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Rearrangement Reactions of the Transient Lewis Acids $(CF_3)_3B$ and $(CF_3)_3BCF_2$: An Experimental and Theoretical Study

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Short-lived $(CF_3)_3B$ and $(CF_3)_3BCF_2$ are generated as intermediates by thermal dissociation of $(CF_3)_3BCO$ and F^- abstraction from the weak coordinating anion $[B(CF_3)_4]^-$, respectively. Both Lewis acids cannot be detected because of their instability with respect to rearrangement reactions at the B–C–F moiety. A cascade of 1,2-fluorine shifts to boron followed by perfluoroalkyl group migrations and also difluorocarbene transfer reactions occur. In the gas phase, $(CF_3)_3B$ rearranges to a mixture of linear perfluoroalkyldifluoroboranes $C_nF_{2n+1}BF_2$ ($n = 2$–7), while the respective reactions of $(CF_3)_3BCF_2$ result in a mixture of linear ($n = 2$–4) and branched monoperfluoroalkyldifluoroboranes, e.g., $(C_2F_5)(CF_3)FCBF_2$. For comparison, the reactions of $[CF_3BF_3]^-$ and $[C_2F_5BF_3]^-$ with AsF_5 are studied, and the products in the case of $[CF_3BF_3]^-$ are BF_3 and $C_2F_5BF_2$ whereas in the case of $[C_2F_5BF_3]^-$, $C_2F_5BF_2$ is the sole product. In contrast to reports in the literature, it is found that CF_3BF_2 is too unstable at room temperature to be detected. The decomposition of $(CF_3)_3BCO$ in anhydrous HF leads to a mixture of the new conjugate Brønsted–Lewis acids $[H_2F][(CF_3)_3BF]$ and $[H_2F][C_2F_5BF_3]$. All reactions are modeled by density functional calculations. The energy barriers of the transition states are low in agreement with the experimental results that $(CF_3)_3B$ and $(CF_3)_3BCF_2$ are short-lived intermediates. Since CF_2 complexes are key intermediates in the rearrangement reactions of $(CF_3)_3B$ and $(CF_3)_3BCF_2$, CF_2 affinities of some perfluoroalkylfluoroboranes are presented. CF_2 affinities are compared to CO and F^- affinities of selected boranes showing a trend in Lewis acidity, and its influence on the stability of the complexes is discussed. Fluoride ion affinities are calculated for a variety of different fluoroboranes, including perfluorocarboranes, and compared to those of the title compounds.

Introduction

In the course of our recent synthesis of the promising weak coordinating anion $[B(CF_3)_4]^-$,[1] we became interested in studying its stability and decomposition pathways. Since the degradation of the tetrakis(trifluoromethyl)borate anion is initiated by F^- abstraction and the formation of the conjugate Lewis acid $(CF_3)_3BCF_2$, we became interested in studying the properties of the difluorocarbene complex and related trifluoromethylboron Lewis acids, especially $(CF_3)_3B$.

Tricoordinated trifluoromethyl boranes, e.g., $(CF_3)_3B$, are known to be unstable with respect to B−F bond formation and probably loss of difluorocarbene,[1−3] but $B-CF_3$ compounds are still uncommon as difluorocarbene sources.[4] In the presence of strong π-donor ligands tricoordinated trifluoromethylboranes are stable, e.g., $(CF_3)_2BNMe_2$.[2,3] CF_3BF_2 is claimed to be stable at temperatures below −40 °C, and it was trapped with trimethylamine.[5] The syntheses of CF_3BF_2 were also reported by using $^nBu_2BCF_3$ and BF_3 as starting materials,[6,7] but similar reactions did not verify the observation. Hence its existence seems to be doubtful.[2,5] In contrast, a great number of tetracoordinated boron compounds containing trifluoromethyl ligands are well-known in the literature.[1−3] Whereas tricoordinated trifluoromethylboranes are rare, boranes with one perfluoroalkyl substitu-

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(1) Bernhardt, E.; Henkel, G.; Willner, H.; Pawelke, G.; Bürger, H. *Chem. Eur. J.* **2001**, *7*, 4696.
(2) Pawelke, G.; Bürger, H. *Appl. Organomet. Chem.* **1996**, *10*, 147.
(3) Pawelke, G.; Bürger, H. *Coord. Chem. Rev.* **2001**, *215*, 243.
(4) Brahms, D. L. S.; Daily, W. P. *Chem. Rev.* **1996**, *96*, 1585.
(5) Bürger, H.; Grunwald, M.; Pawelke, G. *J. Fluorine Chem.* **1985**, *28*, 183.
(6) Parsons, T. D.; Baker, E. D.; Burg, A. B.; Juvinall, G. L. *J. Am. Chem. Soc.* **1961**, *83*, 250.
(7) Parsons, T. D.; Self, J. M.; Schaad, L. H. *J. Am. Chem. Soc.* **1967**, *89*, 3446.

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ent, e.g., $C_nF_{2n+1}BF_2$ ($n = 3, 6$), are stable.[8–10] To our knowledge no unstabilized tricoordinate boranes of the types $(C_nF_{2n+1})_2BF$ and $(C_nF_{2n+1})_3B$ have been reported so far.

The tetrakis(trifluoromethyl)borate anion, $[B(CF_3)_4]^-$, is synthesized by fluorination of the tetracyanoborate anion, $[B(CN)_4]^-$,[11,12] in anhydrous HF according to eq 1.[1]

$$K[B(CN)_4] \xrightarrow[ClF_3/aHF]{} K[B(CF_3)_4] \qquad (1)$$

$[B(CF_3)_4]^-$ forms many stable salts with a wide variety of highly reactive cations, e.g., $[Co(CO)_5]^+$ [13] and NO^+,[14] and is stable under reductive (Na/NH_3) and oxidative conditions (F_2/aHF), respectively.[1] However, in the presence of concentrated sulfuric acid, $K[B(CF_3)_4]$ is converted to the borane carbonyl $(CF_3)_3BCO$ according to eq 2.[15,16]

$$[B(CF_3)_4]^-(solv) + H_3O^+ \xrightarrow[\text{conc. } H_2SO_4]{25\ °C} (CF_3)_3BCO(g) + 3HF(solv) \qquad (2)$$

The transformation of one of the CF_3 groups to the CO ligand involves the difluorocarbene complex $(CF_3)_3BCF_2$, which is immediately hydrolyzed in sulfuric acid. The released borane carbonyl, $(CF_3)_3BCO$, is stable up to 0 °C and at room temperature in suitable solvents, such as SO_2 or CH_2Cl_2, for a prolonged period of time.[15,16] In anhydrous HF, $(CF_3)_3BCO$ forms a new conjugated Brønsted−Lewis acid, $[H_2F][(CF_3)_3BF]$, (see eq 3) which has been shown to be a useful reaction medium for the formation of the so far unknown $[Co(CO)_5]^+$ cation in a salt with the weak coordinating anion $[(CF_3)_3BF]^-$.[17]

$$(CF_3)_3BCO(solv) + 2HF(l) \rightarrow [H_2F][(CF_3)_3BF](solv) + CO(g) \qquad (3)$$

The tris(trifluoromethyl)fluoroborate anion is formed by exchange of CO against F^-. In contrast, in nonacidic media, $(CF_3)_3BCO$ reacts with fluoride ions under addition to the carbonyl carbon atom, resulting in the formation of $[(CF_3)_3BC(O)F]^-$.[18]

In this study we report (i) the rearrangement and decomposition reactions of the intermediate $(CF_3)_3B$ in anhydrous HF and in the gas phase at room and elevated temperatures, (ii) the reactions of $K[B(CF_3)_4]$ with selected Lewis acids and the rearrangement as well as degradation reactions of the intermediate $(CF_3)_3BCF_2$, (iii) the heterogeneous reactions of $K[CF_3BF_3]$ and $K[C_2F_5BF_3]$ with AsF_5, (iv) a detailed ab initio study on the stabilities, fluoride ion affinities, and reaction pathways of fluoro(perfluoroalkyl)boron compounds and a comparison to related fluoroboron species, and (v) a ^{19}F NMR spectroscopic study on the reaction products.

Experimental Section

General Procedures and Reagents. (a) Apparatus. Volatile materials were manipulated in stainless steel or glass vacuum lines of known volume equipped with capacitance pressure gauges (type 280E Setra Instruments, Acton MA, or type 221AHS-1000 MKS Baratron, Burlinton, MA). The stainless steel line was fitted with bellow valves (type BPV25004 Balzers and type SS4BG Nupro) as well as with Gyrolok and Cajon fittings, while the glass vacuum line was fitted with PTFE stem valves (Young, London) and NS14.5 standard tapers. The glass vacuum line was equipped with three U-traps and connected to an IR gas cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of the FTIR instrument. Anhydrous HF was stored in a PFA tube (12 mm o.d., 300 mm long), heat sealed at the bottom, and connected at the top to a stainless steel needle valve (3762 H46Y Hoke, Cresskill, NJ). For synthetic reactions in HF, a reactor was used that consists of a 100 mL PFA bulb with a NS29 socket standard taper (Bohlender, Lauda, Germany) in connection with a PFA NS29 cone standard taper and a PFA needle valve (type 204−30 Galtek, Fluoroware, Chaska, Minnesota). The parts were held together with a metal compression flange, and the reactor was leakproof ($<10^{-5}$ mbar L s^{-1}) without using grease. Alternatively, a V-shaped reactor consisting of two PFA tubes (12 mm o.d., 100 mm length) and a PFA needle valve (Fluoroware, MN) with an approximate volume of 25 mL was used. Volatile products were stored in flame-sealed glass ampules under liquid nitrogen in a storage Dewar vessel. The ampules were opened and resealed using an ampule key.[19]

Matrix-isolated samples were prepared by passing a gas stream of Ar (∼3 mmol h^{-1}) over the sample placed in a small U-trap in front of the matrix support. The U-trap containing $C_2F_5BF_2$ was kept at −150 °C. Details of the matrix apparatus have been described elsewhere.[20]

(b) Chemicals. Anhydrous HF (Solvay AG, Hannover, Germany) as well as all standard chemicals and solvents were obtained from commercial sources. $(CF_3)_3BCO$ was prepared through the acidic hydrolysis of $K[B(CF_3)_4]$ with H_2SO_4 as reported.[15,16] $K[B(CF_3)_4]$ was synthesized as described previously from $K[B(CN)_4]$.[1] $K[CF_3BF_3]$ was formed as side product in some syntheses of $K[B(CF_3)_4]$. A sample of $K[C_2F_5BF_3]$ was obtained from Dr. N. V. Ignat'ev (Merck KGaA, Darmstadt, Germany).[21]

(c) Synthetic Reactions. (1) Decomposition of $(CF_3)_3BCO$ in aHF in the Presence of KHF_2. A 100 mL PFA reactor, fitted with a PTFE coated magnetic stirring bar, was charged with 1.20 g (15.4 mmol) of KHF_2. The PFA vessel was connected to a glass vacuum apparatus and set under vacuum to remove all volatile compounds. A 810 mg (3.3 mmol) portion of $(CF_3)_3BCO$ was condensed in vacuo into the PFA reactor at −196 °C. The PFA vessel was

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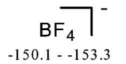
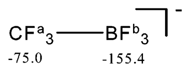
(8) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2001**, *627*, 15.
(9) Bardin, V. V.; Idemskaya, S. G.; Frohn, H.-J. *Z. Anorg. Allg. Chem.* **2002**, *628*, 883.
(10) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1853.
(11) Bernhardt, E.; Henkel, G.; Willner, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 560.
(12) Bernhardt, E.; Finze, M.; Willner, H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1229.
(13) Bernhardt, E.; Finze, M.; Berkei, M.; Lehmann, C. W.; Willner, H.; Aubke, F. Paper in preperation.
(14) Bernhardt, E.; Finze, M.; Willner, H. Paper in preparation.
(15) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. *J. Am. Chem. Soc.* **2002**, *124*, 15385.
(16) Terheiden, A.; Bernhardt, E.; Willner, H.; Aubke, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 799.
(17) Bernhardt, E.; Finze, M.; Willner, H.; Lehmann, C. W.; Aubke, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 2077.
(18) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1052.
(19) Gombler, W.; Willner, H. *J. Phys. E: Sci. Instrum.* **1987**, *20*, 1286.
(20) Argüello, G. A.; Grothe, H.; Kronberg, M.; Willner, H.; Mack, H. G. *J. Phys. Chem.* **1995**, *99*, 17525.
(21) Ignat'ev, N. V.; Schmidt, M.; Welz-Biermann, U.; Weiden, M.; Heider, U.; Miller, A.; Willner, H.; Sartori, P. (Merck KGaA). German Patent DE 10216998.5y, 2002.

