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Reactions of Perfluorinated Alkenyl-, Alkynyl-, Alkyltrifluoroborates, and Selected Hydrocarbon Analogues with the Halogenating Agents Hal_2 (Hal = F, Cl, Br), "BrF" (BrF_3–Br_2 1:1), and ICl

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Dedicated to Professor Helge Willner on the Occasion of His 65th Birthday

Keywords: Alkenyltrifluoroborates; Alkynyltrifluoroborates; Alkyltrifluoroborates; 1,2-Halogen addition; Bromofluorination; Halodeboration; Stereospecifity; NMR spectroscopy

Abstract. Reactions of $[Bu_4N][RBF_3]$ [$R = C_nF_{2n+1}CF{=}CF$ (*cis*, *trans*), $CF_2{=}CF$, $CF_2{=}C(CF_3)$, *trans*-$C_4H_9CF{=}CF$, *trans*-$C_6H_5CF{=}CF$, $C_4H_9CH{=}CH$ (*cis*, *trans*), $CF_3C{\equiv}C$, and $C_4H_9C{\equiv}C$] with chlorine, bromine, BrF_3 + Br_2 (as equivalent of "BrF"), and ICl in solution (CH_2Cl_2, $CHCl_3$, $CF_3CH_2CF_2CH_3$) led to 1,2-addition of halogen and/or replacement of boron by halogen (halodeboration). The reaction of $[Bu_4N][CF_3C{\equiv}CBF_3]$ with less than equimolar amounts of diluted fluorine (5%) in 1,1,1,3,3-pentafluorobutane (PFB) showed only $[Bu_4N][CF_3CF_2CF_2BF_3]$ as fluorine addition product besides extensive fluorodeboration. Suspensions of the insoluble $K[CF_2{=}CFBF_3]$ salt reacted with Cl_2 and Br_2 in CH_2Cl_2 giving preferentially products of halogen addition across the C=C bond. In reactions with ICl iododeboration with formation of $CF_2{=}CFI$ occurred besides 1,2-addition with formation of $[CF_2I–CFClBF_3]^-$. The halodeboration reaction of $[Bu_4N][$*trans*-$C_4H_9CF{=}CFBF_3]$ with Br_2, "BrF", and ICl, of $K[$*trans*-$C_6H_5CF{=}CFBF_3]$ with Br_2, and of $[Bu_4N][$*trans*-$C_4F_9CF{=}CFBF_3]$ with ICl proceeded stereospecifically.

Introduction

During the last decade we elaborated convenient protocols for the synthesis of perfluorinated aryl-, alkenyl-, alkynyl-, alkyltrifluoroborates, and related analogues.[1,2] These borates were mainly used as precursors for the corresponding organyldifluoroboranes by fluoride abstraction with boron trifluoride or arsenic pentafluoride. Organyldifluoroboranes were the reagents by choice to introduce the corresponding organyl groups into hypervalent moieties of halogen fluorides and xenon fluorides and allowed the synthesis of organyliodonium(III and V),[3] organylbromonium(III),[4,5] and organylxenonium(II and IV)[6] salts. Other reactivities of polyfluoroorganyl(fluoro)borates are only rarely investigated. Potassium polyfluorophenyltrifluoroborates and trifluoroethenyltrifluoroborates were involved in platinum-catalyzed cross-coupling reactions with carbon electrophiles to give polyfluorobiphenyls or polyfluorostyrenes, respectively.[7–9] The nickel-catalyzed hydrodefluorination of potassium pentafluorophenyltrifluoroborate with zinc in aqueous DMF, DMA, or NMP displayed the unexpected *ortho*-directing effect of the weakly coordinating BF_3^- substituent and resulted in the formation of the 2,3,4,5-tetrafluorophenyltrifluoroborate anion and 1,2,3,4-tetrafluorobenzene.[10] We reported the carbon–boron bond cleavage in a series of polyfluorinated organyltrifluoroborates and their hydrocarbon analogues (hydrodeboration reactions) with protic acids of different strength[11] and had found the stereospecific replacement of the BF_3^- group by hydrogen in $K[RCF{=}CFBF_3]$ to form the corresponding polyfluoroalkenes *R*CF=CFH. Fluorine addition across the C=C bond took place when perfluoroalkenyltrifluoroborates were treated with xenon difluoride in super acidic anhydrous hydrogen fluoride (aHF).[12] When XeF_2 was reacted with *R*CF=$CFBF_2$ (*R* = H, F, *cis*-CF_3, *cis*-C_2F_5) in halocarbon solvents (CH_2Cl_2, $CF_3CH_2CF_2CH_3$) xenonium salts [*R*CF=CFXe]*X* were formed with two types of anions, *X* = $[BF_4]^-$ and $[RCF_2–CF_2BF_3]^-$.[13] Analogous products were observed in the reaction of XeF_2 with $CF_2{=}CClBF_2$ in PFB,[14] whereas no organyltrifluoroborate anions were formed in reactions of alkynyldifluoroboranes $RC{\equiv}CBF_2$ [*R* = CF_3, C_3F_7, $(CF_3)_2CF$, $CF_3CF{=}CF$ (*cis* and *trans*), C_6F_5, C_4H_9, $(CH_3)_3C$] with XeF_2 under similar conditions.[15]

In the course of systematic studies of perfluoroorganylboron compounds, we investigated reactions of perfluorinated alk-

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Dedicated Cluster

1-enyltrifluoroborates, alk-1-ynyltrifluoroborates, and selected low-fluorinated and non-fluorinated analogues and alkyltrifluoroborates with halogenating agents of different nature [fluorine, chlorine, bromine, bromine trifluoride + bromine (1:1, "BrF"), and iodine chloride] in halocarbon solvents (CH_2Cl_2, $CHCl_3$, $CF_3CH_2CF_2CH_3$).

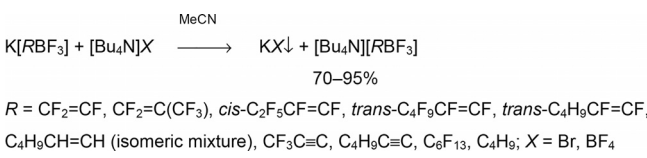
For convenience, the substituent *R′* at C-2 in $R'C^2F = C^1FX$ molecules or ions is specified by *cis* or *trans* relative to the position of $X = BF_3^-$ or Hal. The fluorine atoms in the $F_2C{=}CXY$ moiety are specified by *cis* or *trans* relative to the position of $X = BF_3^-$ and iodine (Y = F, CF_3, CF_2Cl).

Halodeboration of $[RBF_3]^-$ by dihalogen (Cl_2, Br_2) or interhalogen (ICl) should result in *R*Cl, *R*Br, or *R*I and $[BClF_3]^-$ or $[BBrF_3]^-$, respectively. In all reactions with Cl_2 and Br_2 we observed unambiguously only $[BF_4]^-$ (^{19}F, ^{11}B). Principally, equilibration by halide exchange may lead to $[BF_4]^-$: $4[BHalF_3]^- \leftrightarrows 3[BF_4]^- + <[BHal_4]^->$. We did not obtain NMR spectroscopic results, which agree with the reported data of $[BF_nHal_{4-n}]^-$ (Hal = Cl, Br; n = 0–3).[16,17]

Results

Preparation of Tetrabutylammonium Organyltrifluoroborates

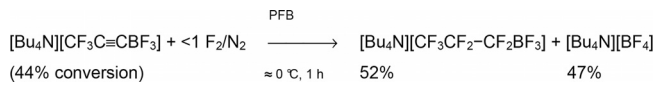
In our current study we compare the reactivities of organyltrifluoroborates towards selected halogenating agents in solution and on the surface of the salts. We chose tetrabutylammonium organyltrifluoroborates as soluble salts in dichloromethane, chloroform, and 1,1,1,3,3-pentafluorobutane (PFB) and potassium organyltrifluoroborates as insoluble salts in dichloromethane. The tetrabutylammonium salts can be easily prepared from the corresponding potassium salts by metathesis with $[Bu_4N]X$ (X = Br, BF_4) in MeCN in high yields (Scheme 1). Compared with reactions of $[Bu_4N]OH$ in aqueous solution or related approaches[18] this procedure guarantees dry products, which is important for the use of $[Bu_4N][RBF_3]$ salts under anhydrous conditions in subsequent reactions.



Scheme 1.

Reaction of Tetrabutylammonium Trifluoropropynyltrifluoroborate with Fluorine in PFB Solution

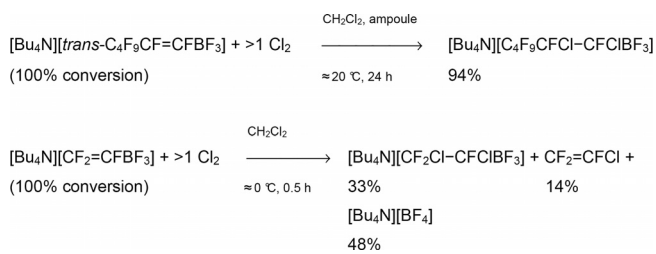
Generally, the result of reactions of organic compounds with elemental fluorine is determined inter alia by a number of process-factors including the design of the reactor. In the current study we bubbled fluorine diluted with nitrogen (5% v/v) through a stirred diluted solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ in PFB at ≈0 °C. Monitoring of the reaction with less than one equivalent of fluorine by ^{19}F NMR spectroscopy confirmed the multiple addition of fluorine across the C≡C bond forming $[Bu_4N][CF_3CF_2{-}CF_2BF_3]$. The yield decreased slightly from 60 to 52% with the increase of conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$ from 10 to 44%. Parallel the cleavage of the carbon–boron bond proceeded, indicated by the ratio $[Bu_4N][BF_4]$ to $[Bu_4N][CF_3CF_2{-}CF_2BF_3]$, which grew from 0.56 to 0.90. The ^{19}F NMR signals of the low boiling perfluorocarbon co-products as well as the resonances (^{11}B, ^{19}F) of the intermediate borate anion $[CF_3CF{=}CFBF_3]^-$ were not detected (Scheme 2).



Scheme 2.

Reactions of Tetrabutylammonium Perfluoroalkenyl- and Perfluoroalkynyltrifluoroborates with Chlorine in Halocarbon Solutions

A solution of $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$ was saturated with Cl_2 (excess) and kept at approximately 20 °C for 24 h in a sealed tube. After evaporation of the volatiles, $[Bu_4N][C_4F_9CFCl{-}CFClBF_3]$ was obtained in 94% yield. $[Bu_4N][CF_2{=}CFBF_3]$ reacted faster than $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$. Bubbling of Cl_2 (excess) into a solution (≈0 °C) of $[Bu_4N][CF_2{=}CFBF_3]$ in dichloromethane resulted in the total conversion of $[Bu_4N][CF_2{=}CFBF_3]$ within 0.5 h with formation of $[Bu_4N][CF_2Cl{-}CFClBF_3]$, $CF_2{=}CFCl$, and $[Bu_4N][BF_4]$ (molar ratio = 33:14:48) (Scheme 3).



Scheme 3.

$[Bu_4N][CF_3C{\equiv}CBF_3]$ reacted with an excess of Cl_2 at approximately 20 °C slower than $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$ and $[Bu_4N][CF_2{=}CFBF_3]$. Bubbling of Cl_2 into a solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (≈0 °C) and reacting the mixture in a sealed tube (≈20 °C) for 24 h resulted in 62% conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$ and gave $[Bu_4N][CF_3CCl{=}CClBF_3]$ (54%, *cis*/*trans* = 46:54), $[Bu_4N][CF_3CCl_2{-}CCl_2BF_3]$ (4%), $[Bu_4N][BF_4]$ (42%), trace quantities of $CF_3C{\equiv}CCl$, $CF_3CCl_2{-}CCl_3$, besides minor amounts of unknown products (Scheme 4).

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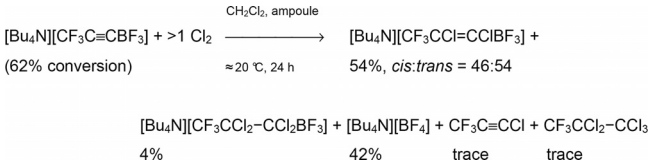


Scheme 4.

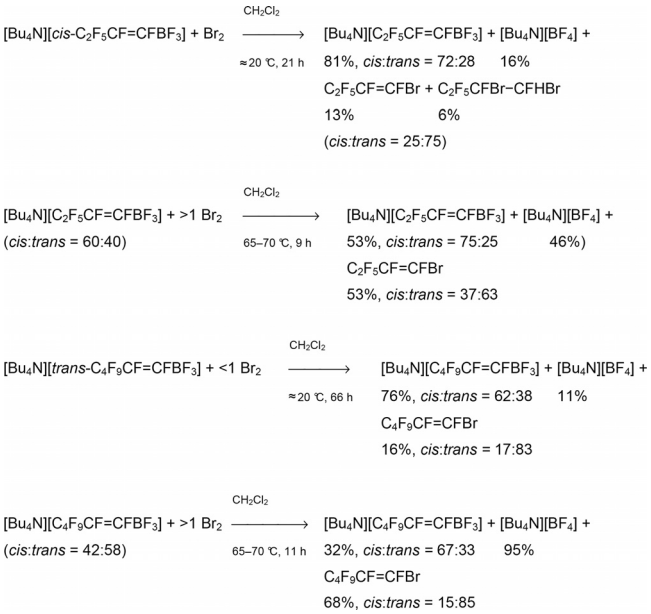
The further treatment of such a solution with a new excess of chlorine (≈20 °C, sealed tube) for additional 33 h led to the total consumption of $[Bu_4N][CF_3C{\equiv}CBF_3]$ and the majority of $[Bu_4N][cis\text{-}CF_3CCl{=}CClBF_3]$. The ^{11}B and ^{19}F NMR spectra displayed the signals of $[Bu_4N][trans\text{-}CF_3CCl{=}CClBF_3]$ (59 %), $[Bu_4N][cis\text{-}CF_3CCl{=}CClBF_3]$ (< 3 %), $[Bu_4N][CF_3CCl_2{-}CCl_2BF_3]$ (8 %), and $[Bu_4N][BF_4]$ (26 %), besides several unknown compounds, which contained CF_3 groups. The formation of $CF_3CCl{=}CCl_2$ was not detected. Noteworthy, that partial chlorination of the tetrabutylammonium cation proceeded, which was deduced from the ^1H NMR spectra of the reaction solution.

Reactions of Tetrabutylammonium Organyltrifluoroborates with Bromine in Halocarbon Solutions

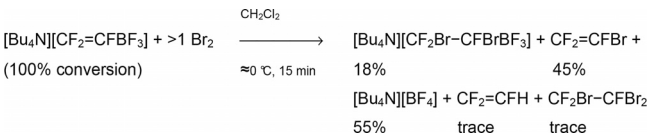
Solutions of $[Bu_4N][C_nF_{2n+1}CF{=}CFBF_3]$ in CH_2Cl_2 reacted with Br_2 at approximately 20 °C slowly forming bromoperfluoroalkenes, -alkanes, and $[Bu_4N][BF_4]$. These reactions were accompanied by *cis*/*trans* isomerization of the starting borates. Perfluoro-1,2-dibromoalkyltrifluoroborates were not detected as intermediates in such isomerization processes. Thus, $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ and an equimolar amount of Br_2 gave after 21 h an isomeric mixture of $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (*cis*/*trans* = 72:28) besides smaller quantities of $C_2F_5CF{=}CFBr$, $C_2F_5CFBr{-}CFHBr$, and $[Bu_4N][BF_4]$. Heating of $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (*cis*/*trans* = 60:40) with Br_2 (in excess) in CH_2Cl_2 (65–70 °C, 9 h) gave $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (*cis*/*trans* = 75:25), $C_2F_5CF{=}CFBr$, and $[Bu_4N][BF_4]$. Similarly, $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$ was partially isomerized (≈20 °C) after 66 h (*cis*/*trans* = 62:38) and $C_4F_9CF{=}CFBr$ (*cis*/*trans* = 17:83), and $[Bu_4N][BF_4]$ were formed. When the reaction was performed in the absence of day-light, or $[Bu_4N][C_4F_9CF{=}CFBF_3]$ was treated with Br_2 at 65–70 °C for 11 h, the same products were obtained (Scheme 5).

$[Bu_4N][CF_2{=}CFBF_3]$ reacted fast with an excess of Br_2 to yield $[Bu_4N][CF_2Br{-}CFBrBF_3]$, $CF_2{=}CFBr$, and $[Bu_4N][BF_4]$ (Scheme 6). The formation of $[Bu_4N][CF_2Br{-}CFBrBF_3]$ was the only example of bromine addition to the C=C bond of an alk-1-enyltrifluoroborate observed in this study.

