Organonickelpentafluoro-*ortho*tellurates and Strong Methylation Agents

Inaugural-Dissertation

to obtain the academic degree

Doctor rerum naturalium (Dr. rer. nat.)

submitted to the

Department of Biology, Chemistry, Pharmacy

of Freie Universität Berlin

by

Sebastian Hämmerling

2020

The work for this dissertation was done in the time period from April 2016 to June 2020 under the supervision of Prof. Dr. Sebastian Hasenstab-Riedel at the Institute of Chemistry and Biochemistry of Freie Universität Berlin.

1st Referee:	Prof. Dr. Sebastian Hasenstab-Riedel
2nd Referee:	Prof. Dr. Thomas Braun (Humboldt-Universität zu Berlin)
Date of defense:	25.03.2021

Acknowledgments

First, I would like to thank my doctoral supervisor Prof. Dr. Sebastian Hasenstab-Riedel for giving me the chance to work at these interesting topics.

I would like to thank Prof. Dr. Thomas Braun for his time and effort to assess my work as a second reviewer.

Many thanks to Dr. Simon Steinhauer for many productive discussions and great ideas on my topics, the correction of my manuscripts and overall support. Also many thanks to Dr. habil. Helmut Beckers for many genius corrections in posters and manuscripts.

I thank my two favorite lab colleagues Dr. Lisa Mann and Sofiya Kotsyuda for the good mood during daily lab work and many helpful discussions.

I would like to thank all former and present group members of the Riedel group for their support and the nice atmosphere, especially Dr. Karsten Sonnenberg, Dr. Jan Hendrik Nissen, Dr. Benjamin Schmidt, Tyler Gully, Patrick Voßnacker, Marlon Winter, Gene Senges and Paul Golz.

Special thanks to Dr. Anja Wiesner for developing the Aluminium-Pentrafluoro-*ortho*tellurate system as a rock-hard fundament of my work.

Many thanks to Dr. Günther Thiele for prompt and accurate proofreading of the manuscript of this thesis.

Finally, I would like to thank my friends, my family and especially my parents for their support, their encouragement and understanding over all these years.

Abstract

The synthesis of the first organonickelpentafluoro-*ortho*tellurates is described. The obtained complexes [Ni(*H*acac)$_2$(OTeF$_5$)$_2$] and *cis*-[Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$] are characterized by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The binuclear complex [{Ni(*H*acac)(H$_2$O)(OTeF$_5$)(μ-OTeF$_5$)}$_2$] is characterized by single crystal X-ray diffraction, extending the group of metals of which bridging pentafluoro-*ortho*tellurato ligands are known.

The facile one-pot synthesis of the strong methylation agent [Me$_2$Cl][Al(OTeF$_5$)$_4$] is described. This reaction requires a Brønsted super acid. The dimethylchloronium salt is used to methylated several weakly basic molecules like PF$_3$, P(CF$_3$)$_3$ and cyanuric fluoride under formation of strongly Lewis acidic cations. Subsequent decomposition reactions of the formed salts are investigated. This leads to new insides on the electron withdrawing properties of the pentafluoro-*ortho*tellurato group. When incorporated in a hypervalent 3-center-4-electron bond the pentafluoro-*ortho*tellurato ligand is more electron withdrawing than the fluorido ligand. The decomposition reactions also leads to new insides on the stability of the weakly coordinating anion. The aluminate anion [Al(OTeF$_5$)$_4$]$^-$ is not the perfect anion for these organic cations, but it is the best available on a large scale.

The role of the dimethylchloronium cation in the classical Friedel-Crafts-Methylation is evaluated by quantum chemical calculations. In similarity to the Friedel-Crafts-Methylation, the salt [Me$_2$Cl][Al(OTeF$_5$)$_4$] is used to methylate electron deficient aromatic molecules like 1,2,3,4-tetrafluorobenzene.

Zusammenfassung

Es werden die Synthesen der ersten Organonickelpentafluoro-*ortho*tellurato Verbindungen beschrieben. Die dargestellten Komplexe [Ni(*H*acac)$_2$(OTeF$_5$)$_2$] und *cis*-[Ni($^{i\text{Pr}}$Im)$_2$(OTeF$_5$)$_2$] werden mittels NMR Spektroskopie, Massenspektrometrie und Einkristallröntgendiffraktometrie charakterisiert. Der zweikernige Komplex [{Ni(*H*acac)(H$_2$O)(OTeF$_5$)(*μ*-OTeF$_5$)}$_2$] wird mittels Einkristallröntgendiffraktometrie charakterisiert. Dadurch wird die Gruppe der Metalle bei denen verbrückende Pentafluoro-*ortho*tellurato Liganden bekannt sind um Nickel erweitert.

Es wird eine einfache Eintopfreaktion zu Synthese des starken Methylierungsmittels [Me$_2$Cl][Al(OTeF$_5$)$_4$] vorgestellt. Diese Synthese erfordert eine Brønsted Supersäure. Dieses Dimethylchloroniumsalzes wird verwendet um schwach basische Moleküle wie PF$_3$, P(CF$_3$)$_3$ und Cyanurfluorid zu methylieren. Die dabei gebildeten Kationen sind starke Lewissäuren. Die Zersetzungsreaktionen dieser Salze wird untersucht, was zu neuen Erkenntnissen zu den Bindungseigenschaften der Pentrafluoro-*ortho*tellurat Gruppe führt. Als Teil einer hypervalenten 3-Zentren-4-Elektronenbindung ist der Pentrafluoro-*ortho*tellurato-Ligand stärker elektronenziehend als der Fluorido-Ligand. Die Zersetzungsreaktionen führen außerdem zu neuen Erkenntnissen zur Stabilität des schwach koordinierenden Anions. Das Aluminat Anion [Al(OTeF$_5$)$_4$]$^-$ nicht das perfekte Anion für diese organischen Kationen ist, aber es ist das am besten zugängliche.

Die Rolle des Dimethylchloroniumkations in der klassischen Friedel-Crafts-Methylierung wird mittels quantenmechanischer Berechnungen untersucht. In Analogie zur Friedel-Crafts-Methylierung werden elektronenarme fluorierte aromatische Moleküle wie 1,2,3,4-Tetrafluorbenzol methyliert.

List of Abbreviations

acac	acetylacetonat
*a*HF	*anhydrous* hydrogenfluoride
Ar	aryl
B3LYP	Becke three-parameter Lee-Yang-Parr
COSMO	conductor-like screening model
Cp	cyclopentadienyl
D3	Grimme dispersion correction from 2010
ΔH	enthalpy
$\Delta E^{\ddagger}$	ZPE corrected relative energy of transition state
ε_R	relative permittivity
Et	ethyl
EXSY	exchange spectroscopy
FIA	fluoride ion affinity
*H*acac	acetylaceton
η	hapticity
$^{i\text{Pr}}$Im	1,3-diisopropylimidazol-2-ylidene
MCA	methyl cation affinity
Me	methyl
MeCl	chloromethane
nbd	2,5-Norbornadiene, Bicyclo[2.2.1]hepta-2,5-diene
NBO	natural bonding orbital
*n*Bu	*n*-butyl
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NPA	natural population analysis
RI	resolution of identity
solv	solvent
SIMes	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
TZVPP	triple-ζ with two sets of polarization functions
VSEPR	valence shell electron pair repulsion
WCA	weakly coordinating anion
XRD	X-ray diffraction
ZPE	zero point energy

Contents

1 Introduction

1.1 Pentafluoro-*ortho*tellurates

The pentafluoro-*ortho*telluric acid, $HOTeF_5$, was first synthesized by Engelbrecht and Sladky in 1964.[1] They described the acid as a volatile glass like solid with a melting point of 40 °C and a boiling point of 60 °C. The synthesis is usually performed in 100 g batches starting from telluric acid and fluorosulfuric acid (equation 1.1).[2] Since $HOTeF_5$ rapidly hydrolyses in water, the acidity cannot be directly compared to water based pKa values of common strong acids.[3] In pure acetic acid the acidity of $HOTeF_5$ is larger than that of nitric acid but smaller than that of hydrogen chloride HCl.[4]

$$ML_n + Xe(OTeF_5)_2 \longrightarrow ML_n(OTeF_5)_2 + Xe\uparrow \qquad (1.8)$$

Synthesis of Pentafluoro-*ortho*tellurates

Based on the strong electron withdrawing properties this group is used to stabilize high oxidation states and unusual coordination arrangements.[5] The most common synthesis routes of pentafluoro-*ortho*tellurates are presented in the following section.

The reaction of binary chlorides (equation 1.2) or flourides (equation 1.3) with pentafluoro-*ortho*telluric acid is the easiest and oldest[1] way to synthesis pentafluoro-*ortho*telluratesalts. The formation of gaseous HCl or stable HF is the driving force of these reactions. Under stoichiometric conditions the reaction with pentafluoro-*ortho*telluric acid enables also the synthesis of complexes bearing organic ligands, like $[M(Cp)_2(OTeF_5)_2]$ (M = Ti, Zr, Hf, Mo, W, $Cp = C_5H_5^-$) without replacement of the cyclopentadienyl ligand.[6] Furthermore, all other pentafluoro-*ortho*tellurato transfer reagents are synthesized from the corresponding fluorides ($AgOTeF_5$[7] and $Xe(OTeF_5)_2$[8]) or chlorides ($B(OTeF_5)_3$[9] and $Me_3SiOTeF_5$[10]) through reaction with pentafluoro-*ortho*telluric acid.

$$MCl_n + n\ HOTeF_5 \longrightarrow M(OTeF_5)_n + n\ HCl\uparrow \qquad (1.2)$$

$$MF_n + n\ HOTeF_5 \longrightarrow M(OTeF_5)_n + n\ HF \qquad (1.3)$$

Related, but rarely used, is the reaction of organometallic precursors (equation 1.4) – like dimethylmercury – with $HOTeF_5$, leading to the formation of an alkane as leaving group.[11,10] The two complexes $[M(CO)_5(OTeF_5)]$ (M = Mn, Re)[12,13] where synthesized through protonation of a methyl group of $[M(CO)_5Me]$ (M = Mn, Re). More recently the anions $[Al(OTeF_5)_4]^-$[14] and $[GaEt(OTeF_5)_3]^-$[15] were synthesized from the corresponding triethyl compounds $AlEt_3$ and $GaEt_3$. In some cases, like $HgMe(OTeF_5)$[11] and $[GaEt(OTeF_5)_3]^-$[15], not all alkyl groups react.

$$MR_n + n\ HOTeF_5 \longrightarrow M(OTeF_5)_n + n\ HR\ (\uparrow) \qquad (1.4)$$

The formation of solid, insoluble silver chloride is the driving force for reactions between $AgOTeF_5$ and element halides (equation 1.5). The possible light and temperature sensitivity of $AgOTeF_5$[16] and the necessary filtration after the reaction, makes this route a rarely used one. However, the compounds $Si(OTeF_5)_4$ and $Me_3GeOTeF_5$ were synthesized through this route.[10]

$$MCl_n + n\ AgOTeF_5 \longrightarrow M(OTeF_5)_n + n\ AgCl\downarrow \quad (1.5)$$

The precursors $B(OTeF_5)_3$ and $Me_3SiOTeF_5$ (equation 1.6 and 1.7) both combine a strong element fluorine bond and a volatile reaction product, BF_3 and Me_3SiF respectively, that are formed. The boron compound has been used frequently for the synthesis of $E(OTeF_5)_3$ (E = As[17], Sb[18]), $U(OTeF_5)_6$[19], $Xe(OTeF_5)_n$ (n = 4, 6)[20]. The silicon compound was used recently to exchange the fluorine atom *trans* to the carbene ligand of $[AuF_3(SIMes)]$ (SIMes = 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) by an $OTeF_5$ group.[21]

$$MF_n + n\ Me_3SiOTeF_5 \longrightarrow M(OTeF_5)_n + n\ Me_3SiF\uparrow \quad (1.6)$$

$$MF_n + {}^{n}/_{3}\ B(OTeF_5)_3 \longrightarrow M(OTeF_5)_n + {}^{n}/_{3}\ BF_3\uparrow \quad (1.7)$$

The xenon compound $Xe(OTeF_5)_2$ is outstanding in the group of pentafluoro-*ortho*tellurato precursors. It enable the introduction of $OTeF_5$ groups without replacing ligands at the metal center, instead the central metal is oxidized (equation 1.8). The precursor was used in the synthesis of $[M(CO)_4(OTeF_5)_2]$ (M = Mn, Ru, Os)[22]. Furthermore, $Xe(OTeF_5)_2$ allows the synthesis of highly oxidized compounds, like $As(OTeF_5)_5$[18], $I(OTeF_5)_5$[23] and $Te(OTeF_5)_6$[24].

$$ML_n + Xe(OTeF_5)_2 \longrightarrow ML_n(OTeF_5)_2 + Xe\uparrow \quad (1.8)$$

Properties of Pentafluoro-*ortho*tellurates

Due to the five fluorine atoms, the pentafluoro-*ortho*tellurato ligand is strongly electron withdrawing. Various studies have been performed to compare the electron withdrawing properties of the pentafluoro-*ortho*tellurato ligand with the fluorido ligand. It is important to note, that the concept of electronegativity cannot be extended to polyatomic groups in a strictly theoretical approach. For most of the following studies, the measured physical quantity depends on more properties than only the electronic ones.

According to the VSEPR model[25] the equatorial positions of a square pyramidal should be occupied by the more electronegative substituent.[23] This is confirmed by the observed geometries of $^{ax}CF_3{-}IF_4$[26] and $^{ax}CH_3O{-}IF_4$[27]. In case of $IF_{5-x}(OTeF_5)_x$ the $OTeF_5$ group is only for $I(OTeF_5)_5$ in the axial position, leading to the assumption the $OTeF_5$ group is stronger electron withdrawing then fluorine.[23]

However in a ^{1}H NMR study the chemical shift of the protons in CH_3X (X = I, Br, Cl, F, $OTeF_5$) shows, that the electron withdrawing properties of F and $OTeF_5$ are – in the range of precision – equal.[23] Evaluation of the vibrational and multinuclear NMR spectroscopic data for POF_2X (X = Br, Cl, F, $OTeF_5$) leads to the same assumption.[23]

The difference of the chemical shifts between the protons of the CH_3 and the CH_2 group of CH_3CH_2X (X = I, Br, Cl, F, $OTeF_5$) leads to the assumption that the $OTeF_5$ group less electron withdrawing than fluorine.[28] This is also confirmed by ^{125}Te and ^{129}Xe NMR studies off TeX_4, TeX_6, XeX_2, XeX_4 and $OXeX_4$ (X = F, $OTeF_5$, not mixed) and the quadrupolar splitting observed by Mößbauer spectroscopy of IFX_4, XeX_2, XeX_4 and $OXeX_4$ (X = F, $OTeF_5$, not mixed).[28]

From all this methods the quadrupolar splitting observed in ^{127}I or ^{129}Xe NMR spectroscopy contains the least number of influences beside the electron withdrawing properties of the ligands.[28] Therefore, it might assumed as the most accurate comparison.

The comparison attempts mentioned so far have in common that only properties of discrete molecules were used. As a further characterization, the reactivity of fluorido and pentafluoro-*ortho*tellurato compounds can be compared. For this propose the Lewis acidity of BX_3[9] and EX_5[29] (X = F, $OTeF_5$; E = P, As, Sb) have been quantified by the reaction enthalpy for the addition of a test base. For BX_3 the reaction enthalpy was determined calorimetrically for the coordination of pyridine in a solution of nitrobenzene (equation 1.9).[9] While for the pentels, the enthalpy was determined quantum chemically with a fluoride anion as test base. This leads to the determination of the fluoride ion affinity (FIA, equation 1.10).[29] In both cases, the reactions are more exothermic when replacing F by $OTeF_5$. This shows that the pentafluoro-*ortho*tellurate analogs are stronger Lewis acids.

$$BX_3 + NC_5H_5 \longrightarrow X_3B\text{-}NC_5H_5 \qquad (1.9)$$

$$EX_5 + F^- \longrightarrow [EFX_5]^- \qquad (1.10)$$

A fundamental difference between the pentafluoro-*ortho*tellurato ligand and the fluorido ligand is the size. The negative charge in $OTeF_5^-$ is distributed over a significant larger area. This makes pentafluoro-*ortho*tellurates ideal for weakly coordinating anions. But the good stabilization of a negative charge is also the definition of a good leaving group.[30] As a result, the $OTeF_5$ ligand is more easily replaced from a low valent metal center by a coordinating solvent molecule than the chlorido ligand.[12,13,31,32] Another result of the steric demand of the $OTeF_5$ ligand is the widening of the M−O−Te angle. This varies from 123.4(3)° in $[Pt(OTeF_5)_2(nbd)]$[32] (nbd = 2,5-norbornadiene) up to 171(1)° in $U(OTeF_5)_6$[33] which is nearly linear. Furthermore, bridging pentafluoro-*ortho*tellurato ligands occurs only with Lewis acidic low coordinated central ions like, Ag^+[16], Tl^+[34], Zn^{2+}[35], Hg^{2+}[36], Au^{3+}[37], in absence of stronger coordinating agents.

For pure pentafluoro-*ortho*tellurato compounds, like $Ti(OTeF_5)_4$[38], $Te(OTeF_5)_6$[24] and $U(OTeF_5)_6$[19], the molecular surface is completely terminated by fluorine atoms. This leads to very low intermolecular interaction. As a result, this three compounds all sublime in vacuum at moderate temperatures of 40 °C, 110 °C and 60 °C (all at 0.01 mbar), respectively. The low intermolecular interactions make pentafluoro-*ortho*tellurates also ideal for weakly coordinating anions.

Reactivity of Pentafluoro-*ortho*tellurates Compared to Fluorido Analogs

Beside the already mentioned pentafluoro-*ortho*tellurates with central elements in high oxidation states, some pentafluoro-*ortho*tellurates were used as strong oxidizers. The cation $[Xe(OTeF_5)]^+$[39] is one prominent example, showing similarities to the fluoro analog $[XeF]^+$[40]. In the solid state the compounds $[XeF][AsF_6]$[41], $[XeF][Sb_2F_{11}]$[42] and $[XeOTeF_5][AsF_6]$[43] all contains bridging fluorine atoms with E−F−Xe (E = As, Sb) structural motives. The F−Xe contacts are much shorter than the sum of the van der Waals radii.[44] Therefore the alternatively description as Y−Xe−F (Y = F, $OTeF_5$) adducts to strong Lewis acids like AsF_5 or Sb_2F_{10} is much better suitable. This shows the strong Lewis acidic character of the xenonium ions. With the less basic weakly coordinating anion $[Sb(OTeF_5)_6]^-$ a less coordinated $[Xe(OTeF_5)]^+$ can be stabilized.[39] This less coordinated $[Xe(OTeF_5)]^+$ cation reacts with CBr_4 under formation of $[CBr_3]^+$ and $BrOTeF_5$ (equation 1.11).[45] The formed $BrOTeF_5$ can react with further $[Xe(OTeF_5)]^+$ to the bromonium ion $[Br(OTeF_5)_2]^+$ (equation 1.12).[45] A similar formal Br^- abstraction reaction is possible between $[XeF]^+$ and an excess of bromine under the formation of the bromonium ion $[Br_5]^+$ (equation 1.13).[46]

$$CBr_4 + [Xe(OTeF_5)]^+ \longrightarrow [CBr_3]^+ + BrOTeF_5 + Xe \quad (1.11)$$

$$BrOTeF_5 + [Xe(OTeF_5)]^+ \longrightarrow [Br(OTeF_5)_2]^+ + Xe \quad (1.12)$$

$$8\ Br_2 + 3\ [XeF]^+ \longrightarrow 3\ [Br_5]^+ + BrF_3 + 3\ Xe \quad (1.13)$$

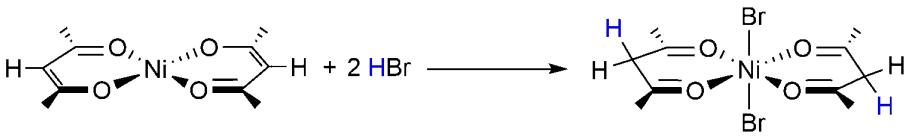
1.2 Nickel Precursors

One element where no synthetic procedures yielding pentafluoro-*ortho*tellurato compounds are known is nickel. As a group 10 metal the main oxidation state of nickel is +II, in which pure ionic compounds mainly exist in the high spin triplet state.[47]

Anhydrous nickel(II) halides are not useful as precursors because of their high lattice energy.[48] An ideal precursor for nickel chemistry should be well soluble in aprotic solvents, molecular and well characterized. When dealing with pentafluoro-*ortho*tellurates, all other ligands should be either inert and stably bond to the metal center or easily to remove. One example for ligands that are known to be problematic in combination with pentafluoro-*ortho*tellurates are phosphines.[49] They can be easily oxidized by pentafluoro-*ortho*tellurates[32], therefore phosphines

should be excluded as spectator ligands. Only a few nickel(II) precursors meet all requirements.

One common nickel(II) precursor is di(acetylacetonato)nickel(II) [$Ni(acac)_2$]. The acetylacetonato ligand can be protonated by Brønsted acids under formation of coordinated acetylaceton (*H*acac, equation 1.14).[50] In the presence of a chelating ligand, the acetylaceton can be completely replaced at the nickel(II) center.[51] Alternatively, the acetylaceton ligand stays coordinated and stabilizes the [$(Ni^{2+})(X^{-})_2$] fragment as a versatile ligand.[52]



(1.14)

One ligand class that is commonly strongly bonded to the metal center are N-heterocyclic carbenes (NHCs), or Arduengo carbenes.[53] As shown in figure 1.1, those consist of a carbon heterocycle with a carbon bearing an electron sextet. The carbenoid carbon is stabilized through a +M effect of neighboring heteroatoms. For nickel(II) many complexes of the general formula [$Ni(NHC)_2X_2$] exist, which are all low spin complexes enabling NMR analysis.[54a,54b,55,54c,56,57] The bromido complex [$NiBr_2(^{i\text{Pr}}Im)_2$] ($^{i\text{Pr}}$Im = 1,3-diisopropylimidazol-2-ylidene) is a versatile precursor, because it is easily accessible and suitable for metathesis reactions with silver(I) salts.[56]

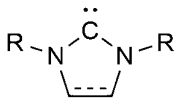


Figure 1.1: Structural motive of NHCs.

There are less compounds known with nickel in a higher oxidation state than +II and none of them is easily accessible. NiF_4 is one of the rare example for nickel in oxidation state +IV[58] and is a strong oxidizer.[47] As shown in figure 1.2 there are some more examples known for nickel in high oxidation states. However, in most cases, the electronic structure of the nickel center differs from the formal oxidation state of +IV (see figure 1.2 left and middle).

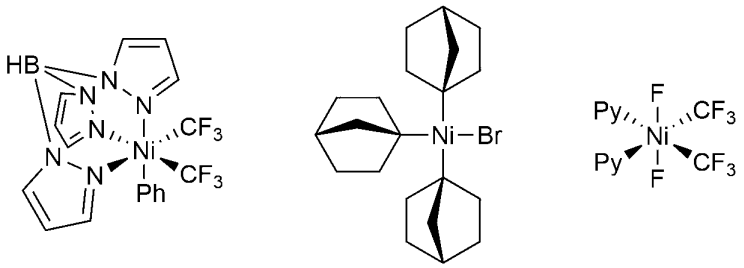


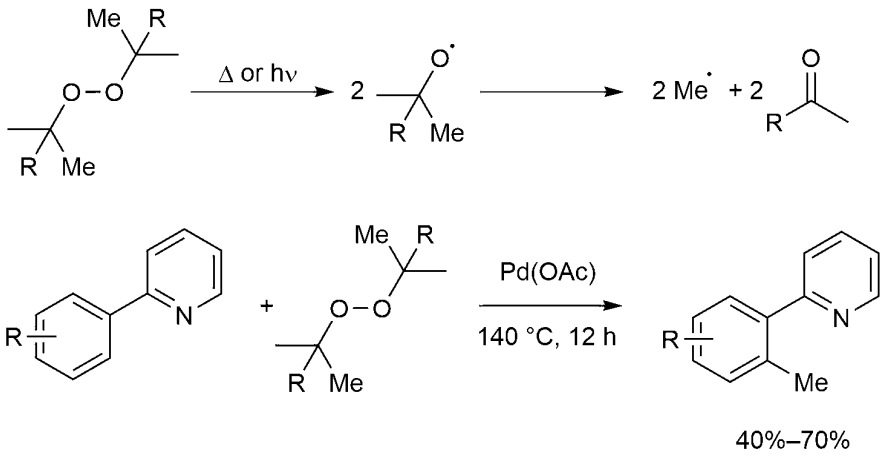
Figure 1.2: Three complexes with nickel in the formal oxidation state +IV.[59]

1.3 Methylation Agents

One important reaction in organic chemistry is the methylation.[60] There are different reaction mechanisms possible. In nucleophilic methylation reactions, a negatively polarized methyl group is necessary. This formal methyl anion is stabilized by a metal cation. Methyllithium is the most prominent example for nucleophilic methylation agents.[61] Through the addition of a chelating ligand like tetramethylethylendiamin (TMEDA), the reactivity of methyllithium can be increased.[62] If less reactivity is required, compounds with less ionic metal carbon bonds like trimethylalumane can be used.[63] In inorganic synthesis, methyllithium and methylmagnesium-halides are wildly used for metathesis (equation 1.15).[64]

$$P(OC_6H_5)_3 + 3\ MeMgCl \longrightarrow PMe_3 + 3\ C_6H_5OMgCl \qquad (1.15)$$

There are numerous publications of metal catalyzed formally radical methylations.[60] In these reactions, an organic peroxide is used as source of methyl radicals (scheme 1.1 top). However, these are not free radical reactions as the methyl radical is immediately trapped by a metal complex (example reaction see scheme 1.1 bottom). The underlying reaction mechanism is always marked as “tentative” or “proposed”. It is claimed that the methylation accords through reductive elimination after C−H activation.[65,66]



Scheme 1.1: Generation of methyl radicals from organic peroxides (top) and palladium catalyst methylation with organic peroxide as methylation source (bottom).[65]

Electrophilic Methylation Agents

For electrophilic methylation agents, the reactive Me^+ group is either stabilized by an anionic leaving group (X^-, equation 1.16) or is part of a cation with a labile Me-Y bond where Y is a neutral leaving group (equation 1.17).

$$Nu + Me\text{-}X \longrightarrow [Me\text{-}Nu]^+ + X^- \qquad (1.16)$$

$$Nu + [Me\text{-}Y]^+X^- \longrightarrow [Me\text{-}Nu]^+ + X^- + Y \qquad (1.17)$$

In organic chemistry dimethyl carbonate[67], iodomethane[68], dimethyl sulfate, methyl triflate[69] and trimethyloxoniumsalts[70] are widely used and belong to textbook knowledge[30] (see figure 1.3). The reactivity of these reagents can be ranked by measuring the kinetics in different solvolysis experiments.[71]

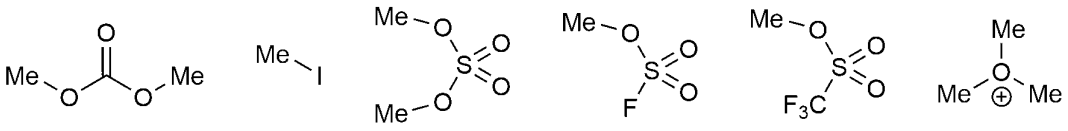


Figure 1.3: Common electrophilic methylation reagents, increasing strength from left to right.

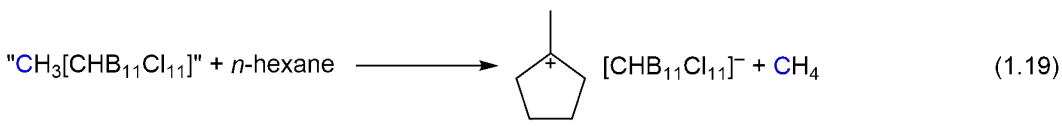
Strong Electrophilic Methylation Agents

The mixture of fluoromethane with antimony pentafluoride[72,73] is a much stronger methylation agent (equation 1.18) which also methylates the weakly basic solvents SO_2 and SO_2ClF according to multinuclear NMR spectroscopy[74]. The similar system with arsenic pentafluoride is a bit weaker as it does not methylate SO_2ClF. The structure of the salts $[SO_2Me][AsF_6]$ and $[SO_2Me][Sb_2F_{11}]$ have been determined in the solid state by X-ray diffraction.[75]

$$MeF + SbF_5 + SO_2 \rightleftharpoons [SO_2Me][SbF_6] \qquad (1.18)$$

The systems MeF/EF_5 (E = Sb, As) were also used in *anhydrous* HF to methylate $P(CF_3)_3$ resulting in the formation of $[MeP(CF_3)_3)][Sb_2F_{11}]$[76]. Note the similarity to the Brønsted super acid HF/SbF_5[77], where the acidity of the weak acid HF is strongly enhanced through the coordination to a strong Lewis acid. One drawback of the MeF/SbF_5 is the presence of free SbF_5 in the equilibrium, which – as strong oxidizer – oxidizes for example electron deficient aromatic systems, like $C_6H_2F_4$ or C_6F_6[78].

The *closo*-carborate compounds $Me[CHB_{11}Me_5X_6]$ (X = Cl, Br) are also very strong electrophilic methylation agents.[79,80] The ^1H NMR spectra of this compounds indicates a dynamic exchange of the methyl group between the inequivalent halogen atoms of the carborates. Therefore, these carborates do not contain free Me^+ cations. With the less basic perchlorinated anion $[CHB_{11}Cl_{11}]^-$, the corresponding $Me[CHB_{11}Cl_{11}]$ could not be isolated. Attempts to synthesize $Me[CHB_{11}Cl_{11}]$ lead to hydride abstraction from hexane (equation 1.19) even at temperatures of −78 °C.[80] Therefore it is not used in further synthesis.[81] The general drawback of the carborate compounds is their limited, small scale accessibility, because of their time consuming and expensive synthesis.[82,83] The pure chlorocarborate compound $Me_2[B_{12}Cl_{12}]$ is a promising candidate for a strong and large scale available methylation agent unfortunately, it could not yet be synthesized as a pure compound.[84]



$$\text{"}CH_3[CHB_{11}Cl_{11}]\text{"} + n\text{-hexane} \longrightarrow [CHB_{11}Cl_{11}]^- + CH_4 \qquad (1.19)$$

Another class of strong methylation agents are dimethylhalonium ions.[85,86] Their reactivity increases from $[Me_2I]^+$ to $[Me_2F]^+$.[87] The dimethylfluoronium ion is not known in condensed phase as it readily decomposes under formation of HF and $CH_3CH_2^+$.[88] However, all dimethylhalonium ions, including $[Me_2F]^+$, are used in gas phase reactions in mass spectrometers, because they can be easily synthesized by chemical ionization of the halomethanes.[89] The dimethylchloronium cation can be isolated as $[SbF_6]^-$[85] or carborate ($[CHB_{11}Cl_{11}]^-$)[90] salt. As $[Me_2Cl][SbF_6]$ slowly decomposes in solution at room temperature[85] it inherits all disadvantages of the MeF/SbF_5 system. As a carborate salt $[Me_2Cl][CHB_{11}Cl_{11}]$ is not accessible on large a scale. However, $[Me_2Cl][CHB_{11}Cl_{11}]$ is interesting because it is synthesized from chloromethane by the Brønsted super acid $H[CHB_{11}Cl_{11}]$ (see equation 1.20).[90] The first step in the underlying reaction mechanism is the protonation of MeCl. However, the intermediate $[MeClH]^+$ could not be detected.[90] Therefore, $[Me][CHB_{11}Cl_{11}]$ could be assumed as intermediate[88]. This reaction is also possible for the higher substituted chloroalkanes EtCl and *i*PrCl.[88,90] The corresponding halonium ions $[Et_2Cl]^+$ and $[iPr_2Cl]^+$ are less stable and decomposes in solution under formation of oligomeric cations and HCl.[88]

$$2\ MeCl + H[CHB_{11}Cl_{11}] \longrightarrow [Me_2Cl][CHB_{11}Cl_{11}] + HCl\uparrow \qquad (1.20)$$

These strong and – in condensed phase usable – methylation agent, MeF/SbF_6, $Me[CHB_{11}Me_5X_6]$ (X = Cl, Br) and $[Me_2Cl][CHB_{11}Cl_{11}]$, could be ranked by their reactivity with weakly basic molecules. Hydrocarbons might be used as prototype for weakly basic molecules. $Me[CHB_{11}Me_5X_6]$ (X = Cl, Br) reacts with linear alkanes at room temperature under hydride abstraction similarly to $Me[CHB_{11}Cl_{11}]$.[91] For MeF/SbF_5 reactions with the hydrocarbons isobutene and neopentane are also known.[92] Since the $[Me_2Cl]^+$ cation reacts neither with SO_2 nor with hydrocarbons, it is the weakest methylation agent of these three strong methylation agents.

Methyl Cation Affinity

In the previous paragraphs weak test bases where introduced to demonstrate and rank the reactivity – i.e. the strength – of methylation agents. Usually the proton affinity (PA) is used to choose a test base. This strategy will lead to wrong assumptions when performing methylation reactions. The PA of SO_2 is 672.3 $kJ \cdot mol^{-1}$[93], which is higher than that of MeCl 647.3 $kJ \cdot mol^{-1}$[93]. This means that protonated MeCl will protonate SO_2 (equation 1.21). However, methylated SO_2 reacts with MeCl under formation of $[Me_2Cl]^+$[85] (equation 1.22). Another example is methylated acetonitrile, $[MeCN\text{-}Me]^+$, which can be synthesized with the Meerweinsalts $[Me_3O][BF_4]$[94] or $[Me_3O][Al(OC(CF_3)_3)_3]$[95] (equation 1.23). This reactions is also wrongly predicted by PA values as the PA of acetonitrile 792.0 $kJ \cdot mol^{-1}$[93] is higher than that of dimethylether 779.6 $kJ \cdot mol^{-1}$[93].

$$[MeClH]^+ + SO_2 \longrightarrow MeCl + [SO_2H]^+ \quad (1.21)$$

$$[SO_2Me]^+ + MeCl \longrightarrow SO_2 + [Me_2Cl]^+ \quad (1.22)$$

$$[Me_3O]^+ + MeCN \longrightarrow Me_2O + [MeCN\text{-}Me]^+ \quad (1.23)$$

The determination of experimental methyl cation affinities (MCA) as negative gas-phase reaction enthalpy according to equation 1.24 leads to correct prediction of methylation reactions. The MCA of SO_2 254 kJ·mol^{-1}[96] is lower than the MCA of MeCl 260 kJ·mol^{-1}[96]. Since there are much less MCAs available in the literature than PAs, quantum chemical calculations are often necessary.

$$Me^+ + base \longrightarrow [Me\text{-}base]^+ \quad (1.24)$$

For many molecules there is a linear correlation between PA and MCA values.[96] One reason for the deviation from this trend for some molecules are the additional orbitals that are present in a methyl group. These orbitals are available for hyper conjugation.[97] Both positive and negative hyper conjugation are possible for methyl groups[98], but not for protons.

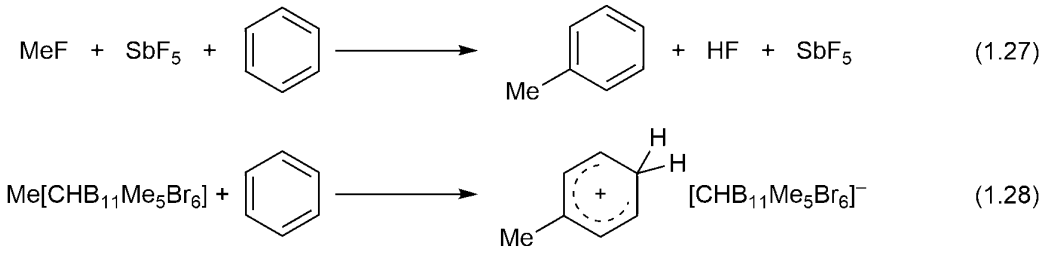
Reactivity of Methylated Molecules

Obviously, cations are generated through methylation of weakly basic, neutral molecules, like Br_2 or OPF_3. It is important to note that those cations – $[MeBr_2]^+$ and $[MeOPF_3]^+$ – are strong Lewis acids. For example methylated phosphoryl trifluoride $[MeOPF_3]^+$ readily abstracts a fluoride ion from $[AsF_6]^-$ (equation 1.25).[99] This shows that the Lewis acidity of $[MeOPF_3]^+$ is higher than those of AsF_5. Similarly, methylated bromine $[MeBr_2]^+$ is a stronger Lewis acid as SbF_5 (equation 1.26).[100] This shows that strong methylation agents need low basic weakly coordinating anions (see section 1.5).

$$MeOPF_3^+ + AsF_6^- \longrightarrow \{MeOPF_4 + AsF_5\} \longrightarrow PF_5 + ½[MeOAsF_4]_2 \quad (1.25)$$

$$MeBr_2^+ + SbF_6^- \longrightarrow MeBr + BrF + SbF_5 \quad (1.26)$$

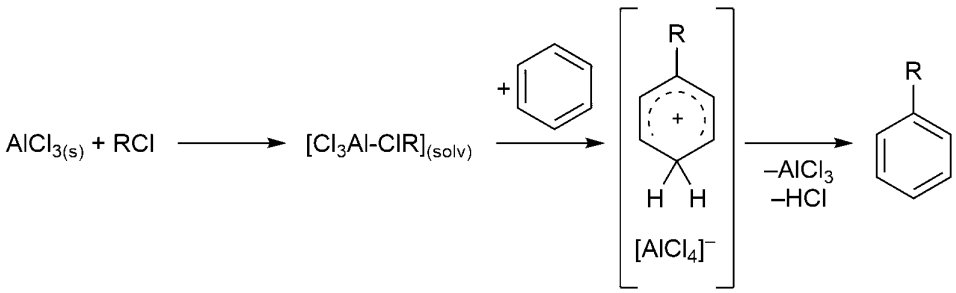
In presence of an aromatic compound MeF/SbF_5 is transformed to HF/SbF_5 under formation a methylated aromat (equation 1.27).[72] This reaction is – with a more convenient Lewis acid like $AlCl_3$ – also known as Friedel-Crafts alkylation[101,102] and is widely used in organic chemistry[103]. With $Me[CHB_{11}Me_5X_6]$ (X = Cl, Br) as methylation agent the Wehland intermediate, i.e. protonated toluene, can be isolated (equation 1.28).[79]



This shows that methylated weakly basic molecules can react as methylation agents, Lewis acids or Brønsted acids.

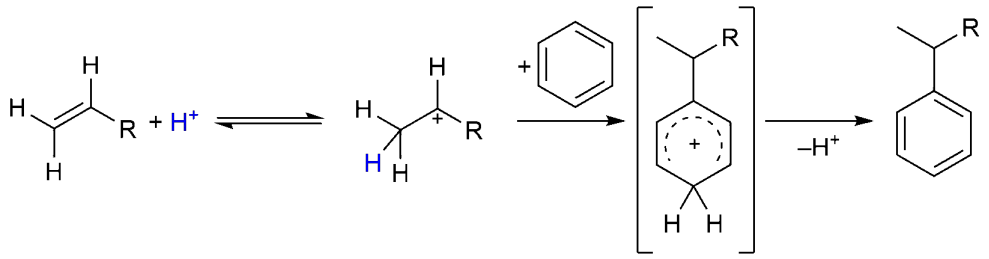
Friedel-Crafts Alkylation

The Friedel-Crafts alkylation reaction is based on the polarization of an alkyl halide – mostly an alkyl chloride – by a Lewis acid like $AlCl_3$. This resulting intermediate reacts as an electrophilic reagent with an aromatic molecule to form an arenium ion (Wheland intermediate, scheme 1.2).[101,102] Rearomatization occurs through elimination of HCl. Depending on the stabilizing effects of the alkyl group, that alkylating species has a distinct carbocationic character.



Scheme 1.2: $AlCl_3$ catalyzed Friedel-Crafts alkylation.

The Lewis acid is a catalyst in Friedel-Crafts alkylation reactions. However, the catalysts load is usually larger than 10%.[104] As a more environmental friendly variation, the electrophilic agent can be generated from an olefin and a strong Brønsted acid, like HCl (scheme 1.3).[105] For intermolecular reactions with higher olefins there are a lot of isomerization reactions.[106] For intramolecular reactions, this Brønsted acid catalyzed Friedel-Crafts alkylation is widely used in organic synthesis.[107]



Scheme 1.3: Brønsted acid catalyzed Friedel-Crafts alkylation of benzene.

1.4 Halonium Ions

According to the definition of the IUPAC, halonium ions contain a formally positively charged halogen atom in their Lewis structure.[108] In organic reaction mechanism, halonium ions are known as intermediates e.g. in electrophilic halogenation reactions.[109]

One well-known class of isolatable halonium ions are polyhalogen cations. Polyhalogen cations are commonly synthesized through oxidation of elemental halogens by a strong oxidizer like $[XeF]^+$[46] (equation 1.13, synthesis of $[Br_5]^+$), AsF_5[110] (equation 1.29) or SbF_5[111] (equation 1.30). The crystal structures of $[X_2]^+$ (X = Br, I)[111,112], $[X_3]^+$ (X = Cl, Br, I)[113], $[Cl_4]^+$[114], $[I_4]^{2+}$[110], $[X_5]^+$ (X = Br, I)[46,115,116], $[I_7]^+$[117] and $[I_{15}]^{3+}$[116] are known.

$$2\ I_2 + 3\ AsF_5 \longrightarrow [I_4]^{2+}[AsF_6]_2^- + AsF_3 \qquad (1.29)$$

$$5\ I_2 + 5\ SbF_5 \longrightarrow 2\ [I_2]^+[Sb_2F_{11}]^- + SbF_3 \qquad (1.30)$$

The prototype structure of polyhalogen cations with an odd atom number to charge ratio is a C_{2v} symmetric bent structure. This structure can be rationalized as a mono halonium cation X^+ that coordinates to a dihalogen molecule X_2. The positive charge is delocalized over the entire molecule, with a maximum at the central atom (see figure 1.4). For higher polyhalogene cations with an odd atom number to charge ratio this motive coordinates additional dihalogen molecules in a chain like structure.

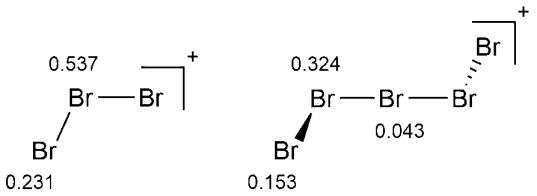


Figure 1.4: NBO charges of the atoms in $[Br_3]^+$ and $[Br_5]^+$ at B3LYP/ATZ-PP level of theory, formal charges are omitted for clarity.[118]

Polyhalogene cations with an even atom number to charge ratio are formally derived from an dihalogen radical cation $[X_2]^{+\bullet}$, that either dimerizes ($[I_4]^{2+}$) or coordinates a halogen molecule ($[Cl_4]^{+\bullet}$).

It is worth mentioning, that halonium ions are also strong oxidizers. Halonium ions bearing organic or electron donating moieties are usually weaker oxidizer, but still highly reactive, as seen in section 1.3. For elements that are less electronegative than carbon, the methylation is a formal oxidation of the element.

The bend structure of triatomic halogen cations $[X_3]^+$ is also present in organic halonium ions $[R_2X]^+$ (R = Me, Me_3Si; X = F, Cl, Br, I). As shown in table 1.1, the bond angle at the central halogen decreases for the heavier homologs as expected with increasing s-p separation. This is already visible for chloronium ions. However, the steric demand of the organic sidechains (R = Me, Me_3Si) leads to a widening of the central bonding angle. This can be evaluated by comparing with the ions $[H_2X]^+$ (X = F, Cl, Br, I).

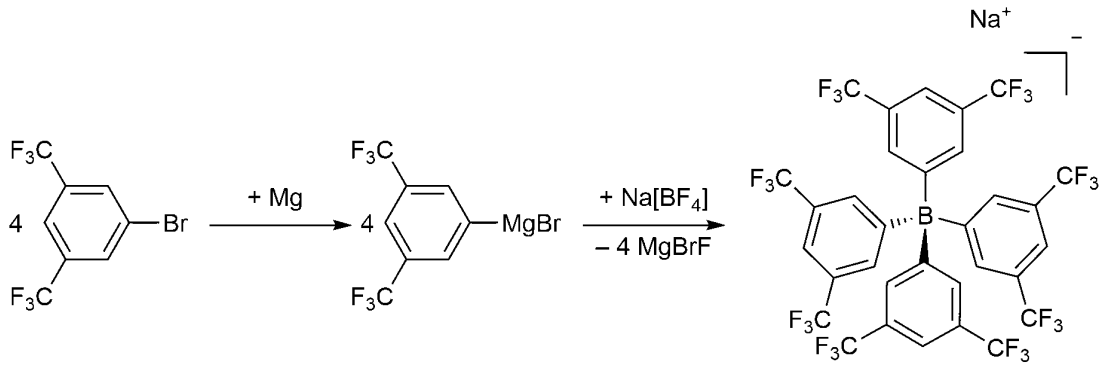
Table 1.1: Bond angles at the central halogen of $[R_2X]^+$. Values in *italics* are on BP86/TZ2P (R = H)[119] or B3LPY/6-311++G(d,p) (R = Me)[120] level of theory. The other values are determined by single crystal X-ray diffraction.

R =	X = F	Cl	Br	I
H	*111.9*[119]	*93.5*[119]	*91.2*[119]	*90.4*[119]
Me	*122.4*[120]	*104.9*[120] 101.5(2)[90]	*101.3*[120]	*98.1*[120]
Me_3Si	163.0(3)[121]	119.0(2)[121]	114.2(1)[121]	111.8(1)[121]

1.5 Weakly Coordinating Anions

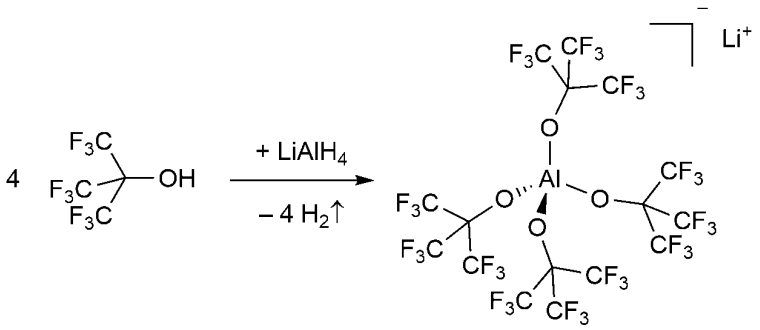
As seen in the previous sections, weakly basic and weakly nucleophilic anions can be used to stabilize reactive cations. As a keyword for these anions the term weakly coordinating anions commonly abbreviated with WCA where introduced over 30 years ago.[122] The determination of when to call an anion weakly coordinating changed over the time. This starts after salts of the fluorinated anions $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ where examined by single crystal X-ray diffraction. Here, significant interactions between anion and cation are visible by elongation of one E−F bond.[123] However, the anions $[AsF_6]^-$, $[SbF_6]^-$ and the related binuclear anions $[As_2F_{11}]^-$, $[Sb_2F_{11}]^-$ directly form upon protonation with the super acidic mixtures *a*HF/EF_5 (E = As, Sb) and are those widely present.[124] The other important classes of WCAs are briefly introduced in the following paragraphs.

A versatile class of WCA are the borate anions $[B(Ar)_4]^-$.[125] Depending on the aromatic substituent, many of these anions are easily accessible and can be synthesized in lab courses for bachelor students (scheme 1.4).[126] Replacing C−H groups in $[B(C_6H_5)_4]^-$ by C−F or C−CF_3 drastically reduces the coordination ability.[83] This can be straightforwardly achieved through fluorinated aromatic precursors. However the reduction potential of the anions stays undesirable high, i.e. the borate anions $[B(Ar)_4]^-$ are not compatible with strong oxidants.[29,83]



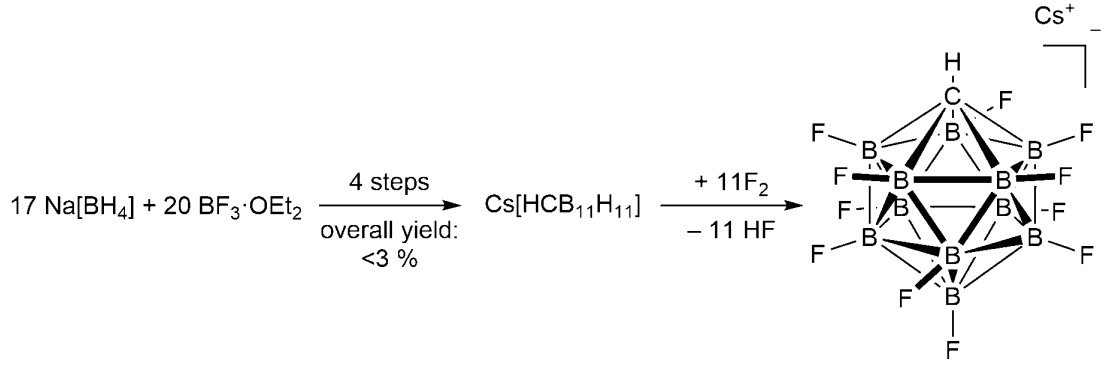
Scheme 1.4: Synthesis of $Na[B(C_6H_3(CF_3)_2)_4]$.[126]

Quite similar is the class of alkoxyaluminate WCAs $[Al(OR^F)_4]^-$. The most prominent member of this groups is the anion $[Al(OC(CF_3)_3)_4]^-$.[127] These anions are easily accessible from reactions of a fluorinated alcohol and an aluminum precursor, like $LiAlH_4$ (scheme 1.5) or $AlEt_3$.[128] Depending on the steric demand of the alkoxygroup, small cations like Li^+ tend to coordinate to the oxygens.[129]



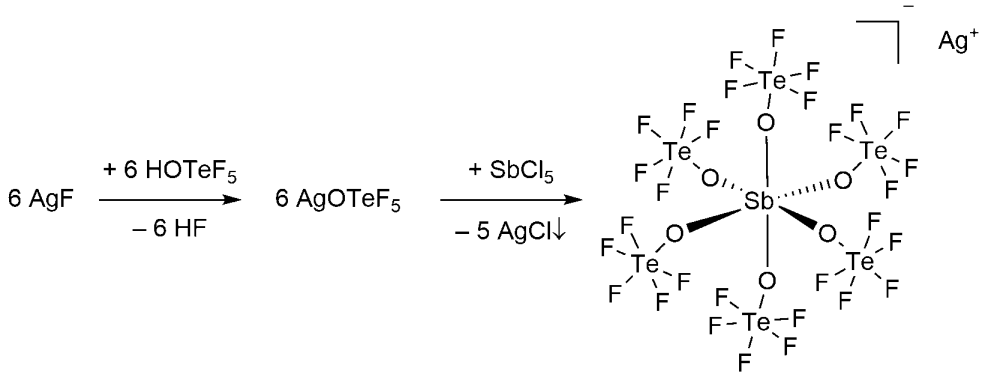
Scheme 1.5: Synthesis of $Li[Al(OC(CF_3)_3)_4]$.[127]

Complete different are the *close*-carborate anions, formally derived from $[HCB_{11}H_{11}]^-$.[130] Again, the partial or complete exchange of hydrogens by halogens strongly reduces the coordination ability. In contrast to the borate anions shown above, elemental halogens or interhalogens are necessary for the synthesis of $[HCB_{11}Cl_{11}]^-$[131] or $[HCB_{11}F_{11}]^-$ (scheme 1.6).[132] However, these two anions belong the least coordinating anions known.[83]



Scheme 1.6: Synthesis of $Cs[HCB_{11}F_{11}]$[132] from commercially available precursors through optimized route.[133]

A reemerging class of WCAs are those of pentafluoro-*ortho*tellurato based anions $[E(OTeF_5)_x]^-$. That started in 1981 with $[B(OTeF_5)_4]^-$[134], went on with $[E(OTeF_5)_6]^-$ (E = As[135], Sb[136], Nb[137], Ta[137], Bi[138]) and recently led to the development of $[Al(OTeF_5)_4]^-$[14]. The boron anion is less stable against electrophiles, thus decomposes under $OTeF_5^-$ abstraction.[139] The hexacoordinated anions are not accessible directly from pentafluoro-*ortho*telluric acid, resulting in additional synthetic steps (scheme 1.7).



Scheme 1.7: Synthesis of $Ag[Sb(OTeF_5)_6]$.[136]

In total, no WCA is ideal for all cases. Hence, the design of a WCA is a complex task.[140,83] It is necessary to find an optimal compromise between coordination ability, oxidation stability and electrophilic stability.[141]

Stability of Weakly Coordinating Anions

While the coordination ability of a WCA is important for the interpretation and the reactivity of the obtained salts, their oxidation stability and their electrophilic stability directly limits the usability of a WCA. The electrophilic stability of a WCA, which is a crucial point in the work, is discussed in more details.

A common decomposition pathway for anions of the formula $[ML_n]^-$ is the ligand abstraction.[139,142] To model the different possible reactions three parameters can be used: the ligand affinity (LA), the proton decomposition (PD) and the copper decomposition (CuD) (see table 1.2).[29] For all these parameters, larger values – i.e. more positive values – indicate a more stable WCA. The PD mimics the stability against hard and the CuD against soft electrophiles. The LA not only includes the Lewis acidity of the fragment $[ML_{n-1}]^-$, but also the stabilization of the ligand precursor L^-. Therefore, the values for pentafluoro-*ortho*tellurate based anions are smaller than for the small fluorido base anions. For the carborate based anions these values cannot be directly accessed, therefore these anions where not included by *Krossing and Rabe*.[29] The borate-based anions are the least stable according to PD and CuD values. For the other anions, the size matters – e.g. larger anions are showing better stability values. This not only includes more bulky ligands (fluorido vs. pentafluoro-*ortho*tellurato) but also heavier

and more Lewis acidic central elements. The three presented parameters provide good standard values for fast evaluation of a new WCA. However, these three parameters only represent thermodynamic properties of the anions. The anions $[SbF_6]^-$ and $[Sb(OTeF_5)_6]^-$, which both combine the best stability data according to table 1.2, may corroborate this limitation. Due to the steric demand of the pentafluoro-*ortho*tellurato ligands the anions $[Sb(OTeF_5)_6]^-$ is kinetically much less labile than $[SbF_6]^-$, therefore much stronger electrophiles can be stabilized by $[Sb(OTeF_5)_6]^-$ (see also end of section 1.1).[39,43] In total, the anion $[Sb(OTeF_5)_6]^-$ combines the best electrophilic stability data.

Table 1.2: Calculated properties in kJ·mol^{-1} of different WCA by *Krossing and Rabe* (LA, PD, CuD)[29] and Lewis acids by *Krossing et al.* (FIA)[143]

Anion	LA[a]	PD[b]	CuD[c]	FIA[d]	Lewis acid
$[BF_4]^-$	338	−1212	−521	342	BF_3
$[AlF_4]^-$	-	-	-	471	AlF_3
$[AsF_6]^-$	426	−1124	−433	430	AsF_5
$[SbF_6]^-$	489	−1061	−371	493	SbF_5
$[B(OTeF_5)_4]^-$	274	−1040	−420	552	$B(OTeF_5)_3$
$[Al(OTeF_5)_4]^-$	-	-	-	552[e][144]	$Al(OTeF_5)_3$
$[As(OTeF_5)_6]^-$	290	−1023	−403	559	$As(OTeF_5)_5$
$[Sb(OTeF_5)_6]^-$	341	−973	−353	625	$Sb(OTeF_5)_5$
$[Al(OC(CF_3)_3)_4]^-$	342	−1081	−395	543	$Al(OC(CF_3)_3)_3$
$[B(C_6H_5)_4]^-$	324	−1402	−649	-	$B(C_6H_5)_3$
$[B(C_6H_3(CF_3)_2)_4]^-$	382	−1251	−506	482	$B(C_6H_3(CF_3)_2)_3$
$[B(C_6F_5)_4]^-$	296	−1256	−538	452	$B(C_6F_5)_3$

[a] Ligand affinity, ΔH for reaction $[ML_n]^- \rightarrow [ML_{n-1}] + L^-$.
Sum of reactions $[ML_n]^- + AlF_3 \rightarrow [ML_{n-1}] + [AlF_3L]^-$ (BP86/SV(P)) and $[AlF_3L]^- \rightarrow AlF_3 + L^-$ (MP2/TZVPP).
[b] Proton decomposition, ΔH for reaction $[ML_n]^- + H^+ \rightarrow [ML_{n-1}] + HL$ at BP86/SV(P) level of theory.
[c] Copper decomposition, ΔH for reaction $[ML_n]^- + Cu^+ \rightarrow [ML_{n-1}] + CuL$ at BP86/SV(P) level of theory.
[d] Fluoride ion affinity at BP86/SV(P) level of theory with TMS^+/TMSF as anchor point.
[e] In $Al(OTeF_5)_3$ two $OTeF_5^-$ ligands are coordinated η^2[14], leading to an additional stabilization of the Lewis acid in gas phase. This coordination motive is not present in $B(OTeF_5)_3$.

Due to its recent development, the newest pentafluoro-*ortho*tellurate based WCA, $[Al(OTeF_5)_4]^-$, was not included by *Krossing and Rabe*.[29] Based on the general trend of the Lewis acidity (see FIA values also of the fluorides, table 1.2 right), this aluminate based anion is probably more stable than $[B(OTeF_5)_4]^-$, but it may not reach the stability properties of $[Sb(OTeF_5)_6]^-$.[144] However, $[Al(OTeF_5)_4]^-$ is accessible in a simple one pot reaction on larger scales[14], just like $[Al(OC(CF_3)_3)_4]^-$. In contrast to the alkoxy based WCA, a corresponding Brønsted super acid $[ArH][Al(OTeF_5)_4]$ (Ar = $C_6H_4F_2$) exists, just like the carboranes $H[HCB_{11}R_5X_5]$ (R = H, Me, X = Cl, Br).[145] Therefore, the anion shows a rapidly developing chemistry.[146] One outstanding result of this development is $[P_4H][Al(OTeF_5)_4]$, protonated white phosphorous.[147]

2 Objectives

The pentafluoro-*ortho*tellurato ligand has been used widely to stabilize high oxidation states and should be suitable to stabilize nickel in high oxidation states. Since no nickelpentafluoro-*ortho*tellurates are known, one scope of this thesis is to first synthesize and characterize nickel(II)-pentafluoro-o*rthot*ellurates.

The anion $[Al(OTeF_5)_4]^-$ combines the large scale accessibility of the BArF anions $[B(Ar^F)_4]^-$ with the existence of a Brønstedt super acid. The second scope of this thesis is to extend the chemistry of the super acidic reaction mixture of triethylalumane with four equivalents of pentafluoro-*ortho*telluric acid to a non-arene solvent, and synthesize a strong electrophilic methylation agent based on the anion $[Al(OTeF_5)_4]^-$. The application of this aluminate base methylation agent should be demonstrated by methylation of several weakly basic molecules. Since the resulting cations are expected to be strong Lewis acids, this will also lead to new findings on the reactivity of the anion $[Al(OTeF_5)_4]^-$ and on the bonding properties of the pentafluoro-*ortho*tellurate group.

3 Outline

This chapter contains a brief outline of the results obtained in this work. Chapter 4 contains the complete results by means of three peer-reviewed articles, which includes all experimental procedures. The sequence of the results is changed to provide a more coherent view.

3.1 Organonickelpentafluoro-*ortho*tellurates

All attempts to synthesize nickelpentafluoro-*ortho*tellurates from nickel(II)-halides failed as the salts are insoluble in all tested aprotic solvents. The slow addition of pentafluoro-*ortho*telluric acid to a solution of nickel(II) acetylacetonate in 1,2-difluorobenzene yields in the formation of $[Ni(Hacac)_2(OTeF_5)_2]$ (**1**) (Hacac = $MeC(O)CH_2C(O)Me$) as a turquoise colored precipitate (equation 3.1). Crystals suitable for X-ray diffraction were obtained from 1,2-difluorobenzene at 0 °C. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (see figure 3.1).

$$[Ni(acac)_2] + 2\ HOTeF_5 \longrightarrow [Ni(Hacac)_2(OTeF_5)_2] \qquad (3.1)$$

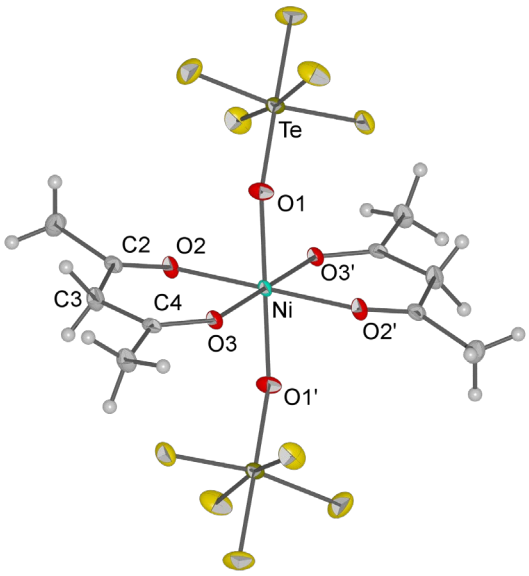


Figure 3.1: Molecular structure of $[Ni(Hacac)_2(OTeF_5)_2]$ (**1**). Thermal ellipsoids drawn at a 50% probability level. Selected bond length (pm) and angles (°): Ni-O1 202.6(2), Ni-O2 204.2(2), Ni-O3 203.1(2), O1-Te1 178.6(2), O2-C2 122.3(2), O3-C4 122.4(1), C2-C3 149.9(1), C4-C3 150.7(1), O2-Ni-O3 89.3(1), O3-Ni-O2' 90.7(1), O1-Ni-O2 87.7(1), O1-Ni-O3 85.5(1) Ni-O1-Te 133.7(1), C2-C3-C4 121.0(2).

From the primary reaction mixture of $[Ni(Hacac)_2(OTeF_5)_2]$ in 1,2-difluorobenzene also crystals of $[\{Ni(Hacac)(H_2O)(OTeF_5)(\mu\text{-}OTeF_5)\}_2]$ (**2**) were grown. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ (see figure 3.2). There is a loss of one acetylacetone ligand, which is compensated by bridging pentafluoro-*ortho*tellurato ligands. This extends the group metals of which bridging pentafluoro-*ortho*tellurato ligands are known by nickel.

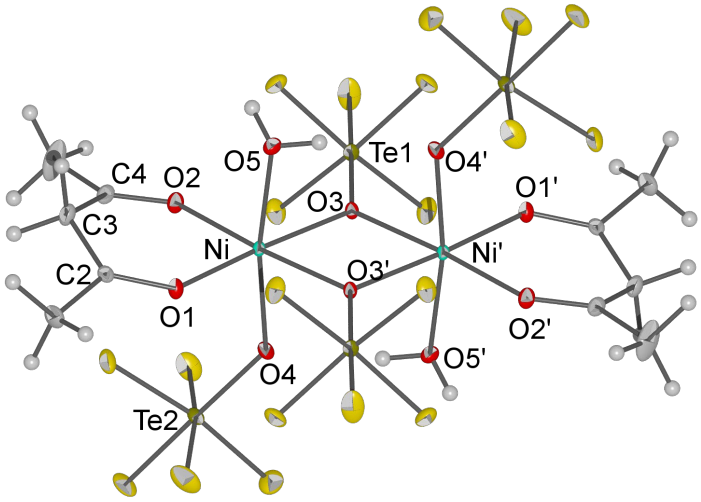
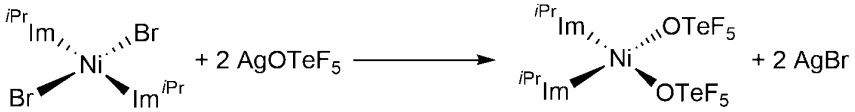


Figure 3.2: Molecular structure of [{Ni(Hacac)(H_2O)($OTeF_5$)(μ-$OTeF_5$)}$_2$] (**2**). Thermal ellipsoids drawn at a 50% probability level. Selected bond length (pm) and angles (°): Ni-O1 200.5(2), Ni-O2 200.3(2), Ni-O3 206.7(2), Ni-O4 205.2(2), Ni-O5 206.9(2), O4-Te2 179.6(2), O3-Te1 180.9(2), Ni-Ni' 315.4(1), O1-C2 122.8(2), O2-C4 122.6(2), C2-C3 150.8(3), C3-C4 150.3(3), O1-Ni-O2 89.0(1), O1-Ni-O3' 94.5(1), O2-Ni-O3 95.5(1), O3-Ni-O3' 81.1(1), O5-Ni-Ni' 85.0(1), O4-Ni-Ni' 85.4(1), Ni-O4-Te2 134.6(1), Ni-O3-Te1 131.2(7), Ni'-O3-Te2 129.7(1), C2-C3-C4 118.8(2).

The nickel complex [Ni($^{i\mathrm{Pr}}$Im)$_2$Br$_2$] ($^{i\mathrm{Pr}}$Im = 1,3-diisopropylimidazol-2-ylidene) is a common soluble nickel precursor.[56] The reaction of pentafluoro-*ortho*telluric acid with [Ni($^{i\mathrm{Pr}}$Im)$_2$Br$_2$] do not yield in the formation of a nickel pentafluoro-*ortho*tellurate complex. Using silver pentafluoro-*ortho*tellurate as a transfer reagent yields quantitatively [Ni($^{i\mathrm{Pr}}$Im)$_2$($OTeF_5$)$_2$] (**3**) (equation 3.2). Crystals suitable for X-ray diffraction were grown by recrystallization from dichloromethane at 0 °C. Compound **3** crystalizes in the monoclinic space group $P2_1/n$ (see figure 3.3).



(3.2)

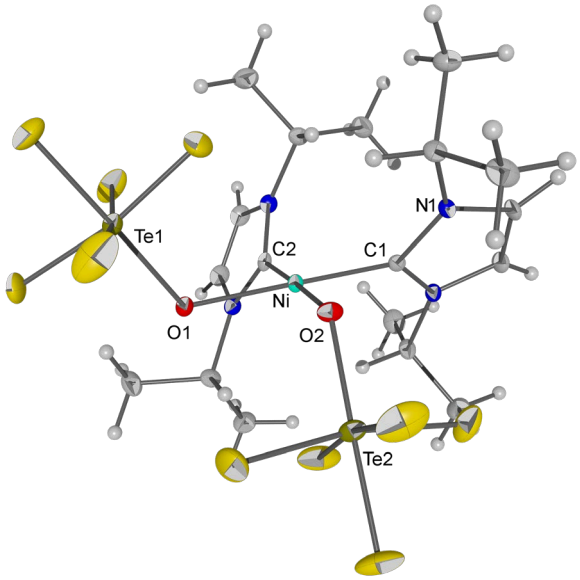


Figure 3.3: Molecular structure of [Ni($^{i\text{Pr}}$Im)$_2$(OTeF$_5$)$_2$] (**3**). Thermal ellipsoids are drawn at a 50% probability level. Selected bond length (pm) and angles (°): Ni-O1 192.7(2), Ni-O2 193.1(2), Ni-C1 187.4(2), Ni-C2 187.5(2), O1-Te1 179.6(2), O2-Te2 179.7(2), O1-Ni-O2 88.1(1), C1-Ni-C2 92.1(1), O1-Ni-C2 89.3(1), O2-Ni-C1 90.6(1), N-O1-Te1 120.0(1), Ni-O2-Te2 119.3(1).

The carbene carbon shift of complex **3** exceeds with 141 ppm the usual range of 210 to 160 ppm for neutral [Ni($^{i\text{Pr}}$Im)$_2$X$_2$] complexes (see table 3.1). However this value is comparable to those published by Braunstein *et al.* for [Ni(NHC)$_2$(H$_2$O)$_2$]$^{2+}$ of 147 to 145 ppm.[57] This points out the strong Lewis acid character[148] of the [Ni(OTeF$_5$)$_2$]$^{2+}$ fragment. There is virtually no influence of the *cis*/*trans* constitution on the carbenoid shift.[149] Complex **3** is one of the rare examples of NHC *cis* coordination to a nickel(II) center.[57,149,150,151] However, the electron withdrawing properties of the anionic ligands are not necessarily the only reason for the *cis*/*trans* constitution. By comparing the free enthalpy for the isomerization reaction from *trans* to *cis*, it becomes apparent that solvation effects are important for the *cis*/*trans* constitution.

Table 3.1: Solution and gas phase free enthalpy for the reaction *cis*-[Ni($^{i\text{Pr}}$Im)$_2$X$_2$]→*trans*-[Ni($^{i\text{Pr}}$Im)$_2$X$_2$] on RI-B3LYP-D3/def2-TZVPP level of theory (for COSMO: ε_R MeCN) and experimental ^{13}C NMR shift of the carbene carbon atom in solution.

X	experimental isomer	δ_{NCN} (ppm)	ΔG^0_{solv} (kJ·mol^{-1})	ΔG^0_{gas} (kJ·mol^{-1})
OTeF$_5$	*cis*	140.9	+8.8	−19.1
Br	*trans*	170.4[56]	−5.8	−52.6
CN	*trans*	171.5[55]	−16.0	−43.7
NCS	*trans*[a]	173.1[149]	+6.7	−33.8
Cl	*trans*[a]	177.8[152]	+9.3	−37.5
Me	*trans*	203.4[56]	−22.0	−29.4

[a] *cis* for different NHC.[149,150]

3.2 $[Me_2Cl][Al(OTeF_5)_4]$ as Strong Methylation Agent

The reaction of four equivalents of pentafluoro-*ortho*telluric acid with triethylalumane in chloromethane yield in the formation of $[Me_2Cl][Al(OTeF_5)_4]$ (**4**) (equation 3.3). This reaction, but in an aromatic solvent like 1,2-dilfuorobenzene, is similar to the synthesis of the Brønsted Super acid $[ArH][Al(OTeF_5)_4]$ (*Ar*=*ortho*-$C_6H_4F_2$).[14] However the proton affinity of the solvent chloromethane is 647.3 kJ·mol^{-1}[93] which is much lower than that of 1,2-difluorobenzene 731.2 kJ·mol^{-1}[93]. The reaction enthalpy for equation 3.4 is −723.5 kJ·mol^{-1} on RI-B3LYP-D3/def2-TZVPP level of theory. This value can be interpreted as the negative proton affinity of a chloromethane dimer, which is much larger than the proton affinity of a single molecule of chloromethan 649.2 kJ·mol^{-1} on RI-B3LYP-D3/def2-TZVPP level of theory.

$$2\ MeCl + AlEt_3 + 4\ HOTeF_5 \xrightarrow[-40\ °C,\ 15\ min]{MeCl} [Me_2Cl][Al(OTeF_5)_4] + HCl\uparrow + 3\ C_2H_6\uparrow \quad (3.3)$$

$$2\ MeCl + H^+ \longrightarrow [Me_2Cl]^+ + HCl\uparrow \quad (3.4)$$

From a solution of **4** in a MeCl/n-pentane mixture colorless crystals suitable for X-ray diffraction where grown at −80 °C. **4·MeCl** crystallizes in the monoclinic space group $P2_1/n$ (figure 3.4). Both, solvate MeCl and the aluminate anion are disordered. The structure of the cation in the solid state is similar to that of $[Me_2Cl][CHB_{11}Cl_{11}]$.[90]

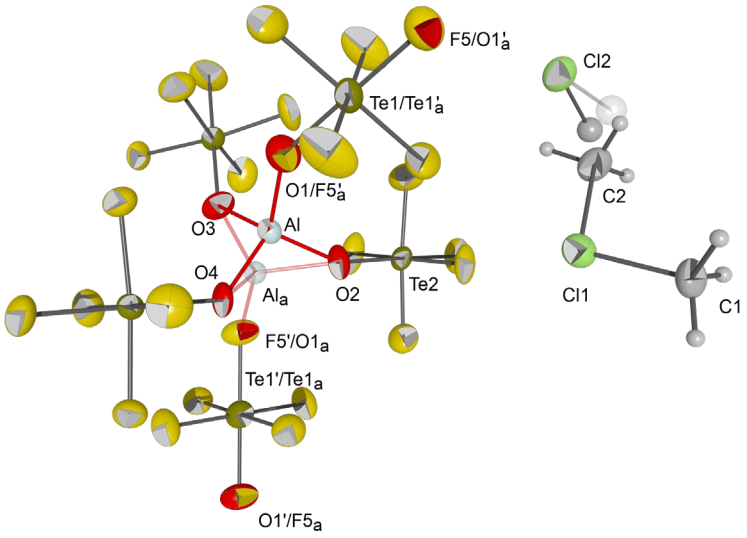


Figure 3.4: Molecular structure of **4·MeCl** in the solid state. H-Atoms of solvate MeCl are omitted for clarity. Thermal ellipsoids drawn at 50% probability level. Selected bond length (pm) and angles (°): C1-Cl1 183.9(16), C2-Cl1 180.1(19), C1-Cl1-C2 101.0(7), Al-O1/F_a' 184.5(14), Al O2 166.4(14), Al-O3 178.7(14), Al-O4 176.1(14), O1/F_a'-Te1/$Te1_a$' 180.7(11), O1/F_a'-Al-O2 112.0(7), O1/F_a-Al-O3 107.0(7), O1/F_a-Al-O4 110.8(7), O2 Al O3 114.6(8), O3-Al-O4 105.0(7), O4-Al-O2 107.4(7).

To demonstrate the wide scope of **4** as methylation agent, several weakly basic molecules are methylated with **4** according to equation 3.5. A summary of substrates and products is given in table 3.2. Most of the reactions are completed after 30 minutes at temperatures between −10 °C to room temperature. The only exception is the methylation of $P(CF_3)_3$ which takes days as room temperature. This observation is in agreement with the energies of the transition states calculated at RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2).

$$[Me_2Cl][Al(OTeF_5)_4] + Nu \xrightarrow{SO_2} [Me\text{-}Nu][Al(OTeF_5)_4] + MeCl \qquad (3.5)$$

Table 3.2: Isolated salts of methylated weak bases, methyl cation affinity (MCA), reaction time and energy of the transition state. Energies and Enthalpies in kJ·mol^{-1} on RI-B3LYP-D3/def2-TZVPP level of theory.

base	MCA[a]	reaction time	$\Delta E^{\ddagger}$[b]	salt	literature known salt of cation[c]
MeCl	279.2	-	40.6[d]	$[Me_2Cl][Al(OTeF_5)_4]$	$[Me_2Cl][SbF_6]$[85], $[Me_2Cl][CHB_{11}Cl_{11}]$[90]
MeBr	294.4	<5 min	33.5	$[Me_2Br][Al(OTeF_5)_4]$	$[Me_2Br][SbF_6]$[85]
MeI	323.7	<5 min	26.1	$[Me_2I][Al(OTeF_5)_4]$	$[Me_2I][SbF_6]$[85]
$N_3C_3F_3$	358.5	<30 min	34.1	$[MeN_3C_3F_3][Al(OTeF_5)_4]$	-
$P(CF_3)_3$	367.2	2 days	53.7	$[MeP(CF_3)_3][Al(OTeF_5)_4]$	$[MeP(CF_3)_3][SbF_6]$[76]
PF_3	370.2	20 min	44.4	$[MePF_3][Al(OTeF_5)_4]$	-
NC_5F_5	376.7	<30 min	31.3	$[MeNC_5F_5][Al(OTeF_5)_4]$	-
NC_5F_4I	400.0	<30 min	31.2	$[MeNC_5F_4I][Al(OTeF_5)_4]$	-

[a]: MCA = $-\Delta H0$ for reaction Me^+ + base → $[Me\text{-base}]^+$ in gas phase.

[b]: $\Delta E^{\ddagger}$ difference of ZPE corrected energies between substrate−$[Me_2Cl]^+$ complex and transition state including COSMO (ε_R SO_2).

[c]: all literature known salts, beside $[Me_2Cl][CHB_{11}Cl_{11}]$, are synthesized with the MeF/SbF_5 system.

[d]: slow dynamic exchange between $[Me_2Cl]^+$ and excess MeCl is observed by EXSY.

The complexes between the substrates and the $[Me_2Cl]^+$ ion are dominated by a weak lone pair to σ* interaction (see figure 3.5 for one example). A similar weak interaction is present in the complexes between MeCl and the products. The distortion from the ideal C_{2v} structure of the $[Me_2Cl]^+$ ion in the substrate complexes is small. For all educt and product complexes which are considered for table 3.2, the energy gain through complexation is below 7.6 kJ·mol^{-1} on RI-B3LYP-D3/def2-TZVPP level of theory including COSMO (ε_R SO_2).

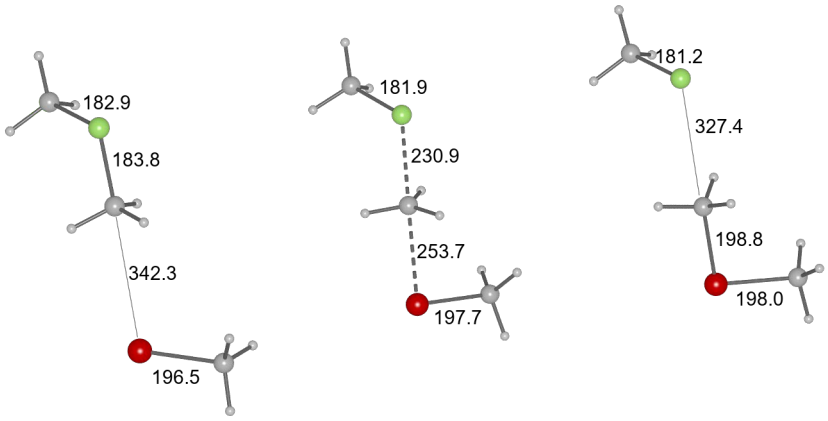


Figure 3.5: Structure of $[Me_2Cl]^+$−MeBr complex (left), transition state (middle) and MeCl−$[Me_2Br]^+$ complex (right) on RI-B3LPY-D3/def2-TZVPP level of theory including COSMO (ε_R SO_2), distances in pm.

From a solution of the salt $[MeNC_5F_4I][Al(OTeF_5)_4]$ (**5**) in dichloromethane colorless crystals suitable for X-ray diffraction where grown by cooling to −80 °C. The salt **5** crystallizes in the triclinic space group $P\bar{1}$(see figure 3.6). The anion cation interactions are limited to one F−C interaction (C1−F7') and one halogen-halogen bond between I1 and F5. As the halogen bond acceptor is a weakly coordinating anion (WCA) the bond strength of the halogen bond is expected to be low with a normalized contact (observed distance divided by sum of van der Waals radii)[153] of 0.92. For stronger halogen bonds with participation of tetrafluoro-4-iodo-pyridine the normalized contact is in the range of 0.75 to 0.80.[154]

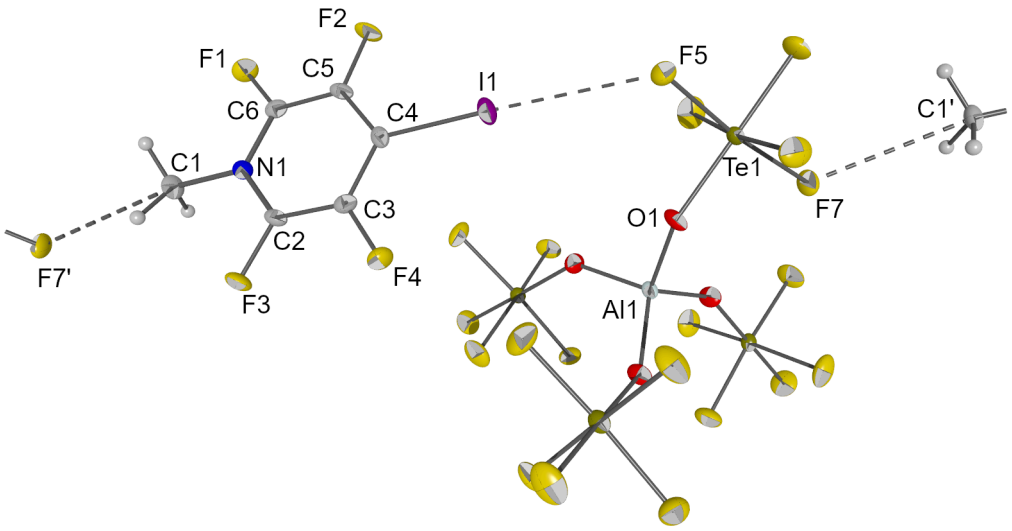


Figure 3.6: Molecular structure of $[MeNC_5F_4I][Al(OTeF_5)_4]$ (**5**) in the solid state. Thermal ellipsoids set at 50 % probability. Selected bond lengths [pm] and angles [°]: C1-N1 150.1(4), N1-C2 134.4(3), C2-C3 136.6(4), C3-C4 138.5(4), C4-C5 138.6(4), C5-C6 137.0(4), C6-N1 134.9(3), C2-F3 131.4(3), C3-F4 132.8(3), C4-I1 205.9(3), C5-F2 132.9(3), C6-F1 130.7(3), I1-F5 320.6(2), C1-F7' 307.2(4); C4-I1-F5 172.2(1), C2-N1-C6 118.5(2), C3-C4-C5 116.9(3), F7'-C1-N1 170.2(2).

From a solution of [$MeN_3C_3F_3$][$Al(OTeF_5)_4$] (**6**) in dichloromethane crystals of [$MeN_3C_3F(OTeF_5)_2$][$Al(OTeF_5)_4$] (**7**) suitable for X-ray diffraction were grown by slowly cooling the solution to −40 °C. Compound **7** crystallizes in monoclinic space group $P2_1/c$ (see figure 3.7). At room temperature, a colorless solution of **6** in dichloromethane decomposes within one day to a two phase system with a dark and oily lower phase. This decomposition shows the highly Lewis acidic character of the $[MeN_3C_3F_3]^+$ cation.

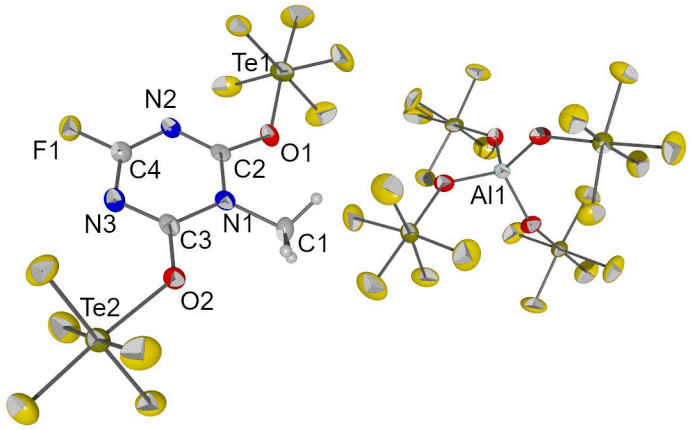
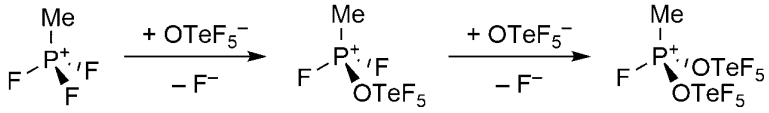


Figure 3.7: Molecular structure of [$MeN_3C_3F(OTeF_5)_2$][$Al(OTeF_5)_4$] (**7**) in the solid state. Thermal ellipsoids are shown at 50 % probability. Selected bond lengths [pm] and angles [°]: C1-N1 148.7(8), N1-C2 135.6(8), C2-N2 131.3(8), N2-C4 131.7(9), C4-N3 131.6(8), N3-C3 130.8(8), C3-N1 137.3(9), C2-O1 131.3(9), C4-F1 129.9(7), C3-O2 129.8(8), O1-Te1 193.8(5), O2-Te2 194.0(5); C2-N1-C3 116.1(6), N1-C2-N2 123.7(6), C2-N2-C4 114.0(6), N2-C4-N3 129.0(6), C4-N3-C3 114.2(6), N3-C3-N1 123.1(6), C2-O1-Te1 127.9(5), C3-O2-Te2 126.9(5), N2-C2-O1-Te1 9.3(9), N3-C3-O2-Te2 4.0(9).

The decomposition reaction of [$MeN_3C_3F_3$][$Al(OTeF_5)_4$] is similar to that of [$MePF_3$][$Al(OTeF_5)_4$] in solution (equation 3.6). In both cases the source of pentafluoro-*ortho*tellurate ions is the weakly coordinating anion $[Al(OTeF_5)_4]^-$. The decomposition reactions of $[MePF_3]^+$ and $[MeN_3C_3F_3]^+$ in solution show the strong Lewis acidic character of the methylated weakly basic molecules. This also indicated by the high fluoride ion affinities (FIAs) of the cations (see table 3.3).



(3.6)

Table 3.3: Fluoride ion affinities (FIA) of selected Lewis acids in kJ·mol^{-1}.

Compound	FIA[a]	Compound	FIA[a]
BF_3	356	$[MePF_3]^+$	851
PF_5	385	$[MeN_3C_3F_3]^+$	779
AsF_5	445	$[FP(C_6F_5)_3]^+$	773
SbF_5	500	$[MeOPF_3]^+$	863

[a] RI-B3LYP-D3/def2-TZVPP level using TMS^+/TMSF as anchor point.[143]

Since the FIAs are defined and calculated for gas phase molecules, the values for cations must be much higher than those for neutral Lewis acids because of the coulomb attraction. However, the cation $[MePF_3]^+$ is a stronger Lewis acid then the previously reported exceptional strong Lewis acid $[FP(C_6F_5)_3]^+$.[155,144] For a more accurate determination of the Lewis acidity of $[MePF_3]^+$, solutions of $[n\text{Bu}_4\text{N}][EF_6]$ (E = P, As, Sb) are added to a solutions of $[MePF_3][Al(OTeF_5)_4]$. In case of the hexafluorophosphate salt, the formation of $MePF_4$ shows, that the cation $[MePF_3]^+$ is a stronger Lewis acid than PF_5. Since $[SbF_6]^-$ is stable in the presence of $[MePF_3]^+$, SbF_5 is a stronger Lewis acid then the cation. The addition of $[AsF_6]^-$ did not yield the formation of $MePF_4$, instead less specific decomposition reaction take place. Note, that $[MeOPF_3]^+$, with a FIA value only slightly higher than that of $[MePF_3]^+$, readily reacts with $[AsF_6]^-$ in a multi-step reaction (see also equation 1.25).[99]

As the decomposition products $[MePF(OTeF_5)_2]^+$ and $[MeN_3C_3F(OTeF_5)_2]^+$ are more stable than their parent ions, one might conclude that the Lewis acidity decreases upon F to $OTeF_5$ exchange. This is in agreement with decreasing FIA values of the cations (see table 3.4).

Table 3.4: Fluoride ion affinities (FIA) of selected Lewis acids after F-$OTeF_5$ exchange in kJ·mol^{-1}.

Compound	FIA[a]	Compound	FIA[a]
$[MePF_3]^+$	851	$[MeN_3C_3F_3]^+$	779
$[MePF_2(OTeF_5)]^+$	811	$[MeN_3C_3F_2(OTeF_5)]^+$	752
$[MePF(OTeF_5)_2]^+$	782	$[MeN_3C_3F(OTeF_5)_2]^+$	722
$[MeP(OTeF_5)_3]^+$	767	$[MeN_3C_3(OTeF_5)_3]^+$	713

[a] RI-B3LYP-D3/def2-TZVPP level using TMS^+/TMSF as anchor point.[143]

3.3 Binding Properties of $OTeF_5$

The decreasing Lewis acidity through F to $OTeF_5$ exchange for the cations contradicts the literature known Lewis acids EX_5 (E = P, As, Sb; X = F, $OTeF_5$, not mixed) where the FIA increases upon introduction of $OTeF_5$ groups.[29] As shown in figure 3.7 (left) the FIA for the cations $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$ also decreases with increasing x. However the FIA of $PF_{5-x}(OTeF_5)_x$ increases monotonically with increasing x. Interestingly, the natural population analysis (NPA) charge at the central atoms decreases in all considered molecules with gradual introduction of $OTeF_5$ groups (see figure 3.8 right).

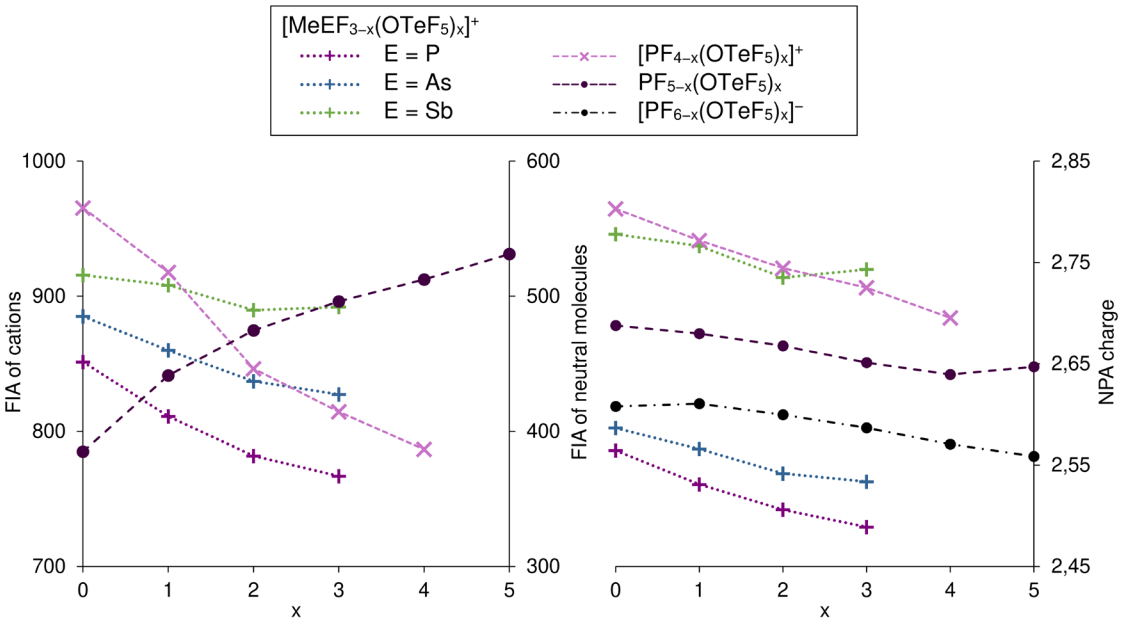


Figure 3.8: left: FIA of $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$ and $PF_{5-x}(OTeF_5)_x$ in $kJ \cdot mol^{-1}$ on RI-B3LYP-D3/def2-TZVPP level of theory using $TMS^+/TMSF$[143] as anchor point. right: NPA charge of central atom in $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$, $PF_{5-x}(OTeF_5)_x$ and $[PF_{5-x}(OTeF_5)_x]^-$ on RI-B3LYP-D3/def2-TZVPP level of theory.

For simplicity natural bonding orbital (NBO) analysis is carried out for the molecules $[PF_3(OTeF_5)]^+$, PF_4OTeF_5, $[PF_5(OTeF_5)]^-$. In the cation $[PF_3(OTeF_5)]^+$, the P−F bonds are slightly more ionic than the P−O bond (see table 3.5). In this cation, the phosphorous is only incorporated in ordinary 2-center-2-electrons bonds. The opposite is observed in the hypervalent anion $[PF_5(OTeF_5)]^-$. Furthermore the lone pair to σ* interaction differs between molecules with and without hypervalent 3-center-4-electron bonds (see figure 3.9). The $OTeF_5$ group stabilizes 3-center-4-electron bonds in hypervalent species compared to a fluorido ligand, because it allows for a more efficient charge delocalization via the σ*(P–O) orbitals than the σ*(P−F) orbitals. This is most apparent in the two isomers of PF_4OTeF_5. With the $OTeF_5$ group in axial position and those incorporated in a 3-center-4-electron bond, the donation of the oxygen lone pairs is lower than with the $OTeF_5$ group on equatorial position. More important is the donation of the fluorine lone pairs into the σ*(P−O) orbital, which is much larger for the $OTeF_5$ group in axial – hypervalent – position.

Table 3.5: Average X-atom contribution at the P−X (X = F, O) natural bonding orbitals in $[PF_3(OTeF_5)]^+$, PF_4OTeF_5 and $[PF_5(OTeF_5)]^-$.

Compound	P−F	P−O
$[PF_3(OTeF_5)]^+$	80.7%	78.2%
$PF_4(OTeF_5)^{eq}$	81.0%	79.6%
$PF_4(OTeF_5)^{ax\,[a]}$	81.0%	81.0%
$[PF_5(OTeF_5)]^-$	82.2%	84.2%

[a] The isomer with $OTeF_5$ ligand axial is less stable by 8.8 $kJ{\cdot}mol^{-1}$.

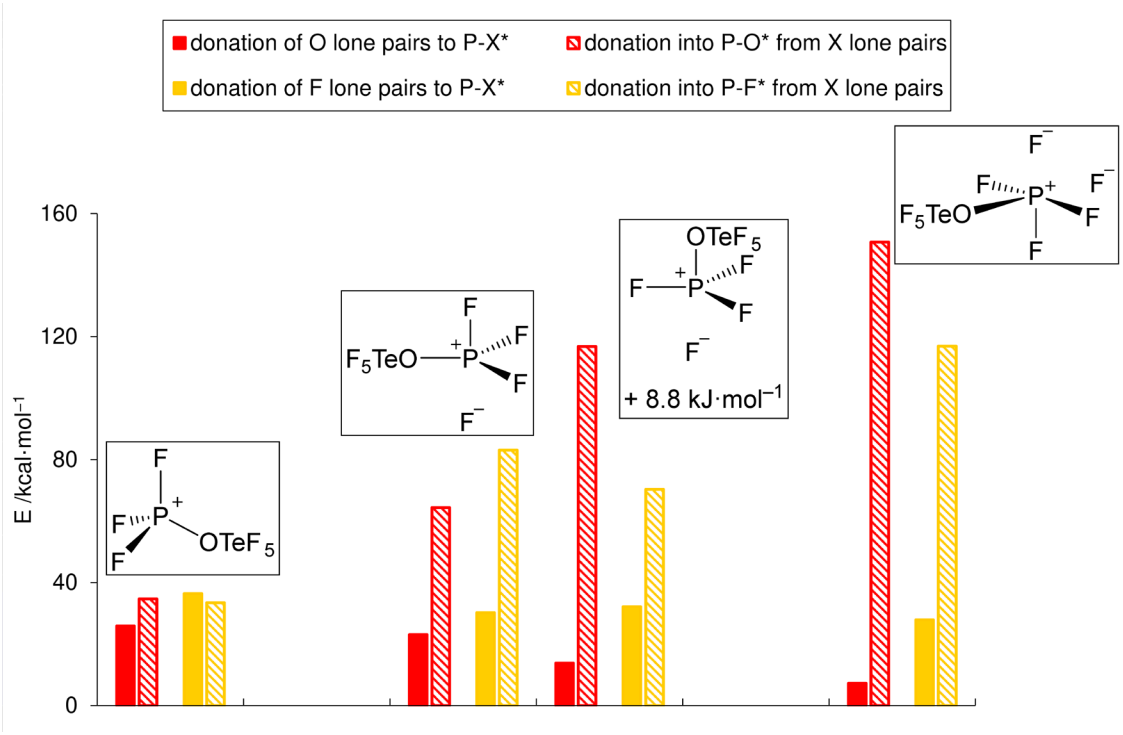


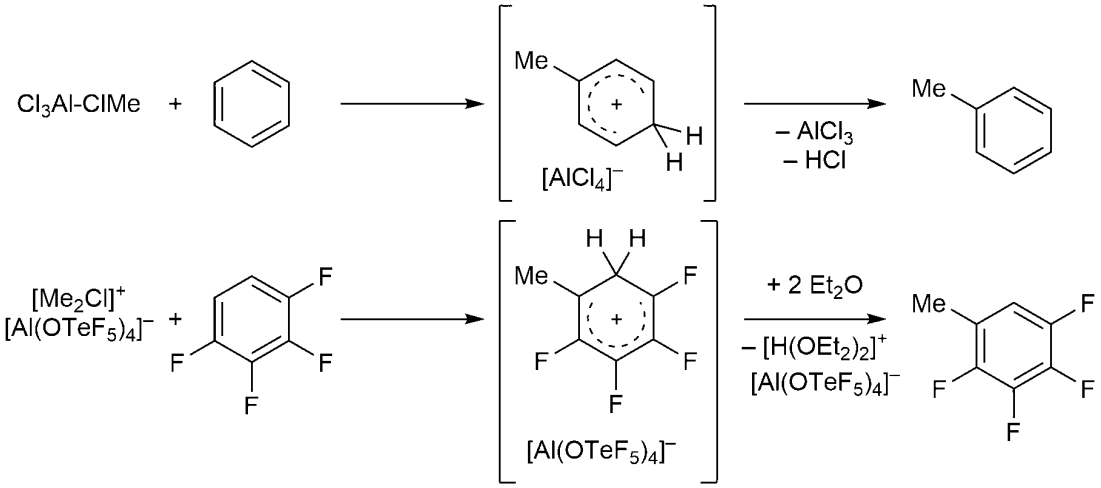
Figure 3.9: Sum of interaction energies obtained from second order perturbation theory analysis of the fock matrix in the NBO basis for $[PF_3(OTeF_5)]^+$, PF_4OTeF_5 and $[PF_5(OTeF_5)]^-$. (donation of Y (Y = O, F) lone pairs to P−X*: sum of donation of all lone pairs of one Y into all P−X* orbitals, donation into P−Y* from X lone pairs: sum of donation of all lone pairs into one P−X* orbital, for Y = F: average over the three covalently bonded fluorine atoms).

These results of the binding properties of the pentafluoro-*ortho*tellurate group are in agreement with the ambiguous literature known comparisons of the electron withdrawing properties of F and $OTeF_5$, which are described in section 1.1 and which all depend on more properties than only the electronic properties. The NMR analysis of CH_3X[23] and CH_3CH_2X[28] (X = I, Br, Cl, F, $OTeF_5$) are both without the presence hypervalent 3-center-4-electron bonds, therefore $OTeF_5$ seems to be not stronger electron withdrawing than fluorine. For the structures of $IF_{5-x}(OTeF_5)_x$[23], hypervalent 3-center-4-electron bonds are present, therefore $OTeF_5$ seems to be stronger electron withdrawing than fluorine. For the methods where the s-electron density at the nuclear core is important, regardless of presence of 3-center-4-electron bonds or not, the NPA charge decreases when replacing F by $OTeF_5$, therefore fluorine seems to be stronger electron withdrawing. This includes ^{31}P-NMR studies of OPF_2X (X = Br, Cl, F, $OTeF_5$)[23], ^{125}Te-

NMR studies of TeX_4, TeX_6(X = F, $OTeF_5$, not mixed)[28] and also ^{129}Xe-NMR and ^{129}Xe Mößbauer spectroscopy of XeX_2, XeX_4 and $OXeX_4$ (X = F, $OTeF_5$, not mixed)[28]. The $OTeF_5$ ligands of *cis*-[Ni($^{i\text{Pr}}$Im)$_2$($OTeF_5$)$_2$] are incorporated in hypervalent 3-center-4-electron bonds, therefore they are strong electron withdrawing.

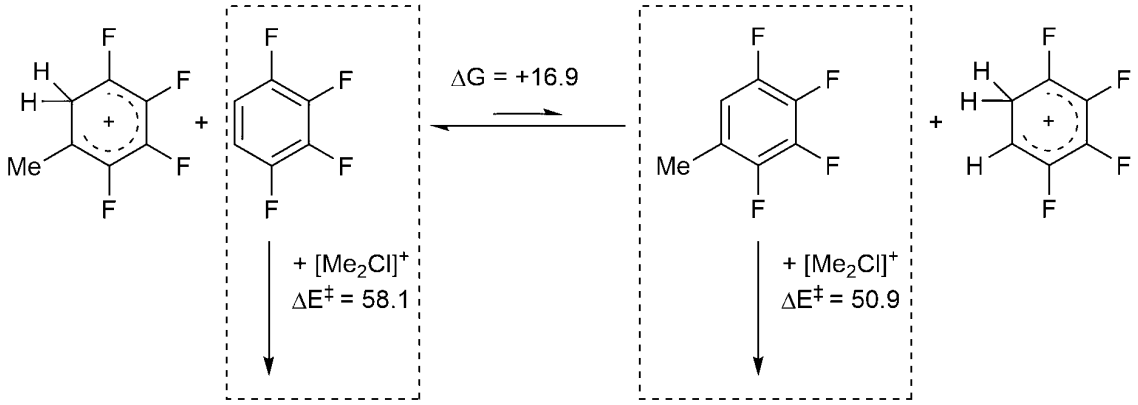
3.5 Friedel-Crafts Like Methylation

The dimethylchloronium salt **4** readily reacts with the fluorinated arenes 1,2-difluorobenzene, 1,2,3-trifluorobenzene and 1,2,3,4-tetrafluorobenzene. This reactivity is similar to the classical Friedel-Crafts methylation[101,102] (see scheme 3.1). One difference is the rearomatization of the Wheland intermediate. In the Friedel-Crafts methylation, HCl is eliminated permanently during the reaction. With **4** as methylation agent the rearomatization occurs only through addition of diethyl ether in a separate step. Even trough, multi methylation occurs in both cases.



Scheme 3.1: Comparison of Friedel-Crafts alkylation of benzene with the $AlCl_3$/MeCl system in MeCl (top) and the methylation of 1,2,3,4-tetrafluorobenzene with [Me_2Cl][Al($OTeF_5$)$_4$] (bottom).

The presence of multi-methylated products indicates, that there must be a fast equilibrium in which methyltetrafluorobenzene and protonated tetrafluorobenzene are formed (see scheme 3.2). On RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2) this step is only disfavored by 16.9 kJ·mol^{-1} of free enthalpy. The calculated transition state for the methylation by [Me_2Cl]$^+$ is for methyltetrafluorobenzene 7.2 kJ·mol^{-1} lower in energy than for tetrafluorobenzene. The more basic methyltetrafluorobenzene reacts faster with the dimethylchloronium cation than tetrafluorobenzene. The barrier for the methylation of 1,2,3,4-tetrafluorobenzene is 58.1 kJ·mol^{-1}, which is higher than that for the methylation of $P(CF_3)_3$ 53.7 kJ·mol^{-1} (see also table 3.2). Hence, a reaction time longer than two days would be required to methylate 1,2,3,4-tetrafluorobenzene quantitatively.



Scheme 3.2: Equilibrium in the reaction mixture of $[Me_2Cl][Al(OTeF_5)_4]$ (**4**) with 1,2,3,4-tetrafluorobenzene; values given in kJ·mol^{-1} on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2).

The less fluorinated and more basic aromatic compounds 1,2,3-trifluorobenzene and 1,2-difluorobenzene reacts faster with **4** than 1,2,3,4-tetrafluorobenzene (see table 3.6). The methylation occurs preferentially in *para* position to a fluorine atom. This is in agreement with quantum-chemical calculations on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2) where the transition state for the methylation of 1,2-difluorobenzene with $[Me_2Cl]^+$ in 4-position is by 3.1 kJ·mol^{-1} lower in energy than in 3-position.

Table 3.6: Methyl cation affinities (MCA) of fluorinated aromatic molecules and energy of the transition state for their methylation with **4**. Energies and Enthalpies in kJ·mol^{-1} on RI-B3LYP-D3/def2-TZVPP level of theory. The consumption of **4** is given after 30 minutes at room temperature.

substrate	**MCA[a]**	**$\Delta E^{\ddagger}$[b]**	**consumption of 4**
1,2,3,4-tetraflourobenzene	310.0	58.1	10%
methyl-1,2,3,4-tetrafluorobenzene	338.3	50.9	-
1,2,3-trifluorobenzene	361.4	52.3	100%
1,2-difluorobenzene	369.0	51.7 (4 position) 54.7 (3 position)	100%

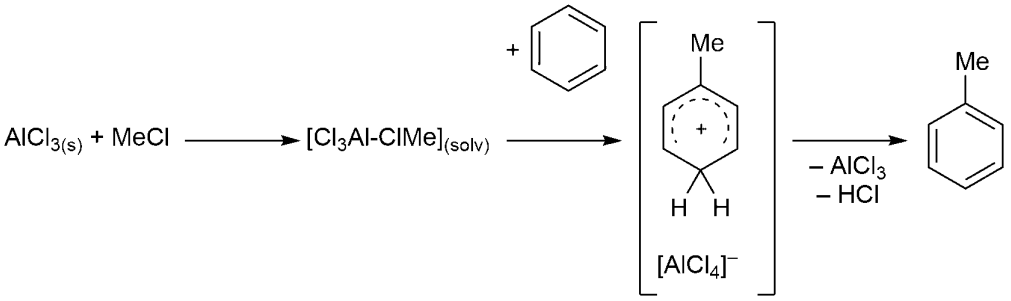
[a]: MCA = $-\Delta H0$ for reaction Me^+ + base → $[Me\text{-base}]^+$ in gas phase.

[b]: $\Delta E^{\ddagger}$ difference of ZPE corrected energies between pre complex and transition state including COSMO (ε_R SO_2).

The less reactive bromonium ion $[Me_2Br]^+$ reacts slower with 1,2,3-triflourobenzene than $[Me_2Cl]^+$. In contrast, the iodonium ion $[Me_2I]^+$ does not react with 1,2,3-trifluorobenzene or 1,2-difluorobenzene. These observations are in agreement with increasing reaction barriers as calculated on RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2). For the methylation of 1-2-difluorobenzene in 4-position the energy of the transition states increases from 51.7 kJ·mol^{-1} ($[Me_2Cl]^+$) to 56.6 kJ·mol^{-1} ($[Me_2Br]^+$) and 73.6 kJ·mol^{-1} ($[Me_2I]^+$).

3.6 The Role of the $[Me_2Cl]^+$ Cation in Friedel-Crafts Type Methylation Reactions

In classical Friedel-Crafts alkylation reaction, with a Lewis acid like $AlCl_3$ and a methyl source like MeCl, the presents of multi-methylated products is explained by continuous rearomatization through elimination of HCl (see scheme 3.3). The methylation agent faster attacks the methylated product because it is more basic. However, this is not the only possible mechanism for the formation of multi-methylated product as those products are – as described above – also formed through the methylation with the dimethylchloronium salt **4** where methylation and rearomatization are separated steps. As the dimethylchloronium cation was suggested by Olah as intermediate in Friedel-Crafts methylation[85] a reevaluation of the mechanism of the classical Friedel-Crafts alkylation is appropriate.



Scheme 3.3: Friedel-Crafts alkylation of benzene with $[Cl_3Al{-}ClMe]$.

The reaction mechanism for the methylation of 1,2-difluorobenzene with $[Cl_3Al{-}ClMe]$ in MeCl has been evaluated on RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R MeCl). As shown in figure 3.10 the formation of the contact ion pair $[Me_2Cl][AlCl_4]$ from $[Cl_3Al{-}ClMe]$ and MeCl is disfavored by 22.6 $kJ{\cdot}mol^{-1}$. However, the route over the contact ion pair is still overall favored, as TS1 is higher in energy than TS2 and TS3. In the presence of a more polar solvent than MeCl the formation of solvent separated ions would by more favored (route through TS3a). In this case, there would be an additional competing equilibrium between $[Cl_3Al{-}ClMe]$ and $[Cl_3Al{-}solv]$.

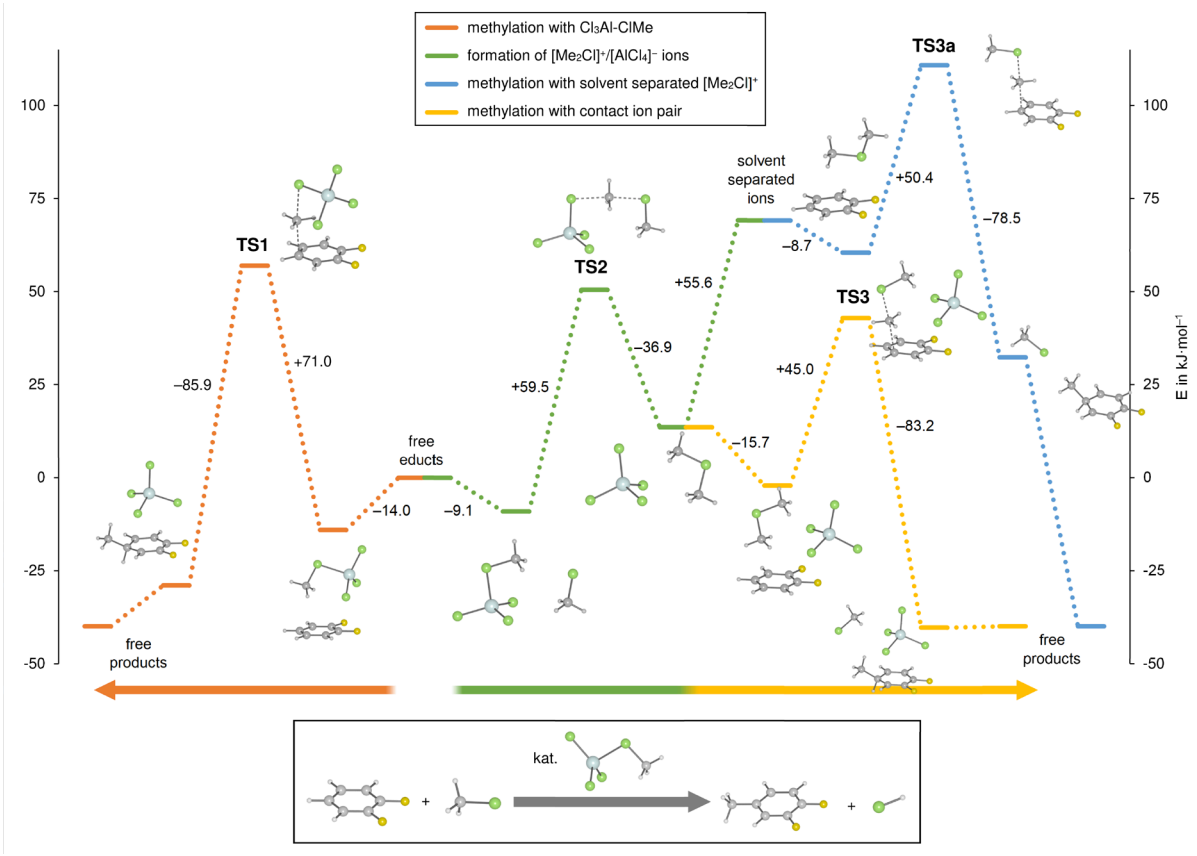
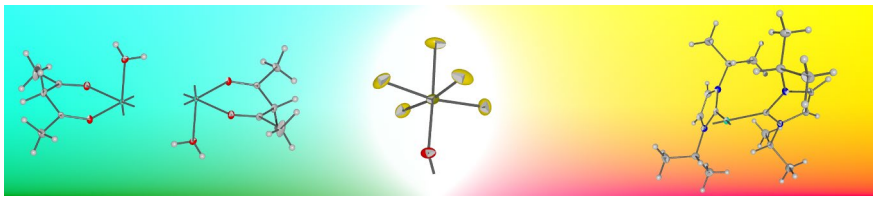


Figure 3.10: Reaction profiles for the methylation of 1,2-difluorobenzene with the $AlCl_3$-MeCl system. Energies (ZPE corrected) in $kJ \cdot mol^{-1}$ on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R MeCl). The final steps (rearomatization and catalyst recovery) are omitted for clarity, and energy differences between linked energy levels are indicated.

4 Publications

4.1 Investigation of Organonickel-Pentafluoro-*ortho*tellurates



Sebastian Hämmerling, Lisa Mann, Simon Steinhauer, Maximilian W. Kuntze-Fechner, Udo Radius, and Sebastian Riedel*

Z. Anorg. Allg. Chem. **2018**, *644*(17), 1047-1050.

https://doi.org/10.1002/zaac.201800177

Author contribution

Sebastian Hämmerling contributed to the project design, performed all experiments, the product characterization, quantum-chemical calculations and wrote the manuscript. Lisa Mann and Simon Steinhauer conducted the crystallographic studies. Maximilian W. Kuntze-Fechner synthesized [$NiBr_2(^{i\mathrm{Pr}}Im)_2$]. Simon Steinhauer and Sebastian Riedel supervised the project and provided scientific guidelines. Simon Steinhauer, Sebastian Riedel and Udo Radius revised the manuscript.

Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

DOI: 10.1002/zaac.201800177

ARTICLE

Investigation of Organonickel-Pentafluoroorthotellurates

Sebastian Hämmerling,[a] Lisa Mann,[a] Simon Steinhauer,[a] Maximilian W. Kuntze-Fechner,[b] Udo Radius,[b] and Sebastian Riedel*[a]

Dedication to Prof. Dr. Alexander Filippou on the Occasion of his 60th Birthday

Abstract. The pentafluoroorthotellurate (F_5TeO–, teflato) group was transferred to two organonickel precursors resulting in the formation of $[Ni(Hacac)_2(OTeF_5)_2]$ and $[Ni(^{iPr}Im)_2(OTeF_5)_2]$. These complexes show completely different behavior in their stability against stronger coordinating agents, coordination arrangement, and their spin state. Interestingly, traces of water did not hydrolyze the teflato ligand, instead coordinating to the central nickel atom with formation of a dinuclear complex $[\{Ni(Hacac)(H_2O)(OTeF_5)(\mu\text{-}OTeF_5)\}_2]$.

Introduction

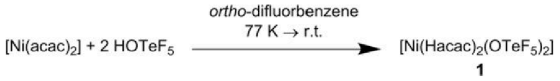
Based on its strong electron withdrawing properties the pentafluoroorthotellurate (F_5TeO–, teflato) group has been used to stabilize unusual oxidation states and coordination arrangements[1] e.g. $Xe(OTeF_5)^+$ [2] and $[Hg(OTeF_5)_5]^{3-}$.[3] This is further supported by the high steric demand and delocalization of the negative charge, which results in a versatile inorganic coordination chemistry. This has led to thorough investigation of teflates starting in the middle of the last century[4] and recently to the development of a new superacid $H[Al(OTeF_5)_4]$.[5]

Combining these properties of the teflato ligand with nickel as a central metal resulted in a challenging research field. Even though *McQuiston* and *Strauss* mentioned in 1993 the $[Ni(OTeF_5)_4]^{2-}$ anion in a review about weakly coordinating anions, no experimental details on any nickel teflates have been published so far.[6] The synthesis of nickel teflates were hampered for long time due to the lack of a good soluble, easily accessible precursor.

Herein we present the facile synthesis of $[Ni(Hacac)_2(OTeF_5)_2]$ (**1**) and $[Ni(^{iPr}Im)_2(OTeF_5)_2]$ (**3**), which are the first examples of well characterized nickel-teflate compounds.

Results and Discussion

The reaction of two equivalents of teflic acid with nickel(II) acetylacetonate in *ortho*-difluorobenzene yields bis(acetylacetone)bis(pentafluoro-*ortho*-tellurato)nickel(II), $[Ni(Hacac)_2(OTeF_5)_2]$ (**1**), as a turquoise colored precipitate (Scheme 1). The acetylacetonato ligands are protonated by the teflic acid ($HOTeF_5$) and the $OTeF_5$ group coordinates to the nickel forming an octahedral coordinated complex. Crystals suitable for X-ray diffraction were grown through recrystallization from *ortho*-difluorobenzene at 0 °C. The compound $[Ni(Hacac)_2(OTeF_5)_2]$ crystallizes in the monoclinic space group $P2_1/c$ (see Figure 1).



Scheme 1. Reaction between teflic acid and nickelacetylacetonate.

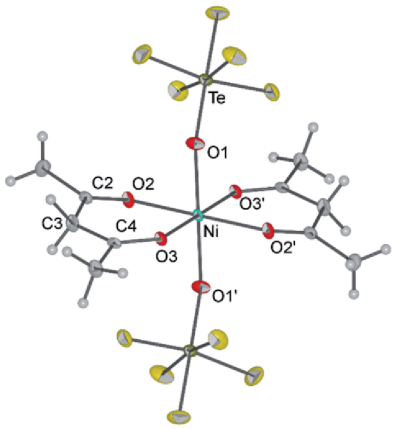


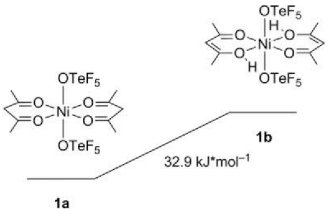
Figure 1. Molecular structure of $[Ni(Hacac)_2(OTeF_5)_2]$ (**1**); thermal ellipsoids drawn at a 50% probability level. Selected bond length /pm and angles /°: Ni–O1 202.6(2), Ni–O2 204.2(2), Ni–O3 203.1(2), O1–Te1 178.6(2), O2–C2 122.3(2), O3–C4 122.4(1), C2–C3 149.9(1), C4–C3 150.7(1), O2–Ni–O3 89.3(1), O3–Ni–O2' 90.7(1), O1–Ni–O2 87.7(1), O1–Ni–O3 85.5(1) Ni–O1–Te 133.7(1), C2–C3–C4 121.0(2).

* Prof. Dr. S. Riedel
E-Mail: s.riedel@fu-berlin.de
[a] Institut für Chemie und Biochemie
Freie Universität Berlin
Fabeckstr. 34/36
14195 Berlin, Germany
[b] Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland
97074 Würzburg, Germany
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201800177** or from the author.

Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

ARTICLE

The oxygen atoms of the acetylacetone ligands form a nearly perfect plane with O–Ni–O angles of 89.3(1)° (O2–Ni–O3) and 90.7(1)° (O3–Ni–O2'), while the angle between the acetylacetone plane and the teflato ligands is with 84.1(1)° slightly distorted. It is notable that the carbon backbones of the acetylacetone ligands are almost flat, the angle between the oxygen plane and the plane defined by the three central carbon (C2–C3–C4) atoms is only 6.4(1)°. The equal C–O bond lengths [*d*(C2–O2) = 122.3(2) pm, *d*(C4–O3) = 122.4(2) pm] as well as the C–C bond lengths [*d*(C4–C3) = 150.7(1) pm, *d*(C2–C3) = 149.9(1) pm] clearly show the coordination of acetylacetone. The C–C bond length are similar to distances determined for [$NiBr_2(Hacac)_2$] of 151 and 152 pm.[7] This excludes an acetylacetonato ligand with C–C bond length of 139.9(1) to 141.3(1) pm.[8] The presence of a CH group and consequently an enol-like structure (see Scheme 2) with alternating single and double bonds can be excluded in view of the experimental structure and those optimized on RI-B3LYP-D3/def2-TZVPP level of theory (see Table 1).



Scheme 2. Isomers of compound **1** with energy difference at RI-B3LYP-D3/def2-TZVPP level of theory.

Table 1. Comparison of experimental and calculated (RI-B3LYP-D3/def2-TZVPP) bond lengths /pm and angles /° of compound **1**.

Structure	Angle C2–C3–C4	Distance C–C	Distance C–O
XRD	121.0(2)	149.9(1)	122.3(1)
		150.7(1)	122.4(1)
1a	115.1	149.8	121.7
		150.6	121.8
1b	127.8	135.1	123.9
		145.0	135.4

Upon dissolving compound **1** in acetonitrile for an ESI-MS a color change to a blue solution is observed. Only solvolysis products like $[Ni(MeCN)_6]^{2+}$ and $[Ni(MeCN)_5(OTeF_5)]^+$ are observed in the positive ESI. The observation is supported by ^{19}F NMR studies, where in [D_3]acetonitrile sharp resonances of non-coordinated teflate ions are observed, whereas the NMR spectra recorded in [D_2]dichloromethane are strongly broadened due to the paramagnetic nature of **1**.

From the primary reaction mixture of **1** in *ortho*-difluorobenzene also crystals of [{Ni(Hacac)(H_2O)($OTeF_5$)(μ-$OTeF_5$)}$_2$] (**2**) were grown. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ (see Figure 2). There is a loss of one acetylacetone, which is compensated through bridging teflato ligands. The bridging teflato ligands and the oxygen atoms of the acetylacetone form a common plane for both central nickel atoms. Again the positions perpendicular to this plane are slightly distorted from 90° with angles of 85.3(1)° ($OTeF_5$) and 85.1(1)° (OH_2). This structure is additionally stabilized by a hydrogen bond between the water ligand and the teflato ligand with a O5–O4' distance of 280.9(3) pm, which is in agreement with a strong hydrogen bond.[9]

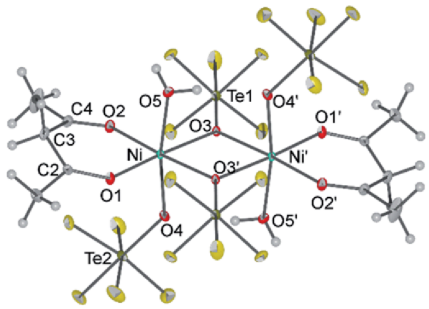
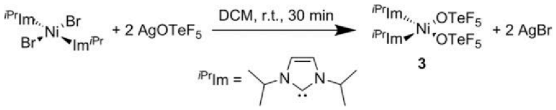


Figure 2. Molecular structure of [{Ni(Hacac)(H_2O)($OTeF_5$)(μ-$OTeF_5$)}$_2$] (**2**); thermal ellipsoids drawn at a 50% probability level. Selected bond length /pm and angles /°: Ni–O1 200.5(2), Ni–O2 200.3(2), Ni–O3 206.7(2), Ni–O4 205.2(2), Ni–O5 206.9(2), O4–Te2 179.6(2), O3–Te1 180.9(2), Ni–Ni' 315.4(1), O1–C2 122.8(2), O2–C4 122.6(2), C2–C3 150.8(3), C3–C4 150.3(3), O1–Ni–O2 89.0(1), O1–Ni–O3' 94.5(1), O2–Ni–O3 95.5(1), O3–Ni–O3' 81.1(1), O5–Ni–Ni' 85.0(1), O4–Ni–Ni' 85.4(1), Ni–O4–Te2 134.6(1), Ni–O3–Te1 131.2(7), Ni'–O3–Te2 129.7(1), C2–C3–C4 118.8(2).

Another good soluble nickel complex is [Ni($^{i\mathrm{Pr}}$Im)$_2$Br$_2$] featuring the advantage of low spin complexes for NMR studies.[10] The reaction of teflic acid with [Ni($^{i\mathrm{Pr}}$Im)$_2$Br$_2$] in *ortho*-difluorobenzene results in a partial substitution of the bromido ligand and formation of the imidazolium salt (H$^{i\mathrm{Pr}}$Im)($OTeF_5$) as a side reaction. Using silver teflate as a transfer reagent yields quantitatively [Ni($^{i\mathrm{Pr}}$Im)$_2$($OTeF_5$)$_2$] (**3**) accompanied by the formation of silver bromide (Scheme 3). Crystals suitable for X-ray diffraction were grown by recrystallization from dichloromethane at 0 °C. The compound *cis*-[Ni($^{i\mathrm{Pr}}$Im)$_2$($OTeF_5$)$_2$] crystallizes in the monoclinic space group $P2_1/n$ (see Figure 3).



Scheme 3. Formation of *cis*-[Ni($^{i\mathrm{Pr}}$Im)$_2$($OTeF_5$)$_2$] (**3**).

As expected for a fourfold coordinated closed shell d^8 system, nickel is square-planar coordinated with a sum of bond angles of 360°. The O–Ni–O angle is slightly contracted to 88.1(1)° while the C–Ni–C angle is expanded to 92.1(1)°. In contrast to the starting compound, complex **3** features a *cis* conformer in the solid state. Note, that this structural motive is one of the rare examples of NHC *cis* coordination in a nickel(II) complex.[11–13] According to calculations in the gas phase at RI-B3LYP-D3/def2-TZVPP level of theory, complex **3** shows a *trans* coordinated minimum structure which is –19.1 kJ·mol^{-1} lower in energy as the *cis* coordinated one (see Table S1, Supporting Information). Taking solvent effects into

Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

ARTICLE

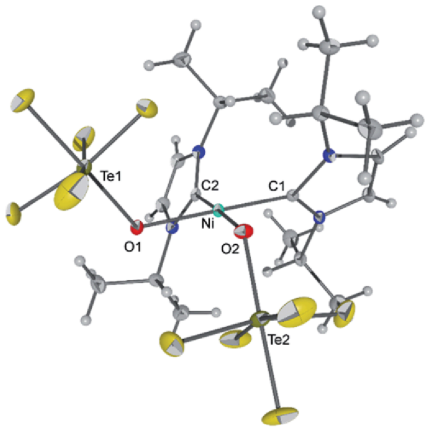


Figure 3. Molecular structure of [Ni(i^{Pr}Im)$_2$(OTeF$_5$)$_2$] (**3**); thermal ellipsoids are drawn at a 50 % probability level. Selected bond length / pm and angles /°: Ni–O1 192.7(2), Ni–O2 193.1(2), Ni–C1 187.4(2), Ni–C2 187.5(2), O1–Te1 179.6(2), O2–Te2 179.7(2), O1–Ni–O2 88.1(1), C1–Ni–C2 92.1(1), O1–Ni–C2 89.3(1), O2–Ni–C1 90.6(1), N–O1–Te1 120.0(1), Ni–O2–Te2 119.3(1).

account, using the COSMO model implemented in the Turbomole program package, complex **3** is predicted to be *cis* configured.

The experimental Ni–O–Te and Te–F vibrations at 818 cm^{-1} and 655 cm^{-1} indicates ionic Ni-OTeF$_5$ bonding.[14] The same conclusion can be drawn by evaluating the AB$_4$X spin system in the ^{19}F NMR spectrum.[9] Especially the differnce between δ_{FA} and δ_{FB} of 18.2 ppm is comparable to those of [(PS)H](OTeF$_5$) of 17.4 ppm (PS = protone sponge = 1,8-bis(dimethylamino) naphthalene).[15] The methyl groups show two discrete resonances in the NMR spectra due to hindered rotation around the C–C bond between the ring and the isopropyl groups shown by 2D NMR (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC, ^{1}H,^{13}C-HMBC, see Figures S1–S3, Supporting Information). This proves in agreement with our quantum-chemical calculations at RI-B3LYP-D3/def2-TZVPP COSMO ε_R = 35.94 that the *cis* configuration is also present in solution.

Comparing the ^{13}C NMR shifts of **3** with other nickel complexes bearing the same NHC ligand it becomes apparent that the more electron withdrawing the anionic ligands are, the further low field shifted the resonance of the carbene carbon is (see Table S2, Supporting Information). Due to the strong electron withdrawing properties of the teflato ligands, the carbene carbon shift of complex **3** exceeds with 140.9 ppm the usual range of 210 to 160 ppm for neutral [Ni(NHC)$_2X_2$] complexes. However this value is comparable to those published recently by *Braunstein* et al. for [Ni(NHC)$_2$(H$_2$O)$_2$]$^{2+}$ of 147 to 145 ppm.[13] This points out the strong Lewis acid character[16] of the [Ni(OTeF$_5$)$_2$] fragment. Note, that there is virtually no influence of the *cis*/*trans* constituent on the carbenoid shift.[11]

Conclusions

The complex [Ni(Hacac)$_2$(OTeF$_5$)$_2$] (**1**) was prepared by the reaction of nickel(II) acetylacetonate with teflic acid in a simple protonation reaction. During characterization it was found that both ligands (acetylacetone and teflato) can be easily replaced by stronger coordinating agents such as acetonitrile. Trace amounts of water lead to the formation of the teflate bridged compound [{Ni(Hacac)(H$_2$O)(OTeF$_5$)(μ-OTeF$_5$)}$_2$] (**2**).

Through the reaction of silver teflate and [Ni(i^{Pr}Im)$_2$Br$_2$] the complex *cis*-[Ni(i^{Pr}Im)$_2$(OTeF$_5$)$_2$] (**3**) was obtained. In contrast to **1**, this NHC complex is stable in acetonitrile. Complex **3** is one of the rare examples for Ni(II) NHC complexes where the NHC ligands are coordinated in cis-position to each other.

Experimental Section

The experiments were performed under exclusion of air and moisture using standard Schlenk techniques. The solvents CH$_2$Cl$_2$, CD$_2$Cl$_2$ and *ortho*-difluorobenzene were dried with CaH$_2$ while acetonitrile and [D$_3$]acetonitrile were dried with Sicapent®. Nickel(II)-acetylacetonate was purchased from abcr, dried 1 h at 120 °C under dynamic vacuum and recrystallized from *ortho*-difluorobenzene before storing and handling in a glovebox in a dry argon atmosphere, as all other solids. Teflic acid[17], [Ni(i^{Pr}Im)$_2$Br$_2$][10] and silver teflate[18] were prepared according to literature. IR spectra were recorded with a Bruker ALPHA FTIR spectrometer inside a glovebox equipped with a diamond ATR attachment (resolution 4 cm^{-1}). Raman spectra were recorded with a Bruker MultiRAM II equipped with a low-temperature Ge detector (1064 nm, 30–80 mW, resolution 2 cm^{-1}). Elemental analysis was performed with an Elementar vario el III. Double determination was performed to ensure homogeneous samples. NMR spectra were recorded with a JEOL 400 MHz ECS or ECZ spectrometer. For strongly coupled spin systems all chemical shifts and coupling constants are reported as simulated in gNMR.[19] All reported chemical shifts are referenced to the Ξ values given in IUPAC recommendations of 2008[20] using the ^{2}H signal of the deuterated solvent as internal reference. Mass spectra were recorded with an Advion Compact mass spectrometer expression L with a quadrupole mass filter. Samples were either inserted direct using ASAP sampling with APCI or dissolved in a dry solvent (CH$_3$CN or CH$_2$Cl$_2$) with ESI. Crystal data were collected with a Bruker D8 Venture diffractometer with a Photon 100 CMOS area detector with Mo-K_α radiation. Using Olex2,[21] the structure was solved with the ShelXT[22] structure solution program by intrinsic phasing and refined with ShelXL[23] refinement package using least square minimization. CCDC identifiers and further crystallographic data are given in the Supporting Information. Crystal structures were visualized with Diamond[24]. For density functional calculations the program package TURBOMOLE[25] was used with its implementations of RI[26], MARI-J[27], B3LYP[28], Grimme-D3,[29] and def2-TZVPP.[30] SCF energies were corrected with chemical potential taken from the in TURBOMOLE implemented freeh script, to get free enthalpies.

[Ni(Hacac)$_2$(OTeF$_5$)$_2$] (1): Teflic acid (216 mg, 0.90 mmol) was condensed on top of a frozen solution of nickelacetylacetonate (115 mg, 0.45 mmol) in 4 mL *ortho*-difluoro-benzene. The light green solution, which was formed upon melting, was filtered off to leave **1** as a turquoise colored solid (307 mg, 0.42 mmol, yield 93 %). Cooling down, a saturated solution in *ortho*-difluorobenzene to 0 °C yielded to the formation of crystals suitable for X-ray diffraction. C$_{10}$H$_{16}$F$_{10}$NiO$_6$Te$_2$ (736.11 g·mol^{-1}): C 16.35 (calcd. 16.32); H 2.25 (calcd. 2.19) %. **^{1}H NMR** (400.5 MHz, CD$_2$Cl$_2$, 20 °C): δ = 0.40 (s br), –1.00 (s br) ppm. **^{19}F NMR** (376.9 MHz, CD$_3$CN, 20 °C): δ = –42.7 (s br) ppm. **IR** (ATR, 25 °C): $\tilde{\nu}$ = 2892 (w), 1704 (s), 1376 (s), 1223 (w), 1169 (m),

Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

ARTICLE

987 (w), 863 (s), 713 (w), 663 (vs), 650 (vs), 605 (w), 589 (m), 572 (m) cm^{-1}. **FT-Raman** (25 °C): $\tilde{\nu}$ = 3086 (s), 2925 (m), 2893 (w), 1620 (w), 1269 (m), 1162 (w), 1104 (w), 1025 (s), 871 (m), 763 (vs), 667 (m), 657 (m), 595 (w), 567 (m), 296 (m), 198 (m) cm^{-1}. **ESI** (positive mode, MeCN) *m/z* = 504.3 ($[Ni(MeCN)_5(OTeF_5)]^+$, 1 %), 463.2 ($[Ni(MeCN)_4(OTeF_5)]^+$, 6 %), 420.1 ($[Ni(MeCN)_3(OTeF_5)]^+$, 1 %), 239.2 ($[Ni(acac)(MeCN)_2]^+$, 20 %), 152.1 ($[Ni(MeCN)_6]^{2+}$, 100 %), 131.6 ($[Ni(MeCN)_5]^{2+}$, 4 %). **ESI** (negative mode, MeCN) *m/z* = 241.0 ($OTeF_5^-$, 100 %), 225.0 (TeF_5^-, 10 %). **APCI** (ASAP, positive mode) *m/z* = 671.3 ($[Ni_3(acac)_5]^+$, 1 %), 413.3 ($[Ni_2(acac)_3]^+$, 6 %), 257.2 ($[Ni(acac)(Hacac)]^+$, 100 %). **APCI** (ASAP, negative mode) *m/z* = 241.1 ($OTeF_5^-$, 100 %), 225.0 (TeF_5^-, 7 %).

