Journal of Fluorine Chemistry 131 (2010) 922–932

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Bis(perfluoroorganyl)bromonium salts $[(R_F)_2Br]Y$ (R_F = aryl, alkenyl, and alkynyl)

Hermann-Josef Frohn [a,*], Matthias Giesen [a], Dirk Welting [a], Vadim V. Bardin [b]

[a] Inorganic Chemistry, University of Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany
[b] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Ave. 9, 630090 Novosibirsk, Russia

ARTICLE INFO

Article history:
Received 6 May 2010
Received in revised form 8 June 2010
Accepted 9 June 2010
Available online 17 June 2010

Keywords:
Bromine trifluoride
Perfluoroorganylbromine difluorides
Bis(perfluoroorganyl)bromonium salts
Difluorobromonium salts
Perfluoroorganylboron difluoride
Tris(pentafluorophenyl)borane
Pentafluorophenyltrifluorosilane
Pentafluorophenyltrimethylsilane
Perfluoroorganyltrifluoroborate salts
NMR spectroscopy

ABSTRACT

Bromonium salts $[(R_F)_2Br]Y$ with perfluorinated groups R_F=C_6F_5, CF_3CF=CF, C_2F_5CF=CF, and CF_3C≡C were isolated from reactions of BrF_3 with R_FBF_2 in weakly coordinating solvents (wcs) like $CF_3CH_2CHF_2$ (PFP) or $CF_3CH_2CF_2CH_3$ (PFB) in 30–90% yields. $C_6F_5BF_2$ formed independent of the stoichiometry only $[(C_6F_5)_2Br][BF_4]$. 1:2 reactions of BrF_3 and silanes $C_6F_5SiY_3$ (Y = F, Me) ended with different products – $C_6F_5BrF_2$ or $[(C_6F_5)_2Br][SiF_5]$ – as pure individuals, depending on Y and on the reaction temperature (Y = F). With $C_6F_5SiF_3$ at ≥−30 °C $[(C_6F_5)_2Br][SiF_5]$ resulted in 92% yield whereas the reaction with less Lewis acidic $C_6F_5SiMe_3$ only led to $C_6F_5BrF_2$ (58%). The interaction of $K[C_6F_5BF_3]$ with BrF_3 or $[BrF_2][SbF_6]$ in anhydrous HF gave $[(C_6F_5)_2Br][SbF_6]$. Attempts to obtain a bis(perfluoroalkyl)bromonium salt by reactions of $C_6F_{13}BF_2$ with BrF_3 or of $K[C_6F_{13}BF_3]$ with $[BrF_2][SbF_6]$ failed. The 3:2 reactions of BrF_3 with $(C_6F_5)_3B$ in CH_2Cl_2 gave $[(C_6F_5)_2Br][(C_6F_5)_nBF_{4-n}]$ salts (n = 0–3). The mixture of anions could be converted to pure $[BF_4]^-$ salts by treatment with BF_3·base.

1. Introduction

The first preparation of a bis(organyl)bromonium salt was reported in 1955 by Nesmeyanov. He obtained a bis(phenyl)bromonium salt by the decomposition of benzenediazonium tetrafluoroborate in bromobenzene [1]. Improvement allowed to increase the yield of isolated bis(phenyl)bromonium tetrafluoroborate to 6–7% [2]. Further progress was achieved by reactions of BrF_3 with benzenes, C_6H_5R [3], bis(aryl)mercury, Ar_2Hg [4], and tetrakis(aryl)stannanes, Ar_4Sn [5] (Eqs. (1)–(3)).

$$BrF_3 + 2C_6H_5R + BF_3 \cdot OEt_2 \xrightarrow{CH_2Cl_2,\,-70\,^\circ C} [(RC_6H_4)_2Br][BF_4] + \cdots$$
$$R = H(50\%), 4\text{-}F(41\%), 4\text{-}Cl(13\%), 3\text{-}MeOC(O)(20\%), 3\text{-}NO_2(6\%), 3\text{-}CF_3(49\%) \quad (1)$$

$$BrF_3 + 2(RC_6H_4)_2Hg + BF_3 \cdot OEt_2 \xrightarrow{CH_3CN,CH_2Cl_2,\,-70\,^\circ C} [(RC_6H_4)_2Br][BF_4] + \cdots$$
$$R = H, 4\text{-}F, 4\text{-}Cl, 3\text{-}EtOC(O), 4\text{-}CH_3(16-96\%) \quad (2)$$

$$BrF_3 + (RC_6H_4)_4Sn + BF_3 \cdot OEt_2 \xrightarrow{CH_3CN,CH_2Cl_2,\,-70\,^\circ C} [(RC_6H_4)_2Br][BF_4] + \cdots$$
$$R = H, 4\text{-}CH_3O, 4\text{-}CH_3(52-96\%) \quad (3)$$

An alternative route to symmetric bromonium salts consists in the electrophilic alkylation of alkyl bromides with carbocations [6,7] (Eq. (4)).

$$AlkBr + AlkF + SbF_5 \xrightarrow{SO_2,\,-70\,^\circ C} [(Alk)_2)Br][SbF_6]$$
$$Alk = Me, Et, i\text{-}Pr, cyclo\text{-}C_3H_5 \quad (4)$$

All methods compiled before are not adequate for the preparation of bis(perfluoroorganyl)bromonium salts, $[(R_F)_2Br]Y$, where R_F represent perfluorinated alkyl, alkenyl, alkynyl, and aryl groups. For example, the reaction of C_6F_5H with BrF_3 in weakly coordinating solvents (CCl_2FCClF_2, 0 °C [8], SO_2ClF, −80 °C [9,10]), or with $[BrF_2]Y$ (Y = BF_4, SbF_6) (SO_2ClF, −80 °C [9,10]) and with BrF_3 or $[BrF_2][SbF_6]$ in a highly acidic solvent (aHF, −70 °C) led to C_6F_5Br and polyfluorinated 1-X-cyclohexa-1,4-dienes (X = H, Br). In contrast to the successful electrophilic alkylation of RBr with CH_3F-SbF_5 in SO_2 to methylbromonium salts, $[CH_3(R)Br][SbF_6]$, the attempted methylation of 1,4-dibromotetrafluorobenzene failed [7]. Nesmeyanov reported the inertness of BrF_3 towards $(C_6F_5)_2Hg$ [4] and $(C_6F_5)_4Sn$ [5] (CH_2Cl_2 + 2CH_3CN + 3BF_3·OEt_2) at −78 to −25 °C and the decomposition of the solvent and the organometallic compounds at higher temperature. Later the formation of $C_6F_5BrF_2$ was shown besides C_6F_5R (R = H, F, Br, C_6F_5) when BrF_3 was reacted with $(C_6F_5)_2M$ (M = Hg, Cd, Zn) in the absence of a Lewis acid (CH_2Cl_2 + 2 CH_3CN, −78 to −25 °C) and no bromonium salts, $[(C_6F_5)_2Br]Y$, were found under those non-acidic conditions [11].

* Corresponding author. Tel.: +49 203 379 3310; fax: +49 203 379 2231.
E-mail address: h-j.frohn@uni-due.de (H.-J. Frohn).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.06.006

Up to now the bis(pentafluorophenyl)bromonium salts, $[(C_6F_5)_2Br]Y$ (Y = BF_4, AsF_6, SbF_6, PF_6), are the only reported bromonium compounds bearing perfluorinated organic groups at bromine(III) (see review [12]). Salt $[(C_6F_5)_2Br][AsF_6]$ was the product of pentafluorophenylation of C_6F_5Br with molten $[C_6F_5Xe][AsF_6]$ but only in 6% yield [13]. $[(C_6F_5)_2Br][BF_4]$ was obtained by the reaction of $C_6F_5BrF_2$ with bis(pentafluorophenyl)cadmium and $BF_3{\cdot}NCCH_3$ in a satisfactory yield and in excellent yield from BrF_3 and $(C_6F_5)_2BF$ [11] (Eqs. (5) and (6)).

Hexafluorometallates $[(C_6F_5)_2Br][EF_6]$ were prepared from the parent tetrafluoroborate by metathesis with $K[PF_6]$ (E = P) or by displacement of BF_3 using stronger Lewis acids like AsF_5 or SbF_5 [11] (E = As, Sb).

$$Cd(C_6F_5)_2 + 2C_6F_5BrF_2 + 2BF_3\cdot NCCH_3 \xrightarrow[-78\text{ to }20\,^\circ C]{CH_2Cl_2/<MeCN} \underset{20-30\%}{[(C_6F_5)_2Br][BF_4]} \quad (5)$$

$$(C_6F_5)_2BF + BrF_3 \xrightarrow[-78\text{ to }20\,^\circ C,1\text{ h}]{CH_2Cl_2/<MeCN*} \underset{80-100\%}{[(C_6F_5)_2Br][BF_4]} \quad (6)$$

*MeCN was added to increase the solubility of BrF_3 at low temperatures.

Based on our experience in the preparation of polyfluoroorganylxenonium salts [14,15] and polyfluoroorgano derivatives of polyvalent iodine and bromine [12], we studied selected promising routes to bis(perfluoroorganyl)bromonium salts. One was based on the direct introduction of two perfluoroorganyl groups into BrF_3 or $[BrF_2]^+$ with different types of organoboron compounds (R_FBF_2, $(C_6F_5)_3B$, $M[R_FBF_3]$). The second used pentafluorophenyl silanes, $C_6F_5SiF_3$ and $C_6F_5SiMe_3$, of different Lewis acidity.

2. Results

2.1. New basic information about bromine trifluoride in organic solvents

Bromine trifluoride is a highly reactive compound and the choice of appropriate weakly coordinating organic solvents for reactions with Lewis acidic perfluoroorganylboranes and -silanes is very limited. In the past some reactions of BrF_3 with organic compounds were performed in SO_2ClF, CCl_3F, and CCl_2FCClF_2. To increase the solubility in dichloromethane at low temperature small quantities (2–4 equiv.) of CH_3CN were added. In the absence of MeCN, CH_2Cl_2 reacts with BrF_3 above ca. −20 °C. Bromine trifluoride is moderately soluble in trichlorofluoromethane, but above 5–10 °C it reacts with CCl_3F to produce mainly CCl_2F_2. Saturated solutions of BrF_3 in 1,1,2-trichlorotrifluoroethane showed no decomposition at 22–25 °C within 26 h, but after 3 d the ^{19}F NMR signal of BrF_3 disappeared and a significant amount of $CClF_2CClF_2$ was formed. Bromine trifluoride is insoluble in perfluorohexane, perfluoromethylcyclohexane, perfluoro-2-methylpent-2-ene, and perfluorotributylamine. Fortunately, the commercially available fluorohydrocarbons, 1,1,1,3,3-pentafluoropropane (PFP) (HFC-245fa) (mp. −103 °C, bp. 15 °C) and 1,1,1,3,3-pentafluorobutane (PFB) (Solkane® 365mfc) (mp. ∼−36 °C, bp. 40 °C) displayed satisfactory properties as solvents for reactions of bromine trifluoride e.g. with perfluoroorganyldifluoroboranes. PFP and PFB solutions of bromine trifluoride can be stored over weeks at 5–25 °C without remarkable decomposition.

For BrF_3 solutions in PFB, we have found that bubbling of BF_3 at −15 °C caused the formation of a second high density phase, which completely dissolved above 0 °C. The ^{11}B and ^{19}F NMR spectra showed no resonances of the starting fluorides BrF_3 and BF_3. Instead, a new ^{19}F resonance appeared at −72 ppm in case of a molar ratio 1:1 and its integral intensity was equal to the sum of those of BrF_3 and BF_3. Parallel, a singlet at 0.16 ppm was observed in the ^{11}B NMR spectrum. No changes in the ^{11}B and ^{19}F NMR spectra occurred at 24 °C over a period of 24 h. Decantation of the solvent phase from the heavy density phase at −20 °C and redissolution of the latter in a fresh portion of PFB resulted only in a small shift of the NMR resonance. We assume that the above mentioned ^{19}F and ^{11}B signal belong to an adduct, formally described as "$BrF_3{\cdot}BF_3$" with a highly polarized bromine-fluorine bond. Noteworthy, that Cyr and Brownstein [16] presented the ^{19}F NMR spectrum of BrF_3 and BF_3 (1:1) in SO_2ClF at −120 °C, which consisted of three resonances at −60.6, −70.5, and −127.7 ppm in the integral ratio 1:1:4. The ^{19}F NMR spectrum of an equimolar solution of BrF_3 and AsF_5 in SO_2ClF at −120 °C also contained three resonances at −61.0, −68.3 and −56.3 (As-F) ppm. With an excess of either BrF_3 or LA (LA = BF_3, AsF_5) there was a rapid exchange between all fluorine atoms over the entire temperature range (−120 to 25 °C). This picture was interpreted to arise from a structure like F-Br(F)···F-LA with two magnetically non-equivalent fluorine atoms bonded to the bromine atom. In case of individual $[BrF_2][SbF_6]$ we were not able to measure its ^{19}F NMR spectrum in SO_2ClF because of the too low solubility even at 24 °C. However, this salt is well soluble in aHF (>163 mg (0.46 mmol) per mL at 0 °C). The ^{19}F NMR spectrum of $[BrF_2][SbF_6]$ in aHF at −40 °C consisted of a singlet at −73.5 ppm ($\Delta\nu_{1/2}$ = 106 Hz) ($[BrF_2]^+$), very broad Sb-F resonances in the range of ca. −120 to −125 ppm and the signal of the solvent at −190 ppm. Acidification of the solution with SbF_5 (fivefold molar excess) did not really affect the chemical shift of the $[BrF_2]^+$ cation ($\delta(F)$ = −72.9). Variation of the temperature caused reversible broadening of this resonance from $\Delta\nu_{1/2}$ = 47–53 Hz (−40 °C) to ∼240 Hz (−20 °C) and >1000 Hz (0 °C). For comparison, the ^{19}F NMR spectrum of BrF_3 presents a singlet at −16.3 ppm (neat liquid, 35 °C) [17], −16.5 ppm (SO_2ClF, −20 °C) [16], −17.3 ppm ($\Delta\nu_{1/2}$ = 56 Hz) (PFP, −10 °C), and −17.9 ppm ($\Delta\nu_{1/2}$ = 27 Hz) (PFB, 24 °C).