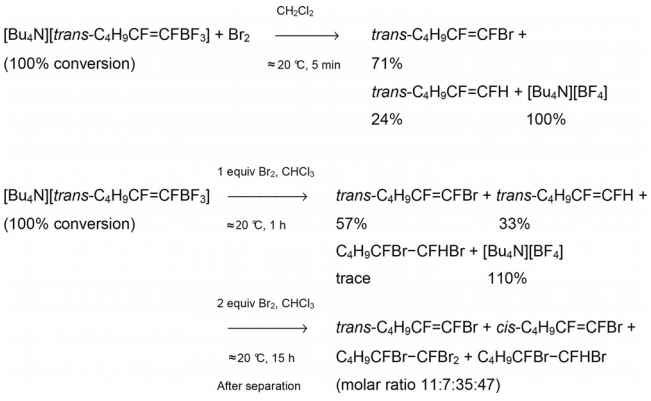
$[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ reacted with Br_2 (1 equiv.) in CH_2Cl_2 to yield *trans*-$C_4H_9CF{=}CFBr$, *trans*-$C_4H_9CF{=}CFH$, and $[Bu_4N][BF_4]$. The reaction in $CHCl_3$ proceeded in a similar way. When adding a second equivalent of Br_2 *trans*-$C_4H_9CF{=}CFBr$ was partially isomerized to *cis*-$C_4H_9CF{=}CFBr$ and both isomers underwent partial addition of bromine to form $C_4H_9CFBr{-}CFBr_2$. *Trans*-$C_4H_9CF{=}CFH$ added Br_2 and was completely converted to $C_4H_9CFBr{-}CFHBr$ (Scheme 7).



Scheme 5.

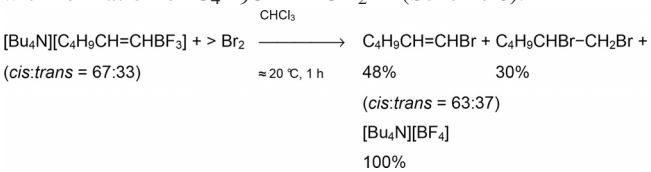


Scheme 6.



Scheme 7.

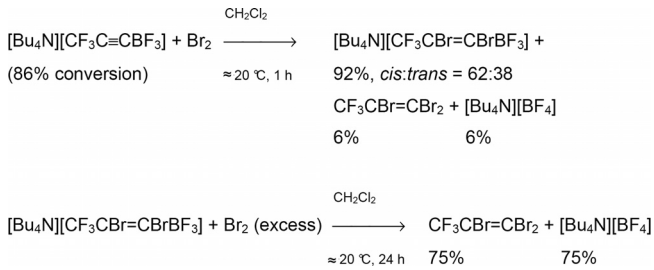
$[Bu_4N][C_4H_9CH{=}CHBF_3]$ (*cis*/*trans* = 67:33) and an excess of Br_2 underwent bromodeboration in $CHCl_3$ at approximately 20 °C to $C_4H_9CH{=}CHBr$ (*cis*/*trans* = 63:37). Furthermore $C_4H_9CHBr{-}CH_2Br$ and $[Bu_4N][BF_4]$ were present. Hex-1-ene was not detected, presumable due to a fast addition of bromine with formation of $C_4H_9CHBr{-}CH_2Br$ (Scheme 8).



Scheme 8.

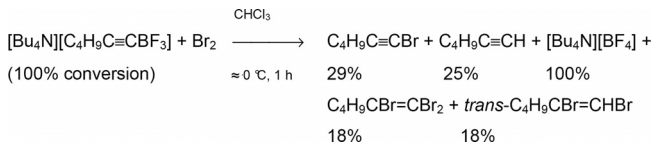
The conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$ with Br_2 (1 equiv.) was 86 % after 1 h at approximately 20 °C and resulted in

$[Bu_4N][CF_3CBr{=}CBrBF_3]$ (*cis*/*trans* = 62:38), small amounts of $CF_3CBr{=}CBr_2$, and $[Bu_4N][BF_4]$. $[Bu_4N][CF_3CBr{=}CBrBF_3]$ and an excess of Br_2 underwent C–B bond splitting to alkene $CF_3CBr{=}CBr_2$. Bromine addition across the C=C bond of $[Bu_4N][CF_3CBr{=}CBrBF_3]$ did not occur (Scheme 9).



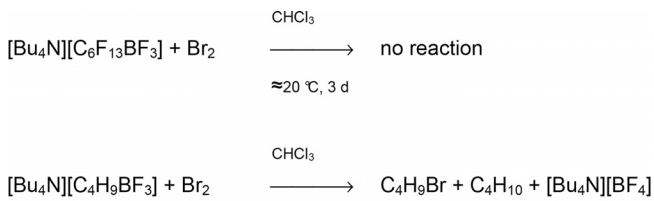
Scheme 9.

Bromine and a cold $CHCl_3$ solution of $[Bu_4N][C_4H_9C{\equiv}CBF_3]$ formed $C_4H_9C{\equiv}CBr$, $C_4H_9C{\equiv}CH$, besides $[Bu_4N][BF_4]$, $C_4H_9CBr{=}CBr_2$, and *trans*-$C_4H_9CBr{=}CHBr$, whereas *cis*-$C_4H_9CBr{=}CHBr$ was only present as a trace (Scheme 10). With an excess of bromine hexynes $C_4H_9C{\equiv}CH$ and $C_4H_9C{\equiv}CBr$ were completely converted into the alkenes *trans*-$C_4H_9CBr{=}CHBr$ and $C_4H_9CBr{=}CBr_2$, respectively.



Scheme 10.

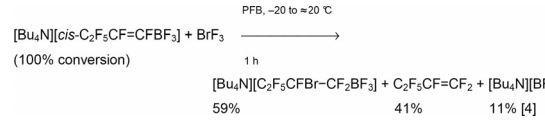
Noteworthy that $[Bu_4N][C_6F_{13}BF_3]$ did not react with bromine, while $[Bu_4N][C_4H_9BF_3]$ reacted within 1 h under C–B bond cleavage under bromo- and protodeboration (Scheme 11).



Scheme 11.

Reactions of Tetrabutylammonium Fluoroalkenyl- and Fluoroalkynyltrifluoroborates with BrF_3–Br_2 (1:1, Equivalent of "BrF") in Halocarbon Solutions

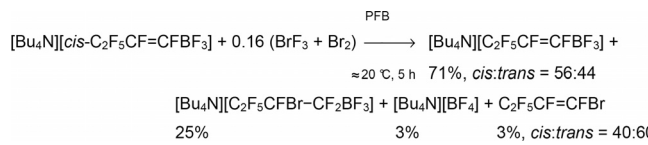
In a preceding paper[4] we showed that the reaction of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ with BrF_3 in PFB followed two routes: (a) addition of BrF across the C=C bond with formation of $[Bu_4N][C_2F_5CFBr–CF_2BF_3]$ and (b) cleavage of the C–B bond with formation of $C_2F_5CF{=}CF_2$ (ratio $[Bu_4N][C_2F_5CFBr–CF_2BF_3]/C_2F_5CF{=}CF_2$ = 59:41) and $[Bu_4N][BF_4]$ (Scheme 12).



Scheme 12.

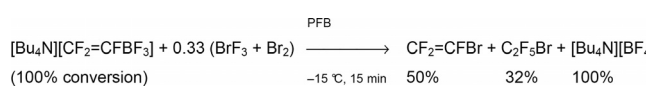
The equimolar mixture of bromine trifluoride and bromine is often described as an equivalent of "BrF" although the nature of the key reactive species is not doubtless proven as well as the mechanism of bromofluorination reactions with such mixtures.[19–21] We prepared solutions of BrF_3–Br_2 (1:1) in PFB and found that this solvent is not attacked at 20–25 °C at least for 2 days. The ^{19}F NMR spectrum displayed a broad singlet at –23 ppm ($\Delta\nu_{1/2}$ = 1512 Hz at 24 °C). This resonance is in the same region as the signal of BrF_3 in PFB (δ = –17.9; s, $\Delta\nu_{1/2}$ = 27 Hz).[4]

The interaction of BrF_3–Br_2 (1:1, ≈0.5 equiv. "BrF") with a PFB solution of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ showed partial isomerization of $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (*cis*/*trans* = 56:44) and in a smaller quantity yield of $[Bu_4N][C_2F_5CFBr–CF_2BF_3]$, $C_2F_5CF{=}CFBr$, and $[Bu_4N][BF_4]$ (Scheme 13).



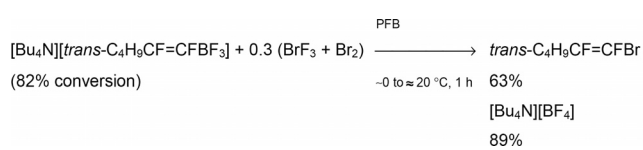
Scheme 13.

$[Bu_4N][CF_2{=}CFBF_3]$ reacted fast with BrF_3–Br_2 (1:1) in PFB already at –15 °C to yield $CF_2{=}CFBr$, C_2F_5Br, and $[Bu_4N][BF_4]$. Polyfluorinated ethyltrifluoroborates were not found (Scheme 14).



Scheme 14.

$[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ reacted with BrF_3–Br_2 (1:1) under cleavage of the C–B bond giving *trans*-$C_4H_9CF{=}CFBr$ and $[Bu_4N][BF_4]$ (Scheme 15).



Scheme 15.

Treatment of $[Bu_4N][CF_3C{\equiv}CBF_3]$ with BrF_3–Br_2 (1.2 equiv. "BrF") in PFB resulted in 28% conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$ yielding $[Bu_4N][CF_3CBr{=}CBrBF_3]$, $[Bu_4N][CF_3CBr_2–CF_2BF_3]$, $[Bu_4N][CF_3CBr_2–CFBrBF_3]$, $CF_3C{\equiv}CBr$, $CF_3CBr{=}CBr_2$, and $[Bu_4N][BF_4]$. The reaction with further BrF_3–Br_2 (4.8 equiv. "BrF") led to the total conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$, the transformation of $[Bu_4N][CF_3CBr{=}CBrBF_3]$ to $CF_3CBr{=}CBr_2$, and an increased yield of $[Bu_4N][CF_3CBr_2–CF_2BF_3]$ and of $[Bu_4N][BF_4]$.

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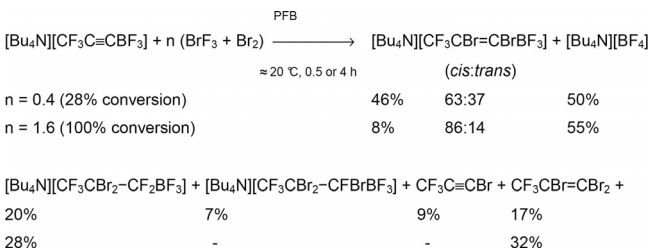
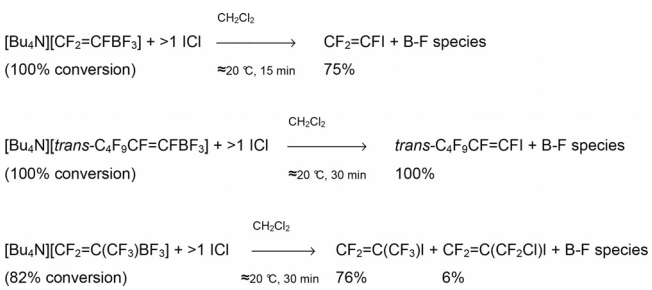
$[Bu_4N][CF_3CBr{=}CFBF_3]$ was not detected as precursor of $[Bu_4N][CF_3CBr_2{-}CF_2BF_3]$ and $[Bu_4N][CF_3CBr_2{-}CFBrBF_3]$ (Scheme 16).



Scheme 16.

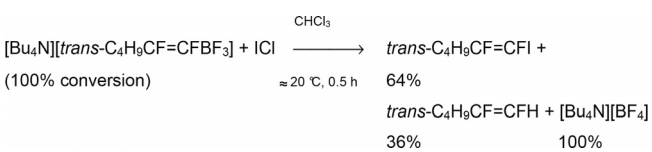
Reactions of Tetrabutylammonium Organyltrifluoroborates with Iodine Chloride in Halocarbon Solutions

Carbon–boron bond cleavage occurred fast in reactions of perfluoroalkenyltrifluoroborates with iodine chloride in dichloromethane at approximately 20 °C. Thus, $[Bu_4N][CF_2{=}CFBF_3]$ underwent 75% conversion into $CF_2{=}CFI$ within 15 minutes. The exhaustive formation of *trans*-$C_4F_9CF{=}CFI$ from $[Bu_4N][$*trans*-$C_4F_9CF{=}CFBF_3]$ and ICl indicates the regiospecifity of this process. Noteworthy, that the formation of $CF_2{=}C(CF_3)I$ (major) from $[Bu_4N][CF_2{=}C(CF_3)BF_3]$ was accompanied by $CF_2{=}C(CF_2Cl)I$ (minor) (Scheme 17).



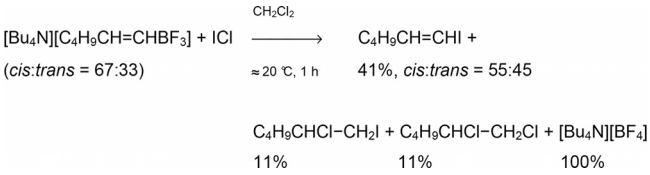
Scheme 17.

Treatment of $[Bu_4N][$*trans*-$C_4H_9CF{=}CFBF_3]$ with 1 equiv. of iodine chloride in $CHCl_3$ led to the quantitative cleavage of the carbon–boron bond with formation of *trans*-$C_4H_9CF{=}CFI$ and *trans*-$C_4H_9CF{=}CFH$ (Scheme 18).



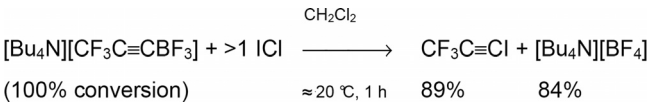
Scheme 18.

Besides $[Bu_4N][BF_4]$, $C_4H_9CH{=}CHI$ (*cis*/*trans* = 55:45) was the main organic product of the 1:1 reaction of $[Bu_4N][C_4H_9CH{=}CHBF_3]$ (*cis*/*trans* = 67:33) with ICl. In addition, $C_4H_9CHCl{-}CH_2I$ and $C_4H_9CHCl{-}CH_2Cl$ were found (Scheme 19).



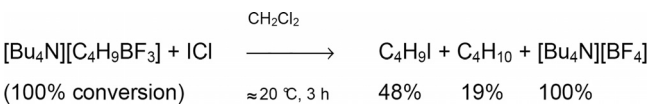
Scheme 19.

$[Bu_4N][CF_3C{\equiv}CBF_3]$ underwent complete iododeboration within 1 h forming $CF_3C{\equiv}CI$ and $[Bu_4N][BF_4]$ (Scheme 20).



Scheme 20.

The 1:1 reaction of $[Bu_4N][C_4H_9BF_3]$ with ICl in CH_2Cl_2 gave mainly iodobutane (iododeboration) and a significant amount of butane (protodeboration) (Scheme 21).

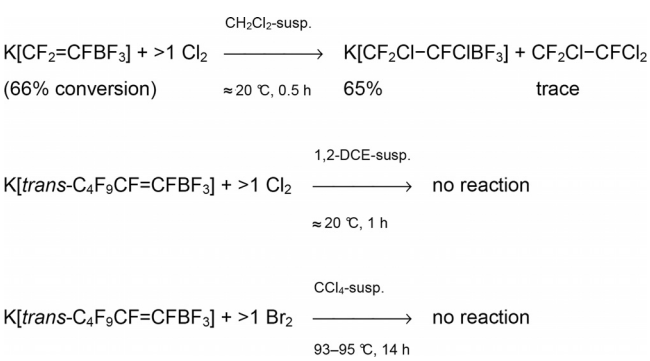


Scheme 21.

Surface Reactions of Potassium Organyltrifluoroborates with Halogenating Agents

In contrast to the well soluble tetrabutylammonium organyltrifluoroborate salts, the corresponding potassium salts are insoluble in CH_2Cl_2, $CHCl_3$, and PFB (^{19}F NMR). Nevertheless, some of them reacted with halogenating agents in halocarbon suspensions.

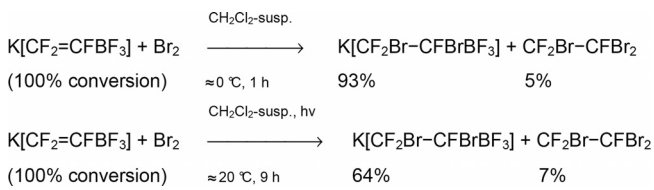
Bubbling of an excess of chlorine into a stirred suspension of $K[CF_2{=}CFBF_3]$ in CH_2Cl_2 at approximately 20 °C led to salt $K[CF_2Cl{-}CFClBF_3]$ and $CF_2Cl{-}CFCl_2$ (trace). In contrast, a suspension of K[*trans*-$C_4F_9CF{=}CFBF_3$] in 1,2-dichloroethane did not react with chlorine under those conditions (Scheme 22).