$[Ni(^{iPr}Im)_2(OTeF_5)_2]$ (3): DCM (2 mL) was added to a mixture of silver teflate (182 mg, 0.525 mmol) and $[Ni(^{iPr}Im)_2Br_2]$ (132 mg, 0.252 mmol). The slurry was stirred for 30 min before the orange colored solution was filtered of. The yellow residue was extracted twice with 2 mL acetonitrile. After removing of the solvent in vacuo **3** was obtained as a yellow solid (187 mg, 0.222 mmol, yield 88 %). Cooling down, a saturated DCM solution to 0 °C yielded to the formation of crystals suitable for X-ray diffraction., $C_{18}H_{32}F_{10}N_4NiO_2Te_2$ (840.36 g·mol^{-1}): C 25.92 (calcd. 25.72); 3.92 (calcd. 3.84); N 6.60 (calcd. 6.67) %. **^{1}H NMR** (400.5 MHz, CD_3CN, 20 °C): δ = 7.34 (s, 4 H, CH), 5.45 [sept, $^3J(^1H,^1H)$ = 6.6 Hz, 4 H, *i*Pr-CH], 1.45 [d, $^3J(^1H,^1H)$ = 6.6 Hz, 12 H, *i*Pr-CH_3], 1.16 [d, $^3J(^1H,^1H)$ = 6.6 Hz, 12 H, *i*Pr-CH_3'] ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, CD_3CN, 20 °C): δ = 140.9 ($C_{carbene}$), 121.3 (CH), 53.3 (*i*Pr-CH), 23.3 (*i*Pr-CH_3), 21.4 (*i*Pr-CH_3') ppm. **^{19}F NMR** (376.9 MHz, CD_3CN, 20 °C): δ = –19.8 [m, $^2J(^{19}F,^{19}F)$ = 170.1, $^1J(^{125}Te,^{19}F)$ = 2630 Hz, 1 F, F_A], –38.0 [m, $^2J(^{19}F,^{19}F)$ = 170.1, $^1J(^{125}Te,^{19}F)$ = 3651 Hz, 4 F, F_B]. **IR** (ATR, 25 °C): $\tilde{\nu}$ = 2985 (w), 2945 (w), 2882 (w), 1567 (m), 1468 (m), 1428 (m), 1416 (m), 1401 (s), 1376 (m), 1329 (w), 1302 (w), 1206 (s), 1177 (w), 1131 (m), 1065 (w), 1035 (w), 1000 (w), 936 (w), 823 (w), 829 (s), 818 (vs), 731 (m), 704 (w), 689 (w), 655 (vs), 606 (w), 657 (m), 486 (m), 467 (s), 440 (m) cm^{-1}. **FT-Raman** (25 °C) $\tilde{\nu}$ = 2987 (m), 2948 (s), 2918 (m), 2875 (w), 1569 (m), 1467 (m), 1446 (m), 1391 (m), 1334 (m), 1133 (w), 1037 (w), 947 (w), 885 (m), 830 (vs), 664 (vs), 630 (w), 610 (s), 460 (m), 366 (w), 334 (w), 310 (w), 285 (m), 228 (w), 159 (w), 103 (m) cm^{-1}. **APCI** (ASAP, positive mode): *m/z* = 602.9 ($[M - OTeF_5^-]^+$, 100 %). **APCI** (ASAP, negative mode): *m/z* = 240.9 ($OTeF_5^-$, 100 %), 224.8 (TeF_5^-, 80 %). **ESI** (acetonitrile, positive mode): *m/z* = 643.7 ($[M - OTeF_5^- + MeCN]^+$, 100 %).

Supporting Information (see footnote on the first page of this article): Carbene carbon shifts and computational results for $[Ni(i^{Pr}Im)_2X_2]$ complexes as well as further crystallographic details and 2D nmr spectra of **3**.

Acknowledgements

The authors gratefully acknowledge the research training network "Fluorine as a key element" for financial support, Solvay Fluor GmbH for donating of chemicals and the Zentraleinrichtung für Datenverarbeitung (ZEDAT) of the Freie Universität Berlin for computational time and support. UR and MWKF acknowledge support from Julius-Maximilians-Universität Würzburg and the Deutsche Forschungsgemeinschaft (DFG RA720/12–2).

Keywords: Carbene ligands; Metathesis; Pentafluoroortho-telurates; Nickel; Fluorine chemistry

References

[1] K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 877; *Angew. Chem.* **1982**, *94*, 890.
[2] B. A. Fir, H. P. A. Mercier, J. C. P. Sanders, D. A. Dixon, G. J. Schrobilgen, *J. Fluorine Chem.* **2001**, *110*, 89.
[3] J. R. DeBackere, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* **2015**, *54*, 1606.
[4] a) A. Engelbrecht, F. Sladky, *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 15; b) D. Lentz, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 66; *Angew. Chem.* **1979**, *91*, 68; c) F. Sladky, H. Kropshofer, O. Leitzke, *J. Chem. Soc., Chem. Commun.* **1973**, 134; d) F. Sladky, H. Kropshofer, *J. Chem. Soc., Chem. Commun.* **1973**, 600.
[5] A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; *Angew. Chem.* **2017**, *129*, 8375.
[6] S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927.
[7] S. Koda, S.'i. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, S. Kawaguchi, *J. Chem. Soc. D* **1971**, 1321.
[8] A. Lennartson, L. U. Christensen, C. J. McKenzie, U. G. Nielsen, *Inorg. Chem.* **2014**, *53*, 399.
[9] a) J. Emsley, *Chem. Soc. Rev.* **1980**, *9*, 91; b) P. E. Hansen, J. Spanget-Larsen, *Molecules* **2017**, *22*; c) H. Zhao, S. Tang, L. Du, *Spectrochim. Acta Part A* **2017**, *181*, 122.
[10] P. Fischer, T. Linder, U. Radius, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1491.
[11] R. Jothibasu, K.-W. Huang, H. V. Huynh, *Organometallics* **2010**, *29*, 3746.
[12] D. Zhang, S. Zhou, Z. Li, Q. Wang, L. Weng, *Dalton Trans.* **2013**, *42*, 12020.
[13] S. Hameury, P. de Frémont, P.-A. R. Breuil, H. Olivier-Bourbigou, P. Braunstein, *Organometallics* **2015**, *34*, 2183.
[14] M. C. Crossman, University of Leicester, Leicester, **1995**.
[15] P. K. Miller, K. D. Abney, A. K. Rappe, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1988**, *27*, 2255.
[16] W. A. Herrmann, O. Runte, G. Artus, *J. Organomet. Chem.* **1995**, *501*, C1-C4.
[17] K. Seppelt, D. Nothe, *Inorg. Chem.* **1973**, *12*, 2727.
[18] M. R. Colsman, T. D. Newbound, L. J. Marshall, M. D. Noirot, M. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson, S. H. Strauss, *J. Am. Chem. Soc.* **1990**, *112*, 2349.
[19] Adept Scientific, *gNMR V 5.0*, **2005**.
[20] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Magn. Reson. Chem.* **2008**, *46*, 582.
[21] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[22] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3.
[23] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3.
[24] K. Brandenburg, *DIAMOND*, Crystal Impact GbR, Bonn, **2014**.
[25] a) TURBOMOLE GmbH, *TURBOMOLE V7.0.1*, A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989–2015**; b) M. von Arnim, R. Ahlrichs, *J. Comput. Chem.* **1998**, *19*, 1746; c) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346.
[26] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
[27] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136.
[28] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[29] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[30] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

Received: April 30, 2018
Published online: July 25, 2018

Z. Anorg. Allg. Chem. **2018** · ISSN 0044–2313

SUPPORTING INFORMATION

Title: Investigation of Organonickel-Pentafluoroorthotellurates
Author(s): S. Hämmerling, L. Mann, S. Steinhauer, M. W. Kuntze-Fechner, U. Radius, S. Riedel*
Ref. No.: z201800177

Supporting Information

Referred in article

Tab. S1: Gas phase reaction energies (SCF-ZPE corrected), free enthalpies and solution free enthalpies (COSMO ε_R = 35,94 for acetonitrile)[1] for reaction *cis*-[Ni(^{iPr}Im)$_2$(X)$_2$]→*trans*-[Ni(^{iPr}Im)$_2$(X)$_2$] on RI-B3LYP-D3/def2-TZVPP level of theory.

X	experimental isomer	characterization methodf	ΔE (kJ*mol^{-1})	ΔG^0 (kJ*mol^{-1})$^{(b)}$	ΔG^0_{solv} (kJ*mol^{-1})$^{(c)}$
$OTeF_5$	*cis*	XRD+NMR	-6.4	-19.1	8.8
Cl	*trans*$^{(a)}$	NMR[2]	-35.3	-37.5	9.3
NCS	*trans*$^{(a)}$	XRD+NMR[3]	-28.5	-33.8	6.7
Br	*trans*	XRD+NMR[4]	-44.7	-52.6	-5.8
CN	*trans*	XRD+NMR[5]	-35.5	-43.7	-16.0
Me	*trans*	NMR[4]	-21.4	-29.4	-22.0

(a) *cis* for different NHC ligands.[3,6] (b) μ taken from TURBOMOLES freeh script. (c) $E_{tot+Occorr}$ of COSMO optimized structure, μ taken from TURBOMOLES freeh script for structure without COSMO.

Tab. S2: Selected ^{13}C NMR resonances of different Ni-NHC complexes.

Complex	Solvent	δ_{NCN} (ppm)
[Ni(^{iPr}Im)$_2$($OTeF_5$)$_2$]	CD_3CN	140.9
[Ni(^{iPr}Im)$_2$(C_6F_5)(SO_3CF_3)][7]	$CDCl_3$	165.7
[Ni(^{iPr}Im)$_2$$Br_2$][2,4]	C_6D_6	171.2
	Aceton-d^6	170.4
[Ni(^{iPr}Im)$_2$(CN)$_2$][5]	CD_2Cl_2	171.5
[Ni(^{iPr}Im)$_2$(NCS)$_2$][3]	$CDCl_3$	173.1
[Ni(^{iPr}Im)$_2$(C_6F_5)F][7]	C_6D_6	175.4
[Ni(^{iPr}Im)$_2$$Cl_2$][2]	Aceton-d^6	177.8
[Ni(^{iPr}Im)$_2$(CN)(Me)][5]	CD_2Cl_2	188.7
[Ni(^{iPr}Im)$_2$(C_6F_5)(Me)][7]	C_6D_6	191.0
[Ni(^{iPr}Im)$_2$(Me)$_2$][4]	C_6D_6	203.4

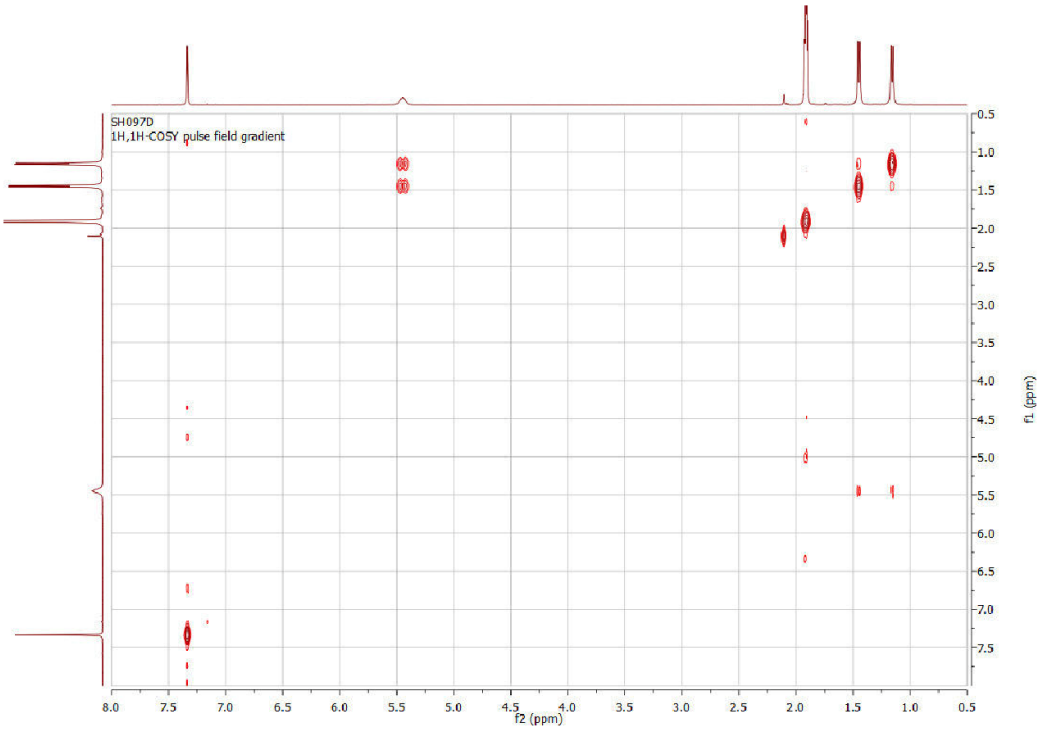


Fig. S1: $^{1}H,^{1}H$-COSY of *cis*-[Ni(^{iPr}Im)$_2$(OTeF$_5$)$_2$] (400.5 MHz, CD_3CN, 20 °C).

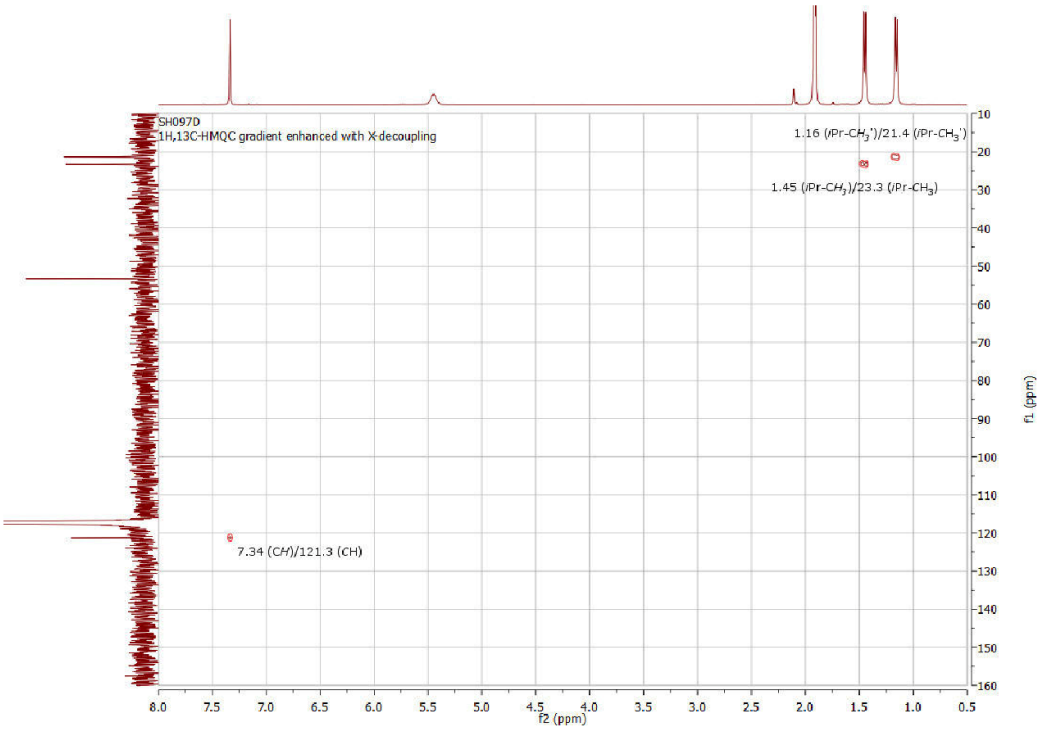


Fig. S2: $^{1}H,^{13}C$-HMQC of *cis*-[Ni(^{iPr}Im)$_2$(OTeF$_5$)$_2$] (400.5 MHz/100.7 MHz, CD_3CN, 20 °C).

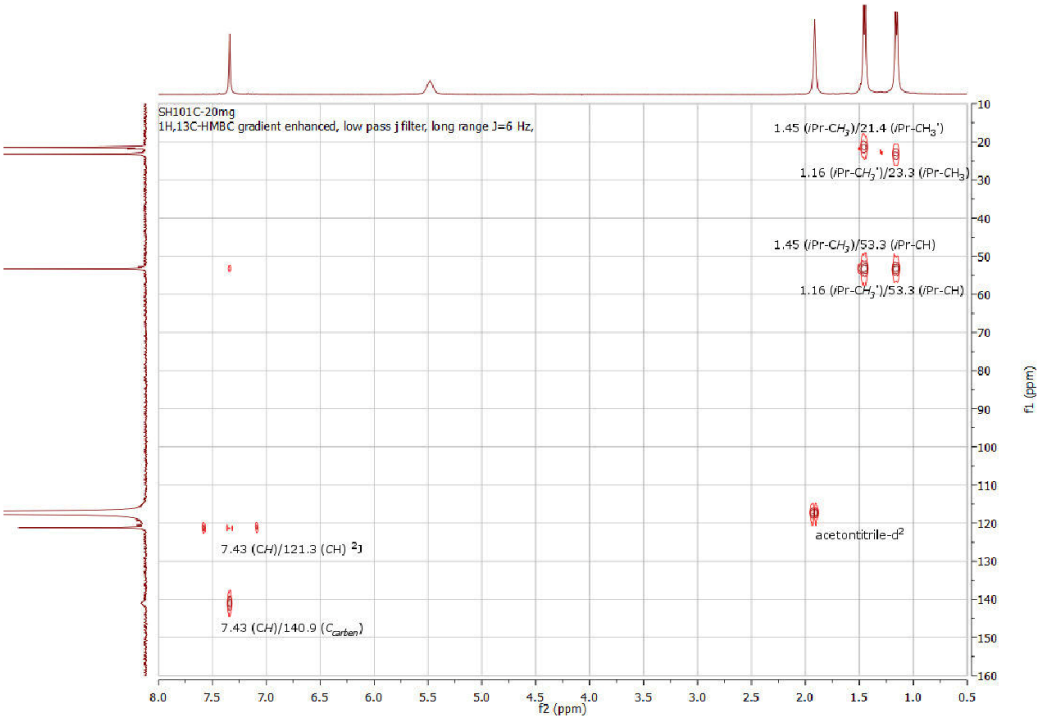


Fig. S3: $^{1}H,^{13}C$-HMBC of *cis*-[Ni($^{i^{Pr}}$Im)$_2$(OTeF$_5$)$_2$] (400.5 MHz/100.7 MHz, CD_3CN, 20 °C).

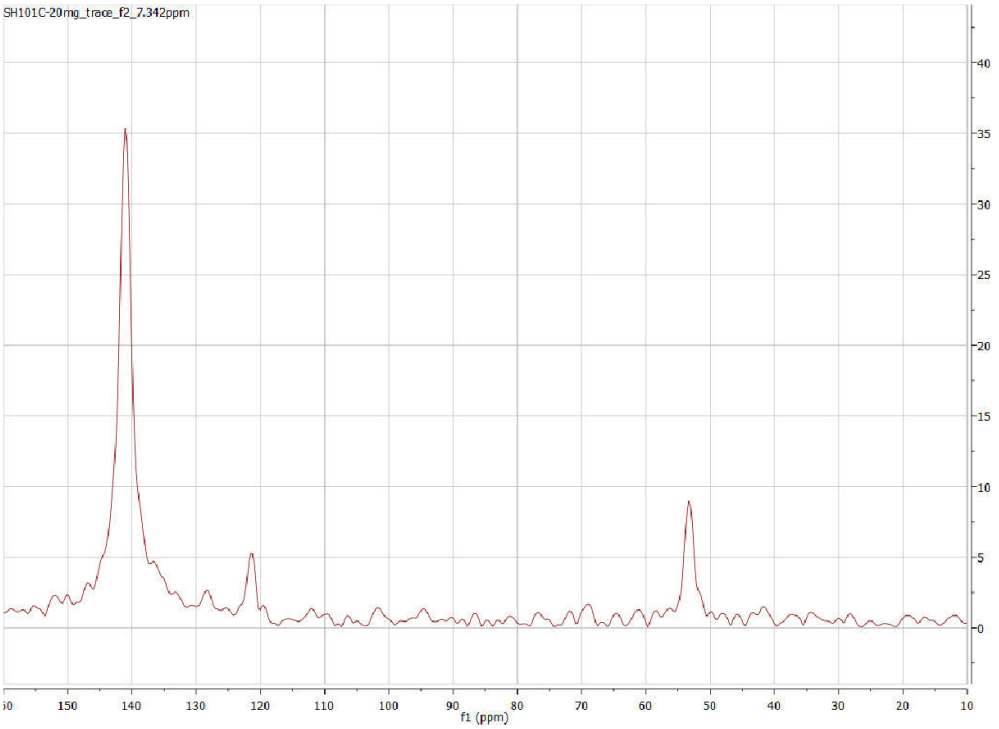


Fig. S4: Slices along f1 through $^{1}H,^{13}C$-HMBC of *cis*-[Ni($^{i^{Pr}}$Im)$_2$(OTeF$_5$)$_2$] at 7.342 ppm (400.5 MHz/100.7 MHz, CD_3CN, 20 °C).

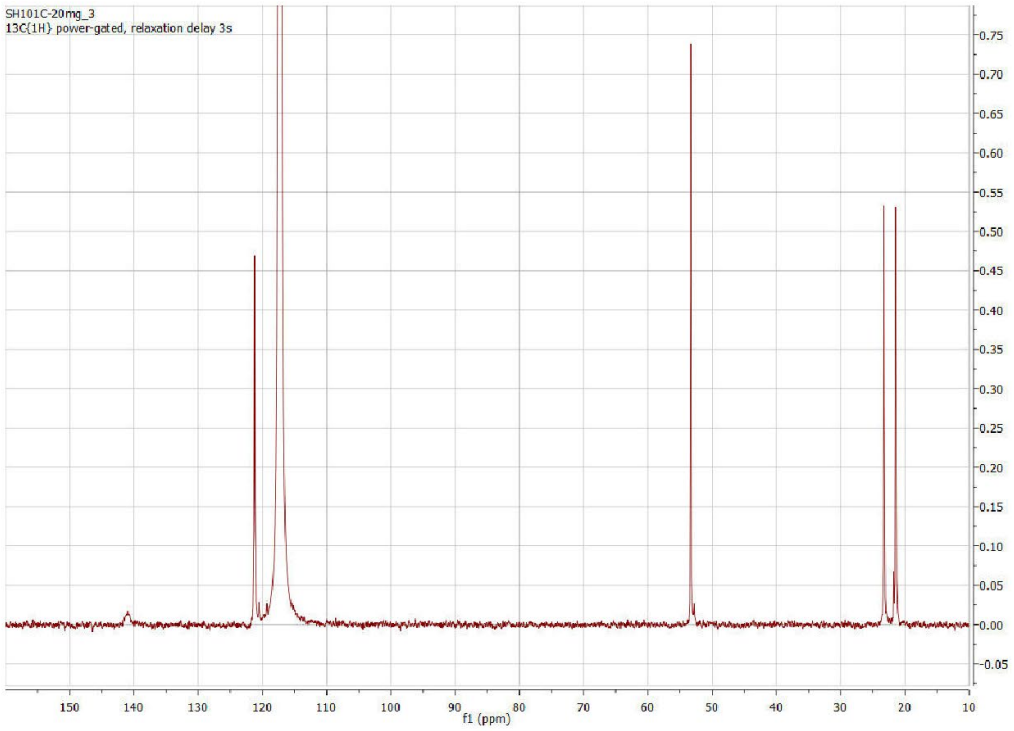


Fig. S5: 13C{1H} nmr spectrum of [Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$] (100.7 MHz, CD_3CN, 20 °C).

Crystallographic Data

Compound	**[Ni(acetylacetone)$_2$ (OTeF$_5$)$_2$] (1)**	**[{Ni(acetylacetone)(H$_2$O) (OTeF$_5$)(μOTeF$_5$)}$_2$] (2)**	***cis*-[Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$] (3)**
CCDC	1939291	1839617	1839393
Formula	$C_{10}H_{16}F_{10}NiO_6Te_2$	$C_{10}H_{20}F_{20}Ni_2O_{10}Te_4$	$C_{18}H_{32}F_{10}N_4NiO_2Te_2$
$D_{calc.}$/ g cm^{-3}	2.474	2.794	1.976
μ/mm^{-1}	3.992	5.049	2.801
Formula Weight	736.14	1308.08	840.38
Colour	clear bluish green	clear light green	Clear yellow
Shape	block	cuboid	block
Size/mm^3	0.30×0.18×0.08	0.18×0.12×0.09	0,21×0,18×0,30
T/K	102.33	102(2)	102(2)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	P2$_1$/c	P2$_1$/n	P2$_1$/n
a/Å	9.9468(14)	8.8658(5)	10.4314(5)
b/Å	8.7447(13)	11.9327(7)	16.3549(8)
c/Å	11.8048(18)	15.0646(8)	16.6616(9)
α/°	90	90	90
β/°	105.766(6)	102.639(2)	96.494(2)
γ/°	90	90	90
V/Å^3	988.2(3)	1555.11(15)	2824.3(2)
Z	2	2	4
Z'	0.5	0.5	1
Wavelength/Å	0.710730	0.710730	0.710730
Radiation type	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$
Θ_{min}/°	2.940	2.198	2.326
Θ_{max}/°	26.472	30.544	33.205
Measured Refl.	13909	27683	70494
Independent Refl.	2035	4760	10768
Reflections Used	1947	4547	8248
R_{int}	0.0347	0.0317	0.0504
Parameters	135	218	342
Restraints	0	0	0
Largest Peak	0.891	0.649	0.707
Deepest Hole	-1.274	-1.597	-0.920
GooF	1.070	1.175	1.089
wR_2 (all data)	0.0544	0.0475	0.0525
wR_2	0.0525	0.0469	0.0472
R_1 (all data)	0.0220	0.0201	0.0573
R_1	0.0208	0.0187	0.0315

Quantum Chemical Calculations at RI-B3LYP-D3/def2-TZVPP

[Ni(Hacac)$_2$(OTeF$_5$)$_2$] – 1a

$coord

2.50327776219637	0.71334023681878	4.86865324160893	c
4.57316326838483	0.26967665576515	6.73884665153671	c
4.98242105570861	1.99954751380669	7.78701320131077	h
3.92768703403465	-1.13735587184364	8.10827156823948	h
6.25315668347875	-0.42323354705705	5.78546964824087	h
2.77895218740244	0.11825320598167	2.66263500415435	o
-2.33487609303985	0.63478606858903	4.98454126612245	c
-2.58670805611127	-0.27917417067581	2.88980594471489	o
-4.46823327312733	0.61881237573822	6.83748096784578	c
-6.12193549391508	-0.26846858562075	6.00702646351163	h
-3.90562418251353	-0.37151777126455	8.55898738902910	h
-4.90332255235894	2.56760624494542	7.36710041010941	h

```
  -2.45086740916013   -0.66452722735703   -4.99347132591065  c
  -4.48719966497434   -0.26103830089789   -6.91027542586028  c
  -4.93271102338336   -2.03559127581502   -7.86576084281531  h
  -6.15831877843324    0.52402605519567   -6.01441003366078  h
  -3.79252921454775    1.04718859610607   -8.35133320711953  h
  -2.75105173433054    0.01278717320736   -2.81424378293272  o
   2.38813337764847   -0.66001610064218   -5.03373594502445  c
   2.60977327225259    0.34560056571848   -2.97785331595901  o
   4.56235059959223   -0.76980341194879   -6.83623030033308  c
   4.06005525206695    0.15041284034423   -8.61435080641818  h
   6.21529668371825    0.12171539824571   -6.00873391211813  h
   4.96913831574695   -2.74901605185973   -7.26637307356421  h
  -0.00646036732043    0.06394059548301   -0.05061622926284  ni
  -0.11540150857521    3.87909611990088    0.26374714121407  o
  -2.55962430569320    6.23338108915143   -0.21415378659595  te
  -0.24692893267919    8.83696724495024   -0.84627205843184  f
  -5.03492928252018    8.72304483133517   -0.60458558846510  f
  -2.59418947034268    7.11396723931053    3.26093179794472  f
  -2.92206878122715    5.66903033302668   -3.71547423388594  f
  -5.29735894381724    4.04584037929239    0.42461993548489  f
   0.09089973533518    1.93081157639574    5.81333948678911  c
   0.12420790710187    2.17690115053003    7.85304629987098  h
   0.01150247803431    3.80847342527920    4.93516897509716  h
  -0.04286348244444   -1.94928528981266   -5.85896241986669  c
  -0.00471964062473   -3.79569869089091   -4.91358714103884  h
  -0.04781889740667   -2.26366797287759   -7.88967194693546  h
   0.07872344217009   -3.75983166560532   -0.36635981153928  o
   2.41378085805706   -6.15711146917588    0.36764463764313  te
   2.64048030889787   -5.37377625985199    3.84378515861317  f
   4.78720008748874   -8.68646202641335    1.03785749889478  f
   5.24486803024751   -4.09650028969294   -0.28582786302595  f
  -0.00976254033441   -8.63956986859538    1.07018485899974  f
   2.56043528931709   -7.26356106721916   -3.03387449621198  f
$end
Etot = -3885.0329204660 H, triplet state
ZPE = 727.7 kJ*mol^-1
μ = 530.52 kJ*mol^-1
```

$[Ni(Hacac)_2(OTeF_5)_2]$ – 1b, enol isomer

```
$coord
   2.33544621607931    0.31551705349931    5.04099715863195  c
   4.64162463391560    0.04792379386525    6.66988292080823  c
   4.62294168604749    1.37285584335626    8.24660181217460  h
   4.64354322474292   -1.86708588172351    7.44670148391667  h
   6.33516559965108    0.29513699506467    5.53602721605353  h
   2.61647907945288    0.21330889353565    2.71895253798302  o
  -2.38981050081483    0.77353817797093    5.27945164630535  c
  -2.78729672458083    0.07428847826661    2.85039174638521  o
  -4.70948066453849    1.58169973794167    6.65237569746504  c
  -6.16749111093759    0.12768589829335    6.52064681122606  h
  -4.31566240882852    1.97824079425360    8.62741940440361  h
  -5.43850205891525    3.30215121255649    5.76845883781448  h
  -2.33658029507407   -0.31804310811914   -5.03836699141839  c
  -4.64451485455144   -0.04690808278097   -6.66403590275389  c
  -4.61353905343235   -1.34274276296114   -8.26424265613722  h
  -6.33597192620444   -0.32940481555740   -5.53510747953190  h
  -4.66466345784444    1.88235735335576   -7.40476778578937  h
  -2.61644426038397   -0.22242243415664   -2.71576018391434  o
   2.38883948497499   -0.77107093728923   -5.27969378583765  c
   2.78625898848351   -0.08087010326968   -2.84823885209080  o
   4.70893188066539   -1.57193421520953   -6.65621771739517  c
   4.31504407469221   -1.96151650242199   -8.63263665914441  h
   6.16550365746667   -0.11693998319406   -6.51940539160508  h
   5.44001475676323   -3.29489665295688   -5.77884768051284  h
   0.00010961264024   -0.00417656763577    0.00119604575850  ni
```

-0.20306007255858	3.85409486224705	-0.13218910771969	o
-2.81329131313347	6.04547185199690	-0.39439019061802	te
-0.78549246808636	8.83812534090474	-1.12282503784773	f
-5.54912721344189	8.26498463611286	-0.61867050104894	f
-2.81799259036798	6.85912987481627	3.07784538755779	f
-3.39788605548304	5.45988182179541	-3.86055757339127	f
-5.39206185293436	3.58470278518758	0.40047613893702	f
-0.05835299013820	0.70110573254917	6.31640429549001	c
0.04512460186157	1.08560225980682	8.31703805040220	h
0.05704291857556	-0.69658383679237	-6.31599092432718	c
-0.04635945972608	-1.07364806261580	-8.31799112959783	h
0.20419153357062	-3.86204160519274	0.13907093002786	o
2.81649865087492	-6.05206206769357	0.39194027043909	te
3.40654149868626	-5.47271530479335	3.85795856068584	f
5.55403959763242	-8.27041224349575	0.60681514333477	f
5.39306822657162	-3.58829250008308	-0.40216837920773	f
0.79166762014707	-8.84752766793197	1.11775865749852	f
2.81627943071172	-6.85805474556170	-3.08218349654315	f
-4.29890993006209	0.86422486641996	2.14424697017943	h
4.29813428783112	-0.87267818235987	-2.14437029704624	h

$end

Etot = -3885.0256713840 H, triplet state

ZPE = 734.5 kJ*mol^{-1}

μ = 544.43 kJ*mol^{-1}

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$]

$coord

-1.52917015975371	-2.10833730720306	0.41596799700907	c
1.52917015975371	2.10833730720306	0.41596799700907	c
0.47889228025511	3.57098294138265	2.22190452376849	n
4.05063316665751	2.49620703359273	0.59974947536468	n
-0.47889228025511	-3.57098294138265	2.22190452376849	n
-4.05063316665751	-2.49620703359273	0.59974947536468	n
-4.56697396938730	-4.20203233646443	2.50989779219346	c
-6.45204403056831	-4.80051046952155	2.96088965129204	h
-2.32594438265474	-4.87710851451565	3.53171777402096	c
-1.89730524000504	-6.17379815287107	5.03143663538092	h
4.56697396938730	4.20203233646443	2.50989779219346	c
6.45204403056831	4.80051046952155	2.96088965129204	h
2.32594438265474	4.87710851451565	3.53171777402096	c
1.89730524000504	6.17379815287107	5.03143663538092	h
-2.26077728335643	3.84344747888520	2.63873338253040	c
-3.11605888180724	2.84428970216401	1.06293059328930	h
5.98302644619800	1.42487862727419	-1.11821042184198	c
4.97358055162436	0.08944658308007	-2.31005331938441	h
2.26077728335643	-3.84344747888520	2.63873338253040	c
3.11605888180724	-2.84428970216401	1.06293059328930	h
-5.98302644619800	-1.42487862727419	-1.11821042184198	c
-4.97358055162436	-0.08944658308007	-2.31005331938441	h
-8.00697092791520	-0.00997546496563	0.37232457947650	c
-9.31402271504254	0.88487272321329	-0.94237484347165	h
-9.09600831088091	-1.28437856176684	1.57376743252317	h
-7.18926001515773	1.45804554241082	1.55896914421525	h
-7.09296968630648	-3.49927486625771	-2.78506169791960	c
-8.12059523299933	-4.88857175912988	-1.65767722693683	h
-8.41128366762771	-2.66538394057048	-4.12980271809028	h
-5.61213158156123	-4.45239089276942	-3.83928562842277	h
3.02287504191686	-2.58567195107574	5.12001089178825	c
2.08558636754751	-3.48702848104730	6.72088948679288	h
5.05555043874727	-2.75424845381972	5.40431764852127	h
2.53413757790232	-0.58548092396934	5.11709315808119	h
3.04747587225297	-6.61189660143621	2.47540851992730	c
5.10190912020478	-6.74159193378895	2.54446041517322	h
2.29611288837464	-7.70926763393258	4.05179779681641	h
2.39671147880788	-7.44408739300864	0.71154827168206	h
7.09296968630648	3.49927486625771	-2.78506169791960	c

8.12059523299933	4.88857175912988	-1.65767722693683	h
8.41128366762771	2.66538394057048	-4.12980271809028	h
5.61213158156123	4.45239089276942	-3.83928562842277	h
8.00697092791520	0.00997546496563	0.37232457947650	c
7.18926001515773	-1.45804554241082	1.55896914421525	h
9.31402271504254	-0.88487272321329	-0.94237484347165	h
9.09600831088091	1.28437856176684	1.57376743252317	h
-3.02287504191686	2.58567195107574	5.12001089178825	c
-2.08558636754751	3.48702848104730	6.72088948679288	h
-5.05555043874727	2.75424845381972	5.40431764852127	h
-2.53413757790232	0.58548092396934	5.11709315808119	h
-3.04747587225297	6.61189660143621	2.47540851992730	c
-5.10190912020478	6.74159193378895	2.54446041517322	h
-2.29611288837464	7.70926763393258	4.05179779681641	h
-2.39671147880788	7.44408739300864	0.71154827168206	h
0.00000000000000	-0.00000000000000	-2.03479788119327	ni
-1.31946299672281	-2.18316754082377	-4.64377237898006	o
0.43347050418879	-5.00903342227073	-5.54307045219723	te
2.17719063414744	-7.96066960125851	-6.39670481520998	f
1.95445261176090	-3.59444634890258	-8.39712459009089	f
-2.22745788744089	-6.26683770607051	-7.50017665814863	f
3.35105608987685	-4.20361820829766	-3.59210135187183	f
-0.75194552731524	-6.91844894095387	-2.75100012668391	f
1.31946299672281	2.18316754082377	-4.64377237898006	o
-0.43347050418879	5.00903342227073	-5.54307045219723	te
-2.17719063414744	7.96066960125851	-6.39670481520998	f
-1.95445261176090	3.59444634890258	-8.39712459009089	f
2.22745788744089	6.26683770607051	-7.50017665814863	f
-3.35105608987685	4.20361820829766	-3.59210135187183	f
0.75194552731524	6.91844894095387	-2.75100012668391	f

$end

Etot = -4117.5186602530 H

ZPE = 1352 kJ*mol^{-1}

μ = 1146.38 kJ*mol^{-1}

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$]-COSMO

$coord

-1.05765034057723	-1.04262893302278	2.16982418592322	c
1.42563582213744	1.55710390755176	-1.56133113307723	c
1.11846223071011	3.97780987616331	-0.82705711535791	n
3.77497613948029	1.43434516775428	-2.56631010880871	n
0.77200167907896	-1.36522710048772	3.91362544713352	n
-3.21107428825131	-0.65025322873927	3.49379540805177	n
-2.71994919140392	-0.72896053678246	6.06011768466226	c
-4.16509488509690	-0.46931644586902	7.46113001551095	h
-0.21899748496356	-1.17579940153664	6.32547144851339	c
0.91502490347627	-1.37628254505042	7.99644310949435	h
4.92772586979019	3.77785703249106	-2.45631689936802	c
6.80320206351794	4.11078935398872	-3.15661327326220	h
3.26186550188889	5.37567203675330	-1.36255510814736	c
3.41761852163891	7.35315703683877	-0.93394099685217	h
-1.19706372179548	5.02363345492391	0.31827044767560	c
-2.55650360454579	3.48846994127747	0.21749607487917	h
4.92384073443245	-0.81216036150803	-3.77578306962813	c
3.60759808880364	-2.35227516523436	-3.42263075263163	h
3.44425658921736	-1.91896873079394	3.34805692295715	c
3.49138828193286	-2.18852490471996	1.31334983238759	h
-5.77075525440743	-0.34783000540325	2.40443413885140	c
-5.48496072458556	-0.22617151526783	0.37144091795556	h
-7.01096132121361	2.08282872939395	3.33765836682615	c
-8.83258935245918	2.31119579204554	2.40570431948412	h
-7.34321321791766	2.02301871843220	5.37054828218663	h
-5.86333610254321	3.73676728615520	2.91929018410640	h
-7.37559792933023	-2.67297406823963	2.98629092491525	c
-7.69995177730232	-2.85114513390652	5.01468127004188	h
-9.20523130379648	-2.49362922350456	2.05746715435670	h
-6.45863285511002	-4.37885984089192	2.30260016526938	h

5.09922185526814	0.32870520933860	4.06900260029585	c
4.98235499326694	0.70330562994819	6.09244124797687	h
7.06646459964139	-0.06804863416673	3.61052835333182	h
4.52459579470335	2.02573183924425	3.05387577220921	h
4.25919003504471	-4.38035420334571	4.60693776112791	c
6.16984570922892	-4.85315909213365	4.00082663723103	h
4.27060350561401	-4.20740233960193	6.66056690221223	h
2.99906416986597	-5.91869726801826	4.07602504770768	h
5.14135518538496	-0.40076874867509	-6.62255923633643	c
6.45334287311014	1.13314839524702	-7.04360924139514	h
5.85433786966938	-2.11653600888690	-7.51145063787120	h
3.30863420350687	0.04508890559434	-7.43532538547823	h
7.47004168429489	-1.44299904511827	-2.57737524059328	c
7.30896796017212	-1.73732283351194	-0.54879643795340	h
8.20299703281607	-3.17168182528370	-3.42202582494475	h
8.84621211174386	0.05517650715568	-2.90652106412406	h
-0.71612941053942	5.71748967537281	3.07477365552422	c
0.73410017955960	7.17491961775506	3.21932987096282	h
-2.43945166337029	6.45152570069058	3.92862958452644	h
-0.10417831240119	4.07451801325705	4.15497768112012	h
-2.19899484649016	7.22504101751207	-1.24933111310640	c
-4.01190435582968	7.83381195922081	-0.48493829265133	h
-0.91450272822000	8.83568560834481	-1.19229535617143	h
-2.46732059606418	6.65731275070636	-3.20955386596240	h
-0.86458398557233	-1.18968379753553	-1.40102073680249	ni
-3.15789764429917	-4.07499819464560	-1.38882452793736	o
-1.94334085468825	-7.26433186510678	-1.03723573882479	te
-0.76618258634422	-10.59313907801291	-0.63825748779786	f
-2.09983504077172	-8.08716440969703	-4.49211967012034	f
-5.17979597240449	-8.66060521062352	-0.57857904384371	f
1.51544194102226	-6.41458851556098	-1.40269147632078	f
-1.55605333057887	-7.07315899895722	2.50731382836264	f
-0.82746378096467	-1.42324975242711	-5.07779808369141	o
-2.96030930269478	0.48306425738452	-6.97156030961145	te
-5.10371108450110	2.45525005593002	-9.00635832504443	f
-5.34349759112373	-2.09520536947185	-7.53073006413431	f
-1.34283258971284	-0.38018318938707	-10.01623302966236	f
-4.93790348828403	1.70104195481014	-4.24753967155502	f
-0.98291560986394	3.45082008984429	-6.78765692470358	f

$end
Etot+OCcorr= -4117.5506396964 H

trans-[Ni(*i*^{Pr}Im)$_2$(OTeF$_5$)$_2$]

$coord

0.00000000000000	-0.00000000000000	3.63652930413809	c
-0.00000000000000	-0.00000000000000	-3.77747819840783	c
-1.80987631860614	0.91835657399772	-5.31506812882203	n
1.80987631860614	-0.91835657399772	-5.31506812882203	n
2.00271356285565	-0.32661111491178	5.18174336200245	n
-2.00271356285565	0.32661111491178	5.18174336200245	n
-1.26088498090365	0.20686259841407	7.68303542075794	c
-2.56100698985992	0.42458456318532	9.22522879237225	h
1.26088498090365	-0.20686259841407	7.68303542075794	c
2.56100698985992	-0.42458456318532	9.22522879237225	h
1.14232365774353	-0.57385817375978	-7.81902964088629	c
2.31797357837187	-1.16404916682357	-9.36314997930142	h
-1.14232365774353	0.57385817375978	-7.81902964088629	c
-2.31797357837187	1.16404916682357	-9.36314997930142	h
-4.19871479665408	2.02725060749575	-4.40159610218941	c
-3.86653057759005	2.40424586172204	-2.40632609987555	h
4.19871479665408	-2.02725060749575	-4.40159610218941	c
3.86653057759005	-2.40424586172204	-2.40632609987555	h
4.61415637127017	-0.77439992469155	4.31694551670381	c
4.50284085829630	-0.71776713616894	2.26602050389082	h
-4.61415637127017	0.77439992469155	4.31694551670381	c
-4.50284085829630	0.71776713616894	2.26602050389082	h
-5.50858597068239	3.38880851660366	5.14247661639018	c

-7.38875409277559	3.75008387986776	4.38109600735710	h
-5.62395887813017	3.52510980882218	7.19736465833370	h
-4.23238336482797	4.84682905028531	4.45088857929371	h
-6.34338260517872	-1.35821396215262	5.19659792062340	c
-6.53084900835464	-1.37034070046239	7.25104010211644	h
-8.22279026769721	-1.10143792190284	4.39344244355244	h
-5.61246444032443	-3.18247744731810	4.59141072673688	h
6.34338260517872	1.35821396215262	5.19659792062340	c
6.53084900835464	1.37034070046239	7.25104010211644	h
8.22279026769721	1.10143792190284	4.39344244355244	h
5.61246444032443	3.18247744731810	4.59141072673688	h
5.50858597068239	-3.38880851660366	5.14247661639018	c
7.38875409277559	-3.75008387986776	4.38109600735710	h
5.62395887813017	-3.52510980882218	7.19736465833370	h
4.23238336482795	-4.84682905028532	4.45088857929371	h
4.72887782009243	-4.53920427349292	-5.70933480832670	c
5.13994055169068	-4.28152452392186	-7.71406340315605	h
6.37551123385015	-5.42321742490154	-4.84461052106785	h
3.12564738704598	-5.81458729187222	-5.51287990003613	h
6.34067261159079	-0.11239993320440	-4.65308411226428	c
5.88392657360217	1.60706937664436	-3.61793854949632	h
8.08255359740286	-0.90360179507381	-3.88694275887338	h
6.67288471048354	0.36752670514083	-6.63166064934834	h
-4.72887782009243	4.53920427349292	-5.70933480832670	c
-5.13994055169068	4.28152452392186	-7.71406340315605	h
-6.37551123385015	5.42321742490154	-4.84461052106785	h
-3.12564738704598	5.81458729187222	-5.51287990003613	h
-6.34067261159079	0.11239993320441	-4.65308411226428	c
-8.08255359740286	0.90360179507381	-3.88694275887338	h
-6.67288471048354	-0.36752670514083	-6.63166064934834	h
-5.88392657360217	-1.60706937664436	-3.61793854949632	h
0.00000000000000	0.00000000000000	-0.07930430515304	ni
-2.46348129971853	-2.75548855480195	-0.12895387057909	o
-1.64320434420775	-6.10598301630883	0.09225932070881	te
-0.87863190519215	-9.54212115931612	0.31540122327471	f
-1.20739002258364	-6.50918670598717	-3.41558440650308	f
-5.02627646207587	-7.08817784374590	-0.17940471738736	f
1.88767457454953	-5.57273845291729	0.39340135675596	f
-1.87776780576544	-6.19681296271225	3.64025133908493	f
2.46348129971853	2.75548855480195	-0.12895387057909	o
1.64320434420775	6.10598301630883	0.09225932070881	te
0.87863190519215	9.54212115931612	0.31540122327471	f
1.20739002258364	6.50918670598717	-3.41558440650308	f
5.02627646207588	7.08817784374590	-0.17940471738736	f
-1.88767457454953	5.57273845291729	0.39340135675596	f
1.87776780576544	6.19681296271225	3.64025133908493	f

$end
Etot = -4117.5199405550 H
ZPE = 1349 kJ*mol^{-1}
μ = 1130,60 kJ*mol^{-1}

trans-[Ni($^{i\mathrm{Pr}}$Im)$_2$(OTeF$_5$)$_2$]-COSMO

$coord

0.00023553447739	0.00016504358863	3.70697675302487	c
-0.00032238050605	-0.00068671046913	-3.70737376340227	c
-1.95840476604259	0.53348746294044	-5.24903849168077	n
1.95775629036017	-0.53455558726132	-5.24914117116918	n
1.96055833406035	-0.52579087839266	5.24874351783460	n
-1.95976166756074	0.52696475529438	5.24886374886240	n
-1.23423988128518	0.33365575096091	7.75306786683521	c
-2.50538560463956	0.68108884268261	9.29732234752082	h
1.23559005485849	-0.33101805629280	7.75299324002559	c
2.50706839260490	-0.67751013190467	9.29718247102381	h
1.23331056755118	-0.33739475804457	-7.75337277629674	c
2.50327205803269	-0.68907330438232	-9.29763157504702	h
-1.23397827713625	0.33673404665175	-7.75331104860824	c

-2.50393075937581	0.68866028421537	-9.29751765391363	h
-4.51046808850768	1.24082331524359	-4.37719698370090	c
-4.38081684267019	1.25268668889849	-2.32543351430572	h
4.50971266155700	-1.24243995393572	-4.37745000666221	c
4.38040872164376	-1.25348916004521	-2.32566284480854	h
4.51496458081490	-1.22533998127021	4.37745092118613	c
4.38749059632402	-1.23178927203023	2.32560836876359	h
-4.51424523879952	1.22646658384210	4.37776256483728	c
-4.38765430260478	1.23029368623700	2.32586184471165	h
-5.19213281692331	3.88052646039496	5.27589670790609	c
-7.02076652613363	4.42400815467406	4.49927571556263	h
-5.32208404334447	3.96137440767218	7.33195019303149	h
-3.78181473318610	5.24267621860775	4.64643172213884	h
-6.42976105761381	-0.77250947652049	5.17899793674256	c
-6.59985368240890	-0.85737185184789	7.23224521919907	h
-8.27997862495542	-0.30781703642333	4.40236702246399	h
-5.86921394170600	-2.62614276555914	4.48172728689225	h
6.42997921604292	0.77541242824957	5.17544721850826	c
6.60072613461764	0.86285441033657	7.22852598433379	h
8.28010249362429	0.31049244514865	4.39873488423906	h
5.86838206568664	2.62788834117918	4.47598047768362	h
5.19436403938999	-3.87803729482598	5.27846080935205	c
7.02283447078984	-4.42170348916492	4.50158000673003	h
5.32539276758933	-3.95643620620477	7.33454562758642	h
3.78428527251341	-5.24154563198643	4.65139561584737	h
5.18326713125998	-3.89472705232790	-5.28393375791837	c
5.31735093104799	-3.96838582603879	-7.33998375016875	h
7.00906943929269	-4.44522583432272	-4.50560389211293	h
3.76859928669578	-5.25594638138581	-4.66233787820732	h
6.43030622865437	0.75536064856226	-5.16937854862613	c
5.87339537107596	2.60735736826633	-4.46491845409276	h
8.27898958357290	0.28345025687970	-4.39343065900384	h
6.60173989751503	0.84798002317138	-7.22219592071745	h
-5.18520431217365	3.89252426723429	-5.28449692229792	c
-5.31992755910381	3.96540230583160	-7.34053007627873	h
-7.01100138833470	4.44261098525031	-4.50586249990670	h
-3.77087785277263	5.25449763597944	-4.66379189940132	h
-6.43044597853538	-0.75799612662396	-5.16807764640120	c
-8.27920562075342	-0.28654752569451	-4.39205793980604	h
-6.60210498681464	-0.85139633808179	-7.22084305777514	h
-5.87268741699239	-2.60950445631090	-4.46299682650113	h
-0.00005884539560	-0.00038874428774	-0.00032335311468	ni
-2.61316107032985	-2.62279289970993	-0.00007017158817	o
-1.95779027212186	-6.00248340623269	0.00201194973373	te
-1.39923361696812	-9.50704155085927	0.00458438079174	f
-1.90048923004149	-6.31156933569206	-3.54475041006982	f
-5.40795282536170	-6.82921571214469	0.00374241367550	f
1.60278496940330	-5.72255222204663	0.00074033855884	f
-1.89810445492376	-6.30652475103096	3.54918894566996	f
2.61290167019192	2.62215043608233	-0.00069986978841	o
1.95740070314720	6.00180392018669	-0.00383595343556	te
1.39865487856146	9.50633874796480	-0.00616869878944	f
1.89812228415547	6.30549821043924	-3.55103106890004	f
5.40752152398335	6.82869305779918	-0.00532498169716	f
-1.60316270858935	5.72175823931989	-0.00278338916410	f
1.89968322351608	6.31126427956696	3.54289335408496	f

$end

Etot+OCcorr= -4117,5412942519 H

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$Cl$_2$]

$coord

-1.34631910505923	-2.30963191034790	0.46838671428255	c
1.34631910505923	2.30963191034790	0.46838671428255	c
0.56016193739895	4.72168586358577	0.08622657475264	n
3.37674785980630	2.02975998144921	-1.06380949247398	n
-0.56016193739895	-4.72168586358577	0.08622657475264	n

```
  -3.37674785980630   -2.02975998144921   -1.06380949247398 n
  -3.89455120247580   -4.25534632595283   -2.34280703880179 c
  -5.44490895806870   -4.44995297886057   -3.63603978971847 h
  -2.11848345729278   -5.94013681872660   -1.62598499299119 c
  -1.83595963726127   -7.87045055550479   -2.18323936240960 h
   3.89455120247580    4.25534632595283   -2.34280703880179 c
   5.44490895806870    4.44995297886057   -3.63603978971847 h
   2.11848345729278    5.94013681872660   -1.62598499299119 c
   1.83595963726127    7.87045055550479   -2.18323936240960 h
  -1.46210209296741    5.99135627543891    1.52592822612082 c
  -2.32208720144941    4.50052777210119    2.65612872515023 h
   5.02685044882225   -0.20450104254622   -1.01137302769057 c
   3.83457375256039   -1.68782045867613   -0.24232338908668 h
   1.46210209296741   -5.99135627543891    1.52592822612082 c
   2.32208720144941   -4.50052777210119    2.65612872515023 h
  -5.02685044882225    0.20450104254622   -1.01137302769057 c
  -3.83457375256039    1.68782045867613   -0.24232338908668 h
  -7.22908780686707   -0.23340843002864    0.80122856641295 c
  -8.35954270305500    1.48293985526552    0.96365558687796 h
  -8.45153517999671   -1.74758955095751    0.11514003636709 h
  -6.51392039429786   -0.74697425270093    2.66357189633853 h
  -5.86122193572203    0.95140587303834   -3.66581664021597 c
  -7.09014367318496   -0.47295811108328   -4.50973217129367 h
  -6.93521727660271    2.70664115177517   -3.58079875449408 h
  -4.24014102715264    1.23680034212958   -4.90567466013096 h
   0.34020117310392   -7.95136289221626    3.32137766357165 c
  -0.57954964364393   -9.47231179367692    2.27223427368418 h
   1.84206076103822   -8.78076755912217    4.46283908166062 h
  -1.02423083876854   -7.05642959275102    4.57149679724579 h
   3.42636424133873   -7.13231841309401   -0.25489643613164 c
   5.01162186911751   -7.85926217640452    0.84079253958005 h
   2.63793020400489   -8.70621074309791   -1.33003269058252 h
   4.14117570542449   -5.74160131117265   -1.59261818315056 h
   5.86122193572203   -0.95140587303834   -3.66581664021597 c
   7.09014367318496    0.47295811108328   -4.50973217129367 h
   6.93521727660271   -2.70664115177517   -3.58079875449408 h
   4.24014102715264   -1.23680034212958   -4.90567466013096 h
   7.22908780686707    0.23340843002864    0.80122856641295 c
   6.51392039429786    0.74697425270093    2.66357189633853 h
   8.35954270305500   -1.48293985526552    0.96365558687796 h
   8.45153517999671    1.74758955095751    0.11514003636709 h
  -0.34020117310392    7.95136289221626    3.32137766357165 c
   0.57954964364393    9.47231179367692    2.27223427368418 h
  -1.84206076103822    8.78076755912217    4.46283908166062 h
   1.02423083876854    7.05642959275102    4.57149679724579 h
  -3.42636424133873    7.13231841309401   -0.25489643613164 c
  -5.01162186911751    7.85926217640452    0.84079253958005 h
  -2.63793020400489    8.70621074309791   -1.33003269058252 h
  -4.14117570542449    5.74160131117265   -1.59261818315056 h
   0.00000000000000   -0.00000000000000    2.90213566193589 ni
   2.25387174364451    2.19222109918210    5.74507211615875 cl
  -2.25387174364451   -2.19222109918210    5.74507211615875 cl
$end
Etot = -3352.7450536800 H
ZPE = 1270 kJ*mol^-1
μ = 1111.12 kJ*mol^-1
```

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$Cl$_2$]-COSMO

```
$coord
  -1.16258603128306   -2.32027452128171    0.87743388627095 c
   1.16258603128306    2.32027452128171    0.87743388627095 c
   0.31073808533126    4.72129236813308    0.58087590587148 n
   2.92337173648878    2.00968953762802   -0.94578033974027 n
  -0.31073808533126   -4.72129236813308    0.58087590587148 n
  -2.92337173648878   -2.00968953762802   -0.94578033974027 n
  -3.17902637031432   -4.18877453250344   -2.37372389721012 c
```

-4.47969899527823	-4.34019006589464	-3.92436187255624	h
-1.53989192976795	-5.89071869477801	-1.41051000155103	c
-1.15359992831208	-7.80414418042162	-1.96621961260068	h
3.17902637031432	4.18877453250344	-2.37372389721012	c
4.47969899527823	4.34019006589464	-3.92436187255624	h
1.53989192976795	5.89071869477801	-1.41051000155103	c
1.15359992831208	7.80414418042162	-1.96621961260068	h
-1.51096761871954	6.02667728316268	2.25012961526142	c
-2.18604288280059	4.57715546488004	3.54423640915513	h
4.42239474667504	-0.30000980521359	-1.34295218108760	c
3.88504136948756	-1.53034129669988	0.21084796933814	h
1.51096761871954	-6.02667728316268	2.25012961526142	c
2.18604288280059	-4.57715546488004	3.54423640915513	h
-4.42239474667504	0.30000980521359	-1.34295218108760	c
-3.88504136948756	1.53034129669988	0.21084796933814	h
-7.24016150138879	-0.27049724960150	-1.12635583240900	c
-8.30880181067021	1.48535386963189	-1.25402797883469	h
-7.87579340342115	-1.50990645352215	-2.64553249648544	h
-7.66449310729380	-1.16659265246850	0.67912639960557	h
-3.71258112828885	1.53454126006897	-3.85096231792457	c
-4.13686904790994	0.27966406710362	-5.43070235085760	h
-4.78886159068028	3.26980912439269	-4.11551296524697	h
-1.70758999116140	1.99948786003817	-3.90241743358556	h
0.16555433200405	-8.07975891304827	3.76763907443831	c
-0.53700754938425	-9.56808278011510	2.52430863278622	h
1.48918064058899	-8.92956355718271	5.09834367997812	h
-1.40664875141578	-7.27564351399792	4.81998861221525	h
3.73307516447732	-7.08667181179590	0.74715577105838	c
5.07953855227218	-7.94346561671991	2.04824553976661	h
3.11738945967936	-8.54226796304284	-0.57614781870506	h
4.71040511442133	-5.62232536320565	-0.31419219224274	h
3.71258112828885	-1.53454126006897	-3.85096231792457	c
4.13686904790994	-0.27966406710362	-5.43070235085760	h
4.78886159068028	-3.26980912439269	-4.11551296524697	h
1.70758999116140	-1.99948786003817	-3.90241743358556	h
7.24016150138879	0.27049724960150	-1.12635583240900	c
7.66449310729380	1.16659265246850	0.67912639960557	h
8.30880181067021	-1.48535386963189	-1.25402797883469	h
7.87579340342115	1.50990645352215	-2.64553249648544	h
-0.16555433200405	8.07975891304827	3.76763907443831	c
0.53700754938425	9.56808278011510	2.52430863278622	h
-1.48918064058899	8.92956355718271	5.09834367997812	h
1.40664875141578	7.27564351399792	4.81998861221525	h
-3.73307516447732	7.08667181179590	0.74715577105838	c
-5.07953855227218	7.94346561671991	2.04824553976661	h
-3.11738945967936	8.54226796304284	-0.57614781870506	h
-4.71040511442133	5.62232536320565	-0.31419219224274	h
0.00000000000000	-0.00000000000000	3.39105336798983	ni
2.18153743759134	2.23752118316917	6.33554111129714	cl
-2.18153743759134	-2.23752118316917	6.33554111129714	cl

$end
Etot+OCcorr= -3352,7869723235 H

trans-[Ni(*i*Prlm)$_2$Cl$_2$]

$coord

0.00000000000000	0.00000000000000	3.65722398929647	c
0.00000000000000	0.00000000000000	-3.65722398929647	c
-0.52928793966162	-1.95857428945757	-5.20443720952736	n
0.52928793966162	1.95857428945757	-5.20443720952736	n
-0.52928793966162	1.95857428945757	5.20443720952736	n
0.52928793966162	-1.95857428945757	5.20443720952736	n
0.32313415536937	-1.23710477490133	7.71130616159066	c
0.64876075959435	-2.50402387844621	9.26077565077352	h
-0.32313415536937	1.23710477490133	7.71130616159066	c
-0.64876075959435	2.50402387844621	9.26077565077352	h
0.32313415536937	1.23710477490133	-7.71130616159066	c

```
  0.64876075959435    2.50402387844621   -9.26077565077352  h
 -0.32313415536937   -1.23710477490133   -7.71130616159066  c
 -0.64876075959435   -2.50402387844621   -9.26077565077352  h
 -1.07320907995917   -4.51182688926787   -4.23209215402224  c
 -2.06795506548105   -4.17815852198130   -2.46038724414046  h
  1.07320907995917    4.51182688926787   -4.23209215402224  c
  2.06795506548105    4.17815852198130   -2.46038724414046  h
 -1.07320907995917    4.51182688926787    4.23209215402224  c
 -2.06795506548105    4.17815852198130    2.46038724414046  h
  1.07320907995917   -4.51182688926787    4.23209215402224  c
  2.06795506548105   -4.17815852198130    2.46038724414046  h
 -1.39645604817335   -5.90423692841967    3.68864562966849  c
 -1.00254561106684   -7.71969895603879    2.79377960875113  h
 -2.44119412352692   -6.25439844551594    5.43344690517316  h
 -2.58356781697827   -4.78137504361223    2.43395323441323  h
  2.82149713972354   -5.96329779401515    5.99846764524431  c
  1.89551470896062   -6.43974046591725    7.77958169920652  h
  3.37157540115525   -7.73212344230559    5.09860016294635  h
  4.53000851979998   -4.88619321731270    6.40198130755401  h
 -2.82149713972354    5.96329779401515    5.99846764524431  c
 -1.89551470896062    6.43974046591725    7.77958169920652  h
 -3.37157540115525    7.73212344230559    5.09860016294635  h
 -4.53000851979998    4.88619321731270    6.40198130755401  h
  1.39645604817335    5.90423692841967    3.68864562966849  c
  1.00254561106684    7.71969895603879    2.79377960875113  h
  2.44119412352692    6.25439844551594    5.43344690517316  h
  2.58356781697827    4.78137504361223    2.43395323441323  h
  2.82149713972354    5.96329779401515   -5.99846764524431  c
  1.89551470896062    6.43974046591725   -7.77958169920652  h
  3.37157540115525    7.73212344230559   -5.09860016294635  h
  4.53000851979998    4.88619321731270   -6.40198130755401  h
 -1.39645604817335    5.90423692841967   -3.68864562966849  c
 -2.58356781697827    4.78137504361223   -2.43395323441323  h
 -1.00254561106684    7.71969895603879   -2.79377960875113  h
 -2.44119412352692    6.25439844551594   -5.43344690517316  h
 -2.82149713972354   -5.96329779401515   -5.99846764524431  c
 -1.89551470896062   -6.43974046591725   -7.77958169920652  h
 -3.37157540115525   -7.73212344230559   -5.09860016294635  h
 -4.53000851979998   -4.88619321731270   -6.40198130755401  h
  1.39645604817335   -5.90423692841967   -3.68864562966849  c
  1.00254561106684   -7.71969895603879   -2.79377960875113  h
  2.44119412352692   -6.25439844551594   -5.43344690517316  h
  2.58356781697827   -4.78137504361223   -2.43395323441323  h
  0.00000000000000    0.00000000000000    0.00000000000000  ni
  4.21043021562050    0.00000000000000    0.00000000000000  cl
 -4.21043021562050    0.00000000000000    0.00000000000000  cl
$end
Etot = -3352.7584845170 H
ZPE = 1270 kJ*mol^-1
μ = 1108.86 kJ*mol^-1
```

trans-[Ni($^{i\mathrm{Pr}}$Im)$_2$Cl$_2$]-COSMO

```
$coord
  0.00000000000000    0.00000000000000    3.66189357057676  c
  0.00000000000000    0.00000000000000   -3.66189357057676  c
 -0.49111196313115   -1.97010084665223   -5.20554627555840  n
  0.49111196313115    1.97010084665223   -5.20554627555840  n
 -0.49111196313115    1.97010084665223    5.20554627555840  n
  0.49111196313115   -1.97010084665223    5.20554627555840  n
  0.29889112603101   -1.24387290066757    7.71445507307964  c
  0.59485102695919   -2.51832916530023    9.26506636164766  h
 -0.29889112603101    1.24387290066757    7.71445507307964  c
 -0.59485102695919    2.51832916530023    9.26506636164766  h
  0.29889112603101    1.24387290066757   -7.71445507307964  c
  0.59485102695919    2.51832916530023   -9.26506636164766  h
 -0.29889112603101   -1.24387290066757   -7.71445507307964  c
```

-0.59485102695919	-2.51832916530023	-9.26506636164766	h
-0.98255089133554	-4.54440286664175	-4.24792083744817	c
-1.93871677704086	-4.24663191609293	-2.44840131935223	h
0.98255089133554	4.54440286664175	-4.24792083744817	c
1.93871677704086	4.24663191609293	-2.44840131935223	h
-0.98255089133554	4.54440286664175	4.24792083744817	c
-1.93871677704086	4.24663191609293	2.44840131935223	h
0.98255089133554	-4.54440286664175	4.24792083744817	c
1.93871677704086	-4.24663191609293	2.44840131935223	h
-1.51227983292172	-5.91618179818234	3.77418403873482	c
-1.15246492640857	-7.75940648290760	2.92495235703405	h
-2.53378789942580	-6.20377448960461	5.54338846799050	h
-2.69788772858721	-4.81587594071043	2.49793266945823	h
2.74577527557994	-5.99911799843917	5.99678617743062	c
1.84585031863601	-6.43224032833264	7.80058356672587	h
3.24839245825558	-7.78688581009494	5.10672501921365	h
4.47734675319757	-4.94231189514426	6.35667132474765	h
-2.74577527557994	5.99911799843917	5.99678617743062	c
-1.84585031863601	6.43224032833264	7.80058356672587	h
-3.24839245825558	7.78688581009494	5.10672501921365	h
-4.47734675319757	4.94231189514426	6.35667132474765	h
1.51227983292172	5.91618179818234	3.77418403873482	c
1.15246492640857	7.75940648290760	2.92495235703405	h
2.53378789942580	6.20377448960461	5.54338846799050	h
2.69788772858721	4.81587594071043	2.49793266945823	h
2.74577527557994	5.99911799843917	-5.99678617743062	c
1.84585031863601	6.43224032833264	-7.80058356672587	h
3.24839245825558	7.78688581009494	-5.10672501921365	h
4.47734675319757	4.94231189514426	-6.35667132474765	h
-1.51227983292172	5.91618179818234	-3.77418403873482	c
-2.69788772858721	4.81587594071043	-2.49793266945823	h
-1.15246492640857	7.75940648290760	-2.92495235703405	h
-2.53378789942580	6.20377448960461	-5.54338846799050	h
-2.74577527557994	-5.99911799843917	-5.99678617743062	c
-1.84585031863601	-6.43224032833264	-7.80058356672587	h
-3.24839245825558	-7.78688581009494	-5.10672501921365	h
-4.47734675319757	-4.94231189514426	-6.35667132474765	h
1.51227983292172	-5.91618179818234	-3.77418403873482	c
1.15246492640857	-7.75940648290760	-2.92495235703405	h
2.53378789942580	-6.20377448960461	-5.54338846799050	h
2.69788772858721	-4.81587594071043	-2.49793266945823	h
0.00000000000000	0.00000000000000	0.00000000000000	ni
4.23021830524365	0.00000000000000	0.00000000000000	cl
-4.23021830524365	0.00000000000000	0.00000000000000	cl

$end
Etot+OCcorr= -3352,7825628091 H

cis-[Ni(*i*^{Pr}Im)$_2$(NCS)$_2$]

$coord
$coord

-0.38320592973007	-2.67251913685570	0.07915528242998	c
0.38320592973007	2.67251913685570	0.07915528242998	c
-1.25228170075246	4.61335509470369	-0.27769338454093	n
2.38161784748892	3.20397054949688	-1.42205100040086	n
1.25228170075246	-4.61335509470369	-0.27769338454093	n
-2.38161784748892	-3.20397054949688	-1.42205100040086	n
-2.01676410438384	-5.46583133933051	-2.68785581154873	c
-3.39407268067509	-6.25364704029496	-3.95123072819329	h
0.26820549817541	-6.34384655171642	-1.97396726536294	c
1.25478521195199	-8.03395057026330	-2.50837976772339	h
2.01676410438384	5.46583133933051	-2.68785581154873	c
3.39407268067509	6.25364704029496	-3.95123072819329	h
-0.26820549817541	6.34384655171642	-1.97396726536294	c
-1.25478521195199	8.03395057026330	-2.50837976772339	h
-3.61964637136902	5.01444584672263	1.14677420859573	c
-3.83807146442207	3.32336761108513	2.30004228444199	h

```
   4.77270188069023    1.78502327953199   -1.38534520811005  c
   4.30185539362426    0.02564121742402   -0.43553685725863  h
   3.61964637136902   -5.01444584672263    1.14677420859573  c
   3.83807146442207   -3.32336761108513    2.30004228444199  h
  -4.77270188069023   -1.78502327953199   -1.38534520811005  c
  -4.30185539362426   -0.02564121742402   -0.43553685725863  h
  -6.73670507359399   -3.19339621131971    0.19262160065010  c
  -8.44234647197364   -2.05053527453797    0.37003238836909  h
  -7.25254943494970   -4.98016660898914   -0.69912403982330  h
  -6.01186839313968   -3.60277037014370    2.07565946014804  h
  -5.66860780762705   -1.20568825954931   -4.06264044267737  c
  -6.12839830403235   -2.92849164372313   -5.09699178932780  h
  -7.38040432757375   -0.06345319251050   -3.98957044064050  h
  -4.23453073404253   -0.17097582935321   -5.12032589357390  h
   3.37031834805063   -7.29208816429319    2.90057551522410  c
   3.17329623494440   -9.03714456133584    1.81791777212121  h
   5.06581637623580   -7.45314726976512    4.05969546639347  h
   1.74336938233570   -7.10493579237774    4.14067782189849  h
   5.86224071968712   -5.26743257415699   -0.65210578707045  c
   7.61214403461091   -5.33735507102271    0.43141062925737  h
   5.74086750319920   -7.00620750758691   -1.75425333324795  h
   5.96824481455491   -3.68697921067037   -1.96392440431696  h
   5.66860780762705    1.20568825954931   -4.06264044267737  c
   6.12839830403235    2.92849164372313   -5.09699178932780  h
   7.38040432757375    0.06345319251050   -3.98957044064050  h
   4.23453073404253    0.17097582935321   -5.12032589357390  h
   6.73670507359399    3.19339621131971    0.19262160065010  c
   6.01186839313968    3.60277037014370    2.07565946014804  h
   8.44234647197364    2.05053527453797    0.37003238836909  h
   7.25254943494970    4.98016660898914   -0.69912403982330  h
  -3.37031834805063    7.29208816429319    2.90057551522410  c
  -3.17329623494440    9.03714456133584    1.81791777212121  h
  -5.06581637623580    7.45314726976512    4.05969546639347  h
  -1.74336938233570    7.10493579237774    4.14067782189849  h
  -5.86224071968712    5.26743257415699   -0.65210578707045  c
  -7.61214403461091    5.33735507102271    0.43141062925737  h
  -5.74086750319920    7.00620750758691   -1.75425333324795  h
  -5.96824481455491    3.68697921067037   -1.96392440431696  h
   0.00000000000000    0.00000000000000    2.53742658691602  ni
   2.00670389624740    4.30916102754182    5.65988684701114  c
  -2.00670389624740   -4.30916102754182    5.65988684701114  c
  -0.88235561372562   -2.51724164318079    4.97055320960490  n
   0.88235561372562    2.51724164318079    4.97055320960490  n
   3.51403862740464    6.80265293244298    6.56728037421337  s
  -3.51403862740464   -6.80265293244298    6.56728037421337  s$end
Etot = -3414.3996119000 H
ZPE = 1320 kJ*mol^-1
μ = 1141.22 kJ*mol^-1
```

cis-[Ni(*i*Prlm)$_2$(NCS)$_2$]-COSMO

```
$coord
  -0.18103565314688   -2.60672114220782    0.35327183711665  c
   0.18103565314688    2.60672114220782    0.35327183711665  c
  -1.50101133846933    4.51811329984704    0.06267459936054  n
   1.92691516212439    2.96679549690256   -1.47380582420425  n
   1.50101133846933   -4.51811329984704    0.06267459936054  n
  -1.92691516212439   -2.96679549690256   -1.47380582420425  n
  -1.34378229426843   -5.07431534438407   -2.90917392777290  c
  -2.48798843245833   -5.69312324288222   -4.46691744311787  h
   0.80686999984786   -6.04863521175269   -1.94005708950628  c
   1.88071279330741   -7.67776648284318   -2.49819850279196  h
   1.34378229426843    5.07431534438407   -2.90917392777290  c
   2.48798843245833    5.69312324288222   -4.46691744311787  h
  -0.80686999984786    6.04863521175269   -1.94005708950628  c
  -1.88071279330741    7.67776648284318   -2.49819850279196  h
  -3.69079589818414    5.04634076549226    1.72065833069789  c
```

-3.77794193547776	3.45759615232820	3.02278999108277	h
4.17126997106373	1.37229396113199	-1.89264851812093	c
4.15564000644704	0.04077072653605	-0.32923693569360	h
3.69079589818414	-5.04634076549226	1.72065833069789	c
3.77794193547776	-3.45759615232820	3.02278999108277	h
-4.17126997106373	-1.37229396113199	-1.89264851812093	c
-4.15564000644704	-0.04077072653605	-0.32923693569360	h
-6.57974042718468	-2.94714578760770	-1.72943577597731	c
-8.21775345875109	-1.70733268944995	-1.87215530440639	h
-6.68766187600187	-4.31678846557392	-3.26533999234392	h
-6.67564983745116	-3.95535726662287	0.06404420825918	h
-3.92855210141318	0.05005136983311	-4.38924776519432	c
-3.86605553239628	-1.26552771721856	-5.97528000394348	h
-5.55280037914418	1.28648756964149	-4.65749629407494	h
-2.22208154921491	1.20238075245764	-4.42308465482246	h
3.23318085814329	-7.46970003208844	3.21874406920768	c
3.17221086174076	-9.10466396458085	1.96330740547601	h
4.77235029245562	-7.74875653398449	4.55857400059360	h
1.46664912004483	-7.37141532231327	4.26520422563333	h
6.14070344282668	-5.17079471131520	0.20310556501757	c
7.71734935600006	-5.46306031332319	1.49452776038067	h
6.11654491596781	-6.73938587562719	-1.13345355203729	h
6.48367202465600	-3.43502454357928	-0.84353923312210	h
3.92855210141318	-0.05005136983311	-4.38924776519432	c
3.86605553239628	1.26552771721856	-5.97528000394348	h
5.55280037914418	-1.28648756964149	-4.65749629407494	h
2.22208154921491	-1.20238075245764	-4.42308465482246	h
6.57974042718468	2.94714578760770	-1.72943577597731	c
6.67564983745116	3.95535726662287	0.06404420825918	h
8.21775345875109	1.70733268944995	-1.87215530440639	h
6.68766187600187	4.31678846557392	-3.26533999234392	h
-3.23318085814329	7.46970003208844	3.21874406920768	c
-3.17221086174076	9.10466396458085	1.96330740547601	h
-4.77235029245562	7.74875653398449	4.55857400059360	h
-1.46664912004483	7.37141532231327	4.26520422563333	h
-6.14070344282668	5.17079471131520	0.20310556501757	c
-7.71734935600006	5.46306031332319	1.49452776038067	h
-6.11654491596781	6.73938587562719	-1.13345355203729	h
-6.48367202465600	3.43502454357928	-0.84353923312210	h
0.00000000000000	0.00000000000000	2.90001251310306	ni
1.17922064967790	4.00997255664917	6.94453398184484	c
-1.17922064967790	-4.00997255664917	6.94453398184484	c
-0.60193398145844	-2.50580192180768	5.43273881716526	n
0.60193398145844	2.50580192180768	5.43273881716526	n
1.96281002572852	6.12374115411284	9.04488976874240	s
-1.96281002572852	-6.12374115411284	9.04488976874240	s

Etot+OCcorr= -3414,4445715188 H

trans-[Ni(^{iPr}Im)$_2$(NCS)$_2$]

$coord

-0.05980062551146	-0.00343881178242	3.71648878211344	c
0.05973948725062	-0.00594973745762	-3.71675218479020	c
-0.88057245316814	-1.78999149174647	-5.28273559090521	n
1.04746660903224	1.78227963513738	-5.24841047238271	n
-1.04683543646129	1.78618480516279	5.24698014654658	n
0.88050516473181	-1.78645824403647	5.28361562117621	n
0.48354662193641	-1.11944047559467	7.78086422767818	c
1.08029063159948	-2.27941913323722	9.33493379099690	h
-0.72521706943363	1.12989321310446	7.75784565773731	c
-1.36823796096584	2.29654020208173	9.28828836602703	h
0.72625752406046	1.12414781997006	-7.75884428394646	c
1.36980639045951	2.28948970305462	-9.29005650343008	h
-0.48293703439290	-1.12498200178824	-7.78038578875972	c
-1.07948928379817	-2.28604961373528	-9.33371799669166	h
-2.11142110354834	-4.14851373305395	-4.45180703331812	c
-2.15421265138888	-4.02093504809398	-2.40141203528876	h

```
   2.24980311806068    4.13980010521596   -4.37385763608952  c
   2.23090023061767    4.00634255008415   -2.32352382980646  h
  -2.24940124112112    4.14298520337888    4.37083924284888  c
  -2.23013705612835    4.00832285586482    2.32057668951991  h
   2.11089553298938   -4.14573546876126    4.45420431402521  c
   2.15322521467783   -4.01974008858764    2.40368894468533  h
   0.51932521738717   -6.42427664681845    5.23001146540533  c
   1.36113874276059   -8.14941778410514    4.48209836738727  h
   0.42107571539730   -6.60847447943463    7.28218328972957  h
  -1.40033005086063   -6.25989695353446    4.50056883549432  h
   4.82491744049701   -4.27292919807747    5.41845278705345  c
   4.88607824160249   -4.36360553352135    7.47890538658217  h
   5.73980909553268   -5.96635412700799    4.68510943784822  h
   5.90783972172472   -2.64129965810269    4.78633497779601  h
  -4.99108286066072    4.27664153122522    5.25228780336411  c
  -5.11435715236550    4.37502786021588    7.30960797997002  h
  -5.88158310594471    5.96809751371373    4.48522642303459  h
  -6.05613789081476    2.64384868609793    4.59343700301952  h
  -0.67943440609018    6.42334549030903    5.18433431812679  c
  -1.49631204573745    8.14593973435567    4.40362422718803  h
  -0.64299853584574    6.61666226957306    7.23769115547219  h
   1.26119211455733    6.25373612268826    4.51396342763932  h
   4.99133548703634    4.27338509290456   -5.25577229463925  c
   5.11434662811447    4.37061950034557   -7.31316389910811  h
   5.88170378894552    5.96538604429304   -4.48977535070623  h
   6.05673115067530    2.64114766464772   -4.59609694428522  h
   0.67932663065309    6.41938609343523   -5.18853576288947  c
  -1.26112464252371    6.24990018300108   -4.51762367424802  h
   1.49610197487944    8.14263581011487   -4.40916875282351  h
   0.64240840281302    6.61125930419692   -7.24202037761831  h
  -4.82522757323370   -4.27614612064735   -5.41659161901443  c
  -4.88592390182107   -4.36829009919062   -7.47698950643278  h
  -5.74049724408750   -5.96890945444080   -4.68220402659967  h
  -5.90810418923624   -2.64396690130402   -4.78582004203106  h
  -0.51990454292013   -6.42782696744877   -5.22546767333351  c
  -1.36211423652801   -8.15230398530469   -4.47646652657189  h
  -0.42109268915761   -6.61359950667016   -7.27746918544163  h
   1.39956780668194   -6.26311776174916   -4.49561169255800  h
  -0.00012084169442   -0.00801358242100    0.00031636440398  ni
  -5.72871168911957    0.00536439868276   -0.09984873430726  c
   5.72847362435578    0.01027226402222    0.10231709116059  c
  -8.77935888207233    0.02261902990730   -0.15751150992960  s
   8.77905790316923    0.03182672949073    0.16188926706261  s
  -3.50966723937244   -0.00783706799497   -0.05779477251682  n
   3.50947942380507   -0.00616774062672    0.05875030937068  n
$end
Etot = -3414.4104614590 H
ZPE = 1320 kJ*mol^-1
μ = 1141.22 kJ*mol^-1
```

trans-[Ni(*i*Pr Im)$_2$(NCS)$_2$]-COSMO

```
$coord
  -0.06022764026661    0.00353929055246    3.71559717666589  c
   0.06046225854844    0.00081550416340   -3.71569017947915  c
  -0.70205650009109   -1.87243642865266   -5.26801813234593  n
   0.87296302298218    1.86943677079816   -5.24800693640258  n
  -0.87243858044180    1.87339350599198    5.24652239200515  n
   0.70190224429745   -1.86874142145195    5.26923695323708  n
   0.36796185486254   -1.17814162237240    7.77183188755201  c
   0.84735328190458   -2.39705014952778    9.32289869367827  h
  -0.61995869667726    1.17894275514546    7.75759137377621  c
  -1.14951230615794    2.39544835481994    9.29416237980420  h
   0.62026264827586    1.17325035844348   -7.75856375568207  c
   1.14994707741685    2.38857444975418   -9.29602384297455  h
  -0.36804943124527   -1.18366784547948   -7.77110491128248  c
  -0.84763393843157   -2.40357370340432   -9.32132663196393  h
```

-1.71922802457852	-4.32437366712039	-4.41580144400134	c
-1.72631082709762	-4.20521541747421	-2.36218591438445	h
1.86276140026223	4.32358792331441	-4.37042517146352	c
1.80243382080804	4.21069458741887	-2.31730965315827	h
-1.86225778779896	4.32684131624109	4.36699410083255	c
-1.80143517722126	4.21246546149765	2.31395850152303	h
1.71887805404538	-4.32129744646505	4.41859473937459	c
1.72592657861394	-4.20340374199457	2.36488744113175	h
-0.02559604864251	-6.46892060241903	5.23177908327505	c
0.67119920072394	-8.25172106967037	4.47111717722620	h
-0.09403011480631	-6.63418040206211	7.28598201186458	h
-1.94014652544630	-6.16064406528014	4.53516086654784	h
4.43224797392371	-4.66209373453351	5.33182783828883	c
4.51808907967440	-4.75455046948779	7.39007891090616	h
5.19503845727263	-6.42220826815768	4.58160115474784	h
5.61954623806202	-3.10828089807110	4.68615609734916	h
-4.60447451163130	4.66446607091256	5.19094390338573	c
-4.75799603209379	4.75352505865819	7.24539478816833	h
-5.34333563833226	6.42533888934041	4.41887228763355	h
-5.76880127284018	3.11094609475545	4.50406370341679	h
-0.14697086821964	6.47408427261108	5.24099625462378	c
-0.81938400386906	8.25775247465419	4.46068872509966	h
-0.14652329990864	6.63590723179662	7.29662385477664	h
1.78976248721344	6.16812233541028	4.60755233659078	h
4.60474199092115	4.66089297037292	-5.19528307320977	c
4.75776663501628	4.74853497439310	-7.24983300162259	h
5.34362805635117	6.42237103436269	-4.42462212756001	h
5.76938123533890	3.10796334756129	-4.50760924490244	h
0.14707373221762	6.47004542372457	-5.24559500702634	c
-1.78946312729265	6.16444066479917	-4.61138047339903	h
0.81959083573195	8.25437063071847	-4.46685283116258	h
0.14600278102550	6.63031315471790	-7.30134759219570	h
-4.43259289608233	-4.66551675207791	-5.32889723003473	c
-4.51835768537860	-4.75906423184024	-7.38710036144264	h
-5.19544107259008	-6.42525904534520	-4.57785193864766	h
-5.61983901004376	-3.11133785075307	-4.68402609951212	h
0.02508207285296	-6.47266273758874	-5.22762357941653	c
-0.67187914384893	-8.25494680477256	-4.46590034064158	h
0.09362973608713	-6.63922609041454	-7.28172292381914	h
1.93964411951678	-6.16412720927465	-4.53115066657042	h
0.00012704064366	0.00467754061256	0.00006936570105	ni
-5.72552374042760	-0.00204381733629	-0.08851984814438	c
5.72568379806344	0.00368965337635	0.09161680791907	c
-8.80226409984896	-0.00848635348753	-0.13275381357403	s
8.80243885409919	-0.00057065419133	0.13898367506313	s
-3.51746883326312	0.00270694375492	-0.05668687879153	n
3.51767026782070	0.00660345603265	0.05742912264665	n

$end

Etot+OCcorr= -3414,4399791756 H

cis-[Ni(*i*^{Pr}Im)$_2$Br$_2$]

$coord

3.03863166092347	1.54849096532458	-6.00382120637846	br
-3.03863166092347	-1.54849096532458	-6.00382120637846	br
2.65607297189703	0.15571077910266	-0.57630327548442	c
-2.65607297189703	-0.15571077910265	-0.57630327548442	c
-4.45415317618570	1.64515182585832	-0.23472675436452	n
-3.27015049295022	-2.01794694308068	1.06497542076373	n
4.45415317618570	-1.64515182585832	-0.23472675436452	n
3.27015049295022	2.01794694308068	1.06497542076373	n
5.45463280562170	1.42096436839925	2.37985894015372	c
6.28477596693701	2.65989376383682	3.75519988849579	h
6.19200207532833	-0.88135586213165	1.56609163258852	c
7.78193062373254	-2.02032532093385	2.10580734122956	h
-5.45463280562170	-1.42096436839925	2.37985894015372	c
-6.28477596693701	-2.65989376383681	3.75519988849579	h

-6.19200207532833	0.88135586213165	1.56609163258852	c
-7.78193062373254	2.02032532093385	2.10580734122956	h
-4.72456085352878	3.94851547295581	-1.78576629140593	c
-3.02833130203097	4.00436679982927	-2.95311001338790	h
-1.99045998274185	-4.48027063670617	1.14871249617301	c
-0.26246021563692	-4.18210116239668	0.08124519650983	h
4.72456085352878	-3.94851547295581	-1.78576629140593	c
3.02833130203097	-4.00436679982927	-2.95311001338790	h
1.99045998274185	4.48027063670617	1.14871249617301	c
0.26246021563692	4.18210116239668	0.08124519650983	h
3.57269041231294	6.46987493217402	-0.21548273144503	c
2.54779128199699	8.25682696564957	-0.28441046135235	h
5.35963589009462	6.79219874068411	0.76448366996248	h
3.96616739550279	5.85178017434528	-2.14040605572744	h
1.32039723007129	5.20091289883272	3.85769201945667	c
3.00818241443181	5.47128760576818	5.01099310463415	h
0.28000718128438	6.97830502723321	3.87061991931602	h
0.15025655633588	3.75224936872394	4.74014403300993	h
7.01892713081851	-3.72854461282489	-3.52078513161855	c
8.76553053659154	-3.63911380029180	-2.42486356330546	h
7.11742204450773	-5.38146700099919	-4.74703525970206	h
6.86315514166732	-2.04698526612589	-4.69314284498307	h
4.83821025466303	-6.30330263146445	-0.12148963001559	c
4.82972601319886	-7.98537183306365	-1.30961037484358	h
6.56592458578189	-6.34320905544660	1.00459563480196	h
3.23581485531689	-6.40713616832535	1.16380943423920	h
-1.32039723007129	-5.20091289883272	3.85769201945667	c
-3.00818241443182	-5.47128760576818	5.01099310463415	h
-0.28000718128438	-6.97830502723321	3.87061991931602	h
-0.15025655633588	-3.75224936872394	4.74014403300993	h
-3.57269041231294	-6.46987493217402	-0.21548273144503	c
-3.96616739550279	-5.85178017434528	-2.14040605572744	h
-2.54779128199699	-8.25682696564957	-0.28441046135235	h
-5.35963589009462	-6.79219874068411	0.76448366996248	h
-7.01892713081851	3.72854461282489	-3.52078513161855	c
-8.76553053659154	3.63911380029180	-2.42486356330546	h
-7.11742204450773	5.38146700099919	-4.74703525970206	h
-6.86315514166732	2.04698526612589	-4.69314284498307	h
-4.83821025466302	6.30330263146445	-0.12148963001559	c
-4.82972601319886	7.98537183306365	-1.30961037484358	h
-6.56592458578188	6.34320905544660	1.00459563480196	h
-3.23581485531689	6.40713616832535	1.16380943423920	h
-0.00000000000000	0.00000000000000	-3.02238730251115	ni

$end

Etot = -7580.5175733070 H

ZPE = 1268 kJ*mol^{-1}

μ = 1101.57 kJ*mol^{-1}

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$Br$_2$]-COSMO

$coord

6.76422148142797	1.41776510189963	-2.38801798714197	br
2.39178146890665	-1.30706490212185	-6.78373846156476	br
2.45628033814740	0.01177183930556	1.21876693101243	c
-1.22186540326145	0.00511171194949	-2.45414050285623	c
-2.67794424263485	1.85513270029889	-3.47196289683000	n
-2.87007773240193	-1.71988468573622	-1.54844097534964	n
3.50129830563238	-1.84281557912960	2.64963831294564	n
1.52847892027228	1.70225058808931	2.89039622769318	n
1.98596387628530	0.92588474836966	5.34812562127972	c
1.39811869362340	2.00015981793999	6.96662302261231	h
3.22813305649556	-1.29810881320275	5.19401667436800	c
3.92937757156409	-2.51707500103528	6.65742599781803	h
-5.33828998242269	-0.96962882530936	-1.99301323694497	c
-6.94193514253679	-2.07307332586931	-1.41864888120501	h
-5.21469354012889	1.27323576066746	-3.20431772915541	c
-6.69471174476231	2.48252208846635	-3.88722642693631	h

-1.74100994547376	4.08652962352600	-4.86997555577124	c
0.30597741406593	4.02993209698264	-4.66068426873905	h
-2.15746325513962	-4.09872628025281	-0.29547357669735	c
-0.11133173343674	-4.16350508661840	-0.45611158504870	h
4.92878053322196	-4.04255281194200	1.68275805966350	c
4.71852776958401	-3.96121922911503	-0.36325609072978	h
0.24158567406958	4.07259164859061	2.21068650575927	c
0.39892905705005	4.16674604956969	0.16548246061358	h
1.61886339967698	6.33965445279809	3.33886970427317	c
0.74388674231601	8.07787582202576	2.66342995449899	h
1.51364493156434	6.33627691968803	5.39743294273706	h
3.60041110937492	6.34124475103656	2.77696845373394	h
-2.53817974960044	3.95062999075706	2.96915009709474	c
-2.73013554142848	3.74214419627972	5.01100123036762	h
-3.49994710546767	5.68499382484486	2.41685673482214	h
-3.48294339360012	2.36545062650563	2.05640365858836	h
7.72441840476497	-3.78150242748198	2.34878147471008	c
8.00059219125884	-3.86305441965744	4.39103329782728	h
8.78034678077485	-5.33202628064772	1.49737930206657	h
8.47224551161591	-2.00347146602143	1.63737111949794	h
3.82353028835637	-6.52018084344206	2.66281297387807	c
4.86041042008765	-8.09492485064428	1.83542288710406	h
3.99470270519026	-6.65573215885658	4.71244042743588	h
1.84007941103114	-6.72756484836986	2.16631379860556	h
-2.91400649283584	-4.02573360322531	2.48650503190472	c
-4.95817970760168	-3.84687886082309	2.68359220395210	h
-2.33768119061764	-5.76602192749967	3.42313719343349	h
-2.02093577003406	-2.44202050244627	3.45233399793683	h
-3.25702610885936	-6.36099081913542	-1.70345012859567	c
-2.69703843216101	-6.32731594284937	-3.68525120220482	h
-2.55789492170372	-8.10234615363015	-0.85361693402108	h
-5.31535705912027	-6.38628196070541	-1.59664851243858	h
-2.40385112182114	3.85385681795589	-7.66887123352699	c
-4.44709120989764	3.91107269830311	-7.94384840418975	h
-1.57401906067342	5.42995565047515	-8.70392233555028	h
-1.66829453468787	2.09591670669873	-8.44044279391288	h
-2.75419832810871	6.53584492369739	-3.73196975397660	c
-1.94767962075378	8.13521413140195	-4.74736615001250	h
-4.80541449021647	6.64636262034039	-3.90212030445613	h
-2.26101684868770	6.72322768025568	-1.74571218651777	h
2.38962735371758	0.03034601704948	-2.39292818386097	ni

$end

Etot+OCcorr= -7580,5587697477 H

trans-[Ni(*i*Prlm)$_2$Br$_2$]

$coord

0.00000000000000	0.00000000000000	4.49238499950885	br
0.00000000000000	-0.00000000000000	-4.49210916130890	br
3.64658033545012	0.20220228108734	0.00024933064656	c
-3.64658033545012	-0.20220228108734	0.00024933064656	c
-5.30271792549791	1.69334684143626	-0.42289917588622	n
-5.08341862008994	-2.26888430382626	0.42379906143779	n
5.30271792549791	-1.69334684143626	-0.42289917588622	n
5.08341862008994	2.26888430382626	0.42379906143779	n
7.62688308973169	1.67637065389654	0.25744530011659	c
9.10122210309312	3.04542523578298	0.51369458800081	h
7.76525391749615	-0.82393103136375	-0.25579392218453	c
9.38169262704234	-2.02199081642228	-0.51153392512904	h
-7.62688308973169	-1.67637065389654	0.25744530011659	c
-9.10122210309312	-3.04542523578298	0.51369458800081	h
-7.76525391749615	0.82393103136375	-0.25579392218453	c
-9.38169262704234	2.02199081642228	-0.51153392512904	h
-4.50046756315424	4.32607478989675	-0.83228204680164	c
-2.59216021715575	4.16276046487500	-1.58876044016343	h
-3.99549764202429	-4.79712813994762	0.83236562642326	c
-2.11697910647656	-4.42435031448253	1.58915417827098	h

4.50046756315424	-4.32607478989675	-0.83228204680164	c
2.59216021715575	-4.16276046487500	-1.58876044016343	h
3.99549764202429	4.79712813994762	0.83236562642326	c
2.11697910647656	4.42435031448253	1.58915417827098	h
3.74843471207808	6.18839674988136	-1.68391780300496	c
2.80228369404504	7.99859690930787	-1.40196830091318	h
5.60527683737619	6.55381239629631	-2.50674097021652	h
2.65276188129141	5.06187304660328	-3.01608223193622	h
5.48497986998196	6.26986163064611	2.80831646050125	c
7.37153422220831	6.76679427450775	2.13765585735585	h
4.49840404414671	8.02754672654037	3.23190049637873	h
5.65928060931167	5.18752771814568	4.55134891254866	h
6.14327646920167	-5.62441855735702	-2.80901256757873	c
8.07342508929059	-5.90969605307649	-2.13895253550194	h
5.35716611411705	-7.48032701672403	-3.23306196735802	h
6.19631138833316	-4.52878436321498	-4.55167222636168	h
4.40870703070152	-5.73710213630660	1.68348273843450	c
3.66841292550073	-7.64065306909088	1.40072772036812	h
6.29452910108041	-5.89545706684337	2.50630340858302	h
3.19521933679467	-4.73909605776120	3.01600690769094	h
-5.48497986998196	-6.26986163064611	2.80831646050125	c
-7.37153422220831	-6.76679427450775	2.13765585735585	h
-4.49840404414671	-8.02754672654037	3.23190049637873	h
-5.65928060931167	-5.18752771814568	4.55134891254866	h
-3.74843471207808	-6.18839674988136	-1.68391780300496	c
-2.65276188129141	-5.06187304660328	-3.01608223193622	h
-2.80228369404504	-7.99859690930787	-1.40196830091318	h
-5.60527683737619	-6.55381239629631	-2.50674097021652	h
-6.14327646920167	5.62441855735702	-2.80901256757873	c
-8.07342508929059	5.90969605307649	-2.13895253550194	h
-5.35716611411705	7.48032701672403	-3.23306196735802	h
-6.19631138833316	4.52878436321498	-4.55167222636168	h
-4.40870703070152	5.73710213630660	1.68348273843450	c
-3.66841292550073	7.64065306909088	1.40072772036812	h
-6.29452910108041	5.89545706684337	2.50630340858302	h
-3.19521933679467	4.73909605776120	3.01600690769094	h
0.00000000000000	-0.00000000000000	0.00017921435804	ni

$end

Etot = -7580.5338439380 H

ZPE = 1266 kJ*mol^{-1}

μ = 1091.63 kJ*mol^{-1}

trans-[Ni((^{iPr}Im)$_2$Br$_2$]-COSMO

$coord

0.00000000000000	0.00000000000000	4.53028014068575	br
-0.00000000000000	0.00000000000000	-4.49227512973839	br
3.65343092637649	0.19988155725519	0.01876512438881	c
-3.65343092637649	-0.19988155725519	0.01876512438881	c
-5.30200856260603	1.70484275101062	-0.38384435320972	n
-5.09099357425014	-2.27028128597282	0.41658487959063	n
5.30200856260603	-1.70484275101062	-0.38384435320972	n
5.09099357425014	2.27028128597282	0.41658487959063	n
7.63510402574003	1.67046038795145	0.25367736737281	c
9.11391012570446	3.03984079030851	0.48937003435781	h
7.76829436601151	-0.83753517628257	-0.23049440577340	c
9.38330856078708	-2.04285043383928	-0.46964083160896	h
-7.63510402574003	-1.67046038795145	0.25367736737281	c
-9.11391012570446	-3.03984079030851	0.48937003435781	h
-7.76829436601151	0.83753517628257	-0.23049440577340	c
-9.38330856078708	2.04285043383928	-0.46964083160896	h
-4.51033867091134	4.34985178460855	-0.76321714492883	c
-2.57596842936162	4.21045966998297	-1.45666782833702	h
-4.01677409731811	-4.81434364025081	0.79924034092825	c
-2.14793553457371	-4.46571831462042	1.59239662626458	h
4.51033867091134	-4.34985178460855	-0.76321714492883	c
2.57596842936162	-4.21045966998297	-1.45666782833702	h

4.01677409731811	4.81434364025081	0.79924034092825	c
2.14793553457371	4.46571831462042	1.59239662626458	h
3.73297719650255	6.16528391905954	-1.73464113571412	c
2.82374399993844	7.99431191760543	-1.45991351757370	h
5.57777629521364	6.48182194407193	-2.60115823930876	h
2.58365739020788	5.03847569138258	-3.02043829753949	h
5.55372091384130	6.32333811107501	2.71042910746470	c
7.42124321856088	6.80227930788035	1.97900430192985	h
4.57403265365104	8.08807426221635	3.12034738276804	h
5.77855268071832	5.27770188264027	4.47107214878935	h
6.11102498577962	-5.63851086655069	-2.78071915462786	c
8.06127700749331	-5.88869391263607	-2.16082892082372	h
5.33495472433071	-7.50629363962184	-3.16931568396050	h
6.10568873015206	-4.55185857109062	-4.53077385531520	h
4.51360556504098	-5.76011818150119	1.75401730229990	c
3.80529241249612	-7.67727317725325	1.48838624993488	h
6.42430900187885	-5.87714645730550	2.52281632016879	h
3.30975201628194	-4.79090252705913	3.11653500001289	h
-5.55372091384130	-6.32333811107501	2.71042910746470	c
-7.42124321856088	-6.80227930788035	1.97900430192985	h
-4.57403265365104	-8.08807426221635	3.12034738276804	h
-5.77855268071832	-5.27770188264027	4.47107214878935	h
-3.73297719650255	-6.16528391905954	-1.73464113571412	c
-2.58365739020788	-5.03847569138258	-3.02043829753949	h
-2.82374399993844	-7.99431191760543	-1.45991351757370	h
-5.57777629521364	-6.48182194407193	-2.60115823930876	h
-6.11102498577962	5.63851086655069	-2.78071915462786	c
-8.06127700749331	5.88869391263607	-2.16082892082372	h
-5.33495472433071	7.50629363962184	-3.16931568396050	h
-6.10568873015206	4.55185857109062	-4.53077385531520	h
-4.51360556504098	5.76011818150119	1.75401730229990	c
-3.80529241249612	7.67727317725325	1.48838624993488	h
-6.42430900187885	5.87714645730550	2.52281632016879	h
-3.30975201628194	4.79090252705913	3.11653500001289	h
0.00000000000000	0.00000000000000	0.02001735395264	ni

$end

Etot+OCcorr= -7580,5572096544 H

cis-[Ni(*i*^{Pr}Im)$_2$(CN)$_2$]

$coord

-1.36747860000918	-2.41739308792831	0.21589953159971	c
1.36747860000918	2.41739308792831	0.21589953159971	c
0.59606178227562	4.82658688583287	-0.19081550098166	n
3.46041631811804	2.14886901714430	-1.23388820131270	n
-0.59606178227562	-4.82658688583287	-0.19081550098166	n
-3.46041631811804	-2.14886901714430	-1.23388820131270	n
-4.01473042188746	-4.37183377429225	-2.49906502354605	c
-5.60943049937716	-4.57293099594711	-3.73600693831872	h
-2.20449474666691	-6.04974630571628	-1.85092466647770	c
-1.93121906546546	-7.97687714197465	-2.42367951816250	h
4.01473042188746	4.37183377429225	-2.49906502354605	c
5.60943049937716	4.57293099594711	-3.73600693831872	h
2.20449474666691	6.04974630571628	-1.85092466647770	c
1.93121906546546	7.97687714197465	-2.42367951816250	h
-1.51277423123281	6.07293459456983	1.14205366551391	c
-2.36342332586840	4.58383962202416	2.28168743660970	h
5.10226629842976	-0.09176867461823	-1.11274618658462	c
3.84723254524495	-1.59994742654529	-0.50323668195004	h
1.51277423123281	-6.07293459456983	1.14205366551391	c
2.36342332586840	-4.58383962202416	2.28168743660970	h
-5.10226629842976	0.09176867461823	-1.11274618658462	c
-3.84723254524495	1.59994742654529	-0.50323668195004	h
-7.14213612027184	-0.28252526655533	0.89471109630275	c
-8.25246751989524	1.44160719200081	1.10311483092018	h
-8.41935868929276	-1.81217562786930	0.36142630346558	h
-6.28729783537815	-0.74726260755573	2.70941791043870	h

-6.17000936534082	0.75682454251789	-3.70384632281405	c
-7.49238076288875	-0.67493125037304	-4.37615757086203	h
-7.20710840181103	2.53165034836396	-3.58098626420900	h
-4.66975911831258	0.97299614513654	-5.09975590364511	h
0.51736548600538	-8.11994901921837	2.91454384706037	c
-0.38942153871585	-9.63829527883648	1.85115128103838	h
2.08637891555682	-8.93553179741025	3.97241237385320	h
-0.82883129558253	-7.32305817627415	4.24930208503125	h
3.45052109900472	-7.08787586426204	-0.74126683707921	c
5.09535441670473	-7.80019299317451	0.27315126559229	h
2.67273883431438	-8.64774670890803	-1.84386581542168	h
4.07235836466027	-5.62807319527138	-2.05266743571766	h
6.17000936534082	-0.75682454251789	-3.70384632281405	c
7.49238076288875	0.67493125037304	-4.37615757086203	h
7.20710840181103	-2.53165034836396	-3.58098626420900	h
4.66975911831258	-0.97299614513654	-5.09975590364511	h
7.14213612027184	0.28252526655533	0.89471109630275	c
6.28729783537815	0.74726260755573	2.70941791043870	h
8.25246751989524	-1.44160719200081	1.10311483092018	h
8.41935868929276	1.81217562786930	0.36142630346558	h
-0.51736548600538	8.11994901921837	2.91454384706037	c
0.38942153871585	9.63829527883648	1.85115128103838	h
-2.08637891555682	8.93553179741025	3.97241237385320	h
0.82883129558253	7.32305817627415	4.24930208503125	h
-3.45052109900472	7.08787586426204	-0.74126683707921	c
-5.09535441670473	7.80019299317451	0.27315126559229	h
-2.67273883431438	8.64774670890803	-1.84386581542168	h
-4.07235836466027	5.62807319527138	-2.05266743571766	h
0.00000000000000	0.00000000000000	2.67551580850641	ni
-1.50864529821596	-2.08406036856734	5.14403170078991	c
1.50864529821596	2.08406036856734	5.14403170078991	c
-2.57247639587918	-3.43990138004736	6.49824763461357	n
2.57247639587918	3.43990138004736	6.49824763461357	n

$end

Etot = -2618.0173102380 H

ZPE = 1307 kJ*mol^{-1}

μ = 1142.84 kJ*mol^{-1}

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$(CN)$_2$]-COSMO

$coord

-1.31212199658419	-2.39294614135172	0.30151987994244	c
1.31212199658419	2.39294614135172	0.30151987994244	c
0.51229190686461	4.78965715285393	-0.11420254395597	n
3.33137562918461	2.09228102167816	-1.23748504797525	n
-0.51229190686461	-4.78965715285393	-0.11420254395597	n
-3.33137562918461	-2.09228102167816	-1.23748504797525	n
-3.81072945124550	-4.28462631747007	-2.58268245059844	c
-5.33451234095738	-4.45725534667285	-3.91068797805550	h
-2.03004140213953	-5.97568542936594	-1.88452537189647	c
-1.71458408326535	-7.88365674397629	-2.50064497561599	h
3.81072945124550	4.28462631747007	-2.58268245059844	c
5.33451234095738	4.45725534667285	-3.91068797805550	h
2.03004140213953	5.97568542936594	-1.88452537189647	c
1.71458408326535	7.88365674397629	-2.50064497561599	h
-1.58154573240483	6.05561028241859	1.22997450583106	c
-2.46078218410485	4.57627633383249	2.36105394963054	h
4.95307773421889	-0.17261713215829	-1.22172391604464	c
3.69731649021417	-1.68852490667204	-0.63923924476142	h
1.58154573240483	-6.05561028241859	1.22997450583106	c
2.46078218410485	-4.57627633383249	2.36105394963054	h
-4.95307773421889	0.17261713215829	-1.22172391604464	c
-3.69731649021417	1.68852490667204	-0.63923924476142	h
-7.03863679543391	-0.11904450325054	0.75059911029873	c
-8.15900570571601	1.60662318823341	0.85027002817500	h
-8.29085062210852	-1.68077328976678	0.25672151117199	h
-6.22640813213268	-0.48564182635466	2.60757206388244	h

-5.96937758353427	0.76162027614077	-3.85012945219335	c
-7.30471539966543	-0.67268176538609	-4.48847009244672	h
-6.97701601713557	2.55682975020501	-3.79835776748369	h
-4.44386777881265	0.90746147683725	-5.22704518934518	h
0.55279174342049	-8.09210951437734	2.99621916478226	c
-0.37128177077861	-9.58995615900316	1.92143587772489	h
2.10776741891136	-8.93034520642495	4.05635951939168	h
-0.79518162128338	-7.28911662566021	4.32511291736882	h
3.50829164781246	-7.11800095378140	-0.63677252596022	c
5.14505376453969	-7.82053436574812	0.39595597769951	h
2.71381381007637	-8.68835558395238	-1.70970164277557	h
4.14379675337859	-5.68866067296741	-1.97303220343968	h
5.96937758353427	-0.76162027614077	-3.85012945219335	c
7.30471539966543	0.67268176538609	-4.48847009244672	h
6.97701601713557	-2.55682975020501	-3.79835776748369	h
4.44386777881265	-0.90746147683725	-5.22704518934518	h
7.03863679543391	0.11904450325054	0.75059911029873	c
6.22640813213268	0.48564182635466	2.60757206388244	h
8.15900570571601	-1.60662318823341	0.85027002817500	h
8.29085062210852	1.68077328976678	0.25672151117199	h
-0.55279174342049	8.09210951437734	2.99621916478226	c
0.37128177077861	9.58995615900316	1.92143587772489	h
-2.10776741891136	8.93034520642495	4.05635951939168	h
0.79518162128338	7.28911662566021	4.32511291736882	h
-3.50829164781246	7.11800095378140	-0.63677252596022	c
-5.14505376453969	7.82053436574812	0.39595597769951	h
-2.71381381007637	8.68835558395238	-1.70970164277557	h
-4.14379675337859	5.68866067296741	-1.97303220343968	h
0.00000000000000	0.00000000000000	2.81705383399943	ni
-1.44937605917440	-2.04377644451166	5.36693801338004	c
1.44937605917440	2.04377644451166	5.36693801338004	c
-2.40005644539383	-3.23353332376636	6.94644096626906	n
2.40005644539383	3.23353332376636	6.94644096626906	n

$end
Etot+OCcorr= -2618,065144613 H

trans-[Ni(*i*^{Pr}Im)$_2$(CN)$_2$]

$coord

0.00000000000000	0.00000000000000	3.67279171397866	c
0.00000000000000	0.00000000000000	-3.67279171397866	c
-0.61220127950783	-1.93649820676765	-5.21871454962617	n
0.61220127950783	1.93649820676765	-5.21871454962617	n
-0.61220127950783	1.93649820676765	5.21871454962617	n
0.61220127950783	-1.93649820676765	5.21871454962617	n
0.37458690980044	-1.22188952166755	7.72435552385402	c
0.75298895018050	-2.47455677792392	9.27314055358663	h
-0.37458690980044	1.22188952166755	7.72435552385402	c
-0.75298895018050	2.47455677792392	9.27314055358663	h
0.37458690980044	1.22188952166755	-7.72435552385402	c
0.75298895018050	2.47455677792392	-9.27314055358663	h
-0.37458690980044	-1.22188952166755	-7.72435552385402	c
-0.75298895018050	-2.47455677792392	-9.27314055358663	h
-1.25900972505721	-4.47324486233197	-4.26058754493604	c
-2.21473529335384	-4.11783339702956	-2.47195456430316	h
1.25900972505721	4.47324486233197	-4.26058754493604	c
2.21473529335384	4.11783339702956	-2.47195456430316	h
-1.25900972505721	4.47324486233197	4.26058754493604	c
-2.21473529335384	4.11783339702956	2.47195456430316	h
1.25900972505721	-4.47324486233197	4.26058754493604	c
2.21473529335384	-4.11783339702956	2.47195456430316	h
-1.15172713186205	-5.98117850306230	3.76243227187009	c
-0.68598904975950	-7.79031519055244	2.89093298069007	h
-2.16422834358695	-6.35012460480219	5.52162099483186	h
-2.40254543241400	-4.93849163335887	2.50149220636123	h
3.09409084585061	-5.82641575946585	6.01674774163150	c
2.21207734533280	-6.32985994850597	7.81235605091857	h

3.71395562249247	-7.57508593785302	5.12359572028002	h
4.75621779830534	-4.66875409657182	6.38737411730834	h
-3.09409084585061	5.82641575946585	6.01674774163150	c
-2.21207734533280	6.32985994850597	7.81235605091857	h
-3.71395562249247	7.57508593785302	5.12359572028002	h
-4.75621779830534	4.66875409657182	6.38737411730834	h
1.15172713186205	5.98117850306230	3.76243227187009	c
0.68598904975950	7.79031519055244	2.89093298069007	h
2.16422834358695	6.35012460480219	5.52162099483186	h
2.40254543241400	4.93849163335887	2.50149220636123	h
3.09409084585061	5.82641575946585	-6.01674774163150	c
2.21207734533280	6.32985994850597	-7.81235605091857	h
3.71395562249247	7.57508593785302	-5.12359572028002	h
4.75621779830534	4.66875409657182	-6.38737411730834	h
-1.15172713186205	5.98117850306230	-3.76243227187009	c
-2.40254543241400	4.93849163335887	-2.50149220636123	h
-0.68598904975950	7.79031519055244	-2.89093298069007	h
-2.16422834358695	6.35012460480219	-5.52162099483186	h
-3.09409084585061	-5.82641575946585	-6.01674774163150	c
-2.21207734533280	-6.32985994850597	-7.81235605091857	h
-3.71395562249247	-7.57508593785302	-5.12359572028002	h
-4.75621779830534	-4.66875409657182	-6.38737411730834	h
1.15172713186205	-5.98117850306230	-3.76243227187009	c
0.68598904975950	-7.79031519055244	-2.89093298069007	h
2.16422834358695	-6.35012460480219	-5.52162099483186	h
2.40254543241400	-4.93849163335887	-2.50149220636123	h
0.00000000000000	0.00000000000000	0.00000000000000	ni
3.58591633738114	0.00000000000000	0.00000000000000	c
-3.58591633738114	0.00000000000000	0.00000000000000	c
5.77890432401430	0.00000000000000	0.00000000000000	n
-5.77890432401430	0.00000000000000	0.00000000000000	n

$end

Etot = -2618.0296814740 H

ZPE = 1304 kJ*mol^{-1}

μ = 1131.65 kJ*mol^{-1}

trans-[Ni(*i*^{Pr}Im)$_2$(CN)$_2$]-COSMO

$coord

0.00000000000000	0.00000000000000	3.68082804081662	c
0.00000000000000	0.00000000000000	-3.68082804081662	c
-0.41107972218549	-1.98883051694053	-5.22183912225233	n
0.41107972218549	1.98883051694053	-5.22183912225233	n
-0.41107972218549	1.98883051694053	5.22183912225233	n
0.41107972218549	-1.98883051694053	5.22183912225233	n
0.24878775360553	-1.25378002870982	7.73062173979914	c
0.49204910317099	-2.54428059140823	9.27784646799172	h
-0.24878775360553	1.25378002870982	7.73062173979914	c
-0.49204910317099	2.54428059140823	9.27784646799172	h
0.24878775360553	1.25378002870982	-7.73062173979914	c
0.49204910317099	2.54428059140823	-9.27784646799172	h
-0.24878775360553	-1.25378002870982	-7.73062173979914	c
-0.49204910317099	-2.54428059140823	-9.27784646799172	h
-0.79538640795740	-4.59233210819534	-4.30181671149896	c
-1.38848362428828	-4.36287192822783	-2.34201366596738	h
0.79538640795740	4.59233210819534	-4.30181671149896	c
1.38848362428828	4.36287192822783	-2.34201366596738	h
-0.79538640795740	4.59233210819534	4.30181671149896	c
-1.38848362428828	4.36287192822783	2.34201366596738	h
0.79538640795740	-4.59233210819534	4.30181671149896	c
1.38848362428828	-4.36287192822783	2.34201366596738	h
-1.69559409359598	-6.04662827969267	4.36932748874153	c
-1.43437560324662	-7.92882523730400	3.57277611694587	h
-2.36612855369676	-6.25284264538943	6.30888556829023	h
-3.13734604725147	-5.06117928532191	3.27612407567045	h
2.90870936069242	-5.90638792021726	5.75141795553897	c
2.38611117067554	-6.23835574365100	7.71751739300296	h

3.28672118437292	-7.73705773448267	4.88709549157283	h
4.63968326604659	-4.79084058422074	5.70504282472023	h
-2.90870936069242	5.90638792021726	5.75141795553897	c
-2.38611117067554	6.23835574365100	7.71751739300296	h
-3.28672118437292	7.73705773448267	4.88709549157283	h
-4.63968326604659	4.79084058422074	5.70504282472023	h
1.69559409359598	6.04662827969267	4.36932748874153	c
1.43437560324662	7.92882523730400	3.57277611694587	h
2.36612855369676	6.25284264538943	6.30888556829023	h
3.13734604725147	5.06117928532191	3.27612407567045	h
2.90870936069242	5.90638792021726	-5.75141795553897	c
2.38611117067554	6.23835574365100	-7.71751739300296	h
3.28672118437292	7.73705773448267	-4.88709549157283	h
4.63968326604659	4.79084058422074	-5.70504282472023	h
-1.69559409359598	6.04662827969267	-4.36932748874153	c
-3.13734604725147	5.06117928532191	-3.27612407567045	h
-1.43437560324662	7.92882523730400	-3.57277611694587	h
-2.36612855369676	6.25284264538943	-6.30888556829023	h
-2.90870936069242	-5.90638792021726	-5.75141795553897	c
-2.38611117067554	-6.23835574365100	-7.71751739300296	h
-3.28672118437292	-7.73705773448267	-4.88709549157283	h
-4.63968326604659	-4.79084058422074	-5.70504282472023	h
1.69559409359598	-6.04662827969267	-4.36932748874153	c
1.43437560324662	-7.92882523730400	-3.57277611694587	h
2.36612855369676	-6.25284264538943	-6.30888556829023	h
3.13734604725147	-5.06117928532191	-3.27612407567045	h
0.00000000000000	0.00000000000000	0.00000000000000	ni
3.57623999014598	0.00000000000000	0.00000000000000	c
-3.57623999014598	0.00000000000000	0.00000000000000	c
5.77045675826954	0.00000000000000	0.00000000000000	n
-5.77045675826954	0.00000000000000	0.00000000000000	n

$end
Etot+OCcorr= -2618,0669948266 H

cis-[Ni($^{i\mathrm{Pr}}$Im)$_2$(Me)$_2$]

$coord

-1.48153258550856	-2.37082400837204	-0.14553449732656	c
1.48153258550856	2.37082400837204	-0.14553449732656	c
0.89932281327353	4.85714647191044	-0.49663671131308	n
3.57299237776162	2.02515861093232	-1.60833505913546	n
-0.89932281327353	-4.85714647191044	-0.49663671131308	n
-3.57299237776162	-2.02515861093232	-1.60833505913546	n
-4.30863239027240	-4.24845498143136	-2.78261409750013	c
-5.92176796410892	-4.38388644849390	-4.00502357950538	h
-2.61496089798732	-6.02789213960290	-2.09165476041586	c
-2.48639887342416	-7.98723662986618	-2.60598889493190	h
4.30863239027240	4.24845498143136	-2.78261409750013	c
5.92176796410892	4.38388644849390	-4.00502357950538	h
2.61496089798732	6.02789213960290	-2.09165476041586	c
2.48639887342416	7.98723662986618	-2.60598889493190	h
-1.20814218709468	6.15126736431148	0.76316230427700	c
-2.14593259195815	4.66661039334256	1.83829081276788	h
4.93101831820204	-0.39391933228131	-1.66141499820832	c
3.44204562425796	-1.79905105931835	-1.47918144355814	h
1.20814218709468	-6.15126736431148	0.76316230427700	c
2.14593259195815	-4.66661039334256	1.83829081276788	h
-4.93101831820204	0.39391933228131	-1.66141499820832	c
-3.44204562425796	1.79905105931835	-1.47918144355814	h
-6.67670335538336	0.61926915759066	0.62646570919795	c
-7.56536537926258	2.48000976058043	0.66476031707076	h
-8.16363404383744	-0.80965503712196	0.55685248970574	h
-5.58865527630636	0.36243409794853	2.35583810137570	h
-6.30317694593346	0.79961242335553	-4.16013080877924	c
-7.89593858767552	-0.49255124761848	-4.37989087346098	h
-7.05932266637250	2.71487963639073	-4.21696268283011	h
-5.03315994899012	0.55667204540971	-5.76481659537617	h

```
  0.23776699854858   -8.15205643157237    2.60423341309446  c
 -0.75435141756891   -9.66139527179620    1.60569012961210  h
  1.82153132810870   -8.99707122471507    3.61713593650588  h
 -1.03947484831288   -7.30813444304550    3.97520742302889  h
  3.04109874830857   -7.26490369006309   -1.17223216640964  c
  4.69316422149937   -8.03455727545473   -0.21103382329026  h
  2.16313999936890   -8.79837459733655   -2.23726669170649  h
  3.67483435912428   -5.83950811828760   -2.51575078487187  h
  6.30317694593346   -0.79961242335553   -4.16013080877924  c
  7.89593858767552    0.49255124761848   -4.37989087346098  h
  7.05932266637250   -2.71487963639073   -4.21696268283011  h
  5.03315994899012   -0.55667204540971   -5.76481659537617  h
  6.67670335538336   -0.61926915759066    0.62646570919795  c
  5.58865527630636   -0.36243409794853    2.35583810137570  h
  7.56536537926258   -2.48000976058043    0.66476031707076  h
  8.16363404383744    0.80965503712196    0.55685248970574  h
 -0.23776699854858    8.15205643157237    2.60423341309446  c
  0.75435141756891    9.66139527179620    1.60569012961210  h
 -1.82153132810870    8.99707122471507    3.61713593650588  h
  1.03947484831288    7.30813444304550    3.97520742302889  h
 -3.04109874830857    7.26490369006309   -1.17223216640964  c
 -4.69316422149937    8.03455727545473   -0.21103382329026  h
 -2.16313999936890    8.79837459733655   -2.23726669170649  h
 -3.67483435912428    5.83950811828760   -2.51575078487187  h
  1.55818949005943    2.04909889046952    5.00109165599228  c
 -1.55818949005943   -2.04909889046952    5.00109165599228  c
  3.07997551915422    3.33732639783313    4.43745334955564  h
  0.09411981047676    3.19088143291246    5.92323608666166  h
  2.32147239341647    0.78771377374762    6.45119110187525  h
 -0.09411981047676   -3.19088143291246    5.92323608666166  h
 -2.32147239341647   -0.78771377374762    6.45119110187525  h
 -3.07997551915422   -3.33732639783313    4.43745334955564  h
 -0.00000000000000   -0.00000000000000    2.22771927579661  ni
$end
Etot = -2512.0742291750 H
ZPE = 1448 kJ*mol^-1
μ = 1289.72 kJ*mol^-1
```

cis-[Ni(^iPrIm)$_2$(Me)$_2$]-COSMO

```
$coord
  1.91580115386352    0.02608140772150    1.99905722284166  c
 -2.04150656455558   -0.03199200085039   -1.87057585357390  c
 -3.63483440496599    1.75023892253296   -2.82678555437267  n
 -3.58507545249523   -2.02363189840836   -1.35673242087618  n
  2.98737486035551   -1.78017136990709    3.48854097812156  n
  1.35209543878324    1.92225918482891    3.64218780245688  n
  2.10340285002827    1.33680971544101    6.08313011620637  c
  1.84141274931535    2.58570093664767    7.66093589886791  h
  3.12248843289629   -1.00265033864657    5.98687041472019  c
  3.89788560396518   -2.15982200303783    7.46447151907368  h
 -6.06688543327515   -1.51690019674824   -2.02697056118937  c
 -7.58112292071961   -2.84626501405115   -1.78673522664303  h
 -6.09879560471000    0.86703226149169   -2.94166908532565  c
 -7.64438018517895    1.98902977718795   -3.63152319960355  h
 -2.83959393020160    4.26507528805443   -3.70339320253266  c
 -0.83147418140216    4.35251873468779   -3.25927373507702  h
 -2.60885879319623   -4.43793131599303   -0.38673633370374  c
 -1.06869285033384   -3.88662536728723    0.85521788314963  h
  3.95455643885637   -4.21510344706112    2.56070011323058  c
  3.46559857356020   -4.23356721585937    0.56120201367449  h
  0.25383239661330    4.33133654255367    2.79793640319856  c
 -0.99795189230811    3.79357357876990    1.26089448584998  h
  2.31135771066216    6.05544340224825    1.73771592632086  c
  1.47190045915178    7.77519945543996    0.97056249597639  h
  3.65109219173867    6.58633974444062    3.21453022048256  h
  3.32355452234446    5.07772685465150    0.23328138464585  h
```

-1.29616094871318	5.59014590966597	4.87115812087451	c
-0.10619111319488	6.26070981385566	6.41577378800249	h
-2.26873714537117	7.22739067053449	4.08609238609258	h
-2.70998715548291	4.30188631429166	5.63807475465709	h
6.82694936126882	-4.34595721907185	2.82316917814312	c
7.38680114768666	-4.30214779644195	4.80837525744080	h
7.52091278676869	-6.10526573701009	2.00406740773952	h
7.71742900655698	-2.76985991465504	1.84791826020467	h
2.66107360894113	-6.42280260742967	3.90052650822203	c
3.24527831294395	-8.19827490846777	3.03442452452696	h
3.18138799879295	-6.48904904348269	5.89505625493558	h
0.61101837501125	-6.28385861623204	3.77983960461060	h
-4.58719379758866	-5.85755119117311	1.14822689129320	c
-6.12749906339288	-6.54463051047944	-0.03789876977846	h
-3.70723652738487	-7.49875046300192	2.02853102507141	h
-5.37785448200807	-4.66977860700742	2.63506817303556	h
-1.52082746982577	-6.01896233398375	-2.54226175264429	c
-0.08554202425583	-4.92953846491395	-3.54071786829363	h
-0.65820032555325	-7.73738223171311	-1.79816434603700	h
-3.00314965201430	-6.55680572355071	-3.87312350621115	h
-3.17787261625204	4.51081822306965	-6.56027646000700	c
-5.17230934867123	4.40205373997444	-7.07681861495495	h
-2.45459291507831	6.33438077252458	-7.19207810958342	h
-2.15597153759895	3.02145157177703	-7.54291911451064	h
-4.24375506320953	6.35038362562127	-2.28145381013696	c
-3.47199855030230	8.18743659710028	-2.80423161793311	h
-6.25150768123495	6.34883178009967	-2.75280638685807	h
-4.06634782477686	6.12665348175515	-0.24306545406035	h
1.73287474857914	-0.13084959475137	-5.45033311447543	c
5.39591178946708	0.45581509803895	-1.84405534930615	c
0.00255667965831	-0.81899344462528	-6.35896333293288	h
2.12747257364699	1.74937818161823	-6.23424667998525	h
3.28739467154595	-1.36936623465234	-6.03957021264568	h
6.25377818798692	-1.36689030128611	-2.34135583485130	h
5.89136956825110	1.78829038248364	-3.35290781198301	h
6.31420598870198	1.10725650368188	-0.10463295308462	h
1.63333926731021	0.07412663898977	-1.67126074049626	ni

$end
Etot+OCcorr= -2512,0933828789 H

trans-[Ni(*i*^{Pr}Im)$_2$(Me)$_2$]

$coord

0.00000000000000	-0.00000000000000	3.67416041754594	c
0.00000000000000	-0.00000000000000	-3.48203624587538	c
0.28087654211472	2.00586316856093	-5.06250925101814	n
-0.28087654211472	-2.00586316856093	-5.06250925101814	n
0.52654388378521	-1.95888986304664	5.25059071992877	n
-0.52654388378521	1.95888986304664	5.25059071992877	n
-0.31837128940562	1.23697541572543	7.76162193867096	c
-0.63602960045473	2.50255074055304	9.31445210981863	h
0.31837128940562	-1.23697541572543	7.76162193867096	c
0.63602960045473	-2.50255074055304	9.31445210981863	h
-0.17238144330450	-1.26434973898123	-7.57468359099089	c
-0.34345929122720	-2.56804364187736	-9.12109855652364	h
0.17238144330450	1.26434973898123	-7.57468359099089	c
0.34345929122720	2.56804364187736	-9.12109855652364	h
0.58391393967153	4.60941943607860	-4.16274549112339	c
0.76428581713578	4.41555935165206	-2.12078124931974	h
-0.58391393967153	-4.60941943607860	-4.16274549112339	c
-0.76428581713578	-4.41555935165206	-2.12078124931974	h
1.05045800936702	-4.50633863654459	4.27752138316582	c
2.06858226350001	-4.17519076128666	2.51629548679345	h
-1.05045800936702	4.50633863654459	4.27752138316582	c
-2.06858226350001	4.17519076128666	2.51629548679345	h
1.42549753095959	5.86338731919840	3.66837615283834	c
1.04444994108901	7.68841136958269	2.78596292516399	h

2.52536188878559	6.18903422838282	5.38392552608564	h
2.54574650913513	4.71692000755342	2.37564125201390	h
-2.73409648422504	6.00687411448243	6.06739037811503	c
-1.75837990659813	6.48347395217231	7.82198759959585	h
-3.27771243885053	7.77717707723066	5.16577156617799	h
-4.44937774004884	4.96323385008083	6.52845375738637	h
2.73409648422504	-6.00687411448243	6.06739037811503	c
1.75837990659813	-6.48347395217231	7.82198759959585	h
3.27771243885053	-7.77717707723066	5.16577156617799	h
4.44937774004884	-4.96323385008083	6.52845375738637	h
-1.42549753095959	-5.86338731919840	3.66837615283834	c
-1.04444994108901	-7.68841136958269	2.78596292516399	h
-2.52536188878559	-6.18903422838282	5.38392552608564	h
-2.54574650913513	-4.71692000755342	2.37564125201390	h
-3.00256019323553	-5.78886670777927	-5.20101873314670	c
-2.91895284844732	-6.00779190681029	-7.25115645264038	h
-3.27880680684874	-7.65913471095974	-4.38084778385016	h
-4.63331687774587	-4.62204634593360	-4.73323699360606	h
1.77116964363919	-6.17078312900118	-4.74929739755862	c
3.44014323966413	-5.28394616688339	-3.93199148814131	h
1.58107095859654	-8.06732832481528	-3.96402602117730	h
2.05770143551299	-6.35093391155663	-6.78505623824352	h
3.00256019323553	5.78886670777927	-5.20101873314670	c
2.91895284844732	6.00779190681029	-7.25115645264038	h
3.27880680684874	7.65913471095974	-4.38084778385016	h
4.63331687774587	4.62204634593360	-4.73323699360606	h
-1.77116964363919	6.17078312900118	-4.74929739755862	c
-1.58107095859654	8.06732832481528	-3.96402602117730	h
-2.05770143551299	6.35093391155663	-6.78505623824352	h
-3.44014323966413	5.28394616688339	-3.93199148814131	h
-0.00000000000000	0.00000000000000	0.10803970156493	ni
-3.83798321178832	0.06542309584375	0.03864756731857	c
3.83798321178832	-0.06542309584375	0.03864756731857	c
-4.56933695321577	-1.64751605225590	-0.87491047548591	h
-4.54375229894818	1.65665640708071	-1.08908516889997	h
-4.74365760402491	0.18571101129572	1.89572459203473	h
4.56933695321577	1.64751605225590	-0.87491047548591	h
4.74365760402491	-0.18571101129572	1.89572459203473	h
4.54375229894818	-1.65665640708071	-1.08908516889997	h

$end
Etot = -2512.0808630090 H
ZPE = 1444 kJ*mol^{-1}
μ = 1277.66 kJ*mol^{-1}

trans-[Ni($^{i\mathrm{Pr}}$Im)$_2$(Me)$_2$]-COSMO

$coord

-0.00000000000000	0.00000000000000	3.69115690175378	c
0.00000000000000	0.00000000000000	-3.49397477160649	c
0.21029390238314	2.01493598603828	-5.07067522503874	n
-0.21029390238314	-2.01493598603828	-5.07067522503874	n
0.48510707267052	-1.97021198355893	5.26383936590184	n
-0.48510707267052	1.97021198355893	5.26383936590184	n
-0.29255807556411	1.24446520113210	7.77700087943279	c
-0.57927989051159	2.51885515627827	9.33011590683592	h
0.29255807556411	-1.24446520113210	7.77700087943279	c
0.57927989051159	-2.51885515627827	9.33011590683592	h
-0.12952645997625	-1.27061832491405	-7.58505417309175	c
-0.25819249773135	-2.58105538644009	-9.13133755321461	h
0.12952645997625	1.27061832491405	-7.58505417309175	c
0.25819249773135	2.58105538644009	-9.13133755321461	h
0.44331298515228	4.63386975659721	-4.17963594858591	c
0.55508384884622	4.46049699227874	-2.13046413329708	h
-0.44331298515228	-4.63386975659721	-4.17963594858591	c
-0.55508384884622	-4.46049699227874	-2.13046413329708	h
0.95538622800902	-4.53683266332675	4.29983897552243	c
1.97326627445782	-4.23745674178766	2.53311385423430	h

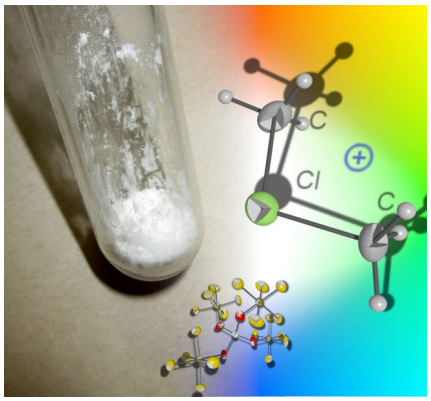
-0.95538622800902	4.53683266332675	4.29983897552243	c
-1.97326627445782	4.23745674178766	2.53311385423430	h
1.54833783622442	5.84687017918183	3.70361637405748	c
1.20219356950484	7.69130474374237	2.84973660006897	h
2.65561386506046	6.12274778145131	5.42307953432988	h
2.63649566152634	4.69782113860300	2.38526252016609	h
-2.60915665284155	6.06481451979684	6.09379002961109	c
-1.62681074561803	6.50162932256937	7.85394848184435	h
-3.10431071047180	7.85190366533146	5.19705666431476	h
-4.35077558198319	5.05948776485559	6.54427451973098	h
2.60915665284155	-6.06481451979684	6.09379002961109	c
1.62681074561803	-6.50162932256937	7.85394848184435	h
3.10431071047180	-7.85190366533146	5.19705666431476	h
4.35077558198319	-5.05948776485559	6.54427451973098	h
-1.54833783622442	-5.84687017918183	3.70361637405748	c
-1.20219356950484	-7.69130474374237	2.84973660006897	h
-2.65561386506046	-6.12274778145131	5.42307953432988	h
-2.63649566152634	-4.69782113860300	2.38526252016609	h
-2.87606764214775	-5.84108183986206	-5.15165640602488	c
-2.85207591184209	-6.02493388264272	-7.20613060873455	h
-3.08921718448513	-7.72717634136659	-4.34940540490867	h
-4.51299481471261	-4.71157639124079	-4.61410192690964	h
1.90761834442643	-6.15941119789099	-4.86645501528503	c
3.59876437949512	-5.26249490050575	-4.10531369006476	h
1.76640416849888	-8.06204532259171	-4.08699595709248	h
2.11493478893140	-6.32088365494116	-6.91279546175185	h
2.87606764214775	5.84108183986206	-5.15165640602488	c
2.85207591184209	6.02493388264272	-7.20613060873455	h
3.08921718448513	7.72717634136659	-4.34940540490867	h
4.51299481471261	4.71157639124079	-4.61410192690964	h
-1.90761834442643	6.15941119789099	-4.86645501528503	c
-1.76640416849888	8.06204532259171	-4.08699595709248	h
-2.11493478893140	6.32088365494116	-6.91279546175185	h
-3.59876437949512	5.26249490050575	-4.10531369006476	h
0.00000000000000	0.00000000000000	0.11180877512265	ni
-3.83384098450998	0.09939322394173	0.04021287741102	c
3.83384098450998	-0.09939322394173	0.04021287741102	c
-4.56045743969745	-1.61525502978079	-0.87623357945095	h
-4.50678910959000	1.70603360248709	-1.08788503475372	h
-4.72692128983546	0.23093440373678	1.90475808210777	h
4.56045743969745	1.61525502978079	-0.87623357945095	h
4.72692128983546	-0.23093440373678	1.90475808210777	h
4.50678910959000	-1.70603360248709	-1.08788503475372	h

$end
Etot+OCcorr= -2512,0971771204 H

References

[1] Y. Marcus, *The properties of solvents*, Wiley, Chichester, **1999**.
[2] T. Zell, U. Radius, *Z. Anorg. Allg. Chem.* **2013**, *639*, 334.
[3] R. Jothibasu, K.-W. Huang, H. V. Huynh, *Organometallics* **2010**, *29*, 3746.
[4] P. Fischer, T. Linder, U. Radius, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1491.
[5] T. Schaub, C. Döring, U. Radius **2007**, 1993.
[6] D. Zhang, S. Zhou, Z. Li, Q. Wang, L. Weng, *Dalton Trans.* **2013**, *42*, 12020.
[7] T. Schaub, M. Backes, U. Radius **2008**, *2008*, 2680.