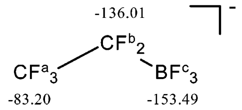
Chart 1. ^{11}B and ^{19}F NMR Data of Linear Perfluoroalkylborates



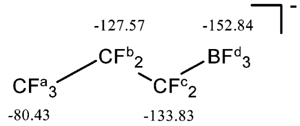
$\delta(^{11}\mathrm{B}) = -1.1 - -1.4$
$^{n}J(^{11}\mathrm{B},^{19}\mathrm{F})$: $^{1}J = 0.2 - 3.5$
$^{1}\Delta^{19}\mathrm{F}(^{10/11}\mathrm{B}) = 0.052 - 0.054$



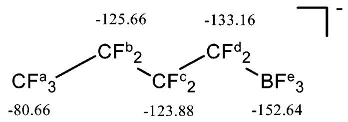
$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{3}J^{ab} = 2.4$
$\delta(^{11}\mathrm{B}) = -1.3$
$^{n}J(^{11}\mathrm{B},^{19}\mathrm{F})$: $^{1}J^{b} = 39.3$; $^{2}J^{a} = 32.5$
$^{1}J(^{13}\mathrm{C},^{19}\mathrm{F})$: $J^{a} = 312$
$^{1}\Delta^{19}\mathrm{F}(^{12/13}\mathrm{C})$: $\Delta^{a} = 0.1276$; $^{1}\Delta^{19}\mathrm{F}(^{10/11}\mathrm{B}) = 0.0648$



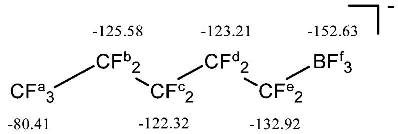
$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{3}J^{ab} = 0.7$; $^{4}J^{ac} = 4.9$; $^{3}J^{bc} = 1.5$
$\delta(^{11}\mathrm{B}) = -0.7$
$^{n}J(^{11}\mathrm{B},^{19}\mathrm{F})$: $^{1}J^{c} = 40.9$; $^{2}J^{b} = 19.6$
$^{1}J(^{13}\mathrm{C},^{19}\mathrm{F})$: $J^{a} = 284.1$; $J^{b} = 259.4$
$^{1}\Delta^{19}\mathrm{F}(^{12/13}\mathrm{C})$: $\Delta^{a} = 0.1209$; $\Delta^{b} = 0.1147$



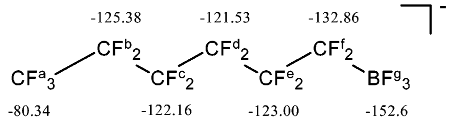
$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{4}J^{ac} = 9.3$; $^{6}J^{ad} = 2.7$; $^{3}J^{bc} = 1.6/1.6$;
$^{4}J^{bd} = 5.2$; $^{3}J^{cd} = 1.8$
$\delta(^{11}\mathrm{B}) = -0.7$
$^{n}J(^{11}\mathrm{B},^{19}\mathrm{F})$: $^{1}J^{d} = 41.0$; $^{2}J^{c} = 19.7$
$^{1}J(^{13}\mathrm{C},^{19}\mathrm{F})$: $J^{a} = 286.9$; $J^{b} = 258.4$; $J^{c} = 261.3$
$^{1}\Delta^{19}\mathrm{F}(^{12/13}\mathrm{C})$: $\Delta^{a} = 0.1249$; $\Delta^{b} = 0.1148$; $\Delta^{c} = 0.1150$



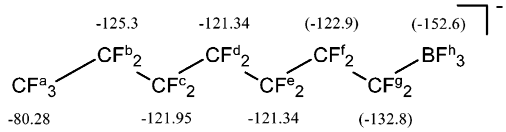
$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{4}J^{ac} = 9.9$; $^{6}J^{ad} = 3.9$; $^{3}J^{bc} = 5.0/0.0$;
$^{4}J^{bd} = 12.7/12.7$; $^{5}J^{be} = 3.1$; $^{3}J^{cd} = (2.5/2.5)$; $^{4}J^{ce} = 5.5$;
$^{3}J^{de} = (1.3)$
$\delta(^{11}\mathrm{B}) = -0.7$
$^{n}J(^{11}\mathrm{B},^{19}\mathrm{F})$: $^{1}J^{d} = 40.9$; $^{2}J^{c} = {\sim}19$
$^{1}J(^{13}\mathrm{C},^{19}\mathrm{F})$: $J^{a} = 286.7$; $^{1}\Delta^{19}\mathrm{F}(^{12/13}\mathrm{C})$: $\Delta^{a} = 0.1252$



$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{4}J^{ac} = 10.1$; $^{6}J^{ad} = 3.1$
$\delta(^{11}\mathrm{B}) = (-0.7)$



$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{4}J^{ac} = 10.2$; $^{6}J^{ad} = 2.8$
$\delta(^{11}\mathrm{B}) = (-0.7)$



$^{n}J(^{19}\mathrm{F},^{19}\mathrm{F})$: $^{4}J^{ac} = {\sim}10$; $^{6}J^{ad} = {\sim}2.5$
$\delta(^{11}\mathrm{B}) = (-0.7)$

attached to a stainless steel vacuum line, and 3 mL of anhydrous HF was added at −196 °C. Upon warming the reaction mixture to room temperature, the HF became liquid, and at approximately −20 °C, the white KHF_2 and $(CF_3)_3BCO$ dissolved in the HF. The reaction mixture was stirred for 1 h at room temperature. After cooling to −100 °C, the gas phase above the clear colorless solution was investigated by IR spectroscopy. The main components of the gas phase were identified as CO and HCF_3, and small quantities of BF_3 were also found. All volatile compounds were removed under reduced pressure, and the white residue was suspended in acetonitrile. The suspension was filtered to remove excess KHF_2. The solvent was removed using a rotary evaporator giving a white solid. The solid was dissolved in CD_3CN and investigated by ^{11}B and ^{19}F NMR spectroscopy. It consisted of 77.1% $K[(CF_3)_3BF]^1$ and 22.9% $K[C_2F_5BF_3]$ (see Chart 1).

(2) Decomposition of $(CF_3)_3BCO$ in Neat aHF. One sidearm of a V-shaped 25 mL PFA reactor was fitted with a PTFE coated magnetic stirring bar and was charged with 160 mg (2.6 mmol) of NaF. The PFA vessel was connected to a glass vacuum apparatus and set under vacuum to remove all volatile compounds. A 310 mg (1.3 mmol) portion of $(CF_3)_3BCO$ was transferred in vacuo into the second sidearm of the PFA reactor at −196 °C. The PFA vessel was attached to a stainless steel vacuum line, and 3 mL of anhydrous HF was added to the borane carbonyl at −196 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The clear colorless reaction mixture was poured at room temperature onto the NaF and stirred for further 10 min. All volatile compounds were removed under reduced pressure, and the white residue was suspended in acetonitrile. The suspension was filtered to remove excess $NaHF_2$. The solvent was removed using a rotary evaporator giving a white solid. The solid was dissolved in CD_3CN and investigated by ^{11}B and ^{19}F NMR spectroscopy. It consisted of 29.5% $Na[(CF_3)_3BF]$,[1] 69.8% $Na[C_2F_5BF_3]$, and 0.7% $Na[BF_4]$ (see Chart 1).

(3) Gas-Phase Decomposition of $(CF_3)_3BCO$: Procedure A. A 100 mL PFA reactor was connected to a glass vacuum apparatus and charged with 320 mg (1.3 mmol) of $(CF_3)_3BCO$ by vacuum transfer at −196 °C. The reactor was warmed to room temperature and kept at this temperature for 20 h.

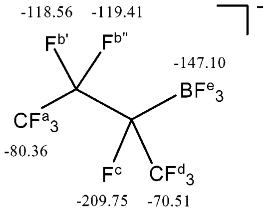
A 50 mL round-bottom glass flask equipped with a valve with a PTFE stem (Young, London), fitted with a PTFE-coated magnetic stirring bar, was charged with 200 mg (4.8 mmol) of NaF and 10 mL of CH_3CN. The PFA reactor was cooled to −196 °C and the CO was removed in vacuo. The content of the PFA reactor was vacuum transferred into the glass flask at −196 °C and stirred for 10 min at room temperature. The suspension was filtered to remove excess NaF, and the solvent was removed using a rotary evaporator yielding a white solid. It consisted of a mixture of linear perfluoroalkyl borates as identified by ^{19}F NMR spectroscopy of the following composition: 1.6% $Na[BF_4]$, 26.0% $Na[C_2F_5BF_3]$, 39.4% $Na[C_3F_7BF_3]$, 22.8% $Na[C_4F_9BF_3]$, 7.9% $Na[C_5F_{11}BF_3]$, 1.6% $Na[C_6F_{13}BF_3]$, and 0.7% $Na[C_7F_{15}BF_3]$ (see Chart 1).

(4) Gas-Phase Decomposition of $(CF_3)_3BCO$: Procedure B. A 40 mg (0.16 mmol) portion of $(CF_3)_3BCO$ was vacuum transferred into a 500 mL round-bottom glass flask equipped with a valve with a PTFE stem (Young, London), at −196 °C. The borane carbonyl was allowed to warm to room temperature and stored for 4 h (∼22 °C). The flask was cooled to −196 °C, and CO formed during the reaction was removed under reduced pressure. The residue was transferred into a 4 mm o.d. NMR tube, and 1.5 mL of dry $CFCl_3$ was added. The NMR tube was flame sealed and warmed to 0 °C. The tube was placed inside a thin walled 5 mm o.d. NMR tube with a CD_3CN film between both tubes. The NMR spectra were recorded at 0 °C. The mixture consisted of BF_3, a mixture of linear perfluoroalkylboranes, and $(CF_3)_3BCO$ as identified by their ^{19}F NMR spectra of the following composition: 2.8% BF_3, 29.4% $C_2F_5BF_2$, 28.0% $C_3F_7BF_2$, 10.6% $C_4F_9BF_2$, 3.1% $C_5F_{11}BF_2$, 0.7% $C_6F_{13}BF_2$, and 25.4% $(CF_3)_3BCO$. NMR data of the boranes, ^{11}B NMR (96.92 MHz, $CFCl_3$, 0 °C, $BF_3{\cdot}OEt_2$): BF_3, δ 9.9 ppm, $^1J(^{11}B,^{19}F) = 16.5$ Hz; $(C_nF_{2n+1})BF_2$ ($n = 2-6$), δ 19.5 ppm; $(CF_3)_3BCO$, δ −18.2 ppm, $^2J(^{11}B,^{19}F) = 33.1$ Hz. ^{19}F NMR (282.41 MHz, $CFCl_3$, 0 °C, $CFCl_3$): BF_3, δ −126.4 ppm, $^1J(^{11}B,^{19}F) = \sim16$ Hz; $C_2F_5BF_2$, $\delta(CF^a{}_3)$ −84.4 ppm, $\delta(CF^b{}_2)$ −134.7 ppm, $\delta(BF^c{}_2)$ −75.6 ppm, $^2J(^{11}B,^{19}F^c) = 20-30$ Hz, $^4J(^{19}F^a,^{19}F^c) = 3.9$ Hz; $C_3F_7BF_2$, $\delta(CF^a{}_3)$ −81.6 ppm, $\delta(CF^b{}_2)$ −129.4 ppm, $\delta(CF^c{}_2)$ −134.3 ppm, $\delta(BF^d{}_2)$ −75.6 ppm, $^2J(^{11}B,^{19}F^d) = 20-30$ Hz, $^4J(^{19}F^a,^{19}F^c) = 8.0$ Hz; $C_4F_9BF_2$, $\delta(CF^a{}_3)$ −81.6 ppm, $\delta(CF^b{}_2)$ −127.3 ppm, $\delta(CF^c{}_2)$ −126.1 ppm, $\delta(CF^d{}_2)$ −134.7 ppm, $\delta(BF^e{}_2)$ −77.0 ppm, $^4J(^{19}F^a,^{19}F^c) = 9.2$ Hz, $^5J(^{19}F^a,^{19}F^d) = 1.9$ Hz; $C_5F_{11}BF_2$, $\delta(CF^a{}_3)$ −81.6 ppm, $\delta(CF^b{}_2)$ −127.0 ppm, $\delta(CF^c{}_2)$ −122.5 ppm, $\delta(CF^d{}_2)$ −126.8 ppm, $^4J(^{19}F^a,^{19}F^c) = 9.8$ Hz, $^5J(^{19}F^a,^{19}F^d) = 2.4$ Hz; $C_6F_{13}BF_2$, $\delta(CF^b{}_2)$ −126.6 ppm, $\delta(CF^c{}_2)$ −123.4 ppm, $\delta(CF^d{}_2)$ −121.7 ppm; $(CF_3)_3BCO$, δ −58.7 ppm, $^2J = \sim33$ Hz.

(5) Reaction of $K[B(CF_3)_4]$ with Gaseous AsF_5. A 10 mL glass finger equipped with a valve that has a PTFE stem (Young, London) was charged with 169 mg (0.52 mmol) of $K[B(CF_3)_4]$. The flask was connected to a glass vacuum apparatus and set under vacuum to remove all volatile compounds. A 51 mg (0.30 mmol) portion of AsF_5 was transferred in vacuo into the glass finger at −196 °C. The reaction mixture was warmed to room temperature and stored for 20 h.

A 50 mL round-bottom flask equipped with a valve with a PTFE stem (Young, London), fitted with a PTFE-coated magnetic stirring bar, was charged with 1.0 g (23.8 mmol) of NaF and 10 mL of CH_3CN. The content of the glass finger was vacuum transferred into the glass flask at −196 °C and stirred for 10 min at room temperature. The suspension was filtered to remove excess NaF, and the solvent was removed using a rotary evaporator yielding a white solid. It consisted of a mixture of perfluoroalkylborates as identified by their ^{19}F NMR spectra. The main components of perfluoroalkylborates were the following: 7.6% $Na[BF_4]$, 43.3% $Na[C_2F_5BF_3]$, 13.1% $Na[C_3F_7BF_3]$, 0.5% $Na[C_4F_9BF_3]$, 32.8% $Na[(C_2F_5)(CF_3)FCBF_3]$, 1.6% $Na[(C_2F_5)_2FCBF_3]$, 1.2% $Na[(C_3F_7)(CF_3)FCBF_3]$ (see Charts 1 and 2).

Chart 2. ^{11}B and ^{19}F NMR Data of $[(C_2F_5)(CF_3)FCBF_3]^-$



$^nJ(^{19}F,^{19}F)$: $^4J^{ac} = 10.6$; $^5J^{ad} = 4.7$; $^5J^{ae} = 5.6$; $^2J^{b'b''} = 294.7$; $^3J^{b'c} = 7.2$; $^3J^{b''c} = 6.2$; $^4J^{b'd} = 7.6$; $^4J^{b''d} = 13.4$; $^4J^{b'e} = 8.5$; $^4J^{b''e} = 5.7$; $^3J^{cd} = 8.8$; $^3J^{ce} = 4.9$; $^4J^{de} = 8.2$

$\delta(^{11}B) = 0.1$

$^nJ(^{11}B,^{19}F)$: $^1J^e = 40.5$; $^2J^c = 12.8$

(6) Reaction of $K[CF_3BF_3]$ with Gaseous AsF_5. A sample of $K[CF_3BF_3]$ (198 mg, 1.13 mmol) was added to a 100 mL PFA reactor. The PFA vessel was connected to a glass vacuum apparatus and set under vacuum to remove all volatile compounds. A 102 mg (0.60 mmol) portion of AsF_5 was transferred in vacuo into the PFA reactor at −196 °C. The reaction mixture was warmed to room temperature and stored for 28 h.