2.2. $[(R_F)_2Br]Y$ salts by reactions of BrF_3 with perfluoroorganylboranes in weakly coordinating solvents

The addition of tris(pentafluorophenyl)borane (**1**) to a stirred suspension of BrF_3 (molar ratio 2:3) in dichloromethane at −78 °C formed a new suspension. Gradual warming up to 35 °C and separation of the precipitate gave bis(pentafluorophenyl)bromonium pentafluorophenylfluoroborates (Eq. (7)).

$$2\underset{\mathbf{1}}{(C_6F_5)_3B} + 3BrF_3 \xrightarrow[-78\text{ to }25\,^\circ C]{CH_2Cl_2} [(C_6F_5)_2Br][(C_6F_5)_nBF_{4-n}] (n = 0-3) \quad (7)$$

The $[(C_6F_5)_3BF]^-$ anion (minor component) together with the $[C_6F_5BF_3]^-$ and $[BF_4]^-$ anions (major components) indicate the participation of the boranes $(C_6F_5)_2BF$ and $C_6F_5BF_2$ as intermediates in the aryl transfer process. To obtain only one type of anion, the reaction was performed in the presence of the fluoride acceptor $BF_3{\cdot}NCCH_3$ and using different sequences of mixing the reagents. In all cases, bis(pentafluorophenyl)bromonium tetrafluoroborate (**2**) was obtained in a good isolated yield (Eq. (8)).

$$2\underset{\mathbf{1}}{(C_6F_5)_3B} + 3BrF_3 + BF_3\cdot NCCH_3 \xrightarrow[-78\text{ to }25\,^\circ C,-MeCN]{CH_2Cl_2} \underset{\mathbf{2}(60-86\%)}{3[(C_6F_5)_2Br][BF_4]} \quad (8)$$

More information about the individual F/C_6F_5-substitution steps in BrF_3 than with $(C_6F_5)_3B$ and $(C_6F_5)_2BF$ [11] were obtained with pentafluorophenyldifluoroborane (**3**). Independent of the molar ratio of reagents salt **2** was isolated (Eq. (9)).

$$2\underset{\mathbf{3}}{C_6F_5BF_2} + BrF_3 \xrightarrow[-20\,^\circ C]{PFB} \underset{\mathbf{2}(83\%)}{[(C_6F_5)_2Br][BF_4]} + BF_3 \quad (9)$$

Pentafluorophenylbromine difluoride was not detected even in the equimolar reaction of borane **3** with BrF_3. Salt **2** was formed in the same yield independent of the ratio of reagents and the stoichiometrical excess of BrF_3 which remained.

The successful pentafluorophenylation of bromine trifluoride with pentafluorophenylboron difluoride inspired us to apply this approach to the preparation of previously unknown bis(organyl)-bromonium salts containing perfluorinated alkynyl, alkenyl, and alkyl groups. We used our convenient synthetic procedure to produce solutions of the required boranes R_FBF_2 by fluoride abstraction from the corresponding borates $K[R_FBF_3]$ with BF_3 in appropriate weakly coordinating solvents [18,19].

Thus trifluoropropynyldifluoroborane (**4**) was easily reacted with BrF_3 in PFP and the desired bis(trifluoropropynyl)bromonium tetrafluoroborate salt (**5**) was isolated in moderate yield (Eq. (10)).

$$2\,\underset{\mathbf{4}}{CF_3C{\equiv}CBF_2} + BrF_3 \xrightarrow[-40\,^\circ C]{PFP} \underset{\mathbf{5}(31\%)}{[(CF_3C{\equiv}C)_2Br][BF_4]} + BF_3 \tag{10}$$

For introducing perfluoroalkenyl groups we took two perfluoroalkenyldifluoroboranes of different configuration, *trans*-pentafluoroprop-1-en-1-yldifluoroborane (**6**) and *cis*-heptafluorobut-1-en-1-yldifluoroborane (**7**). In case of the fluoro/perfluoroalkenyl substitution in XeF_2 we had observed an influence of the configuration on the reaction rate [20].

Borane **6** reacted with BrF_3 giving a solution of salts with bis(*trans*-pentafluoroprop-1-en-1-yl)bromonium ((**8a**), major), (*trans*-pentafluoroprop-1-en-1-yl)(*cis*-pentafluoroprop-1-en-1-yl)(bromonium ((**8b**), minor)) cations and the counteranions *cis*- and *trans*-pentafluoroprop-1-en-1-yltrifluoroborate and perfluoropropyltrifluoroborate (Eq. (11)).

$$\begin{aligned} &2\textit{trans}\text{-}CF_3CF{=}CFBF_2 + BrF_3 \xrightarrow[-40\,\text{to}\,-30\,^\circ C]{PFP} \underset{(\mathbf{8a},\mathbf{b})Y}{[(RCF{=}CF)(R'CF{=}CF)Br]Y} \\ &R = R' = \textit{trans}\text{-}CF_3(\mathbf{8a});\ R = \textit{cis}\text{-}CF_3;\ R' = \textit{trans}\text{-}CF_3(\mathbf{8b}) \\ &Y = [\textit{cis}\text{-and}\,\textit{trans}\text{-}CF_3CF{=}CFBF_3]^- + [C_3F_7BF_3]^- \end{aligned} \tag{11}$$

A related reaction path occurred in the reaction of *cis*-heptafluorobut-1-en-1-yldifluoroborane (**7**) (2 equiv.) and BrF_3 where a solution of salts with bis(heptafluorobut-1-en-1-yl)bromonium cations (**9a–c**) and the counteranions heptafluorobut-1-en-1-yltrifluoroborate and perfluorobutyltrifluoroborate was formed (Eq. (12)).

$$\begin{aligned} &2\textit{cis}\text{-}C_2F_5CF{=}CFBF_2 + BrF_3 \xrightarrow[-20\,^\circ C]{PFB} \underset{(\mathbf{9a-c})Y}{[(RCF{=}CF)(R'CF{=}CF)Br]Y} \\ &R = R' = \textit{cis}\text{-}C_2F_5(\mathbf{9a});\ R = \textit{cis}\text{-}C_2F_5;\ R' = \textit{trans}\text{-}C_2F_5(\mathbf{9b});\ R = R' = \textit{trans}\text{-}C_2F_5(\mathbf{9c}) \\ &Y = [\textit{cis}\text{-and}\,\textit{trans}\text{-}C_2F_5CF{=}CFBF_3]^- + [C_4F_9BF_3]^- \end{aligned} \tag{12}$$

The opposite sequence of mixing, the addition of BrF_3 to a cold solution of **7** (2 equiv.) in PFB, led to a solution of related composition, but with incomplete conversion of **7**. Further addition of BrF_3 (total 1.8 equiv.) to the solution resulted in a suspension. After removal of the volatiles under reduced pressure, bis(heptafluorobut-1-en-1-yl)bromonium salts with tetrafluoroborate and perfluorobutyltrifluoroborate counteranions were isolated. The reaction was accompanied by *cis* to *trans*-isomerization of the heptafluorobutenyl group in the alkenylbromonium moiety and partially in the alkenyltrifluoroborate moiety. It seems that the $[C_2F_5CF{=}CFBF_3]^-$ anion in the bromonium salts did not react preferentially with BrF_3 and furthermore on another route than the "naked" anion. Because the treatment of tetrabutylammonium *cis*-heptafluorobut-1-en-1-yltrifluoroborate (**TBA-10**) with BrF_3 in PFB yielded tetrabutylammonium 2-bromoperfluorobutyltrifluoroborate (**TBA-11**), tetrafluoroborate, and perfluorobut-1-ene (**12**) (Eq. (13)). Borate **11** and alkene **12** were not found in the reaction mixtures (Eq. (12)).

$$\begin{aligned} &\underset{\mathbf{TBA\text{-}10}}{[Bu_4N][\textit{cis}\text{-}C_2F_5CF{=}CFBF_3]} + BrF_3 \xrightarrow{PFB,\,-20\,^\circ C} \underset{\mathbf{TBA\text{-}11}}{[Bu_4N][C_2F_5CFBrCF_2BF_3]} \\ &+ \underset{\mathbf{12}}{C_2F_5CF{=}CF_2} + [Bu_4N][BF_4] \end{aligned} \tag{13}$$

Noteworthy, that solutions of $[(C_6F_5)_2Br]Y$ and $[(RCF{=}CF)(R'CF{=}CF)Br]Y$ in MeCN showed no decomposition at 25 °C over days whereas the salt $[(CF_3C{\equiv}C)_2Br][BF_4]$ decomposed in acetonitrile at −25 °C.

In contrast to perfluorinated aryl-, alkenyl-, and alkynyldifluoroboranes, perfluorohexyldifluoroborane (**13**) (1 equiv.) did not react with BrF_3 (1 equiv.) under formation of the corresponding bis(perfluorohexyl)bromonium salt. The only fluoroorganic products were 1-bromoperfluorohexane (**14**) and perfluorohexane (**15**) (1:1) which were slowly produced at −60 °C. At −10 °C the reaction was completed within 1 h (Eq. (14)). Remarkably, that only 0.5 equiv. of BrF_3 was consumed.

$$2\,\underset{\mathbf{13}}{C_6F_{13}BF_2} + BrF_3 \xrightarrow[-60\,^\circ C]{PFP} \underset{\mathbf{14}}{C_6F_{13}Br} + \underset{\mathbf{15}}{C_6F_{14}} + 2BF_3 \tag{14}$$

A priori, the conversion of **14** to **15** by BrF_3 cannot be excluded. Therefore we performed additional experiments using the closely related 1-bromoperfluorooctane. It did not react with BrF_3 in PFB at 24 °C over a period of 17 h, but in the presence of a Lewis acid replacement of bromine by fluorine occurred (Eqs. (15) and (16)). Bubbling of BF_3 (weak Lewis acid) into a solution of $C_8F_{17}Br$ and BrF_3 in PFB at 0 °C gave "$BrF_3{\cdot}BF_3$" (^{19}F NMR), which converted $C_8F_{17}Br$ slowly into C_8F_{18} at 24 °C (1 h, no reaction; 72 h, complete conversion). Experiment (Eq. (15)) allows to exclude the formation of Alk_F-F from Alk_F-Br and BrF_3.

$$C_8F_{17}Br + BrF_3 \xrightarrow[24\,^\circ C,17\,h]{PFB} \text{no reaction} \tag{15}$$

$$C_8F_{17}Br + \text{"}BrF_3 \cdot BF_3\text{"} \xrightarrow[24\,^\circ C,72\,h]{PFB} C_8F_{18} + \cdots \tag{16}$$

It is noteworthy, that the treatment of $C_8F_{17}Br$ with $[BrF_2][SbF_6]$ in aHF at 24 °C gave C_8F_{18} in a quantitative yield within 3 h.

2.3. Reaction of the pentafluorophenyldifluoroborane-MeCN adduct with BrF_3 in PFB/MeCN

In a preceding paper [11] we reported the synthesis of salt **2** from BrF_3 and $(C_6F_5)_2BF$ in either CH_2Cl_2 as a weakly coordinating solvent or in CH_2Cl_2 with molar admixtures of coordinating CH_3CN in high yields. Actually we investigated the reaction (1:1) of BrF_3 with the adduct $C_6F_5BF_2{\cdot}NCCH_3$ (**16**) in a PFB/MeCN-mixture and obtained salt **2** too, but accompanied by significant amounts of bromopentafluorobenzene (**17**) (Eq. (17)).

$$\underset{\mathbf{16}}{C_6F_5BF_2 \cdot NCCH_3} + BrF_3 \xrightarrow[-20\,\text{to}\,24\,^\circ C]{PFB/MeCN} \underset{\mathbf{2}}{[(C_6F_5)_2Br][BF_4]} + \underset{\mathbf{17}}{C_6F_5Br} \tag{17}$$

2.4. Reactions of BrF_3 with 2 equiv of $C_6F_5SiX_3$ (X = F, Me)

BrF_3 reacted with 2 equiv. of $C_6F_5SiF_3$ (18) in CH_2Cl_2 in the presence of 2 equiv. of MeCN up to −60 °C only under formation of $C_6F_5BrF_2$ (**19**). In a slow reaction at ≥−30 °C the formation of the bromonium salt $[(C_6F_5)_2Br][SiF_5]$ occurred (Eqs. (18) and (19)). The salt was isolated in 92% yield.

$$2\,\underset{\mathbf{18}}{C_6F_5SiF_3} + BrF_3 \xrightarrow[\leq -60\,^\circ C]{CH_2Cl_2^*} \underset{\mathbf{19}}{C_6F_5BrF_2} + C_6F_5SiF_3 + SiF_4 \tag{18}$$

$$2\,\underset{\mathbf{18}}{C_6F_5SiF_3} + BrF_3 \xrightarrow[\geq -30\,^\circ C]{CH_2Cl_2^*} \underset{\mathbf{20}(92\%)}{[(C_6F_5)_2Br][SiF_5]} + SiF_4 \tag{19}$$

*2 equiv. of MeCN were present to increase the solubility of BrF_3 at low temperature

When the reaction of BrF_3 was performed with $C_6F_5SiMe_3$ (**21**) in a similar manner up to 0 °C only $C_6F_5BrF_2$ (**19**) (58% yield after isolation) was formed (Eq. (20)). In a further experiment BrF_3 was reacted with a mixture of 2 equiv. of $C_6F_5SiMe_3$ (**21**) and $BF_3{\cdot}OEt_2$. After 1 h at −78 °C the starting materials BrF_3 and $BF_3{\cdot}OEt_2$ were consumed, but whether $C_6F_5BrF_2$ (**19**) nor $[(C_6F_5)_2Br][BF_4]$ (**2**) were present. Besides $[BF_4]^-$ (major product), C_6F_5Br and Me_3SiF were formed (Eq. (21)).

$$2\,\underset{\mathbf{21}}{C_6F_5SiMe_3} + BrF_3 \xrightarrow[\leq 0\,^\circ C]{CH_2Cl_2} \underset{\mathbf{19}}{C_6F_5BrF_2} + C_6F_5SiMe_3 + Me_3SiF \quad (20)$$

$$BrF_3 + 2\,\underset{21}{C_6F_5SiMe_3}/2BF_3{\cdot}OEt_2 \xrightarrow[\leq -78\,^\circ C]{CH_2Cl_2} [BF_4]^- + C_6F_5SiMe_3 + C_6F_5Br + Me_3SiF \quad (21)$$

2.5. Reactions of potassium perfluoroorganyltrifluoroborates with BrF_3 in aHF

It is known, that dissolution of BrF_3 in aHF leads to a fluoride ion transfer equilibrium [21,22] accompanied by an increase of the electrophilicity and fluorooxidizer power of Br(III) (Eq. (22)).

$$BrF_3 + n\mathrm{HF} \overset{\mathrm{aHF}}{\rightleftharpoons} [BrF_2][F(HF)_n] \quad (22)$$

The dissolution of organyltrifluoroborates in aHF results primarily in the protonation of the fluorine atoms bonded to boron and leads to a organylfluoroborate/-borane equilibrium and a decrease in the acidity of hydrogen fluoride [23]. Thus, the transformation of the organyltrifluoroborate into the corresponding organyldifluoroborane was expected to favor the F/R_F substitution in BrF_3 relative to the oxidative addition of fluorine across C–C double or triple bonds in the R_F-group.

