Fluorinated Butatrienes

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List of Publications

Articles in Journals:

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- Christian Ehm, Floris A. Ackerman, Dieter Lentz (2010) “Fluorinated Butatrienes”, *J. Fluor. Chem.* **2010**, DOI:10.1016/j.jfluchem.2010.06.017.
- Christian Ehm, Dieter Lentz (2010) “Cyclic Dimers of Tetrafluorobutatriene” *Org. Biomol. Chem.*, submitted.

Poster contributions:

“First metal free variant of the Stille-type cross-coupling reaction” 18th International Symposium on Fluorine Chemistry Prag, 2006

Lectures:

“Fluorierte Kumulene: Butatriene” 13. Deutscher Fluortag, Schmitten/Dorfweil 2008

Table of Content

Abbreviations

bipy = 2,2'-bipyridine

B3LYP = Becke 3-Parameter (Exchange), Lee, Yang and Parr (correlation; density functional theory)

CBS = complete basis set method

CCSD(T) = Coupled-Cluster with Single and Double and Perturbative Triple excitations

CFCs = chlorofluorocarbons

d = doublet

DBU = 1,8-diazabicyclo[5.4.0]undec-7ene

DPPE = bisdiphenylphoshinoethane

ΔH = energy difference

DFT = density functional theory

DMF = dimethylformamide

DMSO = dimethyl sulfoxide

dppe = 1,2-bis(diphenylphosphanyl)ethane

EPR = electron paramagnetic resonance

eq. = equivalent or equation

Et_2O = diethylether

G3 = Gaussian-3 theory

GIAO = gauge independent atomic orbital

h = hour

HFCs = hydrofluorocarbons

HV = high vacuum

Hz = Hertz

IR = infrared

KO*t*Bu = tertiary butoxy potassium

LDA = lithium diisopropylamide

min = minute

m = multiplet

MP2 = Møller–Plesset perturbation theory second order

MTBE = *tert.*-butylmethylether

NMR = nuclear magnetic resonance

PE-spectroscopy = photoelectron spectroscopy

PFCs = perfluorocarbons

ppm = parts per million

q = quartet

r.t. = room temperature

s = singlet

t = triplet

THF = tetrahydrofuran

TMS = trimethylsilyl-

UV/vis = ultraviolet/visible

ZPE = zero point energy

Zusammenfassung

Die vorliegende Arbeit liefert tiefere Einblicke in die Chemie fluorierter Butatriene, sowohl experimentell als auch theoretisch.

Die vierstufige Synthese von Tetrafluorbutatrien ausgehend von kommerziell erhältlichem 1,1-Difluorethen konnte auf eine Gesamtausbeute von bis zu 42% gesteigert werden.

1,1,4,4-Tetrafluorbutatrien reagiert in Diels-Alder Reaktionen nur als En-Komponente (Dienophil), nur an der zentralen Doppelbindung und nur mit elektronenreichen Dienen. Es können wohldefinierte Produkte in bis zu quantitativen Ausbeuten erhalten werden. Damit konnte die Tetrafluorbutatrien-Einheit zum ersten Mal in organische Moleküle eingebaut werden. Weder [2+2]-Cycloadditionen noch 1,3-dipolare Cycloadditionen konnten erfolgreich durchgeführt werden.

Es war nicht möglich, neue Tetrafluorbutatrien-Metallkomplexe zu synthetisieren. Dies ist sowohl auf die Instabilität des Triens als auch auf eine teilweise beobachtete Erhöhung der Polymerisationsgeschwindigkeit durch bestimmte Metallzentren zurückzuführen.

Wie sich heraustellte, scheint auch die Isolierung zyklischer Tetrafluorbutatrien-Dimere durch kontrollierte Dimerisierung des Tetrafluorbutatriens unmöglich. Vielmehr konnte bei der Oligomerisierung/Polymerisierung von Tetrafluorbutatrien auch NMR-spektroskopisch intermediär kein bevorzugtes Dimer beobachtet werden. Diese Beobachtung wurde durch die Berechnung der ^{19}F-NMR Verschiebungen möglicher Dimere mit Hilfe der GIAO-Methode gestützt. Dabei ergaben sich Hinweise auf das intermediäre Auftreten einer Vielzahl zyklischer Dimere. Mit Hilfe quantenchemischer Rechnungen auf höchstem Niveau (Coupled Cluster) konnten die Strukturen und relativen Energien möglicher zyklischer Dimere aufgeklärt werden. ESR Messungen lieferten keinen Hinweis auf einen radikalische Reaktionsmechanismus bei der Polymerisation des Triens.

Einige mögliche Strategien zur Synthese teilfluorierter Butatriene wurden experimentell untersucht, doch lieferte keine Methode isolierbare Mengen dieser Substanzen. Dennoch können die bei den Syntheseversuchen gewonnenen Erkenntnisse helfen, in Zukunft eine erfolgreiche Synthese zu entwickeln.

Quantenchemische Rechnungen auf höchstem Niveau (Coupled Cluster) lieferten interessante Informationen über den Einfluß eines steigenden Fluorierungsgrades auf die realtiven Energien von teilfluorierten Butatrienen und ihren Butaenin Isomeren. Dabei

wurde ein Enin-Isomer entdeckt, das erstaunlicherweise stabiler als sein Butatrien Isomer ist, obwohl es an der Dreifachbindung fluoriert ist. Eben jene Fluorierung an der Dreifachbindung ist eigentlich notwendig um die Energie fluorierter But-1-en-3-ine relativ zu ihren Butatrien-Isomeren zu erhöhen.

Betrachtet man längere fluorierte Kumulene als Tetrafluorallen und Tetrafluorbutatrien so stellt sich heraus, dass das Kumulen-Isomer nicht mehr das stabilste Isomer ist.

Abstract

The present study provides deeper insight into the chemistry of fluorinated butatrienes both experimentally and theoretically.

The four step synthesis of tetrafluorobutatriene starting from commercially available 1,1-difluoroethylene could be successfully improved to an overall yield of up to 42% (from 8%).

1,1,4,4-Tetrafluorobutatriene readily undergoes Diels-Alder reactions. The central double bond acts as a dienophile towards electron rich dienes. Well defined products were isloated in up to quantitative yield. This represents the first incorporation of tetrafluorobutatriene into organic molecules. Tetrafluorobutatriene does neither undergo [2+2]-cycloadditions nor 1,3-dipolar cycloadditions.

It was not possible to synthesize new tetrafluorobutatriene metal complexes. The instability of the triene as well as the acceleration of its decomposition by certain metal centers holds responsible for that.

The synthesis of cyclic tetrafluorobutatriene dimers is most likely impossible by controlled dimerization reactions of the monomer and no distinct dimer is intermediately preferred in the starting phase of the polymerization. This is supported by calculations of the ^{19}F-NMR shifts of the possible dimers by the GIAO method which reveal references for the intermediate emergence of several cyclic dimers during the polymerization of tetrafluorobutatriene. Deeper understanding of the structures of tetrafluorobutatriene dimers and their isomerization energies was gained by high level theoretical calculations on the Coupled Cluster level of theory. EPR-spectroscopy gave no evidence for a radiacal polymerization pathway.

Several possible strategies for the successful synthesis of partially fluorinated butatrienes were attempted experimentally, but none of them yielded isolable amounts of these species. This study provides the first set of information necessary to realize a successful synthesis.

High level theoretical calculations on the Coupled Cluster level of theory were employed to gain more information on the influence of increasing fluorination on the relative energies of butatrienes and their enyne isomers and to find promising candidates for a rearrangement reaction of a but-1-en-3-yne to its butatriene isomer. Thereby, a but-1-en-3-yne isomer,

1,1,4-trifluorobut-1en-3-yne, was discovered which is considerably more stable than its butatriene isomer, although it is fluorinated at the acetylenic center. This acetylenic fluorine substitution is crucial in raising the energies of fluorinated but-1-en-3-yne relative to their butatriene isomers.

While the cumulenic isomer is the most stable isomer of the shortest fluorinated cumulenes, tetrafluoroallene and tetrafluorobuatriene, theoretical calculations showed that this is not the case if higher homologues are taken into account.

Auch eine Enttäuschung, wenn sie nur gründlich und endgültig ist, bedeutet einen Schritt vorwärts.

Max Planck

1 Introduction

Fluorine, discovered by *Henry Moissan* in 1886,[1] is a key element although not within the enlivened nature. There are twelve known naturally occurring fluorine compounds compared to 3,500 compounds of the higher halogen homologes.[2,3] Fluorine is present in a large and ever increasing number of pharmaceuticals and agrochemicals, typically as an occasional fluoro or trifluoromethyl substituent on a hydrocarbon-derived molecule; e.g. half of the top ten drugs sold contain C-F bonds.[4,5,6,7,8] Multiple applications underline the important role of fluoropolymers in technology. They are used in automotive hoses and gaskets, biomedical applications, reconstructive surgery and fuel cell membranes for example.[9,10,11,12,13,14] According to Richard D. Chambers "*fluorine is unique, in that it is possible to replace hydrogen in an organic molecule by fluorine either singly or multiply and, in so-doing, create a potentially infinite extension to organic chemistry that is entirely synthetic.*"[15]

Fluorine forms the strongest single bond to carbon[16,17] and the inertness of the C-F bond is crucial to the chemical and physical performance of fluorocarbons.[18] Replacement of hydrogen by fluorine usually results in a dramatic change of the physical, chemical and biological properties of the original compound.[19,20] The importance of strategically placed C-F and C-CF_3 bonds in pharmaceutical, medicinal

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and bioorganic chemistry[4,13,21,22,23,24] has led to the development of new methodologies for their selective generation.[25,26,27,28]

As stated above fluorocarbons are very resistant to chemical change. Although that gives them their utility it is also a downside. Environmentally persistent fluorocarbons are of concern since they have an impact on the long-term global environment. Chlorofluorocarbons (CFCs), once engineered to be inert aerosols, refrigerants, cleaning solvents and foaming agents have been identified as chief culprits in disrupting the ozone balance. Nowadays they are banned under the Montréal Protocol.[29,30] Replacements are environmentally benign hydrofluorocarbons (HFCs) with zero ozone depleting potential.[31] HFCs are non-toxic enough to be used as inhalation anesthetics or drug propellants.[32,33] Unique solvent properties of perfluorocarbons (PFCs)[34,35,36] led to their use in synthesis, separation and combinatorial chemistry.[37] PFCs are inert under ambient conditions, have high global warming potential and atmospheric lifetimes of thousands of years.[28,29,30]

Some fluorocarbon derivatives are detectable world-wide, for example in the bloodstreams of humans.[38] Up to now, little is known about their environmental or metabolic degradation pathways. Recently, the reason for the legendary toxicity of perfluoroisobutene and other highly toxic fluorobutenes was discovered. Unlike alkenes themselves, fluoroalkenes react easily with nucleophiles [39] and the toxicity is

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due to reaction with thiols in the pulmonary tissue.[40]

Induction and resonance effects induced by fluorine substituents result in unique properties regarding the reactivity and stability of fluorinated compounds.[19] This uniqueness makes them interesting, especially regarding their potential as ligands in the organometallic and catalytic chemistry.

Cumulenes are highly reactive molecules. The simplest cumulene, allene (1,2-propadiene), is stable at room temperature and its carbon backbone is a common building block in natural compounds.[41] The first natural molecules containing cumulene units, *pyrethrin I* and *II* ((**1**), chart 1.1), were discovered by *Staudinger* as early as 1924.[42] In contrast, its longer homologue butatriene polymerizes at room temperature and is no common building block in natural occurring substances.[43,44] Both allene and butatriene are capable of binding to metal centers in different ways ranging from η^1- to η^3- and the unusual η^4-modes, respectively.[45,46,47] The stability of cumulenes decreases with increasing carbon skeleton length and consequently higher cumulenes do not occur on earth either.[48,49] Interestingly, the lack of natural occurrence of higher cumulenes is foiled by the appearance of cumulenes in regions of interstellar space where hydrogen is rare.[50,51] Although most of the identified interstellar molecules exhibiting a long carbon chain are polyacetylenes, at least some turned out to have a cumulenic carbon backbone like the C_8H-radicalcarbene ((**2**), chart 1.1).[52]

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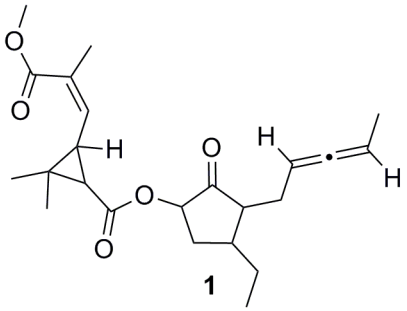

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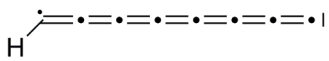

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Chart 1.1 – Naturally occurring cumulenes. *Pyrethrin II* (**1**), one of the first discovered naturally occurring cumulenes; C_8H-radicalcarbene (**2**), discovered in interstellar clouds.

Since long cumulenic carbon chains may be regarded as the simplest "carbon nanowire" they have gained considerable attention for the use in molecular machines in recent years.[53,54] This application may be accomplished by oxidation/reduction of the "wire" and thereby changing its length or by metal atom movement on the "wire".[55] Usually they are stabilized by bulky substituents such as phenyl- or *tert.*-butyl-groups. The capability of cumulenes for different binding modes to metal centers led to studies on their potential use as molecular switches by utilizing haptotropic shifts between these modes.[56]

Beside these experimental efforts, cumulenes have gained much attention by theoretical chemists.[57,58] It has been shown that cumulenes, especially fluorinated cumulenes,[59] may serve in nuclear magnetic resonance quantum computers[60,61] where the nuclear spins of fluorine atoms may be utilized as quantum bits.[62]

The substitution of hydrogen by halogens can change the properties of cumulenes dramatically. While allene dimerizes only if heated over 500°C, tetrafluoroallene

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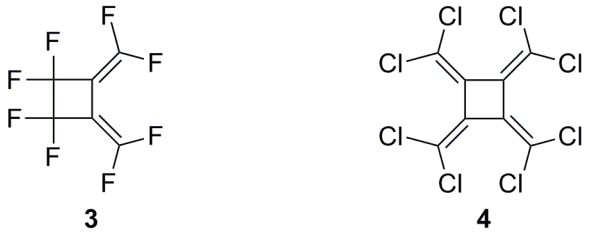
62 Tei, M.; Mizuno, Y.; Manmoto, Y.; Sawae, R.;Takarabe, K.; "Study of decoherence in a NMR quantum computer using tetrafluoropyridine", *Int. J. Quantum Chem.* **2003**, *95*, 554-557.

dimerizes to **3** (chart 1.2) at room temperature[63] and tetrachloroallene dimerizes rapidly already slightly over its melting point of -56°C, sometimes even under the emission of light.[64]

Halogenated cumulenes with a carbon chain length longer than three carbon atoms are only known for the longer homologue buta-1,2,3-triene. Recently, the last missing perhalogenated butatriene, tetrabromobutatriene, was synthesized.[65] Their reactivity depends on the halogen. Tetraiodobutatriene is extremely unstable in solution,[66] tetrafluorobutatriene ((**5**), chart 1.3), the only gas in this series, is known to explode violently when exposed to air or warmed above its boiling point of -5°C.[67] Tetrabromobutatriene and tetrachlorobutatriene[68] are more stable; tetrachloro-butatriene in fact dimerizes to the [4]radialene ((**4**), chart 1.2) only if heated to 100°C.



3 **4**

Chart 1.2 – Dimerization products of halogenated cumulenes. Perfluoro-1,2-dimethylenecyclobutane (**3**), perchloro-[4]radialene (**4**).

While the chemistry of tetrafluoroallene has been studied extensively[69,70] and its longer homologue **5** has been synthesized and characterized by IR- and ^{19}F-NMR-spectroscopy by *Martin* and *Sharkey* as early as 1959, the chemistry of **5** remained almost unexplored due to the compound´s extreme instability.[67] It even polymerizes at -85°C within a short time. The chemistry of **5** is limited to a few derivatives also reported by *Martin* and *Sharkey* using addition of bromine and chlorine and oxidation.

63 Jacobs, T. L.; Bauer, R. S.; "The Synthesis and Polymerization of Perfluoroallene", *J. Am. Chem. Soc.* **1958**, *81*,606-610.
64 Roedig, A.; Bischoff, F.; Heinrich, B.; Märkl, G.; "Perchlorradiallen als Zwischenstufe der Dehydrochlorierung von 3-H-Pentachlorpropen-(1) zu Perchlor-1.2-dimethylen-cyclobutan", *Justus Ann. Chem.* **1963**, *670*, 8-22.
65 Liu, P.-H.; Li, L.; Webb, J. A.; Zhang, Y.; Goroff, N. S.; "Tetrabromobutatriene: Completing the Perhalocumulene Series", *Organic Letters* **2004**, *6*, 2081-2083.
66 Webb, J. A.; Liu, P.-H.; Malkina, O. L.; Goroff, N. S.; "Tetraiodobutatriene: A new Cumulenic Carbon Iodide", *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 3011-3014.
67 Martin, E. L; Sharkey, W. H.; "1,1,4,4-Tetrafluorobuta-1,2,3-triene", *J. Am. Chem. Soc.* **1959**, *81*, 5256-5258.
68 Heinrich, B.; Roedig, A.; "Perchlorbutatriene und Perchlor-[4]radialene", *Angew. Chem Int. Ed. Engl.* **1968**, *7*, 375-376.
69 Lentz, D.; "Organometallic chemistry of fluorinated propadienes and butadienes", *J. Fluorine Chem.* **2004**, *125*, 853-861.
70 Kühnel, M. F.; Lentz, D.; "Hydrometallation of Fluoroallenes", *Dalton Trans.* **2009**, 4747-4755.

Chart 1.3 – Literature known fluorinated butatrienes. Tetrafluorobutatriene (**5**) and 1,1-difluorobutatriene (**6**).

Later, Raman- and PE-spectroscopic data were added[71,72] and its structure and experimental charge density was elucidated by high-resolution X-ray diffraction.[73] Compound **5** decomposes even in anhydrous solvents under vacuum or inert atmosphere within a few hours. Nevertheless it was possible to synthesize two of its transition metal complexes directly from the triene, [M(η^2-C_4F_4)(CO)(PPh_3)$_2$Cl] (M = Ir, Rh).[74] Another tetrafluorobutatriene complex, Ir(η^5-C_5Me_5)(PMe_3)(η^2-C_4F_4), is known but was synthesized by reduction of a *sec.*-perfluorobutyl ligand within the coordination sphere of the metal.[75]

Theoretical and practical studies on partially fluorinated butatrienes or higher cumulenes are rare.[76,77] It is only the synthesis of 1,1-difluorobuta-1,2,3-triene ((**6**), chart 1.3) which has been accomplished and solely within an argon matrix.[78]

71 Miller, F. A.; Elbert, W. F.; Pingitore, W.; "The vibrational spectra of perfluoro- and perchlorobutatriene", *J. Mol. Struct.* **1977**, *40*, 25-42.
72 Barsch, H.; Bieri, G.; Heilbronner, E.; Jones, T. B.; "The Photoelectron Spectrum of Tetrafluorobutatriene", *Helv. Chim. Acta* **1978**, *61*, 46-58.
73 Bach, A.; Lentz, D.; Luger, P.; Messerschmidt, M.; Olesch, C.; Patzschke, M. "Crystal Structure Analysis of 1,1,4,4-Tetrafluorobutadiene and Experimental Determination of the Charge Density of 1,1,4,4-Tetrafluorobutatriene", *Angew. Chem.* **2002**, *114*, 311-314; *Angew. Chem. Int. Ed.* **2002**, *41*, 296-299.
74 F. A. Akkerman, D. Lentz; "Stabilization of Tetrafluorobutatriene by Complex Formation", *Angew. Chem.* **2007**, *119*, 4989-4992; *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 4902-4904.
75 Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L.; "Reductive Activation of Crabon-Fluorine Bonds in Fluoroalkyl Ligands: an Unexpected Route to the Only Known Tetrafluorobutatriene Transition Metal Complex, Ir(η^5-C_5Me_5)(PMe_3)(η^2-C_4F_4)", *J. Am. Chem. Soc.* **2004**, *126*, 2308-2309.
76 Podkopaeva, O. Y.; Chizhov, Y. V.; "DFT study of the geometrical and electronic structure of substituted cumulenes in neutral and cationic forms", *J. Struct. Chem.* **2006**, *47*, 420-426.
77 Amrutha, R.; Sangeetha, L.; Chandran, P.; "Self consistent field molecular orbital studies on chlorinated cumulenes", *Ind. J. Chem. A* **2002**, *41*, 897-903.
78 Kötting, C.; Sander, W.; Senzlober, M.; "Evidence for the non-concerted addition of difluorovinylidene to acetylenes", *Chem. Eur. J.* **1998**, *4*, 2360-2365.

2 Results and Discussion

2.1 Aims of this work

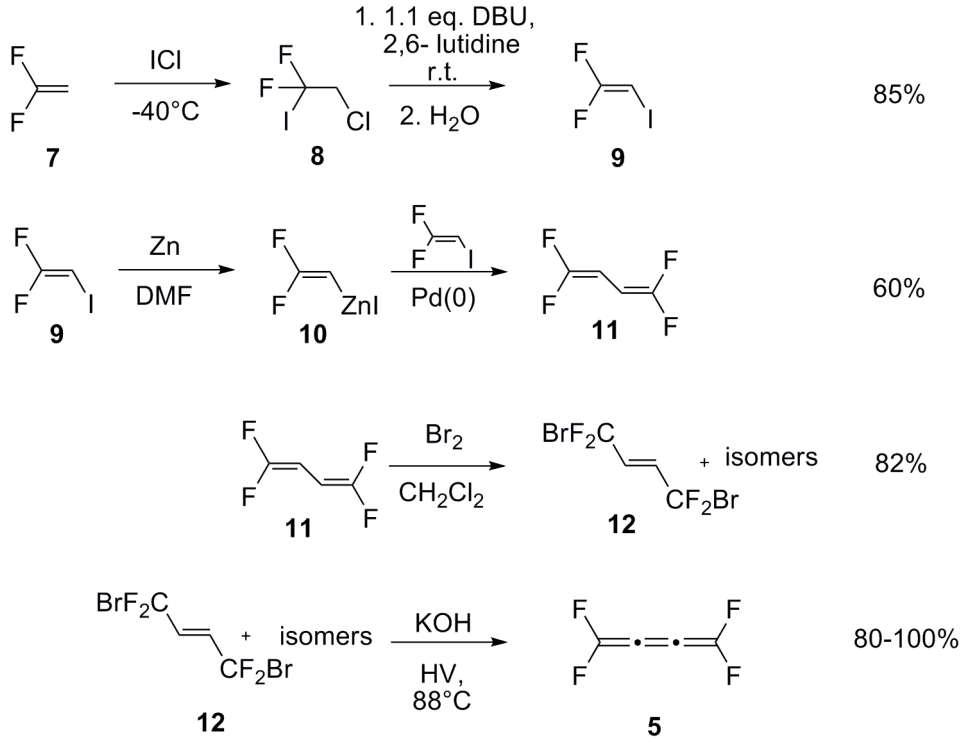
At the beginning of these studies four major questions arose:

1st: How do standard organic reactions with tetrafluorobutatriene (**5**) proceed and which conditions are necessary do reach high yields. Are there other organometallic compounds which are able to stabilize (**5**) to yield isolable compounds?
2nd: Is there a way to develop a lab scale synthesis for partially fluorinated butatrienes, especially for 1,1-difluorobutatriene (**6**)?
3rd: How can the influence of fluorination onto the stabilities of fluorinated butatrienes be determined and what can they tell about the synthetic accessibility of fluorinated cumulenes with a longer carbon chain?
4th: Is it possible to isolate a dimer of tetrafluorobutatriene and how does the polymer look like?

2.2 Tetrafluorobutatriene

2.2.1 Improved Synthesis of Tetrafluorobutatriene

Scheme 2.2.1 shows an improved synthesis of tetrafluorofluorobutatriene (**5**) starting from commercially available 1,1-difluoroethene (**7**).



Scheme 2.2.1 – Improved synthesis of tetrafluorofluorobutatriene (5).

The previously published syntheses of the precursor 2,2-difluoroiodoethene (**9**) for the synthesis of **5** by *Lacher et al.*[79,80] and later *Lentz et al.*[81] could be improved since both suffered from some disadvantages. Regarding the first synthetic method, it was not possible to achieve reproducible high yields in the synthesis of **9**. The elimination of hydrogen chloride from 1-chloro-2,2-difluoro-2-iodoethylene (**8**) by potassium hydroxide in high boiling mineral oil resulted in high conversion to the precursor **9** but due to separation problems during the fractional condensation, yields remained

79 Park, J. D.; Seffl, R. J.; Lacher, R. J.; "The Preparation and Properties of Trifluoroiodoethene", *J. Am. Chem. Soc.* **1956**, *78*, 59-62.
80 Park, J. D.; Abramo, J.; Hein, M. ; Gray, D. N.; Lacher, J. R.; "Preparation and Some Properties of Certain Fluorovinyl Iodides and some Fluorinated Butadienes", *J. Org. Chem.* **1958**, *23*, 1661-1665.
81 Akkerman, F. A.; Kickbusch, R.; Lentz, D.; "Synthesis of fluorinated dienes by palladium-catalyzed coupling reactions", *Chem. Asian J.* **2008**, *3*, 719-731.

rather poor.[82] Most likely this results from the formation of an aceotrope between the ethene **9** and the solvent.

Yields in the revised synthesis of **9** published *Lentz et al.* in 2008 could be further improved. The elimination of hydrogen chloride from **8** by potassium *tert.*-butoxide produces *tert.*-butanol and hence involves the severe problem of separating the product from *tert.*-butanol. Since *tert.*-butanol is a ball-shaped molecule, it passes cooling traps even if they are cooled well beyond its boiling or freezing point due to the high sublimation pressure of such compounds.[83,84] Therefore purification has to be repeated several times which consequently lowers the yield. The second problem is the double elimination of hydrogen bromide from 1,4-dibromo-1,1,4,4-tetrafluorobut-2-ene (**12**) over hot potassium hydroxide.[73] Often the elimination resulted in varying yields and the reasons for that were not fully understood at this time.

The first problem was addressed by investigation of potential bases for the elimination of hydrogen chloride from **8** in different solvents. It turned out, that the elimination employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2,6-lutidine results in a high conversion rate (scheme 2.2.1, line 1), but large amounts of salt precipitate during the reaction and incorporate substantial amounts of the product, thereby lowering the yield, consequently.

This problem can be solved in two different ways. On the one hand one can remove solvent and volatiles and use the content which do not pass a -40°C cooling trap as solvent for another elimination. While yields in the first run are approximately 75%, it increases in every further run to 85-90%. Regarding the limited volatility of 2,6-lutidine this work-up is time consuming and only suitable for small scales. On the other hand one can add the same amount of water to the reaction mixture as the amount of solvent prior to purification. The added water dissolves the salts and after seperation of all volatiles and an easy distillation the yield increases to 85 %. The reaction was scaled up to a two mole scale without any noticeable decrease in yield.

82 F. A. Akkerman, private communication **2006**
83 Ni, N.; Tesconi, M.; Tabibi, S. E.; Gupta, S.; Yalkowsky, S. H.; “The use of pure *t*-butanol as a solvent for freeze drying: a case study”, *Int. J. Pharmaceutics* **2001**, *226*, 39-46.
84 Johnes, A. H.; “Sublimation Pressure of Organic Compounds”, *J. Chem. Eng. Data* **1960**, *5*, 196-200.

The second problem, the double elimination of hydrogen bromide from **12** was solved by careful optimization of the reaction conditions (scheme 2.2.1, last line). The elimination is performed over hot potassium hydroxide in a U-shaped-glass-pipe under high vacuum. The U-pipe is connected to two cooling traps, -78°C to freeze out remaining starting material and water and -196°C to collect the product. It turned out that:

1st decrease of the elimination temperature by 2 degrees to 88°C,

2nd reduction of the stream of the starting material,

3rd use of technical potassium hydroxide flakes instead of chemical grade pellets,

4th use of a thin U-pipe with an inner diameter of below 1 cm,

results in reproducible yields of 80-100%.

Up to 2 g (~ 8 mmol) of the starting material can be converted until the U-pipe is plugged up by the resulting molten potassium hydroxide/water mixture.

It is very important that the pressure in the system must not exceed 10^{-2} mbar otherwise volatiles are produced that even pass the liquid nitrogen cooled trap, most likely carbon monoxide resulting from further reactions of **5** with potassium hydroxide. This can be caused by a too intense stream of starting material. The use of technical grade potassium hydroxide proved to be useful, presumably for two reasons: At first, the surface texture of the technical potassium hydroxide is more rough compared to chemical grade pallets. Hence the contact surface is increased. Secondly, possible admixtures, e.g. potassium carbonate, could play an important role. Consequential, the U-pipe has to have a small diameter since larger ones result in larger amounts of used potassium hydroxide and the contact surface is further increased. However, an oversized contact surface results in a decrease of the yield.

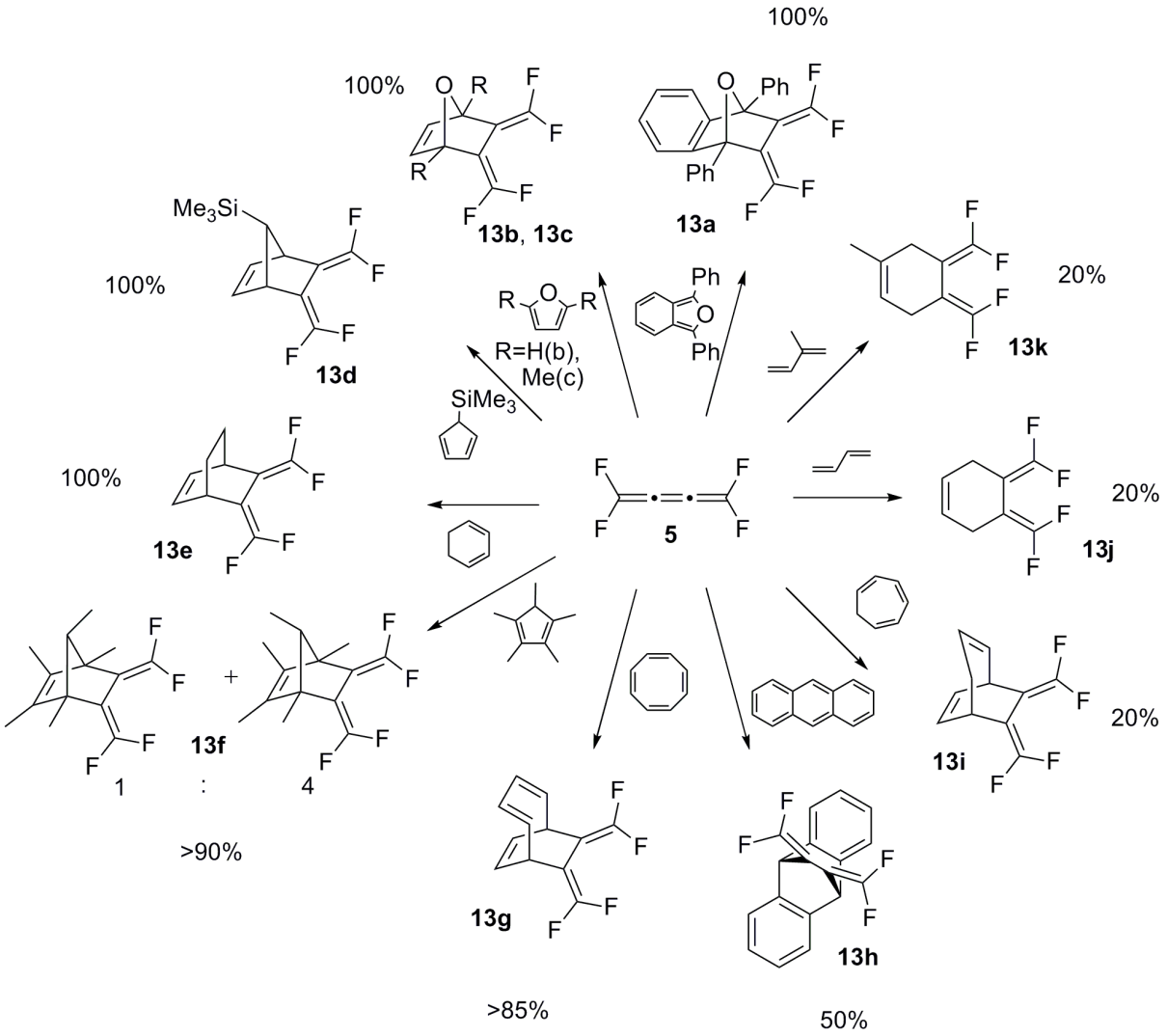
Summing up, there is a complex equilibrium between contact time, contact surface, type of base and temperature which governs the yield. The conditions mentioned above proved to give reliable high yields.

Furthermore it turned out, that careful addition of bromine to 1,1,4,4-tetrafluorobuta-1,3-diene (**11**) followed by addition of sodium thiosulfate saturated water and subsequent work-up furnishes a colorless oil. *Lentz et al.* reported a yellow oil.[73] The reported color was most likely caused by remaining bromine. In addition the yield increases dramatically from 52% to 82%, Compound **12** is air and room temperature stable but within several weeks the color changes to slightly pink. Nevertheless ^{19}F-NMR spectra showed no change of the compound. In conclusion, the overall yield in the four step synthesis of **5** could be improved to 42%.

Martin and *Sharkey* stated that tetrafluorobutatriene explodes when heated above its boiling point or in contact with air.[67] We did not observe such an explosion when tetrafluorobutatriene (1 g) was subjected to room temperature under its own vapor pressure. Nevertheless, small amounts of pure tetrafluorobutatriene **5** polymerize rapidly at room temperature to give a slightly pink to red polymer. Once prepared, it can only be transferred safely by condensation at reduced pressure and must be stored at -196 °C. This method has so far prevented explosion and polymerization.

2.2.2 Organic Reactions Involving Tetrafluorobutatriene

2.2.2.1 Diels – Alder Reactions



Scheme 2.2.2 – Pericyclic reactions I: Diels-Alder reactions of tetrafluorobutatriene (5). Conversion determined by ^{19}F-NMR-spectroscopy, reaction time 1 minute (furane) up to 14 days (anthracene), solvent: CH_2Cl_2 (anthracene and diphenylisobenzofurane), all others in substance.

Honored in 1950 with the Nobel prize, the Diels-Alder reaction is still one of the most remarkable organic reactions.[85,86,87] To study the scope of **5** in this type of reaction it was subjected to various dienes and enes.

85 Diels, O.; Alder; K.; "Synthesen in der hydroarmoatischen Reihe", *Liebigs Ann. Chem.* **1928**, *460*, 98-122.
86 Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G.; "The Diels – Alder Reaction in Total Synthesis", *Angew. Chem. Int. Ed.* **2002**, *41*, 1668-1698.
87 Corey, E. J.; "Catalytic Enantioselective Diels-Alder Reactions: Methods, Mechanistic Fundamentals, Pathways, and Applications", *Angew. Chem. Int. Ed.* **2002**, *41*, 1650-1667.

The Diels-Alder reaction of **5** with various dienes of different reactivity is outlined in scheme 2.2.2. Due to the instability of the triene, all reactions have to be performed at or below ambient temperature. Depending on the reactivity and solubility of the dienes the yields of the products **13a-k** range from almost quantitative to almost zero.

No product could be detected with 9,10-dimethylanthracene, α-terpinene, fullerene-C_{60}, various thiophene derivatives, 1,1-difluorobut-1-en-3-yne[88], hexachlorocyclopentadiene, pyrene, octafluoro-1,2-dimethylene-cyclobutane, tetraphenylcyclopentadienone, 2,5-dimethyl-1,3,4-thiadiazole, N-methylpyrrole, 1-methoxynaphthalene, tetraphenylfurane, pentaphenylcyclopentadiene, acrylonitrile and tetracyanoethylene, respectively. Most likely this is a result of either insufficient solubility of the diene, steric hindrance (e.g. pentaphenylcyclopentadiene for both reasons) or insufficient reactivity. Interestingly, ^{19}F-NMR indicates in some cases (e.g. thiophene derivatives) an increased decomposition rate of the triene (outlined in table 2.2.1).

Tetrafluorobutatriene (**5**) reacts solely as an ene component (dienophile) in these Diels-Alder reactions, as indicated by the lack of reactivity towards the dienophilic cyano-substituted ethenes mentioned above. The perfect linear shape of the three cumulated double bonds is most likely the reason for that since for the diene the *s-cis* configuration is required for sufficient reactivity.[89] Employing the inverse electron demand hexachlorocyclopentadiene or octafluoro-1,2-dimethylene-cyclobutane did not lead to reaction at the terminal double bonds. Since the reaction with electron rich dienes is restricted to the central double bond well defined products result.

Almost quantitative reactions were observed with furane, 2,5-dimethylfurane, 1,3-diphenylisobenzofurane, cyclohexadiene and 1-trimethylsilylcyclopentadiene (products **13a-f**). Single crystals of the Diels-Alder product **13a** of tetrafluorobutatriene with 1,3-diphenylisobenzofurane could be obtained. However, **13a** also isomerized during the crystallization forming a few crystals of the naphthalene derivative ((**14**), scheme 2.2.3)

88 Wessig, P. Müller, G.; "The Dehydro-Diels – Alder Reaction", *Chem. Rev.* **2008**, *108*, 2051-2063.
89 Scharf,H.-D.; Plum, H.; Fleischhauer, J.; Schleker, W.; "Zur Diels-Alder-Reaktivität *s-cis*-fixierter 1,3-Diene", *Chem. Ber.,* **1979,** *112,* 862-882.

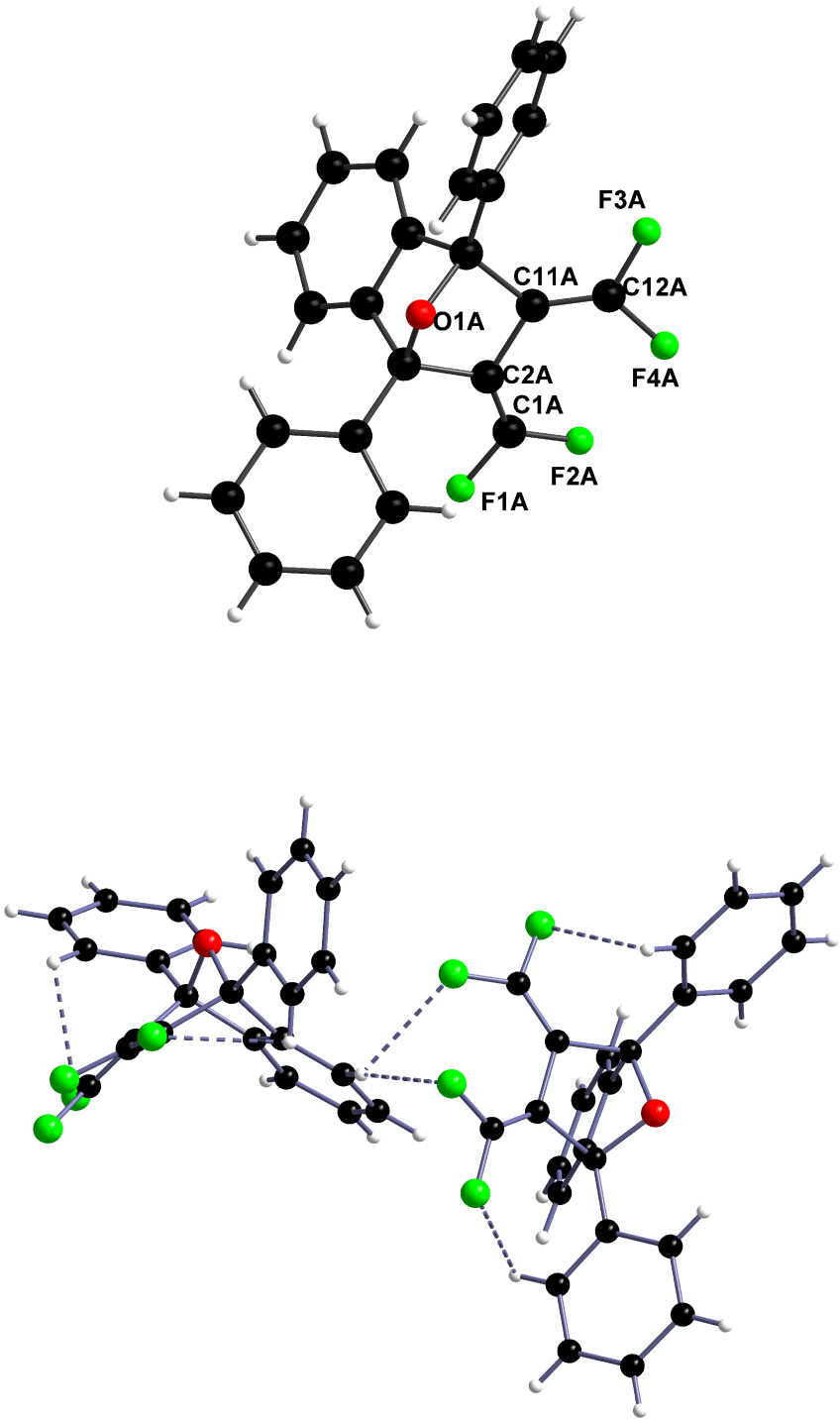
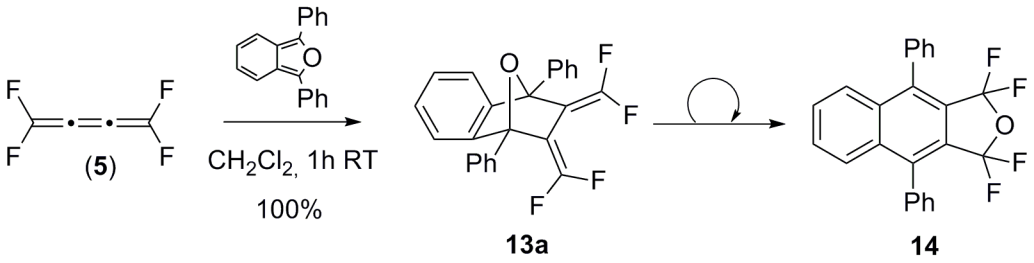


Fig. 2.2.1 – Molecular structure (DIAMOND[90]) of 13a. Inter- and intramolecular H-F contacts between the molecules are symbolized by blue and red dashed lines, respectively. Fluorine atoms of neighboring molecules are drawn as smaller balls.

90 DIAMOND for Windows Visual Crystal Structure Information System, *J. Appl. Cryst*., **1999**, *32*, 1028-1029.

Similar rearrangement reactions have been observed previously.[91] The structures of **13a** and **14** were determined by X-ray crystallography.



Scheme 2.2.3 – Rearrangement of the Diels-Alder product 13a.

As depicted in figure 2.2.1 the asymmetric unit of **13a** consists of two independent molecules which are connected by H-F contacts. The crystal packing of the molecules is dominated to numerous H-F interactions rather than by fluorine segregation.[92,93,94] H-F contacts range from 2.34 Å to 2.79 Å for **13a**. The two phenyl substituents are twisted against each other by 70.5° and 82.1° probably due to intramolecular H-F contacts shown in red. The conjugated *cisoid* double bonds are non planar (C1-C2-C11-C12 -27.6°/-31.5°) to minimize the repulsion of the fluorine atoms F2 and F4. C-F bond lengths range from 1.31 to 1.34 Å. Several O-H contacts can be found: two in the range of 2.40 Å and four in the range of 3.27-3.39 Å.

Several short H-F contacts (ranging from 2.43 Å to 2.78 Å) can be found in the rearranged naphthalene derivative **14** depicted in figure 2.2.2 but again no fluorine segregation can be observed. The phenyl rings are twisted by 15°. The C-F bond lengths are significantly longer than in **13a** (all four bonds are about 1.35 Å in length). Furthermore several intramolecular H-F contacts can be found ranging from 2.83 Å to 3.72 Å.

91 Dufraisse, C.; Priou, R.; "Isomères formés par dièsynthèse dans la série du diphénylisobenzofuran – Leur transformation en diphényl-1.4-naphtalène", *Bull. Soc. Chim. Fr., Memoires* **1938**, *5*, 502-508.

92 Jeannin, O.; Fourmigué, M.; "One- or two-dimensional fluorine segregation in amphiphilic perfluorinated tetrathiafulvalenes", *C. R. Chimie*, **2006**, 9, 1287-1294.

93 Dautel, O. J.; Fourmigué, M.; Faulques, E.; "Fluorine segregation in the solid state organization of the 1:2 mixed-valence salt of bis(2,2-difluoropropylenedithio)tetrathiafulvalene with the isosteric nickel dithiolene complex", *CrystEngComm.* **2002**, *4*, 249-251.

94 Wolf,J. J.; Gredel, F.; Oeser, T.; Irngartiner, H.; Pritzkow H.; "Crystal engineering with symmetrical threefold acceptor-substituted triaminobenzenes", *Chem. Eur. J.* **1999**, *5*, 29-38.