A 50 mL round-bottom flask equipped with a valve that has a PTFE stem (Young, London), fitted with a PTFE-coated magnetic stirring bar, was filled with 100 mg (2.4 mmol) of NaF and 10 mL of CH_3CN. The content of the PFA reactor was vacuum transferred into the glass flask at −196 °C and stirred for 10 min at room temperature. The suspension was filtered to remove excess NaF, and the solvent was removed using a rotary evaporator yielding a white solid. The solid was dissolved in CD_3CN and investigated by ^{11}B and ^{19}F NMR spectroscopy. It consisted of 65% $Na[BF_4]$ and 35% $Na[C_2F_5BF_3]$ (see Chart 1) as well as minor amounts of unidentified products.

(7) Reaction of $K[C_2F_5BF_3]$ with Gaseous AsF_5. A 10 mL glass finger equipped with a valve that has a PTFE stem (Young, London) was charged with 259 mg (1.15 mmol) of $K[C_2F_5BF_3]$. The white salt was dried overnight and then 48 mg (0.28 mmol) of AsF_5 were transferred in vacuo into the PFA reactor at −196 °C. The reaction mixture was warmed to room temperature, and the further reaction was monitored by IR spectroscopy. After 2 h the reaction was completed, and $C_2F_5BF_2$ was obtained with slight impurities of BF_3. ^{11}B NMR (96.92 MHz, $CFCl_3$, 0 °C, $BF_3{\cdot}OEt_2$): δ 19.5 ppm. ^{19}F NMR (282.41 MHz, $CFCl_3$, 0 °C, $CFCl_3$): $\delta(CF^a{}_3)$ −84.4 ppm, $\delta(CF^b{}_2)$ −134.7 ppm, $\delta(BF^c{}_2)$ −75.6 ppm, $^2J(^{11}B,^{19}F^c) = 20-30$ Hz, $^4J(^{19}F^a,^{19}F^c) = 3.9$ Hz.

(d) Instrumentation. (1) Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range 5000−400 cm^{-1} on a Bruker IFS 66v FTIR instrument. Matrix infrared spectra were recorded using another Bruker IFS 66v FTIR spectrometer in the reflectance mode employing a transfer optic. A DTGS detector, together with a KBr/Ge beam splitter, was used in the region 5000−400 cm^{-1}. In this region, 64 scans were CO added for each spectrum using an apodized resolution of 1.2 cm^{-1}.

(2) NMR Spectroscopy. ^{19}F and ^{11}B NMR spectra were recorded at room or at low temperatures on a Bruker Avance DRX-300 spectrometer operating at 282.41 or 96.92 MHz for ^{19}F and ^{11}B nuclei or on a Bruker Avance DRX-500 spectrometer, operating at

470.59 or 160.46 MHz for ^{19}F and ^{11}B nuclei, respectively. The NMR signals were referenced against $CFCl_3$ (^{19}F) as internal standard and $BF_3{\cdot}OEt_2$ in CD_3CN (^{11}B) as external standard. Concentrations of the investigated samples were in the range 0.1−1 mol L^{-1}. Samples were prepared in 5 mm NMR tubes, equipped with special valves with PTFE stems (Young, London).[22] Dry CD_3CN was used as solvent.

(3) Computational Section. Quantum chemical calculations were performed to support the experimental results presented in this study and to understand the reaction pathways for the isomerization reactions of $(CF_3)_3B$ and $(CF_3)_3BCF_2$ mainly leading to $C_3F_7BF_2$ and $(C_2F_5)(CF_3)FCBF_2$, respectively. DFT calculations[23] were carried out using the B3LYP method[24−26] with the basis sets 6-311G(d) and 6-311+G(d) as implemented in the Gaussian 98 program suite.[27] Frequency calculations were performed for all species employing the basis set 6-311G(d), and all structures represent true minima without imaginary frequencies on the respective hypersurface. Geometries and energies were recalculated using the 6-311+G(d) basis set because the accuracy of the energies of anions is improved with the incorporation of diffuse functions.[28] Frequency calculations with the more time demanding basis set 6-311+G(d) were performed only for a few model compounds, for example $(CF_3)_3B$ and $[B(CF_3)_4]^-$, and the wavenumbers are very close to those calculated with the basis set 6-311G(d). Hence, correction terms derived from calculations with 6-311G(d) were used. Transition states exhibit one imaginary frequency, and IRC calculations were performed to verify that the transition states connect the products and reactants, respectively.[29,30] All energies presented herein are zero point corrected. For enthalpies and free energies, the thermal contributions are included for 298 K.

Results and Discussion

(I) Investigation of the Transient Lewis Acids $(CF_3)_3B$ and $(CF_3)_3BCF_2$. All attempts on the synthesis of the free Lewis acid tris(trifluoromethyl)borane, $(CF_3)_3B$, have failed so far. Recently we reported on the synthesis of $(CF_3)_3BCO$ which has been shown to behave in some reactions as a synthon for $(CF_3)_3B$, for example in the formation of $(CF_3)_3BNCCH_3$ with acetonitrile[15] or the reaction with anhydrous HF to $[H_2F][(CF_3)_3BF]$.[17] Furthermore, $(CF_3)_3BCO$ undergoes ligand exchange with ^{13}CO in the gas phase as proven by the synthesis of $(CF_3)_3B^{13}CO$. Since $(CF_3)_3BCO$ is a useful reagent for the generation of weak coordinating anions[17] and the introduction of the $(CF_3)_3B$ fragment into a variety of molecules, it is of interest to investigate the decomposition pathway of $(CF_3)_3BCO$ to gain a deeper insight into the chemistry of the transient Lewis acid $(CF_3)_3B$. The products of the gas-phase decomposition are linear perfluoroalkylboranes which are formed by a cascade of intramolecular fluoride ion abstractions from CF_3 ligands and perfluoroalkyl migrations to the initially formed difluorocarbene complexes. The formation of boranes with perfluoroalkyl chains other than C_3F_7 is also observed and is due to either loss of CF_2 (the formation of $C_2F_5BF_2$) or trapping of CF_2 by $C_nF_{2n+1}BF_2$ followed by migration of C_nF_{2n+1}. A similar degradation reaction of $(CF_3)_3BCO$ was also observed in anhydrous HF, and hence, we have included these results in this report. To prove our proposed reaction mechanism, the fluorine and perfluoroalkyl shifts, we have studied the degradation of $(CF_3)_3B$ giving $C_3F_7BF_2$ by quantum chemical calculations. All reaction intermediates and transition states were calculated. The small barriers found for the fluoride and perfluoroalkyl migrations help to explain why only monoperfluoroalkylboranes are observed as products.

The abstraction of a fluoride ion from $[B(CF_3)_4]^-$ leads to the transient difluorocarbene complex $(CF_3)_3BCF_2$ which should react with HF to give the novel conjugated Brønsted−Lewis acid, $[H_2F][B(CF_3)_4]$. Although ab initio calculations predict an even higher stability for $(CF_3)_3BCF_2$ against loss of the neutral ligand than for $(CF_3)_3BCO$, similar to the attempted synthesis of $(CF_3)_3B$, the isolation of $(CF_3)_3BCF_2$ failed. The products of the gas-phase degradation of $(CF_3)_3BCF_2$ are linear and also branched pefluoroalkylboranes. This result indicates a similar rearrangement process as discussed above for the decomposition of $(CF_3)_3B$. We have studied the degradation process of $(CF_3)_3BCF_2$ by density functional theory to confirm our proposed rearrangement mechanism as already described for $(CF_3)_3B$.

(a) Decomposition Reactions of $(CF_3)_3BCO$ in Anhydrous HF and in the Gas Phase. In anhydrous HF, $(CF_3)_3BCO$ forms the new Brønsted−Lewis acid, $[H_2F][(CF_3)_3BF]$ (see eq 3). In the presence of $Co_2(CO)_8$ mainly $[Co(CO)_5][(CF_3)_3BF]$ is formed (eq 4), and only small quantities of $[C_2F_5BF_3]^-$ salts are observed as side products.[17]

$$Co_2(CO)_8 + 2(CF_3)_3BCO + 2HF \rightarrow 2[Co(CO)_5][(CF_3)_3BF] + H_2 \quad (4)$$

If the reaction is carried out in the presence of KHF_2 instead of $Co_2(CO)_8$, 23% of $[C_2F_5BF_3]^-$ and 77% of $[(CF_3)_3BF]^-$ are formed. The product distribution is reversed to 70% of $[C_2F_5BF_3]^-$ and only 30% of $[(CF_3)_3BF]^-$ if no KHF_2 is added due to the enhanced acidity. The $[(CF_3)_3BF]^-$ anion is the product of the carbonyl group exchange of $(CF_3)_3BCO$ by F^-. For the formation of the $[(C_2F_5)BF_3]^-$ anion, an intramolecular rearrangement mechanism is proposed (Scheme 1). The ratio of both anions formed, $[(CF_3)_3BF]^-$ and $[C_2F_5BF_3]^-$, strongly depends (i) on the availability of F^- in the HF solution (the more F^- is available the more $(CF_3)_3B$ is trapped as $[(CF_3)_3BF]^-$) and (ii) on the acidity of the HF solution (the more acidic the reaction

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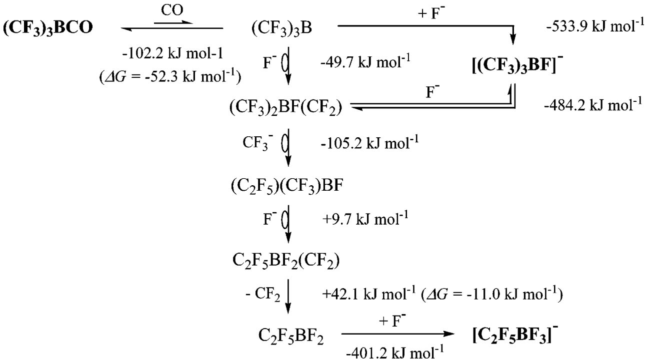
(22) Gombler, W.; Willner, H. *Int. Lab.* **1984**, 84.
(23) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(25) Becke, A. D. *Phys. Rev. B* **1988**, *38*, 3098.
(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *41*, 785.
(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.
(28) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231.
(29) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.
(30) Gonzales, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

Scheme 1. Reaction of $(CF_3)_3BCO$ in Anhydrous HF (ΔE(298 K))[a]

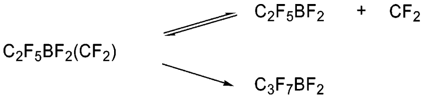


[a] Energy: B3LYP/6-311+G(d). ZPC and thermal corrections: B3LYP/6-311G(d).

medium is, the more the equilibrium between $[(CF_3)_3BF]^-$ and $(CF_3)_2BF(CF_2)$ shifts toward the difluorocarbene complex). The rearrangement is either initiated by an intramolecular fluoride ion shift from one CF_3 group to the B atom of $(CF_3)_3B$ or an intermolecular fluoride ion abstraction from one CF_3 ligand in $[(CF_3)_3BF]^-$. The next step is an intramolecular migration of one CF_3 group in the carbene complex $(CF_3)_2BF(CF_2)$. This step explains the formation of a perfluoroethyl group. A further intramolecular F^- shift from the remaining CF_3 group followed by loss of difluorocarbene and the addition of a fluoride ion from HF results in $[C_2F_5BF_3]^-$. Difluorocarbene is immediately trapped by HF as HCF_3 which was observed by IR spectroscopy in the gas phase over the HF solution.

The decomposition of $(CF_3)_3BCO$ in the gas phase has already been investigated by us,[15] but some of the results must be reinterpreted. To underline the reinterpretation, new additional experiments have been performed as described in the Experimental Section. To prevent side reactions with the glass walls, the reaction was performed in PFA vessels. The resulting gaseous reaction mixture was reacted with sodium fluoride in acetonitrile to convert the boranes into the corresponding borates. This procedure has two advantages: (i) the borates are easier to handle because they are nonvolatile salts, and (ii) borate anions usually exhibit sharper NMR signals as the related boranes.

The formation of the observed linear perfluoroalkylborates $[C_nF_{2n+1}BF_3]^-$ ($n = 2-7$) can be rationalized by initial formation of the carbene complex $C_2F_5BF_2(CF_2)$ as shown in Scheme 1. This carbene complex can undergo two reactions: (i) the reversible dissociation into $C_2F_5BF_2$ and CF_2 or (ii) the irreversible migration of the C_2F_5 group to the carbon atom of the difluorocarbene ligand (eq 5).


$$C_2F_5BF_2(CF_2) \rightleftharpoons C_2F_5BF_2 + CF_2 \qquad C_2F_5BF_2(CF_2) \rightarrow C_3F_7BF_2 \qquad (5)$$

The formation of perfluoroalkyl chains with more than two CF_2 groups is due to trapping of CF_2 by $C_3F_7BF_2$ followed by transfer of the perfluoroalkyl chain to the C atom of the carbene ligand. Repeated CF_2 addition followed by migration of the perfluoroalkyl group leads to chain growth. IR spectra of the gaseous reaction mixture reveal that no formation of C_2F_4 occurs due to the low concentration of CF_2. Addition of BF_3 to $(CF_3)_3BCO$ does not change the course of the reaction, and a nearly identical product composition is observed. Hence, BF_3 is the weakest Lewis acid in this reaction mixture. On the other hand, BF_3 is capable of reacting with CF_2 to yield living polymers under thermal and photolytic conditions with difluorodiazirine as CF_2 source in great access.[31,32]

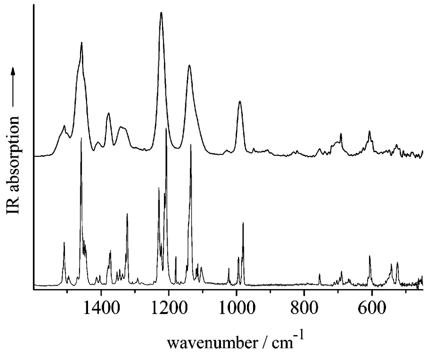


Figure 1. Gas phase and solid state IR (Ar matrix) spectra of $C_2F_5BF_2$.

The reaction of $K[CF_3BF_3]$ with AsF_5 at room temperature led to a mixture of BF_3 and $C_2F_5BF_2$ which were detected as their corresponding borate anions after reaction with NaF in CH_3CN. No $[CF_3BF_3]^-$ was found after treatment with NaF. The instability of CF_3BF_2 is explained by dissociation into CF_2 and BF_3 followed by trapping of CF_2 with CF_3BF_2 as $C_2F_5BF_2$ which is in agreement with the rearrangement reactions discussed above.