However, the addition of bromine trifluoride in aHF to a cold solution of an equimolar amount of potassium pentafluorophenyltrifluoroborate (**K-22**) in aHF gave salt **2** in only 45% yield while the main components derived from BrF-splitting of the B–C bond and fluorine addition across C=C double bonds: bromopentafluorobenzene **17**, 1-bromoheptafluorocyclohexa-1,4-diene (**23**), and 1-bromononafluorocyclohexene (**24**) (Eq. (23)).

$$\underset{\mathbf{K\text{-}22}}{K[C_6F_5BF_3]} + BrF_3 \xrightarrow{\mathrm{aHF},\geq -40\,^\circ C} \underset{\mathbf{2}}{[(C_6F_5)_2Br][BF_4]} + \underset{\mathbf{17}}{C_6F_5Br} + \underset{\mathbf{23}}{cyclo\text{-}1\text{-}Br\text{-}1,4\text{-}C_6F_7} + \underset{\mathbf{24}}{cyclo\text{-}1\text{-}BrC_6F_9} \quad (23)$$

No perfluoroalkenylbromonium salt was obtained when potassium *cis*-heptafluorobut-1-en-1-yltrifluoroborate (**K-10**) was reacted with bromine trifluoride in aHF. Instead, potassium 2-bromoperfluorobutyltrifluoroborate (**K-11**) and 2-bromoperfluorobutane (**25**) were formed (Eq. (24)) (compare with a related reaction in PFB, (Eq. (13))).

$$\underset{\mathbf{K\text{-}10}}{K[cis\text{-}C_2F_5CF=CFBF_3]} + BrF_3 \xrightarrow{\mathrm{aHF},-30\,^\circ C} \underset{\mathbf{K\text{-}11}}{K[C_2F_5CFBrCF_2BF_3]} + \underset{\mathbf{25}}{C_2F_5CFBrCF_3} + K[BF_4] \quad (24)$$

2.6. Reactions of potassium perfluoroorganyltrifluoroborate with $[BrF_2][SbF_6]$ in aHF

When $[BrF_2][SbF_6]$ was added to a solution of $K[C_6F_5BF_3]$ (**K-22**) (2 equiv.) in aHF bromonium hexafluoroantimonate resulted besides unreacted borate **22**. After hydrodeboration of remaining $[C_6F_5BF_3]^-$ with aHF to C_6F_5H and $[BF_4]^-$ at 25 °C, the salt $[(C_6F_5)_2Br][SbF_6]$ was obtained in 31% yield (Eq. (25)).

$$2K\,\underset{\mathbf{K\text{-}22}}{[C_6F_5BF_3]} + [BrF_2][SbF_6] \xrightarrow{\mathrm{aHF},-45\,\mathrm{to}\,25\,^\circ C} [(C_6F_5)_2Br][SbF_6] \quad (25)$$

Potassium perfluorohexyltrifluoroborate (**K-26**) did not react with $[BrF_2][SbF_6]$ in aHF at 25 °C (Eq. (26)).

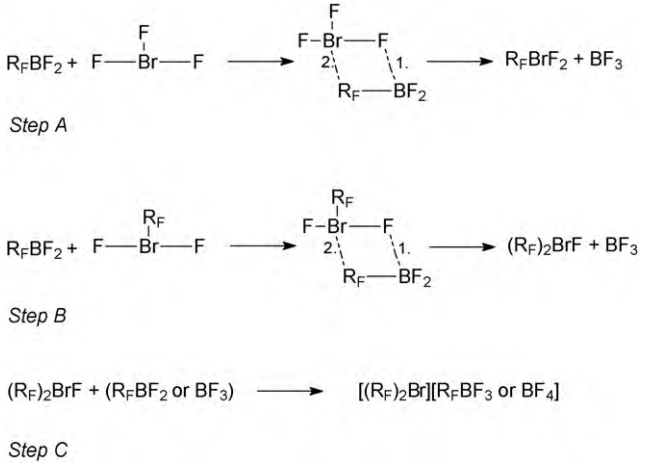
$$2K\,\underset{\mathbf{K\text{-}26}}{[C_6F_{13}BF_3]} + [BrF_2][SbF_6] \xrightarrow{\mathrm{aHF},25\,^\circ C} \text{no reaction} \quad (26)$$

3. Discussion

The formation of organylbromonium(III) salts from BrF_3 and the organyl transfer reagent R_FEX_{n-1} in weakly coordinating solvents like CH_2Cl_2 or PFP includes three steps: (a) $BrF_3 + R_FEX_{n-1} \rightarrow R_FBrF_2 + FEX_{n-1}$, (b) $R_FBrF_2 + R_FEX_{n-1} \rightarrow (R_F)_2BrF + FEX_{n-1}$, and (c) $(R_F)_2BrF + (FEX_{n-1}$ or $R_FEX_{n-1}) \rightarrow [(R_F)_2Br][F_2EX_{n-1}$ or $R_FEX_{n-1}F]$. In step (c) the formation of tris(organyl)bromane is not favored. $(R_F)_2BrF$ is a good fluoride donor comparable with $(R_F)_2IF$ [24]. Furthermore, the bromonium entity is stabilized by two 2c–2e C–Br bonds and the bromonium salt by lattice energy. Therefore bromonium salts are the final products under satisfactory acidic conditions.

When the organyl transfer reagents are perfluoroorganyldifluoroboranes R_FBF_2, these steps are substantiated in Scheme 1.

The success in the carbon-bromine(III) bond formation is mainly determined by two factors of the organyl transfer reagent: (a) Lewis acidity towards fluoride and (b) nucleophilicity of the C^1 carbon atom in the transition state. In step A, the interaction (1) of the acid R_FBF_2 with one fluorine atom of the BrF_2 triad weakens one Br–F bond and makes the bromine centre more electrophilic. Parallel the nucleofugality of the R_F group increases. As a result of the electrophile–nucleophile interaction (2) R_FBrF_2 is formed. The latter was not detected by ^{19}F NMR spectroscopy even at low temperature and local excess of BrF_3 (addition of neat BrF_3 to a diluted solution of R_FBF_2) or stoichiometric excess of BrF_3 (BrF_3:R_FBF_2 = 1:1). Furthermore, reaction mixtures obtained from BrF_3 and $C_6F_5BF_2$ in weakly coordinating solvents did not contain products of the acid-assisted decomposition of $C_6F_5BrF_2$ (C_6F_5Br, bromoperfluorocycloalkenes C_6BrF_7 and C_6BrF_9) which occurred at −80 to −30 °C [25]. Hence, the rate of reaction of R_FBrF_2 with R_FBF_2 (step B) exceeds both: the rate of formation of R_FBrF_2 (step A) and the rate of the acid-assisted decomposition of the latter. Some hint on the intermediate $C_6F_5BrF_2$ may be the increased formation of



Scheme 1.

C_6F_5Br (**17**) from the 1:1 reaction of $C_6F_5BF_2{\cdot}NCCH_3$ and BrF_3 in PFB/MeCN (Eq. (17)). Previously we have found that **17** is the major product of the $BF_3{\cdot}NCCH_3$ assisted decomposition of $C_6F_5BrF_2$ in CH_2Cl_2/MeCN [25].

Taking into account the order of the gas phase fluoride affinity in kcal/mol of fluoroboranes BF_3 (78.8) < $C_6F_5BF_2$ (85.1) < $CF_3C{\equiv}CBF_2$ (89.0) ≤ $CF_3CF=CFBF_2$ (89.0–90.0) < $C_3F_7BF_2$ (96.7) [26], step c should result in $[(R_F)_2Br][R_FBF_3]$ rather than in $[(R_F)_2Br][BF_4]$. The $[R_FBF_3]^-$ type of anion was only observed for R_F = perfluoroalkenyl (Eqs. (11) and (12)). Fluoroborates with more nucleophilic R_F groups ($R_F = C_6F_5$, $CF_3C{\equiv}C$) give tetrafluoroborates, $[(R_F)_2Br][BF_4]$. A closely related pictures was observed for the syntheses of bis(perfluoroorganyl)iodonium [12] and perfluoroorganylxenonium [14,15] salts via boranes R_FBF_2. In the context, which anion is formed, the unique transfer of a perfluoroalkyl group should be mentioned when borane $C_6F_{13}BF_2$ was reacted with $C_6F_5IF_2$ in PFP at −40 °C under formation of $[C_6F_5(C_6F_{13})I][C_6F_{13}BF_3]$ [27].

The attempted preparation of the bis(perfluorohexyl)bromonium salt from $C_6F_{13}BF_2$ and BrF_3 (~2:1) gave $C_6F_{13}Br$ and C_6F_{14} in a 1:1 ratio besides BF_3. This result can be explained via the formation of the intermediate $[(C_6F_{13})_2Br][C_6F_{13}BF_3]$ and its fast decomposition. This assumption is in agreement with the decomposition of $[(C_6F_5)(C_6F_{13})I][C_6F_{13}BF_3]$ in PFB which resulted in C_6F_5I, C_6F_{14}, and $C_6F_{13}BF_2$ [27].

In case of F/C_6F_5 substitution in BrF_3 we have investigated the influence of the nature of the transfer reagent. Concretely, we included $C_6F_5SiF_3$ and $C_6F_5SiMe_3$ in our investigations and compare the result with that of $C_6F_5BF_2$.

From calculated gas phase affinities we know that the tendency to attach a fluoride ion decreases from $C_6F_5BF_2$ via $C_6F_5SiF_3$ to $C_6F_5SiMe_3$ [26]. With both reagents of lower fluoride affinity the first F/C_6F_5 substitution step in BrF_3 is principally successful. The further F/C_6F_5 substitution step in $C_6F_5BrF_2$ was only possible in case of $C_6F_5SiF_3$ but this step proceeded slowly and afforded a temperature of ≥−30 °C. With $C_6F_5SiMe_3$ no bromonium product was formed even at 0 °C. When the reaction of BrF_3 with 2 equiv. $C_6F_5SiMe_3$ was performed in the presence of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 BrF_3 interacted preferentially with the Lewis acid $BF_3{\cdot}OEt_2$ and attacked the solvent and $C_6F_5SiMe_3$. $[BF_4]^-$, C_6F_5Br, and Me_3SiF were formed in decreasing quantities. The comparison of the three C_6F_5-transfer reagents in our present study allows to draw important conclusions. In order to substitute only one fluorine atom in the hypervalent moiety of BrF_3 the equimolar reaction with $C_6F_5BF_2$ is not suitable, because the second F/C_6F_5-substitution step proceeds faster than the first. The opposite sequence of the reaction rates is found for $C_6F_5SiF_3$. For the second F/C_6F_5-substitution step to the bromonium cation a minimum acidity (fluoride affinity) is needed, which is not provided by $C_6F_5SiMe_3$. When we compare the corresponding reactivity of hypervalent F-E-F triads in $C_6F_5IF_2$ and XeF_2 with that in $C_6F_5BrF_2$ we find the same tendency. Thus the unique importance of R_FBF_2 compounds for the introduction of R_F-groups into the Xe(II) moiety under formation of xenonium salts becomes plausible by our actual results.

The results of reactions between $K[R_FBF_3]$ with both, BrF_3 and $[BrF_2][SbF_6]$, in aHF are closely related to those obtained in reactions with XeF_2 in aHF [23,28]. Salt $K[C_6F_5BF_3]$ reacted with both binary fluorides EF_n giving pentafluorophenyl-containing salts, **2** (EF_n=BrF_3) or $[C_6F_5Xe][BF_4]$ ($EF_n = XeF_2$) besides products of fluorine addition across the C=C bond. Salt $K[cis\text{-}C_2F_5CF{=}CFBF_3]$ underwent bromofluorination and further conversion to **25** in reactions with BrF_3, while with XeF_2 fluorine addition across the C=C bond led to $K[C_4F_9BF_3]$. Salt $K[C_6F_{13}BF_3]$ was inert towards both, $[BrF_2][SbF_6]$ and XeF_2, in aHF. This picture shows an increased oxidative potential of $[EF_{n-1}]^+$ (or a related polarized form of EF_n) which can become predominant over an increased electrophilicity (e.g. rate of carbon-E bond formation). Hence, the use of $[EF_{n-1}]Y$ salts for the preparation of organic derivatives of polyvalent halogens or xenon is no perspective route. For the same reason, the presence of very strong polarizing substances (solvents, acidic admixtures, etc.) should be avoided.

4. Experimental

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (300.13 MHz, ^1H; 282.40 MHz, ^{19}F; 96.29 MHz, ^{11}B; 75.47 MHz, ^{13}C). The chemical shifts are referenced to TMS (^1H, ^{13}C), CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), and $BF_3{\cdot}OEt_2/CDCl_3$ (15%, v/v) (^{11}B), respectively. The composition of the reaction mixtures was determined by ^{19}F NMR spectroscopy using the internal integral standards C_6F_6, C_6F_{14}, or PFB. The products $[(C_6F_5)_2Br][BF_4]$ [11], C_4F_9Br [29], $[C_4F_9BF_3]^-$ [23], *cis*-$C_2F_5CF{=}CFBr$ [30], *trans*-$C_2F_5CF{=}CFBr$ [30], *cyclo*-1-Br-1,4-C_6F_7, *cyclo*-1-H-1,4-C_6F_7, and *cyclo*-1-BrC_6F_9 [31] were identified by ^{19}F NMR spectroscopy. As a convention for the presentation of the NMR spectral data, the fluorine atoms F^2 at C^2 in $[RC^2F^2{=}C^1F^1\text{-}X]$ compounds (X = B, Br) are specified by *cis* or *trans* relative to the position of X, e.g. as F^{2trans}.

