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Reactions of fluoroalk-1-en-1-yltrifluoroborate and perfluoroalk-1-yn-1-yltrifluoroborate salts and selected hydrocarbon analogues with hydrogen fluoride and with halogenating agents in aHF and in basic solvents

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ABSTRACT

The relative rate of the electrophilic hydrodeboration of K[R′BF_3] with HF (27–100%) diminishes in the series R′ = $C_4H_9C{\equiv}C$ > $C_4F_9CF{=}CFC{\equiv}C$ > $CF_2{=}C(CF_3)$ > $C_3F_7C{\equiv}C$ ~ $(CF_3)_2CFC{\equiv}C$ > $CF_3C{\equiv}C$. When R′ = $CF_3C{\equiv}C$ the new salt K[CF_3CH_2–CF_2BF_3] was obtained by addition of HF besides $CF_3C{\equiv}CH$ and K[BF_4]. Small amounts of water caused the formation of K[CF_3CH_2–C(O)BF_3] as a by-product. The electrophilic halofluorination of perfluoroalkenyltrifluoroborate salts with NCS or NBS in aHF (anhydrous HF) led to K[R_FCFHal–CF_2BF_3] (from K[$R_FCF{=}CFBF_3$]) and K[R_FCHal_2–CF_2BF_3] (from K[$R_FCHal{=}CFBF_3$] and K[$R_FC{\equiv}CBF_3$]) (Hal = Cl, Br). Treatment of K[$R_FCF{=}CFBF_3$] and K[$R_FC{\equiv}CBF_3$] with 5% F_2/N_2 in MeCN gave the corresponding salts K[R_FCF_2–CF_2BF_3] in 16–25% isolated yield. Reactions of K[*trans*-$C_4F_9CF{=}CFBF_3$] with Cl_2 in MeOH resulted in K[C_4F_9CFCl–C(O)BF_3] (major product). The latter was also obtained in reactions of K[*trans*-$C_4F_9CF{=}CFBF_3$] with Cl_2 in MeCN or sulfolane after sequential methanolysis of the primarily formed products. In contrast, the salts K[$RCF{=}CFBF_3$] (R = C_nF_{2n+1}, *trans*-C_4H_9) and K[$CF_3C{\equiv}CBF_3$] underwent bromodeboration to $RCF{=}CFBr$ and $CF_3C{\equiv}CBr$, respectively, when they were reacted with bromine in the polar solvents MeOH, MeCN, or sulfolane.

1. Introduction

In the preceding paper [1] we described reactions of tetrabutylammonium and potassium perfluorinated alkyl-, alkenyl-, and alkynyltrifluoroborates and selected low- or non-fluorinated analogues with the halogens fluorine, chlorine, and bromine and the interhalogens "BrF" (from Br_2 + BrF_3 (1:1)) and ICl in the halocarbon solvents CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, and $CF_3CH_2CF_2CH_3$. Perfluoroorganyltrifluoroborates with multiple bonds between C^1 and C^2 underwent 1,2-addition of halogen and/or replacement of boron by halogen. [Bu_4N][$C_6F_{13}BF_3$] was inert towards halodeboration. Reactions of M[$RCF{=}CFBF_3$] and of each non-fluorinated hydrocarbon organyltrifluoroborate salt with Cl_2 and Br_2 led to the corresponding organyl chloride or bromide. Under the action of ICl iododeboration occurred fast in all cases, except of the surface reaction of K[$CF_2{=}CFBF_3$] in CH_2Cl_2. These results are in accordance with the known halodeboration reactions of M[RBF_3] with the brominating agents [Bu_4N][Br_3] [2], [NH_4]Br + $CH_3C(O)OOH$ [3], NaBr + Chloramine-T (Na[*p*-$MeC_6H_4S(O)_2NCl$]) [4] and the iodinating agents NaI + Chloramine-T [5], NaI + $CH_3C(O)OOH$ [6] in aqueous THF, and the fluorodeboration of K[R′$CH{=}CHBF_3$] with Selectfluor™ in MeCN [7]. All above compiled results display principally the electronic effect of fluorine in unsaturated fluoroorganyl moieties of organyltrifluoroborate anions on the reaction route with halogenating agents.

In continuation of our studies of fluorinated organyltrifluoroborate salts, we investigated new reactions of fluoroalk-1-en-1-yltrifluoroborates and perfluoroalk-1-yn-1-yltrifluoroborates with selected halogenating agents in the superacidic solvent aHF and in the basic solvents CH_3CN, CH_3OH, and sulfolane *inter alia* with the target to evaluate the influence of fluorine atoms in unsaturated organyl groups of organyltrifluoroborate salts on the reaction route [8].

2. Results

2.1. Reactions of K[R_FBF_3] in anhydrous HF

2.1.1. Selection of alkenyltrifluoroborates and alkynyltrifluoroborates for reactions in aHF

In our previous publications [9,10] we reported the reactivity of a series of perfluorinated aryl-, alkenyl-, and alkyltrifluoroborates and

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$K[CF_2{=}C(CF_3)BF_3]$ + 48% aq HF ⟶ $CF_2{=}C(CF_3)H + K[BF_4]$
50% conversion (4 h) ~20 °C
100% conversion (19 h) ~20 °C

$K[CF_2{=}C(CF_3)BF_3]$ + aHF ⟶ $CF_2{=}C(CF_3)H + K[BF_4]$
50% conversion (25 min) –50 °C
100% conversion (few min) –20 °C
100% conversion (immediately) ~20 °C

Scheme 1.

their hydrocarbon analogues towards protic acids of different strength including aHF. At ~20 °C each borate $K[RBF_3]$ (R = hydrocarbon group) underwent fast hydrodeboration with aHF and formed RH and $K[BF_4]$. The perfluorinated salt $K[CF_2{=}CFBF_3]$ and the partially fluorinated salt K[*trans*-$C_4H_9CF{=}CFBF_3$] also reacted under hydrodeboration. Perfluorinated alkyltrifluoroborates, $K[C_nF_{2n+1}BF_3]$, and alk-1-en-1-yltrifluoroborates, $K[C_nF_{2n+1}CF{=}CFBF_3]$, did not react with aHF over days.

To make the series of organyltrifluoroborates more representative, we examined the reactivity of further organylborates towards both, aqueous HF and anhydrous HF.

In contrast to perfluorinated salts $K[C_nF_{2n+1}CF{=}CFBF_3]$ ($n \geq 0$), the perfluorinated salt $K[CF_2{=}C(CF_3)BF_3]$ reacted with 48% aq HF at ~20 °C with a half-life period of 4 h to yield $CF_2{=}C(CF_3)H$ and $K[BF_4]$. $K[CF_2{=}C(CF_3)BF_3]$ underwent fast hydrodeboration in aHF. At −50 °C the half-life period was only 25 min, at −20 °C hydrodeboration was already completed within a few min and the dissolution of $K[CF_2{=}C(CF_3)BF_3]$ at ~20 °C was accompanied by an immediate conversion (Scheme 1).

The reactivity of alkynyltrifluoroborates $K[RC{\equiv}CBF_3]$ towards hydrodeboration strongly depended on the nature of R. Potassium trifluoropropynyltrifluoroborate, $K[CF_3C{\equiv}CBF_3]$, potassium heptafluoropentynyltrifluoroborate, $K[C_3F_7C{\equiv}CBF_3]$, and potassium heptafluoro-3-methylbutynyltrifluoroborate, $K[(CF_3)_2CFC{\equiv}CBF_3]$, did not react with 48% aq HF at ~20 °C over more than one week. Potassium undecafluorooct-3-en-1-yn-1-yltrifluoroborate, $K[C_4F_9CF{=}CFC{\equiv}CBF_3]$, did not react with 27% aq HF over 2 d, whereas potassium hexynyltrifluoroborate, $K[C_4H_9C{\equiv}CBF_3]$, underwent hydrodeboration in 27% aq HF within 30 min to yield hexyne and $K[BF_4]$ (Scheme 2).

Dissolution of $K[C_4F_9CF{=}CFC{\equiv}CBF_3]$ (*cis*:*trans* = 45:55) in aHF at ~20 °C went along with the complete hydrodeboration to $C_4F_9CF{=}CFC{\equiv}CH$ and $K[BF_4]$ within ≤0.5 h. $K[C_3F_7C{\equiv}CBF_3]$ and $K[(CF_3)_2CFC{\equiv}CBF_3]$ were more stable in aHF. They did not react at 0 °C in 1–2 h but they were slowly converted at ~20 °C to the heptafluoroalkynes $C_3F_7C{\equiv}CH$ and $(CF_3)_2CFC{\equiv}CH$, respectively (Scheme 3).

$K[R_FC{\equiv}CBF_3]$ + 48% aq HF ⟶ (~20 °C) no reaction
R = CF_3 (2 m), C_3F_7 (8 d), and $(CF_3)_2CF$ (8 d)

$K[C_4F_9CF{=}CFC{\equiv}CBF_3]$ + 27% aq HF ⟶ (2 d, ~20 °C) no reaction

$K[C_4H_9C{\equiv}CBF_3]$ + 27% aq HF ⟶ (~20 °C) $C_4H_9C{\equiv}CH + K[BF_4]$
100% conversion (<0.5 h)

Scheme 2.

The reactivity of $K[CF_3C{\equiv}CBF_3]$ towards aHF differed from that of $K[C_3F_7C{\equiv}CBF_3]$ and $K[(CF_3)_2CFC{\equiv}CBF_3]$. At room temperature the addition products 1,1,3,3,3-pentafluoropropyltrifluoroborate, $K[CF_3CH_2{-}CF_2BF_3]$, and 3,3,3-trifluoropropanoyltrifluoroborate, $K[CF_3CH_2{-}C(O)BF_3]$, were formed with a slow rate. The major products, namely $K[BF_4]$ and 3,3,3-trifluoropropyne, $CF_3C{\equiv}CH$, resulted from the slow hydrodeboration reaction (Scheme 4).

The formation of $K[CF_3CH_2{-}C(O)BF_3]$ was probably caused by long-term diffusion of moisture into hygroscopic hydrogen fluoride through the thin FEP-wall or PTFE-stopper of the NMR tube insert or during taking NMR samples repeatedly.