4.2 A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$



Sebastian Hämmerling, Günther Thiele, Simon Steinhauer, Helmut Beckers, Carsten Müller, and Sebastian Riedel*

Angew. Chem. Int. Ed. **2019**, *58*(29), 9807-9810.

https://doi.org/10.1002/anie.201904007

Author contribution

Sebastian Hämmerling contributed to the project design, performed all experiments, the product characterization, most quantum-chemical calculations and wrote the manuscript. Carsten Müller performed quantum-chemical calculations. Günther Thiele and Simon Steinhauer conducted the crystallographic studies. Simon Steinhauer and Sebastian Riedel supervised the project and provided scientific guidelines. Simon Steinhauer, Günther Thiele, Helmut Beckers and Sebastian Riedel revised the manuscript.

Weakly Coordinating Anions | Hot Paper

International Edition: DOI: 10.1002/anie.201904007
German Edition: DOI: 10.1002/ange.201904007

A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$

*Sebastian Hämmerling, Günther Thiele, Simon Steinhauer, Helmut Beckers, Carsten Müller, and Sebastian Riedel**

Dedicated to Professor Hans-Ulrich Reißig on the occasion of his 70th birthday

Abstract: *A new chloronium-containing salt, $[Me_2Cl][Al(OTeF_5)_4]$, was synthesized on multigram scale by means of a simple one-pot procedure. The isolated product can be handled at room temperature and used as a strong electrophilic methylation agent. This is demonstrated by the methylation of the very weak bases $P(CF_3)_3$, PF_3, MeI, and MeBr.*

Strong and easily accessible electrophilic methylation agents are rare. The strongest known methylation systems are MeF/SbF_5 in liquid SO_2[1,2] or anhydrous HF,[3] and the *closo*-carborates $Me(CHB_{11}Me_5X_6)$ (X = Cl, Br).[4] It is possible to crystallize methylated SO_2, that is, $[MeSO_2][SbF_6]$, from a mixture of MeF/SbF_5/SO_2.[1,2] However, because of secondary reactions of the strong Lewis acid SbF_5 as an oxidizer, its synthetic usability is limited.[5] The application of methyl cations stabilized by *closo*-carborates is limited by the small-scale accessibility of these compounds.[6] Another class of strong alkylation agents are salts with dialkylhalonium cations.[7,8] Such cations can be prepared by the reaction of SbF_5·MeF with MeX (X = I, Br, Cl) in liquid SO_2. Their alkylation strength increases from the iodonium cation $[Me_2I]^+$ to the chloronium cation $[Me_2Cl]^+$. The elusive fluoronium cation $[Me_2F]^+$—proposed to be an even stronger methylation agent—has been detected by mass spectrometry.[9] Attempts to synthesize this elusive species have failed thus far, and yielded decomposition products such as HF and $C_2H_5^+$ cations instead.[10] In contrast, a bis-silylated fluoronium salt, $[(Me_3Si)_2F][B(C_6F_5)_4]$,[11] and a cage-like C–F–C hydrocarbon-based system were described recently.[12]

The $[Me_2Cl]^+$ cation can also be accessed by using a Brønsted superacid. Addition of chloromethane to $H(CHB_{11}Cl_{11})$ was reported to yield first HCl and $Me(CHB_{11}Cl_{11})$. The latter reacts further with a second chloromethane molecule to the $[Me_2Cl]^+$ cation.[10,13] We recently reported the synthesis of a new Brønsted superacid, $[ArH][Al(OTeF_5)_4]$ (*Ar* = *ortho*-$C_6H_4F_2$).[14] It was obtained in multigram batches by a simple one-step synthesis based on the reaction of triethylaluminum ($AlEt_3$) and pentafluoroorthotelluric acid ($HOTeF_5$) in *ortho*-difluorobenzene (*o*DFB). We were thus interested in the generation of strong methylation agents, starting from this readily available Brønsted superacid.

Herein, we present the simple one-step synthesis of the dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]$·MeCl (**1·MeCl**) using the superacidic system of in situ generated $H[Al(OTeF_5)_4]$ in neat chloromethane [Eq. (1)]. Upon addition of pentafluoroorthotelluric acid to a solution of triethylaluminum in chloromethane at −40 °C, the initial reaction mixture changed color, from a yellow tinge to a colorless solution, within five minutes. Distillation of excess MeCl from the reaction mixture under reduced pressure led to the formation of a colorless precipitate that still contained solvate MeCl, which can be removed in vacuo at room temperature. Once solvent-free, $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) can be isolated as a colorless powder and is stable for hours at room temperature, where it turns brown within days; however, IR and NMR data indicated the absence of impurities or decomposition. The NMR spectra of **1** contained resonances for the methyl groups with the expected chemical shifts and coupling constants ($\delta(^1H) = 5.61$ ppm; $\delta(^{13}C) = 52.7$ ppm; $^1J(^{13}C,^1H) = 162.1$ Hz; see the Supporting Information, Figure S1 for the ^1H NMR spectrum) and a cross-signal in the $^1H,^{13}C$ HMBC spectrum due to the $^3J(^{13}C,^1H)$ coupling. Its IR data correspond well with literature-reported values.[7,8,13]

$$AlEt_3 + 4\ HOTeF_5 \xrightarrow[-40\ °C,\ 15\ min\ -3\ ethane]{MeCl} \underset{\textbf{(1)}}{[Me_2Cl][Al(OTeF_5)_4]} + HCl\uparrow \qquad (1)$$

Colorless crystals suitable for X-ray diffraction where grown from a MeCl/*n*-pentane mixture at −80 °C. **1·MeCl** crystallizes in the monoclinic space group $P2_1/n$ (Figure 1). Both solvate MeCl and the aluminate anion are disordered as shown in the Supporting Information (Figure S2). The cation $[Me_2Cl]^+$ features a C1-Cl1-C2 bond angle of 101.0(7)°, and a considerably elongated C–Cl bond (d(C1–Cl1) = 183.9(16) pm, d(C2–Cl1) = 180.1(19) pm) compared to free MeCl (d(C–Cl) = 178.1 pm).[15] The structure of the cation is similar to those in $[Me_2Cl][CHB_{11}Cl_{11}]$.[13] The cation shows a weak contact to the embedded MeCl through a weak C2–H–Cl2 hydrogen bridge[16] (d(C2–Cl2) = 339.2(18) pm) and three further contacts to neighboring anions through weak C–H–F hydrogen bridges (d(C1–F) = 316.7(21) pm, d(C2–F) = 313.2(22) pm, and d(C2–F) = 311.2(22) pm; see Figure S3).

Compound **1** is soluble in MeCl, SO_2, and SO_2ClF, but decomposes in solution within days at room temperature,

[*] M. Sc. S. Hämmerling, Dr. G. Thiele, Dr. S. Steinhauer, Dr. H. Beckers, Dr. C. Müller, Prof. Dr. S. Riedel
Freie Universität Berlin
Institut für Chemie und Biochemie
Fabeckstr.34/36, 14195 Berlin (Germany)
E-mail: s.riedel@fu-berlin.de
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201904007.

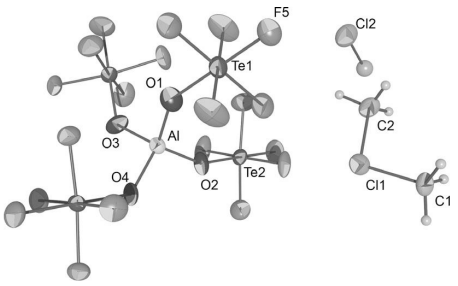


Figure 1. Molecular structure of **1·MeCl** in the solid state. Hydrogen atoms of solvate MeCl are omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: C1–Cl1 183.9(16), C2–Cl1 180.1(19), C1-Cl1-C2 101.0(7), Al–O1 184.5(14), Al–O2 166.4(14), Al–O3 178.7(14), Al–O4 176.1(14), O1–Te1 180.7(11), O1-Al-O2 112.0(7), O1-Al-O3 107.0(7), O1-Al-O4 110.8(7), O2-Al-O3 114.6(8), O3-Al-O4 105.0(7), O4-Al-O2 107.4(7).

yielding $MeOTeF_5$ from the methylation of the weakly coordinating anion. It can thus be used as a Me^+ transfer reagent.

To evaluate this methylation ability, the fluorinated phosphorus(III) compounds $P(CF_3)_3$ and PF_3 were chosen as reagents because of their weak nucleophilicity and basicity.[3,17] The reaction of **1** with $P(CF_3)_3$ [Eq. (2)] proceeds slowly at room temperature with formation of the previously reported cation $[MeP(CF_3)_3]^+$, as confirmed by its characteristic ^{31}P NMR spectrum ($\delta(^{31}P) = 40.6$ ppm, decet of quartets with $^2J(^{31}P,^{19}F) = 127.6$ Hz, $^2J(^{31}P,^1H) = 15.7$ Hz; see Figure 2).[3] The formation of $[MeP(CF_3)_3]^+$ indicates that the methylation strength of **1** is similar to that of the strongest known methylation system MeF/HF/SbF_5. Furthermore, reaction 2 occurs at room temperature while the reaction of MeF/HF/SbF_5 and $P(CF_3)_3$ requires temperatures below −10 °C to prevent secondary reactions of the phosphonium cation in solution.

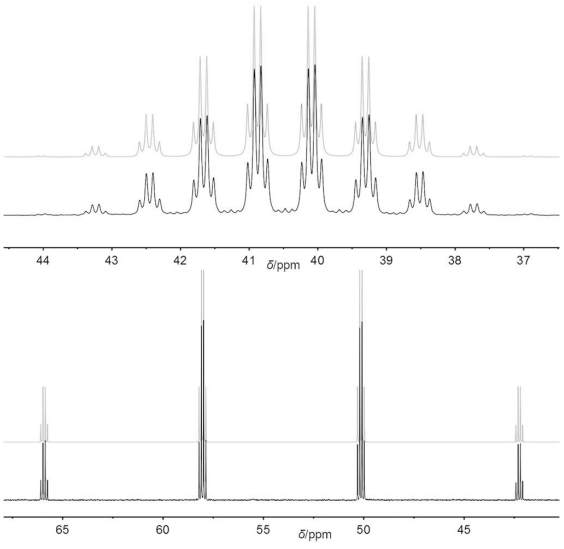
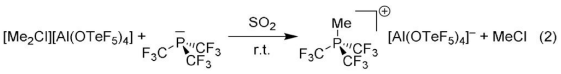
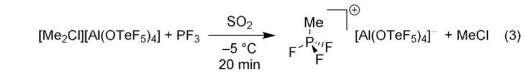


Figure 2. ^{31}P NMR spectra (161.2 MHz, SO_2, 20 °C) of $[MeP(CF_3)_3][Al(OTeF_5)_4]$ (top) and $[MePF_3][Al(OTeF_5)_4]$ (**2**; bottom). Experimental spectra are shown in black, simulated ones are depicted in gray.



An even more challenging cation is $[MePF_3]^+$, which has thus far only been detected in the gas phase by ICR mass spectrometry.[18] Treatment of PF_3 with **1** in liquid SO_2 at −10 °C leads to the formation of the elusive $[MePF_3]^+$ cation in the salt $[MePF_3][Al(OTeF_5)_4]$ (**2**) [Eq. (3)]. This is supported by the observed doublet of quartets in the ^1H NMR spectrum at $\delta(^1H) = 3.35$ ppm with $^2J(^{31}P,^1H) = 18.1$ Hz and $^3J(^{19}F,^1H) = 8.1$ Hz. The signal in the ^{31}P NMR spectrum at $\delta(^{31}P) = 53.1$ ppm revealed a smaller $^1J(^{31}P,^{19}F)$ coupling constant of 1277 Hz compared to the signal obtained for PF_3 in SO_2 solution with 1403 Hz. The reaction product was isolated as an off-white powder, but rapidly decomposed at room temperature to a dark brown oil. The experimental IR spectrum of **2** (see Table S1) is in good agreement with the spectrum calculated at the RI-B3LYP-D3/def2-TZVPP level of theory.



The $[MePF_3][Al(OTeF_5)_4]$ salt decomposes in SO_2 solution at room temperature much faster than **1**, forming initially the $[MePF_2(OTeF_5)]^+$ cation, which further reacts to $[MePF(OTeF_5)_2]^+$, as observed by NMR spectroscopy. Depending on the number of fluorine substituents in $[MePF_{3-x}(OTeF_5)_x]^+$, the ^{31}P resonance shifts from 53.1 ppm ($x = 0$) to 45.2 ppm ($x = 1$) and 37.1 ppm ($x = 2$). Within this series, the $^1J(^{31}P,^{19}F)$ coupling constants decrease from 1277 Hz to 1233 Hz and 1192 Hz. This decomposition pathway of the aluminate anion indicates the strongly Lewis acidic character of the phosphonium cations. We note that the fluoride ion affinity (FIA) of the phosphonium cations $[MePF_{3-x}(OTeF_5)_x]^+$ decreases with increasing number x of the $OTeF_5$ substituents (Table 1). This observation is surprising as it not only indicates an increase in stability by substitution of F by the $OTeF_5$ group, it also contradicts common textbook knowledge that the $OTeF_5$ substituent has a higher group electronegativity than fluo-

Table 1: Fluoride ion affinities (FIAs) of selected Lewis acids in kJ mol^{-1}.

Compound	FIA[a]	Compound	FIA[a]
BF_3	356	$[MeP(OTeF_5)_3]^+$	767
PF_5	385	$[MePF(OTeF_5)_2]^+$	782
AsF_5	445	$[MePF_2(OTeF_5)]^+$	811
SbF_5	500	$[MeP(CF_3)_3]^+$	811
$[FP(C_6F_5)_3]^+$	773	$[MePF_3]^+$	851

[a] At the RI-B3LYP-D3/def2-TZVPP level of theory using TMS^+/TMSF as the anchor point.[20]

rine.[19] Indeed, the fluoride ion affinity of, for example, $E(OTeF_5)_5$ has been shown to be higher than that of EF_5 (E = As, Sb),[20] and this conclusion is in accordance with our observation of an increase in FIA values within the series $PF_{5-x}(OTeF_5)_x$ with x (see Figure S4). These seemingly contradictory results for the two series of the phosphonium cations and the neutral hypervalent species can be attributed to the bonding properties of the $OTeF_5$ group. Our preliminary NBO analysis[21] revealed that substitution of F by the $OTeF_5$ group in $[MePF_{3-x}(OTeF_5)_x]^+$ indeed reduces the NPA charge at the central phosphorus atom and thus decreases its Lewis acidity (Figure S5). This trend is generally found for the series $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$, and also for the neutral species $PF_{5-x}(OTeF_5)_x$ (see Figure S5), which can most probably be attributed to both the higher ionic character of the P–F bond (Table S3) and the stronger π-bonding of the oxygen lone pairs, especially in the two-center-two-electron bonds of these systems. On the other hand, the F_5TeO group preferentially stabilizes three-center-four-electron bonds in hypervalent species compared to a fluorine ligand because it allows for a more efficient charge delocalization via the σ*(P–O) orbitals than the σ*(P–F) orbitals (Figure S6). This most likely results in the higher FIA values for the $OTeF_5$-substituted neutral derivatives.

Based on the very high computed FIA value of $[MePF_3]^+$ (851 kJ mol^{-1}), this is an even stronger Lewis acid than the previously reported exceptionally strong Lewis acid $[FP(C_6F_5)_3]^+$ with a FIA value of 773 kJ mol^{-1}.[22] The experimental determination of the Lewis acidity of the $[MePF_3]^+$ cation by either ^{31}P NMR spectroscopy using triethylphosphine oxide (Gutmann–Beckett method)[23] or IR spectroscopy using an acetonitrile adduct[24] is not possible because of the methylation reactions of the substrates.[25] Therefore, a solution of **2** was combined with a solution of either $[^nBu_4N][PF_6]$ [Eq. (4)] or $[^nBu_4N][SbF_6]$ at −70 °C and allowed to warm to room temperature.

$$[MePF_3][Al(OTeF_5)_4] + [^nBu_4N][PF_6] \xrightarrow[\text{r.t.}]{SO_2} MePF_4 + PF_5 + \underset{[Al(OTeF_5)_4]}{[^nBu_4N]} \quad (4)$$

The reaction of **2** with $[PF_6]^-$ anions yields $MePF_4$[26] as observed in the ^{31}P NMR spectrum (quintet of quartets, $\delta(^{31}P) = -27.0$ ppm, $^1J(^{31}P,^{19}F) = 967.9$ Hz, $^2J(^{31}P,^1H) = 7.2$ Hz). In contrast, the $[SbF_6]^-$ anion is stable in the presence of **2**, and it can be concluded that the Lewis acidity of **2** in solution is higher than that of PF_5, but lower than that of SbF_5. The reaction of the chloronium salt **1** with $[^nBu_4N][PF_6]$ or $[^nBu_4N][SbF_6]$ at room temperature in SO_2 yielded MeF and PF_5 or SbF_5, respectively [Eq. (5)]. This observation exemplifies the high electrophilicity of **1**. $[^nBu_4N][AsF_6]$ reacts with **1** under formation of MeF. The formation of AsF_5 could not be confirmed as the reaction mixture rapidly formed an insoluble gel, even at −40 °C.

$$\underset{E = P, Sb}{[Me_2Cl][Al(OTeF_5)_4] + [^nBu_4N][EF_6]} \xrightarrow[\text{r.t.}]{SO_2} \underset{[^nBu_4N][Al(OTeF_5)_4]}{MeCl + MeF + EF_5} \quad (5)$$

Iodomethane and the even less basic molecule bromomethane are also methylated quantitatively by **1** under formation of $[Me_2I]^+$ or $[Me_2Br]^+$, respectively [Eq. (6)], as confirmed by IR and NMR spectroscopy ($[Me_2I]^+$: $\delta(^1H) = 3.59$ ppm; $\delta(^{13}C) = 11.7$ ppm; $^1J(^{13}C,^1H) = 158.7$ Hz; $^1H,^{13}C$ HMBC: cross-signal; $[Me_2Br]^+$: $\delta(^1H) = 5.31$ ppm; $\delta(^{13}C) = 40.2$ ppm; $^1J(^{13}C,^1H) = 161.4$ Hz; $^1H,^{13}C$ HMBC: cross-signal = .[7,8] $[Me_2I][Al(OTeF_5)_4]$ was obtained as a colorless powder that is stable at room temperature and soluble in dichloromethane without decomposition for months, while $[Me_2Br]^+$ is only as stable as **1**.

$$[Me_2Cl][Al(OTeF_5)_4] + MeX \xrightarrow[\text{r.t.}]{SO_2} \underset{X = Br, I}{Me_2X^{\oplus}\,[Al(OTeF_5)_4]^-} + MeCl \quad (6)$$

According to the proton affinities (PAs), SO_2 should be methylated by **1**. However, this was not observed as **1** can be handled in liquid SO_2 at room temperature. Therefore, the methyl cation affinities (MCAs) were investigated (see Table 2; for more values see Table S2). The MCA predicts the reactivity of **1** in liquid SO_2, that is, the absence of a methylation of SO_2 with **1**, correctly. Furthermore, even more methylation reactions that are predicted wrongly with the PAs were predicted correctly with the MCAs, such as the methylation of acetonitrile with $[Me_3O]^+$.[27] Hence literature values of PA may be a first reactivity hint for methylation reactions, but calculating the MCAs is quite convenient and recommended.

Table 2: Experimental and calculated[a] proton affinities (PAs) and methyl cation affinities (MCAs)[b] in kJ mol^{-1}.

Compound	PA	MCA
SO_2	672.3[28]	*229.1*, 254[29]
MeCl	647.3[28]	*279.2*, 260[29]
MeBr	664.2[28]	*294.4*, 265[29]
MeI	691.7[28]	*323.7*
$P(CF_3)_3$	*690.9*	*367.2*
PF_3	695.3,[28] 669 ± 21[18]	*370.2*
Me_2O	792.0[28]	*374.0*
MeCN	779.6[28]	*414.2*

[a] Values in italics calculated at the RI-B3LYP-D3/def2-TZVPP level of theory. [b] MCA = $-\Delta H^0$ for the reaction $B + Me^+ \rightarrow BMe^+$.

In conclusion, we have reported the simple one-pot synthesis of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**), which is available on multigram scale and can be handled at room temperature and stored for several weeks at −40 °C. The usage of **1** as a strong methylation agent was demonstrated by methylation of very weak bases, yielding the $[MeP(CF_3)_3]^+$, $[Me_2Br]^+$, and $[Me_2I]^+$ cations, as well as the first spectroscopic evidence for the elusive $[MePF_3]^+$ cation. The methylating agent **1** combines the advantages of $Me(CB_{11}Me_5X_6)$[4] and the MeF/SbF_5[1,2] system: a Lewis acid free, non-oxidizing compound with large-scale accessibility.

Acknowledgements

We gratefully acknowledge the DFG research training network 1582 "Fluorine as a key element" for financial support, Solvay Fluor GmbH for donating chemicals, and the Zentraleinrichtung für Datenverarbeitung (ZEDAT) of the Freie Universität Berlin for computational resources and support. The project was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation; Project No. 387284271—CRC 1349: Fluorine-Specific Interactions). G.T. was supported by a Liebig Scholarship of the Fonds der Chemischen Industrie.

Keywords: fluorine chemistry · Lewis acids · methylation · pentafluoroorthotellurates · weakly coordinating anion

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 9807–9810
Angew. Chem. **2019**, *131*, 9912–9915

[1] R. J. Gillespie, F. G. Riddell, D. R. Slim, *J. Am. Chem. Soc.* **1976**, *98*, 8069.
[2] R. Minkwitz, D. Bernstein, H. Preut, W. Sawodny, H. Härtner, *Z. Anorg. Allg. Chem.* **1991**, *606*, 157.
[3] O. Shyshkov, U. Dieckbreder, T. Drews, A. Kolomeitsev, G.-V. Röschenthaler, K. Seppelt, *Inorg. Chem.* **2009**, *48*, 6083.
[4] T. Kato, E. Stoyanov, J. Geier, H. Grützmacher, C. A. Reed, *J. Am. Chem. Soc.* **2004**, *126*, 12451.
[5] M. J. Molski, D. Mollenhauer, S. Gohr, B. Paulus, M. A. Khanfar, H. Shorafa, S. H. Strauss, K. Seppelt, *Chem. Eur. J.* **2012**, *18*, 6644.
[6] a) V. Geis, K. Guttsche, C. Knapp, H. Scherer, R. Uzun, *Dalton Trans.* **2009**, 2687; b) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 13982; *Angew. Chem.* **2018**, *130*, 14178.
[7] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1970**, *92*, 718.
[8] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1969**, *91*, 2113.
[9] a) B. Chiavarino, M. E. Crestoni, S. Fornarini, D. Kuck, *J. Phys. Chem. A* **2003**, *107*, 4619; b) M. Speranza, *J. Chem. Soc. Chem. Commun.* **1981**, 1177; c) W. L. Jolly, C. Gin, *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 27.
[10] E. S. Stoyanov, *J. Phys. Chem. A* **2017**, *121*, 2918.
[11] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2009**, *48*, 7444; *Angew. Chem.* **2009**, *121*, 7580.
[12] a) C. R. Pitts, M. G. Holl, T. Lectka, *Angew. Chem. Int. Ed.* **2018**, *57*, 1924; *Angew. Chem.* **2018**, *130*, 1942; b) M. D. Struble, M. T. Scerba, M. Siegler, T. Lectka, *Science* **2013**, *340*, 57.
[13] E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2010**, *132*, 4062.
[14] A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; *Angew. Chem.* **2017**, *129*, 8375.
[15] S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, J. Kraitchman, *J. Chem. Phys.* **1952**, *20*, 1112.
[16] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441; b) J. Emsley, *Chem. Soc. Rev.* **1980**, *9*, 91.
[17] J. Apel, J. Grobe, *Z. Anorg. Allg. Chem.* **1979**, *453*, 28.
[18] R. R. Corderman, J. L. Beauchamp, *Inorg. Chem.* **1978**, *17*, 1585.
[19] D. Lentz, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 355; *Angew. Chem.* **1978**, *90*, 390.
[20] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489.
[21] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
[22] a) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374; b) L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881.
[23] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235; b) M. A. Beckett, G. C. Strickland, J. R. Holland, K. Sukumar Varma, *Polymer* **1996**, *37*, 4629.
[24] a) I. R. Beattie, T. Gilson, *J. Chem. Soc.* **1964**, 2292; b) K. F. Purcell, R. S. Drago, *J. Am. Chem. Soc.* **1966**, *88*, 919.
[25] a) M. Murray, R. Schmutzler, E. Gründemann, H. Teichmann, *J. Chem. Soc. B* **1971**, 1714; b) B. L. Booth, K. O. Jibodu, M. F. Proença, *J. Chem. Soc. Chem. Commun.* **1980**, 1151.
[26] a) R. Schmutzler, *J. Chem. Soc.* **1964**, 4551; b) J. H. Cameron, A. J. McLennan, D. S. Rycroft, J. M. Winfield, *J. Fluorine Chem.* **1981**, *19*, 135.
[27] a) A. Peter, S. M. Fehr, V. Dybbert, D. Himmel, I. Lindner, E. Jacob, M. Ouda, A. Schaadt, R. J. White, H. Scherer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 9461; *Angew. Chem.* **2018**, *130*, 9605; b) G. A. Olah, T. E. Kiovsky, *J. Am. Chem. Soc.* **1968**, *90*, 4666.
[28] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
[29] T. B. McMahon, T. Heinis, G. Nicol, J. K. Hovey, P. Kebarle, *J. Am. Chem. Soc.* **1988**, *110*, 7591.

Manuscript received: April 2, 2019
Accepted manuscript online: May 3, 2019
Version of record online: June 17, 2019

Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$

*Sebastian Hämmerling, Günther Thiele, Simon Steinhauer, Helmut Beckers, Carsten Müller, and Sebastian Riedel**

anie_201904007_sm_miscellaneous_information.pdf

WILEY-VCH

SUPPORTING INFORMATION

Table of Contents

WILEY-VCH

SUPPORTING INFORMATION

1 Experimental and Computational Details

The experiments were performed under exclusion of air and moisture using standard Schlenk techniques. The solvents SO_2 and *ortho*-difluorobenzene were dried over CaH_2. CH_2Cl_2, CD_2Cl_2 were dried over Sicapent® while diethyl ether was dried over Solvona®. MeCl (purchased from abcr) were used without further purification. Triethylaluminium was purchased from abcr and handled in a glovebox under a dry argon atmosphere. Teflic acid was prepared according to literature[1] as well as $MeOTeF_5$ for comparison.[2] IR spectra were recorded on a Bruker ALPHA FTIR spectrometer inside a glovebox equipped with a diamond ATR attachment (resolution 4 cm^{-1}). Raman spectra were recorded on a Bruker MultiRAM II equipped with a low-temperature Ge detector (1064 nm, 30-80 mW, resolution 2 cm^{-1}). NMR spectra were recorded on a JEOL 400 MHz ECS or ECZ spectrometer. For strongly coupled spin systems all chemical shifts and coupling constants are reported as simulated in gNMR.[3] All reported chemical shifts are referenced to the Ξ values given in IUPAC recommendations of 2008[4] using the ^2H signal of the deuterated solvent as internal reference. For external locking acetone-d6 was flame sealed in a glass capillary and the lock oscillator frequency was adjusted to give $\delta(^1H)$ = 7.26 ppm for a $CHCl_3$ sample locked on the capillary. Crystal data were collected on a Bruker D8 Venture diffractometer with a Photon 100 CMOS area detector with Mo-K_α radiation. Using Olex2[5], the structure was solved with the ShelXT[6] structure solution program by intrinsic phasing and refined with ShelXL[7] refinement package using least square minimization. Crystal structures were visualized with Diamond[8].

For density functional calculations the program package TURBOMOLE[9] was used with its implementations of RI[10], MARI-J[11], B3LYP[12], Grimme-D3[13] together with the basis set def2-TZVPP[14]. SCF energies were corrected with chemical potential taken from TURBOMOLE implemented in the freeh script, to get free enthalpies. No scaling correction was applied to the frequencies. NBO analysis where performed with NBO 7.0[15] executed from Gaussian 16[16]. All CCSD(T) calculations were performed with version 2015.1 of the Molpro program[17]; all SCS-MP2 calculations with the Gaussian 16[16]; these post-HF calculations made use of (augmented) correlation consistent basis sets developed by Dunning et al.[18]

Caution: Chloromethane and SO_2 give a pressure of 4.9 and 3.3 bar, respectively, at room temperature. Care must be taken that reaction vessels resists this pressure.
Gaseous compounds were treated as ideal gases and their amount were measured by pressure measurements in known volumes. When cooled to –70 °C liquefied SO_2 can be easily transferred using inert PFA or PTFE tubes, however some portions of the solvents evaporates by cooling the tube so concentrations are changing.

1.1 $[Me_2Cl][Al(OTeF_5)_4]$

Teflic acid (1.62 g, 6.77 mmol) was condensed on the upper part of a 15 cm long and 1.5 cm diameter Schlenk tube equipped with a teflon stopcock containing a frozen solution of triethylaluminium (190.7 mg, 1.67 mmol) in chloromethane (6.0 mL) at the bottom. The solution was warmed to –40 °C allowing the teflic acid to slowly condense in the reaction mixture. After the initial yellow color of the solution faded, the mixture was stirred for further 10 minutes before the solvent is slowly removed at reduced pressure. The resulting white powder was allowed to reach room temperature to remove all remaining MeCl under dynamic vacuum to give $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) in quantitative yield (1.73 g, 1.65 mmol, 99 %) Cooling down a solution of **1** in MeCl/*n*-pentane (molar ratio 5.7:1) to –80 °C yields to formation of crystals suitable for X-Ray diffraction.

^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.61 (s, 98.9 %, $[CH_3ClCH_3[^+$; d, 1.1 %, $[CH_3Cl^{13}CH_3[^+$, $^1J(^{13}C,^1H)$ = 162.1) ppm.
$^{13}C\{^1H\}$ NMR (100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 52.7 (s) ppm.
$^1H,^{13}C$-HMBC (400.5 MHz/100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.61/52.7 ppm.
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –35.8 (m, **A**B_4, 1F, $^2J(^{19}F,^{19}F)$ = 187.2 Hz, $^1J(^{125}Te,^{19}F)$ = 3336.0 Hz), –43,7 (m, A**B**$_4$, 4F, $^2J(^{19}F,^{19}F)$ = 187.2 Hz, $^1J(^{125}Te,^{19}F)$ = 3460.5 Hz) ppm.
$^{27}Al\{^{19}F\}$ NMR (104.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 47.8 (s, 72.4 %, $[Al(OTeF_5)_4]^-$; d, 22.2 %, $[Al(OTeF_5)_3(O^{125}TeF_5)]^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; d, 2.8 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz; t, 2.6 %, $[Al(OTeF_5)_2(O^{125}TeF_5)_2]^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; t, 0.04 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz) ppm.
IR (ATR, 25 °C): $\tilde{\nu}$ = 3081 (w), 2971 (w), 1422 (m), 1332 (w), 917 (s), 688 (vs), 634 (s), 596 (m), 564 (s), 546 (sh), 431 (m) cm^{-1}.
FT-Raman (25 °C): $\tilde{\nu}$ = 3081 (m), 2971 (s), 1422 (w), 918 (w), 699 (vs), 651 (s), 598 (m), 432 (m), 359 (w), 335 (m), 303 (m), 262 (w), 236 (w), 139 (w) cm^{-1}.

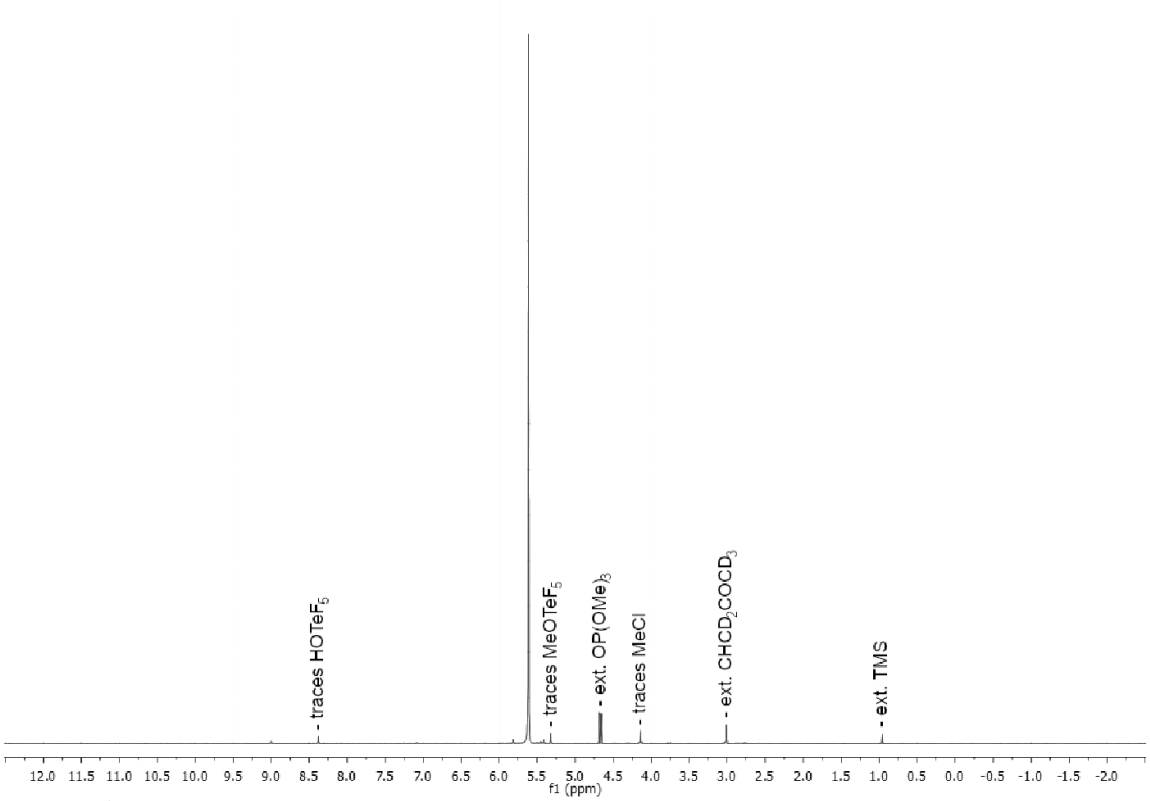


Figure S1: ^{1}H NMR spectrum of **1** in SO_2, ext. [D6]acetone, 20 °C. External standards are shifted due to correction of the different magnetic susceptibility of the capillary (see above).

1.1.1 $MeOTeF_5$ in SO_2

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.53 (91.9%, pd, $^4J(^{19}F_B,^1H)$ = 1.7 Hz, $^4J(^{19}F_A,^1H)$ = 0.5 Hz, 7.1%, dp, $^3J(^{125}Te,^1H)$ = 151.3 Hz, $^4J(^{19}F_B,^1H)$ = 1.7 Hz, $^4J(^{19}F_A,^1H)$ = 0.5 Hz, 0.9%, dp, $^3J(^{123}Te,^1H)$ = 124.6 Hz, $^4J(^{19}F_B,^1H)$ = 1.7 Hz, $^4J(^{19}F_A,^1H)$ = 0.5 Hz) ppm.
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –40.7 (m, **A**B_4X_3, 1F, $^2J(^{19}F,^{19}F)$ = 179.8 Hz, $^4J(^{19}F,^1H)$ = 0.5 Hz, $^1J(^{125}Te,^{19}F)$ = 3352.7 Hz), –54.7 (m, A**B**$_4$$X_3$, 4F, $^2J(^{19}F,^{19}F)$ = 179.8 Hz, $^4J(^{19}F,^1H)$ = 1.7 Hz, $^1J(^{125}Te,^{19}F)$ = 3695.0 Hz) ppm.

1.1.2 Reaction with $[^nBu_4N][PF_6]$

To a solution of **1** (158 mg, 0.15 mmol) in SO_2 (11 mmol, approx. 0.5 mL) a solution of $[^nBu_4N][PF_6]$ (62 mg, 0.16 mmol) in SO_2 (33 mmol, approx. 1.5 mL) is added with a PFA tube. The mixture is stirred at room temperature for 10 minutes before a sample for NMR spectroscopy is prepared. The $[Me_2Cl]^+$ reacts quantitatively under formation of MeF and MeCl. The fluctuating PF_5 is in dynamic exchange with the remaining PF_6^- causing line broadening in the ^{19}F NMR spectrum (–65.5 ppm, d(br), $^1J(^{31}P,^{19}F)$ = 573 Hz, linewidth 1000 Hz) but no signal in the ^{31}P NMR spectrum even not of PF_6^-, the decomposition of the sample within hours excludes prolonged measurement. The ions $[^nBu_4N]^+$ and $[Al(OTeF_5)_4]^-$ stay intact.

MeF

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.45 (d, $^3J(^{19}F,^1H)$ = 45.7 Hz).
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –261.9 (q, $^3J(^{19}F,^1H)$ = 45.7 Hz).

MeCl

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.21 (s).

1.1.3 Reaction with [^{n}Bu$_4$N][AsF$_6$]

To a mixture of solid **1** (30 mg, 28 µmol) and [^{n}Bu$_4$N][AsF$_6$] (16 mg, 37 µmol) in a pressure resistant NMR tube with a teflon stopcock SO_2 (11 mmol, approx. 0.5 mL) is condensed. The SO_2 is allowed to melt at –40 °C dissolving the reactants. While shaking at –40 °C the colorless reaction mixture turned yellow within seconds and partially jellies after further 30 seconds. NMR spectra shows intense line broadening and the complete decomposition of the aluminate anion under formation of three teflate species beside MeF and MeCl. The [^{n}Bu$_4$N]$^+$ ion stays intact. After the 30 minutes at room temperature for the measurement the visual appearance of the sample is unchanged.

MeF

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.49 (d br, $^3J(^{19}F,^1H)$ = 46.5 Hz).

^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –261.8 (q b, $^3J(^{19}F,^1H)$ = 46.5 Hz).

MeCl

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.24 (s br).

1.1.4 Reaction with [^{n}Bu$_4$N][SbF$_6$]

To a solution of **1** (146 mg, 0.14 mmol) in SO_2 (11 mmol, approx. 0.5 mL) a solution of [^{n}Bu$_4$N][SbF$_6$] (43 mg, 0.09 mmol) in SO_2 (33 mmol, approx. 1.5 mL) is added with a PFA tube. The mixture is stirred at room temperature for 10 minutes before a probe for NMR spectroscopy is prepared. The [Me_2Cl]$^+$ reacts quantitatively under formation of MeF and MeCl. The fluctuating SbF_5 gives broad resonances at –105 ppm in the ^{19}F NMR spectrum. Due to the quadrupole moment of ^{121}Sb no signals can be detected in the ^{121}Sb NMR spectrum. The ions [^{n}Bu$_4$N]$^+$ and [Al(OTeF$_5$)$_4$]$^-$ stay intact.

MeF

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.45 (d, $^3J(^{19}F,^1H)$ = 45.7 Hz).

^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –262.0 (q, $^3J(^{19}F,^1H)$ = 45.7 Hz).

MeCl

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.22 (s).

1.2 [MeP(CF$_3$)$_3$][Al(OTeF$_5$)$_4$]

P(CF$_3$)$_3$ (143 mg, 0.60 mmol) is condensed onto a frozen solution of **1** (554 mg, 0.53 mmol) in SO_2 (33 mmol, approx. 1.5 mL). The reaction is stirred at room temperature for two days before the solvent is removed under reduced pressure.

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 3.27 (d, $^2J(^{31}P,^1H)$ = 15.7 Hz) ppm.

^{13}C{^{1}H} NMR (100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 120.0 (qd, CF_3, $^1J(^{19}F,^{13}C)$ = 323.0 Hz, $^1J(^{31}P,^{13}C)$ = 144.5 Hz), –1.5 (d, CH_3, $^1J(^{31}P,^{13}C)$ = 19.3 Hz).

^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –35.8 (m, 1F, $^2J(^{19}F,^{19}F)$ = 187.0 Hz, $^1J(^{125}Te,^{19}F)$ = 3335.5 Hz), –43,8 (m, 4F, $^2J(^{19}F,^{19}F)$ = 187.0 Hz, $^1J(^{125}Te,^{19}F)$ = 3461.5 Hz), –48.6 (d, 9F, $^2J(^{31}P,^{19}F)$ = 127.6 Hz) ppm.

^{27}Al{^{19}F} NMR (104.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 47.8 (s, 72.4 %, [Al(OTeF$_5$)$_4$]$^-$; d, 22.2 %, [Al(OTeF$_5$)$_3$(O^{125}TeF$_5$)]$^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; d, 2.8 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz; t, 2.6 %, [Al(OTeF$_5$)$_2$(O^{125}TeF$_5$)$_2$]$^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; t, 0.04 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz) ppm.

^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 40.6 (dec q, $^2J(^{31}P,^{19}F)$ = 127.6 Hz, $^2J(^{31}P,^1H)$ = 15.7 Hz) ppm.

IR (ATR, 25 °C): $\tilde{\nu}$ = 2995 (w), 2911(w), 1236 (s), 1211 (m), 1108 (s), 927 (s), 902 (m), 771 (w), 688 (vs), 636 (w), 554 (m), 482 (m).

1.3 [MePF$_3$][Al(OTeF$_5$)$_4$]

PF_3 (0.34 mmol) is condensed to a frozen solution of **1** (394 mg, 0.376 mmol) in SO_2 (33 mmol, approx. 1.5 mL). The reaction is stirred at –5 °C for 20 minutes before the solvent is removed under reduced pressure. A mixture of [MePF$_3$][Al(OTeF$_5$)$_4$] is obtained as off white powder containing 10% of the starting compound **1** as determined by NMR spectroscopy.

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 3.35 (dq, $^2J(^{31}P,^1H)$ = 18.1 Hz, $^3J(^{19}F,^1H)$ = 8.1 Hz) ppm.

^{13}C NMR (100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.5 (dd, $^1J(^{13}C,^1H)$ = 140.9 Hz, $^1J(^{31}P,^{13}C)$ = 121.4 Hz) ppm.

^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –35.9 (m, **A**B$_4$, 1F, $^2J(^{19}F,^{19}F)$ = 186.7 Hz, $^1J(^{125}Te,^{19}F)$ = 3335.0 Hz), –43,8 (m, A**B$_4$**, 4F, $^2J(^{19}F,^{19}F)$ = 186.7 Hz, $^1J(^{125}Te,^{19}F)$ = 3462.3 Hz), –65.0 (dq, 3F, $^1J(^{31}P,^{19}F)$ = 1277 Hz, $^3J(^{19}F,^1H)$ = 8.1 Hz) ppm.

^{27}Al{^{19}F} NMR (104.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 47.8 (s, 72.4 %, [Al(OTeF$_5$)$_4$]$^-$; d, 22.2 %, [Al(OTeF$_5$)$_3$(O^{125}TeF$_5$)]$^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; d, 2.8 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz; t, 2.6 %, [Al(OTeF$_5$)$_2$(O^{125}TeF$_5$)$_2$]$^-$, $^2J(^{125}Te,^{27}Al)$ = 74.5 Hz; t, 0.04 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, $^2J(^{123}Te,^{27}Al)$ = 62.8 Hz) ppm.

^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 53.1 (qq, $^1J(^{31}P,^{19}F)$ = 1277 Hz, $^2J(^{31}P,^1H)$ = 18.1 Hz) ppm.

IR (ATR, 25 °C): $\tilde{\nu}$ = 2993 (w), 2912 (w), 1384 (w), 1320 (m), 1095 (s), 1016 (m), 921 (s), 763 (w), 687 (vs), 635 (m), 562 (m), 548 (sh), 454 (m) cm^{-1}.
FT-Raman (25 °C): $\tilde{\nu}$ = 2993 (w), 2912 (m), 1385 (w), 921 (w), 765 (m), 697 (vs), 651 (s), 599 (m), 434 (m), 357 (w), 335 (m), 303 (m), 277 (w), 234 (w), 142 (w) cm^{-1}.

1.3.1 PF_3 in SO_2

^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –33.0 (d, $^1J(^{31}P,^{19}F)$ = 1403 Hz).
^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 105.7 (q, $^1J(^{31}P,^{19}F)$ = 1403 Hz).

1.3.2 Decomposition products

$[MePF_3][Al(OTeF_5)_4]$ decomposes in solution within around 4 hours at room temperature to $[MePF_2(OTeF_5)]^+$ which decompose within around 2 additional hours to $[MePF(OTeF_5)_2]^+$. Even though, the aluminate anion $[Al(OTeF_5)_4]^-$ is the only source of $OTeF_5$ groups, it can be detected by ^{27}Al NMR even after days and complete decomposition of the cation. Hence, the presumed $[AlF(OTeF5)_3]^-$ ions must scramble under reformation of $[Al(OTeF_5)_4]^-$. The only new signal in the $^{27}Al\{^{19}F\}$ NMR spectrum is a broad singlet at –13 ppm at the region of pentagonal/octahedral coordinated aluminium centers.

$[MePF_2(OTeF_5)]^+$
^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.44 (dt, 93.4%, $[MePF_2(OTeF_5)]^+$, $^2J(^{31}P,^1H)$ = 18.3 Hz, $^3J(^{19}F,^1H)$ = 7.8 Hz; dtd, 6.6%, $[MePF_2(O^{125}TeF_5)]^+$, $^2J(^{31}P,^1H)$ = 18.3 Hz, $^3J(^{19}F,^1H)$ = 7.8 Hz, $^4J(^{125}Te,^1H)$ = 7.1 Hz).
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –27.6 (d, 4F, $^2J(^{19}F,^{19}F)$ = 172.9 Hz), –53.4 (quin, 1F, $^2J(^{19}F,^{19}F)$ = 172.9 Hz), –59.5 (dq, 2F, $^1J(^{31}P,^{19}F)$ = 1233 Hz, $^3J(^{19}F,^1H)$ = 7.8 Hz).
^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 45.2 (tq, 93.4%, $[MePF_2(OTeF_5)]^+$, $^1J(^{31}P,^{19}F)$ = 1233 Hz, $^2J(^{31}P,^1H)$ = 18.3 Hz; tdq, 6.6%, $[MePF_2(O^{125}TeF_5)]^+$, $^1J(^{31}P,^{19}F)$ = 1233 Hz, $^2J(^{125}Te,^{31}P)$ = 246.5 Hz, $^2J(^{31}P,^1H)$ = 18.3 Hz).

$[MePF(OTeF_5)_2]^+$
^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.32 (dd, 86.7%, $[MePF(OTeF_5)_2]^+$, $^2J(^{31}P,^1H)$ = 17.9 Hz, $^3J(^{19}F,^1H)$ = 7.9 Hz; ddd, 13.1%, $[MePF(O^{125}TeF_5)(OTeF_5)]^+$, $^2J(^{31}P,^1H)$ = 17.9 Hz, $^3J(^{19}F,^1H)$ = 7.9 Hz, $^4J(^{125}Te,^1H)$ = 5.3 Hz).
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –28.9 (d, 8F, $^2J(^{19}F,^{19}F)$ = 174.3 Hz), –52.4 (p, 2F, $^2J(^{19}F,^{19}F)$ = 174.3 Hz), –55.1 (dq, 1F, $^1J(^{31}P,^{19}F)$ = 1192 Hz, $^3J(^{19}F,^1H)$ = 7.9 Hz).
^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 37.1 (dq, 86.7%, $[MePF(OTeF_5)_2]^+$, $^1J(^{31}P,^{19}F)$ = 1192 Hz, $^2J(^{31}P,^1H)$ = 17.9 Hz;ddq, 13.1%, $[MePF(O^{125}TeF_5)(OTeF_5)]^+$, $^1J(^{31}P,^{19}F)$ = 1192 Hz, $^2J(^{125}Te,^{31}P)$ = 233.2 Hz, $^2J(^{31}P,^1H)$ = 17.9 Hz).

1.3.3 Formation of $MePF_4$

To freshly prepared solution of $[MePF_3][Al(OTeF_5)_4]$ (0.25 mmol) in SO_2 (33 mmol, approx. 1.5 mL) a solution of $[^nBu_4N][PF_6]$ (133 mg, 0.34 mmol) in SO_2 (33 mmol, approx. 1.5 mL) is added whit a PFA tube. The mixture is stirred at room temperature for 10 minutes before a sample for NMR spectroscopy is prepared. The $[MePF_3]^+$ reacts quantitatively to $MePF_4$. The remaining portion of **1** in the starting compound reacts with the PF_6^- under formation of MeF and MeCl. The fluctuating PF_5 is in dynamic exchange with the remaining PF_6^- causing line broadening in the ^{19}F NMR spectrum (–65.8 ppm, d(br), $^1J(^{31}P,^{19}F)$ = 711 Hz, linewidth 64 Hz). The ions $[^nBu_4N]^+$ and $[Al(OTeF_5)_4]^-$ stay intact.
$MePF_4$
^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 3.25 (dp, $^2J(^{31}P,^1H)$ = 20.3 Hz, $^3J(^{19}F,^1H)$ = 7.2 Hz).
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –42.9 (dq, $^1J(^{31}P,^{19}F)$ = 968 Hz, $^3J(^{19}F,^1H)$ = 7.2 Hz).
^{31}P NMR (161.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –27.0 (pq, $^1J(^{31}P,^{19}F)$ = 968 Hz, $^2J(^{31}P,^1H)$ = 20.3 Hz).
MeF
^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.45 (d, $^3J(^{19}F,^1H)$ = 45.7 Hz).
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –261.8 (q, $^3J(^{19}F,^1H)$ = 45.7 Hz).

MeCl
^1H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 4.22 (s).

SUPPORTING INFORMATION

1.3.4 Reaction with [^{n}Bu$_4$N][AsF$_6$]

To freshly prepared solution of [MePF$_3$][Al(OTeF$_5$)$_4$] (0.25 mmol) in SO$_2$ (33 mmol, approx. 1.5 mL) a solution of [^{n}Bu$_4$N][SbF$_6$] (133 mg, 0.28 mmol) in SO$_2$ (33 mmol, approx. 1.5 mL) is added with a PFA tube. The mixture is stirred at –70 °C for 10 minutes before a sample for NMR spectroscopy is prepared. Since this includes contact to a warmer PFA tube the resulting sample contains a jellylike solution. No MePF$_4$ can be detected, but MeF and MeCl. The [MePF$_3$]$^+$ cation has decomposed to [MePF$_2$(OTeF$_5$)]$^+$ while the [^{n}Bu$_4$N]$^+$ cation stays intact. The aluminate anion has decomposed. After the 30 minutes at room temperature for the measurement the visual appearance of the sample is unchanged.

MeF

^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 5.49 (d br, ^3J(^{19}F,^{1}H) = 46.5 Hz).

MeCl

^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 4.24 (s br).

[MePF$_2$(OTeF$_5$)]$^+$

^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 4.42 (dt, 93.4%, [MePF$_2$(OTeF$_5$)]$^+$, ^2J(^{31}P,^{1}H) = 18.3 Hz, ^3J(^{19}F,^{1}H) = 7.8 Hz; dtd, 6.6%, [MePF$_2$(O^{125}TeF$_5$)]$^+$, ^2J(^{31}P,^{1}H) = 18.3 Hz, ^3J(^{19}F,^{1}H) = 7.8 Hz, ^4J(^{125}Te, ^{1}H) = 7.1 Hz).

^{31}P NMR (161.2 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 45.7 (tq, 93.4%, [MePF$_2$(OTeF$_5$)]$^+$, ^1J(^{31}P,^{19}F) = 1232 Hz, ^2J(^{31}P,^{1}H) = 18.3 Hz; tdq, 6.6%, [MePF$_2$(O^{125}TeF$_5$)]$^+$, ^1J(^{31}P,^{19}F) = 1232 Hz, ^2J(^{125}Te,^{31}P) = 246.5 Hz, ^2J(^{31}P,^{1}H) = 18.3 Hz).

1.3.5 Reactivity test with [^{n}Bu$_4$N][SbF$_6$]

To freshly prepared solution of [MePF$_3$][Al(OTeF$_5$)$_4$] (0.20 mmol) in SO$_2$ (22 mmol, approx. 1.0 mL) a solution of [^{n}Bu$_4$N][SbF$_6$] (83 mg, 0.19 mmol) in SO$_2$ (33 mmol, approx. 1.5 mL) is added with a PFA tube. The mixture is stirred at room temperature for 10 minutes before a sample for NMR spectroscopy is prepared. No MePF$_4$ can be detected. The remaining portion of **1** in the starting compound reacts with the SbF$_6^-$ under formation of MeF and MeCl. The fluctuating SbF$_5$ which was formed by the reaction of Me$_2$Cl$^+$ with SbF$_6^-$ gives broad resonances at –105 ppm in the ^{19}F NMR spectrum. Due to the quadrupole moment of ^{121}Sb no signals of SbF$_5$ can be detected in the ^{121}Sb NMR spectrum. The ions [^{n}Bu$_4$N]$^+$ and [Al(OTeF$_5$)$_4$]$^-$ remain intact.

MeF

^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 5.44 (d br, ^3J(^{19}F,^{1}H) = 45.7 Hz).

^{19}F NMR (369.7 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = –261.9 (q br, ^3J(^{19}F,^{1}H) = 45.7 Hz).

MeCl

^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 4.21 (s).

1.4 [Me$_2$I][Al(OTeF$_5$)$_4$]

At –75 °C MeI (0.1 mL 1.65 mmol) is added to a solution of **1** (425 mg, 0.41 mmol) in SO$_2$ (44 mmol, approx. 2.0 mL). The reaction mixture is allowed to reach room temperature. The solvent is removed under reduced pressure. The off-white powder is dissolved in a small amount of CH$_2$Cl$_2$. 5.0 mL *n*-pentane are added to precipitate the salt. The solution is filtered of to leave [Me$_2$I][Al(OTeF$_5$)$_4$] after drying in vacuum as a white powder (455 mg, 0,40 mmol).

^{1}H NMR (400.5 MHz, CD$_2$Cl$_2$, 20 °C): δ = 3.59 (s, 98.9 %, [CH$_3$ICH$_3$]$^+$; d, 1.1 %, [CH$_3$I^{13}CH$_3$]$^+$, ^1J(^{13}C,^{1}H) = 158.7) ppm.
^{1}H NMR (400.5 MHz, SO$_2$, ext. [D6]acetone, 20 °C): δ = 4.75 (s, 98.9%, [CH$_3$ICH$_3$]$^+$; d, 1.1 %, [CH$_3$I^{13}CH$_3$]$^+$, ^1J(^{13}C,^{1}H) = 158.3) ppm.
^{1}H,^{13}C-HMQC (400.5 MHz/100.7 MHz, CD$_2$Cl$_2$, 20 °C): δ = 3.59/11.7 ppm.
^{1}H,^{13}C-HMBC (400.5 MHz/100.7 MHz, CD$_2$Cl$_2$, 20 °C): δ = 3.59/11.7 ppm.
^{19}F NMR (369.7 MHz, CD$_2$Cl$_2$, 20 °C): δ = –38.2 (m, **A**B$_4$, 1F, ^2J(^{19}F,^{19}F) = 188.8 Hz, ^1J(^{125}Te,^{19}F) = 3355.0 Hz), –45.6 (m, A**B$_4$**, 4F, ^2J(^{19}F,^{19}F) = 188.8 Hz, ^1J(^{125}Te,^{19}F) = 3470.9 Hz) ppm.
^{27}Al{^{19}F} NMR (104.2 MHz, CD$_2$Cl$_2$, 20 °C): δ = 46.9 (s, 72.4 %, [Al(OTeF$_5$)$_4$]$^-$; d, 22.2 %, [Al(OTeF$_5$)$_3$(O^{125}TeF$_5$)]$^-$, ^2J(^{125}Te,^{27}Al) = 72.7 Hz; d, 2.8 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, ^2J(^{123}Te,^{27}Al) = 61.2 Hz; t, 2.6 %, [Al(OTeF$_5$)$_2$(O^{125}TeF$_5$)$_2$]$^-$, ^2J(^{125}Te,^{27}Al) = 72.7 Hz; t, 0.04 %, [Al(OTeF$_5$)$_3$(O^{123}TeF$_5$)]$^-$, ^2J(^{123}Te,^{27}Al) = 61.2 Hz;) ppm.
IR (ATR, 25 °C): $\tilde{\nu}$ = 3078 (w), 2968 (w), 1408 (m), 1252 (w), 921 (s), 689 (vs), 563 (s), 515 (sh), 421 (m) cm^{-1}.
FT-Raman (25 °C): $\tilde{\nu}$ = 3079 (w), 2965 (m), 696 (vs), 649 (s), 503 (vs), 427 (m), 357 (m), 335 (m), 303 (m), 222 (w), 141 (w) cm^{-1}.

1.5 [Me$_2$Br][Al(OTeF$_5$)$_4$]

1.3 mL MeI (20.5 mmol) are added to 1-Octyl-3-methylimidazolium bromide (11.4 g, 41.3 mmol). The mixture is stirred three days at room temperature before all volatiles are condensed in another flask. MeBr is obtained in 77% yield (1.5 g, 15.8 mmol) containing MeI as only impurity in less than 5% molar ratio. 0.9 mmol of this mixture are condensed on top of a frozen solution of **1** (348 mg, 0.33 mmol) in SO$_2$ (33 mmol, approx. 1.5 mL). The reaction mixture is allowed to reach room temperature before the solvent is removed under

reduced pressure at –10 °C to leave $[Me_2Br][Al(OTeF_5)_4]$ as a white powder. The remaining MeI in the MeBr reacts preferential with **1** given around 20% $[Me_2I][Al(OTeF_5)_4]$.

^{1}H NMR (400.5 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.31 (s, 98.9 %, $[CH_3BrCH_3]^+$; d, 1.1 %, $[CH_3Br^{13}CH_3]^+$, $^1J(^{13}C,^1H)$ = 161.4 Hz) ppm.
^{1}H,^{13}C-HMQC (400.5 MHz/100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.31/40.2 ppm.
^{1}H,^{13}C-HMBC (400.5 MHz/100.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.31/40.2 ppm.
^{19}F NMR (369.7 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = –35.7 (m, **A**B_4, 1F, $^2J(^{19}F,^{19}F)$ = 187.1 Hz, $^1J(^{125}Te,^{19}F)$ = 3336.2 Hz), –43,8 (m, A**B**$_4$, 4F, $^2J(^{19}F,^{19}F)$ = 187.1 Hz, $^1J(^{125}Te,^{19}F)$ = 3460.1 Hz) ppm.
^{27}Al{^{19}F} NMR (104.2 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 47.8 (s, 72.4 %, $[Al(OTeF_5)_4]^-$; d, 22.2 %, $[Al(OTeF_5)_3(O^{125}TeF_5)]^-$, $^2J(^{125}Te,^{27}Al)$ = 74.3 Hz; d, 2.8 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 62.6 Hz; t, 2.6 %, $[Al(OTeF_5)_2(O^{125}TeF_5)_2]^-$, $^2J(^{125}Te,^{27}Al)$ = 74.3 Hz; t, 0.04 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 62.6 Hz) ppm.
IR (ATR, 25 °C): $\tilde{\nu}$ = 3085 (w), 2972 (w), 1414 (m), 1293 (w), 919 (s), 687 (vs), 563 (sh), 547 (s), 428 (m) cm^{-1}.

SUPPORTING INFORMATION

2 Crystallographic Data

Compound	$[Me_2Cl][Al(OTeF_5)_4]\cdot MeCl$
CCDC	1900575
Formula	$AlO_4Te_4F_{20}C_3H_9Cl_2$
$D_{calc.}$ / g cm^{-3}	3.021
μ/mm^{-1}	5.224
Formula Weight	1094.36
Colour	Colourless
Shape	Block
Size/mm^3	0.58·0.68·0.75
T/K	100
Crystal System	Monoclinic
Space Group	$P2_1/n$
a/Å	8.3862(6)
b/Å	18.1983(14)
c/Å	15.7966(12)
β/°	93.599(3)
V/Å^3	2406.0(3)
Z	4
Radiation	Mo-Kα (0.71073 Å)
Θ_{min}/°	2.238
Θ_{max}/°	26.514
Measured Refl.	450340
Independent Refl.	4961
Refl. (I > 2σ(I))	4881
R_{int}	0.0863
Parameters	321
Restraints	0
Largest Peak	3.578
Deepest Hole	-2.890
GooF	1.277
wR_2 (all data)	0.1590
wR_2	0.1585
R_1 (all data)	0.0740
R_1	0.0724

Comparably high residuals and the nature of the disorder indicates missed twinning effects. Indeed, a second domain can be assigned but twin integration yields an average I/sigma of 2 for the second domain (rotation 160°) and was thus dismissed as no improvement of the structure model could be achieved. Structure solution in non-centrosymmetric space groups with inversion/pseudo-merohedral twinning led to slightly better residual values. However, both, comparison of E-values (0.931) and (thermal) displacement parameters point towards the current space group. We attribute the comparably high residual values to mainly originate from unresolved angular disorder of (TeF_5) groups of Te1, Te2, and Te3, (compare highest residual electron density) and additional rotational disorder of the equatorial F-positions. The crystal dimensions are very large but could not be manually reduced due to the extreme sensitivity of the compound. Thus, numerical absorption correction was attempted but did not yield a satisfactory improvement of the data set. Semi-empiric absorption correction method (SADABS) was finally chosen, accepting a bias from the crystal size and an additional contributor to the residuals and a comparably high residual electron density in the vicinity of the heavy atoms.

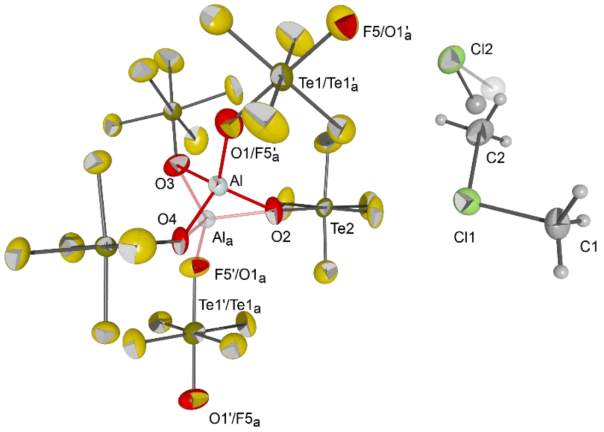


Figure S2: Molecular structure of $[Me_2Cl][Al(OTeF_5)_4]$·MeCl including disordered atoms. H-Atoms of the MeCl are omitted for clarity, thermal ellipsoids drawn at a 50% probability level. Selected bond length (pm) and angles (°): C1-Cl1 183.9(16), C2-Cl1 180.1(19), C1-Cl1-C2 101.0(7), Al-O1/F5$_a$' 184.5(14), Al-O2 166.4(14), Al-O3 178.7(14), Al-O4 176.1(14), O1/F5$_a$'-Te1/Te1$_a$' 180.7(11), Al-F5'O1a 304.0(14), O1/F5$_a$'-Al-O2 112.0(7), O1/F5$_a$'-Al-O3 107.0(7), O1/F5$_a$'-Al-O4 110.8(7), O2-Al-O3 114.6(8), O3-Al-O4 105.0(7), O4-Al-O2 107.4(7).

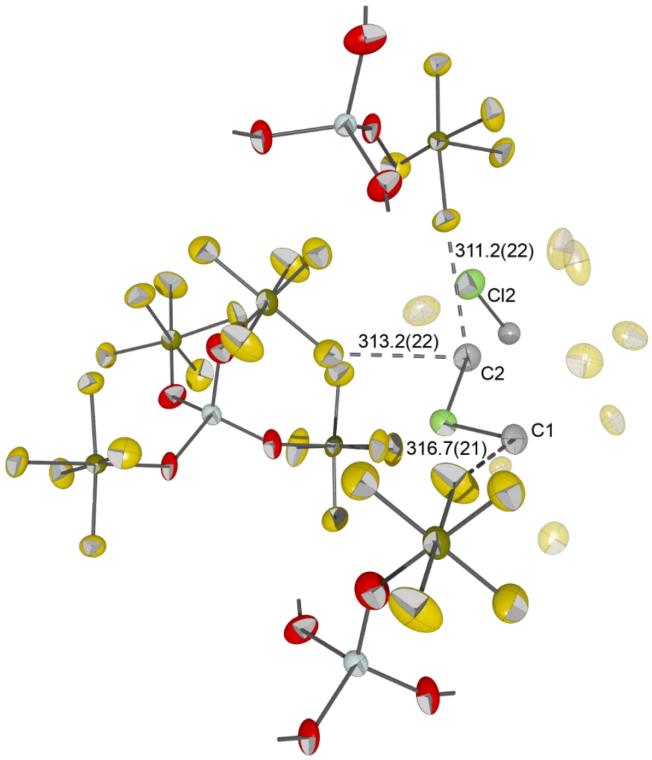


Figure S3: Molecular structure of $[Me_2Cl][Al(OTeF_5)_4]$·MeCl highlighting weak hydrogen bridges[19] between cation and surrounding anions. H-Atoms and disordered atoms are omitted for clarity, thermal ellipsoids drawn at a 50% probability level, bond length in pm. F-Atoms without weak bridges to the cation are shown in transparent. Distance C2-Cl2: 339.2(18) pm features also a weak hydrogen bridge.

SUPPORTING INFORMATION

3 Quantum-chemical calculations

3.1 IR spectrum of $[MePF_3]^+$

Table S1. Comparison of experimental and calculated IR frequencies (> 400 cm^{-1}, intensities in parentheses) of $[MePF_3]^+$ (C_{3v} symmetry).

vibration	symmetry of mode	experimental	RI-B3LYP-D3/ def2-TZVPP	SCS-MP2/ aug-cc-pVTZ	SCS-MP2/ aug-cc-pVTZ anharmonic [a]	SCS-MP2/ aug-cc-pVQZ	CCSD(T)/ aug-cc-pVDZ
$\nu_{as}(C-H)$	*E*	2993 (w)	3117 (29)	3173 (36)	3032 (33)	3176 (36)	3137
$\nu_s(C-H)$	A_1	2912 (w)	3025 (45)	3062 (49)	2947 (51)	3063 (51)	3022
$\delta_{as}(C-H)$	*E*	1384 (w)	1422 (9)	1446 (8)	1403 (8)	1439 (8)	1403
$\delta_s(C-H)$	A_1	1320 (m)	1351 (37)	1358 (36)	1321 (37)	1355 (41)	1321
$\nu_{as}(P-F)$	*E*	1095 (s)	1094 (214)	1198 (209)	1092 (201)	1117 (210)	1053
$\nu_s(P-F)$	A_1	1016 (m)	1007 (168)	1020 (155)	1006 (156)	1027 (157)	980
$\gamma(C-H)$	*E*	n.o. [b]	902 (1)	912 (2)	890 (2)	903 (3)	899
$\nu(P-C)$	A_1	763 (w)	737 (3)	755 (2)	745 (2)	763 (3)	710
$\delta_s(P-F)$	A_1	454 (m)	443 (70)	442 (72)	441 (72)	449 (71)	405

[a] Anharmonically corrected frequencies; [b] not observed, interfered by strong Al-O stretching bands

3.2 Methyl cation affinities

Table S2. Experimental proton affinities and methyl cation affinities (MCA)[a] in kJ*mol^{-1}

Compound	Methyl cation affinity	Experimental proton affinity[20]
CO_2	*150.5*, 207[21]	540.5
$(CF_3)_2O$	*182.8*	670.4
N_2	*186.4*, 203[21]	493.8
AsF_3	*207.4*	636.7
MeF	*207.5*, 230[21]	589.9
Cl_2	*211.3*	-
SO_2	*229.1*, 254[21]	672.3
NF_3	*230.8*	568.4
BrCl	*230.9*	-
Br_2	*242.9*	-
SO_2Cl_2	*258.3*, 260[21]	-
Me_3SiF	*259.3*	-
CH_2Cl_2	*265.4*	-
$CHCl_3$[b]	*267.2*	-
OPF_3	*267.2*	694.0

$N(CF_3)_3$	*267.4*	-
MeCl	*279.2*, 260[21]	647.3
$OCCl_2$	*279.6*	-
I_2	*290.8*	
MeBr	*294.4*, 265[21]	664.2
CCl_4[b]	*297.1*	-
CS_2	*297.8*, 252[21]	681.9
Me_3SiCl	*321.3*	-
CSe_2	*323.0*	725.0
MeI	*323.7*	691.7
$P(CF_3)_3$	*367.2*	-
PF_3	*370.2*	695.3
Me_2O	*374.0*	792.0
CTe_2	*375.1*	771.0
NC_5F_5	*376.7*	764.9
$Me_3SiOSiMe_3$	*383.0*	-
Et_2O	*393.1*	828.4
Me_2CO_3	*401.3*	-
$MeOSiMe_3$	*404.9*	-
PCl_3	*413.5*	-
MeCN	*414.2*	779.6
$OP(OMe)_3$	*447.6*	-
Me_2Se	*457.4*	-
Me_2S	*463.7*	830.9
PC_5H_5	*472.1*	-
$N(SiMe_3)_3$	*486.9*	-
$P(C_6F_5)_3$	*499.1*	-
NC_5H_5	*520.8*	930.0

[a] MCA = $-\Delta H^0$ for the reaction B + Me^+ → BMe^+, values in *italics* obtained at RI-B3LYP-D3/def2-TZVPP level of theory,

[b] Optimised structures suggests the liberation of MeCl.

3.3 FIA discussion

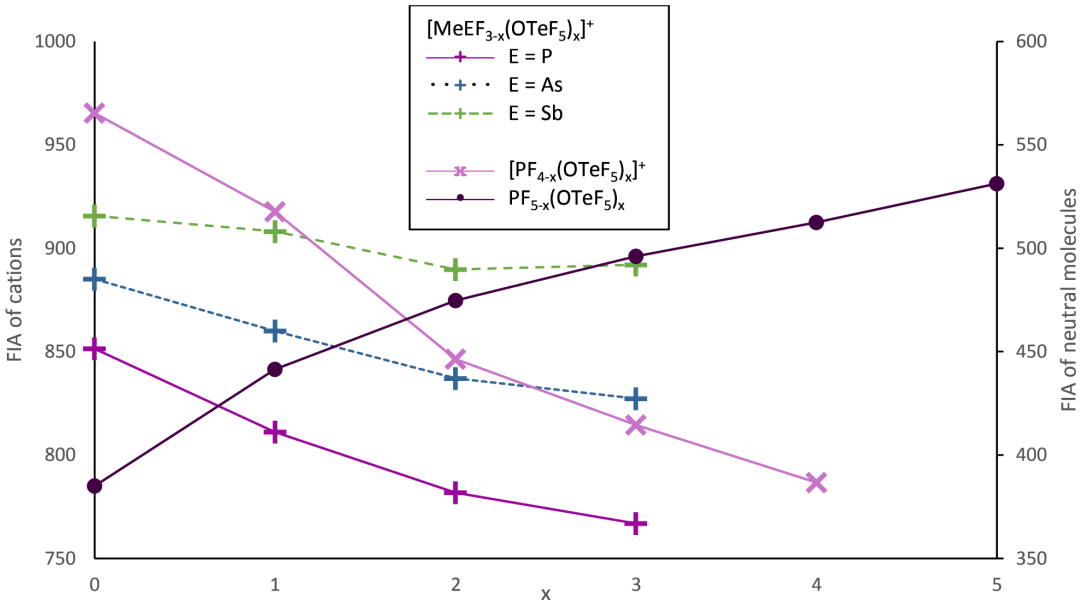


Figure S4: Fluoride ion affinities (FIAs) of $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$ and $PF_{5-x}(OTeF_5)_x$. Note that the FIA for the tetravalent cations (left axis) decreases with the number x of the F_5TeO ligands, while the opposite is observed for the neutral pentavalent $PF_{5-x}(OTeF_5)_x$ (right axis).

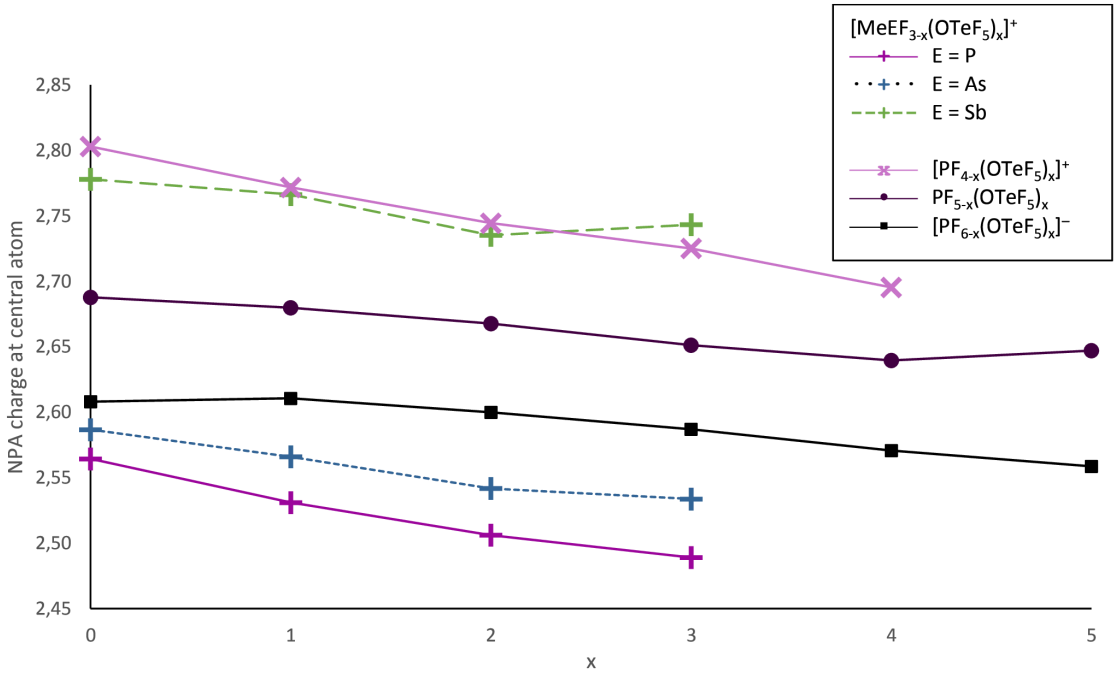


Figure S5: NPA charges at the central atom of $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$, $PF_{5-x}(OTeF_5)_x$ and $[PF_{6-x}(OTeF_5)_x]^-$. Note the general trend of a decreasing charge with increasing number x of the F_5TeO ligands.

SUPPORTING INFORMATION

Table S3: Average X-atom contribution at the P–X (X = F, O) natural bonding orbital in $[PF_3(OTeF_5)]^+$, PF_4OTeF_5 and $[PF_5(OTeF_5)]^-$.

	P–F	P–O
$[PF_3(OTeF_5)]^+$	80.7%	78.2%
$PF_4(OTeF_5)^{eq}$	81.0%	79.6%
$PF_4(OTeF_5)^{ax}$ [a]	81.0%	81.0%
$[PF_5(OTeF_5)]^-$	82.2%	84.2%

[a] The isomer with $OTeF_5$ ligand axial is less stable by 8.8 $kJ{\cdot}mol^{-1}$.

Note that the P–O bond shows a lower ionic character than the P–F bond especially in ordinary 2-center-2-electron bonds. However, the opposite is observed for hyper valent 3-center-4-electron bonds associated with the F_5TeO ligand.

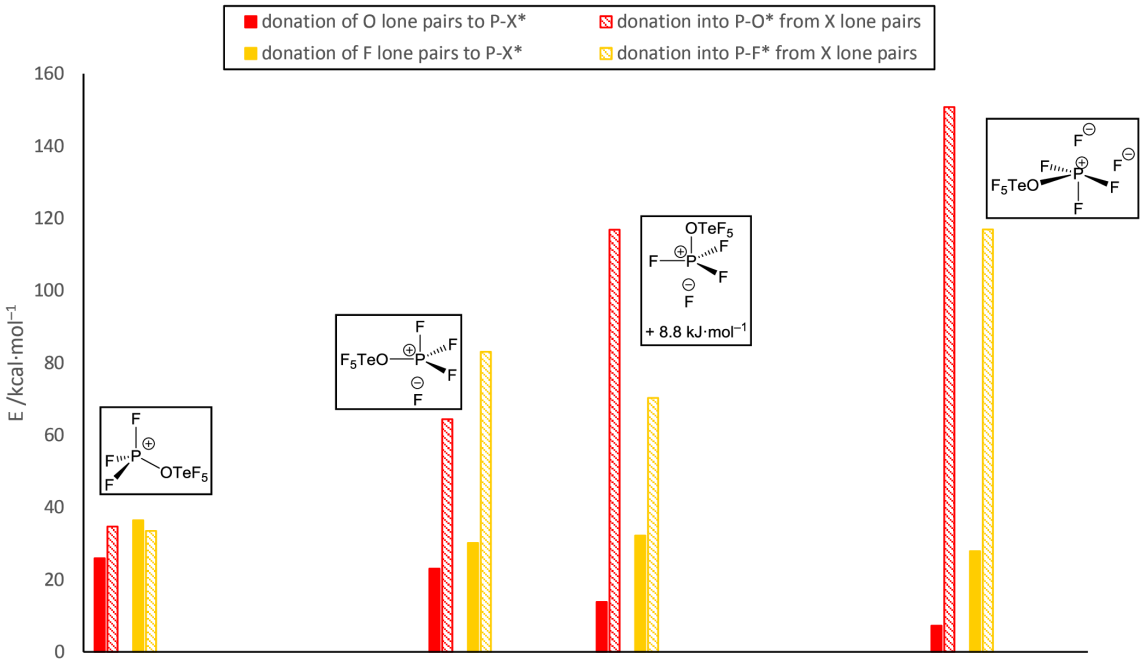


Figure S6: Sum of interaction energies obtained from second order perturbation theory analysis of the fock matrix in the NBO basis for $[PF_3(OTeF_5)]^+$, PF_4OTeF_5 and $[PF_5(OTeF_5)]^-$. The π-interaction energy associated with oxygen lone pairs is generally larger than that based on fluorine ligand lone pairs especially for normal valent species like $[F_3POTeF_5]^+$ cation (note the larger number of fluorine ligands in this species). On the other side, 3-center-4-electron bonds in hyper valent species are also preferentially stabilized by F_5TeO compared to fluorine ligands compared due to a more efficient charge delocalization via the donation into the σ* (P–O) orbital.

SUPPORTING INFORMATION

3.5 Optimized structures for $[MePF_3]^+$ on different levels of theory

SCS-MP2/aug-cc-pVTZ

1	15	0.000000	0.000000	0.787010
2	9	-0.697894	1.208789	1.367050
3	9	-0.697894	-1.208789	1.367050
4	9	1.395789	-0.000000	1.367050
5	6	0.000000	-0.000000	-0.963424
6	1	0.517822	-0.896894	-1.308246
7	1	-1.035644	0.000000	-1.308246
8	1	0.517822	0.896894	-1.308246

SCS-MP2/aug-cc-pVQZ

1	15	0.000000	0.000000	0.786999
2	9	-0.694254	1.202482	1.361863
3	9	-0.694254	-1.202482	1.361863
4	9	1.388507	-0.000000	1.361863
5	6	0.000000	-0.000000	-0.957277
6	1	0.516638	-0.894844	-1.305105
7	1	-1.033277	0.000000	-1.305105
8	1	0.516638	0.894844	-1.305105

CCSD(T)/aug-cc-pVDZ

P	-0.0000167998	0.0000000000	0.7844143741
F	-0.7160902767	1.2402986314	1.3940861442
F	-0.7160902767	-1.2402986314	1.3940861442
F	1.4321959916	0.0000000000	1.3940607913
C	0.0000055620	0.0000000000	-0.9880612495
H	0.5263171719	-0.9115934703	-1.3261819750
H	-1.0526375443	0.0000000000	-1.3262242541
H	0.5263171719	0.9115934703	-1.3261819750

CCSD(T)/aug-cc-pVTZ

P	-0.0000167729	0.0000000000	0.7869563152
F	-0.6973237312	1.2077959538	1.3684902839
F	-0.6973237312	-1.2077959538	1.3684902839
F	1.3946651163	0.0000000000	1.3684713869
C	0.0000052647	0.0000000000	-0.9647845338
H	0.5190329809	-0.8989782682	-1.3091956215
H	-1.0380711076	0.0000000000	-1.3092344931
H	0.5190329809	0.8989782682	-1.3091956215

3.6 Optimized structures for FIA on RI-B3LYP-D3/def2-TZVPP

BF_3

```
$coord
   0.00000000000000      0.00000000000000      0.00000000000000 b
  -1.24395911018455      2.15460038137780      0.00000000000000 f
  -1.24395911018455     -2.15460038137780      0.00000000000000 f
   2.48791822036908      0.00000000000000      0.00000000000000 f
$end
Etot = -324.5936699970 H
ZPE = 32.18 kJ/mol
enthalpy = 43.91 kJ/mol
chem. pot. = -32.16 kJ/mol
```

$[BF_4]^-$

```
$coord
  -0.00000000000000      0.00000000000000      0.00000000000000 b
  -1.54128783872266     -1.54128783872266     -1.54128783872266 f
   1.54128783872266      1.54128783872266     -1.54128783872266 f
  -1.54128783872266      1.54128783872266      1.54128783872266 f
   1.54128783872266     -1.54128783872266      1.54128783872266 f
$end
Etot = -424.5768265395 H
ZPE = 36.61 kJ/mol
enthalpy = 50.71 kJ/mol
chem. pot. = -29.92 kJ/mol
```

PF_5

```
$coord
   0.00000000000000      0.00000000000000      0.00000000000000 p
   1.46469120823919      2.53691959006972      0.00000000000000 f
   0.00000000000000      0.00000000000000     -3.00276064023980 f
   1.46469120823919     -2.53691959006972      0.00000000000000 f
   0.00000000000000      0.00000000000000      3.00276064023980 f
  -2.92938241647836      0.00000000000000      0.00000000000000 f
$end
Etot = -840.7627360223 H
ZPE = 43.28 kJ/mol
enthalpy = 60.16 kJ/mol
chem. pot. = -30.34 kJ/mol
```

$[PF_6]^-$

```
$coord
   0.00000000000000      0.00000000000000     -0.00000000000000 p
   0.00000000000000     -3.07891162410211     -0.00000000000000 f
   0.00000000000000      0.00000000000000      3.07891162410211 f
   3.07891162410211      0.00000000000000     -0.00000000000000 f
  -0.00000000000000      3.07891162410211     -0.00000000000000 f
  -3.07891162410211     -0.00000000000000     -0.00000000000000 f
  -0.00000000000000     -0.00000000000000     -3.07891162410211 f
$end
Etot = -940.7571683556 H
ZPE = 48.67 kJ/mol
enthalpy = 67.45 kJ/mol
chem. pot. = -22.89 kJ/mol
```

SUPPORTING INFORMATION

AsF_5

```
$coord
    0.00000000000000      0.00000000000000     -0.00000000000000  as
   -1.59920933327426      2.76991181716935      0.00000000000000  f
   -1.59920933327426     -2.76991181716935      0.00000000000000  f
    0.00000000000000      0.00000000000000     -3.24104118763331  f
    3.19841866654853      0.00000000000000      0.00000000000000  f
    0.00000000000000      0.00000000000000      3.24104118763331  f
$end
Etot = -2735.1259332800 H
ZPE = 34.25 kJ/mol
enthalpy = 53.66 kJ/mol
chem. pot. = -43.55 kJ/mol
```

$[AsF_6]^-$

```
$coord
    0.00000000000000      0.00000000000000     -0.00000000000000  as
    3.31371102732217     -0.00000000000000     -0.00000000000000  f
   -0.00000000000000      0.00000000000000     -3.31371102732217  f
    0.00000000000000     -0.00000000000000      3.31371102732217  f
   -3.31371102732217      0.00000000000000      0.00000000000000  f
   -0.00000000000000     -3.31371102732217      0.00000000000000  f
    0.00000000000000      3.31371102732217     -0.00000000000000  f
$end
Etot = -2835.1433840220 H
ZPE = 40.10 kJ/mol
enthalpy = 61.72 kJ/mol
chem. pot. = -35.34 kJ/mol
```

SbF_5

```
$coord
    0.00000000000000      0.00000000000000     -0.00000000000000  sb
   -1.76099982462105      3.05014116836355      0.00000000000000  f
   -1.76099982462105     -3.05014116836355      0.00000000000000  f
    0.00000000000000      0.00000000000000     -3.53932911368712  f
    0.00000000000000      0.00000000000000      3.53932911368712  f
    3.52199964924211      0.00000000000000      0.00000000000000  f
$end
Etot = -739.5999956968 H
ZPE = 29.00 kJ/mol
enthalpy = 50.65 kJ/mol
chem. pot. = -53.39 kJ/mol
```

$[SbF_6]^-$

```
$coord
    0.00000000000000      0.00000000000000      0.00000000000000  sb
    3.60833289761330     -0.00000000000000     -0.00000000000000  f
    0.00000000000000      0.00000000000000     -3.60833289761330  f
    0.00000000000000      3.60833289761330      0.00000000000000  f
   -0.00000000000000     -3.60833289761330      0.00000000000000  f
   -0.00000000000000     -0.00000000000000      3.60833289761330  f
   -3.60833289761330      0.00000000000000      0.00000000000000  f
$end
Etot = -839.6387091365 H
ZPE = 34.40 kJ/mol
enthalpy = 58.80 kJ/mol
chem. pot. = -45.83 kJ/mol
```

SUPPORTING INFORMATION

$[FP(C_6F_5)_3]^+$

$coord

-0.00000000000000	-0.00000000000000	-1.35330633550905	p
2.45784520113816	-2.09680642139756	-0.47419122919153	c
2.48306770018147	-4.51339840457184	-1.57000193476317	c
4.38665827148500	-1.49659893729093	1.24098645805633	c
4.36008541606780	-6.24706983824073	-1.03702277345590	c
6.28056956262489	-3.21367520608690	1.80271933714852	c
6.26695045079865	-5.58739314689939	0.66157501030825	c
0.58696502717954	3.17695959345410	-0.47419122919153	c
2.66718382566863	4.40709890995968	-1.57000193476317	c
-0.89723643677176	4.54725696947260	1.24098645805633	c
3.23007847109812	6.89947965210512	-1.03702277345590	c
-0.35716041332900	7.04597039451192	1.80271933714852	c
1.70534918074663	8.22103486809966	0.66157501030825	c
-3.04481022831771	-1.08015317205654	-0.47419122919153	c
-5.15025152585011	0.10629949461216	-1.57000193476317	c
-3.48942183471324	-3.05065803218167	1.24098645805633	c
-7.59016388716591	-0.65240981386439	-1.03702277345590	c
-5.92340914929589	-3.83229518842502	1.80271933714852	c
-7.97229963154527	-2.63364172120027	0.66157501030825	c
-0.00000000000000	-0.00000000000000	-4.28519509714075	f
0.63079966644957	-5.16863324456439	-3.14271659430282	f
4.16076785941276	3.13060515812627	-3.14271659430282	f
-4.79156752586233	2.03802808643812	-3.14271659430282	f
4.44692200862632	0.73803513169695	2.39256565033804	f
-2.86261817724811	3.48212986227005	2.39256565033804	f
-1.58430383137821	-4.22016499396699	2.39256565033804	f
4.34829526389156	-8.50826106973681	-2.09237802459158	f
5.19422259647646	8.01986469655405	-2.09237802459158	f
-9.54251786036802	0.48839637318276	-2.09237802459158	f
8.08865759476608	-2.61438312668580	3.41786262922386	f
-1.78020659444774	8.31217452292426	3.41786262922386	f
-6.30845100031834	-5.69779139623845	3.41786262922386	f
8.05781964316854	-7.21926621181540	1.19396761534839	f
2.22315811453052	10.58790961600492	1.19396761534839	f
-10.28097775769906	-3.36864340418952	1.19396761534839	f

$end

Etot = -2624.3832292380 H
ZPE = 404.9 kJ/mol
enthalpy = 487.24 kJ/mol
chem. pot. = 240.96 kJ/mol

$F_2P(C_6F_5)_3$
both F axial, global minimum

$coord

-0.00000000000000	-0.00000000000000	-0.00023409559385	p
2.40979446048779	-2.46481537363539	-0.00011083571544	c
2.04312662874415	-4.73009781415740	-1.28611487978493	c
4.68291492466971	-2.14918832672964	1.28560255320585	c
3.85539607663934	-6.62336791825681	-1.28623417567309	c
6.53440033253046	-4.00409417622843	1.28670337757480	c
6.11281405447749	-6.25242643289237	0.00006931195228	c
0.92969549896278	3.31935090749913	-0.00011083571544	c
3.07482155507347	4.13444847071959	-1.28611487978493	c
-0.48020577387002	5.13011745189008	1.28560255320585	c
3.80830683750158	6.65055490314893	-1.28623417567309	c
0.20044710949392	7.66100377458308	1.28670337757480	c
2.35835309893936	8.42006547623424	0.00006931195228	c

-3.33948995945057	-0.85453553386375	-0.00011083571544	c
-5.11794818381763	0.59564934343780	-1.28611487978493	c
-4.20270915079970	-2.98092912516044	1.28560255320585	c
-7.66370291414092	-0.02718698489211	-1.28623417567309	c
-6.73484744202438	-3.65690959835465	1.28670337757480	c
-8.47116715341686	-2.16763904334187	0.00006931195228	c
-0.00000000000000	-0.00000000000000	-3.12666456673078	f
-0.11738680326174	-5.17565200447866	-2.51232435309288	f
4.54093951865724	2.48616604854561	-2.51232435309288	f
-4.42355271539550	2.68948595593305	-2.51232435309288	f
5.17714089270496	0.00087336754507	2.51151506953946	f
-2.58932680483335	4.48309884828121	2.51151506953946	f
-2.58781408787161	-4.48397221582628	2.51151506953946	f
3.44009176216583	-8.79128673696776	-2.49522773749107	f
5.89343176508437	7.37485022586906	-2.49522773749107	f
-9.33352352725019	1.41643651109870	-2.49522773749107	f
8.71100426876727	-3.63809325377209	2.49612637443546	f
-1.20482095528022	9.36299761611319	2.49612637443546	f
-7.50618331348705	-5.72490436234110	2.49612637443546	f
7.86730984890371	-8.04667782589915	0.00004503044485	f
3.03497248884575	10.83662910154370	0.00004503044485	f
-10.90228233774946	-2.78995127564455	0.00004503044485	f
-0.00000000000000	-0.00000000000000	3.12680361906440	f

$end
Etot = -2724.5257828610 H
ZPE = 410.3 kJ/mol
enthalpy = 495.16 kJ/mol
chem. pot. = 247.79 kJ/mol

$F_2P(C_6F_5)_3$
one F axial, one F equatorial

$coord

0.24517531712522	2.24435709874741	0.67513610017624	p
0.15049754179931	4.88903678814741	-0.68827772083571	f
0.51350809132259	3.81789703124632	3.35291692899679	f
-2.49289198973056	0.62543565620050	2.07198597586119	c
-2.62209995043526	-1.99745241558388	2.19059052488705	c
-4.54731809109436	1.98635695237831	2.99740453953559	c
-4.68458726501112	-3.24325962735078	3.21430102789430	c
-6.65149291373699	0.77917411703338	3.99592532348944	c
-6.71374523195933	-1.84181026409155	4.11538559116478	c
-0.48832833147951	0.70383386402120	-2.54691117458598	c
0.76743020755514	-1.28542029266735	-3.72781960319053	c
-2.64460013669958	1.57132883184646	-3.80195008326677	c
-0.00704963106751	-2.29371140610031	-6.02735116293502	c
-3.47086648335093	0.60975806785213	-6.09204449568209	c
-2.12946838111460	-1.33885585403662	-7.22489535241856	c
3.43149138424894	1.04071943661999	1.14549842442740	c
5.35868430174008	1.64413832981543	-0.53972287124301	c
4.07890986268510	-0.33906260220406	3.29070422749986	c
7.83510141449903	0.89845187667260	-0.13101983644884	c
6.53520231100527	-1.14211922949970	3.71923831061224	c
8.42009243652296	-0.51273097520984	2.00316072848972	c
4.85037882383993	2.95271832821937	-2.63867172387221	f
9.64115467752802	1.50326689793737	-1.77408812792065	f
10.78054386451784	-1.25727972577698	2.40583445367768	f
7.10122826067453	-2.49099299477207	5.76582982397606	f
2.32814660852364	-0.95352047609970	4.99942829929663	f
2.80733279033534	-2.38484859193212	-2.69592194043143	f
1.28044891315230	-4.18719458301516	-7.08041689430374	f

-2.88669321548335	-2.29104314707999	-9.42250441275123	f
-5.54424508378881	1.51957219168577	-7.19705838925757	f
-4.07786523916730	3.38527221084290	-2.75108544901083	f
-0.69814324303949	-3.39907906388115	1.32784767190631	f
-4.57609407130784	4.49984199527288	2.88846636106687	f
-8.60999288156184	2.11692419173235	4.83349024070647	f
-8.71287992787001	-3.00888511054614	5.08405111999855	f
-4.73089971867244	-5.75637674377627	3.34138792419419	f

$end
Etot = -2724.5026851880 H
ZPE = 409.9 kJ/mol
enthalpy = 494.79 kJ/mol
chem. pot. = 245.18 kJ/mol

$F_2P(C_6F_5)_3$
both F equatorial, optimizes to global minimum with both F axial

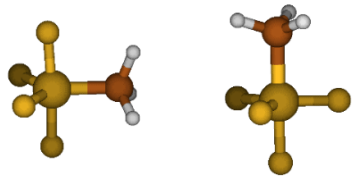
$[MePF_3]^+$

$coord

-0.00000000000000	0.00000000000000	1.48938519485160	p
-1.31703709009327	2.28117515549422	2.58357581500539	f
-1.31703709009327	-2.28117515549422	2.58357581500539	f
2.63407418018653	0.00000000000000	2.58357581500539	f
0.00000000000000	0.00000000000000	-1.81236151102154	c
0.97783850253420	-1.69366596798632	-2.47591704294874	h
-1.95567700506841	0.00000000000000	-2.47591704294874	h
0.97783850253420	1.69366596798632	-2.47591704294874	h

$end
Etot = -680.6147184577 H
ZPE = 125.0 kJ/mol
enthalpy = 142.34 kJ/mol
chem. pot. = 51.05 kJ/mol

$MePF_4$



global minimum +30.5 kJ·mol^{-1}

Me equatorial, global minimum
$coord

0.00524371136091	-0.07762968057505	-0.00212902849119	p
0.07587930459645	-3.46193529494701	-0.34562967889837	c
-1.49110479882910	-4.01001928076635	-1.56114534179830	h
1.81732551313736	-3.94553588310118	-1.33388363682888	h
-0.02013992064058	-4.41717919969735	1.46305653238260	h
-2.54657280576574	1.39913739273713	0.12019305047003	f
0.00369632135559	0.27406255676665	-3.04954806957563	f
0.01297496295390	-0.22069817204719	3.05666357693209	f
2.48848249457484	1.51404507916289	0.12155057125489	f

$end
Etot = -780.7877848719 H
ZPE = 132.2 kJ/mol
enthalpy = 152.26 kJ/mol

chem. pot. = 50.42 kJ/mol

$MePF_4$
Me axial

$coord

0.00000000000000	0.00000000000000	0.07753616425885	p
-1.90404784900424	2.29916044542776	-0.02499393825329	f
2.94315527761891	0.49937358454490	-0.02499393825329	f
-1.03910742861467	-2.79853402997267	-0.02499393825329	f
0.00000000000000	0.00000000000000	-2.95122581926504	f
0.00000000000000	0.00000000000000	3.52616729372953	c
1.22093068962777	-1.50537574694762	4.21248951842430	h
0.69322829428373	1.81004486695151	4.21248951842430	h
-1.91415898391150	-0.30466912000389	4.21248951842430	h

$end
Etot = -780.7761422624 H
ZPE = 132.4 kJ/mol
enthalpy = 152.14 kJ/mol
chem. pot. = 54.60 kJ/mol

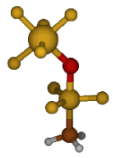
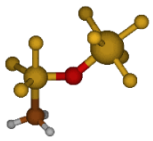
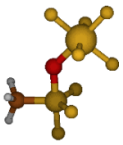
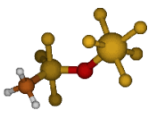
$[MePF_2OTeF_5]^+$

$coord

-0.77220652217466	2.04942934763984	-0.71305938958489	p
0.20219190533020	3.35650801810097	-3.60110822698807	c
-0.45793881870089	2.14883674009322	-5.13658937689015	h
-0.60934093584164	5.24430963420214	-3.78264462329433	h
2.26126797690635	3.46132909550260	-3.62494772491492	h
-3.64592033528125	1.98195789662077	-0.57187674959495	f
-0.01402318000457	3.76610697624600	1.47030300163540	f
0.29522200523066	-0.59040352246448	-0.30381965005908	o
0.44407227785961	-3.26798228044329	2.39275874362528	te
-2.02264027274811	-1.46406222669900	4.06979910887160	f
-2.02056693911150	-4.93018441641262	0.61002977250403	f
2.88071661334157	-4.74180933438931	0.42734158136528	f
0.59959871627547	-5.70369010432017	4.82415855873884	f
2.85956750891873	-1.31034582367673	3.93965497458599	f

$end
Etot = -1423.2969511880 H
ZPE = 163.1 kJ/mol
enthalpy = 201.21 kJ/mol
chem. pot. = 51.47 kJ/mol

$MePF_3OTeF_5$

+37.0 kJ·mol^{-1} | +25.2 kJ·mol^{-1} | global minimum | +1.6 kJ·mol^{-1}

Me equatorial, F axial, global minimum

$coord

0.63460464797883	0.02366797683799	-2.50340226241523	p
1.98375167713498	2.57768397617198	-1.91874689980394	f
2.16578860465192	-2.42376996079002	-1.90974037578187	f

-0.60818220096012	-0.01683716929955	0.51331117525459	o
0.80085550554522	0.03309763987135	3.77245854196347	te
4.11453564304532	0.13009223567684	2.59041702410256	f
0.73695309107228	3.54251169698786	3.87865828559544	f
-2.44019268816113	-0.05753101408610	5.10342922354711	f
2.06013815111816	0.07467568314037	7.04003343364891	f
0.94355788474323	-3.47363498368305	3.89147297592971	f
-2.57228014883391	-0.09626071047681	-3.65388534877940	c
-3.44282529882830	-1.81391146090055	-2.92990900815551	h
-3.59973865455774	1.50170521425590	-2.86671227633434	h
-2.60280703825910	-0.06192738634114	-5.70201747469294	h
1.82584082431030	0.06043826263499	-5.30536701407854	f

$end
Etot = -1523.4544021930 H
ZPE = 169.9 kJ/mol
enthalpy = 210.38 kJ/mol
chem. pot. = 57.71 kJ/mol

$MePF_3OTeF_5$
Me and F equatorial

$coord

0.68123108957019	2.33387546778059	-0.19839555202233	p
3.28662999534684	3.67130067454884	0.18925281877062	f
0.69936852548873	-0.48229771486965	-1.40837157932235	o
0.74074660127995	-3.88560615180379	-0.22331214861549	te
3.34213366079176	-3.33933999345581	2.04688223220366	f
-1.67254223808086	-3.28674770162590	2.24541888635002	f
-1.82917701263817	-4.57072542042472	-2.49657745493056	f
0.74322138070217	-7.25901692002116	0.69303689129871	f
3.09157505324431	-4.60621686744752	-2.70665381440662	f
0.92822244664349	1.21932746368261	2.66061570340997	f
-2.23645524282011	3.93833911431869	0.50216005106971	c
-1.87307360068360	5.96100022255285	0.35385333104128	h
-3.60272878444446	3.44753566695626	-0.95442223442490	h
-2.93548832724989	3.46917085284192	2.36892944528914	h
0.63633645284969	3.38940130696682	-3.07241657571084	f

$end
Etot = -1523.4538167170 H
ZPE = 169.9 kJ/mol
enthalpy = 210.40 kJ/mol
chem. pot. = 56.65 kJ/mol

$MePF_3OTeF_5$
Me and F axial

$coord

-0.13123515369453	-0.00715382973107	-4.25517303997561	p
1.11110372993277	0.07275367603277	-7.46086739664886	c
0.39301805950089	1.73671741943162	-8.43247019716595	h
3.16473164347871	0.14906828817312	-7.39821163040352	h
0.51753081513464	-1.61848501290509	-8.46872531974040	h
1.07014327045897	2.64401121676050	-3.59688548175867	f
1.36477689086057	-2.50525172305134	-3.60580072753095	f
-1.44074531954954	-0.08582832514567	-1.31430919943300	o
-0.03508827628437	-0.00198621894284	1.94923765020799	te
3.28081365410827	0.17294508029071	0.77291775487706	f
-0.17860749670139	3.50118379704578	2.05077940563523	f
-3.27126825322589	-0.17501522464523	3.26224178687653	f
1.22061209470087	0.07393020113017	5.21759036253138	f
0.20148398299174	-3.49945789820650	2.06655232682912	f

-2.94369241308092	-0.17524031748935	-5.20884186515981	f

$end
Etot = -1523.4402347080 H
ZPE = 170.1 kJ/mol
enthalpy = 210.16 kJ/mol
chem. pot. = 59.41 kJ/mol

$MePF_3OTeF_5$
Me axial, F equatorial

$coord

-0.00511150270567	4.28019814795347	-0.11718929494003	p
-0.03545527306529	5.53122298399824	-3.34350915758936	c
-1.73382251106836	4.90595864100514	-4.31550767894543	h
-0.01523327407545	7.58567303817643	-3.23375456794854	h
1.62500530771122	4.87407474379348	-4.35888083700137	h
-2.53919427951095	5.69659546811891	0.56859647551444	f
2.57295389073169	5.64741395265695	0.50142667842436	f
-0.05032652037369	1.40740095736984	-1.27102429069955	o
-0.00221440173520	-2.00352998450034	-0.05797456367590	te
2.57632678147621	-1.39744832026946	2.23222208541515	f
-2.43953568029043	-1.43511657343908	2.39032063750803	f
-2.53615961274766	-2.73382250316261	-2.36481058371237	f
0.04843869049786	-5.37295197131784	0.86967874332998	f
2.39014642719224	-2.71184604831163	-2.51819506074131	f
0.02160923283625	3.18190195698478	2.71720594318809	f

$end
Etot = -1523.4447264180 H
ZPE = 170.3 kJ/mol
enthalpy = 210.20 kJ/mol
chem. pot. = 59.36 kJ/mol

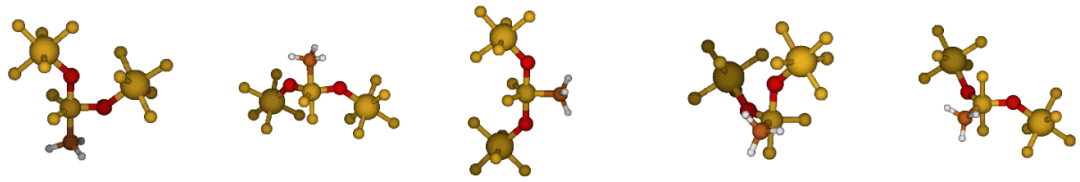
$[MePF(OTeF_5)_2]^+$

$coord

0.21877088545648	-0.04230716328438	-3.26150971562893	p
1.70893097117597	0.56270094087939	-6.17297626740809	c
1.03712421744231	-0.78944886682071	-7.57489733675980	h
1.24372044532755	2.48403147473901	-6.75962968335441	h
3.74648742582821	0.37389765950643	-5.93143645002258	h
-2.63666885692557	0.32224598591691	-3.59679256756862	f
0.69585160558649	-2.80500708163031	-2.48388854742335	o
0.03114422651071	-4.93001156028483	0.53760001893632	te
-1.78644329544161	-2.25648474621311	1.86987658237723	f
-2.84506546160920	-6.03914323203468	-1.05792560366210	f
1.89573029954031	-7.37429280768134	-1.05470054945760	f
-0.56050317553658	-6.90556467847995	3.30500642487131	f
2.92063085786789	-3.59516308461975	1.93566102989303	f
1.10762157745077	1.74812849507492	-1.14532110135158	o
0.03050816207836	4.87053446729719	0.60613173954358	te
1.31329604421015	3.46440012383368	3.50056683257670	f
3.15521393738156	6.15743758194312	-0.17729209214638	f
-1.17521059519725	5.98875304204860	-2.47506352489097	f
-0.92902466051738	7.77286912017436	2.20807908683163	f
-3.04169188425927	3.35793697230898	1.21245032756037	f

$end
Etot = -2165.9733577290 H
ZPE = 201.0 kJ/mol
enthalpy = 257.35 kJ/mol
chem. pot. = 64.43 kJ/mol

$MePF_2(OTeF_5)_2$



+26.4 kJ·mol^{-1} +17.0 kJ·mol^{-1} +0.2 kJ·mol^{-1} +0.9 kJ·mol^{-1} global minimum

Me equatorial, both $OTeF_5$ equatorial, global minimum

$coord

-0.76914935618319	0.00210683118233	-0.95631474008636	p
-3.01785928569963	0.02640097727046	-3.51199046768922	c
-4.26322203586464	-1.59367620422807	-3.27121847102993	h
-4.16603682247534	1.72393487817490	-3.31026792612177	h
-2.09426899272707	-0.01585042062830	-5.33908858902694	h
1.63731892575079	0.06960926042007	-2.86689482104843	f
0.17232605342148	-2.62938489777589	0.30362571742128	o
2.83500024674528	-5.00760133134911	-0.18750304140479	te
5.32955189422210	-2.56657532544361	-0.37631706820596	f
3.23408585896069	-5.11255332717155	3.28167330602243	f
0.43273545718350	-7.53972537975408	0.03892668903719	f
5.30239104822613	-7.45991082265352	-0.51044748524285	f
2.45505157653458	-5.02206186128559	-3.67028436323734	f
0.33542621381770	2.61428500717753	0.21416519061619	o
-0.60318062380951	4.98536000917533	2.76138526904084	te
2.74784843020037	5.09839799582969	3.74263816758668	f
0.02124626811293	7.52942075454989	0.44308768113902	f
-3.97118370124707	5.00044520846509	1.79117859287579	f
-1.35171924117028	7.42563731140185	5.14806293823883	f
-1.20371037966887	2.53379861810277	5.17943667888864	f
-3.06265153432993	-0.06205728146026	1.09614674222665	f

$end

Etot = -2266.1204175270 H

ZPE = 207.6 kJ/mol

enthalpy = 268.61 kJ/mol

chem. pot. = 63.86 kJ/mol

$MePF_2(OTeF_5)_2$

Me equatorial, one $OTeF_5$ equatorial, one $OTeF_5$ axial

$coord

-0.39159514728177	2.67006151087962	-0.23516018803803	p
2.61078500169913	3.48347377555535	1.14227530356486	c
3.33918777789368	5.21287927082692	0.31929257743562	h
2.29551673061789	3.74493550595692	3.16294121640273	h
3.91369337595339	1.91493091551109	0.90164481576724	h
-2.91580839058260	3.03626885843898	1.25425746517174	f
-0.53839030106152	1.51420078295699	-3.03933998308357	o
-0.53542696584903	-1.64831307077546	-4.79565148143489	te
-2.85803744506617	-3.13741455177052	-2.65411520197572	f
-3.16548475644305	-0.41358975960357	-6.73090678893877	f
1.73985870097892	-0.21416848343164	-7.02731550242067	f
-0.52788531901701	-4.55960195201285	-6.72291781255579	f
2.15447113233211	-2.92612070485529	-2.96168649070089	f
-0.21288252477680	-0.40546743061268	0.94505920421491	o
-0.63720130788509	-1.98836612890340	4.07220645545598	te
-0.50324843269990	-5.10521123990205	2.49072951884001	f

2.84743715968314	-2.08252925215406	4.54970608232424	f
-0.72779265510395	1.07500792229990	5.82508609793016	f
-0.97725434712945	-3.63739116066066	7.14119514841597	f
-4.13242489314830	-1.96645103013158	3.82040371655900	f
-0.77751739311360	5.43286622238794	-1.45770415293421	f

$end
Etot = -2266.1201157150 H
ZPE = 207.8 kJ/mol
enthalpy = 268.72 kJ/mol
chem. pot. = 66.90 kJ/mol

$MePF_2(OTeF_5)_2$
Me equatorial, both $OTeF_5$ axial

$coord

0.00071165919321	-0.37254913458443	-0.96707216531841	p
-0.12384784508420	-1.77274377991848	-4.08133993209931	c
-1.73353441873953	-3.05579062407172	-4.09955431210280	h
-0.30152426430817	-0.34937444713927	-5.54030944108746	h
1.58063270710660	-2.89642154282692	-4.32793366485994	h
-2.40152295400304	-0.03089540975118	0.71342121931558	f
-0.44937590927492	2.54190940196837	-2.26288205499822	o
-0.74574909357021	5.83532252111876	-0.91955285662108	te
-0.28305496442485	4.76548755260905	2.39644571743534	f
2.70699457901323	6.37219354147196	-1.22897283651829	f
-1.21832631260100	7.02033976862610	-4.18090296030674	f
-1.05354903229246	9.11728871708490	0.25095514288709	f
-4.21611198272503	5.48039397803576	-0.54907393956631	f
0.43351858936559	-3.34885954125548	0.20710916999406	o
0.80903235634328	-4.70411634277970	3.48041683717230	te
0.91311404226300	-7.89950910039882	2.05127365298594	f
4.30441015299133	-4.49735435382003	3.26343721083039	f
0.71601249347431	-1.55083466707831	5.03025812924159	f
1.19308219576151	-6.16902243000149	6.63414525213701	f
-2.66454851274575	-5.00186435323795	3.87505076672353	f
2.53363651425705	0.51640024594883	0.25508106475569	f

$end
Etot = -2266.1202365890 H
ZPE = 207.2 kJ/mol
enthalpy = 268.35 kJ/mol
chem. pot. = 64.82 kJ/mol

$MePF_2(OTeF_5)_2$
Me axial, one $OTeF_5$ equatorial, one $OTeF_5$ axial

$coord

0.01264596309167	3.65623732972818	0.03779509138607	p
-0.03212137222278	6.84584272252706	-1.28703529238181	c
-1.70928771780518	7.08816012016495	-2.44835593537231	h
-0.06519561896948	8.18693582090208	0.27279692103608	h
1.64982649693664	7.14805014935531	-2.42714233781968	h
-2.56349906303623	4.09766040255620	1.47976854540358	f
0.05685093739552	2.48209392136786	-2.80363490683875	o
0.00368805087745	-0.69773203274739	-4.56103239163883	te
-2.51363017410786	-2.06003552055001	-2.54962624251318	f
-2.45983290378509	0.67570227392273	-6.63649607092408	f
2.46545119105131	0.61335874916976	-6.67732235134640	f
-0.05313476615455	-3.60022706397909	-6.50157039992523	f
2.51568987259898	-2.13026259796814	-2.59337253585549	f
0.06651535033124	0.64316149273191	1.14951132809277	o
0.00096306943912	-0.81403291098236	4.39777128348675	te

0.07395727067665	-3.96510719887529	2.88515643834855	f
3.50109817896577	-0.81752597594209	4.57968895809619	f
-0.07292901651986	2.30128671896692	6.03034051104448	f
-0.05922243202014	-2.37281473101410	7.53053713373607	f
-3.50308331525911	-0.89651484291303	4.40608297245108	f
2.54030861993260	4.19746915218271	1.53261202552747	f

$end
Etot = -2266.1102141030 H
ZPE = 207.5 kJ/mol
enthalpy = 268.24 kJ/mol
chem. pot. = 66.91 kJ/mol

$MePF_2(OTeF_5)_2$
Me axial, both $OTeF_5$ equatorial

$coord

0.12284809733009	0.00242439827040	-3.00167848295076	p
2.81754511277047	0.00037987983139	-5.19217811526220	c
2.68819188628424	-1.67133818151004	-6.38122502406336	h
2.71773173831392	1.69591054938103	-6.34935984297954	h
4.57919631919006	-0.02530335026999	-4.13864604774351	h
-1.84456252400935	0.03871580760994	-5.23930825106577	f
1.06934636859249	-2.72483665723109	-1.89537844355813	o
0.05460857172696	-5.16461103921542	0.58233072755279	te
-3.32750774899861	-5.02231569949038	-0.30492818280823	f
0.54658341527622	-7.65418193784343	-1.83136688805628	f
3.42253135845991	-5.43657309140884	1.50052566609385	f
-0.72462155210405	-7.64365622186246	2.91808315853609	f
-0.40248518808117	-2.74697540818114	3.06938148304836	f
1.10918519049769	2.69299196703503	-1.84713827367230	o
0.05604842176363	5.16019024982507	0.58711644053648	te
3.40179969841964	5.40737365619708	1.58986183058532	f
0.63823312658140	7.62401272881154	-1.83388075445191	f
-3.30261170817148	5.04106012902606	-0.39293258225481	f
-0.76263708242113	7.67036760789477	2.87402358541114	f
-0.49349785609326	2.77538652222688	3.08845549723338	f
-2.24042939426399	-0.00085863935893	-1.06924871846354	f

$end
Etot = -2266.1138343050 H
ZPE = 208.0 kJ/mol
enthalpy = 268.35 kJ/mol
chem. pot. = 68.25 kJ/mol

$[MeP(OTeF_5)_3]^+$

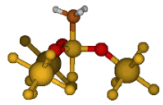
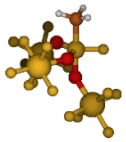
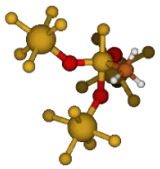
$coord

-0.00000000000000	-0.00000000000000	-2.94329704134501	p
-0.00000000000000	-0.00000000000000	-6.27929349644588	c
-1.42670472863111	-1.32757380276730	-6.94670174956949	h
-0.43636027427964	1.89934944007757	-6.94670174956949	h
1.86306500291075	-0.57177563731027	-6.94670174956949	h
0.44064160999568	-2.73670164000708	-1.98378543885943	o
2.68581745334170	-4.64594406221556	0.27172471488846	te
2.53049360808999	-2.00328233361211	2.54336162831596	f
-0.16387550943209	-6.03419125964374	1.67938394724147	f
2.71961435074354	-7.12023072229710	-2.15881795956799	f
4.76698903755499	-6.45398202419044	2.35500905381873	f
5.39492149074216	-3.09396677330147	-1.28192267110740	f
2.14973233782683	1.74995764822427	-1.98378543885943	o
2.68059685576929	4.64895817562932	0.27172471488846	te
4.80649351094394	5.91537047738918	-2.15881795956799	f

-0.01800692122704	6.21912244905606	-1.28192267110740	f
0.46964658781567	3.19311291552613	2.54336162831596	f
3.20581786973954	7.35532461817977	2.35500905381873	f
5.30770067686154	2.87517527559556	1.67938394724147	f
-2.59037394782251	0.98674399178281	-1.98378543885943	o
-5.36641430911099	-0.00301411341376	0.27172471488846	te
-5.14382516742945	3.15901598404818	1.67938394724147	f
-7.52610786168748	1.20486024490792	-2.15881795956799	f
-5.37691456951513	-3.12515567575459	-1.28192267110740	f
-7.97280690729453	-0.90134259398934	2.35500905381873	f
-3.00014019590566	-1.18983058191401	2.54336162831596	f

$end
Etot = -2908.6486367690 H
ZPE = 238.9 kJ/mol
enthalpy = 318.33 kJ/mol
chem. pot. = 72.74 kJ/mol

$MePF(OTeF_5)_3$


+14.1 kJ·mol^{-1} +35.6 kJ·mol^{-1} global minimum +12.7 kJ·mol^{-1}

Me equatorial, F axial, global minimum
$coord

0.71640992665203	-0.09129476327217	1.79392400934749	p
-1.18409419305490	0.14973495007604	4.61047797209437	c
-2.30612788873899	-1.55979562825453	4.80264099462136	h
-0.01169214447127	0.47779247069459	6.25814497031635	h
-2.47767183220808	1.72945316459939	4.33154943395937	h
-1.85058344554179	-1.25434520440053	0.08148829698813	o
-4.70636042731295	0.08854535789504	-1.51894125345988	te
-2.86419360381523	1.47575844347899	-4.15882153230709	f
-5.07524783266597	-2.89370771191027	-3.30811223029717	f
-6.75257011494357	-1.19206559631573	1.03691645871179	f
-7.60513518828088	1.30091178481562	-3.06134104871436	f
-4.50320626130562	3.13349061523991	0.25450956816126	f
0.86760078646565	2.16937234078645	-0.24920866471709	o
2.86758888043211	5.11494705864038	-0.89770725349298	te
2.91402295983616	6.05233662093779	2.47572777248025	f
5.88376287738176	3.38608453056342	-0.54157335334303	f
2.80395570127690	4.25856323543481	-4.27972648695936	f
4.66439499601888	8.00350624626162	-1.68055923053381	f
-0.10985324495503	6.89194425221659	-1.30650583266322	f
2.19317233486817	-2.68630397050231	1.21334735498263	o
2.16738009525646	-5.42886459060215	-1.13954520202297	te
5.43193168579239	-4.55031293711769	-2.01773245340394	f
3.42545751692537	-7.42413480240812	1.43588114146666	f
-1.06649213131900	-6.43382384180287	-0.28016609336898	f
2.36122967552148	-8.14998460005200	-3.31755480931549	f
0.97824312017913	-3.45850967427350	-3.77099656057565	f
3.23807775200686	0.89070224927132	3.23388403204522	f

$end
Etot = -3008.7890037310 H
ZPE = 245.3 kJ/mol
enthalpy = 326.91 kJ/mol
chem. pot. = 76.99 kJ/mol

SUPPORTING INFORMATION

$MePF(OTeF_5)_3$
Me equatorial, F equatorial

$coord

0.32478853997615	0.21364306293328	0.37337067300474	p
-1.93322307802257	-0.61958892858996	2.78141372498815	c
-3.18007117715064	-2.09685328769909	2.09707747897211	h
-0.96727920016835	-1.17483620032467	4.50203630486906	h
-3.04399200124308	1.07956371291614	3.14643162744474	h
-1.69043875158873	-0.60494875478171	-2.06480394390348	o
-4.62279637059401	0.76193957474223	-3.50529058300250	te
-2.81392842990888	3.07442901256510	-5.41407329252276	f
-4.40917107449139	-1.59190896190803	-6.08036861705587	f
-6.61398218621342	-1.45968711565490	-1.64232837677996	f
-7.55509938381188	2.00362601640675	-4.95147055826003	f
-4.98390942991794	3.14509715268575	-0.93213317511390	f
2.65011044646357	0.99344930083229	2.51319290481892	o
3.19223444259902	3.73411972516946	4.69149823062765	te
4.38305340286148	5.78492875381273	2.11338872941522	f
-0.06866219032410	4.99700893521509	4.22108665272954	f
1.99817176662738	1.84565190318431	7.40842212255228	f
3.78520337133207	6.36282089676598	6.92181738853597	f
6.42726206517828	2.56160043534374	5.30254480602558	f
2.31026968457556	-1.83563592637841	-0.61804119006832	o
2.62534057249073	-4.55513954817885	-2.99157985472782	te
5.87580430591687	-3.44105940475775	-3.58950769858828	f
3.80428984355610	-6.50690274102728	-0.34693916869762	f
-0.60128561205734	-5.74768455992983	-2.36057584720621	f
3.15334482085167	-7.23530447439693	-5.16015955272231	f
1.50611460645162	-2.64617925829772	-5.68949491543046	f
0.44785101661183	2.95785067935236	-0.72551386990434	f

$end
Etot = -3008.7841396990 H
ZPE = 244.8 kJ/mol
enthalpy = 326.85 kJ/mol
chem. pot. = 74.10 kJ/mol

$MePF(OTeF_5)_3$
Me axial, F axial

$coord

-0.00000000000000	-0.00000000000000	-2.06253937481654	p
-0.00000000000000	-0.00000000000000	-5.55065415181939	c
-0.38718784883354	-1.90619381303490	-6.20898237163065	h
-1.45721834220818	1.28841141964395	-6.20898237163065	h
1.84440619104172	0.61778239339095	-6.20898237163065	h
2.34014826606573	-2.01134593175905	-2.09704492079206	o
4.14187148286493	-4.17961567174642	0.17222119295041	te
1.20754582107135	-5.18361780617001	1.79567414960309	f
3.69891376800905	-6.75036249763254	-2.16466995207306	f
7.09606962124510	-3.24648524808800	-1.45423775068821	f
5.96425430312705	-6.39795652312564	2.15977327043768	f
4.69261042280996	-1.68530915375953	2.55850538109273	f
0.57180253966895	3.03230081291455	-2.09704492079206	o
1.54871760835550	5.67677375924456	0.17222119295041	te
-0.73649611276692	7.76861918306527	-1.45423775068821	f
-0.88678467101877	4.90657441309682	2.55850538109273	f
3.88537179311691	3.63757426036653	1.79567414960309	f
2.55866572977164	8.36417400270149	2.15977327043768	f
3.99652852369903	6.57853453832012	-2.16466995207306	f

-2.91195080573468	-1.02095488115550	-2.09704492079206	o
-5.69058909122043	-1.49715808749813	0.17222119295041	te
-7.69544229170808	0.17182795931241	-2.16466995207306	f
-6.35957350847818	-4.52213393497728	-1.45423775068821	f
-3.80582575179119	-3.22126525933730	2.55850538109273	f
-8.52292003289869	-1.96621747957585	2.15977327043768	f
-5.09291761418826	1.54604354580348	1.79567414960309	f
-0.00000000000000	-0.00000000000000	1.00294025032193	f

$end
Etot = -3008.7834980390 H
ZPE = 245.6 kJ/mol
enthalpy = 326.57 kJ/mol
chem. pot. = 80.96 kJ/mol

$MePF(OTeF_5)_3$
Me axial, F equatorial

$coord

0.30710340137597	0.04136080419762	3.08018452841618	p
2.48624912260358	0.51150254975040	5.73150270993233	c
2.51206593295868	-1.17781804358933	6.90196204333968	h
4.37341407763433	0.88613413625122	5.01422442266736	h
1.81736752988611	2.11294797793818	6.83417464781630	h
-1.69441252941720	-0.68018245575294	0.66265901066715	o
-4.96831897048790	0.32253021682629	-0.32265721037635	te
-3.63877868168802	2.56859978051937	-2.66518346391449	f
-4.91264846874193	-2.21441608757842	-2.72710673210558	f
-6.47550358575456	-1.86179488667729	1.96514871651101	f
-8.16586322170449	1.21970780987595	-1.42353808089931	f
-5.13300957000132	2.92937686913472	2.03042739334587	f
0.66764968344121	2.92069970082234	2.00835895322403	o
2.70850923970772	4.60712646944344	-0.39900992563465	te
3.64833211140980	6.88820574049113	2.07638224219467	f
5.45577229409183	2.59226268442751	0.44970153410977	f
1.88128645895980	2.32657268845154	-2.90974239179907	f
4.71756709419194	6.32403437375154	-2.67830483959690	f
0.01471050161190	6.64677956914946	-1.24679615754111	f
2.11269719682176	-2.23907258234672	2.05961570098065	o
2.21019155910910	-4.93950484913347	-0.37148550271912	te
5.50370432044051	-3.99377445583032	-1.08227817620358	f
3.38738036080585	-6.97347513777574	2.22471775596440	f
-1.05719906366130	-5.96885311233422	0.34918068235034	f
2.54351518989737	-7.65109965585088	-2.54653762863545	f
1.11319896809857	-3.00616980067057	-3.06699753200262	f
-1.99799544031063	-0.24847105548207	4.96893538588441	f

$end
Etot = -3008.7752546910 H
ZPE = 244.8 kJ/mol
enthalpy = 326.42 kJ/mol
chem. pot. = 75.44 kJ/mol

$[MeP(CF_3)_3]^+$

$coord

0.00000000000000	0.00000000000000	-0.14450675698320	p
3.01273558170973	1.52846072094725	1.15536953732500	c
-2.83005360388185	1.84487518817227	1.15536953732500	c
-0.18268197782788	-3.37333590911951	1.15536953732500	c
0.00000000000000	0.00000000000000	-3.52214456320291	c
-1.71843750616049	-0.92495850266870	-4.18836056939020	h
0.05818119232273	1.95068978648529	-4.18836056939020	h

1.66025631383776	-1.02573128381663	-4.18836056939020	h
2.73576459829138	2.00219338804906	3.59105267819770	f
0.36606803819400	-3.37033833491903	3.59105267819770	f
-3.10183263648541	1.36814494686996	3.59105267819770	f
-4.86893135721740	1.12064358498446	-0.11403877164062	f
-2.51211866741457	-4.22411556099446	0.77806843830171	f
1.46395986542410	-4.77694003712511	-0.11403877164062	f
4.91425071804966	-0.06350080280487	0.77806843830171	f
-2.40213205063510	4.28761636379933	0.77806843830171	f
3.40497149179328	3.65629645214064	-0.11403877164062	f

$end
Etot = -1393.9087785170 H
ZPE = 212.24 kJ/mol
enthalpy = 255.21 kJ/mol
chem. pot. = 96.72 kJ/mol

$MePF(CF_3)_3$
Me equatorial, F axial, global minimum

$coord

0.01346150941772	0.24091374991669	-0.56253662383576	p
-0.21816575553147	3.55980742546032	0.29279037340118	c
-0.22231275593109	3.88836431767860	2.31264645303301	h
1.36365920081058	4.51717703753125	-0.60841064775321	h
-1.95245664329468	4.26513145692066	-0.56350856654779	h
0.10880763245687	1.03446211548903	-3.60504175023153	f
-3.02332410217947	-1.58941531050201	-1.47259717444564	c
-0.09125932657062	-0.87248266384583	2.98392756133646	c
3.31361280911838	-1.22359675426211	-1.17091249840006	c
-4.09975820311258	-2.87096619556561	0.41255478972038	f
-4.72494365324659	0.09085461222181	-2.33165271339511	f
-2.50159088461567	-3.23206951849527	-3.32143265656760	f
0.00356927416316	-3.37532847205726	3.36972965374803	f
1.85694963068927	0.18455557019941	4.27125253878503	f
-2.23049194020192	0.00291173055178	4.09018664214866	f
4.90631653366023	0.67445190131085	-1.74205151362890	f
4.29165440916120	-2.48659437867646	0.77949353638285	f
3.20627226520667	-2.80817662387590	-3.13443740375025	f

$end
Etot = -1494.0674327320 H
ZPE = 221.7 kJ/mol
enthalpy = 265.36 kJ/mol
chem. pot. = 106.90 kJ/mol

$MePF(CF_3)_3$
Me axial, F axial

$coord

0.00000000000000	0.00000000000000	0.07312700930212	p
0.00000000000000	0.00000000000000	3.60256466165157	c
-0.27641123649283	-1.91235527200233	4.30212012375839	h
1.79435386486153	0.71679848330690	4.30212012375839	h
-1.51794262836870	1.19555678869543	4.30212012375839	h
-0.03259858992883	3.65559557117326	-0.04092396483416	c
3.18213792556235	-1.79956657858071	-0.04092396483416	c
-3.14953933563351	-1.85602899259255	-0.04092396483416	c
0.00000000000000	0.00000000000000	-3.04870816371442	f
-2.34434311815692	4.42256685898155	0.72463570583406	f
0.41697665829844	4.65778308588503	-2.29530869622987	f
1.67524744765968	4.59982580650392	1.58558685784803	f
5.00222680889163	-0.18102273397966	0.72463570583406	f

3.82527014854469	-2.69000392181410	-2.29530869622987	f
-4.82118972524547	-0.84910605595364	1.58558685784803	f
-4.24224680684313	-1.96777916407093	-2.29530869622987	f
-2.65788369073471	-4.24154412500189	0.72463570583406	f
3.14594227758580	-3.75071975055028	1.58558685784803	f

$end
Etot = -1494.0559696630 H
ZPE = 222.5 kJ/mol
enthalpy = 265.79 kJ/mol
chem. pot. = 106.05 kJ/mol