1,1,1,3,3-Pentafluoropropane (PFP) (Honeywell), 1,1,1,3,3-pentafluorobutane (PFB) (Solvay), trichlorofluoromethane (K11, Solvay), 1,1,2-trichlorotrifluoroethane (K113, Solvay), and ether (Baker) were stored over molecular sieves 3 Å before use. Sicapent (Merck), boron trifluoride (Air Liquide), KF, spray-dried (Morita), $[Bu_4N][BF_4]$ (Fluka), $C_6F_{13}I$ (Hoechst), $C_8F_{17}Br$ (Hoechst), 40% and 71–75% aqueous HF (Fluka), $K[HF_2]$ (Riedel-de Haën), were used as supplied. $B(OMe)_3$ (Fluka) was distilled over sodium. Antimony pentafluoride was twice distilled under an atmosphere of dry argon. Acetonitrile (Baker) and dichloromethane (Baker) were purified and dried as described in ref. [32]. Anhydrous HF (aHF) was stored over CoF_3. Tris(pentafluorophenyl)borane [18], $C_6F_5SiF_3$ [33], $C_6F_5SiMe_3$ [34], $Li[C_6F_{13}B(OMe)_3]$ [35], $K[C_6F_5BF_3]$ [36], $K[cis\text{-}C_2F_5CF{=}CFBF_3]$ [37], $BF_3{\cdot}NCCH_3$ [38], and solutions of *cis*-$C_2F_5CF{=}CFBF_2$, *trans*-$CF_3CF{=}CFBF_2$ [39], $CF_3C{\equiv}CBF_2$ [40] in PFB or PFP were prepared as described. Salt $K[C_6F_{13}BF_3]$ [41] and solutions of $C_6F_5BF_2$ [42] and $C_6F_{13}BF_2$ [41] in PFB or PFP were prepared by modified procedures (see below). Bromine trifluoride was prepared by bubbling of fluorine (25%, v/v in N_2) into dry bromine at 8–20 °C and AsF_5 from AsF_3 with undiluted F_2 at ≤20 °C.

All manipulations with BrF_3 and perfluoroorganyldifluoroboranes were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) or PFA (block copolymer of tetrafluoroethylene and perfluoroalkoxytrifluoroethylene) equipment under an atmosphere of dry argon.

4.1. Preparation of $K[C_6F_{13}BF_3]$ (K-26)

(A) The reaction was performed in a three-necked, 1-L flask equipped with a low-temperature thermometer, a gas inlet, a Teflon-coated magnetic stir bar, and a dropping funnel which was connected via a Sicapent-filled tube to a mineral oil gas bubbler. The flask was charged with $C_6F_{13}I$ (25 g, 56 mmol) and ether (400 mL) and cooled to −70 °C under an atmosphere of dry argon. Ethylmagnesium bromide (0.90 M in ether, 62 mL, 56 mmol) was added drop-wise within 30 min. The solution transformed to a white suspension which was stirred at −55 °C for 1.5 h. Subsequently $B(OMe)_3$ (9.0 g, 86 mmol) in ether (10 mL) was added drop-wise using a syringe. The suspension was stirred at −50 °C for 1 h and allowed to warm to −10 °C within 2.5 h. A transparent solution was formed which was transferred to a round bottom flask (1 L). After concentration on an evaporator at 25 °C a suspension resulted, which was diluted with MeOH (50 mL) and poured into a solution of $K[HF_2]$ (23 g, 294 mmol) in water (30 mL) and 40% aqueous HF (30 mL) placed in a polypropylene beaker

(400 mL). The slurry was stirred at 20 °C overnight, diluted with water (50 mL), and neutralized by portion-wise addition of K_2CO_3. The suspension was extracted with MeCN (3× 50 mL). According to ^{19}F NMR data, the extract contained $K[C_6F_{13}BF(OMe)_2]$ (characteristic resonances at −130.8 (CF_2B) and −156.5 (q (1:1:1:1), ^1J(F, B) = 46 Hz, $BF(OMe)_2^-$) ppm), and $K[C_6F_{13}BF_2OMe]$ (characteristic resonances at −131.7 (CF_2B) and −149.1 (q (1:1:1:1), ^1J(F, B) = 50 Hz, BF_2OMe^-) ppm) borate anions in the molar ratio 1:4. The solution was concentrated on an evaporator to 60–70 mL volume, poured into a polypropylene beaker (400 mL) and 71–75% aqueous HF (30 mL) was added in one portion (moderately exothermic reaction). The suspension was stirred for 3.5 h, cooled by addition of crashed ice (60–70 g) and carefully neutralized with concentrated aqueous KOH under cooling (ice bath). The suspension was extracted with MeCN (3× 50 mL) and the combined extracts were dried with KF. The solvent was removed under reduced pressure and the solid was finally dried in a vacuum-desiccator over Sicapent. The salt $K[C_6F_{13}BF_3]$ was obtained in 73% yield (17.5 g, 41 mmol).

(B) The salt $Li[C_6F_{13}B(OMe)_3]$ (2.2 g, 5.1 mmol) was added in portions to a solution of $K[HF_2]$ (1.8 g, 23 mmol) in 71–75% aqueous HF (10 mL). The suspension was stirred for 5 h, diluted with water (3 mL), neutralized with K_2CO_3 and extracted with MeCN (3× 10 mL). The extract was dried with KF and the solvent was removed under reduced pressure. The product was dried in a vacuum-desiccator over Sicapent. The salt $K[C_6F_{13}BF_3]$ was obtained in 74% yield (1.6 g, 3.8 mmol).

Solubility of $K[C_6F_{13}BF_3]$ in MeCN exceeds 533 mg per mL (1.25 mmol per mL).

$K[C_6F_{13}BF_3]$ (**K-26**). ^{19}F NMR (aHF, 0 °C): δ −79.5 (tt, $^4J(F^6, F^4)$ = 10 Hz, $^3J(F^6, F^5)$ = 2 Hz, 3F, F^6), −119.8 (m, CF_2), −120.5 (m, CF_2), −121.3 (m, CF_2), −124.1 (m, 2F, F^5), −132.1 (m, 2F, F^1), −149.0 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3^-). ^{11}B NMR (aHF, 0 °C): δ −0.3 (m, BF_3^-). ^{19}F NMR (D_2O, 24 °C): δ −81.0 (t, $^4J(F^6, F^4)$ = 9 Hz, 3F, F^6), −122.7 (m, CF_2), −123.2 (m, CF_2), −124.6 (m, CF_2), −126.3 (m, 2F, F^5), −134.1 (m, 2F, F^1), −151.9 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3^-). ^{11}B NMR (D_2O, 24 °C): δ −0.7 (m, BF_3^-). ^{19}F NMR (acetone-d_6, 24 °C): δ −80.0 (tt, $^4J(F^6, F^4)$ = 10 Hz, $^3J(F^6, F^5)$ = 3 Hz, 3F, F^6), −120.9 (m, CF_2), −121.6 (m, CF_2), −122.3 (m, CF_2), −125.0 (m, 2F, F^5), −132.3 (m, 2F, F^1), −151.6 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3^-). ^{11}B NMR (acetone-d_6, 24 °C): δ −0.6 (qt, ^1J(B, F) = 41 Hz, ^2J(B, F) = 20 Hz, BF_3^-). $^{13}C\{^{19}F\}$ NMR (acetone-d_6, 24 °C): δ 117.5 (C^6), 121.3 (q (1:1:1:1), $^1J(C^1$, B) = 87 Hz, C^1), 113.5, 112.0, 110.9 ($3CF_2$), 109.1 (q, $^2J(C^5, F^6)$ = 29 Hz, C^5). (lit. [41]: ^{19}F NMR (CD_3CN, 24 °C)): (−80.1 (CF_3), −121.3, −121.9, −122.7, −125.1 ($4CF_2$), −132.6 (CF_2B), −151.8 (BF_3); ^{11}B NMR (CD_3CN, 24 °C): (−0.5 (qt, ^1J(B, F) = 41 Hz, ^2J(B, F^1) = 18 Hz).

4.2. Preparation of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ (TBA-10)

A solution of $K[cis\text{-}C_2F_5CF{=}CFBF_3]$ (428 mg, 1.48 mmol) in MeCN (0.5 mL) was poured into a stirred solution of $[Bu_4N][BF_4]$ (493 mg, 1.50 mmol) in MeCN (0.7 mL). After 15 min the suspension was centrifuged, the colorless mother liquor was decanted and evaporated to dryness at 20 °C (0.66 hPa) to yield the white solid $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ (579 mg, 1.17 mmol).

$[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ (**TBA-10**). ^{19}F NMR (PFB, 24 °C): δ −83.2 (d, $^4J(F^4, F^2)$ = 8 Hz, 3F, F^4), −116.9 (dq, $^3J(F^3, F^2)$ = 13 Hz, $^5J(F^3, BF_3^-)$ = 13 Hz, 2F, F^3), −130.4 (q (1:1:1:1), $^2J(F^1, B)$ = 24 Hz, 1F, F^1), −157.2 (m, 1F, F^2), −140.1 (q (1:1:1:1), ^1J(F, B) = 36 Hz, 3F, BF_3^-). ^{11}B NMR (PFB, 24 °C): δ −0.6 (ddq, $^3J(B, F^2)$ = 7 Hz, ^2J(B, F^1) = 23 Hz, ^1J(B, F) = 37 Hz, BF_3^-).

4.3. Preparation of $C_6F_5BF_2$ in PFB or PFP

(A) A flame dried glass trap (10 mL) equipped with a Teflon-coated magnetic stir bar and topped with a T-piece was charged with $K[C_6F_5BF_3]$ (454 mg, 1.65 mmol), PFB (3 mL) and cooled to −15 to −20 °C under an atmosphere of dry argon. Boron trifluoride (5–7 mmol) was bubbled into the stirred suspension for 25 min. Excess of BF_3 was removed by flushing with dry argon (0 °C, 10 min and 20 °C, 5 min). The suspension was centrifuged at 20 °C, the colorless mother liquor was decanted, the precipitate was washed with PFB (1 mL) and the washing was combined with the mother liquor. Yield of $C_6F_5BF_2$ (1.62 mmol, 98%), determined from the ^{19}F NMR spectrum using C_6F_{14} as quantitative integral reference.

(B) A solution of $C_6F_5BF_2$ (0.94 mmol, 95% yield) in PFP was prepared from $K[C_6F_5BF_3]$ (294 mg, 1.03 mmol) in PFP (3 mL) similarly, but the treatment after the reaction with BF_3 was performed at 0 °C (ice bath).

$C_6F_5BF_2$ (**3**). ^{19}F NMR (PFB, 24 °C): δ −73.7 (s, $\Delta\nu_{1/2}$ = 116 Hz, 2F, BF_2), −128.2 (m, 2F, $F^{2,6}$), −144.0 (tt, $^3J(F^4, F^{3,5})$ = 19 Hz, $^4J(F^4, F^{2,6})$ = 8 Hz, 1F, F^4), −161.2 (m, 2F, $F^{3,5}$). ^{11}B NMR (PFB, 24 °C): δ 22.1 (s, $\Delta\nu_{1/2}$ = 96 Hz).

4.4. Preparation of $C_6F_{13}BF_2$ (13) in PFP

(A) A flame dried glass trap (10 mL) equipped with a Teflon-coated magnetic stir bar and topped with a T-piece was charged with $K[C_6F_{13}BF_3]$ (440 mg, 1.03 mmol), PFP (3 mL) and cooled to −65 °C under an atmosphere of dry argon. Arsenic pentafluoride (1.4 mmol) was condensed. The white slurry was stirred for 1 h while the temperature rose to 0 °C. The suspension was centrifuged at 0 °C (ice bath), the colorless mother liquor was decanted, the precipitate was washed with PFP (2.5 mL), and the washing was combined with the mother liquor. Yield of $C_6F_{13}BF_2$ (0.90 mmol, 90%, determined from the ^{19}F NMR spectrum using PFB as a quantitative integral reference).

(B) A 11.7-mm i.d. PFA trap was charged with $K[C_6F_{13}BF_3]$ (440 mg,1.00 mmol), PFP (2 mL) and cooled to −25 °C under an atmosphere of dry argon. A cold (−20 °C) solution of SbF_5 (0.9 mmol) in PFP (3 mL) was added and the white slurry was stirred for 1 h at −20 °C. The suspension was centrifuged at 0 °C (ice bath), the colorless mother liquor was decanted, the precipitate was washed with PFP (1.5 mL), and the washing was combined with the mother liquor. Yield of $C_6F_{13}BF_2$ (0.80 mmol, 80%, determined from the ^{19}F NMR spectrum using PFB as a quantitative integral reference).

$C_6F_{13}BF_2$ (**13**). ^{19}F NMR (PFP, 0 °C): δ −75.8 (s, $\Delta\nu_{1/2}$ = 150 Hz, 2F, BF_2), −79.9 (t, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6), −119.6 (m, CF_2), −121.3 (m, CF_2), −124.1 (m, CF_2), −124.9 (m, 2F, F^5), −132.8 (m, 2F, F^1). ^{11}B NMR (PFP, 24 °C): δ 18.4 (s, $\Delta\nu_{1/2}$ = 141 Hz). (lit. [41] ^{19}F NMR (CCl_3F): δ −78.3 (s, 2F, BF_2), −81.5 (3F, F^6), −121.7, −123.2, −125.9, −126.7 ($4CF_2$), −134.1 (m, 2F, F^1); ^{11}B NMR (CCl_3F, 24 °C): δ 19.2 (br. s)).

4.5. Preparation of $C_6F_5BF_2{\cdot}NCCH_3$ (16)

A solution of MeCN (14 mg, 0.34 mmol) in PFB (0.1 mL) was added to a solution of $C_6F_5BF_2$ (0.29 mmol) in PFB (0.4 mL). The suspension was centrifuged and the white precipitate was dried in high vacuum (yield 70 mg, 0.27 mmol). Mp. 108 °C.