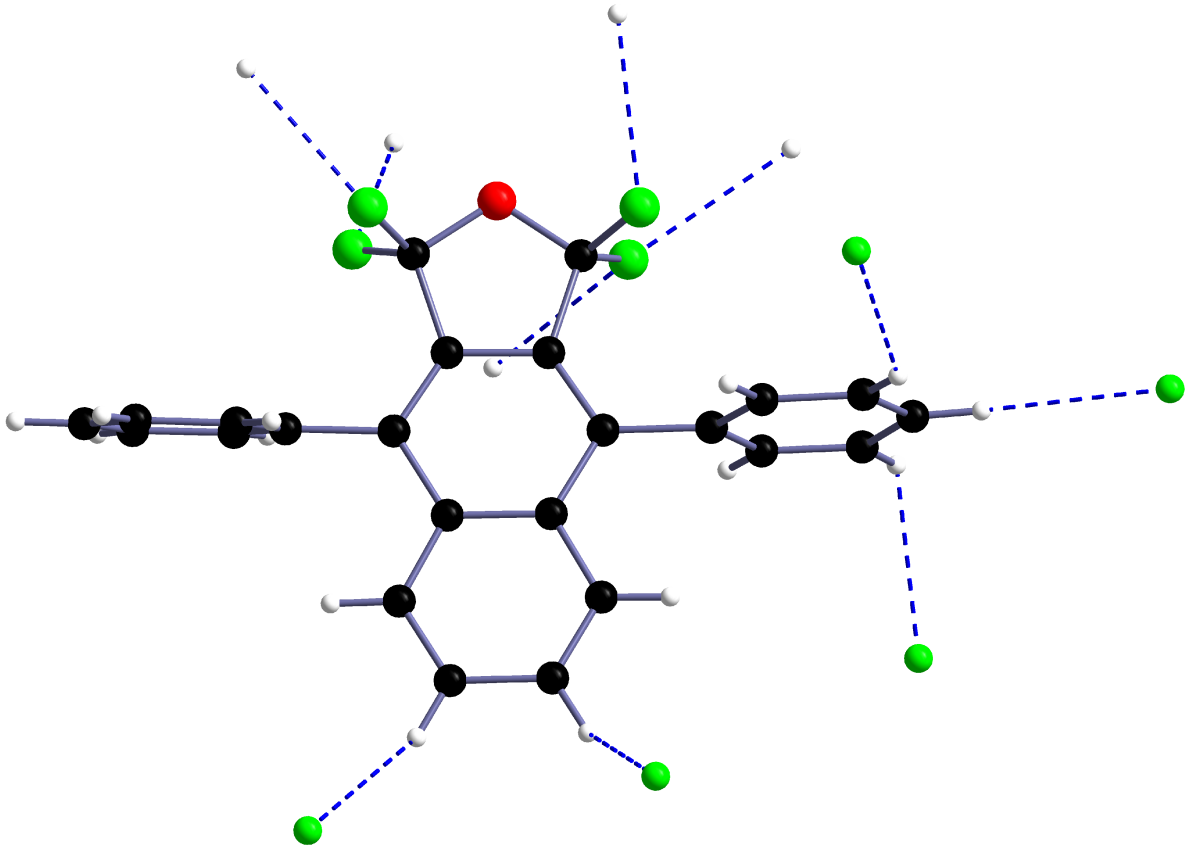


Fig. 2.2.2 – Molecular structure (DIAMOND[80]) of 14. Intermolecular H-F contacts are symbolized by blue dashed lines. Fluorine atoms of neighbouring molecules are drawn as smaller balls.

Attempts to enforce the isomerisation of **13a** to **14** by heating a solution of **13a** in toluene to 160 °C, bubbling air through a hexane solution of **13a**, addition of either potassium hydroxide or sodium fluoride to a THF/water solution of **13a** proved to be unsuccessful. The Diels-Alder product remains stable under all these conditions and not even a trace of **14** could be detected.

All compounds presented exhibit characteristic AA´BB´-type ^{19}F-NMR spectra. The synthesis of **13a-c** has been performed in such a manner that no purification of the product was necessary and all NMR-spectroscopic data was taken. In all other cases the product could not be isolated from the excess diene since starting material and product co-elute and have a comparable volatility.

The AA´BB´-type ^{19}F-NMR spectrum for compound **13a** was analyzed with the gNMR program.[95] The geminal fluorine-fluorine coupling constant and two of the three ^{5}J-couplings exhibit normal values with 38.1 Hz, 16.3 Hz and 8.9 Hz, respectively. In contrast, the coupling constant of the two fluorine atoms standing face-to-face together shows a large ^{5}J through space coupling, resulting in a coupling constant of 62.9 Hz.

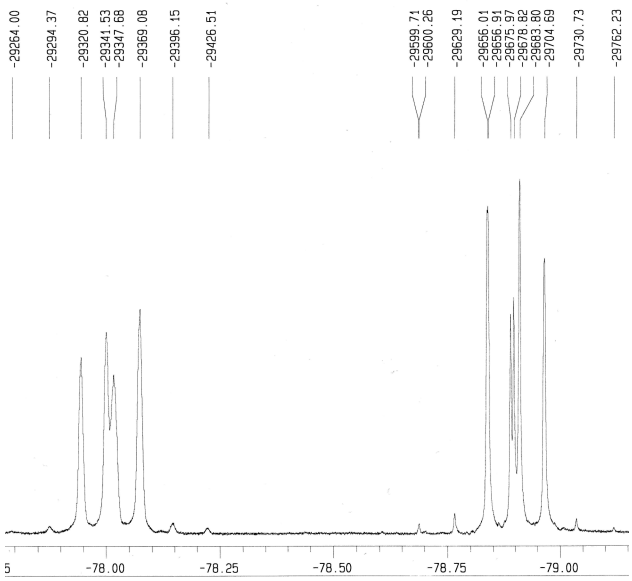


Figure 2.2.3 – ^{19}F-NMR-spectrum of 13a.

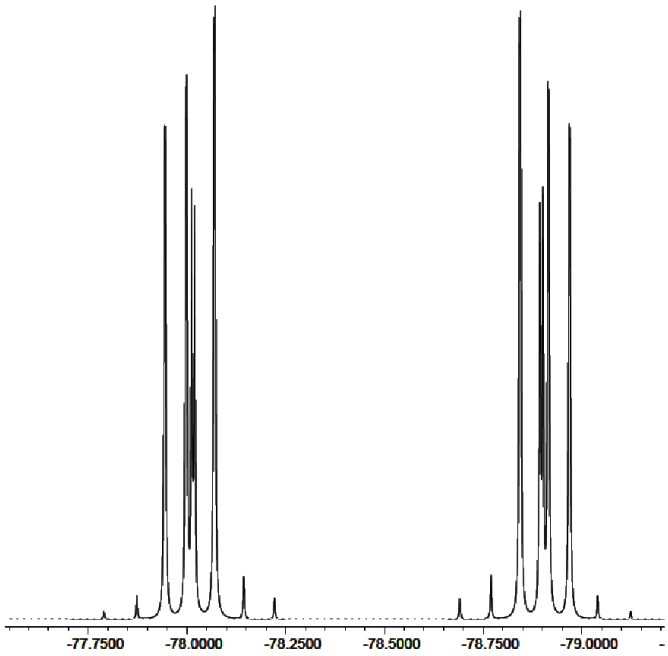


Figure 2.2.4 – Calculated ^{19}F-NMR-spectrum spectrum of 13a (gNMR).

95 P. H. M. Budzelaar, gNMR, © 2002 IvorySoft.

The enormous reactivity of 1,1,4,4-tetrafluorobutatriene (**5**) is best displayed by a comparison to its tetrabromo derivative. While the Diels-Alder reaction with furane in the latter case needs 48 h for completion at room temperature, in the former case the reaction is complete after 1 minute at room temperature.[65]

Table 2.2.1 – Pericyclic reactions with tetrafluorobutatriene (5).

No.	*compound*	*product*	*result*	*No.*	*compound*	*product*	*result*
1	furan	13b	+	*18*	hexachloro-1,3-butadiene	-	-
2	2,5-dimethylfuran	13c	+	*19*	methoxynapthalene	-	-
3	thiophene	-	*dec.*	*20*	acrylontrile	-	-
4	2,5-dimethylthiophene	-	*dec.*	*21*	trimethylsilylazide	-	-
5	2-thiophenealdehyde	-	*dec.*	*22*	tetraphenylcyclopentadienone	-	-
6	anthracene	13h	+	*23*	C_{60}	-	?
7	dimethylanthracene	-	-	*24*	dimethylthiadiazole	-	*dec.*
8	pyrene	-	-	*25*	methylmethacrylate	-	-
9	pentamethylcyclo-pentadiene	13f	+	*26*	pentaphenylcyclo-pentadienone	-	-
10	1,3-cyclohexadiene	13e	+	*27*	1,1-difluoro-1-en-3-yne	-	-
11	1,3,5,7-cyclooctatetraene	13g	+	*28*	pentaphenylcyclopentadiene	-	-
12	α-terpinene	-	-	*29*	isoprene	13k	+
13	hexafluorobuta-1,3-diene	-	-	*30*	pyrrole	-	?
14	octafluoro-1,2-dimethylene-cyclobutane		-	*31*	N-methylpyrrole	-	?
15	1,3-butadiene	13j	-	*32*	hexachlorocyclopentadiene	-	-
16	1,3-diphenyl-isobenzofuran	13a		*33*	1,3,5-cycloheptatriene	13i	
17	1-trimethylsilyl-cyclopentadiene	13d					

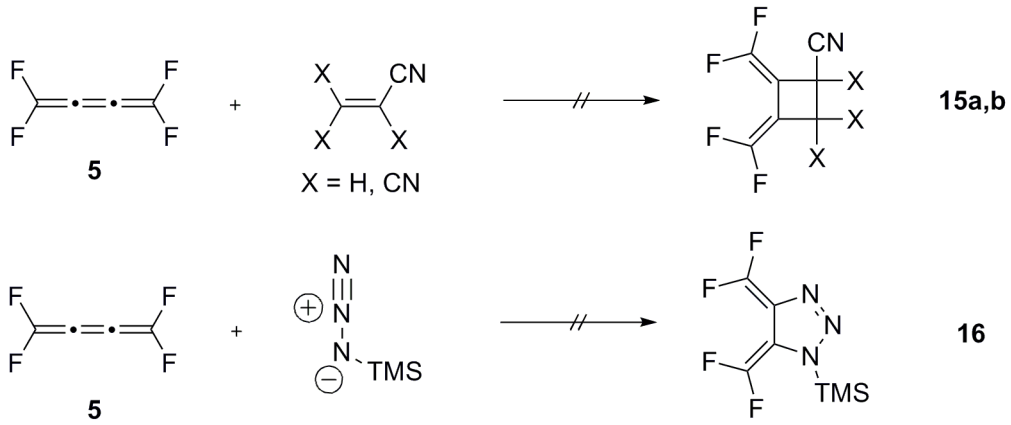
(+ indicates successful reaction, - indicates no reaction, *dec.* indicates enhanced decomposition rate of the triene, ? indicates variation of reaction conditions may lead to successful reaction)

Table 2.2.1 summarizes all substances which were subjected to test their ability to undergo cycloaddition reactions with **5**. In addition to dienes some enes and hetero compounds were tested and given in the table. These reactions will be discussed in

chapter 2.2.3. Some of these reactions showed signals in the ^{19}F-NMR spectra possibly indicative of a successful reaction. However, conversions below 1% leaves these reactions a matter of further optimization. Furthermore, the compounds that accelerate the decomposition of tetrafluorobutatriene (**5**), as mentioned above, are highlighted.

2.2.2.2 Other Pericyclic Reactions

Regarding the reaction cadre of *Sharpless´* famous "click-chemistry" [96] there are two other simple and widespread pericyclic reactions: [2+2]-cycloadditions[97,98] and 1,3-dipolar cycloadditions[99] (Huisgens cycloaddition[100]). Both are relatives of the Diels-Alder reaction but none of them could be successfully performed using tetrafluorobutatriene (scheme 2.2.4).



Scheme 2.2.4 – Pericyclic reactions II: attempted formation of cyclic adducts via [2+2] cycloaddition (first row) and 1,3 – dipolar additions (second row).

96 Kolb, H. C.; Finn, M. G.; Sharpless, K. B.; "Click Chemistry: Diverse Chemical Function from a Few Good Reactions", *Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021.

97 Crellin, R. A.; Lambert, M. C.; Ledwith, A. J.; "Photochemical 2 + 2 cycloaddition via cation-radical chain reaction", *Chem. Soc. D* **1970**, 682-688.

98 Bernardi, F. Olivucci, M.; Robb, M. A.; "Predicting Forbidden and Allowed Cycloaddition Reactions: Potential Surface Topology and Its Rationalization", *Acc. Chem. Res.* **1990**, *23*, 405-412.

99 Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Zunino, E.; Vaccaro, L.; "Synthesis of 4-Aryl-1*H*-1,2,3-triazoles through TBAF-Catalyzed [3 + 2] Cycloaddition of 2-Aryl-1-nitroethenes with $TMSN_3$ under Solvent-Free Conditions", *J. Org. Chem.* **2005**, *70*, 6526-6529.

100 Huisgens, R.; "Centenary Lecture - 1,3-Dipolar Cycloadditions", *Proc. Chem. Soc*. **1961**, *5*, 357-396.

On the one hand [2+2]-Cycloadditions may proceed in a concerted reaction either allowed photochemically or thermally. On the other hand, radical or ionic pathways are also possible. Therefore **5** was condensed onto acrylonitrile and warmed to room temperature. ^{19}F-NMR-measurements revealed no reaction even after 24 hours. The reaction mixture was then irradiated with an UV-lamp for one hour but ^{19}F-NMR revealed again no reaction with the nitrile. After one week, the whole solution had turned into a white polymer. The same observations, with the exception of polymerization, were made when tetracyanoethylene, a very electron-poor olefin, was employed.

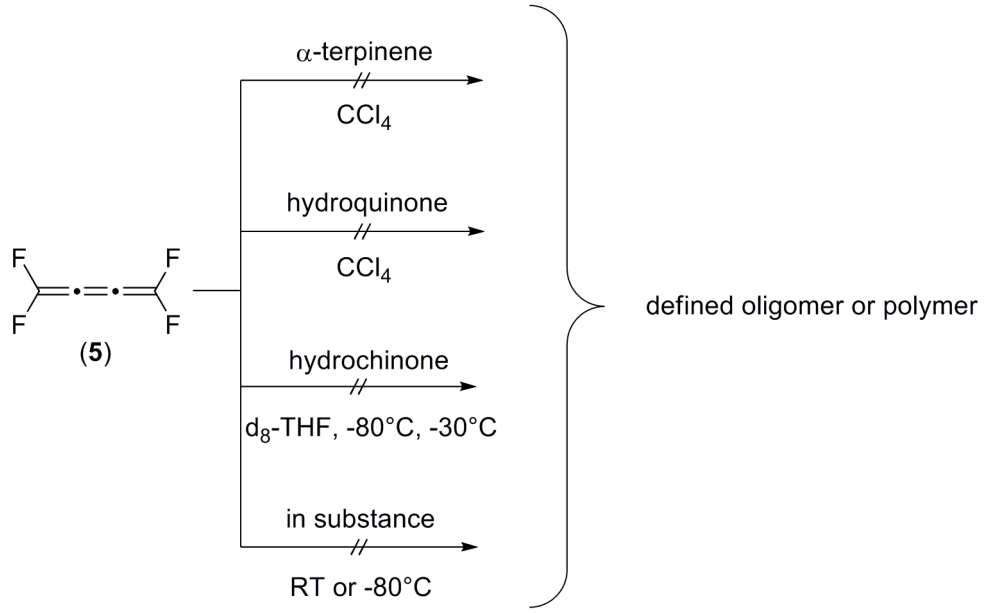
Concerted 1,3-dipolar additions were investigated by condensation of tetrafluorobutatriene (**5**) onto trimethylsilylazide and warming to room temperature. ^{19}F-NMR-measurements first indicated a reaction but continuing measurement revealed that the **5** was not further consumed. Either **5** reacted with impurities in the azide or the impurities were already present in the triene (e.g. decomposition products or hydrolysis product)

In conclusion, tetrafluorobutatriene is neither capable of reacting as an enophile in the Diels-Alder reaction nor of reacting as an ene component in [2+2] cycloaddition reactions be it the [2+2] variant or the 1,3-dipolar variant.

2.3 Dimers and Higher Oligomers of Tetrafluorobutatriene

2.3.1 Tetrafluorobutatriene – Dimers

As mentioned previously 1,1,4,4-tetrafluorobutatriene (**5**) is known to polymerize even at low temperatures within a short time. The pink to red polymer resulting from polymerization in substance is insoluble in any common solvent. Attempts to prevent this undirected polymerization (as shown in scheme 2.3.1) by addition of inhibitors, very high dilution conditions or very low temperature experiments or a combination of these methods revealed no isolable, defined dimeric or oligomeric species. Nevertheless the polymerization in solution is observable by NMR-spectroscopy indicating a highly complex mixture of various compounds. Due to the unique properties of tetrafluorobutatriene a defined polymer might show interesting properties since it is expected to be perfluorinated as well as hyperbranched.[101]



Scheme 2.3.1 – Attempted synthesis of a defined dimer, oligomer or polymer of tetrafluorobutatriene.

Previously reported dimers of substituted butatrienes show an interesting structural diversity (as shown in chart 2.1). While dimerization of the perhydrogen triene[102]

101 Sangermano, M.; Di Gianni, A.; Bongiovanni, R.; Priola, A.; Voit, B.; Pospiech, D.; Appelhans, D.; "Synthesis of Fluorinated Hyperbranched Polymers and Their Use as Additives in Cationic Photopolymerization", *Macromol. Mater. Eng.* **2005** *290*, 721-725.

102 Schubert, M. W.; Liddicoet, T. H.; Lanka, W. A.; "The Synthesis of Butatriene", *J. Am. Chem. Soc.* **1952**, *74*, 569.

results in a cyclooctadiyne[103] the all-chlorine triene[68] forms a [4]radialene-type dimer[68,104,105] and the all-phenyl triene[106] a head-to-head type dimer.[107] For the latter the radialene type dimer is also known but not from dimerization, but from an unusual cyclization of an ate-type complex of a copper carbenoid derived from 1,1-dibromo-2,2-diphenylethylene.[108]

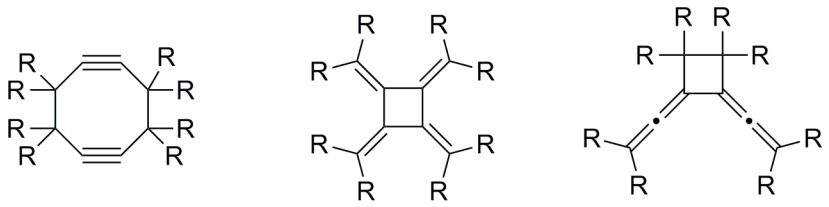


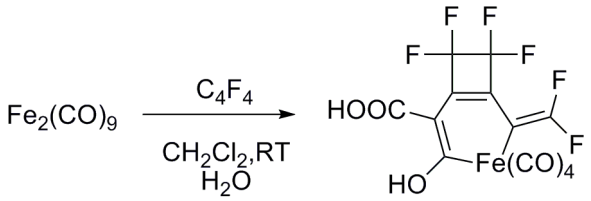
Chart 2.1 – Types of butatriene dimers.

In this respect, the nature of the potential closed-shell dimers and oligomers of tetrafluorobutatriene was investigated by computational methods.

The stabilities of the dimers were determined by CCSD(T)/cc-pVTZ//MP2/cc-pVTZ calculations as the highest order calculations and with a variety of compound methods and lower level computational methods.

Unlike 1,1-difluoroallene and tetrafluoroallene which form η^2-complexes by reactions with several transition metal complexes[69] similar reactions with tetrafluorobutatriene were unsuccessful in most cases. The only tetrafluorobutatriene complexes obtained directly from the triene are $[Ir(\eta^2\text{-}C_4F_4)(CO)(PPh_3)_2Cl]$ and the analogous rhodium compound, as previously mentioned.[73] In one of the many attempts to react tetrafluorobutatriene with enneacarbonyldiiron a few colorless crystals of an unexpected product (**17**) were obtained by *Akkerman*.[109] (scheme 2.3.2)

103 Kloster-Jensen, E.; Wirz, J.; "1,5-Cyclooctadiyne. Preparation and Reactivity", *Helv. Chim. Act*. **1975**, *58*, 162-177.
104 Remoortere, F. P. van; Boer, F. B.; "The Structure of Perchloro-[4]radialene", *Angew. Chem. Int. Ed.* **1969**, *8*, 597-598.
105 Remoortere, F. P. van; Boer, F. B.; "Crystal and molecular structure of perchloro(4)radialene", *J. Am. Chem. Soc.* **1970**, *92*, 3355-3360.
106 Brand, K.; "Über Untersuchungen in der Tetraarylbutan-Reihe und über das 1.1 4.4-Tetraphenyl-butatrien. (4. Mitteilung über die Reduktion organischer Halogen-verbindungen.", *Ber. Dtsch. Chem. Ges B Abhandlungen* **1921**, *54B*, 1987-2006.
107 Berkovitch-Yellin, Z.; Lahav, M.; Leiserowitz, L; "Photochemistry of crystalline cumulenes. Reassignment of the structure of the solid-state photodimer of tetraphenylbutatriene", *J. Am. Chem. Soc.* **1974**, *96*, 918-920.
108 Iyoda, M.; Otani, H.; Oda, M.; "Octaphenyl[4]radialen", *J. Am. Chem. Soc.* **1986**, *108*, 5371-5372.
109 Unpublished results.



17

Scheme 2.3.2 – Synthesis of iron complex 17.

The crystal and molecular structure of the carboxylic acid **17** was elucidated by X-ray crystallography. The formation of similar complexes by hydrolysis of metal-bound fluorocarbyl groups is well known going back to work by *Kemmitt*[110] in the 1960´s and has been recently reviewed by *Hughes*.[7] Despite many further attempts, the synthesis of **17** remained irreproducible. Nevertheless, the formation of this metal complex of a partially hydrolyzed head-to-head type dimer of tetrafluorobutatriene sparked the idea to study the dimerization reaction of **5** in more detail. Recently, a partially hydrolyzed trimer of tetrafluoroallene as well as a manganese complex of the tetrafluoroallene dimer were structurally characterized.[111]

Mass spectrometry (figure 2.3.1) of a freshly oligomerized tetrafluorobutatriene sample shows signals attributed to trimers, tetramers and heptamers. Their apparent existence further increased interest in the potential dimers and higher oligomers of tetrafluorobutatriene (**5**). Since the iron complex **17** is a direct hint to the existence of cyclic dimers and oligomers of **5**, the main focus of this work lies on them. Linear radical oligomerization/polymerization may also take place but was omitted for reasons (e.g. open-shell systems) that will be discussed in detail in the chapter 2.3.2.

110 Kemmitt, R. D. W.; Nichols; “Formation of Metal Carbonyl Complexes in the Reactions with Tetrafluoroethylene”, *Chem. Comm.* **1967**, 919.

111 Lentz, D.; Paschke, M.; “Octafluor-1,2-dimethylencyclobutan, ein perfluorierter Dien-Komplexligand - Carbonyl(η^5-cyclopentadienyl)(η^4-octafluor-1, 2-dimethylencyclobutan)mangan”, *Z. Anorg. Allg. Chem.* **2004**, *630*, 973-976.

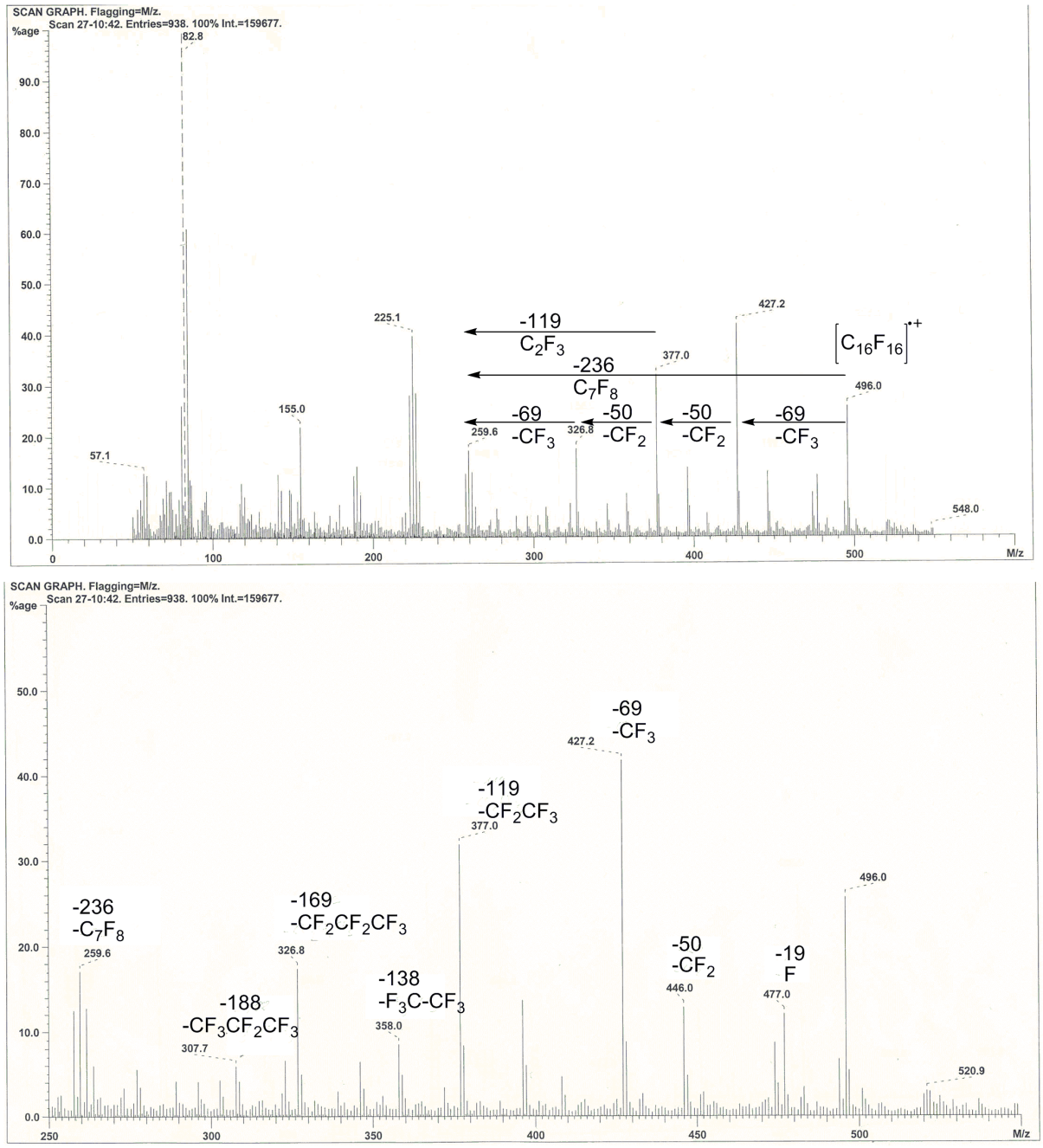
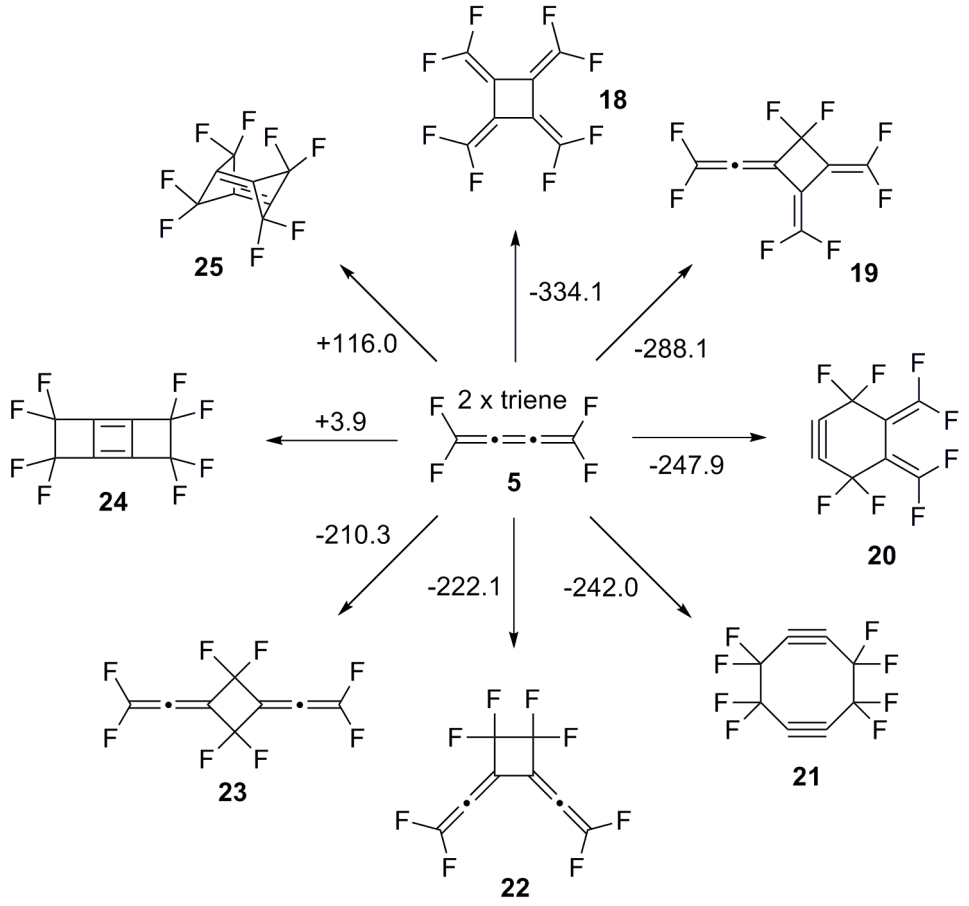


Figure 2.3.1 – Evidences for tetraflurobutatriene oligomers from mass spectroscopy of a freshly polymerized sample.



Scheme 2.3.3 – Dimerization energies of several tetrafluorobutatriene dimers (kJ/mol). Determined at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory including scaled ZPE correction[112], in clockwise order of increasing energy of formation, most stable isomer in 12-o´clock position.

A first look at the structure of a symmetrically substituted buta-1,2,3-triene shows two potential reaction sites at the molecule. Either reactions involve the central double bond or one of the two terminal ones. Schemes 2.3.3 (perfluoro) and 2.3.4 (perhydrogen) show the possible dimers.

Since the two molecules participating in a dimerization reaction do not have to react with the same reaction site, four potential dimers are imaginable as products of a formal [2+2]-cycloaddition reaction.

A symmetrical cycloaddition reaction results either in [4]radialene (**18**, perfluoro) and (**27**, perhydro) or two dimers substituted at the central cyclobutane ring by two

112 Sinha, P.S.; Boesch, E. B.; Gu, C.; Wheeler, R. A.; Wilson, A. K.; "Harmonic Vibrational Frequencies: Scaling Factors for HF, B3LYP, and MP2 Methods in Combination with Correlation Consistent Basis Sets", *J. Phys. Chem. A* **2004**, *108*, 9213-9217.

fluoroallenyl-units on the same side (*Z*-dimer, **22** and **30**, 1,2-bis(allenylidene)-cyclobutane) or on two opposite sides (*E*-dimer, **23** and **31**, 1,3-bis(allenylidene)-cyclobutane) of the ring.

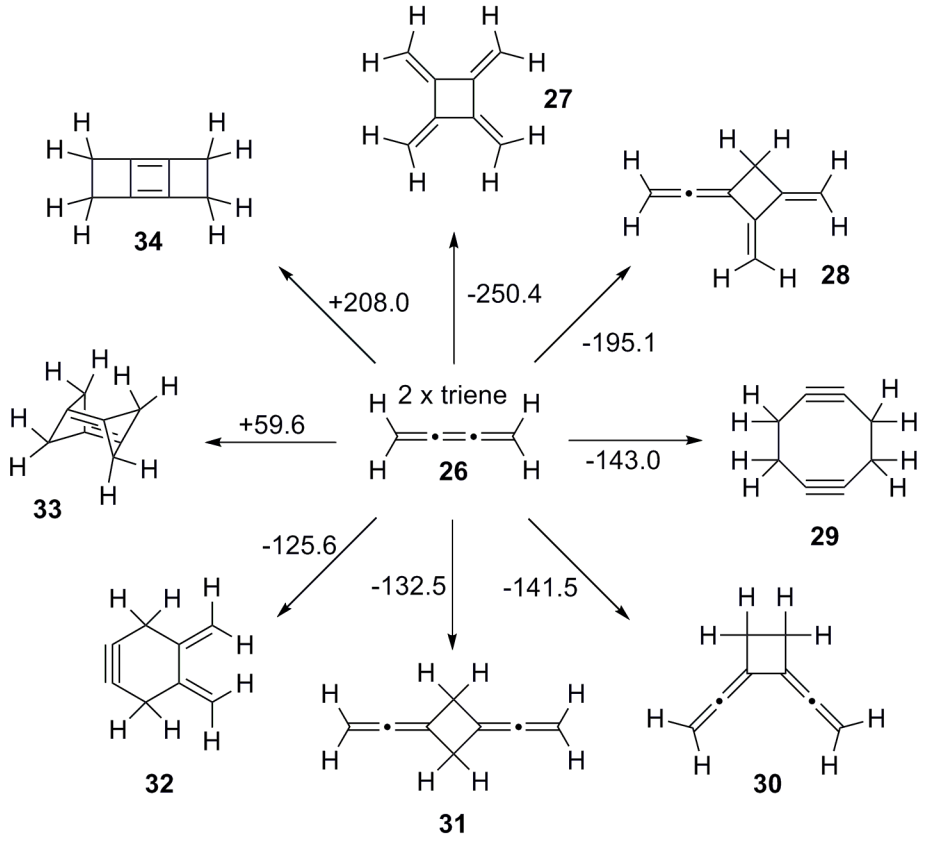
An unsymmetrical cycloaddition on the other hand will produce a head-to-middle-dimer (1,2-bis(methylene)-3-allenylidencyclobutane, **19** and **28**). The possibility of an intramolecular second [2+2]-cycloaddition either simultaneous to the first one or as a second step adds a fifth possible structure which will be further assigned as the "double dimers" **24** and **34**.

Thinking of a formal [4+2]-cycloaddition-reaction (Diels-Alder-type), the reaction product would be a bis(methylene)cyclohexyne, **20** and **32**. A hypothetical second intramolecular Diels-Alder-type reaction produces a "double-topped cyclohexadiene", structures **25** and **33**, clearly a highly unstable compound.

Finally, a potential biradical recombination reaction results in the cyclooctadiynes **21** and **29**, known as the favored dimer[103] of the all-hydrogen butatriene, which was investigated as the eighth and last cyclic dimer. As presented in scheme 2.3.3, six of the potential closed shell dimers are far more stable than the parent perfluorobutatriene, even such an exotic structure like the cyclohexyne structure **20**. The impressive instability of perfluorobutatriene is best displayed by the fact that a cyclobutadiene structure present in the "double-dimer" **24**, i.e. a highly disfavored anti-aromatic cyclic system,[113] is in fact as stable as the triene itself. The most stable dimer is represented in the perfluororinated as well as in the perhydrogen case by the radialene structures **18** and **27**. While it is 334.1 kJ/mol more stable than two triene molecules when the molecules are fully fluorinated, it is only 250.4 kJ/mol more stable if all substituents are hydrogen atoms. In both cases, the molecule exhibits D_{4h}-symmetry with all atoms lying in the same plane.

The geometries of these two and all other structures discussed in this section are shown in figures 2.3.1 (perfluorinated) and 2.3.2 (perhydrogene). In contrast to the perchloro[4]radialene both structures are not puckered.[104,105] The difference in dimerization energies results most likely from the additional destabilization of the triene by fluorine substitution which will be further discussed in chapter 2.4.[114]

113 Bally, T.; "Cyclobutadiene: The Antiaromatic Paradigm?", *Angew. Chem. Int. Ed*. **2006**, 47, 6616-6619.
114 Ehm, C.; Lentz, D.; "Partially Fluorinated Butatrienes: A Coupled Cluster Study", *J. Phys. Chem. A.*, **2010**, DOI:10.1021/jp911213z



Scheme 2.3.4 – Dimerization energies of several butatriene dimers (kJ/mol). (Determined at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory including scaled ZPE correction[112], in clockwise order of increasing energy of formation, most stable isomer in 12-o´clock position.)

Fluorination has a significant effect both on the bond lengths and the angles of the perfluoro[4]radialene (**18**). All C-C bond lengths decrease by fluorination, the cyclobutane bond shrinkage of 0.013 Å represents the major effect. The F-C-F bond angle is reduced by almost 7°. The difluoromethylene unit present in this molecule is also present in the molecules **19** and **20**. In all cases the C-C double bond is approximately 1.33 Å in length while the C-F bond is 1.31 Å in length. The F-C-F bond angle is approximately 111°. This demonstrates that the structure of the rest of the molecule has nearly no influence on the geometry of the difluoromethylene unit.

Interestingly, it was not the thermodynamically most stable dimer that was isolated by *Kloster-Jensen* and *Wirz* from polymerized butatriene but instead the 1,5-cyclooctadiyne **29**.[103] This finding is probably a result of the perfect suitability of the radialene **27** for subsequent Diels-Alder[85,86,87] reactions since all exocyclic double

bonds are *s-cis* configurated. The diyne-dimer was isolated in only 2% yield from a polymeric or oligomeric mixture.

In both cases, the head-to-middle-dimers **19** and **28** represent the second most stable structure. Again, the dimerization energy in the perfluoro case **19** is larger than the dimerization energy of **28** with a difference of 93.0 kJ/mol. The fluorination has major effects on the geometry of the molecule: almost all C-C bonds in the cyclobutane ring of **19** are significantly shorter than in dimer **28** (0.011 to 0.018 Å), both methylene double bonds as well as the terminal allenylidene C-C double bond are also shortened (up to 0.007 Å) and the F-C-F bond angle at the allenylidene group is reduced by 8°. The maximum deviation of the cyclobutane ring angles from 90° decreases from 3.4° in dimer **28** to 2.5° in the perfluorinated dimer **19**. The allenylidene group is also part of the molecules **22** and **23**. The structure of the rest of the molecule has little influence on the allenylidene unit. C-C bond lengths are approximately 1.30 Å to 1.31 Å, C-F bond lengths 1.31 Å. The F-C-F bond angle matches 110° to 111°, similar to the angle in the difluoromethylene unit. Its only the C-C-C bond angle which is indeed slightly influenced. While in dimer **28**, the perfect 180° allenylidene angle is distorted by 1.6° it is nearly not distorted in the molecules **22** and **23**.

The diyne dimer is the third most stable dimer in the perhydrogen case (**29**) and the fourth most stable in the perfluorine case (**21**). It exhibits D_2-symmetry in both cases. The C-C triple bond (1.22 Å) as well as the adjacent single bond (1.47 Å) are nearly unaffected by the fluorination. This subunit also appears in the alkyne dimers **20** and **32** where both bonds are slightly longer by 0.01 Å. Consequently, the sp^3-sp^3 ring bond is affected by fluorination and elongated by 0.013 Å resulting in a bond length of 1.584 Å. This bond length is significantly longer than the typical 1.54 Å for a carbon-carbon single bond. The bond angles in the ring differ only slightly within a maximum of 2°. All dihedral angles are stressed by a maximum of 7°.

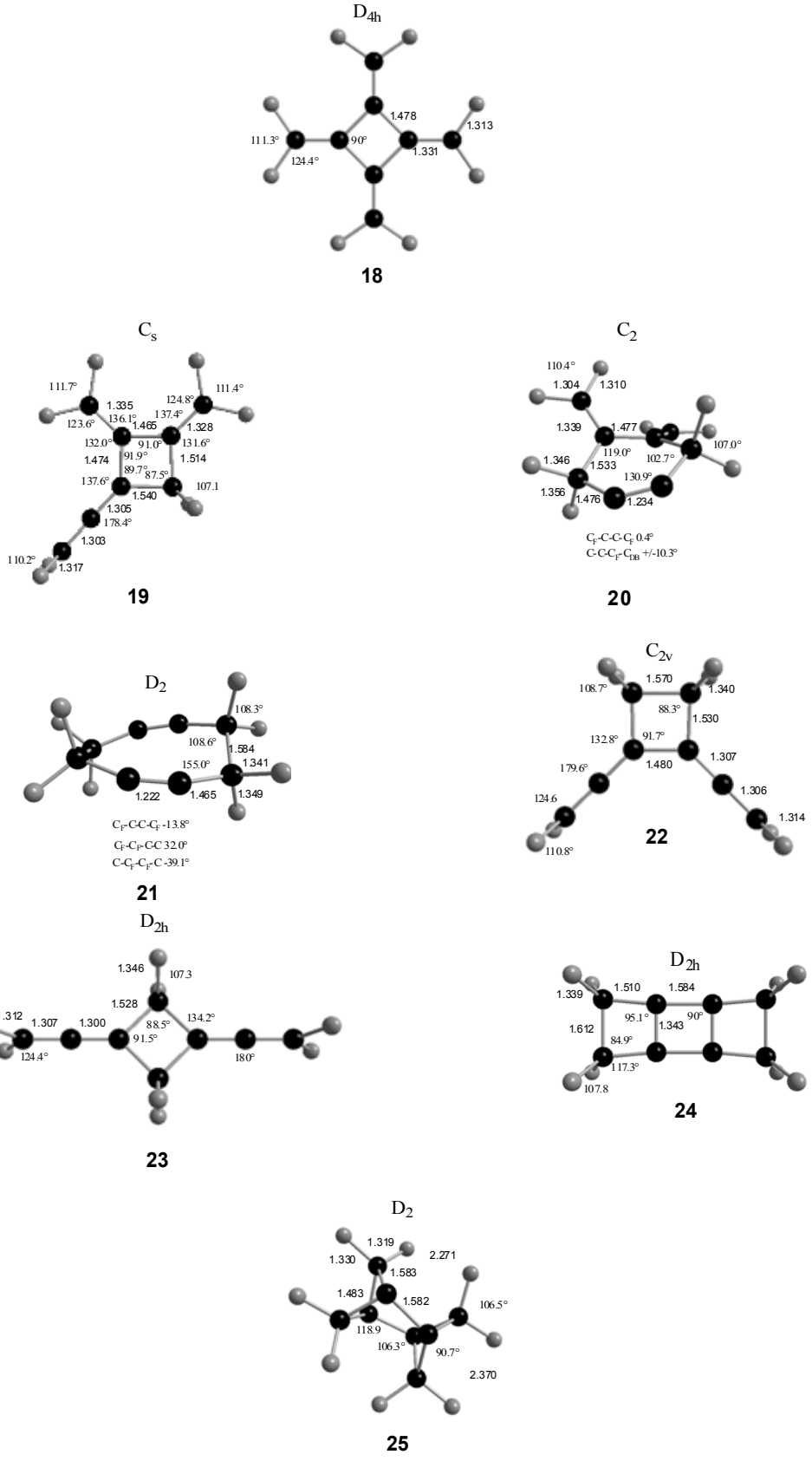


Figure 2.3.1 – Optimized geometries (MP2/cc-pVTZ) of tetrafluorobutatriene dimers. (bond lengths in Å)

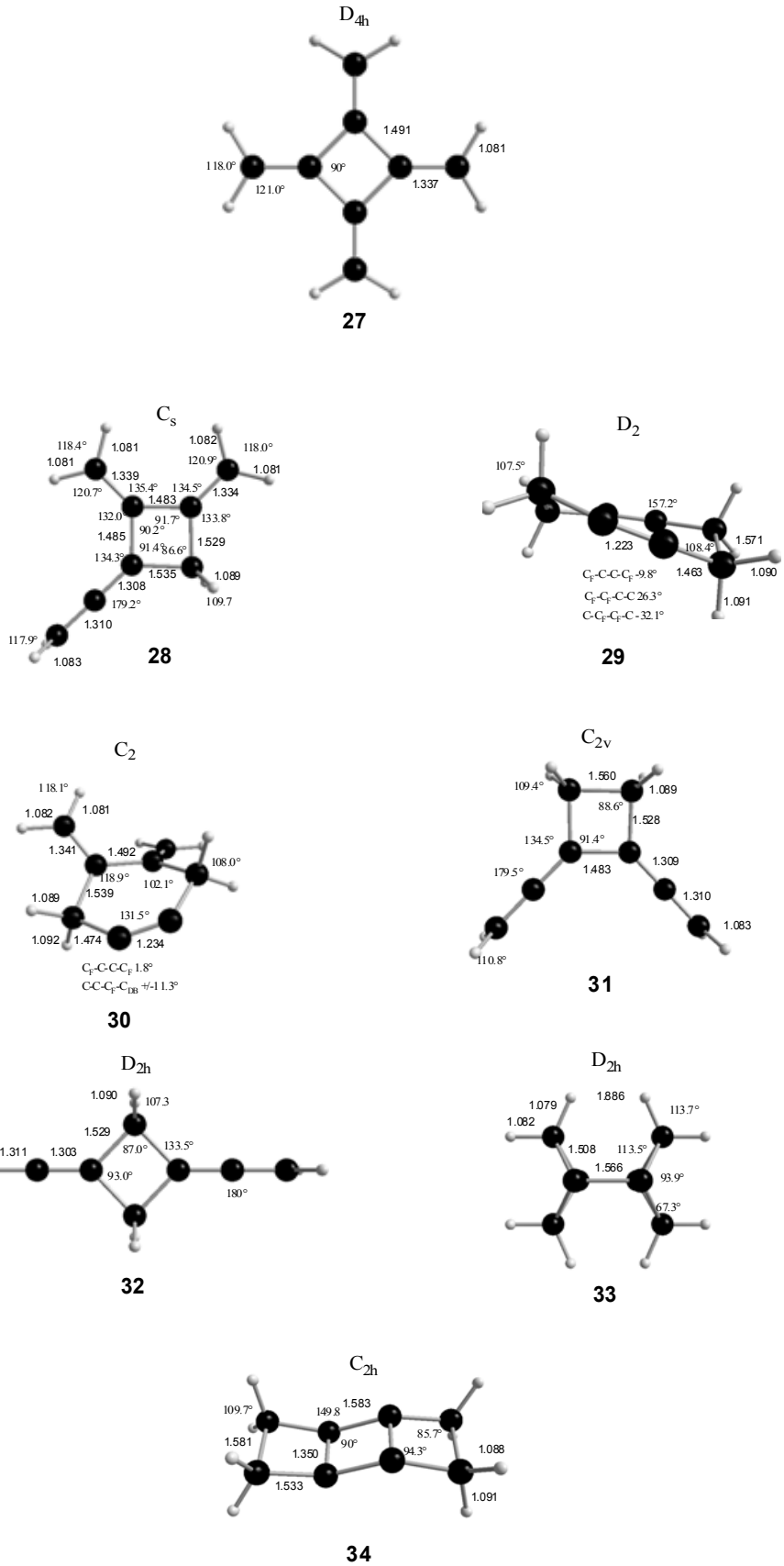


Figure 2.3.2 – Optimized geometries (MP2/cc-pVTZ) of butatriene dimers. (bond lengths in Å)

It is very impressive that the alkyne-dimer **20** in the all fluorine case is more stable than the diyne-dimer **21** (5.8 kJ/mol). On the contrary it is significantly less stable (17.4 kJ/mol) in the perhydrogen case (structures **29** and **32**). Both alkyne dimers have C_2-symmetry. One part of the molecule equals an 1,3-butadiene system similar to half of the radialene structure **18**. This part is in contrast to the radialene distorted by up to 53° in both cases (dihedral C-C-C-C angle). The single bond is shortened in the same manner as in the radialene **18**, while the double bond is significantly less shortened (1.339 Å compared to 1.331 Å in the radialene).