$MePF(CF_3)_3$
Me equatorial, F equatorial

$coord

-0.35458991705785	0.46458653713293	0.00229225078548	p
-1.91369722103318	-2.60105401494207	0.00591935510034	c
-3.87114193273861	-2.24687970292836	-0.54256257128805	h
-1.06121367615729	-3.81706197252735	-1.41304729572491	h
-1.86936750576889	-3.48407540521826	1.85456969460318	h
-0.63554402142202	0.90953437022054	3.67739276132262	c
-0.46950395729001	0.70999465640306	-3.71039039045765	c
3.29982122530958	0.38192622046922	0.07968818136059	c
-1.75835127531214	3.14411358513889	-0.10570124992794	f
0.64506856257826	2.92307624508857	4.54057754992728	f
-3.10008973722164	1.22765449230315	4.27933771241758	f
0.16059984390805	-1.13027451836294	4.99338480871575	f
-2.89960145095898	1.02664087000062	-4.44093593935420	f
0.35681217003347	-1.40038919482021	-4.88921246652301	f
4.27654454509691	-0.85393902416803	-1.89699968254845	f
0.87427747693568	2.66411733051634	-4.61489851923903	f
4.20489102481081	-0.70067252596454	2.17530823174825	f
4.11508584628791	2.78270205165838	0.00527756908217	f

$end
Etot = -1494.0613818940 H
ZPE = 220.8 kJ/mol
enthalpy = 265.05 kJ/mol
chem. pot. = 104.91 kJ/mol

$MePF(CF_3)_3$
Me axial, F equatorial, optimizes to global minimum with Me equatorial and F axial

$[TMS]^+$

$coord

0.00000000000000	0.00000000000000	-0.02110420009278	si
-0.04206233671061	3.45607112267237	0.00752217593567	c
0.80952485759156	4.12139753112963	1.77643787803367	h
1.14927836938218	4.19455039676384	-1.51371530319622	h
-1.93841292139148	4.23788897881015	-0.15634288320100	h
-2.97201422116478	-1.76446261347011	0.00752217593567	c
-4.20722638574267	-1.10197093447700	-1.51371530319622	h
-2.70091305337194	-3.79765932235410	-0.15634288320100	h
-3.97399738984850	-1.35962967389554	1.77643787803367	h
3.01407655787538	-1.69160850920227	0.00752217593567	c
3.16447253225694	-2.76176785723408	1.77643787803367	h
3.05794801636049	-3.09257946228684	-1.51371530319622	h
4.63932597476342	-0.44022965645604	-0.15634288320100	h

$end
Etot = -408.9218468601 H
ZPE = 282.1 kJ/mol

enthalpy = 305.50 kJ/mol
chem. pot. = 197.92 kJ/mol

TMSF

$coord
0.81615731116996 0.00005535589743 0.00018112347328 si
-0.22554087300660 -2.32641252776354 -2.43937166170793 c
0.47312058200833 -4.21848886017854 -2.00586074877708 h
-2.28562981361037 -2.42002904196625 -2.53732812103838 h
0.47285947901099 -1.80340087207381 -4.30879538846769 h
-0.22539806884423 3.27599394730790 -0.79520332053894 c
-2.28547068457563 3.40762860003922 -0.82809495024528 h
0.47253678124699 4.63377951493220 0.59235579374510 h
0.47395180177276 3.84609617955257 -2.65044905985939 h
-0.22529174018130 -0.94957623231181 3.23478178890625 c
0.47328962399648 -2.82997175916255 3.71652725015561 h
0.47319321556270 0.37201025908984 4.65657749008150 h
-2.28537838303647 -0.98776148856422 3.36473596060196 h
3.87760076848636 0.00007692520159 -0.00005615632901 f
$end
Etot = -509.1365793799 H
ZPE = 293.7 kJ/mol
enthalpy = 318.22 kJ/mol
chem. pot. = 210.19 kJ/mol

$[MeAsF_3]^+$

$coord
-0.00000000000000 0.00000000000000 1.54015116228115 as
-1.43499848950232 2.48549029260259 2.82373120087890 f
-1.43499848950232 -2.48549029260259 2.82373120087890 f
2.86999697900465 0.00000000000000 2.82373120087890 f
0.00000000000000 0.00000000000000 -2.06273177454635 c
0.98775796424347 -1.71084697965049 -2.64953766345714 h
-1.97551592848694 0.00000000000000 -2.64953766345714 h
0.98775796424347 1.71084697965049 -2.64953766345714 h
$end
Etot -2574.988187098 H
ZPE = 116.7 kJ/mol
enthalpy = 136.62 kJ/mol
chem. pot. = 37.67 kJ/mol

$MeAsF_4$

$coord
-0.03230550330785 1.39430308639967 0.16686933040742 as
0.04636477001096 -2.21943197880781 -0.20996913970494 c
-1.55716763327532 -2.72672005660775 -1.38971794337675 h
1.79058104704782 -2.66924429492210 -1.19978381581276 h
-0.03663010857080 -3.08797152762955 1.64219718519328 h
-2.80972344962095 3.02130566110390 0.30342370856485 f
-0.02594548134088 1.85621040722910 -3.12249396964239 f
-0.03970237208067 1.28083642986404 3.48393150626268 f
2.66452873113773 3.15071227337047 0.32554313810860 f
$end
Etot = -2675.173943051 H
ZPE = 123.3 kJ/mol
enthalpy = 146.14 kJ/mol
chem. pot. = 35.50 kJ/mol

SUPPORTING INFORMATION

$[MeAsF_2OTeF_5]^+$

$coord

-0.75290227295283	2.03374823947895	-0.75379144882542	as
0.21759758113900	3.59823081726834	-3.84501102168799	c
-0.48272470886234	2.40431862602683	-5.36901011599923	h
-0.65710772176262	5.46217389017148	-3.86429451286099	h
2.27305896489592	3.71132040587042	-3.84381964755801	h
-3.90241641307412	1.81808244881932	-0.50428386455848	f
0.02900573260354	3.80399062592791	1.75394934680165	f
0.50430039839465	-0.86787411224518	-0.38257047816110	o
0.47203114807641	-3.36326237717104	2.44742987737693	te
-1.97021582616078	-1.38184040678729	3.97623964956977	f
-2.01827816991474	-5.06120145573454	0.72488589658209	f
2.89961300695622	-5.05989470814160	0.65162633865579	f
0.46180983924905	-5.65902339256859	5.02202055798586	f
2.92622844141257	-1.43876860091511	3.98662942267908	f

$end
Etot = -3317.670382724 H
ZPE = 154.8 kJ/mol
enthalpy = 195.38 kJ/mol
chem. pot. = 39.38 kJ/mol

$MeAsF_3OTeF_5$

$coord

0.64319473990173	0.02680459765774	-2.57033386251484	as
2.12722170930264	2.80988316109460	-1.91980718560413	f
2.33263020172668	-2.63459336208261	-1.91112773997019	f
-0.65469444794349	-0.01549121055812	0.68371013760798	o
0.81579125135202	0.03356024973461	3.91131892076524	te
4.09967100611645	0.12361054136991	2.65154511991525	f
0.76023812996621	3.54316033230783	4.02584792136867	f
-2.39559463525087	-0.05046710525152	5.32082852532607	f
2.15101350382255	0.07398338005353	7.14944153043314	f
0.95416482862016	-3.47346256192032	4.03701143777964	f
-2.77401898204693	-0.10831591421205	-3.81754380257893	c
-3.60177905260229	-1.83936563849204	-3.08444737362111	h
-3.75931676090553	1.51322676945710	-3.03204289067546	h
-2.70191427225385	-0.07496305233554	-5.86391924530296	h
2.00339278019447	0.07242981317702	-5.58048149292829	f

$end
Etot = -3417.846435222 H
ZPE = 161.3 kJ/mol
enthalpy = 204.53 kJ/mol
chem. pot. = 43.94 kJ/mol

$[MeAsF(OTeF_5)_2]^+$

$coord

0.04741355120758	-0.08299585985342	-3.09976073649922	as
1.59129215276919	0.91902744274791	-6.19415476954379	c
0.91065635923295	-0.36807713606989	-7.64840232620787	h
1.00479371185321	2.85884012278521	-6.54821399599975	h
3.62687914221796	0.76593565719606	-5.93567682375773	h
-3.11579307005324	0.17853674856524	-3.34983465673523	f
0.70901240433322	-3.15696993517193	-2.47582934935980	o
0.04309287252581	-5.32918732517379	0.49289946277286	te
-2.32594714681219	-2.98026463100564	1.55308618335249	f
-2.40505932375820	-6.92780708203411	-1.38130219967604	f
2.46025721258509	-7.45349594291864	-0.79751610736380	f

-0.55338711494904	-7.36217899305670	3.22108772830610	f
2.49441802549482	-3.55909408559820	2.22204766962926	f
0.88865214906156	1.56863808047299	-0.45957056408416	o
0.21633218261830	5.07427600711166	0.55172564226183	te
1.21597309969333	4.17712582309985	3.74247359854669	f
3.50198402309065	5.82216208986440	-0.31753060797639	f
-0.72624853762264	5.67944947184145	-2.79002895316752	f
-0.38641948510979	8.35890522564683	1.43517326758712	f
-3.06747948200867	4.18268696422424	1.26326614083075	f

$end
Etot = -4060.349049083 H
ZPE = 192.8 kJ/mol
enthalpy = 254.06 kJ/mol
chem. pot. = 46.91 kJ/mol

$MeAsF_2(OTeF_5)_2$

$coord

-0.82866681536524	-0.01817542994852	-0.99542598632482	as
-3.25236649401849	0.07409082593755	-3.70195589404452	c
-4.42365118105723	-1.60196280240001	-3.50059261752572	h
-4.39896742911088	1.75310009948699	-3.40053347047010	h
-2.25146319990408	0.11998804351608	-5.48754085887975	h
1.79227464478501	0.05971095958013	-3.04593926830111	f
0.20420490046391	-2.88602043371527	0.36630945553935	o
2.92064096528940	-5.18002851163302	-0.15190137681422	te
5.34529793691544	-2.66538928143815	-0.31414407171571	f
3.34532517854594	-5.33950389790183	3.31465596117795	f
0.60308171358918	-7.79787730102418	0.03953270570549	f
5.46082334705087	-7.55214042073187	-0.52641468020538	f
2.53075232164400	-5.15606641113913	-3.63773333026383	f
0.45044422282800	2.77479180515379	0.31697344132168	o
-0.56361911976737	5.14086739687608	2.82288053322317	te
2.76213935137107	5.32947808923432	3.88113524281496	f
0.05741195862393	7.70790345973949	0.52290213356378	f
-3.91357425305228	5.09357807534475	1.77246806922363	f
-1.41840723854188	7.56826284213184	5.18854634712441	f
-1.17991870951514	2.68901453110023	5.23780582427998	f
-3.24176210077413	-0.11362163816928	1.29897184057068	f

$end
Etot = -4160.515292222 H
ZPE = 198.7 kJ/mol
enthalpy = 260.37 kJ/mol
chem. pot. = 53.79 kJ/mol

$[MeAs(OTeF_5)_3]^+$

$coord

0.00000000000000	-0.00000000000000	-2.08636798264403	as
0.00000000000000	0.00000000000000	-5.68662235522825	c
-1.47765035303897	-1.29585615177741	-6.29422160792595	h
-0.38341917057012	1.92761081953150	-6.29422160792595	h
1.86106952360907	-0.63175466775407	-6.29422160792595	h
0.37394507254632	-3.01661892634987	-0.98832273342376	o
2.69852150213272	-4.71679547549810	1.33390753039624	te
2.57625115706956	-1.93365937526562	3.44274434144005	f
-0.06902229653520	-6.07045740905374	2.93185287356229	f
2.72315770006900	-7.36272112174796	-0.91462177954312	f
4.87992367040646	-6.34328060599845	3.46835841829638	f
5.35362012624048	-3.23228197028060	-0.38870026351130	f
2.42549608748277	1.83215539562003	-0.98832273342376	o

2.73560395517053	4.69538591125455	1.33390753039624	te
5.01472468237947	6.03968430764492	-0.91462177954312	f
0.12242823533719	6.25251201667622	-0.38870026351130	f
0.38647256271122	3.19792863618410	3.44274434144005	f
3.05348031292457	7.39777817010023	3.46835841829638	f
5.29168147709961	2.97545364229983	2.93185287356229	f
-2.79944116002909	1.18446353072981	-0.98832273342376	o
-5.43412545730326	0.02140956424360	1.33390753039624	te
-5.22265918056439	3.09500376675389	2.93185287356229	f
-7.73788238244847	1.32303681410305	-0.91462177954312	f
-5.47604836157766	-3.02023004639559	-0.38870026351130	f
-7.93340398333101	-1.05449756410177	3.46835841829638	f
-2.96272371978080	-1.26426926091847	3.44274434144005	f

$end
Etot = -4803.026481030 H
ZPE = 230.7 kJ/mol
enthalpy = 312.57 kJ/mol
chem. pot. = 63.00 kJ/mol

$MeAsF(OTeF_5)_3$

$coord

0.72457380112876	-0.21818441327935	1.86733130666309	as
-1.23973822389421	0.44769776905370	4.85738971880720	c
-2.49673426483110	-1.15288011420978	5.11956512921431	h
0.05640567284243	0.73051486698692	6.41750092598371	h
-2.33188158523120	2.14156650811169	4.44939835713246	h
-2.08712850883759	-1.43024048619359	0.07905152002688	o
-4.87867917659561	0.10033391947146	-1.44874578951499	te
-3.03273798736730	1.34913892746185	-4.15313414176597	f
-5.55596176729770	-2.83624767443407	-3.22467611277594	f
-6.94592721972734	-1.00388776162104	1.17832807029421	f
-7.71867124715253	1.56201070172196	-2.87915279375100	f
-4.35770673971461	3.12096233883899	0.32699160742292	f
1.14647375698330	1.93671857252707	-0.63901471788578	o
2.83932457700953	5.09196501033435	-1.03206018163927	te
2.37287520637416	5.89804256218797	2.35674506774700	f
5.98619671827669	3.73473915677585	-0.35239905868084	f
3.25905754608029	4.34469254467566	-4.41523846020284	f
4.37176333988672	8.19283203463194	-1.51662039464469	f
-0.23762937531452	6.58171841557759	-1.76045380947900	f
2.06193547752807	-3.23371795490702	1.48193485342122	o
2.33254351404698	-5.59531742247224	-1.22469052322796	te
5.67650373642695	-4.66454717055640	-1.65088376228719	f
3.30757483333762	-7.96568017319524	1.14904098900993	f
-0.98189613370100	-6.64892791812891	-0.88344734987366	f
2.74341782827679	-7.97455591573598	-3.74730720327539	f
1.40919952871647	-3.23547633091603	-3.64113859744086	f
3.57684669274989	0.72673000729262	3.28568535072261	f

$end
Etot = -4903.189937130 H
ZPE = 236.7 kJ/mol
enthalpy = 321.33 kJ/mol
chem. pot. = 62.74 kJ/mol

$[MeSbF_3]^+$

$coord

-0.00000000000000	0.00000000000000	1.65976256853388	sb
-1.57608062132431	2.72985171295841	3.14852352753859	f
-1.57608062132431	-2.72985171295841	3.14852352753859	f

3.15216124264858	0.00000000000000	3.14852352753859	f
-0.00000000000000	0.00000000000000	-2.37496005600107	c
0.99326108739994	-1.72037866855781	-2.91012436504952	h
-1.98652217479991	0.00000000000000	-2.91012436504952	h
0.99326108739994	1.72037866855781	-2.91012436504952	h

$end
Etot = -579.4478184473 H
ZPE = 111.4 kJ/mol
enthalpy = 133.55 kJ/mol
chem. pot. = 25.93 kJ/mol

$MeSbF_4$

$coord

-0.03889612690303	1.49526174818989	0.16435687084506	sb
0.04478919852473	-2.47667284424139	-0.24872707774937	c
-1.25446499528158	-2.94846500487858	-1.76526702476611	h
1.97023449203014	-2.97059134409430	-0.77032095009978	h
-0.48512908747594	-3.29802076019809	1.55279114725085	h
-3.05920276318000	3.33804616100119	0.33921249479155	f
-0.02831456673005	2.03966367558545	-3.41117367590647	f
-0.04162820891338	1.34530034001892	3.77765466833347	f
2.89261205792915	3.47547802861688	0.36147354730085	f

$end
Etot = 530.5775284814 H
ZPE = 117.4 kJ/mol
enthalpy = 142.61 kJ/mol
chem. pot. = 23.08 kJ/mol

$[MeSbF_2OTeF_5]^+$

$coord

-0.81877368253054	2.10885469436123	-0.74126044305058	sb
0.25538358924262	3.86172793607494	-4.18885806890675	c
-0.43135336322508	2.62316987177573	-5.67980304663900	h
-0.66532548446021	5.70061586618342	-4.18120515141009	h
2.30708747181799	3.98791139526296	-4.13083406261540	h
-4.27050866903888	1.57385895031835	-0.49457330623855	f
-0.16441606471949	4.10658106544414	2.05889962974300	f
0.77695724176635	-1.02269811181267	-0.19885236785194	o
0.54727619194835	-3.50729940019282	2.55106695441873	te
-1.76072698400899	-1.36060226279529	4.10094463150507	f
-2.07626597264232	-5.02459661287586	0.83823562293452	f
2.84913535169852	-5.40676608649602	0.78367613700795	f
0.32287901169011	-5.81566090049302	5.11215585848319	f
3.12865136246149	-1.82509640475498	4.17040761261984	f

$end
Etot = -1322.125924648 H
ZPE = 149.3 kJ/mol
enthalpy = 192.21 kJ/mol
chem. pot. = 27.14 kJ/mol

$MeSbF_3OTeF_5$

$coord

0.72736534295819	0.03174291487930	-2.67175443364317	sb
2.39680643906764	3.06775219972061	-1.94717216747756	f
2.62961018227967	-2.86162613108420	-1.93774716224188	f
-0.62376929600150	-0.01111307818237	0.87246157500634	o
0.83217660750082	0.03441545596021	4.09500149921254	te
4.10930944515489	0.11807585830794	2.80938166682390	f

0.78425504170963	3.54447574797353	4.21418206373672	f
-2.36818284392206	-0.04361317167483	5.53374859437182	f
2.19572129706533	0.07253082843678	7.32209605162625	f
0.96478053908114	-3.47326583246506	4.22436124749438	f
-3.03667158503778	-0.12178532534102	-4.00503437111352	c
-3.84631264185587	-1.86080995068963	-3.27294007458894	h
-4.00528702307908	1.50896332521882	-3.21959096763354	h
-2.94869810834606	-0.08739593985046	-6.05240228840575	h
2.18889660342500	0.08165309879037	-5.96459123316764	f

$end
Etot = -1422.320238884 H
ZPE = 155.3 kJ/mol
enthalpy = 201.15 kJ/mol
chem. pot. = 31.05 kJ/mol

$[MeSbF(OTeF_5)_2]^+$

$coord

-0.32070662001157	-0.14787428370950	-1.73731643039833	sb
1.45157431732668	1.00666235404476	-5.14511792289049	c
0.80571912044705	-0.31984561954210	-6.57712597727897	h
0.81045184131449	2.93095572563370	-5.47095346928396	h
3.47350719533215	0.87685605514843	-4.79649342983467	h
-3.82304688474398	-0.10270489473406	-1.97767881086152	f
0.54124437497530	-3.53390084550296	-1.00604796975971	o
-0.21857947883527	-5.73172075688770	1.85546679451501	te
-2.36383208891163	-3.23301247835963	3.08098797425173	f
-2.86932162951728	-7.06848220672904	0.03824080073923	f
1.95821772007142	-8.04245228664741	0.45197286885008	f
-0.92103954270167	-7.79120954343207	4.54450491372732	f
2.41741978507374	-4.25500928327339	3.59809893043604	f
0.42424591127798	1.56526941025271	1.34656018733013	o
-0.13924588006584	5.12600728876315	1.96043749514676	te
0.91943918919029	4.70519070727426	5.22826886871003	f
3.12586300860985	5.76028725194864	0.89888841781145	f
-1.14376815571695	5.28232716716511	-1.46300838945498	f
-0.68948694037995	8.51846659858193	2.34043998490238	f
-3.43865524273492	4.45418964000512	2.82987516334247	f

$end
Etot = -2064.803998733 H
ZPE = 187.2 kJ/mol
enthalpy = 250.85 kJ/mol
chem. pot. = 33.53 kJ/mol

$MeSbF_2(OTeF_5)_2$

$coord

-0.24947916877460	0.00966702206870	-0.33554172293286	sb
-2.80055261007641	0.01014035822533	-3.40425280511611	c
-3.84391538310821	-1.75437685975530	-3.29145157827627	h
-4.04235574674163	1.62028408200226	-3.11591931765689	h
-1.68189895813932	0.15751153891245	-5.11488282584277	h
2.67620636416361	0.61251204902063	-2.37425470150649	f
1.40159876814370	-2.98271507038980	1.05880747159436	o
2.90853464815471	-5.76264201502839	-0.56747802905953	te
5.79189924368158	-3.97955810242934	-1.42014234545047	f
4.37389423638107	-6.74557620866364	2.44589901672317	f
0.10193294375083	-7.74291083706083	0.14057923297312	f
4.30931961379829	-8.54491906591468	-2.15618993479370	f
1.39434695492163	-4.85514458143438	-3.63844678267092	f
0.80479857257914	2.99142560809404	1.56458460285017	o

-1.05220168431348	5.74985095220733	2.82088545065510	te
1.66544683144673	6.69133284797857	4.80203618094505	f
0.13973069619287	7.77173699695024	0.21541680572119	f
-3.82427278020107	4.90169993052948	0.78591381938080	f
-2.85074253899235	8.51703919923189	3.97708987392591	f
-2.39149537593713	3.91681150511427	5.47947831724134	f
-2.83079462693004	-0.58216934965885	2.12786927129573	f

$end
Etot = -2164.991245347 H
ZPE = 193.1 kJ/mol
enthalpy = 259.65 kJ/mol
chem. pot. = 38.03 kJ/mol

$[MeSb(OTeF_5)_3]^+$

$coord

0.00000000000000	-0.00000000000000	-2.26358649639685	sb
-0.00000000000000	0.00000000000000	-6.26238525670164	c
-1.47040030310111	-1.31939300037640	-6.83040784366589	h
-0.40742770435079	1.93310051640611	-6.83040784366589	h
1.87782800745189	-0.61370751602969	-6.83040784366589	h
0.43227099217359	-3.31891439477770	-0.97551301498725	o
2.73035722791028	-4.84967023907859	1.43689676785962	te
2.56714546142322	-1.94641849722501	3.38909980031715	f
-0.00544748507918	-6.16612058278504	3.12382088299932	f
2.83977069797130	-7.63797597141387	-0.63659234379772	f
4.93701210657516	-6.29877950772148	3.67622830374896	f
5.39208101632312	-3.41990203170488	-0.34154196810793	f
2.65812868277656	2.03381485793030	-0.97551301498725	o
2.83475901306428	4.78939384031603	1.43689676785962	te
5.19479587575389	6.27830155107274	-0.63659234379772	f
0.26568152974889	6.37963015525207	-0.34154196810793	f
0.40207513428118	3.19642243341492	3.38909980031715	f
2.98639701323603	7.42496765694621	3.67622830374896	f
5.34274081002954	3.07834263092720	3.12382088299932	f
-3.09039967495015	1.28509953684743	-0.97551301498725	o
-5.56511624097452	0.06027639876253	1.43689676785962	te
-5.33729332495034	3.08777795185783	3.12382088299932	f
-8.03456657372517	1.35967442034108	-0.63659234379772	f
-5.65776254607201	-2.95972812354720	-0.34154196810793	f
-7.92340911981124	-1.12618814922473	3.67622830374896	f
-2.96922059570439	-1.25000393618991	3.38909980031715	f

$end
Etot = -2807.480074733 H
ZPE = 225.3 kJ/mol
enthalpy = 309.46 kJ/mol
chem. pot. = 50.35 kJ/mol

$MeSbF(OTeF_5)_3$

$coord

0.84513890654693	-0.27108888628873	1.84045634019864	sb
-1.34445682841069	0.55745295356962	5.07947364070360	c
-2.63436356243805	-1.01902951048757	5.33130154270706	h
-0.02974909716210	0.80199751807897	6.63243641962207	h
-2.36497152391807	2.28241697776679	4.63190758982048	h
-2.14669569370689	-1.48172625250762	-0.21111737074107	o
-4.96858611978840	0.20598198605052	-1.46808350192074	te
-3.28635990021729	1.34208309069540	-4.32272995683869	f
-6.02811060295458	-2.65932242629958	-3.16680841924015	f
-6.85976631347765	-0.74088236459605	1.35298525304676	f

-7.80949588887507	1.89498588581499	-2.61691839376901	f
-4.05243582809018	3.17047479853734	0.26571478936641	f
1.63023850029864	1.94188189774714	-0.99168952096982	o
2.79324757439404	5.31612634381332	-1.09884792901253	te
1.67080903565014	5.82814064450431	2.21722347523377	f
5.97213578082479	4.46540149956318	0.08252288611877	f
3.87764961709077	4.84301226278853	-4.38259415910135	f
3.84995829018816	8.64595015948467	-1.20060592418562	f
-0.31640790406065	6.39136416738514	-2.28291335737618	f
2.20849730285556	-3.63020779671945	1.37692286201747	o
2.44169784503950	-5.98984384642941	-1.29617102578415	te
5.81956191726985	-5.18572777025397	-1.73807190578910	f
3.33466167550750	-8.42301261993289	1.05072649378394	f
-0.91639286669180	-6.92314216385906	-0.96856048320326	f
2.75860466858884	-8.37011677292572	-3.83505792021953	f
1.58783713032782	-3.59270053111652	-3.71166258893581	f
3.96775388520900	0.59953075561680	3.43016116446827	f

$end
Etot = -2907.668181040 H
ZPE = 231.0 kJ/mol
enthalpy = 318.21 kJ/mol
chem. pot. = 49.13 kJ/mol

$[PF_4]^+$

$coord

0.00000000000000	-0.00000000000000	0.00000000000000	p
-1.62417299493765	-1.62417299493765	-1.62417299493765	f
1.62417299493765	1.62417299493765	-1.62417299493765	f
-1.62417299493765	1.62417299493765	1.62417299493765	f
1.62417299493765	-1.62417299493765	1.62417299493765	f

$end
Etot = -740.5469392146 H
ZPE = 37.53 kJ/mol
enthalpy = 52.04 kJ/mol
chem. pot. = -30.58 kJ/mol

$[PF_3OTeF_5]^+$

$coord

-0.31110043072688	3.45528350591429	1.19198216198387	p
-3.13982804255221	3.73516778076440	1.20565212213783	f
0.62608495979438	5.01509549737374	-0.99074827923329	f
0.64153347487763	4.71017793274465	3.54992798476015	f
0.54816095586406	0.77305462900455	1.09444425045529	o
0.30704391643898	-2.61048630294603	-0.80549429920615	te
-1.24731317483696	-0.78291703566378	-3.32534585303625	f
3.38466597411703	-1.77907201083668	-2.15036129661447	f
1.86893441657747	-3.94056371814708	1.97156073510449	f
0.08970382398727	-5.59873206849037	-2.49070653616461	f
-2.76788587354076	-2.97700820971774	0.74908900981317	f

$end
Etot = -1483.230673510 H
ZPE = 74.44 kJ/mol
enthalpy = 110.27 kJ/mol
chem. pot. = -38.13 kJ/mol

$[PF_2(OTeF_5)_2]^+$

$coord

-0.67317239222748	0.49829768301936	2.29186719599529	p

-3.53189753008027	0.65536193255075	2.26774896154156	f
0.11039280386187	1.95208621738148	4.62181124301163	f
0.17603186198896	-2.20922755264006	2.65164241592583	o
0.44872865595946	-5.37753236619045	0.56946203083676	te
-1.61017870771307	-3.78857240025676	-1.75867800542861	f
3.20255397549142	-3.91800262540178	-0.96016166122404	f
2.46710482508069	-6.57299376082109	3.10593114051074	f
0.69611186209824	-8.24929735827158	-1.31752563371192	f
-2.36962831245794	-6.48514304017627	2.24979802535454	f
0.41348371711782	1.69058720036892	-0.07369412291694	o
0.15104681144243	4.92837998108069	-2.05668315881018	te
-2.15020913943106	5.98177099587310	0.34139364716316	f
2.71986672126861	6.13492604068367	-0.06530100368626	f
2.46042949544316	3.49555751009196	-4.19475860008996	f
-0.08291477757772	7.85243281072194	-3.86152031896914	f
-2.42774987026499	3.41136873198624	-3.81133215550243	f

$end
Etot = -2225.924222946 H
ZPE = 112.4 kJ/mol
enthalpy = 168.83 kJ/mol
chem. pot. = -31.14 kJ/mol

$[PF(OTeF_5)_3]^+$

$coord

0.00000000000000	0.00000000000000	-2.12181212073245	p
0.00000000000000	-0.00000000000000	-4.99384745427033	f
2.65165445726285	0.74898604749282	-1.28301159188908	o
4.71806321871993	3.38529323211202	0.39371243500408	te
1.82399766168704	5.27845006362119	0.81470266161098	f
4.03074726237865	1.75971236890341	3.38784002699359	f
7.40474661178035	1.27321211566470	-0.15347797224693	f
6.67439119356701	5.76665287157100	1.94732945805220	f
5.16254336541086	4.81664505762025	-2.73520858137232	f
-1.97446817284030	1.92190709830148	-1.28301159188908	o
-5.29078154762851	2.39331598801644	0.39371243500408	te
-5.48327067854704	-1.05959672034620	0.81470266161098	f
-3.53932924601335	2.61087334100280	3.38784002699359	f
-4.80500734246194	5.77609261655619	-0.15347797224693	f
-8.33126347837047	2.89686589263868	1.94732945805220	f
-6.75260866361730	2.06257117377450	-2.73520858137232	f
-0.67718628442256	-2.67089314579427	-1.28301159188908	o
0.57271832890857	-5.77860922012846	0.39371243500408	te
3.65927301686000	-4.21885334327496	0.81470266161098	f
-0.49141801636532	-4.37058570990618	3.38784002699359	f
-2.59973926931843	-7.04930473222086	-0.15347797224693	f
1.65687228480343	-8.66351876420967	1.94732945805220	f
1.59006529820647	-6.87921623139473	-2.73520858137232	f

$end
Etot = -2968.600306285 H
ZPE = 149.0 kJ/mol
enthalpy = 212.33 kJ/mol
chem. pot. = 14.74 kJ/mol

$[P(OTeF_5)_4]^+$

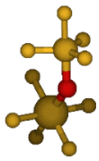
$coord

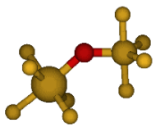
-0.27299845560739	-0.07138363311015	0.04729297969231	p
-3.16400910464498	0.26532801171297	0.02619515772957	o
-5.92802029611149	-0.44348638317126	-2.37695843973882	te
-3.65453080615669	-2.26231473277631	-4.30976036991486	f

-6.62407243735479	-3.30543437373758	-0.54018494875492	f
-7.93911021376864	1.43510285052746	-0.27523953377681	f
-8.50997207487571	-1.06290320190252	-4.58606708678002	f
-4.98819741899578	2.44013355811293	-4.08390469621895	f
0.28637554860760	-2.93305042127112	0.00026388198187	o
3.35497313232506	-4.99316984609401	-0.50211547454750	te
5.25613425229535	-2.12074074147036	0.10879051254481	f
3.28977738019736	-5.63672743345337	2.91035674746729	f
1.22381737594853	-7.66014400087128	-1.07876933270558	f
6.18521151217673	-6.92359756716824	-0.94487078697861	f
3.25186599816947	-4.14802358646383	-3.87444524111215	f
0.98935671074936	1.14158922338843	-2.27520565316464	o
2.49422379527485	4.41322285484656	-3.24684399396648	te
4.75803526360415	4.04081511788526	-0.63035602642495	f
4.58415130458849	2.58817451571883	-5.32303295946203	f
0.10917547240138	4.57645073804098	-5.76024083995410	f
3.89402684195938	7.42837544898620	-4.18665101392543	f
0.26706695672030	5.96410698261340	-1.05292281348903	f
0.75673666954597	1.22395471632856	2.44025681150846	o
0.14449879996655	1.04072839881226	6.11603761424635	te
-1.65513061820276	-1.90247445277231	5.56618625770287	f
3.06709892204899	-0.82319070393840	6.34213239347291	f
1.96885610991726	3.97566544246245	6.34236262484274	f
-0.37383666213722	0.88606927262298	9.52741595120906	f
-2.77150395864138	2.86692394614150	5.62027827851682	f

$end
Etot = -3711.281893393 H
ZPE = 187.3 kJ/mol
enthalpy = 285.53 kJ/mol
chem. pot. = -16.19 kJ/mol

PF_4OTeF_5





+8.8 kJ·mol^{-1} global minimum

$OTeF_5$ equatorial, global minimum

$coord

0.39740730800297	3.36608204994835	-0.15310931930455	p
-1.82492218431385	5.00330045875873	0.83670142815913	f
-0.03763860083633	4.45221494990596	-2.91966323332123	f
0.84948248790613	2.33896322889732	2.65311252059018	f
3.10789240122221	4.48554051113217	-0.14564999323150	f
-0.11150673623859	0.59730666862954	-1.25678328084576	o
-0.34632343098080	-2.79980792545406	0.00403165382516	te
2.58809153639887	-2.51873466999650	1.87791235696020	f
-2.28852778143731	-1.84437350668666	2.74700773824779	f
-3.25350368689879	-3.14821964238865	-1.89564054795514	f
-0.62678515792395	-6.13030082389864	1.00394006772800	f
1.54633384509943	-3.80197129884771	-2.75185939085231	f

$end
Etot = -1583.428296761 H
ZPE = 81.21 kJ/mol
enthalpy = 118.36 kJ/mol
chem. pot. = -27.23 kJ/mol

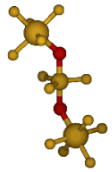
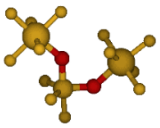
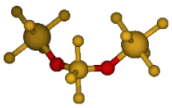
PF_4OTeF_5
$OTeF_5$ axial

$coord
-0.77826296532861 -1.05988832554421 -3.12943235124447 p
-0.94526882039443 -0.91633802269894 -6.11965316106094 f
-2.06435168051637 -3.68535270408856 -3.18211164090101 f
-2.39885729886725 1.37406432299744 -2.92335969239482 f
2.14103830821492 -0.84219852683203 -3.28387556654249 f
-0.67405030752903 -1.35636450829724 0.01486734753332 o
0.57301292210472 0.72753844030092 2.63533329435497 te
1.60995943527685 3.23414186447763 0.39805226516860 f
-2.52927138657385 2.31816875974728 2.96129870725128 f
-0.42875538263279 -1.71329205405303 4.92118764443505 f
1.75758582519570 2.67715686448581 5.28252975592975 f
3.73722135105014 -0.75763611049508 2.42516339747087 f
$end
Etot = -1583.424915485 H
ZPE = 80.96 kJ/mol
enthalpy = 118.24 kJ/mol
chem. pot. = -27.45 kJ/mol

$[PF_5OTeF_5]^-$

$coord
1.03152798215180 0.73333565728068 -3.07753516349184 p
-2.02042808733786 0.71654260363996 -2.98931438959797 f
1.04600843880463 0.75173698993601 -6.11377870482800 f
1.04814525121464 -2.31675648360852 -3.00314972267075 f
4.07280065654203 0.75380339638755 -2.94759004323459 f
1.01031276727719 3.77692981475548 -2.95742028601275 f
1.13958846175663 0.79243206895970 0.34044157748170 o
-0.83028288614075 -0.59247965154103 2.84051231339222 te
-2.67309905739721 -2.91522513051085 0.93059704356032 f
1.53126495476747 -3.11955371785965 3.59917159796550 f
0.74770789718436 1.50742448887846 5.21220764671801 f
-2.65408614973409 -1.85485581855855 5.61758418147569 f
-3.44946022908889 1.76666578224079 2.54827394924262 f
$end
Etot = -1683.444071574 H
ZPE = 85.36 kJ/mol
enthalpy = 122.81 kJ/mol
chem. pot. = -20.68 kJ/mol

$PF_3(OTeF_5)_2$

+18.0 kJ·mol^{-1} +4.7 kJ·mol^{-1} global minimum

both $OTeF_5$ axial

$coord
0.70162590557646 -0.58523434050738 0.00791146254789 p
0.09166739740507 -3.44752530760126 0.12903893893292 f

-1.49005079035242	1.36727026488561	-0.02864304335563	f
3.47399851534878	0.35465054575311	-0.07682207504441	f
0.72916889593876	-0.62875364516943	3.15808092911240	o
1.18135788836407	1.90032166906022	5.64716213890461	te
1.60917341496037	4.43058238895887	3.24442097087594	f
-2.25673407656433	2.55193235836935	5.71153414399926	f
0.77506683139598	-0.56635799915988	8.08122264291973	f
1.60130606157255	4.28583489138121	8.16394189941452	f
4.64075145109315	1.36594633417795	5.67556393794124	f
0.80262276303037	-0.65629128362320	-3.14036723857726	o
-1.57486280360745	-1.57271711154349	-5.65182051429709	te
-4.11532549747028	-2.13052521503933	-3.28600812588692	f
-2.61207111202119	1.75371900171042	-5.97291786114543	f
0.90438796931922	-1.04373505848540	-8.04996114054905	f
-3.81594232492835	-2.43860074265434	-8.18760956370329	f
-0.64614048906080	-4.94051675051284	-5.42472750208935	f

$end
Etot = -2326.087033930 H
ZPE = 118.3 kJ/mol
enthalpy = 176.30 kJ/mol
chem. pot. = -20.07 kJ/mol

$PF_3(OTeF_5)_2$
one $OTeF_5$ equatorial, one axial

$coord

0.09251498399265	1.68838882633970	-2.65513340773400	p
-2.19834297007866	3.48872781120086	-2.28428935358340	f
0.01764265561154	2.21824059380471	-5.60843948031044	f
2.79369809940251	2.83417063975062	-2.52721319754064	f
-0.31974288174335	-1.23598021624635	-3.25118375201682	o
-0.62217683927424	-4.43376452189219	-1.53544712843971	te
2.10778474959153	-3.81196228636397	0.55044841231480	f
-2.85413593156956	-3.19766879088239	0.84849806357986	f
-3.31632404470015	-5.11230673724981	-3.64502825977438	f
-0.93368893178106	-7.61005634291923	-0.13069970008686	f
1.55489018592441	-5.72681950112311	-3.93603821446905	f
0.16093407907086	1.05417514019870	0.44787421689817	o
0.52445767930842	2.98770993616807	3.42716488497233	te
0.84092326574095	5.99971151171146	1.64799847242641	f
-2.93639896019149	3.47636886813384	3.62762101494006	f
0.21860769141243	0.02599696466878	5.25234493851773	f
0.86770211745927	4.76532717613216	6.41544659372103	f
4.00165505182397	2.58974092856810	3.35607589658494	f

$end
Etot = -2326.092428396 H
ZPE = 118.5 kJ/mol
enthalpy = 176.45 kJ/mol
chem. pot. = -19.25 kJ/mol

$PF_3(OTeF_5)_2$
both $OTeF_5$ equatorial, global minimum

$coord

2.23556138345083	1.01539991892475	-0.83459971862596	p
3.22887274004411	1.55794407406108	-3.61811651664400	f
1.27909589475051	0.48656926762832	2.00226465293301	f
4.70659095677979	2.15316770562096	0.26818612098004	f
2.14895485746135	-1.92655575968411	-1.54896861472296	o
1.25436328150663	-5.07266945267261	0.01892482199172	te
2.94888188004378	-4.31558688815203	2.97851992572118	f

-1.72837555927019	-3.78547886044719	1.30398454521228	f
-0.40980947394361	-5.90342688425822	-2.93425980924370	f
0.43740258934641	-8.20094106932611	1.33067001979069	f
4.19994751546475	-6.40777026593480	-1.29321466794225	f
-0.11193303124665	2.83746013005738	-1.42148473515834	o
-2.89471941311858	4.32276768162531	0.37056888887009	te
-3.87826563483836	1.28061462650239	1.77547304924091	f
-0.93324097328570	5.06749948431091	3.16524900849295	f
-1.99055912032884	7.38318556197152	-1.04441819373051	f
-5.62124407133955	5.86731051409489	1.90444076916398	f
-4.87152382147662	3.64051021567756	-2.42321954632912	f

$end
Etot = -2326.094533433 H
ZPE = 118.8 kJ/mol
enthalpy = 176.54 kJ/mol
chem. pot. = -18.41 kJ/mol

$[PF_4(OTeF_5)_2]^-$

global minimum +0.6 kJ·mol^{-1}

$OTeF_5$ cis, global minimum

$coord

-1.87941836798404	1.85866014773728	-0.17340161808418	p
-2.04024157012662	4.87364335399207	-0.38045406465828	f
-1.73360144774648	1.99577962592419	2.85300944656566	f
-4.89384616804124	1.58316666701747	-0.10070883599973	f
-1.83845890125339	1.56368000114651	-3.19106866795507	f
-1.52065887800263	-1.43548287188431	0.21411862666066	o
-2.39758334256764	-4.22616371673610	-1.69004136959765	te
-4.96266858110502	-2.74866245610744	-3.60010916214984	f
-0.07543923387921	-3.61883750820876	-4.27220507965666	f
0.03028348784438	-6.11990832514922	0.02621131976044	f
-3.16950550169242	-7.22526943931989	-3.41034965027096	f
-4.79895696637367	-5.25645282334579	0.68513792850369	f
1.44003114820582	1.99939693406699	-0.41907818815320	o
4.03599068332625	2.65476748823697	1.82188964628571	te
2.41194706107891	5.19308835737550	3.65077466974800	f
3.12208697622200	0.24609626227189	4.22364128123746	f
6.05963135083682	0.25484831327681	0.21492184912930	f
6.84316346299868	3.29574558701916	3.88450386715594	f
5.36724478825957	5.11190440268659	-0.33679199852127	f

$end
Etot = -2426.122971626 H
ZPE = 122.7 kJ/mol
enthalpy = 183.34 kJ/mol
chem. pot. = -21.58 kJ/mol

$[PF_4(OTeF_5)_2]^-$
$OTeF_5$ trans

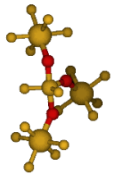
$coord

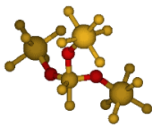
0.16413239126828	-0.19949976788005	0.00746687582914	p
-2.85945264692185	0.10601157175125	0.00106554056648	f
-0.14011773888082	-3.21873746233337	-0.05907862148851	f

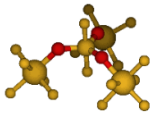
3.18444364903828	-0.49481371435064	0.03431177370406	f
0.46021974920458	2.82501035958477	0.05271727313241	f
0.27904346563781	-0.19500332644221	3.31920944155746	o
-1.86881585736954	-1.33436507781402	5.82398752194146	te
-3.93487039300628	-3.39612918629172	3.85966483348686	f
0.18230460612562	-4.11401610630587	6.54865147307491	f
-0.04506703265736	0.55687522519322	8.17717462520173	f
-3.84595821800448	-2.37425959618366	8.57286237173622	f
-4.15579125016111	1.32947771484613	5.48692089346961	f
0.07767912690795	-0.25214291404762	-3.30292958683028	o
1.76228597161035	1.46604429485979	-5.82839728839011	te
4.15811276137641	3.12802533147584	-3.85860059722519	f
4.04658152166273	-1.17066035086875	-6.36536335574736	f
-0.41696222416910	0.00217621482577	-8.18326417096816	f
3.29309994183487	3.04162661222035	-8.60637859491439	f
-0.34086782349646	4.29438017776094	-5.68002040813636	f

$end
Etot = -2426.122279602 H
ZPE = 122.6 kJ/mol
enthalpy = 180.89 kJ/mol
chem. pot. = -14.15 kJ/mol

$PF_2(OTeF_5)_3$







+9.9 kJ·mol^{-1} +0.4 kJ·mol^{-1} global minimum

two $OTeF_5$ axial, one $OTeF_5$ equatorial

$coord

-1.47003683905759	-0.21385793603931	0.55130695292678	p
-3.61453074005361	-2.20704114044952	0.72012600942635	f
-2.23104125638726	2.58693180136078	0.07205425657914	f
-1.80950989805079	0.16289876656874	3.67185243840806	o
-0.09744523078088	2.18762928803294	6.07454869148801	te
1.78110202659032	3.85933035118958	3.61600278919664	f
-2.56943843770773	4.65320870123766	5.83839957074249	f
-1.92485746729830	0.57596128179477	8.57370083438119	f
1.48802510391580	4.12028084615890	8.51612502581042	f
2.46257225622239	-0.17952152200062	6.41149340998521	f
-1.16371771088625	-0.72169464910748	-2.55198568374960	o
-3.28144266567196	-0.36496148553670	-5.40906438068829	te
-6.04671907951010	0.56915920056951	-3.45421702665538	f
-2.39423923769605	3.00319628685963	-5.74961079865679	f
-0.56367919526880	-1.28978913532182	-7.39700387337656	f
-5.25186426713999	-0.06303215772485	-8.27729668206268	f
-4.25963623494902	-3.71686958027314	-5.17614355948391	f
1.40578174522643	-0.98876053951012	0.96949060119848	o
4.41534446438344	-1.85281505585141	-0.91164161066282	te
2.74642765752601	-4.20599676495163	-2.87820469098572	f
3.88047966635701	0.64797750802466	-3.28946541041034	f
6.11388852189453	0.45005892090027	1.07943438655374	f
7.40574056891110	-2.69417195905594	-2.48969997019602	f
4.97879624943139	-4.31812102687499	1.48979872023166	f

$end

Etot = -3068.757608610 H
ZPE = 155.3 kJ/mol
enthalpy = 234.41 kJ/mol
chem. pot. = -13.69 kJ/mol

$PF_2(OTeF_5)_3$
one $OTeF_5$ axial, two $OTeF_5$ equatorial

$coord

1.39499794104257	0.10076686019891	-1.63376507283660	p
1.26988888584639	0.55585064223873	-4.61631282099707	f
4.10999849040140	1.23143648757742	-1.61914293592389	f
1.00793553959668	-2.84377754848062	-2.17558193387050	o
0.34366670124030	-5.93785733144812	-0.38513690899547	te
3.02066988415239	-5.50809648083225	1.81379279640533	f
-1.86724395106906	-4.41065107981782	1.84758424308198	f
-2.31287450716933	-6.45107695605394	-2.59028623950779	f
-0.32834417039032	-9.02051023052439	1.10009903228101	f
2.49418305383838	-7.50080652563623	-2.64330023448465	f
1.59684849249751	-0.49490728675513	1.47546628724734	o
1.84743430724099	1.51752130650338	4.41787694008349	te
2.25824735133104	4.48908838297314	2.58908074253229	f
-1.61456703480458	2.04257039525509	4.48979448251252	f
1.45133400285206	-1.39754561127296	6.30073722579591	f
2.10210343846286	3.35972069110356	7.37593411903553	f
5.32070320167736	1.09021543184332	4.47905838331445	f
-0.96257007977541	1.91434094964298	-1.09579305886010	o
-3.14745318708840	4.17016084471611	-2.93073696457249	te
-3.78091757358305	1.80220570606512	-5.42051301160941	f
-5.79348926802601	2.87363193978659	-1.06342962953811	f
-2.57023976115015	6.53480256488062	-0.43304065805626	f
-5.33956110387295	6.37872348763783	-4.50252599471476	f
-0.50075065325056	5.50419336039856	-4.77985878832302	f

$end
Etot = -3068.761310495 H
ZPE = 155.8 kJ/mol
enthalpy = 234.61 kJ/mol
chem. pot. = -11.31 kJ/mol

$PF_2(OTeF_5)_3$
all $OTeF_5$ equatorial, global minimum

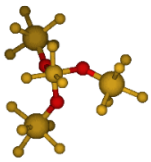
$coord

0.00000000000000	-0.00000000000000	-1.81353034194996	p
0.00000000000000	0.00000000000000	-4.81986759611720	f
0.00000000000000	0.00000000000000	1.24501597468856	f
-1.67317642780919	-2.52803716719397	-1.90994246024676	o
-3.83276214972360	-4.42628756869449	0.29244589256060	te
-1.42175956073642	-4.72872060567554	2.79759156939076	f
-5.09835640946720	-1.52070285936767	1.77189981089842	f
-6.29766587055209	-4.21252690367523	-2.17063679080325	f
-6.00641053725416	-6.34859969124670	2.22989579631418	f
-2.60047079049683	-7.32118856506770	-1.21512620282460	f
-1.35275619459661	2.71303187509304	-1.90994246024676	o
-1.91689640408285	5.53241317267135	0.29244589256060	te
-3.38431239154577	3.59564020050895	2.79759156939076	f
1.23221089691362	5.17565759782966	1.77189981089842	f
-0.49932237743211	7.56020208028200	-2.17063679080325	f
-2.49484334245059	8.37600395644399	2.22989579631418	f
-5.04009988799634	5.91266804890354	-1.21512620282460	f
3.02593262240585	-0.18499470789903	-1.90994246024676	o

5.74965855380645	-1.10612560397687	0.29244589256060	te
4.80607195228222	1.13308040516664	2.79759156939076	f
3.86614551255361	-3.65495473846203	1.77189981089842	f
6.79698824798423	-3.34767517660673	-2.17063679080325	f
8.50125387970479	-2.02740426519731	2.22989579631418	f
7.64057067849319	1.40852051616418	-1.21512620282460	f

$end
Etot = -3068.761487283 H
ZPE = 156.2 kJ/mol
enthalpy = 234.68 kJ/mol
chem. pot. = -5.78 kJ/mol

$[PF_3(OTeF_5)_3]^-$



global minimum +0.2 kJ·mol^{-1}

meridional

$coord

-1.96368819530608	2.04925143467901	0.11098454336011	p
-2.15417736380315	5.06363331632956	-0.08259885043230	f
-1.64732368900038	2.21701040329920	3.11530678378540	f
-2.22918200933891	1.78484146955283	-2.89441661294340	f
-1.77734668459269	-1.19310947697844	0.50756877200870	o
-2.19176165543216	-3.98643186343261	-1.57711974217280	te
-4.87017647592904	-2.71829659418787	-3.46808472039614	f
0.11044446252267	-2.93794120990458	-4.02166346414243	f
0.40857150234314	-5.61855840740815	0.14277421061751	f
-2.53146455026471	-6.95616431837464	-3.46112013572750	f
-4.48940882975707	-5.39987722687274	0.68550809795104	f
1.27057493381975	2.16915334152223	-0.39606219012847	o
4.10642884532620	2.32202377801330	1.65263765922014	te
2.93041451962341	4.92516640754716	3.70940203430076	f
3.05516738305086	-0.08652749013077	3.98891658576700	f
5.65108909778887	-0.21707140029252	-0.23418023194463	f
7.11305429189438	2.50030315205731	3.50217613634320	f
5.54617952540537	4.70791227993680	-0.50300362048492	f
-5.20535909532236	1.69452205566539	0.47404566240379	o
-7.97905466433123	3.79516546981542	0.05820977424626	te
-6.83293489106888	6.32362619355172	2.22433677945340	f
-6.75867281410071	5.55549048639872	-2.73406761409200	f
-9.50533494015452	1.47040788959203	-2.09920086265704	f
-10.92705981401528	5.71796140166657	-0.27438342112101	f
-9.56430100217818	2.22086177687145	2.78096477002861	f

$end
Etot = -3168.797979436 H
ZPE = 159.8 kJ/mol
enthalpy = 241.44 kJ/mol
chem. pot. = -13.45 kJ/mol

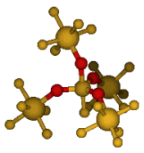
$[PF_3(OTeF_5)_3]^-$
facial, global minimum

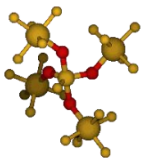
$coord

-2.12149734885352	1.56704092939071	-0.03102780864977	p
-2.74217770163203	4.53167697975044	0.00849647664939	f
-1.71068340075250	1.51405533073126	2.96293480982514	f
-5.05106486533392	0.87142756274490	0.26008540540068	f
-1.27716339108751	-1.59953144615970	-0.10847987400402	o
-2.55584901934607	-4.51081885451936	-1.59163086855210	te
-5.37644367370634	-3.12486848728827	-3.16262777614591	f
-0.69167809312949	-4.08847970842758	-4.54605782114364	f
0.13121839132719	-6.28677696882956	-0.17287459775989	f
-3.59914870783138	-7.61272516792695	-2.92826485692120	f
-4.52702627659512	-5.29723708474763	1.22345387766702	f
1.05370879858311	2.22053705440104	-0.58303123468268	o
3.81990759858965	2.98222835249734	1.43302199481869	te
2.13086816845675	5.16285628103703	3.62164056090134	f
3.40268285542924	0.30723886504540	3.68165119733474	f
5.86124966752651	0.94055141902911	-0.58071158880331	f
6.74969123960728	3.77000088625062	3.24807369727950	f
4.61958377591536	5.71601124804890	-0.63542681266419	f
-2.40557180921706	1.40584952470823	-3.28324392102480	o
-2.40064536041171	3.71493609969007	-5.92777023312493	te
-5.25934837968679	5.44529373245349	-4.81861037556356	f
-0.31747051331049	6.11301867532344	-4.42784107048584	f
0.42109568712141	2.19144290056967	-7.37113700629794	f
-2.46546089782693	5.83231447391253	-8.75525354442384	f
-4.45861574817482	1.53588618880904	-7.76911314889453	f

$end
Etot = -3168.798036658 H
ZPE = 159.6 kJ/mol
enthalpy = 241.37 kJ/mol
chem. pot. = -15.89 kJ/mol

$[PF(OTeF_5)_4]$





global minimum +2.5 $kJ \cdot mol^{-1}$

F axial, global minimum

$coord

-0.39622700031775	-0.43346138144072	0.20634773997811	p
2.49846462178156	-1.32016405991882	0.21785123548520	o
5.00236420692244	-2.59427317217905	-2.08123820716151	te
2.64442526390555	-4.53192947973053	-3.78903399017117	f
4.56402290863521	0.02992531374411	-4.34017060706001	f
7.35411483917705	-0.69586353311233	-0.34313463358967	f
7.52655446795432	-3.87728094137153	-4.11611901728738	f
5.49940904174248	-5.23041304080095	0.15091902686990	f
-2.55303403669306	-2.54571896001060	0.32755609333586	o
-5.20704911168265	-3.81958560246675	-1.78694193245538	te
-5.84052995592250	-0.64184439006610	-3.09835766481498	f
-3.04923119917566	-4.54877661843976	-4.42944586237580	f
-4.58342234642632	-6.97214864549186	-0.43550473664216	f

-7.85401301426565	-5.11453997996540	-3.65065626065827	f
-7.41900516384338	-3.15442231815254	0.82765584764750	f
-1.13824220215098	2.50114777024443	0.37899867955601	o
-1.24723841873013	5.43989496152055	-1.75845829321243	te
1.75070239822935	4.55623173524559	-3.32355045395338	f
-3.08491050885887	3.84510630764569	-4.26107678232687	f
-4.22349399443471	6.31223013755557	-0.16157305338902	f
-1.36121852327327	8.38378593684689	-3.62504943050721	f
0.55064119583280	7.12332982265987	0.70986224108433	f
-0.40865214515785	-0.57091161874195	3.37707524409404	o
1.56998532721226	1.08825137887259	5.85627244015088	te
3.41332424987118	2.93428208489436	3.49757979816820	f
-0.74957147618334	3.70402891007732	6.07146590786106	f
-0.20002363172825	-0.69388758366786	8.28156836324665	f
3.41396739123191	2.62940706716372	8.39443694959866	f
3.99245818564349	-1.44073410103518	5.74975583359720	f
-0.46457136929542	-0.36166599987885	-2.84703447506821	f

$end
Etot = -3811.429257058 H
ZPE = 193.1 kJ/mol
enthalpy = 292.66 kJ/mol
chem. pot. = 1.07 kJ/mol

[PF(OTeF$_5$)$_4$]
F equatorial

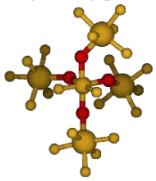
$coord

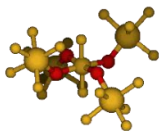
-0.37763917806277	0.80426927241712	-0.14735584361571	p
-0.76357911691098	1.18944941426522	2.97308021874349	o
0.60590449065339	3.40418221232494	5.42319522585860	te
2.32991666071555	5.30048289419241	3.02028881391174	f
-2.14818186039172	5.54145084528092	5.11482447342519	f
-1.08886393062364	1.56414506497749	7.85913872756251	f
1.86220542831539	5.50220263972426	7.91771221382205	f
3.42513149170632	1.36666871494157	5.83271055422421	f
0.01162699355765	0.39504677430634	-3.26351611808491	o
-2.20149532027507	0.17961761834832	-6.06368644924070	te
-5.03855969804705	0.88733713146641	-4.11623946409847	f
-1.80823539579299	3.59575693348285	-6.71217140982463	f
0.57827367495353	-0.52408044519567	-8.05620003037731	f
-4.25007150042572	-0.04536081119241	-8.88449923188478	f
-2.69504547196923	-3.24578186008921	-5.52893541509839	f
-2.19961298531093	-1.59739310014427	-0.08341614273580	o
-3.77880557986112	-3.86931316049036	2.28699110616653	te
-5.26472838420624	-1.28559388331810	4.10316466002716	f
-6.52964085035541	-3.91232929658021	0.14716830591961	f
-2.34864733970231	-6.48267615449299	0.47003035636490	f
-5.34168758616932	-6.18813592957724	4.36736206768668	f
-0.99586897072590	-3.87605392159090	4.39937471043273	f
2.59305120462115	0.52347735707626	0.27511276770417	o
5.64112914025253	-0.31366313810730	-1.53874352608505	te
4.10133624291844	-2.92372629474601	-3.27783522633594	f
4.96860127202765	1.92778496054790	-4.12866599969921	f
7.19995466569483	2.24852195239395	0.23894487200481	f
8.67415948715457	-1.11558154008371	-3.05672649571457	f
6.36374874018301	-2.52849355156340	1.05797186526677	f
-1.52437632392371	3.47778930142575	-0.62907958632573	f

$end
Etot = -3811.428288479 H
ZPE = 192.5 kJ/mol
enthalpy = 292.62 kJ/mol

chem. pot. = -4.97 kJ/mol

$[PF_2(OTeF_5)_4]^-$





global minimum +0.6 kJ·mol^{-1}

F cis, global minimum

$coord

-1.96137391745984	1.84967626604337	0.18225325777569	p
-1.17279973934189	1.87121461559979	3.10198701680233	f
-4.87364964846433	1.43633631515573	0.88460154347636	f
-1.39594552770389	-1.35368534260491	0.17853397436546	o
-2.77387434340541	-4.18984448325403	-1.36366471948285	te
-5.80693694362940	-2.74765308466596	-2.38991572163824	f
-1.34424076482463	-3.50089104027663	-4.50151835414825	f
0.11739217522538	-5.97233641271270	-0.45598887092070	f
-3.94645548355682	-7.20683553526677	-2.77225984424555	f
-4.30379999691081	-5.22125514244745	1.63550867604858	f
1.09854185803255	2.28803676218478	-0.79944310539426	o
4.16851850774824	2.97987903066279	0.78801738611196	te
2.87980125309878	5.25325193529359	3.13448779504532	f
3.92711678619648	0.35716295521352	3.11481796825936	f
5.77472307298200	0.80871384504120	-1.46062708197532	f
7.35453615796985	3.64282423188707	2.15030044906683	f
4.76350075329067	5.63576674766662	-1.43220603389221	f
-2.78572224487305	1.71647424589371	-2.94372882624784	o
-2.03884229314707	3.41044907967283	-5.94227180909380	te
-4.85657768459992	5.48761347167922	-5.60293313317236	f
-0.02733684760536	5.95568676712973	-4.61160915230741	f
0.82584205424401	1.47928045596107	-6.57108807088539	f
-1.52131952442054	4.90586435487388	-9.09515013154586	f
-4.00925877307515	1.03820430831938	-7.62100853130850	f
-2.28206000878950	5.09518976591734	0.15957445164566	o
-4.40045679127649	7.39548212078852	1.76861292530927	te
-7.30625055005285	6.30088944331475	0.11926316395735	f
-5.17059615704299	5.37440190766426	4.53934165725351	f
-1.70647651017840	8.78123440035898	3.55317151399532	f
-6.41568177077627	9.88617279190446	3.25086916413781	f
-3.79739923335563	9.68165339759708	-0.82980354058390	f

$end

Etot = -3911.472051929 H

ZPE = 196.8 kJ/mol

enthalpy = 299.48 kJ/mol

chem. pot. = -0.88 kJ/mol

$[PF_2(OTeF_5)_4]^-$

F trans

$coord

-1.68453910953268	1.60531051660338	-0.09915342649348	p
-1.63816796925129	1.80314456433462	2.91283441216730	f
-1.72821082499906	1.40309091389796	-3.11059932754954	f
-1.44943631054263	-1.61476766111300	0.29255840869892	o
-1.77633752441137	-4.43892837508188	-1.76851382481366	te

-4.36217788463355	-3.16550483583911	-3.77656330802195	f
0.62184984512149	-3.39377269696486	-4.11721152607872	f
0.74988045980260	-6.04292372227305	0.07639116656985	f
-2.04059857305610	-7.42037548840412	-3.63719044727973	f
-4.17089225276094	-5.80763647014881	0.41282282324785	f
1.55167813434096	1.79532264421334	-0.34301644961071	o
4.22879048475377	2.17941965866405	1.89755107883862	te
2.72876762188580	4.70480926601237	3.82723942838263	f
3.14060946096258	-0.27203391026459	4.16916943849516	f
6.04072302142407	-0.27278630786133	0.14716927598169	f
7.07578473287927	2.55522927347929	3.94869241828419	f
5.63385700935641	4.63463485391885	-0.19003240822127	f
-4.92610523559150	1.38422353601807	-0.21958494165150	o
-7.55107665531912	1.53130299762231	2.10816544646002	te
-6.13066139774954	-0.77414606206964	4.34879742950148	f
-6.25279519382972	4.21206936984510	3.97246838352214	f
-9.26804149934127	3.81730634560362	0.06097428511659	f
-10.34620796505253	1.62750678640062	4.25868824692667	f
-9.16536182354329	-1.10450282590731	0.43453299405217	f
-1.90342192628207	4.85024615161377	-0.12696688794686	o
-1.86555570986548	7.36260057307176	-2.57977982748816	te
0.65623017015121	5.92326297339507	-4.55884614397271	f
-4.34780852582057	5.89528199909057	-4.59053876932034	f
-4.35024970431483	9.10588464245735	-0.80760028505688	f
-1.86499310136471	10.05679567389189	-4.85817423929261	f
0.58559708247909	9.12253653596611	-0.77628154217882	f

$end
Etot = -3911.471641864 H
ZPE = 196.6 kJ/mol
enthalpy = 297.12 kJ/mol
chem. pot. = 1.60 kJ/mol

$P(OTeF_5)_5$

$coord

-0.41556128003877	1.58234359440259	-0.26088273392193	p
-0.54147373206147	1.61459111250784	-3.45325945118724	o
1.11102127859419	3.51925877490281	-5.98857115789879	te
2.98704265732082	5.40456611762128	-3.69218789978402	f
3.70951908712225	1.17627843269755	-6.16504212378227	f
-0.70702327925043	1.70389416780846	-8.35515574017450	f
2.63779312272250	5.28971550450997	-8.58635375831839	f
-1.40170518985350	5.95981323376655	-5.90644736077738	f
-0.35936749801104	1.46438614012934	2.92663075854158	o
-1.95691878279623	-0.20222117338461	5.67030561299551	te
-5.14266202989226	0.19969364524339	4.26747268543131	f
-1.64461117322777	-3.36178922965965	4.19159924463908	f
1.15468776347441	-0.61420769397691	7.20481905724124	f
-3.45762567288795	-1.74730017393535	8.42281463641708	f
-2.27444211011995	2.86192656489719	7.31825354591990	f
-2.42671918561608	-0.67361890946376	-0.27499585802537	o
-4.28703045043906	-2.80695335260894	-2.58175233777192	te
-5.37565076794020	-0.10732284120491	-4.50968415322826	f
-1.53615077885521	-3.32829361872706	-4.66897753195990	f
-3.25989603323734	-5.51945361893480	-0.64588270648321	f
-6.17207917306488	-4.95288800155370	-4.58041687088320	f
-7.03345702997404	-2.36826188238881	-0.47809613495731	f
-1.28591277791548	4.47363090796700	-0.28266981573069	o
-1.91108786204898	7.41230926021481	1.74303337937402	te
0.50882230171989	6.55856639179999	4.10869469403107	f
0.53187987140253	9.09313487555006	-0.08890401674063	f

-4.29011934543870	8.32822361837024	-0.63316170922314	f
-2.60020322398055	10.31933367464539	3.53819674360843	f
-4.39085975925604	5.72534076839367	3.53127916963143	f
2.54877022193427	1.04589175293127	-0.45324103487274	o
5.52497830567375	0.23518208736612	1.44730563661998	te
3.86393668346774	-2.36783148290073	3.08262986748235	f
6.36585009036469	-1.96653265872408	-1.12226497129909	f
7.17052786730540	2.80048716828574	-0.24386785525771	f
8.47146023803259	-0.60282490756036	3.10838297712593	f
4.75054538065392	2.46824779652103	4.01506741861674	f

$end
Etot = -4554.094142937 H
ZPE = 229.7 kJ/mol
enthalpy = 350.48 kJ/mol
chem. pot. = 10.78 kJ/mol

$[PF(OTeF_5)_5]^-$

$coord

-2.36232257407634	1.87755194841447	0.21809156333652	p
-1.66731808032095	1.92417583954026	3.16179044324849	f
-2.57596538803260	-1.33767525718451	0.42486964997911	o
-1.72360139963782	-4.18390323693897	-1.48184372384858	te
-4.40224086070377	-3.80682611689219	-3.71775975745182	f
0.40765754638429	-2.59034487310198	-3.76245738601831	f
1.03508609415568	-4.83764492819014	0.59382100258360	f
-0.97313571653079	-7.19819941464084	-3.14896745215879	f
-3.75009861500715	-6.09062844104882	0.65456051640603	f
0.74368846964388	1.72361506642747	-0.66537484414763	o
3.86754779541953	2.33036630407207	0.85950123621614	te
2.74416436795995	4.67069471570028	3.21918206397164	f
3.49647384477081	-0.24868650646162	3.21583217134713	f
5.31610845410568	0.06313506497980	-1.39430727105753	f
7.10595349275231	2.83159228340957	2.15812770508912	f
4.53695588220498	4.94436269043996	-1.38754368229911	f
-3.11311277332112	1.61727977788210	-2.90891904792344	o
-2.96359696350560	3.56565377055662	-5.85071386107933	te
-5.17107523306407	6.00988912914811	-4.63102831501253	f
-0.19084048991098	5.50409391708812	-4.92664841562337	f
-0.80472213856645	1.25902508157574	-7.37560191131059	f
-2.97649780755133	5.32935918280736	-8.90173127495058	f
-5.69803411104135	1.74190573718155	-7.08366072855832	f
-2.18192096352691	5.10531881600997	-0.02065835305480	o
-3.53442139007136	7.93738800260777	1.61206106550541	te
-6.83398621987178	7.35352417720072	0.56821022126395	f
-4.16977967648243	6.32753114447193	4.66338597778201	f
-0.36027643097323	8.88314813723474	2.77387773541836	f
-4.74407312695937	10.89735649953416	3.09833108142080	f
-2.95070980996828	9.81539338909196	-1.29355139666680	f
-5.51644684573251	2.18239816011315	0.87261820684975	o
-8.03374539651638	0.36180181447145	2.53773194096283	te
-5.89232151630838	-1.38024709940566	4.70582174187147	f
-8.39210674642771	2.88883174678610	4.94783830654068	f
-10.42530950401365	1.98678957598846	0.54670414366058	f
-10.71538930671337	-1.28555138299451	4.12649973309483	f
-7.99054142884479	-2.30825164370450	0.25537667723615	f

$end
Etot = -4654.144155025 H
ZPE = 234.0 kJ/mol
enthalpy = 357.43 kJ/mol
chem. pot. = 15.72 kJ/mol

3.7 Optimized structures for MCA on RI-B3LYP-D3/def2-TZVPP

$[Me]^+$

```
$coord
  -0.00000000000000     0.00000000000000     0.00000000000000  c
  -2.06235047617564     0.00000000000000     0.00000000000000  h
   1.03117523808783    -1.78604790387505     0.00000000000000  h
   1.03117523808783     1.78604790387505     0.00000000000000  h
$end
Etot = -39.4671535207 H
ZPE = 81.16 kJ/mol
enthalpy = 91.14 kJ/mol
chem. pot. = 35.41 kJ/mol
```

CO_2

```
$coord
   0.00000000000000     0.00000000000000     0.00000000000000  c
   0.00000000000000     0.00000000000000    -2.19220572030683  o
   0.00000000000000     0.00000000000000     2.19220572030683  o
$end
Etot = -188.5875306968 H
ZPE = 30.43 kJ/mol
enthalpy = 39.78 kJ/mol
chem. pot. = -23.98 kJ/mol
```

$[MeOCO]^+$

```
$coord
   2.77374462063158    -0.85209330766128     0.00000000000000  c
   4.87653044588325    -0.47642247469422     0.00000000000000  o
   0.56893909879228    -1.38976265555729     0.00000000000000  o
  -1.75909100446170     0.47096855322780     0.00000000000000  c
  -3.31583618019990    -0.85540813432423     0.00000000000000  h
  -1.57214349032279     1.55135900950459     1.73061463423377  h
  -1.57214349032279     1.55135900950459    -1.73061463423377  h
$end
Etot = -228.1175684013 H
ZPE = 130.5 kJ/mol
enthalpy = 145.57 kJ/mol
chem. pot. = 58.49 kJ/mol
```

$(CF_3)_2O$

```
$coord
   0.00000000000000     0.00000000000000    -1.41746262391024  o
  -0.00856595620258     2.26063310648605    -0.11869059234312  c
   0.00856595620258    -2.26063310648605    -0.11869059234312  c
   0.69791576332564    -4.02244591522993    -1.75891232138797  f
  -2.28432252941292    -2.82096486559514     0.76504043008693  f
   1.62117011644210    -2.24712551799140     1.82129379559926  f
   2.28432252941292     2.82096486559514     0.76504043008693  f
  -1.62117011644210     2.24712551799140     1.82129379559926  f
  -0.69791576332564     4.02244591522993    -1.75891232138797  f
$end
Etot = -750.5643753334 H
ZPE = 87.12 kJ/mol
enthalpy = 109.33 kJ/mol
chem. pot. = 0.84 kJ/mol
```

$[(CF_3)_2OMe]^+$

```
$coord
   0.58998236986308     0.04491209112456    -0.12526119222453  o
   0.21521770624881     2.51265150604247     1.37999180065889  c
   0.39352609534568    -2.44090191700245     1.32747442171013  c
   1.75602849082381    -4.02817265974848     0.04281441624406  f
  -1.98518628657920    -3.08090681721289     1.36817128254079  f
   1.29159035923721    -2.01704432280787     3.56682565678611  f
   2.24868137864901     2.80369311349876     2.70156233989873  f
  -1.79809603879542     2.22718260020693     2.76501037879223  f
  -0.06441467906148     4.25956829405826    -0.32152982111861  f
  -0.52057941083722    -0.04703086404339    -2.77954956105085  c
  -0.00390550064001    -1.89458121163183    -3.49569495538712  h
  -2.54712841988115     0.21440354360400    -2.62128900704711  h
   0.42428393562687     1.44622664391188    -3.80852575980257  h
$end
Etot = -790.1077670093 H
ZPE = 189.9 kJ/mol
enthalpy = 217.84 kJ/mol
chem. pot. = 95.87 kJ/mol
```

N_2

```
$coord
   0.00000000000000     0.00000000000000     1.03090736663379  n
   0.00000000000000     0.00000000000000    -1.03090736663379  n
$end
Etot = -109.5211262260 H
ZPE = 14.54 kJ/mol
enthalpy = 23.21 kJ/mol
chem. pot. = -33.92 kJ/mol
```

$[MeN_2]^+$

```
$coord
  -0.00000000000000     0.00000000000000    -3.83622277048905  n
   0.00000000000000     0.00000000000000    -1.77504094675310  n
   0.00000000000000     0.00000000000000     0.96512482875548  c
  -0.98859995578909     1.71230535178704     1.54871296282889  h
  -0.98859995578909    -1.71230535178704     1.54871296282889  h
   1.97719991157814     0.00000000000000     1.54871296282889  h
$end
Etot = -149.0651363481 H
ZPE = 117.6 kJ/mol
enthalpy = 129.71 kJ/mol
chem. pot. = 56.96 kJ/mol
```

AsF_3

```
$coord
  -0.00000000000000     0.00000000000000    -1.25668119243432  as
  -1.40377753209014     2.43141400810381     0.41889373081142  f
  -1.40377753209014    -2.43141400810381     0.41889373081142  f
   2.80755506418032     0.00000000000000     0.41889373081142  f
$end
Etot = -2535.4367880100 H
ZPE = 17.31 kJ/mol
enthalpy = 31.71 kJ/mol
chem. pot. = -54.87 kJ/mol
```

SUPPORTING INFORMATION

$[MeAsF_3]^+$

$coord
0.00000000000000 0.00000000000000 1.54116993353040 as
-1.43546741349893 2.48630249278963 2.82237251129210 f
-1.43546741349893 -2.48630249278963 2.82237251129210 f
2.87093482699788 0.00000000000000 2.82237251129210 f
-0.00000000000000 0.00000000000000 -2.06179406151889 c
0.98769718363348 -1.71074170454589 -2.64883113529594 h
-1.97539436726697 0.00000000000000 -2.64883113529594 h
0.98769718363348 1.71074170454589 -2.64883113529594 h
$end
Etot = -2574.9881874380 H
ZPE = 116.8 kJ/mol
enthalpy = 136.63 kJ/mol
chem. pot. = 37.69 kJ/mol

MeF

$coord
0.00000000000000 0.00000000000000 0.12466036507117 c
-0.97506455025163 1.68886134169510 0.79279437311358 h
-0.97506455025163 -1.68886134169510 0.79279437311358 h
1.95012910050324 0.00000000000000 0.79279437311358 h
-0.00000000000000 0.00000000000000 -2.50306521733620 f
$end
Etot = -139.7423874939 H
ZPE = 101.6 kJ/mol
enthalpy = 111.69 kJ/mol
chem. pot. = 45.20 kJ/mol

$[Me_2F]^+$

$coord
0.12385782488976 1.43740470164841 2.05725913213060 c
0.10332347941346 3.47403489037678 2.26469020517029 h
-1.54566152715383 0.48946620225307 2.77130139645307 h
1.90752561332580 0.54897731180681 2.53178183146241 h
-0.12198911986026 -1.46612312510962 -2.03702429684852 c
-1.79091490280028 -2.35628849526971 -1.25074402703853 h
-0.26721738533383 -0.98324092447650 -4.02121546163201 h
1.66236678722130 -2.31179116956477 -1.49230885102360 h
-0.07129076970211 1.16756060833549 -0.82373992867381 f
$end
Etot = -179.2946099648 H
ZPE = 202.8 kJ/mol
enthalpy = 218.67 kJ/mol
chem. pot. = 132.47 kJ/mol

Cl_2

$coord
0.00000000000000 0.00000000000000 1.90326563455308 cl
0.00000000000000 0.00000000000000 -1.90326563455308 cl
$end
Etot = -920.2911191925 H
ZPE = 3.182 kJ/mol
enthalpy = 12.39 kJ/mol
chem. pot. = -54.27 kJ/mol

SUPPORTING INFORMATION

$[Cl_2Me]^+$

```
$coord
   3.93046293867509    -0.88002118100044    -2.19695186414309  cl
   0.17635461189246    -1.37959604734013    -2.07437904522801  cl
  -0.87954948647139     0.38135243307735     0.76302026047504  c
  -0.38588863699624     2.34211971967845     0.42411636742351  h
  -2.91066843530728     0.03249042713029     0.72972753382948  h
   0.06928900820731    -0.49634535154555     2.35446674764303  h
$end
Etot = -959.8434101580 H
ZPE = 101.4 kJ/mol
enthalpy = 115.80 kJ/mol
chem. pot. = 28.37 kJ/mol
```

NF_3

```
$coord
   0.00000000000000     0.00000000000000    -0.86103186774707  n
   1.16960083785459     2.02580807573928     0.28701060941012  f
   1.16960083785459    -2.02580807573928     0.28701060941012  f
  -2.33920167570917     0.00000000000000     0.28701060941012  f
$end
Etot = -354.1162771663 H
ZPE = 26.34 kJ/mol
enthalpy = 38.25 kJ/mol
chem. pot. = -39.68 kJ/mol
```

$[MeNF_3]^+$

```
$coord
   1.98800231278314    -1.23487462224219     2.22600138164508  f
  -2.06343394974201    -1.10422319453130     2.22600138164508  f
   0.07543163695887     2.33909781677350     2.22600138164508  f
   0.00000000000000    -0.00000000000000    -1.57367735224695  c
  -0.05690222267006    -1.97956220614487    -2.12373016568425  h
  -1.68590004755800     1.03905987343649    -2.12373016568425  h
   1.74280227022804     0.94050233270838    -2.12373016568425  h
   0.00000000000000    -0.00000000000000     1.26686371795202  n
$end
Etot = -393.6790017800 H
ZPE = 134.2 kJ/mol
enthalpy = 149.54 kJ/mol
chem. pot. = 63.71 kJ/mol
```

SO_2

```
$coord
  -0.53116767708659    -0.75143872404233     0.00000000000000  s
  -1.64736888845528     1.72770155858090     0.00000000000000  o
   2.17853656554186    -0.97626283453854     0.00000000000000  o
$end
Etot = -548.6008122596 H
ZPE = 18.22 kJ/mol
enthalpy = 28.76 kJ/mol
chem. pot. = -47.05 kJ/mol
```

SUPPORTING INFORMATION

[MeOSO]$^+$

$coord
2.52790399031578 -1.71695872886500 -0.98499917227007 s
5.05850740280964 -1.87406962524757 -0.14902777310819 o
1.01896482056951 0.15416029530062 0.59728610211604 o
-1.73959436648129 0.75071511272258 0.17454074251466 c
-1.77039493459985 2.77599430796889 -0.14355177263020 h
-2.44972051342990 -0.31576596216240 -1.43174472908390 h
-2.64566639918396 0.22592460028288 1.93749660246167 h
$end
Etot = -588.1613543259 H
ZPE = 120.0 kJ/mol
enthalpy = 136.01 kJ/mol
chem. pot. = 46.22 kJ/mol

[MeSO$_2$]$^+$

$coord
1.85223397554647 0.01020415357589 0.00910835027537 s
3.00857936952875 2.40955560634718 -0.01442710777640 o
2.96929558221909 -2.40762294508235 -0.00407452199188 o
-1.53284565242977 0.01937320071702 0.02180092354143 c
-2.07862094771620 -0.58358037155586 -1.88134638572343 h
-2.09760585918800 -1.39017132319182 1.41825433603894 h
-2.12103646796036 1.94224167918997 0.45068440563595 h
$end
Etot = -588.1401332204 H
ZPE = 118.1 kJ/mol
enthalpy = 133.84 kJ/mol
chem. pot. = 41.23 kJ/mol

BrCl

$coord
0.00000000000000 0.00000000000000 2.04713713732770 br
0.00000000000000 0.00000000000000 -2.04713713732770 cl
$end
Etot = -3034.1860042620 H
ZPE = 2.530 kJ/mol
enthalpy = 11.96 kJ/mol
chem. pot. = -59.76 kJ/mol

[MeBrCl]$^+$

$coord
-0.47119416160913 -0.56657513710948 -2.62241265864124 br
-4.29482670066268 0.61577522993080 -2.01091864913710 cl
1.01765360145339 -0.05428674699011 0.81984739928863 c
-0.06282004461698 -1.26864854684829 2.06798903750819 h
2.96071950407938 -0.67946631518656 0.54971111127334 h
0.85046780135608 1.95320151620358 1.19578375970813 h
$end
Etot = -3073.7454287910 H
ZPE = 99.47 kJ/mol
enthalpy = 114.47 kJ/mol
chem. pot. = 22.96 kJ/mol

$[MeClBr]^+$

```
$coord
   4.23171558241260    -0.53418630557110     2.28937636543948  br
   0.25131842982888     0.51457213969387     2.42803648605192  cl
  -0.95798437375379     0.04728729531680    -0.82785393318843  c
  -2.93303940678617     0.59392046628836    -0.62391315138487  h
   0.11600605124320     1.32188443846590    -2.02026660036650  h
  -0.70801628294472    -1.94347803419385    -1.24537916655160  h
$end
Etot = -3073.7440191900 H
ZPE = 100.7 kJ/mol
enthalpy = 115.46 kJ/mol
chem. pot. = 24.46 kJ/mol
```

Br_2

```
$coord
   0.00000000000000     0.00000000000000     2.18994050938778  br
   0.00000000000000     0.00000000000000    -2.18994050938778  br
$end
Etot = -5148.0802122600 H
ZPE = 1.848 kJ/mol
enthalpy = 11.60 kJ/mol
chem. pot. = -61.77 kJ/mol
```

$[MeBr_2]^+$

```
$coord
   4.98757732491813     0.61195353991524     0.00000000000000  br
   1.05599405901103     2.51090884958339     0.00000000000000  br
  -1.25582687111755    -0.49168094261315     0.00000000000000  c
  -0.83596263403593    -1.50966898893787     1.72747117193053  h
  -3.11581924473970     0.38815653099028     0.00000000000000  h
  -0.83596263403593    -1.50966898893787    -1.72747117193053  h
$end
Etot = -5187.6442349460 H
ZPE = 98.72 kJ/mol
enthalpy = 114.16 kJ/mol
chem. pot. = 19.12 kJ/mol
```

$N(CF_3)_3$

```
$coord
   2.32649455009388    -1.39095430019456    -0.04185390184112  c
   0.04135448442476     2.71028053224464    -0.04185390184112  c
  -2.36784903451865    -1.31932623205010    -0.04185390184112  c
   1.38104307689988     3.79765051583234    -1.88266436454410  f
  -2.30749018888839     3.60904132881320    -0.13954904445087  f
   1.05976510610797     3.41365095912078     2.17080097946312  f
  -3.97938335985581    -0.70280686960023    -1.88266436454410  f
  -1.97177637961598    -3.80286578696730    -0.13954904445087  f
  -3.48619100330569    -0.78904197562655     2.17080097946312  f
   2.59834028295593    -3.09484364623210    -1.88266436454410  f
   2.42642589719769    -2.62460898349419     2.17080097946312  f
   4.27926656850437     0.19382445815409    -0.13954904445087  f
   0.00000000000000     0.00000000000000    -0.33238223512655  n
$end
Etot = -1067.7415019240 H
ZPE = 130.1 kJ/mol
enthalpy = 161.79 kJ/mol
```

chem. pot. = 31.75 kJ/mol

$[MeN(CF_3)_3]^+$

$coord
2.83495360053259 -0.13624420027900 0.95719632108914 c
-1.29948586170639 2.52326393675088 0.95719632108914 c
-1.53546773882622 -2.38701973647187 0.95719632108914 c
-0.00000000000000 0.00000000000000 -2.89937858655551 c
-1.92948079950032 -0.27947284448623 -3.52977053831901 h
0.72270981675721 1.81071581072469 -3.52977053831901 h
1.20677098274315 -1.53124296623848 -3.52977053831901 h
2.88817641498287 0.52125718868379 3.33672255647876 f
-0.99266624018601 -2.76186274032811 3.33672255647876 f
-1.89551017479684 2.24060555164433 3.33672255647876 f
-3.30909849188872 2.91316091738431 -0.43491673444024 f
-3.94155442709044 -1.88087168359351 0.64285856472465 f
-0.86832211382243 -4.32234381629254 -0.43491673444024 f
3.59965987279604 -2.47305042246260 0.64285856472465 f
0.34189455429443 4.35392210605613 0.64285856472465 f
4.17742060571114 1.40918289890825 -0.43491673444024 f
-0.00000000000000 0.00000000000000 -0.01687681978068 n
$end
Etot = -1107.3178016940 H
ZPE = 236.9 kJ/mol
enthalpy = 272.09 kJ/mol
chem. pot. = 139.03 kJ/mol

SO_2Cl_2

$coord
0.00000000000000 0.00000000000000 -0.47774690933918 s
0.00000000000000 -2.36300719991997 -1.76040253611013 o
0.00000000000000 2.36300719991997 -1.76040253611013 o
-2.98601559744470 0.00000000000000 1.99927599077973 cl
2.98601559744470 0.00000000000000 1.99927599077973 cl
$end
Etot = -1468.9135688670 H
ZPE = 31.45 kJ/mol
enthalpy = 47.87 kJ/mol
chem. pot. = -45.84 kJ/mol

$[MeOSOCl_2]^+$

$coord
-1.38162087805923 0.85893023391885 1.63944580808888 s
-3.67716831800797 0.66631715398240 0.29127717568574 o
-1.03419576002473 3.94686892651273 3.67809582976562 cl
-0.94129813171187 -1.99655380317975 4.04455034908851 cl
1.03631307200424 0.96355394265703 0.06845551392517 o
1.41282457330082 -0.85195642362077 -2.09786358295378 c
-0.23459761282628 -0.76098745329739 -3.31603044639421 h
3.09185551135164 -0.10824350293367 -3.00355599523519 h
1.72788754397328 -2.71792907403936 -1.30437465197077 h
$end
Etot = -1508.4853376870 H
ZPE = 133.3 kJ/mol
enthalpy = 155.39 kJ/mol
chem. pot. = 46.34 kJ/mol

$[MeClSO_2Cl]^+$

$coord
0.24466577752388 -2.39464603912268 -2.12880283593349 s
-2.25933521837487 -1.45994778778516 -2.23544425322728 o
1.03898972830654 -4.90700801227791 -1.70997195889503 o
2.48490972776853 -0.60214239639845 -4.52286617152246 cl
1.64395153277432 -0.52241657355267 1.71376875620171 cl
-0.52883335542212 2.15372800442553 2.14407152697060 c
-2.39351592118713 1.47949439822727 1.62181871295309 h
-0.39087541811561 2.57151981965099 4.15058966605491 h
0.16004314672654 3.68141858683309 0.96683655739801 h
$end
Etot = -1508.4730835300 H
ZPE = 129.0 kJ/mol
enthalpy = 152.86 kJ/mol
chem. pot. = 38.07 kJ/mol

TMSF

$coord
0.00000000000000 -0.00000000000000 0.81710666227484 si
2.89343241850418 -1.72934629066339 -0.22495747970409 c
2.88683916604700 -3.67239181725634 0.46828415984724 h
3.01216752011753 -1.79359285700580 -2.28509003801075 h
4.60114696418846 -0.80959977425046 0.47780022214582 h
0.05094161040277 3.37045912388978 -0.22495747970409 c
0.04721321815457 3.50541002137903 -2.28509003801075 h
-1.59943951069521 4.38951004465804 0.47780022214582 h
1.73696502337061 4.33627196306475 0.46828415984724 h
-2.94437402890697 -1.64111283322638 -0.22495747970409 c
-3.00170745349327 -3.57991027040759 0.47780022214582 h
-4.62380418941761 -0.66388014580841 0.46828415984724 h
-3.05938073827212 -1.71181716437324 -2.28509003801075 h
0.00000000000000 -0.00000000000000 3.87803604097365 f
$end
Etot = -509.1365801556 H
ZPE = 293.7 kJ/mol
enthalpy = 318.21 kJ/mol
chem. pot. = 212.84 kJ/mol

$[MeTMSF]^+$

$coord
0.06421556788589 0.54924394633156 0.97350385472366 si
-3.26895064670646 -0.28244541949193 1.54761588510770 c
-4.55783205337055 1.04416708156421 0.63784635212716 h
-3.72550002176999 -2.19855629897223 0.93932832557300 h
-3.62921635321241 -0.19436630625280 3.58189660431181 h
0.98351325036477 3.87500113088152 1.38172220424326 c
1.00475512794316 4.31894662519940 3.40081768590895 h
2.87103443763998 4.24369072135580 0.64139853408425 h
-0.35623480342822 5.15379553458747 0.47766822796128 h
2.44058463644222 -1.88486355440907 1.72659477222917 c
1.85925831364541 -3.77124568638996 1.13175709575674 h
4.27986089606552 -1.44727824827840 0.90465328158410 h
2.68744298298844 -1.94976091166621 3.77855260074408 h
-0.15809010335311 -1.68754715563428 -4.37376760498383 c
-0.19906777657765 -0.78622101066542 -6.21053802114112 h
1.48427781161591 -2.87501907549234 -4.08177245086147 h
-1.93039545396873 -2.57996020180559 -3.86616803037422 h

0.15034418779577 0.47241882913825 -2.59110931699456 f
$end
Etot = -548.7086980015 H
ZPE = 393.5 kJ/mol
enthalpy = 425.61 kJ/mol
chem. pot. = 297.34 kJ/mol

CH_2Cl_2

$coord
0.00000000000000 0.00000000000000 -0.28350808651116 c
0.00000000000000 -1.69495000015265 -1.43256677274059 h
0.00000000000000 1.69495000015265 -1.43256677274059 h
-2.81447994362993 0.00000000000000 1.57432081599618 cl
2.81447994362993 0.00000000000000 1.57432081599618 cl
$end
Etot = -959.6196464043 H
ZPE = 75.78 kJ/mol
enthalpy = 87.74 kJ/mol
chem. pot. = 6.85 kJ/mol

$[MeClCH_2Cl]^+$

$coord
-1.82617019480323 0.85527252243172 -1.96769582737317 c
-1.99061835257700 -1.11475766189788 -2.51143791864168 h
-1.84263528975484 2.17055430763157 -3.54366192995546 h
-3.83468977003716 1.69775111419997 0.43292694769967 cl
1.67735713602074 1.12339087245745 -0.97426989331940 cl
1.90491836830991 -0.94837474833839 1.80646346040738 c
1.60463776938902 -2.86527373940098 1.14639058283333 h
3.81890369111291 -0.63164878007545 2.47834824726191 h
0.48829664233965 -0.28691388700803 3.13293633108746 h
$end
Etot = -999.1929682185 H
ZPE = 173.8 kJ/mol
enthalpy = 192.22 kJ/mol
chem. pot. = 93.61 kJ/mol

OPF_3

$coord
-0.00000000000000 0.00000000000000 -0.24949235677682 p
1.29576073194696 -2.24432342218476 1.07379607556053 f
1.29576073194696 2.24432342218476 1.07379607556053 f
-2.59152146389391 0.00000000000000 1.07379607556053 f
0.00000000000000 0.00000000000000 -2.97193181346503 o
$end
Etot = -716.2707448397 H
ZPE = 37.11 kJ/mol
enthalpy = 51.50 kJ/mol
chem. pot. = -34.10 kJ/mol

$[MeOPF_3]^+$

$coord
-1.22862821180909 -0.68615326311410 2.01508725112501 p
0.85957636525260 -1.93666870185875 3.49275093168452 f
-1.64241801346928 1.83734654411282 3.26761331759950 f
-3.57544966992750 -2.21564458318467 2.43708011077364 f
-0.72538721374809 -0.52122823864003 -0.75433689619934 o

1.28569469521713	0.70501459149439	-2.35337202626890	c
0.85616682355206	0.05509863447015	-4.24544489144106	h
1.06324583542855	2.73384047498383	-2.16104378837110	h
3.10719938950361	0.02839454173636	-1.69833400890235	h

$end
Etot = -755.8466089732 H
ZPE = 139.9 kJ/mol
enthalpy = 160.86 kJ/mol
chem. pot. = 54.96 kJ/mol

$OCCl_2$

$coord

0.00000000000000	0.00000000000000	0.37480152272295	c
-2.75332105423819	0.00000000000000	-1.48382644267853	cl
2.75332105423819	0.00000000000000	-1.48382644267853	cl
0.00000000000000	0.00000000000000	2.59285136263412	o

$end
Etot = -1033.6486822160 H
ZPE = 26.97 kJ/mol
enthalpy = 39.90 kJ/mol
chem. pot. = -44.91 kJ/mol

$[MeOCCl_2]^+$

$coord

-0.47727833451584	-1.36287203212029	-1.92230459977721	c
-1.36758070783018	1.22729414396533	-3.51719035777447	cl
-0.59039710386560	-4.17348038472765	-3.33982014766460	cl
0.28398625500341	-1.29910096793904	0.32370320305569	o
0.49767521809497	1.05014706566328	1.85941544157708	c
-1.38017261796929	1.86076016003126	2.03814030243235	h
1.22795808052968	0.38310512787266	3.65051666708522	h
1.80580921055279	2.31414688725439	0.90753949106597	h

$end
Etot = -1073.2292021100 H
ZPE = 131.5 kJ/mol
enthalpy = 149.10 kJ/mol
chem. pot. = 51.78 kJ/mol

$CHCl_3$

$coord

0.00000000000000	0.00000000000000	-0.20247469025037	c
-0.00000000000000	0.00000000000000	-2.24744637454647	h
-1.60327188528118	-2.77694836365375	0.81659084008857	cl
-1.60327188528118	2.77694836365375	0.81659084008857	cl
3.20654377056235	0.00000000000000	0.81659084008857	cl

$end
Etot = -1419.1730056690 H
ZPE = 50.91 kJ/mol
enthalpy = 65.30 kJ/mol
chem. pot. = -23.40 kJ/mol

$[MeClCHCl_2]^+$

$coord

-1.70310797557234	-2.94810038632065	-0.73546704820834	c
-1.41828810311972	-2.54564692907305	-2.72058102228111	h
-4.62398628804355	-3.51244480468172	0.23199562271157	cl
0.77705542475668	-3.94562407514576	0.90764839565026	cl

-1.49961038019760	1.82868552318018	-0.36614939196116	cl
1.70057445388054	2.65990414830036	0.53596334410205	c
2.80997416695877	2.84204971801963	-1.17632705821171	h
1.54981678097053	4.43894282987668	1.54844159012327	h
2.40757192036675	1.18223397584438	1.77447556807523	h

$end
Etot = -1458.7468185710 H
ZPE = 146.3 kJ/mol
enthalpy = 169.29 kJ/mol
chem. pot. = 53.14 kJ/mol

MeCl

$coord

-0.00000000000000	0.00000000000000	0.29006239050744	c
-0.97329303629883	-1.68579298952253	0.93930266393883	h
-0.97329303629883	1.68579298952253	0.93930266393883	h
1.94658607259765	0.00000000000000	0.93930266393883	h
0.00000000000000	0.00000000000000	-3.10797038232392	cl

$end
Etot = -500.0618405244 H
ZPE = 97.67 kJ/mol
enthalpy = 108.12 kJ/mol
chem. pot. = 38.11 kJ/mol

$[Me_2Cl]^+$

$coord

-2.01009662813659	-0.02094899151435	1.86375766979853	c
-2.29344353102282	-1.98477813268909	1.34843687309117	h
-0.56144975887149	0.27199353001293	3.28425698425437	h
-3.76842717334130	0.93571042311285	2.32059560985027	h
-0.92302783894159	1.61101633773991	-1.01147226602583	cl
2.03643101733984	-0.02475746657740	-1.83486094206800	c
2.67497678341471	0.96114150920980	-3.51889446760592	h
3.30574936895173	0.22909766985084	-0.24522570703507	h
1.53928776060745	-1.97847487914549	-2.20659375425948	h

$end
Etot = -539.6407755557 H
ZPE = 197.3 kJ/mol
enthalpy = 213.53 kJ/mol
chem. pot. = 124.52 kJ/mol

I_2

$coord

0.00000000000000	0.00000000000000	2.54901818401283	i
0.00000000000000	0.00000000000000	-2.54901818401283	i

$end
Etot = -595.4367613327 H
ZPE = 1.245 kJ/mol
enthalpy = 11.36 kJ/mol
chem. pot. = -66.49 kJ/mol

$[MeI_2]^+$

$coord

-0.00000116924112	0.09649964245491	-2.72799458713881	i
-0.00000335834854	-0.51595360382495	2.31321711405233	i
0.00007056818152	3.43821951620364	3.46548165150988	c
-1.71362155150206	4.25084607377485	2.69165949233793	h

-0.01451925593067	3.34609326458683	5.51927641498763	h
1.72786993054632	4.24211854198638	2.71448896249571	h

$end
Etot = -635.0186703488 H
ZPE = 96.88 kJ/mol
enthalpy = 113.00 kJ/mol
chem. pot. = 12.52 kJ/mol

MeBr

$coord

0.00000000000000	0.00000000000000	0.36653570605589	c
-0.97575396449039	-1.69005544218411	0.99180936958102	h
-0.97575396449039	1.69005544218411	0.99180936958102	h
1.95150792898076	0.00000000000000	0.99180936958102	h
0.00000000000000	0.00000000000000	-3.34201093690278	br

$end
Etot = -2613.9446109480 H
ZPE = 96.18 kJ/mol
enthalpy = 106.83 kJ/mol
chem. pot. = 33.36 kJ/mol

$[Me_2Br]^+$

$coord

0.04789614574710	1.64928687896576	2.38264994513806	c
-0.16780778353817	3.58823999332894	3.01936307167497	h
1.95191308250680	0.93836850344589	2.64100308685095	h
-1.41743681256646	0.41134390886083	3.10209012922331	h
-0.49775657260575	1.87416190647732	-1.33819294991203	br
-0.02526064512017	-1.73106046202290	-2.32429097590120	c
-0.36567822413537	-1.72571328922035	-4.34802985293239	h
1.90914821402826	-2.20763175714291	-1.84669183618641	h
-1.43501740431623	-2.79699568269250	-1.28790061795526	h

$end
Etot = -2653.5289590470 H
ZPE = 194.3 kJ/mol
enthalpy = 211.23 kJ/mol
chem. pot. = 117.52 kJ/mol

CS_2

$coord

0.00000000000000	0.00000000000000	-0.00000000000000	c
0.00000000000000	0.00000000000000	-2.93662200003438	s
0.00000000000000	0.00000000000000	2.93662200003438	s

$end
Etot = -834.4216330598 H
ZPE = 18.07 kJ/mol
enthalpy = 28.69 kJ/mol
chem. pot. = -42.20 kJ/mol

$[MeSCS]^+$

$coord

-2.00185830070091	0.20852124649757	2.41936167316511	c
-1.95875094467348	0.47501983647142	5.25877000155345	s
-2.24393795508033	-0.08318834929781	-0.62589669903109	s
1.13174480716469	-0.13800085617740	-1.59732847209270	c
1.02509924853645	-0.38995516178376	-3.63601483408143	h
1.98986092789921	1.66216262417332	-1.11660926065310	h

2.05784221685439 -1.73455933988330 -0.70228240886021 h
$end
Etot = -874.0067411716 H
ZPE = 115.6 kJ/mol
enthalpy = 131.74 kJ/mol
chem. pot. = 38.86 kJ/mol

CCl_4

$coord
0.00000000000000 -0.00000000000000 0.00000000000000 c
1.94698654375601 1.94698654375601 -1.94698654375601 cl
-1.94698654375601 -1.94698654375601 -1.94698654375601 cl
1.94698654375601 -1.94698654375601 1.94698654375601 cl
-1.94698654375601 1.94698654375601 1.94698654375601 cl
$end
Etot = -1878.7187050900 H
ZPE = 23.65 kJ/mol
enthalpy = 41.22 kJ/mol
chem. pot. = -51.94 kJ/mol

$[MeClCCl_3]^+$

$coord
-2.72203922941795 -0.73373048739201 3.55680931667667 c
-5.57106198563145 -0.02127207934450 2.48291329131043 cl
-1.12380265902156 1.35482559123686 5.24790120652714 cl
-1.56367948682108 -3.60782493038118 3.11780000624983 cl
-0.52945200880519 1.41259087106670 -1.60985287657864 cl
2.47231742655848 0.51692805887680 -3.00078326179619 c
2.66088536332521 -1.51963875224041 -2.85811310525276 h
2.41954031923045 1.11087594072141 -4.96217705124966 h
3.95729226058316 1.48724578745628 -1.97449752588693 h
$end
Etot = -1918.3051003300 H
ZPE = 121.1 kJ/mol
enthalpy = 148.33 kJ/mol
chem. pot. = 13.65 kJ/mol

TMSCl

$coord
0.00000000000000 0.00000000000000 -0.76691686640188 si
-3.28827361997898 -0.74057717136757 0.28974533446777 c
-4.61975788138222 0.68003629616422 -0.38792926137940 h
-3.89621360559706 -2.57745397897836 -0.42196347575766 h
-3.38969384605984 -0.78474798300710 2.35199628068273 h
1.00277816612236 3.21801707517982 0.28974533446777 c
1.01523523417717 3.32793497324313 2.35199628068273 h
2.89880764866479 3.66080953652830 -0.38792926137940 h
-0.28403382008200 4.66294695050682 -0.42196347575766 h
2.28549545385663 -2.47743990381222 0.28974533446777 c
1.72095023271745 -4.34084583269247 -0.38792926137940 h
4.18024742567906 -2.08549297152848 -0.42196347575766 h
2.37445861188263 -2.54318699023606 2.35199628068273 h
0.00000000000000 0.00000000000000 -4.72616466799684 cl
$end
Etot = -869.4326589242 H
ZPE = 291.3 kJ/mol
enthalpy = 316.62 kJ/mol
chem. pot. = 208.13 kJ/mol

$[TMSClMe]^+$

$coord
0.11593644859349 0.68654681421778 1.05562286640849 si
-3.21810255331809 -0.24119867791646 1.52176889510937 c
-4.52032083129518 1.17080843509392 0.77741742796150 h
-3.65349226619440 -2.07332529815737 0.68522044914613 h
-3.56373695926596 -0.40411891664754 3.55447404389416 h
0.97468200687062 3.96663585485651 1.88048545890358 c
0.94365697395352 4.14038885893805 3.94101061240590 h
2.87192531149569 4.45457338112509 1.24214770399844 h
-0.36765736774380 5.33369777804550 1.12199332415188 h
2.51250030749003 -1.77994149891083 1.66404807269012 c
1.98928980684791 -3.60446518577796 0.86209052749441 h
4.37236841878510 -1.23684733684602 0.96401066149107 h
2.66530304402561 -2.03752507519324 3.71054933285008 h
0.34478147654795 1.12649370599079 -3.34140725988165 cl
-0.28971633366225 -1.99666198259555 -4.72047012773377 c
-0.23799056298442 -1.68360036291574 -6.74541564747002 h
1.20727558153444 -3.24600552018999 -4.09437581942900 h
-2.14670250168041 -2.57545497311702 -4.07917052199068 h
$end
Etot = -909.0276486173 H
ZPE = 389.3 kJ/mol
enthalpy = 422.14 kJ/mol
chem. pot. = 291.15 kJ/mol

MeI

$coord
0.00000000000000 0.00000000000000 0.44732670999904 c
-0.97665414516943 -1.69161460085620 1.06401535131976 h
-0.97665414516943 1.69161460085620 1.06401535131976 h
1.95330829033885 0.00000000000000 1.06401535131976 h
0.00000000000000 0.00000000000000 -3.63942489337836 i
$end
Etot = -337.6094070615 H
ZPE = 94.67 kJ/mol
enthalpy = 105.52 kJ/mol
chem. pot. = 29.67 kJ/mol

$[Me_2I]^+$

$coord
0.32008448734126 -0.15711294507039 -2.61837542073267 i
-3.05227046163348 0.24759220766944 -0.31961401722891 c
-2.82540281804022 1.98215882640034 0.74665887349443 h
-4.58652170958249 0.36183470037218 -1.67779765451929 h
-3.16517118724529 -1.43342445205559 0.84582212115579 h
3.03614162003359 -0.23616455548949 0.45446694876844 c
4.83235114799044 -0.62644242293036 -0.45924496802060 h
2.98768081884942 1.61663906672972 1.32748811228572 h
2.45310810228676 -1.75508042562596 1.70059600479705 h
$end
Etot = -377.2045158694 H
ZPE = 191.5 kJ/mol
enthalpy = 208.93 kJ/mol
chem. pot. = 111.71 kJ/mol

SUPPORTING INFORMATION

CSe_2

$coord
0.00000000000000 0.00000000000000 -0.00000000000000 c
0.00000000000000 0.00000000000000 -3.20966689604278 se
0.00000000000000 0.00000000000000 3.20966689604278 se
$end
Etot = -4840.9892108850 H
ZPE = 13.91 kJ/mol
enthalpy = 25.56 kJ/mol
chem. pot. = -52.79 kJ/mol

$[MeSeCSe]^+$

$coord
-3.17174218973445 0.94898283119465 0.00000000000000 c
-6.00194094808383 -0.36788494962827 0.00000000000000 se
-0.22675024363897 2.55684481613006 0.00000000000000 se
2.05608587512181 -0.45774098628926 0.00000000000000 c
1.70479967883432 -1.52793386372491 -1.71206258341888 h
3.93474814866676 0.37566601604269 0.00000000000000 h
1.70479967883432 -1.52793386372491 1.71206258341888 h
$end
Etot = -4880.5835518260 H
ZPE = 110.1 kJ/mol
enthalpy = 127.65 kJ/mol
chem. pot. = 26.53 kJ/mol

PF_3

$coord
0.00000000000000 0.00000000000000 -1.10720346229832 p
-1.29992804541381 2.25154142084041 0.36904582193829 f
-1.29992804541381 -2.25154142084041 0.36904582193829 f
2.59985609082757 0.00000000000000 0.36904582193829 f
$end
Etot = -641.0003755768 H
ZPE = 21.88 kJ/mol
enthalpy = 34.98 kJ/mol
chem. pot. = -46.82 kJ/mol

Me_2O

$coord
0.00000000000000 0.00000000000000 -1.56277615615345 o
0.12707244603488 2.21720732502181 -0.08648616758858 c
1.81167019732890 2.23157797924060 1.12592010495263 h
0.22167755855242 3.81493050229081 -1.37957903913649 h
-1.54767357482614 2.42680753749067 1.12153317984915 h
-0.12707244603488 -2.21720732502181 -0.08648616758858 c
-0.22167755855242 -3.81493050229081 -1.37957903913649 h
1.54767357482614 -2.42680753749067 1.12153317984915 h
-1.81167019732890 -2.23157797924060 1.12592010495263 h
$end
Etot = -155.0042428580 H
ZPE = 206.5 kJ/mol
enthalpy = 220.31 kJ/mol
chem. pot. = 141.46 kJ/mol

SUPPORTING INFORMATION

$[Me_3O]^+$

$coord

0.00000000000000	-0.00000000000000	0.00000000000000	o
-0.66542590892673	2.70543057356068	0.00000000000000	c
0.11465903455156	3.54135307168908	1.70515672352422	h
0.11465903455156	3.54135307168908	-1.70515672352422	h
-2.71283498466506	2.80453006067112	0.00000000000000	h
-2.01025865041529	-1.92899102824724	0.00000000000000	c
-1.07237678588578	-3.75164904333067	0.00000000000000	h
-3.12423124112858	-1.67137889914948	1.70515672352422	h
-3.12423124112858	-1.67137889914948	-1.70515672352422	h
2.67568455934201	-0.77643954531344	0.00000000000000	c
3.78521177055084	0.94711898265955	0.00000000000000	h
3.00957220657700	-1.86997417253961	1.70515672352422	h
3.00957220657700	-1.86997417253961	-1.70515672352422	h

$end
Etot = -194.6151291792 H
ZPE = 311.8 kJ/mol
enthalpy = 330.09 kJ/mol
chem. pot. = 237.59 kJ/mol

$P(CF_3)_3$

$coord

0.00000000000000	0.00000000000000	-1.88314460716766	p
2.62033090313904	-1.75425538485679	-0.11888872095572	c
0.20906427644209	3.14640082086821	-0.11888872095572	c
-2.82939517958114	-1.39214543601144	-0.11888872095572	c
2.55139191017848	4.08536455338425	-0.43568369881255	f
-1.43949442960251	4.76358115562817	-1.17926980024367	f
-0.27526333173225	3.07071803213080	2.35892076795215	f
-4.81372544204048	0.16688793253251	-0.43568369881255	f
-3.40563507896157	-3.62842932245605	-1.17926980024367	f
-2.52168815781813	-1.77374405407591	2.35892076795215	f
2.26233353186198	-4.25225248591683	-0.43568369881255	f
2.79695148955038	-1.29697397805492	2.35892076795215	f
4.84512950856409	-1.13515183317214	-1.17926980024367	f

$end
Etot = -1354.2962127850 H
ZPE = 113.2 kJ/mol
enthalpy = 149.52 kJ/mol
chem. pot. = 7.57 kJ/mol

$[HP(CF_3)_3]^+$

$coord

0.00000000000000	0.00000000000000	-0.96332072516554	p
0.00000000000000	-0.00000000000000	-3.61392425583211	h
0.06355880932515	3.45233388689896	0.20105763505143	c
2.95802944373778	-1.78121048695933	0.20105763505143	c
-3.02158825306296	-1.67112339993961	0.20105763505143	c
-1.75198032088849	4.69079238235374	-0.98413896518072	f
-0.31707430449583	3.46003928591056	2.66657540125402	f
2.30176103886553	4.40988408076096	-0.35774572100088	f
3.15501907193862	-1.45542524037459	2.66657540125402	f
4.93833552744113	-0.82813672635703	-0.98413896518072	f
2.66819112225081	-4.19832557347928	-0.35774572100088	f
-3.18635520655264	-3.86265565599671	-0.98413896518072	f
-4.96995216111634	-0.21155850728168	-0.35774572100088	f
-2.83794476744279	-2.00461404553593	2.66657540125402	f

$end
Etot = -1354.5695419580 H
ZPE = 138.2 kJ/mol
enthalpy = 176.27 kJ/mol
chem. pot. = 25.77 kJ/mol

$(TMS)_2O$

$coord

0.07704846519523	-2.97659231359532	0.29283912632967	si
0.00000000000000	-0.00000000000000	1.19015814892169	o
-0.07704846519523	2.97659231359532	0.29283912632967	si
-3.15043300553773	-3.93202966426107	-0.81557093437743	c
-3.74404207859133	-2.79817136789813	-2.43454027529252	h
-3.19194307726643	-5.91574065092523	-1.38580189603609	h
-4.54839679859110	-3.67508840198330	0.68057155858492	h
1.05067624433647	-4.90899996802327	3.08972436439101	c
1.11380291314488	-6.91960845675134	2.62617467431358	h
2.92288309590546	-4.35171473379008	3.75452174329263	h
-0.27393523734356	-4.65907050964850	4.65191259069760	h
2.41689358038060	-3.34974836427210	-2.34735952290538	c
4.30023813539690	-2.74427517421879	-1.76014823449092	h
2.54757651669644	-5.31723356355841	-2.95854214081319	h
1.87452251005247	-2.22115816777078	-3.98886012815462	h
-2.41689358038060	3.34974836427210	-2.34735952290538	c
-1.87452251005247	2.22115816777078	-3.98886012815462	h
-4.30023813539690	2.74427517421879	-1.76014823449092	h
-2.54757651669644	5.31723356355841	-2.95854214081319	h
3.15043300553773	3.93202966426107	-0.81557093437743	c
4.54839679859110	3.67508840198330	0.68057155858492	h
3.74404207859133	2.79817136789813	-2.43454027529252	h
3.19194307726643	5.91574065092523	-1.38580189603609	h
-1.05067624433647	4.90899996802327	3.08972436439101	c
0.27393523734356	4.65907050964850	4.65191259069760	h
-1.11380291314488	6.91960845675134	2.62617467431358	h
-2.92288309590546	4.35171473379008	3.75452174329263	h

$end
Etot = -893.7598118451 H
ZPE = 587.2 kJ/mol
enthalpy = 633.37 kJ/mol
chem. pot. = 472.11 kJ/mol

$[(TMS)_2OMe]^+$

$coord

-0.03120366669278	-3.06920404859208	-0.29274972371580	si
-0.09148090479544	-0.00242203588469	1.24985501862137	o
0.03963426107538	3.05341700358890	-0.31623904281508	si
-3.25208563665088	-3.51603078643454	-1.59450604294902	c
-3.67810658305738	-2.25366326677976	-3.16129275401827	h
-3.42111401763762	-5.45229641177256	-2.29311170096354	h
-4.69163660963631	-3.26283091969122	-0.13896853638965	h
0.73738846975499	-5.44775396687175	2.17025348516805	c
0.92001464330196	-7.25650839643557	1.18579946153340	h
2.53591602828649	-5.10000163365293	3.11542464571477	h
-0.73796261954429	-5.68869680632817	3.58808928982844	h
2.55079685468970	-2.85912594446107	-2.65885143880683	c
4.36734678575366	-2.50381947988108	-1.75068425980065	h
2.68677963837773	-4.69064847025003	-3.60519483739920	h
2.26196052016874	-1.44395393652594	-4.12227359902088	h
-1.60964410130820	2.71156180323722	-3.39019596392058	c

-0.79282225768211	1.32942320201477	-4.67338989028250	h
-3.60959570659589	2.28768978658564	-3.13657132419620	h
-1.49169302170703	4.54967839416522	-4.32865714397397	h
3.46636889315676	3.74214637113222	-0.54521317166316	c
4.39063295511223	3.68468083249451	1.29767646912179	h
4.43853808648747	2.42760589511115	-1.79772944675217	h
3.73369695437005	5.64381235403887	-1.30357450004460	h
-1.71871348589781	5.24646802956198	1.78337627489785	c
-0.78752057789196	5.61229082823544	3.58237073414707	h
-1.86748491245583	7.05589294369106	0.79730183193921	h
-3.64225054090627	4.60040488106663	2.15088231429296	h
-0.10023190296101	0.15369548208454	4.03776704802049	c
1.32990227425797	1.50747171149350	4.61702255252385	h
-1.96331389666373	0.74825589135497	4.65655581795805	h
0.35551362860749	-1.68539030091514	4.80222066262816	h

$end
Etot = -933.3808248800 H
ZPE = 695.5 kJ/mol
enthalpy = 745.44 kJ/mol
chem. pot. = 576.85 kJ/mol

NC_5F_5

$coord

-2.13175680248628	0.00000000000000	-1.76609117374860	c
-2.26829141955860	0.00000000000000	0.85422925380889	c
0.00000000000000	0.00000000000000	2.18061115621325	c
2.26829141955860	0.00000000000000	0.85422925380889	c
2.13175680248628	0.00000000000000	-1.76609117374860	c
0.00000000000000	0.00000000000000	-3.02082163234920	n
4.26777532873910	0.00000000000000	-3.08847859869599	f
-4.26777532873910	0.00000000000000	-3.08847859869599	f
-4.46592902999212	0.00000000000000	2.07876752527249	f
0.00000000000000	0.00000000000000	4.68335646286239	f
4.46592902999212	0.00000000000000	2.07876752527249	f

$end
Etot = -744.4652517208 H
ZPE = 125.9 kJ/mol
enthalpy = 150.43 kJ/mol
chem. pot. = 38.86 kJ/mol

$[MeNC_5F_5]^+$

$coord

-0.06297542152629	-2.18170125414344	0.00000000000000	c
2.54419046047328	-2.27402953117702	0.00000000000000	c
3.88696280810764	-0.00138623161991	0.00000000000000	c
2.56969619410052	2.28338683593726	0.00000000000000	c
-0.04276098122677	2.23276738035604	0.00000000000000	c
-1.42330742330835	-4.23481154178539	0.00000000000000	f
3.71891819704425	-4.45635783254555	0.00000000000000	f
6.34583873457141	-0.01495828324914	0.00000000000000	f
3.77117796298255	4.45175820689612	0.00000000000000	f
-1.34370900710712	4.32356064359047	0.00000000000000	f
-4.16859662646559	-0.02574197283846	0.00000000000000	c
-4.86195009198710	1.89831905509271	0.00000000000000	h
-4.79524106205960	-1.01648687840107	-1.68553214861077	h
-4.79524106205960	-1.01648687840107	1.68553214861077	h
-1.34300268153922	0.03216828228849	0.00000000000000	n

$end
Etot = -784.0836887539 H

ZPE = 232.3 kJ/mol
enthalpy = 262.11 kJ/mol
chem. pot. = 135.84 kJ/mol

CTe_2

$coord
0.00000000000000 0.00000000000000 -0.00000000000000 c
0.00000000000000 0.00000000000000 -3.60321518872966 te
0.00000000000000 0.00000000000000 3.60321518872966 te
$end
Etot = -574.1044900081 H
ZPE = 11.16 kJ/mol
enthalpy = 23.71 kJ/mol
chem. pot. = -59.98 kJ/mol

$[MeTeCTe]^+$

$coord
-3.37617896827151 1.12573593400247 0.00000000000000 c
-6.57922790358097 -0.31168400458736 0.00000000000000 te
-0.05395072579386 2.86330970052773 0.00000000000000 te
2.23030295629720 -0.56236578113799 0.00000000000000 c
1.80349534833907 -1.61313850471026 -1.70726576318823 h
4.17206394467102 0.11128116061562 0.00000000000000 h
1.80349534833907 -1.61313850471026 1.70726576318823 h
$end
Etot = -613.7181961337 H
ZPE = 105.8 kJ/mol
enthalpy = 124.57 kJ/mol
chem. pot. = 16.97 kJ/mol

Et_2O

$coord
-0.32231178487182 -0.46142927706485 0.08610924471412 o
-1.33819531359926 1.94480853019331 -0.49955000050289 c
-0.60817452739940 2.59639180343574 -2.33318291607675 h
-0.74072724825091 3.33432087799126 0.92589293440568 h
2.35076197100639 -0.49722646459309 0.22210538403840 c
3.16270827512544 0.12558942599867 -1.58689546356551 h
3.00527455667997 0.83429984997526 1.67756455883349 h
-4.19303515787564 1.73664915565996 -0.56804562975600 c
-4.91380022994522 1.11663981216639 1.25998808268377 h
-5.03850573221114 3.56171469554530 -1.02233540116683 h
-4.78102341897645 0.36868562364232 -1.99232788983855 h
3.19616772491576 -3.16190628816181 0.84087068231032 c
5.25230387477115 -3.25548385174553 0.96572781100884 h
2.40136406651930 -3.76921478601499 2.64227579312947 h
2.56719294411182 -4.47383910702787 -0.61819719021753 h
$end
Etot = -233.6189395271 H
ZPE = 354.0 kJ/mol
enthalpy = 374.50 kJ/mol
chem. pot. = 274.84 kJ/mol

$[Et_2OMe]^+$

$coord
0.67723374293363 2.81469912619912 -0.36931792720067 c
-0.39919343362626 4.27953789169196 0.58709816251465 h

2.63591978227133	2.91479432645460	0.23988573904661	h
1.23926756532331	-1.94733244497778	0.24500483630789	c
0.37701064921068	-2.77752863962488	-1.42856443969782	h
3.10806611336028	-1.23667602845004	-0.21874879792027	h
1.27736654174814	-3.67322747236410	2.50441738985016	c
2.51807345394977	-5.25863779677206	2.05571047239408	h
2.03448458829656	-2.71496220640954	4.16027795765500	h
-0.57381600889415	-4.45387593725140	2.94509685970728	h
0.36524745561920	2.84168822324066	-3.19778819322687	c
1.12364481888091	4.63091647239397	-3.88834222131658	h
1.41932214127798	1.32890030939507	-4.11252214261747	h
-1.60881719929521	2.74928834752305	-3.77115004324027	h
-3.01986868249681	0.07563847290225	0.83277878424767	c
-3.82505159728056	1.82508673654139	1.53610082313569	h
-3.65528146540325	-0.34143197823237	-1.07613914159847	h
-3.43510848058298	-1.46505755029591	2.11572130984993	h
-0.25849998529263	0.40818014803600	0.84048057210958	o

$end
Etot = -273.2438274126 H
ZPE = 461.8 kJ/mol
enthalpy = 486.72 kJ/mol
chem. pot. = 375.75 kJ/mol

Me_2CO_3

$coord

0.01118922757622	0.01617312420551	-0.00171459994178	c
1.31285173546480	1.87254621698112	-0.21800712161895	o
-2.41693232516915	-0.17988671581644	-0.66969383805667	o
0.74281975417882	-2.20704565422662	0.94834224201805	o
-3.49969842643045	2.07062649583891	-1.73523086121549	c
-2.49710096271749	2.61356746272387	-3.44911152242791	h
-5.44845416594524	1.58980345947047	-2.16156576444727	h
-3.41629781213965	3.62226232567354	-0.38515090940893	h
3.33083394410987	-2.31154985795586	1.76325021773001	c
3.60233903528870	-4.21673331582532	2.47548151497361	h
4.60070828389012	-1.94164949900559	0.18593467136617	h
3.67774171189347	-0.92811404206360	3.24746597102916	h

$end
Etot = -343.5884369689 H
ZPE = 247.4 kJ/mol
enthalpy = 268.07 kJ/mol
chem. pot. = 166.43 kJ/mol

$[Me_3CO_3]^+$

$coord

-0.00021659486441	-0.00015781427934	0.00015306277656	c
-2.36998288287359	0.12092283613852	-0.47743427907531	o
1.04081919410917	-2.14350836986418	0.42475402596955	o
1.32821897279064	2.02252076224951	0.05462981234269	o
-3.57871769461260	2.58638402658717	-0.96555627730841	c
-5.54498576818983	2.12100830246786	-1.28931694599884	h
-3.34671214192002	3.78017455870064	0.68753836165900	h
-2.71838612911062	3.43039828753106	-2.62668346871870	h
-0.48142162134845	-4.47949947562237	0.36563385965143	c
-1.23781296912466	-4.72907472507883	-1.52583539693774	h
0.85319053647700	-5.95515733337046	0.84402134426029	h
-1.98048693100941	-4.33474602528821	1.75961744767328	h
4.06019535409182	1.89315708143742	0.60001748454049	c
4.97852236848426	0.79832481539716	-0.87308807600762	h

4.66564363525095	3.84774011199267	0.57434316346497	h
4.33213267184987	1.04151296100129	2.44720588170831	h

$end
Etot = -383.2158578539 H
ZPE = 352.8 kJ/mol
enthalpy = 378.71 kJ/mol
chem. pot. = 264.85 kJ/mol

MeOTMS

$coord

-0.30652690453559	-2.14244003687625	1.73372490149420	o
-0.15877105327453	0.62755733013823	0.27133056767608	si
-2.28158171351032	0.61223783884085	-2.57185860849417	c
-1.70211612503978	-0.81934443766669	-3.94171281508904	h
-4.23672505034055	0.22332684375115	-2.03912113050276	h
-2.23956439566259	2.43846929252046	-3.53397281861602	h
3.17516587370163	1.27397453196365	-0.75713837492010	c
4.46507636505808	1.25641467693570	0.85326223769363	h
3.83821527057952	-0.13256987081286	-2.11477660607180	h
3.32146127105028	3.12265341004580	-1.66467500104029	h
-1.23695375579523	2.99650766188851	2.65536101540664	c
-0.01810953954767	2.97189259621961	4.31915024125061	h
-1.20625562401779	4.90534409175326	1.87056243226548	h
-3.16268338598940	2.59276460341579	3.27413502239540	h
0.31421806822148	-4.49199598326562	0.62124943844114	c
0.16286183860834	-5.95468554070145	2.06498476484754	h
-0.97689103921468	-4.97051190160480	-0.92464652215640	h
2.24917989970892	-4.50959510654532	-0.11585874458017	h

$end
Etot = -524.3744761491 H
ZPE = 396.3 kJ/mol
enthalpy = 426.66 kJ/mol
chem. pot. = 304.00 kJ/mol

[Me_2OTMS]$^+$

$coord

0.26861217010966	-1.60155373411440	1.19113666935512	o
0.15292536682011	1.34194340072539	-0.68038980507875	si
-2.44284648829108	0.77638014539725	-2.95736521786893	c
-2.05905482836031	-0.82393849332200	-4.19978661215062	h
-4.24884512996940	0.45997082120258	-2.01323202262869	h
-2.66659473953519	2.44037366627867	-4.16052858926827	h
3.36003352124691	1.51818640513668	-2.06815909546344	c
4.83047244119842	1.28314434839536	-0.64198529696025	h
3.68065135283457	0.16867737554564	-3.59087042371718	h
3.59339454117641	3.40362769230612	-2.88093968742908	h
-0.47986963211857	3.81345161289876	1.71276423547049	c
0.86107063271828	3.75418625301009	3.27806926568388	h
-0.24701014478832	5.64589942365666	0.78600273606474	h
-2.39822616267124	3.76124002935603	2.46149705998004	h
-1.47200288376951	-2.04322193002672	3.30899410321977	c
-1.73836574966804	-0.25689051901822	4.27138877258220	h
-3.25142378750158	-2.77115753889298	2.57807319706457	h
-0.57888885280602	-3.39906085573400	4.56566390323963	h
1.06068820879938	-3.96427824886181	-0.03310936108491	c
1.96631388180926	-5.12847375163649	1.39514516807493	h
-0.59293174893807	-4.89974016908076	-0.81987030228698	h
2.40189803170432	-3.47876593322187	-1.50249869679831	h

$end

Etot = -564.0037631157 H
ZPE = 503.7 kJ/mol
enthalpy = 538.57 kJ/mol
chem. pot. = 404.69 kJ/mol

PCl_3

```
$coord
  -0.00000000000000    0.00000000000000   -1.33201339309967  p
  -1.74763521785012    3.02699299041312    0.44408062364162  cl
  -1.74763521785012   -3.02699299041312    0.44408062364162  cl
   3.49527043570027    0.00000000000000    0.44408062364162  cl
$end
```

Etot = -1721.8886711640 H
ZPE = 12.11 kJ/mol
enthalpy = 28.37 kJ/mol
chem. pot. = -65.45 kJ/mol

$[MePCl_3]^+$

```
$coord
   0.00000000000000   -0.00000000000000    1.45482286869562  p
  -3.32147183303759   -1.12144486068265    2.72508695237211  cl
   2.63193565481347   -2.31575655502369    2.72508695237211  cl
   0.68953617822415    3.43720141570632    2.72508695237211  cl
   0.00000000000000   -0.00000000000000   -1.91991836813966  c
  -0.39189475577350   -1.91615829201676   -2.57000602871051  h
  -1.46349438067199    1.29746996011811   -2.57000602871051  h
   1.85538913644545    0.61868833189863   -2.57000602871051  h
$end
```

Etot = -1761.5187520440 H
ZPE = 113.5 kJ/mol
enthalpy = 133.80 kJ/mol
chem. pot. = 32.04 kJ/mol

MeCN

```
$coord
   0.00000000000000    0.00000000000000   -0.92426833589338  c
  -0.96673096382151    1.67442714658890   -1.63422594722902  h
  -0.96673096382151   -1.67442714658890   -1.63422594722902  h
   1.93346192764304    0.00000000000000   -1.63422594722902  h
  -0.00000000000000    0.00000000000000    1.82720197562892  c
  -0.00000000000000    0.00000000000000    3.99974420709043  n
$end
```

Etot = -132.7316028351 H
ZPE = 117.5 kJ/mol
enthalpy = 129.47 kJ/mol
chem. pot. = 57.06 kJ/mol

$[MeCNMe]^+$

```
$coord
   0.00000000000000   -0.00000000000000   -1.05990754773939  c
  -0.00000000000000    0.00000000000000   -3.78421403759690  c
   1.17887851993808    1.55030986150379   -4.46573579076511  h
   0.75316846383076   -1.79609367699407   -4.46573579076511  h
  -1.93204698376886    0.24578381549028   -4.46573579076511  h
   0.00000000000000    0.00000000000000    1.09426139947267  n
  -0.00000000000000   -0.00000000000000    3.80140461473582  c
  -1.18180333388244    1.55406959056577    4.44858356010668  h
```

-0.75496207773763	-1.80050650470222	4.44858356010668	h
1.93676541162007	0.24643691413644	4.44858356010668	h

$end
Etot = -172.3631440088 H
ZPE = 220.6 kJ/mol
enthalpy = 238.06 kJ/mol
chem. pot. = 147.16 kJ/mol

Me_2Se

$coord

0.22528336752588	1.14486306812103	-2.19215259862270	se
-2.73343008140992	-0.20696004573954	-0.39965373944895	c
-2.97612871172459	0.76102039026340	1.39786435415438	h
-4.37357107504150	0.13590259170099	-1.59055859283692	h
-2.51472573120560	-2.22908173317022	-0.09914499432393	h
2.73505297243812	0.21634545021576	0.38325886680861	c
2.75204493171484	-1.82198880359834	0.65130922656328	h
4.57037721113553	0.83246397499474	-0.30784518129648	h
2.31509711656724	1.16743510721220	2.15692265900266	h

$end
Etot = -2481.2506631410 H
ZPE = 192.4 kJ/mol
enthalpy = 208.70 kJ/mol
chem. pot. = 117.00 kJ/mol

$[Me_3Se]^+$

$coord

0.00000000000000	0.00000000000000	-1.81343865248181	se
-3.08149616345374	-1.03600829114882	-0.05548895969112	c
-2.76704009884880	-0.92536326355513	1.97070035699530	h
-4.57826810702821	0.23720289752446	-0.65492231795429	h
-3.49968039451649	-2.95826110444795	-0.64774613283722	h
2.43795758039304	-2.15064981364082	-0.05548895969112	c
2.08371031840663	-4.08349793478475	-0.65492231795429	h
4.31176946473757	-1.55168157455367	-0.64774613283722	h
2.18490814339200	-1.93364538711569	1.97070035699530	h
0.64353858306067	3.18665810478963	-0.05548895969112	c
-0.81208907022109	4.50994267900162	-0.64774613283722	h
0.58213195545678	2.85900865067084	1.97070035699530	h
2.49455778862157	3.84629503726028	-0.65492231795429	h

$end
Etot = -2520.8975502950 H
ZPE = 292.8 kJ/mol
enthalpy = 314.32 kJ/mol
chem. pot. = 213.99 kJ/mol

$OPOMe_3$

$coord

-0.49925694085928	2.65186899532450	1.11645930929933	o
2.54621438788899	-0.89356530386242	1.11645930929933	o
-2.04695744702967	-1.75830369146210	1.11645930929933	o
-2.45248988037218	4.27780566804626	0.14700234011690	c
-2.14524499880859	6.12554070865636	0.98959191010555	h
-2.33098162498942	4.40331748469645	-1.90477976729382	h
-4.30561402926444	3.56380679318242	0.69944150034221	h
4.93093332116722	-0.01498429509653	0.14700234011690	c
5.23915423170778	1.94686773164248	0.69944150034221	h
6.37749636501646	-1.20493368801842	0.98959191010555	h

4.97887561517001	-0.18296943935263	-1.90477976729382	h
-2.47844344079503	-4.26282137294971	0.14700234011690	c
-0.93354020244331	-5.51067452482490	0.69944150034221	h
-4.23225136620785	-4.92060702063794	0.98959191010555	h
-2.64789399018059	-4.22034804534380	-1.90477976729382	h
0.00000000000000	-0.00000000000000	-0.18525193744688	p
0.00000000000000	-0.00000000000000	-2.95823310940289	o

$end
Etot = -762.0394542291 H
ZPE = 348.6 kJ/mol
enthalpy = 379.68 kJ/mol
chem. pot. = 253.14 kJ/mol

$[(MeO)_4P]^+$

$coord

-0.00111910522090	-0.00069981874674	0.00222242169868	p
0.15326701366404	-0.46307900642205	2.87830894725629	o
0.13896031689566	-2.61151510496763	-1.29165841065184	o
-2.47424505078542	1.46378295439056	-0.49636406413692	o
2.17778192538895	1.60798452845864	-1.08149102941198	o
0.39933750836290	-3.02734230508919	-4.02067619700345	c
2.19099267199272	-2.24728362477502	-4.65125983726072	h
0.36046031232847	-5.06085798179761	-4.26306513944168	h
-1.17855708649939	-2.15105134776503	-5.00390854568291	h
2.53706117768998	4.32008138547808	-0.63007964513776	c
2.73467032881673	4.66120096014413	1.38703891699289	h
4.26469763401321	4.80728048071135	-1.61670016663064	h
0.93616116726660	5.34799014333809	-1.40249133540493	h
-4.96422261144135	0.78054290057904	0.51425237286047	c
-4.91126480224301	0.89065200278053	2.56392015972113	h
-6.25956701795401	2.16554052504097	-0.25988855885784	h
-5.46602959989908	-1.11071463206797	-0.11465638401062	h
2.02831427169642	-2.07294704164450	4.13551128376244	c
1.62713269417971	-1.90692077126421	6.13722873040534	h
1.78762613588709	-4.00958548454711	3.49710849548468	h
3.91854211586060	-1.38305876183427	3.71664798544933	h