$C_6F_5BF_2{\cdot}NCCH_3$ (16). ^{19}F NMR (CH_3CN, 24 °C): δ −135.4 (m, 2F, $F^{2,6}$), −156.0 (t, $^3J(F^4, F^{3,5})$ = 21 Hz, 1F, F^4), −163.9 (m, 2F, $F^{3,5}$), −138.9 (s, $\Delta\nu_{1/2}$ = 54 Hz, 2F, BF_2). ^{11}B NMR (CD_3CN, 24 °C): δ 1.7 (s, $\Delta\nu_{1/2}$ = 46 Hz). $^{13}C\{^{19}F\}$ NMR (CD_3CN, 24 °C): δ 148.7 ($C^{2,6}$), 141.2 (C^4), 137.5 ($C^{3,5}$), the resonance of C^1 was not detected. ^1H NMR (CD_2Cl_2, 24 °C): δ 2.15 (s, 3H, CH_3). ^{19}F NMR (CD_2Cl_2, 24 °C): δ −135.3 (m, 2F, $F^{2,6}$), −155.8 (t, $^3J(F^4, F^{3,5})$ = 20 Hz, 1F, F^4), −164.4 (m, 2F, $F^{3,5}$), −136.5 (s, $\Delta\nu_{1/2}$ = 33 Hz, 2F, BF_2).

4.6. Preparation of $[BrF_2][SbF_6]$

The synthesis was performed in a 23-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar. The trap was connected to a

stainless steel vacuum line. The trap was charged with BrF_3 (1 mL, 2.8 g, 20 mmol) and SbF_5 (0.8 mL, 2.4 g, 11 mmol) was added in portions within 5 min. The temperature was increased to 60–80 °C, and the reddish solution was stirred for 30 min. All volatiles were removed under reduced pressure at 80–90 °C to yield a fine lemon powder. The product (3.3 g, 85%) was stored inside a glove-box under an atmosphere of dry argon. The ^{19}F NMR spectrum of $[BrF_2][SbF_6]$ in aHF at −40 °C consisted only of one Br*F* resonance at −73.5 ppm ($\Delta\nu_{1/2}$ = 106 Hz) ($[BrF_2]^+$) which became very broad at 0 °C. In the presence of SbF_5 (five fold molar excess) the signal of $[BrF_2]^+$ was located at −72.9 ppm and underwent a reversible broadening from $\Delta\nu_{1/2}$ = 47–53 Hz (−40 °C) to ~240 Hz (−20 °C) and >1000 Hz (0 °C). In both cases, the Sb-F resonances were presented by very broad signals at −120 to −125 ppm.

4.7. Bromine trifluoride in fluoroorganic solvents: stability, behaviour towards BF_3, and NMR properties

A. 3.5-mm i.d. FEP inliners were charged with different organic solvents (0.4 mL) and BrF_3 (20–30 mg). The two-phase systems were maintained for 1 h at 25 °C with periodic shaking before the upper organic phase was decanted. No ^{19}F NMR signal of BrF_3 was detected in case of perfluorohexane, perfluoromethylcyclohexane, perfluoro-2-methylpent-2-ene, and perfluorotributylamine. In case of trichlorofluoromethane and 1,1,2-trichlorotrifluoroethane the upper phase showed the presence of BrF_3. BrF_3 is miscible with PFP (5–10 °C) and PFB (25 °C) in any proportions giving yellowish solutions. No reaction was detected in the solution of BrF_3 in PFP, PFB (25 °C, over weeks), and 1,1,2-trichlorotrifluoroethane (25 °C, 26 h). In contrast, after 3 d the signal of BrF_3 in 1,1,2-$C_2Cl_3F_3$ disappeared and a significant amount of $CClF_2CClF_2$ was formed. With CCl_3F bromine trifluoride reacted above 10 °C to yield predominantly CCl_2F_2 (^{19}F NMR).

The solubility of BrF_3 was determined to 79 mg (0.57 mmol) per mL of 1,1,2-trichlorotrifluoroethane (^{19}F NMR, 24 °C).

BrF_3. ^{19}F NMR (PFB, 24 °C): δ −17.9 (s, $\Delta\nu_{1/2}$ = 27 Hz); (PFP, −10 °C): δ −17.3 (s, $\Delta\nu_{1/2}$ = 56 Hz); (CCl_2FCClF_2, 24 °C): δ −22.6 (s, $\Delta\nu_{1/2}$ = 71 Hz); (CCl_3F, 0 °C): δ −27.2 (s, $\Delta\nu_{1/2}$ = 126 Hz) (lit. ^{19}F NMR (neat, 35 °C): δ −16.3 [17]; (SO_2ClF, −20 °C): δ −16.5 ppm [16]).

(B) A solution of BrF_3 (147 mg, 1.07 mmol) in PFB (0.5 mL) was cooled to −8 °C and BF_3 (2 mmol) was bubbled for 15 min. A high density red phase separated. Warming above 3–5 °C caused the complete dissolution of the dense phase. The NMR spectra contained only one ^{19}F resonance at −74.8 ppm ($\Delta\nu_{1/2}$ = 138 Hz) besides signals of PFB and only one ^{11}B resonance at 0.16 ppm ($\Delta\nu_{1/2}$ = 8 Hz). No individual signals of BrF_3 and BF_3 were detected in both, the ^{11}B and ^{19}F NMR spectra. The solution was kept at −22 °C for 30 min and the mother liquor was decanted from the dense red phase. Cold (−22 °C) PFB (0.5 mL) was added and the inliner was warmed to 24 °C. The solution showed ^{11}B and ^{19}F NMR spectra which were only slightly distinguished from the spectra of the parent solution: ^{19}F NMR (PFB): δ −68.1 (s, $\Delta\nu_{1/2}$ = 553 Hz). ^{11}B NMR (PFB): δ 2.4 (s, $\Delta\nu_{1/2}$ = 8 Hz). No changes were observed when this solution was kept at ~20 °C for 24 h.

4.8. Preparation of $[(C_6F_5)_2Br]Y$ salts with pentafluorophenylboron compounds

4.8.1. Reaction of BrF_3 with $C_6F_5BF_2$ (1:2)

A 23-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of BrF_3 (0.80 mmol) in PFB (1.2 mL) and cooled to −25 °C. Then a cold (−15 °C) solution of $C_6F_5BF_2$ (1.62 mmol) in PFB (4 mL) was added in portions. The white suspension was stirred at −20 °C for 20 min, at 0 °C for 10 min and kept at −30 °C for 30 min without stirring. The mother liquor was decanted, the precipitate was washed with CH_2Cl_2 (4 mL) at 20 °C and pumped in vacuum for 30 min to yield $[(C_6F_5)_2Br][BF_4]$ (333 mg, 83%).

4.8.2. Reaction of BrF_3 with $C_6F_5BF_2$ (1:1)

A 23-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of BrF_3 (146 mg, 1.06 mmol) in PFP (4.5 mL) and cooled to −45 °C. Then a cold (−40 °C) solution of $C_6F_5BF_2$ (0.94 mmol) in PFP (3 mL) was added in portions. The white suspension was stirred at −40 °C for 1 h and at 0 °C for 30 min. The mother liquor was decanted, the precipitate was washed with PFP (2 mL) at 0 °C, dried in vacuum at 0 °C for 30 min and 24 °C for 1 h to yield $[(C_6F_5)_2Br][BF_4]$ (200 mg, 85%). The decanted mother liquor contained *cyclo*-1-Br-1,4-C_6F_7 (yield 3%) and *cyclo*-1-BrC_6F_9 (yield 5%) while resonances of C_6F_5Br and $C_6F_5BrF_2$ were not detected. To prove the presence of BrF_3, pentafluorobenzene (in excess) was added. The ^{19}F NMR spectrum showed the formation of C_6F_5Br and increasing amounts of *cyclo*-1-Br-1,4-C_6F_7 and *cyclo*-1-BrC_6F_9.

4.8.3. Reaction of BrF_3 with $C_6F_5BF_2{\cdot}NCCH_3$ (1:1)

A solution of BrF_3 (37 mg, 0.27 mmol) in PFB (1.2 mL) was cooled to −20 °C and a cold (−20 °C) solution of $C_6F_5BF_2{\cdot}NCCH_3$ (0.27 mmol) in CH_3CN (0.5 mL) was added in portions. The colorless solution was stirred at −20 °C for 30 min and warmed to 24 °C. The ^{19}F NMR spectrum pointed out the formation of $[(C_6F_5)_2Br][BF_4]$ and C_6F_5Br (1:1).

4.8.4. Reaction of BrF_3 with $K[C_6F_5BF_3]$ (1:1)

A cold (−40 °C) solution of BrF_3 (95 mg, 0.69 mmol) in aHF (0.7 mL) was added in portions to a cold (−40 °C) stirred solution of $K[C_6F_5BF_3]$ (190 mg, 0.69 mmol) in aHF (2.5 mL). After stirring at −30 °C for 1 h, the solution contained $[(C_6F_5)_2Br][BF_4]$, C_6F_5Br, and *cyclo*-1-Br-1,4-C_6F_7 (^{19}F NMR). The solution was extracted with CCl_4 at 0 °C. The extract contained C_6F_5Br (0.10 mmol), *cyclo*-1-Br-1,4-C_6F_7 (0.16 mmol), and *cyclo*-4-BrC_6F_9 (0.06 mmol), while the acid phase contained $[(C_6F_5)_2Br][BF_4]$ (0.16 mmol, 45% yield) and weak signals of perfluorinated unsaturated products.

4.8.5. Reaction of $[BrF_2][SbF_6]$ with $K[C_6F_5BF_3]$ (1:2)

A cold (−15 °C) solution of $[BrF_2][SbF_6]$ (90 mg, 0.25 mmol) in aHF (0.5 mL) was added in three portions to a cold (−55 °C) stirred solution of $K[C_6F_5BF_3]$ (143 mg, 0.52 mmol) in aHF (1 mL). The suspension was stirred at −45 °C for 1 h and at −10 °C for 20 min. The pink solution contained $[(C_6F_5)_2Br]^+$, $[C_6F_5BF_3]^-$, $[BF_4]^-$, C_6F_5Br, C_6F_5H (15:32:46:4:3) (^{19}F NMR, −10 °C). The solution was stirred at 0 °C for 1.5 h and at 25 °C for 2 h to complete the conversion of residual $K[C_6F_5BF_3]$ to C_6F_5H and $[BF_4]^-$ [43] (^{19}F NMR). After evaporation in vacuum at 25 °C the residue was washed with pentane (2× 1.5 mL), dried in vacuum, and extracted with MeCN (0.6 mL). The extract contained the salt $[(C_6F_5)_2Br][SbF_6]$ [11] (0.08 mmol (31%) based on $K[C_6F_5BF_3]$).

4.8.6. Reaction of BrF_3 with $(C_6F_5)_3B$ (3:2)

BrF_3 (9.9 mg, 0.072 mmol) was suspended in cold (−78 °C) CH_2Cl_2 (0.25 mL). Solid $(C_6F_5)_3B$ (25 mg, 0.049 mmol) was added and the mixture was vigorously agitated at −78 °C and finally warmed up in steps (−60 °C, −50 °C) under ^{19}F NMR control. The relative molar ratio of products in the suspension did not change: $[(C_6F_5)_2Br]^+$ (100%), $[(C_6F_5)_3BF]^-$ (99%), C_6F_5Br (81%) C_6F_5D (17%), $(C_6F_5)_3B$ (4%). After warming to 35 °C the mother liquor was decanted and the solid residue was dried in vacuum to yield $[(C_6F_5)_2Br]Y$ salts (23.1 mg, 59%) (Y = $[(C_6F_5)_3BF]^-$, $[C_6F_5BF_3]^-$, $[BF_4]^-$) in the molar ratio $[(C_6F_5)_2Br]^+$:$[(C_6F_5)_3BF]^-$:$[C_6F_5BF_3]^-$:$[BF_4]^-$ = 100:2:33:65.

Treatment of the mother liquor with solid $BF_3{\cdot}NCCH_3$ (3 mg, 0.028 mmol) resulted again in a suspension. After separation the precipitate was dissolved in MeCN and the ^{19}F NMR spectrum showed the signals of $[(C_6F_5)_2Br][BF_4]$ besides traces of $BF_3{\cdot}NCCH_3$ and C_6F_5Br. The mother liquor contained $(C_6F_5)_3B{\cdot}NCCH_3$, $(C_6F_5)_2BF{\cdot}NCCH_3$, $BF_3{\cdot}NCCH_3$, C_6F_5Br, and C_6F_5D in the molar ratio 89:26:81:100:37.

4.8.7. Reaction of BrF_3 with $(C_6F_5)_3B$ and $BF_3{\cdot}NCCH_3$ (3:2:1)

Solid $BF_3{\cdot}NCCH_3$ (61 mg, 0.56 mmol) was added to a cold (−70 °C) solution of $(C_6F_5)_3B$ (590 mg, 1.15 mmol) in CH_2Cl_2 (10 mL). The suspension was warmed to 20 °C within 30 min and after 1 h at 20 °C a solution resulted which contained $(C_6F_5)_3B$ ($\delta(F)$ = −129.5, −146.2, and −161.8) and $(C_6F_5)_3B{\cdot}NCCH_3$ ($\delta(F)$ = −134.8, −157.5, and −164.7) in the molar ratio 100:80. Boron trifluoride was not detected by ^{19}F NMR although opening of the trap went along with the escape of a fuming gas, presumably, BF_3. The solution was cooled to −78 °C and formed a suspension which was quantitatively transferred to a suspension of BrF_3 (237.5 mg, 1.74 mmol) in CH_2Cl_2 (1.2 mL, −78 °C). The cold mixture was stirred for 1 h before it was warmed to 20 °C within 0.5 h and finally stored overnight.

The decanted mother liquor showed ^{19}F resonances of $[(C_6F_5)_2Br][(C_6F_5)_3BF]$ and C_6F_5Br (37:63). The solid was washed with CH_2Cl_2 (2× 1.5 mL) and dried in vacuum to give the bromonium salts $[(C_6F_5)_2Br][BF_4]$ and $[(C_6F_5)_2Br][C_6F_5BF_3]$ (554 mg) (94:6) (^{19}F NMR in MeCN).

4.8.8. Reaction of BrF_3 with $(C_6F_5)_3B$ (3:2) and $BF_3{\cdot}NCCH_3$ in CH_2Cl_2

Borane 1 (1.94 g, 3.79 mmol) was added to the cold (−78 °C) suspension of BrF_3 (766 mg, 5.60 mmol) in CH_2Cl_2 (50 mL) and stirred at −70 °C. After 1.5 h the mother liquor did not contain borane **1** (^{19}F NMR). Then $BF_3{\cdot}NCCH_3$ (203 mg, 1.86 mmol) was added. After stirring at −70 °C for 0.5 h, the temperature was increased to 20 °C. The mother liquor was decanted. The solid residue was washed with CH_2Cl_2 (2× 10 mL) and dried in vacuum to yield 2.4 g (4.78 mmol, 86%) of $[(C_6F_5)_2Br][BF_4]$.