Based on these actual results and on previously reported data [9,10] of the reactivity of alkenyltrifluoroborate and alkynyltrifluoroborate salts towards aHF, the compounds K[*trans*-$CF_3CF{=}CFBF_3$], K[*cis*-$C_2F_5CF{=}CFBF_3$], K[*trans*-$C_4F_9CF{=}CFBF_3$], $K[CF_3C{\equiv}CBF_3]$, and $K[C_3F_7C{\equiv}CBF_3]$ were chosen for investigations with halogenating agents in aHF.

2.1.2. Halofluorination in aHF

The systems N-haloimide/aHF or N-haloimide/$(HF)_n$·base were used for halofluorination (Hal-F addition) of unsaturated hydrocarbons [11–13]. Polyfluorinated alkenes are less reactive to electrophilic attacks than the non-fluorinated analogues and thus halofluorination occurs only in strong acids like HSO_3F or

$K[C_4F_9CF{=}CFC{\equiv}CBF_3]$ + aHF ⟶ $C_4F_9CF{=}CFC{\equiv}CH + K[BF_4]$
100% conversion (≤0.5 h) ~20 °C

$K[C_3F_7C{\equiv}CBF_3]$ + aHF ⟶ $C_3F_7C{\equiv}CH + K[BF_4]$
0% conversion (2 h) 0 °C
100% conversion (≤24 h) ~20 °C

$K[(CF_3)_2CFC{\equiv}CBF_3]$ + aHF ⟶ $(CF_3)_2CFC{\equiv}CH + K[BF_4]$
0% conversion (1 h) 0 °C
100% conversion (≤5 h) ~20 °C

Scheme 3.

$K[CF_3C{\equiv}CBF_3]$ + aHF ⟶ (~20 °C) $K[BF_4]$ + $CF_3C{\equiv}CH$ + $K[CF_3CH_2{-}CF_2BF_3]$ + $K[CF_3CH_2{-}C(O)BF_3]$ (formed by penetrating water)

100% conversion (≥43 h)

Scheme 4.

$K[R_FCF{=}CFBF_3]$ + ≥1 NCS ⟶ (aHF, ~20 °C) $K[R_FCFCl{-}CF_2BF_3]$

R_F = *cis*-C_2F_5
0% conversion (1 h)
73% conversion (55 h)
100% conversion (≤102 h) — 59% isolated yield

R_F = *trans*-C_4F_9
8% conversion) (2 h)
83% conversion (20 h)
100% conversion (≤48 h) — 58% isolated yield

Scheme 5.

HSO_3F/SbF_5 [14]. It is worth to mention, that the majority of unsaturated organoelement compounds react with strong acids and cannot be halofluorinated with the above acidic systems.

We found that the potassium perfluoroalkenyltrifluoroborates $K[cis\text{-}C_2F_5CF{=}CFBF_3]$ and $K[C_4F_9CF{=}CFBF_3]$ reacted with *N*-chlorosuccinimide (NCS) in aHF and formed potassium 2-chlorooctafluorobutyltrifluoroborate, $K[C_2F_5CFCl{-}CF_2BF_3]$, and potassium 2-chloroduodecafluorohexyltrifluoroborate, $K[C_4F_9CFCl{-}CF_2BF_3]$, respectively. At room temperature chlorofluorination proceeded slowly and was completed within 2–4 d (Scheme 5).

$K[CF_3C{\equiv}CBF_3]$ reacted with NCS/aHF on two routes, hydrodeboration and chlorofluorination. The primary product of chlorofluorination was potassium (*E*)-2-chlorotetrafluoroprop-1-en-1-yltrifluoroborate, $K[(E)\text{-}CF_3CCl{=}CFBF_3]$, which was detected by ^{19}F NMR as the minor component at 69% conversion of $K[CF_3C{\equiv}CBF_3]$. After total conversion, potassium 2,2-dichloropentafluoropropyltrifluoroborate, $K[CF_3CCl_2{-}CF_2BF_3]$, $CF_3C{\equiv}CH$, and $K[BF_4]$ were the only products (Scheme 6).

Bromofluorination of perfluoroalkenylborate salts with *N*-bromosuccinimide (NBS) in aHF proceeded faster than chlorofluorination. Thus, $K[C_4F_9CF{=}CFBF_3]$ was completely converted at ~20 °C within 2 h giving potassium 2-bromododecafluorohexyltrifluoroborate $K[C_4F_9CFBr{-}CF_2BF_3]$ (Scheme 7).

Treatment of the alkynylborate $K[CF_3C{\equiv}CBF_3]$ with one equivalent of NBS in aHF gave potassium 2-bromotetrafluorobut-1-en-1-yltrifluoroborate, $K[CF_3CBr{=}CFBF_3]$, ((*E*):(*Z*) = 5:1) (minor), $K[CF_3CBr_2{-}CF_2BF_3]$, $CF_3C{\equiv}CH$, and $K[BF_4]$ at 55% conversion of $K[CF_3C{\equiv}CBF_3]$. $K[CF_3C{\equiv}CBF_3]$ reacted with two equivalents of NBS in aHF and gave $K[CF_3CBr_2{-}CF_2BF_3]$, besides $CF_3C{\equiv}CH$ and $K[BF_4]$. In case of a 1:2 stoichiometry the intermediate $K[CF_3CBr{=}CFBF_3]$ was not observed. With four equivalents NBS the longer-chain analogue $K[C_3F_7C{\equiv}CBF_3]$ gave potassium 2,2-dibromononafluoropentyltrifluoroborate, $K[C_3F_7CBr_2{-}CF_2BF_3]$, which was isolated and characterized after complex formation with 18-crown-6 (Scheme 8).

We investigated the reagent molecular bromine in aHF as an alternative for bromofluorination reactions. In the series of unsaturated hydrocarbons this reagent has only a limited application because of by-processes, mainly the addition of two bromine atoms across C=C bonds and some aHF-initiated reactions. $K[trans\text{-}CF_3CF{=}CFBF_3]$ reacted fast with bromine in aHF to form potassium 2-bromohexafluoropropyltrifluoroborate, $K[CF_3CFBr{-}CF_2BF_3]$. In contrast, the alkynylborate $K[CF_3C{\equiv}CBF_3]$ gave potassium 1,2-dibromo-3,3,3-trifluoroprop-1-en-1-yltrifluoroborate, $K[CF_3CBr{=}CBrBF_3]$, (*cis*:*trans* = 94:6) parallel to hydrodeboration (Scheme 9).

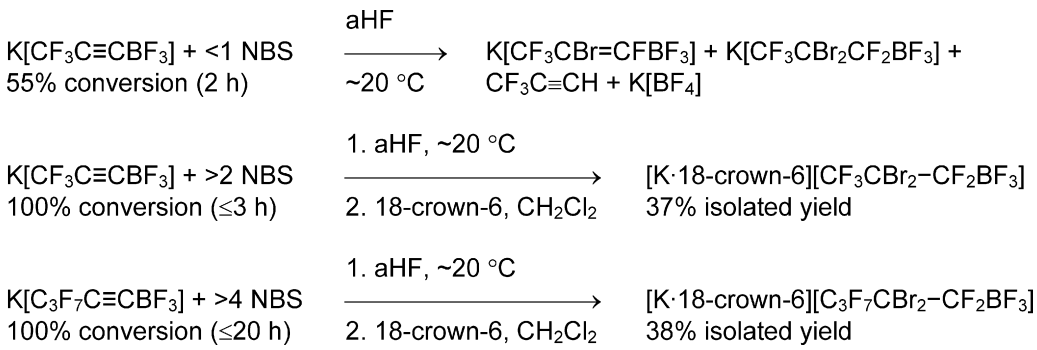
$K[CF_3C{\equiv}CBF_3]$ + >2 NCS ⟶ (aHF, ~20 °C) $K[(E)\text{-}CF_3CCl{=}CFBF_3]$ + $K[CF_3CCl_2{-}CF_2BF_3$ + $CF_3C{\equiv}CH$ + $K[BF_4]$
69% conversion (3 h)

⟶ (aHF, ~20 °C) $K[CF_3CCl_2{-}CF_2BF_3]$ + $CF_3C{\equiv}CH$ + $K[BF_4]$
100% conversion (≤33 h)

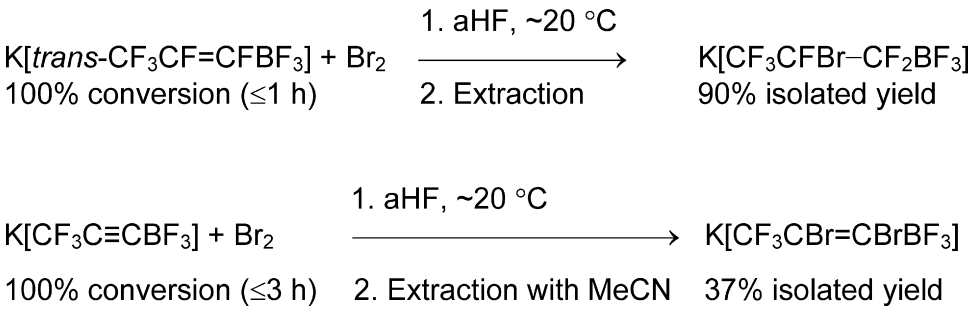
Scheme 6.

$K[trans\text{-}C_4F_9CF{=}CFBF_3]$ + >1 NBS ⟶ (aHF, ~20 °C) $K[C_4F_9CFBr{-}CF_2BF_3]$
100% conversion (≤2 h) — 34% isolated yield

Scheme 7.



Scheme 8.



Scheme 9.

2.2. Reactions of fluoroorganyltrifluoroborate salts with halogenating agents in basic solvents

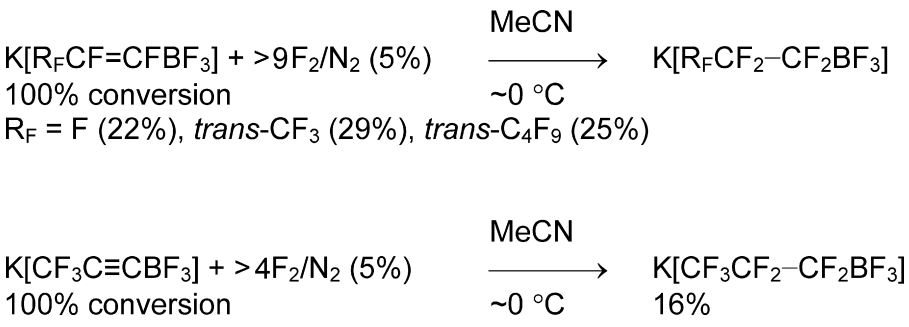
2.2.1. Reactions with fluorine

Fluorine diluted with nitrogen (5%, v/v) was bubbled through a stirred suspension of KF in the solution of $K[R_FCF{=}CFBF_3]$ or $K[CF_3C{\equiv}CBF_3]$ in MeCN at ~0 °C. KF acted as scavenger of HF resulting from the by-reaction of fluorine with acetonitrile. Without KF the solution became dark within a few minutes and the yield of perfluoroalkyltrifluoroborates was significantly reduced.