Scheme 22.

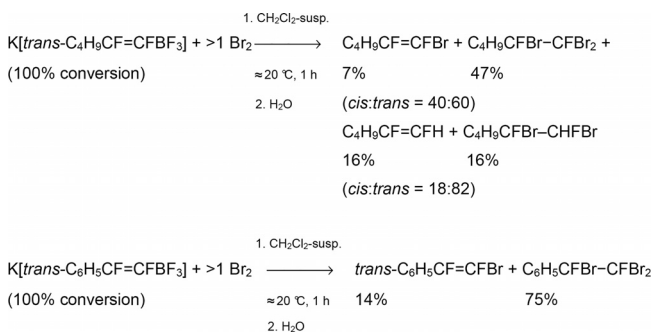
No reaction took place when K[*trans*-$C_4F_9CF{=}CFBF_3$] and bromine were combined, even under more rigorous conditions (CCl_4, sealed tube, ≤ 95 °C, 14 h) (Scheme 22).

The reaction of $K[CF_2{=}CFBF_3]$ (suspension in CH_2Cl_2) with bromine (1 equiv.) at 0 °C gave $K[CF_2Br–CFBrBF_3]$ (93% isolated yield) and a minor amount (5%) of $CF_2Br–CFBr_2$. Irradiation combined with more rigorous conditions did not have a positive effect on the result (Scheme 23).



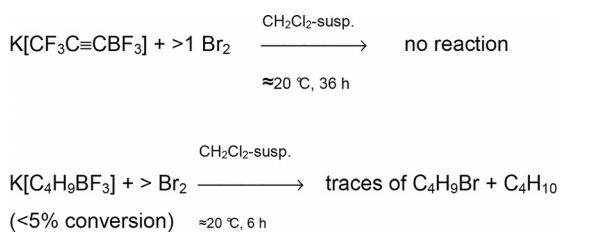
Scheme 23.

K[*trans*-$C_4F_9CF{=}CFBF_3$] in a halocarbon suspension did not react with bromine (CH_2Cl_2, ≈20 °C, 20 h; CCl_4, ≤95 °C, 14 h) as shown in Scheme 22. In contrast, exclusively carbon–boron bond cleavage took place in surface reactions of CH_2Cl_2 suspensions of K[*trans*-$C_4H_9CF{=}CFBF_3$] and K[*trans*-$C_6H_5CF{=}CFBF_3$] with bromine. The primarily formed bromoalkenes $C_4H_9CF{=}CFBr$ and *trans*-$C_6H_5CF{=}CFBr$ added in a second step bromine across the C=C bond yielding the tribromodifluoroalkanes $C_4H_9CFBr–CFBr_2$ and $C_6H_5CFBr–CFBr_2$, respectively, which were the major products (Scheme 24).



Scheme 24.

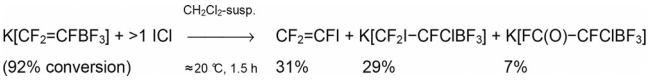
Astonishing, that the alkynyltrifluoroborate salt $K[CF_3C{\equiv}CBF_3]$ did not react with a large excess of bromine in CH_2Cl_2-suspension within 36 h (≈20 °C) (Scheme 25).



Scheme 25.

When a suspension of $K[C_4H_9BF_3]$ in CH_2Cl_2 was stirred with an excess of bromine (≈20 °C, 6 h) only <5% conversion of $K[C_4H_9BF_3]$ was found and traces of C_4H_9Br and C_4H_{10} were observed (Scheme 25).

A CH_2Cl_2-suspension of salt $K[CF_2{=}CFBF_3]$ was treated with ICl and $CF_2{=}CFI$ was formed together with $K[CF_2I–CFClBF_3]$. After working-up the products and isolation of $K[CF_2I–CFClBF_3]$, the ^{19}F NMR spectrum showed an admixture of an additional borate, presumably, $K[FC(O)–CFClBF_3]$ (Scheme 26).



Scheme 26.

Discussion

Reactions of alkenyl- and alkynyltrifluoroborate salts with halogenating agents in halocarbon solvents can principally proceed on two paths, (a) addition across the C=C or C≡C bond and (b) under carbon–boron bond cleavage. The C–B bond of alkyltrifluoroborates remained intact on path (a) under the reaction conditions (halocarbons, mostly ambient temperature), whereas the products of path (b) could underwent further conversions. A detailed analysis of these secondary processes was out of the scope of our current investigation.

The reactions of alkenyl- and alkynyltrifluoroborate salts with halogenating agents in halocarbon solvents were sometimes complex. They can be summarized using simplified descriptions:

1. $[Bu_4N][CF_3C{\equiv}CBF_3]$ reacted with fluorine preferred by fluorine addition across the C≡C triple bond and in a subsequent faster step across the C=C double bond. $[Bu_4N][CF_3CF{=}CFBF_3]$ could not be observed as an intermediate product of this reaction sequence. On an alternative channel the C–B bond was cleaved. $[Bu_4N][BF_4]$ was a characteristic final product of the second channel. The relative contribution of the first channel (fluorine addition to multiple C–C bonds, a typical radical reaction) was estimated to 50–60%.

2. The reaction of $[Bu_4N]$[*trans*-$C_4F_9CF{=}CFBF_3$] with chlorine gave $[Bu_4N][C_4F_9CFCl–CFClBF_3]$ in 94% yield. Replacement of $R = C_4F_9$ in $[Bu_4N][RCF{=}CFBF_3]$ by the less electron-withdrawing substituent R = F led to an increasing contribution of the C–B bond cleavage (Scheme 3). In contrast, in the surface reaction of $K[CF_2{=}CFBF_3]$ with Cl_2 the addition of chlorine to the double bond was the favored reaction channel (65% yield of $K[CF_2Cl–CFClBF_3]$). In CH_2Cl_2 solution the perfluoropropynyltrifluoroborate salt $[Bu_4N][CF_3C{\equiv}CBF_3]$ showed that 1,2-dichlorination was preferred over C–B bond cleavage (ratio $[Bu_4N][CF_3CCl{=}CClBF_3]/[Bu_4N][BF_4]$ = 56:44 at 62% conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$ and 71:29 at 100% conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$). In addition it is worth mentioning that with progressive conversion the *trans* isomer of $[Bu_4N][CF_3CCl{=}CClBF_3]$ increased. The parallel trend of C–B bond cleavage and diminishing of $[Bu_4N]$[*cis*-$CF_3CCl{=}CClBF_3$] with progressive conversion leads to the conclusion that the C–B bond cleavage of $[Bu_4N]$[*cis*-$CF_3CCl{=}CClBF_3$] is favored over $[Bu_4N]$[*trans*-$CF_3CCl{=}CClBF_3$]. The consecutive chlorination reaction of $[Bu_4N][CF_3CCl{=}CClBF_3]$ with Cl_2 proceeded very slowly. This reactivity is different to the second fluorination step of $[Bu_4N][CF_3C{\equiv}CBF_3]$.

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3. Reactions of $[Bu_4N][C_nF_{2n+1}CF{=}CFBF_3]$ with bromine occurred slowly and resulted in a complete C–B bond cleavage. Even $[Bu_4N][CF_2{=}CFBF_3]$ reacted predominantly under C–B bond cleavage. Besides the bromine addition product, $[Bu_4N][CF_2Br–CFBrBF_3]$, was formed. In contrast, $K[CF_2Br–CFBrBF_3]$ was obtained in up to 93% isolated yield from $K[CF_2{=}CFBF_3]$ in the surface reaction in CH_2Cl_2. $[Bu_4N][CF_3C{\equiv}CBF_3]$ and bromine gave $[Bu_4N][CF_3CBr{=}CBrBF_3]$ (92% yield) in CH_2Cl_2 solution. It is important to mention that $[Bu_4N][CF_3CBr{=}CBrBF_3]$ reacted with a further equivalent of bromine slowly under complete C–B bond cleavage. In case of alkyltrifluoroborates the C–B bond cleavage with bromine depended on the nature of the alkyl group: the perfluoroalkyl-B bond was inert, whereas the non-fluorinated alkyl-B bond underwent a fast cleavage in reactions with bromine (bromodeboration and protodeboration). $[Bu_4N][\textit{trans}\text{-}C_4H_9CF{=}CFBF_3]$ reacted significantly faster with bromine than $[Bu_4N][C_nF_{2n+1}CF{=}CFBF_3]$ salts predominantly under bromodeboration and in a lower extent under protodeboration. With an excess of bromine the $[\textit{trans}\text{-}C_4H_9CF{=}CFBF_3]^-$ anion underwent partial isomerization.

H–Hal – necessary for protodeboration – may stem from halogen attacks on C–H bond in the solvent or the cation. A further radical channel is discussed under 7.

A plausible explanation of the *cis*/*trans* isomerization of alkenyl groups in alkenyltrifluoroborate anions is based on addition of a halogen electrophile to C=C followed by C–C bond rotation and elimination of the electrophile.

4. When $[Bu_4N][\textit{cis}\text{-}C_2F_5CF{=}CFBF_3]$ reacted with ca. 0.5 equiv. of "bromine fluoride" ($BrF_3 + Br_2$, 1:1), bromofluorination (addition of $Br^{\delta+}$ at C-2) of the C=C bond was the main reaction channel. In a lower extend bromofluorination proceeded also in case of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (two times) and $[Bu_4N][CF_3CBr{=}CBrBF_3]$. In contrast, salts $[Bu_4N][RCF{=}CFBF_3]$ (R = F, $\textit{trans}\text{-}C_4H_9$) formed no 2-bromo-1-fluoroalkyltrifluoroborates. Instead of BrF addition to the C=C bond bromodeboration proceeded with BrF.

5. Reactions of soluble tetrabutylammonium borates $[Bu_4N][RBF_3]$ ($R = R_FCF{=}CF$, $R_FC{\equiv}C$, or $\textit{trans}\text{-}C_4H_9CF{=}CF$) with ICl underwent exclusively carbon–boron bond cleavage to yield *R*I. However, the surface reaction of $K[CF_2{=}CFBF_3]$ with ICl led to equal amounts of $CF_2{=}CFI$ and $K[CF_2I–CFClBF_3]$ ($I^{\delta+}$ adds to C-2 of the C=C bond).

6. Some of the CH_2Cl_2 insoluble potassium organyltrifluoroborates showed no reaction with halogenating agents under reasonable conditions: $K[\textit{trans}\text{-}C_4F_9CF{=}CFBF_3]/Cl_2$, $K[\textit{trans}\text{-}C_4F_9CF{=}CFBF_3]/Br_2$, $K[CF_3C{\equiv}CBF_3]/Br_2$, and $K[C_4H_9BF_3]/Br_2$. Insoluble $K[CF_2{=}CFBF_3]$ underwent with Cl_2 or Br_2 preferentially halogen addition across the C=C bond. When one of the electron-withdrawing F^2 atoms was substituted by a non-fluorinated alkyl or phenyl group bromodeboration proceeded followed by a fast bromine addition across the C=C bond. $K[CF_2{=}CFBF_3]$ showed in reactions with dipolar ICl both reaction channels: ICl addition and iododeboration. In agreement with the polarity of the C–B σ bond $I^{\delta+}$ was added to C-1 and $CF_2{=}CFI$ was formed and the polarity of the C=C π bond caused the addition of $I^{\delta+}$ to C-2 and $K[CF_2I–CFClBF_3]$ was obtained.

7. We can make some conclusions, e.g., for reactions with bromine concerning electronic and steric influences based on a limited number of experiments: (a) The electrophilic attack of Br_2 on C-1 of the alkenylborate anion $[RCF{=}CFBF_3]^-$ is favored in case of less electron-withdrawing groups *R*. (b) The *trans* isomer of isomeric mixtures of $[R_FCF{=}CFBF_3]^-$ (R_F = C_2F_5, C_4F_9) underwent a faster C–B cleavage than the *cis* isomer, which can be deduced to a steric protection of C-1 in case of the *cis* isomer. (c) Organyltrifluoroborate anions can be formally considered as adducts of the organyl anion and BF_3. This simplification is helpful to rationalize the different reactivity e.g. of the anions $[CF_3C{\equiv}CBF_3]^-$ and $[C_4H_9C{\equiv}CBF_3]^-$ in solution. The organyl group of the latter has a more carbanionic character, which favors in reactions with bromine the formation of $C_4H_9C{\equiv}CBr$ (nucleophilic attack on the electrophile Br_2) and $C_4H_9C{\equiv}CH$ (one-electron oxidation followed by radical attack on C–H bonds). This consideration is additionally supported by the experimental results of alkyltrifluoroborates and bromine. The $[C_6F_{13}BF_3]^-$ anion has a weak C–B bond caused by the repulsion of the partial positive charge on the adjacent carbon and boron atoms. But the weak bond is not accompanied by high reactivity. In contrast, a nucleophilic attack on Br_2 did not proceed because of the low nucleophilicity of the carbanion. The opposite situation can be discussed for the $[C_4H_9BF_3]^-$ anion in reactions with Br_2, which gave C_4H_9Br and C_4H_{10}, the suspected products for interactions of the corresponding carbanion and bromine.

8. Potassium organyltrifluoroborates are insoluble in halocarbons (proven by ^{19}F NMR spectroscopy). In the solid the anions have a fixed orientation on the surface and are less activated by collisions with solvent molecules as in diluted solutions. In conclusion the number of reaction channels is reduced. In our case the addition across the double bond of the alkenyl group became preference over the C–B bond cleavage.

Experimental Section

Materials and Measurements

The NMR spectra were recorded with the Bruker spectrometers AVANCE 300 (^1H at 300.13 MHz, ^{19}F at 282.40 MHz, ^{11}B at 96.29 MHz, ^{13}C at 75.47 MHz) and AVANCE 600 (^{11}B at 192.60 MHz). The chemical shifts are referenced to TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_2/CDCl_3$ (15% v/v) (^{11}B), and CCl_3F [^{19}F, with C_6F_6 as secondary reference (–162.9 ppm)]. The IR spectra were recorded with a Bruker Vector 22 spectrometer and the high resolution mass spectra with a Finnigan MAT 8200 instrument (EI mode).

The composition of the reaction mixtures and the yields of products were determined by ^1H or ^{19}F NMR spectroscopy using the internal integral standards $C_6H_5CF_3$, C_6F_6, or $[Bu_4N][PF_6]$.

1,1,1,3,3-Pentafluorobutane (PFB) (Solvay Fluor und Derivate GmbH) was stored over molecular sieves 3 Å before use. Acetonitrile and dichloromethane were purified and dried using described procedures [22]. Chloroform, carbon tetrachloride, and 1,2-dichloroethane were washed with water (twice), dried with $CaCl_2$, stirred with P_4O_{10} for

several hours and distilled off. The purified solvents were stored over molecular sieves (3 Å) before use. $[Bu_4N][BF_4]$ (Fluka), $[Bu_4N]Br$ (Fluka), and ICl (Fluka) were used as supplied. Chlorine (*n* mmol) was prepared by addition of 37% hydrochloric acid (0.8*n* mL) to $KMnO_4$ (0.8*n* mmol, 126*n* mg)[23] in a slow stream of argon. Crude chlorine in argon was passed through calcinated CaO in a column (D = 0.5 cm, L = 3 cm) to remove HCl and moisture. Bromine was washed with concentrated H_2SO_4 and distilled over P_4O_{10}. Bromine trifluoride was prepared by bubbling of fluorine (25% v/v in nitrogen) into dry bromine at 8–20 °C. The organyltrifluoroborate salts $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$,[4] $K[CF_2{=}CFBF_3]$, $K[trans\text{-}C_4F_9CF{=}CFBF_3]$, $K[trans\text{-}C_4H_9CF{=}CFBF_3]$, $K[trans\text{-}C_6H_5CF{=}CFBF_3]$, $K[cis\text{-}C_2F_5CF{=}CFBF_3]$,[24] $K[CF_2{=}C(CF_3)BF_3]$,[14] $K[CF_3C{\equiv}CBF_3]$,[25] $K[C_4H_9CH{=}CHBF_3]$, $K[C_4H_9BF_3]$,[11] and $K[C_6F_{13}BF_3]$[4] were synthesized using published procedures. Solubilities of selected organylfluoroborate salts in different solvents are given in Table S1 (Supporting Information).