$end
Etot = -801.6843123090 H
ZPE = 452.1 kJ/mol
enthalpy = 489.80 kJ/mol
chem. pot. = 344.02 kJ/mol

Me_2S

$coord

0.00000000000000	0.00000000000000	-2.26089859282945	s
0.12161492935907	2.60654227357500	-0.03692644105580	c
1.81565600785791	2.50398314521250	1.13198504788501	h
0.17361571679874	4.34709345120554	-1.13335337948938	h
-1.54942778166620	2.62878711432744	1.16874406907490	h
-0.12161492935907	-2.60654227357500	-0.03692644105580	c
-0.17361571679874	-4.34709345120554	-1.13335337948938	h
1.54942778166620	-2.62878711432744	1.16874406907490	h
-1.81565600785791	-2.50398314521250	1.13198504788501	h

$end
Etot = -477.9577099317 H
ZPE = 195.9 kJ/mol
enthalpy = 211.21 kJ/mol
chem. pot. = 126.51 kJ/mol

SUPPORTING INFORMATION

$[Me_3S]^+$

$coord

0.00000000000000	0.00000000000000	1.55148690726793	s
-0.25439561670982	-3.05785333071338	0.05983789522972	c
1.33211976216014	-4.19204735975716	0.71300685903202	h
-2.01718984587264	-3.90505887583520	0.69615295268835	h
-0.22685945230014	-2.85452434345147	-1.98615957544277	h
2.77537647379955	1.30861359867457	0.05983789522972	c
4.39047511268352	0.20559178713588	0.69615295268835	h
2.58552032330013	1.23079612294518	-1.98615957544277	h
2.96435962633713	3.24967323479255	0.71300685903202	h
-2.52098085708976	1.74923973203879	0.05983789522972	c
-4.29647938849728	0.94237412496462	0.71300685903202	h
-2.37328526681087	3.69946708869934	0.69615295268835	h
-2.35866087100002	1.62372822050627	-1.98615957544277	h

$end
Etot = -517.6075512304 H
ZPE = 298.6 kJ/mol
enthalpy = 318.35 kJ/mol
chem. pot. = 224.60 kJ/mol

$N(TMS)_3$

$coord

0.00000000000000	-0.00000000000000	-0.35695038569736	n
2.84861783498868	-1.70969995701274	-0.09839350720318	si
-2.90495251311653	-1.61212543226730	-0.09839350720318	si
0.05633467812787	3.32182538928001	-0.09839350720318	si
-5.20909863368353	-0.66544833750695	-2.64342735117471	c
-6.62887522898165	-2.15203437332398	-2.83999355049443	h
-6.20254376532750	1.09255090031114	-2.25962538848529	h
-4.25136205532678	-0.47548865950928	-4.46142168282256	h
3.18084448202891	-4.17848757883531	-2.64342735117471	c
5.17815405160669	-4.66475716015353	-2.83999355049443	h
2.15509504806674	-5.91783591901395	-2.25962538848529	h
2.53746628600981	-3.44404321084358	-4.46142168282256	h
2.02825415165466	4.84393591634226	-2.64342735117471	c
1.45072117737495	6.81679153347749	-2.83999355049443	h
4.04744871726074	4.82528501870282	-2.25962538848529	h
1.71389576931694	3.91953187035282	-4.46142168282256	h
-2.60839341051522	-5.14163956603447	-0.47218761756527	c
-2.13086711191740	-5.67971849589887	-2.40204464838342	h
-1.27183148800933	-6.04635178577460	0.80360056502754	h
-4.47598580279934	-5.92333151004176	-0.05976118445384	h
5.75698718654669	0.31188482644707	-0.47218761756527	c
5.98421405975144	0.99447419694015	-2.40204464838342	h
5.87220999070287	1.92173751493824	0.80360056502754	h
7.36774846413267	-0.91465165718184	-0.05976118445384	h
-3.14859377603147	4.82975473958734	-0.47218761756527	c
-3.85334694783403	4.68524429895868	-2.40204464838342	h
-4.60037850269353	4.12461427083638	0.80360056502754	h
-2.89176266133331	6.83798316722357	-0.05976118445384	h
1.22305575803660	4.28232254980554	3.12593050211990	c
1.35405498328152	6.33792741728754	3.27087403839053	h
-0.09454915120397	3.63181369962684	4.57599455534644	h
3.07524452112541	3.50283173982238	3.57943872606134	h
3.09707223631226	-3.20035863160730	3.12593050211990	c
4.81177865907216	-4.34160972228650	3.27087403839053	h
3.19251750129117	-1.73402488296457	4.57599455534644	h
1.49591901130598	-4.41465574805465	3.57943872606134	h

-4.32012799434887	-1.08196391819825	3.12593050211990	c
-6.16583364235370	-1.99631769500111	3.27087403839053	h
-3.09796835008724	-1.89778881666231	4.57599455534644	h
-4.57116353243133	0.91182400823229	3.57943872606134	h

$end
Etot = -1282.4735752430 H
ZPE = 887.7 kJ/mol
enthalpy = 951.93 kJ/mol
chem. pot. = 759.09 kJ/mol

$[MeN(TMS)_3]^+$

$coord

2.60703524644250	-2.29059643816989	0.16878649357212	si
-3.28723232849455	-1.11246053289568	0.16878649357212	si
0.68019708205203	3.40305697106558	0.16878649357212	si
-5.67990724765766	0.29637375713166	-2.00766232041193	c
-7.51673463324775	-0.37052564923484	-1.33564140519725	h
-5.75532595612184	2.34581734334277	-2.04295094001054	h
-5.47396508102380	-0.38691993052485	-3.93999967979684	h
2.58328642113778	-5.06713084617675	-2.00766232041193	c
4.07925194161494	-6.32442032128145	-1.33564140519725	h
0.84612556608794	-6.15716715673291	-2.04295094001054	h
3.07206502957693	-4.54713285433309	-3.93999967979684	h
3.09662082651992	4.77075708904502	-2.00766232041193	c
3.43748269163280	6.69494597051624	-1.33564140519725	h
4.90920039003390	3.81134981339008	-2.04295094001054	h
2.40190005144686	4.93405278485794	-3.93999967979684	h
-3.56804932638955	-4.60782488093822	-0.22767396285494	c
-3.30888671547440	-5.21795000832648	-2.17703740403079	h
-2.36205501163310	-5.74216584905047	0.98840119274425	h
-5.52379041531925	-5.04866322428812	0.27560582106343	h
5.77451806627726	-0.78610891814022	-0.22767396285494	c
6.17332062062518	-0.25660494968243	-2.17703740403079	h
6.15388900383767	0.82548327931460	0.98840119274425	h
7.13416581504538	-2.25941121270344	0.27560582106343	h
-2.20646873988771	5.39393379907842	-0.22767396285494	c
-2.86443390515075	5.47455495800893	-2.17703740403079	h
-3.79183399220457	4.91668256973584	0.98840119274425	h
-1.61037539972616	7.30807443699152	0.27560582106343	h
1.73807463472872	3.46853076486816	3.52868720733352	c
1.95689061165841	5.46162725032799	4.02664389996841	h
0.36472345840497	2.66689172685119	4.83171142711034	h
3.55548289260829	2.56487206517911	3.85551561291751	h
2.13479843881930	-3.23948216978249	3.52868720733352	c
3.75146263895618	-4.42553060728749	4.02664389996841	h
2.12723425539317	-1.64930564376043	4.83171142711034	h
0.44350291959801	-4.36157454030930	3.85551561291751	h
-3.87287307354806	-0.22904859508568	3.52868720733352	c
-5.70835325061461	-1.03609664304058	4.02664389996841	h
-2.49195771379815	-1.01758608309075	4.83171142711034	h
-3.99898581220627	1.79670247513017	3.85551561291751	h
0.00000000000000	0.00000000000000	-3.71254305226670	c
-1.14153754944704	1.55028003156542	-4.42893344705988	h
1.91335066503891	0.21346050141230	-4.42893344705988	h
-0.77181311559186	-1.76374053297772	-4.42893344705988	h
0.00000000000000	0.00000000000000	-0.83381412819202	n

$end
Etot = -1322.1347072120 H
ZPE = 999.2 kJ/mol
enthalpy = 1065.42 kJ/mol

chem. pot. = 874.78 kJ/mol

PC_5H_5

$coord

-2.51675697342699	-0.02052283228959	-1.70677905750530	c
-2.30884463444039	-0.01827487107239	0.90842588481370	c
0.00000000000000	-0.00000000000000	2.17120158293903	c
2.30884463444039	0.01827487107239	0.90842588481370	c
2.51675697342699	0.02052283228959	-1.70677905750530	c
0.00000000000000	0.00000000000000	4.21693686132021	h
-4.39659753934565	-0.03573902985412	-2.52242698036042	h
-4.02304811235855	-0.03121807097848	2.03238332596380	h
4.02304811235855	0.03121807097848	2.03238332596380	h
4.39659753934565	0.03573902985412	-2.52242698036042	h
0.00000000000000	-0.00000000000000	-3.81134479008277	p

$end
Etot = -534.8023386495 H
ZPE = 219.2 kJ/mol
enthalpy = 234.40 kJ/mol
chem. pot. = 146.03 kJ/mol

$[MePC_5H_5]^+$

$coord

0.25980255808554	0.01643642174134	2.63240958976514	c
2.87524863536404	0.00295984084643	2.33197347172921	c
4.10432287394864	-0.00622682617724	0.00000000000000	c
2.87524863536404	0.00295984084643	-2.33197347172921	c
0.25980255808554	0.01643642174134	-2.63240958976514	c
-0.59861922196806	0.02634359354906	4.48676232650358	h
4.01730329743780	-0.00053311075008	4.02980928725999	h
6.14764302159896	-0.01811605565573	0.00000000000000	h
4.01730329743780	-0.00053311075008	-4.02980928725999	h
-0.59861922196806	0.02634359354906	-4.48676232650358	h
-4.94158766214866	-0.02805774905542	0.00000000000000	c
-5.60962821057660	-1.97563443919683	0.00000000000000	h
-5.62320280209510	0.94588753808453	1.68092162555437	h
-5.62320280209510	0.94588753808453	-1.68092162555437	h
-1.54544205059000	0.04584650314271	0.00000000000000	p

$end
Etot = -574.4546771094 H
ZPE = 318.0 kJ/mol
enthalpy = 339.65 kJ/mol
chem. pot. = 232.69 kJ/mol

$P(C_6F_5)_3$

$coord

0.00000000000000	0.00000000000000	-2.32107100803446	p
-1.06755051566007	2.98693406353877	-0.87500978130017	c
-0.49921924223697	5.18595245820086	-2.21845727715785	c
-2.52034555888034	3.28997785765099	1.30321720019230	c
-1.33337507216815	7.55510781975686	-1.47260322829550	c
-3.40234332844147	5.63245316808913	2.08008274179111	c
-2.80555671318133	7.77524174981192	0.68722736237300	c
-2.05298552062361	-2.41799289815418	-0.87500978130017	c
-1.58903162317391	-3.82767220913116	1.30321720019230	c
-4.24155695050181	-3.02531277493568	-2.21845727715785	c
-3.17667586497058	-5.76274233887136	2.08008274179111	c
-5.87622776415583	-4.93229059514895	-1.47260322829550	c

-5.33077851931182	-6.31730426027897	0.68722736237300	c
3.12053603628368	-0.56894116538457	-0.87500978130017	c
4.74077619273878	-2.16063968326518	-2.21845727715785	c
4.10937718205424	0.53769435148016	1.30321720019230	c
7.20960283632396	-2.62281722460791	-1.47260322829550	c
6.57901919341204	0.13028917078225	2.08008274179111	c
8.13633523249317	-1.45793748953293	0.68722736237300	c
10.49885252350202	-1.87205240981954	1.42865993742126	f
-3.62818131763141	10.02829920084888	1.42865993742126	f
-6.87067120587061	-8.15624679102931	1.42865993742126	f
8.68992682142635	-4.16293569584009	-2.80634174643236	f
-0.73975534379461	9.60716523230303	-2.80634174643236	f
-7.95017147763174	-5.44422953646291	-2.80634174643236	f
3.91512788629461	-3.33249662253175	-4.30419748339252	f
0.92846278999106	5.05684851986188	-4.30419748339252	f
-4.84359067628568	-1.72435189733011	-4.30419748339252	f
7.45845317092398	1.22069014223417	4.17398311238730	f
-4.78637525878601	5.84886484783970	4.17398311238730	f
-2.67207791213796	-7.06955499007385	4.17398311238730	f
2.68197780799413	2.01116632146952	2.77765749385666	f
-3.08271002962537	1.31707775337425	2.77765749385666	f
0.40073222163125	-3.32824407484376	2.77765749385666	f

$end
Etot = -2524.7561664120 H
ZPE = 391.6 kJ/mol
enthalpy = 466.95 kJ/mol
chem. pot. = 241.67 kJ/mol

$[MeP(C_5F_5)_3]^+$

$coord

-0.00000000000000	0.00000000000000	1.32032112201493	p
3.09260505849464	0.90896932441259	0.23827159130605	c
4.25258083068097	3.01641603257683	1.33905356545291	c
4.41588101056882	-0.33797383485201	-1.68205975938385	c
6.63234164593869	3.82785917580841	0.62913426694145	c
6.80729959227587	0.43869862648121	-2.42118209298499	c
7.91932661472286	2.52155182904585	-1.26182810910877	c
-0.75911200304523	-3.13275920673491	0.23827159130605	c
-2.50063443208073	-3.65527821781591	-1.68205975938385	c
0.48600249725373	-5.19105104730487	1.33905356545291	c
-3.02372564099987	-6.11464369132295	-2.42118209298499	c
-0.00114753460990	-7.65770593986461	0.62913426694145	c
-1.77593536644859	-8.11911394373913	-1.26182810910877	c
-2.33349305544945	2.22378988232234	0.23827159130605	c
-4.73858332793471	2.17463501472804	1.33905356545291	c
-1.91524657848812	3.99325205266793	-1.68205975938385	c
-6.63119411132881	3.82984676405619	0.62913426694145	c
-3.78357395127602	5.67594506484173	-2.42118209298499	c
-6.14339124827425	5.59756211469329	-1.26182810910877	c
0.00000000000000	0.00000000000000	4.74092641101318	c
-1.57263995306717	-1.14072761995494	5.40596227900256	h
1.77421907421314	-0.79158234038506	5.40596227900256	h
-0.20157912114594	1.93230996034003	5.40596227900256	h
-5.26185770616304	0.43899041066588	3.10180884178357	f
3.01110570073594	4.33740723930319	3.10180884178357	f
2.25075200542709	-4.77639764996904	3.10180884178357	f
-8.88231983945058	3.73035682612567	1.70838776515865	f
7.67174369633080	5.82713621243986	1.70838776515865	f
1.21057614311972	-9.55749303856555	1.70838776515865	f
-7.92312192192968	7.18404224386705	-1.96257094662566	f

```
  10.18312404601423     3.26960373973893    -1.96257094662566  f
  -2.26000212408458   -10.45364598360602    -1.96257094662566  f
  -3.33335462808643     7.34062183141448    -4.23003483674312  f
   8.02384229962284    -0.78354112796198    -4.23003483674312  f
  -4.69048767153640    -6.55708070345252    -4.23003483674312  f
   0.29229408110995     4.10644107655537    -2.88855967357531  f
   3.41013525088586    -2.30635463789475    -2.88855967357531  f
  -3.70242933199584    -1.80008643866064    -2.88855967357531  f
$end
Etot = -2564.4218792320 H
ZPE = 495.8 kJ/mol
enthalpy = 580.34 kJ/mol
chem. pot. = 324.45 kJ/mol
```

NC_5H_5

```
$coord
  -2.15364789132706     0.00000000000000    -1.71821943813172  c
  -2.25625575594147     0.00000000000000     0.90929559628951  c
   0.00000000000000     0.00000000000000     2.25082192533839  c
   2.25625575594147     0.00000000000000     0.90929559628951  c
   2.15364789132706     0.00000000000000    -1.71821943813172  c
   0.00000000000000     0.00000000000000    -3.02788728956438  n
   0.00000000000000     0.00000000000000     4.29611087165826  h
  -3.88172527869223     0.00000000000000    -2.82072254597581  h
  -4.06112276838806     0.00000000000000     1.86914084733930  h
   4.06112276838806     0.00000000000000     1.86914084733930  h
   3.88172527869223     0.00000000000000    -2.82072254597581  h
$end
Etot = -248.2311226170 H
ZPE = 230.6 kJ/mol
enthalpy = 244.37 kJ/mol
chem. pot. = 160.29 kJ/mol
```

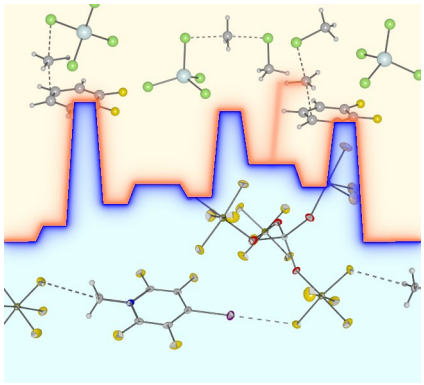
$[MeNC_5H_5]^+$

```
$coord
   1.91828732236686    -1.13508779964517     0.00000000000000  c
   3.25747467186352     1.10314701889762     0.00000000000000  c
   1.95234749407032     3.38188916024714     0.00000000000000  c
  -0.67837624335876     3.35444874822812     0.00000000000000  c
  -1.92664549381109     1.07037934702244     0.00000000000000  c
   2.82786766920573    -2.96077537390824     0.00000000000000  h
   5.29746276787831     1.04002369253041     0.00000000000000  h
   2.96740248888053     5.15534422350119     0.00000000000000  h
  -1.76421280830260     5.08263373362915     0.00000000000000  h
  -3.96214284250573     0.92018610318546     0.00000000000000  h
  -2.05758742870048    -3.53667283476417     0.00000000000000  c
  -0.73896657310563    -5.10627577363507     0.00000000000000  h
  -3.23194144096453    -3.62068881655628     1.68437849553008  h
  -3.23194144096453    -3.62068881655628    -1.68437849553008  h
  -0.62902814255190    -1.12786261217631     0.00000000000000  n
$end
Etot = -287.9049270440 H
ZPE = 338.6 kJ/mol
enthalpy = 357.28 kJ/mol
chem. pot. = 257.64 kJ/mol
```

References

[1] K. Seppelt, D. Nothe, *Inorg. Chem.* **1973**, *12*, 2727.
[2] A. Clouston, R. D. Peacock, G. W. Fraser, *J. Chem. Soc. D* **1970**, 1197.
[3] Adept Scientific, *gNMR V 5.0*, **2005**.
[4] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Magn. Reson. Chem.* **2008**, *46*, 582.
[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[6] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3.
[7] G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3.
[8] K. Brandenburg, *DIAMOND*, Crystal Impact GbR, Bonn, **2014**.
[9] a) TURBOMOLE GmbH, *TURBOMOLE V7.0.1*, **2015**; b) M. von Arnim, R. Ahlrichs, *J. Comput. Chem.* **1998**, *19*, 1746; c) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346.
[10] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
[11] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136.
[12] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[13] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[14] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[15] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, *NBO 7.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2018**.
[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16*, Gaussian, Inc., Wallingford CT, **2016**.
[17] a) H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, *MOLPRO, version 2015.1, a package of ab initio programs*, **2015**; b) H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput Mol Sci* **2012**, *2*, 242.
[18] A. K. Wilson, D. E. Woon, K. A. Peterson, T. H. Dunning, *J. Chem. Phys.* **1999**, *110*, 7667.
[19] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441; b) J. Emsley, *Chem. Soc. Rev.* **1980**, *9*, 91.
[20] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
[21] T. B. McMahon, T. Heinis, G. Nicol, J. K. Hovey, P. Kebarle, *J. Am. Chem. Soc.* **1988**, *110*, 7591.

4.3 Friedel-Crafts Type Methylation with Dimethylhalonium Salts



Sebastian Hämmerling, Patrick Voßnacker, Simon Steinhauer, Helmut Beckers and Sebas-tian Riedel*

Chem. Eur. J., **2020**, *26*(63), 14377-14384.

https://doi.org/10.1002/chem.202001457

Author contribution

Sebastian Hämmerling contributed to the project design, performed all experiments, the product characterization, quantum-chemical calculations and wrote the manuscript. Patrick Voßnacker and Simon Steinhauer conducted the crystallographic studies. Simon Steinhauer and Sebastian Riedel supervised the project and provided scientific guidelines. Simon Steinhauer, Helmut Beckers and Sebastian Riedel revised the manuscript.

Chemistry–A European Journal | Full Paper
doi.org/10.1002/chem.202001457

Fluorinated Ligands

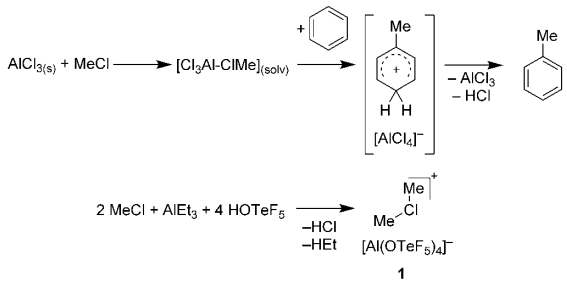
Friedel–Crafts Type Methylation with Dimethylhalonium Salts

Sebastian Hämmerling, Patrick Voßnacker, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel*[a]

Abstract: The dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]$ is used to methylate electron-deficient aromatic systems in Friedel–Crafts type reactions as shown by the synthesis of *N*-methylated cations, such as $[MeNC_5F_5]^+$, $[MeNC_5F_4]^+$, and $[MeN_3C_3F_3]^+$. To gain a better understanding of such fundamental Friedel–Crafts reactions, the role of the dimethylchloronium cation has been evaluated by quantum-chemical calculations.

Introduction

The Friedel–Crafts alkylation is a well-known and widely used but also challenging synthetic tool.[1] The Friedel–Crafts alkylation reaction is based on the polarization of an alkyl halide by a Lewis acid like $AlCl_3$ which further reacts as an electrophilic reagent for example, with an aromatic molecule to form an arenium ion (Wheland intermediate, Scheme 1, top).[2] Rearomatization of the Wheland intermediate occurs through elimination of HCl and recovers the catalyst. Depending on the stabilizing effects of the alkyl group the alkylating species has a distinct carbocationic character. The tendency to form a free CH_3^+ cation[3] is low, therefore Olah and DeMember suggested the formation of the dimethylchloronium cation as an intermediate for Friedel–Crafts reactions[4] and isolated $[Me_2Cl][SbF_6]$[5] as a thermally labile compound. The only other known anion which is able to stabilize the dimethylchloronium cation so far is the carborate anion $[CHB_{11}Cl_{11}]^-$. The salt $[Me_2Cl][CHB_{11}Cl_{11}]$ is considerably more thermally stable.[6] We recently synthesized the easily accessible and room temperature-stable dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]$ (**1**, see Scheme 1 bottom).[7]



Scheme 1. Friedel–Crafts alkylation of benzene with $[Cl_3Al–ClMe]$ (top) and formation of the dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]$ (**1**, bottom).

In this work we report on the role of the dimethylchloronium cation in Friedel–Crafts type methylation reactions, especially in the system MeCl–$AlCl_3$; and the reaction of **1** with electron-deficient aromatic systems.

Results and Discussion

Role of the dimethylchloronium cation in Friedel–Crafts type methylation reactions

The electrophilic intermediate in Friedel–Crafts type methylation reactions is still controversial. While it seems well established that this alkylation proceeds via an Lewis-acid activated alkyl halide such as the $[Cl_3Al–ClMe]$ intermediate shown in Scheme 1, the role of dialkylhalonium intermediates in this process and the relationship between these two intermediates has to our knowledge not been fully elucidated. Previous investigations on the mechanism only considered the direct methylation of the aromatic compound by the Lewis acid-alkyl halide complex.[8]

We have measured ^{27}Al and ^{1}H NMR spectra of a slurry of aluminum trichloride in chloromethane. The solubility of aluminum trichloride at room temperature in pressurized chloromethane is low. However, a broad resonance at $\delta = 108.6$ ppm (FWHM = 357 Hz) can be detected in the ^{27}Al NMR spectrum, which we assign to a $[Cl_3Al–ClMe]$ complex. The signal is broadened by quadrupolar interactions and is in a typical range for donor stabilized tetrahedral coordinated $AlCl_3$.[9] This chemical shift is comparable with that of the $[AlCl_4]^-$ anion at

[a] S. Hämmerling, P. Voßnacker, Dr. S. Steinhauer, H. Beckers, Prof. Dr. S. Riedel
Institut für Chemie und Biochemie, Freie Universität Berlin
Fabeckstr.34/36, 14195 Berlin (Germany)
E-mail: s.riedel@fu-berlin.de

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.202001457.

Chemistry–A European Journal | Full Paper doi.org/10.1002/chem.202001457 | Chemistry Europe European Chemical Societies Publishing

$\delta = 104.2$ ppm, which shows however a significantly lower linewidth of 3 Hz. The ^{1}H NMR spectrum of this solution shows only the signal of MeCl at $\delta = 3.35$ ppm. The addition of 1,2-difluorobenzene to this $[Cl_3Al–ClMe]$/MeCl mixture results in a slow methylation of the aromatic compound within days at room temperature. For comparison, a solution of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) in chloromethane revealed a distinct signal of the cation at $\delta = 4.75$ ppm in the ^{1}H NMR spectrum. The cross signals in an EXSY (exchange spectroscopy) NMR spectrum indicates a slow exchange between $[Me_2Cl]^+$ and the free MeCl at room temperature.

We carried out quantum-chemical calculations at the RI-B3LYP-D3/def2-TZVPP (COSMO, ε_R (relative permittivity) MeCl) level of theory to obtain further information about the relationship between the two intermediates, the activated $[Cl_3Al–ClMe]$ complex and the dimethylchloronium ion $[Me_2Cl]^+$. These calculations support our NMR spectroscopic observation of a $[Cl_3Al–ClMe]$ complex (Figure 1). In the presence of 1,2-difluorobenzene this complex is further stabilized by 14.0 kJ mol^{-1} with respect to the free educts. However, in contrast to common textbook knowledge these calculations disclose that the methylation of 1,2-difluorobenzene does not take place via the electrophilic $[Cl_3Al–ClMe]$ complex but via the contact ion pair $[Me_2Cl][AlCl_4]$. The contact ion pair is 22.6 kJ mol^{-1} less stable and separated from the $[Cl_3Al–ClMe]$ complex by a barrier of 59.5 kJ mol^{-1}. Starting from the contact ion pair the methylation reaction of 1,2-difluorobenzene has a barrier of 45.0 kJ mol^{-1}. The direct methylation of 1,2-difluorobenzene with $[Cl_3Al–ClMe]$ has a higher barrier of 71.0 kJ mol^{-1} (see Figure 1 and S39). The two intermediates are linked by the equilibrium reaction (**1**).

$$[Cl_3Al–ClMe] + MeCl \rightleftharpoons [Me_2Cl][AlCl_4] \quad (1)$$

We point out that the choice of the solvent model or the dispersion correction as well as the selected functional does not change the main conclusion drawn from the computed reaction Scheme (see Figure S40). Therefore, the $[Me_2Cl]^+$ cation, as part of a contact ion pair, is a more reasonable intermediate for the Friedel–Crafts methylation reaction in chloromethane.

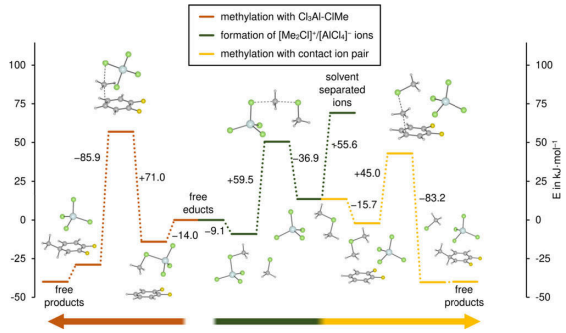
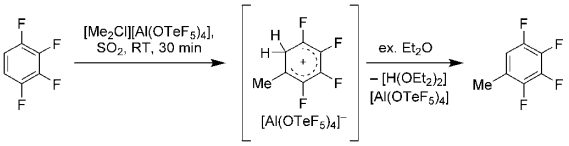


Figure 1. Reaction profiles for the methylation of 1,2-difluorobenzene with the $AlCl_3$–MeCl system. Energies (ZPE corrected) in kJ mol^{-1} on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R MeCl). The final steps (rearomatization and catalyst recovery) are omitted for clarity, and energy differences between linked energy levels are indicated.

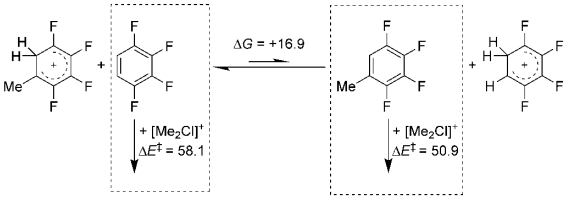
Methylation of electron-deficient aromatic systems

To further investigate the reactivity of the $[Me_2Cl]^+$ cation we treated a series of deactivated aromatic compounds with $[Me_2Cl][Al(OTeF_5)_4]$ (**1**). Upon addition of a twofold excess of 1,2,3,4-tetrafluorobenzene to a solution of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) in SO_2 (Scheme 2) a slow color change from colorless to a pale yellow color is observed within 30 min at room temperature. The yellowish color of the reaction mixture is typical for fluorinated arenium cations.[10] After adding a slight excess of diethyl ether to the reaction mixture the mixture decolorizes immediately, and the formation of protonated and methylated diethyl ether ($[H(OEt_2)_2]^+$ and $[Me(OEt_2)]^+$ (ratio 1:9)) is confirmed by ^{1}H NMR spectroscopy (Scheme 2). Attempts to isolate the Wheland intermediates were so far unsuccessful. In contrast to Friedel–Crafts methylation using the $[Cl_3Al–ClMe]$/MeCl system, where rearomatization of the Wheland intermediate takes places instantaneously during the reaction by liberation of HCl, the rearomatization of the arene intermediate formed in Scheme 2 occurs by the addition of the ether.

The NMR spectroscopic analysis of the purified product mixture in CD_2Cl_2 confirms the formation of 5-methyl-1,2,3,4-tetrafluorobenzene as well as an excess of the starting compound 1,2,3,4-tetrafluorobenzene which is in agreement with the H^+/Me^+ ratio described above. Increasing the reaction time from 30 min to 3 h at room temperature yields a product mixture of $C_6F_4H_2$, C_6F_4HMe, and $C_6F_4Me_2$ in the ratio 18:2.4:1. The formation of a two times methylated product can be explained by a fast equilibrium between methyltetrafluorobenzene and protonated tetrafluorobenzene (see Scheme 3). The more basic methyltetrafluorobenzene (see proton affinities in Table 1)



Scheme 2. Reaction of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) with 1,2,3,4-tetrafluorobenzene.



Scheme 3. Proposed equilibrium between protonated arene intermediates in the reaction mixture of $[Me_2Cl][Al(OTeF_5)_4]$ (1) with 1,2,3,4-tetrafluorobenzene; calculated relative transition-state energies for the methylation reactions (not shown) are given in kJ mol^{-1} on the RI-B3LYP-D3/def2-TZVPP level of with COSMO (ε_R SO_2).

Table 1. Experimental and calculated proton affinities (PAs) and methyl cation affinities (MCAs).[a]

Compound	PA [kJ mol^{-1}]	MCA[b] [kJ mol^{-1}]
MeCl	647.3[11]	260,[12] *279.2*[7]
MeBr	647.3[11]	260,[12] *279.2*[7]
1,2,3,4-tetrafluorobenzene	700.4,[11] *714.9*	*310.0*
MeI	691.7[11]	*323.7*[7]
methyl-1,2,3,4-tetrafluorobenzene	*746,1*	*338.3*
1,2,3-trifluorobenzene	724.3,[11] *738.0*	*361.4*
1,2-difluorobenzene	731.2,[11] *742.9*	*369.0*
4-methyl-1,2,3-trifluorobenzene	*756.0*	*373.8*
4-methyl-1,2-difluorobenzene	*775.3*	*397.6*

[a] Values in *italics* are calculated at the RI-B3LYP-D3/def2-TZVPP level of theory. [b] MCA $= -\Delta H^0$ for the reaction $B + Me^+ \rightarrow BMe^+$ (B = base).

reacts faster with the dimethylchloronium cation than tetrafluorobenzene. This observation is also supported by calculated transition state energies, which is 7.2 kJ mol^{-1} lower in energy for the methylation of methyltetrafluorobenzene by $[Me_2Cl]^+$ than that for tetrafluorobenzene. For longer reaction times unspecific decomposition reactions occurred.

1,2,3-Trifluorobenzene and 1,2-difluorobenzene react within 30 min under quantitative consumption of **1**. After adding diethyl ether to the reaction mixtures, the intense yellow color of the solution vanishes and a quantitative formation of protonated ether is proved ^{1}H NMR spectroscopically. The methylation takes place preferentially in *para* position to a fluorine atom (Table 2). This is in agreement with our quantum-chemical calculations on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2) where the transition state for the methylation of 1,2-difluorobenzene with $[Me_2Cl]^+$ in 4-position is by 3.1 kJ mol^{-1} lower in energy than in 3-position. All multi-methylated isomers up to 4,5,6-trimethyl-1,2,3-trifluorobenzene and 3,4,5,6-tetramethyl-1,2-difluorobenzene are identified by GC/MS and for 1,2,3-trifluorobenzene also by NMR spectroscopy. Detailed analysis of the spin systems of most methylation products were performed and are given in the supporting information.

Table 2. Main products for the methylation with **1** after 30 min of reaction time at room temperature.

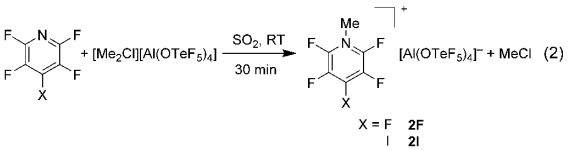
Substrate	Consumption of **1**	Main products (percentage in product mixture)		
	10 %		(> 90 %)	
	100 %		(73 %)	
	100 %		(60 %)	 (20 %)

Reactivity of dimethylbromonium and dimethyliodonium salts

To compare the reactivity of the dimethylchloronium cation with that of the heavier homologues we treated 1,2,3-trifluorobenzene with the corresponding dimethylbromonium and the dimethyliodonium salts. The dimethylbromonium salt $[Me_2Br][Al(OTeF_5)_4]$ reacts slower with 1,2,3-trifluorobenzene than the dimethylchloronium salt **1**. The addition of diethyl ether to the reaction mixture after 1 h reaction time yields protonated and methylated diethyl ether in the ratio 1:2.3. The ratio of the product isomers is similar to that for the reaction of **1** with 1,2,3-trifluorobenzene after 30 min. The dimethyliodonium salt $[Me_2I][Al(OTeF_5)_4]$ does not react with 1,2,3-trifluorobenzene or 1,2-difluorobenzene during 24 h at room temperature or during 2 h at 50 °C. While this observation disagrees with calculated (gas-phase) methyl cation affinity (MCA) values (see Table 1) it is in agreement with our computed transition state energies on the RI-B3LYP-D3/def2-TZVPP level of theory using the COSMO solvent model (ε_R SO_2). These calculations revel increasing transition state energies for the corresponding methylation reaction of 1,2-difluorobenzene from 51.7 kJ mol^{-1} (Me_2Cl^+) to 56.6 kJ mol^{-1} (Me_2Br^+) and 73.6 kJ mol^{-1} (Me_2I^+) (see Figure S41 and S42).

Methylation of weak nitrogen bases

As recently shown, methylation of the weak base PF_3 with the dimethylchloronium salt (**1**) yields highly electrophilic $[MePF_3]^+$, which readily reacts with the weakly coordinating anion $[Al(OTeF_5)_4]^-$.[7] We wanted to expand the scope of methylation reactions using **1** to weakly basic *N*-heteroaromatic compounds. Pentafluoropyridine is known to be a very weak base. The pentafluoropyridinium cation could so far only be isolated as $[HNC_5F_5][EF_6]$ (E = As, Sb)[13] salts. We found that **1** reacts in a fast and quantitative reaction with the fluorinated pyridines NC_5F_4X (X = F, I) under formation of the *N*-methylated products, $[MeNC_5F_4X][Al(OTeF_5)_4]$ (**2F**/**2I**) [Eq. (2)]. The products, isolated as off-white solids, are, unlike **1**, stable in dichloromethane solution (see below). The ^{1}H NMR spectrum of **2F** shows a triplet of doublets at $\delta(^1H) = 4.35$ ppm with couplings to the fluorine atoms in 2-, 6- and 4-position ($^4J(^{19}F,^1H) = 3.3$ Hz, $^6J(^{19}F,^1H) = 1.2$ Hz) and ^{13}C satellites with $^1J(^{13}C,^1H) = 152.7$ Hz. The resonance of **2I** is detected in the ^{1}H NMR spectrum at $\delta(^1H) = 4.25$ ppm and is split into a triplet ($^4J(^{19}F,^1H) = 3.3$ Hz, $^1J(^{13}C,^1H) = 152.1$ Hz). The ^{19}F NMR spectra are of higher order featuring $A_3MM'SXX'$ (**2F**) and $A_3MM'XX'$ (**2I**) spin systems (M, S, X = F; A = H).[14]

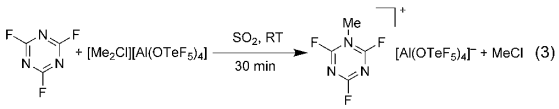


(2)

Chemistry–A European Journal | Full Paper doi.org/10.1002/chem.202001457 | Chemistry Europe European Chemical Societies Publishing

Colorless crystals of **2I** were grown by slowly cooling a dichloromethane solution to −80 °C. It crystallizes in the triclinic space group *P*1(see Figure 2). The shortest contacts between the cation and the anion are a F–C contact (d(F7′–C1) = 307.2(4) pm, ∡(F7′–C1–N1) = 170.2(2)°) and a halogen bond between the iodine and one of the fluorine atoms (F5) of the $OTeF_5$ group (d(F5–I1) = 320.6(2) pm, ∡(C4–I1–F5) = 172.2(1)°). The normalized contact (observed distance divided by sum of van der Waals radii)[15] is with 0.92 quite large, indicating a weak interaction. For comparison, in the solid state structure of tetrafluoro-*para*-iodopyridine a rather strong I–N interaction with a normalized contact of 0.80 is found.[16] No cocrystals were obtained when **2I** was crystallized from dichloromethane solution at −80 °C in the presence of pentafluoropyridine.

An even less basic and therefore more challenging substrate is cyanuric fluoride,[17] which is methylated with **1** by formation of $[MeN_3C_3F_3][Al(OTeF_5)_4]$ (**3**) [Eq. (3)]. This is confirmed by the observed triplet of doublets with ^{13}C satellites in the ^1H NMR spectrum at $\delta(^1H) = 4.34$ ppm ($^4J(^{19}F,^1H) = 1.6$ Hz, $^6J(^{19}F,^1H) = 0.9$ Hz, $^1J(^{13}C,^1H) = 153.0$ Hz). The ^{15}N NMR signals of all heterocycles shift downfield upon methylation (see Table 3).



(3)

From a solution of **3** in dichloromethane crystals of $[MeN_3C_3F(OTeF_5)_2][Al(OTeF_5)_4]$ were grown by slowly cooling a dichloromethane solution to −40 °C. The compound crystallizes in monoclinic space group $P2_1/c$ (see Figure 3). At room temperature a colorless solution of **3** in dichloromethane decomposes within one day to a two-phase system with a dark and oily lower phase. This decomposition shows the highly Lewis-acidic character of the $[MeN_3C_3F_3]^+$ cation.

Also the dimethylchloronium salt **1** decomposes in SO_2 solution within days at room temperature under formation of $MeOTeF_5$.[7] In contrast to this, the addition of dichloromethane at room temperature to solid **1** results in an immediate decomposition to a dark brown suspension. At −40 °C the $[Me_2Cl]^+$ salt **1** has a poor solubility in dichloromethane and decomposes upon slow warming with a quantitative consumption of the weakly coordinating anion $[Al(OTeF_5)_4]^-$ to a yellow solution. Using solvent suppression pulse sequences $CH_2ClOTeF_5$) and $CH_2(OTeF_5)_2$ (ratio 10:1, 1000-fold excess of CH_2Cl_2) can be identified NMR spectroscopically as the only pentafluoro-*ortho*-tellurate-containing species [see Eqs. (4) and (5)].

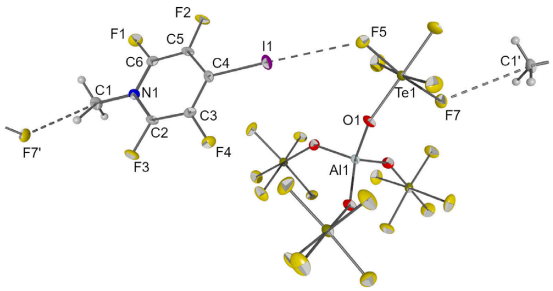


Figure 2. Molecular structure of **2I** in the solid state. Thermal ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: C1-N1 150.1(4), N1-C2 134.4(3), C2-C3 136.6(4), C3-C4 138.5(4), C4-C5 138.6(4), C5-C6 137.0(4), C6-N1 134.9(3), C2-F3 131.4(3), C3-F4 132.8(3), C4-I1 205.9(3), C5-F2 132.9(3), C6-F1 130.7(3), I1-F5 320.6(2), C1-F7′ 307.2(4); C4-I1-F5 172.2(1), C2-N1-C6 118.5(2), C3-C4-C5 116.9(3), F7′-C1-N1 170.2(2).

Table 3. Experimental and calculated PAs and MCAs[a] in kJ mol^{-1} as well as ^{15}N NMR chemical shifts (in ppm) of neutral (δ ^{15}N, educt) and methylated (δ ^{15}N, Me^+) compounds.[a]

Compound	PA	MCA	δ ^{15}N, educt	δ ^{15}N, Me^+
CH_2Cl_2	628 ± 8,[18] *643.1*	*265.4*	–	–
$CH_2Cl(OTeF_5)$	*683.0*	*267.3*	–	–
MeCl	647.3[11]	*279.2*[7]	–	–
$N_3C_3F_3$	*758.5*	*358.5*	−166.3[b]	−220.0 (N1)[b]
NC_5F_5	764.9,[11] *781.6*	*376.7*	−145.5[c]	−213.2[d]
NC_5F_4I	*807.4*	*400.0*	−131.4[c]	−208.0[d]

[a] Values in *italics* are calculated at the RI-B3LYP-D3/def2-TZVPP level of theory. [b] SO_2, ext. [D6]acetone. [c] $CDCl_3$. [d] CD_2Cl_2.

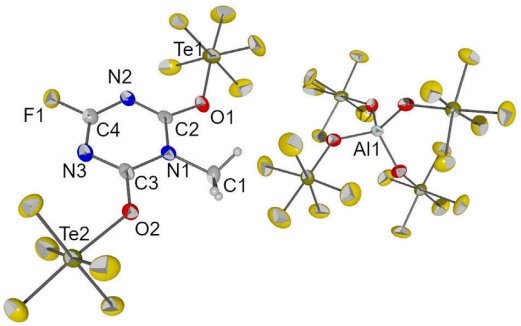
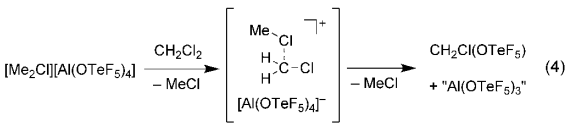
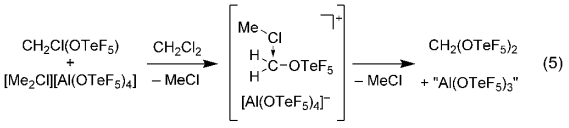


Figure 3. Molecular structure of $[MeN_3C_3F(OTeF_5)_2][Al(OTeF_5)_4]$ in the solid state. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [pm] and angles [°]: C1-N1 148.7(8), N1-C2 135.6(8), C2-N2 131.3(8), N2-C4 131.7(9), C4-N3 131.6(8), N3-C3 130.8(8), C3-N1 137.3(9), C2-O1 131.3(9), C4-F1 129.9(7), C3-O2 129.8(8), O1-Te1 193.8(5), O2-Te2 194.0(5); C2-N1-C3 116.1(6), N1-C2-N2 123.7(6), C2-N2-C4 114.0(6), N2-C4-N3 129.0(6), C4-N3-C3 114.2(6), N3-C3-N1 123.1(6), C2-O1-Te1 127.9(5), C3-O2-Te2 126.9(5), N2-C2-O1-Te1 9.3(9), N3-C3-O2-Te2 4.0(9).



(4)



(5)

These species are likely formed via the intermediates $[MeCl\cdots CH_2Cl]^+$ and $[MeCl\cdots CH_2OTeF_5]^+$, which both can be described as carbenium cations coordinated by a MeCl molecule (see Figure 4). These highly reactive carbenium cations are much less stabilized than the methyl groups in the dimethylchloronium ion. They exhibit considerably longer C–Cl distances than $[Me_2Cl]^+$ and less deviation from a planar geometry at the carbon atom as expressed by their higher angular sums. According to an NBO analysis[19] the $[CH_2OTeF_5]^+$ cation is described as a CH_2O moiety coordinating to a TeF_5^+ group. Thus, the formation of such highly electrophilic carbenium ions ($[MeCl\cdots CH_2OTeF_5]^+$) can probably explain the fast decomposition of the $[Me_2Cl]^+$ salt **1** in dichloromethane.

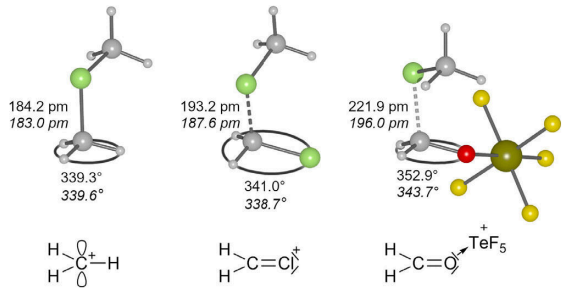


Figure 4. Calculated structures of $[Me_2Cl]^+$, $[MeCl\cdots CH_2Cl]^+$ and $[MeCl\cdots CH_2OTeF_5]^+$ on the RI-B3LYP-D3/def2-TZVPP level of theory; values in *italics* are with COSMO (ε_R CH_2Cl_2); and Lewis structures of underlying $[CH_3]^+$, $[CH_2Cl]^+$ and $[CH_2OTeF_5]^+$ according to the NBO analysis.

Conclusions

We were able to show that dialkylhalonium ions are the key intermediates during the classical Friedel–Crafts methylation reactions. In addition, we reported the methylation of weakly basic oligofluorobenzenes with the dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]$ (**1**),[7] where the electrophilic attack, that is, the methylation step, and the rearomatization are separated in contrast to typical Friedel–Crafts reactions using the $[Cl_3Al–ClMe]$/MeCl system.

The reaction of **1** with weakly basic fluorinated nitrogen-containing heterocycles leads to the formation of *N*-methylated products. It has been shown that the rapid decomposition reaction of **1** in dichloromethane results in the formation of $CH_2Cl(OTeF_5)$ and $CH_2(OTeF_5)_2$. Further investigations on methylation reactions as well as attempts to isolate Wheland intermediates are continuing in our group.

Experimental Section

The experiments were performed under exclusion of air and moisture using standard Schlenk techniques. The solvent SO_2 was dried over CaH_2. The oligofluorobenzenes, CH_2Cl_2 and CD_2Cl_2 were dried over Sicapent while diethyl ether was dried over Solvona. MeCl (purchased from abcr) was used without further purification. Triethylaluminium was purchased from abcr and handled in a glovebox under a dry argon atmosphere. Teflic acid was prepared according to literature[20] as well as cyanuric fluoride[21] and tetrafluoro-*para*-iodopyridine.[16] The salts $[Me_2Cl][Al(OTeF_5)_4]$, $[Me_2Br][Al(OTeF_5)_4]$ and $[Me_2I][Al(OTeF_5)_4]$ where synthesized as already described.[7] The salt $[NEt_4][AlCl_4]$ was synthesized according to the literature with MeCl as a solvent instead of thionyl chloride.[22] IR spectra were recorded on a Bruker ALPHA FTIR spectrometer inside a glovebox equipped with a diamond ATR attachment (resolution 4 cm^{-1}). Raman spectra were recorded on a Bruker MultiRAM II equipped with a low-temperature Ge detector (1064 nm, 30–80 mW, resolution 2 cm^{-1}). NMR spectra were recorded on a JEOL 400 MHz ECS, 400 MHz ECZ or 600 MHz ECZ spectrometer or on a Bruker 700 MHz AVANCE700. For strongly coupled spin systems all chemical shifts and coupling constants were reported as simulated in gNMR.[14] Spin–spin coupling constants calculated with Gauge-Independent Atomic Orbital method (GIAO)[23] on B3LYP/aug-cc-pVTZ-J[24] level of theory and literature data for non-methylated species[25] provided a reasonable first guess, signs of coupling constants were used directly from these sources. All reported chemical shifts were referenced to the Ξ values given in IUPAC recommendations of 2008[26] using the ^2H signal of the deuterated solvent as internal reference. For $^{14}N/^{15}N$ $MeNO_2$ is used as reference. For external locking [D6]acetone was flame sealed in a glass capillary and the lock oscillator frequency was adjusted to give $\delta(^1H) = 7.26$ ppm for a $CHCl_3$ sample. Mass spectra were recorded on an Advion Compact mass spectrometer expression L with a quadrupole mass filter. Samples were dissolved in a dry solvent (CH_3CN or CH_2Cl_2) for ESI (electrospray ionization). GC-MS were measured on a Saturn 2100 GC/MS system from Varian Inc. equipped with a „HP-5 ms Ultra Inert" (length 30 m) column, injection volume 1 µL, split 100. The following temperature program was used: 50 °C for 0.5 min, ramp with 20 °C min^{-1} to 80 °C, hold for 1 min, ramp with 10 °C min^{-1} to 120 °C, ramp with 20 °C min^{-1} to 250 °C, constant helium gas flow of 280 L min^{-1}. Ionization voltage for EI (electron ionization): 80 eV. Crystal data were collected on a Bruker D8 Venture diffractometer with a Photon 100 CMOS area detector with Mo K_α radiation. Using Olex2,[27] the structures were solved with the ShelXT[28] structure solution program by intrinsic phasing and refined with ShelXL[29] refinement package using least square minimization. Crystal structures were visualized with Diamond.[30]

For density functional calculations the program package TURBOMOLE[31] was used with its implementations of RI,[32] MARI-J,[33] B3LYP,[34] Grimme-D3[35] together with the basis set def2-TZVPP.[36] SCF energies were corrected with chemical potential taken from TURBOMOLE implemented in the freeh script to get free enthalpies. For single point calculations the functionals m06[37] and B2-PLYP[38] were used as implemented in TURBOMOLE. For COSMO[39]-optimized structures vibrational spectra were calculated numerically. For MeCl $\varepsilon_R = 10$[40] and for SO_2 $\varepsilon_R = 17.6$[41] were used as 20 °C near values. NBO analysis was performed with NBO 7.0[42] executed from Gaussian 16[43] as well as GIAO calculations.

Caution! Chloromethane and SO_2 give a pressure of 4.9 bar and 3.3 bar, respectively, at room temperature; care must be taken that reaction vessels resist this pressure.

Chloromethane and SO_2 were treated as ideal gases and measured via their pressure in a known volume. When cooled to −70 °C liquefied SO_2 can be easily transferred using inert PFA (perfluoroalkoxy alkane) or PTFE tubes; however, a small amount of the solvent evaporates by cooling the tube so concentrations are changing. This is not possible with MeCl.

Chemistry–A European Journal | Full Paper doi.org/10.1002/chem.202001457 | Chemistry Europe European Chemical Societies Publishing

Methylation of oligofluorobenzenes: general procedure

To a solution of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) in SO_2 a slight excess of the substrate was added at −30 °C. The initially colorless reaction mixture changed color to intense yellow while stirring at room temperature for 30 min. Afterwards, diethyl ether was added at −30 °C, resulting in a decolorization. The $[H(OEt_2)_2]^+$ and $[MeOEt_2]^+$ ratio was determined from this solution by ^{1}H NMR spectroscopy. All volatiles were condensed into a second flask. SO_2 was carefully removed under reduced pressure at −20 °C. The resulting clear colorless liquid was diluted with CD_2Cl_2 and analyzed by NMR spectroscopy.

$[MeOEt_2][Al(OTeF_5)_4]$: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 4.70 (q, 4H, CH_2, $^3J(^1H,^1H)$ = 7.1 Hz), 4.24 (s, 3H, OCH_3), 1.68 (t, 6H, CH_2CH_3, $^3J(^1H,^1H)$ = 7.1 Hz) ppm. ^{1}H NMR (400 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.84 (q, 4H, CH_2, $^3J(^1H,^1H)$ = 7.2 Hz), 5.37 (s, 3H, OCH_3), 2.74 (t, 6H, CH_2CH_3, $^3J(^1H,^1H)$ = 7.2 Hz) ppm ppm^{-1}. ^{1}H,^{13}C-HMQC NMR (400 MHz/101 MHz, CD_2Cl_2, 20 °C): δ = 4.70/88.7 (CH_2/CH_2), 4.24/70.3 (OCH_3/OCH_3), 1.68/11.7 (CH_2CH_3/CH_2CH_3) ppm ppm^{-1}. ^{1}H,^{13}C-HMBC NMR (400 MHz/101 MHz, CD_2Cl_2, 20 °C): δ = 4.70/11.7 (CH_2, CH_2CH_3), 4.24/88.7 (OCH_3/CH_2), 1.68/88.7 (CH_2CH_3/CH_2) ppm.

$[H(OEt_2)_2][Al(OTeF_5)_4]$: ^{1}H NMR (400 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 17.38 (s br, 1H, H), 5.23 (q, 8H, CH_2, $^3J(^1H,^1H)$ = 7.1 Hz), 2.55 (t, 12H, CH_3, $^3J(^1H,^1H)$ = 7.1 Hz).

1,2,3,4-Tetrafluorobenzene

The following amounts were used for a 30 min reaction: **1**: 372 mg, 0.356 mmol, SO_2: 22 mmol, approx. 1.0 mL, 1,2,3,4-tetrafluorobenzene: 0.05 mL, 0.467 mmol.

The following amounts were used for a 3 h reaction: **1**: 401 mg, 0.383 mmol, SO_2: 22 mmol, approx. 1.0 mL, 1,2,3,4-tetrafluorobenzene: 0.05 mL, 0.467 mmol.

5-Methyl-1,2,3,4-tetrafluorobenzene: ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 6.81 (m, 1H, Ar*H*, $^3J(^{19}F,^1H)$ = 10.65 Hz, $^4J(^{19}F,^1H)$ = 8.11 Hz (F2), $^5J(^{19}F,^1H)$ = −2.61 Hz, $^4J(^{19}F,^1H)$ = 6.46 Hz (F4)), 2.23 (m, 3H, CH_3, $^4J(^{19}F,^1H)$ = 2.41 Hz, $^6J(^{19}F,^1H)$ = 1.38 Hz) ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): δ = −142.0 (dddd, 1F, *F*1, $^3J(^{19}F,^{19}F)$ = −21.02 Hz, $^4J(^{19}F,^{19}F)$ = −1.87 Hz, $^5J(^{19}F,^{19}F)$ = 12.49 Hz, $^3J(^{19}F,^1H)$ = 10.65 Hz), −143.9 (dddtd, 1F, *F*4, $^3J(^{19}F,^{19}F)$ = −20.15 Hz, $^4J(^{19}F,^{19}F)$ = −1.67 Hz, $^5J(^{19}F,^{19}F)$ = 12.49 Hz, $^4J(^{19}F,^1H)$ = 6.46 Hz (H5), $^4J(^{19}F,^1H)$ = 2.41 Hz (CH_3)), −158.3 (dddd, 1F, *F*3, $^3J(^{19}F,^{19}F)$ = −20.15 Hz (F4), $^3J(^{19}F,^{19}F)$ = −19.5 Hz (F2), $^4J(^{19}F,^{19}F)$ = −1.87 Hz, $^5J(^{19}F,^1H)$ = −2.61 Hz), −161.3 (ddddt, 1F, *F*2, $^3J(^{19}F,^{19}F)$ = −21.02 Hz (F1), $^3J(^{19}F,^{19}F)$ = −19.45 Hz (F3), $^4J(^{19}F,^{19}F)$ = −1.67 Hz, $^4J(^{19}F,^1H)$ = 8.11 Hz, $^6J(^{19}F,^1H)$ = 1.38 Hz) ppm. GC-MS: t_R = 2.72 min, *m/z* = 163.1 (calc: 163.0 $[M-H]^{\bullet+}$).

Dimethyl-1,2,3,4-tetrafluorobenzene: $AA'_3MM'XX'$ spin system. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 2.15 (m, 6H, CH_3, $H_A/H_{A'}$) ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): $\delta_{MM'}$ = −144.6 ppm (F1/F4), $\delta_{BB'}$ = −162.7 ppm (F2/F3), $J_{MX} = J_{M'X'} = {}^3J(^{19}F,^{19}F)$ = −21.79 Hz, $J_{MX'} = J_{M'X} = {}^4J(^{19}F,^{19}F)$ = 1.61 Hz, $J_{MM'} = {}^5J(^{19}F,^{19}F)$ = 12.68 Hz, $J_{XX'} = {}^3J(^{19}F,^{19}F)$ = −19.30 Hz, $J_{XA} = J_{X'A'} = {}^6J(^{19}F,^1H)$ = 1.43 Hz, $J_{MA'} = J_{M'A} = {}^4J(^{19}F,^1H)$ = 2.48 Hz. GC-MS: t_R = 4.25 min, *m/z* = 178.1 (calc: 178.0 $[M]^{\bullet+}$).

1,2,3-Trifluorobenzene

The following amounts were used for a 30 min reaction: **1**: 495 mg, 0.473 mmol, SO_2: 27 mmol, approx. 1.3 mL, 1,2,3-trifluorobenzene: 0.05 mL, 0.485 mmol.

Main product—4-methyl-1,2,3-trifluorobenzene: ABM_3SVZ spin system. ^{1}H NMR (600 MHz, CD_2Cl_2, 20 °C): δ = 6.89 (m, 1H, *H*5, H_B), 6.86 (m, 1H, *H*6, H_A), 2.21 (m, 3H, CH_3, H_M) ppm. ^{19}F NMR (565 MHz, CD_2Cl_2, 20 °C): δ = −139.0 (m, 1F, *F*3, F_S), −139.8 (m, 1F, *F*1, F_V), −163.0 (m, 1F, *F*2, F_Z) ppm. Coupling constants: $J_{VZ} = {}^3J(^{19}F,^{19}F)$ = −20.19 Hz, $J_{SZ} = {}^3J(^{19}F,^{19}F)$ = −19.85 Hz, $J_{SV=} {}^4J(^{19}F,^{19}F)$ = 5.62 Hz, $J_{AV=} {}^4J(^{19}F,^1H)$ = 5.63 Hz, $J_{AZ} = {}^5J(^{19}F,^1H)$ = −2.53 Hz, $J_{AS} = {}^4J(^{19}F,^1H)$ = 7.92 Hz, $J_{BV=} {}^3J(^{19}F,^1H)$ = 9.89 Hz, $J_{BZ} = {}^4J(^{19}F,^1H)$ = 7.24 Hz, $J_{BS} = {}^5J(^{19}F,^1H)$ = −2.40 Hz, $J_{AB} = {}^3J(^1H,^1H)$ = 8.62 Hz, $J_{AM} = {}^4J(^1H,^1H)$ = −1.00 Hz, $J_{BM} = {}^5J(^1H,^1H)$ = 0.40 Hz, $J_{SM} = {}^4J(^{19}F,^1H)$ = 2.32 Hz, $J_{VM} = {}^6J(^{19}F,^1H)$ 1.33 Hz. GC-MS: t_R = 2.78 min, *m/z* = 145.1 (calc: 145.0 $[M-H]^{\bullet+}$).

1,2-Difluorobenzene

The following amounts were used for a 30 min reaction: **1**: 1.75 g, 1.67 mmol, SO_2: 110 mmol, approx. 5 mL, 1,2-difluorobenzene: 0.17 mL, 1.71 mmol.

4-Methyl-1,2-difluorobenzene: $ABCM_3SX$ spin system. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 7.01 (m, 1H, *H*6, H_A), 6.95 (m, 1H, *H*3, H_B), 6.85 (m, 1H, *H*5, H_C), 2.27 (m, 3H, CH_3, H_M) ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): δ = −140.1 (m, 1F, *F*2, F_S), −144.4 (m, 1F, *F*1, F_X) ppm; coupling constants: $J_{SX} = {}^3J(^{19}F,^{19}F)$ = −21.17, $J_{AS} = {}^3J(^{19}F,^1H)$ = 10.60 Hz, $J_{AX} = {}^4J(^{19}F,^1H)$ = 8.36 Hz, $J_{BS} = {}^4J(^{19}F,^1H)$ = 7.73 Hz, $J_{BX} = {}^3J(^{19}F,^1H)$ = 11.58 Hz, $J_{CS} = {}^4J(^{19}F,^1H)$ = 4.18 Hz, $J_{CX} = {}^5J(^{19}F,^1H)$ = −1.44 Hz, $J_{MS} = {}^6J(^{19}F,^1H)$ = 1.33 Hz, $J_{AC} = {}^3J(^1H,^1H)$ = 8.92 Hz, $J_{AB} = {}^5J(^1H,^1H)$ = 0.30 Hz, $J_{BC} = {}^4J(^1H,^1H)$ = 2.10 Hz, $J_{BM} = {}^4J(^1H,^1H)$ = 0.75 Hz, $J_{CM} = {}^3J(^1H,^1H)$ = −0.75 Hz. GC-MS: t_R = 2.82 min, *m/z* = 127.1 (calc: 127.0 $[M-H]^{\bullet+}$).

4,5-Dimethyl-1,2-difluorobenzene: $AA'M_3M_3'XX'$ spin system. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 6.90 (m, 2H, Ar*H*, $H_A/H_{A'}$), 2.16 (m, 6H, CH_3, $H_M/H_{M'}$) ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): δ = −144.7 (m, 2F, Ar*F*, $F_X/F_{X'}$) ppm; coupling constants: $J_{XX'} = {}^3J(^{19}F,^{19}F)$ = −20.00 Hz, $J_{AX} = J_{A'X'} = {}^3J(^{19}F,^1H)$ = 9.90 Hz, $J_{AX'} = J_{A'X} = {}^4J(^{19}F,^1H)$ = 9.90 Hz, $J_{MX'} = J_{M'X} = {}^6J(^{19}F,^1H)$ = 1.00 Hz, $J_{AA'} = {}^5J(^1H,^1H)$ = 1.20 Hz. GC-MS: t_R = 4.28 min, *m/z* = 142.1 (calc: 142.1 $[M]^{\bullet+}$).

1,2,3-Trifluorobenzene with $[Me_2Br]^+$

The following amounts were used for a 60 min reaction: $[Me_2Br][Al(OTeF_5)_4]$: 332 mg, 0.304 mmol, SO_2: 22 mmol, approx. 1.0 mL, 1,2,3-trifluorobenzene: 0.05 mL, 0.485 mmol. Product ratio according to NMR identical to the activation with **1**. However, $[MeOEt_2]^+$/$[H(OEt_2)_2]^+$ ratio in residual solid was 2.3/1.

Methylation attempts with $[Me_2I]^+$

The following amounts were used for a 24 h reaction: $[Me_2I][Al(OTeF_5)_4]$: 407 mg, 0.357 mmol, SO_2: 27 mmol, approx. 1.3 mL, 1,2,3-trifluorobenzene: 0.05 mL, 0.485 mmol. No color change was observed. No methylation was observed by NMR spectroscopy. To a sample in a Young NMR tube an excess of 1,2-difluorobenzene is added. No color change was observed. No methylation was observed by NMR spectroscopy.

The following amounts were used for 2 h reaction at 50 °C. ***Caution!*** *SO_2 has a vapor pressure of approximately 8 bar at 50 °C!* $[Me_2I][Al(OTeF_5)_4]$: 201 mg, 0.177 mmol, SO_2: 22 mmol, approx. 1.0 mL, 1,2,3-trifluorobenzene: 0.05 mL, 0.485 mmol. No color change was observed. No methylation was observed by NMR spectroscopy. After addition of diethyl ether only $[MeOEt_2]^+$ was detected.

$[MeNC_5F_4I][Al(OTeF_5)_4]$ (2I)

Tetrafluoro-*para*-iodopyridine (103 mg, 0.372 mmol, 1.05 equiv) was sublimed in vacuum onto a frozen solution of **1** (370 mg, 0.354 mmol) in SO_2 (33 mmol, approx. 1.5 mL). The reaction mix-

ture as allowed to melt and stirred at room temperature for 30 min. Removal of all volatiles under reduced pressure at room temperature yielded $[MeNC_5F_4I][Al(OTeF_5)_4]$ (**2I**, 451 mg, 0.354 mmol) as an off-white powder. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 4.25 (t, 98.9 %, $N^{12}CH_3$, $^4J(^{19}F,^1H)$ = 3.27 Hz; dt, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 152.1 Hz, $^4J(^{19}F,^1H)$ = 3.27 Hz) ppm. ^{1}H NMR (400 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.59 (t, 98.9 %, $N^{12}CH_3$, $^4J(^{19}F,^1H)$ = 3.3 Hz; dt, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 152.1 Hz, $^4J(^{19}F,^1H)$ = 3.3 Hz) ppm. $^{13}C\{^{19}F,^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C): δ = 146.7 (*C*3/*C*5), 142.6 (*C*2/*C*6), 107.2 (*C*4), 37.1 (CH_3) ppm. $^1H,^{15}N$ HMBC NMR (400 MHz/41 MHz, CD_2Cl_2, 20 °C): δ = 4.25 ppm/−208 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): cation: $A_3MM'XX'$ spin system. $\delta_{MM'}$ = −99.7 (F2/F6) ppm, $\delta_{XX'}$ = −112.2 (F3/F5) ppm, $J_{MM'} = {}^4J(^{19}F,^{19}F)$ = −18.26 Hz, $J_{MX} = J_{M'X'} = {}^3J(^{19}F,^{19}F)$ = 16.64 Hz, $J_{M'X} = J_{MX'} = {}^5J(^{19}F,^{19}F)$ = −12.73, $J_{XX'} = {}^4J(^{19}F,^{19}F)$ = −2.16 Hz, $J_{MA} = J_{M'A} = {}^4J(^{19}F,^1H)$ = 3.27 Hz; anion: δ = −38.5 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 187.8 Hz, $^1J(^{125}Te,^{19}F)$ = 3366.0 Hz), −46.1 (m, A**B$_4$**X, 4F, $^2J(^{19}F,^{19}F)$ = 187.8 Hz, $^1J(^{125}Te,^{19}F)$ = 3478.0 Hz) ppm. $^{27}Al\{^{19}F\}$ NMR (104 MHz, CD_2Cl_2, 20 °C): δ = 46.8 (s, 73.2 %, $[Al(OTeF_5)_4]^-$; d, 22.2 %, $[Al(OTeF_5)_3(O^{125}TeF_5)]^-$, $^2J(^{125}Te,^{27}Al)$ = 73.2 Hz; d, 2.8 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.2 Hz; t, 2.6 %, $[Al(OTeF_5)_2(O^{125}TeF_5)_2]^-$, $^2J(^{125}Te,^{27}Al)$ = 73.2 Hz; t, 0.04 %, $[Al(OTeF_5)_2(O^{123}TeF_5)_2]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.3 Hz) ppm. IR (ATR, 25 °C): $\tilde{\nu}$ = 1657 (m), 1587 (vw), 1527 (m), 1489 (vw), 1438 (w), 1315 (w), 1285 (w), 1135 (vw), 987 (sh), 945 (sh), 928 (s, ν(Al-O)), 818 (m, ν(C-I)), 687 (vs, ν(Te-F)), 641 (w), 580 (w), 543 (m) cm^{-1}. FT-Raman (25 °C): $\tilde{\nu}$ = 2992 (m), 2964 (w), 1660 (s), 1439 (m), 1387 (m), 1286 (m), 989 (m), 821 (w), 719 (w), 697 (vs), 647 (s), 584 (m), 515 (m), 457 (m), 421 (m), 375 (w), 354 (w), 335 (m), 302 (m), 205 (w), 134 (w) cm^{-1}.

$[MeNC_5F_5][Al(OTeF_5)_4]$ (2F)

Pentafluoropyridine (0.06 mL, 0.547 mmol) was added to a solution of **1** (476 mg, 0.455 mmol) in SO_2 (44 mmol, approx. 2.0 mL) at −30 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. All volatiles were removed under reduced pressure at room temperature to yield $[MeNC_5F_5][Al(OTeF_5)_4]$ (**2F**, 530 mg, 0.455 mmol) as an off-white powder. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 4.35 (td, 98.9 %, $N^{12}CH_3$, $^4J(^{19}F,^1H)$ = 3.32 Hz, $^6J(^{19}F,^1H)$ = 1.24 Hz; dtd, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 152.7 Hz, $^4J(^{19}F,^1H)$ = 3.32 Hz, $^6J(^{19}F,^1H)$ = 1.24 Hz) ppm. ^{1}H NMR (400 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.68 (td, 98.9 %, $N^{12}CH_3$, $^4J(^{19}F,^1H)$ = 3.3 Hz, $^6J(^{19}F,^1H)$ = 1.2 Hz; dtd, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 152.7 Hz, $^4J(^{19}F,^1H)$ = 3.3 Hz, $^6J(^{19}F,^1H)$ = 1.2 Hz) ppm. $^{13}C\{^{19}F,^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C): δ = 155.9 (*C*4), 146.3 (*C*2/*C*6), 136.5 (*C*3/*C*5), 37.0 (CH_3) ppm. $^1H,^{15}N$ HMBC NMR (400 MHz/41 MHz, CD_2Cl_2, 20 °C): δ = 4.35 ppm/−213.2 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): cation: $A_3MM'SXX'$ spin system, $\delta_{MM'}$ = −93.3 (F2/F6) ppm, δ_S = −103.5 (F4) ppm, $\delta_{XX'}$ = −150.8 (F3/F5) ppm, $J_{MM'} = {}^4J(^{19}F,^{19}F)$ = −20.00 Hz, $J_{MS} = J_{M'S} = {}^4J(^{19}F,^{19}F)$ = 25.59 Hz, $J_{MX} = J_{M'X'} = {}^3J(^{19}F,^{19}F)$ = −11.72 Hz, $J_{M'X} = J_{MX'} = {}^5J(^{19}F,^{19}F)$ = 12.69 Hz, $J_{SX} = J_{SX'} = {}^3J(^{19}F,^{19}F)$ −22.95 Hz, $J_{XX'} = {}^4J(^{19}F,^{19}F)$ = 4.42 Hz, $J_{MA} = J_{M'A} = {}^4J(^{19}F,^1H)$ = 3.32 Hz, $J_{SA} = {}^6J(^{19}F,^1H)$ = 1.24 Hz; anion: δ = −38.6 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 187.4 Hz, $^1J(^{125}Te,^{19}F)$ = 3332.0 Hz), −46.3 (m, A**B$_4$**X, 4F, $^2J(^{19}F,^{19}F)$ = 187.4 Hz, $^1J(^{125}Te,^{19}F)$ = 3470.0 Hz) ppm. $^{27}Al\{^{19}F\}$ NMR (104 MHz, CD_2Cl_2, 20 °C): δ = 46.8 (s, 73.4 %, $[Al(OTeF_5)_4]^-$; d, 22.2 %, $[Al(OTeF_5)_3(O^{125}TeF_5)]^-$, $^2J(^{125}Te,^{27}Al)$ = 73.4 Hz; d, 2.8 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.9 Hz; t, 2.6 %, $[Al(OTeF_5)_2(O^{125}TeF_5)_2]^-$, $^2J(^{125}Te,^{27}Al)$ = 73.4 Hz; t, 0.04 %, $[Al(OTeF_5)_2(O^{123}TeF_5)_2]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.3 Hz) ppm. IR (ATR, 25 °C): $\tilde{\nu}$ = 1683 (m), 1605 (w), 1548 (s), 1401 (w), 1352 (w), 1289 (w), 1152 (m), 981 (m), 930 (s, ν(Al-O)), 688 (vs, ν(Te-F)), 641 (m), 614 (w), 550 (s), 450 (w) cm^{-1}. ESI-MS (acetonitrile, positive mode): *m/z* = 184.0 ($[MeNC_5F_5]^+$, calc: 184.1).

$[MeN_3C_3F_3][Al(OTeF_5)_4]$

To a solution of **1** (392 mg, 0.375 mmol) in SO_2 (44 mmol, approx. 2.0 mL) cyanuric fluoride (0.07 mL, 0.816 mmol, 2.2 equiv) was added at −30 °C. The reaction mixture was allowed to reach room temperature and stirred for 30 min. All volatiles were removed under reduced pressure at room temperature. The resulting yellowish oil was dissolved in 0.5 mL CH_2Cl_2. 5.0 mL *n*-pentane were added quickly at room temperature to precipitate the salt. The solution was separated by filtration to leave $[MeN_3C_3F_3][Al(OTeF_5)_4]$ after drying in vacuum as a white powder (396 mg, 0.350 mmol). Cooling a solution of $[MeN_3C_3F_3][Al(OTeF_5)_4]$ in dichloromethane to −40 °C yielded crystals of $[MeN_3C_3F(OTeF_5)_2][Al(OTeF_5)_4]$ suitable for X-ray diffraction. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ = 4.34 (td, 98.9 %, $N^{12}CH_3$, $^4J(^{19}F,^1H)$ = 1.6 Hz, $^6J(^{19}F,^1H)$ = 0.9 Hz; dtd, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 153.0 Hz, $^4J(^{19}F,^1H)$ = 1.6 Hz, $^6J(^{19}F,^1H)$ = 0.9 Hz) ppm. ^{1}H NMR (400 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 5.62 (s br, 98.9 %, $N^{12}CH_3$; d br, 1.1 %, $N^{13}CH_3$, $^1J(^{13}C,^1H)$ = 153.0 Hz) ppm. $^{13}C\{^{19}F,^1H\}$ NMR (101 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = 177.7 (*C*4), 166.1 (*C*2/*C*6), 37.7 (CH_3) ppm. ^{14}N NMR (29 MHz, SO_2, ext. [D6]acetone, 20 °C): δ = −167.4 (3 N/5 N), −220.0 (1 N). $^1H,^{15}N$ HMBC NMR (400 MHz/41 MHz, CD_2Cl_2, 20 °C): δ = 4.34 ppm/−220.3 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, 20 °C): cation: δ = 0.9 (t br, *F*4, $^4J(^{19}F,^{19}F)$ = 16.0 Hz), −26.9 (d br, *F*2/*F*6, $^4J(^{19}F,^{19}F)$ = 16.0 Hz); anion: δ = −38.3 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 187.4 Hz, $^1J(^{125}Te,^{19}F)$ = 3350.0 Hz), −46.0 (m, A**B$_4$**X, 4F, $^2J(^{19}F,^{19}F)$ = 187.4 Hz, $^1J(^{125}Te,^{19}F)$ = 3462.0 Hz) ppm. $^{27}Al\{^{19}F\}$ NMR (104 MHz, CD_2Cl_2, 20 °C): δ = 46.8 (s, 72.9 %, $[Al(OTeF_5)_4]^-$; d, 22.2 %, $[Al(OTeF_5)_3(O^{125}TeF_5)]^-$, $^2J(^{125}Te,^{27}Al)$ = 72.9 Hz; d, 2.8 %, $[Al(OTeF_5)_3(O^{123}TeF_5)]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.4 Hz; t, 2.6 %, $[Al(OTeF_5)_2(O^{125}TeF_5)_2]^-$, $^2J(^{125}Te,^{27}Al)$ = 72.9 Hz; t, 0.04 %, $[Al(OTeF_5)_2(O^{123}TeF_5)_2]^-$, $^2J(^{123}Te,^{27}Al)$ = 61.3 Hz) ppm. IR (ATR, 25 °C): $\tilde{\nu}$ = 1687 (m), 1652 (w), 1626 (w), 1557 (m), 1537 (m), 1522 (w), 1510 (w), 1466 (m), 1440 (w), 1424 (w), 1392 (w), 1196 (m), 1128 (w), 1084 (w), 1060 (w), 933 (s, ν(Al-O)), 817 (w), 802 (m), 689 (vs, ν(Te-F)), 629 (m), 548 (s), 496 (w) cm^{-1}.

Reaction with of 1 CH_2Cl_2

A sample of 6 mL precooled dichloromethane was added to **1** (425 mg, 0.406 mmol) at −40 °C. The initially colorless suspension was allowed to slowly warm up forming a brown solution at room temperature. The ^{19}F NMR spectrum showed the complete decomposition of the anion. All volatiles were condensed into a second flask, yielding $CH_2Cl(OTeF_5)$ and $CH_2(OTeF_5)_2$ in a 10:1 ratio.

$CH_2Cl(OTeF_5)$: ^{1}H NMR (400 MHz, CH_2Cl_2, ext. [D6]acetone, 20 °C): δ = 5.99 (quintet-d, 92.8 %, $^4J(^{19}F,^1H)$ = 2.7 Hz, $^4J(^{19}F,^1H)$ = 0.6 Hz; d-quintet-d, 7.1 %, $^3J(^{125}Te,^1H)$ = 214.7 Hz, $^4J(^{19}F,^1H)$ = 2.7 Hz, $^4J(^{19}F,^1H)$ = 0.6 Hz; d-quintet-d, 1 %, $^3J(^{125}Te,^1H)$ = 180.2 Hz, $^4J(^{19}F,^1H)$ = 2.7 Hz, $^4J(^{19}F,^1H)$ = 0.6 Hz) ppm. $^1H,^{13}C$ HMQC NMR (400 MHz, CH_2Cl_2, ext. [D6]acetone, 20 °C): δ = 5.99 ppm/77.2 ppm. ^{19}F NMR (377 MHz, CH_2Cl_2, ext. [D6]acetone, 20 °C): δ = −43.7 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 181.2 Hz, $^4J(^{19}F,^1H)$ = 0.6 Hz, $^1J(^{125}Te,^{19}F)$ = 3502 Hz), −49.4 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 181.2 Hz, $^4J(^{19}F,^1H)$ = 2.7 Hz, $^1J(^{125}Te,^{19}F)$ = 3765 Hz, $^1J(^{123}Te,^{19}F)$ = 3123 Hz) ppm.

$CH_2(OTeF_5)_2$: ^{1}H NMR (400 MHz, CH_2Cl_2, ext. [D6]acetone, 20 °C): δ = 6.12 (nonet-t, 83 %, $^4J(^{19}F,^1H)$ = 2.5 Hz, $^4J(^{19}F,^1H)$ = 0.4 Hz; d-nonet-t, 14 %, $^3J(^{125}Te,^1H)$ = 207.0 Hz, $^4J(^{19}F,^1H)$ = 2.5 Hz, $^4J(^{19}F,^1H)$ = 0.4 Hz; d-nonet-t, 2 %, $^3J(^{125}Te,^1H)$ = 172.0 Hz, $^4J(^{19}F,^1H)$ = 2.5 Hz, $^4J(^{19}F,^1H)$ = 0.4 Hz) ppm. ^{19}F NMR (377 MHz, CH_2Cl_2, ext. [D6]acetone, 20 °C): δ = −44.6 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 181.2 Hz, $^4J(^{19}F,^1H)$ = 0.4 Hz, $^1J(^{125}Te,^{19}F)$ = 3540 Hz), −49.2 (m, A**B$_4$**X, 1F, $^2J(^{19}F,^{19}F)$ = 181.2 Hz, $^4J(^{19}F,^1H)$ = 2.5 Hz, $^1J(^{125}Te,^{19}F)$ = 3749 Hz, $^1J(^{123}Te,^{19}F)$ = 3110 Hz) ppm.

Chemistry–A European Journal | Full Paper doi.org/10.1002/chem.202001457 | Chemistry Europe European Chemical Societies Publishing

Acknowledgements

We gratefully acknowledge the DFG research training network 1582 "Fluorine as a key element" for financial support, Solvay Fluor GmbH for donating chemicals, and the Zentraleinrichtung für Datenverarbeitung (ZEDAT) of the Freie Universität Berlin for computational resources and support. Gefördert durch die Deutsche Forschungsgemeinschaft (DFG)—Projektnummer 387284271—SFB 1349. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 387284271—SFB 1349. We thank Dr. Carsten Müller for helpful discussions. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: electrophilic substitution · halonium ions · methylation · reaction mechanism · weakly coordinating anion

[1] a) M. M. Heravi, V. Zadsirjan, B. Masoumi, M. Heydari, *J. Organomet. Chem.* **2019**, *879*, 78; b) K. M. Kim, J. H. Kim, D. H. Moon, M. S. Lah, I. N. Jung, B. R. Yoo, *Organometallics* **2005**, *24*, 226; c) M. Rueping, B. J. Nachtsheim, *Beilstein J. Org. Chem.* **2010**, *6*, 6.
[2] a) C. Friedel, J. M. Crafts, *Compt. Rend.* **1877**, *84*, 1392; b) C. Friedel, J. M. Crafts, *J. Chem. Soc.* **1877**, *32*, 725.
[3] L. I. Smith, *Org. Synth.* **1930**, *10*, 32.
[4] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1969**, *91*, 2113.
[5] a) G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1970**, *92*, 718; b) R. Minkwitz, V. Gerhard, *Z. Naturforsch. B* **1991**, *46*, 561.
[6] E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2010**, *132*, 4062.
[7] S. Hämmerling, G. Thiele, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Angew. Chem. Int. Ed.* **2019**, *58*, 9807; *Angew. Chem.* **2019**, *131*, 9912.
[8] a) A. M. Vos, R. A. Schoonheydt, F. de Proft, P. Geerlings, *J. Catal.* **2003**, *220*, 333; b) P. Geerlings, A. M. Vos, R. A. Schoonheydt, *J. Mol. Struct.: THEOCHEM* **2006**, *762*, 69.
[9] F. Bigi, G. Casnati, G. Sartori, G. Predieri, *J. Chem. Soc. Perkin Trans. 2* **1991**, *86*, 1319.
[10] A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; *Angew. Chem.* **2017**, *129*, 8375.
[11] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
[12] T. B. McMahon, T. Heinis, G. Nicol, J. K. Hovey, P. Kebarle, *J. Am. Chem. Soc.* **1988**, *110*, 7591.
[13] a) S. L. Bell, R. D. Chambers, W. K. R. Musgrave, J. G. Thorpe, *J. Fluor. Chem.* **1971**, *1*, 51; b) K. Züchner, T. J. Richardson, O. Glemser, N. Bartlett, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 944; *Angew. Chem.* **1980**, *92*, 956.
[14] Adept Scientific, *gNMR V 5.0*, **2005**.
[15] P. M. J. Szell, A. Siiskonen, L. Catalano, G. Cavallo, G. Terraneo, A. Priimagi, D. L. Bryce, P. Metrangolo, *New J. Chem.* **2018**, *42*, 10467.
[16] J. Schwabedissen, P. C. Trapp, H.-G. Stammler, B. Neumann, J.-H. Lamm, Y. V. Vishnevskiy, L. A. Körte, N. W. Mitzel, *Chem. Eur. J.* **2019**, *25*, 7339.
[17] F. Bernardi, F. Cacace, G. Occhiucci, A. Ricci, I. Rossi, *J. Phys. Chem. A* **2000**, *104*, 5545.
[18] F. Cacace, G. de Petris, F. Pepi, M. Rosi, A. Troiani, *Chem. Eur. J.* **1999**, *5*, 2750.
[19] A. E. Reed, R. . Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
[20] K. Seppelt, D. Nothe, *Inorg. Chem.* **1973**, *12*, 2727.
[21] S. Groß, S. Laabs, A. Scherrmann, A. Sudau, N. Zhang, U. Nubbemeyer, *J. Prakt. Chem.* **2000**, *342*, 711.
[22] J. E. D. Davies, D. A. Long, *J. Chem. Soc. A* **1971**, 1273.
[23] a) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497; b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789; c) F. London, *J. Phys. Radium* **1937**, *8*, 397; d) R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028; e) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.
[24] a) V. Barone, P. F. Provasi, J. E. Peralta, J. P. Snyder, S. P. A. Sauer, R. H. Contreras, *J. Phys. Chem. A* **2003**, *107*, 4748; b) P. F. Provasi, G. A. Aucar, S. P. A. Sauer, *J. Phys. Chem. B* **2001**, *105*, 1324; c) T. Enevoldsen, J. Oddershede, S. P. A. Sauer, *Theor. Chem. Acc.* **1998**, *100*, 275.
[25] V. Wray, L. Ernst, E. Lustig, *J. Magn. Reson.* **1977**, *27*, 1.
[26] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Magn. Reson. Chem.* **2008**, *46*, 582.
[27] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[28] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3.
[29] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3.
[30] K. Brandenburg, *DIAMOND*, Crystal Impact GbR, Bonn, **2014**.
[31] TURBOMOLE GmbH, TURBOMOLE V7.3. a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **2018**.
[32] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
[33] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136.
[34] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[35] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[36] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[37] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
[38] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
[39] A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799.
[40] A. Guha, R. Pal, *J. Indian Chem. Soc.* **2006**, *83*, 49.
[41] L. Pogliani, *J. Comput. Chem.* **2010**, *31*, 295.
[42] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, *NBO 7.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2018**.
[43] Gaussian 16, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

Manuscript received: March 25, 2020
Accepted manuscript online: April 11, 2020
Version of record online: ■■ ▮▮, 0000

Chemistry–A European Journal

Supporting Information

Friedel–Crafts Type Methylation with Dimethylhalonium Salts

Sebastian Hämmerling, Patrick Voßnacker, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel*[a]

Table of Contents

1 Crystallographic Data

Compound	$[MeNC_5F_4I][Al(OTeF_5)_4]$	$[MeN_3C_3F(OTeF_5)_2][Al(OTeF_5)_4)]$
CCDC	1971172	1971173
Formula	$C_6H_3AlF_{24}INO_4Te_4$	$C_4H_3AlF_{31}N_3O_6Te_6$
$D_{calc.}$/ g cm^{-3}	3.264	3.178
μ/mm^{-1}	5.875	5.494
Formula Weight	1273.37	1570.67
Color	colorless	colorless
Shape	block	block
Size/mm^3	0.179·0.125·0.121	0.52·0.323·0.163
T/K	104	100
Crystal System	triclinic	monoclinic
Space Group	$P\bar{1}$	$P2_1/c$
a/Å	9.0178(5)	13.3684(4)
b/Å	10.2547(6)	16.7755(5)
c/Å	14.8980(8)	15.7156(5)
α/°	72.621(2)	90
β/°	89.768(2)	111.357(1)
γ/°	80.618(2)	90
V/Å^3	1295.75(13)	3282.38(17)
Z	2	4
Radiation	Mo-K_α (0.71073 Å)	Mo-K_α (0.71073 Å)
Θ_{min}/°	2.645	2.666
Θ_{max}/°	31.000	25.355
Measured Refl.	72062	37114
Independent Refl.	8192	6023
Refl. (I > 2σ(I))	7144	5577
R_{int}	0.0344	0.0297
Parameters	371	461
Restraints	0	0
Largest Peak	0.646	2.985
Deepest Hole	−1.029	−2.039
GooF	1.137	1.082
wR_2 (all data)	0.0381	0.0865
wR_2	0.0365	0.0842
R_1 (all data)	0.0307	0.0385
R_1	0.0209	0.0353

2 GC/MS and simulated spectra

2.1 $AlCl_3$ in MeCl

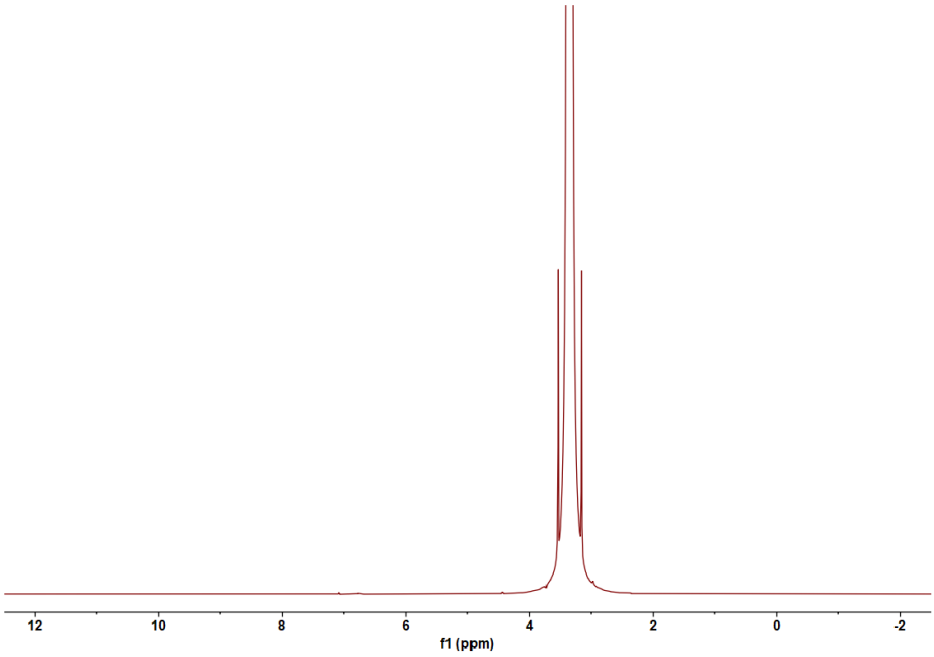


Figure S1: ^{1}H NMR spectrum (400 MHz, MeCl, no lock, r.t.) of $AlCl_3$ in MeCl.

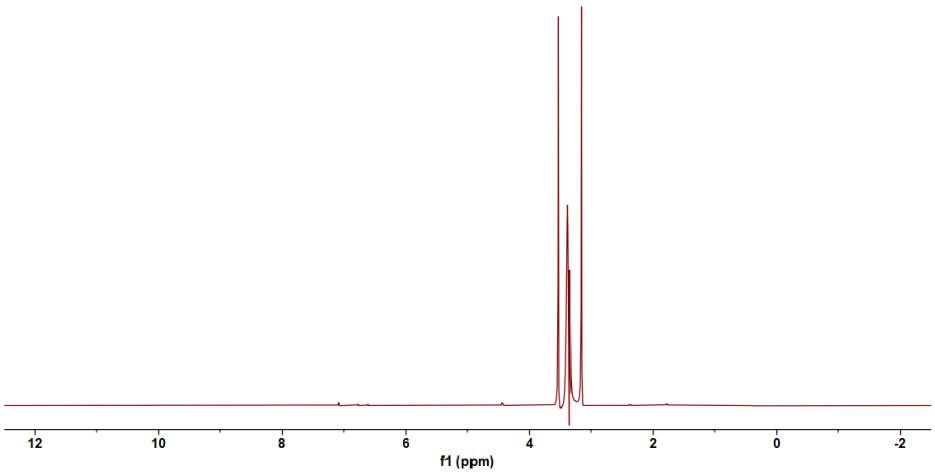


Figure S2: ^{1}H NMR spectrum (400 MHz, MeCl, no lock, r.t.) of $AlCl_3$ in MeCl with presaturation showing the absence of a $[Me_2Cl]^+$ resonance.

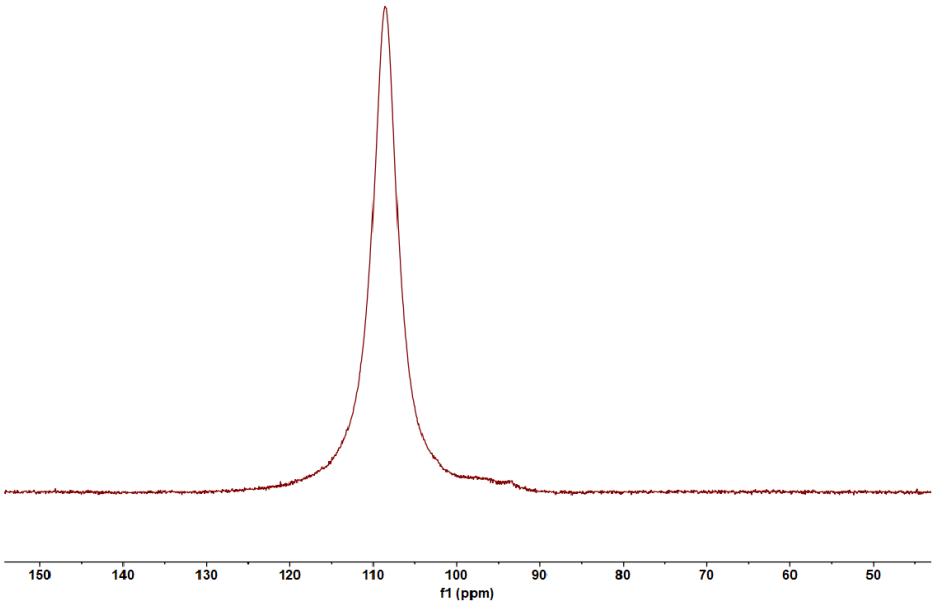


Figure S3: ^{27}Al NMR spectrum (104 MHz, MeCl, no lock, r.t.) of $AlCl_3$ in MeCl.

2.2 $[NEt_4][AlCl_4]$ in MeCl

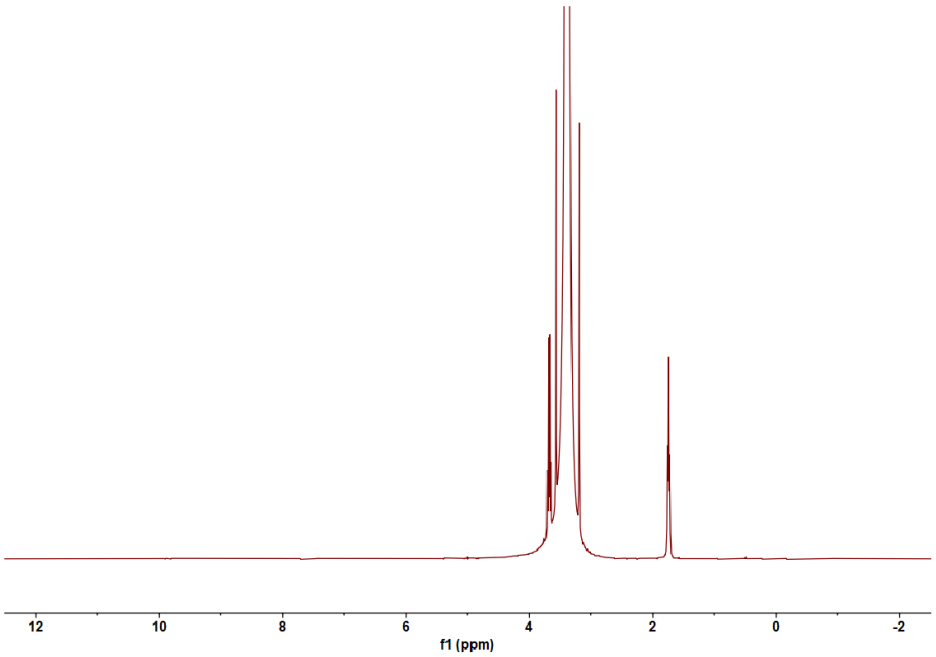


Figure S4: ^{1}H NMR spectrum (400 MHz, MeCl, no lock, gradient shim on MeCl resonance, r.t.) of $[NEt_4][AlCl_4]$ in MeCl.

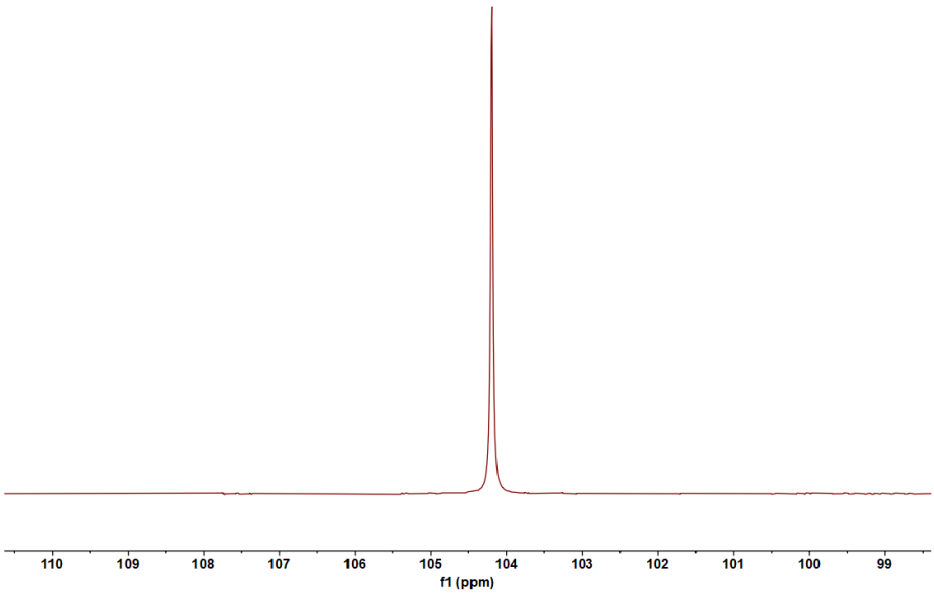


Figure S5: ^{27}Al NMR spectrum (104 MHz, MeCl, no lock, gradient shim on MeCl resonance, r.t.) of $[NEt_4][AlCl_4]$ in MeCl.

2.3 Methylation of oligofluorobenzenes

2.3.1 Methylation of 1,2,3,4-tetrafluorobenzene – 3 hours reaction time

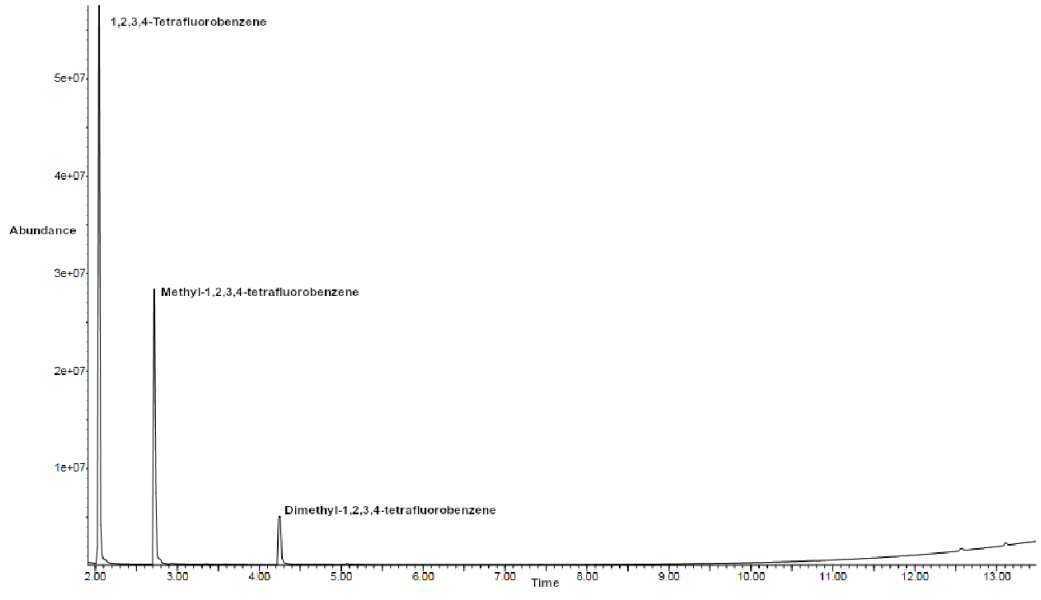


Figure S1: GC/MS TIC of reaction products.

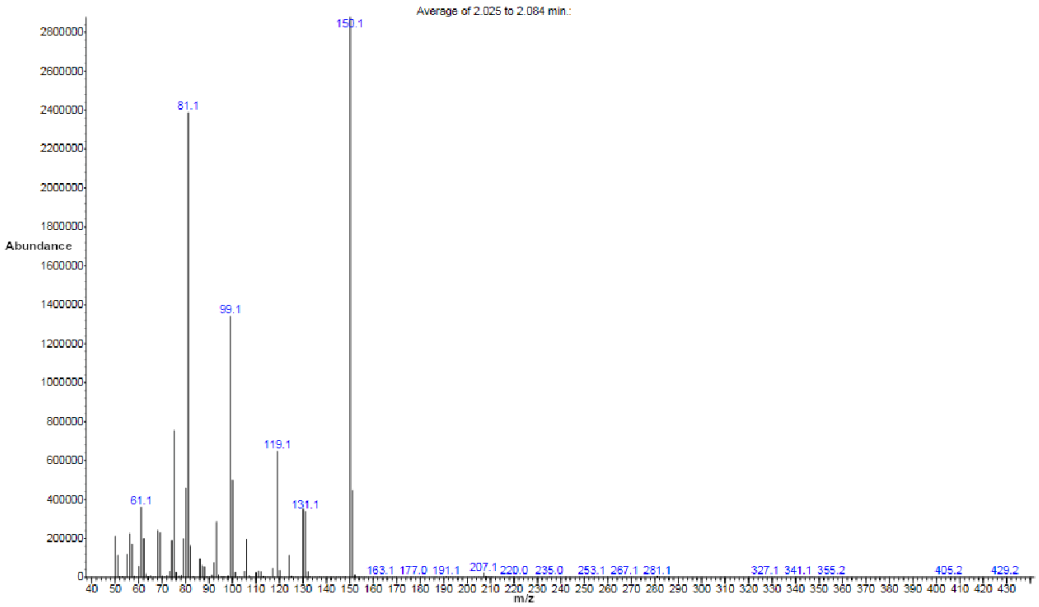


Figure S2: Extracted mass spectrum of 1,2,3,4-tetrafluorobenzene.

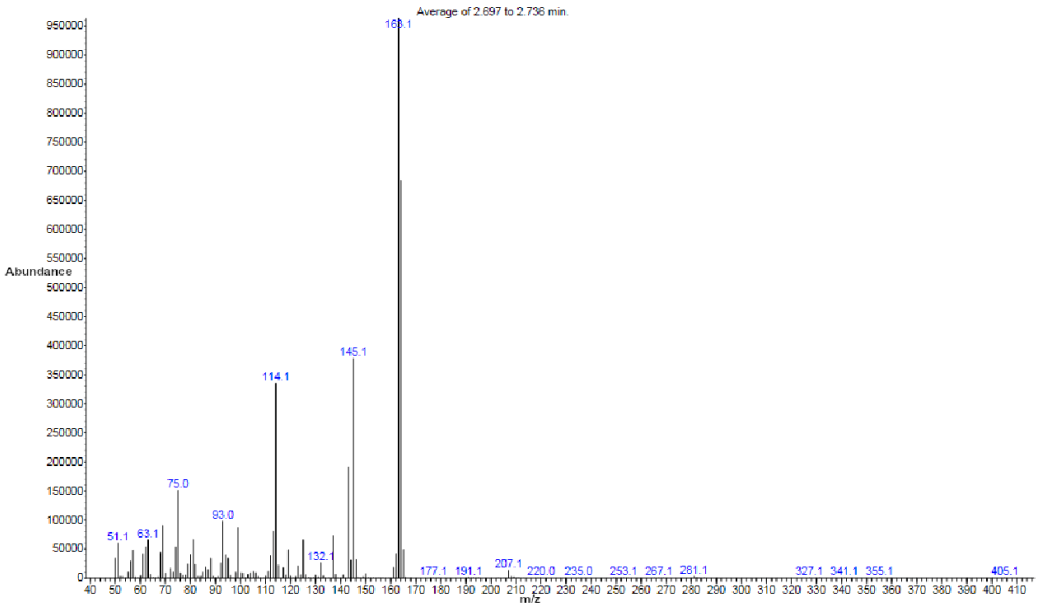


Figure S3: Extracted mass spectrum of methyl-1,2,3,4-tetrafluorobenzene.

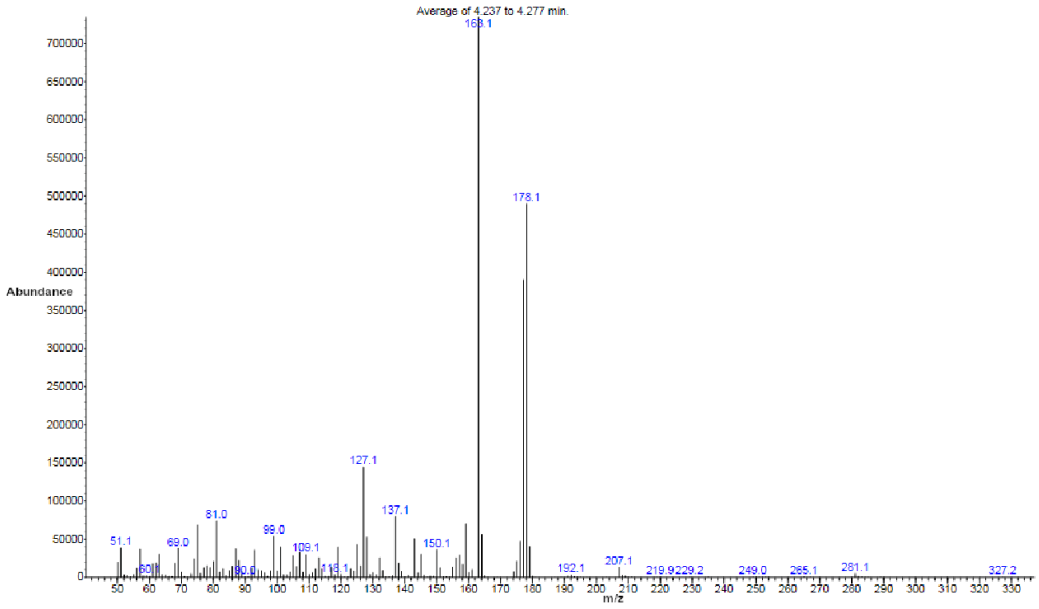


Figure S4: Extracted mass spectrum of dimethyl-1,2,3,4-tetrafluorobenzene.

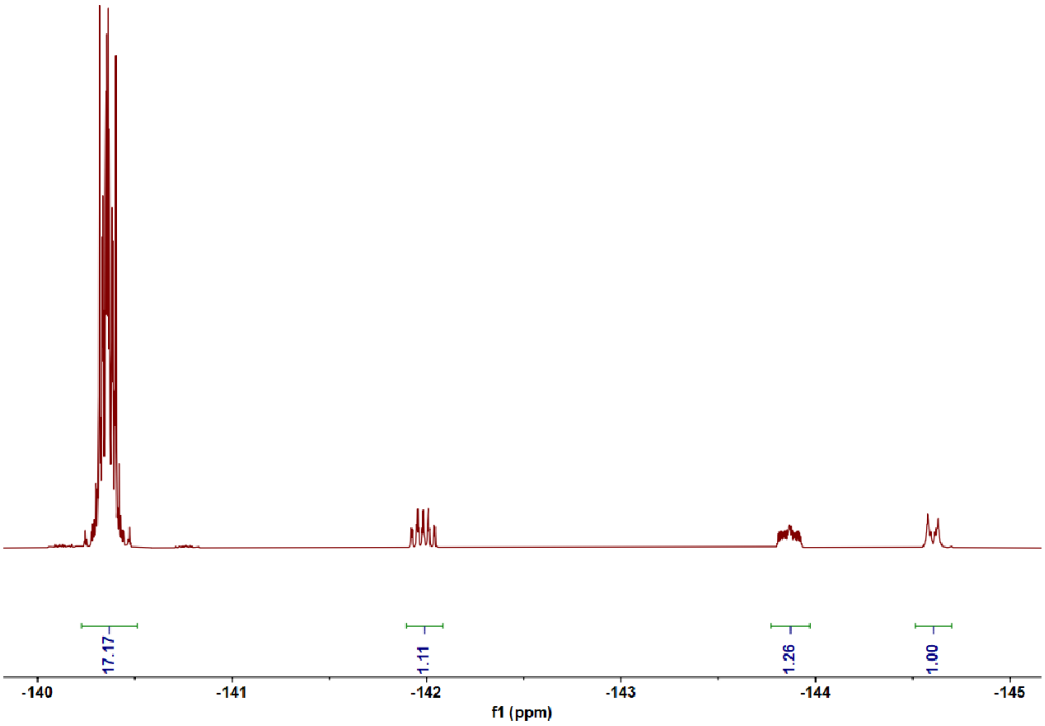


Figure S5: Section of ^{19}F NMR spectrum (377 MHz, CD_2Cl_2, r.t.) of product mixture.

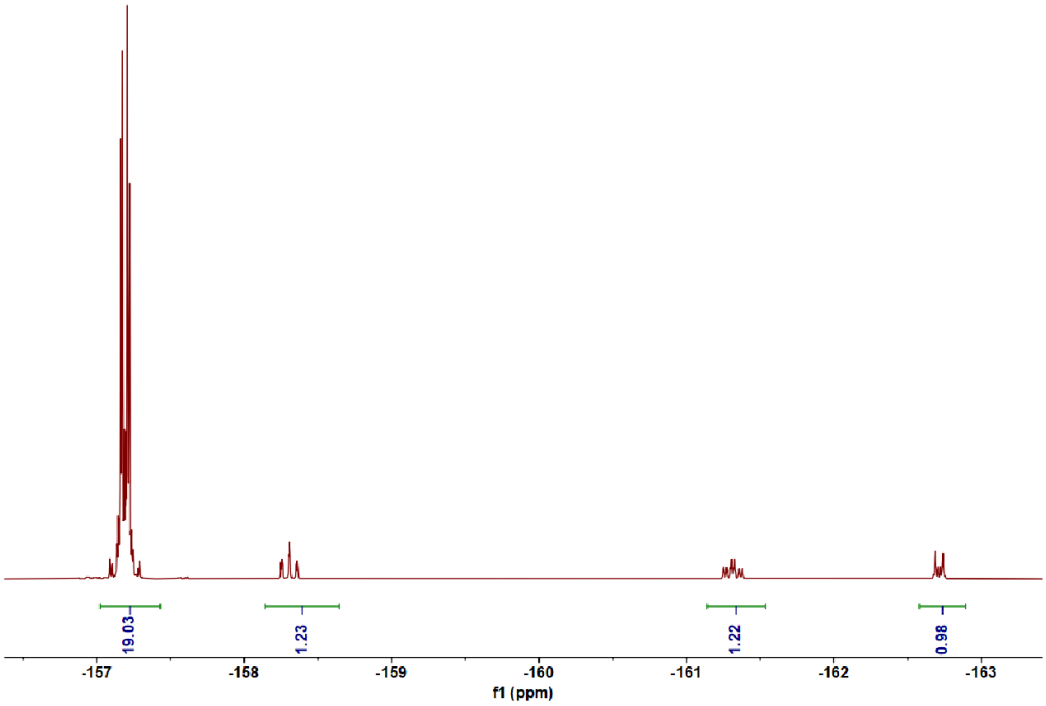


Figure S6: Section of ^{19}F NMR spectrum (377 MHz, CD_2Cl_2, r.t.) of product mixture.

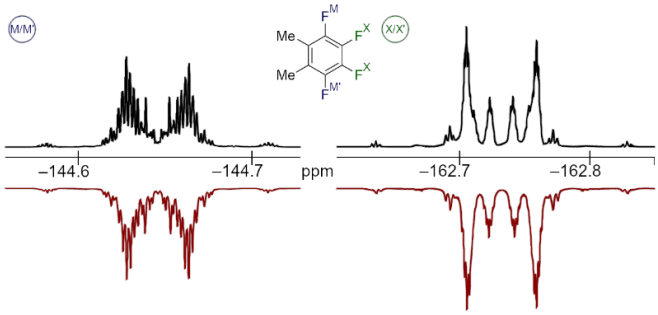


Figure S7: Experimental (top; 377 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of dimethyl-1,2,3,4-tetrafluorobenzene.

2.3.2 Methylation of 1,2,3-trifluorobenzene

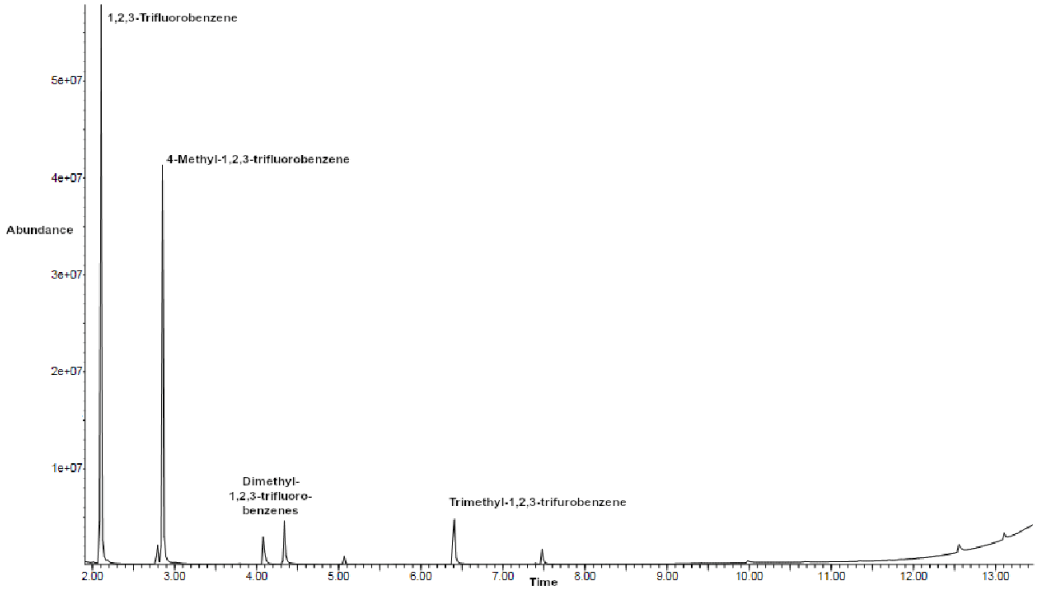


Figure S8: GC/MS TIC of reaction products.

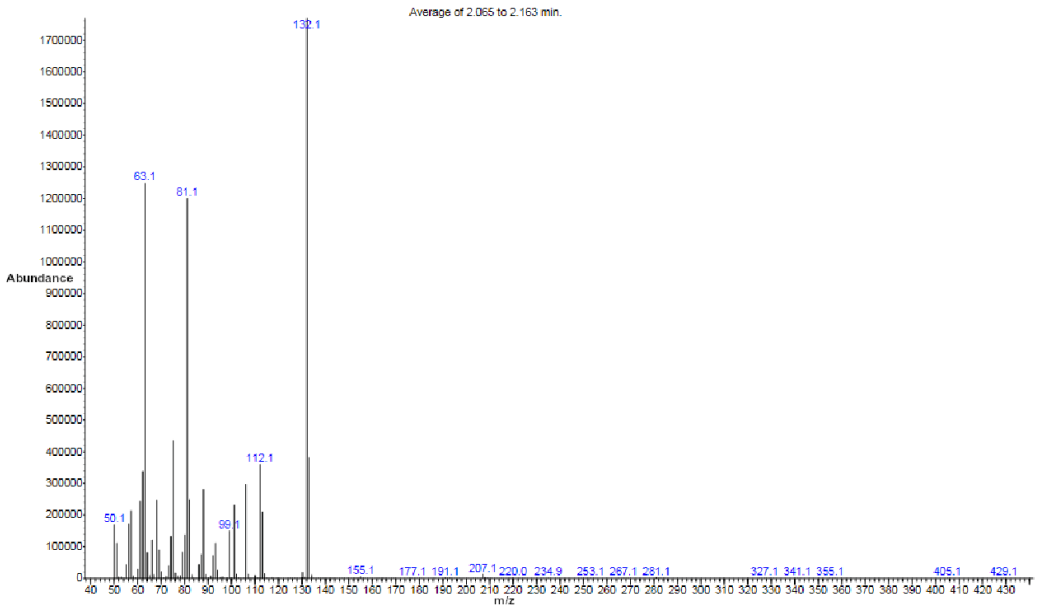


Figure S9: Extracted mass spectrum of 1,2,3-trifluorobenzene.

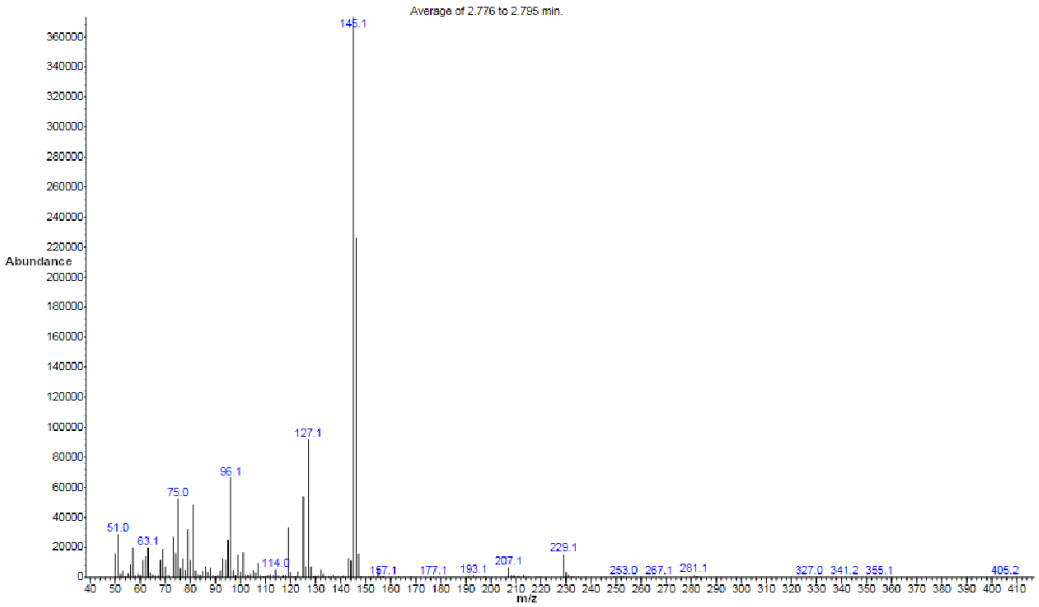


Figure S10: Extracted mass spectrum of 5-methyl-1,2,3-trifluorobenzene.

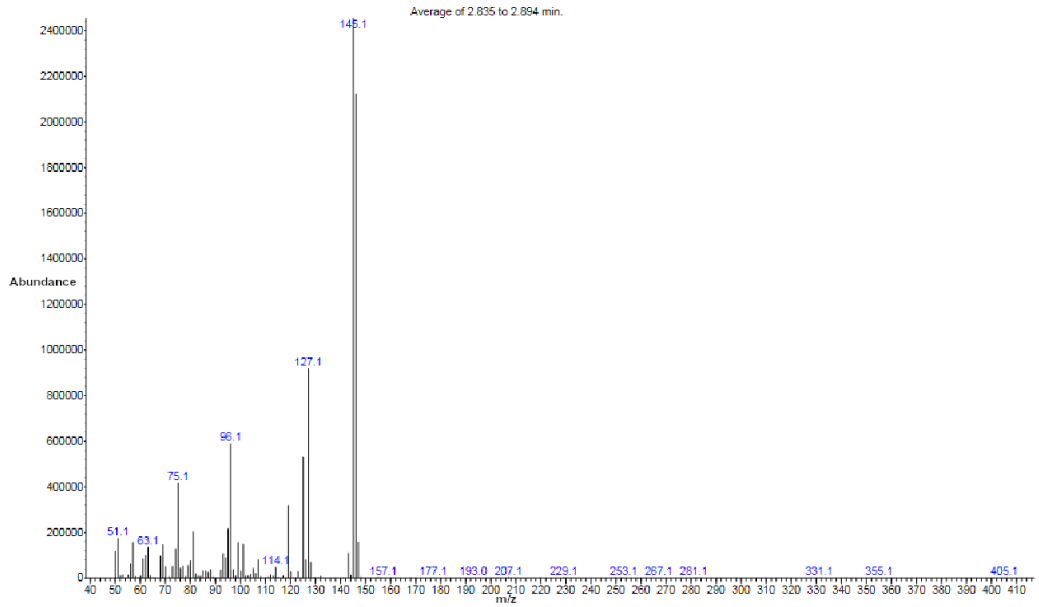


Figure S11: Extracted mass spectrum of 4-methyl-1,2,3-trifluorobenzene.

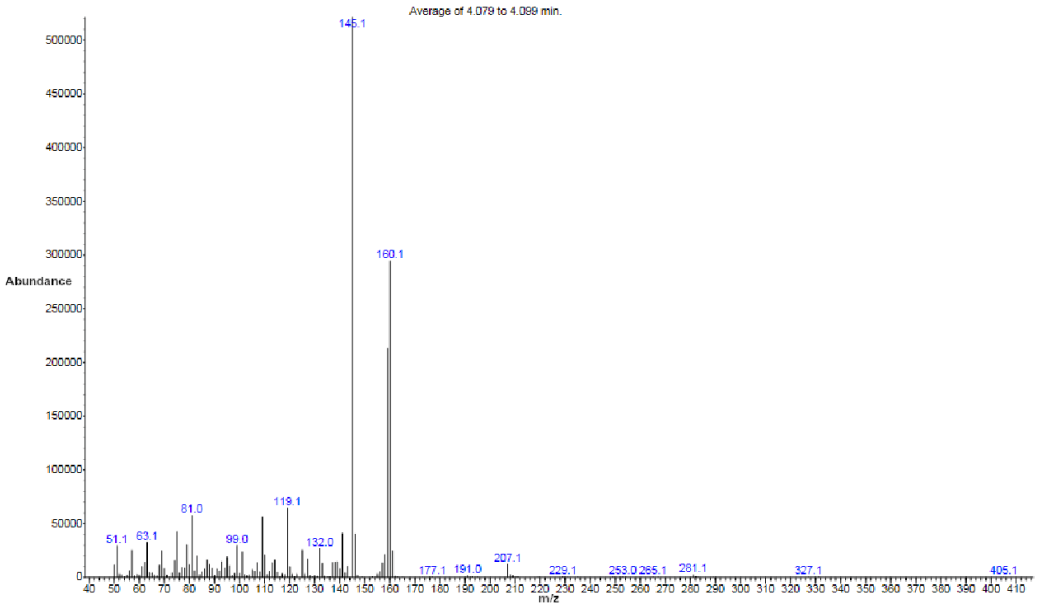


Figure S12: Extracted mass spectrum of 4,6-dimethyl-1,2,3-trifluorobenzene.

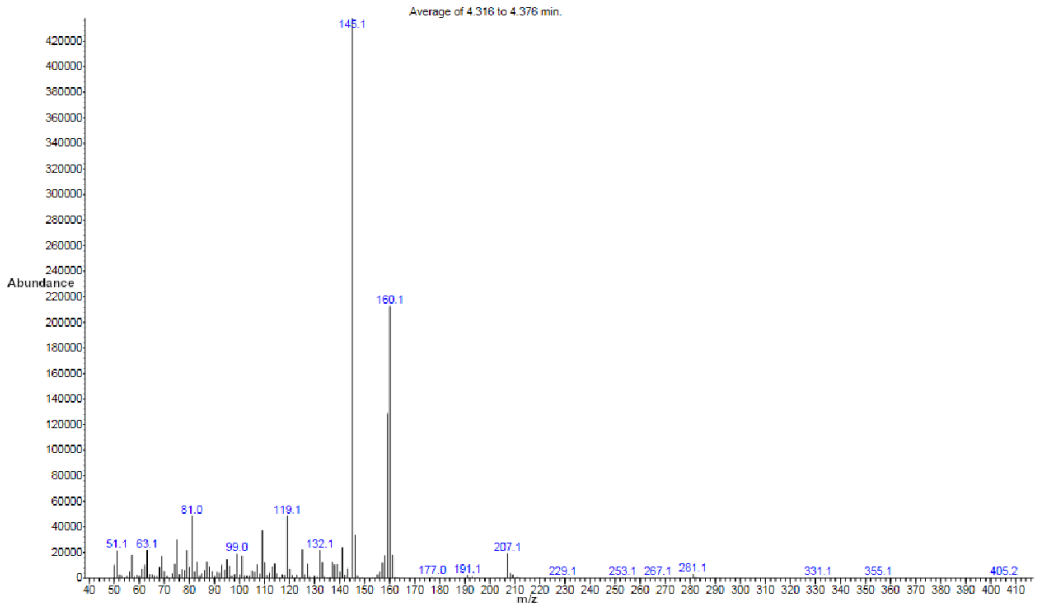


Figure S13: Extracted mass spectrum of 4,5-dimethyl-1,2,3-trifluorobenzene.

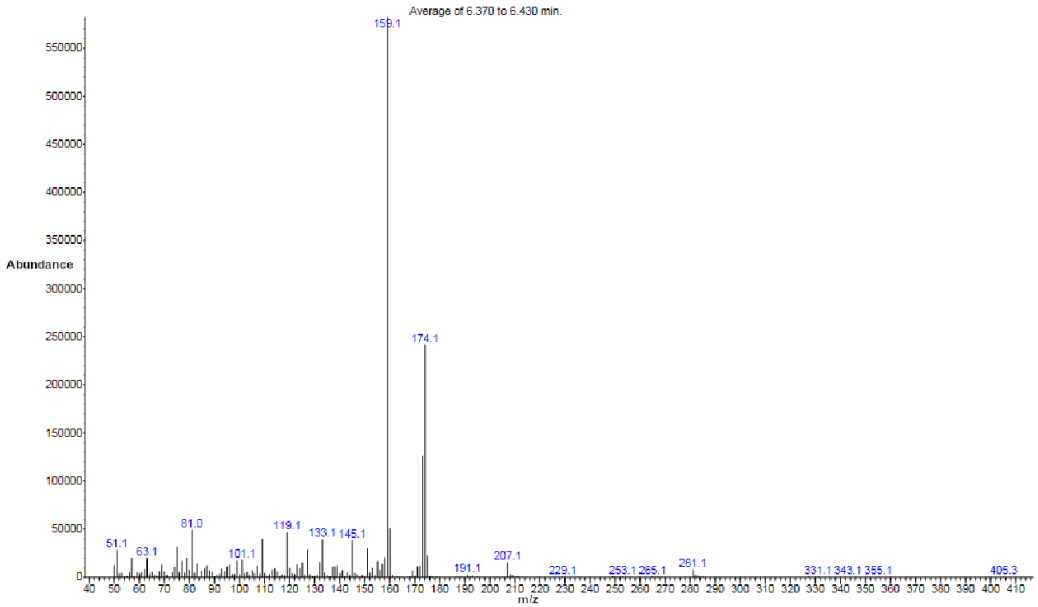


Figure S14: Extracted mass spectrum of trimethyl-1,2,3-trifluorobenzene.

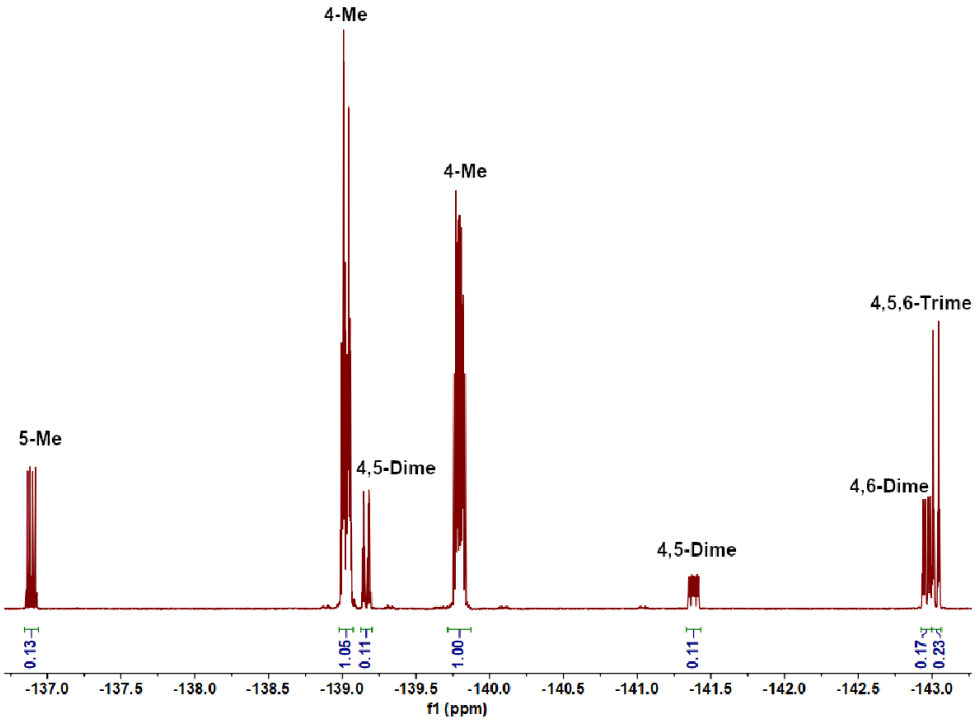


Figure S15: Section of ^{19}F NMR spectrum (565 MHz, CD_2Cl_2, r.t.) of product mixture.

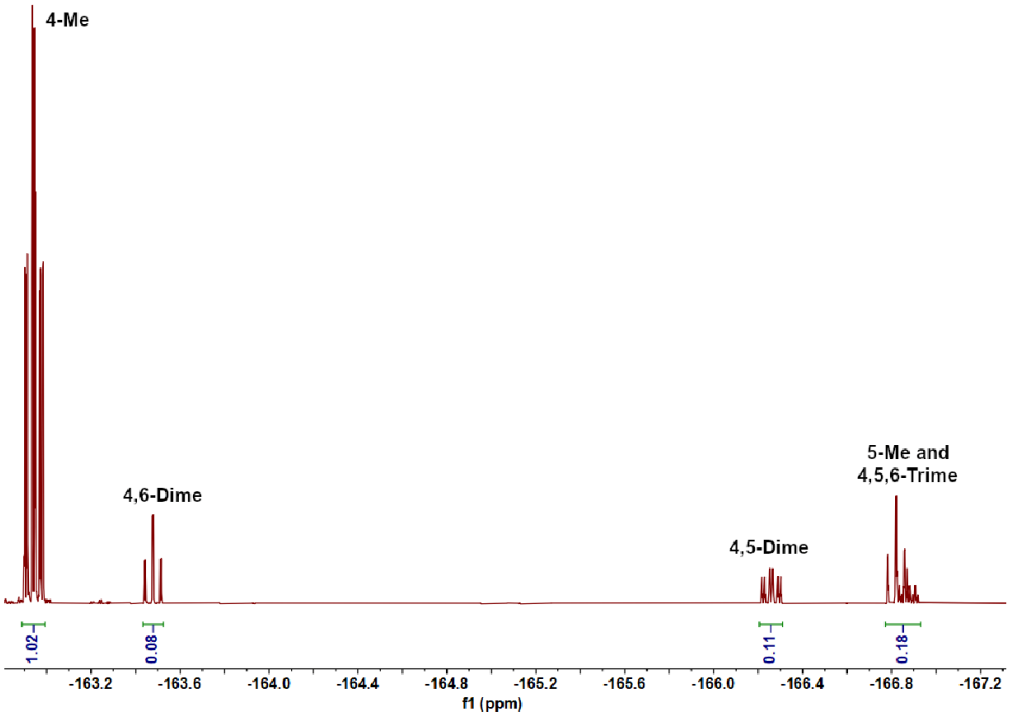


Figure S16: Section of ^{19}F NMR spectrum (565 MHz, CD_2Cl_2, r.t.) of product mixture.