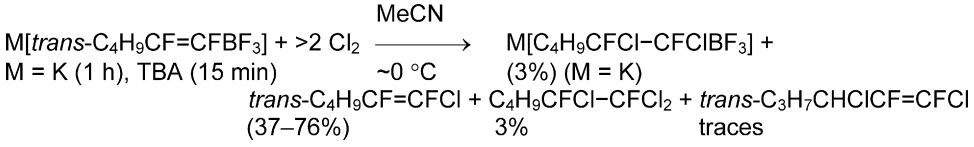
Treatment of a diluted MeCN solution of $K[R_FCF{=}CFBF_3]$ in the presence of suspended KF with an excess of fluorine resulted in the consumption of $K[R_FCF{=}CFBF_3]$ under formation of the corresponding potassium perfluoroalkyltrifluoroborate, $K[R_FCF_2{-}CF_2BF_3]$, in a moderate yield together with $K[BF_4]$ and perfluorocarbons, which were not analyzed. $K[CF_3C{\equiv}CBF_3]$ reacted with fluorine in a similar way to yield potassium perfluoropropyltrifluoroborate $K[CF_3CF_2{-}CF_2BF_3]$ in 16% yield. The intermediate salt $K[CF_3CF{=}CFBF_3]$ was not detected (Scheme 10).

2.2.2. Reactions with chlorine

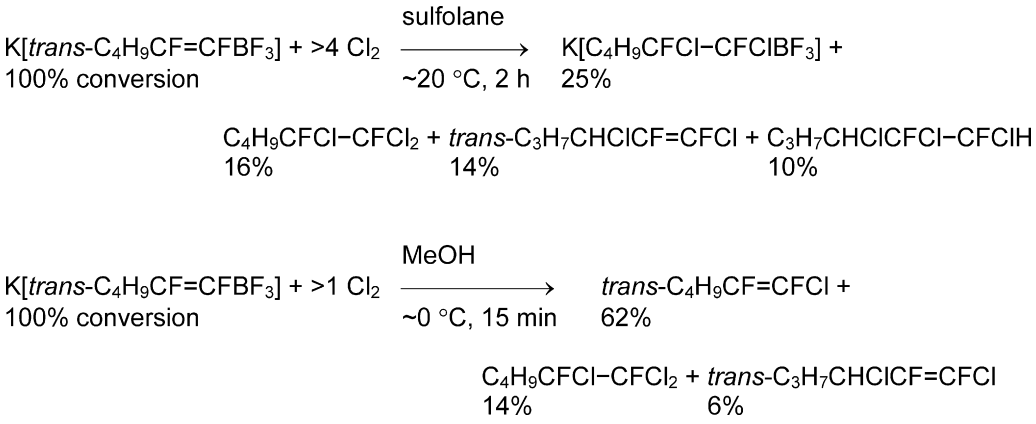
Potassium *trans*-1,2-difluorohex-1-en-1-yltrifluoroborate, $K[trans\text{-}C_4H_9CF{=}CFBF_3]$, reacted with chlorine in MeCN and formed within 1 h *trans*-1-chloro-1,2-difluorohexene, *trans*-$C_4H_9CF{=}CFCl$, as the main product besides very small quantities of $K[C_4H_9CFCl{-}CFClBF_3]$, $C_4H_9CFCl{-}CFCl_2$, and *trans*-$C_3H_7CHClCF{=}CFCl$. The same products were obtained in the reaction of the tetrabutylammonium salt $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ with chlorine (Scheme 11).



Scheme 10.



Scheme 11.



Scheme 12.

Replacement of acetonitrile by sulfolane increased the fraction of chlorine addition products relative to chlorodeboration products, whereas in methanol chlorodeboration dominated (Scheme 12).

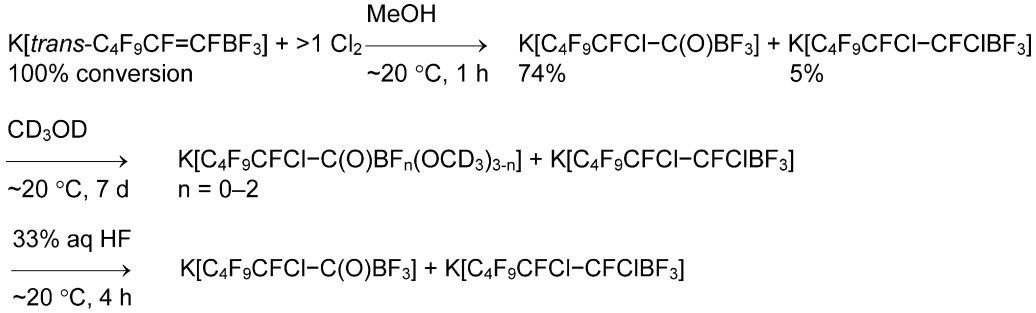
Bubbling of chlorine through the solution of perfluorinated K[*trans*-$C_4F_9CF{=}CFBF_3$] in methanol also led to chlorine addition, but potassium 1,2-dichloroundecafluorohexyltrifluoroborate, K[$C_4F_9CFCl–CFClBF_3$], was formed only in a low yield. Instead, potassium 2-chlorodecafluorohexanoyltrifluoroborate, K[$C_4F_9CFCl–C(O)BF_3$], was the main product. Chlorodeboration did not occur. Noteworthy, that in deuterated methanol K[$C_4F_9CFCl–C(O)BF_3$] underwent slow fluoro/methoxy substitution and formed a mixture of the corresponding fluoro(methoxy)borates, K[$C_4F_9CFCl–C(O)BF_2(OCD_3)$], K[$C_4F_9CFCl–C(O)BF(OCD_3)_2$], and K[$C_4F_9CFCl–C(O)B(OCD_3)_3$]. Treatment of the fluoro(methoxy)borates with aq HF resulted in the quantitative recovery of K[$C_4F_9CFCl–C(O)BF_3$]. Under the same conditions K[$C_4F_9CFCl–CFClBF_3$] did not undergo fluoro/methoxy substitution (^{11}B, ^{19}F NMR) (Scheme 13).

Chlorine addition across the C=C bond occurred when K[*trans*-$C_4F_9CF{=}CFBF_3$] was reacted with an excess of chlorine in sulfolane. The new borate K[$C_4F_9CFCl–CFXBF_3$] was isolated (Scheme 14). Its ^{19}F NMR spectrum was closely related to K[$C_4F_9CFCl–CFClBF_3$]. The ^1H NMR spectrum of a freshly prepared solution of K[$C_4F_9CFCl–CFXBF_3$] in DMSO-d_6 contained signals at 4.48, 3.63, 2.66, and 2.47 ppm with integral intensities of 2:2:2:2. The intensity of each ^1H-signal corresponded to two fluorine atoms in the ^{19}F NMR spectrum ($PhCF_3$ was used as internal integration standard). This allowed the assumption that X in K[$C_4F_9CFCl–CFXBF_3$] contains a $(CH_2)_4$ fragment which derived from one molecule of sulfolane.

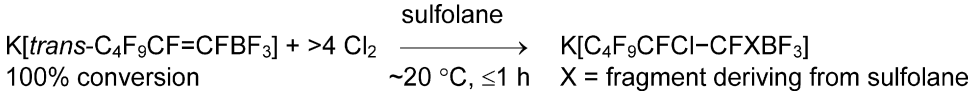
The reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] with chlorine in MeCN proceeded on both reaction channels, chlorodeboration and chlorine addition across the C=C bond. The first channel gave a high-boiling oil soluble in CH_2Cl_2 which consisted at least of two components in the molar ratio 4:1. The second channel gave a solid with a ^{19}F NMR spectrum which looked similar to that of K[$C_4F_9CFCl–CFClBF_3$] and K[$C_4F_9CFCl–CFXBF_3$], and corresponded to K[$C_4F_9CFCl–CFYBF_3$] (Y represents a fragment which derives from the molecule acetonitrile). The constitution of K[$C_4F_9CFCl–CFXBF_3$] and K[$C_4F_9CFCl–CFYBF_3$] was supported by their conversion to K[$C_4F_9CFCl–C(O)BF_3$] in methanol solution (Scheme 15).

2.2.3. Reactions with bromine

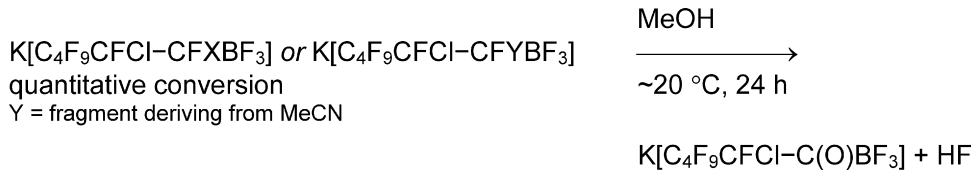
In contrast to chlorine, bromine did not add across double or triple carbon-carbon bonds of 1,2-difluoroalk-1-en-1-yltrifluoroborates and perfluoroalk-1-yn-1-yltrifluoroborates. Thus, potassium *trans*-1,2-difluoro-2-phenylethenyltrifluoroborate, K[*trans*-$C_6H_5CF{=}CFBF_3$], reacted with a slight excess of bromine in acetonitrile to yield *trans*-1-bromo-1,2-difluoro-2-phenylethene, *trans*-$C_6H_5CF{=}CFBr$, and 1,2-dibromo-1,2-difluoro-2-phenylethane, $C_6H_5CFBr–CFBrH$. In a similar way, *trans*-1-bromo-1,2-difluorohexene, $C_4H_9CF{=}CFBr$, and *trans*-1,2-difluorohexene, *trans*-$C_4H_9CF{=}CFH$, were obtained from K[*trans*-$C_4H_9CF{=}CFBF_3$]. The attempt to perform bromofluorination by reacting K[*trans*-$C_4H_9CF{=}CFBF_3$] with the reagent Br_2/AgF in MeCN only led to bromodeboration under formation of an isomeric mixture of $C_4H_9CF{=}CFBr$ (Scheme 16). Assumed that in a fast metathesis insoluble KF was formed from K[*trans*-$C_4H_9CF{=}CFBF_3$] and AgF, we