In contrast to CF_3BF_2, $C_2F_5BF_2$ can be synthesized from $K[C_2F_5BF_3]$ by abstraction of one F^- ion with AsF_5 according to eq 6.

$$K[C_2F_5BF_3] + AsF_5 \rightarrow C_2F_5BF_2 + K[AsF_6] \qquad (6)$$

The product was unambiguously characterized by NMR spectroscopy (see Experimental Section). The gas-phase IR spectrum of $C_2F_5BF_2$ is displayed in Figure 1, and the calculated wavenumbers are in good agreement with the experimental values (Table 1). In addition, calculated and reported[6,7] wavenumbers for CF_3BF_2 are also compared. In contrast to $C_2F_5BF_2$, the experimental values reported for CF_3BF_2 strongly deviate from the calculated data. Hence it is very likely that the IR spectrum of CF_3BF_2 [6,7] has never been observed.

Comparison of the IR spectrum of $C_2F_5BF_2$ in Ar matrix at 16 K (Figure 1) with the reported IR matrix spectrum of the low pressure thermolysis products (180 °C) of $(CF_3)_3BCO$[15] reveals that $C_2F_5BF_2$ is the main product of the thermolysis besides CO and CF_2. Hence the possible thermolysis products of $(CF_3)_3BCO$ like $(CF_3)_3B$, $(CF_3)_2BF$, and CF_3BF_2 are all very short-lived species, and the rearrangement process to yield $C_2F_5BF_2$ must be very fast.

(b) Rearrangement Reactions of $(CF_3)_3BCF_2$. All attempts to isolate the difluorocarbene complex $(CF_3)_3BCF_2$

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(31) Ogden, P. H.; Mitsch, R. A. *J. Heterocycl. Chem.* **1968**, *5*, 41.

(32) Mitsch, R. A.; Ogden, P. H. (Minnesota Mining and Manufacturing Company). United States Patent US3,493,629, 1970.

Table 1. Observed and Calculated[a] Band Positions [cm^{-1}] and IR Intensities [km mol^{-1}] of CF_3BF_2 and $C_2F_5BF_2$

CF_3BF_2				$C_2F_5BF_2$						
calcd[a]		expt[b]		calcd[a]		expt(s)[c]		expt(g)[d]		
$\tilde{\nu}$	I	$\tilde{\nu}$		$\tilde{\nu}$	I	$\tilde{\nu}$		$\tilde{\nu}$		assignment
				1502		1509	m	1509	m	$\nu_{as}(^{10}BF_2)$
1448	336	(1460)	m	1448	355	1458	vs	1457	vs	$\nu_{as}(^{11}BF_2)$
1431	13			1374	103	1374	m	1377	m	$\nu_s(BF_2)$
1137	311		s	1311	194	1323	s	1341	s	$\nu_s(CF_3)$
1156	265	(1190)	s	1218	151	1229	s	1222	vs	$\nu_{as}(CF_3)$
1101	249	(1080)	s	1193	265	1207	vs	1222	vs	$\nu_{as}(CF_3)$
				1133	244	1135	vs	1139	vs	$\nu_s(CF_2)$
				1124	131	1135	vs	1139	vs	$\nu_{as}(CF_2)$
				978	105	980	s	990	s	$\nu(CC)$
753	0.3			748	10	754	w	n.o.		$\delta_s(CF_3)$
692	48	(690)	w	703	16	690	w	691	w	$\pi(BF_2)$
595	51			602	44	607	m	607	w	$\delta_s(BF_2)$
545	0.1			589	0.8					$\delta_{as}(CF_3)$
				545	36	543	m			$\delta_s(CF_2)$
499	9			521	22	525	m			$\delta_{as}(CF_3)$
378	1.8			470	0.1					$\rho(BF_2)$
186	6			356	0.3					$\rho(CF_3)$
174	3.4			347	0.6					$\rho(CF_3)/\tau(CF_2)$
329	0.2			312	0.5					$\nu(BC)$
				267	3.5					$\omega(CF_2)$
				213	1.0					$\tau(CF_2)/\rho(CF_3)$
				179	3.7					$\rho(CF_2)$
				112	1.0					$\delta(BCC)$
				46	0.00					$\tau(CF_3)$
6	0.05			8	0.00					$\tau(BF_2)$

[a] B3LYP/6-311G(d). [b] Attributed band positions for $(CF_3)BF_2$. Further unassigned bands: 1400−1350w, 1255m, 1160w, 1040m, 850m, 845m, 725w.[6] [c] Ar matrix, this work. [d] Gas-phase spectrum at room temperature, this work.

Table 2. Calculated[a] F^-, CF_2, and CO Affinities of Perfluoroalkyl Boranes and Selected Bond Parameters of the Addition Products

	F^- affinity				CF_2 affinity				CO affinity			
compd	$-\Delta E$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}	d(B−F) Å	$-\Delta E$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}	d(B−CF$_2$) Å	$-\Delta E$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}	d(B−CO) Å
BF_3	329.7	332.2	293.4	1.417	18.6	21.1	−19.0	1.771	0.1	2.5[b]	−24.1	2.957[b]
CF_3BF_2	392.6	395.1	349.5	1.412	42.4	44.9	−14.5	1.719	2.1	4.6	−31.2	2.887
$(CF_3)_2BF$	460.8	463.3	422.8	1.413	101.3	103.8	51.3	1.624	25.1	27.6	−15.2	1.722
$(CF_3)_3B$	533.9	536.4	490.9	1.419	171.0	173.4	119.4	1.593	102.2	104.7	52.3	1.589[c]
$C_2F_5BF_2$	401.2	403.6	362.1	1.410	42.1	44.6	−11.0	1.742				
$C_3F_7BF_2$	402.6	405.1	368.3	1.408	39.1	41.5	5.9	1.745				
$C_4F_9BF_2$	406.4	408.9	368.7	1.408								
$(C_2F_5)(CF_3)$-$FCBF_2$	401.9	404.4	363.4	1.404								

[a] Energy: B3LYP/6-311+G(d). ZPC and thermal corrections: B3LYP/6-311G(d). [b] Expt values: $\Delta H = -7.6 \pm 0.3$ kJ mol^{-1},[33] d(B−CO) = 2.886(5) Å.[34] [c] Expt values: d(B−CO) = 1.617(12) Å (gas phase), 1.69(2) Å (solid state).[15]

failed, although DFT calculations predict a higher stability against elimination of CF_2 than of CO from $(CF_3)_3BCO$ (Table 2). Attempted syntheses for this target molecule include (i) the reaction of $[Ph_3C][B(CF_3)_4]$ with Et_3SiH and $^{i}Pr_3Al$, (ii) the reaction of $NO[B(CF_3)_4]$ with $Me_3SiSiMe_3$, (iii) the thermolysis of $[p\text{-}ClC_6H_4N_2][B(CF_3)_4]$ or $[o\text{-}EtC_6H_4N_2][B(CF_3)_4]$, and (iv) the reaction of $K[B(CF_3)_4]$ with SbF_5. All reactions resulted in complex product mixtures, and in some cases, $C_2F_5BF_2$ could be identified as a product.

Since the reaction of $K[B(CF_3)_4]$ with SbF_5 is very vigorous, AsF_5 was chosen as a weaker and gaseous Lewis acid. The boranes formed after the solid−gas reaction of $K[B(CF_3)_4]$ with AsF_5 were vacuum transferred onto NaF with acetonitrile and reacted to the corresponding borates which were analyzed by NMR spectroscopy. The fluoride ion abstraction from $[B(CF_3)_4]^-$ with AsF_5 proceeds easily although the calculated gas-phase F^- affinities of AsF_5 ($\Delta H = 434.4$ kJ mol^{-1}) (Table S1) and $(CF_3)_3BCF_2$ ($\Delta H = 508.5$ kJ mol^{-1}) (Table 3) indicate that no reaction should occur.

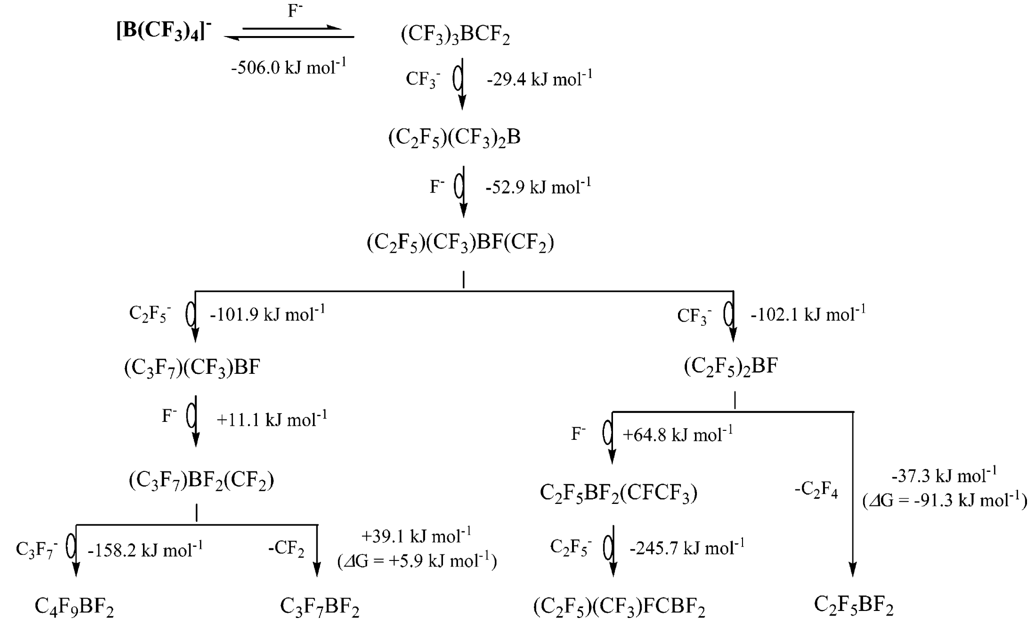
Table 3. Calculated[a] F^--Affinities of the Carbene Complexes $(CF_3)_nBF_{3-n}CF_2$ ($n = 0-3$)

	F^--affinity		
compd	$-\Delta E$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta G$ kJ mol^{-1}
$BF_3(CF_2)$	443.3	445.8	400.2
$CF_3BF_2(CF_2)$	470.9	473.4	438.2
$(CF_3)_2BF(CF_2)$	484.2	486.7	441.8
$(CF_3)_3BCF_2$	506.0	508.5	458.3

[a] Energy: B3LYP/6-311+G(d). ZPC and thermal corrections: B3LYP/6-311G(d).

$$[B(CF_3)_4]^- + AsF_5 \rightarrow (CF_3)_3BCF_2 + [AsF_6]^- \qquad \Delta H = +74.1 \text{ kJ mol}^{-1} \quad (7)$$

Scheme 2. Rearrangement of $(CF_3)_3BCF_2$ in the Gas Phase (ΔE(298 K))[a]



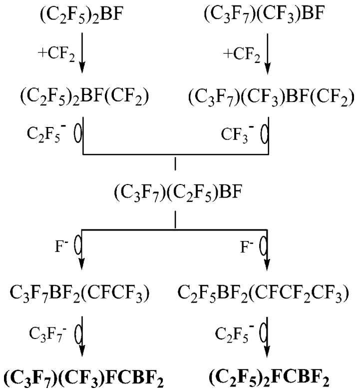
[a] Energy: B3LYP/6-311+G(d). ZPC and thermal corrections: B3LYP/6-311G(d).

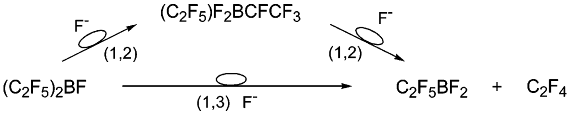
However, the higher lattice energy[35] of $K[AsF_6]$ ($U_{pot} = -579$ kJ mol^{-1}; $V_{mol} = 120$ Å^3) in comparison to $K[B(CF_3)_4]$ ($U_{pot} = -479$ kJ mol^{-1}; $V_{mol} = 244$ Å^3) makes the reaction exothermic.

$$K[B(CF_3)_4] + AsF_5 \rightarrow (CF_3)_3BCF_2 + K[AsF_6] \qquad \Delta H = -25.9 \text{ kJ mol}^{-1} \quad (8)$$

The carbene complex $(CF_3)_3BCF_2$ formed initially is unstable and undergoes rearrangement reactions leading to the formation of linear perfluoroalkylboranes. In addition, branched perfluoroalkylboranes are observed. The formation of the main products $C_2F_5BF_2$ (43.3%), $C_3F_7BF_2$ (13.1%), and $(C_2F_5)(CF_3)FCBF_2$ (32.8%) can be explained according to Scheme 2. The initial step of the rearrangement process is a CF_3 group migration to the CF_2 ligand followed by an intramolecular fluoride ion abstraction from one of the two remaining CF_3 groups. The transfer of either CF_3 or C_2F_5 in $(C_2F_5)(CF_3)BF(CF_2)$ leads to the formation of $(C_2F_5)_2BF$ or $(C_3F_7)(CF_3)BF$, respectively. A further fluoride ion abstraction in $(C_3F_7)(CF_3)BF$ to yield $(C_3F_7)BF_2(CF_2)$ followed by migration of C_3F_7 or loss of CF_2 gives the final products $C_4F_9BF_2$ and $C_3F_7BF_2$, respectively. $(C_3F_7)BF_2(CF_2)$ can dissociate into the borane and CF_2 due to the decreased Lewis acidity of boron compared to boranes with more than one perfluoroalkyl group. Unexpected is the instability of $(C_2F_5)_2BF$ under the reaction conditions: it was not found in the reaction mixture. Since the boron atom in $(C_2F_5)_2BF$ is more Lewis acidic than boron in monoperfluoroalkylboranes, intramolecular fluoride ion abstraction occurs. $(C_2F_5)(CF_3)FCBF_2$ is formed via $C_2F_5BF_2(CFCF_3)$ although the intermediate monofluorocarbene complex is less stabilized than the difluorocarbene complexes that are involved in the reaction steps described above. Alternative reaction pathways for $(C_2F_5)_2BF$ are shown in eq 9.