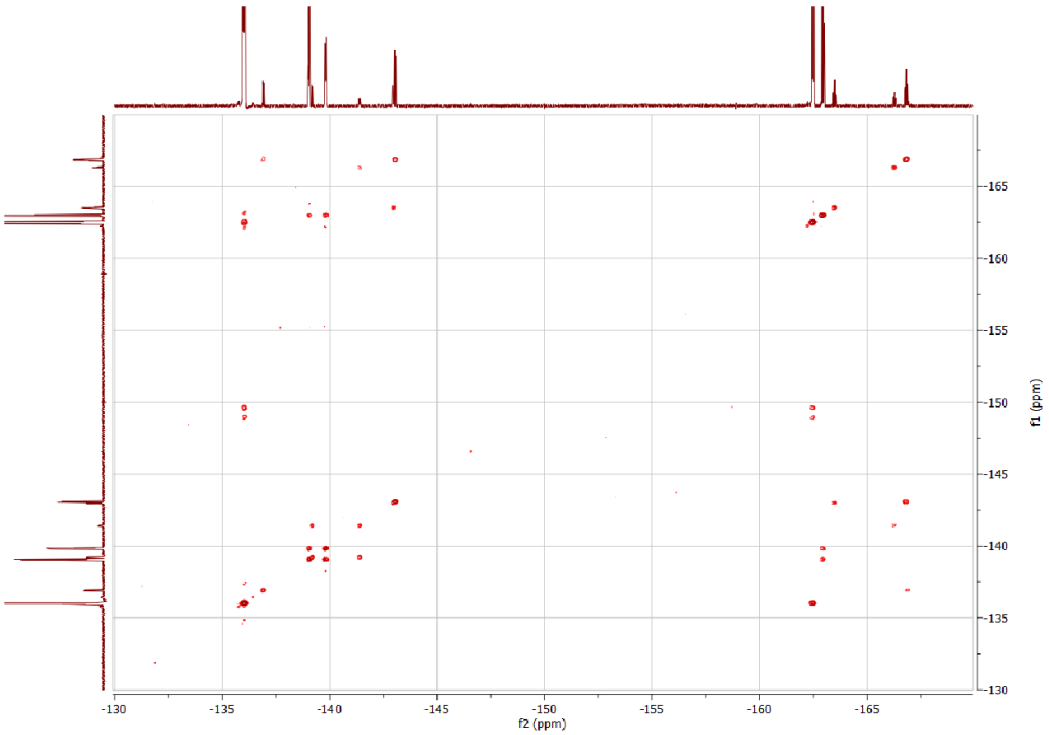


Figure S17: $^{19}F,^{19}F$ COSY NMR spectrum (377 MHz, CD_2Cl_2, r.t.) of product mixture.

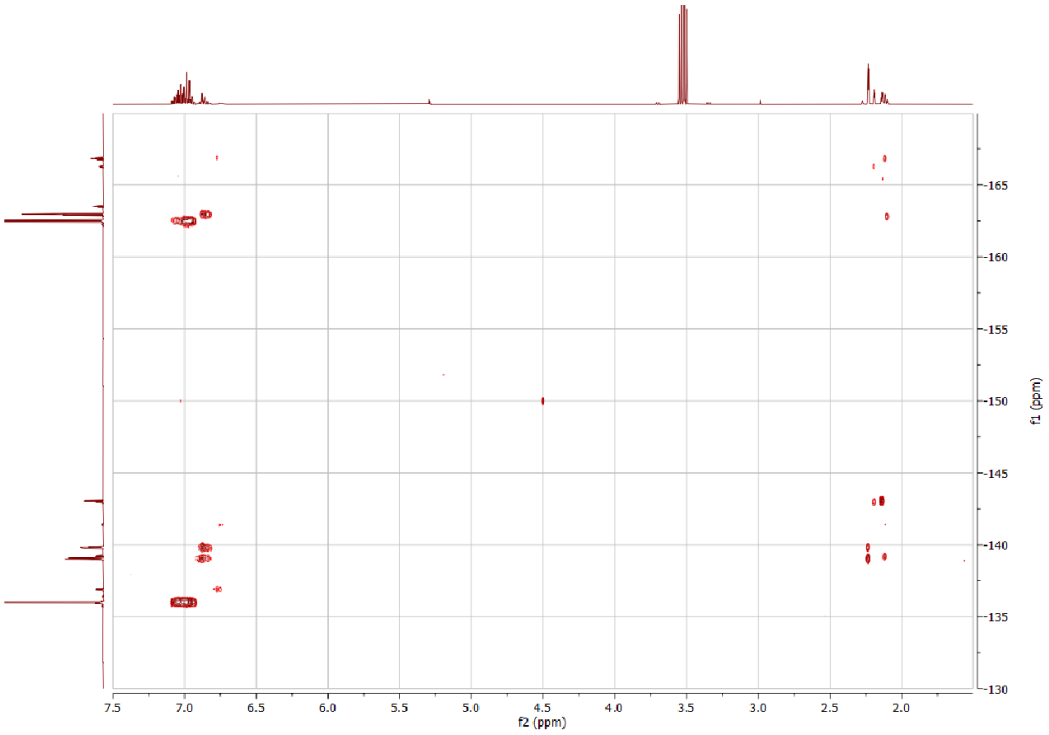


Figure S18: $^{1}H,^{19}F$ HETCOR NMR spectrum (400 MHz/377 MHz, CD_2Cl_2, r.t.) of product mixture.

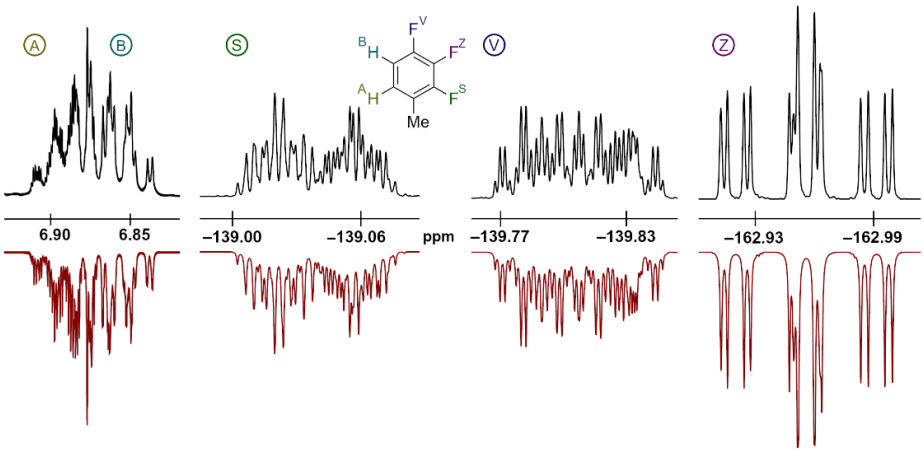


Figure S19: Experimental (top) and iterated (bottom) ^{1}H NMR (700 MHz, CD_2Cl_2, r.t.) and ^{19}F NMR (565 MHz, CD_2Cl_2, r.t.) resonances of 4-methyl-1,2,3-trifluorobenzene.

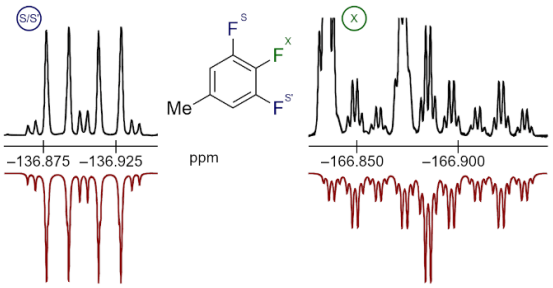


Figure S20: Experimental (top; 565 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of 5-methyl-1,2,3-trifluorobenzene (partially overlapped by low-field resonance of trimethyl-1,2,3-trifluorobenzene). AA'M$_3$SS'X spin system: $\delta_{S/S'}$ = −136.9 (F1/F3) ppm, δ_X = −166.9 (F2) ppm, $\delta_{A/A'}$ = 6.77 (H6/H4) ppm, δ_M (CH_3) not observable due to overlap/low intensity, $J_{SS'}$ = ^4J(^{19}F,^{19}F) = 6.00 Hz, J_{SX} = $J_{S'X}$ = ^3J(^{19}F,^{19}F) = −20.34 Hz, J_{SA} = $J_{S'A'}$ = ^3J(^{19}F,^{1}H) = 10.77 Hz, $J_{S'A}$ = $J_{SA'}$ = ^5J(^{19}F,^{1}H) = −2.11 Hz, J_{XA} = $J_{XA'}$ = ^4J(^{19}F,^{1}H) = 6.52 Hz, $J_{AA'}$ = ^4J(^{1}H,^{1}H) = 2.09 Hz, J_{XM} = ^6J(^{19}F,^{1}H) = 1.50 Hz.

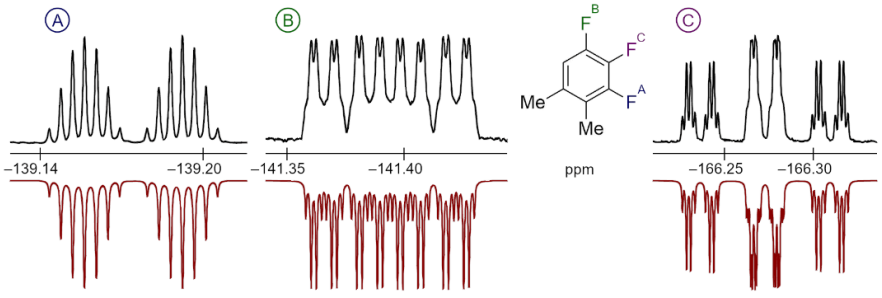


Figure S21: Experimental (top; 565 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of 4,5-dimethyl-1,2,3-trifluorobenzene. δ(^{19}F) = −139.2 (dddq, 1F, *F*3, ^3J(^{19}F,^{19}F) = −20.88 Hz, ^4J(^{19}F,^{19}F) = 4.95 Hz, ^4J(^{19}F,^{1}H) = 2.38 Hz, ^5J(^{19}F,^{1}H) = 2.49 Hz (H6)), −141.4 (dddq, 1F, *F*1, ^3J(^{19}F,^{19}F) = −20.36 Hz, ^4J(^{19}F,^{19}F) = 4.95 Hz, ^3J(^{19}F,^{1}H) = 11.03 Hz, ^6J(^{19}F,^{1}H) = 1.28 Hz), −166.3 (dddq, 1F, *F*2, ^3J(^{19}F,^{19}F) = −20.88 Hz (F3), ^3J(^{19}F,^{19}F) = −20.36 Hz (F1), ^4J(^{19}F,^{1}H) = 7.32 Hz, ^6J(^{19}F,^{1}H) = 1.34 Hz) ppm. δ(^{1}H, from ^{1}H,^{19}F-HETCOR 400 MHz/377 MHz, CD_2Cl_2, r.t.) = 6.76 (Ar*H*), 2.20 (5-CH_3), 2.11 (4-CH_3) ppm.

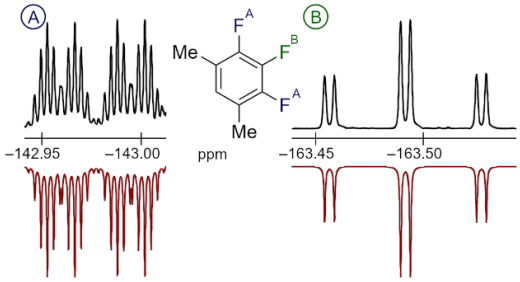


Figure S22: Experimental (top; 565 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of 4,6-dimethyl-1,2,3-trifluorobenzene. $\delta(^{19}F)$ = −143.0 (ddsept, 2F, *F*1/*F*3, $^3J(^{19}F,^{19}F)$ = −19.95, $^4J(^{19}F,^1H)$ = 7.81 Hz (5*H*), $^4J(^{19}F,^1H)$ = 1.80 Hz (CH_3)), −163.5 (dd, 1H, F2, $^3J(^{19}F,^{19}F)$ = −19.95, $^5J(^{19}F,^1H)$ = 2.55 Hz) ppm. $\delta(^1H$, from $^1H,^{19}F$-HETCOR 400 MHz/377 MHz, CD_2Cl_2, r.t.) = 2.19 (CH_3) ppm. Ar*H* not observable due to overlap/low intensity.

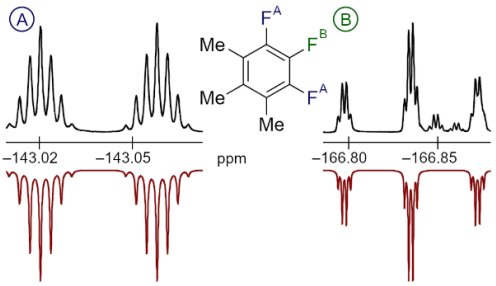


Figure S23: Experimental (top; 565 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of trimethyl-1,2,3-trifluorobenzene (partially overlapped by low-field resonance of 5-methyl-1,2,3-trifluorobenzene): $\delta(^{19}F)$ = −143.0 (dsept, 2F, *F*1/*F*3, $^3J(^{19}F,^{19}F)$ = −21.17 Hz, $^4J(^{19}F,^1H)$ = 1.89 Hz), −166.8 (tq, 1F, *F*2, $^3J(^{19}F,^{19}F)$ = −21.17 Hz, $^4J(^{19}F,^1H)$ = 1.33 Hz). $\delta(^1H$, from $^1H,^{19}F$-HETCOR 400 MHz/377 MHz, CD_2Cl_2, r.t.) = 2.14 (4-CH_3/6-CH_3), 2.12 (5-CH_3).

2.3.3 Methylation of 1,2-difluorobenzene

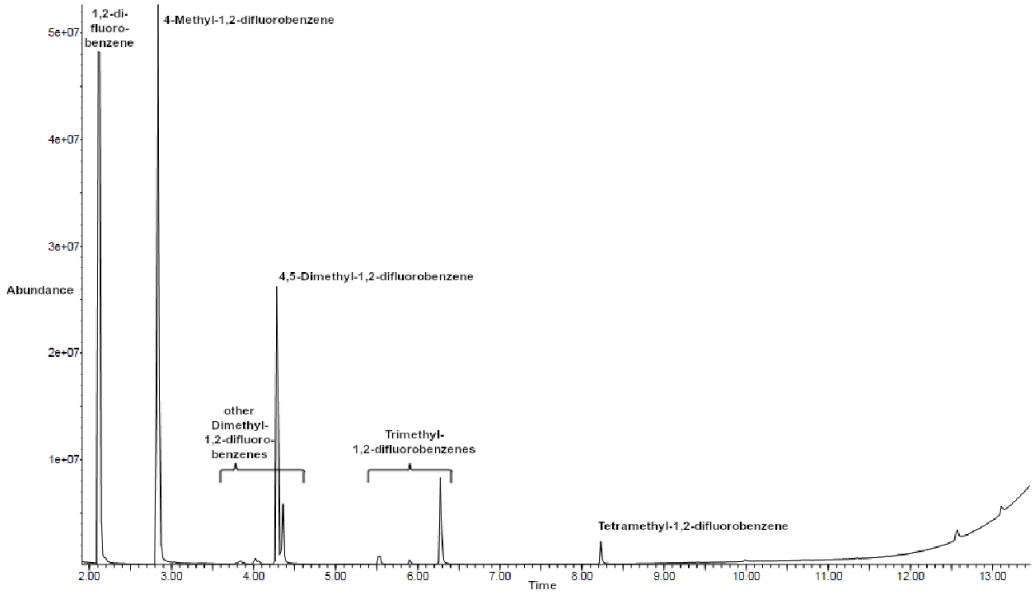


Figure S24: GC/MS TIC of reaction products.

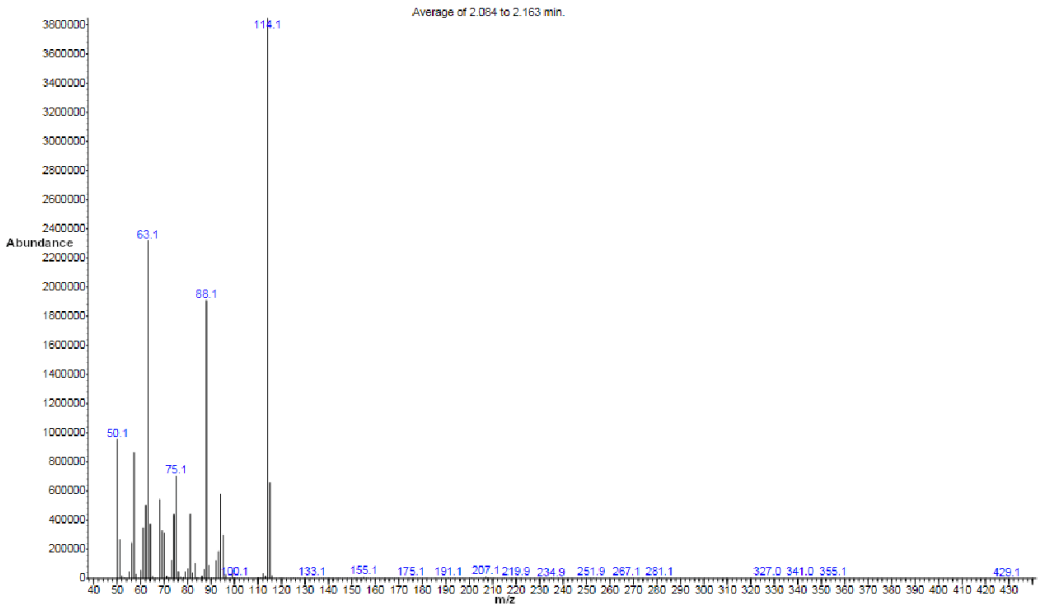


Figure S25: Extracted mass spectrum of 1,2-difluorobenzene.

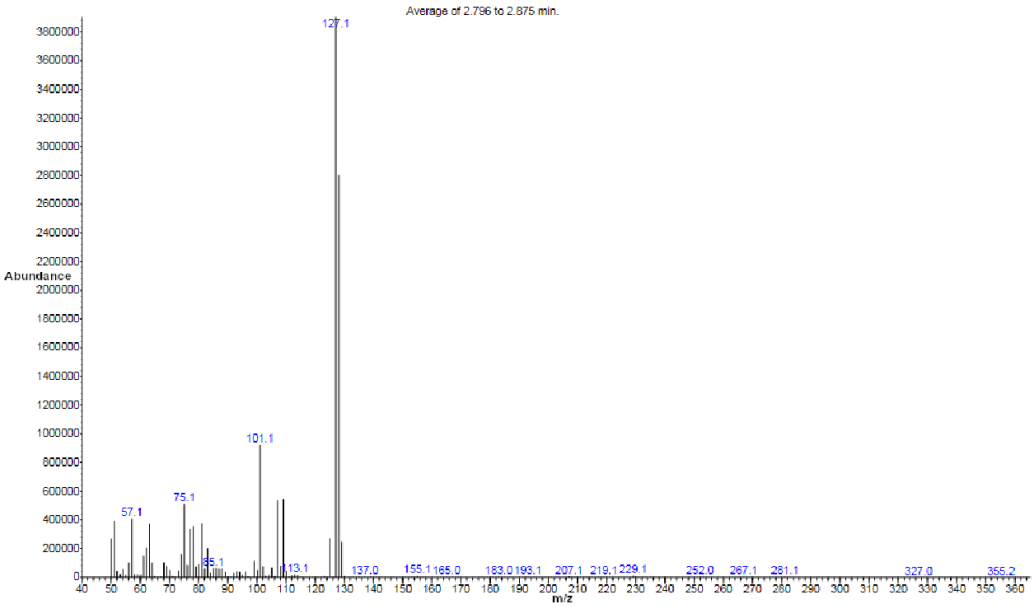


Figure S26: Extracted mass spectrum of 4-methyl-1,2-difluorobenzene.

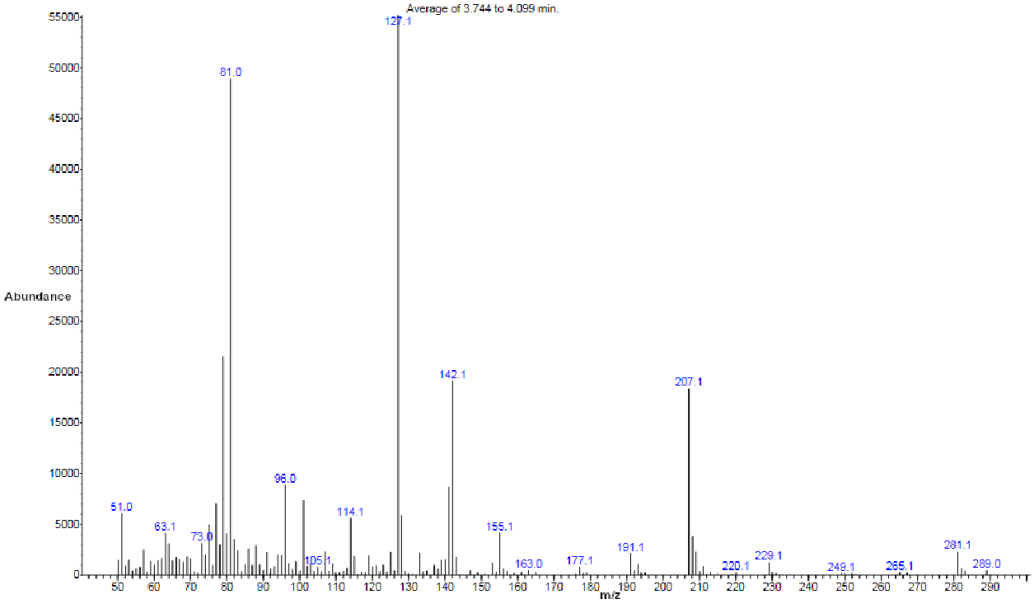


Figure S27: Extracted mass spectrum of dimethyl-1,2-difluorobenzenes, not 4,5-dimethyl-1,2-difluorobenzene.

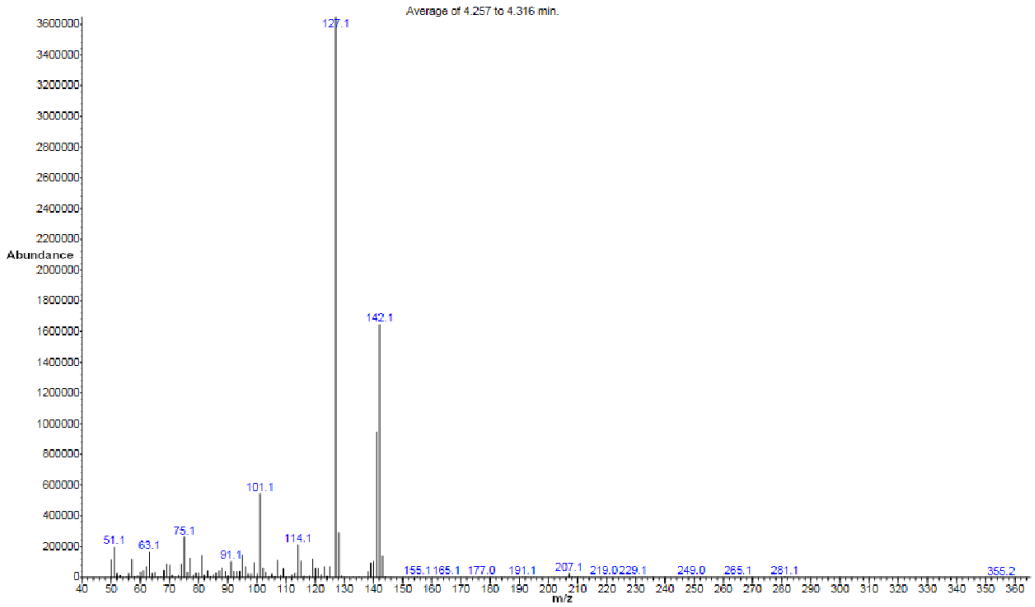


Figure S28: Extracted mass spectrum of 4,5-dimethyl-1,2-difluorobenzene.

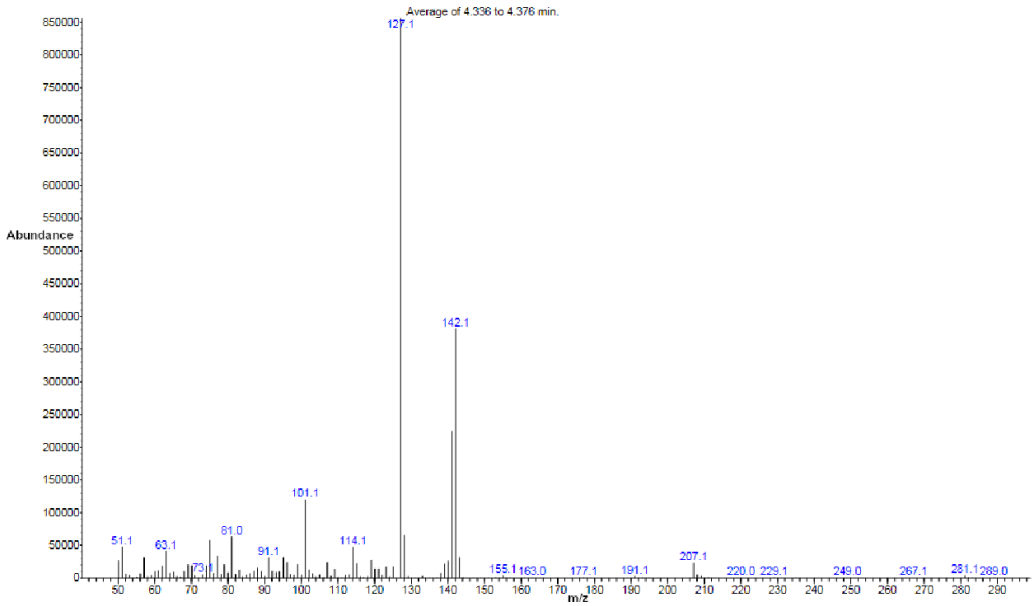


Figure S29: Extracted mass spectrum of the fourth species of dimethyl-1,2-difluorobenzene.

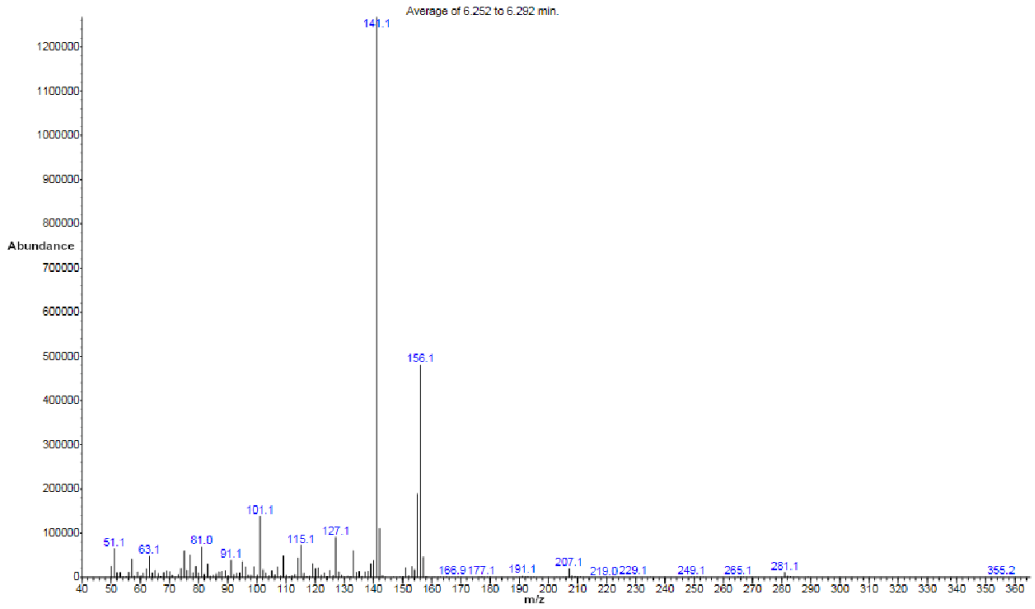


Figure S30: Extracted mass spectrum of the more abundant trimethyl-1,2-difluorobenzene.

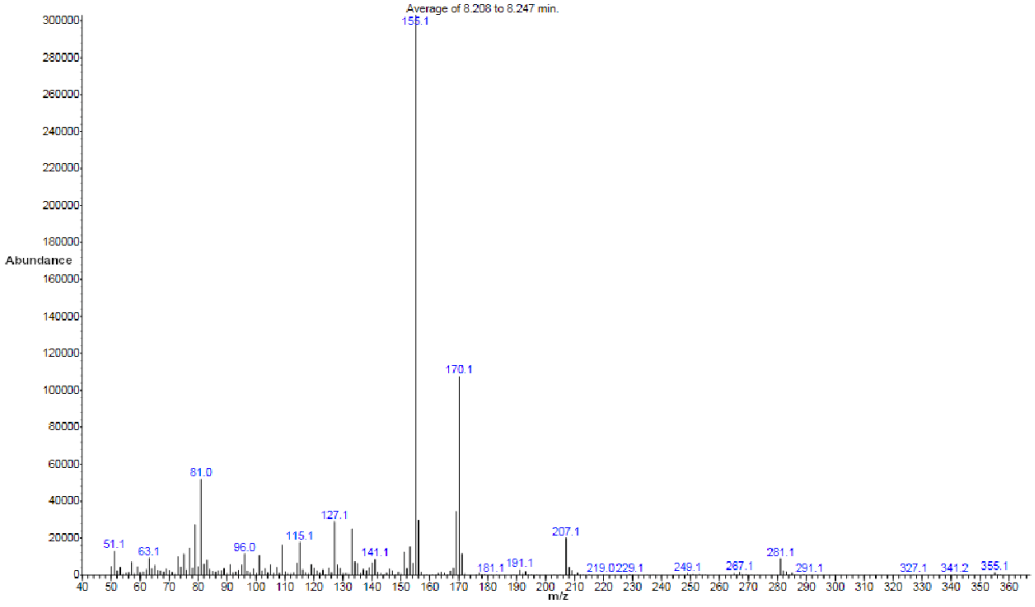


Figure S31: Extracted mass spectrum of tetramethyl-1,2-difluorobenzene.

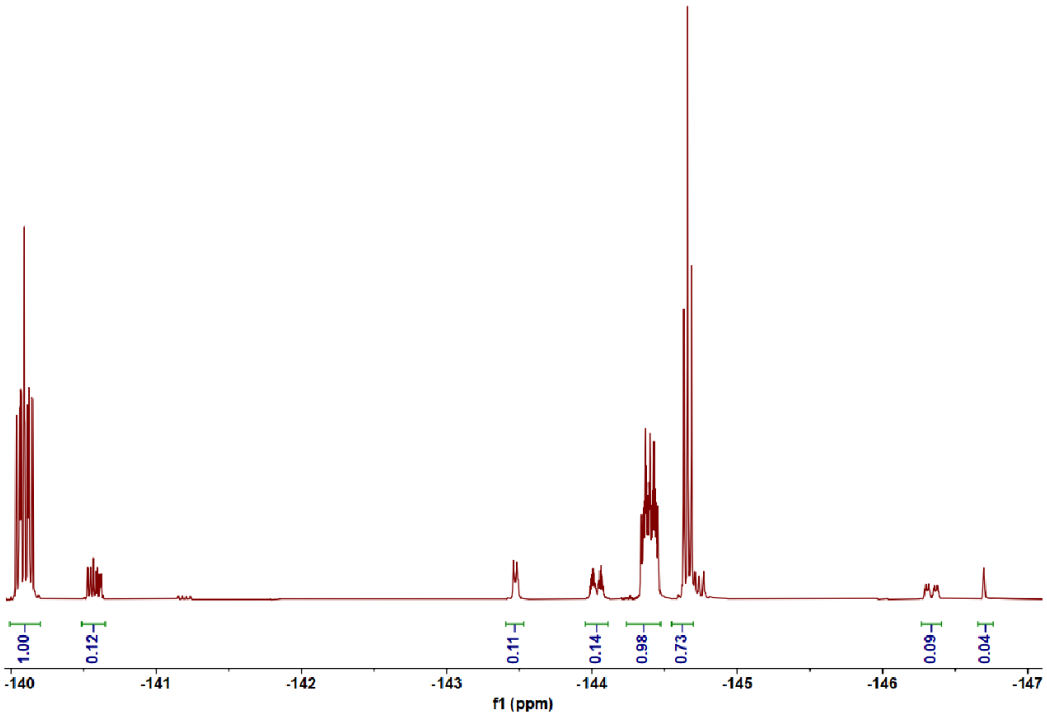


Figure S32: Section of ^{19}F NMR spectrum (377 MHz, CD_2Cl_2, r.t.) of product mixture.

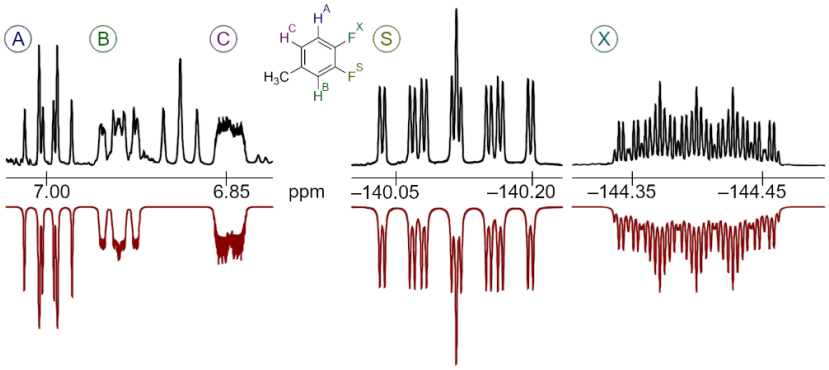


Figure S33: Experimental (top) and iterated (bottom) ^1H NMR (700 MHz, CD_2Cl_2, r.t.) and ^{19}F NMR (377 MHz, CD_2Cl_2, r.t.) resonances of 4-methyl-1,2-difluorobenzene (^1H partially overlapped by resonance of 4,5-dimethyl-1,2-trifluorobenzene).

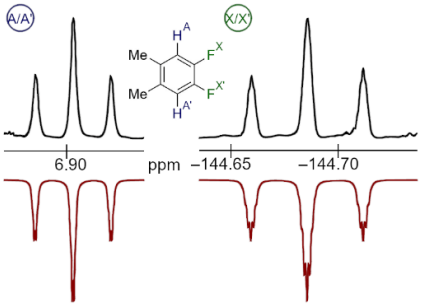


Figure S34: Experimental (top) and iterated (bottom) ^{1}H NMR (700 MHz, CD_2Cl_2, r.t.) and ^{19}F NMR (377 MHz, CD_2Cl_2, r.t.) resonances of 4,5-dimethyl-1,2-difluorobenzene.

2.4 $[MeNC_5F_4I][Al(OTeF_5)_4]$ (2l)

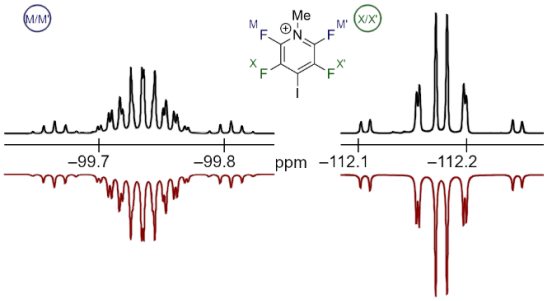


Figure S35: Experimental (top; 377 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of $[MeNC_5F_4I]^+$.

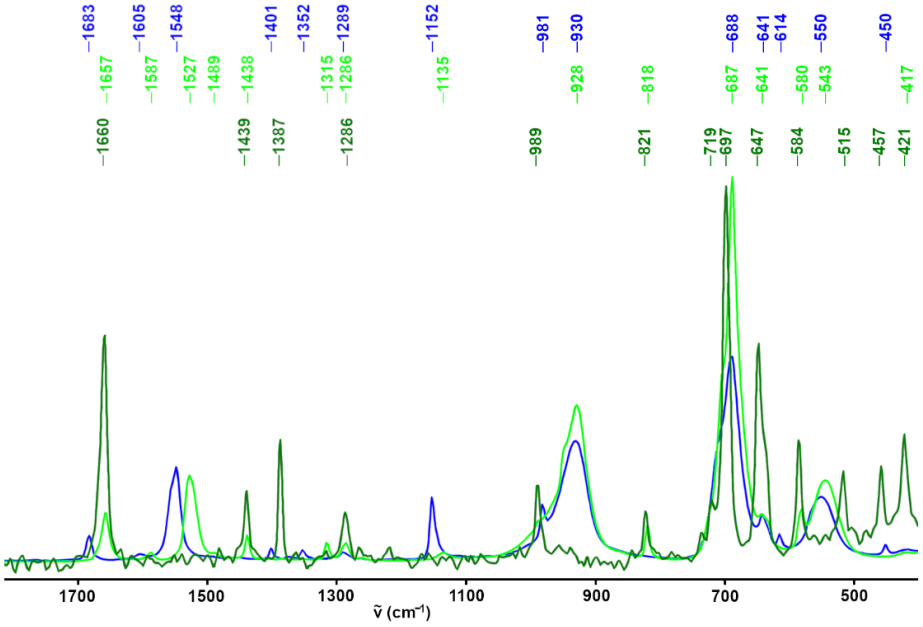


Figure S36: Section of IR spectra of $[MeNC_5F_5][Al(OTeF_5)_4]$ (blue), $[MeNC_5F_4I][Al(OTeF_5)_4]$ (light green) and section of Raman spectrum of $[MeNC_5F_4I][Al(OTeF_5)_4]$ (dark green).

2.5 $[MeNC_5F_5][Al(OTeF_5)_4]$ (2F)

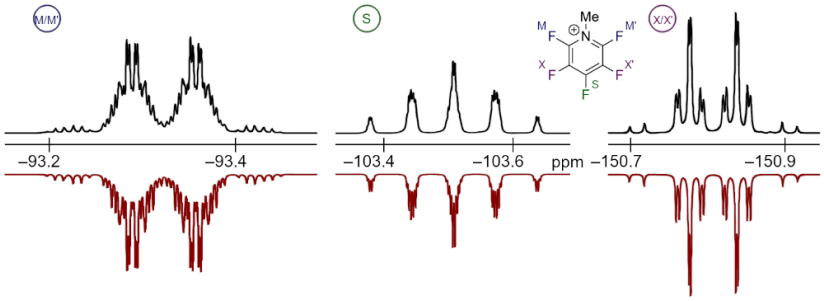


Figure S37: Experimental (top; 377 MHz, CD_2Cl_2, r.t.) and iterated (bottom) ^{19}F NMR resonances of $[MeNC_5F_5]^+$.

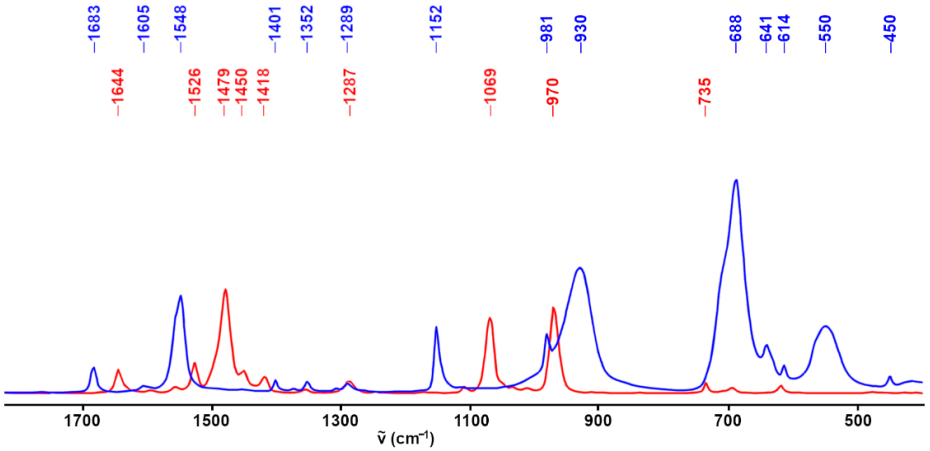


Figure S38: Section of IR spectra of $[MeNC_5F_5][Al(OTeF_5)_4]$ (blue) and NC_5F_5 (red). For comparison IR bands of $[HNC_5F_5][SbF_6]$: 1639, 1538, 1346, 1124, 1075, 1031, 980, 877, 735, 660, 546, 478 cm^{-1}[1].

3 Quantum Chemical Calculations

3.1 Reaction path for methylation of *o*DFB with $AlCl_3$/MeCl

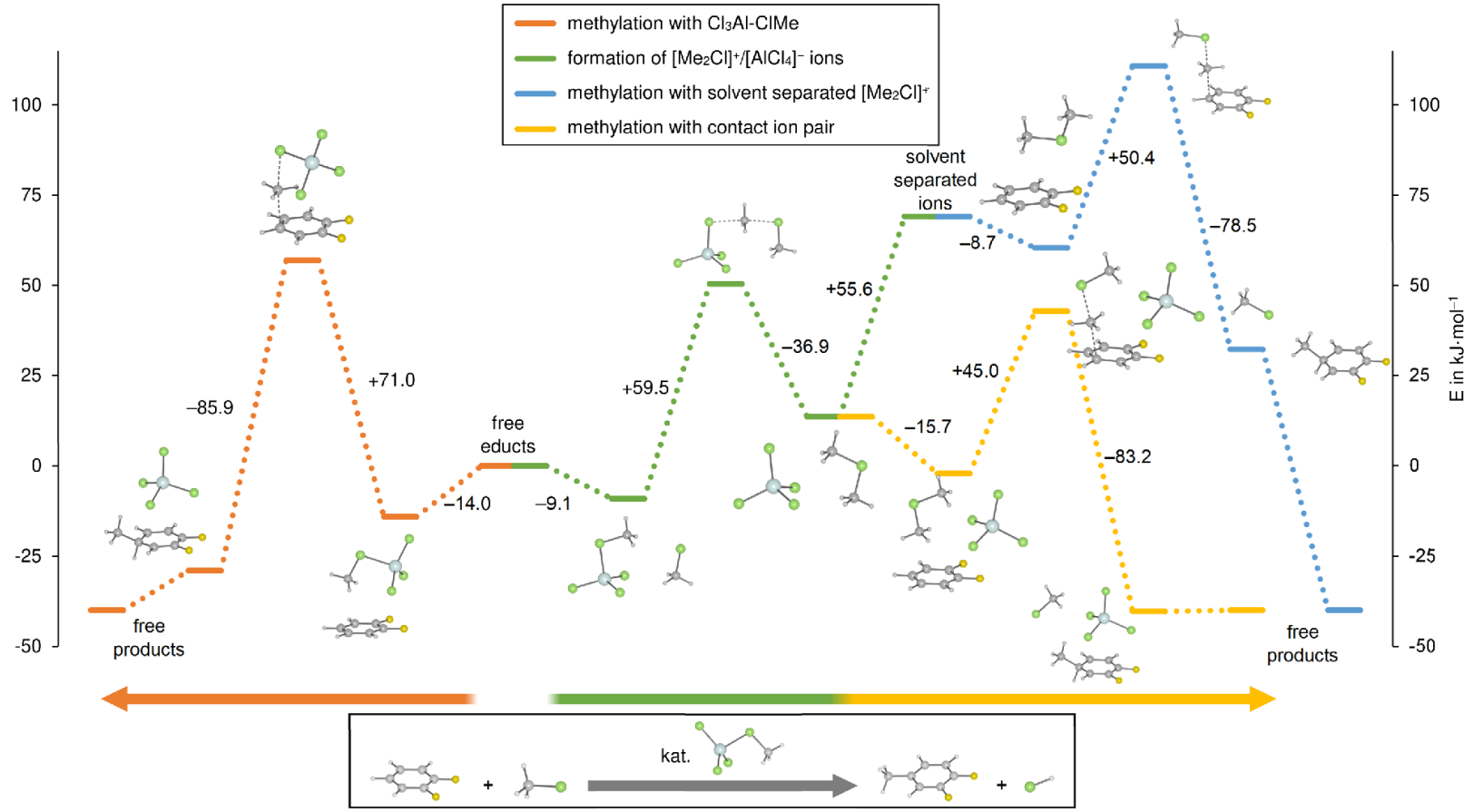


Figure S39: Possible reaction paths for the methylation of 1,2-difluorobenzene with $AlCl_3$/MeCl on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R MeCl, ZPE corrected energies). The final steps (rearomatization, HCl elimination, recovery of $AlCl_3$-MeCl) which are common for all routes are not shown in detail for clarity.

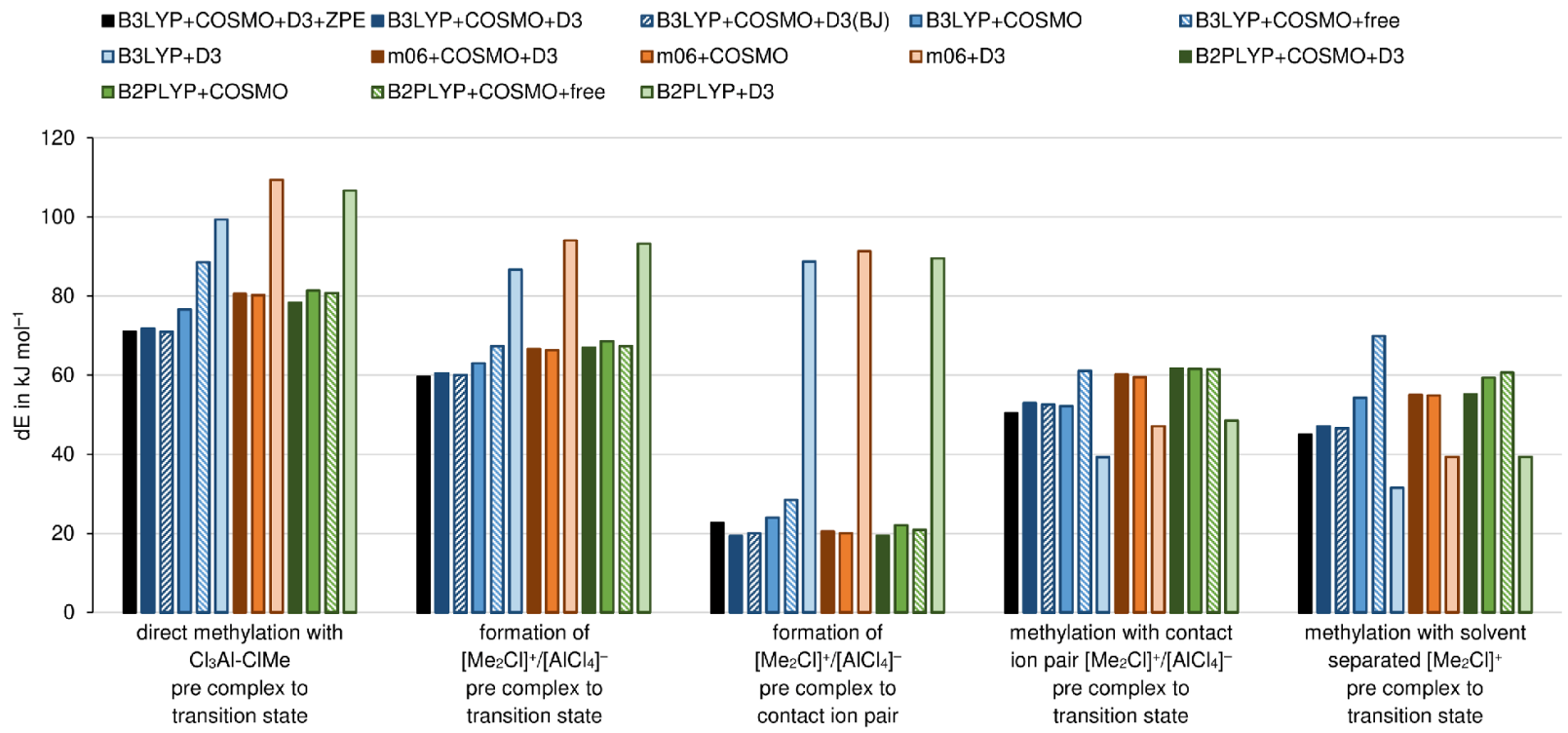


Figure S40: Selected energies from single-point calculations (def2-TZVPP basis set) of structures optimized on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R MeCl). Values in black are equivalent to those in Figure S39. Values named with "+free" are referenced to non-interacting molecules instead of pre-complexes, since the formation of the pre-complexes is disfavored without dispersion correction. Note that even if the formation of the contact ion pair is more disfavored without a solvent model, the relative trend of the transition state is the same.

3.2 Reaction path for methylation with $[Me_2X]^+$

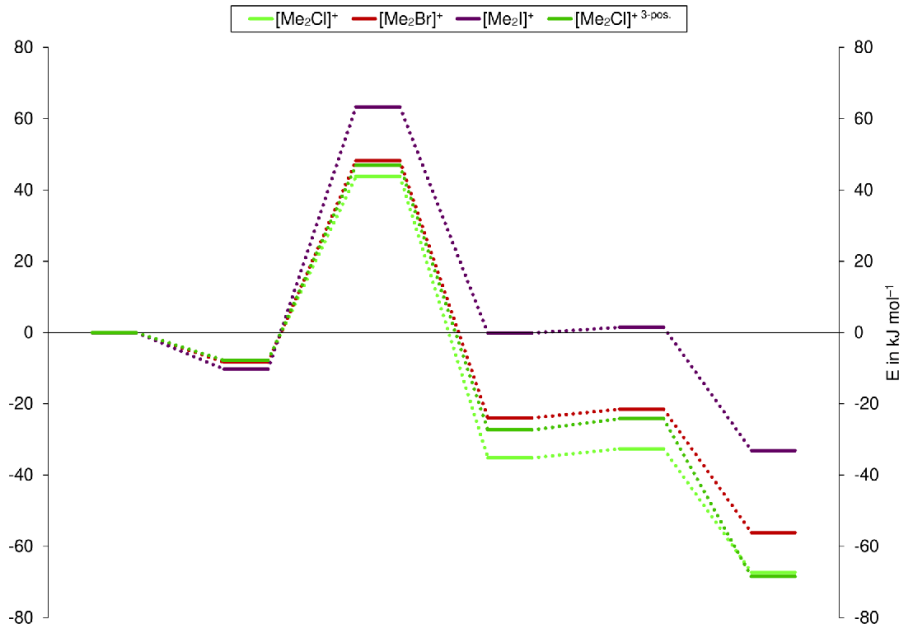


Figure S41: Reaction paths for the methylation of 1,2-difluorobenzene with $[Me_2X]^+$ on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2, ZPE corrected energies).

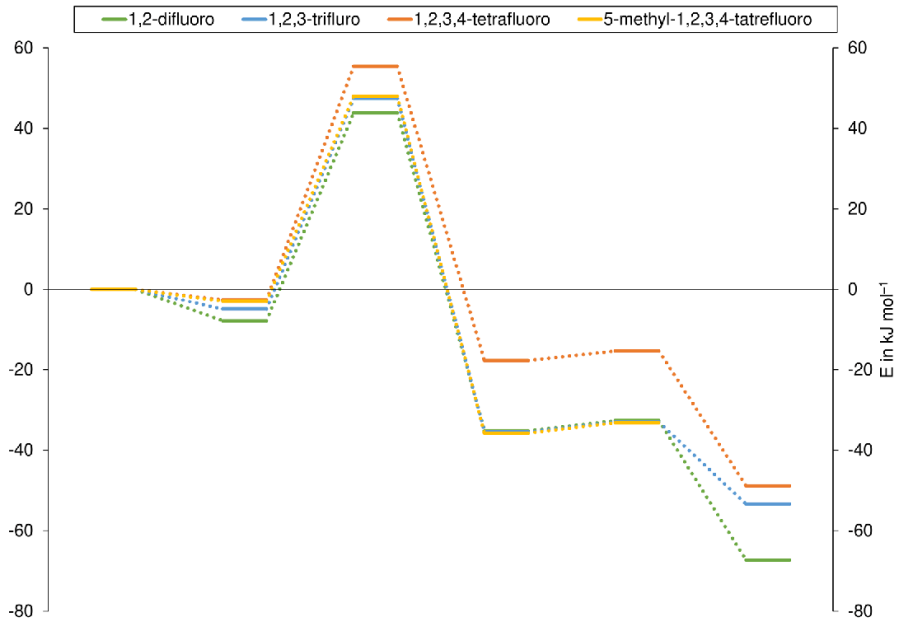


Figure S42: Reaction paths for the methylation of oligofluorobenzenes with $[Me_2Cl]^+$ on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2, ZPE corrected energies).

Table S1: Relative energies in kJ·mol^{-1} of reaction paths for the methylation with $[Me_2X]^+$ on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R SO_2, ZPE corrected energies).

compounds	not interacting reactants to pre-complex	pre-complex to transition state	transition state to product complex	product complex to not interacting products	H^+ shift of Wheland cation
1,2-difluorobenzene $[Me_2Cl]^+$	−7.8	+51.7	−79.0	2.5	−34.6
1,2-difluorobenzene $[Me_2Br]^+$	−8.4	+56.6	−72.2	3.4	−34.6
1,2-difluorobenzene $[Me_2I]^+$	−10.3	+73.6	−63.4	1.6	−34.6
1,2-difluorobenzene $[Me_2Cl]^+$ 3 position	−7.8	+54.7	−74.2	3.1	−44.3
1,2,3-trifluorobenzene $[Me_2Cl]^+$	−4.9	+52.3	−82.9	2.5	−20.4
1,2,3,4-tetrafluoroben-zene $[Me_2Cl]^+$	−2.6	+58.1	−73.1	2.4	−33.5
5-methyl-1,2,3,4-tetra-fluorobenzene $[Me_2Cl]^+$	−3.0	+50.9	−83.7	2.6	n/a

3.3 Fluoride ion affinity of $[MeN_3C_3F_{3-x}(OTeF_5)_x]^+$

Table S3: Fluoride ion affinity (FIA) of the ions $[MeN_3C_3F_{3-x}(OTeF_5)_x]^+$ (x = 0-3) and methyl cation affinity (MCA) of $N_3C_3F_{3-x}(OTeF_5)_x$ in kJ·mol^{-1} on the RI-B3LYP-D3/def2-TZVPP level of theory and NPA charge at the carbon atoms of the cations. For the FIA Me_3SiF/Me_3Si^+[2] was used as anchor point. Note that the basicity of the molecules increases with introduction of pentafluoro-*ortho*tellurates when they are not incorporated in a hypervalent 3-center-4-electron bond. This was already shown in our previous publication[3].

x	MCA	FIA	NPA charge at C2	C4	C6
0	358.5	778.6	0.843	0.829	0.843
1	390.4	752.0	0.762 (C-O)	0.826	0.841
2	413.4	722.4	0.762 (C-O)	0.827	0.761 (C-O)
3	427.1	713.0	0.756	0.743	0.764

3.4 Optimized structures for reaction paths in the $AlCl_3$ system – COSMO MeCl

All structures on RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R = 10 for MeCl at 20 °C[4]).

MeCl

$coord

-0.00000000000000	0.00000000000000	0.30503759877231	c
-0.97535892335006	-1.68937121085797	0.93667402965344	h
-0.97535892335006	1.68937121085797	0.93667402965344	h
1.95071784670010	0.00000000000000	0.93667402965344	h
0.00000000000000	0.00000000000000	-3.11505968773260	cl

$end

E(COSMO) = -500.0657429646 H
ZPE = 98.07 kJ/mol
enthalpy = 108.53 kJ/mol
chem. pot. = 38.47 kJ/mol

$[Me_2Cl]^+$

$coord

-1.98360120477685	-0.02090808471483	1.83393088418715	c
-2.26106970734948	-1.97835324876680	1.29937005869955	h
-0.51359934238604	0.26073558779988	3.23186952105531	h
-3.73568619042416	0.92615434172789	2.32054135723187	h
-0.93222622329660	1.62285488433355	-1.02150424329913	cl
2.00744317945521	-0.02066111904581	-1.80773532536949	c
2.66308371405147	0.94019287189733	-3.49613040468612	h
3.25789959918452	0.24403272350288	-0.20752278047561	h
1.49775617554186	-1.97404795673409	-2.15281906734350	h

$end

E(COSMO) = -539.7233454861 H
ZPE = 200.6 kJ/mol
enthalpy = 215.57 kJ/mol
chem. pot. = 129.95 kJ/mol

1,2-difluorobenzene

$coord

1.31162206342536	0.00000000000000	-2.16918401906098	c
-1.31162206342536	0.00000000000000	-2.16918401906098	c
-2.64335468403867	0.00000000000000	0.07812658019130	c
-1.31495430401535	0.00000000000000	2.35048561207893	c
1.31495430401535	0.00000000000000	2.35048561207893	c
2.64335468403867	0.00000000000000	0.07812658019130	c
-4.68602689915431	0.00000000000000	0.02353198005730	h
-2.34404762081789	0.00000000000000	4.11557725031850	h
2.34404762081789	0.00000000000000	4.11557725031850	h
4.68602689915431	0.00000000000000	0.02353198005730	h
2.54850372039953	0.00000000000000	-4.39867022285120	f
-2.54850372039953	0.00000000000000	-4.39867022285120	f

$end

E(COSMO) = -430.6907320838 H
ZPE = 219.4 kJ/mol
enthalpy = 237.56 kJ/mol
chem. pot. = 142.04 kJ/mol

4-methyl-1,2-difluorocyclohexa-2,6-dien-5-ylium cation

$coord

-0.76808470465442	-3.26992964724035	-0.65035289894714	c
1.90350838286613	-3.20628585560641	-0.73715293516839	c
3.29793006754614	-0.96169305739365	-0.66387065334508	c
2.00489473399269	1.25411332698597	-0.47771842898981	c
-2.07900993647128	-1.08740610804448	-0.46165711301768	c
5.33543224627457	-1.06074598843354	-0.75008731974105	h
3.01846674288333	3.02881546128205	-0.41630978306196	h
-4.12180046146039	-1.12363579348292	-0.38262068111546	h
-1.88647287207475	-5.51980447595306	-0.74179166752216	f
3.09096438634723	-5.35667962166329	-0.90238987156938	f
-0.76448213198015	1.35806516802001	-0.37485397380760	c
-1.32505398493185	2.35089701316919	-2.13445713868449	h
-1.75220113846926	3.09272121955992	1.79610943839738	c
-0.88775835816601	4.94978737359004	1.63333161256084	h
-3.79286263845939	3.27952410793295	1.64533959925994	h
-1.27347033324256	2.27225687727765	3.61848181475212	h

$end

E(COSMO) = -470.3614095711 H

ZPE = 323.1 kJ/mol

enthalpy = 345.77 kJ/mol

chem. pot. = 238.30 kJ/mol

$[AlCl_4]^-$

$coord

-0.00000000000000	0.00000000000000	0.00000000000000	al
2.36258413755740	2.36258413755740	-2.36258413755740	cl
-2.36258413755740	-2.36258413755740	-2.36258413755740	cl
2.36258413755740	-2.36258413755740	2.36258413755740	cl
-2.36258413755740	2.36258413755740	2.36258413755740	cl

$end

E(COSMO) = -2083.5272602171 H

ZPE = 15.12 kJ/mol

enthalpy = 36.36 kJ/mol

chem. pot. = -67.25 kJ/mol

$[AlCl_4H]$

$coord

-0.14432999888736	1.30703967655044	-0.18792593092383	al
1.79476690217931	2.72010320877650	-3.37551990998299	cl
1.15529159189850	2.49290806338780	3.39284139321171	cl
-4.07421841778577	0.69559438060665	-0.52562226494805	cl
1.43632835722188	-3.06504760550980	-0.39676021602734	cl
-0.16783843462657	-4.15059772381169	1.09298692867036	h

$end

E(COSMO) = -2083.9064867914 H

ZPE = 36.39 kJ/mol

enthalpy = 59.96 kJ/mol

chem. pot. = -54.75 kJ/mol

$[AlCl_4Me]$

$coord

0.08160305304419	2.81462867175809	-1.32924821692563	al
2.01079003955966	4.30680626447988	-4.49396450869580	cl
1.29799866919275	4.03504814493417	2.28983508224994	cl

-3.88521369212266	2.35068914892103	-1.66360978335807	cl
1.53478733879697	-1.43483879080622	-1.41774476130605	cl
-0.06805329439596	-2.83722498505905	1.31994844488605	c
-2.07887609199732	-2.67144485712392	0.97003335201242	h
0.56226415510593	-4.78457646772645	1.36216498099658	h
0.54469982281643	-1.77908712937756	2.96258541014056	h

$end
E(COSMO) = -2123.2102972575 H
ZPE = 115.3 kJ/mol
enthalpy = 142.89 kJ/mol
chem. pot. = 18.26 kJ/mol

[$AlCl_4Me$]/MeCl pre complex

$coord

1.28736292935101	3.12804407677777	-2.90146007394298	al
2.82941031929878	5.43080977931968	-5.77641796275453	cl
2.44093343283996	3.89791681074282	0.86277020815303	cl
-2.58003062372487	2.12176415435079	-3.24908412457407	cl
3.34329614553940	-0.76636735379228	-3.72891453485583	cl
2.04697321381006	-2.79992833830572	-1.22833496062150	c
0.01975559734740	-2.84399101793353	-1.50184978053147	h
2.91801822495316	-4.62892308477621	-1.52346192061738	h
2.58728590458502	-1.95163892590004	0.55351310302765	h
-3.07436417631915	-0.02573250317277	3.67998821853283	c
-4.36900609844131	0.32057965777495	5.23101438657380	h
-1.42305209374479	1.18113046519912	3.80928843314894	h
-4.00476821952228	0.21209894037005	1.86965602082179	h
-2.02181455597239	-3.27576266065451	3.90329298763965	cl

$end
E(COSMO) = -2623.2807162483 H
ZPE = 216.6 kJ/mol
enthalpy = 256.75 kJ/mol
chem. pot. = 96.65 kJ/mol

[$AlCl_4$]$^-$/[Me_2Cl]$^+$ product complex

$coord

-0.04862037764516	0.12802308424633	-2.55988593555717	al
-0.09280682419995	1.23094091805765	-6.46473684173792	cl
3.24874086988418	1.65788886809153	-0.65612402038177	cl
-3.39641649903897	1.51718765522227	-0.62799342059195	cl
0.03731574046811	-3.94394875170477	-2.16384585018870	cl
0.00853498019337	-2.34303563453237	4.15267765715521	c
-1.67763755131100	-1.96915501085085	3.05604628879740	h
0.02013014239759	-4.20199911129009	5.01501399375952	h
1.74923667748934	-1.89525112839738	3.17353837386664	h
0.08049503172068	2.94413018627940	5.39064764607791	c
-0.08204374509593	4.23348839455753	6.97575745653485	h
1.90832107064855	3.01796498467959	4.47224199453289	h
-1.49048738352629	3.07137057509755	4.08264326011822	h
-0.13351743752434	-0.18157624488120	6.86877586759051	cl

$end
E(COSMO) = -2623.2733213067 H
ZPE = 219.8 kJ/mol
enthalpy = 257.79 kJ/mol
chem. pot. = 107.26 kJ/mol

[$AlCl_4$Me]/MeCl to [Me_2Cl]$^+$/[$AlCl_4$]$^-$ transition state

$coord

-0.00009461363604	0.08496282481222	-2.73249799222143	al
-0.00548297131103	-0.23709328344099	-6.74678630737370	cl
3.33034390120885	1.87560823645434	-1.23391822222236	cl
-3.31632122428977	1.89480957101589	-1.22690314690663	cl
-0.00784284726355	-3.80845450304230	-1.09800413919473	cl
0.02072839952804	-2.30405872268007	3.20985811174003	c
-1.73471239508545	-1.36646303563462	2.79641466691607	h
-0.00511022908978	-4.20777648708403	3.93067803671709	h
1.79869859830249	-1.41360721292710	2.78969566046712	h
0.00517271744059	2.80322046112228	6.05063241211374	c
0.05846801555196	3.98072885016167	7.72611887564188	h
1.66532953449278	3.06947949368848	4.87897349586707	h
-1.73310608489105	3.05692537574324	4.99573475318852	h
0.05409759603688	-0.44917097867435	7.16761452449441	cl

$end

E(COSMO) = -2623.2576558948 H

ZPE = 215.6 kJ/mol

enthalpy = 253.20 kJ/mol

chem. pot. = 102.51 kJ/mol

[$AlCl_4$]$^-$/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

-0.53139047228232	-3.47126527299218	-1.04795161140233	c
1.95283993880297	-3.52005285613964	-0.07842920747424	c
3.58493571898297	-1.45176567971916	-0.22172967255746	c
2.74991791462736	0.67822296543344	-1.40251663149193	c
-1.39190860086465	-1.38307416176644	-2.24294469461553	c
5.43848712029238	-1.59723398684958	0.62003174302582	h
3.97147646634391	2.30828889479392	-1.55836481744976	h
-3.28610076496307	-1.34998341871542	-3.00444863747524	h
-1.96048093035088	-5.51751173919455	-0.72189112970510	f
2.74490649062217	-5.61659324311425	0.95637728070957	f
0.27474907996175	0.80364755023929	-2.65111737479572	c
0.84319499878899	0.55346442089762	-4.66957512481775	h
-1.04882210447531	3.40041851950261	-2.57926388055275	c
0.26033427596622	4.86117395046737	-3.19579347943928	h
-2.67476745565922	3.38415581936519	-3.83722468876522	h
-1.67251417394045	3.80886016903879	-0.66856056073185	h
-1.86729181906643	0.83375974371700	5.29952004047781	al
1.03046167982298	3.41519155545673	3.97887168981371	cl
-4.85498223996796	0.65850312087247	2.50060540543357	cl
-0.21406771265398	-2.89145500562919	5.65641492817675	cl
-3.34897740998737	2.09324865433605	8.86799042363699	cl

$end

E(COSMO) = -2553.9140237952 H

ZPE = 339.9 kJ/mol

enthalpy = 386.34 kJ/mol

chem. pot. = 217.26 kJ/mol

[AlC_{l4}Me]/ 1,2-difluorobenzene pre complex

$coord

-0.71606574143950	-1.54560211121765	-5.24184154634909	c
1.50546066361727	-0.38374028460119	-6.01664472913306	c
1.51119997604033	2.12263317817555	-6.75594290623937	c
-0.74885555914126	3.47206472016229	-6.71974304044262	c

-2.96349702396884	-0.21467167987414	-5.19222790617758	c
3.26852078554104	2.97872664314395	-7.35076288338538	h
-0.76006974494703	5.43155754870103	-7.29801443395492	h
-4.65795827417610	-1.15800192633840	-4.55467227199195	h
-0.65583162554755	-3.98965438383008	-4.54625100797786	f
3.66297603645156	-1.73491039595028	-6.04812152726723	f
-2.97556570587271	2.30731660424462	-5.94309684418603	c
-4.72799580875577	3.35697390204502	-5.90833550195647	h
-0.05099113788327	4.11081953114004	-0.30568670778022	c
0.14087950188514	6.14560151249581	-0.41289096647210	h
-1.92294910768623	3.46655626505592	-0.81932223127755	h
1.42553466200186	3.12928156961120	-1.32821929740423	h
0.02913873929451	-1.14413280206121	2.99810778179168	al
0.37694080124950	3.33490458822305	3.04944446325148	cl
-3.64006261879178	-1.67281319464712	1.47511037232051	cl
3.01887040404648	-2.15455318306748	0.53516661725184	cl
0.50383629067753	-1.96737491326731	6.88075551916669	cl

$end
E(COSMO) = -2553.9073609475 H
ZPE = 337.3 kJ/mol
enthalpy = 386.14 kJ/mol
chem. pot. = 206.25 kJ/mol

[$AlC_{14}Me$]/ 1,2-difluorobenzene to [$AlCl_4$]$^-$/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-1.22528932886222	-1.17039593230465	-4.93019140964077	c
1.15175527573226	-0.66690520225056	-5.97659201125054	c
1.96776801145497	1.77961877186910	-6.39185797304977	c
0.38708388160233	3.76478237060373	-5.72724049744851	c
-2.80598651541094	0.77313522746639	-4.26938774525757	c
3.80959698001485	2.09464504166967	-7.21414208408886	h
0.98307586584435	5.69139016386601	-6.04609995135933	h
-4.63217298455279	0.35851596475195	-3.45534429801676	h
-1.91403082750461	-3.57953296607869	-4.59737803070531	f
2.63394008667032	-2.61396292098322	-6.57068625821160	f
-1.97075433281409	3.28662589683879	-4.59426264994715	c
-3.28735494480462	4.81942353480740	-4.29528789393954	h
-0.16572430326727	3.72592869149962	-0.73839698705096	c
0.62903564867470	5.58071526904937	-1.00329161509299	h
-2.03282663013244	3.54399940443334	0.03974114185186	h
0.98382407527169	2.08318493706222	-1.06216723722430	h
0.19149640599338	-0.52939636321266	4.00815467029647	al
1.40546564846146	3.49172727736304	3.66780633055674	cl
-3.78247836818533	-0.55012026000093	3.13343473496998	cl
2.23223604894047	-2.54473486640140	1.12022993959317	cl
1.01984000324391	-1.79797578282732	7.74361914648245	cl

$end
E(COSMO) = -2553.8800120345 H
ZPE = 336.5 kJ/mol
enthalpy = 382.76 kJ/mol
chem. pot. = 211.78 kJ/mol

MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

0.76948454182133	-5.56629692184129	-1.80278767280899	c
3.43919227299942	-5.48547431145900	-1.68487853101357	c

4.82647313743952	-3.24400665522078	-1.88172535240271	c
3.52589303493779	-1.04508252330760	-2.18221924189085	c
-0.54901949925134	-3.39987688856244	-2.09681061222167	c
6.86405687979841	-3.33098258925351	-1.78396464150460	h
4.53318783073132	0.72691854298678	-2.34259857457801	h
-2.59137848464948	-3.44708347069551	-2.17776122421921	h
-0.34170909089584	-7.81257161221133	-1.59868542533689	f
4.63324490584134	-7.61847195893954	-1.38747881948004	f
0.75827762950659	-0.96033673518189	-2.32533697367683	c
0.34789390778888	-0.29296321544218	-4.27040536844688	h
-0.40432864165762	1.11147168726950	-0.57923631177186	c
0.47363665138859	2.92354803368411	-0.98610203185355	h
-2.42397408171107	1.24662242116057	-0.92765253290673	h
-0.08252394202991	0.62499171458449	1.39085981760995	h
-3.43204679921443	4.63010275995609	3.99086563239410	cl
-4.88651843546651	7.35941416868696	5.45971083360773	c
-3.65949161759616	8.97087985783851	5.14278793624380	h
-6.71703681554717	7.64321085210919	4.58138762267572	h
-5.08331338423342	6.96598684383887	7.46203147158124	h

$end
E(COSMO) = -970.4294204007 H
ZPE = 423.5 kJ/mol
enthalpy = 459.38 kJ/mol
chem. pot. = 311.69 kJ/mol

[$Me_2Cl]^+$/1,2-difluorobenzene pre complex

$coord

-1.66891517764385	-1.89832024000188	-0.69061499404700	c
0.04648127235565	-2.31721135942973	1.25342522938950	c
2.58111720746947	-2.69815052774330	0.73780350054484	c
3.39273566831381	-2.66040199098982	-1.76731600191432	c
-0.87567929906650	-1.85616190399333	-3.18030992076471	c
3.87475265133222	-3.02072743579766	2.28587424697474	h
5.36912349594858	-2.95983516996494	-2.18726579698011	h
-2.24892343097575	-1.52651323552372	-4.65671511139368	h
-4.11761429579647	-1.51504902569378	-0.11011235076103	f
-0.79652934340545	-2.32761797613324	3.65722563019927	f
1.67254461983709	-2.24309068071536	-3.71463592184018	c
2.30680021659724	-2.21490172118539	-5.65611319574297	h
1.54166202831379	4.17360098461031	-0.77773023620976	c
3.06780854342557	5.40748268628194	-0.19388081863597	h
0.46568886758513	4.86995012464748	-2.37397806868961	h
2.13976913494171	2.22632041450162	-1.00434081754039	h
-0.65623105243260	4.01521523621535	1.88873014917118	cl
-1.58222558337190	7.32176852323199	2.33689827755285	c
0.13786886223661	8.33950676062753	2.78372864224563	h
-2.46971321796648	7.90672959102522	0.58643866426687	h
-2.89549321078583	7.24464593871715	3.90948359108410	h

$end
E(COSMO) = -970.4182898177 H
ZPE = 422.4 kJ/mol
enthalpy = 458.28 kJ/mol
chem. pot. = 315.64 kJ/mol

[$Me_2Cl]^+$/1,2-difluorobenzene to MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-1.33152625302950	-3.67539316609001	-0.81735914932688	c
0.74595549699146	-4.38199765701428	0.65148282888412	c
3.04907295762989	-3.15921036969960	0.42905727920354	c
3.27411964984753	-1.19654289202474	-1.29017945657141	c
-1.13149559060092	-1.73346079196900	-2.52785973274950	c
4.61730867705318	-3.76863158436189	1.58611267563279	h
5.06353437872414	-0.23673630896757	-1.50815398097098	h
-2.74794122432703	-1.22165873687220	-3.66694784260579	h
-3.50725592816887	-4.93707592531629	-0.53453698897053	f
0.47195359625916	-6.27493659610349	2.28994006747475	f
1.17818055906611	-0.42315435419031	-2.73239015212237	c
1.42620390342530	0.92674474676695	-4.24592147855944	h
0.17172145905272	2.80360186034597	0.05054453014585	c
1.98978722968425	3.66434047741117	-0.24265431330357	h
-1.38499674394893	3.28128279417278	-1.16575304987843	h
-0.09348025203183	1.47827039283612	1.57032745099976	h
-0.97529817499185	6.18378483198970	2.84042743267312	cl
-0.41254443792056	8.89500160827697	0.80875515602002	c
1.58474791399877	8.91757977009705	0.35324099509930	h
-1.58791429957144	8.67120807090046	-0.85435219493068	h
-0.95706426285152	10.54165944690571	1.90079067768982	h

$end
E(COSMO) = -970.3981142369 H
ZPE = 419.8 kJ/mol
enthalpy = 454.47 kJ/mol
chem. pot. = 315.07 kJ/mol

HCl

$coord

0.00000000000000	0.00000000000000	-1.21390505723017	cl
0.00000000000000	0.00000000000000	1.21390505723017	h

$end
E(COSMO) = -460.7717134059 H
ZPE = 17.28 kJ/mol
enthalpy = 25.95 kJ/mol
chem. pot. = -29.81 kJ/mol

4-methyl-1,2-difluorobenzene

$coord

-0.65023211120992	-3.30409011592959	0.03045925414114	c
1.97246505952747	-3.32516658175968	0.00283088970811	c
3.29675802508388	-1.07883416235667	-0.02769726121707	c
1.96937907264004	1.19556579446449	-0.03025784245751	c
-0.66633094511619	1.24539133724800	-0.00279974645640	c
-1.96938802955267	-1.05426720372143	0.02779706123429	c
5.33961549233345	-1.12557251407358	-0.04933281709629	h
3.01459838100913	2.95267878691404	-0.05438511902524	h
-1.90578610211027	-5.52524353740089	0.05973058016550	f
3.20271867705380	-5.56175247667663	0.00579030928515	f
-4.01352389978290	-1.11712665933995	0.04945686702332	h
-2.10841487214619	3.69940439600604	-0.00334532959747	c
-3.36167973161540	3.82002399585194	-1.63805125709458	h
-3.28636810917644	3.86409008244769	1.68296417071912	h
-0.83381090693777	5.31489885832611	-0.05315975933212	h

$end
E(COSMO) = -469.9964338503 H
ZPE = 290.9 kJ/mol

enthalpy = 313.46 kJ/mol
chem. pot. = 206.28 kJ/mol

$[AlCl_4]^-$/$[Me_2Cl]^+$/1,2-difluorobenzene pre complex

$coord

-0.67673053920736	-2.70146625521096	-3.58794647026301	c
1.79596848128220	-2.21821899879709	-4.31948121460451	c
2.48906537139214	0.14258332307882	-5.19764278826589	c
0.66678578980866	2.03615601841502	-5.34986999482817	c
-2.49309732248165	-0.83000667835549	-3.72498065369329	c
4.42936289383184	0.46694319084435	-5.74983358646377	h
1.19340894461372	3.88584795338300	-6.04081609070934	h
-4.39621724138329	-1.25336803327321	-3.11963602861011	h
-1.28130520138649	-5.01496904838430	-2.73086038424758	f
3.51841621259906	-4.08327811686596	-4.16555873645893	f
-1.81343537391210	1.55097264639672	-4.61838795088639	c
-3.22552647480873	3.02333770034363	-4.73519447344227	h
0.11140525406233	3.37949634215398	0.94702172235953	c
0.22816537043532	4.90278089633757	-0.41546665869150	h
-1.78247939429917	2.64299863717930	1.18441772411410	h
1.51645369299733	1.91945159497601	0.65858309001109	h
-0.72527944056840	-4.30352035499201	4.12308565515521	al
2.68641633280542	-2.96574893138570	2.28085674415127	cl
-3.86473171304520	-1.95714181055970	2.91184448377739	cl
-1.41312882173167	-8.20895280513716	3.28148762129834	cl
-0.25465859769555	-3.74765782981526	8.15864064268014	cl
0.92494936322967	4.93541093699972	3.94639112816194	cl
0.62421825515469	2.38470105924223	6.28439574121878	c
2.04871183199891	1.00083353006869	5.79472248942940	h
0.98649180980547	3.32322010966250	8.06993071487190	h
-1.29322948349722	1.68959492369524	6.11429727393572	h

$end
E(COSMO) = -3053.9703637609 H
ZPE = 440.1 kJ/mol
enthalpy = 499.98 kJ/mol
chem. pot. = 294.64 kJ/mol

$[AlCl_4]^-$/MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

0.79826366844593	-5.13871714120132	-0.85918695864815	c
3.11581791054971	-4.88315005156298	0.43487812569676	c
4.68294024042465	-2.77875897862708	0.15960018032045	c
3.95564902349966	-0.92462734042236	-1.47233226239319	c
0.04943588235952	-3.32896521677092	-2.50108049464667	c
6.39942721002448	-2.67583765117998	1.25884632571046	h
5.13230100868250	0.72423061441788	-1.73866560303443	h
-1.71483756006708	-3.53167066419925	-3.50910581290850	h
-0.59414225024670	-7.18176536333343	-0.38583373391829	f
3.81640005846986	-6.72730179040595	1.91960099614065	f
1.67915325364414	-1.14411102868611	-3.04316725914930	c
2.53057002875902	-1.67589992042048	-4.90110375627164	h
0.26594847340598	1.35202632367587	-3.57491967325943	c
1.59549757589956	2.77071803803121	-4.24339281396154	h
-1.16572313029659	1.04446796251347	-5.01784874977357	h
-0.63680648268904	2.02851506683656	-1.86385038671189	h
-1.61237071297707	0.01694364669791	4.40864132473545	al
1.38158852464094	2.48917729139529	3.10054384289391	cl

-4.13855450949656	-0.79178630723221	1.28540784063958	cl
0.05715697407189	-3.49441550923331	5.66507522266912	cl
-3.67175307989656	1.82993364846983	7.40709842425696	cl
-3.51868680161185	6.95745953483951	-1.44445688194799	cl
-4.47328978479417	6.35326378832602	1.78553118518597	c
-2.77598137418716	6.24688963524971	2.92770546839621	h
-5.68151292970764	7.89613646077567	2.38745666467001	h
-5.47649121690736	4.56724495204642	1.81455878530886	h

$end
E(COSMO) = -3053.9853590830 H
ZPE = 441.3 kJ/mol
enthalpy = 500.34 kJ/mol
chem. pot. = 296.98 kJ/mol

$[AlCl_4]^-/[Me_2Cl]^+$/1,2-difluorobenzene to $[AlCl_4]^-$/MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-0.89152623391072	-1.73936947352121	-4.47005392932207	c
1.58242161532642	-1.63330449568052	-5.37912918097226	c
2.52956495743174	0.53292806118710	-6.49801611469624	c
0.96932786404011	2.62498940735877	-6.71381634441234	c
-2.45167344033428	0.32448176731470	-4.66051169035700	c
4.45425257213743	0.54367682346309	-7.17940233693123	h
1.66673502878211	4.32496187437744	-7.60520215945181	h
-4.35914474421413	0.21124929561622	-3.94630832476001	h
-1.70353527422853	-3.88241775580134	-3.40390678947271	f
3.04118415871636	-3.67386990809565	-5.14318887869662	f
-1.51002844583016	2.55954206786429	-5.75506465015156	c
-2.80557060666712	4.08319449710587	-6.17216387681665	h
-0.34410689729383	4.74767500965895	-2.12289016139380	c
0.18611860348944	6.32620900295590	-3.28774072108073	h
-2.26238847765384	4.55280668834228	-1.47808105227660	h
1.03727659818835	3.35644688864499	-1.57395275881513	h
-0.73627014888883	-1.75146176831346	3.23936968339059	al
2.60146964339917	-0.78132483055608	1.04764048407033	cl
-3.89200237750276	0.43546047794567	1.78469835571055	cl
-1.51054159795250	-5.72591070680549	2.96902189450050	cl
-0.08762106627529	-0.66116424788123	7.12240231863973	cl
0.68348883226529	7.37299552131424	1.46272349297823	cl
0.65727267029162	5.27711255161650	4.19084701921326	c
2.07751969190660	3.84031962417371	3.86630641784904	h
1.11412450183108	6.45516933398691	5.80453931093650	h
-1.22261874256523	4.48190865837170	4.32910589159936	h

$end
E(COSMO) = -3053.9524216110 H
ZPE = 438.0 kJ/mol
enthalpy = 496.20 kJ/mol
chem. pot. = 297.47 kJ/mol

Single-point energies for above shown structures at different levels of theory, all with def2-TZVPP basis set.

		E(B3LYP+COSMO) in eV	E(B3LYP+D3) in eV
1	MeCl	-13607,45371355	-13607,37439064
2	$[Me_2Cl]^+$	-14686,52112381	-14684,36967036
3	*o*DFB	-11719,52257631	-11719,56811474
4	[4Me4H-*o*DFB]$^+$	-12798,89355985	-12797,13395657
5	$[AlCl_4]^-$	-56695,50503494	-56693,82848653
6	$[AlCl_4H]$	-56705,80303746	-56705,61738367
7	$[AlCl_4Me]$	-57775,21886443	-57775,17952447
8	$[AlCl_4Me]$/MeCl pre complex	-71382,62671960	-71382,81087141
9	$[AlCl_4]^-/[Me_2Cl]^+$ product complex	-71382,37748959	-71381,89128726
10	8 to 9 transition state	-71381,97419864	-71381,91260346
11	$[AlCl_4]^-$/[4Me4H-*o*DFB]$^+$ product complex	-69494,68370425	-69494,61946133
12	$[AlCl_4Me]$/oDFB pre complex	-69494,61727191	-69494,97268284
13	11 to 12 transition state	-69493,82325323	-69493,94201240
14	MeCl/[4Me4H-*o*DFB]$^+$ product complex	-26406,34985256	-26404,71301909
15	$[Me_2Cl]^+$/oDFB pre complex	-26405,95195835	-26404,34104829
16	14 to 15 transition state	-26405,41057723	-26403,93371057
17	HCl	-12538,23753085	-12538,12054729
18	4Me-*o*DFB	-12789,01029192	-12789,13082377
19	$[AlCl_4]^-/[Me_2Cl]^+$/oDFB pre complex	-83101,73898705	-83101,72378767
20	$[AlCl_4]^-$/MeCl/[4Me4H-*o*DFB]$^+$ product complex	-83102,07502133	-83102,29653641
21	19 to 20 transition state	-83101,17595363	-83101,39633469

		E(m06+COSMO+D3) in eV	E(m06+COSMO) in eV	E(m06+D3) in eV
1	MeCl	-13608,07750839	-13608,07716469	-13607,97360666
2	$[Me_2Cl]^+$	-14686,95542403	-14686,94767236	-14684,70938636
3	*o*DFB	-11718,59339329	-11718,56993779	-11718,47389979
4	[4Me4H-*o*DFB]$^+$	-12797,92279323	-12797,88234089	-12795,87493845
5	$[AlCl_4]^-$	-56699,60575555	-56699,60247722	-56697,76612536
6	$[AlCl_4H]$	-56709,88163445	-56709,87363482	-56709,52497370
7	$[AlCl_4Me]$	-57779,19804589	-57779,18128883	-57778,88893103
8	$[AlCl_4Me]$/MeCl pre complex	-71387,38214596	-71387,32799465	-71387,09619894
9	$[AlCl_4]^-/[Me_2Cl]^+$ product complex	-71387,16927269	-71387,11923233	-71386,14937886
10	8 to 9 transition state	-71386,69170374	-71386,64094566	-71386,12135410
11	$[AlCl_4]^-$/[4Me4H-*o*DFB]$^+$ product complex	-69498,26809507	-69498,15777638	-69497,33996958
12	$[AlCl_4Me]$/oDFB pre complex	-69497,99155033	-69497,87727532	-69497,61647468
13	11 to 12 transition state	-69497,15670142	-69497,04648510	-69496,48216919
14	MeCl/[4Me4H-*o*DFB]$^+$ product complex	-26406,03845814	-26405,98510227	-26404,02353602
15	$[Me_2Cl]^+$/oDFB pre complex	-26405,64140045	-26405,56559970	-26403,56303808
16	14 to 15 transition state	-26405,01699309	-26404,94932157	-26403,07454117
17	HCl	-12539,02198809	-12539,02198735	-12538,90742872
18	4Me-*o*DFB	-12787,99006632	-12787,95474678	-12787,86971897
19	$[AlCl_4]^-/[Me_2Cl]^+$/oDFB pre complex	-83105,97122999	-83105,81408200	-83104,92749343
20	$[AlCl_4]^-$/MeCl/[4Me4H-*o*DFB]$^+$ product complex	-83106,50553312	-83106,35092567	-83105,61865513
21	19 to 20 transition state	-83105,40156803	-83105,24546064	-83104,51876417

		E(B2PLYP+COSMO+D3) in eV	E(B2PLYP+COSMO) in eV	E(B2PLYP+D3) in eV
1	MeCl	-13604,95165110	-13604,93490416	-13604,84282181
2	$[Me_2Cl]^+$	-14683,70139576	-14683,64564825	-14681,44889938
3	*o*DFB	-11717,00284693	-11716,91318180	-11716,87693925
4	[4Me4H-*o*DFB]$^+$	-12796,06583343	-12795,90899103	-12794,01682563
5	$[AlCl_4]^-$	-56684,90854128	-56684,81565870	-56683,07439325
6	$[AlCl_4H]$	-56695,18437993	-56695,08082080	-56694,81062065
7	$[AlCl_4Me]$	-57764,34087157	-57764,18348373	-57764,01944394
8	$[AlCl_4Me]$/MeCl pre complex	-71369,39441307	-71369,13092714	-71369,09491334
9	$[AlCl_4]^-/[Me_2Cl]^+$ product complex	-71369,19288576	-71368,90137769	-71368,16624920
10	8 to 9 transition state	-71368,70020288	-71368,41972609	-71368,12160122
11	$[AlCl_4]^-$/[4Me4H-*o*DFB]$^+$ product complex	-69481,64435697	-69481,17803069	-69480,69477926
12	$[AlCl_4Me]$/oDFB pre complex	-69481,50359791	-69481,10262276	-69481,11151262
13	11 to 12 transition state	-69480,69204835	-69480,25921922	-69480,00516253
14	MeCl/[4Me4H-*o*DFB]$^+$ product complex	-26401,07523758	-26400,86928622	-26399,05874770
15	$[Me_2Cl]^+$/*o*DFB pre complex	-26400,81591894	-26400,55980536	-26398,72524165
16	14 to 15 transition state	-26400,17597040	-26399,92171659	-26398,22263472
17	HCl	-12536,06264571	-12536,06260569	-12535,94399596
18	4Me-*o*DFB	-12786,24343889	-12786,11265666	-12786,11808462
19	$[AlCl_4]^-/[Me_2Cl]^+$/oDFB pre complex	-83086,35600067	-83085,80117660	-83085,29768970
20	$[AlCl_4]^-$/MeCl/[4Me4H-*o*DFB]$^+$ product complex	-83086,72546311	-83086,12970134	-83085,82268845
21	19 to 20 transition state	-83085,78461439	-83085,18569752	-83084,88887254

3.5 Optimized structures for reaction paths in the $[Me_2X]^+$ system – COSMO SO_2

All structures on the RI-B3LYP-D3/def2-TZVPP level of theory with COSMO (ε_R = 17.6 for SO_2 at 20 °C[5]).

MeCl

$coord

0.00000000000000	0.00000000000000	0.30637490808900	c
-0.97553808240623	-1.68968152344587	0.93647831279739	h
-0.97553808240623	1.68968152344587	0.93647831279739	h
1.95107616481245	0.00000000000000	0.93647831279739	h
0.00000000000000	0.00000000000000	-3.11580984648114	cl

$end

E(COSMO) = -500.0660811218 H
ZPE = 97.25 kJ/mol
enthalpy = 107.74 kJ/mol
chem. pot. = 34.92 kJ/mol

$[Me_2Cl]^+$

$coord

-1.98180326193356	-0.02131516935396	1.83118016465804	c
-2.26083864247687	-1.97763232425139	1.29387300540267	h
-0.50898001143314	0.25727900959446	3.22657509888194	h
-3.73226963863705	0.92616396555571	2.32187918357650	h
-0.93309760175267	1.62423891208472	-1.02242347055642	cl
2.00548255869734	-0.01993956196023	-1.80522521091350	c
2.66159808781640	0.93702686410424	-3.49538742550695	h
3.25490150105379	0.24800375524369	-0.20492583481124	h
1.49500700866568	-1.97382545101722	-2.14554551073098	h

$end

E(COSMO) = -539.7291366492 H
ZPE = 201.1 kJ/mol
enthalpy = 215.91 kJ/mol
chem. pot. = 130.66 kJ/mol

MeBr

$coord

0.00000000000000	0.00000000000000	0.38271196959917	c
-0.97823546024063	-1.69435351890230	0.98820497983510	h
-0.97823546024063	1.69435351890230	0.98820497983510	h
1.95647092048124	0.00000000000000	0.98820497983510	h
0.00000000000000	0.00000000000000	-3.34737403120829	br

$end

E(COSMO) = -2613.9491087438 H
ZPE = 96.37 kJ/mol
enthalpy = 107.04 kJ/mol
chem. pot. = 33.51 kJ/mol

$[Me_2Br]^+$

$coord

0.05314153946580	1.62387123353746	2.34114357175232	c
-0.17471397329586	3.54793028441753	3.00877559884958	h
1.96158661042506	0.91914650526824	2.56666725811094	h
-1.39505996628559	0.35706564101903	3.03962613056818	h
-0.51090740645040	1.88835889209863	-1.34805855222387	br
-0.03160704956732	-1.70205915411860	-2.28531297103378	c

-0.33563765027720	-1.72248444144125	-4.31187563134162	h
1.89113707682529	-2.16689743641332	-1.75908908036529	h
-1.45793918083973	-2.74493152436763	-1.25187632431644	h

$end
E(COSMO) = -2653.6152620210 H
ZPE = 196.4 kJ/mol
enthalpy = 212.49 kJ/mol
chem. pot. = 121.72 kJ/mol

MeI

$coord

0.00000000000000	0.00000000000000	0.46073540816364	c
-0.97909680493718	-1.69584541167952	1.05930323410005	h
-0.97909680493718	1.69584541167952	1.05930323410005	h
1.95819360987433	0.00000000000000	1.05930323410005	h
0.00000000000000	0.00000000000000	-3.63869723988383	i

$end
E(COSMO) = -337.6136671023 H
ZPE = 95.20 kJ/mol
enthalpy = 106.04 kJ/mol
chem. pot. = 30.18 kJ/mol

$[Me_2I]^+$

$coord

-0.00003414751966	0.00000962792181	-0.53430831156309	i
-3.03179189830635	0.00007607482261	2.18416695708707	c
-2.83178447291680	1.72852531835198	3.26310876171838	h
-4.73840548409708	-0.02881085111426	1.04846728813510	h
-2.79720893198294	-1.70157949952102	3.29824532506166	h
3.03208958518733	0.00006829674999	2.18386918207193	c
4.73901276542950	-0.01251021485839	1.04832085530059	h
2.82214332704637	1.72078136933296	3.27321739911238	h
2.80699469891293	-1.70933864042406	3.28806624420272	h

$end
E(COSMO) = -377.2883560804 H
ZPE = 194.6 kJ/mol
enthalpy = 210.81 kJ/mol
chem. pot. = 117.90 kJ/mol

1,2-difluorobenzene

$coord

1.31150582329906	0.00000000000000	-2.16856719252402	c
-1.31150582329906	0.00000000000000	-2.16856719252402	c
-2.64406784552604	0.00000000000000	0.07811315992355	c
-1.31503671216498	0.00000000000000	2.35030960861693	c
1.31503671216498	0.00000000000000	2.35030960861693	c
2.64406784552604	0.00000000000000	0.07811315992355	c
-4.68677896087381	0.00000000000000	0.02420734630269	h
-2.34371171713491	0.00000000000000	4.11565141404106	h
2.34371171713491	0.00000000000000	4.11565141404106	h
4.68677896087381	0.00000000000000	0.02420734630269	h
2.54760811961374	0.00000000000000	-4.39984715562640	f
-2.54760811961374	0.00000000000000	-4.39984715562640	f

$end
E(COSMO) = -430.6911045433 H
ZPE = 219.5 kJ/mol
enthalpy = 237.60 kJ/mol

chem. pot. = 142.09 kJ/mol

4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation

$coord

-0.76806534264309	-3.26708652465925	-0.64733265745518	c
1.90283027456452	-3.20349476513272	-0.73238009326137	c
3.29703864394969	-0.95954126357027	-0.66491650794870	c
2.00320778998631	1.25647792372052	-0.48481101212735	c
-2.08018116047832	-1.08495767555115	-0.46830312742700	c
5.33449360997307	-1.05775363521029	-0.74936751913608	h
3.01621952450661	3.03143051472277	-0.42563926331447	h
-4.12297644170358	-1.12018072585804	-0.39257448436682	h
-1.88654594725865	-5.51922664475955	-0.73207908257566	f
3.09080193288858	-5.35570913499161	-0.88902143921712	f
-0.76561800803187	1.35976111190817	-0.38200012527424	c
-1.32956512984975	2.35920268838582	-2.13607544184348	h
-1.74955315075034	3.08637693423215	1.79795403522237	c
-0.87844172676384	4.94108787895174	1.64484906264279	h
-3.78944083389397	3.27965372317119	1.64596095602338	h
-1.27420403449539	2.25395959464048	3.61573670005898	h

$end

E(COSMO) = -470.3667835484 H

ZPE = 323.0 kJ/mol

enthalpy = 345.76 kJ/mol

chem. pot. = 237.87 kJ/mol

4-methyl-1,2-difluorocyclohexa-2,6-dien-4-yliumcation

$coord

-2.04882273049047	-3.36225380451209	-0.03195777903573	c
0.49322163204851	-3.41410183196194	-0.07285965615982	c
0.51557080057887	1.36209129953975	0.04825551221889	c
-3.31632475590583	-1.00017813894110	0.06530584214579	c
1.50334084184167	-5.18936564078304	-0.13074618391208	h
-5.78525011924492	-1.04590567763304	0.11363618463998	f
-3.46432665112606	-5.44506017053635	-0.07037664803823	f
1.94953306064026	3.76740926653727	-0.01249531664278	c
2.52121877861267	4.13330235723909	-1.96869230639879	h
0.81150401523410	5.35436906021092	0.62701267623432	h
3.67776030232281	3.63758370110859	1.10033380707393	h
1.92949837839217	-1.03894507005532	-0.01001424588958	c
3.20573951366684	-1.08733621890213	1.63655463897617	h
3.29193350123573	-1.00595890360556	-1.58095207393942	h
-2.08019190395826	1.31527536190953	0.10916277651411	c
-3.20440466384805	3.01907441038566	0.17783277221324	h

$end

E(COSMO) = -470.3788746487 H

ZPE = 320.1 kJ/mol

enthalpy = 343.45 kJ/mol

chem. pot. = 234.95 kJ/mol

3-methyl-1,2-difluorocyclohexa-1,5-dien-4-yliumcation

$coord

-0.08404418850664	-2.26209822396932	-0.52676492982544	c
2.50036879391992	-2.27167386526424	-0.70938356521369	c
3.80395428971337	0.00851344076391	-0.74433612406772	c
2.55031954436830	2.35004115037201	-0.61418136822234	c
-0.01485349752180	2.40448646780844	-0.43643109071428	c

```
   5.84470131032029    -0.06221293502643    -0.88323593166515  h
   3.64744618330584     4.06975505366389    -0.65415160911885  h
  -1.02772690031400     4.17696923531417    -0.33809601705184  h
  -1.32582271460365    -4.39894102934166    -0.48242079974917  f
   3.75263839835753    -4.45015867877545    -0.83546708554500  f
  -1.54561469517157     0.08501766331842    -0.38737489908910  c
  -2.67740460967384     0.13075181644245    -2.14815805833003  h
  -3.51180384357039     0.05480670993919     1.81333787834744  c
  -4.67796149135065     1.73979882525994     1.67878638101869  h
  -4.70144181158832    -1.61017807140046     1.64847720597703  h
  -2.53275476768440     0.03512244089505     3.61940001324947  h
$end
E(COSMO) = -470.3636036517 H
ZPE = 323.1 kJ/mol
enthalpy = 346.05 kJ/mol
chem. pot. = 237.98 kJ/mol
```

3-methyl-1,2-difluorocyclohexa-1,5-dien-3-yliumcation

```
$coord
  -0.05960005099312    -2.36390782114664    -0.03215139045722  c
   2.59041461605517    -2.32391743518297    -0.05112854781688  c
   4.02974874098377    -0.09348210100530    -0.02376896740327  c
   2.76589840699763     2.13476929190543     0.03199568141180  c
  -1.41586418031518    -0.16917839682096     0.02390976992054  c
   6.06618365437362    -0.23225393015556    -0.04565254682716  h
   3.78003704516022     3.90817816041554     0.06027577722073  h
  -4.21773618484117    -0.16991745191720     0.00241386081464  c
  -4.97175180718344     1.66985255932801     0.51834362483028  h
  -4.87471789397975    -0.63545618467424    -1.90352658077024  h
  -4.96349844118307    -1.61943248374464     1.26188637390617  h
  -1.20450156916335    -4.61149302442163    -0.07657443845666  f
   3.76501231630293    -4.49756890024348    -0.10080449540246  f
  -0.00256711410057     2.22936963776407     0.07259075091230  c
  -0.60986241469344     3.32609517009480     1.73765847886231  h
  -0.67719512342020     3.44834290980464    -1.47546735074492  h
$end
E(COSMO) = -470.3791394158 H
ZPE = 319.6 kJ/mol
enthalpy = 343.06 kJ/mol
chem. pot. = 234.48 kJ/mol
```

[$Me_2Cl]^+$/1,2-difluorbenzene pre complex

```
$coord
   1.99009994250624    -1.87137788902849    -2.60751811307687  c
  -0.56469852760366    -2.39913880499734    -2.90609512928192  c
  -1.82506493472790    -3.89798914580658    -1.17668792733569  c
  -0.49397327295916    -4.87619729349828     0.87364491731018  c
   2.06405707930428    -4.34076870978220     1.17707849013439  c
   3.32163174005978    -2.82445604333577    -0.57063543864442  c
  -3.81331534291054    -4.27915077396817    -1.45152393603610  h
  -1.46569742407680    -6.05127648303227     2.23284402398546  h
   3.09135474761421    -5.09735811959729     2.77224343379269  h
   5.30640586658318    -2.37839830269507    -0.38069420374337  h
   3.15023610195760    -0.38924692224770    -4.32651536893425  f
  -1.79897132724640    -1.41369461502593    -4.90305306480046  f
  -1.01961465870669     2.03885868705789     2.51541916982546  c
  -0.24593545937240     0.14306570483650     2.40096319040638  h
```

-0.33852130909536	3.06880505094833	4.14887681494930	h
-3.05410477728309	2.08337005775552	2.29320899325154	h
0.29674440540789	3.63829140151735	-0.25057114658074	cl
-1.00708270611725	6.83378021321277	0.02398829436666	c
-0.23449554354587	7.80944646197289	-1.60504618362121	h
-3.04226561798223	6.62481433170509	-0.06222864832824	h
-0.31678898180586	7.57862119400878	1.80230183236122	h

$end
E(COSMO) = -970.4239864498 H
ZPE = 422.6 kJ/mol
enthalpy = 458.43 kJ/mol
chem. pot. = 315.63 kJ/mol

MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

0.75915934637169	-5.55527931493427	-1.69576170311792	c
3.42798494726331	-5.48337796365936	-1.56832197717986	c
4.82743250541091	-3.25859713786056	-1.84027182785870	c
3.53930349643698	-1.06578979211531	-2.22814685577591	c
-0.54786769895697	-3.39558440201020	-2.07510555363493	c
6.86385275117824	-3.35073968324306	-1.72829810258907	h
4.55649081242985	0.69392268532006	-2.44865269443517	h
-2.59008433457076	-3.43492494735372	-2.16315401661417	h
-0.36473320550752	-7.78844652936523	-1.41271889162280	f
4.60953152209386	-7.61131513621929	-1.18594683049783	f
0.77356039365954	-0.97401008620570	-2.39385440145301	c
0.38766406431582	-0.39777580341908	-4.37388325616761	h
-0.39518935327737	1.17992882278607	-0.75950701327182	c
0.49843806804366	2.96642210106762	-1.23963429192896	h
-2.41031145260581	1.30844230887519	-1.13740995293383	h
-0.09749215551521	0.78196968260770	1.23411393935883	h
-3.50092758310924	4.81995456914065	3.66814213383265	cl
-4.89292406113767	7.30037782323603	5.57517034409024	c
-3.62887638674274	8.91358533657098	5.52572546443232	h
-6.71619807903976	7.76762388335063	4.76275444101374	h
-5.09881359674050	6.58361358343054	7.48476104635393	h

$end
E(COSMO) = -970.4348227302 H
ZPE = 423.7 kJ/mol
enthalpy = 459.46 kJ/mol
chem. pot. = 312.14 kJ/mol

[Me_2Cl]$^+$/1,2-difluorbenzene to MeCl/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-1.33182419449973	-3.68077807704182	-0.82709927213673	c
0.74783907742453	-4.38417541779778	0.64086042533519	c
3.04441967442020	-3.14948417568782	0.42976372757511	c
3.26116290153852	-1.17684612246478	-1.27948139799879	c
-1.14111721448837	-1.73019267524313	-2.52695638889973	c
4.61339429932684	-3.75339082126031	1.58851341387068	h
5.04342130247407	-0.20162758147471	-1.48549875748449	h
-2.75863299691846	-1.21754914925191	-3.66400046777810	h
-3.50194654929278	-4.95631940223310	-0.55047339690733	f
0.47913497950402	-6.28744387156020	2.27013417810836	f
1.16358609807556	-0.40759569404644	-2.72268157295280	c
1.40754777359649	0.94862966620164	-4.23098509641730	h

0.18951403495068	2.78516076800300	0.05688606328290	c
2.01271731361393	3.64323886588075	-0.21089866530604	h
-1.35645467948589	3.28937371471888	-1.16228974450178	h
-0.10324109025465	1.47058782511830	1.58088798035769	h
-0.96132650396897	6.19304333610437	2.85533872739120	cl
-0.40960450604346	8.88402419143914	0.79464663605749	c
1.58345916963921	8.89613127684599	0.32063647248627	h
-1.59895199122049	8.64630717718051	-0.85652737986800	h
-0.94002824410121	10.54358178366292	1.87379526961943	h

$end
E(COSMO) = -970.4033517994 H
ZPE = 420.1 kJ/mol
enthalpy = 454.67 kJ/mol
chem. pot. = 315.52 kJ/mol

MeCl/3-methyl-1,2-difluorocyclohexa-1,5-dien-4-yliumcation product complex

$coord

2.84734372191151	-2.28703867209017	-2.22486959932576	c
5.37771995903123	-2.28555266638436	-1.66801673371347	c
6.58139815062437	-0.01614140802523	-1.12000359000317	c
5.28364675431035	2.30481794626431	-1.13028224776552	c
2.77202230187567	2.34839494822425	-1.68290504436259	c
8.57984582352311	-0.07838084048805	-0.68237937634848	h
6.30388066651363	4.01739183502017	-0.69535468256690	h
1.72842157094988	4.10553959101509	-1.70993592238671	h
1.69670390869990	-4.41531727634824	-2.73133633606064	f
6.66832257242418	-4.44538026195302	-1.63580952189456	f
1.34946784648739	0.03964420569553	-2.29122748919727	c
0.77141543106569	0.26015934201673	-4.29179477192604	h
-1.16514622635129	-0.19612368432792	-0.76641911849354	c
-2.28222553448270	1.49985157606734	-1.06640329710269	h
-2.22173591847785	-1.82792371209531	-1.42485457883538	h
-0.74841031610117	-0.40175784760252	1.23396320767363	h
-5.85165081024008	0.95596065367934	3.73612123331749	cl
-8.99113291841805	0.20833332371786	4.88080605762175	c
-9.01051096106014	0.51324414529964	6.90797168135066	h
-10.31645490855913	1.45439900586031	3.93553019542817	h
-9.37292111372652	-1.75412020354590	4.42719993459079	h

$end
E(COSMO) = -970.4315342973 H
ZPE = 422.9 kJ/mol
enthalpy = 459.27 kJ/mol
chem. pot. = 309.33 kJ/mol

[$Me_2Cl]^+$/1,2-difluorbenzene to MeCl/3-methyl-1,2-difluorocyclohexa-1,5-dien-4-yliumcation transition state

$coord

2.67974148539883	-1.19895338464756	-1.24865971533633	c
4.11559915819411	-0.74815633505807	0.88995616971620	c
4.56335213748251	1.70554193103076	1.68379255058985	c
3.56621025208277	3.73465915130910	0.32651815388191	c
2.12711474322455	3.30208975345264	-1.81289754381143	c
5.68744259491851	2.00258473773256	3.36448880418074	h
3.93427986713840	5.64156405579987	0.95454017450230	h
1.35740765863727	4.85893917429317	-2.88655248491614	h
2.26083204368889	-3.56850238411717	-1.99939007488998	f
5.07414803539403	-2.70950496416895	2.17348519410523	f

1.59819270494123	0.80899973785086	-2.59391976196718	c
0.73665406130456	0.42395737919383	-4.40669334346107	h
-2.19459005062088	0.63461622263629	-0.59687916271176	c
-2.90313049965310	2.14377708712127	-1.75976179692054	h
-2.38146365558044	-1.29452552993475	-1.21496438850812	h
-1.38362521097757	1.04941850969264	1.22218740688745	h
-6.28954630584057	0.31231081353115	1.39022011015995	cl
-8.17193668053100	-0.79561587674850	-1.26002298801238	c
-10.09501595661696	-0.94275039917998	-0.56696395784206	h
-8.01252213633712	0.59894582967433	-2.75241772830741	h
-7.42860652470511	-2.62082380858602	-1.81971985207865	h

$end
E(COSMO) = -970.4021506663 H
ZPE = 420.0 kJ/mol
enthalpy = 454.56 kJ/mol
chem. pot. = 315.35 kJ/mol

[Me_2Br]$^+$/1,2-difluorobenzene pre complex

$coord

-1.59173185327548	-3.59353482930626	0.52779231882701	c
0.75723108694219	-3.49346626553744	1.69913077462211	c
2.95197950960157	-3.41227005451037	0.28188333473324	c
2.77470980706224	-3.44556548950169	-2.34416991077257	c
-1.78172179831781	-3.61567090601062	-2.07890916213938	c
4.75422460754629	-3.33074602761995	1.24056152324517	h
4.48063809434932	-3.38741320471629	-3.46609097351289	h
-3.63187093377881	-3.69051626064665	-2.94209633516373	h
-3.68657534420692	-3.65443173864455	1.97598419397817	f
0.86202379805287	-3.46065984537241	4.24467327755276	f
0.42126050950613	-3.54700942748548	-3.51770576073780	c
0.28990251474988	-3.56818390826210	-5.55597189759411	h
0.36763134846199	3.22899785327689	-1.08596552728291	c
2.02502956488992	4.38746779304843	-0.76972777122630	h
-1.08267516331759	4.12794419853182	-2.21611480122703	h
0.82950582159808	1.34021171728576	-1.73464758393009	h
-1.81921378049632	6.23650963089477	3.24702788906560	c
-2.67953090255942	6.08375488119464	5.10066665480110	h
0.01037546481097	7.15347124529136	3.28228596798594	h
-3.09828909485750	6.96508971434804	1.82489849473405	h
-1.15290325676152	2.67602092374216	2.28649529404164	br

$end
E(COSMO) = -3084.3106534837 H
ZPE = 418.8 kJ/mol
enthalpy = 455.68 kJ/mol
chem. pot. = 308.04 kJ/mol

MeBr/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

1.54901864882099	-5.61214770037832	-2.03365129125503	c
4.08376218293536	-5.23477239405218	-1.27348544226796	c
5.18080265517065	-2.84216696610578	-1.03999074491497	c
3.71569656403417	-0.79073110767351	-1.55257996933724	c
0.06967551094717	-3.59682404866925	-2.54908643675178	c
7.13261837147954	-2.70118820239093	-0.45812102864922	h
4.49703555721805	1.09164652308393	-1.39136877619545	h
-1.87379722147606	-3.87097052029370	-3.12159504509788	h
0.71684117103885	-7.98110935549200	-2.19222266875814	f

5.43677146600386	-7.23409266437072	-0.78239540008962	f
1.07206976034418	-1.01397260013164	-2.35746750704270	c
1.05437375133063	-0.26896569968153	-4.31793272574227	h
-0.72492936260021	0.78573733382677	-0.86983114547595	c
-0.00720699116581	2.70796630922930	-0.97515460687747	h
-2.60288864477365	0.71770012975270	-1.69967044229694	h
-0.82507150460675	0.19746132553950	1.09663454154531	h
-5.91421974038567	7.38184703107752	5.29389828890461	c
-4.69822571552461	8.35540719773405	6.62319241841755	h
-6.69815680962635	8.66488926953367	3.90363720367569	h
-7.37687944921632	6.31208394142291	6.24773899541236	h
-3.78729019994768	4.93220219803908	3.44945178279695	br

$end
E(COSMO) = -3084.3178570300 H
ZPE = 422.1 kJ/mol
enthalpy = 458.34 kJ/mol
chem. pot. = 307.46 kJ/mol

$[Me_2Br]^+$/1,2-difluorobenzene to MeBr/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-1.00526061551273	-4.91323047277864	-1.26948174795438	c
0.18578658511013	-5.62992833336855	0.97704886396716	c
2.54637315412729	-4.70537503217577	1.62540381190522	c
3.73146063834338	-3.03137306197601	-0.00067126550521	c
0.14869383151008	-3.25642920423521	-2.89647185352162	c
3.41174311843412	-5.31347922139999	3.37191910826717	h
5.58103322209831	-2.30044186071281	0.46237582407570	h
-0.78257220428869	-2.73217339649225	-4.63709556145291	h
-3.28062473133386	-5.88804101347659	-1.80175312495939	f
-1.00487615793913	-7.23831947726978	2.50551605203721	f
2.52067012462144	-2.23255560544547	-2.23353076780054	c
3.56297510557011	-1.16040310610367	-3.62567175595761	h
1.09318348751973	1.36988739560487	-0.43165314632189	c
2.97702490893003	1.99586068311747	0.00442881440044	h
0.23832192350974	1.89441438209875	-2.19979857583117	h
0.00290433780890	0.36835448620438	0.96234048824177	h
0.65857332393074	7.85340561231413	-1.15904112198807	c
0.24672862546127	9.74178943031780	-0.48152364762039	h
2.67146228807194	7.52159096547335	-1.33068623599482	h
-0.36441707618116	7.40968091931895	-2.87565453652639	h
-0.60134589582557	5.53767641597671	1.48466606122985	br

$end
E(COSMO) = -3084.2884993251 H
ZPE = 417.2 kJ/mol
enthalpy = 452.76 kJ/mol
chem. pot. = 308.24 kJ/mol

$[Me_2I]^+$/1,2-difluorobenzene pre complex

$coord

-1.69927770189475	-5.27476462719825	0.36974525678203	c
0.63113223948906	-4.77834132866019	1.47644934261035	c
2.82955569489707	-4.88057030635190	0.06442318703669	c
2.67706491247769	-5.52007363151978	-2.48461278773841	c
-1.86306974366263	-5.90315776084704	-2.16138821641410	c
4.61546613243583	-4.47778495265602	0.97065900685109	h
4.38620546549455	-5.61349695964199	-3.59892703683196	h

-3.69742791995836	-6.28832102781911	-2.97375362844854	h
-3.79784165255791	-5.12415016465466	1.80229884015006	f
0.71521334529523	-4.17283995816943	3.95133783115457	f
0.34442325860960	-6.03386737347322	-3.58905542665606	c
0.23144458185066	-6.53411444628167	-5.56639769535687	h
-0.01196383956687	1.11724936204883	-3.37036890193383	c
1.48111737756280	2.43483311182200	-3.84471356246294	h
-1.77784348682704	1.48365826662018	-4.33958497203405	h
0.58682197911809	-0.83703044050222	-3.53564559303904	h
-0.76428408280351	1.63338336421918	0.59603408940873	i
-1.91963055640630	5.53291451817286	0.32347024214387	c
-2.43303929481245	6.04799817112403	2.24029370763597	h
-0.28882488245687	6.56210407338727	-0.36361717768466	h
-3.51758331637032	5.55786458187137	-0.95661070101980	h

$end
E(COSMO) = -807.9841536595 H
ZPE = 416.1 kJ/mol
enthalpy = 453.36 kJ/mol
chem. pot. = 303.50 kJ/mol

MeI/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

1.33920863763666	-5.56679304478438	-2.10351112472438	c
4.00114963456343	-5.40271748620562	-1.92776388265558	c
5.30058695589082	-3.10578689650979	-1.79558283605480	c
3.91735457566099	-0.93666325110028	-1.81978828865132	c
-0.06079292119222	-3.43236683254365	-2.12887321778008	c
7.33837134538005	-3.12773378169648	-1.67321967412868	h
4.85582572407043	0.87705562865923	-1.72097136225567	h
-2.09832979939841	-3.54425025829370	-2.25506478739702	h
0.31488118956349	-7.86184736269268	-2.22340614323449	f
5.27475986704285	-7.51175689353714	-1.89947555854277	f
1.15160370431328	-0.93767939642013	-2.00285155081552	c
0.74292103380943	-0.03041902734447	-3.84879400488529	h
-0.12050358943752	0.83630362005051	-0.02036706533810	c
0.69146035590347	2.71765085909230	-0.16404522015392	h
-2.13787063505176	0.94226820858323	-0.39020396789400	h
0.18632836939348	0.10097991010587	1.87362278631864	h
-3.07252046095874	5.24410246028114	4.95936791756945	i
-6.52894874329802	7.44467958549076	4.80227896999065	c
-6.43905876653190	8.80627878511838	6.32875425846450	h
-6.57352006434868	8.35573276830555	2.96914393492554	h
-8.08290641301113	6.13296240544145	5.04075081724306	h

$end
E(COSMO) = -807.9818923994 H
ZPE = 420.4 kJ/mol
enthalpy = 456.84 kJ/mol
chem. pot. = 303.65 kJ/mol

$[Me_2I]^+$/1,2-difluorobenzene to MeI/4-methyl-1,2-difluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-1.50826567576781	-6.42994740334275	0.10543002331102	c
0.96602604223740	-6.94330612228253	0.87899280917957	c
3.02995777481693	-5.93024361911251	-0.37418007346574	c
2.60887896976387	-4.36998139150671	-2.42922777507133	c
-1.95171239003244	-4.88701152637598	-1.92823105046926	c

4.91231646849458	-6.38725039389089	0.27133383463687	h
4.19152730687201	-3.57141523975115	-3.44264467577383	h
-3.87087679726057	-4.51986393636121	-2.52295115554375	h
-3.42199881440861	-7.48967723646522	1.37933952484435	f
1.31121631538132	-8.44422056425702	2.86813488334641	f
0.12261934943419	-3.75570248674553	-3.17550713577673	c
-0.19270107127761	-2.82203226539154	-4.96536002291537	h
0.09242891875011	-0.10516394914428	-1.17776899138680	c
1.66795263864955	0.62690724537162	-2.23231904649572	h
-1.80077331571548	0.28282673645224	-1.81058672332927	h
0.38940328687159	-0.91717048843492	0.66257418647156	h
-0.08884213503714	4.62827592926761	1.28620356824330	i
-2.21604470429481	6.49136900669745	-1.67082804780920	c
-2.32624232655523	8.46099596063258	-1.11997429406883	h
-1.16455589458579	6.23808002474032	-3.40890401023498	h
-4.05910031228900	5.60236420348043	-1.72690919691189	h

$end
E(COSMO) = -807.9561531740 H
ZPE = 416.2 kJ/mol
enthalpy = 451.68 kJ/mol
chem. pot. = 305.98 kJ/mol

1,2,3-trifluorobenzene

$coord

2.28801502948160	0.00000000000000	-1.41087615615178	c
2.25727956942908	0.00000000000000	1.20217068761598	c
0.00000000000000	0.00000000000000	2.53734936609071	c
-2.25727956942908	0.00000000000000	1.20217068761598	c
-2.28801502948160	0.00000000000000	-1.41087615615178	c
0.00000000000000	0.00000000000000	-2.70751194701200	c
4.08114935454070	0.00000000000000	-2.38812944317907	h
-4.08114935454070	0.00000000000000	-2.38812944317907	h
0.00000000000000	0.00000000000000	-4.74965124417619	h
-4.43287406856290	0.00000000000000	2.52094614652681	f
0.00000000000000	0.00000000000000	5.07159135547361	f
4.43287406856290	0.00000000000000	2.52094614652681	f

$end
E(COSMO) = -529.9341046636 H
ZPE = 198.5 kJ/mol
enthalpy = 218.75 kJ/mol
chem. pot. = 117.81 kJ/mol

[$Me_2Cl]^+$/1,2,3-trifluorobenzene pre complex

$coord

-2.11066889302329	-3.03264220996156	-0.36862591206716	c
-0.42583753641006	-3.48025437435324	1.59499070838651	c
2.10271588066480	-3.89936517453699	1.02523855020271	c
2.95343613189393	-3.87416210996076	-1.44723395008716	c
-1.31284862376869	-2.99395568437136	-2.85747029725640	c
4.93204371467190	-4.20891029074368	-1.82464011848346	h
-4.54692375862241	-2.61644418943308	0.21873148205592	f
-1.22815427643202	-3.50087088264189	3.99678699011864	f
1.22893810332347	-3.42051679350116	-3.38183899426731	c
1.87439156514420	-3.39563896118550	-5.31860036260438	h
1.06397344832332	3.08937424110357	-0.52180308904243	c
2.58027087403565	4.32964544168289	0.07439892227470	h
-0.02984218856449	3.80405433865757	-2.09744733602240	h

1.69071182780192	1.15702976006031	-0.79682234007568	h
-1.11089811811283	2.86422554679915	2.15582090320088	cl
-2.05283225794565	6.15875838189660	2.66237265284372	c
-0.33374708745809	7.17503129978747	3.11541985617149	h
-2.95133120184705	6.76328665420688	0.92445434085706	h
-3.35690669957376	6.04712949882894	4.24014556758737	h
-2.67340429267604	-2.63348823318346	-4.33666749936219	h
3.70691338857515	-4.33228625915079	2.94278992556947	f

$end
E(COSMO) = -1069.6657950631 H
ZPE = 401.4 kJ/mol
enthalpy = 439.52 kJ/mol
chem. pot. = 291.49 kJ/mol

[$Me_2Cl]^+$/1,2,3-trifluorobenzene to MeCl/4-methyl-1,2,3-trifluorocyclohexa-2,6-dien-5-yliumcation transition state

$coord

-3.06063640361632	1.41692548599516	-2.22613438070131	c
1.11223141045630	3.54680698620121	0.20293782268677	c
-1.34916789521382	4.21291261641790	0.86327880370955	c
-3.44063672494728	3.16838713689360	-0.32877663452286	c
-4.65808081629481	0.59537757172568	-3.19534290821263	h
-5.30950007446205	3.75587746725539	0.24426158601274	h
3.07859145105020	4.59005103287109	1.37836226731286	f
-1.65297211983450	5.89732037221583	2.70315202533722	f
-0.60220469439958	0.63332334801959	-2.89193382836872	c
-0.26377568228447	-0.48477651482452	-4.56772517417659	h
-0.61693294051339	-2.86800940420600	-0.41876963395142	c
-2.16144082929975	-3.64919086073759	-1.48562391335503	h
1.30112992473678	-3.23696814203859	-0.98916501042280	h
-0.99075888904408	-1.79014522562929	1.26548760796934	h
1.46072049864838	1.79551913894252	-1.70093853392296	c
3.80296095454590	1.15328494556881	-2.35494046744859	f
-0.51287955296949	-6.62988824074299	2.13465632454270	cl
0.17583840784937	-8.98932496091195	-0.26380664651445	c
0.26399965016121	-10.78576707936241	0.71872355629704	h
-1.35552435948696	-8.94649836557928	-1.62397939890115	h
1.97821911180681	-8.49972280246716	-1.10584991082671	h

$end
E(COSMO) = -1069.6449846757 H
ZPE = 399.1 kJ/mol
enthalpy = 435.88 kJ/mol
chem. pot. = 291.62 kJ/mol

MeCl/4-methyl-1,2,3-trifluorocyclohexa-2,6-dien-5-yliumcation product complex

$coord

-3.38482538975231	0.77293396881671	-2.28799827000506	c
-0.77743512043883	5.42428819667932	-2.54781452318278	c
-3.42539404267351	5.24518439577639	-2.46611882717011	c
-4.74394299393562	2.94263418836913	-2.34493375497420	c
-4.32895945386655	-1.03694772663925	-2.19627605483004	h
-6.78430417169913	2.98255604798726	-2.30245313204760	h
0.31644052755226	7.67189082117223	-2.66717927387837	f
-4.69209298322229	7.35495301618790	-2.51504241419872	f
-0.60102368172632	0.72993990563241	-2.33337867532701	c
-0.05081861383340	-0.28430382312509	-4.07124218609133	h
0.50610725805408	-0.84967134722197	-0.09479582876553	c

-0.27494557115788	-2.74629570030003	-0.17433467054198	h
2.54804735505880	-0.95119009453016	-0.27391179912885	h
0.00754943442285	0.02680660901600	1.69511096929802	h
0.58157407976089	3.23513791119605	-2.49175007443267	c
3.05013008773838	3.33572168356616	-2.56819372023737	f
2.85517980471407	-4.23634018415716	4.99753326920576	cl
4.56463640061401	-7.02139703103626	6.02048529962113	c
5.20855218141064	-6.69490653371420	7.93915171881659	h
3.27662347037818	-8.61404377025427	5.93634210457788	h
6.14890142260151	-7.28695053342115	4.74679984329213	h

$end
E(COSMO) = -1069.6780406515 H
ZPE = 403.0 kJ/mol
enthalpy = 441.35 kJ/mol
chem. pot. = 286.84 kJ/mol

4-methyl-1,2,3-trifluorocyclohexa-2,6-dien-5-yliumcation

$coord

-2.00529333361741	-1.34032467157481	-0.41363620776387	c
0.59972480954493	3.30876640828500	-0.72792317658376	c
-2.04872943478210	3.12731701063364	-0.68472502537807	c
-3.36590811794954	0.82572502143940	-0.53476989205577	c
-2.94924225660538	-3.14907575352205	-0.29891195587407	h
-5.40671992129867	0.86362142449759	-0.52043908044709	h
1.69248364963355	5.55522626491216	-0.87492926115340	f
-3.31731287220510	5.23338188300256	-0.79889520972628	f
0.77927054483339	-1.38179145478342	-0.43258814481881	c
1.32928177436146	-2.38847143625185	-2.17756902413206	h
1.88487925078511	-2.96920043557819	1.79533011119556	c
1.10172354067314	-4.86570576549375	1.70397632622722	h
3.92762518613406	-3.07000998253337	1.61434515114223	h
1.38676805862437	-2.10222052443932	3.59020991770043	h
1.96115371860268	1.12374519906235	-0.60347179160819	c
4.43029540326545	1.22901681234407	-0.63600273672410	f

$end
E(COSMO) = -569.6102582690 H
ZPE = 302.9 kJ/mol
enthalpy = 327.82 kJ/mol
chem. pot. = 214.75 kJ/mol

4-methyl-1,2,3-trifluorocyclohexa-1,3-dien-5-yliumcation

$coord

0.83904361582463	-1.40919660441531	-0.00018592630730	c
2.08361358057330	0.95816609361468	0.01802848644426	c
0.87538392189973	3.32254217783264	0.01778777162455	c
-1.69951975037438	3.36664877378488	-0.00004619456397	c
2.24848754678546	5.41566548969376	0.03446295837105	f
4.55010938925479	0.99097396244240	0.03596111769506	f
-2.90494567967852	5.52333164694063	-0.00119749986488	f
2.37536259441412	-3.78831943319751	0.00218849791560	c
3.62088283131238	-3.84874018046896	-1.63836549044994	h
3.55716296507017	-3.88482061418957	1.68780787925621	h
1.14031422484708	-5.42935363261115	-0.03899122011196	h
-1.73126780199920	-1.32809852524739	-0.01777546096693	c
-2.81382770406872	-3.06116992773608	-0.03225761089104	h
-3.17921805231649	1.04042219540794	-0.01783404402332	c
-4.47183598811057	1.07216016463937	-1.64980981467229	h

-4.48974569343380	1.05978841350961	1.60022655054476	h

$end
E(COSMO) = -569.6169951187 H
ZPE = 300.2 kJ/mol
enthalpy = 325.62 kJ/mol
chem. pot. = 212.27 kJ/mol

4-methyl-1,2,3-trifluorobenzene

$coord

-2.01095197696475	-1.18772444151316	-0.01392540202605	c
0.62463021125639	-1.26864520386724	-0.00240174143826	c
1.88509360446129	1.03608273479329	0.00946456392096	c
0.61507155613896	3.32724646029438	0.00872980207006	c
-2.00632073609738	3.32790425388557	-0.00134595159772	c
-3.33784055035715	1.08383979311326	-0.01266428888956	c
-3.05270186440602	-2.94626997634383	-0.02455598852554	h
-5.37965800691240	1.13068977321062	-0.02169087029020	h
1.90681704658258	5.50982499966815	0.01710068545811	f
4.43381798989923	1.08997390403208	0.02061949662978	f
-3.21864428791539	5.56820551466859	-0.00102340628679	f
2.09501266677373	-3.69894874224357	0.00293393942825	c
3.38822681233566	-3.78876714983554	-1.60094767533181	h
3.23461889375397	-3.87124454735048	1.71405341433309	h
0.82282864145121	-5.31216737251219	-0.09434657745428	h

$end
E(COSMO) = -569.2408597212 H
ZPE = 270.5 kJ/mol
enthalpy = 295.18 kJ/mol
chem. pot. = 183.23 kJ/mol

1,2,3,4-tetrafluorobenzene

$coord

-1.31186114772797	0.00000000000000	-2.19721006997244	c
1.31186114772797	0.00000000000000	-2.19721006997244	c
2.60130765809146	0.00000000000000	0.08767333830251	c
1.31501378087919	0.00000000000000	2.35976982237568	c
-1.31501378087919	0.00000000000000	2.35976982237568	c
-2.60130765809146	0.00000000000000	0.08767333830251	c
2.37041068243037	0.00000000000000	4.10718956182616	h
-2.37041068243037	0.00000000000000	4.10718956182616	h
-5.14333888018899	0.00000000000000	0.03660453164630	f
-2.56191708329083	0.00000000000000	-4.39402718417821	f
2.56191708329083	0.00000000000000	-4.39402718417821	f
5.14333888018899	0.00000000000000	0.03660453164630	f

$end
E(COSMO) = -629.1755247502 H
ZPE = 177.3 kJ/mol
enthalpy = 199.88 kJ/mol
chem. pot. = 93.62 kJ/mol

[$Me_2Cl]^+$/1,2,3,4-tetrafluorobenzene pre complex

$coord

-2.18488986516411	-2.98249004848241	-0.40312450660763	c
-0.54518160173094	-3.44504607390978	1.59316835711142	c
1.99791516130193	-3.88255225000001	1.10388782010976	c
2.91783640356702	-3.86588465662108	-1.34141651997350	c
-1.25547354542019	-2.96648872748818	-2.85871621348359	c

```
   4.90266355607508    -4.21438466730007    -1.66681518426905  h
  -4.62674591343191    -2.54303258998023     0.06043303447800  f
  -1.42546396272234    -3.44674105086650     3.96130897870916  f
   1.27356562954242    -3.40477329344540    -3.34247409359900  c
   1.94262025175746    -3.37965504624427    -5.27084164494208  h
   1.15363408651399     3.14999428933707    -0.60876745183025  c
   2.45753065194194     4.71194952490670    -0.37780557948273  h
  -0.26435373005994     3.45876301396657    -2.05262460204472  h
   2.12088294234199     1.35180127893145    -0.80275144113451  h
  -0.54673975497254     2.86190124255076     2.38732159047951  cl
  -1.97184371917933     5.99817804882016     2.76569468574851  c
  -0.40872005468866     7.31582641376775     2.88191705085042  h
  -3.17994066234576     6.27065103941722     1.13500343554285  h
  -3.01910094783267     5.83811424826992     4.52071972511019  h
   3.54012512887923    -4.32112673046870     3.06937884689540  f
  -2.87832005437269    -2.50500396516101    -4.75349628766812  f
$end
E(COSMO) = -1168.9063177589 H
ZPE = 381.3 kJ/mol
enthalpy = 421.41 kJ/mol
chem. pot. = 268.35 kJ/mol
```

[$Me_2Cl]^+$/1,2,3,4-tetraflurobenzene to MeCl/5-methyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation transition state

```
$coord
   1.19813818442210     2.48018342083545    -2.22702604364857  c
   0.55345103943093     4.17808222982430    -3.15831107803295  h
   3.11344455890256     2.60493397149467    -0.48677239654612  c
   4.19970412715639     4.80258659038705     0.11196681406728  f
   4.00271131173844     0.42059792332749     0.70711606836234  c
   5.84160380289933     0.57201713113471     2.38961462064487  f
   2.94948944423944    -1.92096777261165     0.15058953209186  c
   3.80406354990215    -3.98509744976735     1.29654720588927  f
   1.01780194263228    -2.05577725424069    -1.60892908040351  c
   0.01700135675526    -4.29461759925526    -2.14705416638086  f
   0.05629966721942     0.12824196944253    -2.75698306003903  c
  -1.18417785603878    -0.07628797322989    -4.36693244804101  h
  -3.24795306364820     0.46336574944382    -0.14481204152993  c
  -3.92927817666769     2.06797009421812    -1.19105044648140  h
  -3.85423783637003    -1.41111530213349    -0.65406453842910  h
  -2.09845405524641     0.75087952006325     1.50922002899158  h
  -6.97192177518199     0.77768001187689     2.55344395273395  cl
  -9.44126208550937     0.23490394301911     0.22960692828679  c
 -11.21496445449324     0.32207129621668     1.25257145741474  h
  -9.30469089568757     1.72368159353172    -1.17112623929880  h
  -9.12758774990930    -1.62157309460572    -0.57825444262853  h
$end
E(COSMO) = -1168.8832430307 H
ZPE = 377.6 kJ/mol
enthalpy = 416.65 kJ/mol
chem. pot. = 267.09 kJ/mol
```

MeCl/(5-methyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation product complex

```
$coord
   3.46625171204221     1.11141528437772    -2.00182569721321  c
   3.48082020739088     3.14170108859726    -1.77356178425571  h
   5.65051431134921    -0.19744626326516    -2.04798470815602  c
```