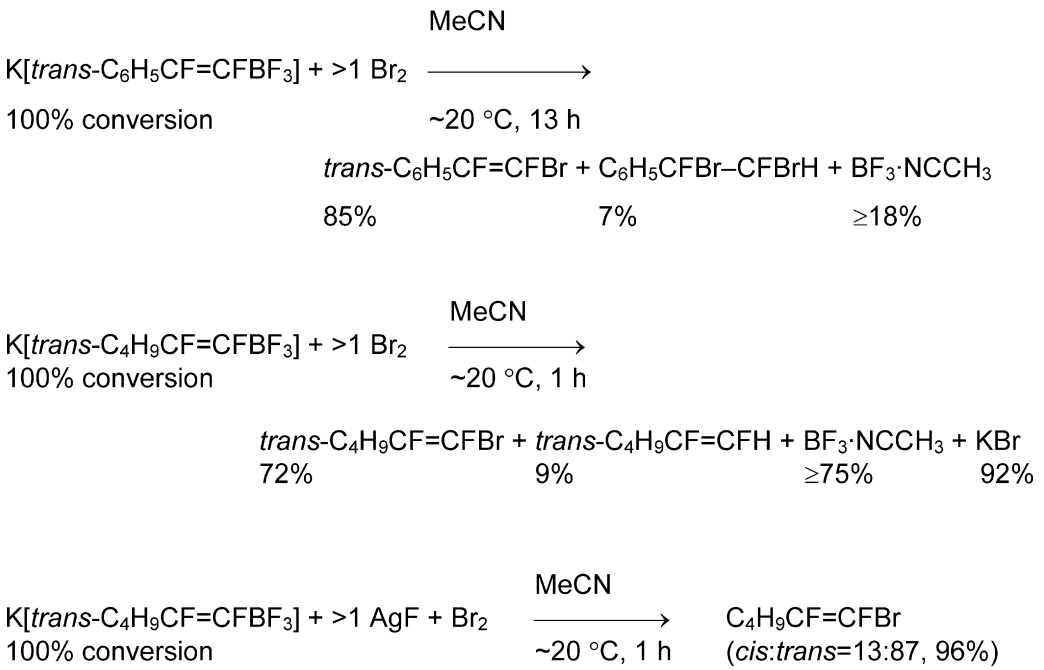
Scheme 13.



Scheme 14.



Scheme 15.

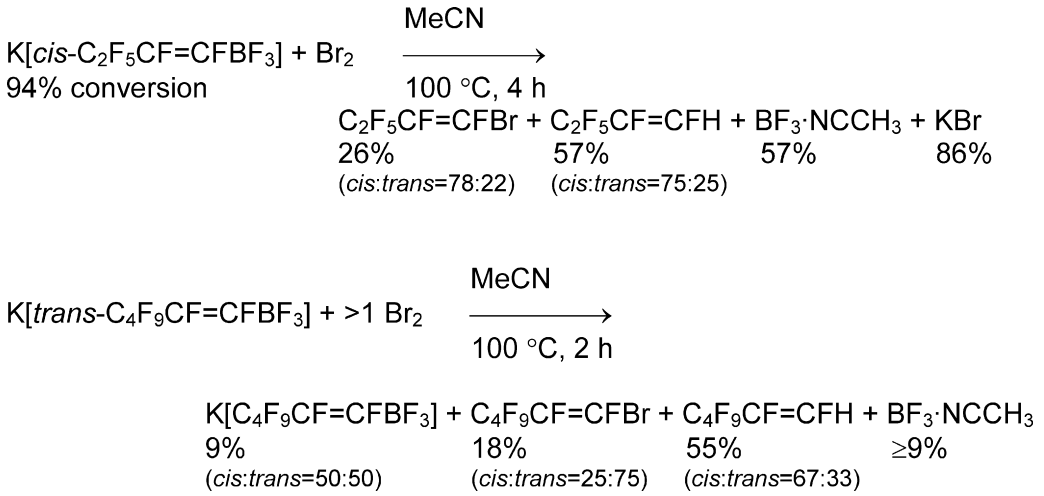


Scheme 16.

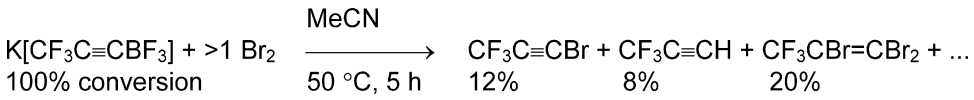
can state that Ag[*trans*-$C_4H_9CF{=}CFBF_3$] and Br_2 in the presence of less than equivalent amounts of AgF (from initial excess) did not even partially react under bromofluorination.

K[*trans*-$C_4F_9CF{=}CFBF_3$] did not react with bromine in MeCN at 50 °C within 6 h. Heating at 100 °C in a sealed tube led to partial *trans* to *cis* isomerization of K[*trans*-$C_4F_9CF{=}CFBF_3$] and isomeric mixtures of the bromodeboration and hydrodeboration products. K[*cis*-$C_2F_5CF{=}CFBF_3$] reacted in a similar way (Scheme 17).

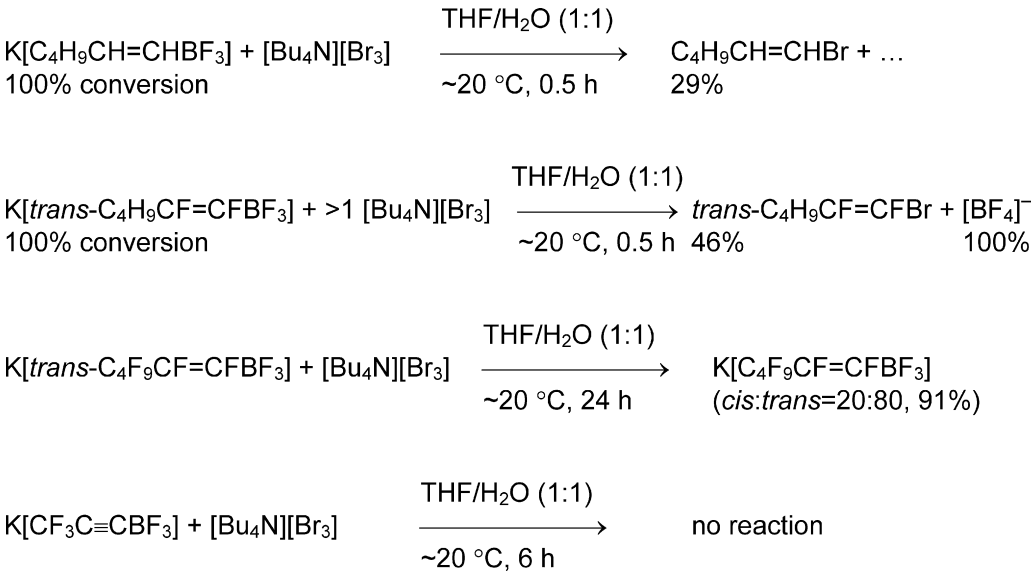
Treatment of K[*trans*-$C_4F_9CF{=}CFBF_3$] with a slight excess of bromine in MeOH at ~20 °C in a sealed tube was even accompanied by partial *trans* to *cis* isomerization with a ratio *cis*:*trans* of 58:42 after 80 h. This result is closely related to the outcome of the photo-induced isomerization of K[*trans*-$C_4F_9CF{=}CFBF_3$] in MeOH in the presence of traces of bromine which gave a ratio *cis*:*trans* of 40:60 after 2 h of irradiation ($\lambda > 280$ nm) [15]. When a solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] and Br_2 in MeOH was heated at 90 °C for 1 h, 50% of the starting



Scheme 17.



Scheme 18.



Scheme 19.

material represented an isomeric mixture *cis*:*trans* = 43:57 besides equal amounts of the alkenes *trans*-$C_4F_9CF{=}CFBr$ and *trans*-$C_4F_9CF{=}CFH$. No signals which could be attributed to $[C_4F_9CFBr–CFBrBF_3]^-$ or $[C_4F_9CFBr–C(O)BF_3]^-$ were observed (^{19}F NMR).

The alkynylborate $K[CF_3C{\equiv}CBF_3]$ reacted slowly with bromine in MeCN at 50 °C to give a complex mixture. After 5 h the conversion was completed. $K[CF_3CBr{=}CBrBF_3]$ or any other organyltrifluoroborate $K[RBF_3]$ was absent: no ^{19}F NMR signals of BF_3 groups in the range −130 to −160 ppm were found. The addition, bromodeboration, and protodeboration products $CF_3CBr{=}CBr_2$, $CF_3C{\equiv}CBr$, and $CF_3C{\equiv}CH$ were formed in 20%, 12%, and 8% yields, respectively (Scheme 18).

Potassium perfluorohexyltrifluoroborate did not react with bromine in MeCN (~20 °C, 40 h).

Recently Kabalka et al. reported the preparation of 1-bromoalkenes and 1-bromoalkynes from potassium alk-1-en-1-yltrifluoroborates or alk-1-yn-1-yltrifluoroborates and $[Bu_4N][Br_3]$ in aq THF (~20 °C, 20 min) [2]. Using the same methodical approach we converted $K[C_4H_9CH{=}CHBF_3]$ to $C_4H_9CH{=}CHBr$. We extended this method to fluoroorganyltrifluoroborates. Under the same conditions, 1,2-difluorinated K[*trans*-$C_4H_9CF{=}CFBF_3$] underwent bromodeboration to *trans*-$C_4H_9CF{=}CFBr$, whereas perfluorinated K[*trans*-$C_4F_9CF{=}CFBF_3$] was partially isomerized to K[*cis*-$C_4F_9CF{=}CFBF_3$] without further transformation. The perfluoroalkynylborate $K[CF_3C{\equiv}CBF_3]$ did not underwent a transformation to the corresponding bromoalkyne (Scheme 19).

