

**Synthetic Methods**

# Fluorinated Dialkyl Chloronium Salts: Synthesis and Reactivity for Fluoroalkylation and Hydride Abstraction

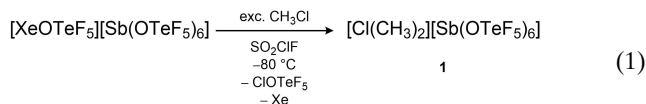
Lukas Fischer, Michael H. Lee, Isaac Kim, Anja Wiesner, Kurt F. Hoffmann, and Sebastian Riedel\*

**Abstract:** A new concept for the synthesis of dialkyl chloronium cations  $[R-Cl-R]^+$  is described ( $R=CH_3, CH_2CF_3$ ), that allows the formation of fluorinated derivatives. By utilizing the xenonium salt  $[XeOTeF_5][M(OTeF_5)_n]$  ( $M=Sb, n=6; M=Al, n=4$ ) chlorine atoms of chloroalkanes or the deactivated chlorofluoroalkane  $CH_2ClCF_3$  are oxidized and removed as  $ClOTeF_5$  leading to the isolation of the corresponding chloronium salt. Since the resulting highly electrophilic cation  $[Cl(CH_2CF_3)_2]^+$  is able to alkylate weak nucleophiles, this compound can be utilized for the introduction of a fluorinated alkyl group to those. In addition, the fluorinated alkyl chloronium cation displays a high hydride ion affinity, enabling the activation of linear hydrocarbons by hydride abstraction even at low temperatures ultimately leading to the formation of branched carbocations.

fluorinated alkyl chloronium compounds to electrophilically transfer fluoroalkyl groups, even to weak nucleophiles.

## Results and Discussion

The first attempts to synthesize fluorinated dialkyl chloronium cations from chlorofluoroalkanes failed. The reaction of  $MF_5$  ( $M=As, Sb$ ) with chlorofluoroalkanes only proceeds unselectively, leading to the decomposition of the starting materials, while the use of the Brønsted superacid  $H[Al(OTeF_5)_4]$ <sup>[7]</sup> showed no reaction between the acid and the chlorofluoroalkanes at all. With the known synthetic pathways failing, we developed a conceptually new route to synthesize dialkyl chloronium salts via the oxidation of chloroalkanes. The strong oxidizer  $[Xe(OTeF_5)][Sb(OTeF_5)_6]$  is known to oxidize the halide substituent of a variety of halogenated methanes yielding the corresponding carbocations  $[CX_3]^+$  and  $[CFX_2]^+$  ( $X=Cl, Br$ ).<sup>[8,9]</sup> Utilizing this oxidative halogen abstraction, we reacted the xenonium salt  $[Xe(OTeF_5)][Sb(OTeF_5)_6]$  with an excess of chloromethane  $CH_3Cl$  in  $SO_2ClF$ , yielding the dimethyl chloronium salt  $[Cl(CH_3)_2][Sb(OTeF_5)_6]$  **1** [Eq. (1)].



The reaction proceeds by condensing an excess of  $CH_3Cl$  at  $-196^\circ C$  onto the yellow solution of freshly prepared  $[Xe(OTeF_5)][Sb(OTeF_5)_6]$  in  $SO_2ClF$ . Warming the mixture up to  $-80^\circ C$  leads to gas evolution due to the formation of xenon and within minutes to the discoloration of the solution. After the reaction is completed, the removal of all volatile compounds in vacuum leads to **1** in quantitative yields as a colorless crystalline powder. The chemical shift of **1** in the  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra ( $\delta(^1H)=4.68$  ppm;  $\delta(^{13}C\{^1H\})=50.9$  ppm;  $^1J_{C-H}=162.1$  Hz) are low field-shifted when compared to the starting material  $CH_3Cl$  ( $\delta(^1H)=3.46$  ppm;  $\delta(^{13}C\{^1H\})=24.6$  ppm). The vibrational bands in the IR spectrum of **1** corresponding to the cation match with the previously reported spectra of the dimethyl chloronium salt  $[Cl(CH_3)_2][Al(OTeF_5)_4]$ .<sup>[3]</sup> By layering a solution of **1** in  $SO_2ClF$  at  $-10^\circ C$  with *n*-pentane and cooling it to  $-80^\circ C$  it was possible to obtain single crystals suitable for x-ray diffraction. The compound crystallizes in the triclinic space