The synthesis of $K[C_4H_9C{\equiv}CBF_3]$ was performed according to ref.[26]. $K[C_4H_9C{\equiv}CBF_3]$. **^{1}H NMR** (CD_3CN): δ = 2.12 [t, $^3J(H^3, H^4)$ = 7 Hz, 2 H, H^3], 1.42 (m, $2CH_2$), 0.91 [t, $^3J(H^6, H^5)$ = 7 Hz, 3 H, H^6]. **^{19}F NMR** (CD_3CN): δ = –133.6 [q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3]. **^{11}B NMR** (CD_3CN): δ = –1.9 [q, ^1J(B, F) = 38 Hz, BF_3]. **^{19}F NMR** ([D_6]DMSO): δ = –131.1 [broadened q (1:1:1:1), 3F, BF_3]. **^{13}C{^{19}F} NMR** ([D_6]DMSO): δ = 92.4 (br. m, C-1), 90.3 (m, C-2), 31.8 [t, ^1J(C-4, H^4) = 125 Hz, C-4], 22.2 [t, ^1J(C-5, H^5) = 124 Hz, C-5], 19.3 [t, ^1J(C-3, H^3) = 128 Hz, C-3], 14.2 [q, ^1J(C-6, H^6) = 125 Hz, C-6]. NMR spectroscopic data in [D_6]acetone (cf.[26,27]) are given in Table S2 (Supporting Information).

Manipulations with fluorine and BrF_3 were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) or PFA (block copolymer of tetrafluoroethylene and perfluoroalkoxytrifluoroethylene) equipment in an atmosphere of dry argon. The NMR spectra of BrF_3 and BrF_3–Br_2 solutions were measured in FEP inliners (D_i = 3.50 ± 0.05 mm, D_o = 4.10 ± 0.05 mm).

Preparation of Tetrabutylammonium Organyltrifluoroborates

Preparation of $[Bu_4N][CF_2{=}CFBF_3]$: A solution of $[Bu_4N][BF_4]$ (0.99 g, 3.0 mmol) in MeCN (5 mL) was added to a solution of $K[CF_2{=}CFBF_3]$ (575 mg, 3.0 mmol) in MeCN (10 mL). The resulting suspension was stirred for 1 h. The mother liquor was separated from $K[BF_4]$ by sequential centrifugation and decantation. Finally the solvent was evaporated under reduced pressure. The colorless viscous product was dried in a vacuum desiccator with Sicapent® and gave a white solid (1.13 g, 2.27 mmol) (yield 92%). **^{11}B NMR** (CD_2Cl_2): δ = 0.5 [ddq ^2J(B, F^1) = 25, ^3J(B, F^{2trans}) = 7, ^1J(B, F) = 41 Hz, BF_3]. **^{13}C{^{19}F^{2cis,2trans}} NMR** (CD_3CN): δ = 160.4 (C-2), 136.6 [q (1:1:1:1) d, ^1J(C-1, B) = 100, ^1J(C-1, F^1) = 220 Hz, C-1] ([$CF_2{=}CFBF_3$]$^-$); 59.2, 24.2, 20.2, 13.5 ([$(C_4H_9)_4N$]$^+$). **^{19}F NMR** (CD_2Cl_2): δ = –102.4 [d, $^2J(F^{2trans}, F^{2cis})$ = 91 Hz, 1F, F^{2trans}], –125.1 [dd, $^2J(F^{2cis}, F^{2trans})$ = 91, $^3J(F^{2cis}, F^1)$ = 112 Hz, 1F, F^{2cis}], –144.3 [q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3], –196.3 [d, $^3J(F^1, F^{2cis})$ = 112 Hz, 1F, F^1] ppm.

Preparation of $[Bu_4N][CF_2{=}C(CF_3)BF_3]$: The salt (310 mg, 70%) was obtained from $[Bu_4N][BF_4]$ (288 mg, 0.87 mmol) and $K[CF_2{=}C(CF_3)BF_3]$ (207 mg, 0.87 mmol) in MeCN (2 mL) as described above. **^{13}C {^{19}F} NMR** (CD_2Cl_2): δ = 157.7 ($F_2C{=}$), 126.8 ($F_3CC{=}$), 84.9 [q (1:1:1:1), ^1J(C-1, B) = 80 Hz, C-1] ([$CF_2{=}C(CF_3)BF_3$]$^-$); 58.9, 23.9, 19.9, 13.0 ([$(C_4H_9)_4N$]$^+$). **^{19}F NMR** (CD_2Cl_2): δ = –55.0 (m, 3F, CF_3), –69.5 (m, 1F, F^{2trans}), –78.2 (m, 1F, F^{2cis}), –138.0 [q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3] ppm.

Preparation of $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$: The salt (485 mg, 82%) was obtained from $[Bu_4N]Br$ (322 mg, 1.0 mmol) and $K[trans\text{-}C_4F_9CF{=}CFBF_3]$ (388 mg, 1.0 mmol) in MeCN (11 mL) as described above. **^{11}B NMR** (CH_2Cl_2): δ = –0.4 [qd, ^1J(B, F) = 38, ^2J(B, F^1) = 27 Hz, BF_3]. **^{19}F NMR** (CH_2Cl_2): δ = –81.3 (3F, F^6), –116.5 (2F, F^3), –124.7, –126.4 (4F, $F^{4,5}$), –143.9 [q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3], –153.3 (1F, F^1), –177.6 (1F, F^2) ppm.

Preparation of $[Bu_4N][CF_3C{\equiv}CBF_3]$: The salt (404 mg, 88%) was prepared from $[Bu_4N][BF_4]$ (374 mg, 1.13 mmol) and $K[CF_3C{\equiv}CBF_3]$ (235 mg, 1.17 mmol) in MeCN (3.5 mL) as described above. **^{11}B NMR** (PFB): δ = –2.7 [q, ^1J(B, F) = 31 Hz, BF_3]. **^{11}B NMR** (CH_2Cl_2): δ = –3.3 [q, ^1J(B, F) = 32 Hz, BF_3]. **^{19}F NMR** (PFB): δ = –47.4 (s, 3F, F^3), –132.8 [q (1:1:1:1), ^1J(F, B) = 31 Hz, 3F, BF_3]. **^{19}F NMR** (CH_2Cl_2): δ = –49.0 (s, 3F, F^3), –136.0 [q (1:1:1:1), ^1J(F, B) = 32 Hz, 3F, BF_3].

Preparation of $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$: Salt $K[C_4H_9CF{=}CFBF_3]$ (392 mg, 1.74 mmol) was suspended in MeCN (5 mL) and $[Bu_4N]Br$ (561 mg, 1.74 mmol) was added in one portion. The suspension was stirred for 1 h. The mother liquor was separated by sequential centrifugation and decantation and evaporated under reduced pressure. The colorless viscous oil was pumped in a vacuum-desiccator with Sicapent® and gave a solid product (707 mg, 95%). **^{1}H NMR** ($CDCl_3$): δ = 2.24 [dtt, $^3J(H^3, F^2)$ = 24, $^4J(H^3, H^5)$ = 7, $^4J(H^3, F^1)$ = 7 Hz, 2 H, H^3], 1.35 (m, $2CH_2$), 0.92 [t, $^3J(H^6, H^5)$ = 7 Hz, 3 H, H^6] [*trans*-$C_4H_9CF = CFBF_3$]$^-$; 3.14 (m, $4CH_2$), 1.54 (m, $4CH_2$), 1.35 (m, $4CH_2$), 0.92 [t, $^3J(H^4, H^3)$ = 7 Hz, $4CH_3$] [$(C_4H_9)_4N$]$^+$. **^{11}B NMR** ($CDCl_3$): δ = 0.7 (br. s, $\Delta\nu_{1/2}$ = 149 Hz, BF_3). **^{19}F NMR** ($CDCl_3$): δ = –158.6 [dtq $^3J(F^2, F^1)$ = 119, $^3J(F^2, H^3)$ = 24, $^4J(F^2, BF)$ = 10 Hz, 1F, F^2], –172.5 [d $^3J(F^1, F^2)$ = 119 Hz, 1F, F^1], –143.6 [broadened q (1:1:1:1), 3F, BF_3].

Preparation of $[Bu_4N][C_4H_9CH{=}CHBF_3]$: The salt (664 mg, 90%) was obtained as a colorless viscous oil from $[Bu_4N]Br$ (603 mg, 1.87 mmol) and $K[C_4H_9CH{=}CHBF_3]$ (*cis*/*trans* = 69:31) (355 mg, 1.87 mmol) in MeCN (15 mL) as described above. **^{1}H NMR** ($CDCl_3$): δ = 5.75 [dt, $^3J(H^2, H^1)$ = 18, $^3J(H^2, H^3)$ = 6 Hz, 1 H, H^2], 5.41 [d, $^3J(H^1, H^2)$ = 18 Hz, 1 H, H^1], 2.03 (m, 2 H, H^3), 1.57 (m, CH_2), 1.25 (m, CH_2), 0.80 (m, 3 H, H^6) [*trans*-$C_4H_9CH{=}CHBF_3$]$^-$; 5.65 (m, 1 H, H^2), 5.31 [dq $^3J(H^1, H^2)$ = 13, $^3J(H^1, BF)$ = 6 Hz, 1 H, H^1], 2.19 (m, 2 H, H^3), 1.57 (m, CH_2), 1.25 (m, CH_2), 0.80 (m, 3 H, H^6) [*cis*-$C_4H_9CH{=}CHBF_3$]$^-$; 3.20 (m, $4CH_2$), 1.57 (m, $4CH_2$), 1.37 (m, $4CH_2$), 0.93 [t, $^3J(H^4, H^3)$ = 7 Hz, $4CH_3$] [$(C_4H_9)_4N$]$^+$. **^{11}B NMR** ($CDCl_3$): δ = 2.9 [q, ^1J(B, F) = 58 Hz, BF_3]. **^{19}F NMR** ($CDCl_3$): δ = –135.6 [broadened q (1:1:1:1), 3F, BF_3] [*cis*-$C_4H_9CH{=}CHBF_3$]$^-$; –140.9 [broadened q (1:1:1:1), 3F, BF_3] [*trans*-$C_4H_9CH{=}CHBF_3$]$^-$.

Preparation of $[Bu_4N][C_4H_9C{\equiv}CBF_3]$: The salt (650 mg, 94%) was obtained as a colorless viscous oil from $[Bu_4N]Br$ (570 mg, 1.77 mmol) and $K[C_4H_9C{\equiv}CBF_3]$ (333 mg, 1.77 mmol) in MeCN (10 mL) as described above. **^{1}H NMR** ($CDCl_3$): δ = 2.03 [t, $^3J(H^3, H^4)$ = 7 Hz, 2 H, H^3], 1.36 (m, $2CH_2$), 0.78 [t, $^3J(H^6, H^5)$ = 7 Hz, 3 H, H^6] [$C_4H_9C{\equiv}CBF_3$]$^-$; 3.19 (m, $4CH_2$), 1.56 (m, $4CH_2$), 1.36 (m, $4CH_2$), 0.92 [t, $^3J(H^4, H^3)$ = 7 Hz, $4CH_3$] [$(C_4H_9)_4N$]$^+$. **^{11}B NMR** ($CDCl_3$): δ = –1.6 (br. s, $\Delta\nu_{1/2}$ = 126 Hz, BF_3). **^{19}F NMR** ($CDCl_3$): δ = –133.9 [broadened q (1:1:1:1), 3F, BF_3].

Preparation of $[Bu_4N][C_4H_9BF_3]$: The salt (710 mg, 91%) was prepared as a colorless viscous oil from $[Bu_4N]Br$ (680 mg, 2.13 mmol) and $K[C_4H_9BF_3]$ (349 mg, 2.13 mmol) in MeCN (10 mL) as described

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above. **^{1}H NMR** ($CDCl_3$): δ = 1.22 (m, $2CH_2$), 0.78 [t, $^3J(H^4, H^3)$ = 7 Hz, 3 H, H^4], 0.14 (m, 2 H, H^1), $[C_4H_9BF_3]^-$; 3.17 (m, $4CH_2$), 1.55 (m, $4CH_2$), 1.36 (m, $4CH_2$), 0.92 [t, $^3J(H^4, H^3)$ = 7 Hz, $4CH_3$] $[(C_4H_9)_4N]^+$. **^{11}B NMR** ($CDCl_3$): δ = 5.4 (br. s, $\Delta\nu_{1/2}$ = 218 Hz, *B*F_3). **^{19}F NMR** ($CDCl_3$): δ = –141.1 [broadened q (1:1:1:1), 3F, B*F*$_3$].

Preparation of $[Bu_4N][C_6F_{13}BF_3]$: The salt (336 mg, 89 %) was prepared as a colorless viscous oil from $[Bu_4N]Br$ (193 mg, 0.60 mmol) and $K[C_6F_{13}BF_3]$ (292 mg, 0.68 mmol) in MeCN (5 mL) as described above. **^{1}H NMR** ($CDCl_3$): δ = 3.20 (m, $4CH_2$), 1.55 (m, $4CH_2$), 1.36 (m, $4CH_2$), 0.90 [t, $^3J(H^4, H^3)$ = 7 Hz, $4CH_3$] $[(C_4H_9)_4N]^+$. **^{19}F NMR** ($CDCl_3$): δ = –80.0 [t, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6], –121.9, –122.6, –123.0 ($3CF_2$), –126.1 (m, 2F, F^5), –131.8 (m, 2F, F^1), –149.6 [q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, B*F*$_3$].

Reaction of $[Bu_4N][CF_3C{\equiv}CBF_3]$ with Fluorine in PFB Solution

A solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (117 mg, 0.29 mmol) in PFB (2 mL) was charged into an 8 mm i. d. FEP trap equipped with a magnetic stir bar and cooled to 0 °C. Less than the equivalent amount of fluorine (0.19 mmol) diluted with nitrogen (5 % v/v) was bubbled in 3 steps into the cold stirred solution. After 15 min the reaction was interrupted, the solution was flushed with dry argon, and a probe was taken in a cold (0 °C) FEP inliner. The solution contained $[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.260 mmol, 10 % conversion), $[Bu_4N][C_3F_7BF_3]$ (0.018 mmol, 60 %) (identified by ^{19}F NMR[28]), and $[Bu_4N][BF_4]$ (0.010 mmol, 33 %). The probe was combined with the main reaction solution and the treatment with fluorine was continued. Similarly as described before, the composition of the reaction solution was determined after 30 min {$[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.230 mmol) (21 % conversion), $[Bu_4N][C_3F_7BF_3]$ (0.035 mmol, 57 %), $[Bu_4N][BF_4]$ (0.030 mmol, 49 %)} and after 60 min {$[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.160 mmol) (44 % conversion), $[Bu_4N][C_3F_7BF_3]$ (0.067 mmol, 52 %), $[Bu_4N][BF_4]$ (0.060 mmol, 47 %)}. In addition, the signals of $CF_3CH_2CF_2CH_2F$ (trace quantities of fluorination of PFB) and HF were detected (^{19}F NMR, 0 °C).

Reactions of Perfluoroalkenyl- and Perfluoroalkynyltrifluoroborates with Chlorine in Halocarbon Solutions

Reaction of $[Bu_4N][$*trans*-$C_4F_9CF{=}CFBF_3]$: A solution of $[Bu_4N][$*trans*-$C_4F_9CF{=}CFBF_3]$ (0.39 mmol) in CH_2Cl_2 in a glass ampoule (3 mL) with a magnetic stir bar was cooled to 0 °C (ice bath) in an atmosphere of dry argon. Chlorine (0.8 mmol) in dry argon was slowly bubbled into the stirred solution within 20 min. The ampoule was sealed and the yellow-greenish solution was stirred for 24 h at ≈20 °C. The ^{19}F NMR spectrum showed the absence of [*trans*-$C_4F_9CF{=}CFBF_3]^-$ and new signals of $[C_4F_9CFCl{-}CFClBF_3]^-$ (0.39 mmol) (C_6F_6, internal integral standard). After evaporation of the volatile components at reduced pressure and ≈20 °C, a colorless viscous oil (243 mg, 94 %) was obtained.