3. Discussion

The combination of previously published data and the currently obtained new results displays generally a diminishing reactivity of organyltrifluoroborates towards protic acids (hydrodeboration) and halogenating agents (halodeboration) with replacement of hydrogen atoms by fluorine atoms in organyltrifluoroborate anions. The earlier reported two qualitative series [9] of relative rates of hydrodeboration can now be supplemented with new members (cf. Section 2.1):

$$K[\textit{trans}\text{-}C_4H_9CF{=}CFBF_3] > K[C_4F_9CF{=}CFC{\equiv}CBF_3] > K[CF_2{=}C(CF_3)BF_3] > K[C_3F_7OCF{=}CFBF_3] \sim K[CF_2{=}CFBF_3] \geq K[ClCF{=}CFBF_3] \sim K[C_6F_5BF_3] > K[C_3F_7C{\equiv}CBF_3] \sim K[(CF_3)_2CFC{\equiv}CBF_3] > K[CF_3C{\equiv}CBF_3] > K[\textit{cis}\text{-}C_2F_5CF{=}CFBF_3] \geq K[\textit{trans}\text{-}C_4F_9CF{=}CFBF_3] > K[C_6F_{13}BF_3]$$

and

$$K[C_4H_9C{\equiv}CBF_3] \sim K[C_4H_9CH{=}CHBF_3] > K[C_6H_5BF_3] > K[C_4H_9BF_3] \sim K[C_8H_{17}BF_3]$$

Hydrodeborations start with the electrophilic addition of H^+ at the carbon atom C^1, whereas halofluorinations and related brominations in aHF start with the addition of the electrophilic species at the carbon atom C^2 of the C–C double and triple bond of the perfluorinated alk-1-en-1-yl and alk-1-yn-1-yltrifluoroborates. The subsequent attachment of the nucleophilic species at C^1 completes the addition across the carbon–carbon multiple bond.

Chlorofluorination and bromofluorination with NCS or NBS in aHF (superacidic solvent) proceeded on the latter route. In halocarbon solvents bromofluorination with $BrF_3–Br_2$ (1:1) [1] represents – at least formally – also that channel.

The conversion of $[CF_3C{\equiv}CBF_3]^-$ in aHF to $[CF_3CH_2–CF_2BF_3]^-$ and to $[CF_3CH_2–C(O)BF_3]^-$ in the presence of less than stoichiometric amounts of water starts with the addition of H^+ to the carbon atom C^2 in $[CF_3C{\equiv}CBF_3]^-$ and is finished after addition of the nucleophiles F^- or OH^- giving $[CF_3CH{=}CXBF_3]^-$ (X = F, OH) (Scheme 4). By the way, this is – to the best of our knowledge – the only example of HF addition across a carbon–carbon multiple bond in organylboron compounds, fluorinated or not.

It is important to stress that the first step of the HF addition in the $[CF_3C{\equiv}CBF_3]^-$ anion (H^+ adds to C^2) proceeds opposite to the HF addition in the $[(C_3F_7C{\equiv}C)_2Br]^+$ cation, where H^+ adds primarily to C^1, and with a low rate $[(Z\text{-}C_3F_7CF{=}CH)_2Br]^+$ is formed [16]. This distinction in reactivity can be explained by the opposite polarization of the sigma and pi electron pairs of the $R_FC^2{\equiv}C^1{-}X$ triple bond by the substituent X (X = BF_3^- and R–Br(III)$^+$).

The formation of the acyltrifluoroborate, $K[C_4F_9CFCl{-}C(O)BF_3]$ and of the borates $K[C_4F_9CFCl{-}CFXBF_3]$ and $K[C_4F_9CFCl{-}CFYBF_3]$ from the borate $K[C_4F_9CF{=}CFBF_3]$ and chlorine in MeOH, sulfolane, or MeCN, respectively, (Schemes 13 and 14) proceeds also on an "ionic route". The ratio "fluorine addition/fluorodeboration" in reactions of perfluoroalkenyltrifluoroborates and perfluoroalkynyltrifluoroborates with fluorine does not depend on the nature of the solvent. This is deduced from the yields of perfluoroalkyltrifluoroborates (20–25%) which are independent of the type of solvent, either CH_2Cl_2 (weakly polar solvent) or MeCN (basic solvent). Such a pattern can be assigned as typical for radical halogen additions. Furthermore, the absence of the intermediate $K[CF_3CF{=}CFBF_3]$ in fluorination reactions of $K[CF_3C{\equiv}CBF_3]$ with F_2 indicates a higher reactivity of the alkenylborate towards fluorine radicals.

In contrast to fluorination, the reaction channel of perfluorinated alk-1-en-1-yl and alk-1-yn-1-yltrifluoroborates with chlorine or bromine depends on the type of solvent. K[*trans*-$CF_3CF{=}CFBF_3$] and bromine underwent the until now unknown reaction path of bromofluorination in aHF solution (Scheme 9) whereas bromodeboration was the exclusive reaction channel of all $M[C_nF_{2n+1}CF{=}CFBF_3]$ salts in CH_2Cl_2 (M = [Bu_4N]) [1] and in MeCN solution (M = K) (except of $M[CF_2{=}CFBF_3]$ [1]). $M[CF_3C{\equiv}CBF_3]$ added only two bromine (differing from the corresponding fluorination) to yield $M[CF_3CBr{=}CBrBF_3]$ in CH_2Cl_2 (M = [Bu_4N]) [1] and in aHF (M = K) (Scheme 9), but in MeCN (M = K) the carbon–boron bond was cleaved completely (Scheme 18).

The new data present additional reactivities of perfluorinated alkenyltrifluoroborates and alkynyltrifluoroborates with respect to their non-fluorinated analogues. In some cases the addition of Hal–Hal or Hal–F across the C=C or C≡C bond allows to prepare new fluoroalkenyltrifluoroborates or fluoroalkyltrifluoroborates which are not easy available by alternative routes.

In 2003 Shellhamer et al. reported many reactions of fluoro-containing alkenes with Cl_2, Br_2, and ICl in MeOH which resulted in dihalogenation and halomethoxylation products [17]. Based on our and literature data, we can conclude a high sensitivity of alkenyltrifluoroborates in "ionic addition reactions" which depends on the alkyl substituent R in the RC=C moiety and the position and number of vinylic fluorine atoms. In future, the mechanistic aspects require further experimental investigations and theoretical explanations.

4. Experimental

4.1. General

The NMR spectra were recorded on the Bruker spectrometers AVANCE 300 (300.13 MHz, ^{1}H; 282.40 MHz, ^{19}F; 96.29 MHz, ^{11}B; 75.47 MHz, ^{13}C) and AVANCE 600 (192.60 MHz, ^{11}B). The chemical shifts are referenced to TMS (^{1}H, ^{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)), respectively. The IR spectra were recorded on a Bruker Vector 22 instrument. High resolution mass spectra were recorded on a Thermo Scientific DFS spectrometer in EI mode. The elemental analysis was performed in the N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (Novosibirsk, Russian Federation). The composition of reaction mixtures and the yields of products were determined by ^{1}H or ^{19}F NMR spectroscopy using the internal integral standards $C_6H_5CF_3$, C_6F_5H, and C_6F_6.

Acetonitrile, dichloromethane, carbon tetrachloride, THF, sulfolane, methanol, pentane, benzene, and ether were purified and dried as described in Ref. [18]. *N*-bromosuccinimide (Aldrich), *N*-chlorosuccinimide (Aldrich), [Bu_4N][BF_4] (Fluka), and anhydrous KF (Merck) were used as supplied. Chlorine (*n* mmol) was prepared by the addition of 37% hydrochloric acid (0.8*n* mL) to $KMnO_4$ (0.8*n* mmol, 126*n* mg) [19] in a slow stream of argon. Crude chlorine in argon was passed through a column (*D* = 0.5 cm, *L* = 3 cm) packed with freshly calcinated CaO to remove HCl and moisture. Bromine was dried with concentrated H_2SO_4 and distilled over P_4O_{10}. [Bu_4N][Br_3] [20] and the salts K[*trans*-$C_4F_9CF{=}CFBF_3$], K[*cis*-$C_2F_5CF{=}CFBF_3$] [21], $K[CF_2{=}C(CF_3)BF_3]$ [22], $K[CF_3C{\equiv}CBF_3]$, $K[C_3F_7C{\equiv}CBF_3]$, $K[(CF_3)_2CFC{\equiv}CBF_3]$, $K[C_4F_9CF{=}CFC{\equiv}CBF_3]$, $K[C_4H_9C{\equiv}CBF_3]$ [23], K[*trans*-$CF_3CF{=}CFBF_3$] [24], K[*trans*-$C_4H_9CF{=}CFBF_3$] [21], [Bu_4N][*trans*-$C_4H_9CF{=}CFBF_3$] [1], and $K[C_4H_9CH{=}CHBF_3]$ [9] were prepared as described. Anhydrous hydrogen fluoride (aHF) was obtained by electrolysis (stainless steel cell, Ni-electrodes).

All manipulations with fluorine and aHF 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.

4.2. Reactions of $K[R_FBF_3]$ with hydrogen fluoride

4.2.1. Reactions of $K[CF_2{=}C(CF_3)BF_3]$

A. $K[CF_2{=}C(CF_3)BF_3]$ (49 mg, 0.21 mmol) was dissolved in 48% aq HF (0.7 mL) which contained $CF_3C(O)OH$ (internal integral standard) (13 mg, 0.11 mmol). The conversion of $K[CF_2{=}C(CF_3)BF_3]$ to $CF_2{=}C(CF_3)H$ and $K[BF_4]$ at ~20 °C was 50% (4 h), 75% (6 h), and 100% (19 h) (^{19}F NMR).

B. $K[CF_2{=}C(CF_3)BF_3]$ (35 mg, 0.15 mmol) was cooled to −55 °C before cold (−50 °C) aHF (0.5 mL) was added. After 25 min at −50 °C the ^{19}F NMR spectrum showed 50% of conversion of $K[CF_2{=}C(CF_3)BF_3]$ to $CF_2{=}C(CF_3)H$ and $K[BF_4]$ (ratio 1:1). Warming to −20 °C within a few min resulted in the complete hydrodeboration of $K[CF_2{=}C(CF_3)BF_3]$ (^{19}F NMR).

C. Cold (−20 °C) aHF (0.5 mL) was added to the pre-cooled (−20 °C) salt $K[CF_2{=}C(CF_3)BF_3]$ (35 mg, 0.14 mmol) and the solution was warmed to ~20 °C. $CF_2{=}C(CF_3)H$ and $K[BF_4]$ were formed immediately in a quantitative yield (^{19}F NMR).