## Introduction

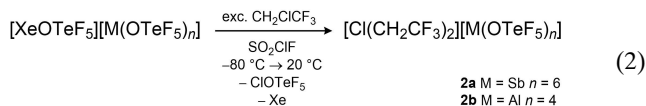
The synthesis of dialkyl chloronium salts has been achieved by reacting an excess of chloroalkanes with either strong Lewis acids like  $SbF_5$ <sup>[1]</sup> or Brønsted superacids like the carborane-based acid  $H[CHB_{10}Cl_{11}]$ <sup>[2]</sup> or the teflate-based acid  $H[Al(OTeF_5)_4]$ <sup>[3]</sup>. However, so far only simple alkyl chloronium cations, such as the dimethyl or the diethyl compounds have been structurally characterized in the solid state.<sup>[2,3]</sup> In general, the variety of alkyl substituents in dialkyl chloronium salts are limited in their complexity. So far, only two halogenated examples, the symmetrical  $[Cl(CH_2Cl)_2]^+$  and the asymmetrical  $[Cl(CH_3)(CH_2Cl)]^+$  cation, have been described in literature.<sup>[4]</sup> Due to their high electrophilicity and their potential to be used as strong alkylation or arylation reagents,<sup>[3,5,6]</sup> we were interested in

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group  $P\bar{1}$  with a disorder of the cation, preventing an accurate analysis of the bond lengths and angles (SI Figure S36). With the successful preparation of the dimethyl chloronium salt **1**, attempts to obtain the fluorinated derivatives were made in an analogous way. However, the reaction of  $[\text{Xe}(\text{OTeF}_5)][\text{Sb}(\text{OTeF}_5)_6]$  with an excess of  $\text{CH}_2\text{ClF}$  or  $\text{CHClF}_2$  did not lead to the desired chloronium cations  $[\text{Cl}(\text{CH}_2\text{F})_2]^+$  and  $[\text{Cl}(\text{CHF}_2)_2]^+$  but to the decomposition of the anion. Calculations of the chloronium ion show that the presence of fluorine atoms in  $\alpha$ -position relative to the chlorine atom drastically destabilizes the C–Cl bond of the cation. The  $\pi$ -donor ability of the  $\alpha$ -F atoms leads to the transfer of electron density from the free electron pairs of the fluorine atom into the  $\sigma^*_{\text{C-Cl}}$  orbital, thus weakening the C–Cl bond. The donor ability of the lone pairs ( $p_{\text{F}}$ ) of the fluorine atom leads to an electron population of 0.118 in the  $\sigma^*_{\text{C-Cl}}$  orbital of the bis(fluoromethyl)chloronium cation  $[\text{Cl}(\text{CH}_2\text{F})_2]^+$  and an electron population of 0.232 in the  $\sigma^*_{\text{C-Cl}}$  orbital of the bis(difluoromethyl)chloronium cation  $[\text{Cl}(\text{CHF}_2)_2]^+$ . The resulting carbocations  $[\text{CH}_2\text{F}]^+$  and  $[\text{CHF}_2]^+$ , in case of a broken C–Cl bond, are stabilized by the  $\alpha$ -fluorine atoms due to the donation of electron density from the lone pairs ( $p_{\text{F}}$ ) into the empty  $p_z$  orbital on the carbon.<sup>[10]</sup> However, the  $[\text{Sb}(\text{OTeF}_5)_6]^-$  anion cannot withstand these highly reactive fluorinated carbocations leading to the observed decomposition.

Therefore, an ideal chlorofluoroalkane for the synthesis of a fluorinated chloronium cation turned out to be 1-chloro-2,2,2-trifluoroethane  $\text{CH}_2\text{ClCF}_3$  because it does not contain fluorine atoms in  $\alpha$ -position relative to the chlorine atom. The reaction of  $[\text{Xe}(\text{OTeF}_5)][\text{Sb}(\text{OTeF}_5)_6]$  with  $\text{CH}_2\text{ClCF}_3$  was carried out similar to the synthesis of **1** [Eq. (2)]. An excess of  $\text{CH}_2\text{ClCF}_3$  is condensed onto a freshly prepared solution of  $[\text{Xe}(\text{OTeF}_5)][\text{Sb}(\text{OTeF}_5)_6]$  in  $\text{SO}_2\text{ClF}$  at  $-196^\circ\text{C}$ . The reaction mixture is warmed up to  $-80^\circ\text{C}$  with no change of the characteristic yellow color of the xenonium salt, indicating no reaction at that temperature. Warming the reaction mixture up to  $20^\circ\text{C}$  over the course of one hour results in the discoloration of the solution. The removal of all volatiles *in vacuo* yields the fluorinated alkyl chloronium salt  $[\text{Cl}(\text{CH}_2\text{CF}_3)_2][\text{Sb}(\text{OTeF}_5)_6]$  **2a** in quantitative yields as a white crystalline powder. The compound is stable at around  $20^\circ\text{C}$  for a few hours but starts to decompose rapidly at around  $30^\circ\text{C}$ . Samples of **2a** can be stored at  $-40^\circ\text{C}$  under inert conditions for weeks without decomposition.