Scheme 3. Formation Pathways of Branched Perfluoroalkylborates





(9)

Both routes, (i) a cascade of two 1,2-fluorine shifts as well as (ii) a 1,3-fluorine shift, lead to the formation of $C_2F_5BF_2$ and C_2F_4.

Since $C_3F_7BF_2(CF_2)$ acts as a difluorocarbene source, the formation of other branched boranes (~3%) can be understood as presented in Scheme 3.

(c) Computational Results for the Model Systems: CF_3BF_2 and $C_2F_5BF_2$. The simplest trifluoromethylfluoroborane, CF_3BF_2, is unstable with respect to reversible dissociation into BF_3 and CF_2 followed by trapping of CF_2 by CF_3BF_2 as shown in the Experimental Section. In contrast to CF_3BF_2, no decomposition at room temperature was observed for $C_2F_5BF_2$. These results are surprising when compared to the isoelectronic carbocations $CF_3CF_2^+$ and

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(33) Sluyts, E. J.; van der Veken, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 440.

(34) Janda, K. C.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Am. Chem. Soc.* **1978**, *100*, 8074.

(35) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609.

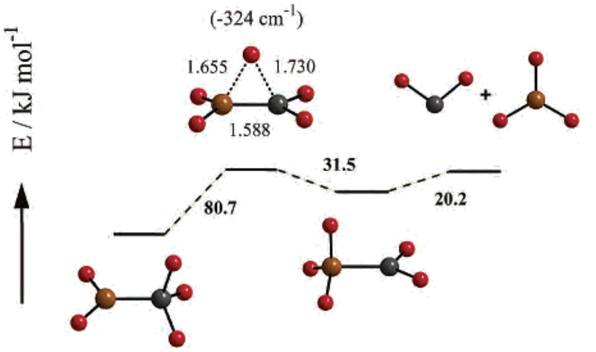

Figure 2. Calculated isomerization of CF_3BF_2 to F_3BCF_2 and dissociation of F_3BCF_2 into CF_2 and BF_3 (energy and geometry, B3LYP/6-311+G(d); wavenumbers and ZPC, B3LYP/6-311G(d)).

$C_2F_5CF_2^+$, because the barrier for a 1,2-fluorine migration in $CF_3CF_2^+$ (72.4 kJ mol^{-1}) is calculated to be significantly higher than the barrier for a 1,3-fluorine shift in $CF_3CF_2CF_2^+$ (27.2 kJ mol^{-1}).[36] Unfortunately, only little is known about fluoride ion migration reactions in carbocations,[37,38] and so, no experimental data are available on the stabilities of $CF_3CF_2^+$ and $C_2F_5CF_2^+$. The transition states for the 1,2-fluorine shifts in CF_3BF_2 and $C_2F_5BF_2$, the 1,3-fluorine shift in $C_2F_5BF_2$, and the thermochemistry for the dissociations of the carbene complexes into BF_3 and the carbene were calculated (Figures 2 and 9). Since in the rearrangement reactions of $(CF_3)_3B$ and $(CF_3)_3BCF_2$ 1,2-fluorine shifts are proposed to be key steps, it is of interest to know the barrier for the fluoride migration in CF_3BF_2 as a reference (Figure 2).

Although the 1,2-fluorine shift in CF_3BF_2 (Figure 2) and the decomposition of CF_3BF_2 into BF_3 and CF_2 are endothermic ($\Delta H = +71.8$ kJ mol^{-1}; $\Delta G = +31.7$ kJ mol^{-1}), the decomposition readily proceeds because it is followed by the loss of CF_2. Since CF_2 can be trapped, e.g., by the more Lewis acidic CF_3BF_2 compared to BF_3 giving $CF_3BF_2(CF_2)$, the loss of CF_2 is irreversible and $C_2F_5BF_2$ is formed via CF_3 group migration (eq 10).

$$2CF_3BF_2 \rightarrow BF_3 + C_2F_5BF_2 \quad \Delta H = -124.3 \text{ kJ mol}^{-1} \quad (10)$$

The small activation barrier for the fluoride ion migration in CF_3BF_2 (80.7 kJ mol^{-1}) is the reason for its instability. The activation barriers for the transfers of perfluoroalkyl chains in difluorocarbene borane complexes are even smaller as will be shown for the isomerization of $(CF_3)_3B$ giving $C_3F_7BF_2$ (Figure 3); hence, the intramolecular transfer of the CF_3 group of $CF_3BF_2(CF_2)$ to give $C_2F_5BF_2$ will readily take place (eq 10). These results are in agreement with our experimental findings. Furthermore, this result is also consistent with earlier reports that BF_3 catalyzes the polymerization of CF_2.[31,32]

The energy of the transition state for a 1,3-fluorine shift in $C_2F_5BF_2$ was computed to be 131.1 kJ mol^{-1} higher than the ground state energy of $C_2F_5BF_2$ (Figure 3). This is nearly twice as high as the barrier calculated for the 1,2-fluoride ion migration in CF_3BF_2 (Figure 2) in agreement with our experimental observations that $C_2F_5BF_2$ does not dissociate into C_2F_4 and BF_3 although the reaction is exergonic (eq 11).

$$C_2F_5BF_2 \rightarrow BF_3 + C_2F_4$$
$$\Delta H = -10.5 \text{ kJ mol}^{-1} \; (\Delta G = -49.9 \text{ kJ mol}^{-1}) \quad (11)$$

The 1,2-fluorine shift from the CF_2 group in $C_2F_5BF_2$ to boron was also calculated, and the value for the transition state is close to the value for the transition state of the 1,3-fluorine shift in $C_2F_5BF_2$ (Figure 3). Since it was not possible to locate a minimum for CF_3CFBF_3 and the geometry of the transition state for the 1,2-fluorine shift is close to that expected for CF_3CFBF_3, it is likely that CF_3CFBF_3 has no local minimum on the respective hypersurface. IRC calculations indicate that CF_3CFBF_3 represents a transition state for a fluoride ion exchange between carbon and boron in $C_2F_5BF_2$. The dissociation of the transient species CF_3CFBF_3 into $CFCF_3$ and BF_3 or a further 1,2-fluorine shift from CF_3 to CF is endothermic. Hence, no decomposition of $C_2F_5BF_2$ is possible (Figure 3).

Similar to our observations for CF_3BF_2 and $C_2F_5BF_2$, phosphoranes with C_2F_5 groups are known to be more stable than the corresponding compounds with CF_3 ligands with respect to loss of CF_2.[39,40]

(d) Computational Results for the Isomerizations of $(CF_3)_3B$ and $(CF_3)_3BCF_2$. The isomerization of $(CF_3)_3B$ to $C_3F_7BF_2$ (Figure 4) was modeled as a reaction cascade of fluoride ion and perfluoroalkyl migrations. All reaction barriers are small, and the overall isomerization energy is -303.6 kJ mol^{-1} ($\Delta H = -305.0$ kJ mol^{-1}). The optimized geometries of the transition states clearly demonstrate that the rearrangement reactions of the difluorocarbene complexes to perfluoroalkyl boranes are transfers of perfluoroalkyl chains from the B atom to the C atom of the carbene ligand and not an insertion reaction of the difluorocarbene into the B−C or C−F bond of the perfluoroalkyl chain (Figure 4). The activation barrier for the fluorine shift of a CF_3 group becomes lower with increasing Lewis acidity of boron due to more perfluoroalkyl chains attached to boron (Figures 2 and 10). Only in the case of three perfluoroalkyl groups attached to boron is the fluoride ion migration exothermic. The reverse trend is observed for the transfer of perfluoroalkyl groups to the carbene ligand. The lower the Lewis acidity of the B atom is, the easier the perfluoroalkyl chain can migrate. The driving forces for the isomerizations are the gains in energy due to the formations of B−F from C−F bonds and of C−C from B−C bonds, respectively.

In Figure 5, the isomerization of $(CF_3)_3BCF_2$ to $(C_2F_5)(CF_3)FCBF_2$ is displayed, and the overall reaction energy is -363.4 kJ mol^{-1} ($\Delta H = -365.3$ kJ mol^{-1}). The calculations reveal the same trends for the C−F activations as well as the perfluoroalkyl transfers involved in the reactions from

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(36) Krespan, C. G.; Dixon, D. A. *J. Fluorine Chem.* **1996**, *77*, 117.
(37) Nguyen, V.; Mayer, P. S.; Morton, T. H. *J. Org. Chem.* **2000**, *65*, 8032.
(38) Shaler, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9222.
(39) Semenii, V. Y.; Stepanov, V. A.; Ignat'ev, N. V.; Furin, G. G.; Yagupol'skii, L. M. *J. Gen. Chem. USSR (Engl. Transl.)* **1985**, *55*, 2415.
(40) Mahler, W. *Inorg. Chem.* **1963**, *2*, 230.

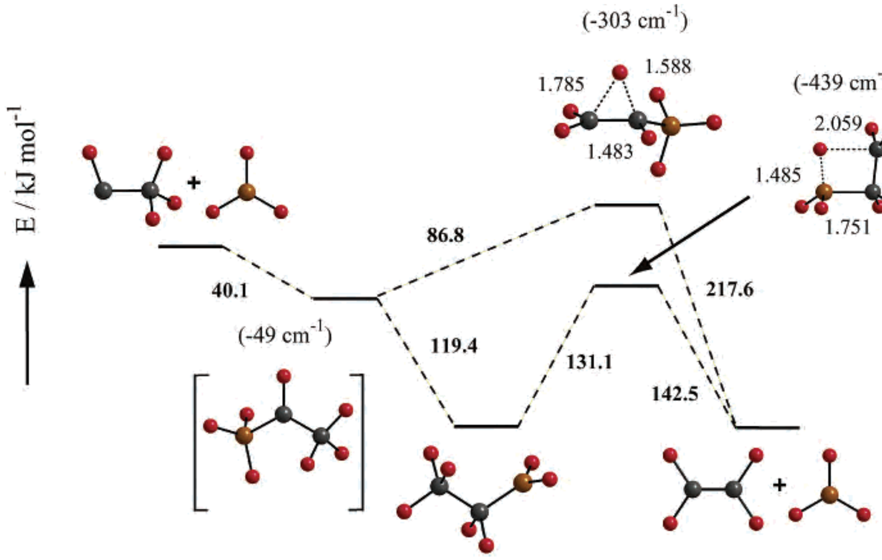

Figure 3. Calculated decomposition of $C_2F_5BF_2$ (energy and geometry, B3LYP/6-311+G(d); wavenumbers and ZPC, B3LYP/6-311G(d)).

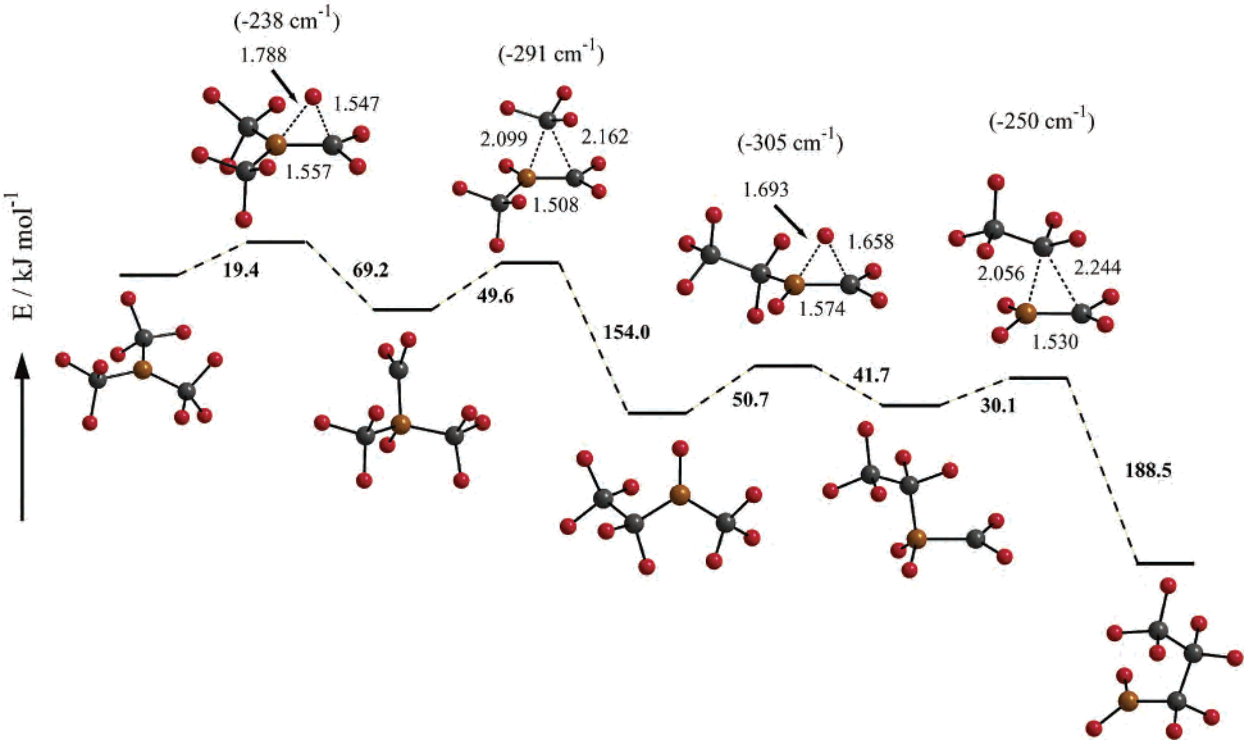

Figure 4. Calculated reaction profile for the isomerization of $(CF_3)_3B$ to $C_3F_7BF_2$ (energy and geometry, B3LYP/6-311+G(d); wavenumbers and ZPC, B3LYP/6-311G(d)).