$[Bu_4N][C_4F_9CFCl{-}CFClBF_3]$: **^{11}B NMR** ($CD_3CN$): δ = 0.2 [dq ^2J(B, F^1) = 17, ^1J(B, F) = 40 Hz] (diastereomer C); 0.0 [dq ^2J(B, F^1) = 18, ^1J(B, F) = 38 Hz] (diastereomer A); –0.5 [dq ^2J(B, F^1) = 20, ^1J(B, F) = 41 Hz] (diastereomer B) (ratio A:B:C = 59:29:12). **^{19}F NMR** (CD_3CN): δ = –79.9 [tt, $^4J(F^6, F^5)$ = 3, $^3J(F^6, F^4)$ = 10 Hz, 3F, F^6], –112.2 [md $^2J(F^{3A}, F^{3B})$ = 286 Hz, 1F, F^{3A}], –113.2 [md $^2J(F^{3B}, F^{3A})$ = 286 Hz, 1F, F^{3B}], –118.0 [md $^2J(F^{4A}, F^{4B})$ = 296 Hz, 1F, F^{4A}], –119.0 [md $^2J(F^{4B}, F^{4A})$ = 296 Hz, 1F, F^{4B}], –124.4 [md $^2J(F^{5A}, F^{5B})$ = 289 Hz, 1F, F^{5A}], –125.3 [md $^2J(F^{5B}, F^{5A})$ = 289 Hz, 1F, F^{5B}], –127.3 (m, 1F, F^1), –135.1 (m, 1F, F^2), –148.0 [q (1:1:1:1), ^1J(F, B) = 36 Hz, 3F, B*F*$_3$] (diastereomer A); –80.0 [tt, $^4J(F^6, F^5)$ = 3 Hz, t $^3J(F^6, F^4)$ = 10 Hz, 3F, F^6], –113.4 [md $^2J(F^{3A}, F^{3B})$ = 286 Hz, 1F, F^{3A}], –115.0 [md $^2J(F^{3B}, F^{3A})$ = 286 Hz, 1F, F^{3B}), –118.0 (md $^2J(F^{4A}, F^{4B})$ = 298 Hz, 1F, F^{4A}), –119.9 (md $^2J(F^{4B}, F^{4A})$ = 298 Hz, 1F, F^{4B}], –121.7 [md $^2J(F^{5A}, F^{5B})$ = 318 Hz, 1F, F^{5A}], –124.8 [md $^2J(F^{5B}, F^{5A})$ = 318 Hz, 1F, F^{5B}], –124.8 (m, 1F, F^1), –134.0 (m, 1F, F^2), –149.7 [q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, B*F*$_3$] (diastereomer B); –80.0 [tt, $^4J(F^6, F^5)$ = 3, $^3J(F^6, F^4)$ = 10 Hz, 3F, F^6], –111.3 [md $^2J(F^{3A}, F^{3B})$ = 286 Hz, 1F, F^{3A}], –113.5 [md $^2J(F^{3B}, F^{3A})$ = 287 Hz, 1F, F^{3B}], –117.2 [md $^2J(F^{4A}, F^{4B})$ = 293 Hz, 1F, F^{4A}}, –119.9 [md $^2J(F^{4B}, F^{4A})$ = 293 Hz, 1F, F^{4B}], –123.4 (m, 1F, F^1), –124.8 (m, 2F, F^5), –134.7 (m, 1F, F^2), –148.1 [q (1:1:1:1), ^1J(F, B) = 36 Hz, 3F, B*F*$_3$] (diastereomer C) (ratio A:B:C = 57:31:12). ^{19}F NMR spectroscopic data in $CDCl_3$ are given in Table S2 (Supporting Information).

Reaction of $[Bu_4N][CF_2{=}CFBF_3]$: A solution of $[Bu_4N][CF_2{=}CFBF_3]$ (0.21 mmol) in CH_2Cl_2 (1 mL) and CD_2Cl_2 (0.2 mL) in a glass tube was cooled to 0 °C (ice bath) in an atmosphere of dry argon and chlorine (0.3 mmol) in argon was slowly bubbled into the solution for 30 min. The colorless solution contained $[Bu_4N][CF_2Cl{-}CFClBF_3]$ (0.07 mmol, 33 %), $CF_2{=}CFCl$ (0.03 mmol, 14 %), and $[Bu_4N][BF_4]$ (0.10 mmol, 48 %). $[Bu_4N][CF_2{=}CFBF_3]$ was totally consumed (^{11}B and ^{19}F NMR).

$[Bu_4N][CF_2Cl{-}CFClBF_3]$: ^{11}B NMR ($CH_2Cl_2$ + CD_2Cl_2): δ = 0.0 [dq ^2J(B, F^1) = 17, ^1J(B, F) = 40 Hz]. **^{19}F NMR** (CH_2Cl_2 + CD_2Cl_2): δ = –60.1 [qdd $^4J(F^{2A}, BF_3)$ = 6, $^3J(F^{2A}, F^1)$ = 13, $^2J(F^{2A}, F^{2B})$ = 167 Hz, 1F, F^{2A}], –61.5 [qdd $^4J(F^{2B}, BF_3)$ = 6, $^3J(F^{2A}, F^1)$ = 12, $^2J(F^{2B}, F^{2A})$ = 167 Hz, 1F, F^{2B}], –143.2 (m, 1F, F^1), –150.9 [dtq (1:1:1:1), $^3J(BF_3, F^1)$ = 6, $^4J(BF_3, F^2)$ = 6, ^1J(F, B) = 40 Hz, 3F, B*F*$_3$].

Reaction of $[Bu_4N][CF_3C{\equiv}CBF_3]$: A. A solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.39 mmol) in CH_2Cl_2 (3 mL) in a glass ampoule with a magnetic stir bar was cooled to 0 °C (ice bath) in an atmosphere of dry argon. Chlorine (1.0 mmol) in dry argon was bubbled into the stirred solution for 10 min. The ampoule was sealed and kept at ≈20 °C for 24 h. The solution contained $[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.15 mmol, 62 % conversion), $[Bu_4N][$*cis*-$CF_3CCl{=}CClBF_3]$ (0.06 mmol, 25 %), $[Bu_4N][$*trans*-$CF_3CCl{=}CClBF_3]$ (0.07 mmol, 29 %), $[Bu_4N][CF_3CCl_2{-}CCl_2BF_3]$ (0.01 mmol, 4 %), and $[Bu_4N][BF_4]$ (0.10 mmol, 42 %) besides traces of $CF_3C{\equiv}CCl$ [δ(F) –50.0 (s)], $CF_3CCl_2{-}CCl_3$,[29] and minor amounts of unknown products.

B. A solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.39 mmol) and chlorine (0.8 mmol) in CH_2Cl_2 (3 mL) was prepared as above and stirred at ≈20 °C for 3 h in a test tube closed with a stopper. A probe showed the presence of $[CF_3C{\equiv}CBF_3]^-$ (0.27 mmol, 31 % conversion), [*cis*-$CF_3CCl{=}CClBF_3]^-$ (0.07 mmol, 18 %), [*trans*-$CF_3CCl{=}CClBF_3]^-$ (0.02 mmol, 5 %), $[CF_3CCl_2{-}CCl_2BF_3]^-$ (0.01 mmol, 3 %), and $[BF_4]^-$ (0.02 mmol, 5 %). This solution was filled into a glass ampoule, treated again with chlorine (0.8 mmol) at 0 °C. The ampoule was sealed and kept at ≈20 °C. After 21 h the yellow-greenish solution contained $[Bu_4N][CF_3C{\equiv}CBF_3]$ (0.15 mmol, 62 % conversion), $[Bu_4N][$*cis*-$CF_3CCl{=}CClBF_3]$ (0.07 mmol, 18 %), $[Bu_4N][$*trans*-$CF_3CCl{=}CClBF_3]$ (0.07 mmol, 18 %), $[Bu_4N][CF_3CCl_2CCl_2BF_3]$ (0.01 mmol, 3 %), and $[Bu_4N][BF_4]$ (0.09 mmol, 23 %). The treatment with chlorine (1.0 mmol) was repeated in an ampoule at ≈20 °C for additional 33 h. The ^{19}F NMR spectrum confirmed the complete conversion of $[Bu_4N][CF_3C{\equiv}CBF_3]$. $[Bu_4N][$*cis*-$CF_3CCl{=}CClBF_3]$ (<0.01 mmol, <3 %), $[Bu_4N][$*trans*-$CF_3CCl{=}CClBF_3]$ (0.23 mmol, 59 %),

$[Bu_4N][CF_3CCl_2–CCl_2BF_3]$ (0.03 mmol, 8 %), and $[Bu_4N][BF_4]$ (0.10 mmol, 26 %) were observed besides unknown products.

$[Bu_4N][cis\text{-}CF_3CCl{=}CClBF_3]$: ^{11}B NMR ($CD_3CN$): δ = 0.0 [q, ^1J(B, F) = 37 Hz, BF_3]. **^{19}F NMR** (CD_3CN): δ = –59.2 [q, $^5J(F^3, BF)$ = 10 Hz, 3F, F^3], –138.5 [qq (1:1:1:1), $^5J(FB, F^3)$ = 10, ^1J(F, B) = 37 Hz, 3F, BF_3]. **^{19}F NMR** (CH_2Cl_2): δ = –60.5 [q, $^5J(F^3, BF)$ = 10 Hz, 3F, F^3], –139.2 [qq (1:1:1:1), $^5J(FB, F^3)$ = 9, ^1J(F, B) = 38 Hz, 3F, BF_3].

$[Bu_4N][trans\text{-}CF_3CCl{=}CClBF_3]$: ^{11}B NMR ($CD_3CN$): δ = 0.7 [q, ^1J(B, F) = 36 Hz, BF_3]. ^{19}F NMR (CD_3CN): δ = –68.7 [q, $^5J(F^3, BF)$ = 8 Hz, 3F, F^3], –145.4 [qq (1:1:1:1), $^5J(FB, F^3)$ = 8, ^1J(F, B) = 35 Hz, 3F, BF_3]. **^{19}F NMR** (CH_2Cl_2): δ = –70.1 [q, $^5J(F^3, BF)$ = 8 Hz, 3F, F^3], –146.3 [qq (1:1:1:1), $^5J(FB, F^3)$ = 7, ^1J(F, B) = 36 Hz, 3F, BF_3].

$[Bu_4N][CF_3CCl_2–CCl_2BF_3]$: ^{11}B NMR ($CD_3CN$): δ = 0.1 [q, ^1J(B, F) = 39 Hz, BF_3] (conformer A); –2.0 [q, ^1J(B, F) = 44 Hz, BF_3] (conformer B); 0.1 [q, ^1J(B, F) = 36 Hz, BF_3] (conformer C) (ratio A:B:C = 56:16:28]. **^{19}F NMR** (CD_3CN): δ = –59.4 (s, 3F, F^3), –140.9 [q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3] (conformer A); –60.0 (s, 3F, F^3),–141.8 [q (1:1:1:1), ^1J(F, B) = 44 Hz, 3F, BF_3] (conformer B); –60.0 (s, 3F, F^3), –135.1 [q (1:1:1:1), ^1J(F, B) = 35 Hz, 3F, BF_3] (conformer C) (ratio A:B:C = 43:24:33).

Reactions of Organyltrifluoroborates with Bromine in Halocarbon Solutions

Reaction of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$: A solution of bromine (51 mg, 0.32 mmol) in CH_2Cl_2 (1.2 mL) was added dropwise to a stirred solution of $[Bu_4N][cis\text{-}C_2F_5CF{=}CFBF_3]$ (152 mg, 0.31 mmol) in CH_2Cl_2 (1 mL) at ≈20 °C. After stirring for 21 h the orange-red solution contained $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (0.25 mmol, 81 %) (*cis*/*trans* = 72:28), $C_2F_5CF{=}CFBr$[30] (0.04 mmol, 13 %) (*cis*/*trans* = 25:75), $C_2F_5CFBr–CFHBr$ (0.02 mmol, 6 %), and $[Bu_4N][BF_4]$ (0.05 mmol, 16 %]. After 48 h, the ^{19}F NMR spectrum of the pale yellow solution showed the resonances of $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (0.15 mmol, 48 %) (*cis*/*trans* = 60:40), $C_2F_5CF{=}CFBr$ (0.05 mmol, 16 %) (*cis*/*trans* = 20:80), *cis*-$C_2F_5CF{=}CFH$[24] (0.01 mmol, 3 %), $C_2F_5CFBr–CFHBr$[30] [δ(F) –85.5 (m, 3F, F^4), –119.9 (m, 2F, F^3), –132.1 (m, 1F, F^2), –148.6 (d, $^2J(F^1, H^1)$ = 52 Hz, 1F, F^1)] (0.01 mmol, 3 %), and $[Bu_4N][BF_4]$ (0.06 mmol, 19 %). To support the identification of $C_2F_5CFBr–CFHBr$ in the reaction solution by NMR spectroscopy, the homologue $C_4F_9CFBr–CFHBr$ was prepared and characterized (cf. last experiment).

Reaction of $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$: A. A solution of bromine (48 mg, 0.30 mmol) in CH_2Cl_2 (1.1 mL) was added dropwise to a solution of $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$ (224 mg, 0.38 mmol) in CH_2Cl_2 (3 mL) at ≈20 °C. The red solution was stirred without protection against light. After 24 h the solution was still red colored. After 66 h, the ^{19}F NMR spectrum of the now pale yellow solution showed the resonances of $[C_4F_9CF{=}CFBF_3]^–$ (0.29 mmol, 76 %) (*cis*/*trans* = 62:38), $C_4F_9CF{=}CFBr$ (0.06 mmol, 16 %) (*cis*/*trans* = 17:83), and $[BF_4]^–$ (0.04 mmol, 11 %). Further maintain at ≈20 °C for 28 h did not change the composition of the reaction solution.

B. A solution of bromine (99 mg, 0.62 mmol) and $[Bu_4N][trans\text{-}C_4F_9CF{=}CFBF_3]$ (259 mg, 0.44 mmol) in CH_2Cl_2 (5.5 mL) was stirred at ≈20 °C in a flask coated with aluminum foil. After 24 h the ^{19}F NMR spectrum of the red solution displayed the signals of $[C_4F_9CF{=}CFBF_3]^–$ (0.35 mmol, 80 %) (*cis*/*trans* = 17:83), *trans*-$C_4F_9CF{=}CFBr$ (0.08 mmol, 18 %), and $[BF_4]^–$ (0.08 mmol, 18 %). After 84 h the ^{19}F NMR spectrum of the still red solution showed the signals of $[C_4F_9CF{=}CFBF_3]^–$ (0.33 mmol, 75 %) (*cis*/*trans* = 24:76), *trans*-$C_4F_9CF{=}CFBr$[31] (0.11 mmol, 25 %), and $[BF_4]^–$ (0.10 mmol, 23 %), besides minor unknown admixtures.

Reactions of $[Bu_4N][(cis \text{ and } trans)\text{-}C_nF_{2n+1}CF{=}CFBF_3]$: A. A solution of $[Bu_4N][C_2F_5CF{=}CFBF_3]$ (0.15 mmol) (*cis*/*trans* = 60:40), and bromine (0.27 mmol) in CH_2Cl_2 (1 mL) was heated at 65–70 °C for 9 h and left overnight at ≈20 °C. The yellow solution was washed with cold water and dried with $MgSO_4$. The ^{19}F NMR spectrum showed the resonances of $[C_2F_5CF{=}CFBF_3]^–$ (0.08 mmol, 53 %) (*cis*/*trans* = 75:25), $C_2F_5CF{=}CFBr$ (0.07 mmol, 46 %) (*cis*/*trans* = 37:63), and $[BF_4]^–$ (0.07 mmol, 46 %).

B. A solution of $[Bu_4N][C_4F_9CF{=}CFBF_3]^–$ (0.19 mmol) (*cis*/*trans* = 42:58), and bromine (0.27 mmol) in CH_2Cl_2 (1 mL) was heated at 65–70 °C for 11 h and left overnight at ≈20 °C. The resulting yellow solution was washed with cold water and dried with $MgSO_4$. The ^{19}F NMR spectrum displayed the resonances of $[Bu_4N][C_4F_9CF{=}CFBF_3]^–$ (0.06 mmol, 32 %) (*cis*/*trans* = 67:33), $C_4F_9CF{=}CFBr$ (0.13 mmol, 68 %) (*cis*/*trans* = 15:85), and $[BF_4]^–$ (0.18 mmol, 95 %).

***cis*-$C_4F_9CF{=}CFBr$: ^{19}F NMR** (CH_2Cl_2): δ = –83.2 [dt, $^3J(F^1, F^2)$ = 16, $^4J(F^1, F^3)$ = 4 Hz, 1F, F^1], –115.6 [td, $^4J(F^3, F^5)$ = 10, $^3J(F^3, F^2)$ = 12 Hz, 2F, F^3], –140.5 (m, 1F, F^2); the resonances of the fluorine atoms $F^{4,5,6}$ overlapped with those of *trans*-C_4F_9CF = CFBr.

Reaction of $[Bu_4N][CF_2{=}CFBF_3]$: A solution of bromine (42 mg, 0.26 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a stirred solution of $[Bu_4N][CF_2{=}CFBF_3]$ (86 mg, 0.22 mmol) in CH_2Cl_2 (0.5 mL) at 0–2 °C. After 15 min, the ^{11}B and ^{19}F NMR spectra of the pale yellow solution showed the absence of $[CF_2{=}CFBF_3]^–$ and the formation of the molecule $CF_2{=}CFBr$ (0.10 mmol, 45 %), of the anions $[CF_2Br–CFBrBF_3]^–$ (0.04 mmol, 18 %) and $[BF_4]^–$ (0.12 mmol, 55 %) besides traces of $CF_2{=}CFH$ and $CF_2Br–CFBr_2$.