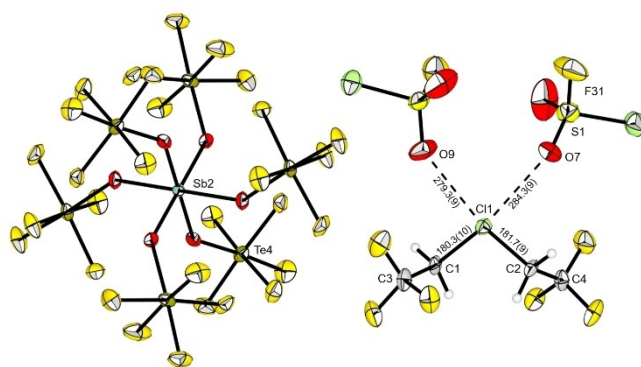
The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR spectra of **2a** ( $\delta(^1\text{H}) = 5.87$  ppm;  $\delta(^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}) = 63.8$  ppm,  $119.7$  ppm;  $^1J_{\text{C-H}} = 167.7$  Hz) show the expected low-field shift of the signals of the methylene group compared to  $\text{CH}_2\text{ClCF}_3$  ( $\delta(^1\text{H}) = 4.06$  ppm;  $\delta(^{13}\text{C}\{^1\text{H}\}) = 40.0$  ppm,  $123.4$  ppm). Furthermore, in the  $^1\text{H}, ^{13}\text{C}$  HMBC spectrum a cross signal can be observed

showing the  $^3J_{\text{C-H}}$  coupling between the methylene groups separated by the chlorine atom. The  $^{19}\text{F}$  NMR spectrum shows the prominent signal of the collapsed  $\text{AB}_4$  spin system of the  $\text{OTeF}_5$  groups in the antimonate anion ( $-42.0$  ppm), which is well described in literature<sup>[11]</sup> and the signal of the  $\text{CF}_3$  groups in the  $[\text{Cl}(\text{CH}_2\text{CF}_3)_2]^+$  cation ( $-67.5$  ppm;  $^1J_{\text{C-F}} = 117.7$  Hz). The aluminate-based chloronium salt  $[\text{Cl}(\text{CH}_2\text{CF}_3)_2][\text{Al}(\text{OTeF}_5)_4]$  **2b** was prepared in a similar fashion as **2a** by usage of the recently reported xenonium salt  $[\text{Xe}(\text{OTeF}_5)][\text{Al}(\text{OTeF}_5)_4]$ <sup>[12]</sup> [Eq. (2)].

Obtaining single crystals of the fluorinated alkyl chloronium salts proved to be a challenging task as the choice of solvent is highly limited due to their extraordinary reactivity. The salts **2a** and **2b** have been found to be soluble without decomposing only in  $\text{SO}_2\text{ClF}$ .

Single crystals suitable for x-ray diffraction could be obtained by condensing isobutane at  $-196^\circ\text{C}$  onto a frozen solution of **2a** in  $\text{SO}_2\text{ClF}$  and immediately storing the still frozen solution in a  $-80^\circ\text{C}$  freezer. Compound **2a** crystallizes in the triclinic space group  $P\bar{1}$  (Figure 1). The anion, which has already been described in detail in literature,<sup>[11,13]</sup> consists of an antimony center coordinated octahedrally by six  $\text{OTeF}_5$  moieties. The cation shows the chlorine atom attached to two  $\text{CH}_2\text{CF}_3$  moieties. The  $\text{CF}_3$  groups point to opposite directions with a torsion angle  $\text{C3-C1-C2-C4}$  of  $150.81(8)^\circ$ . The  $\text{C1-Cl-C2}$  bond angle with  $104.5(4)^\circ$  and the C–Cl bond lengths with  $181.7(9)$  pm and  $180.3(10)$  pm in  $[\text{Cl}(\text{CH}_2\text{CF}_3)_2]^+$  are slightly smaller than the ones in  $[\text{Cl}(\text{CH}_2\text{CH}_3)_2]^+$  ( $105.6(2)^\circ$ ,  $184.0(4)$  pm and  $184.1(6)$  pm).<sup>[2]</sup>