7.90112773035165	0.88803619896334	-1.82073908711308	f
5.61817365806750	-2.85972039934535	-2.34950997950027	c
7.74162159765463	-4.07875259818926	-2.38892851630844	f
3.36737243930616	-4.22231625739346	-2.61762526219363	c
3.45507216715451	-6.70159614553282	-2.89821781036288	f
1.13765633615683	-2.91414881782628	-2.57575789573857	c
-0.98451375787475	-4.14274808821638	-2.82870345489798	f
1.00573094271726	-0.16569361272789	-2.25185260041647	c
0.13671964979814	0.56671948567536	-4.00317319946616	h
-0.84410540638930	0.57678007243610	-0.06716686075061	c
-1.03921496508986	2.61964093317681	-0.03893545906487	h
-2.67875715804580	-0.27604330594564	-0.40955729895373	h
-0.09535150747554	-0.07276548611537	1.73143955813947	h
-4.70126732974677	2.06260661662995	5.01093902230214	cl
-7.73713827665390	3.47227097345419	5.73343839041311	c
-7.93508827692936	3.52515511892909	7.77323067089803	h
-7.75515497728962	5.36341730029849	4.94224127212601	h
-9.19046909649401	2.30348790201915	4.88225070051278	h

$end
E(COSMO) = -1168.9127414870 H
ZPE = 381.9 kJ/mol
enthalpy = 422.45 kJ/mol
chem. pot. = 263.03 kJ/mol

5-methyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation

$coord

1.10760415325323	2.17274977017047	-0.22734600811322	c
1.11118842757617	4.19921774389199	0.03333908718736	h
3.30065202133194	0.88397701593580	-0.35088900482797	c
5.54719005549813	1.98506807775534	-0.16462731506661	f
3.28264070891965	-1.77388372615014	-0.69222295819746	c
5.41401353122630	-2.97416380976929	-0.79846141898405	f
1.03724749390771	-3.15139376509266	-0.92895415662019	c
1.13855570132074	-5.62480137418048	-1.25179289943287	f
-1.20132507970363	-1.86353448976918	-0.81044054481430	c
-3.31888149859947	-3.10575077279216	-1.03194003785516	f
-1.34839521668828	0.87792376380993	-0.43307965928813	c
-2.27291009739800	1.63446341165564	-2.14503552287159	h
-3.13960718241177	1.56027898364605	1.81916031793523	c
-3.34842062558967	3.60167007195757	1.89111681754306	h
-4.97606426817703	0.69661540766466	1.50881295410149	h
-2.33348812446612	0.88156369126656	3.58236034930450	h

$end
E(COSMO) = -668.8448828622 H
ZPE = 281.5 kJ/mol
enthalpy = 308.72 kJ/mol
chem. pot. = 190.08 kJ/mol

5-methyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-5-yliumcation

$coord

3.37791238643561	0.51275610223834	0.24878868894068	c
3.41351773995110	-2.04624267731601	0.00979772872621	c
-1.36962838944185	0.54075329140116	-0.05532385008264	c
5.48921378856172	1.77092451090661	0.50075330764675	f
5.52650607155431	-3.38116149278517	0.02146656749474	f
-1.24518467958033	-2.02060810677864	-0.29351792788789	c
-3.31595449929445	-3.42540881302041	-0.55247579989610	f

1.08341012601034	-3.29703735219717	-0.26609950095429	c
1.10299110302445	-5.74048926357811	-0.50266681046070	f
-3.81102964715645	1.91162117501219	-0.02479264347090	c
-5.12347201269548	1.10885782808707	-1.39325135925713	h
-4.67412697265393	1.69370497197662	1.84379060229135	h
-3.54931391754148	3.91717775392737	-0.38401721331251	h
1.02003593824480	1.95989953266843	0.21899420221757	c
1.14328054763095	3.36718559302089	-1.30819558941495	h
0.93184241695067	3.12806694643689	1.93674959741992	h

$end
E(COSMO) = -668.8565410952 H
ZPE = 278.6 kJ/mol
enthalpy = 306.32 kJ/mol
chem. pot. = 187.36 kJ/mol

5-methyl-1,2,3,4-tetrafluorobenzene

$coord

3.34336367417292	0.74291934354424	0.18122725437157	c
3.41293598887834	-1.86924987487687	0.00486649790376	c
-1.21377102214689	0.74862747112952	0.00277818126727	c
1.07724347473379	2.04166177819308	0.18112436356376	c
5.54768706529058	2.00287015055288	0.35407015216836	f
5.61139581575932	-3.12393717432800	0.00495794427788	f
-1.11586472528387	-1.86910284327882	-0.17247069136871	c
-3.27304771386796	-3.21328725833710	-0.34891599540586	f
1.11312593608335	4.07943680922416	0.32143050267188	h
1.15115154864404	-3.18274486145155	-0.17410213675344	c
1.17455952949597	-5.70694669960904	-0.34669414581913	f
-3.71891677189674	2.08598181885663	-0.00132962688771	c
-4.78086564728577	1.65460873100215	-1.71550110352829	h
-4.87424178290557	1.48729370234187	1.59882634573370	h
-3.45475536967150	4.12186890703683	0.10973245780487	h

$end
E(COSMO) = -668.4825368978 H
ZPE = 249.1 kJ/mol
enthalpy = 276.10 kJ/mol
chem. pot. = 158.67 kJ/mol

[$Me_2Cl]^+$/5-methyl-1,2,3,4-tetrafluorobenzene pre complex

$coord

-2.27419346522672	-2.75677262577688	0.05243473668203	c
0.02908820224624	-3.36782032783714	1.14674660940174	c
-2.43967143662287	-1.38128190472986	-2.17882414558352	c
0.11759636950491	-4.69372286298548	3.29431859074126	f
-4.39241841783465	-3.54278681952851	1.22040871729883	f
-4.97765976564425	-0.76611634957099	-3.29194095216456	c
-5.99096529878102	-2.48973878939410	-3.79697557503766	h
-6.15035515637189	0.25351902835121	-1.93662231007506	h
-4.76917902929083	0.38701184045502	-4.98090301663392	h
2.12073968812215	-1.22351153055001	-2.22717051603577	c
4.28887741025030	-0.46054967891079	-3.31326963502008	f
2.25880451128735	-2.59850097836501	-0.00126085404186	c
-0.18031900616145	-0.61911139003595	-3.30809172744308	c
-0.19777419778448	0.45449111196233	-5.04606634913779	h
-0.19449447243694	3.99754054435151	0.76591639051729	c
-0.62838343485523	2.26990118750762	1.77885916332164	h
1.67418914270652	3.98740409929573	-0.06757605833157	h

-1.67799303241462	4.55520605577435	-0.52901341523492	h
4.48605541568310	-3.17539567813624	1.04350225348090	f
-0.12587054399608	6.40369435105602	3.24844004036031	cl
0.60250149577544	9.27921976601100	1.47129746237083	c
0.65021338516784	10.73955955576720	2.90924689587239	h
2.42703058606370	8.96345699335943	0.59636573347999	h
-0.93027419490951	9.52883247101548	0.13620109204593	h

$end
E(COSMO) = -1208.2139317966 H
ZPE = 453.3 kJ/mol
enthalpy = 497.83 kJ/mol
chem. pot. = 335.05 kJ/mol

[Me_2Cl]$^+$/5-methyl-1,2,3,4-tetrafluorobenzene to MeCl/5,6-dimethyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation transition state

$coord

-2.29303842654565	-2.95419774552121	0.29657340276332	c
0.06301848660306	-3.80609220781875	1.09718497802384	c
-2.54588425992449	-1.16235452881928	-1.58895998944473	c
0.22723629060807	-5.51967368448597	2.91280519975368	f
-4.34431352248136	-3.94362505188077	1.39983733887967	f
-5.10380547429747	-0.31928751994855	-2.44773330301861	c
-6.24413147497788	-1.94463489796324	-3.00114955585152	h
-6.11004317770717	0.63083098584605	-0.91688423143410	h
-4.95803850590473	0.96277730139984	-4.04690658362487	h
2.06104652754034	-1.06616526524930	-1.86438794620876	c
4.15038028214896	-0.15362671882429	-2.92884040440736	f
2.26867249123863	-2.86275757160031	0.01286436284584	c
-0.30213348985947	-0.13518695884312	-2.61772629273931	c
-0.38735905479106	1.02008755196709	-4.30081635186388	h
-0.21894401558903	3.31688876650565	-0.05230125383541	c
-0.24238262526155	2.16898546581332	1.62693171021696	h
1.55322699307318	3.88307844048354	-0.87587980850501	h
-1.96649934567608	3.95735106567801	-0.87159512842234	h
4.50926591347699	-3.70094402622820	0.78725007046354	f
-0.13359988826110	6.99432162845478	2.60106601296069	cl
0.30465451186351	9.50328871421210	0.29655609959382	c
0.34443186443418	11.24928906074040	1.36954175142901	h
2.08669409457832	9.15996717029914	-0.65376667982119	h
-1.28931681406344	9.44267821183594	-0.98869699908407	h

$end
E(COSMO) = -1208.1931702507 H
ZPE = 449.6 kJ/mol
enthalpy = 493.06 kJ/mol
chem. pot. = 335.05 kJ/mol

MeCl/5,6-dimethyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation product complex

$coord

0.93486321773763	-4.85146465564746	-2.50293772508132	c
3.59087474337458	-4.83794755840331	-2.51665994746006	c
-0.41889742409030	-2.66460057603012	-2.39896988880722	c
4.79361218753093	-6.97373675778634	-2.63459877363579	f
-0.18312474786794	-7.10438822454525	-2.61255966654252	f
-3.22101373169092	-2.67824502826437	-2.39019171897031	c
-3.96052255068198	-4.35392977456949	-3.32182018598067	h
-3.88922955181840	-2.71021367106041	-0.43093912315612	h
-3.97447928953381	-0.98431078625486	-3.27988299423327	h

3.73050261034487	-0.37231857868201	-2.31578561244611	c
4.98402253756507	1.75884425313114	-2.25268409537144	f
5.01202133224302	-2.59710095582593	-2.42550797811892	c
0.95542914894573	-0.21829491196087	-2.24324824784905	c
0.40403269515066	0.87870100912369	-3.92341436199737	h
0.09497665785814	1.36295094925538	0.10380876306259	c
0.52954558216172	0.33899724812246	1.83125055387528	h
1.07341641652711	3.16674372003109	0.09824855689703	h
-1.92414369415964	1.70341937531239	-0.01287183169108	h
7.50853780675068	-2.72421337856199	-2.46484000379093	f
-1.87374850829545	4.63628670168936	5.30401433962755	cl
-3.34034528722458	6.98393010690901	7.32064459567907	c
-3.18896673517133	6.32941567256856	9.25742426926508	h
-2.33515977545609	8.75128082068311	7.05875659287695	h
-5.30220364019964	7.16019500076613	6.75276448384851	h

$end
E(COSMO) = -1208.2267758589 H
ZPE = 454.1 kJ/mol
enthalpy = 498.70 kJ/mol
chem. pot. = 331.39 kJ/mol

5,6-dimethyl-1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation

$coord

0.10489881218615	-3.05556515932371	-0.65616077171742	c
2.76084022572940	-3.02687319529008	-0.66666953162648	c
-1.26130579932867	-0.87718194328006	-0.53872760786116	c
3.97578770279331	-5.15461806600140	-0.80126490061008	f
-1.00043440640810	-5.31359001917625	-0.78839508810221	f
-4.06330157142789	-0.90657115729688	-0.54497820331203	c
-4.78701315146192	-2.56819906091521	-1.51403929469587	h
-4.74302912510982	-0.98265421387788	1.40899843558686	h
-4.82159380321122	0.79975773718204	-1.40623494967111	h
2.87447782394460	1.43790874148198	-0.43287465251505	c
4.11478663531453	3.57642031577868	-0.35778472540942	f
4.16914771487894	-0.77843579383541	-0.55839118685118	c
0.09899901555784	1.57429969118302	-0.34857710162061	c
-0.47044446142504	2.70525163129469	-1.99865763302881	h
-0.75449799900583	3.09644330041052	2.04377901461367	c
-0.29389293111991	2.03890772038839	3.74419264676333	h
0.20922929245672	4.90882477255041	2.06599642440738	h
-2.77894925330352	3.41686135628953	1.95118640093268	h
6.66629527894055	-0.89098665756235	-0.60139727528262	f

$end
E(COSMO) = -708.1587189642 H
ZPE = 353.4 kJ/mol
enthalpy = 384.88 kJ/mol
chem. pot. = 257.69 kJ/mol

5,6-dimethyl-1,2,3,4-tetrafluorobenzene

$coord

0.27926738809246	-3.13826485390892	0.17467231690146	c
2.90202944459205	-3.18092809764393	0.14733072256673	c
4.20803343476472	-0.92362923447851	0.00847174014009	c
2.86200396914936	1.32477477480835	-0.10302321899743	c
0.24274104327716	1.39425148750655	-0.08133511874599	c
-1.08841535139390	-0.90564799420912	0.06424283131807	c
4.21675319692064	3.48302938821790	-0.23602833357984	f

6.74121579421680	-0.91761901125740	-0.01803303649447	f
4.16135157443013	-5.37664101425115	0.25537534326354	f
-0.91690383921371	-5.38818276683859	0.31518807134874	f
-3.92889564513059	-0.94722776889046	0.09796717756321	c
-4.68916534548614	-0.11108015363836	-1.62798347136714	h
-4.65333090209274	-2.86148891251733	0.25988788063196	h
-4.65435651659078	0.15694283260039	1.68174598300556	h
-1.13900630087626	3.87304724569132	-0.21047132132694	c
-2.40064461012495	3.91808880883284	-1.84149042795918	h
-2.30418033879537	4.14571347377992	1.46994579037771	h
0.16150300426107	5.45486179619672	-0.35646292864620	h

$end
E(COSMO) = -707.7882986168 H
ZPE = 322.1 kJ/mol
enthalpy = 353.06 kJ/mol
chem. pot. = 227.75 kJ/mol

1,2,3,4-tetrafluorocyclohexa-1,3-dien-6-yliumcation

$coord

2.37266442878536	1.43924826840307	0.00000000000000	c
2.49328725949797	-1.20420006636665	0.00000000000000	c
0.26907348893040	-2.52375323993505	0.00000000000000	c
-2.16033955495244	1.50997334178807	0.00000000000000	c
0.04962322392130	2.77805067649926	0.00000000000000	c
-3.94182982221494	2.50861907825911	0.00000000000000	h
0.18919459429177	5.28189011570471	0.00000000000000	f
4.46873577546719	2.70574672531152	0.00000000000000	f
4.71731292777216	-2.33585703333157	0.00000000000000	f
0.30741216730202	-4.98548311749059	0.00000000000000	f
-2.18545214118271	-1.26460083652097	0.00000000000000	c
-3.28984117380900	-1.95481695616052	1.62553493748310	h
-3.28984117380900	-1.95481695616052	-1.62553493748310	h

$end
E(COSMO) = -629.5425176308 H
ZPE = 207.1 kJ/mol
enthalpy = 230.32 kJ/mol
chem. pot. = 120.82 kJ/mol

[$Me_2Cl]^+$/MeCl complex

$coord

-1.54522947259892	0.96231876107205	-0.07822117683925	c
-1.72177323167473	-0.93059147001155	-0.83428858875768	h
0.10257811687449	1.24252572447253	1.10147829501796	h
-3.27373062012690	1.64020689008797	0.78732431158931	h
-1.13234993061059	3.05473953819922	-2.81770096433479	cl
1.80004145444409	1.87317746498459	-4.21462435927506	c
2.08287238929767	3.07700205238938	-5.84957026674554	h
3.25082515449250	2.11455350074954	-2.78951325537880	h
1.44708823022527	-0.08014221000759	-4.71850742232719	h
-4.18166565102906	-1.48986881032891	6.95309350839407	c
-5.79422395075398	-2.74726289256634	7.09496096939281	h
-3.23179483994577	-1.29818838273607	8.75934537812686	h
-4.73797145938160	0.34116559935938	6.21734158998845	h
-1.96106878871953	-2.88345149673957	4.74923697498550	cl

$end
E(COSMO) = -1039.7975255479 H
ZPE = 299.9 kJ/mol

enthalpy = 328.09 kJ/mol
chem. pot. = 201.17 kJ/mol

$[Me_2Cl]^+$/MeCl transition state

$coord

-0.52662500053527	-0.01190298882634	0.00069208348257	c
-1.58508412716897	-1.70707050764275	-0.38145665177104	h
1.50614445725943	-0.04179274018784	-0.04766998768279	h
-1.51625434492849	1.71541263939896	0.42111090038089	h
-0.59485176869276	1.02635384896473	-4.33585323042164	cl
0.97265933701034	-1.73491478712020	-5.64886303193124	c
1.07229515677123	-1.41813591771629	-7.67101608276342	h
2.83739009875485	-1.83803570751594	-4.80660789627491	h
-0.17990935283807	-3.36619322077463	-5.19351736057163	h
1.04513553305295	1.77011850918601	5.60926853581475	c
-0.33707081681473	3.27866052026512	5.51436722561681	h
1.54251613624735	1.31155240616619	7.54352189214005	h
2.70734478467393	2.16329939326391	4.47742341998049	h
-0.42802566798657	-1.05365572822647	4.31824163325702	cl

$end
E(COSMO) = -1039.7811630978 H
ZPE = 299.8 kJ/mol
enthalpy = 325.49 kJ/mol
chem. pot. = 208.69 kJ/mol

$[Me_2Cl]^+$/MeBr pre complex

$coord

-0.26942577811238	0.47838963481014	-1.28234127893977	c
-0.65658108465314	-1.37076319121949	-2.06792495407680	h
1.34639329930123	0.53233597110183	-0.02845014366731	h
-1.93296958208021	1.37242833919281	-0.48899349091559	h
0.53867645652154	2.51317662712171	-3.97999340895223	cl
3.32157880873151	0.93464215028826	-5.28772325405321	c
3.82696030641574	2.09214136227458	-6.90240572232998	h
4.74259718889816	0.96383133267619	-3.81342878945493	h
2.71372369164680	-0.94725920482938	-5.81960104875702	h
-2.85953270166998	-1.06376816571121	6.19383517578743	c
-4.07932861701945	-2.11657779847337	7.45748462361663	h
-1.23981638789354	-0.28605506401794	7.17610584522945	h
-3.89511520282440	0.37997803972439	5.17523541533750	h
-1.55716039726190	-3.48250003293856	3.66820103117589	br

$end
E(COSMO) = -3153.6803945333 H
ZPE = 300.2 kJ/mol
enthalpy = 328.02 kJ/mol
chem. pot. = 200.46 kJ/mol

$[Me_2Cl]^+$/MeBr to MeCl/$[Me_2Br]^+$ transition state

$coord

-0.79321355193281	0.69626211595754	-5.74298928894403	cl
1.71315906913821	-1.43677897375829	-6.73314819501504	c
1.79032026372903	-1.29244845035571	-8.77596115446231	h
3.44828322110720	-0.78684953697758	-5.85966333859459	h
1.18698270353891	-3.32055232555844	-6.12378146790749	h
1.27267266444429	2.71768681013674	4.11722374144189	c
1.06670135869998	2.98833839684529	6.13666798407529	h
3.22606161182339	2.44890545381022	3.56717921763444	h

0.34494929033244	4.19515304600100	3.04606240940176	h
-0.52110857012877	-0.46506737236525	3.33654097163410	br
-0.68555410380054	0.11415693157062	-1.41929389627779	c
-2.15830888000897	1.49197798014440	-1.15572366615103	h
-1.16928607472829	-1.85325064319443	-1.60374785297127	h
1.26659836744441	0.68067762517915	-1.34683839165785	h

$end
E(COSMO) = -3153.6660212423 H
ZPE = 296.0 kJ/mol
enthalpy = 323.06 kJ/mol
chem. pot. = 200.10 kJ/mol

MeCl/[Me_2Br]$^+$ product complex

$coord

-1.38483745590539	0.44339140814728	-5.17522345577451	cl
0.90458730151504	-1.92437799314802	-6.11196181489708	c
1.05667538974843	-1.87066241318890	-8.15542461130876	h
2.69442754145151	-1.45416800015876	-5.22965645000459	h
0.22117129741017	-3.74875449562125	-5.47363366883889	h
0.40327372756972	2.37170572412455	5.68789388745144	c
0.54423601771316	2.23627295243242	7.72770311453117	h
2.22496471125321	2.53378094928891	4.76865770394512	h
-0.96990250674657	3.75903732513475	5.07175433916942	h
-0.96938477756705	-0.95343507538748	4.66155330662731	br
-1.15594325168460	-0.39329990671275	0.95134389462536	c
-2.46082427132230	1.15955049422063	0.69030447521259	h
-1.86722129454078	-2.17180069483788	0.22819153952454	h
0.75877757110541	0.01275972570655	0.35849773973681	h

$end
E(COSMO) = -3153.6836741088 H
ZPE = 297.0 kJ/mol
enthalpy = 326.14 kJ/mol
chem. pot. = 194.53 kJ/mol

[Me_2Cl]$^+$/MeI pre complex

$coord

-0.31279252113030	0.46654819614972	-1.57278936626335	c
-0.49785775362728	-1.43702769666724	-2.29974498949126	h
1.15631481615969	0.68549818723645	-0.16524622228908	h
-2.10344800827936	1.28129211065342	-1.00195561982061	h
0.65000676617364	2.42743561209574	-4.27916003979189	cl
3.62293027809454	0.94958935073938	-5.24041499068248	c
4.21006703902611	2.04616650129995	-6.86984578228208	h
4.90003935129551	1.14136543520929	-3.65128007377131	h
3.16892191538624	-0.99088706262192	-5.71208986058570	h
-3.05064425211036	-1.00976866422550	6.49368233856138	c
-4.39796931093179	-1.91076074490148	7.74471281200453	h
-1.28064945422577	-0.60694924999311	7.44058406878131	h
-3.83784465221866	0.65683102975037	5.60197284093579	h
-2.22707421361214	-3.69933300472500	3.51157488469484	i

$end
E(COSMO) = -877.3446760280 H
ZPE = 299.3 kJ/mol
enthalpy = 327.10 kJ/mol
chem. pot. = 197.83 kJ/mol

$[Me_2Cl]^+$/MeI to MeCl/$[Me_2I]^+$ transition state

$coord

-0.76965583094040	0.66766515499490	-6.71130403596138	cl
1.75197928535888	-1.42949773312369	-7.74227265751095	c
1.74236136257212	-1.33546570335309	-9.78940581023238	h
3.49903254852475	-0.70881459674193	-6.95218856067138	h
1.29275542959134	-3.30631701460045	-7.06199161767032	h
0.97561803992636	3.52703211261329	3.24161024293923	c
0.51824576996152	3.98745643552332	5.18350377426741	h
2.98677615496525	3.62370711269186	2.87420373932000	h
-0.11603122480293	4.63903853982821	1.91269256373296	h
-0.14019985958232	-0.37454125495430	2.70601123429205	i
-0.49721621476492	0.16605536017676	-2.53876264192541	c
-2.01628391698928	1.46268135086008	-2.14944103265826	h
-0.88868000692608	-1.82961382759310	-2.59532710479289	h
1.42904942216214	0.81127571021214	-2.43902369123543	h

$end

E(COSMO) = -877.3331928894 H

ZPE = 295.3 kJ/mol

enthalpy = 322.11 kJ/mol

chem. pot. = 198.51 kJ/mol

MeCl/$[Me_2I]^+$ product complex

$coord

0.05185204542540	0.61508304478526	-7.24898297758901	cl
1.93397454782122	-1.68173308299097	-8.95415756628785	c
1.65933010804332	-1.34687080595429	-10.95793832674055	h
3.89491950540002	-1.40695093935284	-8.42353863956664	h
1.28031263382339	-3.55087369465281	-8.42344758765111	h
0.67950242590421	3.90419242041838	3.58614739687062	c
0.61085050836226	4.24025200824313	5.60729102830270	h
2.59360208987887	3.83544643468455	2.86297604356366	h
-0.55508969327799	5.15501968858413	2.53596151783728	h
-0.84056507656453	0.15528910416052	3.11819220469638	i
-0.43116862654454	0.03687752181858	-0.94150087090685	c
-1.55922991884486	1.58263570215007	-1.66507415915064	h
-1.16698476775864	-1.79794157801266	-1.47938561857892	h
1.57076822505211	0.22882436029182	-1.31669822902474	h

$end

E(COSMO) = -877.3565011208 H

ZPE = 295.5 kJ/mol

enthalpy = 324.38 kJ/mol

chem. pot. = 192.72 kJ/mol

$P(CF_3)_3$

$coord

-0.00000000000000	0.00000000000000	-1.91758940520388	p
2.61378536549920	-1.74359822575141	-0.12890077771495	c
0.20310767474458	3.13540363943801	-0.12890077771495	c
-2.81689304024381	-1.39180541368660	-0.12890077771495	c
2.55338301441296	4.06937273423644	-0.39689482701746	f
-1.42269989139021	4.77612625232786	-1.18628491747469	f
-0.31574950426779	3.04429819244972	2.34864066949273	f
-4.80087167252302	0.17660818895508	-0.39689482701746	f
-3.42489672050263	-3.62015737406920	-1.18628491747469	f
-2.47856481922264	-1.79559618815315	2.34864066949273	f
2.24748865811002	-4.24598092319158	-0.39689482701746	f

2.79431432349043	-1.24870200429660	2.34864066949273	f
4.84759661189280	-1.15596887825869	-1.18628491747469	f

$end
E(COSMO) = -1354.2988114124 H
ZPE = 113.6 kJ/mol
enthalpy = 149.39 kJ/mol
chem. pot. = 11.03 kJ/mol

$[Me_2Cl]^+/P(CF_3)_3$ pre complex

$coord

-1.06712297044588	0.20071910611732	5.76297566783424	c
0.09419237312285	1.82179620784379	5.29620745470695	h
-0.37393230423606	-1.57770983007680	5.02048233741905	h
-3.05095386470790	0.50999200026991	5.35105650683582	h
-0.97187118264924	-0.08969778257325	9.20145678514564	cl
2.39847724279174	-0.56338790427978	9.81526367610647	c
2.50562916153435	-0.68901115908561	11.85874962942956	h
2.91016772922550	-2.31487912561138	8.88549616917262	h
3.35246618974172	1.09006252840480	9.07308313983740	h
2.30008725139305	-1.17831120779485	-1.00187630317536	c
-2.61824408826758	-1.57563241058299	-3.34599100205580	c
0.16332886028741	3.11647949181875	-3.58542741078743	c
-2.72080823636738	-3.87035942480360	-2.25545434898945	f
-4.98757946112900	-0.71118353618736	-3.60736116150128	f
-1.64086348839327	-1.85337250231207	-5.66186640101537	f
-1.92077010846130	4.00338573773139	-4.73081165057192	f
1.28813463601172	5.04279672928425	-2.37454097539604	f
1.75547354971119	2.30068320595291	-5.37567047108761	f
4.16673400107873	0.46529351899198	-0.46999838363377	f
2.94904961750921	-2.46752846630089	-3.07022945653908	f
2.15900816015518	-2.83719043387046	0.93094604944368	f
-0.81825392812045	0.64488286158017	-1.13824251608722	p

$end
E(COSMO) = -1894.0266534562 H
ZPE = 316.4 kJ/mol
enthalpy = 370.37 kJ/mol
chem. pot. = 179.63 kJ/mol

$[Me_2Cl]^+/P(CF_3)_3$ to MeCl/$[MeP(CF_3)_3]^+$ transition state

$coord

-0.64478695343174	0.95104387164974	4.04900918248671	c
1.28734608888893	1.59353126724308	4.07862687085077	h
-1.08796070441263	-1.03062633162845	4.22497769392059	h
-2.14114425687520	2.28169910141041	3.68173115855842	h
-1.02407195389762	1.52119420449843	8.31624570398120	cl
1.32128408588507	-0.72427258605035	9.44762893997144	c
1.31303473805862	-0.54875669900888	11.48944699249521	h
0.72134044983673	-2.58839865057104	8.84563485456134	h
3.12607780340812	-0.17590718081375	8.64800021591326	h
1.54940268885132	-2.90287499431947	-1.08512640354266	c
-3.06703689225909	-0.22529120387084	-2.67404558106830	c
1.83998493505943	2.43986813895200	-2.61512016085781	c
-4.22428693852172	-2.36031052058394	-1.97366495718896	f
-4.63245932550779	1.72053509817596	-2.31086621504269	f
-2.51015230005621	-0.36591876731365	-5.12760112499314	f
0.43369885951603	4.43088538362901	-3.27091567324090	f
3.80275813588559	3.22903252383310	-1.23452476889271	f

```
   2.71829164328377     1.33889307629770    -4.70536999654188  f
   3.98423736097972    -2.57695620059880    -0.47599591893082  f
   1.40493272886961    -3.79664782205086    -3.43173304024552  f
   0.53944587022051    -4.60678621776893     0.49333353302257  f
  -0.16329197636013     0.22983488423407    -0.57731494386423  p
$end
E(COSMO) = -1894.0049365533 H
ZPE = 313.1 kJ/mol
enthalpy = 366.08 kJ/mol
chem. pot. = 180.37 kJ/mol
```

MeCl/[MeP(CF$_3$)$_3$]$^+$ product complex

```
$coord
  -0.96958212938615     0.26807225089679     2.56428486184604  c
   0.39437279941145     1.50997254251111     3.48101584709820  h
  -0.90870025403529    -1.61990734375044     3.38647438367977  h
  -2.86545730714424     1.05642351560577     2.74296449534333  h
  -1.10234104633289     0.87496904180131     8.97715660549791  cl
   1.95537190284853    -0.37487518548729     9.88003640659931  c
   2.12300863821612    -0.20661344153580    11.91598968881008  h
   2.03010029673102    -2.33955010772004     9.29868763029527  h
   3.39549468329095     0.73555644519804     8.93298421848887  h
   3.12649665075787    -1.23924475855179    -1.18014098454581  c
  -2.44373464904373    -2.14618648435811    -2.47901770398435  c
  -0.33990686627668     3.25042127462653    -2.34064736151137  c
  -1.93915222774981    -4.50792523311745    -1.79939032035113  f
  -4.79710619775715    -1.55040396137057    -1.85809554392662  f
  -2.10383786091257    -1.86671098167613    -4.94608754757873  f
  -2.74811427074847     3.91946426117176    -2.55827219352511  f
   0.89705031941930     4.91497743437597    -0.93350399414671  f
   0.71686232808482     3.08040919324377    -4.60642735837098  f
   4.75871613706228     0.54209754030861    -0.49630000699202  f
   3.46651215089085    -1.84847192333030    -3.58451156371041  f
   3.40938999306933    -3.26287440866661     0.27597932650932  f
  -0.20630124806673     0.04600402451276    -0.68988126050480  p
$end
E(COSMO) = -1894.0512600713 H
ZPE = 314.6 kJ/mol
enthalpy = 369.39 kJ/mol
chem. pot. = 176.29 kJ/mol
```

[MeP(CF$_3$)$_3$]$^+$

```
$coord
   0.00000000000000     0.00000000000000    -0.20073307180163  p
   2.99191455534240     1.49797735993008     1.14720164165633  c
  -2.79324372566457     1.84208533091389     1.14720164165633  c
  -0.19867082967783    -3.34006269084395     1.14720164165633  c
   0.00000000000000     0.00000000000000    -3.54487418605717  c
  -1.66841934477985    -1.01784430009498    -4.20198224508443  h
  -0.04726934858958     1.95381568679222    -4.20198224508443  h
   1.71568869336942    -0.93597138669724    -4.20198224508443  h
   2.72300113353208     1.88024746034860     3.60881432650833  f
   0.26684149929699    -3.29831188634689     3.60881432650833  f
  -2.98984263282910     1.41806442599833     3.60881432650833  f
  -4.87557502128860     1.08808211792741    -0.02751718359643  f
  -2.51125516136462    -4.21765063881813     0.72189341920067  f
   1.49548075511560    -4.76641288545641    -0.02751718359643  f
```

4.90822017818649	-0.06598544571748	0.72189341920067	f
-2.39696501682181	4.28363608453559	0.72189341920067	f
3.38009426617298	3.67833076752901	-0.02751718359643	f

$end
E(COSMO) = -1393.9845428342 H
ZPE = 216.4 kJ/mol
enthalpy = 257.02 kJ/mol
chem. pot. = 108.86 kJ/mol

PF_3

$coord

-0.00000000000000	0.00000000000000	-1.12715514069517	p
-1.29845499870669	2.24899002910176	0.37569638140390	f
-1.29845499870669	-2.24899002910176	0.37569638140390	f
2.59690999741333	0.00000000000000	0.37569638140390	f

$end
E(COSMO) = -641.0037880711 H
ZPE = 21.50 kJ/mol
enthalpy = 34.65 kJ/mol
chem. pot. = -47.21 kJ/mol

$[Me_2Cl]^+/PF_3$ pre complex

$coord

-0.63633618724142	1.14239181165750	-0.75486665533527	c
-0.89264826040884	-0.82445802110260	-1.26118758204035	h
0.83618640590520	1.46338902088325	0.63060926802621	h
-2.39541753797434	2.08176576989144	-0.28318584619206	h
0.39694118741338	2.75002046759692	-3.64316097433791	cl
3.37341874366153	1.14736471270734	-4.36761146318393	c
4.00810772973768	2.05727140217463	-6.09153506880945	h
4.61548650239405	1.50080626745741	-2.77817986363600	h
2.90788227464783	-0.82855074452530	-4.63771221061837	h
-4.67491471429694	-0.77603701095827	6.71477829673964	f
-4.11054387263810	-4.72868133297112	4.64431073923370	f
-0.71313843847085	-2.89331749960040	6.95107601555665	f
-2.71502383272933	-2.09196484321082	4.87666534459717	p

$end
E(COSMO) = -1180.7336967125 H
ZPE = 224.6 kJ/mol
enthalpy = 255.41 kJ/mol
chem. pot. = 121.14 kJ/mol

$[Me_2Cl]^+/PF_3$ to MeCl/$[MePF_3]^+$ transition state

$coord

-0.56003080230850	0.02544089033023	-1.71138014916596	c
0.53090190880697	-1.69431128907402	-1.72917529489872	h
0.38145469940719	1.83115697903880	-1.70295092283358	h
-2.57167825558428	-0.06220671235951	-1.40884359275605	h
-1.03440428212054	0.02795387733696	-5.92922847751214	cl
2.25038499339827	-0.01055522680812	-6.94762238680872	c
2.18912400146756	-0.06237335806971	-8.99529642104405	h
3.12072882125219	1.70849637541277	-6.25264091672549	h
3.10608379581680	-1.70053078282308	-6.16770990637650	h
-2.29311196325482	0.91986615003272	4.70983651016458	f
0.52037581331741	-2.59447824880768	4.31932535973437	f
2.13685102967098	1.62239274270600	4.16547320962080	f
-0.04918683399156	-0.00207215294513	3.03642811721077	p

$end
E(COSMO) = -1180.7161849712 H
ZPE = 223.0 kJ/mol
enthalpy = 252.11 kJ/mol
chem. pot. = 124.81 kJ/mol

MeCl/[MePF$_3$]$^+$ product complex

$coord

-0.31719976101327	0.07523762958525	-0.34323269509123	c
1.46357182146025	-0.63789750880570	-1.09249023582624	h
-0.63611155024198	2.01871365760234	-0.94443724097925	h
-1.88518048503054	-1.12771103650933	-0.92275625860666	h
-1.02404460106646	0.97704152677654	-6.67391947551243	cl
2.16019144017251	-0.17646803945012	-7.17038201035874	c
2.59419651840779	0.01696702367340	-9.16435798157141	h
3.43029377756232	0.96386194003690	-6.03379908870505	h
2.21532082838904	-2.14443827582772	-6.59731350951602	h
-2.51347989873005	0.95862065147675	4.19873684414341	f
0.32699503573965	-2.58907655380492	3.98530934661296	f
1.97719013894090	1.65010253778080	3.95618710921545	f
-0.13319936857481	0.02373811658796	2.92712500401788	p

$end
E(COSMO) = -1180.7775677172 H
ZPE = 226.9 kJ/mol
enthalpy = 256.72 kJ/mol
chem. pot. = 124.59 kJ/mol

[MePF$_3$]$^+$

$coord

-0.00000000000000	0.00000000000000	1.45831898393350	p
-1.31320135025189	2.27453145920433	2.57973023514718	f
-1.31320135025189	-2.27453145920433	2.57973023514718	f
2.62640270050377	0.00000000000000	2.57973023514718	f
-0.00000000000000	0.00000000000000	-1.81661533796142	c
0.97908842385820	-1.69583089522493	-2.46029811713787	h
-1.95817684771637	0.00000000000000	-2.46029811713787	h
0.97908842385820	1.69583089522493	-2.46029811713787	h

$end
E(COSMO) = -680.7100058177 H
ZPE = 126.9 kJ/mol
enthalpy = 143.53 kJ/mol
chem. pot. = 53.98 kJ/mol

NC$_5$F$_4$I

$coord

0.00000000000000	0.00000000000000	-2.09734291699559	c
2.24418715692416	0.00000000000000	-0.73036352038678	c
2.12127184307240	0.00000000000000	1.88790052132779	c
-2.12127184307240	0.00000000000000	1.88790052132779	c
-2.24418715692416	0.00000000000000	-0.73036352038678	c
-4.26691404306162	0.00000000000000	3.21390000792119	f
-4.48863308257502	0.00000000000000	-1.88190867074750	f
4.48863308257502	0.00000000000000	-1.88190867074750	f
4.26691404306162	0.00000000000000	3.21390000792119	f
0.00000000000000	0.00000000000000	3.15820480113705	n
0.00000000000000	0.00000000000000	-6.03991856037077	i

$end

E(COSMO) = -942.3366496984 H
ZPE = 119.5 kJ/mol
enthalpy = 145.74 kJ/mol
chem. pot. = 25.80 kJ/mol

$[Me_2Cl]^+/NC_5F_4I$ pre complex

```
$coord
  -3.92326701306712    -0.52224897422803     1.11795358322606  c
  -5.32556514723404    -1.53004206568443     3.08870885183164  c
  -4.06877953545334    -2.32022989262512     5.25763342523044  c
  -1.45542904844036    -2.04304651542413     5.30554218503364  c
  -0.26149463888695    -1.00806341436476     3.21554243313069  c
  -1.46321204656929    -0.27061274371653     1.18312231447966  n
   2.24602358559912    -0.72933203707069     3.23623929993174  f
  -5.10541303146022     0.24453445975322    -0.97396025236789  f
  -7.82971850542581    -1.72258376872969     2.87287018445399  f
  -0.09193500960852    -2.74819306851880     7.30522295142091  f
   1.32551916102691     1.94686504375680    -3.14592866206949  c
   1.18173264117673    -0.05479678197655    -3.53987683489945  h
   2.41897732144976     2.39860188893792    -1.47775065419066  h
  -0.48265290402493     2.90572402446226    -3.19373914252882  h
   3.05324680399803     3.33058146546487    -5.82913848103927  cl
   6.08582912561217     1.68103972154957    -5.68608121025845  c
   7.13999984437789     2.45301170221874    -7.26563663190012  h
   6.91381336721891     2.15678923737651    -3.87436064268249  h
   5.66615325232650    -0.31081377814096    -5.91096228097984  h
  -6.02382822261554    -3.85718450304010     8.31459956417780  i
$end
```

E(COSMO) = -1482.0690356021 H
ZPE = 321.5 kJ/mol
enthalpy = 366.15 kJ/mol
chem. pot. = 195.11 kJ/mol

$[Me_2Cl]^+/NC_5F_4I$ to MeCl/$[MeNC_5F_4I]^+$ transition state

```
$coord
  -2.36752156449527     0.07655812075697    -1.65091268342147  c
  -2.34130290497655     0.01088846770325     0.96538523442412  c
  -0.03180981352405     0.05064643892786     2.22142674557703  c
   2.14403164295279     0.15539839573412     0.74885360536207  c
   1.91341581225724     0.21341756979633    -1.85713502998125  c
  -0.28871956742531     0.17692455056574    -3.01435238544095  n
   3.96049567037909     0.31165709599550    -3.30187968991075  f
  -4.54570041877383     0.04006427829029    -2.89072073092960  f
  -4.51993957723701    -0.08870019353568     2.21454647757349  f
   4.43483862820303     0.19925911156350     1.78201998983779  f
  -0.48462038948550     0.24981113928829    -7.14295183309354  c
  -0.45401554243502    -1.78118204074437    -7.07435343683215  h
   1.25114631727653     1.30626730162864    -7.11896883805608  h
  -2.25340575789808     1.23733089287972    -6.96918535544016  h
  -0.68254503624143     0.29570308037012   -11.38820745646760  cl
   2.22550362589684    -1.36714769594627   -12.16034017915656  c
   2.28347435416678    -1.46068143503341   -14.20650846956097  h
   3.77574293170209    -0.26098802121423   -11.40556514787634  h
   2.10177665192181    -3.22959195250138   -11.31615067021018  h
   0.16084942564817    -0.04273700329461     6.14989734793647  i
$end
```

E(COSMO) = -1482.0570305965 H

ZPE = 321.2 kJ/mol
enthalpy = 363.96 kJ/mol
chem. pot. = 201.08 kJ/mol

MeCl/[MeNC$_5$F$_4$I]$^+$ product complex

```
$coord
   -2.77599818507812      0.30207421524760      2.73452614012826  c
   -2.70350262239649      0.24741760906548      5.33908278476068  c
   -0.39693973509395      0.25948242875862      6.60254229952493  c
    1.77899292197409      0.32487355974709      5.12655741865083  c
    1.60292875931875      0.37731355205438      2.52703567652013  c
   -0.64834510924304      0.38263106560157      1.34013103315282  n
    3.62324461220929      0.42139869186820      1.10637648839229  f
   -4.92115846773428      0.27524091546965      1.51151934399924  f
   -4.87745368795330      0.17795050970826      6.57216606137009  f
    4.06080242861062      0.33262357928961      6.14879532731167  f
   -0.78465217646019      0.42639372058880     -1.47237773664126  c
   -0.80189149198918     -1.50971355746778     -2.15023192424915  h
    0.84684555461855      1.43759500562518     -2.17766874088337  h
   -2.49871918011277      1.39965125433254     -2.01754882005581  h
   -0.94250108956437      0.49000857900072     -7.81841415491892  cl
    2.00593028905731     -1.15282519722090     -8.39054360568488  c
    2.19330211378656     -1.41577656858944    -10.41481170589916  h
    3.52818817047166      0.00931901295910     -7.65862349608628  h
    1.92119253454799     -2.95774311742386     -7.42164824293771  h
   -0.21026563896906      0.17208474138515     10.51313585354565  i
$end
```

E(COSMO) = -1482.1027275993 H
ZPE = 327.3 kJ/mol
enthalpy = 371.77 kJ/mol
chem. pot. = 199.14 kJ/mol

[MeNC$_5$F$_4$I]$^+$

```
$coord
    3.82611986786914      0.00042783111210      0.00000000000000  c
    2.44240474920006     -2.23790857137076      0.00000000000000  c
   -0.16018159025949     -2.16552494829211      0.00000000000000  c
   -0.14150458220348      2.21952445839645      0.00000000000000  c
    2.46691656608226      2.25068562098977      0.00000000000000  c
   -1.43677452681822      4.32143092457801      0.00000000000000  f
    3.60955292561297      4.47496553018088      0.00000000000000  f
    3.55865276026342     -4.47476883504005      0.00000000000000  f
   -1.51491420402654     -4.23094038525708      0.00000000000000  f
    7.74216386961531     -0.02156367026763      0.00000000000000  i
   -4.25584933639165     -0.02814618902740      0.00000000000000  c
   -4.87055811149920     -1.01739535318928     -1.68899209167588  h
   -4.87055811149920     -1.01739535318928      1.68899209167588  h
   -4.95223105468931      1.89302385733541      0.00000000000000  h
   -1.44323922125604      0.03358508304105      0.00000000000000  n
$end
```

E(COSMO) = -982.0347429190 H
ZPE = 226.9 kJ/mol
enthalpy = 257.87 kJ/mol
chem. pot. = 126.45 kJ/mol

NC_5F_5
$coord
-2.12894023509184 0.00000000000000 -1.76122167788659 c
-2.26491957747676 0.00000000000000 0.85410839222701 c
0.00000000000000 0.00000000000000 2.18045570997674 c
2.26491957747676 0.00000000000000 0.85410839222701 c
2.12894023509184 0.00000000000000 -1.76122167788659 c
0.00000000000000 0.00000000000000 -3.02175284453659 n
4.26848649923801 0.00000000000000 -3.09050040918762 f
-4.26848649923801 0.00000000000000 -3.09050040918762 f
-4.46600322017884 0.00000000000000 2.07670173720560 f
0.00000000000000 0.00000000000000 4.68312104984302 f
4.46600322017884 0.00000000000000 2.07670173720560 f
$end
E(COSMO) = -744.4708147403 H
ZPE = 126.5 kJ/mol
enthalpy = 150.81 kJ/mol
chem. pot. = 39.70 kJ/mol

/home/haemmers/transP/Me2ClNC5F5
$[Me_2Cl]^+/NC_5F_5$ to $MeCl/[MeNC_5F_5]^+$ transition state
$coord
-3.96261230009506 -0.54926100380518 1.16924343028384 c
-5.37663602134386 -1.55782030237363 3.12810364223730 c
-4.08046733706562 -2.33379878260613 5.27588402720827 c
-1.46937105564236 -2.07095437083777 5.37020797019387 c
-0.28982392373162 -1.03186965054817 3.27690348422118 c
-1.50187474373004 -0.29772138315934 1.24812178115604 n
2.21367627061152 -0.74723403751700 3.29319239541494 f
-5.13614034301332 0.21798363509986 -0.92332796511476 f
-7.87749173941519 -1.78684858306449 2.98704304226154 f
-5.32068091749482 -3.31287446596327 7.21307155932544 f
-0.18011965246254 -2.79759407511117 7.40418861998969 f
1.29067496128810 1.92989747920538 -3.09439273512799 c
1.14266531287285 -0.07231495873002 -3.48444590674863 h
2.38458593219798 2.38175054196652 -1.42637108475920 h
-0.51574740738269 2.89214007413465 -3.14381000367665 h
3.02199525366774 3.30394823916312 -5.77873806637944 cl
6.04946565272340 1.64519813317471 -5.63112737541431 c
7.10814531397248 2.41332313426956 -7.20954865516039 h
6.87610266165529 2.11941108096579 -3.81840622344320 h
5.62365408238788 -0.34536070426361 -5.85579193646767 h
$end
E(COSMO) = -1284.2030207190 H
ZPE = 329.1 kJ/mol
enthalpy = 371.42 kJ/mol
chem. pot. = 210.96 kJ/mol

$[Me_2Cl]^+/NC_5F_5$ to $MeCl/[MeNC_5F_5]^+$ transition state
$coord
-2.25871683935557 0.03169652279088 1.24383240725456 c
-2.16606775720358 -0.06878660335718 3.85532120940142 c
0.20223223230078 -0.07301743645303 4.99245591338066 c
2.35772353988412 0.02201159282724 3.49335502984749 c
2.02930892140303 0.11704954006060 0.90111031922723 c
-0.21534672398607 0.12372241996623 -0.17615467648858 n
4.02340391240904 0.20754581035365 -0.60920795533395 f

-4.46925066510121	0.03979036394554	0.07107929558345	f
-4.25475179773833	-0.15943385781396	5.23834257624586	f
0.40267529166813	-0.16662271335833	7.47356485862801	f
4.64176627101817	0.01992814226224	4.52624840354851	f
-0.53779854635798	0.26736930070022	-4.28003207133871	c
-0.50367965769547	-1.76448058800235	-4.25583593967059	h
1.19572629049454	1.32765250851158	-4.29827594955785	h
-2.30208410993630	1.24904547280048	-4.04124971354428	h
-0.86855413345543	0.39250222235033	-8.52860317732157	cl
2.04984620504152	-1.18733296233457	-9.42534709711232	c
2.04849086717070	-1.23299708587416	-11.47397121187701	h
3.59849253666302	-0.06482744250399	-8.69161637253126	h
1.99197038573960	-3.07101226513801	-8.62233103596283	h

$end
E(COSMO) = -1284.1906191687 H
ZPE = 327.8 kJ/mol
enthalpy = 368.59 kJ/mol
chem. pot. = 214.73 kJ/mol

MeCl/[MeNC$_5$F$_5$]$^+$ product complex

$coord

-2.32198586291784	0.00129491581923	1.38481279908570	c
-2.16046819190569	-0.08891871972632	3.98404901489827	c
0.21524267469686	-0.06247474271356	5.10582486788025	c
2.35690184345156	0.04979655208377	3.58699286404534	c
2.05550091771834	0.13553342576165	1.00084316530296	c
-0.24734192288762	0.12801245904799	-0.08648036150349	n
4.00938114406562	0.22615512622545	-0.50012554581172	f
-4.51124604580246	-0.03608946088787	0.25345569665431	f
-4.23136849933088	-0.20462594416765	5.36470692992762	f
0.43425651010522	-0.15051097472673	7.56688981604860	f
4.63964133207806	0.06823732078205	4.58538350170228	f
-0.48889016986019	0.20923366134664	-2.89565927939960	c
-0.41645076652621	-1.71343685708939	-3.60588091964604	h
1.05383947119173	1.32933436174714	-3.63628884318940	h
-2.27510055313681	1.08874489808914	-3.36030384416743	h
-0.92056762470093	0.39469424213272	-9.21945409995121	cl
2.04652860006614	-1.12161353027274	-10.00566328901263	c
2.16393355066020	-1.24473130294981	-12.04845130955779	h
3.56406861702799	0.03331699808719	-9.25285392685317	h
2.04568191445179	-2.98782791757769	-9.15676301392436	h

$end
E(COSMO) = -1284.2348579072 H
ZPE = 336.4 kJ/mol
enthalpy = 378.01 kJ/mol
chem. pot. = 217.44 kJ/mol

[MeNC$_5$F$_5$]$^+$

$coord

-0.06913972885531	-2.17207126289841	0.00000000000000	c
2.53230608132830	-2.26409902246921	0.00000000000000	c
3.87173686514306	-0.00156421054387	0.00000000000000	c
2.55921896316173	2.27336920054527	0.00000000000000	c
-0.04824550362310	2.22496112593508	0.00000000000000	c
-1.42384626721800	-4.23172713156481	0.00000000000000	f
3.71393712850763	-4.45707500843225	0.00000000000000	f
6.34400218410371	-0.01667454071423	0.00000000000000	f

3.76843655168690	4.45212199707694	0.00000000000000	f
-1.34085694489662	4.32321081302511	0.00000000000000	f
-4.16080544697616	-0.02743530364836	0.00000000000000	c
-4.85512062749183	1.89448772760175	0.00000000000000	h
-4.77385085877403	-1.01566862335716	-1.68985435275253	h
-4.77385085877403	-1.01566862335716	1.68985435275253	h
-1.34392153732225	0.03383286280137	0.00000000000000	n

$end
E(COSMO) = -784.1667443792 H
ZPE = 235.2 kJ/mol
enthalpy = 263.83 kJ/mol
chem. pot. = 142.43 kJ/mol

$N_3C_3F_3$
$coord

-1.19485458287165	2.06954884519022	0.00000000000000	c
-1.19485458287165	-2.06954884519022	0.00000000000000	c
2.38970916574332	0.00000000000000	0.00000000000000	c
-2.43620426143100	-4.21962955841431	0.00000000000000	f
-2.43620426143100	4.21962955841431	0.00000000000000	f
4.87240852286201	0.00000000000000	0.00000000000000	f
1.29092931060605	-2.23595515494956	0.00000000000000	n
1.29092931060605	2.23595515494956	0.00000000000000	n
-2.58185862121213	0.00000000000000	0.00000000000000	n

$end
E(COSMO) = -578.1103723863 H
ZPE = 109.0 kJ/mol
enthalpy = 127.40 kJ/mol
chem. pot. = 31.84 kJ/mol

$[Me_2Cl]^+/N_3C_3F_3$ pre complex
$coord

2.47286344344696	-0.01153269599390	-3.82740627219348	c
0.37470507727976	-3.48649321845747	-3.00013816403742	c
3.18559552472681	-3.43563659200813	-6.03965249422789	c
-1.32595293825569	-4.69971739493798	-1.65913202287737	f
2.94743686538400	2.37693697932914	-3.33632055563310	f
4.40747451519309	-4.60414102073141	-7.85295076292106	f
1.51287984756978	-4.79392936187785	-4.78622098289253	n
3.77517614648147	-1.03977374154647	-5.68141606060074	n
0.74353271861918	-1.09603248461492	-2.39760755301778	n
-2.28606858135870	2.47675754026101	6.96429835727060	c
-3.11633391393305	0.60799892312633	6.85269821774178	h
-0.23904770455962	2.47414294250257	7.02444295640919	h
-3.12230835820350	3.63143764865583	8.43719303295951	h
-3.16430907891309	4.10061072956696	4.04291018106928	cl
-1.70360860384154	2.09653605465486	1.60906052589009	c
-2.20469087986508	3.02695717397684	-0.14465139101280	h
0.30603283403523	2.12472131964810	1.98830078729834	h
-2.56337691380622	0.25115719844644	1.80659220077532	h

$end
E(COSMO) = -1117.8420146940 H
ZPE = 312.3 kJ/mol
enthalpy = 348.45 kJ/mol
chem. pot. = 201.40 kJ/mol

$[Me_2Cl]^+/N_3C_3F_3$ to $MeCl/[MeN_3C_3F_3]^+$ transition state

$coord

0.04382413003357	2.11480555879995	-2.19797685480042	c
-0.22645875903132	-2.06841518502577	-2.07820416229819	c
0.15119457205151	-0.09388961231466	-5.70383671814688	c
-0.44860981156970	-4.14147805636503	-0.75517655128637	f
0.09501547702199	4.26825977837990	-0.99202480108679	f
0.31906115565482	-0.17531076017233	-8.16380308829831	f
-0.06768653377984	-2.29100236330102	-4.53886873240607	n
0.22027117800955	2.17592839890737	-4.66675596153360	n
-0.18413270895998	0.06831382705223	-0.76881136940258	n
2.11271205774201	-1.22632686366761	8.47489442237168	c
1.91600150590287	-3.13071881147678	7.74611649933940	h
3.71133584593154	-0.23509843131978	7.66346447954741	h
2.15766505155534	-1.19580506722864	10.52326957976737	h
-0.71990337950540	0.50445037820839	7.58021534653225	cl
-0.44981329188893	0.27371841075776	3.30889113354270	c
-2.19210066389469	1.29696902073529	3.08016281244039	h
1.32373481949407	1.26611739724698	3.29538253292116	h
-0.48013947975316	-1.75826529162654	3.34713750279023	h

$end

E(COSMO) = -1117.8283760645 H

ZPE = 310.6 kJ/mol

enthalpy = 345.28 kJ/mol

chem. pot. = 204.67 kJ/mol

$MeCl/[MeN_3C_3F_3]^+$ product complex

$coord

0.04005304430946	2.19612612053287	-2.28390486221331	c
-0.23997646534316	-2.09716643336424	-2.04939092966613	c
0.14330519959632	-0.15114797848295	-5.71374507659157	c
-0.46186857779746	-4.10142320322668	-0.68107701420678	f
0.08604556729681	4.32901783627479	-1.10500263243619	f
0.30902739012889	-0.29168522473115	-8.14946917835416	f
-0.07704864626216	-2.31496605157962	-4.48515791082097	n
0.21293658722503	2.14506770231880	-4.72418897561705	n
-0.19475136381903	0.12915962282306	-0.79173646561674	n
2.18208407755935	-1.16225402892882	9.00228547652532	c
2.03672097547211	-3.03040559518471	8.17023800423759	h
3.72872304048780	-0.10166179078435	8.17382396970256	h
2.38070519271856	-1.27997665939175	11.03906946289828	h
-0.72478309728037	0.51823223640138	8.33184078684308	cl
-0.39131194865125	0.36767682982745	2.00591169092982	c
-2.06364037098623	1.47461621893623	2.43166950510448	h
1.30209055581349	1.30421162220689	2.68257852160184	h
-0.55095056172743	-1.50563838324016	2.80490091280555	h

$end

E(COSMO) = -1117.8712507004 H

ZPE = 316.9 kJ/mol

enthalpy = 353.13 kJ/mol

chem. pot. = 203.49 kJ/mol

$[MeN_3C_3F_3]^+$

$coord

0.63981853156088	2.17913369090099	0.00000000000000	c
0.61473743271864	-2.13013665993227	0.00000000000000	c
4.18822447298945	-0.00542204091949	0.00000000000000	c

-0.69334685349152	-4.18682458773677	0.00000000000000	f
-0.60755346591904	4.27221284370346	0.00000000000000	f
6.63352521817212	-0.02309609512168	0.00000000000000	f
3.05919367210505	-2.23741268961845	0.00000000000000	n
3.08994001006522	2.23813135401465	0.00000000000000	n
-3.56445982301526	-0.02340292186672	0.00000000000000	c
-4.25098265992170	1.90239273493435	0.00000000000000	h
-4.17772114416574	-1.00977249090429	-1.69109694263308	h
-4.17772114416574	-1.00977249090429	1.69109694263308	h
-0.75365424693234	0.03396935345041	0.00000000000000	n

$end
E(COSMO) = -617.8032586206 H
ZPE = 217.0 kJ/mol
enthalpy = 239.75 kJ/mol
chem. pot. = 130.97 kJ/mol

3.6 Optimized structures for methyl cation affinities

All structures on the RI-B3LYP-D3/def2-TZVPP level of theory

$[CH_3]^+$

```
$coord
   -0.00000000000000      0.00000000000000      0.00000000000000  c
   -2.06235047617564      0.00000000000000      0.00000000000000  h
    1.03117523808783     -1.78604790387505      0.00000000000000  h
    1.03117523808783      1.78604790387505      0.00000000000000  h
$end
Etot = -39.46715352066 H
ZPE = 81.16 kJ/mol
enthalpy = 91.14 kJ/mol
chem. pot. = 35.41 kJ/mol
```

MeCl

```
$coord
   -0.00000000000000      0.00000000000000      0.29006239050744  c
   -0.97329303629883     -1.68579298952253      0.93930266393883  h
   -0.97329303629883      1.68579298952253      0.93930266393883  h
    1.94658607259765      0.00000000000000      0.93930266393883  h
    0.00000000000000      0.00000000000000     -3.10797038232392  cl
$end
Etot = -500.0618405244 H
ZPE = 97.67 kJ/mol
enthalpy = 108.12 kJ/mol
chem. pot. = 38.11 kJ/mol
```

$[Me_2Cl]^+$

```
$coord
   -2.01009662813659     -0.02094899151435      1.86375766979853  c
   -2.29344353102282     -1.98477813268909      1.34843687309117  h
   -0.56144975887149      0.27199353001293      3.28425698425437  h
   -3.76842717334130      0.93571042311285      2.32059560985027  h
   -0.92302783894159      1.61101633773991     -1.01147226602583  cl
    2.03643101733984     -0.02475746657740     -1.83486094206800  c
    2.67497678341471      0.96114150920980     -3.51889446760592  h
    3.30574936895173      0.22909766985084     -0.24522570703507  h
    1.53928776060745     -1.97847487914549     -2.20659375425948  h
$end
Etot = -539.6407755530 H
ZPE = 197.3 kJ/mol
enthalpy = 213.53 kJ/mol
chem. pot. = 124.52 kJ/mol
```

MeBr

```
$coord
    0.00000000000000      0.00000000000000      0.36653570605589  c
   -0.97575396449039     -1.69005544218411      0.99180936958102  h
   -0.97575396449039      1.69005544218411      0.99180936958102  h
    1.95150792898076      0.00000000000000      0.99180936958102  h
    0.00000000000000      0.00000000000000     -3.34201093690278  br
$end
Etot = -2613.944610948 H
ZPE = 96.18 kJ/mol
enthalpy = 106.83 kJ/mol
```

chem. pot. = 33.36 kJ/mol

[Me_2Br]$^+$

$coord

0.04789614574710	1.64928687896576	2.38264994513806	c
-0.16780778353817	3.58823999332894	3.01936307167497	h
1.95191308250680	0.93836850344589	2.64100308685095	h
-1.41743681256646	0.41134390886083	3.10209012922331	h
-0.49775657260575	1.87416190647732	-1.33819294991203	br
-0.02526064512017	-1.73106046202290	-2.32429097590120	c
-0.36567822413537	-1.72571328922035	-4.34802985293239	h
1.90914821402826	-2.20763175714291	-1.84669183618641	h
-1.43501740431623	-2.79699568269250	-1.28790061795526	h

$end

Etot = -2653.528959047 H

ZPE = 194.3 kJ/mol

enthalpy = 211.23 kJ/mol

chem. pot. = 117.52 kJ/mol

MeI

$coord

0.00000000000000	0.00000000000000	0.44732670999904	c
-0.97665414516943	-1.69161460085620	1.06401535131976	h
-0.97665414516943	1.69161460085620	1.06401535131976	h
1.95330829033885	0.00000000000000	1.06401535131976	h
0.00000000000000	0.00000000000000	-3.63942489337836	i

$end

Etot = -337.6094070615 H

ZPE = 94.67 kJ/mol

enthalpy = 105.52 kJ/mol

chem. pot. = 29.67 kJ/mol

[Me_2I]$^+$

$coord

0.32008448734126	-0.15711294507039	-2.61837542073267	i
-3.05227046163348	0.24759220766944	-0.31961401722891	c
-2.82540281804022	1.98215882640034	0.74665887349443	h
-4.58652170958249	0.36183470037218	-1.67779765451929	h
-3.16517118724529	-1.43342445205559	0.84582212115579	h
3.03614162003359	-0.23616455548949	0.45446694876844	c
4.83235114799044	-0.62644242293036	-0.45924496802060	h
2.98768081884942	1.61663906672972	1.32748811228572	h
2.45310810228676	-1.75508042562596	1.70059600479705	h

$end

Etot = -377.2045158694 H

ZPE = 191.5 kJ/mol

enthalpy = 208.93 kJ/mol

chem. pot. = 111.71 kJ/mol

1,2,3,4-tetrafluorobenzene

$coord

-1.31272981463121	0.00000000000000	-2.20059788013987	c
1.31272981463121	0.00000000000000	-2.20059788013987	c
2.60574453109002	0.00000000000000	0.08665000556445	c
1.31466146990386	0.00000000000000	2.35716523186852	c
-1.31466146990386	0.00000000000000	2.35716523186852	c
-2.60574453109002	0.00000000000000	0.08665000556445	c

```
   2.37649039425456      0.00000000000000      4.10020580088497  h
  -2.37649039425456      0.00000000000000      4.10020580088497  h
  -5.13954910275675      0.00000000000000      0.04373279833752  f
  -2.56553514203162      0.00000000000000     -4.38715595651556  f
   2.56553514203162      0.00000000000000     -4.38715595651556  f
   5.13954910275675      0.00000000000000      0.04373279833752  f
$end
Etot = -629.1706470358 H
ZPE = 176.4 kJ/mol
enthalpy = 199.21 kJ/mol
chem. pot. = 92.21 kJ/mol
```

1H-1,2,3,4-tetrafluorobenzeniumcation

```
$coord
   2.28954803246724      1.58837198548894      0.07027723345826  c
   2.33552724925786     -0.98256201221449     -0.19585650569223  c
  -2.44310170485375      1.48724027473053      0.04185601736477  c
  -0.09463207538054      2.78086042895021      0.18186551756249  c
  -4.15484506462752      2.60413954966138      0.05657213744876  h
  -0.11234365623503      5.21246336664826      0.37500571385452  f
   4.35817275681073      2.95575182074224      0.10424678306789  f
   4.43384542684879     -2.19840581087914     -0.44278961777940  f
  -2.43329170178720     -1.05051352598421     -0.19548890655939  c
  -4.15080796340851     -2.14331304409054     -0.39934607672897  h
  -0.03769174127683     -2.51267599411748     -0.01438966315706  c
  -0.02051795117207     -3.18348527113194      1.98362015968337  h
   0.03013839335681     -4.55787176780380     -1.56557279252306  f
$end
Etot = -629.4395305796 H
ZPE = 206.6 kJ/mol
enthalpy = 230.30 kJ/mol
chem. pot. = 119.08 kJ/mol
```

2H-1,2,3,4-tetrafluorobenzeniumcation

```
$coord
   2.27597312609111      1.63017557356880      0.06732489452344  c
   2.37076467962668     -0.93931945244938     -0.20215642064741  c
  -2.40813258101580      1.58098297772934      0.06738685554498  c
  -0.08066341992401      2.84327792913736      0.19226445368458  c
  -4.17251408335482      2.61003993587423      0.08787373400958  h
   4.36491124716903      2.98654252031553      0.09989535320352  f
   4.46624021882434     -2.16205971786128     -0.45746802933482  f
  -2.38529224859325     -0.98093401571700     -0.19044765185555  c
   0.00817167717605     -2.49160152592541     -0.01302052701596  c
   0.00751815227183     -3.13680635188319      1.99252469239336  h
   0.03376583255867     -4.53112729327146     -1.55155865286025  f
  -4.42851733894252     -2.29571679349579     -0.44841182711886  f
  -0.05222526188733      4.88654621397822      0.35579312547338  h
$end
Etot = -629.4371169585 H
ZPE = 206.3 kJ/mol
enthalpy = 230.07 kJ/mol
chem. pot. = 118.62 kJ/mol
```

5H-1,2,3,4-tetrafluorobenzeniumcation

$coord

2.38264471878560	1.44201628903182	0.00000000000000	c
2.50781755048801	-1.21073717469164	0.00000000000000	c
0.27630611864908	-2.53282057813071	0.00000000000000	c
-2.16607886043588	1.51991561132040	0.00000000000000	c
0.04416291783354	2.79140478407268	0.00000000000000	c
-3.94122826806161	2.53420860863057	0.00000000000000	h
0.18669662406973	5.27552264704331	0.00000000000000	f
4.46409222384391	2.70695018776659	0.00000000000000	f
4.71735634489212	-2.33595734644438	0.00000000000000	f
0.30232451157052	-4.98534990617028	0.00000000000000	f
-2.19470326104532	-1.26864718338989	0.00000000000000	c
-3.28969531029482	-1.96825296951928	1.62870661787406	h
-3.28969531029482	-1.96825296951928	-1.62870661787406	h

$end

Etot = -629.4543062214 H

ZPE = 205.2 kJ/mol

enthalpy = 229.05 kJ/mol

chem. pot. = 117.93 kJ/mol

5-methyl-1,2,3,4-tetrafluorobenzene

$coord

3.35058739770098	0.74407009338070	0.18243558207677	c
3.41666619170583	-1.87125379203802	0.00532711538608	c
-1.20999894103874	0.74799867076507	0.00338259394753	c
1.08061233509760	2.03922564872730	0.18228446745415	c
5.54351612815493	2.00653544697407	0.35390423090093	f
5.60713696307055	-3.12223484060062	0.00424460984706	f
-1.11822637180169	-1.87030587615503	-0.17285586103845	c
-3.27602348578673	-3.20125298546250	-0.35013022097460	f
1.12119557449289	4.07665362457751	0.32301321352800	h
1.15124661944244	-3.18580611872586	-0.17417702807208	c
1.17254881441186	-5.70149935157396	-0.34746122582609	f
-3.71780547000306	2.08279562014658	-0.00148322407970	c
-4.78454024997159	1.64741673021913	-1.71140585196263	h
-4.87569040445418	1.48704864349886	1.59770093675288	h
-3.46122510102110	4.12060848626673	0.10522066206007	h

$end

Etot = -668.4778011746 H

ZPE = 247.9 kJ/mol

enthalpy = 275.60 kJ/mol

chem. pot. = 155.92 kJ/mol

1H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

3.18169615764827	-2.08041967827029	0.19090613686944	c
-1.44722708949259	0.79901755652058	-0.01812426608845	c
5.29495726444279	-3.27588550595237	0.43530661724152	f
-1.28269763011560	-1.88156844770036	-0.32195205352314	c
-3.35719717375961	-3.13054404103448	-0.66764656000076	f
0.95953194211022	-3.32448534207094	-0.22754543052183	c
0.83887429636394	-5.79644834254363	-0.43006603879580	f
-3.99917414253087	2.03195089296900	-0.05458504090041	c
-4.92535943626592	1.72782409537720	-1.87136553702425	h
-5.21869746734283	1.22823370130927	1.39976690298791	h
-3.82677538254876	4.05352616636209	0.26640075587935	h

```
   0.76892154433582     2.02663696627917     0.35655397472651  c
   0.83962100229196     4.04589931283356     0.68054232721785  h
   3.26115569556756     0.73971506241141     0.18081941110238  c
   3.91949421306141     1.18714909324202    -1.76992230219355  h
   4.99287620623426     1.64939851026774     1.85091110302324  f
$end
Etot = -668.7540890076 H
ZPE = 278.3 kJ/mol
enthalpy = 306.49 kJ/mol
chem. pot. = 185.46 kJ/mol
```

2H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

```
$coord
  -1.41278641060312     0.89524651235487    -0.04092909708742  c
  -1.40913678810314    -1.78958273798531    -0.16469564320506  c
  -3.60328238434850    -2.98003715960197    -0.32916808624383  f
   0.78155116810929    -3.11831588871987    -0.03846102693679  c
   0.83250398033818    -5.56812867722195    -0.05533211405525  f
  -3.87382747903922     2.20767393702667    -0.14333839042891  c
  -4.92357732324969     1.60694761783592    -1.82261843032254  h
  -5.04232674273625     1.59489777800368     1.45497107417561  h
  -3.68160604015909     4.24934613666587    -0.11928785124292  h
   0.87538954599087     2.25668781878441     0.22150045923754  c
   0.85276763080531     4.29295220680856     0.38363185989131  h
   3.09385779920248     0.98531837566800     0.35557397650095  c
   3.29791802768418    -1.81681063693741    -0.03729340042011  c
   4.03795304363431    -2.03599086892827    -1.98538989358007  h
   5.23309214463412     2.12920727106490     0.71450655881754  f
   4.94150982784031    -2.90941168481812     1.60633000490005  f
$end
Etot = -668.7608188934 H
ZPE = 277.1 kJ/mol
enthalpy = 305.65 kJ/mol
chem. pot. = 183.10 kJ/mol
```

3H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

```
$coord
  -1.36979795652403     0.94976984974266    -0.02719842167814  c
  -1.28406077562810    -1.63890220553507    -0.02656246315319  c
  -3.33051204941490    -2.99102610324865    -0.02014955952147  f
  -3.83006998454898     2.36738920612451    -0.03198020336528  c
  -5.13576650999758     1.56490467659591    -1.40584625341701  h
  -4.72755069206550     2.25020532421334     1.82131996772439  h
  -3.53326778488288     4.35068332049728    -0.48179358820868  h
   0.99205560255066     2.16871628193956     0.09187323435897  c
   1.04245722424702     4.21896179176127     0.11937416406782  h
   3.34981519594623     0.95271050736212     0.22722740385226  c
   5.42175400448059     2.32616689477906     0.43434353422886  f
   1.11516924406496    -3.13061204224995    -0.22708192372710  c
   1.22224185855303    -3.58288977738540    -2.28063792984482  h
   3.46133287303247    -1.62370910479903     0.23785972768345  c
   5.55197740445804    -2.86860636211593     0.46264780432468  f
   1.05422234572886    -5.31376225768166     1.10660450667523  f
$end
Etot = -668.7507228122 H
ZPE = 277.2 kJ/mol
enthalpy = 306.25 kJ/mol
```

chem. pot. = 178.06 kJ/mol

4H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

-1.13246924617471	1.00346429605151	-0.00997829565143	c
-3.61463560947854	2.26153035407453	0.21365048364594	c
-4.87755486047265	1.68780536417023	-1.31802736968483	h
-4.53457983544176	1.62353772646483	1.95595696708679	h
-3.44057075967820	4.30710965857036	0.23999810308851	h
1.12932349072291	2.23803934340017	-0.01254332260928	c
1.25953345757134	4.27634110772177	0.07060221744955	h
3.39630962626681	0.85241914781824	0.02457337064612	c
5.51659458086219	2.07185580114981	0.07472359532450	f
3.54916447476477	-1.82357151712941	0.07947136053997	c
5.76956594868194	-2.92600618649117	0.22892521767178	f
1.34032186048807	-3.13569800200061	0.06197756188439	c
-1.13209022456488	-1.81743676234732	-0.34567673780576	c
-1.48064857293843	-2.06284946582687	-2.40280473264658	h
1.28496123208143	-5.57823567784794	0.19488218053730	f
-3.03322556269028	-2.97830518777820	0.94426940052305	f

$end

Etot = -668.7612731895 H

ZPE = 277.9 kJ/mol

enthalpy = 306.05 kJ/mol

chem. pot. = 185.05 kJ/mol

5H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

3.40221194274794	0.50846110402208	0.23371640352468	c
3.43334048260710	-2.05848784952632	0.00567808167716	c
-1.37308706372256	0.54525812510658	-0.04673549962115	c
5.50125033042261	1.77202460215166	0.47010813543001	f
5.52949396215284	-3.38989355450914	0.01339158318048	f
-1.25125461927575	-2.01815225028925	-0.27304974728488	c
-3.31252035695227	-3.41334656721799	-0.51360428657549	f
1.08865743796887	-3.30628737174379	-0.25172628066081	c
1.09607070240893	-5.73829293035781	-0.47327875206623	f
-3.82469474783150	1.91303155320799	-0.02316963864856	c
-5.09178046544203	1.17273348514306	-1.47096055463536	h
-4.77074352700023	1.59987954070662	1.79170116351575	h
-3.57799772594255	3.93685852908298	-0.28177486145778	h
1.03257045378337	1.96666463216217	0.21064263021493	c
1.15581761683771	3.37185533333727	-1.31941818172735	h
0.96266557723749	3.13769361872398	1.92847980513467	h

$end

Etot = -668.7731691228 H

ZPE = 276.0 kJ/mol

enthalpy = 304.99 kJ/mol

chem. pot. = 180.39 kJ/mol

6H-5-methyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

1.10829506586842	2.18927030671206	-0.27239277296787	c
1.12776983628626	4.21967710380016	-0.02867565475379	h
3.30370985489693	0.89505226150447	-0.34702522231819	c
5.53636343709574	1.98230591329529	-0.14096290119065	f
3.28112013930946	-1.78166527220403	-0.66383982220396	c

```
   5.40340900576529    -2.97959661064829    -0.72480987927126  f
   1.02978575605679    -3.16083211555398    -0.92119783381073  c
   1.12392423074949    -5.62378278051807    -1.21950619842904  f
  -1.21051502585259    -1.85590351349198    -0.85567741350653  c
  -3.32658509940159    -3.08005830851461    -1.11197443692594  f
  -1.35807683737756     0.89524185779637    -0.47448823816930  c
  -2.33342009899763     1.66141970195421    -2.15113838729817  h
  -3.11466781424123     1.54084277325305     1.83421807228870  c
  -3.35814931609141     3.57837072033953     1.93311521237736  h
  -4.94674116015864     0.65287909137419     1.56339456996970  h
  -2.26622197390777     0.86677887090167     3.58096090620974  h
$end
Etot = -668.7623293583 H
ZPE = 279.6 kJ/mol
enthalpy = 307.34 kJ/mol
chem. pot. = 187.28 kJ/mol
```

dimethyl-1,2,3,4-tetrafluorobenzene

```
$coord
   0.27740142023480    -3.14217322830333     0.17408489755863  c
   2.90292307695971    -3.18382843152168     0.14514692769478  c
   4.21083463897980    -0.92280132983951     0.00863747808816  c
   2.86449293697783     1.32835489777717    -0.10109320195857  c
   0.24372160691414     1.39251027675546    -0.08075175963194  c
  -1.08635867459652    -0.90530128780691     0.06371685547230  c
   4.20620884383498     3.48619967515528    -0.23011523096220  f
   6.73469980725887    -0.91589874201998    -0.01660342586380  f
   4.15692982890829    -5.37213430947921     0.25084848058061  f
  -0.92498179145194    -5.38051663334003     0.31617959083946  f
  -3.92827825609968    -0.95357769428862     0.09811306123771  c
  -4.69921174904081    -0.12640251146202    -1.62807653022297  h
  -4.64248696339120    -2.87126367189643     0.26349903298996  h
  -4.66447925292437     0.14796249047458     1.67936393936116  h
  -1.13304807735939     3.87564571199614    -0.21114321003346  c
  -2.39876827935573     3.92980402733888    -1.83928299006989  h
  -2.29493484461902     4.16326557131975     1.46966154678390  h
   0.17533572877020     5.45015518914066    -0.36218546186392  h
$end
Etot = -707.7836024446 H
ZPE = 320.6 kJ/mol
enthalpy = 352.36 kJ/mol
chem. pot. = 224.32 kJ/mol
```

1H-dimethyl-1,2,3,4-tetrafluorobenzeniumcation

```
$coord
   0.14425217598261    -3.16731522501599    -0.05105847966836  c
   2.81976865533535    -3.31079359061527     0.12169849661818  c
   4.13488315684947    -1.11487348723648     0.23071721941770  c
  -0.01883700574231     1.32130598233482     0.00960567163367  c
  -1.31218731446061    -0.92896326456087    -0.08759533971445  c
   6.57256521672009    -1.05676812704474     0.47820523606906  f
   3.90917760215849    -5.54204448541580     0.24963977746939  f
  -1.00981866701209    -5.33221589162122    -0.12935312344202  f
  -4.15055525775077    -1.07077915784837    -0.13081466978081  c
  -4.87634445002117    -0.34092720459369    -1.91821891487583  h
  -4.82594910726754    -2.99516638876366     0.09293180438419  h
  -4.94902470359401     0.07464292861348     1.38305083830382  h
```

-1.29763601421178	3.81025149405185	0.14970657093347	c
-2.84980699343053	3.92441291174452	-1.20425844057621	h
-2.14792008354563	4.02209749615129	2.02804641465537	h
-0.00139173862596	5.37639248874488	-0.13010168658655	h
2.81203294425212	1.34498301729043	-0.16160449407037	c
3.16335612118261	1.77452852965425	-2.18920801258727	h
3.88343546318179	3.21123197413059	1.25861113181700	f

$end
Etot = -708.0717749888 H
ZPE = 349.5 kJ/mol
enthalpy = 382.47 kJ/mol
chem. pot. = 249.67 kJ/mol

2H-dimethyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

0.03086263516935	-3.19060577008159	0.17546598951349	c
2.59271643293982	-3.25922813860127	0.26608431861734	c
-0.01269848870285	1.51773963589846	-0.03802535599160	c
-1.29803606374549	-0.85861036172993	0.02946017845558	c
3.84549354383210	-5.35377019477123	0.49832550071474	f
-1.26563262278267	-5.32960586306473	0.29948345415915	f
-4.09262587652020	-0.92603498459415	-0.03597245051583	c
-4.74089972852782	-0.14774027928665	-1.84413202672059	h
-4.85720398714628	-2.81235338920551	0.19400997094989	h
-4.86603739843612	0.32970627907240	1.41101096256025	h
-1.43599085667478	3.97282736683171	-0.12240319848289	c
-2.71925137337338	4.01704226900653	-1.73375867020414	h
-2.56321216614757	4.22485715458074	1.58533356383450	h
-0.15143055067390	5.56564217399961	-0.27832660487641	h
4.11604691315191	-0.90755504999241	-0.06477572823354	c
4.83989161391314	-0.98806206630911	-2.02929142924888	h
2.55693974882541	1.45435176375998	0.04457691176055	c
3.90608223212290	3.51712816207708	0.09128940363346	f
6.11498599277648	-0.82572870758997	1.55164521007485	f

$end
Etot = -708.0722515383 H
ZPE = 349.8 kJ/mol
enthalpy = 382.52 kJ/mol
chem. pot. = 250.70 kJ/mol

6H-dimethyl-1,2,3,4-tetrafluorobenzeniumcation

$coord

0.09494204729406	-3.05152021260256	-0.62876333868481	c
2.76474975214770	-3.02293003958434	-0.62876203897488	c
-1.27267874686352	-0.87009068611921	-0.55584465630414	c
3.97031417398312	-5.14649496427633	-0.71781073456344	f
-1.00383075706076	-5.29965445905674	-0.73141819970521	f
-4.08169794986484	-0.91079023885134	-0.58687199541050	c
-4.78937887650203	-2.56936643984168	-1.57566578142656	h
-4.79477633150975	-1.01579749587330	1.35470041580530	h
-4.85414440050459	0.79358724149303	-1.44194379620102	h
2.87586427018075	1.45406730177088	-0.48283939705289	c
4.10003080464720	3.59475416597855	-0.45438140278594	f
4.17928604848997	-0.76788678820652	-0.55972671464690	c
0.09163594215240	1.58780711604228	-0.37367799833495	c
-0.50501734020240	2.75890430590229	-1.98485904186374	h
-0.71640353671406	3.07270510500977	2.07066600439904	c

```
  -0.23076948882178     1.98884548616975     3.74943204911126  h
   0.25175985454184     4.88315329772624     2.11548565869723  h
  -2.74254138740422     3.39856015660207     2.02839607462178  h
   6.66265592201092    -0.87785285228276    -0.59611510667972  f
$end
Etot = -708.0802768351 H
ZPE = 351.5 kJ/mol
enthalpy = 383.70 kJ/mol
chem. pot. = 253.91 kJ/mol
```

1,2,3-trifluorobenzene

```
$coord
   2.28472225443595     0.00000000000000    -1.40994405688642  c
   2.25961459270098     0.00000000000000     1.20522230901210  c
   0.00000000000000     0.00000000000000     2.54262230555036  c
  -2.25961459270098     0.00000000000000     1.20522230901210  c
  -2.28472225443595     0.00000000000000    -1.40994405688642  c
   0.00000000000000     0.00000000000000    -2.70806066465918  c
   4.08112044180603     0.00000000000000    -2.38008632236133  h
  -4.08112044180603     0.00000000000000    -2.38008632236133  h
   0.00000000000000     0.00000000000000    -4.75024652248982  h
  -4.43242061134481     0.00000000000000     2.50934077110240  f
   0.00000000000000     0.00000000000000     5.06661947986518  f
   4.43242061134481     0.00000000000000     2.50934077110240  f
$end
Etot = -529.9292766527 H
ZPE = 197.5 kJ/mol
enthalpy = 218.01 kJ/mol
chem. pot. = 116.63 kJ/mol
```

1H-1,2,3-trifluorobenzeniumcation

```
$coord
   0.22266535616007    -2.42273897696534    -1.45696109486181  c
   0.09819008130458    -2.51099928173640     1.17047527225719  c
  -0.25222487676855    -0.29572488610098     2.50175655935946  c
   0.42126325501374    -4.21075003665054    -2.43958190789167  h
  -0.55224796074696    -0.27396041926541     4.91602663502436  f
   0.16242461822300    -4.69089698878771     2.37020284734881  f
  -0.24998373719149     2.08956542682994    -1.62135812710849  c
  -0.45585824276244     3.88220860882776    -2.58505688825369  h
   0.04713649551605    -0.14378645312949    -2.84931773653920  c
   0.08285446664058    -0.22526274415877    -4.88976796908865  h
  -0.07665468858587     2.17583513034605     1.17030018319479  c
   1.99018855246717     2.60256716058950     1.41821232104389  h
  -1.43775331926991     4.02394346020142     2.29506990551499  f
$end
Etot = -530.1933016924 H
ZPE = 226.0 kJ/mol
enthalpy = 247.46 kJ/mol
chem. pot. = 142.01 kJ/mol
```

2H-1,2,3-trifluorobenzeniumcation

```
$coord
   0.19838456041537    -2.47359257525920    -1.43079851210179  c
   0.07251212261846    -2.59131060072974     1.22121586067771  c
  -0.19056206435267    -0.38465892846682     2.51408631008402  c
   0.35527695545211    -4.24132512121867    -2.45338914400575  h
```

-0.46041828330717	-0.30390298384379	4.94381685107549	f
-0.19012918417571	1.98762329270351	-1.58694692762633	c
0.07037572498350	-0.23345280963959	-2.85519260756655	c
0.08368180201031	-0.26606950021835	-4.89754886675396	h
-0.00767815282770	2.14139147488558	1.23877997508471	c
1.99362106998965	2.70505870844049	1.56509763728074	h
-1.55564270439919	3.90344518224242	2.25786281801112	f
-0.45618372865266	4.13469261123421	-2.72829187706514	f
0.08676188224567	-4.37789875012997	2.21130848290575	h

$end
Etot = -530.2061392753 H
ZPE = 227.8 kJ/mol
enthalpy = 249.30 kJ/mol
chem. pot. = 143.44 kJ/mol

4H-1,2,3-trifluorobenzeniumcation

$coord

-0.00043814777272	-2.52281980901371	-1.33149991987799	c
0.00009203601749	-2.44212373343399	1.34170367921979	c
0.00039065381844	-0.18913120913455	2.76102489470825	c
-0.00038695599129	2.04853298737781	1.46099170300268	c
-0.00013869884256	-0.31620080551303	-2.62277420011230	c
-0.00032126236164	-4.35258232518631	-2.24111383773514	h
-0.00052773749609	-0.29900954699381	-4.66731681420613	h
-0.00201038744158	4.18231986953471	2.67681075177607	f
0.00100816957479	-0.28324612652270	5.24177039369346	f
0.00027018401297	-4.54886614600568	2.58613214093896	f
0.00028949599461	2.14867769814723	-1.31599586890376	c
1.62809076139351	3.28665198902624	-1.94439363392547	h
-1.62631811090598	3.28779715771781	-1.94533928857839	h

$end
Etot = -530.2218454026 H
ZPE = 226.4 kJ/mol
enthalpy = 248.11 kJ/mol
chem. pot. = 142.44 kJ/mol

5H-1,2,3-trifluorobenzeniumcation

$coord

0.00000000000000	-2.37666351569655	-1.09432266552255	c
0.00000000000000	-2.34414515206907	1.46914929147357	c
0.00000000000000	0.00000000000000	2.76822291453691	c
0.00000000000000	2.34414515206907	1.46914929147357	c
0.00000000000000	-4.16248204404300	-2.09239404238054	h
0.00000000000000	4.41542865783279	2.84759162333735	f
0.00000000000000	0.00000000000000	5.20305339954338	f
0.00000000000000	-4.41542865783279	2.84759162333735	f
0.00000000000000	2.37666351569655	-1.09432266552255	c
0.00000000000000	4.16248204404300	-2.09239404238054	h
0.00000000000000	0.00000000000000	-2.52365269714496	c
1.60967242947668	0.00000000000000	-3.85383601537549	h
-1.60967242947668	0.00000000000000	-3.85383601537549	h

$end
Etot = -530.2132744326 H
ZPE = 224.7 kJ/mol
enthalpy = 246.41 kJ/mol
chem. pot. = 142.59 kJ/mol

4-methyl-1,2,3-trifluorobenzene

$coord

-2.01335628206396	-1.18760357124420	-0.01360847000023	c
0.61985411678631	-1.26701892494540	-0.00366021120754	c
1.88602662059909	1.03624816008690	0.00727909794043	c
0.61792849605238	3.33149732589792	0.00659991349626	c
-2.00685021707846	3.33228560326554	-0.00087758802340	c
-3.33555250077998	1.08458810122298	-0.01112931517650	c
-3.05452682795949	-2.94671999934391	-0.02367839500696	h
-5.37663244912480	1.14045188062362	-0.01824411520884	h
1.90572621808045	5.50415737712283	0.01344370841306	f
4.42685971778268	1.07554362796209	0.01809843400421	f
-3.22311339411335	5.55824528251535	0.00100830659610	f
2.09492762314938	-3.69514200809958	0.00321718079000	c
3.39878663055776	-3.78093930137002	-1.59179212870214	h
3.22988002229210	-3.87143345661254	1.71678429459376	h
0.83004222581986	-5.31416009708163	-0.10344071250818	h

$end

Etot = -569.2361291878 H

ZPE = 269.1 kJ/mol

enthalpy = 294.37 kJ/mol

chem. pot. = 180.50 kJ/mol

1H-4-methyl-1,2,3-trifluorobenzeniumcation

$coord

-1.95156826965264	-1.44396596456250	0.04234223880826	c
0.74999982462455	-1.47563480279099	-0.05487158847625	c
2.11278943907748	0.81289087534721	0.02878203122577	c
0.88314905257112	3.07654687347733	0.22319641089671	c
-3.24641485068361	0.74916427067070	0.20351418548698	c
-2.93407472139850	-3.23532385113938	0.05482194452632	h
-5.28443701984704	0.82090780866911	0.36415471931567	h
2.09694118757534	5.18623769010873	0.44325108848654	f
4.61319502823585	0.74489963033193	0.04011942857856	f
2.17884132470536	-3.87088438017461	-0.17222015246251	c
3.49837481586708	-3.83302915905952	-1.76590914362163	h
3.38228045058885	-4.03694805801661	1.50685806063183	h
0.95401099360181	-5.51074757208893	-0.30751497322197	h
-1.92289994304512	3.21311512684241	-0.01357427141329	c
-2.19834685750555	3.73009170472747	-2.03936342893071	h
-2.93184045471483	5.07267980765755	1.44641345016979	f

$end

Etot = -569.5163864054 H

ZPE = 297.0 kJ/mol

enthalpy = 323.32 kJ/mol

chem. pot. = 205.80 kJ/mol

2H-4-methyl-1,2,3-trifluorobenzeniumcation

$coord

-1.98656885935798	-1.34703945937437	-0.14674015768685	c
0.67443264312254	-1.50846607048431	-0.01448350762895	c
1.91100254749918	0.75006922439667	0.20623543350467	c
-3.43070126149193	0.88379250086843	-0.05236061018147	c
-3.01573411138013	-3.11432029439114	-0.28018049616142	h
-5.47231704663556	0.82575023453517	-0.06985308311567	h
4.35229041545776	0.87397800195301	0.45266256906475	f
2.05101849090569	-3.99187720814611	-0.03635726933568	c

2.60293859536673	-4.48484589271577	-1.96222342659064	h
3.76088435085388	-3.90355650380853	1.10213942987500	h
0.85290213024541	-5.49638916272911	0.69196105777936	h
0.62894122957874	3.26707959871299	-0.00322700016468	c
0.95321002545809	3.81350260189855	-2.00912219408911	h
-2.18920949767987	3.11806171242872	0.18031922470501	c
1.65199794203713	5.04939087182588	1.52451859999996	f
-3.34508759397970	5.26486984502991	0.41671143002575	f

$end
Etot = -569.5190609535 H
ZPE = 298.8 kJ/mol
enthalpy = 325.50 kJ/mol
chem. pot. = 204.58 kJ/mol

3H-4-methyl-1,2,3-trifluorobenzeniumcation

$coord

-2.13416793253276	-1.30758662905101	-0.25513844114038	c
0.44607760725858	-1.44213777080475	-0.01339929957274	c
0.43122108820262	3.36538136447756	0.29258363835897	c
-2.14344765609847	3.34787159503286	0.04556791725509	c
-3.38724952666864	1.02726382585373	-0.22806145630622	c
-3.24311249813597	-3.01998793837946	-0.35950655909431	h
-5.43104773429964	1.08829442825016	-0.36821607884501	h
1.70509575872572	5.41845401524898	0.66055259380635	f
-3.45414515232263	5.46584360931462	0.17256107685722	f
1.90499724386726	-3.80701218725719	0.22908868020849	c
3.39002044373963	-3.91538876048697	-1.20503953011605	h
2.89821534298343	-3.80780511851349	2.04636339434463	h
0.70146460533098	-5.46535318497943	0.10001054905251	h
1.88972698333520	0.98619668347418	-0.11771721437672	c
2.32480317077380	1.11266229189574	-2.18159807479307	h
4.10154825584084	0.95330377592436	1.18194880436128	f

$end
Etot = -569.5149232775 H
ZPE = 297.4 kJ/mol
enthalpy = 323.43 kJ/mol
chem. pot. = 207.91 kJ/mol

4H-4-methyl-1,2,3-trifluorobenzeniumcation

$coord

-2.00979853128861	-1.35707239188885	-0.46661812185526	c
0.61287227628407	3.31470491483906	-0.71470238502453	c
-2.03956255609992	3.13272696109776	-0.64614232409934	c
-3.36027707106849	0.81400366497720	-0.52772684744973	c
-2.96013367516344	-3.16607114287768	-0.37597691003243	h
-5.40263572570357	0.86515526439602	-0.49472136020391	h
1.70451321808524	5.54461428160308	-0.83485010336637	f
-3.31385510436205	5.22336023737629	-0.70566221270167	f
0.78314459283327	-1.40209539767651	-0.48452052426728	c
1.37715823952270	-2.45097650015413	-2.18675362661571	h
1.86424181687776	-2.93390849932441	1.81446097211136	c
1.11403901559013	-4.84590894548771	1.75661649301683	h
3.91225534776716	-3.01037807030535	1.68004822231944	h
1.32093401614048	-2.03989930967755	3.58409632197558	h
1.96949346919183	1.11196629428176	-0.65837460979552	c
4.42761067139349	1.19977863882111	-0.73917298401145	f

$end

Etot = -569.5294647194 H
ZPE = 300.9 kJ/mol
enthalpy = 326.44 kJ/mol
chem. pot. = 211.74 kJ/mol

5H-4-methyl-1,2,3-trifluorobenzeniumcation

```
$coord
   0.85733722445299    -1.17235233644777    -0.00566140016058  c
   2.09925534182395     1.10240390325532    -0.00157017145675  c
   0.76131424078031     3.39226818815241     0.00139832820533  c
  -1.92871601194624     3.48091904074039     0.00394472325829  c
  -3.25908909215082     1.30466364147476     0.00009625655249  c
  -5.30343277741224     1.34662197054922    -0.00018863907784  h
   2.00321603982398     5.49550103672102     0.00183147866161  f
   4.59663722196810     1.21787666427099    -0.00051728892785  f
  -2.99041107762028     5.73517489731005     0.00745725700882  f
   2.26851718731290    -3.59479633547781     0.00193035249870  c
   3.62303277762466    -3.64178265751470    -1.55706092129826  h
   3.39431657463844    -3.74609935197750     1.73074682937757  h
   1.01646484691285    -5.21812808348863    -0.12667192374987  h
  -1.93466357544764    -1.14257729075924    -0.01043793191546  c
  -2.60733745230616    -2.29356445746128     1.59164967639854  h
  -2.59644146845491    -2.26612882934722    -1.63694662537466  h
$end
```

Etot = -569.5329284615 H
ZPE = 295.8 kJ/mol
enthalpy = 322.40 kJ/mol
chem. pot. = 204.80 kJ/mol

6H-4-methyl-1,2,3-trifluorobenzeniumcation

```
$coord
   0.83173488808393    -1.41774226140950    -0.00109879620423  c
   2.08713135050095     0.96288120170786     0.01636865173438  c
   0.88378372150097     3.33719227096095     0.01583219299782  c
  -1.69969869062214     3.38119029772454    -0.00002333217601  c
   2.24930499410107     5.41410355860795     0.03065639728254  f
   4.54077849050920     0.98355119608663     0.03387433929505  f
  -2.90957077773454     5.52160827843202    -0.00082217076572  f
   2.37856831274389    -3.79337641975292     0.00211429445018  c
   3.63809278657651    -3.84703423903663    -1.62846504938123  h
   3.55728061079329    -3.89252218752288     1.69043822315421  h
   1.16164010241904    -5.44781011681281    -0.04963571966960  h
  -1.73568265816591    -1.33677573303859    -0.01729442441869  c
  -2.81511893629595    -3.07413497815460    -0.03106089798187  h
  -3.19002498074348     1.04383539043650    -0.01642851009669  c
  -4.48152432334974     1.08864622125419    -1.64990833543861  h
  -4.49669489031704     1.07638752051725     1.60545313721837  h
$end
```

Etot = -569.5354845601 H
ZPE = 298.2 kJ/mol
enthalpy = 324.35 kJ/mol
chem. pot. = 208.86 kJ/mol

5-methyl-1,2,3-trifluorobenzene

$coord

-0.70971566412244	-1.23463390814548	-0.03462727215667	c
1.92608978516312	-1.20760162471483	-0.02163169235912	c
3.21489376414347	1.06712856984017	0.00505754679092	c
1.93950629866613	3.35874718994361	0.01784222210133	c
-0.68381372006162	3.31504060654438	-0.00091772603210	c
-2.00687976709826	1.06142630978260	-0.02788864801130	c
3.01029431920150	-2.93955125732386	-0.03578410792292	h
-4.04907736873064	1.13200098013915	-0.04669661059502	h
-1.92884965508458	5.52409824898153	0.00010029979914	f
3.20108626179766	5.54737203310469	0.03473053577016	f
5.75047046608123	1.09434630921693	0.01111552126068	f
-2.13535027343562	-3.69783499353271	0.00662166785510	c
-1.02772272703004	-5.22123685814902	-0.82569402127305	h
-2.58993151134790	-4.24554404062576	1.94531843969456	h
-3.91100020814198	-3.55375756506133	-1.02754615492183	h

$end

Etot = -569.2352927214 H

ZPE = 268.5 kJ/mol

enthalpy = 294.02 kJ/mol

chem. pot. = 178.20 kJ/mol

1H-5-methyl-1,2,3-trifluorobenzeniumcation

$coord

-0.77412266777001	-1.44690040936363	-0.00670088692682	c
1.91667146164112	-1.35636730603626	-0.02431236645768	c
3.32952300303910	0.85752211269017	0.09711499782197	c
2.10029468490689	3.14678711905803	0.27794042019569	c
2.97832920153478	-3.11007986840345	-0.09520842410395	h
3.29830983627475	5.24786801717059	0.56371649004038	f
5.81893063001491	0.76331506450344	0.17935017608244	f
-2.07966214317236	-3.96590066571090	-0.04361856697143	c
-1.66606064251915	-4.96397687137311	-1.80070682227022	h
-1.41963750177835	-5.14704432901226	1.51200503260651	h
-4.11771470216343	-3.75654702659231	0.11522309041518	h
-2.03777273446400	0.79555452356511	0.11450893462441	c
-4.07939223105373	0.90946593972961	0.18806813930066	h
-0.68248614388361	3.23562404648186	-0.07375907272533	c
-0.79540944151220	3.60247781178481	-2.16187117239609	h
-1.78980060909476	5.18820184150823	1.15825003076425	f

$end

Etot = -569.5061284416 H

ZPE = 297.1 kJ/mol

enthalpy = 323.24 kJ/mol

chem. pot. = 207.25 kJ/mol

2H-5-methyl-1,2,3-trifluorobenzeniumcation

$coord

-0.83028622776626	-1.45401095823090	-0.09803695716927	c
1.85128449258006	-1.49247133914480	-0.00894464295134	c
3.13232444385328	0.71379599489101	0.14952246839424	c
-0.94949702266978	3.06218723885675	0.14809441316375	c
-2.21179525657922	0.84631159555035	-0.00930170901253	c
2.86970336185962	-3.26362000878813	-0.00146300298845	h
-4.25503364278736	0.83536826585983	-0.00202127669977	h
-2.10897689940158	5.21883845084016	0.34069858081225	f

```
   5.57872184706355     0.79482434749485     0.34527105565945  f
  -2.23135539154356    -3.87413056134539    -0.17037939446532  c
  -1.10930513940065    -5.41154089768226    -0.94707318960952  h
  -2.70136875706323    -4.38402173955260     1.78928569922589  h
  -4.01913498689043    -3.70148738426380    -1.17603940424952  h
   1.87498427420869     3.24968858446839    -0.03267868001003  c
   2.26472471156558     3.92496267663384    -1.97570982567380  h
   2.84501019297124     4.93530573441278     1.64877586557399  f
$end
Etot = -569.5275946370 H
ZPE = 298.0 kJ/mol
enthalpy = 324.65 kJ/mol
chem. pot. = 203.00 kJ/mol
```

4H-5-methyl-1,2,3-trifluorobenzeniumcation

```
$coord
  -0.49039296018711    -1.40555609921739    -0.02734938710642  c
   2.08674773007485    -1.33181136623609    -0.10202157110937  c
   3.34446451537212     1.00595436415672    -0.08011881279513  c
   2.11768151205836     3.37700008781796     0.01052445475330  c
  -0.45524084516227     3.36718978977491     0.07695694155766  c
   3.22961438530948    -3.02461051720774    -0.17229744577436  h
  -1.71549907068060     5.48159278349879     0.15429145541813  f
   3.45940225402514     5.46997502152775     0.02395342257053  f
   5.79557739744922     1.02856681710320    -0.14585746180820  f
  -1.93924489162511    -3.81038141818488    -0.00403359213051  c
  -0.72203845172534    -5.44433266520470    -0.26367922615604  h
  -2.93260672358642    -4.01260949836004     1.79932949391126  h
  -3.39111631036742    -3.80828444318577    -1.47221849363562  h
  -1.93672988910751     1.00780204114766     0.05539355211522  c
  -3.24780618281476     1.08506515108181    -1.55649218745381  h
  -3.20281246903268     1.01443995148779     1.70361885764337  h
$end
Etot = -569.5397864749 H
ZPE = 297.6 kJ/mol
enthalpy = 324.13 kJ/mol
chem. pot. = 206.71 kJ/mol
```

5H-5-methyl-1,2,3-trifluorobenzeniumcation

```
$coord
   1.99859406859623    -1.27880295690221    -0.49230612049071  c
   3.23898541141483     0.96073991510480    -0.61440660443224  c
  -0.83066869537727     3.26043286544909    -0.68550575412812  c
  -2.11236244936346     1.04416762325916    -0.56483679318528  c
   3.06837232322016    -3.02165882947565    -0.42019294413837  h
  -4.15848087471557     1.06192933547352    -0.54820659335744  h
  -1.96514240028692     5.47659762608177    -0.78481190816253  f
   5.72450077371802     1.13140743943567    -0.65021795503441  f
  -0.77733513096296    -1.38934780037659    -0.43453962644442  c
  -1.34941852885717    -2.45563135731026    -2.14258867873739  h
  -1.75892207244900    -3.05541351725033     1.82245047078265  c
  -3.79780215350866    -3.26742647237426     1.67887960130237  h
  -0.88384197958096    -4.91245972290871     1.73188667681165  h
  -1.28786749461744    -2.16333246044364     3.61291750715275  h
   1.84607969934653     3.24498151136577    -0.70120475555869  c
   3.04530950342361     5.36381680087182    -0.80731652237973  f
$end
```

Etot = -569.5197701889 H
ZPE = 299.2 kJ/mol
enthalpy = 324.77 kJ/mol
chem. pot. = 210.04 kJ/mol

4,5-dimethyl-1,2,3-trifluorobenzene

```
$coord
    2.90823125797853    -1.37928415430422    -0.04615882799575  c
    4.20871038182591     0.88656229307589     0.03049680672910  c
    0.29481207295791     3.11270678815541     0.10691057573564  c
   -1.07741242365690     0.87641970766113     0.03034544756096  c
    3.98594817308192    -3.11418791575051    -0.10601477731050  h
   -0.90813426205851     5.35319987085356     0.18358840561284  f
    6.74656209207625     0.91130053978217     0.02949724066424  f
    2.92032226583484     3.16088688857905     0.10883281569917  c
    4.16302756134548     5.36081786660039     0.18483771894522  f
    0.27608304341476    -1.40924590485256    -0.04679795740126  c
   -3.91981894751701     0.93340786350576     0.02992294322579  c
   -4.63412695578935     2.85721988192446     0.10068925314810  h
   -4.67536311240219     0.03057216448291    -1.66508330282618  h
   -4.67905564429094    -0.09298210913830     1.65127936697292  h
   -1.11955887517678    -3.88665359763188    -0.13151415347538  c
   -2.33857454397281    -4.11873359068899     1.51836295044427  h
   -2.33733635085773    -4.00619279714833    -1.79423811427498  h
    0.18568426720668    -5.47581379510599    -0.18495639145426  h
$end
```

Etot = -608.5414383100 H
ZPE = 341.3 kJ/mol
enthalpy = 370.61 kJ/mol
chem. pot. = 248.50 kJ/mol

1H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

```
$coord
    2.60580261755756    -1.49716572233956    -0.21762336358431  c
    0.03570477371650     3.16556145521692     0.08157556403895  c
   -1.28479040429569     0.85093839142446     0.08557659222881  c
    3.70200779506591    -3.21285623096890    -0.41858727169585  h
   -1.23465063854687     5.32352035667934     0.13189097184859  f
    2.61233162849977     3.23002973397990    -0.08983198277735  c
    3.84366636649373     5.33722672768128    -0.23456348681456  f
    0.04694125850908    -1.52834891593480    -0.09430598364114  c
   -4.07685169845684     0.90320453460447     0.20369986337426  c
   -4.83370367597662     2.78143550198405     0.51759535666545  h
   -4.83793160473882     0.16421829969656    -1.57712327053335  h
   -4.75120963349750    -0.38860382802873     1.66767302176431  h
   -1.41691126157406    -3.95760634944135    -0.21152425262565  c
   -2.48747631935929    -4.25984011840003     1.52554055596873  h
   -2.76323434638385    -3.94594445574578    -1.77209755111752  h
   -0.15478434926821    -5.55887158081338    -0.46459287474905  h
    4.09732199163664     0.85379189488528     0.09151637292292  c
    4.66588921142392     0.81525210041116     2.12123412630904  h
    6.23187828919456     0.92405820510904    -1.34605238758228  f
$end
```

Etot = -608.8272965980 H
ZPE = 369.6 kJ/mol
enthalpy = 399.80 kJ/mol
chem. pot. = 274.82 kJ/mol

2H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

2.81152469253966	-1.61085454542698	0.09450985293267	c
0.03072613028932	2.90143603575617	-0.31000692589775	c
-1.30772489435659	0.72049081590221	-0.08191717297494	c
3.81737596749573	-3.38640862452117	0.18521467387265	h
-1.07956544152642	5.08587678705251	-0.60395835504356	f
0.12828486934738	-1.56483884172537	0.14313081228368	c
-4.14682104327113	0.70973861303624	-0.13016218718566	c
-4.90222845649254	-0.03584181293173	1.63725260792431	h
-4.89082714209848	2.60408737545138	-0.39385707480011	h
-4.85202853531318	-0.47456523273715	-1.66193585035033	h
-1.23589765549297	-3.99730788409614	0.38141821006965	c
-2.54847386211006	-3.92570436772903	1.97820892375251	h
-2.42521906309394	-4.29502959275688	-1.28721711370797	h
0.02488999596003	-5.60017684440625	0.60364760121048	h
2.84863644279753	3.09560848281979	-0.09411643051570	c
3.20319810611356	3.84194803088621	1.83015074073499	h
4.11409315399556	0.57117576332141	-0.15224592290812	c
6.56470517719882	0.63192575344609	-0.32337997058682	f
3.84535155801778	4.72844008865868	-1.81473641880997	f

$end

Etot = -608.8391758041 H

ZPE = 371.1 kJ/mol

enthalpy = 401.39 kJ/mol

chem. pot. = 275.75 kJ/mol

3H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

2.83842411484141	-1.48551028016768	0.12721744540678	c
-1.17538594596097	0.59745634105041	-0.04039708150948	c
3.93398223805893	-3.21557998424311	0.22423408971226	h
0.18138212308157	-1.63376052876310	0.12891709410622	c
-3.94922897163448	0.78392424713949	-0.31379317403980	c
-4.74281886763392	2.15485028141934	1.01040426400033	h
-4.37671744876341	1.54005103600491	-2.19662646982478	h
-4.89526485164484	-1.01989829267368	-0.08775890144964	h
-1.08595452240841	-4.18304204030136	0.17335623784688	c
-2.39603416548356	-4.33051519626633	1.75666558653736	h
-2.15684361304536	-4.50230458967942	-1.55855626123839	h
0.29322317029379	-5.69657449162841	0.34798641721999	h
4.24401186928353	0.75089593135148	-0.06415987713099	c
6.73619576059931	0.64313517462125	-0.17686671315158	f
3.00101811309282	3.00491091589038	-0.22832092687178	c
0.21814809464906	3.04598391172398	0.17434186110984	c
0.10276967354691	3.39100314594862	2.25587337673946	h
-0.92026291987548	5.00523236276238	-1.03613505806815	f
4.14935614900322	5.14974205581085	-0.49638190939447	f

$end

Etot = -608.8245848083 H

ZPE = 368.7 kJ/mol

enthalpy = 399.54 kJ/mol

chem. pot. = 272.01 kJ/mol

4H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

2.74627136804179	-1.53321101031697	0.53463291868911	c
3.86186834937147	-3.24481228808351	0.58695348973357	h
0.16535268079451	-1.56694886876505	0.52170619905169	c
-1.27287721423076	-3.98145616883507	0.55542319740111	c
-2.90600208629130	-3.87097672450733	1.80874990247382	h
-2.00265414792493	-4.38439730018342	-1.33886228819714	h
-0.08690206167117	-5.56220568826438	1.11844016791350	h
4.04314817661261	0.77799638394599	0.50323844307375	c
6.49733605627213	0.76296723016669	0.51031781235304	f
2.84371598687219	3.15975138925006	0.49320162242503	c
4.20718570906911	5.24165360991701	0.50657029383904	f
-1.28268755731808	0.85536885560465	0.42084494140668	c
-2.51430245434302	0.91862679028940	2.09520185233479	h
-3.08536810576040	0.96090016706552	-1.93182512641450	c
-4.44462192988507	-0.57321645617168	-1.82186670160583	h
-4.10123455192284	2.74566606434735	-1.93395033981179	h
-1.99659228050647	0.79046366646923	-3.66840498261367	h
0.27041648091516	3.17696035931697	0.50018365710588	c
-0.94205241809492	5.32686998875458	0.53944494084200	f

$end

Etot = -608.8462322807 H

ZPE = 372.8 kJ/mol

enthalpy = 402.66 kJ/mol

chem. pot. = 278.31 kJ/mol

5H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

2.94362758756586	-1.42826646649955	0.46936902687466	c
4.01771363306194	-3.16909478658675	0.46234302111678	h
4.16269370730992	0.81104996412741	0.47158067513616	c
6.64904163626064	1.01970638630629	0.47490929356196	f
2.73645363189530	3.08628857336346	0.47570053717270	c
3.92261022894575	5.22243587466963	0.47823986281584	f
0.08430262558246	3.07841447079511	0.49738670180339	c
-1.06581573325850	5.30235903544570	0.52320490060130	f
-1.25201620708162	0.85928807979694	0.51102405013945	c
-4.05734791688111	0.88087014092901	0.56357003465572	c
-4.77520534942819	0.95154694111194	-1.37921231400131	h
-4.81500798575169	-0.81575933748850	1.44458540454623	h
-4.77617228080653	2.55201167162976	1.52321060280052	h
0.15750750853281	-1.56553981841320	0.42548565974464	c
-0.41602578210664	-2.63263168594254	2.12185341185166	h
-0.72651491593453	-3.23886437210480	-1.86660598611692	c
0.21071789142821	-5.06528616895518	-1.77828349570386	h
-2.75629071163504	-3.53331918046655	-1.77932161411771	h
-0.24427156769896	-2.31520932171822	-3.63903977288125	h

$end

Etot = -608.8383017022 H

ZPE = 371.3 kJ/mol

enthalpy = 401.27 kJ/mol

chem. pot. = 276.83 kJ/mol

6H-4,5-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

4.10820939268861	1.10136076700101	0.02309292360856	c
0.12001354835713	3.13420774933854	-0.02658441632337	c
-1.31463084909864	0.88371674853696	-0.02029489386027	c
-1.08596956924857	5.27957517316268	-0.05421569271599	f
6.57441174674850	1.09535135078099	0.04292017154458	f
2.78668296603869	3.30273168288973	-0.00621799739320	c
3.87878956995985	5.53869859793127	-0.01575580901706	f
0.00630378890583	-1.35463825492900	0.01287872307002	c
-4.14587518011512	1.11719184365367	-0.04532226639977	c
-4.80585914524534	2.09282610989210	1.64697452251309	h
-4.76678162381856	2.22805770050126	-1.66636410254293	h
-5.05985233952160	-0.71593744518555	-0.13089000756719	h
-1.25708834645403	-3.87332480569810	0.02517026736391	c
-2.51773357270001	-4.04628708031275	1.65123125679607	h
-2.43155581304070	-4.10078587220303	-1.65873878126849	h
0.09833006777382	-5.41680573314910	0.08382464079773	h
2.81671144663039	-1.35579692051152	0.03549061354980	c
3.48513729999909	-2.43936498065076	1.68044429969472	h
3.51075661214064	-2.47077663104836	-1.57764345185011	h

$end

Etot = -608.8503522643 H

ZPE = 369.4 kJ/mol

enthalpy = 400.51 kJ/mol

chem. pot. = 268.22 kJ/mol

4,6-dimethyl-1,2,3-trifluorobenzene

$coord

1.83931601292887	-1.44585849344794	0.07051627195986	c
3.10255701791368	0.85133038280362	-0.03510664214058	c
5.64553775290080	0.90586293516238	-0.03526384205854	f
1.81045464724049	3.12947916676221	-0.14221028934710	c
3.07488441215010	5.31521504587968	-0.24232588428237	f
-0.81077229178748	3.11019728530003	-0.14443477177147	c
-2.03345749624828	5.33823479502038	-0.24925737806060	f
-2.17249833111385	0.86973597514928	-0.04197361709896	c
-5.01338701382353	0.93430423043952	-0.04556810960166	c
-5.73506754989747	1.88710060088137	-1.72620059113258	h
-5.78502951309417	-0.97237025892736	0.00079651575108	h
-5.73703675808719	1.96697335145693	1.58684702698671	h
-0.79529811756125	-1.37493707354956	0.06430489819158	c
-1.81918180508234	-3.14460768257980	0.14567505487650	h
3.31355391463566	-3.87264833871411	0.17882169496219	c
4.47281311987379	-4.11525481765979	-1.51016996604316	h
4.59499403927037	-3.89546410300743	1.79424425825529	h
2.04761795978186	-5.48729300096936	0.33130537055376	h

$end

Etot = -608.5428781342 H

ZPE = 340.7 kJ/mol

enthalpy = 370.75 kJ/mol

chem. pot. = 245.99 kJ/mol

1H-4,6-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

1.59633810745181	-1.60369135487205	0.06259070713240	c
1.54552650836730	3.16969120580885	-0.36162615620236	c
2.80715231688464	5.24515220900018	-0.70685781923795	f
-1.01889970977846	3.12765028867812	-0.24506531543585	c
-2.33629509170228	5.24447357870562	-0.48322758461794	f
-2.32677130334350	0.80868684692341	0.04560389735792	c
-5.12114324326528	0.87649555683278	0.11676379177700	c
-5.83824758631111	1.67299331585229	-1.65523111062186	h
-5.94162668947664	-0.97889978460369	0.42096020628617	h
-5.75984271082738	2.18347075630230	1.58725011395447	h
3.08175974452080	-3.96756312019445	-0.05164140959267	c
4.17191110486157	-4.00204144904021	-1.81036696037788	h
4.48096885091230	-4.03634115103661	1.46807141779329	h
1.88226615883046	-5.63128762923498	0.04556827736460	h
-0.97798312211045	-1.49802954520012	0.18610247338734	c
-2.05655167304564	-3.23075956609558	0.29410269492507	h
3.04137723393206	0.83110799106676	0.14547282200624	c
3.55245065679774	1.01654966690295	2.17559140534989	h
5.21761044730193	0.77234218420458	-1.23406145124787	f

$end

Etot = -608.8366224308 H

ZPE = 368.7 kJ/mol

enthalpy = 399.40 kJ/mol

chem. pot. = 273.01 kJ/mol

2H-4,6-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

1.83417054290148	-1.61086719250693	0.02898800336363	c
-1.00015485996107	3.00291031505710	-0.19140354590096	c
-2.11582596836675	5.18457752545155	-0.41578729143981	f
-2.31366935768460	0.79412476104281	0.01891922509761	c
-5.15103692940207	0.67562966061000	0.03035249672409	c
-5.83450673705313	-0.26986622259456	-1.66945598665931	h
-5.81437705082647	-0.39551257221331	1.66047597881701	h
-5.98226996325297	2.55200199957939	0.10093728907628	h
3.15722036792230	-4.12405091924877	0.03166031714683	c
3.03224927562025	-4.99993975929934	-1.83154532999347	h
5.14599604117613	-3.92240207079987	0.50563630977483	h
2.28209219267408	-5.39739481467059	1.39174983941911	h
-0.82682167699456	-1.42242258732730	0.13699706400102	c
-1.85452071341898	-3.19240765985388	0.28771963149073	h
1.81566996285302	3.13998717451921	0.01502976579819	c
2.13797921729615	3.70135213882577	2.01510547504825	h
3.09614331181550	0.62870718934050	-0.18475275174889	c
5.54302791273945	0.73989843932636	-0.40859127800724	f
2.84863443196220	4.91567459476183	-1.52203521200795	f

$end

Etot = -608.8315987317 H

ZPE = 370.1 kJ/mol

enthalpy = 401.79 kJ/mol

chem. pot. = 268.95 kJ/mol

4H-4,6-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

-0.83092409087799	3.00907518258007	0.37655322057744	c
-2.05772826379590	5.13595776553273	0.32014995618357	f
-2.23777726880331	0.72259510407164	0.50729854208268	c
-5.06986777754869	0.84393938498032	0.58447971850183	c
-5.80725737966000	1.77526802638710	-1.10011123540870	h
-5.87065851838422	-1.04477896855525	0.69623139387631	h
-5.71045165974768	1.93043387904986	2.21470680150204	h
-0.85698902037420	-1.44350420057839	0.55265015663729	c
-1.81152726398049	-3.25118578443448	0.64724176215958	h
3.16358061316230	0.95732574478793	0.36877017084998	c
5.62602367872179	1.01882271929530	0.33021507938825	f
1.82260703334235	3.16487732166264	0.31272705718333	c
1.93303753088293	-1.53275660882483	0.44439307101605	c
2.59463319731222	-2.46011263553549	2.19123319581803	h
2.88096218843763	-3.24890566855862	-1.78062521334183	c
4.93179260763659	-3.35404663008208	-1.73925840835758	h
2.10580168981007	-5.13746109127570	-1.54805837947303	h
2.26622572048457	-2.47726721422115	-3.58429678569196	h
2.92851698338203	5.39172367371844	0.20569989649677	f

$end

Etot = -608.8426189999 H

ZPE = 372.7 kJ/mol

enthalpy = 402.71 kJ/mol

chem. pot. = 278.23 kJ/mol

5H-4,6-dimethyl-1,2,3-trifluorobenzeniumcation

$coord

2.01020594998613	-1.36491676377714	-0.02208476959534	c
3.22334635393806	0.90760450698795	-0.02741823325834	c
5.72156867379296	1.07023720342473	-0.05027690648342	f
1.84610809661709	3.18763659971069	0.00437076243235	c
3.07383783793567	5.30529688825098	0.00579810148808	f
-0.81868668371146	3.25094980327841	0.03318698829035	c
-1.91143519968269	5.50348734649816	0.04779599845593	f
-2.18915534702346	1.07035388855344	0.03222957172332	c
-4.99766329163062	1.08625970630983	-0.00179340854091	c
-5.65689220951148	1.34917597243840	-1.94716414637159	h
-5.77707268236771	-0.68556751628895	0.69273354549329	h
-5.74908848853514	2.65892158430338	1.09342952784113	h
3.42687887992875	-3.79039811722038	-0.00566458512978	c
4.97140330397853	-3.74659169989695	-1.37092563689550	h
4.30163734559649	-4.07129700954396	1.84870502485746	h
2.20350332604780	-5.39511170023634	-0.39562795029019	h
-0.78993357956452	-1.35599288864966	0.01244137622359	c
-1.47016744898744	-2.49277544921346	-1.59258176467343	h
-1.41839483680698	-2.48727235492922	1.64284650443294	h

$end

Etot = -608.8506930910 H

ZPE = 367.0 kJ/mol

enthalpy = 398.71 kJ/mol

chem. pot. = 267.14 kJ/mol

trimethyl-1,2,3-trifluorobenzene

$coord

-0.41731945717032	-0.74882837176417	0.05015869314247	c
2.23733402930282	-0.77117352205294	0.01520428625269	c
3.49129239880619	1.53613928991057	-0.08184121531829	c
2.20786874109374	3.81406481902700	-0.15270953674392	c
-0.40854929857513	3.78351338008915	-0.12914042690478	c
-1.76450524886703	1.53999458703749	-0.03413678468067	c
-1.61554022637487	6.02432333917113	-0.20332248735073	f
3.47077637965272	6.00339775669749	-0.24430409003971	f
6.03648856496801	1.62439755370933	-0.11340556810838	f
-4.60897079696887	1.60948644944390	-0.02391717066276	c
-5.36299579417067	0.90121751733295	1.76294842753714	h
-5.31066736541494	3.52073394700953	-0.29078720189130	h
-5.38528652660394	0.42317195031763	-1.52159743980508	h
-1.89230705784792	-3.18613896853561	0.14914638365772	c
-3.35156526442087	-3.11682650274301	1.60404466143036	h
-2.85671974227044	-3.54060011019758	-1.64416617033825	h
-0.70201443248627	-4.81075339575232	0.54191144816940	h
3.76256833161413	-3.17842255621963	0.06784747517692	c
3.43546387657940	-4.23332179024161	1.81038008066842	h
3.26133327737385	-4.41230200177445	-1.50628873277855	h
5.77331561178050	-2.78207337046495	-0.05602463141268	h

$end

Etot = -647.8451155601 H

ZPE = 413.7 kJ/mol

enthalpy = 447.48 kJ/mol

chem. pot. = 314.93 kJ/mol

1H-trimethyl-1,2,3-trifluorobenzeniumcation

$coord

-0.48160971009341	-0.95701365636280	-0.00751918617398	c
2.22147794085122	-0.90624092211619	-0.09390060654049	c
3.58979897620767	1.39335937143099	0.00041623683911	c
2.36398116157964	3.64313738746739	0.11085671494642	c
-1.80617052174094	1.27551030493268	0.07945758823277	c
3.55231204708795	5.78325847219354	0.28883053732660	f
6.09582244688140	1.34175339378773	0.06284304137968	f
-4.60691276584370	1.46283491466160	0.27119391923409	c
-5.23835382259091	0.65738832547865	2.06749717575415	h
-5.25668761297578	3.40713486520051	0.18657624800658	h
-5.52498668740603	0.37434075853813	-1.22258550599047	h
-1.79200505135999	-3.48156047100088	0.05340318256435	c
-3.80289736959818	-3.29921213608383	0.40554077333958	h
-1.56030739245121	-4.46983288483272	-1.74355807653745	h
-1.00844205736119	-4.69231556026662	1.52406184745098	h
3.69330416640230	-3.29027950266401	-0.20085353883261	c
3.56596550915580	-4.23577274383238	1.63983424568852	h
2.87545577019561	-4.59707796525189	-1.56846224646229	h
5.67549282351532	-2.97766519757449	-0.61962083310595	h
-0.42425404728332	3.73228286712773	-0.19436368093315	c
-0.67584675185909	4.18667423571335	-2.23259024785433	h
-1.45513705131322	5.64929614345345	1.19294241166791	f

$end

Etot = -648.1425063730 H

ZPE = 441.6 kJ/mol

enthalpy = 476.30 kJ/mol

chem. pot. = 340.84 kJ/mol

2H-trimethyl-1,2,3-trifluorobenzeniumcation

$coord

-0.49707998539353	-0.90939646185419	0.00785819640392	c
2.21221717861809	-0.99499034341031	0.05129656722747	c
3.44250098461921	1.25826727827491	0.07367246760112	c
-1.94040752602348	1.38926930611814	-0.00814951643894	c
5.90493751479503	1.40439452206237	0.20359552466990	f
-4.78225086768928	1.38391895291262	0.02137900740428	c
-5.49928880957346	0.56834803576660	1.77384590451572	h
-5.52245512165008	3.29166249426960	-0.13547208828011	h
-5.53433501480950	0.27283504564326	-1.54142925633077	h
-1.93910176078824	-3.31257206978148	-0.00839132616617	c
-3.40298954323213	-3.28720612601258	1.44703563267712	h
-2.96210834008610	-3.46695276517255	-1.80474626476160	h
-0.77933605668848	-4.98111886488913	0.22380773812592	h
3.66775261925535	-3.43833651629846	0.13160559190536	c
3.21155444588827	-4.51454489580355	1.82837947425456	h
3.22697001776315	-4.60782041832409	-1.50611592773138	h
5.68943466061216	-3.08533121495506	0.13338607292261	h
-0.62908830039358	3.59255640142888	0.01783854268647	c
-1.75628817120741	5.78982049359025	0.10339520169694	f
2.17611881250219	3.76239819226903	-0.20621992686729	c
2.54063971257556	4.34840210516841	-2.18267388818435	h
3.17260355090636	5.53639684899731	1.37610227266910	f

$end

Etot = -648.1485567012 H

ZPE = 443.8 kJ/mol

enthalpy = 478.34 kJ/mol

chem. pot. = 342.58 kJ/mol

4H-trimethyl-1,2,3-trifluorobenzeniumcation

$coord

-0.53371324018049	-0.89903237375317	-0.42765323495350	c
3.57463773635666	1.46040342636671	-0.58791174582592	c
-1.82788514421608	1.35973517888545	-0.46689086505286	c
6.04480206148169	1.42979096361405	-0.67226438555171	f
-4.66635783130216	1.51706285346500	-0.46039383226105	c
-5.44475004218113	0.45105803379670	1.12109514932231	h
-5.32519278205946	3.45479019973754	-0.31513348894667	h
-5.43814573401414	0.71078241513809	-2.19470069979700	h
-1.91762654553463	-3.34856321915714	-0.43706939240076	c
-2.97338371068411	-3.58611183663272	1.32610229578155	h
-3.32164672621679	-3.37236960288587	-1.94977656792252	h
-0.67070140412705	-4.96270982308872	-0.67229956663830	h
-0.36938043121753	3.58617013909322	-0.56810123719823	c
-1.51340495255591	5.76697849309867	-0.62753865934143	f
2.27896150036662	-0.98906060758060	-0.32705517384096	c
2.94756920581249	-2.21335212408873	-1.86508646370229	h
3.18974625505309	-2.26242469005859	2.20481802873544	c
5.24130277114166	-2.36063351561028	2.20705761784132	h
2.55318310277872	-1.15934685591942	3.81940385982989	h
2.43098019788122	-4.16457679279760	2.33675462502959	h
2.29919396490525	3.68586649063229	-0.64957061227427	c
3.44181174851199	5.89554324774519	-0.79378565083270	f

$end

Etot = -648.1564288299 H
ZPE = 444.8 kJ/mol
enthalpy = 479.13 kJ/mol
chem. pot. = 345.14 kJ/mol

5H-trimethyl-1,2,3-trifluorobenzeniumcation

$coord

3.47878273410451	1.36895608496161	-0.38929523939041	c
-1.91647409491802	1.50286482947762	-0.48462563111169	c
5.97965003123751	1.54716281113533	-0.39006286795515	f
-4.72437839564557	1.55378814623232	-0.60391424727995	c
-5.50101735268892	1.81510532798600	1.29733048562947	h
-5.38232600064747	3.14705870363210	-1.72926716200804	h
-5.48799335453636	-0.19572780379861	-1.36703800643215	h
-0.55986705975210	3.69097352196818	-0.42468963460065	c
-1.66707738976826	5.94011631234792	-0.45830058226863	f
2.09997658688117	3.64556880477953	-0.37129244618903	c
3.32029826420665	5.76847584645994	-0.34297287182744	f
2.27192306983319	-0.90511347949171	-0.44430023749672	c
3.72693956264338	-3.30919406654873	-0.51345035047363	c
4.21314417923629	-3.88660142680730	1.41459511949013	h
2.64046204872291	-4.83048199327816	-1.37066813272720	h
5.50326085894254	-3.06892379302063	-1.52369742195698	h
-0.54031034810223	-0.94756690190548	-0.35580553368793	c
-1.18608424700945	-2.09497002910314	-1.96188556545801	h
-1.41250082608226	-2.42312934697782	2.07933499443040	c
-0.57269606389909	-4.29617563981835	2.09453748435800	h
-0.82807362568419	-1.40120042491625	3.76579393289974	h
-3.45563857707431	-2.62098548331440	2.07967391405580	h

$end
Etot = -648.1553202684 H
ZPE = 443.5 kJ/mol
enthalpy = 477.86 kJ/mol
chem. pot. = 343.85 kJ/mol

1,2-difluorobenzene

$coord

1.31302604494639	0.00000000000000	-2.17453051221147	c
-1.31302604494639	0.00000000000000	-2.17453051221147	c
-2.63792204727101	0.00000000000000	0.07840144570120	c
-1.31381884439180	0.00000000000000	2.35109250678418	c
1.31381884439180	0.00000000000000	2.35109250678418	c
2.63792204727101	0.00000000000000	0.07840144570120	c
-4.67999866420115	0.00000000000000	0.01811387504152	h
-2.34289136743646	0.00000000000000	4.11612150823824	h
2.34289136743646	0.00000000000000	4.11612150823824	h
4.67999866420115	0.00000000000000	0.01811387504152	h
2.55314575760179	0.00000000000000	-4.38933164281983	f
-2.55314575760179	0.00000000000000	-4.38933164281983	f

$end
Etot = -430.6862496890 H
ZPE = 218.6 kJ/mol
enthalpy = 236.85 kJ/mol
chem. pot. = 141.08 kJ/mol

1H-1,2-difluorobenzeniumcation

$coord

1.43961770171065	2.44371060680316	0.23399361053900	c
-1.19091304801471	2.57145263747046	0.10097479848088	c
-2.48906388428733	0.35451838703823	-0.23703189187247	c
2.47680210229449	4.19942751026511	0.42778768420807	h
-2.19024048064422	4.35341660349366	0.13823447843325	h
-4.91024925714493	0.30974611231579	-0.54565004277557	f
1.59584549723031	-2.06360726034010	-0.24752515454687	c
2.54924409685642	-3.85961426004499	-0.47585626624596	h
2.83538372138096	0.15810323830655	0.05223650861046	c
4.87651929788282	0.22806139725225	0.07154530537844	h
-1.19890902215781	-2.14094264103195	-0.06338562594812	c
-1.47180690393541	-2.57714682364984	1.99384232573473	h
-2.32222982117119	-3.97712550787829	-1.44916572999583	f

$end

Etot = -430.9612355453 H

ZPE = 247.5 kJ/mol

enthalpy = 266.79 kJ/mol

chem. pot. = 166.86 kJ/mol

3H-1,2-difluorobenzeniumcation

$coord

-2.25324116324002	-1.08116076022719	0.00000000000000	c
2.45918475197037	-0.94155943767794	0.00000000000000	c
2.34726254274225	1.62554751438135	0.00000000000000	c
-0.02870852891567	2.84431280840541	0.00000000000000	c
-2.30350811692733	1.52304275031290	0.00000000000000	c
4.24862886815044	-1.93057359419247	0.00000000000000	h
4.04561119481173	2.75941104147036	0.00000000000000	h
-0.13705332112947	4.89094305258357	0.00000000000000	h
-4.47666027106348	2.74306274722699	0.00000000000000	f
-4.33788172260019	-2.37373188023507	0.00000000000000	f
0.13892767457475	-2.47898105737823	0.00000000000000	c
0.14871904581332	-3.79015659233485	-1.62176316129782	h
0.14871904581332	-3.79015659233485	1.62176316129782	h

$end

Etot = -430.9757903162 H

ZPE = 246.0 kJ/mol

enthalpy = 265.66 kJ/mol

chem. pot. = 165.19 kJ/mol

4H-1,2-difluorobenzeniumcation

$coord

-2.39842950984992	-1.34233094714170	0.00000000000000	c
2.05716727498228	1.61153866630302	0.00000000000000	c
-0.21081282970076	2.82006531547465	0.00000000000000	c
-2.42017001977315	1.34457218930175	0.00000000000000	c
3.80067563574832	2.68174428764069	0.00000000000000	h
-0.39527490710075	4.85549410654609	0.00000000000000	h
-4.59603560736488	2.46090232696769	0.00000000000000	f
-4.59300479949517	-2.52090701007372	0.00000000000000	f
2.22712772106607	-1.15833167373883	0.00000000000000	c
3.40642947449169	-1.77302568387852	-1.60888369000245	h
3.40642947449169	-1.77302568387852	1.60888369000245	h
-0.15907159377998	-2.58045747863103	0.00000000000000	c
-0.12503031371540	-4.62623841489157	0.00000000000000	h

$end
Etot = -430.9801399267 H
ZPE = 246.1 kJ/mol
enthalpy = 265.58 kJ/mol
chem. pot. = 165.48 kJ/mol