$(CF_3)_3BCF_2$ to $(C_2F_5)_2BF$ compared to the isomerization of $(CF_3)_3B$. A more complex case is the last step, the rearrangement of $(C_2F_5)_2BF$ giving $(C_2F_5)(CF_3)FCBF_2$. The isomerization should proceed under C−F activation via a transition state to give the carbene complex $C_2F_5BF_2(CFCF_3)$ which rearranges via a second transition state to the final product $(C_2F_5)(CF_3)FCBF_2$. It was not possible to verify by IRC calculations that the found transition states connect the reactants and the products. All calculations performed indicate that the energies of the transition states are very similar to the energy of the minimum of $C_2F_5BF_2(CFCF_3)$ and hence the potential is very flat in this area. In Figure 5, one minimum of the monofluorocarbene complex is depicted. The energies of the located transition states and the energy of $C_2F_5BF_2(CFCF_3)$ differ by only ± 3 kJ mol^{-1}, and so, the value for the activation barrier as shown in Figure 5 represents the overall activation barrier for this process very well. A comparison with the activation barriers found for 1,2- and 1,3-fluorine shifts in $C_2F_5BF_2$ which are very close indicates that for the degradation of $(C_2F_5)_2BF$ both reaction pathways are possible. The 1,2-fluorine migration followed by C_2F_5 group transfer leads to the formation of $(C_2F_5)(CF_3)$-$FCBF_2$ as already outlined whereas the 1,3-fluorine shift is followed by dissociation into $C_2F_5BF_2$ and C_2F_4. Since in the reaction mixture $C_2F_5BF_2$ is one of the main components, the assumption of a competitive decomposition is very likely.

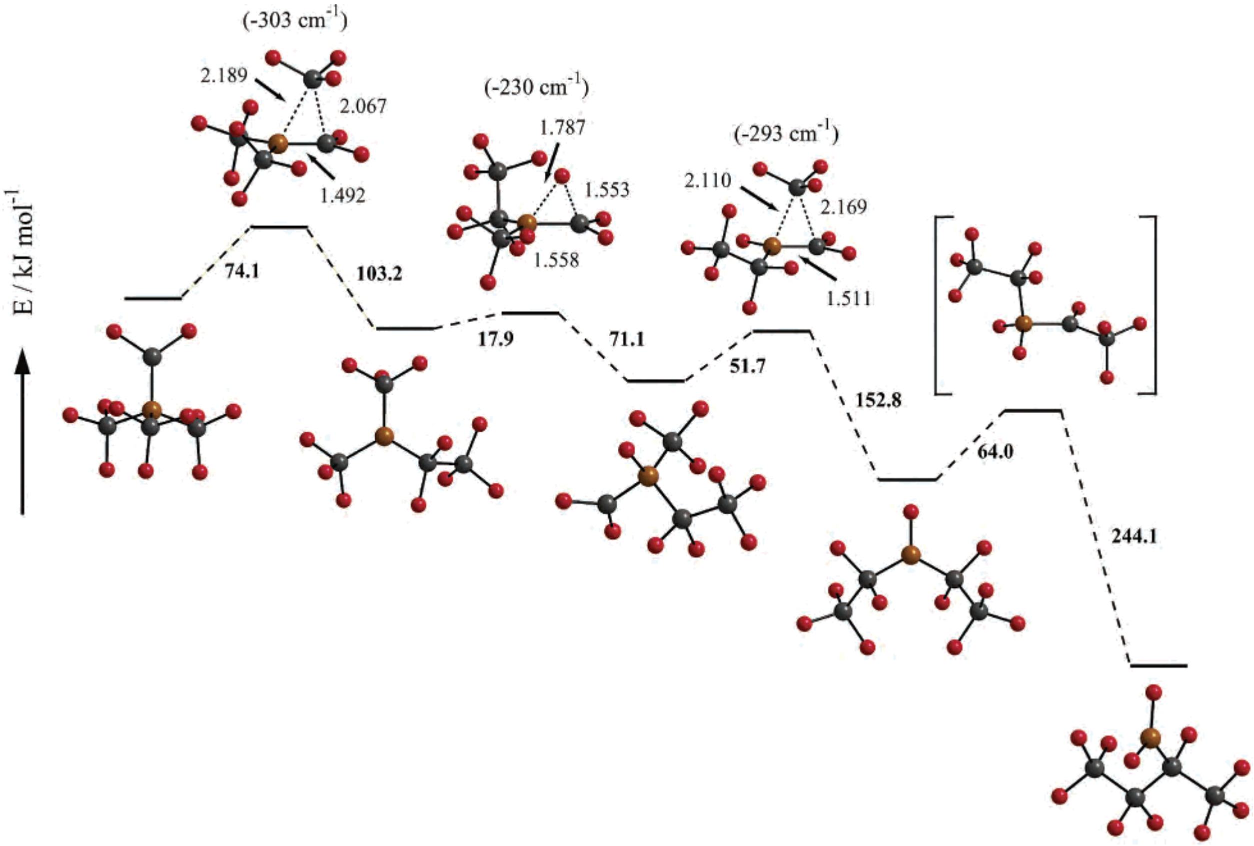

Figure 5. Calculated reaction profile for the isomerization of $(CF_3)_3BCF_2$ to $(C_2F_5)(CF_3)FCBF_2$ (energy and geometry, B3LYP/6-311+G(d); wavenumbers and ZPC, B3LYP/6-311G(d)).

(e) Discussion and Summary of the Results on the Stability of $(CF_3)_3B$ and $(CF_3)_3BCF_2$. Both strong Lewis acids $(CF_3)_3B$ and $(CF_3)_3BCF_2$ are unstable with respect to degradation to mono perfluoroalkylfluoroboranes at room temperature as shown experimentally and verified by density functional calculations. Furthermore, the computational results on the stabilities of CF_3BF_2 and $C_2F_5BF_2$ are also in agreement with the experimentally observed behavior which shows that the calculations display the real behavior very well.

As mentioned above the intramolecular fluoride migrations presented in this study are the first examples for reactions of this type in boron chemistry, whereas for other elements intramolecular C−F activations have been observed in the past.[41] In main group chemistry only for phosphorus and arsenic compounds have similar reactions been reported to our knowledge.[42,43] In variance to the well-known feature of C−F activations at α-C atoms of perfluoroalkyl ligands, the examples for intramolecular transfer reactions onto the carbene ligand derived through the activation process are rare. One example is the synthesis of $(Et_3P)(BF_4)Ni\{CF(PEt_3)(CF_2)_3\}$ from BF_3 and $(Et_3P)_2Ni\{(CF_2)_4\}$.[44] Examples for similar perfluoroalkyl transfer reactions to CF_2 complexes in the literature are very limited in general,[41] e.g., the synthesis of $C_6F_5(CF_2)_2Cu$ from C_6F_5Cu and CF_3Cu in DMF is a typical exception.[45,46]

(f) F^-, CF_2, and CO Affinities: A Measure for the Lewis Acidity of Perfluoroalkylfluoroboranes. The replacement of a F atom against a perfluoroalkyl group on boron leads to an enhanced Lewis acidity due to the reduction of π-back-donation from fluorine to boron. We have studied the F^-, CF_2, and CO affinities of the series of fluoro(trifluoromethyl)borates (Figure 6, Tables 2 and 3) to demonstrate the changes in the Lewis acidity and some of its effects. F^- and CF_2 affinities were calculated because F^- abstraction from trifluoromethyl substituents leading to CF_2 ligands is the initial step of the decomposition reactions of trifluoromethylboranes studied in this contribution. CO affinities are of interest because during the degradation of $(CF_3)_3BCO$ carbon monoxide is released and hence present in the reaction mixture.

A general trend for the bond strength of F^-, CF_2, and CO to boron in the investigated boranes is that CO is bound more weakly than CF_2 and F^- (Table 2). CO complexes of BF_3 and CF_3BF_2 are only stabilized by weak van der Waals interactions. The values calculated for F_3BCO are close to values derived from experimental studies.[33,34]

The F^- affinities underline the trend for the Lewis acidities as outlined above, for example $(CF_3)_3B$ is a stronger Lewis acid than BF_3 (Table 2). The electron affinity of the F atom

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(41) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373.

(42) Eujen, R.; Haiges, R. *Z. Naturforsch., B: Chem. Sci.* **1998**, *53b*, 1455.

(43) Eujen, R.; Hoge, B. *J. Organomet. Chem.* **1995**, *503*, C51.

(44) Burch, R. R.; Calabrese, J. C.; Ittel, S. D. *Organometallics* **1988**, *7*, 1642.

(45) Yang, Z.-Y.; Wiemers, D. M.; Burton, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 4402.

(46) Yang, Z.-Y.; Burton, D. J. *J. Fluorine Chem.* **2000**, *102*, 89.

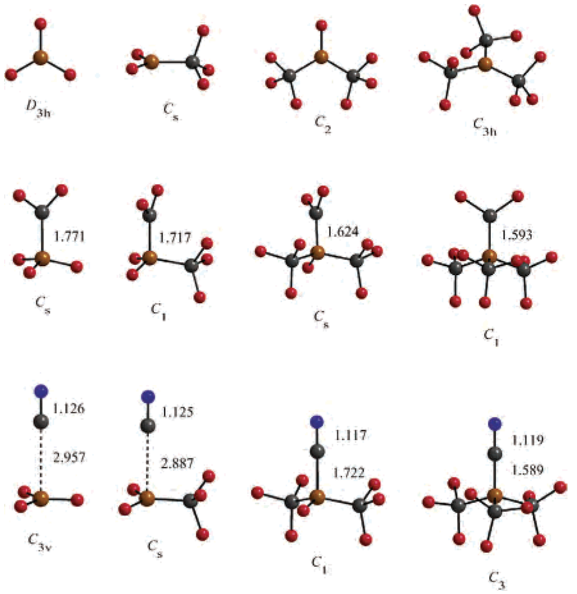

Figure 6. Comparison of the computed structures of $(CF_3)_nBF_{3-n}$ (n = 0−3) and related CF_2 and CO complexes (B3LYP/6-311+G(d)).

Table 4. Calculated[a] F^--Affinities of Selected Boron and Carbon Lewis Acids

	F^- affinity			
compd[b]	-Δ*E* kJ mol^{-1}	-Δ*H* kJ mol^{-1}	-Δ*G* kJ mol^{-1}	symmetry
$(CF_3)_2BFCF_2$	484.2	486.7	441.8	C_s
$(CF_3)_3B$	**533.9**	**536.4**	**490.9**	**C_{3h}**
$(CF_3)_3B$ tetrahedral[c]	**617.5**	**620.0**	**584.0**	**C_3**
β-BC_9F_{15}[d]	426.1	428.6	374.4	C_s
α-BC_9F_{15}[d]	527.9	530.4	485.3	C_s
γ-BC_9F_{15}[d]	602.4	604.9	556.5	C_s
***i*-BC_9F_{15}**[d]	**623.8**	**626.3**	**587.7**	**C_{3v}**
***i*-$BC_{19}F_{19}$**[e]	**638.0**	**640.4**	**600.6**	**C_{3v}**
i-$CB_{11}F_{11}$[g]	699.4	701.8	651.9	C_s
***m*-$CB_{11}F_{11}$**[g]	**752.8**	**755.3**	**708.6**	**C_s**
***p*-$CB_{11}F_{11}$**[g]	**769.1**	**771.6**	**727.7**	**C_{5v}**
***o*-$CB_{11}F_{11}$**[g]	**784.3**	**786.8**	**739.9**	**C_s**

[a] Energy: B3LYP/6-311+G(d). ZPC and thermal corrections: B3LYP/6-311G(d). [b] Compounds in bold letters are boron Lewis acids. [c] ∠(CBC) = 110.81° (adopted from $[(CF_3)_3BF]^-$). [d] Perfluoro-1-boradamantane (perfluoro-1-boratricyclo[3.3.1.1^{3,7}]decane). [e] Perfluoroboradodecahedrane; *i*, α, β, γ, δ, ε: bonds between B atom and unsaturated center, F^- abstraction in α, β, γ, δ, ε position leads to opening of the cage. [f] Energy without zero point correction. [g] *i*, *o*, *m*, and *p* position of the unsaturated center.

was calculated (336.3 kJ mol^{-1}) to investigate the performance of the method applied for the calculations because electron affinities and hence also F^- affinities are known to be critical cases for calculations.[28,47] The difference of the computational value for the electron affinity of the F atom to the experimental value (328.1 kJ mol^{-1})[28] is 8.2 kJ mol^{-1} (Table S1), so no further correction of the computational data seems to be necessary. Furthermore, the F^- affinity calculated for BF_3 (332.2 kJ mol^{-1}) (Table 2) is also in good agreement with the experimental value (331 ± 8 kJ mol^{-1}).[48,49] Some of the F^- affinities presented in this study correspond very well to those reported in the literature.[47,50]

In the series BF_3, CF_3BF_2, $(CF_3)_2BF$, and $(CF_3)_3B$, the Lewis acidity toward F^- increases for each step by about 70−80 kJ mol^{-1}. These increments display the loss of π-back-donation in the free Lewis acids. In Table 3, the F^- affinities of the corresponding difluorocarbene complexes are listed, and interestingly, in the case of $[(CF_3)_3BF]^-$ the fluoride ion is bound more strongly to boron than to carbon (Tables 2 and 3, Scheme 1). In the cases of the remaining borates, the fluoride anion is easier to remove from boron than from one of the CF_3 groups. The increase in F^- affinity and hence in Lewis acidity from BF_3 to $(CF_3)_3B$ is due to the loss of stabilization for the planar three coordinate borane by π-back-donation from the fluorine ligands.

The increases in the F^- affinities from BF_3 to $(CF_3)_3B$ underline the trends found for the activation barriers for 1,2-fluorine shifts as discussed above. The highest barrier is found for the transition state connecting CF_3BF_2 and $BF_3(CF_2)$ (80.7 kJ mol^{-1}) whereas the lowest barrier is found between $(CF_3)_3B$ and $(CF_3)_2BF(CF_2)$ (19.4 kJ mol^{-1}). The gain in Lewis acidity and hence also in F^- affinity from CF_3BF_2 to difluoroboranes with longer perfluoroalkyl chains is rather small (Table 2).

The decrease of the CF_2 affinities from $(CF_3)_3B$ to BF_3 helps to explain that $C_nF_{2n}BF_2(CF_2)$ is in equilibrium with the free borane and CF_2 and, hence, why CF_3BF_2 is unknown. The occurrence of an equilibrium is the main reason for the formation of linear monoperfluoroalkyldifluoroboranes with carbon chains longer than three C atoms in the decomposition of $(CF_3)_3BCO$, where $(C_2F_5)BF_2(CF_2)$ formed from $(C_2F_5)(CF_3)BF$ acts as CF_2 source. The trend in CF_2 affinity also gives a clue for the observation of smaller quantities of reaction products that are due to CF_2 transfer in the rearrangement reaction of $(CF_3)_3BCF_2$ because in this case only a minor fraction decomposes via $(C_3F_7)(CF_3)BF$ which then forms $(C_3F_7)BF_2(CF_2)$ and partially dissociates whereas the main route is via $(C_2F_5)_2BF$ which cannot serve as a CF_2 source (Scheme 2).