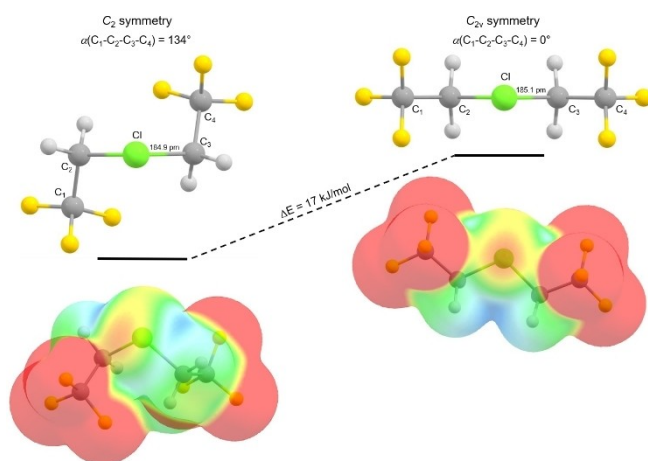
Interestingly, two molecules of the weakly basic solvent  $\text{SO}_2\text{ClF}$  coordinate to the Cl1 atom ( $\text{Cl1-O7}$   $284.3(9)$  pm,  $\text{Cl1-O9}$   $279.3(9)$  pm), which suggests a high Lewis acidity at this atom. In general,  $\text{SO}_2\text{ClF}$  is rarely reported to act as a donor, with only a few examples described in literature.<sup>[9,14–16]</sup> Quantum-chemical calculations in the gas phase of the chloronium cation  $[\text{Cl}(\text{CH}_2\text{CF}_3)_2]^+$  indeed show a high positive NBO charge of 0.523 at the chlorine atom of the optimized structure. The visualization of the electrostatic potential on the electron density reveals two  $\sigma$ -holes at the



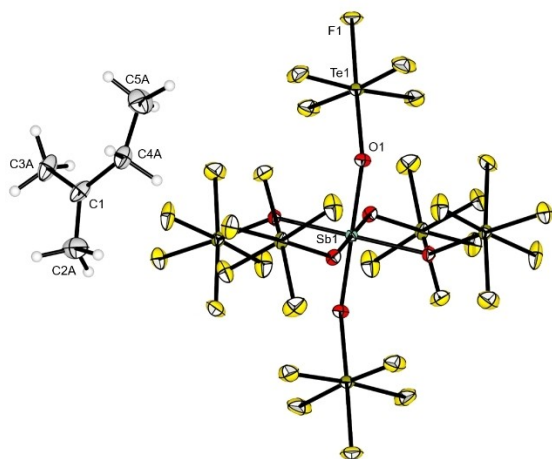
**Figure 1.** Molecular structure of the chloronium salt **2a** in the solid state. A third co-crystallized solvent molecule  $\text{SO}_2\text{ClF}$  is omitted for clarity. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [ $^\circ$ ]: C1–C3 150.3(14), C2–C4 151.2(13), C1–Cl1–C2 104.5(4), O7–Cl1–O9 284.3(9). For crystallographic details see Supporting Information.

Cl1 atom (Figure 2), which can interact with the oxygen atoms at the SO<sub>2</sub>ClF molecules. As a result of the high directionality of halogen bonding,<sup>[17]</sup> the Cl1 atom is surrounded by C1, C2, O7 and O9 in an almost planar fashion. A comparable planar coordination at the Cl atom has been reported for the difluorochloronium cation [ClF<sub>2</sub>]<sup>+</sup> which interacts with the fluorine atoms of the counterion in the solid state. The result are either dimeric as in [ClF<sub>2</sub>][BF<sub>4</sub>] and [ClF<sub>2</sub>][AuF<sub>4</sub>] or chain-like arrangements as in [ClF<sub>2</sub>][MF<sub>6</sub>] (M=Nb, Ta, Ru, Os, Ir, Sb, Bi).<sup>[18]</sup>

However, the extremely weakly coordinating nature of the [Sb(OTeF<sub>5</sub>)<sub>6</sub>]<sup>-</sup> anion in **2a** prevents interactions with the [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation resulting in the coordination of the SO<sub>2</sub>ClF molecules. The same phenomena has also been



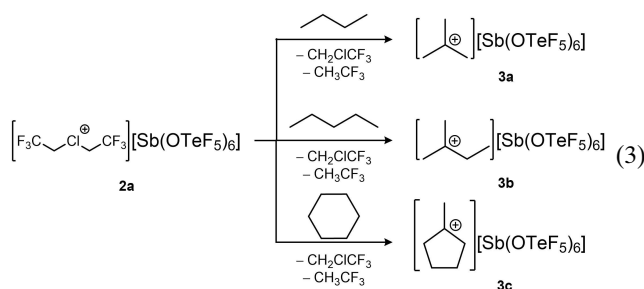
**Figure 2.** Electrostatic potential of the optimized structures of [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in C<sub>2</sub> (left) and C<sub>2v</sub> (right) symmetry in the gas phase in the range of 0.19 a.u. (red) to 0.27 a.u. (blue) mapped onto the electron density (isosurface value 0.003 a.u.); calculated at the B3LYP/def2-TZVPP level of theory.