$K[CF_2{=}C(CF_3)BF_3]$. The fluorine atoms at C-2 in $[F_2C^2{=}C^1(CF_3)BF_3]^-$ are specified by *cis* or *trans* relative to the position of BF_3. ^{19}F NMR (48% aq HF) δ −55.8 (3F, CF_3), −66.9 (1F, F^{2trans}), −76.0 (1F, F^{2cis}), −136.5 (q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3) (the signals of fluorine bonded to carbon were not resolved). ^{19}F NMR (aHF, −50 °C): δ −53.9 (dd, $^4J(CF_3, F^{2trans})$ = 22 Hz, $^4J(CF_3, F^{2cis})$ = 12 Hz, 3F, CF_3), −62.5 (br s, 1F, F^{2trans}), −71.6 (qd, $^4J(F^{2cis}, CF_3)$ = 12 Hz, $^2J(F^{2cis}, F^{2trans})$ = 15 Hz, 1F, F^{2cis}), −134.4 (br s, $\Delta\nu_{1/2}$ = 313 Hz, 3F, BF_3). ^{11}B NMR (aHF, −50 °C): δ 2.9 (br s, $\Delta\nu_{1/2}$ = 45 Hz) (cf. with ^{11}B and ^{19}F NMR spectra in CD_3CN [22]).

$CF_2{=}CHCF_3$. ^{19}F NMR (aHF, −20 °C): δ −56.5 (ddd, $^3J(F^3, H^2)$ = 7 Hz, $^4J(F^3, F^{1trans})$ = 11 Hz, $^4J(F^3, F^{1cis})$ = 18 Hz, 3F, F^3), −72.0 (ddq, $^3J(F^{1cis}, H^2)$ = 22 Hz, $^2J(F^{1cis}, F^{1trans})$ 14 Hz, $^4J(F^{1cis}, F^3)$ = 18 Hz, 1F, F^{1cis}), −75.7 (dq, $^2J(F^{1trans}, F^{1cis})$ = 14 Hz, $^4J(F^{1trans}, F^3)$ = 11 Hz, 1F, F^{1trans}) (cf. ^{19}F NMR (ether): δ −57.4 (ddd, $^3J(F^3, H^2)$ = 7 Hz, $^4J(F^3, F^{1trans})$ = 11 Hz, $^4J(F^3, F^{1cis})$ = 18 Hz, 3F, F^3), −72.0 (ddq, $^3J(F^{1cis}, H^2)$ = 22 Hz, $^2J(F^{1cis}, F^{1trans})$ 13 Hz, $^4J(F^{1cis}, F^3)$ = 18 Hz, 1F, F^{1cis}), −76.7 (dq, $^2J(F^{1trans}, F^{1cis})$ = 13 Hz, $^4J(F^{1trans}, F^3)$ = 11 Hz, 1F, F^{1trans}) [22]).

4.2.2. Reactions of K[$CF_3C{\equiv}CBF_3$]

A. A solution of K[$CF_3C{\equiv}CBF_3$] (50 mg, 0.25 mmol) in 27% aq HF (0.5 mL) and $CF_3C(O)OH$ (12 mg) (internal integral standard) was maintained at ~20 °C for 2 months. The periodic control by ^{11}B and ^{19}F NMR spectroscopy displayed no reaction. The same result was obtained for a solution of K[$CF_3C{\equiv}CBF_3$] (50 mg, 0.25 mmol) in 48% aq HF (0.5 mL) and $CF_3C(O)OH$ (12 mg) (~20 °C, 2 months).

B. K[$CF_3C{\equiv}CBF_3$] (462 mg, 2.31 mmol) was suspended in cold (−40 °C) aHF (4 mL). Warming above 10 °C led to the complete dissolution of K[$CF_3C{\equiv}CBF_3$] without reaction after 0.5 h (^{19}F NMR). The solution was stirred at ~20 °C with periodic control by ^{19}F NMR spectroscopy. For this purpose probes of the solution were taken under argon from the reactor in a cold (~0 °C) inliner and the measurement was performed at 10 °C. With progress of the reaction the integral intensity of the very broad $[BF_4]^-$ signal (^{19}F) increased strongly whereas the quantity of the co-product of the hydrodeboration, $CF_3C{\equiv}CH$, appeared significantly lower, caused by its high volatility and diffusion through the FEP wall. The molar ratio K[$CF_3C{\equiv}CBF_3$]:K[$CF_3CH_2{-}CF_2BF_3$]:K[$CF_3CH_2{-}C(O)BF_3$] was 83:12:5 (3 h), 15:68:17 (22 h), and 1:86:12 (43 h) (all spectra contained additional signals of minor unknown compounds). Stirring was continued for additional 30 h. Then all volatiles were removed under reduced pressure. The residue was suspended in water (3 mL), neutralized with KF (excess) and extracted with MeCN (2× 5 mL). The combined extracts were dried with KF. The solution contained K[$CF_3CH_2{-}CF_2BF_3$] (0.18 mmol) and K[$CF_3CH_2{-}C(O)BF_3$] (0.18 mmol) (^{19}F NMR) (internal integral standard C_6F_5H).

C. K[$CF_3C{\equiv}CBF_3$] (1.1 g, 5.5 mmol) was dissolved in aHF (5 mL) and stirred at ~20 °C for 4 d. All volatiles were distilled off, the residue was diluted with ice water (10 mL), neutralized with KF (excess) and stirred with charcoal to remove colored impurities. The suspension was filtered, saturated with KF and extracted with MeCN (2× 5 mL). The colorless combined extracts were dried with KF and evaporated to dryness to yield a white solid mixture of K[$CF_3CH_2{-}CF_2BF_3$] and K[$CF_3CH_2{-}C(O)BF_3$] (43:57) (185 mg).

K[$CF_3C{\equiv}CBF_3$]. ^{11}B NMR (48% aq HF): δ −3.3 (q, ^1J(B, F) = 32 Hz). ^{11}B NMR (aHF, −20 °C): δ −2.3 (s, $\Delta\nu_{1/2}$ = 46 Hz). ^{19}F NMR (48% aq HF): δ −48.5 (s, 3F, F^3), −132.9 (q (1:1:1:1), ^1J(F, B) = 32 Hz, 3F, BF_3). ^{19}F NMR (aHF, −20 °C): δ −49.5 (s, 3F, F^3), −133.3 (s, 3F, BF_3). (cf. with ^{11}B and ^{19}F NMR spectra in CD_3CN, acetone-d_6 or DMSO-d_6 [23]).

K[$CF_3CH_2{-}CF_2BF_3$]. ^1H NMR (CD_3CN): δ 2.64 (tq, $^3J(H^2, F^1)$ = 19 Hz, $^3J(H^2, F^3)$ = 11 Hz, 2H, H^2). ^1H NMR (acetone-d_6): δ 2.56 (tq, $^3J(H^2, F^1)$ = 19 Hz, $^3J(H^2, F^3)$ = 11 Hz, 2H, H^2). ^{11}B NMR (aHF, 0 °C): δ 0 (m). ^{11}B NMR (CD_3CN): δ −0.3 (tq, ^2J(B, F^1) = 23 Hz, ^1J(B, F) = 46 Hz). ^{11}B NMR (acetone-d_6): δ −0.2 (tq, ^2J(B, F^1) = 23 Hz, ^1J(B, F) = 46 Hz). $^{13}C\{^{19}F\}$ NMR (CH_3OD): δ 124 (C-3), 116.4 (C-1), 36.6 (t, ^1J(C-2, H^2) = 127 Hz, C-2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 126.0 (q, ^1J(C-3, F^3) = 276 Hz, C-3), 116.7 (t, ^1J(C-1, F^1) = 238 Hz, C-1), 37.8 (tq, ^2J(C-2, F^1) = 24 Hz, ^2J(C-2, F^3) = 24 Hz, C-2). ^{19}F NMR (aHF, 0 °C): δ −59.6 (tt, $^3J(F^3, H^2)$ = 10 Hz, $^4J(F^3, F^1)$ = 10 Hz, 3F, F^3), −116.4 (m, 2F, F^1), −151.7 (q (1:1:1:1), ^1J(F, B) = 44 Hz, 3F, BF_3). ^{19}F NMR (CD_3CN): δ −59.3 (tt, $^3J(F^3, H^2)$ = 10 Hz, $^4J(F^3, F^1)$ = 10 Hz, 3F, F^3), −120.9 (m, 2F, F^1), −155.6 (q (1:1:1:1), ^1J(F, B) = 47 Hz, 3F, BF_3). ^{19}F NMR (CH_3OD): δ −60.2 (ttq, $^3J(F^3, H^2)$ = 11 Hz, $^4J(F^3, F^1)$ = 9 Hz, $^5J(F^3, BF_3)$ = 1 Hz, 3F, F^3), −121.1 (m, 2F, F^1), −156.4 (q (1:1:1:1), ^1J(F, B) = 47 Hz, 3F, BF_3). ^{19}F NMR (acetone-d_6): δ −58.9 (ttq, $^3J(F^3, H^2)$ = 10 Hz, $^4J(F^3, F^1)$ = 10 Hz, $^5J(F^3, BF_3)$ = 1 Hz, 3F, F^3), −121.6 (m, 2F, F^1), −155.7 (q (1:1:1:1), ^1J(F, B) = 46 Hz, 3F, BF_3).

K[$CF_3CH_2{-}C(O)BF_3$]. ^1H NMR (CD_3CN): δ 3.34 (q, $^3J(H^2, F^3)$ = 11 Hz, 2H, H^2). ^1H NMR (acetone-d_6): δ 3.29 (q, $^3J(H^2, F^3)$ = 12 Hz, 2H, H^2). ^{11}B NMR (aHF, 0 °C): δ 0 (m). ^{11}B NMR (CD_3CN): δ −2.3 (q, ^1J(B, F) = 51 Hz). ^{11}B NMR (acetone-d_6): δ −2.2 (q, ^1J(B, F) = 50 Hz). $^{13}C\{^{19}F\}$ NMR (CH_3OD): δ 236 (C-1), 123 (C-3), 45 (t, ^1J(C-2, H^2) = 134 Hz, C-2). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 125.5 (q, ^1J(C-3, F^3) = 277 Hz, C-3), 45.7 (q, ^2J(C-2, F^3) = 21 Hz, C-2), (C-1 was not observed because of the low concentration and S/N caused by couplings with boron and fluorine atoms of the BF_3 group). ^{19}F NMR (aHF, 0 °C): δ −61.2 (t, $^3J(F^3, H^2)$ = 9 Hz, 3F, F^3), −149.5 (q (1:1:1:1), ^1J(F, B) = 33 Hz, 3F, BF_3). ^{19}F NMR (CD_3CN): δ −60.6 (t, $^3J(F^3, H^2)$ = 12 Hz, 3F, F^3), −150.4 (q (1:1:1:1), ^1J(F, B) = 50 Hz, 3F, BF_3). ^{19}F NMR (acetone-d_6): δ −60.4 (t, $^3J(F^3, H^2)$ = 12 Hz, 3F, F^3), −150.6 (q (1:1:1:1), ^1J(F, B) = 49 Hz, 3F, BF_3). ^{19}F NMR (CH_3OD): δ −61.6 (t, $^3J(F^3, H^2)$ = 11 Hz, 3F, F^3), −151.4 (q (1:1:1:1), ^1J(F, B) = 47 Hz, 3F, BF_3).