The yne parts of both molecules exhibit equatorial and axial fluorine positions which are not equivalent. The axial fluorine-carbon bond is elongated by 0.01 Å compared to the equatorial one. The sp^2-sp^3 ring bond is elongated by 0.006 Å compared to the perhydrogen dimer **32**. The two remaining C-C bonds (triple bond and adjacent single bond) are again not affected by the fluorination. The same holds true for the angles within the molecule (less than 1° deviation). The only exception is the difluoromethylene angle which is reduced in the same manner as in the radialene **18**.

The *Z*-dimer, structures **22** and **30**, and the *E*-dimer, structures **23** and **31**, represent the last structures where dimerization is thermodynamically preferred. Both dimers are in the perhydrogen case more stable than the alkyne dimer **32**. The *Z*-dimer is more stable in the perfluoro (11.8 kJ/mol) as well as perhydrogen case (9.0 kJ/mol). Most likely this finding results from the fact that the *Z*-dimers possess a conjugated allenic system while the *E*-dimers have isolated allenic subunits. Consequently, a distortion of the central cyclobutane ring results from the conjugation. Regarding the perfluorinated molecules, the *E*-dimer has four identical 1.528 Å sp^2-sp^2 bonds while the *Z*-dimer has two bonds of 1.53 Å, an elongated bond between the two CF_2-groups, 1.57 Å in length and a shortened single bond as part of the conjugated system between the two allenylidene subunits, 1.48 Å in length.
In comparison to octafluoro-1,2-dimethylenecyclobutane **3** – the dimer of tetrafluoroallene – the cyclobutane ring bonds in the related *Z*-dimer are elongated by 0.02 Å. In contrast to that, the bond between the two CF_2-groups is identical in length to the analogous bond in the tetrafluoroallene dimer **3**.[115]

115 Lentz, D.; Patzschke, M.; Bach, A.; Scheins, S.; Luger, P.; "Experimental charge density of octafluoro-1,2-dimethylenecyclobutane: atomic volumes and charges in a perfluorinated hydrocarbon", *Org. Biomol. Chem* .**2003**, *1*, 409-414.

The sp^3-sp^3 ring bond is the only one in the cyclobutane subunit in which the *Z*-dimers **22** and **30** differ noticeably by fluorination. It is elongated by 0.01 Å if the molecule is fully fluorinated. Within the allenylidene subunits, C-C bond lengths differ only slightly. The cumulene bond on the ring side of the molecule is 0.006 to 0.007 Å shorter in the *E*-dimer **23** than in the *Z*-dimer **22**. This shortening is again a consequence of the conjugated allenic system in the *Z*-dimers The bond angles in the cyclobutane ring deviate about 1.5° from the ideal 90° in case in the fluorinated *Z*-dimer **22**, the non-fluorinated *Z*-dimer **30** and the fluorinated *E*-dimer **23**. In the non-fluorinated E-dimer **31**, this deviation doubles to 3°. The allene units are not distorted within the E-dimers **23** and **31** and only slightly distorted within the Z-dimers **22** and **30** by a maximum of 0.5°.

The double-dimer **24** is only slightly destabilized in the perfluorinated case in comparison with two free triene molecules (3.9 kJ/mol). In the perhydrogen case double-dimer **34** this structure is the least stable one, highly destabilized by 208 kJ/mol in respect to two triene molecules. These energy differences again emphasize the additional destabilization of the triene by fluorination.

The perfluorinated molecule **24** has D_{2h}-symmetry and all carbon atoms are in the same plane. On the contrary the perhydrogen dimer **34** has only C_{2h}-symmetry and the outer cyclobutene rings form two different planes, resulting in a C-C-C_H angle of 149.8°. The single bonds of the cyclobutadiene are in both cases identical in length while the double bonds are shortened by fluorination by 0.007 Å. The effect on the bond lengths of the outer cyclobutene rings is even more dramatic. The bond opposite to the double bond is stretched by fluorination by 0.031 Å to 1.612 Å. Furthermore, the C-H bonds are not equal: the *endo* C-H bond is 0.003 Å shorter than the *exo* C-H bond.

The last structures to be discussed in this section are the double capped cyclohexa-1,3-diene **25** and **33**, respectively. They are highly destabilized in both cases. It is 116 kJ/mol less stable than two tetrafluorobutatriene molecules and just the half, 59.6 kJ/mol, compared to two triene molecules. The non-fluorinated molecule has D_{2h}-symmetry which is distorted to D_2-symmetry by fluorination. As a result the two equal bonds within the three-membered rings (1.508 Å) of **33** become inequivalent

(1.583 Å and 1.483 Å) in compound **25**. The central rectangle of the carbon atoms resembles much more a cyclobutane unit than a diene system. The C-C bond lengths are 1.566 Å, 1.671 Å and 1.582 Å, 1.765 Å in compound **33** and **25**, respectively. All fluorine atoms within molecule **25** are in close contact of 2.122 Å to 2.370 Å compared to the double van der Waals radii of 3.0 Å – 3.2 Å of fluorine.[116] The instability of the molecule clearly reflects these distances and distortion.

To study methods and basis set effects, the dimerization energies of tetrafluorobutatriene were not only analyzed by the CCSD(T)/cc-pVTZ level of theory but also by the lower level methods (B3LYP[117,118], B3PW91[119], MP2) and compound methods. The complete basis set methods CBS-4M[120], CBS-Q[121] and CBS-QB3[122] by *Petterson et. al* were chosen and the G3[123] and G3(MP2)[124] methods by *Curtiss* and *Pople*. All these compound methods are complex energy computations involving several to many pre-defined calculations on the specified system. All of these distinct steps are performed automatically and each method has been tested for reliability on a molecule set including up to hundreds of molecules. The CBS models use the known asymptotic convergence of a pair natural expansions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit.[125]

Values are only given for three different dimers in table 2.3.1 and discussed below. The trends for all other dimers are comparable to this small test set.

As expected B3LYP, does not perform well on the given problem as it overestimates the triene stabilization energy, hence underestimating the dimerization energy.[126,127]

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118 Lee, C.; Yang, W.; Parr, R. G.; “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density”, *Phys. Rev.* B **1988**, *37*, 785-789.
119 Perdew, J. P.; Burke, K.; Wang, Y.; “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density”, *Phys. Rev. B* **1996**, *54*, 16533-16539.
120 Ochterski, J. W.; Petterson, G. A.; Frisch, M. J.; Montgomery, J. A. Jr.; “A complete basis set model chemistry. VI. Use of the minimum population localization method”, *J. Chem. Phys.* **2000**, *112*, 6532-6542.
121 Ochterski, J. W.; Petterson, G. A.; Montgomery, J. A. Jr.; “A complete basis set model chemistry. V. Extension to six or more heavy atoms”, *J. Chem. Phys.* **1996**, *104*, 2598-2619.
122 Ochterski, J. W.; Petterson, G. A.; Frisch, M. J.; Montgomery, J. A. Jr.; “A complete basis set model chemistry. VII. Use of density funtional geometries and frequencies”, *J. Chem. Phys.* **1999**, *110*, 2822-2827.
123 Curtiss, L. A.;Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A.; “Gaussian-3 (G3) theory for molecules containing first and second-row atoms”, *J. Chem. Phys.* **1998**, *109*, 7764-7776.
124 Curtiss, L. A.;Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A.; “Gaussian-3 theory using reduced Møller-Plesset order”, *J. Chem. Phys.* **1999**, *110*, 4703-4709.
125 Foresman, J. B.; Frisch, A.; “Exploring Chemistry with Electronic Structure Methods”, 2nd. Ed. **1996** Gaussian, Inc. Pittsburgh.
126 Woodcock, H. L.; Schaefer, H. F. III; Schreiner, P. R.; “Problematic Energy Differences between Cumulenes and Poly-ynes: Does This Point to a Systematic Improvement of Density Functional Theory?”, *J. Phys. Chem. A* **2002**, *106*, 11923-11931.
127 Zhao, Y.; Truhlar, D. G.; “Assessment of Density Functionals for π Systems: Energy Differences between Cumulenes and Poly-ynes; Proton Affinities, Bond Length Alternation, and Torsional Potentials of Conjugated Polyenes; and Proton

To our surprise, CBS-Q does also perform rather poorly. The other compound methods, complete basis set (CBS) and G3 methods, in contrast perform very well. Taking the CCSD(T)/cc-pVTZ calculation as the most reliable value, B3LYP and CBS-Q deviate by up to 20%.

Table 2.3.1 – Dimerization energies (kJ/mol) of perfluorinated butatriene – dependence on theoretical method.

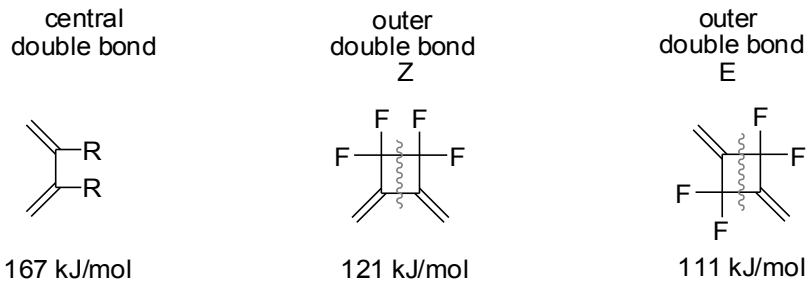
level of theory / basis set	*radialene (18)*	*double dimer (24)*	*Z-dimer (22)*
B3LYP/6-311G(d,p)	-282.2	+121.5	-164.4
B3LYP/6-311++G(3df,3pd)	-269.8	+122.9	-163.4
B3PW91/6-311G(d,p)	-312.5	+64.4	-188.8
MP2/6-311G(d,p)	-359.3	-21.9	-232.8
MP2/cc-pVTZ	-360.3	-25.9	-235.7
CBS-4M	-347.9	-9.5	-230.9
CBS-Q	-274.2	+55.8	-182.7
CBS-QB3	-338.2	-5.5	-228.8
G3	-332.9	+5.7	-225.8
G3(MP2)	-327.1	+7.9	-222.0
CCSD(T)/cc-pVTZ//MP2/cc-pVTZ[a]	-334.1	+3.9	-222.1

[a] includes scaled MP2/cc-pVTZ ZPE correction

In the dimerization reaction of **5** forming the compounds **18**, **19**, **22** and **23** two double bonds are converted into four single bonds. Therefore the relative amount of energy released per double bond during dimerization can be determined (shown in scheme 2.3.5).

As expected, the central double bond releases the highest amount of energy since two cumulenic centers are converted to two vinylic centers. The relative amounts of energy released per bond type are approximately additive.

Affinities of Conjugated Shiff Bases", *J. Phys. Chem. A* **2006**, *110*, 10478-10486.



Scheme 2.3.5 – Dimerization energies released per bond type.

To allow the identification of the discussed dimers in the complicated mixture which is formed upon thermal decomposition of **5**, ^{19}F-NMR shifts were determined by the gauge-independent atomic orbital (GIAO) method.[128,129,130]

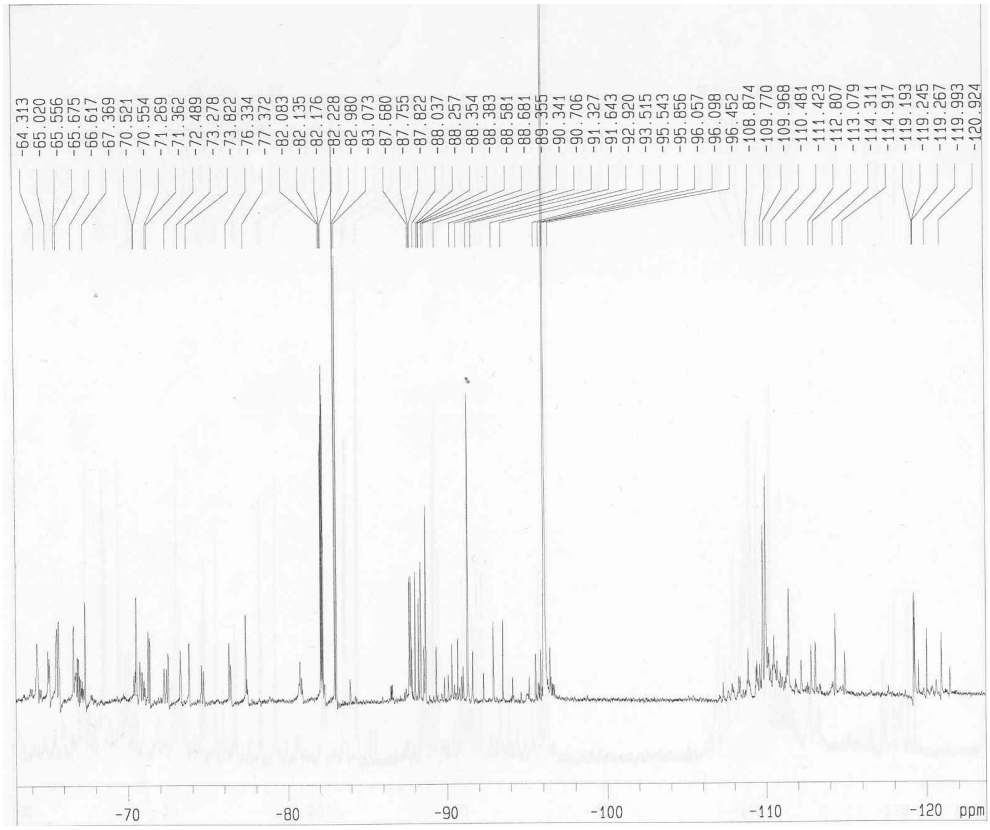


Figure 2.3.3 – Example for ^{19}F-NMR spectrum of freshly polymerized tetrafluorobutatriene. Attempted stabilization of tetrafluorobutatriene by the scavenger hydrochinone in tetrachloromethane.

128 London, F.; "Quantum theory of interatomic currents in aromatic compounds", *J. Phys. Radium* **1937**, *8*, 397-409.
129 Ditchfield, R.; "Self-consistent perturbation theory of diamagnetism. I. A gage-invariant LCAO(linear combination of atomic orbitals) method for NMR chemical shifts", *Mol. Phys.* **1974**, *27*, 789-807.
130 Wolinski, K.; Himton, J. F.; Pulay, P.; "Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations.", *J. Am. Chem. Soc.* **1990**, *112*, 2, 8251-8260.

The calculated shifts are given in table 2.3.2. The ^{19}F-NMR spectrum of freshly, in solution oligomerized tetrafluorobutatriene shows two principal regions (between -60 ppm and -95 ppm and between -105 ppm and -120 ppm) where various signals appear (figure 2.3.3). As mentioned previously it is not possible to dissolve polymerized **5**.

Based on calculations, cyclic dimers exclusively exhibit signals in the ^{19}F-NMR spectrum between -90 ppm and -140 ppm. Possibly linear oligomers derived by radical dimerization are responsible for the observed signals in the -60 ppm to -90 ppm region. Dimerizations of fluorinated double bonds may take place by a radical mechanism rather than a pericyclic mechanism, as recently proven by EPR spectroscopy for the cyclopolymerization of aromatic trifluorovinyl ethers.[131] Nevertheless EPR spectroscopy of a freshly prepared sample of tetrafluorobutatriene did not prove the existence of radical intermediates. Since most of the resulting dimers are themselves highly reactive molecules it is not surprising that no specific dimer could be isolated up to now.

Looking at iron complex **17**, it turns out that it is a partially hydrolyzed complex of the *Z*-dimer **22**. Two coordination sites of the central iron are occupied by the dimer. Whether the dimerization took place before coordination to the metal center or afterwards remains unclear. *Z*-dimer **22** is the only dimer with two allenylidene units presented to the iron atom in a perfect cone angle and that is most likely the reason for its formation. Additionally, the cyclobutane side of the molecule is unreactive in contrast to the other dimers.

131 Mifsud, N.; Mellon, V.; Jin, J.; Topping, C. M.; Echegoyen, L.; Smith, D. W. “First identification of biradicals during thermal [2p + 2p] cyclopolymerization of trifluorovinyl aromatic ethers”, *Polym. Int.* **2007**, *56*, 1142–1146.

Table 2.3.2 – Calculated ^{19}F-NMR chemical shifts of potential cyclic closed-shell dimers.

dimer	*^{19}F-chemical shifts*			
radialene **19**	*-61.6*/**-97.6**			
head-to-middle **20**	*-53.8*/**-89.8**	*-55.9*/**-91.9**	*-73.3*/**-109.3**	*-82.0*/**-118.0**
cyclohexyne **21**	*-54.8*/**-90.8**	*-54.1*/**-93.1**	*-67.9*/**-103.9**	*-80.6*/**-116.6**
diyne **22**	*-80.5*/-**116.5**	*-103.3*/**-139.3**		
Z-dimer **23**	*-75.2*/**-111.2**	*-96.3*/**-132.3**		
E-dimer **24**	*-75.4*/**-111.4**	*-80.8*/**-118.8**		
double-dimer **25**	*-78.1*/**-124.1**			
double-topped cyclohexadiene **26**	*-63.9*/**-99.9**	*-71.0*/**-107.0**		
tetrafluorobutatriene **5**	*-60.1*/**-96.1**			

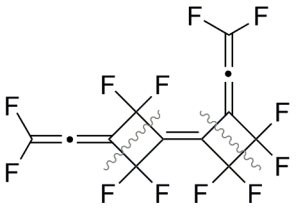
Determined by the GIAO MP2/cc-pVTZ method. Italic numbers indicate the calculated shifts. Bold values indicate calibrated (reference tetrafluorobutatriene) chemical shifts. Calibration was derived by comparison of the calculated/real value for perfluorobutatriene.

2.3.2 Higher Oligomers of Tetrafluorobutatriene – Some Comments on the Constitution of the Tetrafluorobutatriene Polymer

The next question to be answered concerns the fate of the dimers. Notwithstanding the highly destabilized dimers **25** and **26**, the question arises, why none of the six other potential dimers (**19**-**24**) has been isolated so far. Three of these dimers possess highly reactive allenylidene units, three of them possess *s-cis* configurated butadiene units. Both units are potential sites for further reactions leading to an oligomeric or polymeric species. Assuming that most of these dimers are formed, reactions with **5** or any of its dimers yield an almost unlimited number of oligomeric species. This is in good agreement with the observed highly complex ^{19}F-NMR-spectra with hundreds of detectable signals. This assumption also explains the insolubility of the polymer. Random build-up by different oligomerization paths forms a highly branched structure.

NMR-findings indicate that both, cyclic and linear oligomerizations take place. Theoretical calculations on dimers and oligomers are focused on the cyclic derivatives for two reasons: First, an iron complex of a cyclic dimer was isolated and characterized and second, linear polymerizations involve radical (open shell) species for which unrestricted calculations have to be perfomed. This adds additional computational costs especially regarding the size of the discussed systems and possibly the reliability of calculated energies may be questioned.

Scheme 2.3.6 shows the plausible trimers and tetramers **35** - **39**. It is evident that subsequent cycloaddition reactions of these molecules with remaining triene are highly exergonic. Reactions between the dimers are also thermodynamically favorable as indicated by tetramer **39**. Additionally it explains why the reaction does not stop at the dimeric stage but subsequent reactions lead to higher oligomers. Calculations were performed at the MP2/6-311G(d,p) level of theory due to the size of the systems (up to 32 heavy atoms for the tetramers). As shown in table 2.2.1, this theory level performs well on the given problem, only slightly overestimating the oligomerization energy.

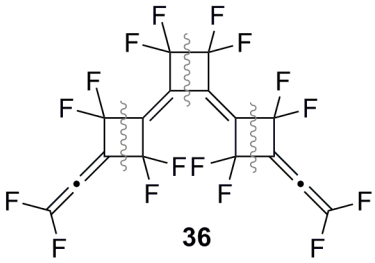


35

-505.5

-242.5 per triene

Z-dimer + triene [2+2]-cycloaddition

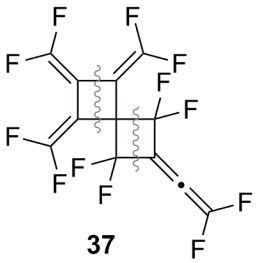


36

-415.8

-263.4 per triene

Z-dimer + 2 trienes [2+2]-cycloaddition

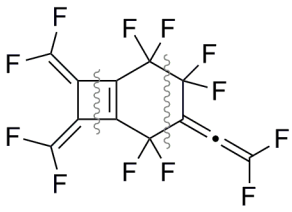


37

-464.9

-269.4 per triene

radialene + triene
[2+2]-cycloaddition

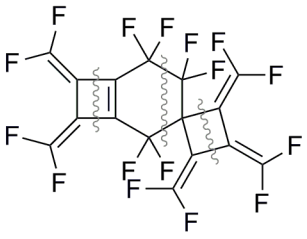


38

-541.5

-294.9 per triene

radialene + triene
[4+2]-cycloaddition



39

-357.3

-260.9 per triene

radialene + radialene
[4+2]-cycloaddition

Scheme 2.3.6 – Oligomerization energies in kJ/mol of possible tetrafluorobutatriene oligomers.
MP2/6-311G(d,p) level of theory including scaled ZPE correction.[112]

2.4 Partially Fluorinated Butatrienes

2.4.1 Partially Fluorinated Butatrienes and their Enyne Isomers – Theoretical Considerations

2.4.1.1 State of the Art

The only known partially fluorinated butatriene, 1,1-difluorobutatriene (**6**) was spectroscopically characterized by low temperature matrix-isolation experiments by *Sander et al.*[78] No other partially fluorinated butatriene did appear in the literature up to now.

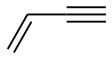
In their work on the singlet C_4H_4 potential energy surface, *Mebel et al.*[132] determined heats of formation of 14 different C_4H_4 isomers including species like tetrahedrane, bicyclobutane and some carbene type species. For this energy surface carbene type species represent highly energetic molecules. This finding was shown by *Sander et al.*[78] to be also true for C_4F_4. Table 2.4.1 illustrates the relative energies of a series of C_4H_4- and C_4F_4-isomers determined by *Wiberg et al.*[133] Interestingly, comparing the relative stability of the fluorinated (C_4F_4) and non-fluorinated (C_4H_4) isomers to the corresponding but-3-en-1-yne isomer, it turns out that full fluorination stabilizes all isomers relative to but-3-en-1-yne. The only exception is the tetrahedrane isomer. Remarkably, full fluorination reverses the relative stabilities between perfluoroenyne and perfluorotriene. In contrast, as shown by *Sander et al.*, 1,1-difluorobutatriene (**6**) does not represent the global energy minimum on the $C_4H_2F_2$ potential energy surface.

This finding prompted the investigation of the effect of fluorination on the relative stabilities of various partially fluorinated trienes compared to their enyne isomers. High level *ab initio* calculations, were performed. Relative energies were determined by the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory.

132 Mebel, A. M.; Kislov, V. V.; Kaiser, R. I.; "Ab initio/Rice-Ramsperger-Kassel-Marcus study of the singlet C4H4 potential energy surface and of the reactions of C2(X 1S g+) with C2H4(X 1A1g) and C(1D) with C3H4 (allene and methylacetylene)", *J. Chem. Phys.* **2006**, *125*, 133113/1-133113/15.

133 Wiberg, K. B.; Marquez, M.; "Effect of Fluorine Substitution on the Energies of Small Ring Compounds", *J. Am. Chem. Soc.* **1998**, *120*, 2932-2938

Table 2.4.1 Calculated relative Energies of C_4H_4 and C_4F_4 Isomers in kJ/mol.[a]

Compound		***C_4H_4***	***C_4F_4***
		MP2/6-311+G*	MP2/6-311+G*
but-3-ene-1-yne		0.0	0.0
butatriene		51.5	-14.7
methylenecyclopropene		108.4	95.9
cyclobuta-1,3-diene		157.4	128.5
tetrahedrane		259.2	455.9
bicyclo[1.1.0]but-1(2)-ene		268	70.3
cyclobutyne		327	186.3

[a] taken from reference 133, chemical structures display the carbon backbone.

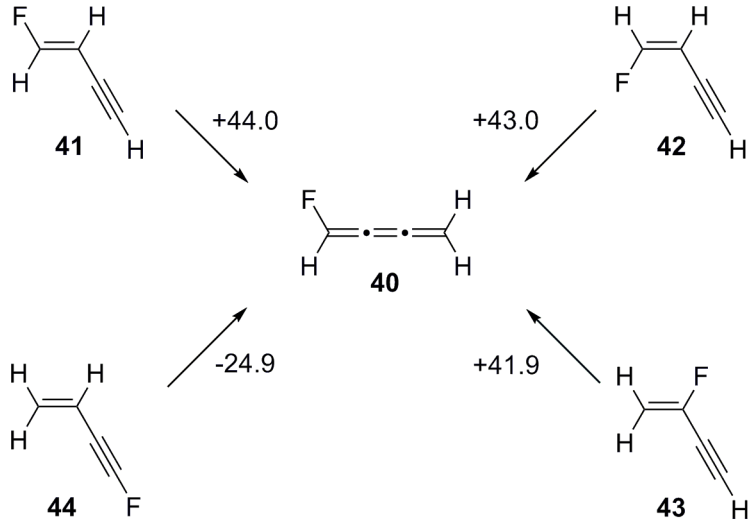
To the best of my knowledge, only perfluorobutatriene[67], butatriene[43] but-1-en-3-yne[134], and 1,1-difluorobut-1-en-3-yne[135] have been synthesized so far. Experimental structures are available for the perfluoro-[73], the non-fluorinated butatriene[136] and the non-fluorinated enyne[137] only. Reliability of the calculated structures was verified by comparison of the calculated structures with related compounds like fluorinated ethylenes[138,139,140], acetylenes[141,142], allenes[143,144,145,146,147] and propenes.[148] The

134 Willstatter, R.; Wirth, T.; "Über Vinyl-acetylen", *Ber. Dtsch. Chem. Ges.* **1913**, *46,* 535-538.
135 E. I. du Pont de Nemours & Co., Pat. GB 809319, **1959**.
136 Almenningen, A.; Bastiansen, O.; Trætterber, M.; "An electron-diffraction investigation of the molecular structure of butatriene", *Acta Chem. Scand.* **1961**, *15*, 1557-1562.
137 Fukuyama, T.; Kuchitsu, K.; Morino, Y.; "Structure of vinylacetylene determined by electron diffraction and spectroscopy", *Bull. Chem. Soc. Jpn.* **1969**, *42*, 379-82.
138 Carlos, C. L. Jr; Karl, R. R. Jr; Bauer, S. H.; "Gas phase electron diffraction study of six fluoroethylenes" *J. Chem. Soc. Faraday Trans. II* **1974**, *70*, 177-187.
139 Mom, V.; Huisman, P. A. G,; Mijlhoff, F. C.; Renes, G. H.; "The molecular structure of trifluoroethene in the gas phase as determined from electron diffraction and microwave data", *J. Mol. Struct.* **1980**, *62*, 95-103.
140 Lentz, D.; Bach, A.; Buschmann, J.; Luger, P.; Messerschmidt, M.; "Crystal and molecular structures and experimentally determined charge densities of fluorinated ethenes", *Chem. Eur. J.* **2004**, *10*, 5059-5066.
141 Tyler, J. K.; Sheridan, J.; "Structural studies of linear molecules by microwave spectroscopy", *Trans. Faraday Soc.* **1963**, *59*, 2661-2770.
142 Bürger, H.; Senzlober, S.; Sommer, S.; "Ground state and equilibrium structure of FCCF from high-resolution IR spectra of F12C13CF", *J. Mol. Spectrosc.* **1994**, *164*, 570-573.
143 Maki, A. G.; Toth, R. A. J.; "Infrared measurements on allene and allene-d4", *J. Mol. Spectrosc.* **1965**, *17*, 136-155.
144 Ogata, T.; Fujii, K.; Yoshikawa, M.; Hirota, F.; "Microwave spectra and substitution structure of fluoroallene", *J. Am. Chem. Soc.* **1987**, *109*, 7639-7641.
145 Durig, J. R.; Li, Y.S.; Tong, C. C.; Zens, A. P.; Ellis, P. D.; "Microwave spectra of 1,3-difluoroallene and fluoroallene", *J. Chem. Phys.* **1975**, *62*, 1311-1313.
146 Ogata, T.; Ando, B.-I.;"Infrared measurements on allene and allene-d4", *J. Mol. Spectrosc.* **1986**, *118*, 70-75.
147 Buschmann, J.; Koritsánsky, T.; Lentz, D.; Luger, P.; Nickelt, N.; Willemsen, S.; "Topological analysis of the experimental electron densities of small organic molecules. 4. Structure and charge density studies on 1,1-difluoroallene and tetrafluoroallene", *Z. Kristallogr.* **2000**, *215*, 487-494.
148 Weiss, V. W.; Beak, P.; Flygare, W. H.; "Barrier studies in the halopropenes. II. Microwave spectra, molecular structure, dipole moment, and the barrier to internal rotation of the methyl group in 1,1-difluoropropene", *J. Chem. Phys.* **1967**, *46*, 981-988.

theoretically determined bond distances are slightly shorter than the experimental values as typical for *ab initio* calculations[149] since: first, all *ab initio* calculations are approximate and second, they refer to vibrationless states at 0 K, whereas all experimental observations are of vibrationally averaged structures.[150]

2.4.1.2 C_4H_3F

Scheme 2.4.1 shows the isomerization energies between the enyne and triene C_4H_3F-isomers. Only a fluorine substitution on the terminal acetylenic sp-centre in **44** destabilizes the system in such a manner that it should thermodynamically favor an isomerization to the triene **40** via *γ*-hydrogen shift.



Scheme 2.4.1 – Calculated relative energies (kJ/mol) of different C_4H_3F isomers. Determined at the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory including scaled ZPE correction[112], in clockwise order of increasing energy of formation, most stable isomer in 10-o´clock position.

This finding is expected since both fluoroacetylene[151,152] and difluoroacetylene[153,154], although synthetically accessible, are dangerously explosive and extraordinarily reactive. Isodesmic reactions predicted they are destabilized relative to acetylene by

149 Dixon, D. A.; Smart, B. E.; "Molecular structures, electronic properties and energetics of fluorinated allenes and isomeric acetylenes", *J. Phys. Chem.* **1989**, *93*, 7772-7780.
150 de Smedt, J.; Vanhouteghem, F.; van Alsenoy, C.; Geise, H. J.; Schäfer, L.; "Empirical corrections of SCF geometries with special examples from 4-21G calculations", *J. Mol. Struct. (Theochem)* **1992**, *259*, 289-305.
151 Middelton, W. J.; Sharkey, W. H.; "Fluoroacetylene", *J. Am. Chem. Soc.* **1959**, *81*, 803-804.
152 Borro, A. F.; Mills, I. M.; "The equilibrium structure of monofluoroacetylene", *J. Mol. Struct* **1994**, *320*, 237-242.
153 Heicklen, J.; Knight, V.; "Difluoroacetylene", *J. Phys. Chem.* **1965**, *69*, 2484-2485.
154 Bürger, H.; Schneider, W.; Sommer, S.; Thiel, W.; "The vibrational spectrum and rotational constants of difluoroethyne (FCCF). Matrix and high resolution infrared studies and ab initio calculations", *J. Phys. Chem.* **1991**, *95*, 5660

57.3 kJ/mol for the former and 169.0 kJ/mol for the latter.[155] This destabilization derives from the preference of fluorine to be bonded to carbon orbitals having high p-character.[156,157,158,] Fluorine has only a relatively weak *π*-stabilizing effect owing to weaker interactions of the low-energy lone-pair fluorine electrons with *π**-type orbitals. *Greenberg* and *Liebman* concluded that in fluoroacetylene the destabilizing *σ* effect (inductive destabilization) dominates over the *π* effect.[159] As expected, different substitution patterns at the vinyl moiety slightly affect the stability of the isomers. The 2-substituted isomer **43** represents the least stable vinylic substituted isomer, 2.1 kJ/mol below the *trans*-isomer **41** with the *cis*-isomer **42** energetically right in the middle of the two. With the *trans* isomer representing the most stable isomer there is no "*cis*-effect" [160,161] in this system as it has been reported recently for 1-fluoropropene[162] and for 1,4-difluorobuta-1,3-diene.[163] *Wiberg* concluded for the 1-fluoropropene that the preference of the *cis*-isomer over the *trans*-isomer is due to Coulombic attractions between the negatively charged fluorine and the positively charged terminal methyl group. This is not the case here, since an actylene substituent may be regarded as negatively charged.

As shown in figure 2.4.1, fluorination has little effect on the geometries of the molecules. Only the F-C-H and the F-C-$C_{acetylene}$ bond angle at the vinylic carbons differ noticeably. They become more acute than in the non-fluorinated structures by up to 5.3°. The perfect linear shape of the carbon skeleton in the non-fluorinated triene (**58**, figure 2.4.4) is distorted by 3.2° on the fluorinated side of **40** and very slightly by 0.8° on the non-fluorinated side. While *Trinquier et al.* and *Goddard et al.* describe the occurrence and extent of this distortion as a result of the singlet-triplet

155 Smart, B.E. in *Molecular Structure and energetics*, Vol. 3 (Eds: J. Liebman, A. Greenberg), VCH Publishers, Inc., Weinheim, **1986**, pp. 170-173. and references therein.
156 Smart, B. E. in *Molecular Structure and energetics*, Vol. 3 (Eds: J. Liebman, A. Greenberg), VCH Publishers, Inc., Weinheim, **1986**, pp. 141.
157 Papprott, G.; Seppelt, K.; "Reactions of 1,2,3,4,5-pentafluorocyclopentadiene", *Chem Ber.* **1988**, *121*, 727-733.
158 Wang, S. Y.; Borden, W.; "Why is the p bond in tetrafluoroethylene weaker than that in ethylene? An ab initio investigation", *J. Am. Chem. Soc.* **1989**, *111*, 7282-7283.
159 Dill, J. D.; Greenberg, A.; Liebman, J. F.; "Substituent effects on strain energies", *J. Am. Chem. Soc.* **1979**, *101*, 6814-26.
160 Kanakaraju, R.; Senthilkumar, K.; Kolandaivel, P.; "Origin of the cis effect – nonbonded intramolecular interactions: quantum chemical studies on 1,2-dihaloethylene molecules", *J. Mol. Struct. (Theochem)* **2002**, *589-590*, 95-102.
161 Craig, N. C.; Entemann, E. A.; "Thermodynamics of cis-trans isomerizations, the 1,2-difluoroethylenes", *J. Am. Chem. Soc.* **1961**, *83*, 3047-3050.
162 Wiberg, K. B.; Wang, Y.; Petersson, G. A.; Bailey, W. F.; "Intramolecular Nonbonded Attractive Interactions: 1-Substituted Propenes", *J. Chem. Theory Comput.* **2009**, *5*, 1033-1037.
163 Hu, H.-R.; Gong, M.-C.; Tian, A.; Wong, N.-B.; "Origin of cis preference among the three isomers of 1,4-difluorobutadiene", *Int. J. Quantum Chem.* **2003**, *91*, 675-684.

separation of the interacting fragments forming the multiple bond.[164,165,166] *Allen et al.* interpreted it on the basis of a second order Jahn-Teller effect.[167]

Regarding the enynes **41 – 44**, the C-C double bond length is marginally shortened by a maximum of 0.008 Å in **43** compared to the non fluorinated isomers. This effect is in the same order as the shortening of the fluorinated C-C triple bond (0.007 Å, **44**) The fluorine influences on the C-C single bond and the C-H bonds are again somewhat smaller, a maximum shortening of 0.006 Å (**42**) for the former and only 0.003 Å for the latter (**43**).

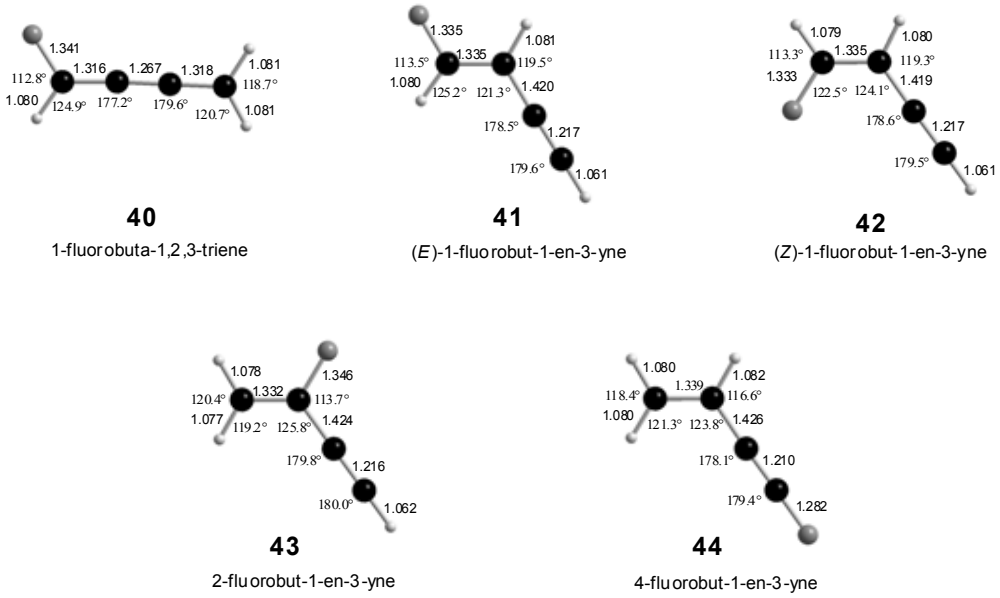


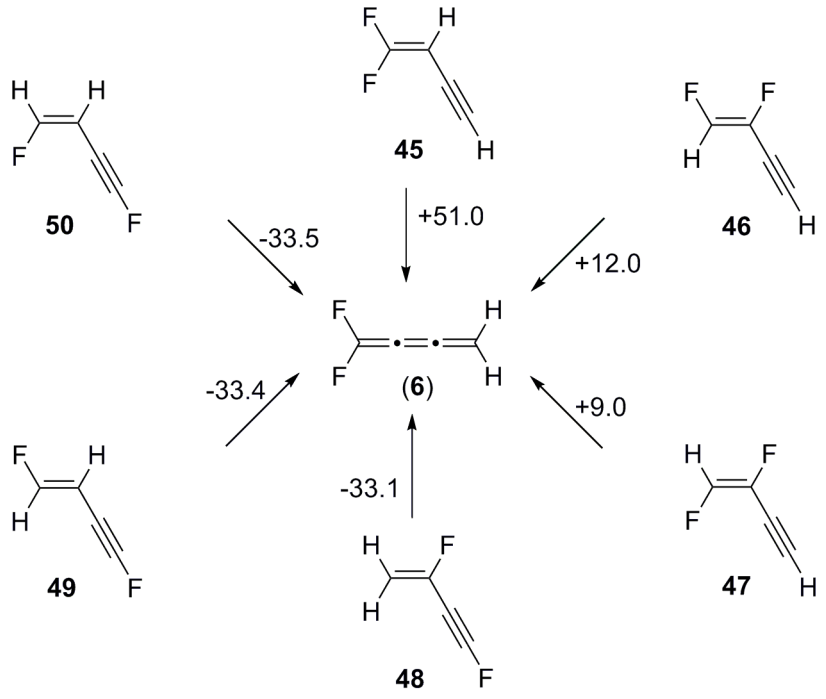
Figure 2.4.1 – Calculated structures of C_4H_3F derivatives. MP2/cc-pVTZ geometries, bond lengths in Å.

164 Trinquier, G.; Malrieu, J.-P.; "Nonclassical distortions at multiple bonds", *J. Am. Chem. Soc.* **1987**, *109*, 5303-5315.
165 Trinquier, G.; Malrieu, J.-P.; "Trans bending at double bonds: scrutiny of various rationales through valence-bond analysis", *J. Phys. Chem.* **1990**, *94*, 6184-6196.
166 Charter, E. A.; Goddard, W.A. III.; "Relation between singlet-triplet gaps and bond energies", *J. Phys. Chem.* **1986**, *90*, 998-1001.
167 Liang, C.; Allen, L. C.; "Double bond deformation: cumulenes, cumulenones, and Group IV ethylene analogs", *J. Am. Chem. Soc.* **1991**, *113*, 1873-1884.

2.4.1.3 $C_4H_2F_2$

As mentioned above, 1,1-difluorobutatriene (**6**) does not represent the global energy minimum regarding the variety of other $C_4H_2F_2$-Isomers. With the introduction of a second fluorine substituent competing fluorine substituent, effects govern the stabilities of the isomers. As introduction of fluorine may act stabilizing or destabilizing, the effects of two fluorines oppose or amplify each other.

As shown in scheme 2.4.2, the geminally substituted enyne **45** represents the by far most stable structure, 51.0 kJ/mol more stable than the triene. This energy difference is substantially more than the 30 kJ/mol reported by *Sander*[78] but the employed B3LYP calculations are known to overestimate the triene stabilization energy.[126,127]



Scheme 2.4.2 – Calculated relative energies (kJ/mol) of different $C_4H_2F_2$ isomers. Determined at the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory including scaled ZPE correction[112], in clockwise order of increasing energy of formation, most stable isomer in 12-o´clock position.

Changing the geminal fluorine substitution at the vinyl moiety to a vicinal substitution leads to a decrease in stability. 1,1-disubstituted ethylenes are in general more stable than either of the 1,2-isomers when the substituents are identical.[168] Irradiation of

168 Bock, C. W.; George, P.; Mains, G. J.; Trachtman, M.; "An ab initio study of the stability of the symmetrical and

difluorobut-3-en-1-ynes substituted at both vinyl carbons, e. g. **46** and **47** may result in a *γ*-fluorine migration. Unfortunately all *γ*-migrations either by fluorine or hydrogen with the exception of a rearrangement of **48** to **6** will result in the formation of a 1,4-disubstituted triene (scheme 2.4.3, **51** and **52**). Both are far more destabilized than the 1,1-disubstituted analogue.

Nevertheless, this decrease makes an isomerization of the enynes **46** and **47** into 1,4-difluorobutatriene thermodynamically more easily accessible. The energy difference declines to a maximum of 44.5 kJ/mol. *Sander et al.* used a wavelength of 193 nm for the isomerization of **45** to **6**.[78] Unfortunately this wavelength is of no practical use for lab synthesis since it does not pass standard glassware. With decreasing difference in thermodynamic stability this rearrangement should be activated at a substantially longer wavelength.

The energy gap between structures **46** and **47** is governed by the so called "*cis* effect". Electron delocalization, in particular halogen lone pair delocalizations into the C-C double bond antibonding orbitals (LP effect), holds responsible for the preference of the *cis*-structure **46** over the *trans*-structure **47**.[169,170,171,172] Compounds that gain their instability from an acetylenic fluorine substituent like structures **48**–**50** will be an interesting synthetic aim for UV-irradiation induced rearrangement. As these compounds are extremely unstable, a spontaneous rearrangement is also possible.

Interestingly, not only the fluorine substituted acetylenic center present in the enyne structures **48**–**50** destabilizes the system in such a manner that the 1,1-difluorobutatriene represents the more stable structure. A non geminal fluorine substitution of the butatriene core present in structures **51** and **52** (scheme 2.4.3) is as destabilizing as the long known effect of fluorine substitution at a sp-carbon center. Both butatrienes represent angle strained butatrienes[173] and the deformation

unsymmetrical difluoroethylenes relative to ethylene and monofluoroethylene", *J. Chem. Soc., Perkin Trans 2* **1979**, 814-821.

169 Yamamoto, T.; Kaneno, D.; Tomoda, S.; "The origin of cis effect in 1,2-dihaloethenes: the quantitative comparison of electron delocalizations and steric exchange repulsions", *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1415-1422.

170 Kanakaraju, R.; Senthilkumar, K.; Kolandaivel, P.; "Origin of the cis effect-nonbonded intramolecular interactions: quantum chemical studies on 1,2-dihaloethylene molecules", *J. Mol. Struct. (Theochem)* **2002**, *95*, 589-590.

171 Cremer, D.; "The role of correlation in calculations on 1,2-difluoroethylenes. The cis-trans energy difference", *Chem. Phys. Lett.* **1981**, *81*, 481-485.