**Figure 3.** Molecular structure of the isopentyl salt **3b** in the solid state. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: C1–C2A 143.0(5), C1–C3A 142.9(4), C1–C4A 148.3(4), C4A–C5A 153.1(11), C2A–C1–C3A 122.4(3), C3A–C1–C4A 119.8(3), C2A–C1–C4A 117.8(3). For crystallographic details see Supporting Information.

observed in the molecular structure of [Xe(OTeF<sub>5</sub>)(SO<sub>2</sub>ClF)][Sb(OTeF<sub>5</sub>)<sub>6</sub>], whereby one SO<sub>2</sub>ClF molecule coordinates the xenonium cation with a short Xe–O<sub>solvent</sub> contact of 247.9(4) pm<sup>[14]</sup> or 242.6(4) pm,<sup>[15]</sup> respectively. Again, no cation-anion interaction is observed. When the bulky [Sb(OTeF<sub>5</sub>)<sub>6</sub>]<sup>-</sup> anion is exchanged with the smaller [AsF<sub>6</sub>]<sup>-</sup> anion, strong anion-cation interactions lead to a F<sub>anion</sub>–Xe contact of 224(3) pm in the [XeOTeF<sub>5</sub>][AsF<sub>6</sub>] salt.<sup>[19]</sup> Removing all volatiles under dynamic vacuum leads to the SO<sub>2</sub>ClF-free chloronium salts **2a** and **2b** as proven by IR spectroscopy with the absence of any traces of SO<sub>2</sub>ClF (SI Figure S32).

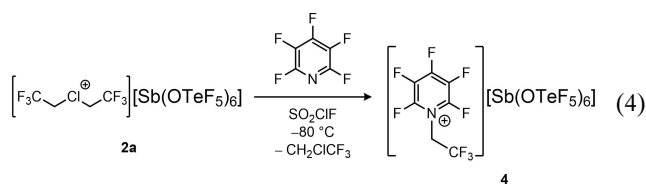
First attempts to crystallize the [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> salts led to the discovery of their extraordinary reactivity. Layering a solution of **2a** in SO<sub>2</sub>ClF at –30 °C with *n*-pentane and cooling to –80 °C gave colorless crystals which turned out to be the tertiary isopentyl carbocation stabilized by the antimonate anion (Figure 3). This reaction shows the ability of the fluorinated chloronium cation to activate *n*-pentane via hydride abstraction [Eq. (3)]. The activation of alkanes and the subsequent formation of stable branched carbocations has been reported by Olah et al. in superacidic media like FSO<sub>3</sub>H–SbF<sub>5</sub> or HF–SbF<sub>5</sub>.<sup>[20]</sup> The highly acidic protons in these systems are able to abstract a hydride ion from alkanes with the release of H<sub>2</sub>.



With a higher thermodynamic stability for tertiary carbocations compared to primary or secondary ones, the branched tertiary isopentyl cation is obtained after the activation of *n*-pentane since hydrogen- or methyl-1,2-shifts can easily occur in carbocations.<sup>[21]</sup> The exclusive formation of the branched carbocations from linear alkanes has been confirmed by NMR spectroscopy. For the preparation of NMR samples **2a** was suspended in *n*-butane, *n*-pentane or a mixture of cyclohexane and isobutane (1:1) and left stirring for several days at –20 °C. The <sup>19</sup>F NMR spectrum of the alkane solutions show the expected formation of the by-products CH<sub>3</sub>CF<sub>3</sub> and CH<sub>2</sub>ClCF<sub>3</sub> (SI Figure S17). Removing all volatiles from the reaction mixtures under vacuum lead to a colorless solid in all cases. The <sup>1</sup>H NMR spectra show the formation of the *tert*-butyl cation **3a** (SI Figure S14), the isopentyl cation **3b** (SI Figure S15) and the methyl cyclopentyl cation **3c** (SI Figure S16), respectively. Interestingly, under the same condition isobutane does not react with **2a**. This leads us to conclude that the chloronium cation is not able to abstract a hydride ion from the CH<sub>3</sub> groups of isobutane to form the intermediate primary carbocation, while the H atom at the tertiary atom may be too sterically shielded by the CH<sub>3</sub> groups to be attacked.

A similar observation of the selective formation of the branched carbocations from alkanes has been made by Reed et al., using the highly electrophilic “CH<sub>3</sub><sup>+</sup>” reagent CH<sub>3</sub>(CHB<sub>11</sub>Me<sub>5</sub>Br<sub>6</sub>) to abstract a hydride ion.<sup>[24]</sup> In contrast to the fluorinated [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation and the “CH<sub>3</sub><sup>+</sup>” reagent, the non-fluorinated chloronium cation [Cl(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> does not show any reactivity towards alkanes. For comparison, the calculated hydride ion affinities (HIA) and fluoride ion affinities (FIA) of selected cations are displayed in table 1 (for more computational details see SI). Note, that the hydride or fluoride abstraction leads to the decomposition of the cation by forming the corresponding neutral molecules. The high HIA of the fluorinated chloronium cation [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> with 1130 kJ/mol surpasses the non-fluorinated chloronium cations by more than 100 kJ/mol and the trityl cation [C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup>, which is commonly used as a hydride abstracting reagent, by more than 300 kJ/mol.