$[Bu_4N][CF_2Br–CFBrBF_3]$: ^{11}B NMR (CH_2Cl_2 + CD_2Cl_2): δ = –0.8 [dq ^2J(B, F^1) = 16, ^1J(B, F) = 40 Hz]. **^{19}F NMR** (CH_2Cl_2 + CD_2Cl_2): δ = –50.4 [d, $^2J(F^{2A}, F^{2B})$ = 165 Hz, 1F, F^{2A}], –52.3 [dd, $^3J(F^{2A}, F^1)$ = 22, $^2J(F^{2B}, F^{2A})$ = 165 Hz, 1F, F^{2B}], –138.0 (m, 1F, F^1), –147.8 (BF_3, overlapping with the signal of the other conformers) (conformer A); δ = –48.0 [qd, $^4J(F^{2A}, BF_3)$ = 17, $^2J(F^{2A}, F^{2B})$ = 161 Hz, 1F, F^{2A}], –52.1 [qdd $^4J(F^{2B}, BF_3)$ = 8, $^3J(F^{2B}, F^1)$ = 27, $^2J(F^{2B}, F^{2A})$ = 161 Hz, 1F, F^{2B}], –134.0 (m, 1F, F^1), –147.8 (BF_3, overlapping with the signal of the other conformers) (conformer B); δ = –48.3 [qdd $^4J(F^{2A}, BF_3)$ = 9, $^3J(F^{2A}, F^1)$ = 10, $^2J(F^{2A}, F^{2B})$ = 167 Hz, 1F, F^{2A}], –52.2 [qdd $^4J(F^{2B}, BF_3)$ = 8, $^3J(F^{2B}, F^1)$ = 15, $^2J(F^{2B}, F^{2A})$ = 167 Hz, 1F, F^{2B}], –134.0 (m, 1F, F^1), –147.8 (BF_3, overlapping with the signal of the other conformers) (conformer C) (ratio A:B:C = 53:25:22).

Reaction of $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$: A. A solution of bromine (0.30 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ (0.30 mmol) in $CHCl_3$ (1 mL) at 0 °C within 15 min. The color of bromine disappeared immediately after addition. The yellow solution was stirred for 1 h at ≈20 °C and diluted with $CDCl_3$. The ^{1}H and ^{19}F NMR spectra showed the resonances of *trans*-$C_4H_9CF{=}CFBr$ (0.17 mmol, 57 %), *trans*-$C_4H_9CF{=}CFH$[32] (0.10 mmol, 33 %), and $[Bu_4N][BF_4]$ (0.33 mmol, 110 %) besides a trace of $C_4H_9CFBr–CFHBr$.

The solution was treated with a further equivalent of bromine (0.30 mmol) in $CHCl_3$ (1 mL) and stirred at ≈20 °C for 15 h. All volatiles were distilled off at 80 °C (bath). The residue was cooled to ≈20 °C and extracted with CCl_4 (2 × 1 mL). The extract was passed through a short column (2 cm length) with anhydrous $MgSO_4$ and a

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probe was diluted with $CDCl_3$. The ^1H and ^{19}F NMR spectra showed the resonances of *trans*-$C_4H_9CF{=}CFBr$, *cis*-$C_4H_9CF{=}CFBr$, $C_4H_9CFBr–CFBr_2$, and $C_4H_9CFBr–CFHBr$ (molar ratio = 11:7:35:47), besides minor amounts of unknown products.

B. A solution of bromine (0.21 mmol) in CH_2Cl_2 (0.7 mL) was added dropwise to a solution of $[Bu_4N][$*trans*-$C_4H_9CF{=}CFBF_3]$ (0.21 mmol) in CH_2Cl_2 (2.5 mL) at ≈20 °C within 5 min. The color of bromine disappeared immediately after addition. The ^{19}F NMR spectrum showed the resonances of *trans*-$C_4H_9CF{=}CFBr$ (0.15 mmol, 71 %), *trans*-$C_4H_9CF{=}CFH$ (0.05 mmol, 24 %), and $[Bu_4N][BF_4]$ (0.21 mmol, 100 %).

***trans*-$C_4H_9CF{=}CFBr$: ^1H NMR** ($CDCl_3$ + CCl_4): δ = 2.41 [tdd, $^3J(H^3, H^4)$ = 7, $^4J(H^3, F^1)$ = 6, $^3J(H^3, F^2)$ = 21 Hz, 2 H, H^3], 1.54 (m, CH_2), 1.37 (m, CH_2), 0.93 [t, $^3J(H^6, H^5)$ = 7 Hz, 3 H, H^6]. **^{19}F NMR** ($CDCl_3$ + CCl_4): δ = –127.3 [td, $^4J(F^1, H^3)$ = 5, $^3J(F^1, F^2)$ = 134 Hz, 1F, F^1], –140.0 [td, $^3J(F^2, H^3)$ = 22, $^3J(F^2, F^1)$ = 134 Hz, 1F, F^2].

***cis*-$C_4H_9CF{=}CFBr$: ^1H NMR** ($CDCl_3$ + CCl_4): δ = 2.50 [td, $^3J(H^3, H^4)$ = 7, $^3J(H^3, F^2)$ = 21 Hz, 2 H, H^3], 1.5–1.3 (m, $2CH_2$), 0.9 [t, $^3J(H^6, H^5)$ = 7 Hz, 3 H, H^6]. **^{19}F NMR** ($CDCl_3$ + CCl_4): δ = –108.7 [d, $^3J(F^1, F^2)$ = 14 Hz, 1F, F^1], –128.4 [td, $^3J(F^2, H^3)$ = 22, $^3J(F^2, F^1)$ = 14 Hz, 1F, F^2].

$C_4H_9CFBr–CFHBr$: ^1H NMR ($CDCl_3$ + CCl_4): δ = 6.57 [dd, $^3J(H^1, F^2)$ = 5, $^2J(H^1, F^1)$ = 48 Hz, 1 H, H^1], 2.2 (m, $2H^3$), 1.5–1.3 (m, 4H, $H^{4,5}$), 0.91 [t, $^3J(H^6, H^5)$ = 7 Hz, 3H, H^6] {cf. $C_7H_{15}CFBrCFHBr$ ($CDCl_3$): δ = 6.6 [dd, $^3J(H^1, F^2)$ = 5, $^2J(H^1, F^1)$ = 48.1 Hz, 1 H, H^1] (diastereomer A); 6.5 [dd, $^3J(H^1, F^2)$ = 10, $^2J(H^1, F^1)$ = 48.1 Hz, 1 H, H^1] (diastereomer B); the signals of the C_7H_{15} moiety were not given[33]}. **^{19}F NMR** ($CDCl_3$ + CCl_4): δ = –113.1 [dddd, $^3J(F^2, H^1)$ = 4, $^3J(F^2, F^1)$ = 32, $^3J(F^2, H^{3A})$ = 8, $^3J(F^2, H^{3B})$ = 28 Hz, 1F, F^2], –143.8 [dd, $^3J(F^1, F^2)$ = 32, $^2J(F^1, H^1)$ = 48 Hz, 1F, F^1]. {cf. $C_7H_{15}CFBrCFHBr$ ($CDCl_3$): δ = –112.6 [d, $^3J(F^2, F^1)$ = 31.3 Hz, 1F, F^2], –142.9 [dd, $^3J(F^1, F^2)$ = 31.3, $^2J(F^1, H^1)$ = 48.1 Hz, 1F, F^1] (diastereomer A); δ –115.7 [d, $^3J(F^2, F^1)$ = 24.4 Hz, 1F, F^2], –142.1 [dd, $^3J(F^1, F^2)$ = 24.4, $^2J(F^1, H^1)$ = 48.1 Hz, 1F, F^1] (diastereomer B)[33]}.

$C_4H_9CFBr–CFBr_2$: ^{19}F NMR ($CDCl_3$ + CCl_4): δ –62.8 [d, $^3J(F^1, F^2)$ = 22 Hz, 1F, F^1], –110.5 [dd, $^3J(F^2, F^1)$ = 25, $^3J(F^2, H^{3A})$ = 35 Hz, 1F, F^2] {cf. $C_7H_{15}CFBrCFBr_2$ ($CDCl_3$): δ = –62.1 [d, $^3J(F^1, F^2)$ = 25.9 Hz, 1F, F^1], –109.7 [dd, $^3J(F^2, F^1)$ = 25.9, $^3J(F^2, H^{3A})$ = 38.2 Hz, 1F, F^2) [33]}.

Reaction of $[Bu_4N][C_4H_9CH{=}CHBF_3]$: A solution of bromine (0.33 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of $[Bu_4N][C_4H_9CH{=}CHBF_3]$ (0.33 mmol) (*cis*/*trans* = 67:33) in $CHCl_3$ (1 mL) at ≈20 °C within 10 min. The color of bromine disappeared immediately after addition. The yellow solution was stirred for 1 h. The ^1H and ^{19}F NMR spectra displayed the resonances of $C_4H_9CH{=}CHBr$[34] (0.16 mmol, 48 %) (*cis*/*trans* = 63:37), $C_4H_9CHBr–CH_2Br$[35] (0.10 mmol, 30 %), and $[Bu_4N][BF_4]$ (0.33 mmol, 100 %).

Reaction of $[Bu_4N][CF_3C{\equiv}CBF_3]$: Bromine (89 mg, 0.55 mmol) dissolved in CH_2Cl_2 (0.5 mL) was added to a stirred cold (0 °C) solution of $[Bu_4N][CF_3C{\equiv}CBF_3]$ (230 mg, 0.57 mmol) in CH_2Cl_2 (1.5 mL). After 10 min the bath was removed and the solution was stirred at ≈20 °C over a period of 1 h. The ^{11}B and ^{19}F NMR spectra showed the formation of $[Bu_4N][CF_3CBr{=}CBrBF_3]$ (*cis*/*trans* = 62:38) (0.45 mmol, 92 %), $[Bu_4N][BF_4]$, and $CF_3CBr{=}CBr_2$ (both ~0.03 mmol, 6 %]. The conversion of the starting borate was determined to 86 %. A second portion of bromine (107 mg, 0.66 mmol) (total 196 mg, 1.22 mmol) in CH_2Cl_2 (0.8 mL) was added. After stirring at ≈20 °C for 24 h, the red solution contained $[Bu_4N][BF_4]$ (0.43 mmol, 75 %), $CF_3CBr{=}CBr_2$ (0.43 mmol, 75 %), and $[Bu_4N][CF_3CBr{=}CBrBF_3]$ (0.09 mmol, 16 %) (*cis*/*trans* = 62:38), (^{19}F NMR). The solution was concentrated on an evaporator and the oil was extracted with CCl_4 (0.5 mL). The pale yellow extract contained $CF_3CBr{=}CBr_2$ (0.40 mmol, 70 %) (^{13}C, ^{19}F NMR).

$[Bu_4N][CF_3CBr{=}CBrBF_3]$: ^{11}B NMR (CH_2Cl_2): δ = 0.3 [q, ^1J(B, F) = 38 Hz, BF_3]. **^{19}F NMR** (CH_2Cl_2): δ = –57.4 [q, $^5J(F^3, BF_3)$ = 11 Hz, 3F, F^3], –137.5 [q (1:1:1:1)q, ^1J(F, B) = 37, $^5J(BF_3, F^3)$ = 11 Hz, 3F, BF_3] ([*cis*-$CF_3CBr{=}CBrBF_3]^-$); –57.8 [q, $^5J(F^3, BF_3)$ = 1 Hz, 3F, F^3], –140.4 [q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3] ([*trans*-$CF_3CBr{=}CBrBF_3]^-$).

$CF_3CBr{=}CBr_2$: ^{13}C NMR (CCl_4): δ = 121.0 [q, $^1J(C\text{-}3, F^3)$ = 275 Hz, C-3], 115.8 [q, $^2J(C\text{-}2, F^3)$ = 39 Hz, C-2], 99.9 [q, $^3J(C\text{-}1, F^3)$ = 3 Hz, C-1]. **^{19}F NMR** (CCl_4): δ = –58.6 (s, 3F, F^3).

Reaction of $[Bu_4N][C_4H_9C{\equiv}CBF_3]$: A solution of bromine (0.30 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of $[Bu_4N][C_4H_9C{\equiv}CBF_3]$ (0.28 mmol) in $CHCl_3$ (1 mL) at 0 °C within 15 min. The color of bromine disappeared immediately after addition. The yellow solution was stirred for 1 h at ≈20 °C. The ^1H and ^{19}F NMR spectra showed the resonances of $C_4H_9C{\equiv}CBr$[36] (0.08 mmol, 29 %), $C_4H_9C{\equiv}CH$ (0.07 mmol, 25 %), *trans*-$C_4H_9CBr{=}CHBr$[36] (0.05 mmol, 18 %), $C_4H_9CBr{=}CBr_2$[36] (0.05 mmol, 18 %), and $[Bu_4N][BF_4]$ (0.28 mmol, 100 %).

To confirm the presence of the alkynes $C_4H_9C{\equiv}CH$ and $C_4H_9C{\equiv}CBr$, the solution was treated with bromine (0.33 mmol) in $CHCl_3$ (1 mL) and stirred at ≈20 °C for 15 h. All volatiles were distilled off at 80 °C (bath), the residue was cooled to ≈20 °C and extracted with CCl_4 (2 × 1 mL). The extract was passed through a short column (2 cm length) with anhydrous $MgSO_4$ and a probe was diluted with $CDCl_3$. The ^1H and ^{19}F NMR spectra showed the resonances of *trans*-$C_4H_9CBr{=}CHBr$, *cis*-$C_4H_9CBr{=}CHBr$,[36] and $C_4H_9CBr{=}CBr_2$ (molar ratio = 40:16:44) besides minor amounts of unknown products and the absence of the alkynes and of $[Bu_4N][BF_4]$.

Reaction of $[Bu_4N][C_4H_9BF_3]$: A solution of bromine (0.30 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of $[Bu_4N][C_4H_9BF_3]$ (0.30 mmol) in $CHCl_3$ (1 mL) at 0 °C within 15 min. The color of bromine disappeared immediately after addition. The yellow solution was stirred for 1 h at ≈20 °C. The ^1H and ^{19}F NMR spectra showed the resonances of C_4H_9Br (0.15 mmol, 50 %), C_4H_{10} (0.13 mmol, 43 %), and $[Bu_4N][BF_4]$ (0.28 mmol, 93 %).

Attempted Reaction of $[Bu_4N][C_6F_{13}BF_3]$ with Bromine: A solution of $[Bu_4N][C_6F_{13}BF_3]$ (0.30 mmol) in $CHCl_3$ (2.3 mL) and bromine (0.30 mmol) in $CHCl_3$ (1 mL) was stirred at ≈20 °C for 3 d. No reaction was detected (^{19}F NMR).

Reactions of Fluoroalkenyl- and Fluoroalkynyltrifluoroborates with Bromine Trifluoride-Bromine (1:1, Equivalent of "BrF")

Preparation of Bromine Trifluoride-bromine (1:1) Solutions: A solution of BrF_3 (100 mg, 0.73 mmol) in PFB (0.4 mL) was stirred with dried NaF (32 mg) for 2 h and centrifuged. The mother liquor was transferred into a 8 mm. i. d. FEP trap equipped with a magnetic stir bar in an atmosphere of dry argon. A solution of bromine (116 mg, 0.73 mmol) in PFB (0.5 mL) was added in one portion. A red-brown solution resulted which was diluted with PFB (0.1 mL).

(BrF_3–Br_2) (1:1): ^{19}F NMR (PFB 24 °C): δ = –23.0 (s, $\Delta\nu_{1/2}$ = 1512 Hz) {cf. with ^{19}F NMR spectrum of BrF_3 in PFB at 24 °C: δ = –17.9 (s, $\Delta\nu_{1/2}$ = 27 Hz)[4]}.

The solubility of bromine in PFB (160 mg, 1.00 mmol per mL of PFB; 21 °C) was determined visually by portion-wise addition of PFP to Br_2 in a narrow-diameter tube.

Reaction of [Bu_4N][*cis*-C_2F_5CF=$CFBF_3$] with "BrF": A solution of BrF_3 (0.10 mmol) and Br_2 (0.10 mmol) (0.30 mmol "BrF") in PFB (0.1 mL) was added to a stirred solution of [Bu_4N][*cis*-C_2F_5CF=$CFBF_3$] (0.63 mmol) in PFB (2 mL). The red-orange solution was stirred at ≈20 °C for 5 h and changed the color to yellow. The ^{19}F NMR spectrum showed the resonances of [Bu_4N][C_2F_5CF=$CFBF_3$] (0.45 mmol, 71 %) (*cis*/*trans* = 56:44), [Bu_4N][C_2F_5CFBr–CF_2BF_3] (0.16 mmol, 25 %) besides C_2F_5CF=CFBr (0.02 mmol, 3 %) (*cis*/*trans* = 40:60) and [Bu_4N][BF_4] (0.02 mmol, 3 %). No changes were observed after further 50 h at ≈20 °C.