172 Hu, H.-R.; Tian, A. Wong, N.-B.; Li, W. K.; "Theoretical Study on the Low-Energy and High-Energy Conformers of the Three Isomers of 1,4-Difluorobutadiene", *J. Phys. Chem. A* **2001**, *105*, 10372-10378.

173 Daoust, K. J.; Hernandez, S. M.; Konrad, K. M.; Mackie, I. D.; Winstanley, J. Jr.; Johnson, R. P.; "Strain Estimates for Small-Ring Cyclic Allenes and Butatrienes", *J. Org. Chem.* **2006**, *71*, 5708-5714.

of the butatriene carbon chain by more than 2° is likely to be responsible for that as well as fluorine substituent effects now present on two sp^2-carbon-centres.

Comparison of the least stable isomer non fluorinated at the acetylenic center with the most stable isomer fluorinated at the acetylenic center reveals an energy difference of 42.1 kJ/mol. This difference is substantially lower than the energy difference of 66.8 kJ/mol derived from the same comparison regarding the monofluorinated isomers. The introduction of a second fluorine substituent has therefore a stabilizing effect on enynes which are fluorinated at the acetylenic position since the destabilization induced by an acetylenic fluorine is reduced by the introduction of the second fluorine.

A detailed look at the geometries of the various $C_4H_2F_2$ isomers (figure 2.4.2) reveals nearly the same observations as in the case of the monofluorinated molecules. An increasing fluorination does only slightly affect the bond lengths of the carbon chain and the C-H bonds.

Again, the position of the fluorine substitution has only a minor effect on bond lengths. Fluorine substitution at the acetylene moiety results in a marginal shortening of the C-C triple bond by only 0.008 Å. Introduction of a second fluorine substituent at the sp^2 carbon atom results in a further decrease of the F-C-F bond angle to 110.0° and 110.8° in 1,1-difluorobutatriene (**6)** and 1,1-difluoro-1-en-3-yne (**45**), respectively. The H-C-F bond angles range from 113.4° to 115.7°.

The substitution pattern of fluorine at the vinylic positions only affect a CF_2 group. This substitution pattern lowers the C-F bond lengths by 0.02Å (**45**). Consequently, the C-C double bond length shrinks by 0.01 Å in the triene **6**, by 0.008 Å in the enyne **45**. All other substitution patterns lead to a smaller shrinkage of the C-C double bond (0.003 Å in **46** to 0.008 Å in **18**). Only direct fluorination affects the C-C triple bond. Remarkably, only two fluorine substitution patterns affect the distortion of the acetylenic unit which is present in the non fluorinated molecule (1.3°, (**58**), figure 2.4.4). Only the vicinal fluorine substitution present in **46** and **47** enforces the nearly perfect 180° angle at the sp-carbons.

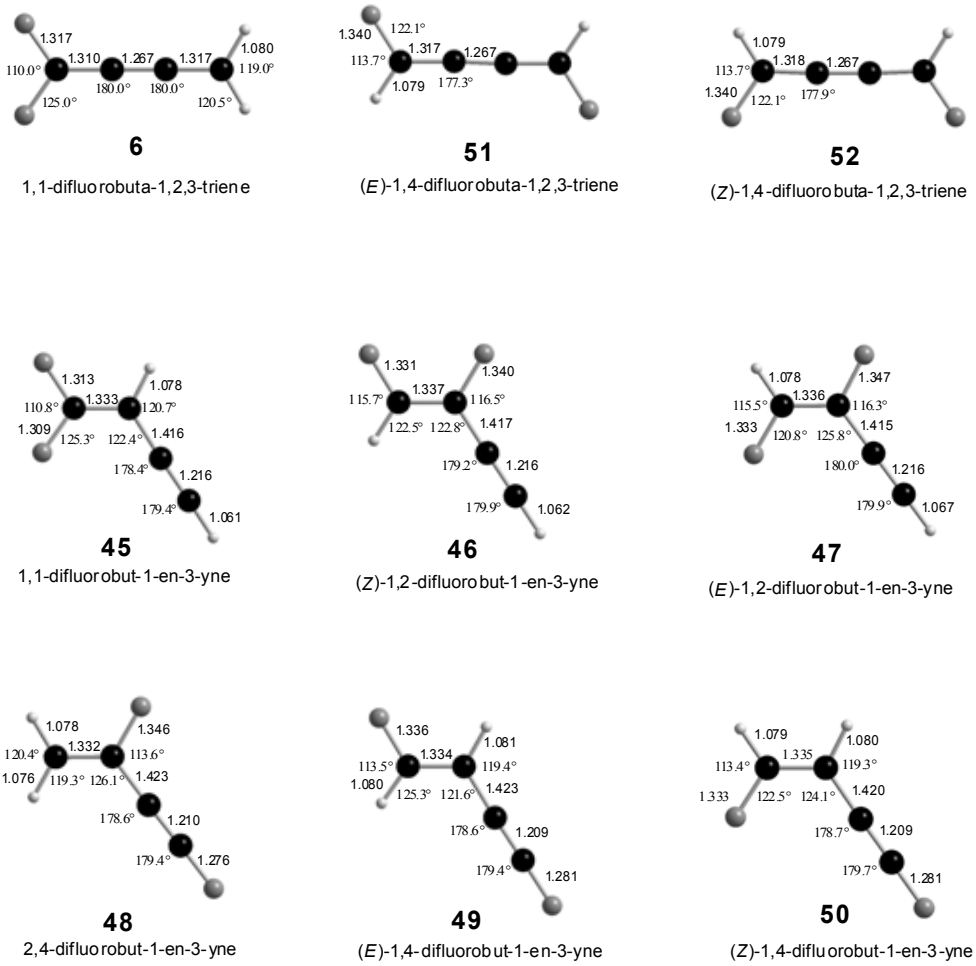
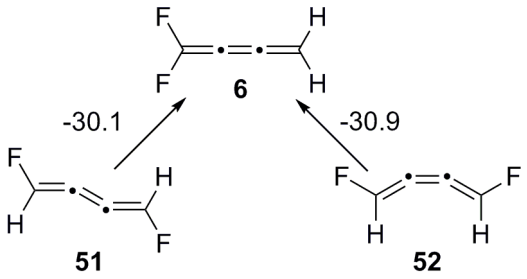


Figure 2.4.2 – Calculated structures of $C_4H_2F_2$ derivatives. MP2/cc-pVTZ geometries, bond lengths in Å.

Regarding the triene structures one is again encountered by a distortion of the cumulenic bonds. While 1,1-difluorbutatriene (**6**) is perfectly linear both other isomers are not. In the *cis* isomer **52** this distortion is somewhat smaller than in the *trans* isomer **51** (2.1° vs. 2.7°). Since the distortion is directed onto the opposite side of the fluorine substituent a “horseshoe” shape results in case of the *cis*-fluorination (**52**) while a *trans*-fluorination (**51**) results in a “serpentine” shape of the triene. Interestingly, it is only th C_F-C-C bond angle that differs in both molecules. All other angles and bond lengths are exactly the same.

The difference in stability between the 1,1-isomer and both 1,4-isomers (scheme 2.4.3) is more than twice as large as the difference between 1,1-difluoroallene and

1,3-difluoroallene.[174] There are two distorted cumulenic centers in 1,4-difluorobutatriene isomers in comparison to one distorted cumulenic center in 1,3-difluoroallene.

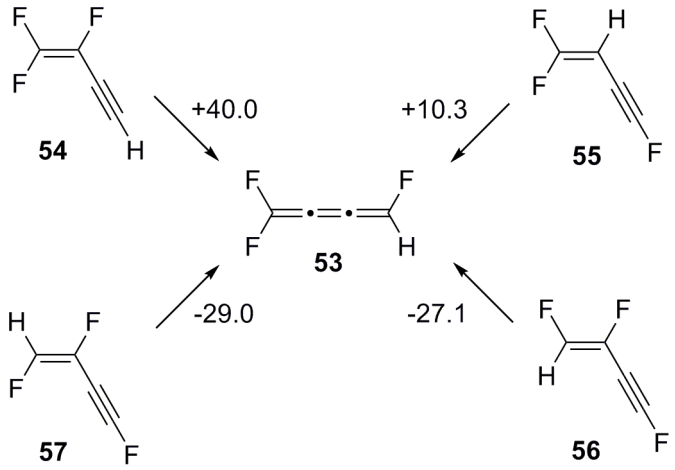


Scheme 2.4.3 – Calculated relative energies (kJ/mol) of the 3 different difluorobutatrienes. Determined at the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory including scaled ZPE correction.[112]

2.4.1.4 C_4HF_3

In the trifluorinated triene and enyne isomers, the situation is completely different. Acetylenic fluorine substitution is not sufficient in all cases to make the triene structure the more stable isomer.

As shown in scheme 2.4.4 enyne **55** with an acetylenic fluorine substituent accompanied by a geminal fluorine substitution pattern at the terminal vinyl carbon is considerably more stable than the triene itself.



Scheme 2.4.4 – Calculated relative energies (kJ/mol) of different C_4HF_3 isomers. Determined at the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory including scaled ZPE correction[112], in clockwise order of increasing energy of formation, most stable isomer in 10-o´clock position.

174 Novak, I.; "An ab Initio Study of the Thermochemistry of Haloallenes", *J. Org. Chem.* **2001**, *66*, 3600-3601.

Only vicinal fluorine substitution at the vinyl carbons (enyne **56** and **57**) leads to a further decrease in stability. This finding is a perfect example for the destabilization of double bonds by this substitution pattern.[174] Conversely, geminal substitution clearly stabilizes the system in isomer **55** similar to the 1,1-difluorobutenyne **45** which shows the biggest difference in thermodynamic stability to its butatriene isomer.

A detailed look at the structures (figure 2.4.3) reveals no further special conspicuity. The triene structure **53** is distorted on the partially fluorinated side of the molecule by 2.4° compared to the monofluorinated butatriene **40**. While **57** displays the most distorted acetylenic angle (2.3°, *cis*-fluorinated) of all enyne structures the same angle is almost undistorted in structure **57** (*trans*-fluorinated). Here, mixed vicinal fluorine substitution leads to a different situation compared to the $C_4H_2F_2$ derivatives. Full fluorination of the vinylic unit leads to the shortest bond length (shrinkage by 0.012 Å) of the neighboring C-C single bond in isomer **54**. Interestingly no other bond length is further shortened compared to the mono or difluoro derivatives. An increasing fluorine substitution does not lead to further bond contraction.

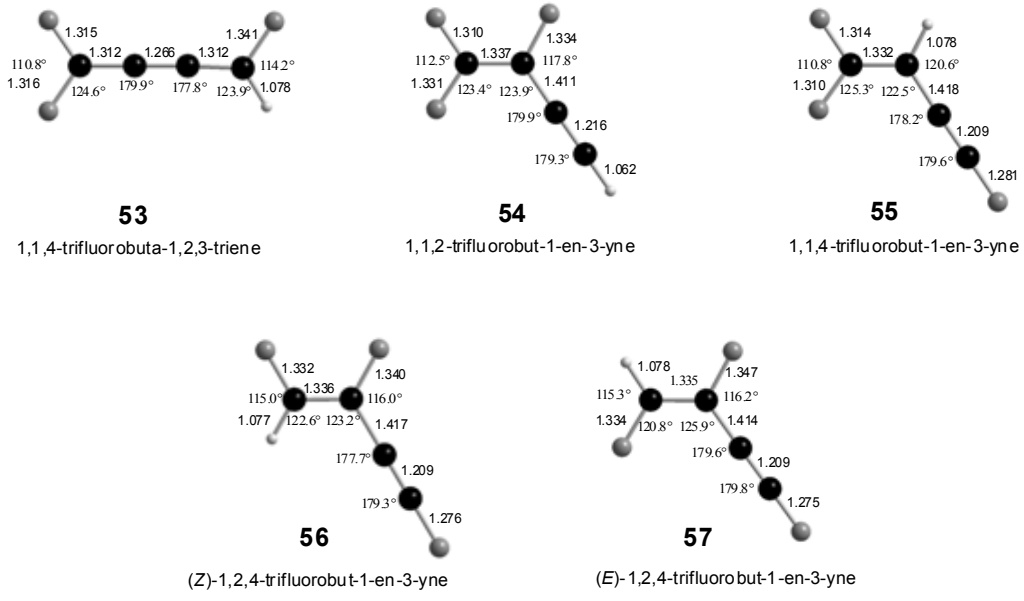
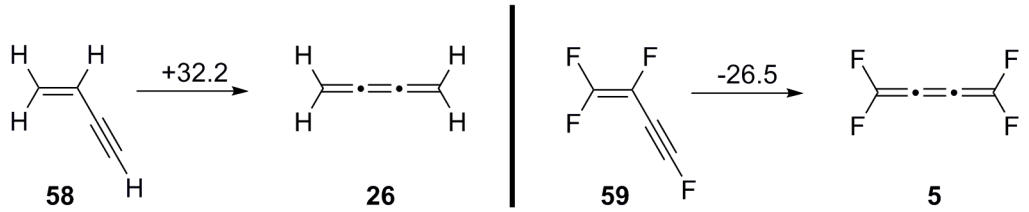


Figure 2.4.3 – Calculated structures of C_4HF_3 derivatives. MP2/cc-pVTZ geometries, bond lengths in Å.

2.4.1.5 C_4H_4 and C_4F_4

As seen in scheme 2.4.5, the relative energies between the enyne and triene isomers for the non fluorinated and the fully fluorinated isomers determined by the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory differ slightly from the B3LYP values obtained by *Wiberg et al.*[133] It is remarkable, that the full fluorination turns the energy difference between both possible isomers upside down. Destabilization of double bonds by full fluorination as well as the unfavorable acetylenic fluorination is most likely responsible for that.

Complete substitution of hydrogen by fluorine has no further effects on the structure. The ene part of the perfluoroenyne (**59**) shows no differences to the 1,1,2-trifluorobutenyne (**54**) while the yne part matches the *(E)*-1,2,4-trifluorobutenyne **57** except for the C-C-C angle which is less acute by 1°.



Scheme 2.4.5 – Calculated relative energies (kJ/mol) of the C4H4 and C4F4 isomers. Determined at the CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory including scaled ZPE correction.[112]

The slight changes in the structure by introduction of fluorine atoms has a substantial effect only on the nearest neighboring atoms. Regarding the triene structure **5**, fluorination marginally shortens the C-C bond lengths by 0.006 Å and 0.005 Å, respectively.

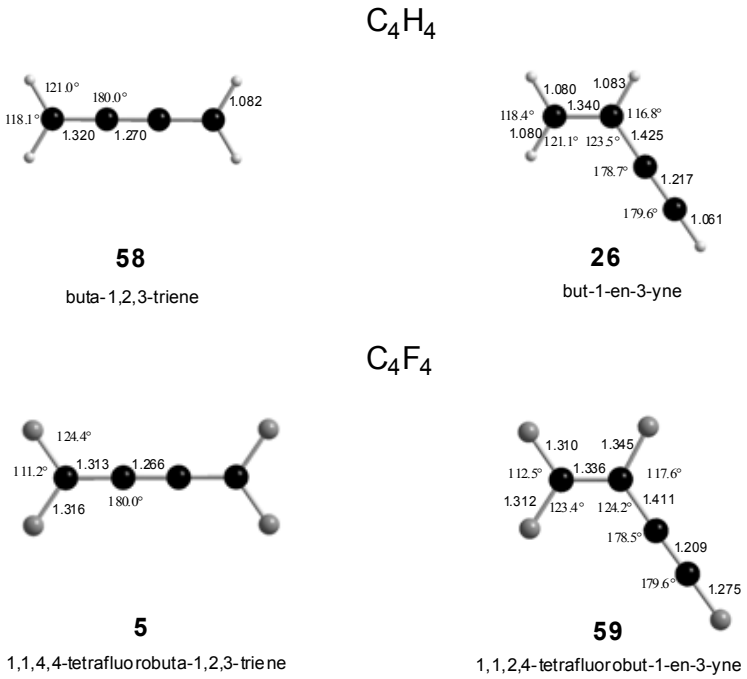


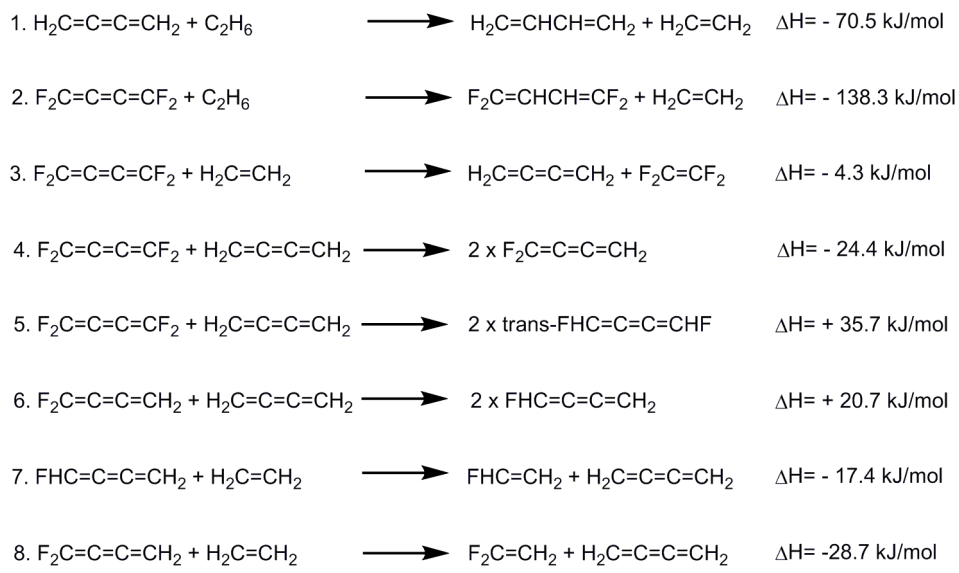
Figure 2.4.4 – Calculated structures of C_4H_4 and C_4F_4 derivatives MP2/cc-pVTZ geometries, bond lengths in Å.

2.4.1.6 Isodesmic Reactions – Stabilization or Destabilization of Tetrafluorobutatriene by Fluorination?

The question arises whether fluorine substitution has a stabilizing or destabilizing effect on butatriene. Isodesmic reactions can quantify the effect of increasing fluorine substitution (scheme 2.4.6).[175] Isodesmic reactions are hypothetical reactions involving a transfer of atoms and/or bonds between two molecules. They give a clear insight in substitution effects. For reliability reasons, these calculations were performed on the same high level as that used for calculating the isomerization energies.

Increasing fluorine substitution destabilizes butatriene. The central double bond is strongly destabilized by 68 kJ/mol in comparison to the non fluorinated butatriene (eq. 1 and 2). The same holds true for the terminal double bonds.

175 IUPAC. Compendium of Chemical Terminology, 2nd ed. Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford.



Scheme 2.4.6 – Isodesmic reactions. Energy differences, CCSD(T)/cc-pVQZ//MP2/cc-pVTZ level of theory, including scaled ZPE correction derived from the MP2 calculation.[112]

In comparison to tetrafluoroethylene, a commonly known, highly unstable molecule, tetrafluorobutatriene (**5**) is further destabilized by 43 kJ/mol (eq. 3). A geminal difluoro substitution is strongly preferred in contrast to a 1,4-difluoro substitution (eq. 4, 5, 6, 7). Both 1,4-difluoro substituted butatrienes are angle strained butatrienes while there is no angle strain in 1,1-difluorobutatriene and monofluoroethylene.The central double bond is destabilized by 29 kJ/mol if the molecule is fully fluorinated on one side (eq. 8).

2.4.1.7 Conclusions

In case of the partially fluorinated butatrienes (in contrast to the fully fluorinated triene) none of them represents the global energy minimum on the isomeric enyne/triene energy potential surface. Therefore, only precursors that cannot form an enyne structure during elimination are reasonable candidates for the synthesis of the desired trienes. Once generated, the trienes themselves will be even less stable than tetrafluorobutatriene.

In principle, enynes bearing an acetylenic fluorine substituent are promising precursors for a γ-hydrogen or γ-fluorine migration since these rearrangements are in most cases thermodynamically favored. But-3-en-1-yne isomers with vinylic fluorine

substituents should be more stable and are therefore interesting targets for isomerization via UV-irradiation. The synthesis of 1,1,2-trifluorobut-1-en-3-yne (**54**) will be of outstanding interest since an UV-irradiation induced rearrangement should be accessible at a wavelength suitable for lab purposes. This rearrangement requires a γ-fluorine migration of which examples are rare up to now.[176,177,178]

Regarding the stability of the different isomers related to the degree of fluorination different trends can be found. The energy difference between the least stable enyne non-fluorinated at the acetylenic center and the most stable enyne fluorinated at the acetylenic center decreases from 66.8 kJ/mol in the monofluorinated system to 29.7 kJ/mol in the triple fluorinated system. The acetylenic fluorine substitution is crucial in raising the energies of fluorinated but-1-en-3-yne relative to their butatriene isomers, which confirms *Greenberg* and *Liebman´s* comment on the sigma destabilization of fluorinated acetylenes. Within the triple fluorinated system and unprecedented for all discussed molecules 1,1,4-trifluoro-but-1-en-3-yne represents the only molecule fluorinated at the acetylenic center which is more stable than its triene isomer.

Fluorination induces only slight effects on the geometries of the molecules in sharp contrast to the dramatic effects on the energies**.**

176 McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Csizmadia, I. G.; "Theoretical structures and stabilities of allyl and 3,3,3-trifluoro-2-propenyl cations", *J. Org. Chem.* **1991**, *56*, 575-580.

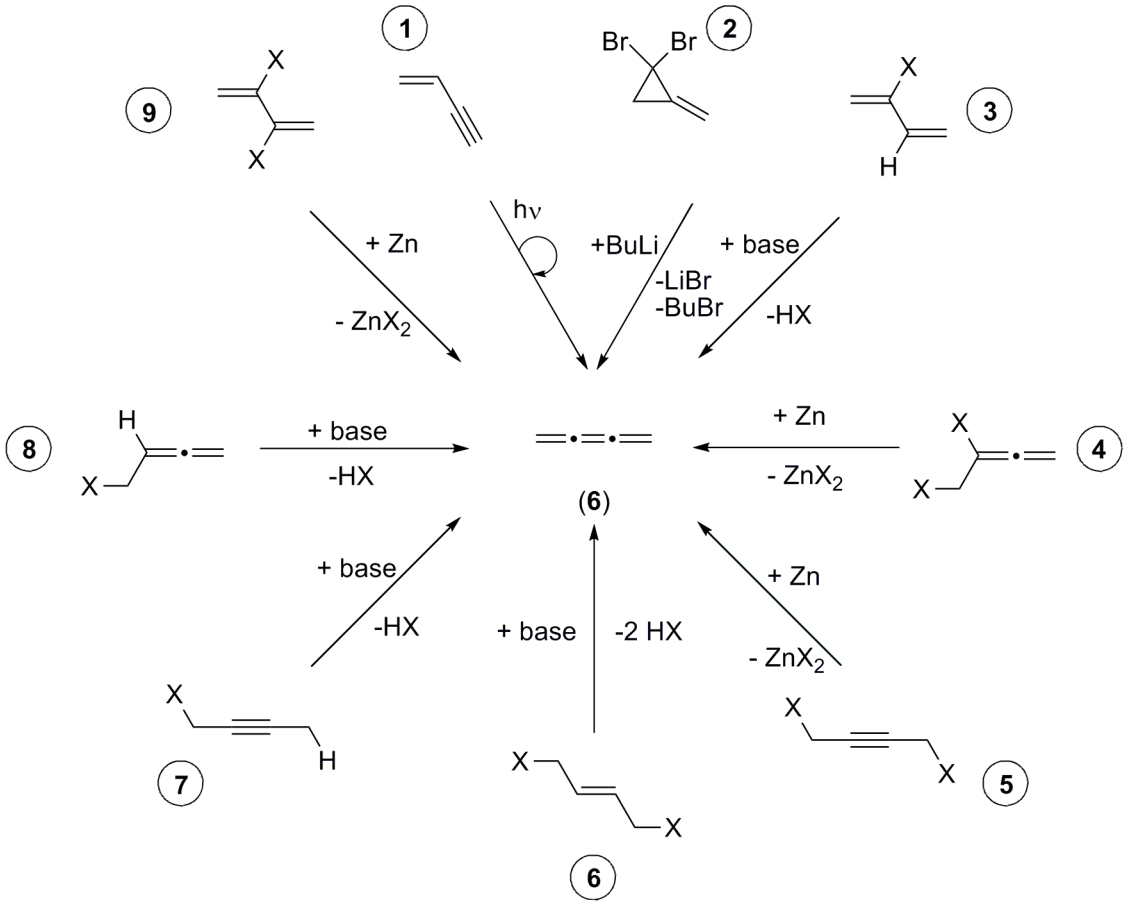
177 Avent, A. G; Taylor, R., "Fluorine takes a hike: remarkable room-temperature rearrangement of the *C*1 isomer of $C_{60}F_{36}$ into the *C*3 isomer via a 1,3-fluorine shift", *Chem. Comm.* **2002**, 2726-2727.

178 Nguyen, V.; Mayer,P. S.; Morton, T. H.; "Intramolecular Fluorine Migration via Four-Member Cyclic Transition States" *J. Org. Chem.* **2000**, *65,* 8032-8040

2.4.2 Partially Fluorinated Butatrienes – Synthetic Strategies

2.4.2.1 Synthetic Strategies for the Synthesis of Butatrienes

As mentioned earlier, only 1,1-difluorobutatriene (**6**) has been prepared so far in matrix-isolation experiments by *Sander et al*.[78] In order to establish a lab scale synthesis of **6** the syntheses of several promising precursors were investigated synthetically. Wherever possible, the potential of these precursors to synthesize the triene was investigated.



Scheme 2.4.7 – Possible strategies for the synthesis of butatrienes. Only carbon backbone and relevant substitution patterns displayed.

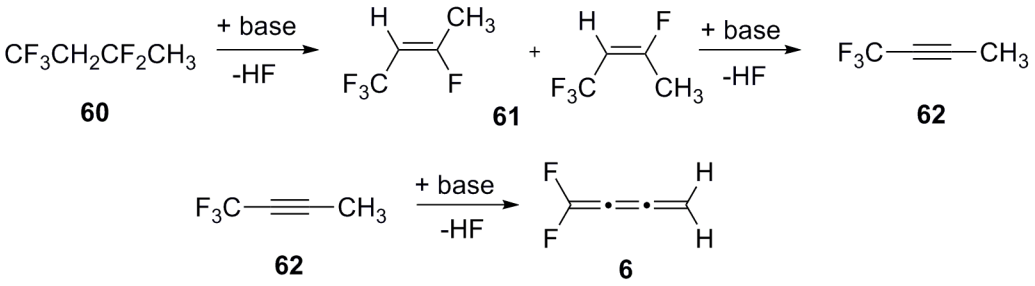
The synthesis of cumulenes is usually achieved by elimination reactions.[179] As depicted in scheme 2.4.7 most of the employed reactions are based on the elimination of either hydrogen halides by treatment with strong bases or dihalide

179 For references please see the detailed description of the syntheses on the following pages (ref. 181-199)

elimination with zinc (strategies 3-9). 1,2- and 1,4-eliminations were examined. One attempt was made to use a rearrangement induced by UV-light for the triene synthesis (strategy 1). Furthermore one attempt was planned to achieve the triene synthesis by a cyclopropane ring-opening reaction with butyllithium but was omitted since the precursor could not be synthesized (strategy 2).

Up to now none of the these reactions is suitable for producing isolable amounts of the triene. Nevertheless, some of them give arguments that the synthesis of **6** is possible and that it has a comparable stability to tetrafluorobutatriene (**5**).

2.4.2.1 Attempted Synthesis of 1,1-Difluorobutatriene by Multiple Hydrogen Fluoride Elimination from 1,1,1,3,3-Pentafluorobutane



Scheme 2.4.8 – Attempted synthesis of 1,1-difluorobutatriene (6) by subsequent elimination of hydrogen fluoride from 1,1,1,3,3-pentafluorobutane (61).

Scheme 2.4.8 shows a potential synthesis of 1,1-difluorobutatriene starting from the commercially available hydrofluorocarbon 1,1,1,3,3-pentafluorobutane (Solkane® 365 mfc[180], **60**). The elimination of two equivalents hydrogen fluoride by strong bases forms 1,1,1-trifluorobut-2-yne (**62**). Further base treatment should result in a third elimination to give the triene **6**. Indeed, the dehydrofluorination takes place but unfortunately the reaction is not controllable. Table 2.4.2 specifies the bases that were used to investigate the elimination and the applied reaction conditions. All bases have in common that if they are capable of eliminate hydrogen fluoride one time the reaction does not stop when the precursor **62** is formed. Dehydrofluorination of the intermediates seems to be preferred and the high reaction temperature (room

180 Registered Trademark of SOLVAY FLOUR GmbH

temperature and above) required for the first two eliminations lead to complex product mixtures. Elimination with *tert*.-butyllithium and *n*-butyllithium show promising ^{19}F-NMR-spectra during the reaction with substantial formation of precursor **62** but after 24 hours at room temperature large amounts of starting material remain.

Table 2.4.2 – Bases applied for the dehydrofluorination of 1,1,1,3,3-pentafluorobutane.

run	*base*	*solvent*	*conditions*	*ratio product/starting material (^{19}F-NMR) butyne:butene(isomers): butane*
1	tri-n-butylamine	THF	130°C, 1h	no reaction
2	tri-ethylamine	THF	RT., 24h	no reaction
3	potassium *tert.*-butoxide	THF	RT, 24h	0:4:3, several unidentified new peaks
4	potassium hydroxide	THF	RT, 24h	0:1:2
5	sodium hydride	THF	RT, 3d	0:1:200
6	lithium diisoproylamide	THF	-78°C up to RT, 16h	1:40:250
7	n-butyllithium	DME	-78°C up to RT, 16h	1:11:46
8	potassium hydroxide	H_2O/THF	RT, 1h	no reaction
9	potassium hydroxide	H_2O/propanol	RT, 30min	butene isomers + KF
10	potassium hydroxide	H_2O/ethanol	80°C, 16h	quantitative formation of KF
11	sodium amide	toluene	RT, 1h	traces of butene and butyne
12	*tert.*-butyllithium	THF	-100°C, 1h	1:14:70
13	*n*-butyllithium	pentane	RT, 16h	9:2:30
14	*n*-butyllithium	pentane	RT, 72h, 5 eq.	75:50:1

Addition of further equivalents of butyllithium does not increase the starting material to product ratio. Instead an “over-elimination” occurs and leads to the formation of lithium fluoride with no fluorinated hydrocarbons remaining in the reaction mixtures. The intermediate formation of 1,1-difluorobutatriene or a polymeric decomposition product could not be observed in the ^{19}F-NMR-spectra.

Workup of run *14* (350 mmol) by three-time fractional condensations over -78°C (product), -110°C and -196°C cooling traps afforded 4.4 g of a mixture containing 750 mg (7 mmol) of the butyne **62**, a small amount of butenes **61** and large amounts

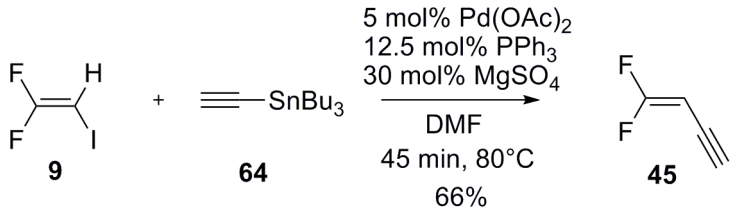
of butane (from *n*-butyllithium) which could not be separated further. Since no trace of the triene was observed during the reactions and the required elimination temperatures are very high no further attempts were made to generate triene **6** by this reaction route.

2.4.2.2 Attempted Synthesis of 1,1-Difluorobutatriene by Rearrangement Reactions of 1,1-Difluorobuta-1-en-3-yne

Sander et. al. reported the synthesis of 1,1-difluorobutatriene (**6**) by laser induced (193 nm) rearrangement of 1,1-difluorobuta-1-en-3-yne (**45**) within an argon matrix.[78] The only other report on **45** is a patent by E. I. Du Pont de Nemours & Co.[181] They claim the synthesis of this compound by pyrolysis of 1-ethynyl-2,2,3,3-tetrafluorocyclobutane and the use of its group I and II metal salts as an additive to fuels for internal-combustion engines and as bactericides.

A new synthesis was developed based on palladium-catalyzed Stille cross-coupling of acetylene-tri-*n*-butylstannane (**64**) with 1,1-difluoro-2-iodo-ethylene (**9**) (scheme 2.4.9).

The crude product was purified by fractional condensation (-78°C and -196°C cooling traps) to give >95% pure **45** according to ^{19}F-, ^{1}H- and ^{13}C-NMR-spectra. Addition of magnesium sulfate[182] to the reaction mixture proved to be useful, under identical conditions a run without magnesium sulfate yielded only 41%.



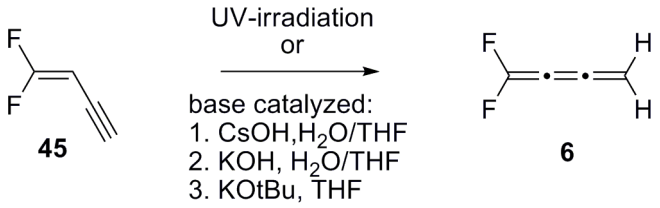
Scheme 2.4.9 – Palladium–catalyzed synthesis of 1,1-difluorobut-1-en-3-yne (45).

An UV-Vis spectrum of the enyne **45** showed bands at 214, 225 and 230 nm and the enyne was therefore subjected to gas phase UV-irradiation but no rearrangement

181 E. I. Du Pont de Nemours & Co., "4,4-difluorobut-3-ene-1-yne and salts thereof" **1959**, GB809319 (A).
182 Farina,V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction,* Wiley & Sons, Inc., New York, 1998.

was observed after 24 hours of irradiation.

A potential base-catalyzed rearrangement[183] of **45** was analyzed by employing reaction conditions according to scheme 2.4.10 but no traces of the triene could be observed. New signals did appear in the ^{19}F-NMR-spectra but none of them in the typical region expected for fluorinated cumulenes. Interestingly, the water phase of the attempted rearrangement by cesium hydroxide in a water/THF mixture (entry 2) showed large amounts of cesium fluoride. It is most likely that base treatment of the enyne results either in fluoride abstraction and therefore substitutions at the CF_2-group or the formation of stable salts of potassium or cesium according to the patent description mentioned above. Although tetrafluorobutatriene is not stable against water at all, it has a considerably long lifetime in a water/organic solvent mixture.



Scheme 2.4.10 – Attempted rearrangement of 1,1-difluorobut-1-en-3-yne 45.

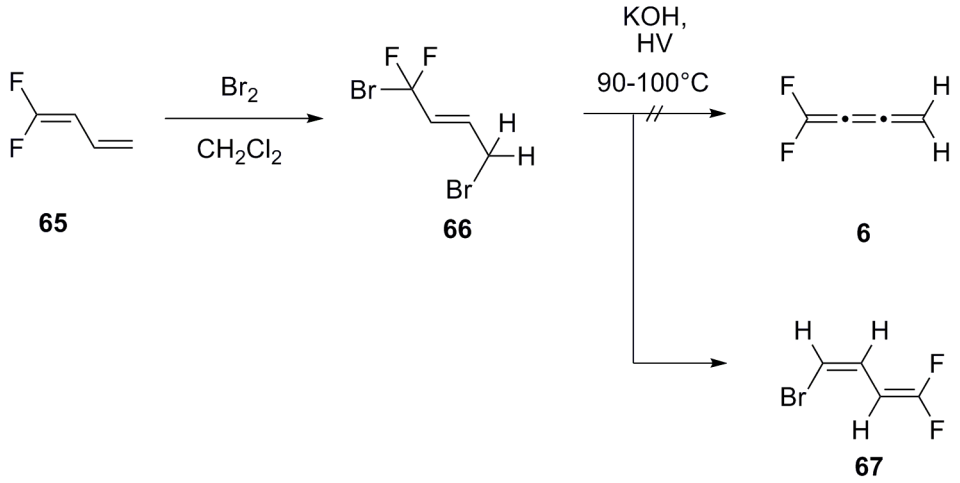
2.4.2.3 Attempted Synthesis of 1,1-Difluorobutatriene by Elimination of Hydrogen Bromide from Suitable Precursors

The experiences gained from the handling and synthesis of tetrafluorobutatriene (**5**) advise a similar synthetic strategy for the synthesis of 1,1-difluorobutatriene (**6**): gas phase hydrogen halide elimination from a suitable precursor and immediate cooling to -196°C.

A reasonable starting point was an analogous synthetic route to the earlier described synthesis of **5** according to scheme 2.4.11. However, the dehydrobromination of **66** gives *Z*-1-bromo-4,4-difluorobutadiene (**67**) but does not proceed further to yield **6**. This finding was earlier described by *Akkerman*.[184] Increasing the temperature from the mentioned 90°C gradually to 100°C did not result in a successful synthesis of **6**.

183 Brandsma, L. "Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques" **2004**, Elsevier Ldt., Oxford p328ff.

184 F. Akkerman; "Mangankomplexe fluorierter Butadiene – auf dem Weg zum 1,1-Difluorbuatrien", Diploma Thesis, Freie Universität Berlin **2003**.



Scheme 2.4.11 – Proposed synthesis of 1,1-difluorobutatriene by a bromination/double dehydrobromination sequence and observed reaction.

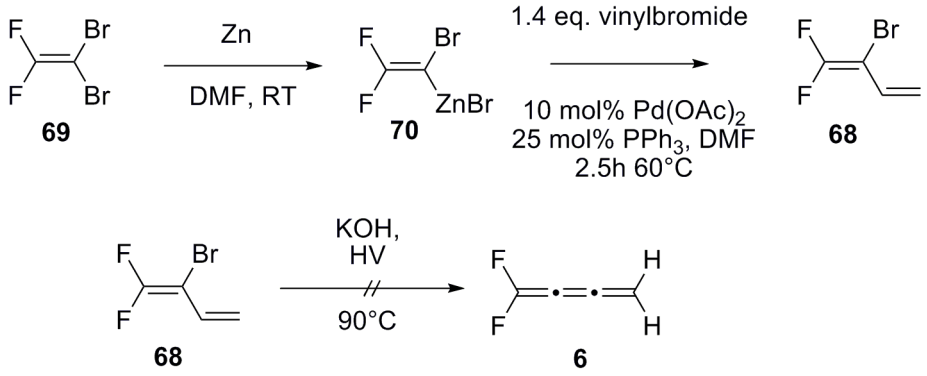
It seemed necessary to use a brominated diene **68** which is only capable of eliminating hydrogen bromide in the desired modality (scheme 2.4.12). Elimination of hydrogen bromide from **68** has to yield **6**, no other product can result. After numerous unsuccessful attempts, it turned out that only Negishi cross-coupling of 1,1-dibromo-2,2-difluoroethene (**69**) with vinylbromide affords isolable yields of the desired diene **68**.

Previous experiments, where 1,1-dibromo-2,2-difluoroethene (**69**) was subjected to cross-coupling reactions with vinylmagnesiumchloride (Grignard reaction[185,186,187]), vinyltri-*n*-butylstannane (Stille-type cross-coupling reaction[188,189]) or vinylzincbromide (Negishi-type cross-coupling reaction[190]) proved unsuccessful. Changing the reaction direction by lithiation of **69** was unsuccessful.

According to *Burton* (1-halo-2,2-difluoro)tributylstannanes are not stable at room

185 Grignard, V.; "Sur quelques nouvelles combinaisons organométaliques du magnésium et leur application à des synthèses d'alcools et d'hydrocabures", *Compt. Rend.* **1900**, *130*, 1322-1325.
186 Nobe, Y; Arayama, K.; Urabe, H.; "Air-Assisted Addition of Grignard Reagents to Olefins. A Simple Protocol for a Three-Component Coupling Process Yielding Alcohols", *J. Am. Chem. Soc.* **2005**, *127*, 18001-18007.
187 Lindsell, W. E. in*Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G.A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, pp 167-169.
188 Milstein, D.; Stille, J. K.; "A general, selective, and facile method for ketone synthesis from acid chlorides and organotin compounds catalyzed by palladium", *J. Am. Chem. Soc.* **1978**, *100*, 3636-3638.
189 Espinet, P.; Echavarren, A.M.; "The Mechanisms of the Stille Reaction", *Angew. Chem. Int. Ed.* **2004**, *43*, 4704-4734.
190 King, A. O.; Okukado, N.; Negishi, E.; "Highly general stereo-, regio-, and chemo-selective synthesis of terminal and internal conjugated enynes by the Pd-catalysed reaction of alkynylzinc reagents with alkenyl halides", *J. Chem. Soc., Chem. Comm.* **1977**, 683-684.

temperature when the halogen is a higher homologue to fluorine.[191] This finding precludes a Stille type cross-coupling using this reagent.



Scheme 2.4.12 – Palladium–catalyzed synthesis of 2-bromo-1,1-difluorobuta-1,3-diene 67 and attempted dehydrobromination.

As mentioned above, it is only the Negishi-type cross-coupling of the mono zinc reagent of **69** with vinylbromide that successfully affords diene **68**. The synthesis of the α-halo-β,β-difluorovinylzinc compounds has previously been reported by *Burton*.[192,193] Since no excess of zinc can be employed in this reaction the zinc dust has to be carefully activated with dilute hydrogen chloride and subsequently washed with ethanol and acetone and finally dried in high vacuum. Furthermore only the finest zinc powder has to be employed to assure complete conversion. An excess of zinc may lead to the incorporation of zinc in both carbon-bromine bonds.

As shown in scheme 2.4.12, it turned out that elimination of hydrogen bromide from **68** over hot potassium hydroxide under high vacuum conditions is not possible. **68** passes the reaction zone unchanged. In contrast to the synthesis of tetrafluorobuatriene (**6**) where hydrogen bromide is eliminated two times, this precursor has to undergo one elimination step thereby forming two cumulenic centers. It is most likely, that the energy released by elimination of one equivalent of hydrogen bromide is not sufficient to build up two highly strained cumulenic centers

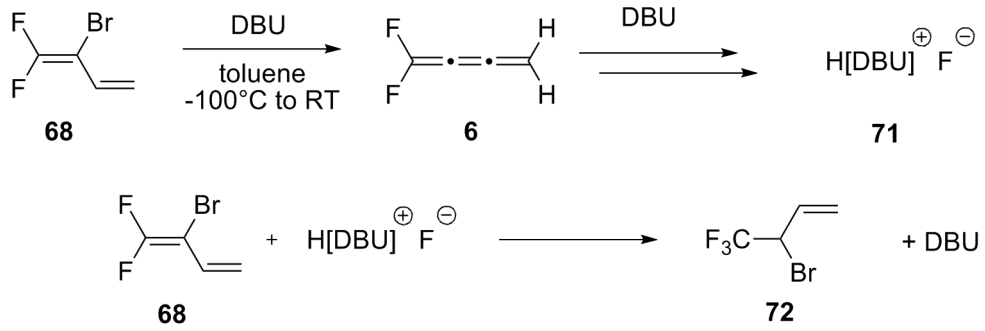
191 Burton, D.J.; Jairaj, V.; "Fluorinated Stannanes Part 2. The Stereospecific Synthesis of Fluorinated Stannanes via Barbier-type Reaction Between Fluorinated Halides and Tributyltin Chloride Mediated by Zinc or Cadmium.", *J. Fluor. Chem.* **2005**, *126*, 797-801.

192 Anilkumar, R.; Burton, D.J.; "Room Temperature Preparation of α-chloro-β,β-difluoroethenylziinc Reagent (F_2C=CClZnCl) by the Metallation of HCFC-133a (CF_3CH2Cl) and a High Yield One-Pot Synthesis of α-chloro-β,β-difluorostyrenes.", *J. Fluor. Chem.* **2005**, *126*, 835-843.

193 Raghavanpillai, A.; Burton, D.J.; "The First Preparation of the α-iodo-β,β-difluorovinylzinc Reagent (F_2C=ClZnCl) and a High Yield One-Pot Synthesis of α-iodo-β,β-diflurostyrenes.", *J. Fluor. Chem.* **2005**, *126*, 457-463.

at a time. The driving force of this reaction is the subsequent conversion of hydrogen bromide into potassium bromide (and hence the release of considerable amounts of lattice energy) and water by the reaction with hot potassium hydroxide.

Since the elimination of hydrogen bromide over hot potassium hydroxide proved unsuccessful, an alternative elimination from **68** in solution by a strong hindered base (DBU) was examined (scheme 2.4.13). The reaction was monitored by ^{19}F-NMR spectroscopy. A new signal at -99.5 ppm was detected close to that where the related tetrafluorobutatriene (**5**) signal appears. This signal vanishes within one hour when the reaction mixture is subjected to room temperature.



Scheme 2.4.13 – Attempted synthesis of 1,1-difluorobutatriene by elimination of hydrogen bromide from 68 by treatment with DBU and formation of unexpected 3-bromo-4,4,4-trifluoro-but-1-ene (72).