To further evaluate the alkylation power of the [Cl(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cation we choose the weakly nucleophilic pentafluoropyridine (C<sub>5</sub>F<sub>5</sub>N) as a reagent. For the alkylation reaction, **2a** is dissolved in SO<sub>2</sub>ClF and cooled to –80 °C. To the colorless solution a few drops of C<sub>5</sub>F<sub>5</sub>N are added via a syringe. The addition instantly leads to a yellow color, which upon warming to room temperature turns dark purple, indicating the immediate alkylation of the pyridine and the consequential formation of the pyridinium salt **4** [Eq. (4)].



The chemical shifts of the pyridinium cation in the <sup>19</sup>F NMR spectrum (F<sub>o</sub> = –94.1 ppm, F<sub>m</sub> = –151.1 ppm, F<sub>p</sub> = –99.1 ppm) are shifted compared to the ones of the starting material C<sub>5</sub>F<sub>5</sub>N (F<sub>o</sub> = –88.2 ppm, F<sub>m</sub> = –162.2 ppm, F<sub>p</sub> = –134.8 ppm) as it was already reported for the methylated pentafluoropyridinium cation.<sup>[5]</sup>

**Table 1:** Hydride ion affinities (HIA) and fluoride ion affinities (FIA) of selected halonium cations and carbocations. The ion affinities were calculated using Me<sub>3</sub>SiH or Me<sub>3</sub>SiF as anchor points, respectively (B3LYP/def2-TZVPP).<sup>[22]</sup>

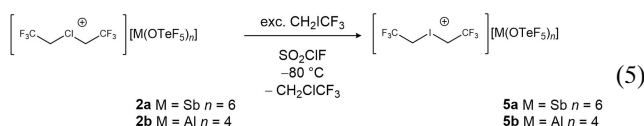
| Compound  | HIA [kJ/mol]]       | FIA [kJ/mol]]       |
|---|---------------------|---------------------|
| [Cl(CH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> a | 1130                | 907                 |
| [Cl(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> a | 986                 | 794                 |
| [Cl(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> a                 | 1048                | 828                 |
| [CH <sub>3</sub> ] <sup>+</sup>                                     | 1327                | 1107                |
| [I(CH <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> a  | 1074                | 851                 |
| [C(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sup>+</sup>      | 801 <sup>[23]</sup> | 599 <sup>[23]</sup> |
| [C(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>+</sup>      | 955 <sup>[23]</sup> | 697 <sup>[23]</sup> |

a) The HIA and FIA for the chloronium cations are calculated using the negative reaction enthalpy for the reaction [X(R)<sub>2</sub>]<sup>+</sup> + YSi(CH<sub>3</sub>)<sub>3</sub> → RX + RY + [Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, using Me<sub>3</sub>SiH or Me<sub>3</sub>SiF as anchor points, respectively.

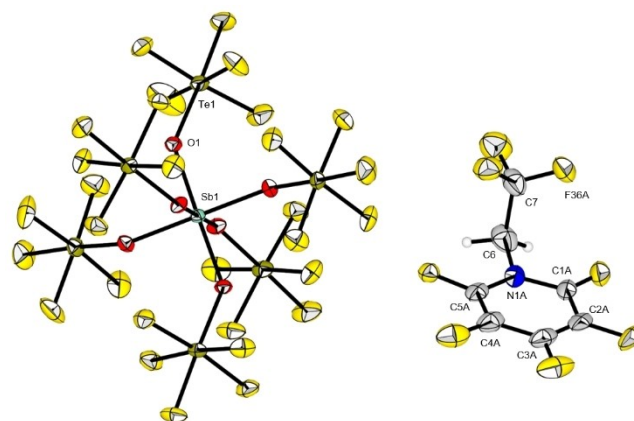
The signal of the CF<sub>3</sub> group (–71.0 ppm) shows the coupling to the methylene group (<sup>3</sup>J<sub>F-H</sub> = 7.0 Hz) and the long-range coupling to the *ortho*-fluorine atoms of the pyridine ring (<sup>5</sup>J<sub>F-F</sub> = 9.6 Hz), resulting in a triplet of triplets. The anion gives the expected collapsed AB<sub>4</sub> pattern at –42.2 ppm.

By layering a solution of the pyridinium salt **4** in SO<sub>2</sub>ClF at –10 °C with *n*-pentane and cooling it to –80 °C, it was possible to obtain single crystals suitable for x-ray diffraction. The compound crystallizes in the triclinic space group *P* $\bar{1}$  (Figure 4). The cation is disordered preventing an accurate analysis of the bond length and angles. However, it can be observed that the CF<sub>3</sub> group is nearly perpendicular to the ring plane (torsion angle: C5A–N1A–C6–C7 = 90.6(18)°, C5B–N1B–C6–C7 = 92.6(20)°).