4.8.9. Reaction of $(C_6F_5)_3B$ with BrF_3 (2:3) and $BF_3{\cdot}NCCH_3$ in CH_2Cl_2

A solution of $(C_6F_5)_3B$ (945 mg, 1.85 mmol) in CH_2Cl_2 (20 mL) was prepared in a FEP trap and cooled to −78 °C forming a suspension. Bromine trifluoride BrF_3 (385 mg, 2.81 mmol) was dropped onto the cold wall of the FEP trap and solidified. After knocking at the trap, BrF_3 released from the wall and sunk into the stirred suspension of **1**. Within 2 h the temperature was increased to −60 °C under stirring. The ^{19}F NMR spectrum showed the absence of $(C_6F_5)_3B$ and the presence of resonances at −133.0, −142.7, and −156.5 ppm (2:1:2) (presumably $(C_6F_5)_2BrF$) and C_6F_5Br (10:9) besides C_6F_6 (traces). Then $BF_3{\cdot}NCCH_3$ (101 mg, 0.93 mmol) was added to the suspension and the temperature was increased to 20 °C within 1 h. The precipitate was separated, dissolved in MeCN (2 mL) and re-precipitated by addition of CH_2Cl_2 (15 mL). The mother liquor was decanted and the solid dried in vacuum to yield $[(C_6F_5)_2Br][BF_4]$ (1.134 g, 2.26 mmol, 82%).

4.9. Reaction of BrF_3 with $C_6F_5SiF_3$ (1:2)

A 23-mm i.d. FEP trap was charged with $C_6F_5SiF_3$ (5.283 g, 20.05 mmol), CH_2Cl_2 (10 mL) and NaF (102 mg, 2.43 mmol) and cooled to −60 °C. In a second 23-mm i.d. FEP trap BrF_3 (1.43 g, 10.45 mmol) was frozen at −78 °C and cold (−78 °C) CH_2Cl_2 (35 mL), cold (−40 °C) MeCN (1.1 mL, 21.05 mmol) and NaF (106 mg, 2.52 mmol) were added in sequence. CAUTION! BrF_3 can react violently with neat MeCN [44]. The suspension was stirred at −78 °C for 10 min to remove traces of HF and the light-yellow mother liquor (BrF_3 in CH_2Cl_2/MeCN) was added drop-wise to the trap with $C_6F_5SiF_3$ within 15 min. The suspension was stirred for further 1.5 h at −78 °C and 1 h at −60 °C. The amount of solid corresponded to the NaF quantity. A probe of the mother liquor contained $C_6F_5BrF_2$ and $C_6F_5SiF_3$ in a molar ratio of 1:1 (^{19}F NMR). When the temperature was increased to −30 °C overnight, a colorless solid precipitated. The suspension was warmed to −15 °C within 7 h before mother liquor (A) was decanted from precipitate (A) (3.99 g, including NaF). Stirring of mother liquor (A) at −40 to −10 °C for 12 h and at 0 °C for 24 h resulted in a suspension again. Precipitate (B) was separated and dried in vacuum to give product (B) (1.15 g). Both solids (A) and (B) were washed with CH_2Cl_2, dried in vacuum and extracted with MeCN. The solvent was evaporated under reduced pressure forming the colorless salt $[(C_6F_5)_2Br][SiF_5]$ (4.93 g, 92%).

$[(C_6F_5)_2Br][SiF_5]$. ^{19}F NMR (CD_3CN): δ −129.0 (m, 4F, $F^{2,6}$), −137.1 (s, $\Delta\nu_{1/2}$ = 9 Hz, 5F, SiF_5^-), −139.0 (tt, $^3J(F^4, F^{3,5})$ = 20 Hz, $^4J(F^4, F^{2,6})$ = 7 Hz, 2F, F^4), −154.7 (m, 4F, $F^{3,5}$).

Salt $[(C_6F_5)_2Br][SiF_5]$ decomposed exothermically at 207 °C (DTA). A $CDCl_3$ solution of the decomposition product exhibited a 1:0.8 molar ratio of C_6F_5Br and C_6F_6.

4.10. Reaction of BrF_3 with $C_6F_5SiMe_3$ (1:2) in the presence of MeCN

A 23-mm i.d. FEP trap was charged with $C_6F_5SiMe_3$ (2.15 g, 8.95 mmol), CH_2Cl_2 (5 mL) and NaF (50 mg, 1.19 mmol) and cooled to −90 °C. A solution of BrF_3 (610 mg, 4.46 mmol) in CH_2Cl_2 (15 mL) and MeCN (0.465 mL, 8.9 mmol) over NaF (50 mg, 1.19 mmol) was prepared in a 23-mm i.d. FEP trap as described above (4.9). After 10 min of stirring at −78 °C (to remove traces of HF) the BrF_3 solution was added drop-wise to the trap with $C_6F_5SiMe_3$ (−90 °C). After 4 h at −90 °C, the reaction mixture was kept at −70 °C for 12 h and then warmed to 0 °C. The mother liquor was separated from the precipitate, evaporated to dryness in vacuum and the solid residue was re-crystallized from CCl_3F yielding $C_6F_5BrF_2$ (730 mg, 2.56 mmol) (58% related to BrF_3). Dissolution of the precipitate in an aqueous solution of $Na[BF_4]$ confirmed the absence of $[(C_6F_5)_2Br]Y$ salts (^{19}F NMR).

4.11. Reaction of BrF_3 with $C_6F_5SiMe_3$ (1:2) in the presence of $BF_3{\cdot}OEt_2$

The reaction was performed in analogy to the above one (*4.10*). A cold (−78 °C) solution of $C_6F_5SiMe_3$ (4.33 g, 14.8 mmol) and $BF_3{\cdot}OEt_2$ (1.8 mL, 14.6 mmol) in CH_2Cl_2 (8 mL) was stirred over NaF (86 mg, 2.05 mmol) before being added drop-wise to a cold suspension of BrF_3 (1.01 g, 7.38 mmol) in CH_2Cl_2 (25 mL) and MeCN (0.77 mL, 14.7 mmol) which contained NaF (90 mg, 2.14 mmol). The light-yellow suspension discolored after 1 h at −78 °C. The mother liquor contained $C_6F_5SiMe_3$, C_6F_5Br, Me_3SiF, and $[BF_4]^-$ in the molar ratio 30:19:9:42, while no BrF_3 or $C_6F_5BrF_2$ was found (^{19}F NMR). This composition was not changed after 12 h at −78 °C. The liquid phase was separated. The solid was dried in vacuum at −30 to 20 °C and suspended in MeCN. The ^{19}F NMR spectrum of the MeCN suspension showed signals of $[BF_4]^-$ as major component with its $^{10/11}B$ isotopomers (−150.65/−150.70 ppm) besides a minor unknown species (−65.1 ppm, q, J = 17 Hz).

*4.12. Preparation of $[(CF_3C{\equiv}C)_2Br][BF_4]$ (**5**)*

A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of BrF_3 (97 mg, 0.70 mmol) in PFP (1 mL) and cooled to −45 °C. A cold (−45 °C) solution of $CF_3C{\equiv}CBF_2$ (0.80 mmol) in PFP (2 mL) was added in portions within 2 min. The white suspension was stirred at −40 °C for 1 h, centrifuged at −78 °C and the mother liquor was decanted. The white precipitate was washed with cold (−40 °C) PFP (2 mL)

and dried in vacuum at −30 °C for 1 h to yield $[(CF_3C{\equiv}C)_2Br][BF_4]$ (56 mg, 31%).

Attempts to dissolve $[(CF_3C{\equiv}C)_2Br][BF_4]$ in cold (−25 °C) MeCN led to vigorous reactions and formation of a complex mixture (^{19}F).

$[(CF_3C{\equiv}C)_2Br][BF_4]$ (**5**). ^{19}F NMR (aHF, −40 °C): δ −52.6 (s, 6F, F^3), −148.6 (q (1:1:1:1), ^1J(F, B) = 12 Hz, $[BF_4]^-$). ^{11}B NMR (aHF, −40 °C): δ −2.1 (quintet, ^1J(B, F) = 12 Hz, $[BF_4]^-$). ^{13}C NMR (aHF, −40 °C): δ 112.4 (q, $^1J(C^3, F^3)$ = 264 Hz, C^3), 83.2 (q, $^2J(C^2, F^3)$ = 61 Hz, C^2), 44.1 (q, $^3J(C^1, F^3)$ = 8 Hz, C^1).

4.13. Preparation of $[(CF_3CF{=}CF)_2Br]Y$ salts

A 8-mm i.d. FEP trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of BrF_3 (0.14 mmol) in PFP (1 mL) and cooled to −45 °C. Then a cold (−45 °C) solution of *trans*-$CF_3CF{=}CFBF_2$ (0.29 mmol) in PFP (1.5 mL) was added in portions. After stirring at −40 °C for 1 h and at −30 °C for 1 h, [(*trans*-$CF_3CF{=}CF)_2Br]^+$ (**8a**), [*trans*-$CF_3CF{=}CFBF_3]^-$ and *trans*-$CF_3CF{=}CFBF_2$ were the major components of the colorless solution (^{19}F NMR, −30 °C). A second portion of cold (−10 °C) BrF_3 (0.14 mmol) in PFP (1 mL) was added to the cold (−40 °C) stirred reaction solution. The solution was stirred at −35 °C for 40 min and then evaporated at −10 °C in vacuum to dryness. A solution of the product in MeCN contained [(*trans*-$CF_3CF{=}CF)_2Br]^+$ (**8a**), [(*cis*-$CF_3CF{=}CF$)(*trans*-$CF_3CF{=}CF)Br]^+$ (**8b**) (94:6), [*trans*-$CF_3CF{=}CFBF_3]^-$, [*cis*-$CF_3CF{=}CFBF_3]^-$, and $[C_3F_7BF_3]^-$ (60:32:8) (yield 0.13 mmol).

$[(CF_3CF{=}CF)_2Br][CF_3CF{=}CFBF_3/C_3F_7BF_3]$. ^{19}F NMR (CH_3CN, −10 °C): δ −67.8 (dd, $^3J(F^3, F^2) = {}^3J(F^{3'}, F^{2'})$ = 10 Hz, $^4J(F^3, F^1) = {}^4J(F^{3'}, F^{1'})$ = 19 Hz, 6F, F^3, $F^{3'}$), −106.4 (qdd, $^4J(F^1, F^3) = {}^4J(F^{1'}, F^{3'})$ = 19 Hz, $^3J(F^1, F^2) = {}^3J(F^{1'}, F^{2'})$ = 129 Hz, $^5J(F^1, F^{2'}) = {}^5J(F^{1'}, F^2)$ = 5 Hz, 2F, F^1,$F^{1'}$), −139.4 (md, $^3J(F^2, F^1) = {}^3J(F^{2'}, F^{1'})$ = 129 Hz, 2F, F^2,$F^{2'}$) (*trans*, *trans*-isomer (**8a**)); −66.5 (dd, $^3J(F^3, F^2)$ = 11 Hz, $^4J(F^3, F^1)$ = 7 Hz, 3F, F^3), −94.5 (qd, $^4J(F^1, F^3)$ = 7 Hz, $^3J(F^1, F^2)$ = 42 Hz, 1F, F^1), −121.3 (qd, $^3J(F^2, F^3)$ = 11 Hz, $^3J(F^2, F^1)$ = 42 Hz, 1F, F^2) (*cis*-moiety *of cis*, *trans*-isomer (**8b**)), −67.4 (dd, $^3J(F^{3'}, F^{2'})$ = 11 Hz, $^4J(F^{3'}, F^{1'})$ = 22 Hz, 3F, $F^{3'}$), −107.5 (qd, $^4J(F^{1'}, F^{3'})$ = 20 Hz, $^3J(F^{1'}, F^{2'})$ = 129 Hz, 1F, $F^{1'}$), −140.0 (d, $^3J(F^{2'}, F^{1'})$ = 128 Hz, 1F, $F^{2'}$) (*trans*-moiety *of cis*, *trans*-isomer (**8b**)); −80.4 (tt, $^3J(F^3, F^2)$ = 3 Hz, $^4J(F^3, F^1)$ = 9 Hz, 3F, F^3), −127.7 (m, 2F, F^2), −134.0 (m, 2F, F^1), −150.9 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3^-) ($[C_3F_7BF_3]^-$); −66.4 (m, 3F, F^3), −137.1 (m, 1F, F^1), −158.8 (m, 1F, F^2), −140.9 (q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3^-) ([*cis*-$CF_3CF{=}CFBF_3]^-$); −66.8 (dd, $^3J(F^3, F^2)$ = 11 Hz, $^4J(F^3, F^1)$ = 23 Hz, 3F, F^3), −156.1 (d, $^3J(F^1, F^2)$ = 129 Hz, 1F, F^1), −179.6 (d, $^3J(F^2, F^1)$ = 129 Hz, 1F, F^2), −142.2 (q (1:1:1:1), ^1J(F, B) = 39 Hz, 3F, BF_3^-) ([*trans*-$CF_3CF{=}CFBF_3]^-$).

4.14. Preparation of $[(C_2F_5CF{=}CF)_2Br]Y$ salts

(A) A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of BrF_3 (0.5 mmol) in PFB (0.7 mL) and cooled to −20 °C. A cold (−20 °C) solution of *cis*-$C_2F_5CF = CFBF_2$ (1.0 mmol) in PFB (1.5 mL) was added in portions. After stirring at −20 °C for 2 h the ^{19}F NMR spectrum (−20 °C) of the colorless solution showed signals of [(*cis*-$C_2F_5CF{=}CF)_2Br]^+$ (**9a**), [(*cis*-$C_2F_5CF{=}CF$)(*trans*-$C_2F_5CF{=}CF)Br]^+$ (**9b**), [*cis*-$C_2F_5CF{=}CFBF_3]^-$, $[C_4F_9BF_3]^-$, C_4F_9Br, and $C_2F_5CFBrCF_2Br$ (molar ratio 21:4:55:6:9:5) besides a trace of [(*trans*-$C_2F_5CF{=}CF)_2Br]^+$ (**9c**). Resonances of BrF_3, $C_2F_5CF{=}CF_2$, $[BF_4]^-$, and $[C_2F_5CFBrCF_2BF_3]^-$ were not detected. Volatiles were removed in vacuum at 20 °C, the residue was washed with CCl_3F (2 mL) at 15 °C and the solid was dried in vacuum at 20 °C for 3 h to yield $[(C_2F_5CF{=}CF)_2Br]Y$ [(*cis*, *cis*):(*cis*, *trans*):(*trans*, *trans*) = 90:8:2] (Y = $[C_2F_5CF{=}CFBF_3]^-$ (*cis*:*trans* = 63:37):$[C_4F_9BF_3]^-$ = 70:30) (114 mg).