(K[$CF_3CH_2{-}CF_2BF_3$] + K[$CF_3CH_2{-}C(O)BF_3$]). IR (KBr): 3014w (C–H), 2978w (C–H), 2963w (C–H), 2951w (C–H), 2926w (C–H), 1685m (C=O), 1419w, 1386w, 1361 m, 1263s, 1188s, 1126s, 1051s, 937m, 865m, 784w, 683w, 615w, 602w cm^{-1}.

4.2.3. Reactions of K[$C_3F_7C{\equiv}CBF_3$]

A. A solution of K[$C_3F_7C{\equiv}CBF_3$] (60 mg, 0.20 mmol) in 48% aq HF (1 mL) and $CF_3C(O)OH$ (24 mg, 0.21 mmol) (internal integral standard) was maintained at ~20 °C for 8 d. The periodic control by ^{11}B and ^{19}F NMR spectroscopy displayed no reaction.

B. A solution of K[$C_3F_7C{\equiv}CBF_3$] (26 mg, 0.09 mmol) and $C_6H_5CF_3$ (5 μL, 0.041 mmol) (internal integral standard) in aHF (0.5 mL) was kept at 0 °C for 2 h without reaction. The complete hydrodeboration of K[$C_3F_7C{\equiv}CBF_3$] to $C_3F_7C{\equiv}CH$ (>98% yield) and K[BF_4] occurred when this solution was maintained at ~20 °C for 24 h (^{11}B, ^{19}F NMR).

K[$C_3F_7C{\equiv}CBF_3$]. ^{11}B NMR (aHF, 0 °C): δ −1.7 (br s). ^{19}F NMR (aHF, −20 °C): δ −80.4 (t, $^4J(F^5, F^3)$ = 9 Hz, 3F, F^5), −98.5 (m, 2F, F^3), −127.0 (m, 2F, F^4), −134.6 (br s, 3F, BF_3) (cf. with ^{11}B and ^{19}F NMR spectra in CH_3CN [23]).

$C_3F_7C{\equiv}CH$. ^{19}F NMR (aHF, −10 °C): δ −78.5 (t, $^4J(F^5, F^3)$ = 9 Hz, 3F, F^5), −98.0 (dtq, $^4J(F^3, H^1)$ = 5 Hz, $^3J(F^3, F^4)$ = 4 Hz, $^4J(F^3, F^5)$ = 9 Hz, 2F, F^3), −125.3 (t, $^3J(F^4, F^3)$ = 4 Hz, 2F, F^4) (cf. with ^{19}F NMR spectra of the neat liquid, and in ether or CCl_4 solutions [23]).

4.2.4. Reaction of K[$(CF_3)_2CFC{\equiv}CBF_3$]

A. A solution of K[$(CF_3)_2CFC{\equiv}CBF_3$] (56 mg, 0.19 mmol) in 48% aq HF (0.7 mL) and $CF_3C(O)OH$ (24 mg, 0.21 mmol) (internal integral standard) was maintained at ~20 °C for 8 d. The periodic control by ^{11}B and ^{19}F NMR spectroscopy displayed no decomposition.

B. K[$(CF_3)_2CFC{\equiv}CBF_3$] (62 mg, 0.21 mmol) was cooled to −40 °C and cold (−40 °C) aHF (0.8 mL) was added. The solution was kept at −15 °C for 20 min and at 0 °C for 1 h (no reaction of K[$(CF_3)_2CFC{\equiv}CBF_3$]) (^{11}B, ^{19}F NMR). Stirring at ~20 °C for 5 h resulted in the complete hydrodeboration to $(CF_3)_2CFC{\equiv}CH$ and K[BF_4] (ratio 1:1) (^{11}B, ^{19}F NMR).

K[$(CF_3)_2CFC{\equiv}CBF_3$]. ^{11}B NMR (48% aq HF): δ −3.1 (q, ^1J(B, F) = 32 Hz). ^{11}B NMR (aHF, 0 °C): δ −2.2 (s, $\Delta\nu_{1/2}$ = 20 Hz). ^{19}F NMR (48% aq HF): δ −77.9 (d, $^3J(CF_3, F^3)$ = 10 Hz, 6F, $2CF_3$), −163.4 (sept, $^3J(F^3, CF_3)$ = 10 Hz, 1F, F^3), −134.7 (q (1:1:1:1), ^1J(F, B) = 31 Hz, 3F, BF_3). ^{19}F NMR (aHF, 0 °C): δ −75.8 (d, $^3J(CF_3, F^3)$ = 10 Hz, 6F, $2CF_3$), −165.2 (sept, $^3J(F^3, CF_3)$ = 10 Hz, 1F, F^3), −133.3 (br s, $\Delta\nu_{1/2}$ = 390 Hz, 3F, BF_3) (cf. with ^{11}B and ^{19}F NMR spectra in CH_3CN or DMSO-d_6 [23]).

$(CF_3)_2CFC{\equiv}CH$. ^{19}F NMR (aHF, 0 °C): δ −75.9 (d, $^3J(CF_3, F^3)$ = 10 Hz, 6F, $2CF_3$), −167.4 (dsept, $^4J(F^3, H^1)$ = 6 Hz, $^3J(F^3, CF_3)$ = 10 Hz, 1F, F^3) (cf. with ^{19}F NMR spectrum in ether [23]).

4.2.5. Reaction of K[$C_4F_9CF{=}CFC{\equiv}CBF_3$]

A. A solution of K[$C_4F_9CF{=}CFC{\equiv}CBF_3$] (*cis*:*trans* = 45:55) (49 mg, 0.12 mmol) in 27% aq HF (0.5 mL) was maintained at ~20 °C for 2 d. The periodic control by the ^{11}B and ^{19}F NMR spectroscopy displayed no reaction.

B. A solution of K[$C_4F_9CF{=}CFC{\equiv}CBF_3$] (*cis*:*trans* = 45:55) (41 mg, 0.10 mmol) and $C_6H_5CF_3$ (5 μL, 0.04 mmol) (internal integral standard) in aHF (0.6 mL) was kept at ~20 °C for 0.5 h. The ^{11}B and ^{19}F NMR spectra displayed the quantitative conversion of K[$C_4F_9CF{=}CFC{\equiv}CBF_3$] to $C_4F_9CF{=}CFC{\equiv}CH$ (*cis*:*trans* = 44:56) and K[BF_4].

K[*cis*-$C_4F_9CF{=}CFC{\equiv}CBF_3$]. ^{11}B NMR (27% aq HF): δ −2.6 (br s). ^{19}F NMR (27% aq HF): δ −80.4 (tt, $^3J(F^8, F^7)$ = 2 Hz, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −114.6 (d, $^3J(F^3, F^4)$ = 10 Hz, 1F, F^3), −115.2 (dt, $^3J(F^5, F^4)$ = 13 Hz, $^4J(F^5, F^7)$ = 13 Hz, 2F, F^5), −123.0 (m, 2F, F^6), −125.4 (m, 2F, F^7), −132.7 (purely resolved q, 3F, BF_3), −142.6 (m, 1F, F^4).

K[*trans*-$C_4F_9CF{=}CFC{\equiv}CBF_3$]. ^{11}B NMR (27% aq HF): δ −2.6 (br s). ^{19}F NMR (27% aq HF): δ −80.8 (tt, $^3J(F^8, F^7)$ = 2 Hz, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −116.8 (dtd, $^3J(F^5, F^4)$ = 13 Hz, $^4J(F^5, F^7)$ = 13 Hz, $^4J(F^5, F^3)$ = 25 Hz, 2F, F^5), −123.7 (m, 2F, F^6), −125.7 (m, 2F, F^7), −132.7 (poorly resolved q, 3F, BF_3), −135.2 (dt, $^3J(F^3, F^4)$ = 140 Hz, $^4J(F^3, F^5)$ = 25 Hz, 1F, F^3), −160.0 (d, $^3J(F^4, F^3)$ = 140 Hz, 1F, F^4) (cf. with ^{11}B and ^{19}F NMR spectra in CH_3CN [23]).

cis-$C_4F_9CF{=}CFC{\equiv}CH$. ^{19}F NMR (aHF, 0 °C): δ −79.6 (t, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −114.5 (m, 2F, F^5), −119.0 (dd, $^3J(F^3, F^4)$ = 6 Hz, $^4J(F^3, H^1)$ = 5 Hz, 1F, F^3), −121.8 (m, 2F, F^6), −124.4 (m, 2F, F^7), −138.6 (m, 1F, F^4).

trans-$C_4F_9CF{=}CFC{\equiv}CH$. ^{19}F NMR (aHF, 0 °C): δ −79.6 (t, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −116.0 (m, 2F, F^5), −122.5 (m, 2F, F^6), −124.4 (m, 2F, F^7), −138.3 (dt, $^3J(F^3, F^4)$ = 139 Hz, $^4J(F^3, F^5)$ = 26 Hz, 1F, F^3), −156.4 (d, $^3J(F^4, F^3)$ = 139 Hz, 1F, F^4).

4.2.6. Reaction of K[$C_4H_9C{\equiv}CBF_3$]

A three-phase system of K[$C_4H_9C{\equiv}CBF_3$] (69 mg, 0.36 mmol) and C_6F_5H (20 mg, 0.12 mmol, internal integral standard) in CCl_4 (0.7 mL) and 27% aq HF (1 mL) was stirred at ~20 °C for 30 min. The colorless organic phase at the bottom of the final three-phase system contained $C_4H_9C{\equiv}CH$ (quantitative yield) (^1H NMR).