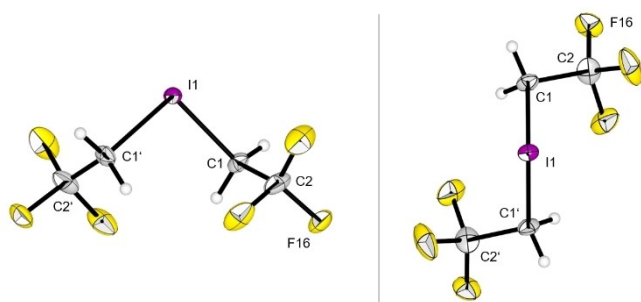
Furthermore, the chloronium salts **2a** and **2b** readily react with 1-iodo-2,2,2-trifluoroethane (CH<sub>2</sub>ICF<sub>3</sub>) at –80 °C in SO<sub>2</sub>ClF yielding the iodonium salts [I(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>][Sb(OTeF<sub>5</sub>)<sub>6</sub>] **5a** and [I(CH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>][Al(OTeF<sub>5</sub>)<sub>4</sub>] **5b** [Eq. (5)].



The iodonium salts are soluble in DCM at 20 °C without any sign of decomposition. The neat salts can be stored for an indefinite time at room temperature under inert conditions. By layering a solution of **5a** in DCM with *n*-pentane and cooling it to –80 °C it was possible to obtain single crystals suitable for x-ray diffraction (Figure 5). A detailed discussion of NMR data, structural features in the solid state and reactivity of **5a** and **5b** can be found in the SI.



**Figure 4.** Molecular structure of the pyridinium salt **4** in the solid state. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: C1A–C2A 137.0(13), C2A–C3A 135.9(14), C3A–C4A 138.9(13), C4A–C5A 134.5(10), N1A–C1A 134.9(9), N1A–C5A 134.1(10), N1A–C6 145.1(10), C6–C7 149.9(6), C1A–N1A–C5A 123.7(9), N1A–C6–C7 105.3(16). For crystallographic details see Supporting Information.



**Figure 5.** Molecular structure of the iodonium cation **5a** in the solid state. The anion is omitted for clarity. The cation is depicted from two different perspectives to show the structural arrangement of the  $\text{CH}_2\text{CF}_3$  groups. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: I1–C1 213.5(3), C1–C2 149.4(4), C1–I1–C1' 98.78(16), I1–C1–C2 111.0(2), C2–C1–C1'–C2' 139.3(4). For crystallographic details see Supporting Information.

## Conclusion

In conclusion, we report on a conceptually new way of synthesizing alkyl chloronium salts by oxidation of the chloride substituent of chloroalkanes and chlorofluoroalkanes. This approach allows for the quantitative synthesis and characterization of the first fluorinated alkyl chloronium salts **2a** and **2b**. The high electrophilicity of these salts has been demonstrated by the activation via hydride abstraction of linear alkanes giving the branched carbocations **3a**, **3b** and **3c**, and the alkylation of the weakly nucleophilic nitrogen base  $\text{C}_5\text{F}_5\text{N}$  and the iodofluoroalkane  $\text{CH}_2\text{ICF}_3$ , yielding the pyridinium salt **4** and the fluorinated alkyl iodonium salts **5a** and **5b**.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[25–40]</sup>