(B) A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with a solution of *cis*-$C_2F_5CF{=}CFBF_2$ (1.0 mmol) in PFB (1.5 mL) and cooled to −20 °C. Then a cold (−20 °C) solution of BrF_3 (0.5 mmol) in PFB (0.7 mL) was added in portions. After stirring at −20 °C for 2.5 h the ^{19}F NMR spectrum (−20 °C) of the colorless solution showed signals of [(*cis*-$C_2F_5CF{=}CF)_2Br]^+$ (**9a**), [(*cis*-$C_2F_5CF{=}CF$)(*trans*-$C_2F_5CF{=}CF)Br]^+$ (**9b**), [*cis*-$C_2F_5CF{=}CFBF_3]^-$, $[C_4F_9BF_3]^-$, C_4F_9Br, $C_2F_5CFBrCF_2Br$, *cis*-$C_2F_5CF{=}CFBr$, and *trans*-$C_2F_5CF{=}CFBr$ (molar ratio 29:8:29:8:6:3:5:12) besides a trace of [(*trans*-$C_2F_5CF{=}CF)_2Br]^+$ (**9c**). Resonances of BrF_3 and $[BF_4]^-$ were not detected. In order to react still present *cis*-$C_2F_5CF{=}CFBF_2$, a further portion of BrF_3 (0.3 mmol) in PFB (0.1 mL) was added at −15 °C. Stirring at −15 °C for 1 h resulted in a suspension and the ^{19}F NMR spectrum showed the complete consumption of *cis*-$C_2F_5CF{=}CFBF_2$. Volatiles were removed in vacuum at 20 °C, the residue was washed with CCl_3F (2× 2 mL) at 15 °C and the solid was dried in vacuum at 20 °C for 1 h to yield $[(C_2F_5CF{=}CF)_2Br]Y$ [(*cis*, *cis*):(*cis*, *trans*):(*trans*, *trans*) = 80:18:2] (Y = $[C_4F_9BF_3]^-/[BF_4]^-$(24:76)] (167 mg).

1,2-Dibromooctafluorobutane. ^{19}F NMR (PFB, −20 °C): δ −56.5 (d, $^2J(F^{1A}, F^{1B})$ = 178 Hz, 1F, F^{1A}), −57.4 (d, $^2J(F^{1B}, F^{1A})$ = 178 Hz, 1F, F^{1B}), −77.6 (ddd, $^4J(F^4, F^2)$ = 11 Hz, $^3J(F^4, F^{3A})$ = 5 Hz, $^3J(F^4, F^{3B})$ = 6 Hz, 3F, F^4), −124.8 (m, 2F, $F^{3A, 3B}$), −131.1 (m, 1F, F^2).

$[(C_2F_5CF{=}CF)_2Br][C_4F_9BF_3]$. ^{19}F NMR (PFB, −20 °C): δ −82.0 (t, $^3J(F^4, F^3) = {}^3J(F^{4'}, F^{3'})$ = 6 Hz, 6F, F^4,$F^{4'}$), −92.9 (md, $^3J(F^1, F^2) = {}^3J(F^{1'}, F^{2'})$ = 48 Hz, 2F, F^1,$F^{1'}$), −114.5 (md, $^3J(F^2, F^1) = {}^3J(F^{2'}, F^{1'})$ = 48 Hz, 2F, F^2,$F^{2'}$), −116.9 (m, 4F, F^3,$F^{3'}$) (*cis*, *cis*-isomer **9a**); −82.2 (m, 3F, F^4), −90.2 (dd, $^3J(F^1, F^2)$ = 48 Hz, $^4J(F^1, F^{1'})$ = 6 Hz, 1F, F^1), −115.0 (d, $^3J(F^2, F^1)$ = 48 Hz, F, F^2), −117.2 (m, 2F, F^3) (*cis*-moiety of *cis*, *trans*-isomer **9b**), −82.7 (m, 3F, $F^{4'}$), −107.9 (dt, $^3J(F^{1'}, F^{2'})$ = 130 Hz, $^4J(F^{1'}, F^{3'})$ = 25 Hz, 1F, $F^{1'}$), −120.3 (dd, $^4J(F^{3'}, F^{1'})$ = 25 Hz, $^3J(F^{3'}, F^{2'})$ = 12 Hz, 2F, $F^{3'}$), −130.8 (d, $^3J(F^{2'}, F^{1'})$ = 130 Hz, 1F, $F^{2'}$) (*trans*-moiety of *cis*, *trans*-isomer **9b**); −82.8 (m, 6F, F^4,$F^{4'}$), −107.0 (dt, $^3J(F^1, F^2) = {}^3J(F^{1'}, F^{2'})$ = 130 Hz, $^4J(F^1, F^3) = {}^4J(F^{1'}, F^{3'})$ = 25 Hz, 2F, F^1,$F^{1'}$), −120.4 (m, 4F, F^3,$F^{3'}$), −132.7 (d, $^3J(F^2, F^1) = {}^3J(F^{2'}, F^{1'})$ = 130 Hz, 2F, F^2,$F^{2'}$) (*trans*, *trans*-isomer **9c**); −80.1 (t, $^4J(F^4, F^2)$ = 10 Hz, 3F, F^4), −123.5 (m, 2F, F^2), −125.5 (m, 2F, F^3), −133.6 (m, 2F, F^1), ∼−150 (very br, 3F, BF_3^-) ($[C_4F_9BF_3]^-$) (bromonium salt with $[BF_4]^-$ counteranion is insoluble in PFB).

$[(C_2F_5CF = CF)_2Br][BF_4 + C_4F_9BF_3]$. ^{19}F NMR (CH_3CN, 24 °C): δ −81.5 (m, 6F, F^4,$F^{4'}$), −89.8 (md, $^3J(F^1, F^2) = {}^3J(F^{1'}, F^{2'})$ = 44 Hz, 2F, F^1,$F^{1'}$), −116.8 (m, 4F, F^3,$F^{3'}$), −119.1 (md, $^3J(F^2, F^1) = {}^3J(F^{2'}, F^{1'})$ = 44 Hz, 2F, F^2,$F^{2'}$) (*cis*, *cis*-isomer **9a**); −81.7 (m, 3F, F^4), −87.2 (d, $^3J(F^1, F^2)$ = 44 Hz, 1F, F^1), −116.9 (m, 2F, F^3), −118.8 (d, $^3J(F^2, F^1)$ = 44 Hz, F, F^2) (*cis*-moiety of *cis*, *trans*-isomer **9b**), −82.6 (m, 3F, $F^{4'}$), −106.5 (dt, $^3J(F^{1'}, F^{2'})$ = 130 Hz, $^4J(F^{1'}, F^{3'})$ = 25 Hz, 1F, $F^{1'}$), −120.3 (ddq, $^4J(F^{3'}, F^{1'})$ = 25 Hz, $^3J(F^{3'}, F^{2'})$ = 12 Hz, $^3J(F^{3'}, F^{4'})$ = 2 Hz, 2F, $F^{3'}$), −136.1 (d, $^3J(F^{2'}, F^{1'})$ = 128 Hz, 1F, $F^{2'}$) (*trans*-moiety of *cis*, *trans*-isomer **9b**); −82.7 (m, 6F, F^4,$F^{4'}$), −105.6 (dt, $^3J(F^1, F^2) = {}^3J(F^{1'}, F^{2'})$ = 128 Hz, $^4J(F^1, F^3) = {}^4J(F^{1'}, F^{3'})$ = 26 Hz, 2F, F^1,$F^{1'}$), −120.4 (dd, $^3J(F^3, F^2) = {}^3J(F^{3'}, F^{2'})$ = 13 Hz, $^4J(F^3, F^1) = {}^4J(F^{3'}, F^{1'})$ = 26 Hz, 4F, F^3,$F^{3'}$), −135.4 (d, $^3J(F^2, F^1) = {}^3J(F^{2'}, F^{1'})$ = 128 Hz, 2F, F^2,$F^{2'}$) (*trans*, *trans*-isomer **9c**); −80.6 (tt, $^3J(F^4, F^3)$ = 3 Hz, $^4J(F^4, F^2)$ = 10 Hz, 3F, F^4), −123.8 (m, 2F, F^2), −125.4 (m, 2F, F^3), −133.0 (m, 2F, F^1), −150.9 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3^-) ($[C_4F_9BF_3]^-$); −148.0 (s, $[BF_4]^-$).

4.15. Reaction of $C_6F_{13}BF_2$ with BrF_3

A cold (−15 °C) solution of BrF_3 (0.30 mmol) in PFP (0.5 mL) was added in one portion to a cold (−65 °C) solution of $C_6F_{13}BF_2$ (0.50 mmol) in PFP (3 mL). After stirring at −60 °C for 1 h the solution contained still residual $C_6F_{13}BF_2$ besides the products $C_6F_{13}Br$ and C_6F_{14} (55:22:23) (^{19}F NMR). A second portion of BrF_3 (0.20 mmol) in PFP (0.2 mL) was added at −60 °C. The solution was stirred at −60 °C for 1 h and then at −10 °C for 1 h. The NMR spectra displayed resonances of $C_6F_{13}Br$ and C_6F_{14} (1:1) besides traces of $C_6F_{13}BF_2$ (^{19}F NMR) and BF_3 (^{11}B NMR). To determine the quantity of unreacted BrF_3, the solution was treated with C_6F_5H

(93 mg, 0.55 mmol) at −5 °C for 1.5 h. The ^{19}F NMR spectrum showed partial conversion of C_6F_5H (0.30 mmol, unreacted) into C_6F_5Br (0.11 mmol), 1-H-heptafluorocyclohexa-1,4-diene (0.08 mmol) and 1-bromoheptafluorocyclohexa-1,4-diene (trace). Thus, ca. 0.30 mmol of BrF_3 had reacted with $C_6F_{13}BF_2$.

4.16. Reactions of $C_8F_{17}Br$ with BrF_3 and with $[BrF_2][SbF_6]$

(A) A solution of $C_8F_{17}Br$ (179 mg, 0.35 mmol) and BrF_3 (35 mg, 0.25 mmol) in PFB (0.5 mL) was stirred at 24 °C for 17 h. The ^{19}F NMR spectrum displayed resonances of the unchanged starting materials $C_8F_{17}Br$ (−62.7 (CF_2Br), −80.3 (CF_3), −116.2, −119.7, −120.5, −121.5, −125.1 ($6CF_2$) ppm) and BrF_3 (−14.6 ppm) besides PFB.

(B) The above solution was cooled to 0 °C and BF_3 was bubbled into the solution for 5 min before the solution was kept at 24 °C for 1 h. The ^{19}F and ^{11}B NMR spectra showed the formation of "$BrF_3{\cdot}BF_3$" ($\delta(F)$: −87 ppm and $\delta(B)$: 2.4 ppm) besides unchanged $C_8F_{17}Br$. When the solution was kept at 24 °C for 3 d, perfluorooctane was formed in quantitative yield.

(C) A solution of $[BrF_2][SbF_6]$ (46 mg, 0.13 mmol) in aHF (1 mL) was cooled to −40 °C and $C_8F_{17}Br$ (0.4 mL) was added. The mixture was stirred at 24 °C for 3 h before the upper acidic phase was decanted at 10 °C. The ^{19}F NMR spectrum of the organic phase confirmed the quantitative formation of C_8F_{18}.

4.17. Reaction of K[cis-$C_2F_5CF{=}CFBF_3$] with BrF_3 in aHF

A solution of K[*cis*-$C_2F_5CF{=}CFBF_3$] (190 mg, 0.66 mmol) in aHF (1.6 mL) was cooled to −40 °C and a cold (−30 °C) solution of BrF_3 (94 mg, 0.68 mmol) in aHF (0.6 mL) was added in portions. The reaction mixture was stirred at −30 °C for 2 h and at −20 °C for 0.5 h forming a suspension. The ^{19}F NMR spectrum showed the complete consumption of [*cis*-$C_2F_5CF{=}CFBF_3]^-$, but signals of $[(C_2F_5CF{=}CF)_2Br]^+$ were not detected. The reaction mixture was extracted with CCl_2FCClF_2 (1 mL). The extract contained $C_2F_5CFBrCF_3$ (0.40 mmol, 60%) (^{19}F NMR). The acidic phase was evaporated to dryness in vacuum and the solid residue was extracted with MeCN (1 mL). The ^{11}B and ^{19}F NMR spectra showed the formation of $K[C_2F_5CFBrCF_2BF_3]$ (0.10 mmol, 15%).