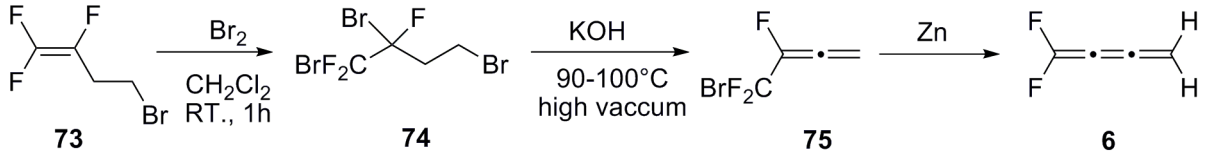
Unfortunately, even at -50°C the predominant signal of 3-bromo-4,4,4-trifluorobut-1-ene **72** is rapidly formed. The elimination may take place and triene **6** is formed but further reaction with DBU leads to defluorination. Since the diene **68** is the only fluorine source in the reaction, it is most likely that DBU-hydrogen fluoride is formed intermediately which then subsequently adds hydrogen fluoride to the remaining diene **68**. This finding is comparable to the hydrofluorination of alkenes by Olah´s reagent (x(HF) • pyridine).[194]

Butene **72** was isolated from the reaction mixture by fractional condensation over two cooling traps, -100°C and -196°C, where the product was collected, and identified by its ^{19}F-, ^{1}H- and ^{13}C-NMR spectra.

194 Olah, G. A.; Nojima, M.; Kerekes, I.; "Synthetic Methods and Reactions II. Hydrofluorination of Alkenes, Cyclopropane and Alkynes with Poly-Hydrogen-Fluoride/Pyridine (Trialkylamine) Reagents", *Synthesis* **1973**, 779-780.

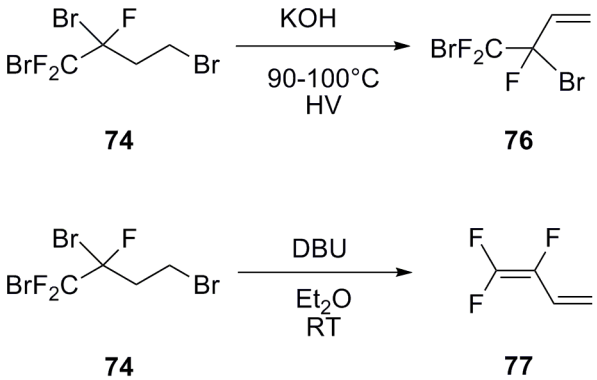
In addition, the elimination was attempted using LDA in pentane. The sample was quickly subjected to a room temperature NMR measurement but no traces of fluorinated compounds could be detected.

Finally, 1,1,2-trifluoro-4-bromo-but-1-ene (**73**) was brominated using bromine in dichloromethane. The reaction product **74** was isolated by fractional condensation over a -30°C trap where the product was collected in excellent yield (95%) and purity (>99%) (scheme 2.4.13).



Scheme 2.4.14 – Proposed mechanism for the synthesis of 1,1-difluorobutatriene by bromination/dehydrobromination of 4-bromo-1,1,2-trifluorobut-1-ene and subsequent elimination of zinc(II)halide.

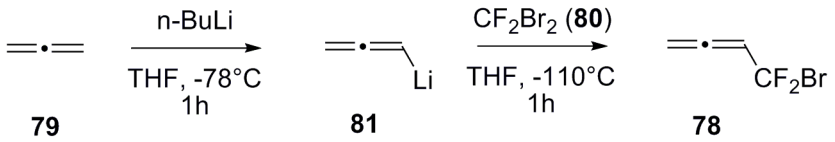
The tribromo compound **74** was then subjected to high vacuum elimination over hot potassium hydroxide. NMR-spectroscopy of the product revealed that only one elimination of hydrogen bromide took place forming butene **76** (scheme 2.4.15). Additionally double hydrogen bromide elimination was attempted by the treatment of **74** with two equivalents DBU in diethylether at room temperature.



Scheme 2.4.15 – Attempted synthesis of 1,1-difluorobutatriene by bromination/ dehydrobromination of 4-bromo-1,1,2-trifluorobut-1-ene (74). Formation of the mono-elimination product (76) and 1,1,2-trifluorobuta-1,3-diene (77) by treatment of 74 with DBU.

Surprisingly, the major product of this reaction is 1,1,2-trifluorobuta-1,3-diene (**77**). The formation of **77** requires the elimination of one equivalent hydrogenbromide and a subsequent debromination. The reasons for this finding still remains unclear but most likely a sequence of addition/elimination reactions involving DBU-hydrogen halides occurs.

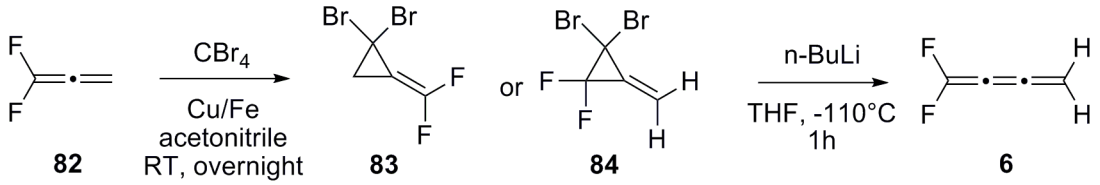
2.4.2.4 Attempted Synthetic Approaches to Potential Precursors of 1,1-Difluorobutatriene



Scheme 2.4.16 – Attempted synthesis of 4-bromo-4,4-difluorobuta-1,2-diene (78).

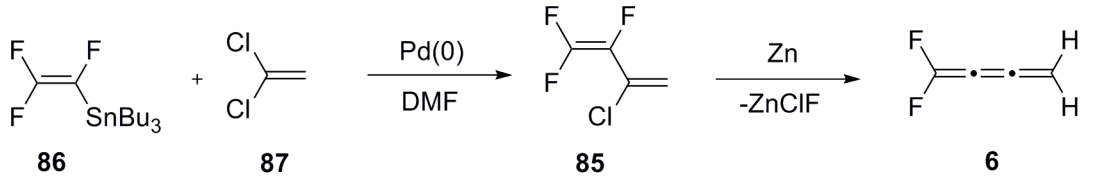
A reaction sequence for the synthesis of bromodifluoromethylallene (**78**) starting from allene (**79**) is depicted in scheme 2.4.16. Hydrogen bromide elimination of **78** could yield **6** with formation of only one cumulenic center. Although trace amounts of the allene **78** could be detected in the ^{19}F-NMR spectrum of the reaction mixture, all attempts failed to obtain a pure product in reasonable yields. Neither lowering the reaction temperature nor changing the solvent to diethylether nor variations of the addition technique of dibromodifluoromethane (**80**) (condensation, pre-cooling, mixing with solvent) did lead to a successful reaction. *Hammond* reported very exothermic reactions when **80** was added to lithiated acetylenes.[195,196] This finding was also observed and may lead to decomposition of the lithiated allene **81** or further reaction of **81** with the product.

195 Wang, Z.; Hammond, G. B.; "A highly efficent synthesis of triisopopylsilyldifluorobromopropyne yields a versatile *gem*-difluoromethylene building block", *Chem. Comm.* **1999**, 2545-2546.
196 Hammond, G. B.; "Nucleophilic and electrophilic substitutions of difluoropropargyl bromides", *J. Fluorine Chem.* **2006**, *127*, 476-488.



Scheme 2.4.17 – Proposed reaction for the synthesis of 1,1-difluorobutatriene (6) by cyclopropanation of 1,1-difluoroallene (82) and subsequent ring opening.

Scheme 2.4.17 shows another potential reaction series which may lead to 1,1-difluorobutatriene (**6**). *Léonel* described the cyclopropanation of nucleophilic olefins using tetrahalomethanes by iron/copper activation.[197] Applying the described reaction conditions to 1,1-difluoroallene (**82**) resulted in no detectable reaction. **82** remained unchanged in the reaction mixture, no traces of the methylcyclopropenes **83** or **84** could be detected. The cyclopropane ring opening by halogen-lithium exchange, subsequent elimination and rearrangement was therefore omitted.[198,199]



Scheme 2.4.18 – Proposed reaction for the synthesis of 1,1-difluorobutatriene (6) by a palladium catalyzed Stille cross coupling of tributyltrifluorovinylstannane and 1,1-dichloroethene and subsequent elimination of zinc(II)halide.

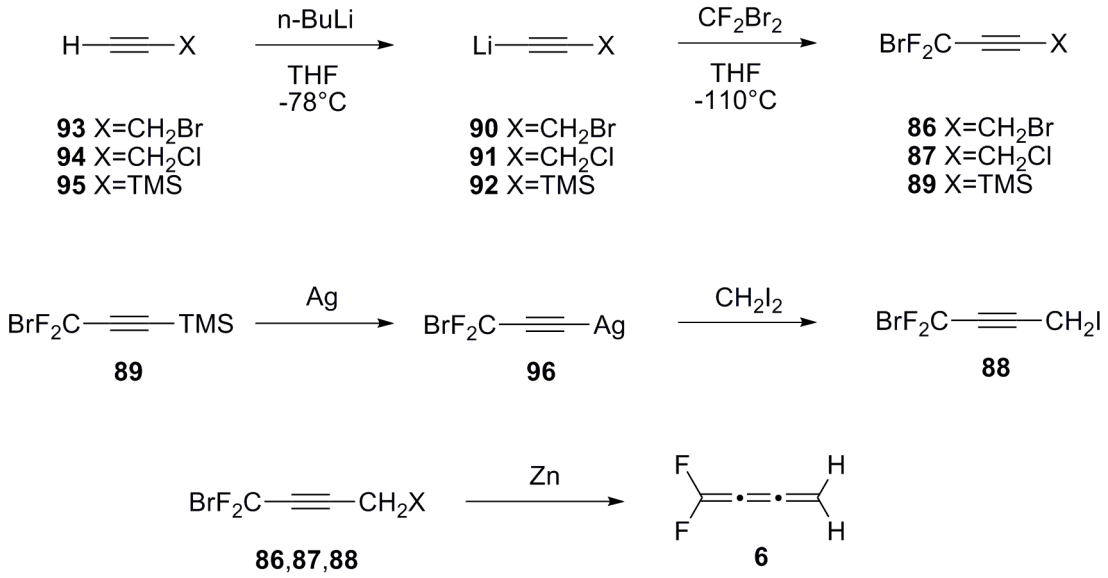
The attempted synthesis of 2-chloro-3,4,4-trifluorobut-1,3-diene (**85**) is depicted in scheme 2.4.18. Trace amounts of the product were detected in the reaction mixture employing palladium acetate/triphenylphosphine as the catalyst system. This reaction would be an interesting goal for optimization. The elimination of one equivalent hydrogen bromide is not sufficient to yield the formation of two cumulenic centers at a time (scheme 2.4.12). It is most likely that similar problems may arise here so no further optimization attempts were made.

197 Leonel, E.; Lejaye, M.; Oudeyer, S.; Paugam, J.-P.; Nedelec, J.-Y.; "gem-Dihalocyclopropane formation by iron/copper activation of tetrahalomethanes in the presence of nucleophilic olefins. Evidence for a carbene pathway", *Tetrahedron Lett.* **2004**, *45*, 2635-2638

198 Santelli-Rouvier, C.; Toupet, L.; Santelli, M.; "Cumulated Trienephosphine Oxides. Bimolecular Trapping of an Alkylidenecyclopylidene", *J. Org. Chem.* **1997**, *62*, 9039-9047.

199 Maercker, A.; Wunderlich, H.; Girreser, U.; "Polylithiumorganic Compounds – 23. 3,4-Dilithio-1,2-butadienes by addition of Lithium Metal to 1,4-unsymmetrically Substituted Butatrienes", *Tetrahedron* **1996**, *52*, 6149-6172.

Finally, numerous attempts were made to develop a synthetic procedure leading to 1,4-dihalo-1,1-difluorobut-2-ynes **86**, **87** and **88** (scheme 2.4.19). The standard precursors in the synthesis of perhydrogen butatriene are 1,4-dibromo-but-2-yne and 1,4-dichloro-but-2-yne which are converted to butatriene by treatment with zinc dust.[200,201] An analogous reaction series for the synthesis of 1,1-difluorobutatriene (**6**) would be of reasonable interest. Initially, the synthesis of 1-bromo-1,1-difluoro-3-trimethylsilylpropyne (**89**) described by *Hammond* could not be reproduced in high yields.[196] Variation of temperature, stirring velocity or method of addition of dibromodifluoromethane (**80**) to the lithiated propynes **90** - **92** did not improve the poor yield significantly.



Scheme 2.4.19 – Proposed synthetic procedure for the synthesis of 1,4-dihalobutynes and subsequent 1,4-dehalogenation.

Hammond describes the addition of precooled dibromodifluoromethane to the lithiated alkyne **92** in THF. Reversing the order, addition of precooled lithiated alkyne to a slight excess of dibromodifluoromethane in THF improved the yield significantly. Applying this procedure a yield of 80% in the synthesis of trimethylsilyl protected propyne **89** could be achieved (10 mmol scale).

200 Schubert, W. M.; Liddicoet, Thomas H.; Lanka, Wayne A; "The action of metals on unsaturated 1,4-dihalides and derivatives. I. Synthesis and some properties of butatriene.", *J. Am. Chem. Soc* **1954**, *76*, 1929-1932.

201 Wille, F.; Dirr, K.; Kerber, H.; "Preparation and properties of 1,4-diiodobutyne; an example of 1,4-addition in butatriene." *Liebigs Ann. Chem.* **1955**, *591,* 177-191.

The next step, the silver promoted cleavage of the trimethylsilyl group[202], did not result in the isolation of the bromodifluoropropenylsilver (**96**). These preliminary results indicate that although silver salts of alkynes are known to be stable even towards water[203] **96** is unstable. Whether this is a result of the fact that **96** possesses a *δ*-bromine atom as well as fluorine atoms in the same position which may lead to an inherent instability or a result of insufficient course of reaction (e.g. traces of light) has to be clarified. The possible silver promoted carbon-carbon bond formation[204] was omitted.

The successful optimization of the described synthetic procedure for **89** may be used along with further optimizations to synthesize butynes **86** and **87** in considerable amounts and high yields.

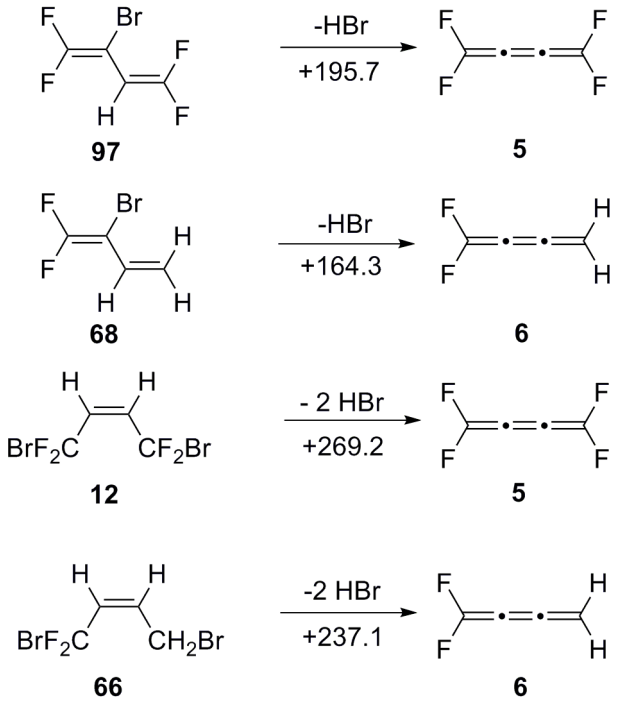
2.4.2.5 Elimination of Hydrogen Halides to Form Cumulenic Centers – Theoretical Considerations

As mentioned earlier, 2-bromo-1,1-difluorobuta-1,3-diene (**68**) fails to eliminate hydrogen bromide and thereby forming two highly strained cumulenic centers. To gain a better understanding of the reasons for this experimental finding, MP2/cc-pVTZ calculations on the energetics of the elimination reactions leading to **5** and **6** were performed.

The elimination of hydrogen bromide from an organic molecule is an endothermic processes since a carbon-carbon double bond is formed. The overall process, the reaction of hydrogen bromide with the employed base and thereby the formation of water and salts and the release of considerable amounts of lattice energy, is exergonic. These amounts of energy are the same for each reaction and according to the principles of thermodynamics it is sufficient to consider only the first part of the reaction sequence.

202 Vitérisi, A.; Orsini, A.; Weibel, J.-M., Pale, P.; “A mild access to silver acetylides from trimethylsilyl acetylenes”, *Tetrahedron Lett.* **2006**, *47*, 2779-2781.
203 Halbes-Letinois, U.; Weibel, J.-M.; Pale, P.; “The organic chemistry of silver acetylides”, *Chem. Soc. Rev.* **2007**, *36*, 759-769.
204 Isabelle, M. E.; Leitch, L. C.“Organic Deuterium Compounds. XIX. Synthesis of Some Deuterated Lauric Acids and Their Methyl Esters”, *Can. J. Chem.* **1958**, *36*, 440-448.

As depicted in scheme 2.4.20 the elimination of hydrogen bromide and the subsequent formation of two cumulenic centers are highly endothermic. As expected, they are more endothermic than the formation of a double bond without formation of a cumulenic center (~84 kJ/mol).[205]



Scheme 2.4.20 – Elimination of hydrogen bromide from different precursors. Reaction enthalpy in kJ/mol, energies determined by MP2/cc-pVTZ level of theory including ZPE correction.[112]

The elimination of two equivalents hydrogen bromide is even more endothermic than the single hydrogen bromide elimination regarding the overall process. In addition it is more endothermic when the target molecule is fully fluorinated. The destabilization of butatrienes by fluorination was pointed out earlier.

Taking these results into account, the synthesis of 1,1-difluorobutatriene (**6**) should be easier than that of 1,1,4,4-tetrafluorobutatriene (**5**). The experimental results indicate the opposite. The elimination of only one equivalent hydrogen bromide requires approximately 50% more energy than the double elimination referred per hydrogen bromide molecule. Most likely this additionally required energy makes the synthesis of **6** starting from **68** impossible. Whether this is also the case in the

205 Lacher, J. R.; Billings, T. J.; Campion, D. E.; Lea, K. R.; Park, J. D.; "Vapor Phase Heats of Formation of the Isomeric Butenes", *J. Am. Chem. Soc.* **1952**, *74*, 5291-5292.

synthesis of **5** from 2-bromo-1,1,4,4-buta-1,3-diene (**90**) remains unclear but it is most likely the case. As pointed out in chapter 2.4.2.6, the successful synthesis of **90** is far from trivial since it involves coupling of two fluorinated C_2 building blocks.

Regarding the double elimination, there is no simple explanation why the synthesis of **6** could not be accomplished. The differences in isomerisation of trienes to their enyne isomers was pointed out earlier. Either only starting material or a complex decomposition mixture was observed when **66** was subjected to elimination over hot potassium hydroxide. This leaves the possibility, that a rearrangement of **6** to **45** followed by the deprotonation of the acetylenic carbon of **45** may take place. The resulting potassium salt would remain on the potassium hydroxide, maybe followed by decomposition. In any way, neither triene **6** nor enyne **45** would be observable.

2.4.2.6 Comments on the Synthesis of Small Fluorinated Molecules by Coupling Reactions Involving Fluorinated Ethylene or Methane Building Blocks

Richard. D. Chambers stated that "*the excitement of the chemistry* [of organofluorine systems] *stems from the unique reactions that ensue and the "special effects" that introduction of fluorine impart"*.[15] Although this short statement already contains all necessary information, some comments shall be made for a better understanding of the difficulties faced working with "simple" and small fluorinated molecules.

Burton observed the formation of $Cd(CF_3)_2$ by treating difluorodibromomethane with cadmium in DMF instead of formation of $Cd(CBrF_2)_2$.[206] This is particularly a result of the favored formation of highly stabilized singulett difluorocarbene.[207] While the fluorinated carbene can be regarded as an actual intermediate, the comparable dihydrocarbene in the Simmons-Smith reaction generated from diiodomethane and zinc represents only a carbenoid species, not a free triplett carbene .[208]

Lithiated organofluorine compounds often exhibit a tendency towards α- or ß-fluoride

206 Burton, D. J.; Wiemers, D. M.; "A Remarkable Simple Preparation of (Trifluoromethyl)cadmium and -zinc Reagents Directly from Difluorodihalomethanes", *J. Am. Chem. Soc.* **1985**, *107*, 5014-5015.
207 Brahms, D. L. S.; Daiely, W. P.; "Fluorinated Carbenes", *Chem. Rev.* **1996**, *96*, 1585-1632.
208 Simmons, H. E. Jr.; Smith, R.D.; "4-Substituted-2,3,5-pyrrolidinetriones", *J. Am. Chem. Soc.* **1958**, *80*,: 3924-3928.

elimination which limits their stability and application.[209] Furthermore, olefin metathesis reactions, although known for hydrocarbons since the early 1970s, and honoured with the nobel prize in 2005 for *Y. Chauvin, R. Grubbs and R. R. Schrock*,[210,211,212] have not been successfully performed using perfluoroalkenes up to now. There is only one example where a Grubbs II catalyst reacts with 1,1-difluoroethylene to give a single turnover and a $Ru=CF_2$ complex.[213] This is most likely a result of the altered characteristics of difluorocarbene metal complexes formed intermediately.

Keeping these examples for the difficulties in organofluorine chemistry in mind, it is no surprise, that during the studies discussed above similar difficulties were observed.

Attempted lithiation of 1,1-dibromo-2,2-difluoroethylene (**69**) results in violent reactions on the surface of the reaction mixture (“little explosions”) even at -110°C. Nevertheless, only the ^{19}F-NMR-signal of the starting material is observable afterwards. Most likely, immediate decomposition with formation of a fluorobromoacetylene occurs. This species is much more reactive towards a halogen-lithium exchange than the starting material and reacts further.

Analogous experiences were made when fluorinated C_1 compounds were employed. Sometimes reactions that were expected to occur did not take place and the starting material remained unchanged.

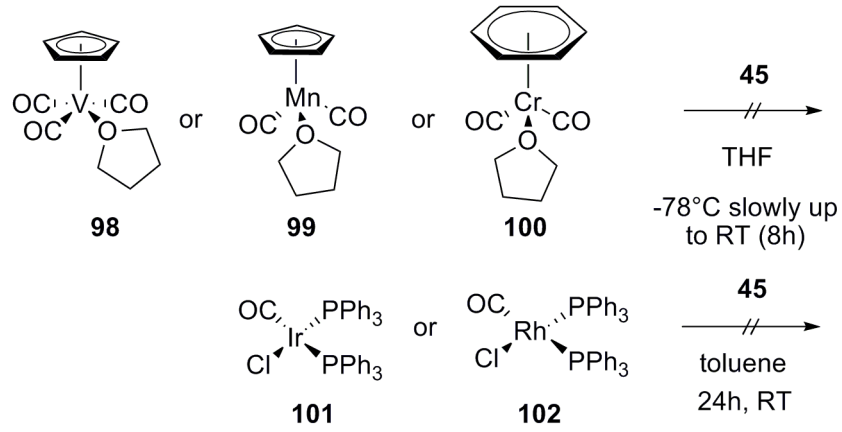
Furthermore, the synthetic routes that were tested commonly involved dichloro, dibromo or diiodo compounds. Frequently, the double functionalization could not be circumvent.

Metal catalyzed cross-coupling reactions turned out to be problematic in general. The successful optimization of the synthesis of **68** took very long and the only possible way is the synthesis described earlier. It is typical for this type of reactions that conditions published to work with certain kinds of starting materials are not

209 See for example: Seyferth, D.; Welch, D. E.; Raab, G.; “The Preparation of Organolithium Compounds by the Transmetalation Reaction. V. Perfluorovinyllithium”, *J. Am. Chem. Soc.* **1962**, *84*, 4266-4269.
210 Chauvin, Y.; “Olefin Methathesis: The Early Days (Nobel Lecture)”, *Angew. Chem. Int. Ed.* **2006**, *45*, 3740-3747.
211 Schrock, R. R.; "Multiple Metal-Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture)", *Angew. Chem. Int. Ed.* **2006**, *45*, 3748-3759.
212 Grubbs, R. H.; "Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials (Nobel Lecture)", *Angew. Chem Int. Ed.* **2006**, 3760-3765.
213 Trnka, T. M.; Day, M. W.; Grubbs, R. H."Olefin Metathesis with 1,1-Difluoroethylene", *Angew. Chem. Int. Ed.* **2001**, *40*, 3441-3444. "

transferrable. Every cross-coupling reaction that was investigated during this work required much effort in optimization.

2.4.2.7 Attempted Synthesis of 1,1-Difluorobut-1-en-3-yne Metal Complexes – Potential Precursors for 1,1-Difluorobutatriene Metal Complexes



Scheme 2.4.21 – Attempted synthesis of 1,1-difluorobut-1-en-3-yne (45) metal complexes.

1,1-Difluorobut-1-en-3-yne **45** was synthesized as depicted in scheme 2.4.9. It was then subjected to reactions with metal complexes that are known to bind to double or triple bonds (scheme 2.4.21). Unfortunately, no reaction was observed with tricarbonyl (η^5-cycloplentadienyl)(tetrahydrofuran)vanadium (**98**),[214] dicarbonyl-(η^5-cycloplentadienyl)(tetrahydrofuran)manganese (**99**),[215] dicarbonyl(η^6-benzene) (tetrahydro-furan)chromium (**100**),[216] and Vaska´s complex (**101**),[217] or its rhodium analog **102**.

214 Hoch, M.; Rehder, D.; "Syntheses with η^5-$C_5H_5V(CO)_3THF$: generation and substitution reactions. First observation of vanadium-51-tin-117, 119 coupling", *J. Organomet. Chem.* **1985**, 288, C25-C29.

215 Nesmeyanov, A. N.; Antonova, A. B.; Kolobova, N. E.; Anisimov, K. N.; "Reaction of the $CpMn(CO)_2$-tetrahydrofuran complex with phenylacetylene.", *Izv. Akad. Nauk, Ser. Khim.* **1974**, *12*, 2873-2874.

216 Alt, H. G.; Engelhardt, H. E.; Filippou, A. C. "Acetylene as a building block for carbene and vinylidene ligands of chromium", *J. of Organomet. Chem.* **1988**, *355*, 139-148.

217 Vaska, L.; DiLuzio, John W.; "Carbonyl and hydrido-carbonyl complexes of iridium by reaction with alcohols-hydrido complexes by reaction with acid", *J. Am. Chem. Soc.* **1961**, *83*, 2784-2785.

2.4.2.8 Conclusions

The problem of developing a successful synthesis for partially fluorinated butatrienes remains still to be solved. It turned out, that the single or multiple elimination of hydrogen halides is rather unpromising. Either elimination of hydrogen halides is unfavorable indicated by the lack of reactivity towards elimination agents or the formed triene is not stable under the applied conditions and cannot be trapped.

Instead, the successful synthesis of a precursor that possesses two halide atoms in 1,4-position and a central triple bond is very promising. The subsequent elimination of both halides under formation of the butatriene carbon backbone by treatment with zinc dust may be successful. Fast removal of the triene by reduced pressure may than lead to isolation of the triene.

2.5 Higher Homologues of Tetrafluorobutatriene – Tetrafluorinated Pentatetraene and Hexapentaene

As mentioned earlier, fluorinated cumules with a carbon backbone longer than 4 carbon atoms are unknown. To clarify the synthetic accessibility of longer fluorinated cumulenes MP2/cc-pVTZ calculations were performed on the C_5F_4 and C_6F_4 potential energy surface. Potential isomers of the cumulenes were restricted to closed-shell acyclic systems (scheme 2.5.1 and figure 2.5.1).

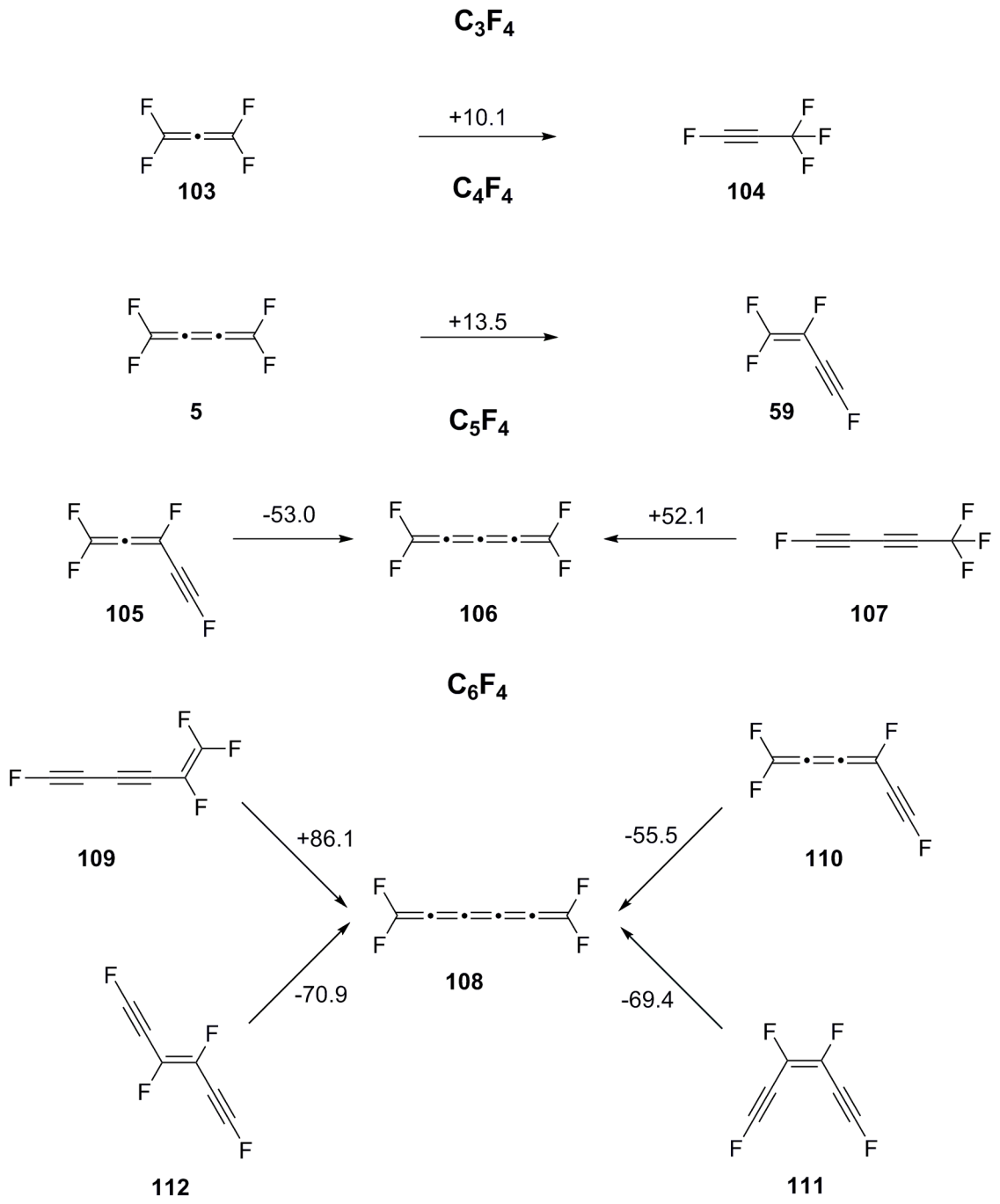
The long known tetrafluoroallene **103** and tetrafluorobutatriene **5** are considerably more stable than their corresponding acyclic closed-shell isomer. The acetylenic fluorine substitution is crucial in raising the energies of fluorinated non cumulenic isomers above their cumulenic isomers due to the sigma destabilization of fluorinated acetylenes (see section 2.4).

Regarding the next two homologues with lengthened carbon skeleton, tetrafluoropentatetrene (**106**) and tetrafluorohexapentaene (**108**), both do not represent the energetic minimum among the possible isomers. While for the C_5F_4 system, there are three possible acyclic closed-shell isomers, there are five non-cyclic closed shell isomers in the C_6F_4 system. Systems with longer cumulene chains will exhibit even more isomers.

The hydrocarbon analogues of **106** and **108** are known for over 30 years and even longer cumulenes have been synthesized (carbon skeleton length of 8 and 10).[218,219] Substituted long cumulenes are known for even longer times, the phenyl stabilized octaheptaene has been synthesized nearly 60 years ago.[220] The hydrogen analogue of the pentatetraene in fact is described as even more stable than its butatriene relative.

In the C_5F_4 case the most stable isomer is represented by the diyne isomer **107**. It is 52.1 kJ/mol more stable than **106** which itself is 53.0 kJ/mol more stable than the allenylacetylene isomer **105**. The diyne **107** is destabilized by an acetylenic fluorine substitution which is opposed by a stabilizing acetylenic CF_3 substitution.

218 Ripol, J. L.; "Synthesis of Pentatetraene by Thermal Decomposition of Vinylallene", *J.C.S. Chem. Comm.* **1976**, 235-236.
219 S. Patai (Ed.); "The Alkenes", Interscience, New York, **1964**.
220 Kuhn, H.; Zahn, H.; "Über Kumulene; Oktahepatene", *Chem. Ber.* **1951**, *84*, 566-570.



Scheme 2.5.1 – Calculated relative energies (kJ/mol) of the C_xF_4-isomers (x = 3-6).

The allenylacetylene **105** is also destabilized by an acetylenic fluorination and further destabilized by a triple fluorination of the cumulated double bonds.

In the C_6F_4 case the by far the most stable isomer is represented by a vinyldiyne structure (**109**) which is 86.1 kJ/mol more stable than the tetrafluorohexapentaene

isomer **108**. Three other isomers are considerably less stable than the hexapentaene (**110**-**112**). While the acetylenic substituted triene **110** exhibits cumulenic fluorine as well as acetylenic fluorine destabilization, the other two isomers **111** and **112** possess two fluorinated acetylenenic units which destabilize them so that they represent the least stable isomers. The *cis*-isomer **111** is slightly more stable than the *trans*-isomer **112**, again triggered by the *cis*-effect.

The additional bonds introduced by lengthening of the cumulenic carbon chain increase resemblance. In case of tetrafluoropentatetraene (**106**) the fluorinated double bonds are shortened by 0.004 Å to 1.309 Å while the central double bonds lengthen by 0.008 Å to 1.274 Å compared to tetrafluorobutatriene (**5**).

In contrast, in the case of tetrafluorohexapentaene (**108**) the fluorinated double bonds are lengthened by 0.002 Å to 1.315 Å but the central double bonds are much more similar to each other (central bond 1.290 Å, adjacent bond 1.269 Å). *Burk et al*. observed no substantial alternation in C-C bond lengths and a rapid decrease to the asymptotic limit as the number of carbons in the chain increase regarding perhydrogen cumulenes.[221] They also observed only a small end-effect (both external C-C double bonds differ from the inner bonds). The same is supposed to happen when the molecules are fluorinated, as indicated by the development in the carbon length range 3-6.

The synthetic accessibility of perfluorinated pentatetraene **106** and hexapentaene **108** is hampered by the existence of more stable isomers in both cases. The difference in stabilities is even larger than the value between 1,1-difluorobut-1-en-3-yne (**45**) and 1,1-difluorobutatriene (**6**). This is a sincere limitation and a clear challenge for a successful synthesis.

221 Mölder, U.; Burk, P.; Koppel, I. A.; “Quantum chemical calculations of linear cumulene chains”, *J. Mol. Struct.* **2004**, *712*, 81-89.

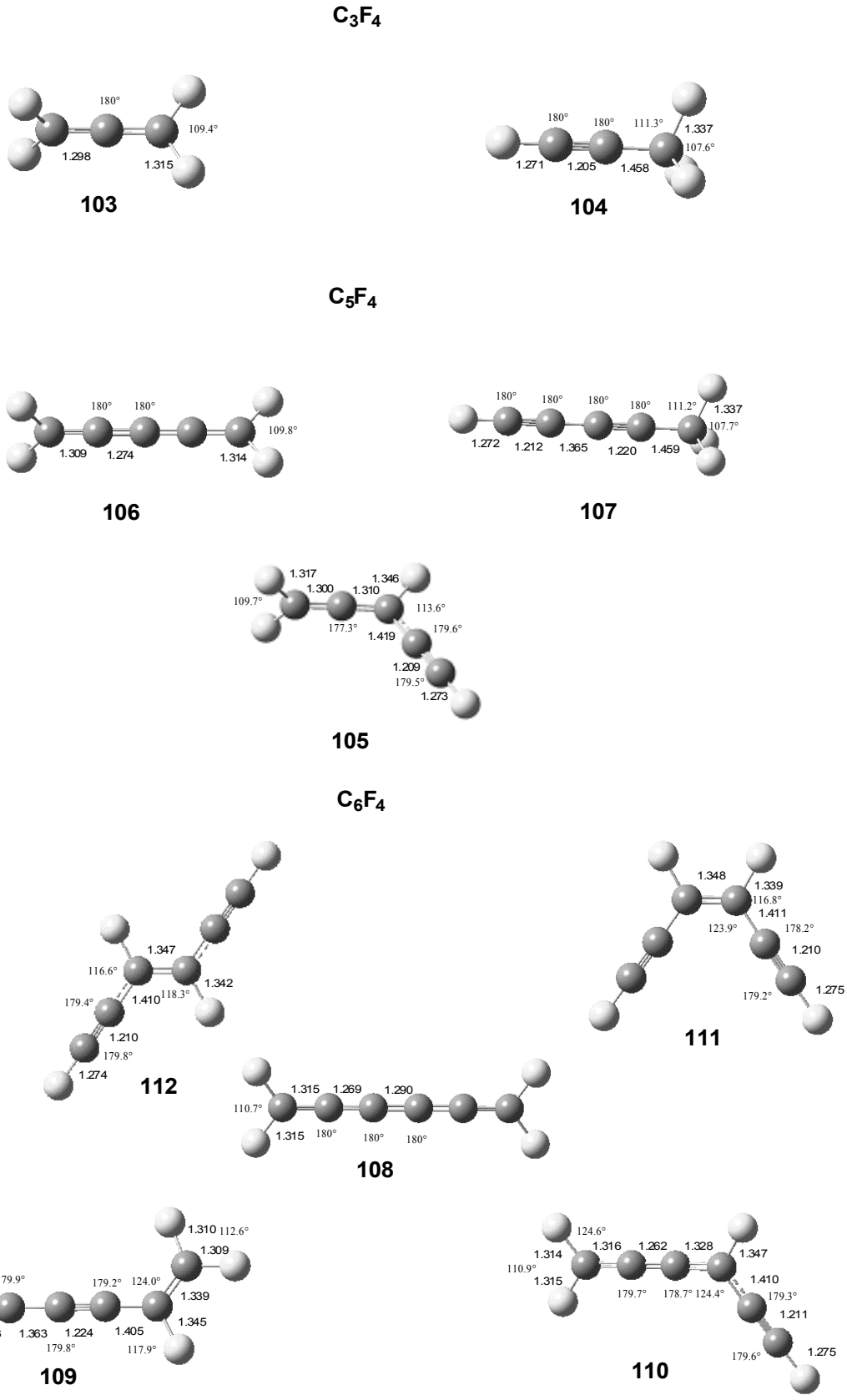
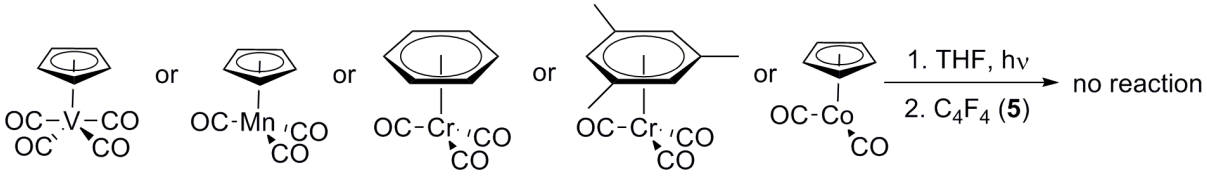


Figure 2.5.1 – Optimized geometries (MP2/cc-pVTZ) of C_3F_4, C_5F_4 and C_6F_4 isomers. Bond lengths in Å.

2.6 Attempted Syntheses of Tetrafluorobutatriene Transition Metal Complexes – Considerations on the Instability of Tetrafluorobutatriene

As mentioned earlier, only three tetrafluorobutatriene metal complexes are known by now. Further studies on the reactions of tetrafluorobutatriene with metal complexes were undertaken involving nearly the complete first transition metal row and some second and third row metals (shown in schemes 2.6.1 to 2.6.5). None of these reactions yielded isolable amounts of a metal complex containing the tetrafluorobutatriene moiety.

First, the reaction of tetrafluorobutatriene with complexes containing a labile tetrahydrofuran ligand (scheme 2.6.1) was examined. This approach proved successful in the synthesis of other fluorocumulene complexes.[222] Therefore, THF solutions of tetracarbonyl(η^5-cycloplentadienyl)vanadium **98**,[214] tricarbonyl-(η^5-cycloplentadienyl)manganese **99**,[215] tricarbonyl(η^6-benzene)chromium **100**,[216] tricarbonyl(η^6-mesitylene)chromium (**116**)[223] and dicarbonyl(η^5-cycloplentadienyl) cobalt (**117**) [224] were irradiated to replace a carbon monoxide ligand by tetrahydrofuran. The resulting solution was frozen in liquid nitrogen, triene **5** was condensed into the irradiation reactor and the reaction mixture was allowed to warm to room temperature overnight. After removal of all volatiles, the residue was solved in THF, insoluble parts were filtered off. ^{19}F-NMR spectra of the solution revealed no detectable fluorine containing species.

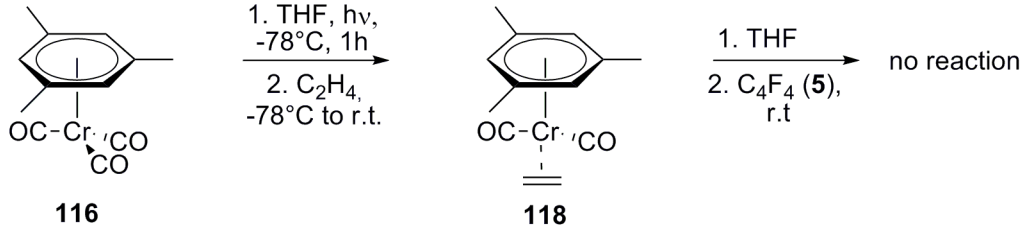


98 **99** **100** **116** **117**

Scheme 2.6.1 – Attempted synthesis of tetrafluorobutatriene metal complexes I.

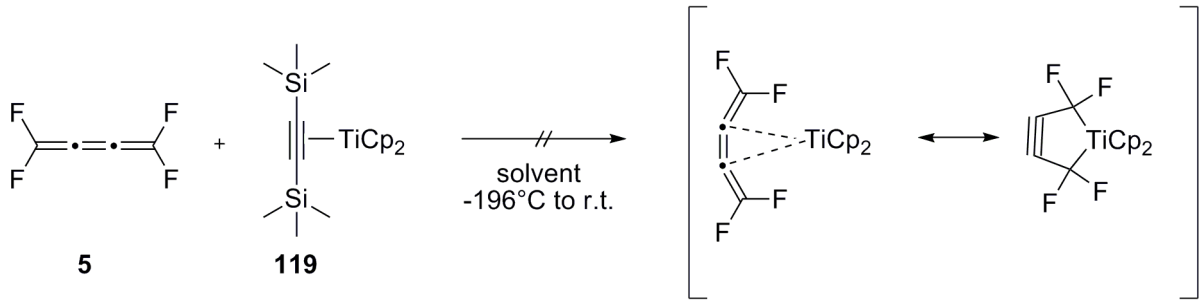
222 Lentz, D.; Willemsen, S.; "Coordination Chemistry of Fluorinated Allenes", *Organometallics* **1999**, *18*, 3962-3964.
223 Oishi, S.; "(η^6-Anisole)(η^2-benzene)dicarbonylchromium(0): an intermediate in the photochemical carbonyl substitution of (η^6-anisole)tricarbonylchromium(0) in benzene.", *J. Organomet. Chem.* **1987**, *335,* 207-212.
224 Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; "IR flash kinetic spectroscopy of transients generated by irradiation of cyclopentadienylcobalt dicarbonyl in the gas phase and in solution.", *J. Am. Chem. Soc.* **1988**, *110*, 6076-6084.

Replacement of a carbon monoxide ligand in **116** by a labile ethylene ligand yields a stable *π*–complex (**118**).[225] However, no reaction of **118** with tetrafluorobutatriene could be observed (scheme 2.6.2).



Scheme 2.6.2 – Attempted synthesis of tetrafluorobutatriene metal complexes II.

According to *Rosenthal*,[226] the bis(trimethylsilyl)acetylene ligand in the titanium complex **119** is easily removable for example by substituted butatrienes. Similar reactions were described by *Suzuki* using the `Negishi reagent´ dibutyldicyclopentadienylzirconium.[227] The titanium complex **119** neither reacts with **5** to yield a defined species in the originally described solvents toluene and THF nor in diethylether, *tert.*-butylmethylether, 1,2-dimethoxyethane, acetonitrile, dichloromethane, chloroform or pentane (scheme 2.6.3). Although a reaction was indicated by color changes, the reaction mixture turned black when it was allowed to warm to room temperature. The black precipitate is insoluble in any solvent. A low temperature NMR experiment revealed no fluorine containing species which could be assigned to a titanium tetrafluorobutatriene complex.



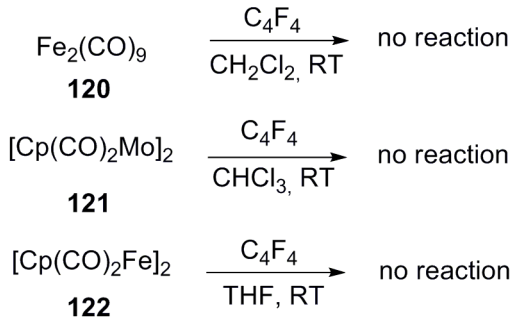
Scheme 2.6.3 – Attempted synthesis of tetrafluorobutatriene metal complexes III.

225 Fischer, E. O.; Kuzel, P.; "Ethylene-metal complexes. II. Mesitylene ethylene chromium(0) dicarbonyl", *Z. Naturforsch. B* **1961**, 475-476.