3-methyl-1,2-difluorobenzene

$coord

-0.01391340887065	-2.14757050322651	-0.13262637512623	c
2.60812416359910	-2.16920269231710	-0.12876322485065	c
3.95985557646030	0.06378488708711	0.00219575386376	c
2.63771148718880	2.33016512436973	0.13414020876107	c
0.01051152584858	2.33968523949196	0.13884012552823	c
-1.37153194850509	0.09704698759768	0.00604483108055	c
6.00089006326918	-0.00952789229163	0.00204778415750	h
3.66554528548985	4.09301800420504	0.23745954823264	h
-0.99999909156407	4.11405892544991	0.24922871467159	h
-4.21149467165560	0.03314914002404	0.00395556970986	c
-4.98423765630580	1.91922483852626	0.28304428911930	h
-4.93585091105424	-0.70747351886472	-1.78044319666929	h
-4.92826824520192	-1.19575063163510	1.49624488169151	h
-1.26006119878552	-4.36355392269122	-0.26403701790587	f
3.82271903008716	-4.39705398572555	-0.24733189226406	f

$end
Etot = -469.9933163800 H
ZPE = 290.3 kJ/mol
enthalpy = 313.18 kJ/mol
chem. pot. = 204.94 kJ/mol

3H-3-methyl-1,2-difluorobenzeniumcation

$coord

-0.11093197381230	-2.26348832939520	-0.60918386795884	c
2.49199737877306	-2.28437094999058	-0.68880752722190	c
3.78933048303658	0.00147735921125	-0.67914456779449	c
2.53195937006666	2.35340535882228	-0.60061696418266	c
-0.03589779017273	2.41588220590557	-0.51486863057773	c
5.83591505721058	-0.07809480176363	-0.74368385602024	h
3.63468353599404	4.07212335793213	-0.61116976316984	h
-1.04580202094847	4.19355038072287	-0.45239453266532	h
-1.35939209538718	-4.38109968374082	-0.63390777476016	f
3.73491242514255	-4.44676283033637	-0.77372848198318	f
-1.57230149442500	0.09221623290020	-0.47008820620450	c
-2.79817969061824	0.12317676581092	-2.16021026750134	h
-3.44617380359071	0.05350890598362	1.84152247447205	c
-4.64675141259593	1.71775282520168	1.75142548381078	h
-4.61338148875918	-1.63286385375863	1.74045409376264	h
-2.38998647991379	0.06358705649474	3.60440238799476	h

$end
Etot = -470.2831995481 H
ZPE = 320.7 kJ/mol
enthalpy = 344.23 kJ/mol
chem. pot. = 234.52 kJ/mol

4H-3-methyl-1,2-difluorobenzeniumcation

$coord

-0.06652546109389	-2.37028520385666	-0.03168375098941	c
2.59270086746079	-2.33362850582797	-0.05049310012051	c

```
   4.03535156410074    -0.08982340757021    -0.02560579290937  c
   2.78199745322380     2.13968595828550     0.03147149114021  c
  -1.41850728309880    -0.16686099683680     0.02301465660113  c
   6.07286160235095    -0.23886706305453    -0.04933644241566  h
   3.80418119844967     3.91072180753541     0.05932543037525  h
  -4.22390579731386    -0.17363401353896     0.00168610097507  c
  -5.00016723963958     1.65820187895359     0.51693790307806  h
  -4.89120609988881    -0.64983272975590    -1.90012568158629  h
  -4.96893774566768    -1.63165584296162     1.25377216142620  h
  -1.20957793196178    -4.59703066329946    -0.07535596831476  f
   3.76545853066842    -4.48821456038879    -0.09618172486294  f
   0.00109773153800     2.24187739331539     0.07426047708997  c
  -0.60354345092138     3.33104738170954     1.74582924517005  h
  -0.67127793820656     3.45829856729130    -1.47751500465700  h
$end
Etot = -470.2991267779 H
ZPE = 317.3 kJ/mol
enthalpy = 341.60 kJ/mol
chem. pot. = 229.50 kJ/mol

5H-3-methyl-1,2-difluorobenzeniumcation
$coord
  -0.19062750009017    -2.27992696494176    -0.11166331953672  c
   2.49177575383835    -2.38696101082442    -0.12235214279090  c
   3.84520598508396    -0.22050314166775    -0.01983759945072  c
  -1.62257015118895    -0.02583223117354     0.00326109232695  c
   5.88954019193558    -0.28038427431875    -0.02757183166553  h
  -4.45377747945245    -0.16386935366408     0.00252469532124  c
  -5.27208715077569     1.71632398985867     0.12796719929807  h
  -5.13727750153762    -1.06921906244866    -1.71881624642650  h
  -5.12899175409128    -1.28752177003034     1.59315507556810  h
  -1.38547723620520    -4.42028359658585    -0.21467362292354  f
   3.55622110274775    -4.64005830112128    -0.23387668625699  f
  -0.25343767265671     2.16135604908681     0.10793130054171  c
  -1.22565291074075     3.96005285616015     0.19980170375741  h
   2.52009955557131     2.21195857202768     0.10241820419438  c
   3.18866628524623     3.28467105599040     1.76325897567642  h
   3.17839048231556     3.44019718365269    -1.45152679763339  h
$end
Etot = -470.2938079636 H
ZPE = 317.8 kJ/mol
enthalpy = 341.80 kJ/mol
chem. pot. = 231.72 kJ/mol

6H-3-methyl-1,2-difluorobenzeniumcation
$coord
  -0.33937705498782    -2.22337855825689    -0.08233695967153  c
   2.24581664223326    -2.27283519935907    -0.09164582325445  c
  -1.65031932950971     0.08880393292324     0.02024364767871  c
  -4.44765931361002     0.04520807950653     0.01747450158476  c
  -5.25541148906989     1.90902221855656     0.30697125924346  h
  -5.11565482022222    -0.71335841895870    -1.79132928004647  h
  -5.15020885652930    -1.26847470516813     1.44881418473136  h
  -1.63433277750546    -4.36469786190849    -0.16760358787907  f
   3.45614087881835    -4.41534763842478    -0.17990325618978  f
  -0.27161573677304     2.40094950245219     0.10619789308901  c
  -1.32419871485405     4.15022664575386     0.18294151560963  h
```

2.28742087547878	2.41579642605218	0.09503970160574	c
3.33166183006336	4.17246130654462	0.16042752003561	h
3.75608048367876	0.05081293064588	-0.00416511432720	c
5.04977813378282	0.07726814070653	-1.63621085842187	h
5.06187924900631	-0.05245680106565	1.61508465621208	h

$end
Etot = -470.2973419865 H
ZPE = 317.3 kJ/mol
enthalpy = 341.54 kJ/mol
chem. pot. = 229.81 kJ/mol

4-methyl-1,2-difluorobenzene

$coord

-0.65138068139780	-3.31070540390344	0.03129140061203	c
1.97460158633958	-3.33142263582575	0.00360696623377	c
3.29206774880240	-1.07982982704162	-0.02726884585301	c
1.96836591117456	1.19520583629746	-0.03007845988169	c
-0.66456599600877	1.24467424589538	-0.00251140639863	c
-1.96334156181761	-1.05528887005609	0.02786313793122	c
5.33445880674837	-1.13143650325676	-0.05008882734946	h
3.01318517163398	2.95285805197036	-0.05478611912796	h
-1.90897323249740	-5.51712760815824	0.05886663766022	f
3.20713280112883	-5.55295901991100	0.00570004438920	f
-4.00718475663217	-1.12111380838421	0.04873555122822	h
-2.10892416061468	3.69790017097639	-0.00312486968045	c
-3.36124691196777	3.82398397559428	-1.63829341294746	h
-3.28604269081900	3.86861398613129	1.68324618587700	h
-0.83815203407248	5.31664740967184	-0.05315798269306	h

$end
Etot = -469.9919629670 H
ZPE = 289.5 kJ/mol
enthalpy = 312.77 kJ/mol
chem. pot. = 201.70 kJ/mol

3H-4-methyl-1,2-difluorobenzeniumcation

$coord

-1.81961653577995	-3.53468611842758	0.00172313220212	c
0.81965444727820	-3.44948671008902	0.00285192522399	c
2.19496207993205	-1.18379855190342	0.00152560138594	c
0.98223615917842	1.10941662968791	-0.00062074303563	c
-3.13140415824958	-1.30450514507856	-0.00032531453669	c
1.80686256475255	-5.24532315513311	0.00422000720556	h
4.23575672450700	-1.27239099237675	0.00192645840767	h
-5.59204051838574	-1.27394696908896	-0.00359213330272	f
-3.01027015402368	-5.72920600960614	0.00189848884477	f
2.34607201458771	3.56171978822956	-0.00249058096197	c
1.80640710589101	4.68954200209386	-1.64846985034177	h
1.82937120201082	4.67730929468197	1.65949963711455	h
4.38380036185293	3.30454921629959	-0.01665954106921	h
-1.82604229481257	1.14949594212116	-0.00048415920483	c
-2.51277304208608	2.25080598070347	1.62568310018972	h
-2.51297595665305	2.25050479788602	-1.62668602812154	h

$end
Etot = -470.2934741462 H
ZPE = 317.1 kJ/mol
enthalpy = 341.75 kJ/mol
chem. pot. = 228.15 kJ/mol

4H-4-methyl-1,2-difluorobenzeniumcation

$coord

-0.78155023605351	-3.27296812842695	-0.64333524397774	c
1.90085808968200	-3.20826924902962	-0.69428575768051	c
3.29290409218720	-0.94839674687059	-0.65548604262021	c
1.99971906688090	1.26980309778721	-0.53981813666050	c
-2.08682794013138	-1.07605745366003	-0.52649850933474	c
5.33294159090798	-1.05486556715443	-0.71596314151782	h
3.01466150467596	3.04653364642490	-0.50593232160704	h
-4.13232973880071	-1.11955922203910	-0.47724627966780	h
-1.89333378276806	-5.50526610641571	-0.70238809681014	f
3.09214858451231	-5.34438161361488	-0.78881573685518	f
-0.77667515122859	1.37851649677204	-0.44031729102222	c
-1.37281586317119	2.43072753189582	-2.14759145420732	h
-1.72779420235258	3.05387606930082	1.81768100730392	c
-0.86874586310162	4.91736518892098	1.70211772779366	h
-3.77025140311059	3.25319134344233	1.70980772230484	h
-1.22290874812808	2.17975071266722	3.60807155455883	h

$end

Etot = -470.2862595296 H

ZPE = 320.7 kJ/mol

enthalpy = 343.97 kJ/mol

chem. pot. = 234.65 kJ/mol

5H-4-methyl-1,2-difluorobenzeniumcation

$coord

-2.05842607199063	-3.38436967674793	-0.03257533497598	c
0.48805985083202	-3.42711521737251	-0.07113333580504	c
0.51633752771352	1.36761770654495	0.04713693582309	c
-3.32714171222556	-1.00890690157725	0.06474633737879	c
1.48486712820852	-5.21230378458043	-0.12787632863220	h
-5.77818559883155	-1.04312180712401	0.11252546863616	f
-3.46102755491007	-5.44694767577501	-0.07270107401390	f
1.95233627557779	3.77824102193916	-0.01441080696228	c
2.52187989361965	4.16514085520711	-1.96870211319911	h
0.82250298585124	5.36845782177710	0.63323513957627	h
3.68646477109549	3.66236335734739	1.09272609897838	h
1.93572849464823	-1.04589715514718	-0.00787736034694	c
3.20652603913435	-1.08838764371649	1.64366929972178	h
3.29351258461121	-1.01021448036026	-1.58403945320113	h
-2.07655762683266	1.31172018821163	0.10864532502461	c
-3.20687698650150	3.01372339137392	0.17663120199753	h

$end

Etot = -470.2982377919 H

ZPE = 317.3 kJ/mol

enthalpy = 341.60 kJ/mol

chem. pot. = 229.80 kJ/mol

6H-4-methyl-1,2-difluorobenzeniumcation

$coord

-2.08176045284411	-3.13938183462995	0.00014385085856	c
0.76725041815330	1.44895974223395	0.00001979665846	c
-3.32274246287806	-0.85259956587067	0.00088716913257	c
-5.81669169576537	-0.76625320949760	0.00006728331662	f
-3.33065195853075	-5.25362136210336	-0.00238958274935	f
2.08582994820640	3.96199279220746	-0.00182690909270	c
1.54636988072054	5.06245283906038	-1.66010471180108	h

1.56199151117440	5.05674526095311	1.66526494746316	h
4.12866696135841	3.73730342850763	-0.01176364582126	h
-1.91690324781812	1.36766355465606	0.00150219582270	c
-2.97947462981724	3.12203142413407	0.00213157620010	h
2.01666501428953	-0.80931158948648	-0.00001648397206	c
4.06083262777613	-0.87476837964292	-0.00139337538084	h
0.68046068734730	-3.25066718038122	0.00139756062301	c
1.30097696047867	-4.40702288376207	-1.61924810894261	h
1.29918043814893	-4.40352303637838	1.62532843768473	h

$end
Etot = -470.2877719875 H
ZPE = 317.2 kJ/mol
enthalpy = 341.47 kJ/mol
chem. pot. = 230.48 kJ/mol

3,6-dimethyl-1,2-difluorobenzene

$coord

0.00148031733469	-1.31396437637717	-2.33950311678008	c
0.00228171109932	-2.69196820772449	-0.09485803831056	c
0.00055258361243	-1.30924911732291	2.13816943335163	c
-0.00055258361243	1.30924911732291	2.13816943335163	c
-0.00228171109932	2.69196820772449	-0.09485803831056	c
-0.00148031733469	1.31396437637717	-2.33950311678008	c
0.00294063820650	-2.32410985065858	-4.11806944394755	h
-0.00294063820650	2.32410985065858	-4.11806944394755	h
0.00048022956177	-2.53142404910599	4.37305073706866	f
-0.00048022956177	2.53142404910599	4.37305073706866	f
-0.00202084889302	5.53110693104047	-0.01318005090021	c
-1.63664296915288	6.24759816616353	1.02063531504360	h
1.67568524916351	6.24853468376649	0.94929773527259	h
-0.04225675928237	6.31405888745343	-1.91554257079813	h
0.00202084889302	-5.53110693104047	-0.01318005090021	c
1.63664296915288	-6.24759816616353	1.02063531504360	h
-1.67568524916351	-6.24853468376649	0.94929773527259	h
0.04225675928237	-6.31405888745343	-1.91554257079813	h

$end
Etot = -509.3001833682 H
ZPE = 361.9 kJ/mol
enthalpy = 389.52 kJ/mol
chem. pot. = 272.38 kJ/mol

1H-3,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.23701933129542	-1.29086497689567	-2.24588567071177	c
-0.00411079177775	-2.76186423491497	-0.03928566398063	c
0.21510992727600	-1.40308910606373	2.15152867791442	c
0.01872729964522	2.77768165354239	-0.18884948667255	c
-0.21554627043928	1.36662962928071	-2.34329128469551	c
-0.37717839467399	-2.29924459872994	-4.02443592136898	h
-0.27671450593087	2.28797895124354	-4.16611572314229	h
0.54056660280652	-2.51423052211934	4.32239142772110	f
0.29915003340504	5.55463208204086	-0.10282654875626	c
-1.18504086706497	6.41158772812708	1.05354445766646	h
2.07903877929644	6.03586184195148	0.83617025727028	h
0.26278902407298	6.38240252072372	-1.98165097998674	h
0.10788130570677	-5.59843294818653	-0.05570390476907	c
1.86462406132211	-6.26514863493477	0.78962593308603	h

-1.44371313787360	-6.39435110892659	1.04289350483942	h
-0.00961979257213	-6.32641770251009	-1.97382579266801	h
-0.14722001936466	1.38864048359666	2.26326360387221	c
-2.21053728106597	1.52283171128329	2.68647341700824	h
1.15065812865460	2.49087956570899	4.18984102961362	f

$end
Etot = -509.5948665398 H
ZPE = 390.2 kJ/mol
enthalpy = 419.00 kJ/mol
chem. pot. = 294.86 kJ/mol

3H-3,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.41404601114066	-1.25340083346122	-2.42881424936683	c
0.49890564842869	-1.28893960603324	2.23177077184883	c
0.54076656398506	1.29614388085701	2.23002956849476	c
0.51646507989809	2.65051234063698	-0.05603053413846	c
0.46054255358741	1.30559184842676	-2.38542261743382	c
0.36860145086292	-2.26642459363446	-4.20542839982003	h
0.45662177072213	2.38036049118610	-4.12293685927236	h
0.53481222722543	-2.51901529789319	4.37022005367202	f
0.60495572864982	2.55247455953604	4.39849577941572	f
0.56197790591333	5.44711118370981	0.03615485155346	c
-1.02816064119215	6.14128899988403	1.16191318805402	h
2.25525531110144	6.08578997672993	1.03962292842154	h
0.51009218289474	6.28849151651278	-1.83434139613846	h
0.38756423108318	-2.79278898003161	-0.10299013153010	c
2.09768050196702	-3.98648322951711	-0.12221392142589	h
-1.90069261314406	-4.67644074799717	-0.05719519350627	c
-1.80780039989517	-5.88694607422137	-1.71480459364189	h
-1.79647997309291	-5.83884336880449	1.63278568679761	h
-3.67515354013567	-3.63848206588557	-0.07081493198381	h

$end
Etot = -509.6042352800 H
ZPE = 391.8 kJ/mol
enthalpy = 419.97 kJ/mol
chem. pot. = 299.32 kJ/mol

4H-3,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.00305681279574	-2.67680169187512	0.12785996178486	c
0.00534064719870	-1.28745719656942	2.30470383000505	c
0.00527216837370	1.36945205518103	2.23229058058046	c
-0.00150227340764	2.84202364702441	-0.01201887498072	c
-0.00376686151017	1.50574541678963	-2.20764284223196	c
-0.00800238372664	2.49081566827814	-4.00115790528990	h
0.00725994200625	-2.39653016478196	4.55231779153149	f
0.01105394868365	2.54603546624057	4.39335534134127	f
-0.00456552123889	5.67005271545397	0.17376097450607	c
-1.65523085487729	6.33155343277548	1.21602161771075	h
1.66321933451121	6.33680412613718	1.18520949137955	h
-0.02307881339820	6.51831679616759	-1.69741683911222	h
0.00056733844847	-5.48271436536967	0.17647165831583	c
1.62757395839227	-6.18029957437694	1.24164078560628	h
-1.67044791188386	-6.17397312136552	1.17709185442721	h
0.03345211349945	-6.28428306861197	-1.71476455511960	h
0.00106727918557	-1.27513898232407	-2.28445641436984	c

-1.60911428775533	-1.93074026190755	-3.43382943288008	h
1.61784536470305	-1.92286089686576	-3.42943702320453	h

$end
Etot = -509.6121599805 H
ZPE = 389.0 kJ/mol
enthalpy = 417.88 kJ/mol
chem. pot. = 295.46 kJ/mol

4,5-dimethyl-1,2-difluorobenzene

$coord

0.18841596309976	-2.60723350394525	1.82615611734692	c
0.09464066926585	-1.30447882885128	4.08997417081826	c
-0.09464066926585	1.30447882885128	4.08997417081826	c
-0.18841596309976	2.60723350394525	1.82615611734692	c
-0.09533906349129	1.32524624313681	-0.47303092126669	c
0.09533906349129	-1.32524624313681	-0.47303092126669	c
0.33559708040576	-4.64544313302462	1.89157992964459	h
-0.33559708040576	4.64544313302462	1.89157992964459	h
-0.18651066550281	2.56363470524457	6.29635968176699	f
0.18651066550281	-2.56363470524457	6.29635968176699	f
0.19694700992318	-2.77573099399623	-2.91889261267568	c
0.35870170827473	-4.79945825219663	-2.58342422009160	h
-1.49751371472733	-2.45507037481976	-4.05468296095588	h
1.80626180479413	-2.19362341240564	-4.07403918458686	h
-0.19694700992318	2.77573099399623	-2.91889261267568	c
-1.80626180479413	2.19362341240564	-4.07403918458686	h
-0.35870170827473	4.79945825219663	-2.58342422009160	h
1.49751371472733	2.45507037481976	-4.05468296095588	h

$end
Etot = -509.2977057541 H
ZPE = 362.1 kJ/mol
enthalpy = 388.90 kJ/mol
chem. pot. = 274.47 kJ/mol

1H-4,5-dimethyl-1,2-difluorobenzeniumcation

$coord

0.13906852509176	-2.77646579465707	1.61846477684862	c
-0.13161350427867	-1.52507650938347	3.84685798149976	c
-0.34787642510704	2.55878037214213	1.50021424554825	c
-0.12455132179417	1.31604896751876	-0.72604574838324	c
0.15222783941401	-1.40837739126663	-0.66655297751222	c
0.24803073603975	-4.81691236825850	1.61714991254594	h
-0.62951596264031	4.58388381193019	1.58609050738032	h
-0.30131899011198	-2.71520428575470	5.98476468893940	f
0.38886567377866	-2.81574692136424	-3.07193082604828	c
0.58455880772231	-4.83975639204070	-2.79925294970517	h
-1.25627073448102	-2.44362514059373	-4.27067016021187	h
2.01099757727346	-2.10834712935658	-4.14460193746897	h
-0.24035915628673	2.68781487682211	-3.20928877094593	c
-1.79920203665751	2.00217495067093	-4.37120270447693	h
-0.50008823132539	4.70538009530605	-2.92045632462434	h
1.49657446750783	2.41788217186075	-4.28777436806922	h
-0.05346738388656	1.28049602306463	3.97875672055095	c
1.94712800906797	1.66093277616412	4.51624024997446	h
-1.58318788932634	2.23611788719594	5.81923768415846	f

$end
Etot = -509.5934433373 H

ZPE = 391.0 kJ/mol
enthalpy = 418.83 kJ/mol
chem. pot. = 299.75 kJ/mol

3H-4,5-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.01761692968653	-1.24732079168898	4.21484005317652	c
-0.05138528889985	1.33209569276894	4.15759924511888	c
-0.04316103520729	2.55986961058126	1.81543959502332	c
-0.00077980020549	1.32627900988115	-0.53655881833705	c
0.03422127124432	-1.29111498469898	-0.55396020036130	c
-0.07129145771003	4.60861552579690	1.87593369511102	h
-0.09020911643477	2.67485921471863	6.26564023901146	f
-0.02194668076573	-2.49640592777606	6.34128748742920	f
0.08163825877471	-2.76855455749436	-2.94044407445973	c
0.10617119967124	-4.79749878971575	-2.61717004980999	h
-1.56100905750716	-2.30125818191920	-4.10587322266282	h
1.73715991772526	-2.25520976240651	-4.06769878203642	h
0.00941112901892	2.83471831006191	-2.94452876412829	c
-1.61597015922783	2.35654081082021	-4.11999598978625	h
-0.04736164899553	4.85477628132556	-2.57249214346943	h
1.70260271353903	2.43796792736469	-4.05326122218241	h
0.02179228629507	-2.70950590636648	1.86051042163657	c
-1.59745532598856	-4.01942186460867	1.87157321714901	h
1.65123842422526	-4.00413764904433	1.90856832920254	h

$end
Etot = -509.6037054236 H
ZPE = 389.0 kJ/mol
enthalpy = 417.52 kJ/mol
chem. pot. = 297.29 kJ/mol

4H-4,5-dimethyl-1,2-difluorobenzeniumcation

$coord

0.61882771523737	-2.63497925991971	1.84202191127517	c
0.55936198793413	-1.31495138430279	4.01848266871431	c
0.41293350922414	1.36836648254698	3.90896841358429	c
0.34728612750351	2.71899895185759	1.64821333567043	c
0.39487857843217	1.44784111391275	-0.61365385913705	c
0.73449971159353	-4.67672849659960	1.89910722458247	h
0.26968413554292	4.75937000311817	1.75189564129156	h
0.36097444748436	2.59065021787763	6.03588267824105	f
0.63676173958635	-2.38734760768243	6.27297153185946	f
0.31441226587565	2.83785412937044	-3.05295151865262	c
-1.61579299557225	2.78488644835847	-3.80272074270026	h
0.83938215349911	4.81200135609307	-2.82635026327477	h
1.52422589992056	1.96133024111424	-4.47157943017834	h
0.49881585203360	-1.36337214891947	-0.64369606356077	c
2.26623098811127	-1.85387557014598	-1.63726817034510	h
-1.66077685472144	-2.54577741178540	-2.29035020776634	c
-1.57196123111971	-1.81606940451895	-4.20730222783737	h
-1.43441930622360	-4.58718367403710	-2.35723934892823	h
-3.49532472434174	-2.10101398633776	-1.47443157283772	h

$end
Etot = -509.6034046010 H
ZPE = 392.6 kJ/mol
enthalpy = 420.21 kJ/mol
chem. pot. = 301.46 kJ/mol

4,6-dimethyl-1,2-difluorobenzene

$coord

-0.74696846341009	-1.37748778745723	0.03494225878800	c
1.89034524791362	-1.41205274296897	0.02428342747748	c
3.18055572018358	0.88245332507759	-0.06101117421670	c
1.83552930311953	3.12261244205994	-0.12739778782336	c
-0.78234689169923	3.11704388533045	-0.11081924319562	c
-2.12979815775275	0.86445775495277	-0.03001486051235	c
-1.76850639712792	-3.15080996732312	0.09147721932752	h
5.22273776259859	0.96594757755656	-0.08169338186057	h
-4.97030337688391	0.91805839570835	-0.02621338553018	c
-5.69013899712513	1.99850454125874	1.57638446568932	h
-5.69762576285258	1.82279635670457	-1.73144757976275	h
-5.73771446465606	-0.98803686484659	0.07609234184994	h
3.31265621985571	-3.87541192168427	0.15773374028770	c
3.46582919522455	-4.53218402148666	2.11001298148520	h
2.35409647798805	-5.35165815147919	-0.91418521624847	h
5.22430364257796	-3.68483857972580	-0.58447866305938	h
-2.03044609833052	5.33699298085274	-0.18620061909739	f
3.06779504037656	5.34361277746994	-0.21746452359845	f

$end

Etot = -509.2989339377 H

ZPE = 361.2 kJ/mol

enthalpy = 389.13 kJ/mol

chem. pot. = 267.54 kJ/mol

1H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-2.40200870157581	-2.00758321851562	0.01897596621431	c
-0.06612282710180	-3.33127965772392	0.07954797642649	c
2.27282941097996	-2.03385599673890	0.00515856555133	c
2.25486206436806	0.51926273516718	-0.16933972296767	c
-2.52067648800651	0.55781295599601	-0.14736187433599	c
-4.12863504702888	-3.08433796741418	0.21964185703444	h
4.04508440856304	-3.03690377516571	0.16960434452860	h
-4.87666901933470	2.05548722178973	0.01030264372807	c
-4.75853712551014	3.34773132846573	1.62120047653873	h
-5.09631021255600	3.26053603219703	-1.65426744880206	h
-6.53261089855569	0.85803737086385	0.21113555584485	h
-0.08075181412068	-6.12745248173543	0.24339074849551	c
-1.69165597919695	-6.82187428580903	1.32250427768323	h
-0.29531689805640	-6.87527322775124	-1.68186951772051	h
1.67283598673077	-6.88483170192749	1.00352865109656	h
4.32568829651759	1.84428533119505	-0.12923780246549	f
-0.11622080701373	1.97890069745852	-0.62827553281969	c
-0.11016535703428	2.24583870154387	-2.71176858076484	h
-0.06355776361746	4.30351576919666	0.48662996818462	f

$end

Etot = -509.6023949982 H

ZPE = 390.0 kJ/mol

enthalpy = 418.49 kJ/mol

chem. pot. = 296.95 kJ/mol

2H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.79777582895369	-1.45447708434534	-0.04151771236894	c
1.89925535481513	-1.56384640256837	0.05130827231864	c
3.17789155084452	0.66253553175700	0.12719025394501	c
-0.96420195326157	2.97124601204044	0.10657787884271	c
-2.28712867722398	0.73135518319998	-0.01421452938974	c
-1.79546670899908	-3.24640486152370	-0.08087142712497	h
5.21673875687477	0.77213853077986	0.25280428899155	h
-5.12532988997281	0.69370292475717	0.01959170222881	c
-5.84615180620442	1.63274817153407	1.70649144349201	h
-5.88424806268582	1.69721928026301	-1.61296011946184	h
-5.83522406730053	-1.23431840692206	-0.00802533365329	h
3.18084340287052	-4.09487148426942	0.14250052352717	c
2.47398882944108	-5.21001546279045	1.72622948093350	h
2.80000247074900	-5.15879840997234	-1.58309596765489	h
5.21691393961810	-3.90062748869430	0.34290120159208	h
-2.12716833427183	5.12237143373954	0.29057957781272	f
1.82279290078186	3.08769553113020	-0.18312982213305	c
1.98234721046162	3.40951893103102	-2.27103426874563	h
2.89192091241707	5.08282807085377	1.02867455684815	f

$end

Etot = -509.5863677620 H

ZPE = 390.0 kJ/mol

enthalpy = 418.78 kJ/mol

chem. pot. = 296.61 kJ/mol

3H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.77233067268395	-1.44782815135509	-0.01141808488795	c
1.80780783553185	-1.52054056167341	0.05349611431670	c
1.73530333022466	3.22443044674050	-0.01366161046435	c
-0.83521787743869	3.18010076678216	-0.07324011012520	c
-2.13689957163965	0.85032713292954	-0.07368316284200	c
-1.83862572329177	-3.19146437330921	-0.01305968330989	h
-4.93649039591743	0.89718337681185	-0.13993813201212	c
-5.65808459605212	1.97947215570451	1.46811739825778	h
-5.58024614688255	1.92258729011998	-1.81709208895644	h
-5.74769880106301	-0.98722227448504	-0.12721120445573	h
3.26471466864741	-3.92129333935419	0.14047881571202	c
4.36186405461875	-4.02728731984131	1.88971214356457	h
2.03955402970817	-5.56681752680265	0.03628604677149	h
4.62895540346442	-4.00480012672293	-1.40830670920420	h
-2.14704951741089	5.31612198332096	-0.13176419459371	f
2.96980300544199	5.36271571148695	-0.01393112805679	f
3.24653755807933	0.89217304832067	0.04770902236379	c
4.51197116247058	0.96787205600541	1.69460947297895	h
4.55875329714458	0.92163894708201	-1.56457244362795	h

$end

Etot = -509.6140158644 H

ZPE = 388.8 kJ/mol

enthalpy = 417.76 kJ/mol

chem. pot. = 295.22 kJ/mol

4H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.85367849341151	-1.45946729570079	-0.34687472714158	c
3.21924984581247	0.90768877195057	-0.48083436344883	c
1.87391926396760	3.07345341175336	-0.65566496945078	c
-0.80585157435808	2.97256814027428	-0.66352215740459	c
-2.23024655894931	0.71823832009474	-0.52515194364225	c
-1.83193137221924	-3.25430913308357	-0.22796903873117	h
5.26390036761671	0.97534207463929	-0.46331660470078	h
-5.06256585073414	0.84419284237845	-0.57184410711914	c
-5.76867212508257	1.97966535869988	0.99688967461076	h
-5.72384946328355	1.72901180897796	-2.31231471551214	h
-5.87461428090963	-1.03840330922332	-0.44073731432046	h
-2.00206145174006	5.11126767087281	-0.81723775480769	f
2.94700527963305	5.32365076182865	-0.81023607829514	f
1.92418984440160	-1.54360889839838	-0.29024364724986	c
2.49589517167737	-2.64173835364099	-1.97756094358689	h
2.92827865017775	-3.14032193277408	1.99752183094756	c
2.07852429526489	-5.01128439547219	1.96048839134500	h
4.96968953566861	-3.33352816078033	1.85962021589868	h
2.45281891646819	-2.21241768239637	3.76898825260933	h

$end

Etot = -509.5994643977 H

ZPE = 392.4 kJ/mol

enthalpy = 420.19 kJ/mol

chem. pot. = 300.96 kJ/mol

5H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.01339993069273	-3.39859576293075	0.02110543824346	c
2.22279041771696	-2.11899155514134	-0.11880598579102	c
2.18895308182665	0.52672913150157	-0.22311938007462	c
-0.04350264394592	1.99261846976352	-0.20779652008430	c
-2.34321209703035	0.85211784185275	-0.06178841732902	c
4.03555139914648	-3.06188166365727	-0.15952158103056	h
-4.74388779627401	2.30868780679685	-0.09186805546121	c
-4.44908574711867	4.28344681079012	0.39049976184357	h
-5.55428127629395	2.23864394820236	-1.99584969512112	h
-6.13308935592361	1.47861280201039	1.18341476991328	h
-0.14388232519324	-6.20407625384682	0.09349917794660	c
-1.32587576770404	-6.84748372958683	1.65875449527166	h
-1.03321267225826	-6.90507195352824	-1.63731311578886	h
1.71579462783733	-7.06070881757340	0.25923951640338	h
0.20491928555272	4.48329168172811	-0.34831007227098	f
4.32911485355117	1.72788517958801	-0.35106400493216	f
-2.41730132110663	-1.94938134611141	0.10811233795928	c
-3.39064087072233	-2.44883181437359	1.87844838275497	h
-3.71920721289700	-2.68290573116062	-1.33368873762357	h

$end

Etot = -509.6159401905 H

ZPE = 388.7 kJ/mol

enthalpy = 418.06 kJ/mol

chem. pot. = 292.82 kJ/mol

6H-4,6-dimethyl-1,2-difluorobenzeniumcation

$coord

-0.77378336700908	-1.51723745367191	-0.40963074300316	c
1.80679362884247	-1.54571272170493	-0.43266970044829	c
3.05701874757918	0.82675598502650	-0.51013837945969	c
1.80119492111429	3.13144539944103	-0.57867106081489	c
-0.79986313538833	3.16191469237295	-0.55908505655957	c
-1.82755365875327	-3.27041295333278	-0.34922361574045	h
5.10657443638676	0.89405588545827	-0.52747694176798	h
3.34301481491508	-3.93237224343605	-0.37620676490121	c
4.53520503867547	-3.98760071649899	1.30557928953030	h
2.13954613861502	-5.59848586315751	-0.36884007051165	h
4.58477350571952	-4.03723947846745	-2.01874094057130	h
-2.01599649600257	5.29974556000532	-0.63402529043809	f
3.09119212304605	5.26981506546012	-0.65944718877103	f
-2.28290837584472	0.82530488529232	-0.43655373411638	c
-3.44318409008955	0.79019459414510	-2.17348334683170	h
-4.23775156288558	0.91174092221837	1.79967187856658	c
-5.38436165740315	2.60804894473236	1.64151098550383	h
-5.45306880066642	-0.74047186678565	1.68713150083545	h
-3.24684221085100	0.91051136290285	3.60029917949931	h

$end

Etot = -509.5947172890 H

ZPE = 391.9 kJ/mol

enthalpy = 420.02 kJ/mol

chem. pot. = 299.84 kJ/mol

5,6-dimethyl-1,2-difluorobenzene

$coord

0.28490064962471	-3.22318358201266	0.12121888879871	c
2.91201984279286	-3.25589088692310	0.01777924870117	c
4.18629834583403	-0.98827692229630	-0.12721707068083	c
2.85783714884925	1.27519163492152	-0.16858186667801	c
0.23661685012814	1.34349499789891	-0.06792514091392	c
-1.07066883033753	-0.96799420355837	0.08150456640637	c
-0.72512397632615	-4.99763497832031	0.23596042751491	h
3.97461609278647	-4.99997960578635	0.04844648820874	h
4.19045551561620	3.44272170621382	-0.31010719299891	f
6.72587412179970	-0.93395234322237	-0.22918278244097	f
-1.13522264793639	3.83277473478561	-0.11227608087165	c
-2.22222225967263	4.10260572134957	1.62169436447399	h
0.16581509740679	5.40960243707097	-0.30349290323643	h
-2.47435286782760	3.90731006828227	-1.68017295615881	h
-3.91341157750737	-0.98860421728363	0.19608546375753	c
-4.61361856314665	0.07229606942524	1.82316142113671	h
-4.74451209484144	-0.11996226427917	-1.48292041952233	h
-4.63530084724250	-2.91051836626561	0.33602554450382	h

$end

Etot = -509.2983907361 H

ZPE = 362.5 kJ/mol

enthalpy = 389.40 kJ/mol

chem. pot. = 273.08 kJ/mol

1H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.16024984117737	-3.22683369475136	0.00938892500487	c
2.80937006659627	-3.36620881410734	0.10238251191120	c
4.11354174246583	-1.15525153209259	0.13341537439899	c
-0.01034571786898	1.29960940908821	0.00728725839208	c
-1.27835244313900	-0.98322414018007	-0.02581856435475	c
-0.86173509864295	-5.00230876103444	0.02921554346170	h
3.78354687962786	-5.15633413604733	0.23460822300010	h
6.55894621073125	-1.05781368497635	0.33021705084830	f
-1.30014230335160	3.77907200207108	0.15120728401814	c
-2.31594105266314	3.90865726524467	1.95141083914460	h
0.00094353130724	5.36006005047821	0.02758147294131	h
-2.74169420873354	3.93763216761311	-1.32075234156793	h
-4.11774000209755	-1.09251381336372	0.03628991178286	c
-4.85686366801441	-0.12730465773029	1.70196853829723	h
-4.92695046483417	-0.16317285201489	-1.61761251488666	h
-4.79687737698944	-3.03183188676763	0.07291473199924	h
2.79972687572988	1.29478776532653	-0.28909183043513	c
2.99198915416689	1.51213929525263	-2.38189149014265	h
3.98832803453214	3.27084001799155	0.84727907618660	f

$end

Etot = -509.5916875514 H

ZPE = 390.3 kJ/mol

enthalpy = 418.61 kJ/mol

chem. pot. = 297.89 kJ/mol

2H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.06778015142802	-3.24218073066992	0.21455573190340	c
2.61285754107932	-3.31073686955015	0.26245266946746	c
2.56125298637862	1.40558546205895	0.02959362466235	c
-0.02320643667417	1.47625685733540	-0.03510408812369	c
-1.28071586233413	-0.89679980709549	0.04850691327506	c
-1.01437336173343	-4.96748607803914	0.37701825747263	h
3.67922992426945	-5.04308941859428	0.47339239202593	h
3.89605380744353	3.47408605507797	0.08154572311320	f
-1.43607335823597	3.93801594339217	-0.08423567344510	c
-2.59411925538877	4.15133451549582	1.60809457971750	h
-0.15164495657758	5.53534680146571	-0.18412348579415	h
-2.69464860172223	4.01936059791629	-1.71453651375440	h
-4.07878186704582	-0.95665439250382	0.03059173211590	c
-4.82831101527098	0.17907676364272	1.58896622828670	h
-4.79023987052710	-0.05253198570769	-1.69081253137922	h
-4.83416064381822	-2.86035356813862	0.15146171717509	h
4.07636532796978	-0.96286424795047	-0.15612859301136	c
4.56957538611588	-1.04188101111518	-2.20216532335321	h
6.26316010464375	-0.84448488702042	1.20092663964605	f

$end

Etot = -509.5940764717 H

ZPE = 391.0 kJ/mol

enthalpy = 419.11 kJ/mol

chem. pot. = 299.17 kJ/mol

3H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.18531356863456	-3.19482517571679	0.12687133382409	c
4.24107615720016	-0.86674004912507	-0.13709945436504	c
2.91004535866151	1.34945089761744	-0.17734022868129	c
0.25292740658741	1.34968684464433	-0.07033533679566	c
-1.13072521102184	-0.98826024096026	0.08603036361762	c
-0.80161566320223	-4.98243953151011	0.24375907199373	h
4.15596103080750	3.52066551893173	-0.31929118714735	f
6.70232299150910	-0.85400210684644	-0.23682101902187	f
-1.10138474017828	3.80140517417385	-0.11631387838767	c
-2.23636884584721	3.99203133584488	1.60291664849517	h
0.15760840743051	5.40980331285214	-0.27781358824333	h
-2.45320895092295	3.82229385935054	-1.68019608927322	h
-3.96726638472061	-0.94434339386521	0.19878063635781	c
-4.63251011655205	0.12440625485164	1.83178140624808	h
-4.76561999350998	-0.05629375839541	-1.48241461670972	h
-4.72503335508440	-2.84964461074757	0.33261703780969	h
2.96451609293722	-3.31174783466738	0.01890391314158	c
3.70431197790099	-4.35341187012844	1.66351166263842	h
3.57277706309000	-4.49252806578805	-1.58506755167089	h

$end

Etot = -509.6075160266 H

ZPE = 389.9 kJ/mol

enthalpy = 417.98 kJ/mol

chem. pot. = 298.67 kJ/mol

4H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

3.05761404434735	-3.26144798329091	0.01040407881391	c
4.25552573592881	-1.02292698456363	-0.13137541579682	c
2.81917152333504	1.25908500396018	-0.16731104192017	c
0.17491997087484	1.39159141426436	-0.06645361135047	c
-1.10585841540666	-0.88580867766266	0.08217808352433	c
4.11546650139732	-5.01052762354543	0.03971520192754	h
4.12026903436968	3.34420289161647	-0.30518374671652	f
6.74166022749741	-0.81114950340227	-0.24151818185373	f
-1.15023168909117	3.90260080202741	-0.11692859973857	c
-2.25061075161005	4.16939572668415	1.60626403653704	h
0.17065172461028	5.46364409018263	-0.28140753251115	h
-2.45837193895699	3.99431769264081	-1.70731541340661	h
-3.91030759489168	-0.96948382480045	0.19981158863301	c
-4.59469220272558	0.11530985735757	1.82076114618908	h
-4.72420804771049	-0.06377768416729	-1.47105885865156	h
-4.63415997176282	-2.88777403113855	0.33096091385715	h
0.28156882487818	-3.30990382714254	0.12741989373857	c
-0.45277199482220	-4.51384363159006	-1.40663410286418	h
-0.31801824466138	-4.37598441931868	1.81449682319281	h

$end

Etot = -509.6097623025 H

ZPE = 389.7 kJ/mol

enthalpy = 417.98 kJ/mol

chem. pot. = 297.93 kJ/mol

5H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.26364299345650	-3.28015613008716	-0.33301449989000	c
2.81904249264738	-3.25011721276124	-0.45137320569431	c
4.02349653397239	-0.88034690885910	-0.60794694621924	c
2.70246618407245	1.42656923799093	-0.66290125407664	c
0.12020923295533	1.48004052741464	-0.56213875638740	c
-0.74043036697400	-5.05876226889104	-0.21141300933445	h
3.97089398875164	-4.93730427690952	-0.43840590963794	h
4.05300767163308	3.53190316260844	-0.83284816899243	f
6.47369290670197	-0.80178255678166	-0.72681842537010	f
-1.27224129899632	3.91655806029945	-0.64439548375604	c
-1.57459582608137	4.59442731685237	1.28990997124264	h
-0.19715033155182	5.36639880878129	-1.62850928421522	h
-3.12295708692373	3.70035925269402	-1.51699115746797	h
-1.27218272946806	-0.95082879397891	-0.32964101451683	c
-2.52260107205341	-1.07076637814105	-1.99495248515521	h
-3.10341238426792	-0.94354682663308	2.00297515967081	c
-4.39162641468918	0.65062300943247	1.88215357221251	h
-4.20538177501341	-2.67827985447984	2.01785266984260	h
-2.02387271817156	-0.81498816855114	3.74845822774517	h

$end

Etot = -509.6042997848 H

ZPE = 392.8 kJ/mol

enthalpy = 420.44 kJ/mol

chem. pot. = 301.54 kJ/mol

6H-5,6-dimethyl-1,2-difluorobenzeniumcation

$coord

0.25583918640608	-3.30133037355336	0.14971035065143	c
2.90051214649709	-3.25730347346576	0.06236044326189	c
4.28139859927375	-1.01706345443318	-0.12272136332645	c
2.99727708625370	1.22601386343081	-0.21021274364813	c
-1.12014335647294	-1.10065746964058	0.08579655773223	c
-0.69309285315009	-5.10780246992698	0.25178496457273	h
3.96145134458237	-5.00943870836242	0.11440334960399	h
4.21993268064679	3.35747941103093	-0.42846431846781	f
6.77763124333109	-1.07869250343357	-0.23659842884922	f
-3.92718331245785	-1.10409148704452	0.18261102071702	c
-4.55437142885468	-0.70467364361482	2.11584085331472	h
-4.74098859965515	0.35744286856467	-1.02031969413800	h
-4.69699605497644	-2.93457736510599	-0.34882507487148	h
0.22103134659936	1.37223636821396	-0.02385140925690	c
-0.43172987022676	2.36826899557861	-1.73026150383017	h
-0.52064532467514	3.12344147266082	2.26288209742813	c
-2.54145376485786	3.47872128731418	2.21926247818276	h
-0.01945836089029	2.21401600480616	4.03753833001087	h
0.47638630814089	4.91101390719980	2.10083764941678	h

$end

Etot = -509.5998223952 H

ZPE = 392.7 kJ/mol

enthalpy = 420.47 kJ/mol

chem. pot. = 301.24 kJ/mol

CH_2Cl_2
$coord
0.00000000000000 0.00000000000000 -0.28350808651116 c
0.00000000000000 -1.69495000015265 -1.43256677274059 h
0.00000000000000 1.69495000015265 -1.43256677274059 h
-2.81447994362993 0.00000000000000 1.57432081599618 cl
2.81447994362993 0.00000000000000 1.57432081599618 cl
$end
Etot = -959.6196464043 H
ZPE = 75.78 kJ/mol
enthalpy = 87.74 kJ/mol
chem. pot. = 6.85 kJ/mol

$[MeCH_2Cl_2]^+$
$coord
-1.82617019480323 0.85527252243172 -1.96769582737317 c
-1.99061835257700 -1.11475766189788 -2.51143791864168 h
-1.84263528975484 2.17055430763157 -3.54366192995546 h
-3.83468977003716 1.69775111419997 0.43292694769967 cl
1.67735713602074 1.12339087245745 -0.97426989331940 cl
1.90491836830991 -0.94837474833839 1.80646346040738 c
1.60463776938902 -2.86527373940098 1.14639058283333 h
3.81890369111291 -0.63164878007545 2.47834824726191 h
0.48829664233965 -0.28691388700803 3.13293633108746 h
$end
Etot = -999.1929682185 H
ZPE = 173.8 kJ/mol
enthalpy = 192.22 kJ/mol
chem. pot. = 93.61 kJ/mol

$[HCH_2Cl_2]^+$
$coord
-0.85633958300171 0.95968521890862 -0.12440301612330 c
-0.39905259055511 1.57985605945970 1.77309057068251 h
-0.46908920386836 2.24196691364704 -1.67593485106395 h
-3.36954290193866 -0.90124573783698 -0.43825333548955 cl
2.43251777697246 -2.72150619830662 1.16911129400408 h
2.66150650239143 -1.15875625587169 -0.70361066200979 cl
$end
Etot = -959.8725970944 H
ZPE = 93.41 kJ/mol
enthalpy = 108.91 kJ/mol
chem. pot. = 18.33 kJ/mol

$CH_2ClOTeF_5$
$coord
0.33519267491892 -2.88454683766945 -1.47125123283604 c
1.87908489606404 -2.49001535594465 -2.76483428251886 h
-1.49208203577579 -2.49499543381484 -2.32373066959910 h
0.66633177644307 -1.51234235887580 0.83519702657854 o
-0.15790229159999 1.97314924960077 1.03316798877056 te
-3.39332807586879 1.40740650114992 -0.24868637851367 f
0.98310303110695 2.56415859942374 -2.25483595722006 f
-0.95872453942594 5.36661734925822 1.28167134855268 f
-1.32759920257812 1.50600428439727 4.29626113848393 f
3.02950364937042 2.70430645937170 2.28820086069889 f
0.43642011734522 -6.13974245689676 -0.67115984239689 cl

$end
Etot = -1341.985524008 H
ZPE = 118.6 kJ/mol
enthalpy = 149.78 kJ/mol
chem. pot. = 14.85 kJ/mol

$[MeClCH_2OTeF_5]^+$

$coord

1.96018985111497	-0.96507830292168	-2.31698887969489	c
3.50817145253533	-2.28978732423588	-2.55291132901901	h
1.06875713328374	-0.17906082942305	-3.99085850700094	h
2.08708523945759	0.34318612600174	-0.25426151537656	o
0.04994180504140	3.47865163884697	0.44409548660994	te
-2.81087564667363	1.69066558396666	-0.50246452125975	f
0.49002033624923	4.40082238000026	-2.89580599263498	f
-1.79617419769646	6.30279680406606	1.15357430792111	f
-0.28865567271157	2.22650623047676	3.67083394025163	f
3.04539065241402	4.99081823445437	1.30187026108317	f
-0.91913420025016	-3.98228017898132	-1.87249514960855	cl
-1.52712428631493	-3.99426309381945	1.52372489545779	c
-3.29949622730110	-3.00954500656821	1.80737753166866	h
-1.61880427884898	-5.97141910155911	2.05716298234000	h
0.05070803970033	-3.04201316030414	2.42714648926230	h

$end
Etot = -1381.565613376 H
ZPE = 216.3 kJ/mol
enthalpy = 254.65 kJ/mol
chem. pot. = 103.90 kJ/mol

$[HClCH_2OTeF_5]^+$

$coord

1.40926930157772	-1.76207548886829	-1.71241422109744	c
2.82584289466447	-3.22385495235496	-1.99524794249481	h
-0.04500229513135	-1.43654838464310	-3.12977138989995	h
1.78721682394333	-0.26410883813728	0.08208887860677	o
-0.46411738880873	2.82657244178329	0.92261985137181	te
-3.20682404491320	0.74227324581586	0.36552625539294	f
-0.42963672571349	3.53072230572151	-2.49323729955186	f
-2.41909025807285	5.54948268029321	1.69392464783316	f
-0.28278589334589	1.69776033922539	4.19042000200380	f
2.52366923465362	4.52793749494885	1.30657572639197	f
-1.63280838709701	-5.29467492488835	-0.09519251204267	cl
-0.06573326175659	-6.89348591889616	0.86470800348640	h

$end
Etot = -1342.256191841 H
ZPE = 135.1 kJ/mol
enthalpy = 170.99 kJ/mol
chem. pot. = 25.77 kJ/mol

NC_5F_5

$coord

-2.13175680248628	0.00000000000000	-1.76609117374860	c
-2.26829141955860	0.00000000000000	0.85422925380889	c
0.00000000000000	0.00000000000000	2.18061115621325	c
2.26829141955860	0.00000000000000	0.85422925380889	c
2.13175680248628	0.00000000000000	-1.76609117374860	c
0.00000000000000	0.00000000000000	-3.02082163234920	n

```
   4.26777532873910      0.00000000000000     -3.08847859869599  f
  -4.26777532873910      0.00000000000000     -3.08847859869599  f
  -4.46592902999212      0.00000000000000      2.07876752527249  f
   0.00000000000000      0.00000000000000      4.68335646286239  f
   4.46592902999212      0.00000000000000      2.07876752527249  f
$end
Etot = -744.4652517208 H
ZPE = 125.9 kJ/mol
enthalpy = 150.43 kJ/mol
chem. pot. = 38.86 kJ/mol
```

$[MeNC_5F_5]^+$

```
$coord
  -0.06297542152629     -2.18170125414344      0.00000000000000  c
   2.54419046047328     -2.27402953117702      0.00000000000000  c
   3.88696280810764     -0.00138623161991      0.00000000000000  c
   2.56969619410052      2.28338683593726      0.00000000000000  c
  -0.04276098122677      2.23276738035604      0.00000000000000  c
  -1.42330742330835     -4.23481154178539      0.00000000000000  f
   3.71891819704425     -4.45635783254555      0.00000000000000  f
   6.34583873457141     -0.01495828324914      0.00000000000000  f
   3.77117796298255      4.45175820689612      0.00000000000000  f
  -1.34370900710712      4.32356064359047      0.00000000000000  f
  -4.16859662646559     -0.02574197283846      0.00000000000000  c
  -4.86195009198710      1.89831905509271      0.00000000000000  h
  -4.79524106205960     -1.01648687840107     -1.68553214861077  h
  -4.79524106205960     -1.01648687840107      1.68553214861077  h
  -1.34300268153922      0.03216828228849      0.00000000000000  n
$end
Etot = -784.0836887539 H
ZPE = 232.3 kJ/mol
enthalpy = 262.11 kJ/mol
chem. pot. = 135.84 kJ/mol
```

$[HNC_5F_5]^+$

```
$coord
  -2.29919131249498      0.00000000000000     -1.27674196880174  c
   0.00000000000000      0.00000000000000     -2.58961494934371  c
   2.29919131249498      0.00000000000000     -1.27674196880174  c
   2.23518308047427      0.00000000000000      1.33113270273271  c
  -2.23518308047427      0.00000000000000      1.33113270273271  c
   0.00000000000000      0.00000000000000      4.48452213106983  h
   4.25289924990766      0.00000000000000      2.72652794998835  f
   4.45805582862935      0.00000000000000     -2.48586343826002  f
   0.00000000000000      0.00000000000000     -5.04402507243016  f
  -4.45805582862935      0.00000000000000     -2.48586343826002  f
  -4.25289924990766      0.00000000000000      2.72652794998835  f
   0.00000000000000      0.00000000000000      2.55900739938550  n
$end
Etot = -744.7763604628 H
ZPE = 160.6 kJ/mol
enthalpy = 185.62 kJ/mol
chem. pot. = 73.29 kJ/mol
```

NC_5F_4I

```
$coord
   0.00000000000000      0.00000000000000     -2.09313612482296  c
   2.24842271768006      0.00000000000000     -0.73019337137702  c
   2.12575756516087      0.00000000000000      1.89318284731361  c
  -2.12575756516087      0.00000000000000      1.89318284731361  c
  -2.24842271768006      0.00000000000000     -0.73019337137702  c
  -4.26706387205152      0.00000000000000      3.21150995630949  f
  -4.48646458897778      0.00000000000000     -1.88725334624425  f
   4.48646458897778      0.00000000000000     -1.88725334624425  f
   4.26706387205152      0.00000000000000      3.21150995630949  f
   0.00000000000000      0.00000000000000      3.15608010925613  n
   0.00000000000000      0.00000000000000     -6.03743615643678  i
$end
Etot = -942.3305763184 H
ZPE = 119.0 kJ/mol
enthalpy = 145.49 kJ/mol
chem. pot. = 24.85 kJ/mol
```

$[MeNC_5F_4I]^+$

```
$coord
   3.84309722846643      0.00058943999955      0.00000000000000  c
   2.45188909773188     -2.24537682800510      0.00000000000000  c
  -0.15406131639222     -2.17451310967299      0.00000000000000  c
  -0.13584486672565      2.22701663023108      0.00000000000000  c
   2.47533428443425      2.25824054651286      0.00000000000000  c
  -1.44039950543165      4.32232548491605      0.00000000000000  f
   3.61202900198368      4.47302413802316      0.00000000000000  f
   3.56332237891046     -4.47226647751947      0.00000000000000  f
  -1.51642002775640     -4.23352682988385      0.00000000000000  f
   7.75009488583997     -0.02004639403002      0.00000000000000  i
  -4.26234319151568     -0.02662438855754      0.00000000000000  c
  -4.89207227684617     -1.01871947035875     -1.68392379618668  h
  -4.89207227684617     -1.01871947035875      1.68392379618668  h
  -4.95858456245618      1.89630352813081      0.00000000000000  h
  -1.44396885339651      0.03229320057307      0.00000000000000  n
$end
Etot = -981.9577117529 H
ZPE = 224.8 kJ/mol
enthalpy = 256.67 kJ/mol
chem. pot. = 121.42 kJ/mol
```

$[HNC_5F_4I]^+$

```
$coord
   0.00000000000000      0.00000000000000     -2.52409343019722  c
   2.27133951170660      0.00000000000000     -1.15977499090742  c
   2.22741070047243      0.00000000000000      1.44643461994788  c
  -2.22741070047243      0.00000000000000      1.44643461994788  c
  -2.27133951170660      0.00000000000000     -1.15977499090742  c
   0.00000000000000      0.00000000000000      4.60906602941398  h
   0.00000000000000      0.00000000000000      2.68567162442685  n
  -4.47921403934048      0.00000000000000     -2.30178374052736  f
  -4.25232433917254      0.00000000000000      2.84330649595364  f
   4.25232433917254      0.00000000000000      2.84330649595364  f
   4.47921403934048      0.00000000000000     -2.30178374052736  f
   0.00000000000000      0.00000000000000     -6.42700899257716  i
$end
```

Etot = -942.6512551506 H
ZPE = 153.1 kJ/mol
enthalpy = 180.06 kJ/mol
chem. pot. = 58.70 kJ/mol

$[N_3C_3F_3]$

```
$coord
  -1.19604163577979     2.07160488113841     0.00000000000000  c
  -1.19604163577979    -2.07160488113841     0.00000000000000  c
   2.39208327155962     0.00000000000000     0.00000000000000  c
  -2.43613096161762    -4.21950259941334     0.00000000000000  f
  -2.43613096161762     4.21950259941334     0.00000000000000  f
   4.87226192323524     0.00000000000000     0.00000000000000  f
   1.29178260036823    -2.23743309617122     0.00000000000000  n
   1.29178260036823     2.23743309617122     0.00000000000000  n
  -2.58356520073648     0.00000000000000     0.00000000000000  n
$end
```

Etot = -578.1027710451 H
ZPE = 108.7 kJ/mol
enthalpy = 127.22 kJ/mol
chem. pot. = 31.34 kJ/mol

$[MeN_3C_3F_3]^+$

```
$coord
   0.65153035098513     2.18790841204294     0.00000000000000  c
   0.62775424070340    -2.14101241369815     0.00000000000000  c
   4.21308130951005    -0.00474739597299     0.00000000000000  c
  -0.68749021098619    -4.19299064101403     0.00000000000000  f
  -0.60610000956939     4.27508673161593     0.00000000000000  f
   6.63764855196507    -0.02094300915328     0.00000000000000  f
   3.06694957666461    -2.23980390163782     0.00000000000000  n
   3.09551224719108     2.24115867616036     0.00000000000000  n
  -3.57465730995438    -0.02199579164784     0.00000000000000  c
  -4.26185132316029     1.90570502411633     0.00000000000000  h
  -4.20419195009216    -1.01028516474308    -1.68664552423017  h
  -4.20419195009216    -1.01028516474308     1.68664552423017  h
  -0.75399352316471     0.03220463867461     0.00000000000000  n
$end
```

Etot = -617.7139873235 H
ZPE = 214.1 kJ/mol
enthalpy = 238.05 kJ/mol
chem. pot. = 123.51 kJ/mol

$[HN_3C_3F_3]^+$

```
$coord
   0.00000000000000     0.00000000000000     2.84809479631941  c
   2.18806059877226     0.00000000000000    -0.71468490951850  c
  -2.18806059877226     0.00000000000000    -0.71468490951850  c
   0.00000000000000     0.00000000000000    -3.98694327241193  h
   4.22144081835305     0.00000000000000    -2.04082493188351  f
   0.00000000000000     0.00000000000000     5.26598267278582  f
  -4.22144081835305     0.00000000000000    -2.04082493188351  f
   0.00000000000000     0.00000000000000    -2.06178045829594  n
  -2.25296634313502     0.00000000000000     1.72283297220332  n
   2.25296634313502     0.00000000000000     1.72283297220332  n
$end
```

Etot = -578.4047107374 H

ZPE = 142.4 kJ/mol
enthalpy = 161.50 kJ/mol
chem. pot. = 61.82 kJ/mol

[MeClH]$^+$

```
$coord
  -0.56543589300053    -0.36595011229166     0.84366837533605  c
   0.00902878109819    -2.31821496407070     0.60793658359676  h
   0.49975301972127     0.70282796314041     2.22936512447792  h
  -2.59703792136928    -0.12147386391676     1.00418239174122  h
   0.10715085437041     1.20430991727270    -2.28547316478282  cl
   2.54654115917995     0.89850105986599    -2.39967931036916  h
$end
```

Etot = -500.3181038919 H
ZPE = 119.3 kJ/mol
enthalpy = 131.74 kJ/mol
chem. pot. = 54.77 kJ/mol

[CH_2Cl]$^+$

```
$coord
   0.00000000000000     0.00000000000000    -0.24865678245851  c
   1.79435207712726     0.00000000000000    -1.25843652536337  h
  -1.79435207712726     0.00000000000000    -1.25843652536337  h
   0.00000000000000     0.00000000000000     2.76552983318522  cl
$end
```

Etot = -499.0776514221 H
ZPE = 65.24 kJ/mol
enthalpy = 75.39 kJ/mol
chem. pot. = 6.21 kJ/mol

[CH_2OTeF_5]$^+$

```
$coord
  -2.93838527963546    -1.62488838468461    -1.42155449697117  c
  -2.30843900110580    -3.33653502236333    -0.45005207899562  h
  -4.66098325498029    -1.63038952016151    -2.56165608838860  h
  -1.76551698006863     0.38580080250463    -1.29237563887305  o
   1.63697425258115     0.99670558815141     0.76153018728010  te
   2.83708984502832    -1.80347045933679    -0.91927953350751  f
   0.27161530418833    -1.14405583738148     3.14769761938237  f
   4.53774488968276     1.55178986231382     2.50820484479678  f
   2.49049060932415     2.97166859507379    -1.94182946469044  f
  -0.10059038501457     3.63337437588409     2.16931464996713  f
$end
```

Etot = -881.4713170005 H
ZPE = 111.3 kJ/mol
enthalpy = 139.74 kJ/mol
chem. pot. = 15.87 kJ/mol

[Me_2Cl]$^+$ with COSMO (ε_R DCM)

```
$coord
  -1.98405009229510    -0.02098963202409     1.83432600895542  c
  -2.26206448398021    -1.97841915296400     1.29995197966391  h
  -0.51419326178527     0.26049715452948     3.23248347308744  h
  -3.73601684120484     0.92648095396826     2.32071763536219  h
  -0.93210416562440     1.62263899880372    -1.02135660568787  cl
   2.00794224185052    -0.02067827978101    -1.80809485426875  c
   2.66316059735374     0.94035457441494    -3.49659912813942  h
```

```
   3.25878431744139     0.24427253642967    -0.20820464147197  h
   1.49854168824412    -1.97415715337698    -2.15322386750094  h
$end
E(COSMO) = -539.7221153427 H
ZPE = 200.5 kJ/mol
enthalpy = 215.54 kJ/mol
chem. pot. = 129.91 kJ/mol
```

[MeCl···CH_2Cl]$^+$ with COSMO (ε_R DCM)

```
$coord
  -1.74581571389478     0.83827298606909    -1.93478644464126  c
  -1.89950779852708    -1.15216934744983    -2.38933623648056  h
  -1.82444251466985     2.07709179754972    -3.56542836078661  h
  -3.84301373831243     1.73799074760944     0.42009043307158  cl
   1.62319869850949     1.23407424029674    -0.90801806056359  cl
   1.87197466651857    -0.93933529955150     1.77660982244547  c
   1.51812795200163    -2.81525530953295     1.03564168233934  h
   3.80412684008161    -0.67839020294229     2.41182797033054  h
   0.49535160829285    -0.30227961204843     3.15339919428518  h
$end
E(COSMO) = -999.2732013724 H
ZPE = 177.2 kJ/mol
enthalpy = 194.43 kJ/mol
chem. pot. = 99.44 kJ/mol
```

[MeCl···CH_2OTeF_5]$^+$ with COSMO (ε_R DCM)

```
$coord
   1.41003836726465    -1.01985872400031    -1.88989615068370  c
   2.97596161872049    -2.34323091576330    -1.84484552669293  h
   1.01370527271234    -0.20626508449059    -3.73264353675659  h
   1.50121972737910     0.53962585913106     0.11750158846426  o
  -0.12808032984581     3.83880294266345     0.21487893037597  te
  -3.02013492865032     2.50358589970600    -1.25704954360283  f
   1.09704457684645     4.57479482037963    -2.98429295394972  f
  -1.63419109468748     6.96430603176835     0.39483184397900  f
  -1.35064544103051     3.01337795117142     3.37701145743994  f
   2.77676341635017     5.10371739867902     1.65952620690663  f
  -1.47330259248276    -3.32424401503535    -1.58442059837046  cl
  -0.84676968583680    -4.73554504386411     1.51402433213741  c
  -0.72754840944797    -3.18135519327657     2.84295513412816  h
  -2.48398087888630    -5.92363379028668     1.84549575921246  h
   0.88992038159433    -5.80407813678197     1.32692305741238  h
$end
E(COSMO) = -1381.6416963833 H
ZPE = 219.9 kJ/mol
enthalpy = 256.25 kJ/mol
chem. pot. = 114.83 kJ/mol
```

3.7 Optimized structures for fluoride ion affinities

All structures on the RI-B3LYP-D3/def2-TZVPP level of theory, see also section 3.6 for necessary structures.

2,2,4,6-tetrafluoro-1-methyl-1,3,5-triazine

$coord

0.09941750421381	-0.60449281709045	2.36297232064804	c
0.02435762263131	-4.16830225816490	0.23692919186585	c
0.21884590083266	0.73463243030198	4.46759673829239	f
0.05619209441420	-6.66123314462667	0.38401803906994	f
-0.08431984242552	-3.19447073845026	-1.96502791986116	n
0.12271720685180	-3.02726954762072	2.52944623001091	n
0.03205074601634	3.54476162591456	0.22775963559796	c
1.97522118831202	4.21365691599137	0.32007491704237	h
-0.83046742779319	4.18402680235571	-1.51898397769682	h
-1.03328552660262	4.27853873903208	1.81996581252335	h
-0.04126164114326	0.77131719121715	0.25438086210968	n
-0.12993643198738	-0.57801794285471	-2.13854746187593	c
1.84096973813024	0.28784598465962	-3.58205977231524	f
-2.25050113145046	0.21900675933532	-3.39852461541137	f

$end

Etot = -717.8586031889 H

ZPE = 219.3 kJ/mol

enthalpy = 246.05 kJ/mol

chem. pot. = 126.15 kJ/mol

2,4,4,6-tetrafluoro-1-methyl-1,3,5-triazine

$coord

-0.01669286729766	-0.28260756178390	2.19136241349766	c
-0.01618735684844	1.11507110363620	4.27640712090085	f
0.02830305885835	-2.66547977648749	-2.29272305487868	n
0.00430667072822	-2.64569894162950	2.34119262749899	n
0.00256370755930	3.92304729952177	-0.05416996801002	c
1.86994911910782	4.59766236762855	-0.59489823003445	h
-1.38406189394624	4.59411932640813	-1.41085864678694	h
-0.46909923639553	4.63419905838426	1.80683018001147	h
-0.04543325353970	1.14744728522205	0.01355721305261	n
0.00558740594496	-0.30276940555522	-2.15025661386026	c
0.02913382587844	1.10135876111549	-4.23113697645830	f
0.00538439931136	-4.04215272625176	0.03088119608341	c
-2.06548331517242	-5.57234196623794	0.02629946902500	f
2.05172973581152	-5.60185482397061	0.04751326995867	f

$end

Etot = -717.8487796134 H

ZPE = 218.7 kJ/mol

enthalpy = 245.98 kJ/mol

chem. pot. = 121.17 kJ/mol

2-pentafluoro-*ortho*tellurato-4,6-difluoro-1,3,5-triazine

$coord

-4.67545612319515	1.97927920163241	1.89144421688085	c
-4.10601684817995	-1.61500473853918	-0.08411967577297	c
-0.85172962920546	0.88145008988750	0.67000448000783	c
-5.01348803087810	-3.71908062860258	-1.03226976912062	f
-6.19142682130341	3.60131697420106	2.99742468406693	f
-1.64865205792291	-1.27725898354057	-0.31765406545004	n
-2.26849919033808	2.60548602585784	1.81213294221416	n

```
  -5.75102088272372    -0.08527044411069     0.98922483291476  n
   1.61404707087723     1.49390244929587     0.56921455282830  o
   4.32613082157465    -0.38220979770258    -1.00637031608099  te
   2.48632385950757    -1.08582998979905    -3.89530178852532  f
   5.35685586804224     2.63250259043368    -2.44199235524164  f
   6.24610520030036     0.35755892262107     1.81708170254678  f
   7.08586431632219    -1.97346870727660    -2.43245179229806  f
   3.39096244712250    -3.41337296435818     0.46363235103002  f
$end
Etot = -1320.779486963 H
ZPE = 146.2 kJ/mol
enthalpy = 185.35 kJ/mol
chem. pot. = 33.23 kJ/mol
```

2-pentafluoro-*ortho*tellurato-4,6-difluoro-1-methyl-1,3,5-triazinium

```
$coord
  -4.56946207327888     0.91711993836128     1.28319975403742  c
  -3.91232766776122    -2.88327149255018    -0.29889088420039  c
  -0.57087265331146    -0.32879701465585     0.02151027381275  c
  -4.81812590808289    -5.04834820885971    -0.94951664544299  f
  -6.00510735348624     2.65404854357292     2.23175464646099  f
  -1.46811767201342    -2.53880925509059    -0.64795444719221  n
   1.78132830937463     0.31867222392737    -0.18281997490268  o
   4.70768215874546    -1.65837762230484    -1.61051613754405  te
   2.73584112658322    -2.57504754798663    -4.32467438063191  f
   5.51045267255917     1.30920915242863    -3.22643258921011  f
   6.42243437395101    -0.55702129228723     1.20122011500883  f
   7.47665187975642    -3.28389855415577    -2.87805191737451  f
   3.67797486318398    -4.47151763705296     0.15263804584213  f
  -5.54605579665575    -1.23239465581871     0.65645985217631  n
  -1.02442837743798     4.02728080326772     1.76034590426771  c
   0.36001834100854     3.73323481805966     3.24838194458982  h
  -0.12000001547689     4.85713193133657     0.11473607051544  h
  -2.54384837047348     5.22697028558713     2.42254133428006  h
  -2.09403783718414     1.53381558422113     1.02606903550763  n
$end
Etot = -1360.403113666 H
ZPE = 252.5 kJ/mol
enthalpy = 296.89 kJ/mol
chem. pot. = 133.39 kJ/mol
```

2-pentafluoro-*ortho*tellurato-2,4,6-trifluoro-1-methyl-1,3,5-triazine

```
$coord
  -3.89232412115368     0.63685517612704     2.55439978401198  c
  -3.43054487890985    -3.24658104277084     1.16018305012961  c
   0.06198406153074    -0.72707197855752     0.88995014814392  c
  -4.53162159107779    -5.45259259331032     0.79178950229588  f
  -5.21245486235852     2.50820193452150     3.54157147844566  f
  -1.10825111531064    -3.05293525962036     0.54346720598014  n
   0.84443795185634     0.39486045719977    -1.43013514949172  o
   3.28822398336337    -0.90716498035418    -3.75071065016725  te
   0.83880525042949    -2.70752508792304    -5.49112102610398  f
   2.58725644037199     1.91456486822874    -5.70833441613016  f
   5.85000886667367     0.87396895177439    -2.13659863438527  f
   5.62144232454358    -1.90472806053512    -6.15822319825619  f
   4.09063465309027    -3.74933174561406    -1.87579987455911  f
  -4.99885593034164    -1.48863224427064     2.16683533717111  n
```

-0.39472631608074	3.72395147069860	2.53203439442832	c
1.64603936140255	3.53852239791821	2.55448545756986	h
-0.95135980226707	5.02114093593063	1.03688967475709	h
-1.03596917563196	4.43070318267528	4.34848024461269	h
-1.47712759668293	1.20557207668243	2.08253406628927	n
2.20440249655290	-1.01177845880027	2.34830260525809	f

$end
Etot = -1460.532971900 H
ZPE = 256.7 kJ/mol
enthalpy = 303.92 kJ/mol
chem. pot. = 133.83 kJ/mol

2-pentafluoro-*ortho*tellurato-4,4,6-trifluoro-1-methyl-1,3,5-triazine

$coord

-4.36265837330984	1.10882524275640	1.30988760432440	c
-0.39830348663490	-0.17777330533700	0.04094333049916	c
-5.74520799274379	2.95938411066203	2.29156246236806	f
-1.18751620916634	-2.32258804102652	-0.62486626298274	n
2.05433671803935	0.55269125093409	-0.14910389111520	o
4.78588286361931	-1.43812380526678	-1.53597749516991	te
2.97311150331579	-2.42318643637377	-4.34963012323464	f
5.77029110600116	1.46347417856971	-3.23002730890800	f
6.68616501422710	-0.38589486933582	1.20961988537983	f
7.59045574954821	-3.08370347773845	-2.80598695786778	f
3.92328063287077	-4.33043411461911	0.21157458424903	f
-5.38342347065803	-0.94682551082539	0.72623954244394	n
-0.76331986903289	4.19958997534893	1.78126448342626	c
0.63910609447051	3.93574577654268	3.26065815436322	h
0.12794248398841	5.07757446812600	0.15125434854686	h
-2.26694490379657	5.40451347162238	2.47012545606460	h
-1.84952842804537	1.74740251070587	1.05436334654515	n
-3.81030143985329	-2.86604173468383	-0.32482826548718	c
-4.02347307145871	-4.96941677047377	1.14426201959419	f
-4.75989492138088	-3.50521291958762	-2.63133491303926	f

$end
Etot = -1460.527663808 H
ZPE = 256.8 kJ/mol
enthalpy = 304.45 kJ/mol
chem. pot. = 131.17 kJ/mol

2-pentafluoro-*ortho*tellurato-4,6,6-trifluoro-1-methyl-1,3,5-triazine

$coord

-3.62008225489380	-2.94664019329542	-0.39649770081882	c
-0.33527404602955	-0.38140830192265	-0.06139852668420	c
-4.40047015952060	-5.20941844594801	-1.11038209565037	f
-1.11279145018667	-2.59394370056832	-0.75335476372542	n
2.11210994035014	0.30363863654849	-0.26196400408959	o
4.84616804421860	-1.70300738602729	-1.64078321328546	te
3.03212263637014	-2.69379802357159	-4.45242342188696	f
5.83215625450799	1.19066986907983	-3.34172857158215	f
6.73514850724028	-0.64687390767547	1.10759712692665	f
7.64702070203186	-3.36088648036973	-2.89934685578572	f
3.96852320139891	-4.58698348357740	0.11444501308465	f
-5.26821460248858	-1.44060797649053	0.50736616126265	n
-0.77879835088125	3.92465597059836	1.67397395170088	c
0.54537478104419	3.70464128952658	3.23106712035327	h
0.16766629442004	4.82356233472629	0.08728128216159	h

```
  -2.35645394810589     5.08504603679651     2.27498587692799  h
  -1.78283503081489     1.45292334564778     0.90856009309035  n
  -4.45901918643368     0.93875131359497     1.25591446958681  c
  -5.76875354050539     2.78926821014400    -0.00046973950438  f
  -5.00359779172189     1.35041089278362     3.75715779791828  f
$end
Etot = -1460.537410725 H
ZPE = 257.1 kJ/mol
enthalpy = 304.39 kJ/mol
chem. pot. = 133.36 kJ/mol
```

4-pentafluoro-*ortho*tellurato-2,6-difluoro-1-methyl-1,3,5-triazinium

```
$coord
  -2.73703274819351     2.36047391378223     1.54978581601376  c
  -2.24290748701017    -1.43098414069654    -0.46130231605289  c
   1.08766339189802     1.02371807876100     0.36318138179026  c
  -3.29302442874137    -3.45125584059425    -1.35660061112303  f
  -4.24590318576293     3.98108841712978     2.59026661284714  f
   0.16365642994421    -1.13315622175560    -0.61570783742925  n
  -0.35063599904851     2.80574509279770     1.47017474376743  n
   3.47964696547216     1.52185402110910     0.29230688401527  o
   6.36767098797592    -0.51872954198320    -1.04962474930072  te
   4.53917040498972    -1.26017554940257    -3.92210722878598  f
   7.42826795856843     2.43900419853782    -2.52175445700072  f
   7.99318791681723     0.35822932635882     1.88717071297696  f
   9.11190365813959    -2.26866671739830    -2.21512445563021  f
   5.08831235421573    -3.35189557609007     0.52807189971092  f
  -6.64612905447811    -0.24451415682353     0.69966224586194  c
  -6.98538795189659    -1.86138275094667     1.92032188804292  h
  -7.57608673090417     1.41918566271141     1.44478759847507  h
  -7.30609686736286    -0.63750460416044    -1.20399019693769  h
  -3.87627561462269     0.24896638866313     0.60048206875866  n
$end
Etot = -1360.399094183 H
ZPE = 251.6 kJ/mol
enthalpy = 296.50 kJ/mol
chem. pot. = 127.18 kJ/mol
```

2,4-bis(pentafluoro-*ortho*tellurato)-6-fluoro-1,3,5-triazine

```
$coord
  -2.21574534077028     4.00154182659088     1.15473462609456  c
  -1.44290560462994    -0.07476293944734     0.75458456146917  c
   1.50046996164028     2.74099986628717    -0.22199022497725  c
  -3.77443427210373     5.82912553589123     1.77297014523565  f
   0.88778041645448     0.32288980743241    -0.07095071539918  n
   0.03641734389340     4.69342704164725     0.36421471826890  n
  -3.10086180270072     1.68248274206900     1.40088023072633  n
   3.81513141442203     3.41466679944179    -1.03165806680415  o
   6.44379676149969     1.23515924273672    -2.33659586376123  te
   4.23707527097515    -0.63808796233645    -4.29930370147221  f
   6.79341232406312     3.50990103474723    -4.96685445204546  f
   8.70386657745636     3.12826556861244    -0.46220573789348  f
   9.10089784735049    -0.62185526466590    -3.63028187254072  f
   6.20818680730108    -1.04096406569637     0.30551081282706  f
  -2.05379220089365    -2.53595889103140     0.92924501551035  o
  -5.34017733727891    -3.97907006987162     1.62149745050017  te
  -5.92895250030319    -1.95221407239879     4.40576262362860  f
```

-6.99367012921816	-1.73874263046065	-0.49559130412967	f
-4.79355413922984	-6.09904222452794	-1.10177684756854	f
-8.37282901821936	-5.59776494261044	2.22460000121569	f
-3.71011237970818	-6.27999640240916	3.68320860111542	f

$end
Etot = -2063.456474298 H
ZPE = 183.6 kJ/mol
enthalpy = 243.49 kJ/mol
chem. pot. = 40.52 kJ/mol

2,6-bis(pentafluoro-*ortho*tellurato)-4-fluoro-1-methyl-1,3,5-triazinium

$coord

-2.11120688909353	0.40998623256463	0.58298306238752	c
-1.65414785842453	-3.55335542002975	-0.73824448874202	c
1.82382260696219	-1.17501648236401	-0.63079610462430	c
-2.67871913948862	-5.71744246045439	-1.22673473606612	f
0.80176096951859	-3.37441766598935	-1.13168489478586	n
4.22331764686037	-0.71708319253676	-0.91886225522548	o
6.93889258378010	-2.99860169998180	-2.24659265072609	te
4.85538931646264	-4.01013044840712	-4.84238494910182	f
7.90900713533040	-0.24514593127569	-4.13350214938496	f
8.82861125589802	-1.79708584904587	0.41026854898886	f
9.55715586815558	-4.91543639774458	-3.43373023659983	f
5.79142629426791	-5.58862813887508	-0.23012540096536	f
-3.18194221451385	-1.76706572819163	0.10135734250084	n
1.53218442768192	3.34385156505087	0.83059513995644	c
3.52322640185896	3.31102303686653	0.36948017118916	h
0.56086802493888	4.76403195902447	-0.28934544976253	h
1.26635375309051	3.73316568777668	2.82957662398817	h
0.42836142463029	0.82947484887390	0.24657436445089	n
-3.33555960117937	2.37120879295023	1.42361043230181	o
-7.04556088261159	2.76029736306375	2.07864596713812	te
-7.08674060664125	-0.26853554008609	3.78732653737771	f
-6.05460807244954	4.36931623677500	4.99446253253188	f
-6.72843450166145	5.76123486245716	0.35366215949438	f
-10.39166417344018	3.32343313123833	2.73238263991194	f
-7.77179376993212	1.15092123834071	-0.91892220623327	f

$end
Etot = -2103.089052987 H
ZPE = 290.2 kJ/mol
enthalpy = 355.51 kJ/mol
chem. pot. = 140.95 kJ/mol

2,4-bis(pentafluoro-*ortho*tellurato)-6-fluoro-1-methyl-1,3,5-triazinium

$coord

-2.54636198699958	2.67073524788625	1.21346891851390	c
-1.69102375455081	-1.39698328571487	0.53123197873988	c
1.30869189182677	1.45930700152146	-0.42921048274550	c
0.62174157096148	-0.90126068465108	-0.35262242087118	n
3.50102509146541	2.23112878978048	-1.24169448009055	o
6.42286561846150	0.16037595195479	-2.47124093332089	te
4.28594340318941	-1.74519029805845	-4.44596185777541	f
6.63705715150863	2.51602264606112	-5.01687870995992	f
8.35254250100528	2.22251393114880	-0.44543263535036	f
9.20041779901753	-1.54877110752196	-3.61490667473852	f
6.01471473890585	-2.03375245188230	0.19820888596578	f
-3.32713619691442	0.36924335546594	1.33517275866974	n

0.59920865907123	6.07780344434994	0.23098378446932	c
2.30903257915616	6.27707639376499	1.34944377453451	h
0.98504963429191	6.55614707391269	-1.72827561301346	h
-0.88420381434506	7.27296341539434	0.97765171157957	h
-0.24675431400634	3.40390702925969	0.35385971704412	n
-4.02628050355368	4.47863685711077	1.95706600508966	f
-2.29120461083136	-3.78170181672484	0.56988844609380	o
-5.45751647352566	-5.46400983221950	1.69438034032357	te
-5.52401012992393	-3.49978541034971	4.57441326165233	f
-7.36835921670809	-3.09872097694668	-0.01169487641219	f
-5.20279130957149	-7.32636408953135	-1.22617586778478	f
-8.29752637644130	-7.17425008718673	2.68686942008651	f
-3.37512195148946	-7.72507109682360	3.31145554930017	f

$end
Etot = -2103.085905928 H
ZPE = 290.1 kJ/mol
enthalpy = 355.30 kJ/mol
chem. pot. = 141.56 kJ/mol

2,4,6-tris(pentafluoro-*ortho*tellurato)-1,3,5-triazine

$coord

-1.31808592834816	2.02580011901524	-0.26982976808768	c
-1.09535140188264	-2.15439595782790	-0.26982976808768	c
2.41343733023082	0.12859583881264	-0.26982976808768	c
1.40068789940917	-2.16509464558390	-0.26994750207650	n
1.17468301496870	2.29557862645372	-0.26994750207650	n
-2.57537091437789	-0.13048398086985	-0.26994750207650	n
4.95545865296241	0.11246554958181	-0.28278078393197	o
7.20494652077188	2.97257793626209	0.07608834915157	te
5.32399938295996	4.40244112491405	2.65464625211414	f
8.94899968268505	1.08598887174079	2.44451982900488	f
9.15549403604211	1.53538925414813	-2.44047471312715	f
9.55842124712063	5.52589647124192	0.42734757425732	f
5.56226539024240	4.88951374815563	-2.33956735011367	f
-2.38033130349278	-4.34778585565973	-0.28278078393197	o
-1.02814525285386	-7.72595568802781	0.07608834915157	te
1.15062616136092	-6.81193927783304	2.65464625211414	f
-3.53400589018777	-8.29305549953453	2.44451982900488	f
-3.24806091923115	-8.69658504648344	-2.44047471312715	f
0.00635609921797	-11.04078385570038	0.42734757425732	f
1.45331042293483	-7.26182000461866	-2.33956735011367	f
-2.57512734946962	4.23532030607793	-0.28278078393197	o
-6.17680126791803	4.75337775176570	0.07608834915157	te
-6.47462554432091	2.40949815291897	2.65464625211414	f
-5.41499379249728	7.20706662779372	2.44451982900488	f
-5.90743311681098	7.16119579233534	-2.44047471312715	f
-9.56477734633863	5.51488738445842	0.42734757425732	f
-7.01557581317722	2.37230625646308	-2.33956735011367	f

$end
Etot = -2806.133839636 H
ZPE = 220.9 kJ/mol
enthalpy = 301.65 kJ/mol
chem. pot. = 52.34 kJ/mol

2,4,6-tris(pentafluoro-*ortho*tellurato)-1-methyl-1,3,5-triazinium

$coord

-0.96804724309378	1.91670509975977	-0.30716634504860	c
-0.34278695444735	-2.22635269963025	0.42325583018152	c
3.08126077183033	0.20718540654846	-0.11686501513544	c
2.17284424428752	-2.03761723327296	0.31391155575961	n
5.49732318244533	0.70141828029856	-0.26251855779737	o
8.41971800089358	-1.65483533841611	0.07363565649867	te
6.86479110158741	-3.94809063271772	-2.03168475014787	f
9.69629841323377	-0.00514426093406	-2.70896982672822	f
9.79226000381301	0.80112016454351	2.11745237071080	f
11.23791424297039	-3.64134433872963	0.34528911072377	f
6.97178165752722	-3.13466532789265	2.86954197800880	f
-1.94413608799778	-0.30500851239732	0.12784570120206	n
2.75193938353187	4.80900646195530	-0.96454539226415	c
3.94477876631980	4.65797972714511	-2.62837959349686	h
1.26462014435752	6.17565368759568	-1.27760455301982	h
3.88928377428613	5.34957458255687	0.65772277949114	h
1.58787383674287	2.30675089633321	-0.46274351319295	n
-1.17949826627487	-4.51496329438937	0.85291166502915	o
-4.67628285501513	-5.70921665686907	1.41931202293603	te
-5.29199880337717	-3.02888389750788	3.56901352495938	f
-5.85522327942935	-3.84876316456363	-1.28727033012779	f
-3.89427699676859	-8.31584528275595	-0.74035733622170	f
-7.84801733382018	-6.98164054512818	1.99005839586802	f
-3.37064223051556	-7.52142353998299	4.08108307985590	f
-2.33986108449170	3.94632555743528	-0.62165274737241	o
-6.08759075018302	4.25306439911973	-0.86185023579586	te
-6.19145717701805	1.50046000800982	-2.99056239557971	f
-6.52090228600500	2.20033139496403	1.91301681471992	f
-5.71709552138887	6.99079863460343	1.24710822041983	f
-9.49887157604953	4.74835228303411	-1.14720386547595	f
-5.44599907795112	6.30906814128475	-3.59178424895985	f

$end

Etot = -2845.771664437 H

ZPE = 327.5 kJ/mol

enthalpy = 413.80 kJ/mol

chem. pot. = 148.33 kJ/mol

2,6-bis(pentafluoro-*ortho*tellurato)-2,4-difluoro-1-methyl-1,3,5-triazine

$coord

-1.81448361776664	0.25003148585672	1.34798958416249	c
-1.45095897768500	-3.78676196425010	0.30898796689016	c
2.17975494602599	-1.47249889710187	0.12063163921340	c
-2.64579340463110	-5.95897518380970	0.04288961637247	f
0.92240319066906	-3.76745735884812	-0.10399765065968	n
3.14450985793020	-0.58400708684651	-2.23645408416510	o
5.49381492792151	-2.28518600232578	-4.39043348160000	te
2.94039077291488	-4.13391117730435	-5.92110290974206	f
4.94992300637300	0.32868438024517	-6.66140028586780	f
8.16037930688140	-0.47529189131027	-2.99200768185385	f
7.75505421815188	-3.69289287834774	-6.65802256214510	f
6.14629631962793	-4.92757870661320	-2.19236795615771	f
-2.98766285028518	-1.86734376791576	1.00487134901859	n
1.88533665344012	3.09404227122758	1.44334750385252	c
3.91254091380576	2.83177397464812	1.31638096681929	h
1.26988570148210	4.42157955891269	-0.00057651845538	h

```
   1.40262469615489     3.81886709994123     3.30288118102048  h
   0.67750002962685     0.62154205586167     1.05913231242137  n
  -3.03873624249620     2.35900388931415     2.07118707124644  o
  -6.62186079876086     2.69397834764515     2.77361444185299  te
  -6.79701446279076    -0.24220969038102     4.64889993507134  f
  -5.68849596875699     4.43297586597571     5.66056296166053  f
  -6.46209827242506     5.69732981907353     0.99092375146725  f
  -9.97497087669019     3.32610321416449     3.49473596673004  f
  -7.58068612639241     1.04489592612553    -0.14643890552967  f
   4.22234705767484    -1.72669328393722     1.71576578837706  f
$end
Etot = -2203.211784854 H
ZPE = 294.3 kJ/mol
enthalpy = 362.30 kJ/mol
chem. pot. = 140.48 kJ/mol
```

2,6-bis(pentafluoro-*ortho*tellurato)-4,4-difluoro-1-methyl-1,3,5-triazine

```
$coord
  -2.04137710077565     0.51952910344977     0.59416264558993  c
   1.85842967345090    -1.04422370742784    -0.61439797697270  c
   0.95625462576962    -3.19160627347539    -1.11384176180310  n
   4.34843339149247    -0.49035839012024    -0.88317129725907  o
   6.91807922807624    -2.76336220983192    -2.14503435437131  te
   4.99070671017386    -3.88011799455285    -4.82908802791019  f
   8.03615887811685    -0.08880797719884    -4.10872536010546  f
   8.93967238192655    -1.58835188256085     0.45963464845656  f
   9.58919305988807    -4.68409728648862    -3.31015729410561  f
   5.92673980289866    -5.42948837161810    -0.12665627183208  f
  -3.14524082778040    -1.54445617077416     0.15961155786304  n
   1.59362216828367     3.51090368768678     0.83789856143880  c
   3.58532822120568     3.48503886326088     0.37600297055974  h
   0.64758443231154     4.95318992954915    -0.27817955248153  h
   1.35511482918800     3.93435836490163     2.83500285013913  h
   0.50556025327365     1.01563737121857     0.26210877701490  n
  -3.24772098524317     2.60159298350040     1.48418793863100  o
  -6.83563452445352     2.90386508592966     2.10629593929379  te
  -7.04758547700067    -0.09554817278956     3.87362371053791  f
  -5.97342039644939     4.55208343160007     5.07096345641092  f
  -6.66498768379776     5.97688533311444     0.43666995427466  f
 -10.20552109672980     3.50470999875893     2.78918033160253  f
  -7.74806805619954     1.36776884919521    -0.88991869060140  f
  -1.67939321910612    -3.59758708048297    -0.77482909014774  c
  -1.98536366337993    -5.59372161631327     0.82236691045212  f
  -2.67656462513973    -4.33383586853101    -3.03371057467480  f
$end
Etot = -2203.205993763 H
ZPE = 294.2 kJ/mol
enthalpy = 362.86 kJ/mol
chem. pot. = 134.88 kJ/mol
```

2,4,6-tris(pentafluoro-*ortho*tellurato)-2-fluoro-1-methyl-1,3,5-triazine

```
$coord
  -1.26910633926403     2.15611715552684     0.14800002970387  c
  -0.25322020193765    -1.89158422439448     1.31733017979989  c
   2.94956416196951     0.54631708933675     0.12472782919016  c
   2.25594824250321    -1.69000074628376     0.82541702007690  n
   5.37925971236498     1.08703930884980    -0.39626189781942  o
```

8.22927408427902	-1.21511558543074	-0.19000122731824	te
6.58765009252544	-3.76191442820536	-1.91765366345328	f
9.26509334438266	0.14207924509422	-3.24121814569799	f
9.93112802652195	1.35904709067003	1.45550255043289	f
11.11781000701659	-3.16632799681178	-0.09909851104641	f
7.28367923357655	-2.51217162067989	2.90735626327829	f
-1.96231334813248	-0.19970854149034	1.07386675489922	n
2.34488835371609	5.04023140453971	-0.98726462485853	c
3.01894935469776	4.93611607685529	-2.92637172386430	h
0.78440751322606	6.36161351895889	-0.87165016439580	h
3.86521108751810	5.66540572008325	0.24330351402365	h
1.42486374577775	2.55589452592876	-0.14901770750284	n
-0.83416121726960	-4.24125314221874	2.15728653133232	o
-4.06562767289900	-5.36558954596335	3.41513761498910	te
-4.58546279290027	-2.49424666355753	5.34359348577037	f
-5.89045219952708	-4.04668155588826	0.74380503806699	f
-3.57623177816542	-8.30696273939556	1.58731758158707	f
-7.03152357768943	-6.69722790454466	4.69621710483111	f
-2.33365641629809	-6.80581633793690	6.09335376123561	f
-2.28492559227276	2.65251377508880	-2.30008712613644	o
-5.77376641630031	2.62717611645251	-3.24205419260371	te
-5.69463719743424	-0.82430840277736	-3.83968004069219	f
-7.00900449015020	2.08759290457134	-0.01328018215147	f
-5.99724841022392	6.09445770843919	-2.73161637247244	f
-9.06104619214638	2.67449954894764	-4.43515699041814	f
-4.65144847880284	3.20705001416279	-6.51122039423122	f
-2.16389463866190	4.02575823207291	1.71941770544511	f

$end
Etot = -2945.890783857 H
ZPE = 331.6 kJ/mol
enthalpy = 420.46 kJ/mol
chem. pot. = 147.36 kJ/mol

2,4,6-tris(pentafluoro-*ortho*tellurato)-4-fluoro-1-methyl-1,3,5-triazine

$coord

-1.21134170470830	1.75586776701127	0.54545134714267	c
-0.70784841534904	-2.50456960251079	1.15334213124220	c
2.77000382710028	0.07075300412907	1.18968181720805	c
1.89253033694872	-2.09350587434149	1.69371035798396	n
5.23614549876057	0.67282932124772	1.49594962395251	o
8.00901841929667	-1.71446865345158	1.63951465748061	te
6.57263491421814	-3.86573024051842	-0.70317449966096	f
9.46231688089875	0.10213006160274	-0.98074779794940	f
9.50229761732714	0.49186081255972	3.90194963542030	f
10.84447211854438	-3.74207148207014	1.75040574033373	f
6.66021774987057	-3.50742488625278	4.30674530110434	f
-2.27804650100840	-0.32721297130377	1.00999985491373	n
2.50117229481052	4.59415105048434	-0.24218315449587	c
4.38686740297410	4.28965907073763	-0.98109522604043	h
1.34940448653201	5.50720225899671	-1.67035580787810	h
2.59986051443871	5.79011458564411	1.42960233139251	h
1.37444813219937	2.12582778648774	0.37228100067317	n
-0.68087996563567	-3.82873484370937	-1.21582160189860	o
-3.53385571934736	-4.98918617090373	-3.07951056918543	te
-5.90484555782290	-4.30013401532632	-0.59052937900147	f
-4.04024567778734	-1.80156055666210	-4.48798624678885	f
-1.29234990205351	-5.73630956144737	-5.66994097713764	f

```
  -6.13446067970900   -6.16318460275912   -5.10957459430644  f
  -3.16326205421518   -8.24527917763066   -1.83107328585643  f
  -2.48226630726274    3.94317416544222    0.19957217700054  o
  -6.10377813900461    4.43133171754641    0.45740986029487  te
  -6.92491421107592    1.56891768148321   -1.34554162594572  f
  -6.31502515733937    2.72591838429603    3.49422360572070  f
  -5.34136701251859    7.37205947824445    2.19528181126290  f
  -9.49121845903692    5.23342272483414    0.67861166778052  f
  -5.87950167147044    6.22544741489335   -2.53645767631581  f
  -1.67618305857480   -4.08129464675337    2.93025952155375  f
$end
Etot = -2945.882352172 H
ZPE = 331.4 kJ/mol
enthalpy = 420.48 kJ/mol
chem. pot. = 147.07 kJ/mol
```

$[Me_3Si]^+$

```
$coord
   0.00000000000000    0.00000000000000   -0.02110420009278     si
  -0.04206233671061    3.45607112267237    0.00752217593567     c
   0.80952485759156    4.12139753112963    1.77643787803367     h
   1.14927836938218    4.19455039676384   -1.51371530319622     h
  -1.93841292139148    4.23788897881015   -0.15634288320100     h
  -2.97201422116478   -1.76446261347011    0.00752217593567     c
  -4.20722638574267   -1.10197093447700   -1.51371530319622     h
  -2.70091305337194   -3.79765932235410   -0.15634288320100     h
  -3.97399738984850   -1.35962967389554    1.77643787803367     h
   3.01407655787538   -1.69160850920227    0.00752217593567     c
   3.16447253225694   -2.76176785723408    1.77643787803367     h
   3.05794801636049   -3.09257946228684   -1.51371530319622     h
   4.63932597476342   -0.44022965645604   -0.15634288320100     h
$end
Etot = -408.9218468601 H
ZPE = 282.1 kJ/mol
enthalpy = 305.50 kJ/mol
chem. pot. = 197.92 kJ/mol
```

Me_3SiF

```
$coord
   0.81615731116996    0.00005535589743    0.00018112347328  si
  -0.22554087300660   -2.32641252776354   -2.43937166170793  c
   0.47312058200833   -4.21848886017854   -2.00586074877708  h
  -2.28562981361037   -2.42002904196625   -2.53732812103838  h
   0.47285947901099   -1.80340087207381   -4.30879538846769  h
  -0.22539806884423    3.27599394730790   -0.79520332053894  c
  -2.28547068457563    3.40762860003922   -0.82809495024528  h
   0.47253678124699    4.63377951493220    0.59235579374510  h
   0.47395180177276    3.84609617955257   -2.65044905985939  h
  -0.22529174018130   -0.94957623231181    3.23478178890625  c
   0.47328962399648   -2.82997175916255    3.71652725015561  h
   0.47319321556270    0.37201025908984    4.65657749008150  h
  -2.28537838303647   -0.98776148856422    3.36473596060196  h
   3.87760076848636    0.00007692520159   -0.00005615632901  f
$end
Etot = -509.1365793346 H
ZPE = 293.7 kJ/mol
enthalpy = 318.22 kJ/mol
chem. pot. = 210.19 kJ/mol
```

$(MeO)^{ax}PF_4$

$coord

-0.45980711572844	1.13516379858483	-1.80522583781724	p
-1.47816008628210	-1.55919371864389	-2.50120172208298	f
-0.25003620459523	1.73593744545735	-4.76679644730418	f
2.48929570006702	1.37644139194551	-1.62965309243785	f
-2.24842004340770	3.46276997384458	-1.56404032614548	f
-0.78585290847361	0.68774423485157	1.19753907243274	o
0.46057089129951	-1.33570380524817	2.49559241308910	c
2.50845183859560	-1.13054292496871	2.38656640272638	h
-0.13409439948970	-1.20763731470978	4.45724965829672	h
-0.10194767198530	-3.16497908111330	1.72996987924285	h

$end

Etot = -856.0114791769 H

ZPE = 147.1 kJ/mol

enthalpy = 169.36 kJ/mol

chem. pot. = 61.87 kJ/mol

$(MeO)^{eq}PF_4$

$coord

0.08717980431942	-2.13514295925814	0.48854060777968	p
-0.91825324262419	-2.99066432626798	3.19553446951168	f
-1.87235691932052	-3.93061564820832	-0.78677129832099	f
1.14261056953783	-1.43355251627652	-2.29194371757110	f
2.72847656193472	-3.27839971813242	1.12569649643098	f
-0.58406126093453	0.68254437542104	1.15230661438440	o
-0.20379276288664	2.86057388848583	-0.45174073589904	c
-1.28615216126866	2.67742159751378	-2.18796675926422	h
-0.88270499480480	4.45415834856472	0.64875056635384	h
1.78905440604738	3.09367695815813	-0.89240624340513	h

$end

Etot = -856.0238831319 H

ZPE = 148.1 kJ/mol

enthalpy = 169.93 kJ/mol

chem. pot. = 63.90 kJ/mol

4 References

[1] S. L. Bell, R. D. Chambers, W.K.R. Musgrave, J. G. Thorpe, *J. Fluor. Chem.* **1971**, *1*, 51.
[2] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489.
[3] S. Hämmerling, G. Thiele, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Angew. Chem. Int. Ed.* **2019**, *58*, 9807; *Angew. Chem.*, **2019**, *131*, 9912.
[4] A. Guha, R. Pal, *J. Indian Chem. Soc.* **2006**, *83*, 49.
[5] L. Pogliani, *J. Comput. Chem.* **2010**, *31*, 295.

5 Conclusion

The first experimental procedures yielding organonickelpentafluoro-*ortho*tellurates are published. Even though the complex [{Ni(*H*acac)(H_2O)($OTeF_5$)(μ-$OTeF_5$)}$_2$] (Hacac = acetylacetone) was not synthesized in bulk, it extends the group of pentafluoro-*ortho*tellurate bridged metal complexes by the group 10 metal nickel. The high field shift of the carbene carbon atoms in the ^{13}C NMR spectrum of *cis*-[Ni($^{i\text{Pr}}$Im)$_2$($OTeF_5$)$_2$] ($^{i\text{Pr}}$Im = 1,3-diisopropylimidazol-2-ylidene) shows the strong electron withdrawing properties of the pentafluoro-*ortho*tellurato ligand.

With the dimethylchloronium salt [Me_2Cl][$Al(OTeF_5)_4$] a strong electrophilic methylation reagent was synthesized in a simple one-pot reaction. The salt is room temperature stable for days and can be synthesized in multigram scales. It was used to methylate weakly basic molecules like fluorinated nitrogen heterocycles (NC_5F_4I, NC_5F_5, $N_3C_3F_3$), fluorinated phosphines (PF_3, $P(CF_3)_3$), fluorinated aromatic systems and MeI, as well as MeBr. While some of the molecules only have been used to demonstrate the wide substrate scope, three of the methylated molecule lead to further results.

The cation [$MeNC_5F_4I$]$^+$ is a halogen bridge donor. Even though, no cocrystals with weak halogen bond acceptors were obtained, there is a weak halogen bond between the cation and one fluorine atom of the weakly coordinating anion [$Al(OTeF_5)_4$]$^-$.

The decomposition reactions of [$MePF_3$][$Al(OTeF_5)_4$] and [$MeN_3C_3F_3$][$Al(OTeF_5)_4$] are examined. In both cases pentafluoro-*ortho*tellurate groups are abstracted from the weakly coordinating anion [$Al(OTeF_5)_4$]$^-$. The phosphonium cations [$MePF_2(OTeF_5)$]$^+$ and [$MePF(OTeF_5)_2$]$^+$ is detected by multinuclear NMR spectroscopy. While the structure of the salt [$MeN_3C_3F(OTeF_5)_2$][$Al(OTeF_5)_4$] is determined by single crystal X-ray diffraction. The higher stability of the decomposition products shows, that the Lewis acidity of the cations decreases through “introduction” of pentafluoro-*ortho*tellurate groups. This is in agreement with the quantum chemically calculated fluoride ion affinity (FIA) of the cations.

Quantum chemical calculations for the systems [$MeEF_{3-x}(OTeF_5)_x$]$^+$ (E = P, As, Sb), [$PF_{4-x}(OTeF_5)_x$]$^+$, [$EF_{5-x}(OTeF_5)_x$] and [$EF_{6-x}(OTeF_5)_x$]$^-$ show that a decreasing electron density at the central atom (increasing NPA charge) do not correlated always with an increasing FIA value. The ambiguous effect of pentafluoro-*ortho*tellurate replacement of a fluorine atom for the Lewis acidic character of a molecule is a result of the different bonding properties in situation with and without hypervalent 3-center-4-electron bonds. This result also clarifies the ambiguous literature known comparisons of the electron withdrawing properties of the pentafluoro-*ortho*tellurato ligand and the fluorido ligand.

Because the tendency of carbon to participate as the central atom in hypervalent 3-center-4-electron bonds is lower than for heavier main-group elements, the pentafluoro-*ortho*tellurate group is not expected to be an extraordinary strong electron withdrawing group in organic molecules.

The decomposition reactions of $[MePF_3][Al(OTeF_5)_4]$ and $[MeN_3C_3F_3][Al(OTeF_5)_4]$ also show the limits of the weakly coordinating anion $[Al(OTeF_5)_4]^-$. In combination with highly Lewis acidic cations bearing fluorido substituents, exchange reactions with the anion should always be considered as a known weak point.

The methylation of fluorinated aromatic systems like 1,2-difluorobenzene, 1,2,3-trifluorobenzene and 1,2,3,4-tetrafluorobenzene is similar to the Friedel-Crafts alkylation. Therefore, the role of the dimethylchloronium cation in the Friedel-Crafts like methylation of 1,2-difluorobenzene with the system $AlCl_3$/MeCl is evaluated by quantum chemical calculations of possible reaction paths, including the calculation of the transition states. The contact ion pair $[Me_2Cl]^+/[AlCl_4]^-$ is a reasonable intermediate for this system.

For all performed methylation reactions with $[Me_2Cl][Al(OTeF_5)_4]$, calculated methyl cation affinities on RI-B3LYP-D3/def2-TZVPP level of theory provide good predictions of the reactivity. These calculations predicted all performed reactions in a homogenous solution correctly. For the optimization of reaction conditions or prediction of the reaction speed, the calculation of transition states on RI-B3LYP-D3/def2-TZVPP level of theory with the solvent model COSMO for SO_2 provides accurate enough values in reasonable computational time. Through the structure of the dimethylchloronium-substrate complexes the transition states for the methylation reactions are comparable easy to find.

6 References

[1] A. Engelbrecht, F. Sladky, *Angew. Chem. Int. Ed.* **1964**, *3*, 383; *Angew. Chem.*, **1964**, *76*, 379.

[2] K. Seppelt, D. Nothe, *Inorg. Chem.* **1973**, *12*, 2727.

[3] J. Reijenga, A. van Hoof, A. van Loon, B. Teunissen, *Anal. Chem. Insights* **2013**, *8*, 53.

[4] a) W. Porcham, A. Engelbrecht, *Z. phys. Chemie* **1971**, *248*, 177; b) W. Porcham, A. Engelbrecht, *Monatsh. Chem.* **1971**, *102*, 333.

[5] K. Seppelt, *Angew. Chem. Int. Ed.* **1982**, *21*, 877; *Angew. Chem.*, **1982**, *94*, 890.

[6] M. C. Crossman, E. G. Hope, G. C. Saunders, *J. Chem. Soc., Dalton Trans.* **1996**, 509.

[7] E. Mayer, F. Sladky, *Inorg. Chem.* **1975**, *14*, 589.

[8] F. Sladky, *Monatsh. Chem.* **1970**, *101*, 1559.

[9] F. Sladky, H. Kropshofer, O. Leitzke, *J. Chem. Soc., Chem. Commun.* **1973**, 134.

[10] F. Sladky, H. Kropshofer, *J. Chem. Soc., Chem. Commun.* **1973**, 600.

[11] F. Sladky, H. Kropshofer, O. Leitzke, P. Peringer, *J. Inorg. Nucl. Chem.* **1976**, *28*, 69.

[12] S. H. Strauss, K. D. Abney, K. M. Long, O. P. Anderson, *Inorg. Chem.* **1984**, *23*, 1994.

[13] K. D. Abney, K. M. Long, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1987**, *26*, 2638.

[14] A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; *Angew. Chem.* **2017**, *129*, 8375.

[15] A. Wiesner, L. Fischer, S. Steinhauer, H. Beckers, S. Riedel, *Chem. Eur. J.* **2019**, *25*, 10441.

[16] S. H. Strauss, M. D. Noirot, O. P. Anderson, *Inorg. Chem.* **1985**, *24*, 4307.

[17] K. Seppelt, *Chem. Ber.* **1977**, *110*, 1470.

[18] D. Lentz, K. Seppelt, *Z. Anorg. Allg. Chem.* **1983**, *502*, 83.

[19] K. Seppelt, *Chem. Ber.* **1976**, *109*, 1046.

[20] a) D. Lentz, K. Seppelt, *Angew. Chem. Int. Ed.* **1978**, *17*, 356; *Angew. Chem.*, **1978**, *90*, 391–392; b) D. Lentz, K. Seppelt, *Angew. Chem. Int. Ed.* **1979**, *18*, 66; *Angew. Chem.*, **1979**, *91*, 68.

[21] M. A. Ellwanger, C. von Randow, S. Steinhauer, Y. Zhou, A. Wiesner, H. Beckers, T. Braun, S. Riedel, *Chem. Commun.* **2018**, *54*, 9301.

[22] a) M. C. Crossman, *PhD thesis*, University of Leicester, Leicester, **1995**; b) M. C. Crossman, E. G. Hope, L. J. Wootton, *J. Chem. Soc., Dalton Trans.* **1998**, 1813.

[23] D. Lentz, K. Seppelt, *Z. Anorg. Allg. Chem.* **1980**, *460*, 5.

[24] D. Lentz, H. Pritzkow, K. Seppelt, *Inorg. Chem.* **1978**, *17*, 1926.

[25] a) R. J. Gillespie, *Angew. Chem. Int. Ed.* **1967**, *6*, 819; *Angew. Chem.*, **1967**, *79*, 885; b) I. Hargittai, B. Chamberland, *Comput. Math. Appl.* **1986**, *12*, 1021.

[26] a) O. R. Chambers, G. Oates, J. M. Winfield, *J. Chem. Soc., Chem. Commun.* **1972**, 839; b) G. Oates, J. M. Winfield, *J. Chem. Soc., Dalton Trans.* **1974**, 119.

[27] a) G. Oates, J. M. Winfield, *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1093; b) G. Oates, J. M. Winfield, O. R. Chambers, *J. Chem. Soc., Dalton Trans.* **1974**, 1380.

[28] T. Birchall, R. D. Myers, H. de Waard, G. J. Schrobilgen, *Inorg. Chem.* **1982**, *21*, 1068.

[29] I. Krossing, I. Raabe, *Chem. Eur. J.* **2004**, *10*, 5017.

[30] K. Peter, C. Vollhard, Neil E. Schore, *Organische Chemie,* 4. Aufl., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2009**.

[31] K. Schröder, F. Sladky, *Chem. Ber.* **1980**, *113*, 1414.

[32] M. R. Colsman, M. C. Manning, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1987**, *26*, 3958.

[33] L. K. Templeton, D. H. Templeton, N. Bartlett, K. Seppelt, *Inorg. Chem.* **1976**, *15*, 2720.

[34] S. H. Strauss, M. D. Noirot, O. P. Anderson, *Inorg. Chem.* **1986**, *25*, 3850.

[35] P. K. Hurlburt, P. J. Kellett, O. P. Anderson, S. H. Strauss, *J. Chem. Soc., Chem. Commun.* **1990**, 576.

[36] J. R. DeBackere, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* **2015**, *54*, 1606.

[37] P. Huppmann, H. Hartl, K. Seppelt, *Z. Anorg. Allg. Chem.* **1985**, *524*, 26.

[38] K. Seppelt, *Chem. Ber.* **1975**, *108*, 1823.

[39] H. P. A. Mercier, M. D. Moran, J. C. P. Sanders, G. J. Schrobilgen, R. J. Suontamo, *Inorg. Chem.* **2005**, *44*, 49.

[40] F. O. Sladky, P. A. Bulliner, N. Bartlett, *J. Chem. Soc. A* **1969**, *14*, 2179.

[41] A. Zalkin, D. L. Ward, R. N. Biagioni, D. H. Templeton, N. Bartlett, *Inorg. Chem.* **1978**, *17*, 1318.

[42] V. M. McRae, R. D. Peacock, D. R. Russell, *J. Chem. Soc. D* **1969**, 62.

[43] B. A. Fir, H. P.A. Mercier, J. C.P. Sanders, D. A. Dixon, G. J. Schrobilgen, *J. Fluor. Chem.* **2001**, *110*, 89.

[44] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[45] H. P. A. Mercier, M. D. Moran, G. J. Schrobilgen, C. Steinberg, R. J. Suontamo, *J. Am. Chem. Soc.* **2004**, *126*, 5533.

[46] H. Hartl, J. Nowicki, R. Minkwitz, *Angew. Chem. Int. Ed.* **1991**, *30*, 328; *Angew. Chem.*, **1991**, *103*, 311.

[47] A. F. Holleman, N. Wiberg, *Lehrbuch der anorganischen Chemie,* 102. Aufl., de Gruyter, Berlin, **2007**.

[48] D. R. Lide, *CRC Handbook of Chemistry and Physics*. *A Ready-Reference Book of Chemical and Physical Data,* 85. Aufl., CRC Press, Boca Raton, FL., London, **2004**.

[49] a) S. A. Brewer, L. A. Buggey, J. H. Holloway, E. G. Hope, *J. Chem. Soc. Dalton Trans.* **1995**, 2941; b) L. A. Buggey, E. G. Hope, *J. Fluor. Chem.* **1995**, *73*, 247.

[50] S. Koda, S.'i. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, S. Kawaguchi, *J. Chem. Soc. D* **1971**, 1321.

[51] a) K.-I. Hong, H. Yoon, W.-D. Jang, *Chem. Commun.* **2015**, *51*, 7486; b) T. Zhao, P. Ghosh, Z. Martinez, X. Liu, X. Meng, M. Y. Darensbourg, *Organometallics* **2017**, *36*, 1822.

[52] M. Seco, *J. Chem. Educ.* **1989**, *66*, 779.

[53] a) A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361; b) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.

[54] a) W. A. Herrmann, G. Gerstberger, M. Spiegler, *Organometallics* **1997**, *16*, 2209; b) D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert, *Organometallics* **2002**, *21*, 175; c) T. Schaub, M. Backes, U. Radius **2008**, *2008*, 2680.

[55] T. Schaub, C. Döring, U. Radius, *Dalton Trans.* **2007**, 1993.

[56] P. Fischer, T. Linder, U. Radius, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1491.

[57] S. Hameury, P. de Frémont, P.-A. R. Breuil, H. Olivier-Bourbigou, P. Braunstein, *Organometallics* **2015**, *34*, 2183.

[58] B. Zemva, K. Lutar, A. Jesih, W. J. Casteel, N. Bartlett, *J. Chem. Soc., Chem. Commun.* **1989**, 346.

[59] a) V. Dimitrov, A. Linden, *Angew. Chem. Int. Ed.* **2003**, *42*, 2631; *Angew. Chem.*, **2003**, *115*, 2735; b) J. R. Bour, N. M. Camasso, M. S. Sanford, *J. Am. Chem. Soc.* **2015**, *137*, 8034; c) F. D'Accriscio, P. Borja, N. Saffon-Merceron, M. Fustier-Boutignon, N. Mézailles, N. Nebra, *Angew. Chem. Int. Ed.* **2017**, *56*, 12898; *Angew. Chem.*, **2017**, *129*, 13078.

[60] Q. Dai, Y. Jiang, J.-T. Yu, J. Cheng, *Synthesis* **2016**, *48*, 329.

[61] S. D. Lipsky, S. S. Hall, R. E. Ireland, P. J. Clendening, K. D. Crossland, A. K. Willard, *Org. Synth.* **1976**, *55*, 7.

[62] N. Meyer, D. Seebach, *Chem. Ber.* **1980**, *113*, 1304.

[63] E. Negishi, H. Matsushita, P. J. Sanfilippo, A. S. Kende, *Org. Synth.* **1984**, *62*, 31.

[64] a) C. Elschenbroich, *Organometallchemie,* 6. Aufl., Vieweg+Teubner Verlag / GWV Fachverlage GmbH Wiesbaden, Wiesbaden, **2008**; b) M. L. Luetkens, A. P. Sattelberger, H. H. Murray, J. D. Basil, J. P. Fackler, R. A. Jones, D. E. Heaton in *Inorganic Synthesis - Volume 28* (Hrsg.: R. J. Angelici, F. Basolo), John Wiley & Sons, New York, **1990**, S. 305–310.

[65] Y. Zhang, J. Feng, C.-J. Li, *J. Am. Chem. Soc.* **2008**, *130*, 2900.

[66] a) D. A. Dirocco, K. Dykstra, S. Krska, P. Vachal, D. V. Conway, M. Tudge, *Angew. Chem. Int. Ed.* **2014**, *53*, 4802; *Angew. Chem.*, **2014**, *126*, 4902; b) S. Guo, Q. Wang, Y. Jiang, J.-T. Yu, *J. Org. Chem.* **2014**, *79*, 11285.

[67] a) W. C. Shieh, S. Dell, O. Repic, *Org. Lett.* **2001**, *3*, 4279; b) C. B. Kreutzberger in *Kirk, Othmer (Hg.) 2004 – Kirk-Othmer Encyclopedia of Chemical Technology*, S. 225.

[68] a) J. G. Avila-Zárraga, R. Martínez, *Synth. Commun.* **2001**, *31*, 2177; b) G. A. Sulikowski, M. M. Sulikowski, M. H. Haukaas, B. Moon in *Encyclopedia of reagents for organic synthesis* (Hrsg.: L. A. Paquette), Wiley, Chichester, **1995**, S. 742.

[69] a) *Org. Synth.* **1993**, *71*, 107; b) R. W. Alder, J. G. E. Phillips, L. Huang, X. Huang in *Encyclopedia of reagents for organic synthesis* (Hrsg.: L. A. Paquette), Wiley, Chichester, **1995**, S. 983.

[70] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, E. Pfeil, *J. Prakt. Chem.* **1937**, *147*, 257.

[71] a) E. S. Lewis, S. Vanderpool, *J. Am. Chem. Soc.* **1977**, *99*, 1946; b) D. N. Kevill, G. M. L. Lin, *Tetrahedron Lett.* **1978**, *19*, 949; c) P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, *1982*, 85.

[72] G. A. Olah, J. R. DeMember, R. H. Schlosberg, *J. Am. Chem. Soc.* **1969**, *91*, 2112.

[73] a) G. A. Olah, D. J. Donovan, H. C. Lin, *J. Am. Chem. Soc.* **1976**, *98*, 2661; b) P. E. Peterson, R. Brockington, D. W. Vidrine, *J. Am. Chem. Soc.* **1976**, *98*, 2660.

[74] G. A. Olah, D. J. Donovan, *J. Am. Chem. Soc.* **1978**, *100*, 5163.

[75] a) R. Minkwitz, D. Bernstein, H. Preut, W. Sawodny, H. Härtner, *Z. Anorg. Allg. Chem.* **1991**, *606*, 157; b) R. J. Gillespie, F. G. Riddell, D. R. Slim, *J. Am. Chem. Soc.* **1976**, *98*, 8069.

[76] O. Shyshkov, U. Dieckbreder, T. Drews, A. Kolomeitsev, G.-V. Röschenthaler, K. Seppelt, *Inorg. Chem.* **2009**, *48*, 6083.

[77] G. A. Olah, *Superacid chemistry,* 2. Aufl., Wiley, Hoboken, N.J., **2009**.

[78] M. J. Molski, D. Mollenhauer, S. Gohr, B. Paulus, M. A. Khanfar, H. Shorafa, S. H. Strauss, K. Seppelt, *Chem. Eur. J.* **2012**, *18*, 6644.

[79] D. Stasko, C. A. Reed, *J. Am. Chem. Soc.* **2002**, *124*, 1148.

[80] T. Kato, E. Stoyanov, J. Geier, H. Grützmacher, C. A. Reed, *J. Am. Chem. Soc.* **2004**, *126*, 12451.

[81] Y. Zhang, C. A. Reed, *Dalton Trans.* **2008**, 4392.

[82] V. Geis, K. Guttsche, C. Knapp, H. Scherer, R. Uzun, *Dalton Trans.* **2009**, 2687.

[83] I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 13982; *Angew. Chem.* **2018**, *130*, 14178.

[84] C. Bolli, J. Derendorf, M. Kessler, C. Knapp, H. Scherer, C. Schulz, J. Warneke, *Angew. Chem. Int. Ed.* **2010**, *49*, 3536; *Angew. Chem.*, **2010**, *122*, 3616.

[85] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1969**, *91*, 2113.

[86] G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1970**, *92*, 718.

[87] G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, J. A. Olah, *J. Am. Chem. Soc.* **1974**, *96*, 884.

[88] E. S. Stoyanov, *J. Phys. Chem. A* **2017**, *121*, 2918.

[89] a) M. Speranza, N. Pepe, R. Cipollini, *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179; b) R. O'Hair, M. Freitas, J. Schmidt, M. Hatley, T. Williams, *Eur. Mass Spectrom.* **1995**, *1*, 457; c) B. Chiavarino, M. E. Crestoni, S. Fornarini, D. Kuck, *J. Phys. Chem. A* **2003**, *107*, 4619.

[90] E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2010**, *132*, 4062.

[91] T. Kato, C. A. Reed, *Angew. Chem. Int. Ed.* **2004**, *43*, 2908; *Angew. Chem.*, **2004**, *116*, 2968.

[92] G. A. Olah, J. R. DeMember, R. H. Schlosberg, Y. Halpern, *J. Am. Chem. Soc.* **1972**, *94*, 156.

[93] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

[94] G. A. Olah, T. E. Kiovsky, *J. Am. Chem. Soc.* **1968**, *90*, 4666.

[95] A. Peter, S. M. Fehr, V. Dybbert, D. Himmel, I. Lindner, E. Jacob, M. Ouda, A. Schaadt, R. J. White, H. Scherer et al., *Angew. Chem. Int. Ed.* **2018**, *57*, 9461; *Angew. Chem.*, **2018**, *130*, 9605.

[96] T. B. McMahon, T. Heinis, G. Nicol, J. K. Hovey, P. Kebarle, *J. Am. Chem. Soc.* **1988**, *110*, 7591.

[97] C. L. Deasy, *Chem. Rev.* **1945**, *36*, 145.

[98] a) R. J. Mulder, C. F. Guerra, F. M. Bickelhaupt, *J. Phys. Chem. A* **2010**, *114*, 7604; b) Z. Boughlala, C. Fonseca Guerra, F. M. Bickelhaupt, *ChemistryOpen* **2016**, *5*, 247.

[99] E. Lork, B. Görtler, C. Knapp, R. Mews, *Solid State Sci.* **2002**, *4*, 1403.

[100] R. Minkwitz, V. Gerhard, *Z. Naturforsch., B* **1991**, *46*, 1470.

[101] C. Friedel, J. M. Crafts, *Compt. Rend.* **1877**, *84*, 1392.

[102] C. Friedel, J. M. Crafts, *J. Chem. Soc.* **1877**, *32*, 725.

[103] a) M. Rueping, B. J. Nachtsheim, *Beilstein J. Org. Chem.* **2010**, *6*, 6; b) M. M. Heravi, V. Zadsirjan, B. Masoumi, M. Heydari, *J. Organomet. Chem.* **2019**, *879*, 78.

[104] K. M. Kim, J. H. Kim, D. H. Moon, M. S. Lah, I. N. Jung, B. R. Yoo, *Organometallics* **2005**, *24*, 226.

[105] S. O. Ojwach, J. Darkwa, *Catal. Sci. Technol.* **2019**, *9*, 2078.

[106] C. Perego, P. Ingallina, *Catal. Today* **2002**, *73*, 3.

[107] B. Maji, *Adv. Synth. Catal.* **2019**, *361*, 3453.

[108] M. Nič, J. Jirát, B. Košata, A. Jenkins, A. McNaught (Hrsg.) *IUPAC Compendium of Chemical Terminology*, IUPAC, Research Triagle Park, NC, **2009**.

[109] a) I. Roberts, G. E. Kimball, *J. Am. Chem. Soc.* **1937**, *59*, 947; b) R. C. Fahey, *J. Am. Chem. Soc.* **1966**, *88*, 4681; c) G. A. Olah, J. M. Bollinger, *J. Am. Chem. Soc.* **1967**, *89*, 4744; d) M. F. Ruasse, *Acc. Chem. Res.* **1990**, *23*, 87.

[110] R. J. Gillespie, R. Kapoor, R. Faggiani, Lock, Colin J. L., M. Murchie, J. Passmore, *J. Chem. Soc., Chem. Commun.* **1983**, 8.

[111] C. G. Davies, R. J. Gillespie, P. R. Ireland, J. M. Sowa, *Can. J. Chem.* **1974**, *52*, 2048.

[112] A. J. Edwards, G. R. Jones, *J. Chem. Soc. A* **1971**, 2318.

[113] a) J. Passmore, G. Sutherland, P. S. White, *Inorg. Chem.* **1981**, *20*, 2169; b) K. O. Christe, R. Bau, D. Zhao, *Z. Anorg. Allg. Chem.* **1991**, *593*, 46; c) T. Drews, W. Koch, K. Seppelt, *J. Am. Chem. Soc.* **1999**, *121*, 4379.

[114] S. Seidel, K. Seppelt, *Angew. Chem. Int. Ed.* **2000**, *39*, 3923; *Angew. Chem.*, **2000**, *112*, 4072.

[115] A. Apblett, F. Grein, J. P. Johnson, J. Passmore, P. S. White, *Inorg. Chem.* **1986**, *25*, 422.

[116] J. Passmore, P. Taylor, T. Whidden, P. S. White, *Can. J. Chem.* **1979**, *57*, 968.

[117] S. Hoyer, *PhD thesis*, Freie Universität Berlin, **2004**.

[118] Thanthiriwatte, K. Sahan, J. M. Spruell, D. A. Dixon, K. O. Christe, Jenkins, H. Donald B., *Inorg. Chem.* **2014**, *53*, 8136.

[119] M. Swart, E. Rösler, F. M. Bickelhaupt, *J. Comput. Chem.* **2006**, *27*, 1486.

[120] A. Jubert, N. Okulik, M. d. C. Michelini, C. J. A. Mota, *J. Phys. Chem. A* **2008**, *112*, 11468.

[121] M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2009**, *48*, 7444; *Angew. Chem.*, **2009**, *121*, 7580.

[122] K. S. Wolfgang Beck, W. Beck, K. Suenkel, *Chem. Rev.* **1988**, *88*, 1405.

[123] a) A. A. G. Tomlinson, M. Bonamico, G. Dessy, v. Fares, L. Scaramuzza, *J. Chem. Soc., Dalton Trans.* **1972**, 1671; b) A. P. Gaughan, Z. Dori, J. A. Ibers, *Inorg. Chem.*

1974, *13*, 1657; c) H. Nakai, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1637; d) K. Shelly, T. Bartczak, W. R. Scheidt, C. A. Reed, *Inorg. Chem.* **1985**, *24*, 4325.

[124] a) H. Willner, F. Aubke, *Angew. Chem. Int. Ed*. **1997**, *36*, 2402; *Angew. Chem.*, **1997**, *109*, 2506; b) R. Minkwitz, C. Hirsch, T. Berends, *Eur. J. Inorg. Chem.* **1999**, *1999*, 2249; c) R. Minkwitz, F. Neikes, *Inorg. Chem.* **1999**, *38*, 5960.

[125] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[126] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920.

[127] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490.

[128] T. J. Barbarich, S. T. Handy, S. M. Miller, O. P. Anderson, P. A. Grieco, S. H. Strauss, *Organometallics* **1996**, *15*, 3776.

[129] S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson, S. H. Strauss, *Chem. Eur. J.* **2001**, *7*, 503.

[130] T. Jelínek, J. Plešek, S. Heřmánek, B. Štíbr, *Coll. Czech. Chem. Comm.* **1986**, *51*, 819.

[131] M. Juhasz, S. Hoffmann, E. Stoyanov, K.-C. Kim, C. A. Reed, *Angew. Chem. Int. Ed.* **2004**, *43*, 5352; *Angew. Chem.*, **2004**, *116*, 5466.

[132] S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *J. Am. Chem. Soc.* **1998**, *120*, 4224.

[133] A. Hepp, R. Labbow, F. Reiß, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2018**, *2018*, 2905.

[134] H. Kropshofer, O. Leitzke, P. Peringer, F. Sladky, *Chem. Ber.* **1981**, *114*, 2644.

[135] M. J. Collins, G. J. Schrobilgen, *Inorg. Chem.* **1985**, *24*, 2608.

[136] D. M. Van Seggen, P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1995**, *34*, 3453.

[137] K. Moock, K. Seppelt, *Z. Anorg. Allg. Chem.* **1988**, *561*, 132.

[138] H. P. A. Mercier, J. C. P. Sanders, G. J. Schrobilgen, *J. Am. Chem. Soc.* **1994**, *116*, 2921.

[139] D. M. Van Seggen, P. K. Hurlburt, M. D. Noirot, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1992**, *31*, 1423.

[140] I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066; *Angew. Chem*. **2004**, *116*, 2116.

[141] T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, *Chem. Soc. Rev.* **2016**, *45*, 789.

[142] a) Bochmann, M. J. Sarsfield, *Organometallics* **1998**, *17*, 5908; b) W. v. Konze, B. L. Scott, G. J. Kubas, *Chem. Commun.* **1999**, 1807; c) D. A. Walker, T. J. Woodman, D. L. Hughes, M. Bochmann, *Organometallics* **2001**, *20*, 3772.

[143] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489.

[144] L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881.

[145] a) Christopher A. Reed, Kee-Chan Kim, Robert D. Bolskar, Leonard J. Mueller, *Science* **2000**, *289*, 101; b) C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, *125*, 1796.

[146] a) K. F. Hoffmann, A. Wiesner, N. Subat, S. Steinhauer, S. Riedel, *Z. Anorg. Allg. Chem.* **2018**, *644*, 1344; b) S. Kotsyuda, A. Wiesner, S. Steinhauer, S. Riedel, *Z. Anorg. Allg. Chem.* **2020**, DOI: 10.1002/zaac.202000101.

[147] A. Wiesner, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Chem. Sci.* **2018**, *9*, 7169.

[148] W. A. Herrmann, O. Runte, G. Artus, *J. Organomet. Chem.* **1995**, *501*, C1-C4.

[149] R. Jothibasu, K.-W. Huang, H. V. Huynh, *Organometallics* **2010**, *29*, 3746.

[150] D. Zhang, S. Zhou, Z. Li, Q. Wang, L. Weng, *Dalton Trans.* **2013**, *42*, 12020.

[151] a) T. Zell, T. Schaub, K. Radacki, U. Radius, *Dalton Trans.* **2011**, *40*, 1852; b) S. Wellens, N. R. Brooks, B. Thijs, L. van Meervelt, K. Binnemans, *Dalton Trans.* **2014**, *43*, 3443.

[152] T. Zell, U. Radius, *Z. Anorg. Allg. Chem.* **2013**, *639*, 334.

[153] P. M. J. Szell, A. Siiskonen, L. Catalano, G. Cavallo, G. Terraneo, A. Priimagi, D. L. Bryce, P. Metrangolo, *New J. Chem.* **2018**, *42*, 10467.

[154] J. Schwabedissen, P. C. Trapp, H.-G. Stammler, B. Neumann, J.-H. Lamm, Y. V. Vishnevskiy, L. A. Körte, N. W. Mitzel, *Chem. Eur. J.* **2019**, *25*, 7339.

[155] C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374.

7 List of Publications

[1] **Sebastian Hämmerling**, Lisa Mann, Simon Steinhauer, Maximilian W. Kuntze-Fech-ner, Udo Radius and Sebastian Riedel*,
Investigation of Organonickel-Pentafluoro-*ortho*tellurates,
Z. Anorg. Allg. Chem. **2018**, *644*(17), 1047-1050.
https://doi.org/10.1002/zaac.201800177

[2] **Sebastian Hämmerling**, Günther Thiele, Simon Steinhauer, Helmut Beckers, Carsten Müller and Sebastian. Riedel,
A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$,
Angew. Chem. Int. Ed. **2019**, *58*(29), 9807-9810,
https://doi.org/10.1002/anie.201904007
Ein sehr starkes Methylierungsmittel: $[Me_2Cl][Al(OTeF_5)_4]$
Angew. Chem., **2019**, *131*(29), 9912-9915,
https://doi.org/10.1002/ange.201904007

[3] **Sebastian Hämmerling**, Patrick Voßnacker, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel*
Friedel-Crafts Type Methylation with Dimethylhalonium Salts
Chem. Eur. J., **2020***, 26*(63)*, 14377-14384.*
https://doi.org/10.1002/chem.202001457

Conference Contributions – Oral Presentations

[1] GRK 1582 “Fluorine as a Key Element” Workshop **2017**, Zeuthen, Germany
Title: Computational and Experimental Approaches to Nickel(II)-teflates

[2] GRK 1582 “Fluorine as a Key Element” Meeting **2018**, Berlin, Germany
Title: Nickel(II)-teflates – The Fight Against the Lattice Energy

[3] GRK 1582 “Fluorine as a Key Element” Workshop **2018**, Potsdam, Germany
Title: Teflates for Methylation Reactions?

Conference Contributions – Poster Presentations

[1] GDCh Wissenschaftsforum Chemie **2017**, Berlin, Germany
Poster title: Pentafluoro*ortho*tellurates – a Pathway to Highly Oxidized Nickel