(g) Comparison of the Influence of π-Back Donation and Geometry at Boron on the Lewis Acidity of Selected Perfluoroalkylfluoroboranes, Perfluoroalkylfluoroborate Anions, Carboranes, and Carboronate Anions. Since our initial aim is the use of perfluoroborates as weak coordinating anions, a comparison of the F^- affinities of perfluoroalkylfluoroborates with other perfluoroborates is of interest. Especially the evaluation of the stabilizing and destabilizing parameters for the design of novel boron based weak coordinating anions is essential. The comparison of the F^- affinities of some different perfluoroboron species with perfluoroalkylfluoroborates leads to a qualitative view on the influence of π-back-donation from fluorine to boron and the geometry at boron (Table 4).

The Lewis acidity of $(CF_3)_3B$ is reduced by 90 kJ mol^{-1} due to the planar configuration at boron in comparison to

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(47) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151.

(48) Veljkovic, M.; Neskovic, O.; Zmbov, K. F.; Borshchevsky, A. Y.; Vaisberg, V. E.; Sidorov, L. N. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 37.

(49) Aleshina, V. E.; Borshchevsky, A. Y.; Korobov, M. V.; Sidorov, L. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1996**, *70*, 1170.

(50) Dixon, D. A.; Christe, K. O. *Book of Abstracts—225th ACS National Meeting*; New Orleans, LA; American Chemical Society: Washington, DC, 2003.

Table 5. Calculated[a] and Experimental B−F Bond Length in Boranes and Borate Anions

borane	d(B−F)[b] calcd[a]	borate anion	d(B−F)[b] calcd,[a] Å	d(B−F)[b] expt, Å	cation	ref
BF_3	1.317[c]	$[BF_4]^-$	1.417	1.406[d]	$[NH_4]^+$	54
CF_3BF_2	1.312	$[CF_3BF_3]^-$	1.412	1.391	K^+	55
$(CF_3)_2BF$	1.306	$[(CF_3)_2BF_2]^-$	1.413	1.391	Cs^+	56
$(CF_3)_3B$		$[(CF_3)_3BF]^-$	1.419	1.407	$[Co(CO)_5]^+$	17
$RCB_{11}F_{10}$		$[RCB_{11}F_{11}]^-$	1.365[e]	1.369[f]	$[Rh(CO)_4]^+$	57

[a] B3LYP/6-311+G(d). [c] Expt d(B−F): 1.310 Å.[58] [d] Corrected for thermal motion. [e] R = F. [f] R = Et.

$(CF_3)_3B$ with a tetrahedral arrangement (geometry increment). To model the maximum of the Lewis acidity for perfluoroalkylboranes, perfluoro-1-boradamantane and perfluoroboradodecahedrane were investigated. The fluoride ion at boron in perfluoro-1-boradamantane and perfluoroboradodecahedrane is bound as strong as in $(CF_3)_3B$ with a tetrahedral arrangement. But as for $[(CF_3)_3BF]^-$, the fluoride ion will be removed from one of the C atoms and not from the B atom. The position with the weakest bound fluorine ion in perfluoro-1-boradamantane is in β-position. The abstraction of the fluoride ion is followed by destruction of the carbon cage and the formation of a C−C double bond (Figure S1). This reaction is also predicted for the β-position in perfluoroboradodecahedrane (Figure S2) by density functional calculations. This type of acid catalyzed β-elimination is an analogue to the Hofmann elimination of alkenes in tetraalkylammonium cations by β-hydrogen elimination catalyzed by F^-.[51,52]

The F^- affinities for the four different fluorine positions in perfluorocarborane, $[CB_{11}F_{12}]^-$, are listed in Table 4, and the structures of the Lewis acids as well as the anion are displayed in Figure S3. The fluoride ion at the C atom is weakest bound in perfluorocarborane. The reason for this unexpected behavior is the stabilization of the resulting Lewis acid through a pseudo-Jahn−Teller effect.[53] The Lewis acidities of perfluorocarborane are higher than the ones in perfluoroalkylboranes (enhanced by 100−200 kJ mol^{-1}). The enhancement of the Lewis acidity for perfluorocarborane in comparison to the B atom in perfluoro-1-boradamantane and $(CF_3)_3B$ in the tetrahedral arrangement is due to a gain in π-back-donation from the fluorine atoms of about 130−170 kJ mol^{-1}. While in the system $[BF_4]^-/BF_3$ the Lewis acid BF_3 is stabilized by π-back-donation, in $[CB_{11}F_{12}]^-/CB_{11}F_{11}$ the anion $[CB_{11}F_{12}]^-$ is stabilized by π-back-donation.

Additional evidence for the contrary influence of π-back-donation from fluorine to boron is also displayed in the trend in B−F bond length in fluoroboranes, fluoroborate anions, and fluorocarboranate anions (Table 5). The shorter B−F bond length in fluoroboranes compared to the related fluoroborate anions (Table 5) is due to two effects: (i) the less steric hindrance in the boranes due to the reduction of the coordination number from four (borate anion) to three (borane) and (ii) the occurrence of π-back-bonding from fluorine to boron. Hence π-back-donation stabilizes the borane in these systems. The averaged B−F bond length in $[CB_{11}F_{12}]^-$ compared to B−F bond lengths in fluoroborate anions (Table 5) is shorter. This finding is unprecedented taking into account that the coordination number on boron in $[CB_{11}F_{12}]^-$ is six whereas in $[(CF_3)_xBF_{4-x}]^-$ ($x = 0-3$) only four substituents are bound to boron. The shortening of the B−F bond length in fluorocarborante anions is attributed to π-back-bonding from fluorine to boron and hence leading to stabilization of the anion against fluoride ion abstraction.

closo-Carboranes containing CF_3 groups instead of fluorine substituents are less stable, probably due to a loss of stabilization through π-back-donation. The extreme example $[CB_{11}(CF_3)_{12}]^-$ tends to explode,[59] whereas other trifluoromethylcarboranes, e.g., $(CF)_2B_{10}(CF_3)_{10}$, exhibit higher stability.[60] The decomposition is probably initiated by a fluoride ion abstraction from a CF_3 group followed by opening of the cluster at the electron deficient C atom, similar to reactions described for the N atom in $MeNB_{11}H_{11}$.[61] The resulting strong Lewis acid can attack one of the remaining CF_3 groups, and the decomposition can proceed. The reaction should be highly exothermic as the comparison to the energies for the rearrangement reactions described herein implies. In contrast, the high stability of $[CB_{11}F_{12}]^-$ [62] or $[RCB_{11}F_{11}]^-$ (R = Me, Et, ^{n}Bu)[57,63] is demonstrated by the formation of salts with highly electrophilic cations, e.g., $[{}^iPr_3Si][EtCB_{11}F_{11}]$ and $[AlMe_2][MeCB_{11}F_{11}]$.[63]

(h) Comparison of the Stability of Some Borate Anions with the Sum-Formula $[BC_4F_{12}]^-$. Geometries and energies of some isomers of borate anions with the sum-formula $[BC_4F_{12}]^-$ have been calculated (Figure 7). A comparison of the relative stabilities is of interest since $[B(CF_3)_4]^-$ is a weak coordinating anion.[1] In the investigated series of fluoro(perfluoroalkyl)borates the stability increases with an increased number of F atoms attached to boron and for every additional F atom on boron the species become more stable by −70 to −80 kJ mol^{-1}. A further trend is the gain in energy if the BF_3 group is attached to a secondary C atom and a tertiary C atom. Although $[(CF_3)_3CBF_3]^-$ is the most stable isomer of the series, $[B(CF_3)_4]^-$ has an enhanced stability against fluoride ion abstraction, and so, it is suitable as a weak coordinating anion. The reason is the high fluoride ion

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(51) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J.-A. *J. Am. Chem. Soc.* **1990**, *112*, 7619.
(52) Mahjoub, A. R.; Zhang, X.; Seppelt, K. *Chem. Eur. J.* **1995**, *1*, 261.
(53) Bersuker, I. B. *Vibronic Interactions in Molecules and Crystals*; Springer-Verlag: Berlin, 1989.
(54) Yeh, H. J. C.; Ragle, J. L. *J. Phys. Chem.* **1968**, *72*, 3688.
(55) Brauer, D. J.; Bürger, H.; Pawelke, G. *Inorg. Chem.* **1977**, *16*, 2305.
(56) Brauer, D. J.; Bürger, H.; Pawelke, G. *J. Organomet. Chem.* **1980**, *192*, 305.
(57) Lupinetti, A. J.; Havighurst, M. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 11920.
(58) Beeker, K.; Mrinal, K. D.; Gragg, B. R.; Keller-Rudek, H.; List, H.; Sawodny, W. In *Gmelin Handbuch der Anorganischen Chemie*—*Borverbindungen*; Niedenzu, K., Buschbeck, K.-C., Merlet, P., Eds.; Springer-Verlag: Berlin, 1978; Vol. 53, Teil 18.
(59) King, B. T.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10255.
(60) Herzog, A.; Callahan, R. P.; Macdonald, C. L. B.; Lynch, V. M.; Hawthorne, M. F.; Lagow, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2121.
(61) Paetzold, P.; Lomme, P.; Englert, U. *Z. Anorg. Allg. Chem.* **2002**, *628*, 632.
(62) Strauss, S. H.; Ivanov, S. V.; Lupinetti, A. J. (Colorado State University Research Foundation). United States Patent US 6,130,357, 2000.
(63) Strauss, S. H.; Ivanov, S. V. (Colorado State University Research Foundation). Patent WO 02/36557/A2, 2002.

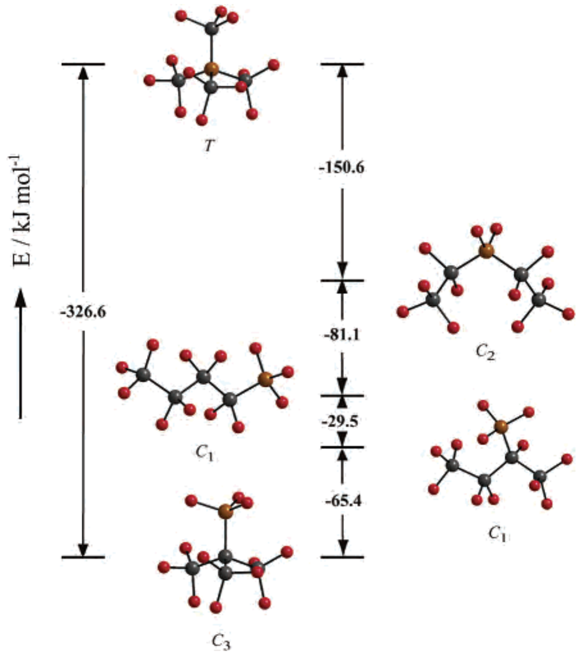

Figure 7. Comparison of the relative stabilities (Δ*H*) of some $[C_4BF_{12}]^-$ anions (energy and geometry, B3LYP/6-311+G(d); ZPC and thermal corrections, B3LYP/6-311G(d)).

affinity of the corresponding Lewis acid $(CF_3)_3BCF_2$ compared to monoperfluoroalkylborates (Tables 2 and 3).

(II) NMR Studies of Perfluoroalkylborates: Application of the SERF Method in ^{19}F NMR Spectroscopy and Trends in ^{19}F NMR Chemical Shifts. ^{19}F NMR spectroscopy offers the best possibility to analyze the complex reaction mixtures obtained in this study. The advantages are the characteristic ^{19}F NMR chemical shifts as well as the high sensitivity and access to the quantitative product distribution. In most cases, it was possible to elucidate the connectivity of the atoms by using the relative intensities and the coupling constants. Since the influence of the quadrupolar moment of the ^{11}B nucleus leads to a broadening of the lines, the ^{19}F NMR spectra were also recorded applying ^{11}B broad band decoupling. Furthermore by this procedure the number of parameters, the couplings with ^{11}B, is reduced. The largest contribution to couplings of ^{19}F nuclei is often not due to dipolar interactions; hence, other interactions dominate, e.g., through-space coupling, and it is often impossible to predict and to assign these coupling constants.[64] For example, the $^3J(^{19}F, ^{19}F)$ values are significantly smaller than the $^4J(^{19}F, ^{19}F)$ values, and in many cases, they cannot be observed. In some cases, even long-range couplings, e.g., $^5J(^{19}F, ^{19}F)$ and $^6J(^{19}F, ^{19}F)$, are resolved. The $^nJ(^{19}F, ^{19}F)$ coupling constants between the F atoms of one CF_2 group to the F atoms of another CF_2 group are different and can only be equivalent by accident.[65,66] To solve this problem we have used the selective refocusing method (SERF).[67,68] To our knowledge this is the first example for the use of this method in ^{19}F NMR spectroscopy. Because the coupling constants are directly measured, the SERF method offers an easier and more reliable tool for the determination and assignment of coupling constants in complex systems than selective decoupling. In this manner it was possible to assign all signals and coupling constants for $[(C_2F_5)(CF_3)FCBF_3]^-$, and in Figure 8, the $^{19}F\{^{11}B\}$ NMR spectrum of the CF_3 group at −70.5 ppm and the spectra of the corresponding coupling constants (F2 projections) are shown. In the case of $[C_4F_9BF_3]^-$, a few SERF experiments were performed to prove the proposed assignment of the signals of the CF_2 groups. In addition to the SERF measurements the spectra were also simulated using the program gNMR.[69]

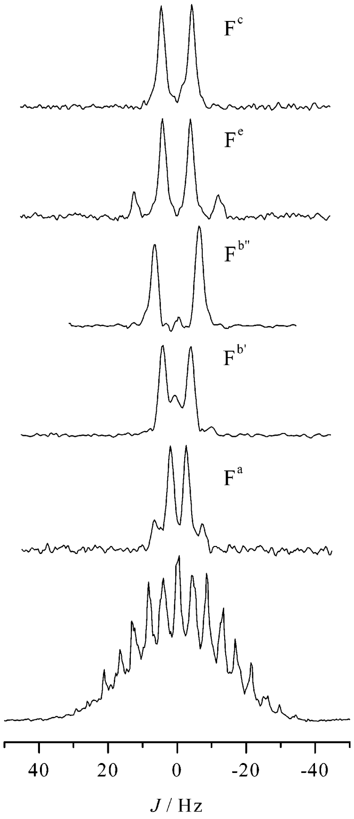

Figure 8. $^{19}F\{^{11}B\}$ NMR spectrum of $[(CF^a_3CF^{b'}F^{b''})(CF^d_3)F^cCBF^e_3]^-$ (bottom) and F2 projections, $^nJ(^{19}F,^{19}F)$, obtained by SERF experiments.