226 Rosenthal, U.; "Discovering Chemical Terra Incognita: Unusual Metallacycles and Their Reactions", *Angew. Chem. Int. Ed.* **2008**, *47*, 5118-5121.

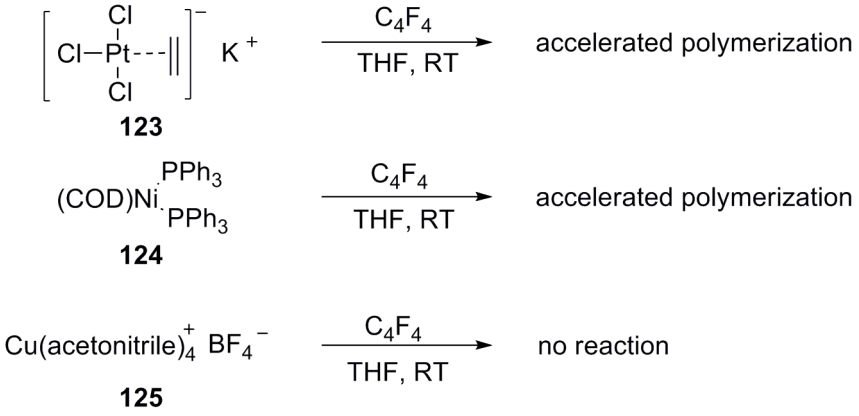
227 Suzuki, N.; Nishiura, M.; Wakatsuki, Y.; "Isolation and Structural Characterization of 1-Zorconacyclopen-3-yne, Five-Membered Cyclic Alkynes", *Science* **2002**, *295*, 660-663.

Other reactions based on the reactivity of metal-metal bonds in enneacarbonyldiiron (**120**), bis[(dicarbonyl)(η^5-cycloplentadienyl)iron] (**121**) and bis[(dicarbonyl)-(η^5-cycloplentadienyl)molybdenum (**122**) successfully yield difluoroallene complexes.[228] Employing tetrafluorobutatriene did not result in successful reactions (scheme 2.6.4).



Scheme 2.6.4 – Attempted synthesis of tetrafluorobutatriene metal complexes IV.

Further reactions based on the replacement of labile ligands like ethylene in Zeise´s salt (**123**),[229] cyclooctadiene in bis(triphenylphosphine)(cyclooctadiene)nickel (**124**)[230] and acetonitrile in tetraacetonitrilecopper(I)-tetrafluoroborate (**125**)[231] (scheme 2.6.5) did not yield isolable tetrafluorobutatriene complexes, too.



Scheme 2.6.5 – Attempted synthesis of tetrafluorobutatriene metal complexes V.

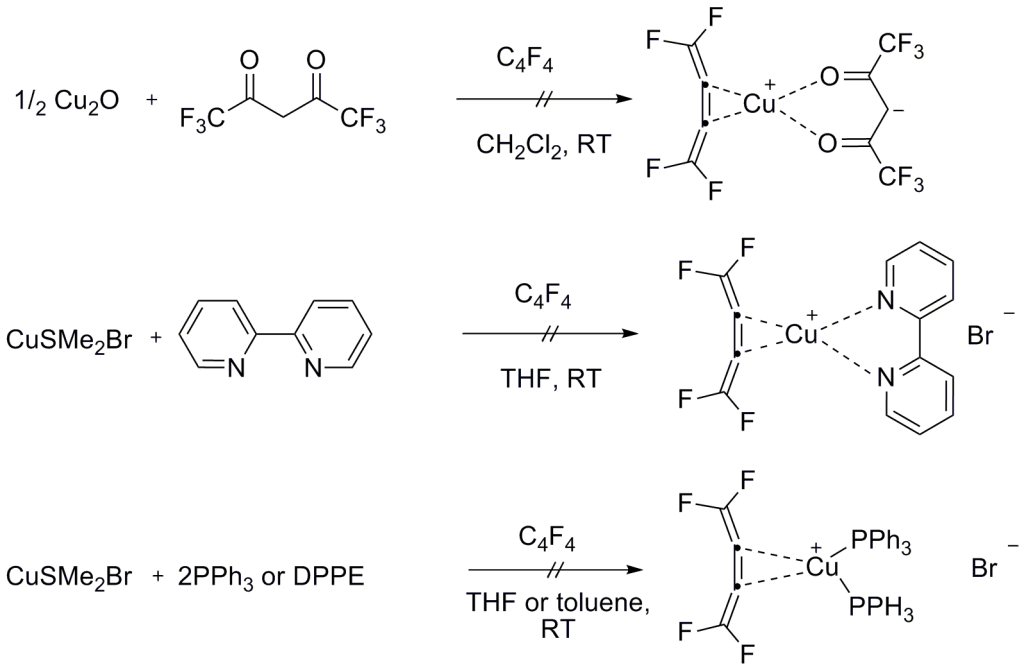
228 Lentz, D.; Nickelt, N.; Willemsen, S.; "Organometallic Chemistry of Fluorinated Allenes", *Chem. Eur. J.* **2002**, *8*, 1205-1217.

229 Haschke, Elliot M.; Fitch, John W.; "Vinylmetallics ligands. III. Synthesis and characterization of potassium trichloro(trimethylvinylsilane)platinate(II).", *J. Organomet. Chem.* **1973**, *57*, C93-C94.

230 Maciejewski, H.; Sydor, A.; Marciniec, B.; Kubicki, M.; Hitchcock, P. B.; "Intermediates in nickel(0)-phosphine complex catalyzed dehydrogenative silylation of olefins", *Inorg. Chim. Act.* **2006**, *359*, 2989-2997.

231 Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A.; "Studies of Copper(I) Olefin Complexes. Formation Constants of Copper Olefin Complexes with 2,2´-Bipyridine, 1,10-Phenanthroline, and Their Derivatives" *Inorg. Chem.* **1986**, *25*, 2622-2627.

Instead of forming a coordination product, accelerated polymerization was observed employing the platinum complex **123** and the nickel complex **124**.Finally, more copper (I) complexes were examined (scheme 2.6.6)[231,232,233] but tetrafluorobutatriene copper complex (**126** - **128**) formation was not observed.



Scheme 2.6.6 – Attempted synthesis of tetrafluorobutatriene metal complexes VI.

Although no new tetrafluorobutatriene metal complex could be synthesized, some new findings could be made. Several metals turned out to catalyze the polymerization in terms of an accelerated undirected polymerization. This finding is significant for nickel, platinum and titanium. Furthermore, the stability of tetrafluorobuatriene (**5)** in different solvents rises in the row pentane < diethylether ≈ THF < CH_2Cl_2 ≈ $CHCl_3$. High dilution conditions stabilize tetrafluorobutatriene (**5)** but has a decelerating effect on the reaction rate. There is no clear indication whether the other mentioned metals have an effect on the polymerization rate. The influence of concentration and/or solvent cannot be separated from the influence of the metal.

232 Wang, X.-S.; Zhao, H.; Li, Y.-H.; Xiong, R.-G.; You, X.-Z.; "Olefin - Copper (I) Complexes and their Properties.", *Top. Catal.* **2005**, *35*, 43-61.

233 Pampaloni, G.; Riccardo, P.; Graiff, C.; Tiripicchio, A.; "Synthesis Characterization, and Olefin/CO Exchange Reactions of Copper(I) Derivatives Containing Bidentate Oxygen Ligands", *Organmetallics* **2005**, *24*, 4475-4482.

3 Summary and Outlook

The present study provides deeper insight into the chemistry of fluorinated butatrienes both experimentally and theoretically.

The four step synthesis of tetrafluorobutatriene starting from commercially available 1,1-difluoroethylene could be successfully improved to an overall yield of up to 42% (from 8%).

1,1,4,4-Tetrafluorobutatriene readily undergoes Diels-Alder reactions. The central double bond acts as a dienophile towards electron rich dienes. Well defined products were isloated in up to quantitative yield. This represents the first incorporation of tetrafluorobutatriene into organic molecules. Tetrafluorobutatriene does neither undergo [2+2]-cycloadditions nor 1,3-dipolar cycloadditions.

It was not possible to synthesize new tetrafluorobutatriene metal complexes. The instability of the triene as well as the acceleration of its decomposition by certain metal centers holds responsible for that.

The synthesis of cyclic tetrafluorobutatriene dimers is most likely impossible by controlled dimerization reactions of the monomer and no distinct dimer is intermediately preferred in the starting phase of the polymerization. This is supported by calculations of the ^{19}F-NMR shifts of the possible dimers by the GIAO method which reveal references for the intermediate emergence of several cyclic dimers during the polymerization of tetrafluorobutatriene. Deeper understanding of the structures of tetrafluorobutatriene dimers and their isomerization energies was gained by high level theoretical calculations on the Coupled Cluster level of theory. EPR-spectroscopy gave no evidence for a radiacal polymerization pathway.

Several possible strategies for the successful synthesis of partially fluorinated butatrienes were attempted experimentally, but none of them yielded isolable amounts of these species. This study provides the first set of information necessary to realize a successful synthesis. Some experiments suggest that after major improvements this may be accomplished. 1,4-Dihalogen-1,1-difluorobut-2-ynes represent the most promising candidates for the synthesis of 1,1-difluorobutatrienes

but further experimental efforts are necessary.

High level theoretical calculations on the Coupled Cluster level of theory were employed to gain more information on the influence of increasing fluorination on the relative energies of butatrienes and their enyne isomers and to find promising candidates for a rearrangement reaction of a but-1-en-3-yne to its butatriene isomer. Thereby, a but-1-en-3-yne isomer, 1,1,4-trifluorobut-1en-3-yne, was discovered which is considerably more stable than its butatriene isomer, although it is fluorinated at the acetylenic center. This acetylenic fluorine substitution is crucial in raising the energies of fluorinated but-1-en-3-yne relative to their butatriene isomers. Only these acetylenic fluorinated but-1-en-3-ynes represent promising rearrangement candidates.

While the cumulenic isomer is the most stable isomer of the shortest fluorinated cumulenes, tetrafluoroallene and tetrafluorobuatriene, this is not the case for the longer cumulenes. The occurrence of more stable isomers may represent a sincere hindrance for the synthetic accessibility of fluorinated cumulenes with longer carbon chains than butatriene.

4 Theoretical Background

4.1 Introduction

As a molecule may be considered as a number of electrons surrounding a set of positively charged nuclei, Coulombic attraction between these two types of differently charged particles (charges q_i and q_j) separated by a distance r_{ij} is given by the interaction potential.[234]

$$V_{ij} = V(r_{ij}) = \frac{q_i q_j}{r_{ij}} \frac{1}{4\pi\varepsilon_0} \tag{4.1}$$

In classical mechanics Newton´s second law describes the dynamics of a system, i.e. how the system evolves in time.

$$F = ma \tag{4.2}$$

$$\frac{-dV}{dr} = m\frac{d^2 r}{dt^2}$$

With F = force, a = acceleration, r = position vector and m = particle mass

Since electrons are very light particles and cannot be described by classical mechanics – they display both wave and particle characteristics – they must be described in terms of a wave function, Ψ. The quantum mechanical equation corresponding to Newtons second law is the time-dependent Schrödinger equation:

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{4.3}$$

with H being the Hamilton operator corresponding to the total energy of the system.

If the Hamilton operator, H, is independent of time, the time dependence of the wave function can be separated out as a simple phase factor.

$$H(r,t) = H(r)$$

$$\Psi(r,t) = \Psi(r)\,\mathrm{e}^{-iEt/\hbar} \tag{4.4}$$

$$H(r)\Psi(r) = E\Psi(r)$$

234 The Theoretical Background chapter is based upon: Jensen, F. “Introduction to Computational Chemistry” **1999**, John Wiley & Sons, Chichester, 1-168.

The time-dependent Schrödinger equation describes the particle-wave duality, the square of the wave function giving the probability of finding the particle at a given position.

For a general *N*-particle system the Hamilton operator contains kinetic (*T*) and potential (*V*) energy for all particles.

$$H = T + V$$

$$H = \sum_{i=1}^{N} T_i = -\sum_{i=1}^{N} \frac{\hbar^2}{2\mathrm{m}_i} \nabla_i^2 \quad \text{with:} \quad \nabla_i^2 = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \tag{4.5}$$

$$V = \sum_{i=1}^{N} \sum_{j>1}^{N} V_{ij}$$

The potential energy operator is the Coulomb potential between all charged particles. The nuclei are much heavier than electrons and therefore their velocities are much smaller. A good approximation is the separation of the Schrödinger equation into two parts, one which describes the electronic wave function for a fixed nuclear geometry, and another part which describes the nuclear wave function. The energy from the electronic wave function is a potential energy for the nuclear wave function.

The electronic wave function depends only on the position of the nuclei, not their momenta and the separation is called the *Born-Oppenheimer approximation*.[235] The picture is that the nuclei move on *Potential Energy Surfaces* (PES), which are solutions to the electronic Schrödinger equation.

Denoting nuclear coordinates with R and subscribt n, and electron coordinates with r and e, this can be expressed as follows.

$$H_{tot} \Psi_{tot}(R;r) = E_{tot} \Psi_{tot}(R;r)$$

$$H_{tot} = H_e + T_n$$

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn} \tag{4.6}$$

$$\Psi_{tot}(R;r) = \Psi_n(R) \Psi_e(R;r)$$

$$H_e \Psi_e(R;r) = E_e(R) \Psi_e(R;r)$$

$$(T_n + E_e(R)) \Psi_n(R) = E_{tot} \Psi_n(R)$$

235 Kolos, W.; Wolniewicz, L; "Accurate Adiabatic Treatment of the Ground State of the Hydrogen Molecule", *J. Chem. Phys.* **1964**, *41*, 3663-3673.

The Born-Oppenheimer approximation is usually very good (the error for the hydrogen molecule is of the order 10^{-4}, for systems with heavier nuclei, the approximation becomes even better), neglect of the coupled nuclear-electron motion is usually only a minor approximation compared with other errors.

Once the electronic Schrödinger equation has been solved for a large number of nuclear geometries (and possibly also for several electronic states), the PES is known. This can then be used for solving the nuclear part of the Schrödinger equation.

For *N* nuclei, there are 3*N* coordinates that define the geometry, three of them describe the overall translation of the molecule and three describe the overall rotation of the molecule with respect to three axes. A linear molecule requires only two coordinates for the description of the rotation. Therefore, 3*N*-6(5) coordinates describe the internal movement of the nuclei, the vibrations. Often they are referred to as “vibrational normal coordinates”.

Nuclei behave to a good approximation as classical particles since they are heavy enough for quantum effects to be almost negligible. The concept of molecular structure (i.e. different configurations and conformations) would not have any meaning if nuclei showed significant quantum aspects as they would simply tunnel through barriers to end in the global minimum. It would be impossible to speak of molecular geometry: *Heisenberg´s uncertainty principle* would not permit a measure of nuclear positions to an accuracy much smaller than the molecular dimension.

4.2 Electronic Structure Methods

4.2.1 Self-consistent Field Theory

The electronic Schrödinger equation can only be solved exactly for the H_2^+ molecule and similar one-electron systems. In the general case only approximate (numerical) methods are used. By neglecting relativistic effects, the electron spin has to be introduced as an *ad hoc* quantum effect. Each electron has a spin quantum number of ½. In the presence of an external magnetic field there are two possible states (alignment along or opposite to the field). The corresponding spin functions are

denoted α and β, and obey the following orthonormality conditions

$$\langle\alpha|\alpha\rangle=\langle\beta|\beta\rangle=1 \qquad \text{and} \qquad \langle\alpha|\beta\rangle=\langle\beta|\alpha\rangle=0 \tag{4.7}$$

To generate approximate solutions the variational principle is employed. The variational principle states that any approximate wave function has an energy above or equal to the exact energy. The equality holds only if the wave function is the exact function. By making a trial wave function containing a number of parameters, the "best" trial function of the given form may be generated by minimizing the energy as a function of these parameters.

The energy of an approximate wave function can be calculated as the expectation value of the Hamilton operator, divided by the norm of the wave function.

$$E_e=\frac{\langle\Psi|H_e|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{4.8}$$

For a normalized wave function the denominator is 1 and therefore: $E_e=\langle\Psi|H_e|\Psi\rangle$

The total electronic wave function must be antisymmetric (change sign) with respect to the interchange of any two electron coordinates. The *Pauli principle*, which states that two electrons cannot have all quantum numbers equal, is a direct consequence of this antisymmetry requirement. The antisymmetry of the wave function can be achieved by building it from *Slater determinants*. The columns in a Slater determinant are single electron wave functions, *orbitals*, while the electron coordinates are along the rows. The one-electron functions are thus *Molecular Orbitals* (MO), which are given as a product of a spatial orbital times a spin function (*α* or *β*), also known as *spinorbitals*, and may be taken to be orthonormal. For the general case of *N* electrons and *N* spinorbitals, a Slater determinant is given as

$$\Psi_{\mathrm{SD}}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(1) & \phi_2(1) & \cdots & \phi_N(1)\\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2)\\ \cdots & \cdots & \cdots & \cdots\\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N)\end{vmatrix}, \langle\phi_i|\phi_j\rangle=\delta_{ij} \tag{4.9}$$

Making one further approximation, taking the trial wave function to consist of a single Slater determinant, the variational principle can be used to derive the *Hartree-Fock* (HF) equations. A single determinant trial wave function implies that electron-electron

correlation is neglected, or equivalently, the electron-electron repulsion is only included as an average effect. The HF model is a kind of branching point, either additional approximations may be invoked, leading to semi-empirical methods, or it can be improved by additional determinants, generating solutions which can be made to converge towards the exact solution of the Schrödinger equation.[236]

4.2.2 The Energy of a Slater Determinant

It is convenient to write the Slater Determinat as a sum of permutations over the "diagonal" of the deteminant (*Π* denotes diagonal product, *Ψ* represents the determinant wave function).

$$\Psi = A[\phi_1(1)\phi_2(2)\cdots\phi_N(N)] = A\Pi \tag{4.10}$$

$$A = \frac{1}{\sqrt{N!}}\sum_{p=0}^{N-1}(-1)^p P = \frac{1}{\sqrt{N!}}[1 - \sum_{ij} P_{\mathrm{ij}} + \sum_{ijk} P_{\mathrm{ijk}} - \cdots]$$

The *1* operator is the identity, while P_{ij} generates all possible permutations of two electron coordinates, P_{ijk} all possible permutations of three electron coordinates etc. The antisymmetrizing operator *A* commutes with *H* and *A* acting twice gives the same as *A* acting once, multiplied by the square root of *N* fractional.

$$AH = HA \tag{4.11}$$

$$AA = \sqrt{N!}\,A$$

Considering the Hamilton operator, the nuclear-nuclear repulsion does not depend on electron coordinates and is a constant for a given nuclear geometry. The nuclear-electron attraction is a sum of terms, each depending only on one electron coordinate. The same holds for the electron kinetic energy. The electron-electron repulsion, however, depends on two electron coordinates.

236 Simons, J.; "An experimental chemist's guide to ab initio quantum chemistry", *J. Phys. Chem.* **1991**, *95*, 1017-1029.

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn}$$

$$T_e = -\sum_i^1 \frac{1}{2}\nabla_i^2$$

$$V_{\mathrm{ne}} = -\sum_i^N \sum_a \frac{Z_a}{|R_a - r_i|} \tag{4.12}$$

$$V_{\mathrm{ee}} = \sum_i^N \sum_{j>i}^N \frac{1}{|r_i - r_j|}$$

$$V_{\mathrm{nn}} = \sum_a \sum_{b>a} \frac{Z_a Z_b}{|R_a - R_b|}$$

The operators may be collected according to the number of electron indices.

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_a \frac{Z_a}{|R_a - r_i|}$$

$$g_{\mathrm{ij}} = \frac{1}{|r_i - r_j|} \tag{4.13}$$

$$H_e = \sum_{i=1}^N h_i + \sum_{i=1}^N \sum_{i>j}^N g_{\mathrm{ij}} + V_{nn}$$

The one electron operator h_i describes the motion of electron i in the field of all the nuclei and g_{ij} is a two electron operator giving the electron-electron repulsion. The zero point of the energy corresponds to the particles being at rest (T_c = 0) and infinitely removed from each other (V_{ne} = V_{ee} = V_{nn} = 0).

The energy, written in terms of the permutation operator (using eqs. 2.10 – 2.11) is:

$$E = \langle \Psi | H | \Psi \rangle = \langle A\Pi | H | A\Pi \rangle = \sqrt{N!}\langle \Pi | H | A\Pi \rangle = \sum_p (-1)^p \langle \Pi | H | A\Pi \rangle \quad (2.14)$$

Since the nuclear repulsion operator does not depend on electron coordinates it can immediately be integrated to yield a constant.

$$E = \langle \Psi | V_{\mathrm{nn}} | \Psi \rangle = V_{\mathrm{nn}} \langle \Psi | \Psi \rangle = V_{\mathrm{nn}} \tag{4.15}$$

For the one-electron operator only the identity operator can give a non-zero contribution.

For coordinate 1 this yields

$$\langle \Pi | h_1 | \Pi \rangle = \langle \phi_1(1) | h_1 | \phi_1(1) \rangle = h_1 \tag{4.16}$$

as all MOs Φ_i are normalized. All matrix elements involving a permutation operator give zero since they contain overlap integrals between two different MOs which are orthogonal.

For the two electron operator, only the identity and P_{ij} operators can give a non-zero contribution. A three electron permutation will again give at least one overlap integral between two different MOs, which will be zero. The term arising from the identity operator is

$$\langle \Pi | g_{12} | \Pi \rangle = \langle \phi_1(1)\phi_2(2) | g_{12} | \phi_1(1)\phi_2(2) \rangle = J_{12} \tag{4.17}$$

and is called *Coulomb* integral. It represents a classical repulsion between two charge distributions. The term arising from P_{ij} operator is

$$\langle \Pi | g_{12} | P_{12}\Pi \rangle = \langle \phi_1(1)\phi_2(2) | g_{12} | \phi_2(1)\phi_1(2) \rangle = K_{12} \tag{4.18}$$

and is called *exchange* integral, which has no classical analogy. The order of MOs in the *J* and *K* matrix elements is according to the electron indices. The energy can thus be written as

$$E = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ij}) + V_{nn} \tag{4.19}$$

where the factor of ½ allows the double sum to run over all electrons (the Coulomb "self interaction" J_{ii} is exactly cancelled by the corresponding "exchange" element K_{ii}).

For the purpose of deriving the variation of the energy, it is convenient to express the energy in terms of Coulomb and Exchange operators.

$$E = \sum_{i}^{N} \langle \phi_i | h_i | \phi_i \rangle + \frac{1}{2} \sum_{ij}^{N} (\langle \phi_j | J_i | \phi_j \rangle - \langle \phi_j | K_i | \phi_j \rangle) + V_{nn} \tag{4.20}$$

$$J_i | \phi_j(2) \rangle = \langle \phi_i(1) | g_{12} | \phi_i(1) \rangle | \phi_j(2) \rangle$$

$$K_i | \phi_j(2) \rangle = \langle \phi_i(1) | g_{12} | \phi_j(1) \rangle | \phi_i(2) \rangle$$

The *J* operator involves “multiplication” by a matrix element with the same orbital on both sides while the *K* operator “exchanges” two functions on the right hand side of the g_{12} operator.

The objective is now to determine a set of MOs which makes the energy a minimum, or at least stationary with respect to a change in the orbitals. The variation, however, must be carried out in such a way that the MOs remain orthogonal and normalized. This is a constrained optimization and can be handled by means of *Lagrange multipliers*. The condition is, that the Lagrange function is stationary with respect to an orbital variation.

$$L = E - \sum_{ij}^{N} \lambda_{ij}(\langle \phi_i | \phi_j \rangle - \delta_{ij}) \tag{4.21}$$

$$\delta L = \delta E - \sum_{ij}^{N} \lambda_{ij}(\langle \phi_i | \phi_j \rangle - \langle \phi_i | \delta_{ij} \phi_j \rangle) = 0$$

The variation of the energy is given by (4.22)

$$\delta E = \sum_{i}^{N} (\langle \delta\phi_i | h_i | \phi_i \rangle + \langle \phi_i | h_i | \delta\phi_j \rangle) + \frac{1}{2} \sum_{ij}^{N} (\langle \delta\phi_i | J_i - K_j | \phi_i \rangle + \langle \phi_i | J_j - K_j | \delta\phi_j \rangle) + (\langle \delta\phi_j | J_i - K_i | \phi_j \rangle + \langle \phi_j | J_i - K_i | \delta\phi_j \rangle)$$

The third and the fifth term are identical, as are the fourth and sixth terms (since the summation over all *i* and *j*) They may be collected to cancel the factor of *½* and the variation can be written in terms of a *Fock operator*, F_i.

$$\delta E = \sum_{i}^{N} (\langle \delta\phi_i | h_i | \phi_i \rangle + \langle \phi_i | h_i | \delta\phi_j \rangle) + \sum_{ij}^{N} (\langle \delta\phi_i | J_j - K_j | \phi_i \rangle + \langle \phi_i | J_j - K_j | \delta\phi_j \rangle)$$

$$\delta E = \sum_{i}^{N} (\langle \delta\phi_i | F_i | \phi_i \rangle + \langle \phi_i | F_i | \delta\phi_j \rangle) \tag{4.23}$$

$$F_i = h_i + \sum_{j}^{N} (J_j - K_j)$$

The Fock operator is an effective one-electron energy operator, describing the kinetic energy of an electron, the attraction to all nuclei and the repulsion to all other electrons (via the *J* and *K* operators). The Fock operator is associated with the

variation of the total energy, not the energy itself. The Hamilton operator is not a sum of Fock operators.

The variation of the Lagrange function now becomes

$$\delta L=\sum_{i}^{N}(\langle\delta\phi_i|F_i|\phi_i\rangle+\langle\phi_i|F_i|\delta\phi_i\rangle)-\sum_{ij}^{N}\lambda_{ij}(\langle\phi_i|\phi_j\rangle-\langle\phi_i|\delta_{ij}\phi_j\rangle) \quad (4.24)$$

The variational principle states that the desired orbitals are those that make *δL = 0*. Using the fact that $\langle\delta\phi_i|\phi_i\rangle=\langle\phi_i|\delta\phi_i\rangle^*$ and $\langle\delta\phi_i|F|\phi_i\rangle=\langle\phi_i|F|\delta\phi_i\rangle^*$ equation 2.24 becomes

$$\delta L=\sum_{i}^{N}\langle\delta\phi_i|F_i|\phi_i\rangle-\sum_{ij}^{N}(\lambda_{ij}\langle\delta\phi_i|\phi_i\rangle\langle\phi_i|\delta\phi_i\rangle) \quad (4.25)$$
$$+\sum_{i}^{N}\langle\delta\phi_i|F_i|\phi_i\rangle^*-\sum_{ij}^{N}(\lambda_{ij}\langle\delta\phi_i|\phi_i\rangle\langle\phi_i|\delta\phi_i\rangle)^*=0$$

The variation of either $\langle\delta\phi|\text{or}\langle\delta\phi|^*$ should make *δL = 0*. The first two terms in eq. 2.25 should thus be zero and the last two terms should be zero. Taking the complex conjugate of the last two terms and subtracting them from the first two gives

$$\sum_{ij}^{N}(\lambda_{ij}-\lambda_{ij}^*)\langle\delta\phi_i|\phi_j\rangle=0 \quad (4.26)$$

which means that the Lagrange multipliers are elements of a Hermitian matrix. $(\lambda_{ij}=\lambda_{ij}^*)$

The final set of *Hartree-Fock equations* may be written as

$$F_i\phi_i=\sum_{j}^{N}\lambda_{ij}\phi_j \quad (4.27)$$

The equations may be simplified by choosing a unitary transformation which makes the matrix of Lagrange multipliers diagonal, i.e. $\lambda_{ij} \rightarrow 0$ and $\lambda_{ij} \rightarrow \varepsilon_i$. This special set of molecular orbitals (Φ´) are called *canonical* MOs, and they transform this equation into a set of pseudo-eigenvalue equations.

$$F_i\phi_i'=\varepsilon_i\phi_i' \quad (4.28)$$

The Lagrange multipliers can be interpreted as MO energies, i.e. they are the expectation value of the Fock operator in the MO basis.

$$\varepsilon_i = \langle \phi_i' | F_i | \phi_i' \rangle \tag{4.29}$$

The Hartree-Fock equations form a set of pseudo-eigenvalue equations, as the Fock operator depends on all occupied MOs (via the Coulomb and Exchange operators). A specific orbital can only be determined if all the other occupied orbitals are known and iterative methods must therefore be employed for determining the orbitals. A set of functions which is a solution to eq. 2.28 are called *Self-consistent Field* (SCF) orbitals.

The canonical MOs may be considered as a convenient set of orbitals for carrying out the variational calculation. The total energy, however, depends only on the total wave function, which is a Slater determinant written in terms of the occupied MOs.

The orbital energies can be considered as matrix elements of the Fock operator with MOs (dropping the prime notation and letting Φ be the canonical orbitals). The total energy can be written in two ways:

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + V_{nn} \tag{4.30}$$

$$\varepsilon_i = \langle \phi_i | F_i | \phi_i \rangle = h_i + \sum_j^N (J_{ij} - K_{ij})$$

The total energy is not simply a sum of MO orbital energies. The Fock operator contains terms describing the repulsion to all other electrons (*J* and *K* operators) and the sum over MO energies therefore counts the electron-electron repulsion twice, which must be corrected for. It is also clear, that the total energy cannot be exact since the electron-electron repulsion is only accounted for in an average fashion. This is due to the approximation of a single Slater determinant as the trial wave function.

4.2.3 The Basis Set Approximation

Essentially all calculations use a basis set expansion to express the unknown MOs in terms of a set of known functions. Any type of basis may in principle be used: exponential, Gaussian, polynominal, cube etc. See chapter 4.4 for details.

Each MO is expanded in terms of the basis functions, conventionally called *atomic orbitals* (MO = *LCAO*, *Linear Combination of Atomic Orbitals*), although they are generally not solutions to the atomic HF problem.

$$\Phi_i = \sum_{\alpha}^{M} c_{\alpha i} \chi_i \tag{4.32}$$

The Hartree Fock equations may be written as:

$$F_i \sum_{\alpha}^{M} c_{\alpha i} \chi_i = \varepsilon_i \sum_{\alpha}^{M} c_{\alpha i} \chi_i \tag{4.33}$$

Multiplying from the left by a specific basis function and integrating yields the *Roothan-Hall* equations (for a closed shell system).[237,238] These are the Fock equations in the atomic orbital basis and all the *M* equations may be collected in a matrix notation.

$$\begin{aligned} F\,C &= S\,C\,\varepsilon \\ F_{\alpha\beta} &= \langle \chi_\alpha | F | \chi_\beta \rangle \\ S_{\alpha\beta} &= \langle \chi_\alpha | \chi_\beta \rangle \end{aligned} \tag{4.34}$$

The *S* matrix contains the overlap elements between basis functions and the *F* matrix contains the Fock matrix elements. Each $F_{\alpha\beta}$ element contains two parts from the Fock operator, integrals involving the one-electron operators and a sum over ocupied MOs of coefficients multiplied with two-electron integrals involving the electron-electron repulsion operator. The latter is often written as a product of a density matrix and two-electron integrals:

237 Roothan, C. C. J.; “New Developments in Molecular Orbital Theory”, Rev. Mod. Phys. **1951**, 23, 69–89.
238 Hall, G. G.; “The Molecular Orbital Theory of Chemical Valency. VIII. A Method of Calculating Ionization Potentials”, *Proc. R. Soc. Lond. A* **1951**, *A205*, 541-552

$$\begin{aligned}\langle\chi_\alpha|F|\chi_\beta\rangle&=\langle\chi_\alpha|h|\chi_\beta\rangle+\sum_j^{\text{occ. MOs}}\langle\chi_\alpha|J_j-K_j|\chi_\beta\rangle\\&=\langle\chi_\alpha|h|\chi_\beta\rangle+\sum_j^{\text{occ. MOs}}\left(\langle\chi_\alpha\phi_j|g|\chi_\beta\phi_j\rangle-\langle\chi_\alpha\phi_j|g|\phi_j\chi_\beta\rangle\right)\\&=\langle\chi_\alpha|h|\chi_\beta\rangle+\sum_j^{\text{occ. MOs}}\sum_\gamma^{\text{AO}}\sum_\delta^{\text{AO}}c_{\gamma l}c_{\delta l}\left(\langle\chi_\alpha\chi_\gamma|g|\chi_\beta\chi_\delta\rangle-\langle\chi_\alpha\chi_\gamma|g|\chi_\delta\chi_\beta\rangle\right)\\&=\langle\chi_\alpha|h|\chi_\beta\rangle+\sum_\gamma^{\text{AO}}\sum_\delta^{\text{AO}}D_{\gamma\delta}\left(\langle\chi_\alpha\chi_\gamma|g|\chi_\beta\chi_\delta\rangle-\langle\chi_\alpha\chi_\gamma|g|\chi_\delta\chi_\beta\rangle\right)\end{aligned}$$

$$D_{\gamma\delta}=\sum_j^{\text{occ. MO}}c_{\gamma j}c_{\delta j} \tag{4.35}$$

The total energy in terms of integral over basis functions is given as

$$E=\sum_i^N\langle\phi_i|h_i|\phi_i\rangle+\frac{1}{2}\sum_{ij}\left(\langle\phi_i\phi_j|g|\phi_i\phi_j\rangle-\langle\phi_i\phi_j|g|\phi_j\phi_i\rangle\right)+V_{nn}$$

$$\begin{aligned}E=&\sum_i^N\sum_{\alpha\beta}c_{\alpha i}c_{\beta i}\langle\chi_\alpha|h_i|\chi_\beta\rangle\\&+\frac{1}{2}\sum_{ij}^N\sum_{\alpha\beta\gamma\delta}^M c_{\alpha i}c_{\gamma j}c_{\beta i}c_{\delta j}\left(\langle\chi_\alpha\chi_\gamma|g|\chi_\beta\chi_\delta\rangle-\langle\chi_\alpha\chi_\gamma|g|\chi_\delta\chi_\beta\rangle\right)+V_{nn}\end{aligned} \tag{4.36}$$

$$E=\sum_{\alpha\beta}^M D_{\alpha\beta}h_{\alpha\beta}+\frac{1}{2}\sum_{\alpha\beta\gamma\delta}^M D_{\alpha\beta}D_{\gamma\delta}\left(\langle\chi_\alpha\chi_\gamma|g|\chi_\beta\chi_\delta\rangle-\langle\chi_\alpha\chi_\gamma|g|\chi_\delta\chi_\beta\rangle\right)+V_{nn}$$

The one- and two-electron integrals in the atomic basis are given as

$$\langle\chi_\alpha|h|\chi_\beta\rangle=\int\chi_\alpha(1)\left(-\frac{1}{2}\nabla^2\right)\chi_\beta(1)\,\mathrm{d}\,r_1+\sum_a\int\chi_\alpha(1)\frac{Z_a}{|R_a-r_1|}\chi_\beta(1)\,\mathrm{d}\,r_1 \tag{4.37}$$

$$\langle\chi_\alpha\chi_\gamma|g|\chi_\beta\chi_\delta\rangle=\int\chi_\alpha(1)\chi_\gamma(2)\frac{1}{|r_1-r_2|}\chi_\beta(1)\chi_\delta(2)\,\mathrm{d}\,r_1\,\mathrm{d}\,r_2 \tag{4.38}$$

The two-electron integrals written in a notation without the *g* operator and a change to the *Mulliken* notation (both functions depending on electron 1 on the left and the functions depending on electron 2 on the right) gives

$$\int\chi_\alpha(1)\chi_\beta(1)\frac{1}{|r_1-r_2|}\chi_\gamma(2)\chi_\delta(2)\,\mathrm{d}\,r_1\,\mathrm{d}\,r_2=\langle\chi_\alpha\chi_\beta|g|\chi_\gamma\chi_\delta\rangle \tag{4.39}$$

The Rothan-Hall equation is a determination of the eigenvalues of the Fock matrix. To determine the unkonown MO coefficients $c_{\alpha k}$, the Fock matrix must be diagonalized. However, the Fock matrix is only known, if all the MO coefficients are known. The procedure therefore starts off by some guess of the MO coefficients, forms the F matrix and diagonalizes it. The new set of coefficients is then used for calculating a new Fock matrix etc. This is continued until the set of coefficients used for constructing the Fock matrix is equal to those resulting from the diagonalization (to within a certain threshold). This set of coefficients determines an SCF solution.

To construct the Fock matrix, integrals over all pairs of basis functions and the one-electron operator *h* are needed. For M basis functions there are of the order of M^2 of such one-electron integrals (describing the interaction of an electron with the whole set of bare nuclei). The second part of the Fock matrix involves integrals over four basis functions and the *g* two-electron operator. There are of the order of M^4 of these two-electron integrals. For these integrals, the four basis functions may be located on 1, 2, 3 or 4 different atomic centers. As the number of basis functions increases, the accuracy of the MOs becomes better. As the size of the basis set is increased, the variational principle ensures, that the results become better (at least in an energetic sense). The quality of a result can therefore be assessed by running calculations with increasingly larger basis sets.

4.3 Electron Correlation Methods

4.3.1 Introduction

In the solutions to the Schrödinger equation in the Hartree-Fock method real electron-electron interaction is replaced by an average interaction. Giving a sufficiently large basis set, the HF wave function accounts for ~99% of the total energy but the remaining ~1% is often very important for describing chemical phenomena. The difference in energy between the HF and the lowest possible energy in a given basis set is called *Electron Correlation* (EC) energy.[239] The physical meaning is that the motion of the electrons is correlated, on average they are nearer

239 Bartlett, R. J.; Stanton, J. F.; “Applications of Post-Hartree-Fock Methods: A Tutorial”, *Rev. Comput. Chem.* **1994**, 5, 65-169.

than described by the HF wave function.

The HF method determines the best one-determinant trial wave function (within the given basis set). In order to improve HF results, the starting point must be a trial wave function which contains more than one Slater determinant. Electron correlation methods normally use the HF wave function as a starting point.

A generic multi determinant wave function may be written as

$$\Psi = a_0 \Phi_{\mathrm{HF}} + \sum_{k=1} a_k \Phi_k \tag{4.31}$$

where a_0 is usually close to 1. Electron correlation methods differ in how they calculate the coefficients in front of the other determinants, a_0 being determined by the normalization condition.

The multi-determinant wave function can be considered as describing the total wave function in a “coordinate” system of Slater determinants. The basis set determines the size of the one-electron basis (and thus limits the description of the one-electron functions, the MOs), while the number of determinants included determines the size of the many-electron basis (and thus limits the description of electron correlation).

4.3.2 Excited Slater determinants

With *N* electrons and *M* basis functions, solutions of the Roothaan-Hall equations for the RHF case yield *N/2* occupied MOs and *M-N/2* unoccupied (virtual) MOs. Except for a minimum basis, there will be always more virtual than occupied MOs. A Slater determinant is determined by *N/2* spatial MOs multiplied by two spin functions to yield N spinorbitals. Replacement of occupied MOs in the HF determinant by virtual MOs generates a whole series of determinants. Depending on how many occupied MOs have been replaced Slater determinants can be *singly, doubly, triply* etc. *excited* relative to the HF determinant, up to a maximum of *N* excited states. These determinants are called *Singles (S), Doubles (D), Triples (T*) etc.

The total number of determinants that can be generated depends on the size of the basis set. If all possible determinants in a given basis set are included, all electron correlation is recovered (within the given basis set). For an infinite basis set the

Schrödinger equation is then solved exactly (within the limitations of the Born-Oppenheimer approximation and the neglect of relativistic effects). Therefore methods which include electron correlation are two-dimensional: the larger the one-electron expansion (basis set size) and the larger the many-electron expansion (number of determinants), the better are the results.

There are three main methods for calculating electron correlation: *Configuration Interaction* (CI), *Many Body Perturbation Theory* (MTBT) and *Coupled Cluster* (CC).

4.3.3 Configuration Interaction

The method is based on the variational principle, analogous to the HF method. Although not employed in this thesis it is the easiest method to understand. Chapter 2.3.8 illustrates the connections between CI, MTBT and CC. The trial wave function is written as a linear combination of determinants with the expansion coefficients determined by requiring that the energy should be a minimum (or at least stationary). The MOs used for building the excited Slater determinants are taken from a Hartree-Fock calculation and held fixed.

$$\Psi_{\mathrm{CI}} = a_0 \Phi_{\mathrm{SCF}} + \sum_S a_S \Phi_S + \sum_D a_D \Phi_D + \sum_T a_T \Phi_T \ldots = + \sum_{k=0} a_k \Phi_k \qquad (4.40)$$

This is an example of a constrained optimization, the energy should be minimized under the constraint that the total CI wave function is normalized. Introducing a Lagrange multiplier, this can be written as

$$L = \langle \Psi_{\mathrm{CI}} | H | \Psi_{\mathrm{CI}} \rangle - \lambda [\langle \Psi_{\mathrm{CI}} | \Psi_{\mathrm{CI}} \rangle - 1] \qquad (4.41)$$

The first bracket is the energy of the CI wave function, the second bracket is the norm of the wave function. In terms of determinants this can be written as

$$\langle \Psi_{\mathrm{CI}} | H | \Psi_{\mathrm{CI}} \rangle = \sum_{k=0} \sum_{l=0} a_k a_l \langle \Phi_k | H | \Phi_l \rangle = \sum_{k=0} a_k^2 E_k + \sum_{k=0} \sum_{l \neq k} a_k a_l \langle \Phi_k | H | \Phi_l \rangle$$

$$\langle \Psi_{\mathrm{CI}} | \Psi_{\mathrm{CI}} \rangle = \sum_{k=0} \sum_{l=0} a_k a_l \langle \Phi_k | \Phi_l \rangle = \sum_{k=0} a_k^2 \langle \Phi_k | \Phi_k \rangle = \sum_{k=0} a_k^2 \qquad (4.42)$$

The diagonal elements in the sum involving the Hamilton operator are energies of the

corresponding determinants. The overlap elements between different determinants zero as they are build from orthogonal MOs The variational procedure corresponds to setting all derivatives of the Lagrange function with respect to the a_k expansion coefficients equal to zero.

$$\frac{\partial L}{\partial a_k} = 2\sum_l a_l \langle \Phi_k | H | \Phi_l \rangle - 2\lambda a_k = 0 \tag{4.43}$$

$$a_k(\langle \Phi_k | H | \Phi_k \rangle - \lambda) + \sum_{l \neq k} a_l \langle \Phi_k | H | \Phi_l \rangle = 0$$

$$a_k(E_k - \lambda) + \sum_{l \neq k} a_l \langle \Phi_k | H | \Phi_l \rangle = 0$$

If there is only one determinant in the expansion (a_0 = 1), the last equation shows that the Lagrange multiplier is the (CI) energy, $\lambda = E$. If there is one equation for each k, the variational problem is transformed into solving a set of CI *secular equations*. With $H_{kl} = \langle \Phi_k | H | \Phi_l \rangle$ the matrix equation becomes

$$\begin{pmatrix} H_{00}-E & H_{01} & \cdots & H_{0l} & \cdots \\ H_{10} & H_{11} & \cdots & H_{1l} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ H_{l0} & \cdots & \cdots & H_{ll}-E & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} = \begin{pmatrix} a_0 \\ a_1 \\ \cdots \\ a_l \\ \cdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdots \\ 0 \\ \cdots \end{pmatrix} \tag{4.44}$$

which in shorthand notation may be written as $Ha = Ea$. Solving the secular equations is equivalent to diagonalizing the CI matrix. The CI energy is obtained as the lowest eigenvalue of the CI matrix and the corresponding eigenvector contains the a_k coefficients in front of the determinants. The second lowest eigenvalue corresponds to the first excited state etc.

The CI matrix elements H_{kl} can be evaluated by the strategy employed for calculating the energy of a single determinant used for deriving the Hartree-Fock equations (expanding the determinants in a sum of products of MOs and thereby expression of the CI matrix elements in terms of MO integrals).

Some general features make many of the CI matrix elements equal to zero (different spin of two determinants since the Hamilton operator contains no spin, symmetry

reasons, difference of two determinants by more than 2 MOs).

The last fact is known as the *Slater-Condon rules*: CI matrix elements can only be non-zero if the two determinants differ by 0, 1 or 2 MOs and they may be expressed in terms of integrals of one- and two-electron operators over MOs. If two determinants are identical, the matrix element is simply the energy of a single determinant wave function. If they differ by 1 (exciting an electron from orbital *i* to *a*) or 2 (two electrons from k and l to *a* and *b*) MOs the results are

$$\langle \Phi_0 | H | \Phi_k^a \rangle = \langle \phi_k | h | \phi_a \rangle + \sum_l \left(\langle \phi_k \phi_l | \phi_a \phi_l \rangle - \langle \phi_k \phi_l | \phi_l \phi_a \rangle \right) = \langle \phi_k | F | \phi_a \rangle \quad (4.45)$$

$$\langle \Phi_0 | H | \Phi_{kl}^{ab} \rangle = \langle \phi_k \phi_l | \phi_a \phi_b \rangle - \langle \phi_k \phi_l | \phi_b \phi_a \rangle$$

where the *g* operator is implicit in the notation of the two-electron integrals and the matrix element between the HF and a singly excited determinant is a matrix element of the Fock operator between two different MOs.

This is an occupied-virtual off-diagonal element of the Fock matrix in the MO basis and is identical to the gradient of the energy with respect to an occupied-virtual mixing parameter. If the determinants are constructed from optimized canonical HF MOs, the gradient is zero (the MOs are eigenfunctions of the Fock operator).

$$F \phi_a = \varepsilon_a \phi_a \quad (4.46)$$

$$\langle \phi_k | F | \phi_a \rangle = \varepsilon_a \langle \phi_k | \phi_a \rangle = \varepsilon_a \delta_{ka}$$

The disappearance of matrix elements between the HF reference and singly excited states is known as *Brillouins theorem*. The HF reference state therefore only has zero-matrix elements with doubly excited determinants and the full CI matrix acquires a block diagonal structure.