2-Bromoperfluorobutane (**25**). ^{19}F NMR (CCl_2FCClF_2, 24 °C): δ −75.9 (qdd, $^5J(F^1, F^4)$ = 5 Hz, $^4J(F^1, F^{3A})$ = 8 Hz, $^4J(F^1, F^{3B})$ = 12 Hz, 3F, F^1), −79.0 (qd, $^5J(F^4, F^1)$ = 5 Hz, $^4J(F^4, F^2)$ = 11 Hz, 3F, F^4), −116.6 (qdd, $^4J(F^{3A}, F^1)$ = 8 Hz, $^3J(F^{3A}, F^2)$ = 8 Hz, $^2J(F^{3A}, F^{3B})$ = 286 Hz, 1F, F^{3A}), −118.1 (qdd, $^4J(F^{3B}, F^1)$ = 12 Hz, $^3J(F^{3B}, F^2)$ = 10 Hz, $^2J(F^{3B}, F^{3A})$ = 286 Hz, 1F, F^{3B}), −140.9 (qt, $^4J(F^2, F^4)$ = 11 Hz, $^3J(F^2, F^3)$ = 9 Hz, 1F, F^2) (lit. [45]: ^{19}F NMR (neat, −20 °C): δ −76.3 (3F), −79.3 (3F), −117.8 (2F), −141.4 (1F)). ^{19}F NMR (aHF, −20 °C): δ −74.3 (qdd, $^5J(F^1, F^4)$ = 4 Hz, $^4J(F^1, F^{3A})$ = 9 Hz, $^4J(F^1, F^{3B})$ = 12 Hz, 3F, F^1), −77.4 (qd, $^5J(F^4, F^1)$ = 4 Hz, $^4J(F^4, F^2)$ = 11 Hz, 3F, F^4), −115.3 (qdd, $^4J(F^{3A}, F^1)$ = 8 Hz, $^3J(F^{3A}, F^2)$ = 8 Hz, $^2J(F^{3A}, F^{3B})$ = 287 Hz, 1F, F^{3A}), −116.2 (qdd, $^4J(F^{3B}, F^1)$ = 12 Hz, $^3J(F^{3B}, F^2)$ = 11 Hz, $^2J(F^{3B}, F^{3A})$ = 287 Hz, 1F, F^{3B}), −139.7 (qt, $^4J(F^2, F^4)$ = 11 Hz, $^3J(F^2, F^3)$ = 9 Hz, 1F, F^2).

$K[C_2F_5CFBrCF_2BF_3]$ (**K-11**). ^{19}F NMR (CH_3CN, 24 °C): δ −77.3 (dt, $^4J(F^4, F^2)$ = 5 Hz, $^3J(F^4, F^3)$ = 9 Hz, 3F, F^4), −114.3 (qddd, $^3J(F^{3A}, F^4)$ = 8 Hz, $^3J(F^{3A}, F^{1A})$ = 12 Hz, $^3J(F^{3A}, F^{1B})$ = 20 Hz, $^2J(F^{3A}, F^{3B})$ = 284 Hz, 1F, F^{3A}), −115.6 (md, $^2J(F^{3B}, F^{3A})$ = 284 Hz, 1F, F^{3B}), −118.7 (d, $^2J(F^{1A}, F^{1B})$ = 319 Hz, 1F, F^{1A}), −122.0 (d, $^2J(F^{1B}, F^{1A})$ = 319 Hz, 1F, F^{1B}), −136.1 (m, 1F, F^2), −149.4 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3^-). ^{11}B NMR (CH_3CN, 24 °C): δ −0.7 (tq, $^2J(B, F^1)$ = 20 Hz, $^1J(B, F)$ = 41 Hz, BF_3^-). ^{19}F NMR (aHF, −20 °C): δ −76.8 (ddd, $^4J(F^4, F^2)$ = 4 Hz, $^3J(F^4, F^{3A})$ = 8 Hz, $^3J(F^4, F^{3B})$ = 11 Hz, 3F, F^4), −114.2 (md, $^2J(F^{3A}, F^{3B})$ = 286 Hz, 1F, F^{3A}), −115.8 (md, $^2J(F^{3B}, F^{3A})$ = 286 Hz, 1F, F^{3B}), −117.8 (md, $^2J(F^{1A}, F^{1B})$ = 326 Hz, 1F, F^{1A}), −122.6 (md, $^2J(F^{1B}, F^{1A})$ = 326 Hz, 1F, F^{1B}), −136.6 (m, 1F, F^2), −146.8 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3^-). ^{11}B NMR (aHF, −20 °C): δ −0.2 (s, $\Delta\nu_{1/2}$ = 90 Hz, BF_3^-).

4.18. Reaction of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ with BrF_3 in PFB

A cold (−20 °C) solution of BrF_3 (0.29 mmol) in PFB (0.1 mL) was added to a cold (−20 °C) stirred solution of $[Bu_4N][cis\text{-}C_2F_5CF = CFBF_3]$ (0.29 mmol) in PFB (0.6 mL). The colorless solution was stirred at −20 °C for 1 h and warmed to 20 °C. The ^{11}B and ^{19}F NMR spectra showed resonances of $[C_2F_5CFBrCF_2BF_3]^-$, $C_2F_5CF{=}CF_2$, and $[BF_4]^-$ (53:37:10) besides signals of PFB.

$[Bu_4N][C_2F_5CFBrCF_2BF_3]$ (**TBA-11**). ^{19}F NMR (PFB, 24 °C): δ −77.1 (dt, $^4J(F^4, F^2)$ = 5 Hz, $^3J(F^4, F^3)$ = 10 Hz, 3F, F^4), −113.6 (d, $^2J(F^{3A}, F^{3B})$ = 284 Hz, 1F, F^{3A}), −115.1 (d, $^2J(F^{3B}, F^{3A})$ = 284 Hz, 1F, F^{3B}), −117.5 (d, $^2J(F^{1A}, F^{1B})$ = 324 Hz, 1F, F^{1A}), −121.1 (d, $^2J(F^{1B}, F^{1A})$ = 324 Hz, 1F, F^{1B}), −134.6 (m, 1F, F^2), −147.0 (m, 3F, BF_3^-). ^{11}B NMR (PFB, 24 °C): δ −1.0 (tq, $^2J(B, F^1)$ = 20 Hz, $^1J(B, F)$ = 40 Hz, BF_3^-).

4.19. Reaction of $K[C_6F_{13}BF_3]$ with $[BrF_2][SbF_6]$

A cold (−15 °C) solution of $[BrF_2][SbF_6]$ (56 mg, 0.15 mmol) in aHF (0.7 mL) was added in portions to a cold (−15 °C) stirred solution of $K[C_6F_{13}BF_3]$ (151 mg, 0.35 mmol) in aHF (1.5 mL). After stirring at 20 °C for 6 h only signals of unchanged $K[C_6F_{13}BF_3]$ were detected in the solution.

5. Conclusions

Reactions of BrF_3 with R_FBF_2 (R_F = perfluorinated aryl, alkenyl, and alkynyl group) in weakly coordinating solvents like CH_2Cl_2 or better in PFB, PFP present a convenient preparative route to bis(perfluoroorganyl)bromonium salts. Comparing reactions of BrF_3 with $C_6F_5BF_2$, $C_6F_5SiF_3$, and $C_6F_5SiMe_3$ showed the influence of the acidity (fluoride affinity) on the reaction rate for the first and second F/C_6F_5 substitution step: $C_6F_5BF_2$ gives only bromonium salts, $C_6F_5SiF_3$ allowed the aimed synthesis as well of $C_6F_5BrF_2$ as of $[(C_6F_5)_2Br]^+$ salts, whereas in case of $C_6F_5SiMe_3$ only $C_6F_5BF_2$ is accessible. The 1:2 reaction of BrF_3 with $C_6F_{13}BF_2$ in PFP gave $C_6F_{13}Br$ and C_6F_{14} (1:1) as the only perfluoroalkyl compounds, which may be considered as products of decomposition of the unstable salt $[(C_6F_{13})_2Br][C_6F_{13}BF_3]$. The instability can be attributed to electrostatic repulsion between high partial positive charge on bromine and both ipso carbon atoms of the perfluoroalkyl groups. The 3:2 molar reaction of BrF_3 with $(C_6F_5)_3B$ (more acidic than $C_6F_5BF_2$) ended with $[(C_6F_5)_2Br][(C_6F_5)_nBF_{4-n}]$ salts with anion mixtures (n = 0–3) and showed that boranes $(C_6F_5)_nBF_{3-n}$ (n = 1–3) operate here as intermediate transfer reagents. Finally, salts $[(C_6F_5)_2Br]Y$ can be prepared from BrF_3 or $[BrF_2][SbF_6]$ (Br^{III}-electrophile) and $K[C_6F_5BF_3]$ (C-nucleophile) in aHF. This route failed for the synthesis of perfluoroalkenylbromonium and -alkylbromonium salts $[(R_F)_2Br]Y$.

Acknowledgement

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

[1] A.N. Nesmeyanov, T.P. Tolstaya, L.S. Isaeva, Dokl. Akad. Nauk SSSR 104 (1955) 872–875 (Chem. Abstr. 50 (1956) 11266).
[2] A.N. Nesmeyanov, T.P. Tolstaya, L.S. Isaeva, Dokl. Akad. Nauk SSSR 117 (1957) 996–999 (Chem. Abstr. 52 (1958) 8069).
[3] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, N.S. Khrushcheva, T.P. Tolstaya, Dokl. Akad. Nauk SSSR 254 (1980) 652–656 (Chem. Abstr. 94 (1981) 174489).
[4] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Lazarev, T.P. Tolstaya, Dokl. Akad. Nauk. SSSR 255 (1980) 1136–1140 (Chem. Abstr. 95 (1981) 24402).

[5] A.N. Nesmeyanov, A.N. Vanchikov, I.N. Lisichkina, V.V. Grushin, T.P. Tolstaya, Dokl. Akad. Nauk. SSSR 255 (1980) 1386–1389 (Chem. Abstr. 95 (1981) 6664).
[6] G.A. Olah, Halonium Ions, Wiley, New York, 1975.
[7] G.A. Olah, K.K. Laali, Q. Wang, Onium Ions, Wiley, New York, 1998, 246-268.
[8] T.W. Bastock, M.E. Harley, A.E. Pedler, J.C. Tatlow, J. Fluorine Chem. 6 (1975) 331–355.
[9] V.V. Bardin, G.G. Furin, G.G. Yakobson, Zh. Org. Khim. 17 (1981) 999–1004; V.V. Bardin, G.G. Furin, G.G. Yakobson, J. Org. Chem. USSR (Eng. Transl.) 17 (1981) 879–884.
[10] V.V. Bardin, G.G. Furin, G.G. Yakobson, J. Fluorine Chem. 23 (1983) 67–86.
[11] H.-J. Frohn, M. Giesen, D. Welting, G. Henkel, Eur. J. Solid State Inorg. Chem. 33 (1996) 841–853.
[12] H.-J. Frohn, M. Hirschberg, A. Wenda, V.V. Bardin, J. Fluorine Chem. 129 (2008) 459–473.
[13] J. Helber, H.-J. Frohn, A. Klose, T. Scholten, ARKIVOC vi (2003) 71–82.
[14] H.-J. Frohn, V.V. Bardin, Organometallics 20 (2001) 4750–4762.
[15] H.-J. Frohn, V.V. Bardin, in: K.K. Laali (Ed.), Recent Developments in Carbocation and Onium Ion Chemistry, ACS Symposium Series 965, ACS, Washington, DC, 2007, pp. 428–457.
[16] T. Cyr, S. Brownstein, J. Inorg. Nucl. Chem. 39 (1977) 2143–2145.
[17] H.-J. Frohn, M. Giesen, J. Fluorine Chem. 24 (1984) 9–15.
[18] K. Koppe, V. Bilir, H.-J. Frohn, H.P.A. Mercier, G.J. Schrobilgen, Inorg. Chem. 46 (2007) 9425–9437.
[19] V.V. Bardin, H.-J. Frohn, Main Group Met. Chem. 25 (2002) 589–613.
[20] H.-J. Frohn, V.V. Bardin, Mendeleev Commun. 17 (2007) 137–138.
[21] T. Surles, H.H. Hyman, L.A. Quaterman, A.I. Popov, Inorg. Chem. 10 (1971) 611–613.
[22] H. Meinert, U. Gross, J. Fluorine Chem. 2 (1972/1973) 381–386.
[23] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 628 (2002) 1853–1856.
[24] H.-J. Frohn, P. Barthen, F. Bailly, K. Koppe, in: Proceedings 1st Int. Conf. Hypervalent Iodine, Thessalonki September, (2001), pp. 109–111.
[25] H.-J. Frohn, F. Bailly, D. Welting, V.V. Bardin, J. Fluorine Chem. 130 (2009) 301–307.
[26] A. Abo-Amer, H.-J. Frohn, Chr. Steinberg, U. Westphal, J. Fluorine Chem. 127 (2006) 1311–1323.
[27] H.-J. Frohn, F. Bailly, V.V. Bardin, Mendeleev Commun. 19 (2009) 67–68.
[28] H.-J. Frohn, T. Schroer, J. Fluorine Chem. 112 (2001) 259–264.
[29] (a) E.S. Lo, J.D. Readio, S.D. Osborn, J. Org. Chem. 38 (1973) 907–909; (b) B.-N. Huang, A. Haas, M. Lieb, J. Fluorine Chem. 36 (1987) 49–62.
[30] T.I. Filyakova, M.I. Kodess, A.Ya. Zapevalov, Zh. Org. Khim. 34 (1998) 1317–1323; T.I. Filyakova, M.I. Kodess, A.Ya. Zapevalov, Russ. J. Org. Chem. 34 (1998) 1256–1259.
[31] V.V. Bardin, J. Fluorine Chem. 89 (1998) 195–211.
[32] H.-J. Frohn, M.E. Hirschberg, R. Boese, D. Bläser, U. Flörke, Z. Anorg. Allg. Chem. 634 (2008) 2539–2550.
[33] H.-J. Frohn, M. Giesen, A. Klose, A. Lewin, V.V. Bardin, J. Organomet. Chem. 506 (1996) 155–164.
[34] M. Fild, O. Glemser, G. Christoph, Angew. Chem. 76 (1964) 953.
[35] N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, Z. Anorg. Allg. Chem. 633 (2007) 647–652.
[36] H.-J. Frohn, H. Franke, P. Fritzen, V.V. Bardin, J. Organomet. Chem. 598 (2000) 127–135.
[37] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 627 (2001) 2499–2505.
[38] A.W. Laubengayer, D.S. Sears, J. Am. Chem. Soc. 67 (1945) 164–167.
[39] H.-J. Frohn, N.Yu. Adonin, V.V. Bardin, Z. Anorg. Allg. Chem. 629 (2003) 2499–2508.
[40] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, J. Fluorine Chem. 128 (2007) 699–702.
[41] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 627 (2001) 15–16.
[42] H.-J. Frohn, F. Bailly, V.V. Bardin, Z. Anorg. Allg. Chem. 628 (2001) 723–724.
[43] V.V. Bardin, S.G. Idemskaya, H.-J. Frohn, Z. Anorg. Allg. Chem. 628 (2002) 883–895.
[44] T.E. Stevens, J. Org. Chem. 26 (1961) 1627–1630.
[45] P.L. Coe, S.F. Sellers, J.C. Tatlow, H.C. Fielding, G. Whittaker, J. Fluorine Chem. 18 (1981) 417–439.