Reaction of [Bu_4N][CF_2=$CFBF_3$] with "BrF": A solution of [Bu_4N][CF_2=$CFBF_3$] (136 mg, 0.34 mmol) and [Bu_4N][PF_6] (35 mg, 0.09 mmol) (internal integral standard) in PFB (2.1 mL) in a 11.7 mm. i. d. PFA trap was cooled to –15 °C. Afterwards, a solution of BrF_3 (0.11 mmol) and Br_2 (0.11 mmol) (0.33 mmol of "BrF") in PFB (0.15 mL) was added in one portion with stirring. Within 1 min a colorless solution was formed. After 15 min at –15 °C, the solution contained [Bu_4N][BF_4] (0.34 mmol, 100 %), CF_2=CFBr (0.17 mmol, 50 %), and CF_3–CF_2Br (0.11 mmol, 32 %) and traces of CF_2=CFH and [Bu_4N][CF_2=$CFBF_3$] besides the standard [Bu_4N][PF_6] (^{11}B, ^{19}F NMR).

Reaction of [Bu_4N][*trans*-C_4H_9CF=$CFBF_3$] with "BrF": A cold (0 °C) solution of BrF_3 (0.10 mmol) and Br_2 (0.10 mmol) (0.30 mmol "BrF") in PFB (0.1 mL) was added to a cold (0 °C) stirred solution of [Bu_4N][*trans*-C_4H_9CF=$CFBF_3$] (0.33 mmol) in PFB (9 mL). The pale-yellow solution was stirred at 0 °C for 30 min and at ≈20 °C for 30 min. The ^{19}F NMR spectrum showed the resonances of [Bu_4N][*trans*-C_4H_9CF=$CFBF_3$] (0.06 mmol, 82 % conversion), *trans*-C_4H_9CF=CFBr (0.17 mmol, 63 %), and [Bu_4N][BF_4] (0.24 mmol, 89 %). The volatile components were distilled off and collected and the residue was extracted with CCl_4 (2 mL). The extract was combined with the distillate and concentrated to a volume of 2 mL. The ^{1}H and ^{19}F NMR spectra showed the presence of *trans*-C_4H_9CF=CFBr (0.24 mmol, 73 %), besides an admixture of PFB and traces of *cis*-C_4H_9CF=CFBr, *cis*- and *trans*-C_4H_9CF=CFH.

C_4H_9CF=CFBr: MS (EI) calcd. for $C_6H_9BrF_2$ 197.9850209 (^{79}Br), found 197.9852 (^{79}Br).

Reaction of [Bu_4N][$CF_3C{\equiv}CBF_3$] with "BrF": A solution of [Bu_4N][$CF_3C{\equiv}CBF_3$] (101 mg, 250 μmol) and [Bu_4N][PF_6] (59 mg, 153 μmol) (internal integral standard) in PFB (1.3 mL) in a 8.0 mm. i. d. FEP trap was cooled to ≈0 °C. Afterwards, solutions of BrF_3 (100 μmol) and Br_2 (100 μmol) (300 μmol of "BrF") in PFB (0.1 mL) were added. The solution was stirred at ≈20 °C for 0.5 h till discoloration. It contained [Bu_4N][$CF_3C{\equiv}CBF_3$] (180 μmol, 28 % conversion), [Bu_4N][CF_3CBr=$CBrBF_3$] (32 μmol, 46 %) (*cis*/*trans* = 63:37), [Bu_4N][CF_3CBr_2–$CFBrBF_3$] (5 μmol, 7 %), [Bu_4N][CF_3CBr_2–CF_2BF_3] (14 μmol, 20 %), [Bu_4N][BF_4] (35 μmol, 50 %), $CF_3C{\equiv}CBr$ (6 μmol, 9 %), and CF_3CBr=CBr_2 (12 μmol, 17 %) (^{19}F NMR). The solution was reacted with further BrF_3 (300 μmol) and Br_2 (300 μmol) (total amount: 1200 μmol of "BrF") in PFB (0.1 mL). The red-orange solution was stirred at ≈20 °C for 4 h and became pale yellow. It contained [Bu_4N][CF_3CBr=$CBrBF_3$] (21 μmol, 8 %) (*cis*/*trans* = 86:14), [Bu_4N][CF_3CBr_2–CF_2BF_3] (70 μmol, 28 %), [Bu_4N][BF_4] (138 μmol, 55 %), and CF_3CBr=CBr_2 (80 μmol, 32 %) (^{19}F NMR). The solvent was removed on an evaporator at <30 °C (bath) and the remaining yellow oil was extracted with CCl_4 (1 mL). The extract contained CF_3CBr=CBr_2 besides residual PFB (^{19}F NMR). In all cases, signals of minor unrecognized components were observed besides PFB. In the first step, the presence of [Bu_4N][CF_3CBr_2–$CFBrBF_3$] (≤5 μmol) {signals at δ = –57.7 [dq $^4J(F^3, F^1)$ = 9, $^5J(F^3, BF_3)$ = 9 Hz, 3F, F^3), –68.0 (m, 1F, F^1), –139.7 [q, ^1J(F,B) = 38 Hz, 3F, BF_3} was assumed.

Reactions of Tetrabutylammonium Organyltrifluoroborates with Iodine Chloride in Halocarbon Solutions

Reaction of [Bu_4N][*trans*-C_4F_9CF=$CFBF_3$]: A solution of [Bu_4N][*trans*-C_4F_9CF=$CFBF_3$] (190 mg, 0.32 mmol) in CH_2Cl_2 (0.5 mL) was treated with portions of a solution of ICl (67 mg, 0.41 mmol) in CH_2Cl_2 (0.3 mL) at ≈20 °C. The addition of the first portion of ICl (0.12 mmol, 0.38 equiv.) ended with a molar ratio of [Bu_4N][*trans*-C_4F_9CF=$CFBF_3$] to *trans*-C_4F_9CF=CFI of 64:36 which did not change within 20 h. The addition of following portions of ICl and sequential NMR measurements after 30 min showed the fast conversion of [Bu_4N][*trans*-C_4F_9CF=$CFBF_3$] to *trans*-C_4F_9CF=CFI (*n* equiv. ICl/ratio ([Bu_4N][*trans*-C_4F_9CF=$CFBF_3$]:*trans*-C_4F_9CF=CFI): 0.38/56:44; 0.53/32:68; 1.28/0:100). The ^{19}F NMR spectra contained a broadened signal ($\Delta\nu_{1/2}$ = 255 Hz) of a *F*-B resonance at δ = –144 ppm.

***trans*-C_4F_9CF=CFI: ^{19}F NMR** (CH_2Cl_2): δ = –81.8 [tt, $^3J(F^6, F^5)$ = 3, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6], –106.9 [ttd, $^5J(F^1, F^4)$ = 6, $^4J(F^1, F^3)$ = 27, $^3J(F^1, F^2)$ = 150 Hz, 1F, F^1], –117.4 [dtd $^3J(F^3, F^2)$ = 13, $^4J(F^3, F^5)$ = 13, $^4J(F^3, F^1)$ = 26 Hz, 2F, F^3], –125.2 (m, 2F, F^4), –127.1 (m, 2F, F^5), –145.9 [md $^3J(F^2, F^1)$ = 150 Hz, 1F, F^2] {ref.[31] **^{19}F NMR** (CH_2Cl_2): δ = –81.7 (3F, F^6), –106.6 [ttd, $^5J(F^1, F^4)$ = 5.5, $^4J(F^1, F^3)$ = 27, $^3J(F^1, F^2)$ = 151 Hz, 1F, F^1], –117.0 (2F, F^3), –124.8 (2F, F^4), –126.9 (2F, F^5), –144.8 [d, $^3J(F^2, F^1)$ = 151 Hz, 1F, F^2]}.

Reaction of [Bu_4N][CF_2=$C(CF_3)BF_3$]: A solution of ICl (120 mg, 0.73 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a solution of [Bu_4N][CF_2=$C(CF_3)BF_3$] (273 mg, 0.62 mmol) in CH_2Cl_2 (0.7 mL) at ≈20 °C over a period of 30 min. The ^{19}F NMR spectrum showed the formation of CF_2=$C(CF_3)$I (0.47 mmol, 76 %) and CF_2=$C(CF_2Cl)$I (0.04 mmol, 6 %) and contained a broadened *F*-B signal at δ = –144 ppm ($\Delta\nu_{1/2}$ = 347 Hz). The ^{11}B NMR spectrum contained unresolved signals at 3.5 and 0 ppm in the integral ratio 3:100.

CF_2=$C(CF_3)$I: ^{19}F NMR (CH_2Cl_2): δ = –58.6 [dd, $^4J(F^3, F^{1cis})$ = 11, $^4J(F^3, F^{1trans})$ = 22 Hz, 3F, F^3], –61.7 [dq $^2J(F^{1trans}, F^{1cis})$ = 3, $^4J(F^{1trans}, F^3)$ = 22 Hz, 1F, F^{1trans}], –61.9 [dq $^2J(F^{1cis}, F^{1trans})$ = 3, $^4J(F^{1cis}, F^3)$ = 11 Hz, 1F, F^{1cis}] {ref.[37] **^{19}F NMR** (DMF): δ = –58.8 [d 22 Hz, d 11 Hz, 3F, F^3], –61.6 [q 22 Hz, d 2 Hz, 1F], –62.0 [q 11 Hz, d 3 Hz, 1F]}.

CF_2=$C(CF_2Cl)$I: ^{19}F NMR (CH_2Cl_2): δ = –43.7 [dd, $^4J(F^3, F^{1cis})$ = 9, $^4J(F^3, F^{1trans})$ = 29 Hz, 2F, F^3], –61.4 [dt, $^2J(F^{1trans}, F^{1cis})$ = 4, $^4J(F^{1trans}, F^3)$ = 29 Hz, 1F, F^{1trans}], –63.3 [dt, $^2J(F^{1cis}, F^{1trans})$ = 4, $^4J(F^{1cis}, F^3)$ = 9 Hz, 1F, F^{1cis}].

Reaction of [Bu_4N][CF_2=$CFBF_3$]: A dark solution of ICl (66 mg, 0.40 mmol) in CH_2Cl_2 (0.3 mL) was added dropwise to a stirred solution of [Bu_4N][CF_2=$CFBF_3$] (110 mg, 0.28 mmol) in CH_2Cl_2 (0.5 mL) at ≈20 °C. The yellowish solution was stirred for 15 min. The ^{19}F NMR spectrum displayed the formation of CF_2=CFI (0.21 mmol, 75 %) and contained a broadened *F*-B signal at δ = –144 ppm ($\Delta\nu_{1/2}$

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= 268 Hz). The ^{11}B NMR spectrum contained unresolved signals at 2.5 and –1.0 ppm in the ratio 1:100 and no resonances of either $[CF_2{=}CFBF_3]^-$ nor $[CF_2X{-}CFYBF_3]^-$.

Reaction of [Bu$_4$N][*trans*-C$_4$H$_9$CF=CFBF$_3$]: A solution of ICl (0.38 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of [Bu$_4$N][*trans*-C$_4$H$_9$CF=CFBF$_3$] (0.36 mmol) in $CHCl_3$ (1.1 mL) at ≈20 °C within 5 min. The color of ICl disappeared immediately after dropping. The yellow solution was stirred for 0.5 h at ≈20 °C and diluted with $CDCl_3$. The ^{1}H and ^{19}F NMR spectra showed the resonances of *trans*-C$_4$H$_9$CF=CFI (0.23 mmol, 64 %), *trans*-C$_4$H$_9$CF=CFH (0.13 mmol, 36 %), and [Bu$_4$N][BF$_4$] (0.36 mmol, 100 %; a singlet at δ = –152.2 ppm) besides a weak resonance at δ = –126 ppm ($\Delta\nu_{1/2}$ = 97 Hz).

***trans*-C$_4$H$_9$CF=CFI: ^{1}H NMR** ($CDCl_3$ + $CHCl_3$): δ = 2.46 [tdd, ^3J(H^3, H^4) = 7, ^4J(H^3, F^1) = 6, ^3J(H^3, F^2) = 21 Hz, 2H, H^3], 1.6–1.3 (m, 4H, H$^{4,\ 5}$), 0.87 [t, ^3J(H^6, H^5) = 7 Hz, 3H, H^6] {ref.[38] δ = 2.65 [dq ^3J(H^3, F^2) = 20, ^4J(H^3, F^1) = 7.5 Hz, 2H, H^3], 1.5 (4H), 0.95 (t, 3H, H^6)}. **^{19}F NMR** ($CDCl_3$ + $CHCl_3$): δ = –129.1 [td, ^4J(F^1, H^3) = 6, ^3J(F^1, F^2) = 141 Hz, 1F, F^1], –130.9 [td, ^3J(F^2, H^3) = 22, ^3J(F^2, F^1) = 141 Hz, 1F, F^2] {ref.[38] δ = –128.2 (dt, 1F, F^1), –130.6 (dt, 1F, F^2); ^3J(F^1, F^2) = 141 Hz}.

Reaction of [Bu$_4$N][C$_4$H$_9$CH=CHBF$_3$]: A solution of ICl (0.27 mmol) in CH_2Cl_2 (0.9 mL) was added dropwise within 5 min to a solution of [Bu$_4$N][C$_4$H$_9$CH=CHBF$_3$] (*cis*/*trans* = 67:33) (0.27 mmol) in CH_2Cl_2 (1 mL) at 20 °C. The color of ICl disappeared immediately after dropping. After the last drop a red-brownish solution remained which was stirred for 1 h at 20 °C. The ^{1}H NMR spectrum showed the resonances of C$_4$H$_9$CH=CHI[39] (0.11 mmol, 41 %) (*cis*/*trans* = 55:45), C$_4$H$_9$CHCl–CH$_2$I[40] (0.03 mmol, 11 %), C$_4$H$_9$CHCl–CH$_2$Cl[41] (0.03 mmol, 11 %), and [Bu$_4$N][BF$_4$] (0.27 mmol, 100 %). To remove the latter salt, the solution was diluted with CCl_4 (2 mL), and the volatile components were distilled off at 70 °C (bath). The yellow distillate contained drops of a dense red oil, which were removed by passing through a short column (length 1.5 cm) filled with anhydrous $MgSO_4$. The yellow liquid phase contained C$_4$H$_9$CH=CHI[39] (31 %) (*cis*/*trans* = 58:42), C$_4$H$_9$CHCl–CH$_2$I (32 %), C$_4$H$_9$CH=CHCl (5 %) (*cis*/*trans* = 40:60), besides minor unknown products (GC-MS data).

Reaction of [Bu$_4$N][CF$_3$C≡CBF$_3$]: A solution of ICl (85 mg, 0.52 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a solution of [Bu$_4$N][CF$_3$C≡CBF$_3$] (152 mg, 0.38 mmol) in CH_2Cl_2 (0.9 mL) at ≈20 °C over a period of 1 h. The ^{19}F NMR spectrum showed the formation of CF$_3$C≡CI (0.34 mmol, 89 %) (δ = –50.7 ppm) (proved by the addition of the pure substance[42]) besides [Bu$_4$N][BF$_4$] {δ(F) = –152 ppm [q, ^1J(F, B) = 1 Hz]} (0.32 mmol, 84 %).

Reaction of [Bu$_4$N][C$_4$H$_9$BF$_3$]: A solution of ICl (0.31 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of [Bu$_4$N][C$_4$H$_9$BF$_3$] (0.31 mmol) in CH_2Cl_2 (0.9 mL) at 20 °C. The color of ICl disappeared immediately after dropping. After the last drop a red-brownish solution remained. The solution was stirred for 3 h at 20 °C. The ^{1}H and ^{19}F NMR spectra showed the resonances of C$_4$H$_9$I (0.15 mmol, 48 %), C$_4$H$_{10}$ (0.06 mmol, 19 %), [Bu$_4$N][BF$_4$] {δ(F) = –152 ppm (s)} (0.31 mmol, 100 %) and a very broad resonance at δ = –132 ppm.

Reactions on the Surface of Potassium Perfluoroalkenyltrifluoroborates with Chlorine in Halocarbons

Reaction of K[CF$_2$=CFBF$_3$]: Chlorine (4.5 mmol) was bubbled into a stirred suspension of K[CF$_2$=CFBF$_3$] (173 mg, 0.92 mmol) in CH_2Cl_2 (2 mL) at ≈20 °C for 0.5 h. The separated mother liquor showed the presence of CF$_2$Cl–CFCl$_2$ (0.01 mmol, 1 %) (^{19}F NMR). The solid part was dried in vacuo, extracted with MeCN (2 mL). The extract was evaporated to dryness to yield a white solid, K[CF$_2$Cl–CFClBF$_3$], (155 mg, 65 %).

When a stirred suspension of K[CF$_2$Cl–CFClBF$_3$] (155 mg) in dichloromethane (2 mL) was treated with further chlorine (4.5 mmol) (≈20 °C, 30 min), no further reaction occurred. The ^{19}F NMR spectrum of the mother liquor showed no fluoroorganic compounds. After evaporation of the suspension in vacuo to dryness, K[CF$_2$Cl–CFClBF$_3$] (145 mg) was recovered.