In order to evaluate the CI matrix elements one- and two-electron integrals over MOs are needed. These can be expressed in terms of the corresponding AO integrals and the MO coefficients.

$$\langle \phi_k | h | \phi_l \rangle = \sum_{\alpha}^{M} \sum_{\beta}^{M} c_{\alpha k} c_{\beta l} \langle \chi_\alpha | h | \chi_\beta \rangle \tag{4.47}$$

$$\langle \phi_k \phi_l | \phi_m \phi_n \rangle = \sum_{\alpha}^{M} \sum_{\beta}^{M} \sum_{\gamma}^{M} \sum_{\delta}^{M} c_{\alpha k} c_{\beta l} c_{\gamma m} c_{\delta n} \langle \chi_\alpha \chi_\beta | \chi_\gamma \chi_\delta \rangle$$

Such MO integrals are required for all electron correlation methods. The two-electron AO integrals are the most numerous and the above equation appears to involve a computational effect proportional to M^8 (M^4 AO integrals each multiplied by four sets of M MO coefficients) but by performing the transformation one index at a time the computational effort can be reduce to M^5. In the large basis set limit, all electron correlation methods scale as at least M^5 since this is the scaling for the AO to MO integral transformation.

The size of the CI matrix grows with the size of the system and the considered excitation level. In addition it grows factorial with the size of the basis set, which makes the full CI method infeasible for all but the very smallest systems. The full CI calculations are not a routine computational procedure for including electron correlation but a useful reference for developing more approximate methods, full CI gives the best result that can be obtained in a given basis set.

In order to develop a computational tractable model, the number of excited Slater determinants in the CI expansion must be reduced.

CIS CI with Singles (no improvement, matrix elements between HF wave function and single exited determinants are zero)

CID CI with Doubles

CISD CI with Singles and Doubles (relatively few singly excited determinants compared to the doubly excited, therefore computationally only a marginal increase, singly excited determinants enter the wave function indirectly since they have non-zero matrix elements with the doubly excited determinants, scales M^6 in the large basis set limit)

CISDT Scales M^8

CISDTQ Scales M^{10}

Since only doubly excited determinants have non-zero matrix elements with the HF state, they are the most important. In terms of energy the contribution from singly excited determinants follow and then the quadruples and triples.

4.3.4 Size Consistency and Size Extensivity

Size Consistency guarantees the consistency of the energy behaviour when interaction between the involved molecular systems is nullified. This means that the energy of a system *A-B* is equal to sum of *A* and *B*. A very similar, but not identical concept, is *Size Extensivity*. Size consistency is only defined if the two fragments are non-interacting (separated by ~100 Å) while size extensivity implies that the method scales properly with the number of particles, i.e. the fragments can be interacting (separated by e.g. 5 Å) Full CI is size consistent (and extensive), but all forms of truncated CI are not and the quality of description decreases with increasing size of the system.

4.3.5 Many Body Pertubation Theory

The idea in pertubation methods is that a problem at hand only differs slightly from a problem which has already been solved (exactly or approximately). The solution to the given problem should therefore in some sense be close to the solution of the already known system. Mathematically this is described by defining a Hamilton operator which consists of two parts, a reference ($H^{(0)}$) and a pertubation (H'). The premise of pertubation methods is that the H' operator in some sense is “small” compared to H_0. In quantum mechanics, pertubation methods can be used for adding corrections to solutions which employ an independent particle approximation and the theoretical framework is then called *Many-Body Pertubation Theory* (MBPT).

If the Schrödinger equation for the reference Hamilton operator is solved

$$H = H^{(0)} + \lambda H' \tag{4.48}$$

$$H^{(0)} \Phi_i = E_i \Phi_i \quad , \mathrm{i} = 0,1,2,...,\infty$$

the solutions for the unperturbed Hamilton operator form a complete set (since $H^{(0)}$ is hermitian) which can be chosen to be orthonormal and λ is a (variable) parameter determining the strength of the pertubation. In the following only the lowest energy state is considered. The perturbed Schrödinger equation is

$$H\Psi = W\Psi \tag{4.49}$$

If $\lambda = 0$, then $H = H^{(0)}$, $\Psi = \Phi_0$ and $W = E_0$. As the perturbation is increased from zero to a finite value, the new energy and wave function must also change continuously and can be written as a Taylor expansion in powers of the perturbation parameter λ.

$$W = \lambda^0 W^{(0)} + \lambda^1 W^{(1)} + \lambda^2 W^{(2)} + \lambda^3 W^{(3)} + \ldots \tag{4.50}$$

$$\Psi = \lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \lambda^3 \Psi^{(3)} + \ldots$$

For $\lambda = 0$, it is seen that $\Psi = \Phi_0$ and $W = E_0$, these are the *unperturbed*, or *zero-order* wave functions and energy. The other indices define the *first-*, *second-* etc. order corrections. The λ parameter will eventually be set equal to 1 and the *n*th order energy and wave function become a sum of all terms up to order *n*. It is convenient to chose the perturbed wave function to be intermediately normalized, i.e. the overlap with the unperturbed wave function should be 1. This has the consequence that all correction terms are orthogonal to the reference wave function.

$$\langle \Psi^{(0)} | \Phi_0 \rangle = 1 \tag{4.51}$$

$$\langle \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots | \Phi_0 \rangle = 1$$

$$\langle \Psi^{(0)} | \Phi_0 \rangle + \lambda \langle \Psi^{(1)} | \Phi_0 \rangle + \lambda^2 \langle \Psi^{(2)} | \Phi_0 \rangle + \ldots = 1$$

$$\langle \Psi^{(i \neq 0)} | \Phi_0 \rangle = 0$$

Once all the correction terms have been calculated, it is trivial to normalize the total wave function. The Schrödinger equation becomes

$$\begin{aligned} &(H^{(0)} + \lambda H')(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots) \\ &= (\lambda^0 W^{(0)} + \lambda^1 W^{(1)} + \lambda^2 W^{(2)} + \ldots)(\lambda^0 \Psi^{(0)} + \lambda^1 \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \ldots) \end{aligned} \tag{4.52}$$

Since this holds for any value of λ, terms with the same power of λ can be collected to give

$$\lambda^n : H^{(0)}\Psi^{(n)} + H'\Psi^{n-1} = \sum_{i=0}^{n} W^{(i)}\Psi^{(n-1)} \tag{4.53}$$

The zero order equation is just the Schrödinger equation for the unperturbed problem. The first-order equation contains two unknowns, the first-order correction to the energy, W_1, and the first-order correction to the wave function

$$\lambda^1 : H^{(0)}\Psi^{(1)} + H'\Psi^{(0)} = W^{(0)}\Psi^{(1)} + W^{(1)}\Psi^{(0)} \tag{4.54}$$

The *n*th-order energy correction can be calculated by multiplying from the left by Φ_0 and integrating and use of the "turnover $\langle \Phi_0 | H_0 | \Psi_i \rangle = \langle \Psi_i | H_0 | \Phi_0 \rangle^*$ rule".

$$\langle \Phi_0 | H^{(0)} | \Psi^{(n)} \rangle + \langle \Phi_0 | H' | \Psi^{(n-1)} \rangle = \sum_{i=0}^{n-1} W^{(i)} \langle \Phi_0 | \Psi^{(n-1)} \rangle + W^{(n)} \langle \Phi_0 | \Psi^{(0)} \rangle \tag{4.55}$$

$$E_0 \langle \Phi_0 | \Psi^{(n)} \rangle + \langle \Phi_0 | H' | \Psi^{(n-1)} \rangle = W^{(n)} \langle \Phi_0 | \Psi^{(0)} \rangle$$

$$W^{(n)} = \langle \Phi_0 | H' | \Psi^{(n-1)} \rangle$$

From this it would appear that the *(n-1)*th-order wave function is required for calculating the *n*th-order energy. However, by using the turnover rule and the *n*th and lower-order pertubation equations it can be shown that knowledge of the *n*th-order wave function actually allows a calculation of the *(2n+1)*th-order energy.

$$W^{(2n+1)} = \langle \Psi^{(n)} | H' | \Psi^{(n)} \rangle - \sum_{k,l=1}^{n} W^{(2n+1-k-l)} \langle \Psi^{(k)} | \Psi^{(l)} \rangle \tag{4.56}$$

The first-order equation is one equation with two unknowns. Since the solutions to the unperturbed Schrödinger equation generates a complete set of functions, the unknown first-order correction to the wave function can be expanded in these functions. This is known as *Rayleigh-Schrödinger* perturbation theory and the λ^1 equation becomes

$$\Psi_i = \sum_i c_i \Phi_i \tag{4.57}$$

$$(H^{(0)} - W^{(0)})(\sum_i c_i \Phi_i) + (H' - W^{(1)})\Phi_0 = 0$$

Multiplying from the left by Φ_0^* and integrating yields

$$\sum_i c_i \langle \Phi_0 | H^{(0)} | \Phi_i \rangle - W^{(0)} \sum_i c_i \langle \Phi_0 | \Phi_i \rangle + \langle \Phi_0 | H' | \Phi_0 \rangle - W^{(1)} \langle \Phi_0 | \Phi_0 \rangle = 0$$

$$\sum_i c_i E_i \langle \Phi_0 | \Phi_i \rangle - c_0 E_0 + \langle \Phi_0 | H' | \Phi_0 \rangle - W^{(1)} = 0$$

$$c_0 E_0 - c_0 E_0 + \langle \Phi_0 | H' | \Phi_0 \rangle - W^{(1)} = 0 \tag{4.58}$$

$$\langle \Phi_0 | H' | \Phi_0 \rangle = W^{(1)}$$

since the Φ_is are orthonormal. The latter equation shows that the first-order correction to the energy is an average of the perturbation operator over the unperturbed wave function. The first-order correction to the wave function can be obtained in an analogous manner by multiplying from the left by a function other than Φ_0 (Φ_j) and integrating to give

$$c_j = \frac{\langle \Phi_j | H' | \Phi_0 \rangle}{E_0 - E_j} \tag{4.59}$$

The expansion coefficients determine the first-order correction to the perturbed wave function and they can be calculated for the known unperturbed wave functions and energies.

Starting from second-order perturbation equation,

$$\lambda^2 : H^{(0)}\Psi^{(2)} + H'\Psi^{(1)} = W^{(0)}\Psi^{(2)} + W^{(1)}\Psi^{(1)} + W^{(2)}\Psi^{(0)} \tag{4.60}$$

$$\Psi^{(2)} = \sum_i d_i \Phi_i$$

analogous formulas can be generated for the second-order corrections. Using intermediate normalization ($c_0 = d_0 = 0$), the second-order energy correction is after transformation

$$W^{(2)}=\sum_i c_i\langle\Phi_0|H'|\Phi_i\rangle=\sum_{i\neq 0}\frac{\langle\Phi_0|H'|\Phi_i\rangle\langle\Phi_i|H'|\Phi_0\rangle}{E_0-E_i} \tag{4.61}$$

This shows that the second-order energy correction can be written in terms of the first-order wave function (c_i) and matrix elements over unperturbed states. The second-order wave function correction is

$$d_j=\sum_{i\neq 0}\frac{\langle\Phi_j|H'|\Phi_i\rangle\langle\Phi_i|H'|\Phi_j\rangle}{(E_0-E_j)-(E_0-E_i)}-\frac{\langle\Phi_j|H'|\Phi_0\rangle\langle\Phi_0|H'|\Phi_j\rangle}{(E_0-E_j)^2} \tag{4.62}$$

The formulas for higher-order corrections become increasingly complex. The main point, however, is that all corrections can be expressed in terms of matrix elements of the perturbation operator over the unperturbed wave functions and the unperturbed energies.

So far the theory has been completely general. In order to apply pertubation theory to the calculation of correlation energy, the unperturbed Hamilton operator must be selected. The most common choice is to take this as a sum over Fock operators, leading to *Møller-Plesset* (MP) perturbation theory, which satisfies the requirement that solutions to the unperturbed Schrödinger equation should be known. Furthermore, this is the only choice which leads to a size extensive method, which is a desirable feature. (4.63)

$$H^{(0)}=\sum_{i=1}^{N}F_i=\sum_{i=1}^{N}\left(h_i+\sum_{j=1}^{N}(J_{ij}-K_{ij})\right)=\sum_{i=1}^{N}h_i+2\langle V_{ee}\rangle=\sum_{i=1}^{N}h_i+\sum_{i=1}^{N}\sum_{j=1}^{N}\langle g_{ij}\rangle$$

$$H'=H-H^{(0)}=V_{ee}-\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij}-K_{ij})=V_{ee}-2\langle V_{ij}\rangle=\sum_{i=1}^{N}\sum_{j=1}^{N}g_{ij}-\sum_{i=1}^{N}\sum_{j=1}^{N}\langle g_{ij}\rangle$$

The zero-order wave function is the HF determinant and the zero-order energy is just a sum of MO energies. The first-order energy correction is the average of the perturbation operator over the zero-order wave function.

$$W^{(1)}=\langle\Phi_0|H'|\Phi_0\rangle=\langle V_{ee}\rangle-2\langle V_{ee}\rangle=-\langle V_{ee}\rangle \tag{4.64}$$

This yields a correction for the overcounting of the electron-electron repulsion at zero-order. The first-order energy (sum of W_0 and W_1) is exactly the HF energy.

Using the notation E(MP*n*) to indicate the correction at order n and MP*n* to indicate the total energy up to order *n*

$$E(MP0)=\sum_{i=1}^{N}\varepsilon_i \tag{4.65}$$

$$E(HF)=E(MP0)+E(MP1) \tag{4.66}$$

Electron correlation energy thus starts at order 2 with this choice of H_0.

In developing perturbation theory it was assumed that the solutions to the unperturbed problem formed a complete set but this requires an infinite number of functions which is impossible. The lowest energy solution to the unperturbed problem is the HF wave function, additional higher energy solutions are excited Slater determinants, analogously to the CI method. When a finite basis set is employed it is only possible to generate a finite number of excited determinants. The expansion of the many-electron wave function is therefore truncated.

Regarding the expression for the second-order energy correction this involves matrix elements of the perturbation operator between the HF reference and all possible excited states. Since the perturbation is a two-electron operator, all matrix elements involving triple, quadruple etc. excitations are zero. When canonical HF orbitals are used, matrix elements with singly excited states are also zero, which follows from:

$$\begin{aligned}\langle\Phi_0|H'|\Phi_i^a\rangle &=\langle\Phi_0|H-\sum_{j=1}^{N}F_j|\Phi_i^a\rangle=\langle\Phi_0|H'|\Phi_i^a\rangle-\sum_{j=1}^{N}\langle\Phi_0|F_j|\Phi_i^a\rangle \\ &=\langle\Phi_0|H'|\Phi_i^a\rangle-\varepsilon_a\langle\Phi_0|\Phi_i^a\rangle\end{aligned} \tag{4.67}$$

The first bracket is zero due to Brillouins theorem and the second set of brackets is zero due to the orbitals being eigenfunctions of the Fock operators and being orthogonal to each other. The second-order correction to the energy, which is the first contribution to the correlation energy, therefore only involves a sum over doubly excited determinants. These can be generated by promoting two electrons from occupied orbitals *i* and *j* to virtual orbitals *a* and *b*. The summation must be restricted so that each excited state is only counted once.

$$W^{(2)} = \sum_{i \neq j}^{\text{occ}} \sum_{a<b}^{\text{vir}} \frac{\langle \Phi_0 | H' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | H' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}} \tag{4.68}$$

The matrix elements between the HF and a doubly excited state are given by two electron integrals over MOs. The difference in total energy between two Slater determinants becomes a difference in MO energies (essentially *Koopmans´ theorem*)[240] and the explicit formula for the second-order Møller-Plesset correction is

$$E(MP2) = \sum_{i \neq j}^{\text{occ}} \sum_{a<b}^{\text{vir}} \frac{\left[\langle \phi_i \phi_j | \phi_a \phi_b \rangle - \langle \phi_i \phi_j | \phi_b \phi_a \rangle \right]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{4.69}$$

Once the two-electron integrals over MOs are available, the second-order energy correction can be calculated as a sum over such integrals. There are of the order of M^4 integrals, thus the calculation of the energy (only) increases as M^4 with the system size. However, the transformation of the integrals from the AO to the MO basis grows as M^5. MP2 is an M^5 method, but fairly inexpensive as not all two-electron integrals over MOs are required. Only those corresponding to the combination of two occupied and two virtual MOs are needed.

The most important contribution to the energy in a CI procedure comes from doubly excited determinants. This is also shown by the perturbation expansion, the second- and third-order energy corrections only involve doubles. At fourth order the singles, triples and quadruples enter the expansion for the first time. The MP2 contribution describes the correlation between pairs of electrons while MP3 describes the interaction between pairs. MP2 typically overshoots the correlation effect, but often gives better answers than MP3.

CI methods determine the energy by a variational procedure and the energy is consequently an upper bound to the exact energy. There is no such guarantee for perturbation methods but limitations in the basis set often mean that the error in total energy is several a.u. anyway. Furthermore, the interest is not in total energies, but in energy differences (keeping the errors constant).

240 Koopmans, T. A.; “Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms”, *Physica* **1933**, *1*, 104-113.

4.3.6 Coupled Cluster Methods

Perturbation methods add all types of corrections (S, D, T, Q etc.) to the reference wave function to a given order (2, 3, 4 etc.) The idea in *Coupled Cluster* (CC) methods is to include all corrections of a given type to infinite order.[241] The (intermediate normalized) coupled cluster wave function is written as

$$\Psi_{\mathrm{CC}} = e^{T}\Phi_0 \tag{4.70}$$

$$e^{T} = 1 + T + \frac{1}{2}T^2 + \frac{1}{6}T^3 + \ldots = \sum_{k=0}^{\infty}\frac{1}{k!}T^k$$

where the cluster operator *T* is given by

$$T = T_1 + T_2 + T_3 + \ldots + T_N \tag{4.71}$$

The T_i operator acting on a HF reference wave function generates all *i*th excited Slater determinants

$$T_1\Phi_0 = \sum_{i}^{\mathrm{occ}}\sum_{a}^{\mathrm{vir}} t_k^a \Phi_k^a \tag{4.72}$$

$$T_2\Phi_0 = \sum_{k\neq l}^{\mathrm{occ}}\sum_{a\neq b}^{\mathrm{vir}} t_{kl}^{ab}\Phi_{kl}^{ab}$$

The expansion coefficients *t* are called *amplitudes*. From equations 2.70 and 2.71 the exponential operator may be written as

$$\begin{aligned} e^{T} = 1 + T_1 + (T_2 + \frac{1}{2}T_1^2) + (T_3 + T_2T_1 + \frac{1}{6}T_1^3) \\ + (T_4 + T_3T_1 + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{24}T_1^4) + \ldots \end{aligned} \tag{4.73}$$

The first term generates the reference HF and the second all singly excited states. The first parenthesis generates all doubly excited states, which may be considered as *connected* (T_2) or *disconnected* (T^2_1). The second parenthesis generates all triply excited states, which again may be either "true" (T_3) or "product" triples (e.g. T_2T_1). The quadruply excited states can similarly be viewed as composed of five terms, a

241 Bartlett, R. J. "Coupled-cluster approach to molecular structure and spectra: a step toward predictive quantum chemistry", *J. Phys. Chem.* **1989**, *93*, 1697-1708.

true quadruple and four product terms. Physically a connected type such T_4 corresponds to four electrons interacting simultaneously, while a disconnected term such as T^2_2 corresponds to two non-interacting pairs of interacting electrons.

With the coupled cluster wave function the Schrödinger equation becomes

$$H\, e^T \Phi_0 = E\, e^T \Phi_0 \tag{4.74}$$

Multiplying from the left by Φ_0^* and integrating gives

$$\langle \Phi_0 | H\, e^T | \Phi_0 \rangle = E_{\mathrm{CC}} \langle \Phi_0 | e^T \Phi_0 \rangle$$

$$\langle \Phi_0 | H\, e^T | \Phi_0 \rangle = E_{\mathrm{CC}} \langle \Phi_0 | (1 + T_1 + T_2 + \ldots) \Phi_0 \rangle \tag{4.75}$$

$$E_{\mathrm{CC}} = \langle \Phi_0 | H\, e^T | \Phi_0 \rangle$$

Expanding out the exponential and using the fact that the Hamilton operator contains only one- and two-electron operators yields

$$E_{\mathrm{CC}} = \langle \Phi_0 | H | (1 + T_1 + T_2 + \frac{1}{2} T_1^2) \Phi_0 \rangle \tag{4.76}$$

$$E_{\mathrm{CC}} = \langle \Phi_0 | H | \Phi_0 \rangle + \langle \Phi_0 | H | T_1 \Phi_0 \rangle + \langle \Phi_0 | H | T_2 \Phi_0 \rangle + \frac{1}{2} \langle \Phi_0 | H | T_1^2 \Phi_0 \rangle$$

$$E_{\mathrm{CC}} = E_0 + \sum_i^{\mathrm{occ}} \sum_a^{\mathrm{vir}} t_k^a \langle \Phi_0 | H\, \Phi_k^a \rangle + \sum_{k \neq l}^{\mathrm{occ}} \sum_{a \neq b}^{\mathrm{vir}} (t_{kl}^{ab} + t_k^a t_l^b - t_k^b t_l^a) \langle \Phi_0 | H | \Phi_{kl}^{ab} \rangle$$

When using HF orbitals for constructing the Slater determinants, the first matrix elements are zero (Brillouins theorem) and the second matrix elements are just two-electron integrals over MOs.

$$E_{\mathrm{CC}} = E_0 + \sum_{k \neq l}^{\mathrm{occ}} \sum_{a \neq b}^{\mathrm{vir}} (t_{kl}^{ab} + t_k^a t_l^b - t_k^b t_l^a)(\langle \phi_k \phi_l | \phi_a \phi_b \rangle - \langle \phi_k \phi_l | \phi_b \phi_a \rangle) \tag{4.77}$$

The coupled cluster correlation energy is therefore determined completely by the singles and doubles amplitudes and the two-electron MO integrals.

Only equation for the amplitudes is obtained by multiplying the Schrödinger equation from the left by a singly excited determinant and integrating.

$$\langle \Phi_m^e | H\, e^T | \Phi_0 \rangle = E_{\mathrm{CC}} \langle \Phi_m^e | e^T \Phi_0 \rangle \tag{4.78}$$

$$\langle \Phi_m^e | H | (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_3 + T_1 T_2 + \frac{1}{6} T_1^3) \Phi_0 \rangle = E_{\mathrm{CC}} \langle \Phi_m^e | T_1 \Phi_0 \rangle$$

$$\langle \Phi_m^e | H | \Phi_0 \rangle + \langle \Phi_m^e | H | T_1 \Phi_0 \rangle + \langle \Phi_m^e | H | T_2 \Phi_0 \rangle + \frac{1}{2} \langle \Phi_m^e | H | T_1^2 \Phi_0 \rangle$$
$$+ \langle \Phi_m^e | H | T_3 \Phi_0 \rangle + \langle \Phi_m^e | H | T_1 T_2 \Phi_0 \rangle + \frac{1}{6} \langle \Phi_m^e | H | T_1^3 \Phi_0 \rangle = E_{\mathrm{CC}} \langle \Phi_m^e | T_1 \Phi_0 \rangle$$

The first term in the last equation is zero due to Brillouins theorem and the remaining forms a coupled set of equations of all singles, doubles and triples amplitudes. Other equations connecting amplitudes may be obtained by multiplying from the left by a double, triple etc. excited determinant and integrating.

If all cluster operators up to T_N are included in T, all possible excited determinants are generated and the coupled cluster wave function is equivalent to full CI, but this is impossible for all but the smallest systems. Therefore the cluster operator must be truncated at some excitation level. When the T operator is truncated, some of the terms in the amplitude equations will become zero and the amplitudes derived from these approximate equations will no longer be exact. The lowest level of approximation is $T = T_2$ (*Coupled Cluster Doubles*, (CCD)). Including only Singles gives no improvement compared to HF. Using $T = T_1 + T_2$ gives the CCSD model which is only slightly more demanding than CCD. Both methods scale as M^6 in the limit of a large basis set. The next higher level is CCSDT which scales as M^8 and is more demanding than CISDT.

The important aspect in coupled Cluster methods is that excitations of higher order than the truncation of the T operator enter the amplitude equation. Quadruply excited states, for example, are generated by the T^2_2 operator in CCSD and they enter the amplitude equations with a weight given as a product of double amplitudes. Quadruply excited states influence the doubles amplitudes and thereby also the CCSD energy. It is the inclusion of these products of excitations that makes the coupled cluster theory size extensive.

4.3.7 Connections between Coupled Cluster, Configuration Interaction and Perturbation Theory

The general Cluster operator is given by

$$e^T = 1 + T_1 + (T_2 + \frac{1}{2} T_1^2) + (T_3 + T_2 T_1 + \frac{1}{6} T_1^3) + (T_4 + T_3 T_1 + \frac{1}{2} T_2^2 + \frac{1}{2} T_2 T_1^2 + \frac{1}{24} T_1^4) + \ldots \quad (4.79$$

where terms have been collected according to the excitation they generate. Each of the operators in a given parenthesis generates all the excited determinants of a given type. Both T_2 and T^1_2 generate all doubly excited determinants and the terms in the above equation generate all determinants which are included in a CISDTQ calculation. This cluster expansion can be viewed as a method of dividing up the contributions from each excitation type. The total contribution from double excitations is the sum of two terms, one which is the square of the singles contributions and the remaining is (by definition) the connected doubles. Similarly the total contribution from triple excitations is a sum of three terms, the cube of the singles contributions, the product of singles and doubles contribution and the remaining is the connected triples.

When canonical HF orbitals are used the T_1 effect is small, although not zero since singles enter indirectly via the doubly excited states. It is known from CI that the effect of doubles is the most important. In coupled cluster theory the doubles contribution is divided into T^2_1 and T_2. If T_1 is small, then T^2_1 must also be small and the most important term is T_2. For the same reasons for the triples T_3, the connected triples, is the most important term. For the quadruple excitations, all terms involving T_1 must again be small and since T_2 is large the disconnected quadruples T^2_2 are the dominant term and the connected quadruples T_4 is small.

The principal deficiency of CISD is the lack of the T^2_2 term, which is the main reason for CISD not being size extensive. Furthermore, this term becomes more and more important as the number of electrons increases and CISD recovers a smaller and smaller percentage of the correlation energy as the system increases.

Coupled cluster is closely connected with Møller-Plesset perturbation theory. The infinite Taylor expansion of the exponential operator ensures that the contributions from a given excitation level are included to infinite order. Perturbation theory indicates that doubles are the most important, they are the only contributors to MP2 and MP3. At fourth order, there are contributions from singles, doubles, triples and quadruples. The MP4 quadruples contribution is actually the disconnected T^2_2 term in the coupled cluster language and the triples contribution corresponds to T_3. This is consistent with the above analysis, the most important is T_2 (and products thereof) followed by T_3. The CCD energy is equivalent to MP2 ∞ (D) where all disconnected contributions of products of doubles are included. If the perturbation series is reasonable converged at fourth order, it is expected that CCD ~ MP4(DQ) and CCSD ~ MP4(SDQ). The MP2, MP3 and MP4(SDQ) results may be obtained in the first iteration for the CCSD amplitudes, allowing a direct test of the convergence of the MP series. This also points out the principal limitation of the CCSD method, the neglect of the connected triples. Including them in the *T* operator leads to the CCSDT method which is too demanding computationally for all but the smallest systems. Alternatively the triples contribution may be evaluated by perturbation theory and added to the CCSD results. Several such hybrid method exist; two of the most common are known by the acronyms CCSD+(T)CCSD and CCSD(T).[242] In both cases the triples contribution is calculated from the formula given by MP4, but using the CCSD amplitudes instead of the perturbation coefficients for the wave function corrections. For the CCSD(T) method an additional term arising from fifth-order perturbation theory, describing coupling between singles and triples, is also included. This is computationally inexpensive to calculate and the latter method is usually preferred.

Another commonly used method is *Quadratic* CISD (QCISD).[243] It was originally derived from CISD by including enough higher-order terms to make it size extensive. In fact, the resulting equations are identical to CCSD where some of the terms have been omitted. The omitted terms are computational inexpensive and there appears to be no reason for using the less complete QCISD over CCSD (or QCISD(T) in place

242 Scuseria, G. E., Lee, T. J.; "Comparison of coupled-cluster methods which include the effects of connected triple excitations", *J. Chem. Phys.* **1990**, *93*, 5851-5855.

243 Pople, J. A., Head-Gordon, M.; Raghavachari, K.; "Quadratic configuration interaction. A general technique for determining electron correlation energies", *J. Chem. Phys.* **1987**, *87*, 5968-5975.

of CCSD(T)), although in practice they normally give very similar results.[244]

In summary in terms of accuracy with a medium sized basis set the following order of performance is often observed.

$$HF << MP2 < CISD < MP4(SDQ) \sim CCSD < MP4 < CCSD(T)$$

Given a sufficiently large basis set, the CCSD(T) method is able to meet the goal of an accuracy of ~ 1 kcal/mol for most systems. This method was employed in the present thesis to calculate relative energies of different isomers. The geometry optimization of these isomers was done using the MP2 method.

4.4 Basis Sets

One of the approximations inherent in essentially all *ab initio* methods is the introduction of a basis set (chapter 2.3.2). Expanding an unknown function, such as a molecular orbital, in a set of known functions is not an approximation if the basis set is complete. However, a complete basis set means an infinite number of functions. When a finite basis is used, only the components of an MO along the coordinate axes corresponding to the selected basis can be represented. The smaller the basis, the poorer the representation. The type of basis functions used also influence the accuracy. The better a single basis function is able to reproduce the unknown function, the fewer are basis functions necessary to achieve a given level of accuracy.

4.4.1 Slater and Gaussian Type Orbitals

There are two types of basis functions (also called *Atomic Orbitals*, AO, although in general they are not solutions to an atomic Schrödinger equation) commonly used in electronic structure calculations: *Slater Type Orbitals* (STO)[245] and *Gaussian Type Orbitals* (GTO).[246]

244 Lee, T. J.; Rendall, A. P.; Taylor, P. R.; "Comparison of the quadratic configuration interaction and coupled-cluster approaches to electron correlation including the effect of triple excitations", *J. Phys. Chem.* **1990**, *94*, 5463-5468.
245 Slater, J. C.; "Atomic Shielding Constants", *Phys. Rev.* **1930**, *36*, 57-64.
246 Boys, S. F.; "Electronic Wave Functions. I. A General Method of Calculation for the Stationary States of Any Molecular System", *Proc. R. Soc. Lon. A* **1950**, *200*, 542-554.

The former have the functional form:

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi)=N\,Y_{l,m}(\theta,\varphi)\,r^{n-1}e^{-\zeta r} \tag{4.81}$$

N is a normalization constant and $Y_{l,m}$ are the usual spherical harmonic functions. The exponential dependence on the distance between the nucleus and the electron mirrors the exact orbitals for the hydrogen atom. However, STOs do not have any radial nodes, nodes in the radial part are introduced by making linear combinations of STOs.

Gaussian type orbitals can be written in terms of polar or cartesian coordinates

$$\chi_{\alpha,n,l,m}(r,\theta,\varphi)=N\,Y_{l,m}(\theta,\varphi)\,r^{(2n-2-l)}e^{-\alpha r^2} \tag{4.82}$$

$$\chi_{\alpha,l_x,l_y,l_z}(x,y,z)=N\,x^{l_x}y^{l_y}z^{l_z}e^{\alpha r^2}$$

where the sum of l_x, l_y and l_z determines the type of orbital (for example $l_x + l_y + l_z = 1$ is a p-orbital). The r^2 dependence in the exponential makes the GTO inferior to the STOs in two aspects. At the nucleus the GTO has zero slope, in contrast to the STO which has a “cusp” (discontinous derivative) and GTOs have problems representing the proper behaviour near the nucleus. The other problem is that GTOs falls off too rapidly far from the nucleus compared with an STO and the “tail” of the wave function is consequently represented poorly. These considerations indicate that more GTOs are necessary for achieving a certain accuracy compared with STOs (~3 times more). The increase in number of basis functions, however, is more than compensated for by the ease by which the required integrals can be calculated. GTOs are therefore preferred and used almost universally as basis functions in electronic structure calculations.

4.4.2 Classification of Basis Sets

Another important factor beside the type of function is the number of functions used. The smallest possible is a *minimum basis set*. Only enough functions are employed to contain all the electrons for the neutral atom(s), e.g for hydrogen this means a single s-function. The next improvement in the basis set is a doubling of all basis

functions, producing a *Double Zeta* (DZ) type basis. The term zeta stems from the fact that the exponent of STO basis function is often denoted by the greek letter *ζ*. A DZ basis thus employs two s-functions for hydrogen, four s-functions and two p-functions for first row elements and six s-functions and for p-functions for second row elements. Doubling the number of basis functions allows for a much better description of the electron distribution if it is different in different directions. A variation of the DZ type basis only doubles the number of valence orbitals, producing a *split valence basis*. In actual calculations a doubling of the core orbitals would rarely be considered (chemical bonding occurs between valence orbitals) and the term DZ basis is also used for split valence basis sets (or sometimes VDZ, for valence double zeta). Next levels are *Triple Zeta* (TZ), *Quadruple Zeta* (QZ) and *Quintuple Zeta* (5Z). So far only the number of s- and p-functions for each atom has been discussed. In most cases higher angular momentum functions are also important, these are denoted *polarization functions*. If for example the electron distribution along a bond is different than that perpendicular to the bond, a p-orbital may introduce polarization to a s-type bond orbital. Similarly, d-orbitals can be used for polarizing p-orbitals, f-orbitals for polarizing d-orbitals etc. For single determinant wave functions where electron correlation is not considered, the first set of polarized functions (i.e. p-functions for hydrogen and d-functions for heavy atoms) is by far the most important and will in general describe all the important charge polarization effects.

If methods including electron correlation are used, higher angular momentum functions are essential. Two types of correlation can be identified. The *radial correlation* refers to the situation where one electron is close and one far from the nucleus. To describe this, the basis set needs functions of the same type, but with different exponents. The *angular correlation* refers to the situation where two electrons are on opposite sides of the nucleus. To describe this, the basis set needs functions of same magnitude exponents, but different angular momenta, e.g. to describe an angular correlation of an s-function, p- (and d-, f-, g-functions etc.) are needed. A single set of polarization functions added to the DZ basis forms a *Double Zeta plus Polarization* (DZP) type basis.

4.4.3 Contracted Basis Sets

Combining the full set of basis functions, known as the *primitive* GTOs (PGTOs), into a smaller set of functions by forming linear combinations is known as basis set contraction, and the resulting functions are called *contracted* GTOs (CGTOs).

$$\chi(CGTO)=\sum_{i}^{k} a_i \chi_i(PGTO) \tag{4.83}$$

There are many different contracted basis sets available in the literature or built into the Gaussian 03 program package. Within this thesis occasionally derivatives of the Pople style basis set *6-311G* are used.[247] This is a *triple split valence* basis set, where the core orbitals are a contraction of six PGTOs and the valence split into three functions, represented by three, one and one PGTOs, respectively.

4.4.4 Correlation Consistent Basis Sets

The *correlation consistent* (cc) basis sets by Dunning are geared toward recovering the correlation energy of the valence electrons.[248,249] The name correlation consistent refers to the fact that the basis sets are designed so that functions which contribute similar amounts of correlation energy are included at the same stage, independently of the function type. For example, the first d-function provides a large energy lowering, but the contribution from a second d-function is similar to the first f-function. The energy lowering from a second d-function is similar to that from the second f-function and the first g-function. Addition of polarization functions should therefore be done in the order: 1d, 2d1f, 3d2f1g. An additional feature of the cc basis sets is that the energy error from the sp-basis should be comparable to (or at least not exceed by) the correlation error arising from the incomplete polarization space and the sp-basis therefore also increases as the polarization space is extended. Several different size of basis sets are available in the terms of final number of contracted

247 Krishnan, R. Binkley, J. S. Seeger, R. Pople, J. A.; "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions", *J. Chem. Phys.* **1980**, *72*, 650-654.
248 Dunning, T. H. Jr.; "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen", *J. Chem. Phys.* **1989**, *90*, 1007-1023.
249 Wilson, A. K.; van Mourik, T.; Dunning, T. H.; "Gaussian basis sets for use in correlated molecular calculations. VI. Sextuple zeta correlation consistent basis sets for boron through neon", *J. Mol. Struct.* **1996**, 3*88, 339-349.*

functions. These are known by their acronyms: *cc-pVDZ* up to *cc-pV6Z* (*correlation consistent polarized Valence Double* (or higher) *Zeta*. A step up in terms of quality increases each type of basis function by one and adds a new type of higher-order polarization function. The vast majority of ab initio calculations presented in this thesis represents coupled cluster calculations employing the *cc-pVTZ* and *cc-pVQZ* basis sets which are composed as follows

Basis	*Primitive functions*	*Contracted functions*
cc-pVTZ	10s,5p,2d,1f/5s,2p,1d	4s,3p,2d,1f/3s,2p,1d
cc-pVQZ	12s,6p,3d,2f,1g/6s,3p,2d,1f	5s,4p,3d,2f,1g/4s,3p,2d,1f

Where the number of primitives with heavy atoms (first row elements) is denoted before the slash and hydrogen after. The main advantage of cc basis sets is the ability to generate a sequence of basis sets which converges towards the basis set limit and consistently reduces errors (both HF and correlation) for each step up in quality. In tests it has been found that the cc-pVTZ basis set can provide ~85% of the total (valence) correlation energy while the cc-pVQZ basis set provides ~93%. The main difficulty with in using the cc basis is that each step up in quality almost doubles the number of basis functions which severely effects the computational requirements. A further step up and the employment of the cc-pV5Z basis set to the presented calculations was impossible due to the lack of sufficient disk space on the abacus4 super computer of the ZEDAT.

4.4.5 Extrapolation Procedures

In principle the large majority of systems can be calculated with high accuracy by using a highly correlated method such as CCSD(T) and performing a series of calculations with systematically larger basis sets (like the correlation consistent sets) in order to extrapolate to the basis set limit. In practice this is too demanding. Various approximation procedures have therefore been developed for estimating the “infinite correlation, infinite basis basis” limit as efficiently as possible. These models rely on the fact that different properties converge with different rates as the level of sophistication increases and that effects from extending the basis set to a certain

degree are additive. There are three main steps in these procedures:

(1) Selection of geometry.

(2) Selecting a basis set for calculating the HF energy.

(3) Estimating the electron correlation energy.

Given a certain target accuracy, the error from each of these four steps should be reduced below the desired tolerance (typically ~ 1 kcal/mol, “chemical accuracy”). The error at a given level may be defined as the change which would occur if the calculation were taken to the “infinite correlation, infinite basis” limit.

Several models (different *Gaussian-3* (G3) and *Complete Basis Set* (CBS) levels) have been employed in this thesis.[120-124] They all match the mentioned accuracy compared to experimental results. They are calibrated on a reference set involving at least 125 atomic and molecular properties (atomization energies, ionization potentials, electron and proton affinities).

4.4.6 Frozen Core Approximation

In order to calculate total energies with a “chemical accuracy” of ~1 kcal/mol, it is necessary to use sophisticated methods for including electron correlation and large basis sets, which is only feasible for small systems. Instead the focus is usually on calculating relative energies, trying to make the errors as constant as possible. The important chemical changes take place in the valence orbitals; the core orbitals are almost constant. Limiting the number of determinants to only those which can be generated by exciting the valence electrons is known as the *frozen core approximation*. The frozen core approximation is not justified in terms of total energy. However it is essentially a constant factor, which drops out when calculating relative energies.

4.5 NMR-Spectroscopy and GIAO-Method

Nuclear magnetic resonance or *NMR* is a phenomenon which occurs when nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field.[250] When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary (shielding). This is called the chemical shift phenomenon. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol δ.

The chemical shift of a NMR-signal depends on the strength of the shielding σ_i of the nucleus.[251]

$$\sigma_i = \sigma_{dia} + \sigma_{para} + \sum_{i \neq j} \sigma_j \tag{4.84}$$

The diamagnetic part describes the shielding by electrons of the nucleus in spherical symmetry. This term dominates in the ^{1}H spectroscopy. The paramagnetic part describes all the deviations from the spherical charge distribution (excited states, orbital magnetic moment, bonds, electron density). This term dominates all hetero nucleus spectroscopy. The third component describes the effects of the other atoms in the sample (anisotropy by bonds, ring currents, electric field of polar groups in the molecule, solvent effects etc.)

To calculate chemical shifts and the shielding tensors the magnetic-field dependent Schrödinger equation has to be used.[252,253,]

$$H(B,\mu)\Psi(B,\mu) = E(B,\mu)\Psi(B,\mu) \tag{4.85}$$

Hamiltonian, wave function and energy depend on an external magnetic field *B* and the nuclear magnetic moment *μ*. Regarding the electronic Hamiltonian only the

250 Hornak, J. P.; “The Basics of NMR” http://www.cis.rit.edu/htbooks/nmr/bnmr.htm
251 Kalinowski, H.-O.; Berger, S.; Braun, S. “^{13}C-NMR Spektroskopie”, **1984**, Thieme, Stuttgart, p78.
252 Zuschneid, T. L. “Methoden-, Basissatz- und Geometrieabhängigkeit GIAO-berechneter NMR-chemischer Verschiebungen kleiner Kohlenwasserstoffmoleküle”, Dissertation, **2007**, Tübingen 35-36.
253 Ditchfield, R. “Self-consistent perturbation theory of diamagnetism”, *Mol. Phys.* **1974**, *27*, 789-807.

operator for the kinetic energy is affected.

$$T_e(B,\mu)=\frac{1}{2}\sum_j (p_j+A(r_j))^2 \qquad (4.86)$$

The operator for the momentum of electron *j* is expanded by the vector potential *A* which describes the effective magnetic field at the position of the electron. r_j is the distance vector to an arbitrary chosen origin. The dependence on a gauge origin of the magnetic field causes problems when non-infinite basis sets are used.[254] To solve this problem several solutions have been developed, e.g. the GIAO method.

The *GIAO* method, *Gauge Independent Atomic Orbitals*, is a method for calculating chemical shifts. Ditchfield proposed this method to cancel out the arbitrariness of the choice of origin and form (gauge) of the vector potential used to introduce the magnetic field in the Hamiltonian when calculating chemical shielding and chemical shift tensor. An exponential term containing the vector potential and local gauge origins at the nucleus is included with each atomic orbital. Originally developed based on Hartree-Fock it has been extended by to post-HF methods such as MP2 by Gauss.[255]

254 Helgaker, T.; Jaszunski, M.; Ruud, K.;"Ab Initio Methods for the Calculation of NMR Shielding and Indirect Spin−Spin Coupling Constants", Chem. Rev. **1999**, *99*, 293-252.

255 Gauss, J.; "Effects of electron correlation in the calculation of nuclear magnetic resonance chemical shifts", *J. Chem. Phys.* **1993**, *99*, 3629-3674.

5 Experimental

5.1 General Comments

5.1.1 General Working Procedures

All manipulations of air and moisture sensitive compounds were performed on a standard vacuum line in flame dried flasks under an atmosphere of argon. The argon, purification grade 4.8, was provided by *LINDE*. Solvents were distilled under argon from sodium (toluene, pentane, hexane, benzene), sodium/benzophenone (THF, DME, diethyl ether, tert.-butylmethyl ether) or phosphorous pentoxide (DMF, dichloromethane, chloroform, tetrachloromethane, acetonitrile). Solvents were stored over sodium-potassium alloy (ethers and hydrocarbons) or 3 Å molecular sieve (DMF, acetonitrile and chlorohydrocarbons) in flasks with *NORMAG* or *YOUNG* plug valve and transferred to the reaction vessels via standard vacuum techniques (condensation) or Schlenk technique. Air sensitive compounds were stored and weighted in a glovebox (MBraun Labmaster sp). Unless otherwise noticed all manipulations were carried out using standard Schlenk techniques in a argon counterflow to exclude moisture and air. Cooling of reaction mixtures up to -125°C was performed by ethanol/liquid nitrogen mixtures. Lower temperatures up to -160°C were obtained by *iso*-pentane/liquid nitrogen mixtures. Unless otherwise noted all reaction temperatures are internal temperatures, especially involving exothermic reactions at low temperatures.

5.1.2 Chemicals

Basic chemicals were ordered either directly at *ABCR*, *Acros*, *Aldrich*, *Fluka* or *Alfa Aesar* or purchased via the material stores at the *Institut für Chemie und Biochemie der Freien Universität Berlin*. 1,1-difluoroethylene and 1,1-dibromo-2,2-difluoroethylene were ordered from *SynQuest Labs, Inc*. Metal complexes employed in the reactions were either purchased or were synthesized by students in the advance inorganic chemistry lab course. bis(trimethylsilyl)dicyclopenta-

dienenyltitanium was a gift from the group of U. Rosenthal (*Catalysis, Leibnitz Institut für Katalyse e.V.*). Deuterated solvents were obtained from *euriso-top* or *chemotrade*. 1,1,1,3,3-pentafluorobutane was a gift of *Honeywell*.