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- [1] a) R. Minkwitz, V. Gerhard, *Z. Naturforsch. B* **1991**, *46*, 561; b) G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1970**, *92*, 718; c) G. A. Olah, J. R. DeMember, *J. Am. Chem. Soc.* **1969**, *91*, 2113.
- [2] E. S. Stoyanov, I. V. Stoyanova, F. S. Tham, C. A. Reed, *J. Am. Chem. Soc.* **2010**, *132*, 4062.
- [3] S. Hämmerling, G. Thiele, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Angew. Chem. Int. Ed.* **2019**, *58*, 9807; *Angew. Chem.* **2019**, *131*, 9912.
- [4] E. S. Stoyanov, *Phys. Chem. Chem. Phys.* **2016**, *18*, 12896.
- [5] S. Hämmerling, P. Voßnacker, S. Steinhauer, H. Beckers, S. Riedel, *Chem. Eur. J.* **2020**, *26*, 14377.
- [6] M. Nakajima, K. Miyamoto, K. Hirano, M. Uchiyama, *J. Am. Chem. Soc.* **2019**, *141*, 6499.
- [7] A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; *Angew. Chem.* **2017**, *129*, 8375.
- [8] H. P. A. Mercier, M. D. Moran, G. J. Schrobilgen, in *ACS Symposium Series, Vol. 965*, American Chemical Society **2007**, S. 394–427.
- [9] H. P. A. Mercier, M. D. Moran, G. J. Schrobilgen, C. Steinberg, R. J. Suontamo, *J. Am. Chem. Soc.* **2004**, *126*, 5533.
- [10] K. O. Christe, X. Zhang, R. Bau, J. Hegge, G. A. Olah, Prakash, G. K. Surya, J. A. Sheehy, *J. Am. Chem. Soc.* **2000**, *122*, 481.
- [11] H. P. A. Mercier, J. C. P. Sanders, G. J. Schrobilgen, *J. Am. Chem. Soc.* **1994**, *116*, 2921.
- [12] A. N. Toraman, L. Fischer, A. Pérez-Bitrián, A. Wiesner, K. F. Hoffmann, S. Riedel, *Chem. Commun.* **2024**, *60*, 1711.
- [13] a) D. M. Van Seggen, P. K. Hurlburt, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1995**, *34*, 3453; b) W. J. Casteel, P. Kolb, N. LeBlond, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* **1996**, *35*, 929.
- [14] H. P. A. Mercier, M. D. Moran, J. C. P. Sanders, G. J. Schrobilgen, R. J. Suontamo, *Inorg. Chem.* **2005**, *44*, 49.
- [15] P. Ulferts, K. Seppelt, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1589.
- [16] a) T. Drews, K. Seppelt, *Z. Anorg. Allg. Chem.* **1991**, *606*, 201; b) P. A. W. Dean, R. J. Gillespie, *J. Am. Chem. Soc.* **1969**, *91*, 7260; c) K. F. Hoffmann, A. Wiesner, S. Steinhauer, S. Riedel, *Chem. Eur. J.* **2022**, e202201958.
- [17] M. Saccone, G. Cavallo, P. Metrangolo, A. Pace, I. Pibiri, T. Pilati, G. Resnati, G. Terraneo, *CrystEngComm* **2013**, *15*, 3102.
- [18] a) B. Scheibe, R. Haiges, S. I. Ivlev, A. J. Karttunen, U. Müller, K. O. Christe, F. Kraus, *Eur. J. Inorg. Chem.* **2020**, 4483; b) M. Y. Antipin, A. M. Ellern, V. F. Sukhovkikhov, Y. T. Struchkov, Y. A. Buslaev, *Russ. J. Inorg. Chem.* **1988**, 171.
- [19] B. A. Fir, H. P. A. Mercier, J. C. P. Sanders, D. A. Dixon, G. J. Schrobilgen, *J. Fluorine Chem.* **2001**, *110*, 89.
- [20] a) G. A. Olah, J. Lukas, *J. Am. Chem. Soc.* **1967**, *89*, 4739; b) G. A. Olah, J. Lukas, *J. Am. Chem. Soc.* **1968**, *90*, 933; c) G. A. Olah, *Science* **1970**, *168*, 1298.
- [21] V. G. Shubin, G. I. Borodkin, *Stable Carbocation Chemistry/Eds. GKS Prakash and P. v. R. Schleyer* **1997**, New York: John Wiley & Sons.
- [22] a) P. Erdmann, L. Greb, *ChemPhysChem* **2021**, *22*, 935; b) H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489.

- [23] K. F. Hoffmann, D. Battke, P. Golz, S. M. Rupf, M. Malischewski, S. Hasenstab-Riedel, *Angew. Chem. Int. Ed.* **2022**, e202203777; *Angew. Chem.* **2022**, *134*, e202203777.
- [24] T. Kato, C. A. Reed, *Angew. Chem. Int. Ed.* **2004**, *43*, 2908.
- [25] K. Seppelt, D. Nothe, *Inorg. Chem.* **1973**, *12*, 2727.
- [26] D. Lentz, K. Seppelt, *Z. Anorg. Allg. Chem.* **1983**, *502*, 83.
- [27] OriginLab Corporation, *OriginPro, Version 2022*, Northampton, MA, USA.
- [28] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3.
- [29] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3.
- [30] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
- [31] H. Putz, K. Brandenburg, *DIAMOND*, Crystal Impact GbR, Bonn **2020**.
- [32] F. Béke, J. T. Csenki, Z. Novák, *Chem. Rec.* **2023**, *23*, e202300083.
- [33] *Turbomole 7.4.1 ed., a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, Karlsruhe* **2019**.
- [34] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
- [35] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136.
- [36] E. Caldeweyher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2017**, *147*, 34112.
- [37] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [38] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, *NBO 7.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI **2018**.
- [39] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16*, Gaussian, Inc., Wallingford CT **2016**.
- [40] G. A. Zhurko, *Chemcraft - graphical program for visualization of quantum chemistry computations*. <https://www.chemcraft-prog.com>, Ivanovo (Russia) **2005**.

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