K[CF$_2$Cl–CFClBF$_3$]: ^{11}B NMR (CH_3CN): δ = –0.1 [dq ^2J(B, F^1) = 16, ^1J(B, F) = 39 Hz]. **^{19}F NMR** (CH_3CN): δ = –60.2 [qdd ^4J(F^{2A}, B*F*$_3$) = 7, ^3J(F^{2A}, F^1) = 13, ^2J(F^{2A}, F^{2B}) = 169 Hz, 1F, F^{2A}], –61.5 [qdd ^4J(F^{2B}, B*F*$_3$) = 6, ^3J(F^{2B}, F^1) = 12, ^2J(F^{2B}, F^{2A}) = 169 Hz, 1F, F^{2B}], –142.0 (m, 1F, F^1), –149.5 [dtq (1:1:1:1), ^3J(B*F*$_3$, F^1) = 6, ^4J(B*F*$_3$, F^2) = 6, ^1J(F, B) = 39 Hz, 3F, B*F*$_3$]. Anal. for $C_2BCl_2F_6K$ (258,83): calcd. C 9.28; Cl 27.40 %; F 44.04; found: C 9.1; Cl 27.2; F 44.5 %.

Attempted Reaction of K[*trans*-C$_4$F$_9$CF=CFBF$_3$]: Chlorine (3 mmol) in argon was slowly bubbled into a stirred suspension of K[*trans*-C$_4$F$_9$CF=CFBF$_3$] (249 mg, 0.64 mmol) in 1,2-dichloroethane (2.5 mL) for 1 h. The solid was filtered off. After drying on air 222 mg of the starting borate was recovered (^{19}F NMR).

Reactions on the Surface of Potassium Organyltrifluoroborates with Bromine in Halocarbons

Reaction of K[CF$_2$=CFBF$_3$]: A. Bromine (95 mg, 0.59 mmol) was added to a suspension of K[CF$_2$=CFBF$_3$] (110 mg, 0.55 mmol) in CH_2Cl_2 (1 mL) at ≈0 °C. The suspension was stirred for 1 h before the mother liquor was separated. The precipitate was washed with CH_2Cl_2 (2 × 2 mL). The combined extracts contained CF$_2$Br–CFBr$_2$ (0.03 mmol, 5 %) (^{19}F NMR). The solid residue was dried in vacuo and extracted with MeCN. The extract was evaporated to dryness yielding K[CF$_2$Br–CFBrBF$_3$] (178 mg, 93 % yield).

B. The reaction of bromine (160 mg, 1.00 mmol) and K[CF$_2$=CFBF$_3$] (190 mg, 1.00 mmol) in CH_2Cl_2 suspension (1 mL) was performed at ≈20 °C for 24 h as above. The combined CH_2Cl_2 extracts contained CF$_2$Br–CFBr$_2$ (0.08 mmol, 8 %) and a trace of CF$_2$Br–CFHBr (^{19}F NMR). Borate K[CF$_2$Br–CFBrBF$_3$] was isolated in 70 % yield (242 mg).

C. K[CF$_2$=CFBF$_3$] (116 mg, 0.61 mmol) was suspended in CH_2Cl_2 (0.5 mL) in a quartz tube and bromine (99 mg, 0.61 mmol) was added. The suspension was stirred at ≈20 °C for 9 h under irradiation with a photo lamp (100 W). The mother liquor was separated. The solid part was washed with CH_2Cl_2 (2 × 2 mL). The combined extracts contained CF$_2$Br–CFBr$_2$ (0.04 mmol, 7 %) (^{19}F NMR). The solid residue was dried in vacuo and extracted with acetone. The extract was evaporated to dryness yielding K[CF$_2$Br–CFBrBF$_3$] (135 mg, 0.39 mmol, 64 % yield).

K[CF$_2$Br–CFBrBF$_3$]: ^{11}B NMR (CH_3CN): δ = 0.0 [dq ^2J(B, F^1) = 16, ^1J(B, F) = 39 Hz]. **^{19}F NMR** (CH_3CN): δ = –50.7 [qdd ^4J(F^{2A}, B*F*$_3$) = 6, ^3J(F^{2A}, F^1) = 18, ^2J(F^{2A}, F^{2B}) = 167 Hz, 1F, F^{2A}], –52.7 [qdd ^4J(F^{2B}, B*F*$_3$) = 6, ^3J(F^{2B},F^1) = 21, ^2J(F^{2B}, F^{2A}) = 167 Hz, 1F, F^{2B}], –138.5 (m, 1F, F^1), –147.7 [q (1:1:1:1)dt, ^1J(F, B) = 39, ^3J(B*F*$_3$, F^1) = 6, ^4J(B*F*$_3$, F^2) = 6 Hz, 3F, B*F*$_3$] (conformer A, cf. reaction of [Bu$_4$N][CF$_2$=CFBF$_3$] with Br$_2$). NMR spectroscopic data in DMSO

are given in Table S2 (Supporting Information). Anal. for $C_2BBr_2F_6K$ (347,73): calcd. C 6.91; Br 45.96; F 32.78 %; found: C 6.8; Br 45.7; F 33.0 %.

$CF_2Br–CFBr_2$. ^{19}F NMR (CH_3CN): δ = –59.0 [d, $^3J(F^2, F^1)$ = 17 Hz, 2F, F^2], –70.4 [t, $^3J(F^1, F^2)$ = 17 Hz, 1F, F^1) {ref.[43] (in CF_2Cl_2) (–36 °C): δ = –59.1 (2F F^2), –68.9 (1F F^1)}.

$CF_2Br–CFHBr$: ^{19}F NMR (CH_2Cl_2): δ = –59.6 [ddd, $^3J(F^{2A}, H^1)$ = 3, $^3J(F^{2A}, F^1)$ = 24, $^2J(F^{2A}, F^{2B})$ = 172 Hz, 1F, F^{2A}], –63.9 [ddd, $^3J(F^{2B}, H^1)$ = 9, $^3J(F^{2B}, F^1)$ = 21, $^2J(F^{2B}, F^{2A})$ = 172 Hz, 1F, F^{2B}], –149.4 [ddd, $^2J(F^1, H^1)$ = 47, $^3J(F^1, F^{2A})$ = 24, $^3J(F^1, F^{2B})$ = 21 Hz, 1F, F^2] {ref.[44] (in CCl_3F): δ = –59.3 (1F, F^{2A}), –63.8 (1F, F^{2B}), –149.3 (1F, F^1); $^3J(F^{2A}, H^1)$ = 3.4, $^3J(F^{2A}, F^1)$ = 24.0, $^2J(F^{2A}, F^{2B})$ = 172.5, $^3J(F^{2B}, H^1)$ = 9.1, $^3J(F^{2B}, F^1)$ = 20.6, $^2J(F^1, H^1)$ = 47.0 Hz)}.

Attempted Reaction of K[*trans*-C_4F_9CF=$CFBF_3$]: A. K[*trans*-C_4F_9CF=$CFBF_3$] (118 mg, 0.30 mmol) was suspended in a solution of bromine (64 mg, 0.40 mmol) in CCl_4 (1 mL) and stirred at 93–95 °C (sealed tube) for 14 h. After cooling to 20 °C, the solid part was isolated, washed with CH_2Cl_2 (4 mL), and dried in vacuo. The starting material K[*trans*-C_4F_9CF=$CFBF_3$] (113 mg, 96 %) (^{19}F NMR) was recovered.

B. K[*trans*-C_4F_9CF=$CFBF_3$] (186 mg, 0.48 mmol) was suspended in a solution of bromine (87 mg, 0.54 mmol) in CH_2Cl_2 (1.5 mL) and stirred at ≈20 °C for 20 h. The solid part was separated, washed with CH_2Cl_2 (2 mL), and dried in vacuo to give K[*trans*-C_4F_9CF=$CFBF_3$] (168 mg, 90 %) (^{19}F NMR).

Reaction of K[*trans*-C_4H_9CF=$CFBF_3$]: A solution of bromine (118 mg, 0.74 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a suspension of K[*trans*-C_4H_9CF=$CFBF_3$] (98 mg, 0.43 mmol) in CH_2Cl_2 (2 mL) at ≈20 °C within 5 min. The color of bromine disappeared within a few min. The suspension was stirred for 1 h, the mother liquor was separated by centrifugation, washed with water and dried with $MgSO_4$. The ^{19}F NMR spectrum showed the resonances of C_4H_9CF=CFBr (*cis*/*trans* = 40:60) (0.03 mmol, 7 %), C_4H_9CF=CFH (*cis*/*trans* = 18:82) (0.07 mmol, 16 %), $C_4H_9CFBr–CFBr_2$ (0.20 mmol, 47 %), and $C_4H_9CFBr–CFHBr$ (0.07 mmol, 16 %). The precipitate was washed with CH_2Cl_2 and dried in vacuo. The acetone extract contained only traces of fluoroorganics (^{19}F NMR).

Reaction of K[*trans*-C_6H_5CF=$CFBF_3$]: A solution of bromine (78 mg, 0.49 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a suspension of K[*trans*-C_6H_5CF=$CFBF_3$] (71 mg, 0.28 mmol) in CH_2Cl_2 (2 mL) at ≈20 °C within 5 min. The suspension was stirred for 1 h, the mother liquor was separated after centrifugation, washed with water and dried with $MgSO_4$. The ^{19}F NMR spectrum showed the resonances of *trans*-C_6H_5CF=CFBr (0.04 mmol, 14 %) and $C_6H_5CFBr–CFBr_2$ (0.21 mmol, 75 %) besides minor amounts of unknown products. The precipitate was washed with CH_2Cl_2 and dried in vacuo. The acetone extract contained only traces of fluoroorganics (^{19}F NMR).

Attempted Reaction of K[$C_4H_9BF_3$]: A solution of bromine (0.54 mmol) in CH_2Cl_2 (1.8 mL) was added to a suspension of K[$C_4H_9BF_3$] (78 mg, 0.47 mmol) in CH_2Cl_2 (1 mL) at ≈20 °C. The red suspension was stirred for 6 h. The mother liquor contained only traces of C_4H_9Br and C_4H_{10} (^1H NMR).

Attempted Reaction of K[CF_3C≡CBF_3]: A suspension of salt K[CF_3C≡CBF_3] (100 mg, 0.50 mmol) and bromine (252 mg, 1.57 mmol) was stirred in CH_2Cl_2 (1 mL) at ≈20 °C for 36 h. The ^{19}F NMR spectrum of the decanted mother liquor showed a negligible amount of fluoroorganic compounds. The solid was washed with CH_2Cl_2 (2 mL) and dried in vacuo to recover K[CF_3C≡CBF_3] (92 mg, 92 %) (^{19}F NMR).

Reaction on the Surface of K[CF_2=$CFBF_3$] with Iodine Chloride in Halocarbon

A solution of ICl (1.13 mmol) in CH_2Cl_2 (5 mL) was added dropwise to the stirred suspension of K[CF_2=$CFBF_3$] (174 mg, 0.92 mmol) in CH_2Cl_2 (1 mL) at ≈20 °C. The suspension was stirred for 1.5 h and centrifuged. The mother liquor was decanted. The dark violet solution contained CF_2=CFI (0.26 mmol, 31 %) and unknown products (^{19}F NMR). The solid part was washed with CH_2Cl_2 (2 × 2 mL), dried in vacuo at ≈20 °C for 1 h and extracted with MeCN (2 × 2 mL). The solvent was removed under reduced pressure at 25 °C to give a yellowish solid (122 mg). The ^{11}B and ^{19}F NMR spectra in CD_3CN showed the resonances of K[CF_2=$CFBF_3$] (0.07 mmol, 92 % conversion), K[$CF_2I–CFClBF_3$] (0.25 mmol, 29 %) besides an admixture of presumably K[FC(O)–$CFClBF_3$] (0.06 mmol, 7 %) {signals at δ = 18.8 [qd, $^4J(F^2, BF_3)$ = 6, $^3J(F^2, F^1)$ = 44 Hz, 1F, F^2], –148.3 (m, 1F, F1), –150.6 [ddq (1:1:1:1), $^4J(BF_3, F^2)$ = 6, $^3J(BF_3, F^1)$ = 10, ^1J(F, B) = 38 Hz, 3F, BF_3] (^{19}F NMR) and at 0.8 [dq ^2J(B, F^1) = 15, ^1J(B, F) = 39 Hz] (^{11}B NMR)}.

K[$CF_2I–CFClBF_3$]: ^{11}B NMR (CD_3CN): δ = 0.6 [dq ^2J(B, F^1) = 15, ^1J(B, F) = 38 Hz]. **^{19}F NMR** (CD_3CN): δ = –54.2 [dd, $^3J(F^{2A}, F^1)$ = 19, $^2J(F^{2A}, F^{2B})$ = 165 Hz, 1F, F^{2A}], –57.4 [qdd $^4J(F^{2B}, BF_3)$ = 7, $^3J(F^{2B}, F^1)$ = 20, $^2J(F^{2B}, F^{2A})$ = 165 Hz, 1F, F^{2B}], –147.0 (m, 1F, F^1), –147.4 [q (1:1:1:1), ^1J(F, B) = 39 Hz, 3F, BF_3].

Reaction of trans-C_4F_9CF=CHF with Bromine

The heterogeneous mixture of *trans*-C_4F_9CF=CHF (1.0 g, 3.5 mmol) and bromine (0.6 g, 3.6 mmol) was stirred in a quartz tube at 30 °C under irradiation with a super-high-pressure mercury lamp (λ >365 nm, 240 W) (two lamps DRK 120) for 15 h. The bottom and the upper phase contained *cis*-C_4F_9CF=CHF and $C_4F_9CFBr–CHFBr$. The signals of *trans*-C_4F_9CF=CHF were not detected. After addition of a new portion of bromine (0.6 g, 3.6 mmol) the irradiation was continued for 24 h. The reaction mixture was washed with aqueous $Na_2S_2O_5$, with water, and finally dried with $MgSO_4$. The ^{19}F NMR spectrum showed the signals of $C_4F_9CFBr–CHFBr$ and a trace of *cis*-C_4F_9CF=CHF. Distillation gave pure $C_4F_9CFBr–CHFBr$ (0.82 g, 0.85 mmol, 53 %) (b. p. 135–138 °C).

$C_4F_9CFBr–CHFBr$: ^1H NMR ($CDCl_3$): δ = 6.80 [d, $^2J(H^1, F^1)$ = 48 Hz, 1H, H^1] (diastereomer A); 6.68 [dd, $^3J(H^1, F^2)$ = 12, $^2J(H^1, F^1)$ = 48 Hz, 1H, H^1] (diastereomer B) (A:B = 55:45). **^{19}F NMR** ($CDCl_3$): δ = –81.7 [tt, $^3J(F^6, F^5)$ = 3, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6], –111.7 [md $^2J(F^{3A}, F^{3B})$ = 289 Hz, 1F, F^{3A}], –114.0 [md $^2J(F^{3B}, F^{3A})$ = 289 Hz, 1F, F^{3B}], –120.1 [md $^2J(F^{4A}, F^{4B})$ = 298 Hz, 1F, F^{4A}], –121.0 [md $^2J(F^{4B}, F^{4A})$ = 298 Hz, 1F, F^{4B}], –126.6 [md $^2J(F^{5A}, F^{5B})$ = 294 Hz, 1F, F^{5A}], –127.2 [md $^2J(F^{5B}, F^{5A})$ = 294 Hz, 1F, F^{5B}], –129.3 [md $^3J(F^2, F^1)$ = 41 Hz, 1F, F^2], –146.0 [ttdd, $^5J(F^1, F^4)$ = 3, $^4J(F^1, F^3)$ = 12, $^3J(F^1, F^2)$ = 40, $^1J(F^1, H^1)$ = 48 Hz, 1F, F^1] (diastereomer A); –81.7 [tt, $^3J(F^6, F^5)$ = 3, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6], –112.4 [md $^2J(F^{3A}, F^{3B})$ = 291 Hz, 1F, F^{3A}], –112.9 [md $^2J(F^{3B}, F^{3A})$ = 291 Hz, 1F, F^{3B}], –120.9 (m, 2F, F^4), –126.9 (m, 2F, F^5), –133.1 (m, 1F, F^2), –143.9 [md $^2J(F^1, H^1)$ = 48 Hz, 1F, F^1] (diastereomer B) (A:B = 55:45). **IR** (neat): $\tilde{\nu}$ = 2991 (C-H), 1750, 1356, 1328, 1240, 1224, 1211, 1142, 1101, 1064, 1033, 911, 812, 778, 743, 712, 700, 662, 629, 595, 577, 531 cm^{-1}. **MS** (EI) calcd. for $C_6HBr_2F_{11}$ 439.82703 (^{79}Br), found 439.82704 (^{79}Br).

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Supporting Information (see footnote on the first page of this article): Solubilities of selected organylfluoroborate salts in different solvents. NMR spectroscopic data of $K[C_4H_9C{\equiv}CBF_3]$ in $[D_6]$acetone.

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