5.1.3 Analytical Instruments and Techniques

NMR measurements were carried out on a *JOEL* Lambda 400 spectrometer at 20°C (if not indicated differently). Temperatures below room temperature were reached by evaporation of liquid nitrogen. Temperature sensitive compounds were transferred into the precooled spectrometer without interruption of the cold chain. Air and moisture sensitive compounds were measured in sealed NMR tubes (*Young*) or flame sealed 4-mm-Duran-glass tubes. Chemical shifts δ are given by definition as dimensionless number. The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplett (m). Spectra were referenced with internal standards: for ^{1}H- and ^{13}C-NMR (solvent signal) and external standards for ^{19}F- and ^{119}Sn-NMR ($CFCl_3$ and tetramethyltin). Measurement frequencies are 399.65 MHz (^{1}H), 100.40 MHz (^{13}C), 376.00 MHz (^{19}F) and 148.95 MHz (^{119}Sn).
EPR investigations were performed in collaboration with the group of Prof. Abram at the *Institiut für Anorganische Chemie* of the *Freie Universität Berlin*. Mass spectra were recorded at the *Institiut für Organische Chemie* of the *Freie Universität Berlin* on a *Varian* MAT 711.
Crystal structure data were collected on a *Bruker* SMART-CCD-1000-TM diffractometer with Mo-K_α-radiation at -100°C. A suitable crystal was selected on an installation described in the literature[256] using a microscope, mounted onto a glass fiber using silicon grease and transferred into the cold gas stream of the diffractometer. The data was collected by the *SMART* program. Data reduction was done with the *SAINT* program. Empirical absorption correction was done with *SADABS*.[257] Structure solution and refinement was done using the least square refinement method implemented in the *SHELX* program suite. Pictures were created

256 Veith, M.; Baernighausen, H.; "Crystal and molecular structure of bis(trimethylsilyl)diimide", *Act. Cryst. B* **1974**, *30*, 1806-1813.
257 All three programs by Bruker, included in the scope of delivery of the SMART-CCD-1000-TM diffractometer.

using *Diamond 3*. Crystal structures are published at the *Cambridge Crystallographic Data Center* (CSD).

5.2 Preparation and Characterization

5.2.1 Revised Synthesis of Tetrafluorobutatriene (5)

5.2.1.1 1,1-difluoro-2-iodoethylene (9)

100 g (0.6 mol) iodinemonochloride (ICl) in a flame dried 2L-flask with a Normag type teflon plug valve and a magnetic stir bar were cooled to -196°C and evacuated (3 times). The reaction vessel and the difluoroethylene gas flask were connected to the vacuum line. At 0°C (icebath) 40 g (0.62 mol) difluoroethylene were added in portions over the vacuum line, monitored by a vacuum gauge. Then 300 mL of 2,6-lutidine were added at 0°C followed by the fast addition of 110g (0.72 mol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The valve at the reaction was then closed and the mixture slowly warmed to room temperature and stirred overnight. All volatiles were condensed into a -196°C cooling trap. 3 portions of 50 mL of water were added to the reaction mixture and the mixture was stirred for 5 minutes. Again all volatiles were condensed into the trap. 1,1-difluoro-2-iodoethylene was distilled off (b.p. 35°C) to yield 97 g (85%) of the pure product (purity > 99%). A scale up of the reaction to 2 mol iodine monochloride gave an equal yield.

Physical data:

^{1}H-NMR ($CDCL_3$, 20°C): δ = 4.82 (dd, $^{3}J(H\text{-}F_{trans})$ = 22.8 Hz, $^{3}J(H\text{-}F_{cis})$ = 2.1 Hz, =C*H*I)

^{19}F-NMR ($CDCL_3$, 20°C): δ = -71.36 (dd, $^{2}J(F\text{-}F)$ = 26.2 Hz, $^{3}J(F_{cis}\text{-}H)$ =2.1 Hz, =C*F*2);
-75.79 (dd, $^{2}J(F\text{-}F)$ = 26.2 Hz, $^{3}J(F_{trans}\text{-}H)$ = 23.6 Hz, =C*F*2)

all other spectroscopic data see reference 81.

5.2.1.2 1,1,4,4-tetrafluorobuta-1,3-diene (11)

The previously published method was modified as follows. Zinc was carefully activated by treatment with dilute hydrogen chloride and subsequently washed with water, ethanol and acetone and finally dried in high vacuum. Only the finest powder was employed in the following synthesis. 1,1-difluoro-2-iodoethylene (13 g, 68.45 mmol) was added dropwise to activated zinc powder (8 g) in DMF (50 mL) at room temperature. An exothermic reaction occurs. ^{19}F-NMR measurement revealed complete conversion to the zinc compound. The zinc reagent was transferred to a second flask containing [Pd(PPh3)4] (2g, 1.7mmol, 2.5 mol%) and 1,1-difluoro-2-iodo ethylene (13 g, 68.45 mmol) via a small diameter teflon tube. The reaction temperature was maintained at 75°C for 4 hours. Meanwhile the product was collected as a colorless liquid in a trap kept at -78°C which was connected to the reflux condenser. Fractional condensation under vacuum (10^{-3} mbar) yielded 5.2 g (61%) in the trap kept at -120°C.

Physical data (1,1,4,4-tetrafluorobuta-1,3-diene):

^{1}H-NMR ($CDCL_3$, 20°C): δ = 4.52 (m, 2H, =C*H*-)

19F-NMR ($CDCL_3$, 20°C): δ = -86.77 (m, 2F, =C*F*2); -88.09 (m, 2F, =C*F*2)

all other spectroscopic data see reference 73.

Physical data ((2,2-difluoroehylene)zinkiodide):

^{19}F-NMR ($CDCL_3$, 20°C): δ = -64.12 (dd, ^{2}J(F-F) = 56.2 Hz, ^{3}J(F_{trans}-H) =12.8 Hz, =C*F*2); -77.41 (dd, ^{2}J(F-F) = 56.2 Hz, ^{3}J(F_{trans}-H) = unresolved, overall signal collapses to a triplett, =C*F*2)

5.2.1.3 1,4-dibromo-1,1,4,4-tetrafluorobuta-1,3-diene (12)

The previously published method was modified as follows. Compound (**11**) (5.2 g, 40 mmol) was condensed onto bromine (6.4 g, 42 mmol) in CH_2Cl_2 (10 mL) in a 100 mL glass flask. The reaction mixture was rapidly warmed to room temperature

and stirred for 5 h at ambient temperature. 5 ml of sodium thiosulfate saturated water were added and the mixtures was stirred for 5 minutes. The layers were seperated, the water phase extracted 3 times with 2 mL of dichloromethane. Fractional condensation of the combined organic phases under vacuum yielded (**12**) (9.87 g, 82%) as a colourless liquid in the trap kept at -60C.

Physical data:

^{1}H-NMR ($CDCL_3$, 20°C): δ = 6.33 (m, 2H, =C*H*-)

^{19}F-NMR ($CDCL_3$, 20°C): δ = -50.30 (m, 4F, -C*F*2Br)

all other spectroscopic data see reference 73.

5.2.1.4 1,1,4,4-Tetrafluorobuta-1,2,3-triene (5) – General Procedure for Elimination in the Gas Phase Over Hot Potassium Hydroxide

Compound (**12**) (1 g, 3.5 mmol) was passed over technical grade KOH which was filled into a U-shaped tube with a diameter of no more than 1 cm and heated to 88°C by evaporation under vacuum (10^{-3} mbar). The volatile materials were collected in traps kept at -78°C (water) and -196 °C (product). No repetition was necessary. A yield of up to 100% was determined by weighting in a Young-valve tube.

For further descriptions of the procedure please see chapter 2.2.1.

Physical data:

^{19}F-NMR (CD_2Cl_2 , 193 K): δ = 96.1 (s);

all other spectroscopic data see reference 73.

5.2.2 Pericyclic Reactions

5.2.2.1 General Procedure for Diels-Alder Reactions of Tetrafluorobutatriene (5) Using Liquid Starting Materials

The reactions were carried out in flame dried 4-mm-Duran-glass tubes using vacuum line techniques. Tetrafluorobutatriene (0.1 mmol) was condensed onto the liquid nitrogen cooled diene (0.2 mL) and the tube was flame sealed and rapidly warmed to room temperature. The reaction was monitored by ^{19}F-NMR spectroscopy until all of the triene was consumed or polymerized.

Physical data:

13b:

^{19}F-NMR ($CDCL_3$, 20°C): δ = -85.9 (2F, m), -86.4 (2F, m)

^{1}H-NMR (C_6D_6, 20°C): δ = 6.57 (2H, dd, 1.0,1.0), 5.48 (2H, m)

^{13}C{^{1}H}-NMR ($CDCL_3$, 20°C): δ = 153.5 (2C, m, CF_2), 135.7 (2C), 88.1 (2C), 78.8 (2C)

13c:

^{19}F-NMR($CDCL_3$, 20°C): δ = -82.4 (2F, m); -88.2 (2F, m)

^{1}H-NMR ($CDCL_3$, 20°C): δ = 6.32 (2H, s); 2.38 (6H, s)

^{13}C{^{1}H}-NMR ($CDCL_3$, 20°C): δ = 152.5 (2C, m, CF2), 140.7 (2C), 95.0 (2C, m), 87,8 (2C), 95.5 (2C, m, C=CF2), 17.0 (2C)

13d:

^{19}F-NMR (neat, 20°C): δ = -85.9 (2F, m), -87.4 (2F, m)

13e:

^{19}F-NMR (neat, 20°C): δ = -85.5 (2F, m), -92.5 (2F, m)

13f:

^{19}F-NMR (neat, 20°C):δ = Isomer 1: -78.1 (2F, m), -89.0 (2F, m)
Isomer 2 (minor) -75.6 (2F, m), -90.7 (2F, m);
Isomer ratio 3.8:1

13g:

^{19}F-NMR ($CDCL_3$, 20°C): δ = -81.6 (2F, m), -88.3 (2F, m)

^{13}C{^{1}H}-NMR ($CDCL_3$, 20°C): δ = 150.8 (2C, m, CF2), 132.8 (2C), 128.3 (2C), 127.5 (2C), 86.8 (2C, m, C=CF2), 42.5 (2C)

13i:

^{19}F-NMR (neat): -84.6 (2F, m), -91.5 (2F, m)

13j:

^{19}F-NMR (neat): -86.8 (2F, m), -88.6 (2F, m)

13k:

^{19}F-NMR (neat): -86.9 (2F, m), -88.9 (2F, m)

5.2.2.2 General Procedure for Diels-Alder Reactions of Tetrafluorobutatriene (5) Using Solid Starting Materials

The reactions were carried out in flame dried Young-valve 100-mL-flasks. Tetrafluorobutatriene (0.1 mmol) was condensed onto the liquid nitrogen cooled diene (0.05 mmol) in dichloromethane. The amount of solvent was defined by the minimum amount that was necessary to dissolve the diene. In case of anthracene high dilution conditions were employed (100 mL of solvent, pentane was used in this single case) and in the case of 1,3-diphenylisobenzofurane 10 mL of dichloromethane were employed. The reaction was monitored by ^{19}F-NMR spectroscopy until all of the triene was consumed or polymerized. The reaction with 1,3-diphenylisobenzofurane can be monitored by a color change from yellow to colorless. In this case the excess of tetrafluorobutatriene was removed by evaporation to dryness.

Physical data:

13 a:

^{19}F-NMR (C_6D_6, 20°C): δ = -78.5 (4F, 62.9, 38.1, 16.3, 8.9 Hz) see Chapter 2.2.2.1 for assignments

^{1}H-NMR (C_6D_6): δ = 7.80 (4H, m), 7.38 (1H, d, 5.5), 7.37 (1H, d, 5.5), 7.21 (6H, m), 7.03 (1H, d, 5.5), 7.02 (1H, d, 5.5)

^{13}C{^{1}H}-NMR (C_6D_6): δ = 151.5 (2C, m, CF2), 146.4 (2C), 133.7 (2C), 130.0 (2C), 129.1 (2C), 128.,9 (2C), 128.2 (2C), 121,4 (2C), 95.5 (2C, m, C=CF2), 89.7 (2C)

13 h:

^{19}F-NMR ($CDCl_3$, 20°C): δ = -81.4 (2F, m), -87.4 (2F, m)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 7.36 (4H, m), 7.20 (4H, m), 5.08 (2H, m, 5.5)

^{13}C{^{1}H}-NMR ($CDCl_3$, 20°C): δ = 152.5 (2C, m, CF2), 141.6 (4C), 125.3 (4C), 123.9 (4C), 88.7 (2C, m, C=CF2), 45.,2 (2C, m, bridging C´s)

5.2.3 Partially fluorinated butatrienes – Synthetic Approaches

5.2.3.1 Attempted Synthesis of 1,1-Difluorobutatriene (6) by Multiple Hydrogen Fluoride Elimination from 1,1,1,3,3-pentafluorobutane (60)

10 mmol (1.5 g) 1,1,1,3,3-pentafluorobutane were diluted with the appropriate solvent (see table 2.4.2) in a flame dried Young-valve 50-mL-flask. With the exception of butyllithium and LDA (addition temperature, reaction time see table) all bases were added at room temperature. The reaction was monitored by NMR spectroscopy (see table for results).

Physical data of observed intermediates:

1,1,1,3,3-pentafluorobutane (60):

^{19}F-NMR ($CDCl_3$, 20°C): δ = -64.15 (3F, m), -88.95 (2F, m)

1,1,1,3-tetrafluorobut-2-ene (61):

^{19}F-NMR ($CDCl_3$, 20°C): δ = isomer 1: -59.16 (3F, m), -83.2 (1F, m)

isomer 2: -57.84 (3F, m), -83.3 (1F, m)

1,1,1-trifluorobut-2-yne (62):

^{19}F-NMR ($CDCl_3$, 20°C): δ = -50.41 (3F, q, ^{5}J(F-H)= 4 Hz)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 1.95 (3H, q, ^{5}J(H-F)= 4 Hz)

4.2.3.2 1,1-Difluorobuta-1-en-3-yne (45)

In a flame dried Young-valve 50-mL-flask 7.56 g acetylenetri-*n*-butylstannane (24 mmol, 1.04 eq.) and 4.37 g 1,1-difluoro-2-iodoethylene (23 mmol) were added to 250 mg palladium(II) acetate (5 mol%), 750 mg triphenylphosphine (12.5 mol%) and 1 g magnesium sulfate in 20 ml DMF. The reaction vessel was heated to 80°C (bath-temperature) for 45 min. The color of the reaction mixture changes to black during heating. The reaction mixture was subjected to fractional condensation in high vacuum (10-3 mbar) over a -78°C cooling trap. The product, 1.4g (66% yield) of a colorless gas, was collected in a -196°C cooling trap and stored in a Young-valve flask in the fridge at 4°C.

Physical data:

^{19}F-NMR ($CDCl_3$, 20°C): δ = -76.53 (1F, d, ^{3}J(F-H) = 22.8 Hz), -81.70 (1F, s) no geminal F-F coupling observable.

^{1}H-NMR ($CDCl_3$, 20°C): δ = 5.22 (1H, dm, ^{3}J(H-F) = 22.8 Hz), all other coupling constants could not be resolved, 3.58 (1H, m)

^{13}C{^{1}H}-NMR ($CDCl_3$, 20°C): δ = 163.9 (1C,dd, *C*F2, ^{2}J(C-F) = 293 Hz, 300 Hz), 81.2 (1C, dd, J(C-F) = 4 Hz, 9 Hz)), 71.9 (1C, dd, J(C-F) = 4Hz, 12 Hz), 64.4 (1C, J(C-F) = 19.5 Hz, 43 Hz), 88.7 (2C, m, C=CF2), 45.,2 (2C, m, bridging C´s)

5.2.3.3 Attempted Rearrangement of 1,1-Difluorobutatriene (6)

Attempt 1: 1 mmol (ca. 100 mg) (**45**) was condensed into a Normag-valve 2 L-flask and irradiated at room temperature for 4 hours. All volatiles were condensed onto $CDCl_3$ in a 4-mm-glass-tube. ^{19}F-NMR revealed only starting material.

Attempt 2: 1 mmol of (**45**) was condensed into a 25-mL-Schlenk-flask witch was charged with a magnetic stir bar and 250 mg cesium hydroxide or 250 mg potassium

hydroxide in 5 mL of THF/water mixture 1:1 or 250 mg potassium *tert.*-butoxide in 5 mL THF. ^{19}F-NMR revealed no signals in the expected region of the spectrum for a fluorinated triene.

5.2.3.4 2-Bromo-1,1-difluorobuta-1,3-diene (68)

In a flame dried 50-mL-Schlenk-flask, equipped with a magnetic stir bar, were added 2.2 g (10 mmol) 1,1-dibromo-2,2-difluoroethylene, 654 mg activated zinc dust (finest powder) and 30 mL DMF. A mild exothermic reaction occurred. The solution was stirred overnight. The solution was then transferred via a teflon pipe to another 50-mL-Schlenk-flask, equipped with a magnetic stir bar and 225 mg palladium(II) acetate and 655 mg triphenylphosphine (25 mol%).The reaction mixture was frozen in liquid nitrogen and degassed. 1.5 g vinylbromide which was synthesized according to literature methods were condensed onto the reaction mixture.[258] The reaction mixture was heated to 60°C (bath-temperature) for 2.5 hours. Afterwards the mixture was subjected to fractional condensation over cooling traps (-40°C, -100°C and -196°C). The product was collected in the -100°C trap (1.52 g, 80% purity). The calculated yield was 72%.

Physical data:

^{19}F-NMR ($CDCl_3$, 20°C): δ = -81.03 (1F, dddd, ^{3}J(F-F) = 23.9 Hz, ^{4}J(F-H) = 1.6Hz, ^{5}J(F-H) = 2.1 Hz, ^{5}J(F-H) = unresolved), -84.23 (1F, dddd, ^{3}J(F-F) = 23.9 Hz, ^{4}J(F-H) = 2.4 Hz, ^{5}J(F-H) = 1.8 Hz, ^{5}J(F-H) = 0.8 Hz)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 6.44 (1H, dddd, ^{3}J(H-H) = 16.3 Hz, ^{3}J(H-H) = 10.3 Hz, ^{4}J(H-F) = 2.4 Hz, ^{4}J(H-F) = 1.6 Hz, C*H*=), 5.51 (1H, ddd, ^{3}J(H-H) = 16.3 Hz, ^{5}J(H-F) = 0.8 Hz, ^{2}J(H-H) = 0.9 Hz, =CH_2, trans H), 5.34 (1H, dddd, ^{3}J(H-H) = 10.3 Hz, ^{5}J(H-F) = 2.1 Hz, ^{5}J(H-F) = 1.8 Hz, ^{2}J(H-H) = 0.9 Hz, =CH_2, cis H)

258 Wang, Z.; " Improved preparation of dl-α -phenylbutyric anhydride and vinyl bromide." Youji Huaxue **1986**, 2, 167-168.

$^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 20°C): δ = 154.8 (1C,dd, *C*F2, ^{1}J(C-F) = 292 Hz, 288 Hz), 126.1 (1C, s, H_2C=)), 119.4 (1C, dd, J(C-F) = 11.6 Hz, 3.5 Hz), 83.0 (1C, J(C-F) = 32 Hz, 24 Hz, *C*Br)

5.2.3.5 Attempted Elimination of Hydrogen Bromide from 2-Bromo-1,1-difluorobuta-1,3-diene

Attempt 1: The attempted elimination was performed according to the general procedure described in 4.2.1.4. A temperature of 90°C was employed. According to ^{19}F-NMR data the starting compound (**68**) was recovered unchanged.

Attempt 2: A flame dried 4mm-Duran-glass tube was charged under argon with 0.05 mL (0.3 mmol) DBU and 0.25 mL toluene-d^8. The tube was frozen in liquid nitrogen and degassed. Approximately 50 mg of diene (**68**) were condensed into the tube. The tube was flame sealed and unfreezed at -80°C. A temperature depended NMR study was performed (-80°C up to +10°C). Predominantly compound (**72**) is formed, a small signal in the low temperature ^{19}F-NMR spectra is observable at -99.5 ppm which might result from the formation of (**6**).

Physical data for 3-bromo-4,4,4-trifluorobut-1-ene (**72**):

^{19}F-NMR ($CDCl_3$, 20°C): δ = -72.75 (3F, d, ^{3}J(F-H) = 7.1 Hz)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 5.53 (1H, m) 4.80 (2H, m), 3.84 (1H, m)

$^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 20°C): δ = 129.5 (1C,q, *C*F_3, ^{1}J(C-F) = 284 Hz);129.5 (1C,q, *C*F_3, ^{3}J(C-F) = 2 Hz), 125.0 (1C, s), 122.6 (1C, s) 46.50 (1C,q, ^{2}J(C-F) = 34 Hz)

5.2.3.6 1,2,4-tribromo-1,1,2-trifluorobutane (74)

In a flame dried 25-mL-Schlenk flask bromine (1.6 g, 10 mmol) was added dropwise at room temperature to a stirred solution of 1.89 g (10 mmol) 4-bromo-1,1,2-trifluorobut-1-ene (**73**) in 10 mL dichloromethane. The solution was stirred for 1 hour. Fractional condensation in high vacuum (10-3 mbar) yielded 3.3 g (95%) (**72**) in >99% purity in the cooling trap kept at -30°C.

Physical data for 1,2,4-tribromo-1,1,2-trifluorobutane (**74**):

^{19}F-NMR ($CDCl_3$, 17°C): δ = -59.00 (1F, m, C*F*$_2$Br), -117.54 (1F, m, C*F*Br)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 3.65 (1H, m, C*H*$_2$Br), 3.55 (1H,m, C*H*$_2$Br), 2.93 (1H, m, C*H*$_2$), 2.80 (1H, m, C*H*$_2$)

^{13}C{^{1}H}-NMR ($CDCl_3$, 20°C): δ = 119.05 (1C,ddd, *C*F$_2$Br, ^{1}J(C-F) = 310 Hz, 312 Hz, ^{2}J(C-F) = 33 Hz), 104.90 (1C, ddd, *C*FBr, ^{1}J(C-F) = 266 Hz, ^{2}J(C-F) = 31 Hz, 28 Hz), 41.70 (1C, d, *C*H$_2$, J(C-F) = 20 Hz), 23.90 (1C, m, *C*H$_2$Br)

5.2.3.7 Attempted Synthesis of 4-bromo-3,4,4-trifluorobuta-1,2-diene (75)

Attempt 1: The attempted elimination was performed according to the general procedure described in 4.2.1.4. A temperature of 90°C was employed. According to ^{19}F-, ^{1}H- and ^{13}C-NMR data 3,4-dibromo-3,4,4-trifluorobut-1-ene (**76**) is formed by a single hydrogen bromide elimination.

Physical data for 3,4-dibromo-3,4,4-trifluorobut-1-ene (**76**):

^{19}F-NMR ($CDCl_3$, 17°C): δ = -59.2 (1F, m, C*F*$_2$Br), -125.35 (1F, m, C*F*Br)

^{1}H-NMR ($CDCl_3$, 20°C): δ = 3.65 (1H, m, C*H*$_2$Br), 3.55 (1H,m, C*H*$_2$Br), 2.93 (1H, m, C*H*$_2$), 2.80 (1H, m, C*H*$_2$)

$^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 20°C): δ = 131.45 (1C,d, *C*H=, ^{2}J(C-F) = 18 Hz), 121.00 (d, =CH_2, ^{3}J(C-F) = 10 Hz118.50 (1C, ddd, *C*F_2Br, ^{1}J(C-F) = 314 Hz, 310 Hz, ^{2}J(C-F) = 35 Hz), 104.90 (1C, ddd, *C*FBr, ^{1}J(C-F) = 266 Hz, ^{2}J(C-F) = 32 Hz, 29 Hz), 41.70 (1C, d, *C*H_2, J(C-F) = 20 Hz), 23.90 (1C, m, *C*H_2Br)

Attempt 2: In a flame dried 25-mL-Schlenk flask DBU (236 mg, 4 mmol, 2 eq.) was added dropwise at room temperature to a stirred solution of 775 mg (2 mmol) 1,2,4-tribromo-1,1,2-trifluorobutane (**74**) in 10 mL diethylether. The solution was stirred for 1 hour. Fractional condensation in high vacuum (10^{-3} mbar) yielded 1,1,2-trifluorobuta-1,3-diene (**77**) as the major component according to ^{19}F-NMR spectra.

Physical data for 1,1,2-trifluorobuta-1,3-diene (**77**):

^{19}F-NMR ($CDCl_3$, 20°C): δ = -103.31 (dd, 1F, dddd, ^{2}J(F-F) = 64.5 Hz, ^{3}J(F-F) = 28.4Hz, =C*F*$_2$), -119.23 (ddd, 1F, ^{3}J(F-F) = 107.1 Hz, ^{2}J(F-F) = 64.5 Hz, ^{4}J(F-H) = 1.5 Hz, =C*F*$_2$), -183.87 (dddd, 1F, ^{3}J(F-F) = 107.1 Hz, ^{3}J(F-F) = 28.4 Hz, ^{3}J(F-H) = 28.4 Hz, ^{4}J(F-H) = 1.4 Hz =C*F*-)

For all other spectroscopic data please see reference 81.

5.2.3.8 Attempted Synthesis of 4-bromo-,4,4-trifluorobuta-1,2-diene (78)

100 mg (2.5 mmol) allene (**74**) and 25 mL of THF or Et_2O or MTBE were condensed into a flame dried 50-mL -2-neck-Schlenk flask, equipped with a magnetic stir bar and a thermometer. At -78°C 1 mL *n*-butyllithium was added dropwise to the reaction mixture. The mixture was stirred for 1 hour at -78°C to assure complete generation of lithated allene. Addition of dibromodifluoromethane (525 mg, 2.5 mmol) was done in different ways:

1. The reaction temperature was lowered to -110°C. Dibromodifluoromethane in 10 mL of the appropriate solvent was cooled to the same temperature and

carefully added via a teflon tube. The addition temperature did not exceed -100°C.

2. The reaction mixture was frozen in liquid nitrogen and dibromodifluoromethane was condensed into the reaction vessel. The mixture was slowly warmed. An uncontrollable exothermic reaction occurred when the reaction mixture was partly unfreezed.
3. Difluorodibromomethane was condensed into the stirred reaction mixture at -110°C. The reaction temperature exceeded -55°C since the exothermic reaction started with noticeable delay.

Only traces of supposed product (^{19}F-NMR: -47 ppm) were observed

5.2.3.9 Attempted Synthesis of 1,1-dibromo-2-difluormethylenecyclopropane (83)

A solution of CBr_4 (30 mmol, 10 g) diluted in 5mL of acetonitrile was added to a well-stirred mixture of copper powder (1 g), iron powder (1.5 g) and 1,1-difluoroallene (10 mmol, 760 mg) in acetonitrile (25 mL). The reaction was exothermic and the temperature was controlled by an ice/water bath then stirring was continued at room temperature overnight. A ^{19}F-NMR spectrum showed that 1,1-difluoroallene remained unchanged in the reaction mixture.

5.2.3.10 Attempted Synthesis of 3-chloro-1,1,2-trifluorobuta-1,3-diene (85)

A flame dried 4mm-Duran-glass tube was charged under argon with 0.25 mL (0.3 mmol) DMF, 0.05 mL 50 mg tri-nbutyltrifluorovinylstannane and 100 mg dichloroethylene, 5 mg of palladium(II) acetate and 20 mg triphenylphisphine. The tube was frozen in liquid nitrogen and degassed, flame sealed and and heated to 80°C. A ^{19}F-NMR spectrum revealed the predominant formation of trifluoroethylene but traces of the product are also observable.

5.2.3.11 1-bromo-1,1-difluoro-3-trimethylsilylprop-2-yne (89)

The synthesis was performed according to Hammond. See reference 196. In difference to the published method the precooled lithiated alkyne was added to cooled diluted dibromodifluoromethane.

5.2.3.12 Attempted Synthesis of silver(I) 3-bromo-3,3-difluoroprop-1-enide (96)

To a solution of 230 mg (87) (1 mmol) in 4 ml MeOH/H_2O was added 170 mg silver nitrate (1 mmol) at room temperature. The starting materials rapidly disappeared and a white precipitate formed within 5–15 min. This solid was recovered by filtration and washed with cold methanol (0°C). The solid was dried in vacuo. The solid was unexpectedly insoluble in C_6D_6 and stable towards light. Maybe decomposition had already taken place during the synthesis.

5.2.3.13 Attempted synthesis of 1,4-dibromo-1,1-difluorobut-2-yne (86) and 1-bromo-4-chloro-1,1-difluorobut-2-yne (87)

The attempts to synthesize (85) and (86) were conducted in an analogous manner to 4.2.3.8. Although traces of products were observable (triplett at -31 ppm, region for acetylene substituted CF_2Br, see reference 196) in ^{19}F-NMR spectra the optimization was unsuccessful.

5.2.4 Attempted Synthesis of Tetrafluorobuatriene or 1,1-Difluorobut-1-en-3-yne Metal Complexes

5.2.4.1 General Procedure for the Generation of Metal-THF Complexes 98, 99, 100, 116 and 117 the Attempted Synthesis of Tetrafluorobutatriene and/or 1,1-Difluorobut-1-en-3-yne Complexes thereof

A photoreactor with water-cooled Pyrex-light, circulation pipe and magnetic stir bar was charged with 0.25 mmol (1 eq.) of the metal complex. The reactor was evacuated for several minutes and afterwards frozen in liquid nitrogen. 50-100 mL pentane and 5-10 mL THF were condensed into the reactor (depending on the size of the reactor). The solvent was degassed again by melting/freezing. The solution was irradiated at -78°C with a mercury-high-pressure light (Philips HPK-125) for one hour.

The reaction mixture was frozen in liquid nitrogen and 0.5 mmol tetrafluorobutatriene (A) or 1,1-difluorobut-1-en-3-yne (B) or ethylene (C) were condensed into the reactor. The solution was warmed to room temperature overnight. The solution was filtered under inert condition over a G4-frit and the solvent was removed in high vacuum (for A and B). NMR-spectra of the residue revealed no fluorine containing complex.

The solution of C was frozen in liquid nitrogen again and 0.5 mmol tetrafluorobutatriene were condensed into the reactor. The solution was stirred overnight. After a work-up similar to A and B no evidence for the formation of a fluorine containig species was found in ^{19}F-NMR, too.

5.2.4.1 General Procedure for Attempted Synthesis of 1,1-Difluorobuta-1-en-3-yne Complexes of 101 and 102

In a flame dried 10-mL-Schlenk flask, equipped with a magnetic stir bar, were added 0.1 mmol of Vaskas Complex **101** or it rhodium analog **102** in 5 mL toluene. The solution was frozen in liquid nitrogen and degassed. 0.25 mmol tetrafluorobutatrine were condensed into the reaction vessel. The solution was warmed to -30°C and argon was added to the vessel for pressure compensation. The reaction mixture was

stirred overnight at room temperature. After removal of all volatiles in high vacuum the residue was dissolved in dried d^8-toluene. ^{19}F-NMR spectra showed no evidence for the formation of a fluorine containing complex.

5.2.4.3 General Procedure for Attempted Synthesis of a Tetrafluorobutatriene Complex of 119

In a flame dried 10-mL-Normag-valve flask, equipped with a magnetic stir bar, were added 0.1 mmol of titanium complex **119** and 5 mL of solvent (either toluene, THF, diethylether, *tert.*-butylmethylether, 1,2-dimethoxyethane, acetonitrile, dichloromethane, chloroform or pentane). The solution was frozen in liquid nitrogen and degassed. 0.25 mmol tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed very slowly to room temperature. Already below -80°C the solution turned black. ^{19}F-NMR spectra showed no evidence for the formation of a fluorine containing titanium complex. A run employing toluene in a Normag-NMR-tube was monitored starting from -100°C. Nevertheless no evidence for a fluorine containing titanium species was found either.

5.2.4.4 General Procedure for Attempted Synthesis of a Tetrafluorobutatriene Complexes of 120, 121, 122, 123 and 125

In a flame dried 25mL-Schlenk flask, equipped with a magnetic stir bar, was added 0.1 mmol of the metal complex and 10 mL of solvent (please see scheme 2.6.4 and 2.6.5 for details. The reaction mixture was frozen in liquid nitrogen and degased. 0.25 mmol of tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed to -30°C and argon was added to the vessel for pressure compensation. The reaction mixture was stirred overnight at room temperature. After removal of all volatiles in high vacuum the residue was dissolved in dried d^8-toluene or d^8-THF. ^{19}F-NMR spectra showed no evidence for the formation of a fluorine containing complex.

5.2.4.5 General Procedure for Attempted Synthesis Tetrafluorobutatriene Complex 126 – 128 and Attempted Synthesis of a Tetrafluorobutatriene Complexes of 124

In a flame dried 25mL-Schlenk flask, equipped with a magnetic stir bar, was added: (**124**) 0.1 mmol dicyclooctadienenickel(0) and 0.2 mmol triphenylphosphine in 10 mL THF

(**126**) 0.1 mmol copper(I) oxide and 0.2 mmol hexafluoropenta-2,4-dione in 10 mL dichloromethane

(**127**) 0.1 mmol (dimethylsulfide)copper(I) bromide and 0.1 mmol 2,2´-bipyridine and 10 mL THF

(**128**) 0.1 mmol (dimethylsulfide)copper(I) bromide and 0.1 mmol DPPE (toluene) or 0.2 mmol triphenylphosphine (THF) and 10 mL of solvent

The reaction mixture was frozen in liquid nitrogen and degased. 0.25 mmol of tetrafluorobutatriene were condensed into the reaction vessel. The solution was warmed to -30°C and argon was added to the vessel for pressure compensation. The reaction mixture was stirred overnight at room temperature. After removal of all volatiles in high vacuum the residue was dissolved in dried d^8-toluene or d^8-THF. ^{19}F-NMR spectra showed no evidence for the formation of a fluorine containing complex.

5.2 Computational Details

All calculations were performed using computational time on the *abacus 4* of the high- performance computing group at the *ZEDAT of the Freie Universität Berlin*. *Abacus 4* has the following specifications:

Host Name	abacus4.zedat.fu-berlin.de
IP-Nr	130.133.8.138
Nodes	8x IBM p575
Processors	128 POWER 5+ (16 pro Knoten) Prozessoren 1.9 GHz, dual core, 1.9MB L2 Cache, 36MB L3-Cache, Simultaneous Multi-Threading
Main Memory	8x 128 GB = 1 TB
Hard Disks	RAID-Array, 15 TB Fibre Channel, 23 TB SATA
File System	General Parallel File System (GPFS)
Operating System	AIX
Network Link	Gigabit-Ethernet - TCP/IP
Interconnect	Infiniband

Up to 16 processors and 64 gigabyte of main memory were used. A scratch space of up to 5 terrabyte was necessary for the high level Coupled Cluster Calculations.

All calculations involving partially fluorinated butatrienes and enynes were performed with the Gaussian 03 program package.[259,260,261,262,263] Geometries and vibrations were calculated at the MP2(full)/cc-pVTZ level of theory (cc-pVTZ defined as correlation-consistent polarized valence-triple-ζ (Dunning) basis set). All structures represent local minima indicated by the absence of imaginary frequencies. Final energies were calculated at the CCSD(T, full)/cc-pVQZ (correlation consistent polarized valence-

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261 Head-Gordon, M.; Pople, J. A:; Frisch, M. J.; "MP2 energy evaluation by direct methods", *Chem. Phys. Lett.* **1988**, *153*, 503-506.

262 Čížek, J.; "On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods", *J. Chem. Phys.* **1966**, *45*, 4256-4266.

263 Pople, J. A.; Head-Gordon, M.; Raghavachari, K.; "Quadratic configuration interaction. A general technique for determining electron correlation energies", *J. Chem. Phys.* **1987**, *87*, 5968-5975.

quadruple-ζ (Dunning) basis set) level of theory and were corrected by the scaled MP2(full)/cc-pVTZ zero point energy.[112]

Tables containing the final energies of Coupled Cluster calculations and lower level methods used for calculations of dimerization energies are given. All output files of the performed GAUSSIAN 03 calculations can be found on the enclosed CD.

6. Appendices

6.1 Crystallographic Data

Crystallographic Data of 13a and 14 are available at the Cambridge Crystal Structure Database: CCDC 752618 and 752619.

6.2 Final Energies - Tables

See the following pages.

energy differences

	MP2/cc-pVTZ//MP2/cc-pVTZ					CCSD(T)/cc-pVQZ//MP2/cc-pVTZ		
	Total Energy(incl. ZPE)	ZPE(kJ/mol)	ZPE(corrected)	ΔE(kJ/mol)	ZPE(Hartree)	Total Energy	Total Energy(incl. ZPE)	ΔE(kJ/mol)
C4F4								
perfluoorbutatrienee	-550,950101	83,59	0,031304	**0,00**	0,031839	-551,354432	-551,323128	
perfluoroobut-3-en-1-yne	-550,944605	83,71	0,031347	**-14,43**	0,031883	-551,344364	-551,313017	**-26,55**
C4F3H								
1,1,4-trifluorobutatriene	-451,801736	103,63	0,038806	**0,00**	0,039469	-452,161445	-452,122639	**0**
1,1,4-trifluorobut-1-en-3-yne	-451,812210	104,96	0,039304	**27,50**	0,039976	-452,165888	-452,126584	**10,36**
1,1,2-trifluorobut-1-en-3-yne	-451,821894	101,71	0,038089	**52,92**	0,038740	-452,175947	-452,137858	**39,96**
1,2,4-trans-trifluorobut-1-en-3-yne	-451,795484	104,04	0,038962	**-16,41**	0,039628	-452,150551	-452,111588	**-29,01**
1,2,4-cis-trifluorobut-1-en-3-yne	-451,796009	104,19	0,039015	**-15,04**	0,039682	-452,151347	-452,112332	**-27,06**
C4F2H2								
1,1-difluorobutatriene	-352,665660	121,85	0,045630	**0,00**	0,046410	-352,978231	-352,932601	**0**
3,4-difluorobu-1-en-3-yne	-352,657306	123,42	0,046220	**-21,93**	0,047010	-352,966209	-352,919988	**-33,11**
1,1-difluorobuta-1-en-3-yne	-352,690289	122,70	0,045950	**64,66**	0,046735	-352,997972	-352,952022	**50,99**
1,2-trans-difluorobut-1-en-3-yne	-352,672380	121,81	0,045615	**17,64**	0,046394	-352,981638	-352,936023	**8,99**
1,2-cis-difluorobut-1-en-3-yne	-352,673313	122,15	0,045741	**20,09**	0,046523	-352,982903	-352,937161	**11,97**
1,4-trans-difluorobut-1-en-3-yne	-352,657119	124,29	0,046545	**-22,42**	0,047340	-352,966417	-352,919872	**-33,42**
1,4-cis-difluorobut-1-en-3-yne	-352,657140	125,33	0,046932	**-22,37**	0,047734	-352,966792	-352,919860	**-33,45**
cis-1,4-difluorobutatriene	-352,651641	123,40	0,046211	**-36,81**	0,047001	-352,967044	-352,920832	**-30,9**
trans-1,4-difluorobutatriene	-352,651980	123,93	0,046208	**-35,92**	0,046998	-352,967352	-352,921143	**-30,08**
C4FH3								
monofluorobutatriene	-253,513143	141,37	0,052943	**0,00**	0,053848	-253,781687	-253,728743	**0**
1-trans-fluorobut-1-en-3-yne	-253,535237	142,04	0,053191	**58,01**	0,054100	-253,798700	-253,745509	**44,02**
1-cis-fluorobut-1-en-3-yne	-253,534853	142,83	0,053487	**57,00**	0,054401	-253,798591	-253,745104	**42,96**
2-fluorobut-1-en-3-yne	-253,534313	141,15	0,052861	**55,58**	0,053764	-253,797568	-253,744707	**41,91**
4-fluorobut-1-en-3-yne	-253,509140	143,87	0,053871	**-10,51**	0,054792	-253,773141	-253,719270	**-24,87**
C4H4								
butatriene	-154,369975	158,50	0,059523	**0,00**	0,060540	-154,592291	-154,532768	**0**
buta-1-en-3-yne	-154,386893	161,38	0,060435	**44,42**	0,061468	-154,604979	-154,544543	**30,92**

isodesmic reactions

	MP2/cc-pVTZ//MP2/cc-pVTZ				CCSD(T)/cc-pVQZ//MP2/cc-pVTZ	
	Total Energy(incl. ZPE)	**ZPE(kJ/mol)**	**ZPE(Hartree)**	**ZPE(corrected)**	**Total Energy**	**Total Energy(incl. ZPE)**
butadiene	-155,604025	226,19	0,086150	0,084703	-155,858396	-155,773694
ethane	-79,586047	199,76	0,076086	0,074808	-79,758698	-79,683890
ethene	-78,378318	135,68	0,051678	0,050810	-78,520608	-78,469798
tetrafluoroethene	-474,958031	58,01	0,022093	0,021722	-475,283531	-475,261809
tetrafluorobutadiene	-552,210626	148,11	0,056411	0,055463	-552,645187	-552,589723
monofluoroethene	-177,527946	117,44	0,044731	0,043980	-177,716361	-177,672381
difluoroethene	-276,684616	98,17	0,037391	0,036763	-276,917473	-276,880711

	ΔE(Hartree)	**ΔE(kJ/mol)**
triene+ethane -> butadiene + ethene	-0,026833	**-70,45**
perfluorotriene + ethane -> tetrafluorobutadiene + ethene	-0,052664	**-138,27**
perfluorotriene + ethen -> triene + tetrafluoroethene	-0,001652	**-4,34**
perfluorotriene+ triene -> 2x 1,1 difluorotriene	-0,009305	**-24,43**
perfluorotriene+ triene -> 2x trans - difluorotriene	0,013609	**35,73**
1,1-difluorotriene + triene -> 2 x monofluorotriene	0,007882	**20,69**
monofluorotriene + Ethen -> monofluoroethene + triene	-0,006608	**-17,35**
1,1-difluorotriene + ethene -> triene + difluoroethene	-0,010925	**-28,68**

dimerization energies

hydrogen dimers	ZPE	Scaled ZPE	CCSDT(Hartree)	corrected CCSDT	ΔE(Hartree)	ΔE(kJ/mol))
27	0.128396	0.126238947	-308.9658735	-308.8396345	-0.09535535	**-250.3554613**
28	0.128454	0.126295973	-308.9448693	-308.8185733	-0.07429415	**-195.0592706**
29	0.133118	0.130881618	-308.9296346	-308.798753	-0.05447384	**-143.0210646**
30	0.128512	0.126352998	-308.9245391	-308.7981861	-0.05390694	**-141.5326667**
31	0.12825	0.1260954	-308.9208222	-308.7947268	-0.0504476	**-132.4501661**
32	0.13195	0.12973324	-308.921852	-308.7921187	-0.04783957	**-125.6027839**
33	0.133902	0.131652446	-308.8532338	-308.7215813	0.02269783	**59.59313516**
34	0.130271	0.128082447	-308.7931344	-308.6650519	0.07922721	**208.0110122**
2 x triene	0.060133	0.059122766	-154.4312623	-154.3721396		

scaling factor

0.9832

fluorinated dimers	ZPE	Scaled ZPE	CCSDT	corrected CCSDT	ΔE(Hartree)	**ΔE(kJ/mol))**
18	0.069152	0.067990246	-1102.01495	-1101.94696	-0.12726136	**-334.1246774**
19	0.068531	0.067379679	-1101.996791	-1101.929411	-0.10971283	**-288.0510083**
20	0.069715	0.068543788	-1101.982648	-1101.914104	-0.09440542	**-247.8614098**
21	0.068309	0.067161409	-1101.979038	-1101.911877	-0.0921783	**-242.0141046**
22	0.067763	0.066624582	-1101.97093	-1101.904306	-0.08460713	**-222.1359921**
23	0.067611	0.066475135	-1101.966285	-1101.89981	-0.08011147	**-210.3326545**
24	0.067781	0.066642279	-1101.884867	-1101.818225	0.00147367	**3.869123417**
25	0.06828	0.067132896	-1101.842647	-1101.775514	0.04418469	**116.0068888**
2 x triene	0.03147	0.030941304	-550.9407906	-550.9098492		

other theory levels (fluorinated dimers)

	radialene(18)		***double dimer (24)***		***Z-dimer(22)***	
	Total Energy(incl. ZPE)	ΔE(kJ/mol)	Total Energy(incl. ZPE)	ΔE	Total Energy(incl. ZPE)	ΔE
Level of theory/basis set						
B3LYP/6-311G(d,p)	-1103.666726	-282.19	-1103.512974	121.49	-1103.621857	**-164.39**
B3LYP/6-311++G(3df,3pd)	-1103.771163	-269.79	-1103.62159	122.91	-1103.73065	**-163.4**
B3PW91/6-311G(d,p)	-1103.246736	-312.45	-1103.103224	64.35	-1103.19964	**-188.79**
MP2/6-311G(d,p)	-1101.160045	-359.28	-1101.031555	-21.93	no minimum found	
MP2/cc-pvtz	-1101.813599	-360.31	-1101.686236	-25.92	-1101.766132	**-235.69**
CBS-4M	-1102.366448	-347.89	-1102.237574	-9.53	-1102.321884	**-230.89**
CBS-Q	-1102.261404	-274.22	-1102.135706	55.8	-1102.226536	**-182.68**
CBS-QB3	-1102.272612	-338.19	-1102.145892	-5.48	-1102.23094	**-228.76**
G3	-1102.934522	-332.94	1102.805557	5.66	-1102.893701	**-225.76**
G3(MP2)	-1102.278481	-327.13	-1102.150863	7.93	-1102.238438	**-222**

oligomers

	Oligomer	Total energy (Hartree)
MP2/6-311G(d,p) + ZPE	[2+2]-trimer	**-1651.749825**
scaling factor 0,9877	Z-trimer	**-1651.719176**
	[4+2]-trimer	**-1651.779034**
	Z-tetramer	**-2202.324073**
	[4+2]-tetramer	**-2202.32086**