In Chart 1, the NMR spectroscopic data of the linear perfluoroalkyl borates are depicted. To offer a complete overview of the ^{11}B and ^{19}F NMR spectroscopic data of linear perfluoroalkyl borates known so far, the values of the $[CF_3BF_3]^-$ anion are included.[1] For $[C_nF_{2n+1}BF_3]^-$ ($n = 3-4$, 6), the ^{11}B and ^{19}F chemical shifts and a few coupling constants have been reported previously,[8−10] which are in good agreement with our results. The ^{19}F and the $^{19}F\{^{11}B\}$ NMR spectra of the $[C_2F_5BF_3]^-$ anion are displayed in Figure 9. In the ^{11}B decoupled spectrum, small $^{19}F-^{19}F$ coupling constants are resolved that cannot be extracted from the corresponding ^{11}B coupled spectrum. In Figure 10, the ^{11}B coupled and decoupled spectra of $[C_3F_7BF_3]^-$ are displayed,

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[64] Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR-Spektroskopie von Nichtmetallen—19F NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1994; Vol. 4.

[65] Harris, R. K.; Woodman, C. M. *J. Mol. Spectrosc.* **1968**, *26*, 432.

[66] Hopkins, R. C. *J. Mol. Spectrosc.* **1966**, *20*, 321.

[67] Fäcke, T.; Berger, S. *J. Magn. Reson.* **1995**, *113A*, 114.

[68] Eberstadt, M.; Gemmecker, G.; Mierke, D. F.; Kessler, H. *Angew. Chem.* **1995**, *107*, 1813.

[69] Budzelaar, P. H. M. *gNMR*, V4.1.0; Chem Research GmbH, 1995−1999.

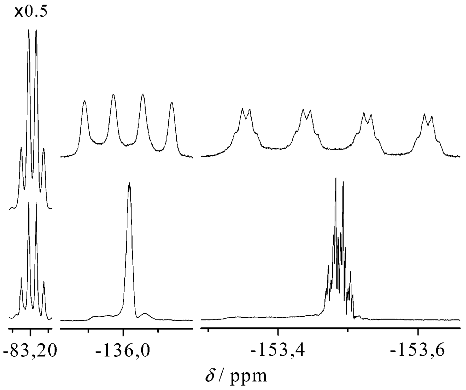

Figure 9. ^{19}F NMR (top) and ^{19}F{^{11}B} NMR spectrum (bottom) of [$C_2F_5BF_3$]$^-$.

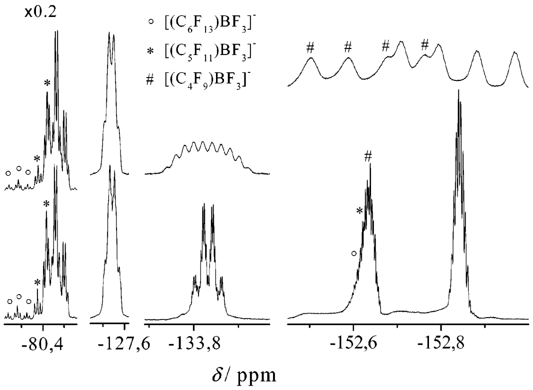

Figure 10. ^{19}F NMR (top) and ^{19}F{^{11}B} NMR spectrum (bottom) of [$C_3F_7BF_3$]$^-$.

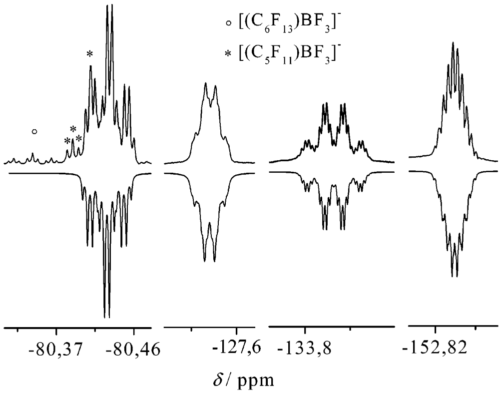

Figure 11. Simulated ^{19}F{^{11}B} NMR (bottom) and ^{19}F{^{11}B} NMR spectrum (top) of [$C_3F_7BF_3$]$^-$.

and they illustrate that except for the CF_3 group the signals become very complex and that special methods as mentioned above are necessary to assign the coupling constants and the signals. The measured and simulated spectra of [$C_3F_7BF_3$]$^-$ (Figure 11) are in good agreement. The comparison of the ^{19}F NMR chemical shifts of the linear perfluoroalkyl borates reveals an interesting trend; the CF_2 groups in the middle of the perfluoroalkyl chain converge against -121.3 ppm (Figure 12). The closer a CF_2 group is located to any of the two ends of the anion, the lower the ^{19}F NMR chemical shifts becomes. By accident the ^{19}F NMR chemical shifts of the BF_3 groups fit into this trend. The ^{19}F NMR chemical shifts of the CF_3 groups are in a different region (-75 to -84 ppm).

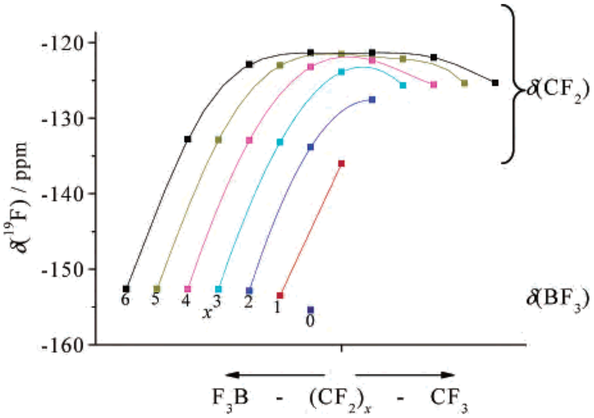

Figure 12. Trends of the ^{19}F NMR chemical shifts of the CF_2 and BF_3 groups in linear perfluoroalkylborates.

The NMR spectroscopic data obtained for [(C_2F_5)(CF_3)-$FCBF_3$]$^-$ are summarized in Chart 2. The data for [(C_3F_7)-(CF_3)$FCBF_3$]$^-$ and [(C_2F_5)$_2FCBF_3$]$^-$ are limited because these species were only formed in small quantities; [(C_2F_5)(CF_3)-$FCBF_3$]$^-$ could be investigated in detail by ^{19}F NMR spectroscopy. The measured coupling constants for the two diastereotopic F atoms attached to the C^b atom (Chart 2) were corrected to the values of the real coupling constants.[70] Since the signs of the effective coupling constants are unknown, two different sets of coupling constants are obtained from the corrections. The simulation with gNMR shows that both sets give the expected line distribution, but the intensity distribution obtained with the values presented in Chart 2 is in closer agreement to the measured spectrum. In Figure 13, the ^{19}F and ^{19}F{^{11}B} NMR spectra are depicted and compared to the simulated ^{19}F NMR spectrum. A similar study was already performed for perfluoroisopropyl groups attached to aryl systems.[71] The spectra reveal similarities, but especially, the coupling constants differ significantly due to the different influences of the attached groups.

In the cases of [(C_3F_7)(CF_3)$FCBF_3$]$^-$ and [(C_2F_5)$_2FCBF_3$]$^-$, very complex spectra are expected in comparison to the simpler spectra of isoelectronic $C_3F_7CF(CF_3)_2$ and (C_2F_5)$_2$-$CFCF_3$.[72] The observation of signals with similar chemical shifts and intensities as found for [(C_2F_5)(CF_3)$FCBF_3$]$^-$ and a related trend as reported for the series $C_2F_5CF(CF_3)_2$, C_3F_7-$CF(CF_3)_2$, and (C_2F_5)$_2CFCF_3$[73,74] indicates the formation of the above-mentioned species during the rearrangement and CF_2 transfer reactions of (CF_3)$_3BCF_2$.

Summary and Conclusion

The investigations of the rearrangement reactions of the unstable intermediates (CF_3)$_3$B and (CF_3)$_3BCF_2$ formed from

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(70) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Pergamon Press: Oxford, 1967; Vol. 1.

(71) Chambers, R. D.; Sutcliffe, L. H.; Tiddy, G. J. T. *Trans. Faraday Soc.* **1970**, *66*, 1025.

(72) Burdon, J.; Creasey, J. C.; Procter, L. D.; Plevey, R. G.; Yeoman, J. R. N. *J. Chem. Soc., Perkin Trans. 2* **1991**, 445.

(73) Coe, P. L.; Sellers, S. F.; Tatlow, J. C. *J. Fluorine Chem.* **1981**, *18*, 417.

(74) Sartori, P.; Velayutham, D.; Ignat'ev, N. V.; Noel, M. *J. Fluorine Chem.* **1998**, *87*, 31.

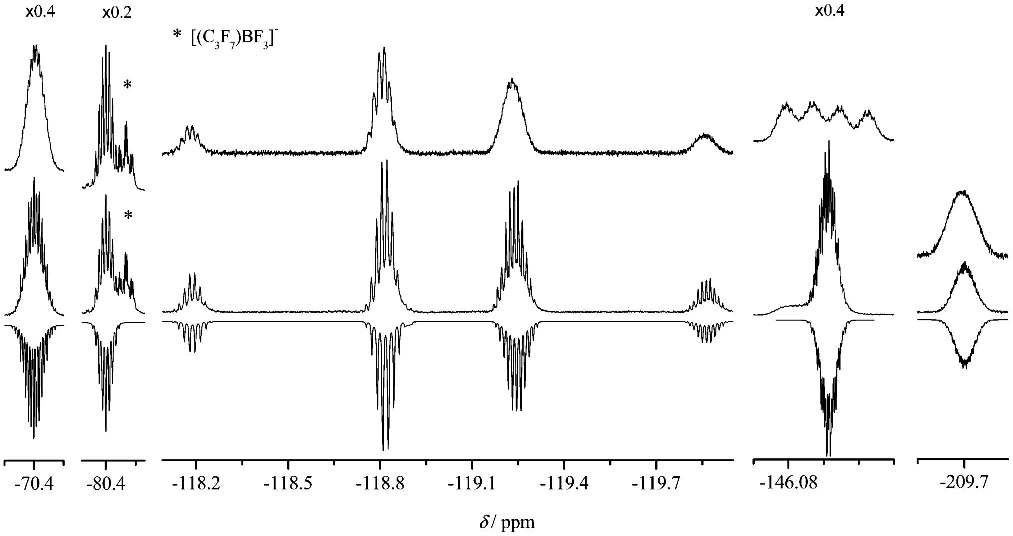

Figure 13. Simulated $^{19}F\{^{11}B\}$ NMR (bottom), $^{19}F\{^{11}B\}$ NMR (middle), and ^{19}F NMR spectrum (top) of $[(C_2F_5)(CF_3)FCBF_3]^-$.

the precursors $(CF_3)_3BCO$ and the weak coordinating anion $[B(CF_3)_4]^-$ revealed unprecedented rearrangement reactions. The results rationalized the degradation chemistry of perfluoroalkylfluoroborate anions which are of interest as weak coordinating anions. In the case of $(CF_3)_3B$, the final product of the decomposition in anhydrous HF is $[C_2F_5BF_3]^-$, and in the gas phase, a mixture of linear perfluoroalkylboranes $C_nF_{2n+1}BF_2$ is observed. For $(CF_3)_3BCF_2$, a mixture of linear and branched perfluoroalkylboranes is obtained with the interesting borane $(C_2F_5)(CF_3)FCBF_2$ as a main product. The boranes are formed in a cascade of 1,2-fluorine shifts from a CF_3 or a C_2F_5 group to boron followed by perfluoroalkyl migrations. The difluorocarbene complexes formed as intermediates can also serve as CF_2 sources. The 1,2-fluorine shifts observed are the first examples for intramolecular C−F activation in boron chemistry, and the intramolecular transfer reactions of the perfluoroalkyl groups are unusual reactions in general.

Quantum chemical calculations were performed to gain a deeper insight into the reaction cascades described above. The geometries and energies of the transition states for the rearrangement reactions were calculated, and the low barriers are in agreement with the experimental findings that neither $(CF_3)_3B$, $(CF_3)_3BCF_2$, nor the intermediates could be isolated. As precedents for the C−F activations, the barrier of the 1,2-fluorine shift in CF_3BF_2 was compared to the barrier of the 1,2- and 1,3-fluorine shift in $C_2F_5BF_2$. Since the activation energy for the isomerization of $C_2F_5BF_2$ is nearly twice as large as for the isomerization of CF_3BF_2, the borane $C_2F_5BF_2$ is easily obtained at room temperature whereas CF_3BF_2 remains unknown.

F^- affinities of a variety of different fluoroboron species were investigated by theoretical methods. The F^- affinities are closely related to the calculated barriers for the observed intramolecular fluoride ion abstractions. Because the fluoride ion affinities are a good measure for the stability of weak coordinating anions, their knowledge is of broad interest. Especially, the influence of π-back-donation and the geometry at boron are discussed. Tricoordinated (perfluoroalkyl)fluoroboranes are stabilized by π-back-donation from fluorine ligands to boron and planar arrangement of the ligands leads to a further gain in energy as modeled with perfluoro-1-boradamantane. In contrast to tetracoordinated (perfluoroalkyl)fluoroborates, *closo*-carboranate anions are stabilized by π-back-donation from fluorine.

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Supporting Information Available: Table of energies, enthalpies and free energies of all compounds and transition states investigated by DFT calculations, and figures displaying the calculated structures of the carboranate, adamantane, and dodecahedrane derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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