4.3. Reactions of perfluoroalkenyl- and perfluoroalkynyltrifluoroborates with N-chlorosuccinimide in aHF

4.3.1. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$]

A solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (166 mg, 0.43 mmol) in aHF (1 mL) was cooled to ~0 °C and *N*-chlorosuccinimide (70 mg, 0.52 mmol) was added in one portion. The solution was stirred at ~20 °C for 2 h (8% conversion), 20 h (83% conversion), and 48 h (100% conversion). KF (2–3 g) was added and the slurry was diluted with water (1:1, v/v). The suspension was extracted with ether (4× 1 mL). The combined extracts were dried with KF and the solvent was removed under reduced pressure. After further drying in vacuum (13.3 hPa) K[$C_4F_9CFCl{-}CF_2BF_3$] was obtained as a white solid (114 mg, 0.25 mmol, 58%).

K[$C_4F_9CFCl{-}CF_2BF_3$]. ^{11}B NMR (CH_3CN): δ −0.6 (qt, $^1J(B, F)$ = 40 Hz, $^2J(B, F^1)$ = 20 Hz). ^{19}F NMR (CH_3CN): δ −79.9 (tt, $^4J(F^6, F^4)$ = 10 Hz, $^3J(F^6, F^5)$ = 3 Hz, 3F, F^6), −113.5 (md, $^2J(F^{3A}, F^{3B})$ = 295 Hz, 1F, F^{3A}), −114.6 (md, $^2J(F^{3B}, F^{3A})$ = 295 Hz, 1F, F^{3B}), −117.9 (md, $^2J(F^{4A}, F^{4B})$ = 300 Hz, 1F, F^{4A}), −119.9 (md, $^2J(F^{4B}, F^{4A})$ = 300 Hz, 1F, F^{4B}), −124.5 (ddddd, $^3J(F^{5A}, F^{4A})$ = 4 Hz, $^3J(F^{5A}, F^{4B})$ = 8 Hz, $^4J(F^{5A}, F^{3A})$ = 12 Hz, $^4J(F^{5A}, F^{3B})$ = 20 Hz, $^2J(F^{5A}, F^{5B})$ = 292 Hz, 1F, F^{5A}), −125.2 (ddddd, $^3J(F^{5B}, F^{4B})$ = 3 Hz, $^3J(F^{5B}, F^{4A})$ = 8 Hz, $^4J(F^{5B}, F^{3B})$ = 15 Hz, $^4J(F^{5B}, F^{3A})$ = 19 Hz, $^2J(F^{5B}, F^{5A})$ = 292 Hz, 1F, F^{5B}), −121.9 (br m, $\Delta\nu_{1/2}$ = 72 Hz, d, $^2J(F^{1A}, F^{1B})$ = 319 Hz, 1F, F^{1A}), −124.9 (br m, $\Delta\nu_{1/2}$ = 71 Hz, d, $^2J(F^{1B}, F^{1A})$ = 319 Hz, 1F, F^{1B}), −134.1 (m, 1F, F^2), −150.0 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3).

Anal. Calcd for $C_6BClF_{15}K$ (442.40): C, 16.29; Cl, 8.01; F, 64.42. Found: C, 16.3; Cl, 7.6; F, 63.9.

4.3.2. Reaction of K[*cis*-$C_2F_5CF{=}CFBF_3$]

A solution of K[*cis*-$C_2F_5CF{=}CFBF_3$] (327 mg, 1.14 mmol) in aHF (1 mL) was cooled to ~0 °C and *N*-chlorosuccinimide (157 mg, 1.18 mmol) was added in one portion. The solution was stirred at ~20 °C for 1 h (no reaction), 24 h (37% conversion), 55 h (73% conversion), and 102 h (100% conversion). KF (2–3 g) was added and the slurry was diluted with water (1:1, v/v). The suspension was extracted with ether (4× 1 mL). The combined extracts were dried with KF and the solvent was removed under reduced pressure. After additional drying in vacuum (13.3 hPa) K[$C_2F_5CFCl{-}CF_2BF_3$] was obtained as a white solid (229 mg, 0.67 mmol, 59%).

K[$C_2F_5CFCl{-}CF_2BF_3$]. ^{11}B NMR (CD_3CN): δ 2.8 (qt, $^1J(B, F)$ = 41 Hz, $^2J(B, F^1)$ = 20 Hz). ^{19}F NMR (CD_3CN): δ −74.5 (ddd, $^3J(F^4, F^{3B})$ = 5 Hz, $^3J(F^4, F^{3A})$ = 7 Hz, $^4J(F^4, F^2)$ = 11 Hz, 3F, F^4), −114.1 (qdtd, $^3J(F^{3A}, F^4)$ = 7 Hz, $^3J(F^{3A}, F^2)$ = 8 Hz, $^4J(F^{3A}, F^1)$ = 12 Hz, $^2J(F^{3A}, F^{3B})$ = 284 Hz, $1F^{3A}$), −115.5 (qtd, $^3J(F^{3B}, F^4)$ = 4 Hz, $^4J(F^{3B}, F^1)$ = 12 Hz, $^2J(F^{3B}, F^{3A})$ = 284 Hz, $1F^{3B}$), −119.3 (br m, $\Delta\nu_{1/2}$ = 66 Hz, d, $^2J(F^{1A}, F^{1B})$ = 321 Hz, 1F, F^{1A}), −122.2 (br m, $\Delta\nu_{1/2}$ = 67 Hz, d, $^2J(F^{1B}, F^{1A})$ = 321 Hz, 1F, F^{1B}), −131.4 (m, 1F, F^2), −146.7 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3).

Anal. Calcd for $C_4BClF_{11}K$ (342.39): C, 14.03; Cl, 10.35; F, 61.04. Found: C, 13.8; Cl, 10.3; F, 60.2.

4.3.3. Reaction of K[$CF_3C{\equiv}CBF_3$]

N-chlorosuccinimide (300 mg, 2.25 mmol) was added in one portion to a cold (~0 °C) stirred solution of K[$CF_3C{\equiv}CBF_3$] (200 mg, 1 mmol) in aHF (1 mL). The yellow solution was stirred for 1 h at ~0 °C and at ~20 °C for 3 h. The ^{19}F NMR spectrum showed the presence of K[$CF_3C{\equiv}CBF_3$], K[(*E*)-$CF_3CCl{=}CFBF_3$], K[$CF_3CCl_2{-}CF_2BF_3$], $CF_3C{\equiv}CH$, and K[BF_4] (molar ratio 100:13:34:31:172). After stirring at ~20 °C for 33 h the total conversion of K[$CF_3C{\equiv}CBF_3$] to K[$CF_3CCl_2{-}CF_2BF_3$], $CF_3C{\equiv}CH$, and K[BF_4] was achieved (signals of $[CF_3CCl{=}CFBF_3]^-$ were no more detected). Volatiles were evaporated in vacuum and the semi-solid was stirred with charcoal (100 mg) in water (2 mL) at ~20 °C for 0.5 h and the solid was filtered off. The filtrate was saturated with KF and extracted with acetonitrile (5× 1 mL). The combined extracts were treated with K_2CO_3 and the solvent was evaporated to yield crude K[$CF_3CCl_2{-}CF_2BF_3$] (300 mg). It was washed with CH_2Cl_2 (5× 1 mL) and stirred with 18-crown-6 (250 mg, 0.95 mmol) in CH_2Cl_2 (2 mL) for 1 h. After filtration the solution was evaporated at ~20 °C overnight. The solid was washed with pentane (5× 2 mL) and ether (5× 2 mL) and dried in a vacuum desiccator over Sicapent®. The salt [K·18-crown-6][$CF_3CCl_2{-}CF_2BF_3$] (230 mg, 0.40 mmol) was isolated.

K[(*E*)-$CF_3CCl{=}CFBF_3$]. ^{19}F NMR (aHF, 0 °C): δ −60.7 (d, $^4J(F^3, F^1)$ = 25 Hz, 3F, F^3), −105.4 (m, 1F, F^1), −140.0 (q (1:1:1:1), $^1J(F, B)$ = 39 Hz, 3F, BF_3).

K[$CF_3CCl_2{-}CF_2BF_3$]. ^{11}B NMR (aHF, 0 °C): δ −0.7 (m). ^{11}B NMR (CD_3CN): δ −0.5 (tq, $^2J(B, F^1)$ = 20 Hz, $^1J(B, F)$ = 41 Hz). $^{13}C\{^{19}F\}$ NMR (CD_3CN): δ 122.3 (q (1:1:1:1), ^1J(C-1, B) = 86 Hz, C-1), 120.9 (m, C-3), 86.4 (m, C-2). ^{19}F NMR (aHF, 0 °C): δ −71.7 (m, 3F, F^3), −115.3 (m, 2F, F^1), −145.1 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3). ^{19}F NMR (CD_3CN): δ −72.7 (tq, $^4J(F^3, F^1)$ = 10 Hz, $^5J(F^3, BF_3)$ = 6 Hz, 3F, F^3), −115.6 (qq (1:1:1:1), $^4J(F^1, F^3)$ = 10 Hz, $^2J(F^1, B)$ = 19 Hz, 2F, F^1), −148.7 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3).

[K·18-crown-6][$CF_3CCl_2{-}CF_2BF_3$]. Anal. Calcd for $C_{15}H_{24}BCl_2F_8KO_6$ (573.15): C, 31.43; H, 4.22. Found: C, 32.6; H, 4.4.

4.4. Reactions of perfluoroalkenyl- and perfluoroalkynyltrifluoroborates with N-bromosuccinimide in aHF

4.4.1. Reaction of K[trans-$C_4F_9CF{=}CFBF_3$]

A solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (197 mg, 0.51 mmol) in aHF (1.5 mL) was cooled to −10 °C and NBS (110 mg, 0.62 mmol) was added in one portion. The yellow solution was stirred at ~20 °C for 2 h to show the quantitative formation of K[C_4F_9CFBr–CF_2BF_3] (^{19}F NMR). The solution was concentrated at 50 °C to a volume of ca. 1 mL, diluted with water (1 mL) and neutralized with concentrated aq KOH. A precipitate was formed which was filtered off. The solid was washed with water (2–3 mL) and dried in a vacuum desiccator over Sicapent® to give a solid mixture (284 mg) which consisted of K[C_4F_9CFBr–CF_2BF_3] and succinimide (77:23) (^{1}H, ^{19}F NMR). Sequential washing with 20% aq KOH, water (2 mL) and drying in vacuum over Sicapent® gave analytically pure K[C_4F_9CFBr–CF_2BF_3] (167 mg, 34%).

K[C_4F_9CFBr–CF_2BF_3]. ^{11}B NMR (CD_3CN): δ −0.5 (qt, ^1J(B, F) = 41 Hz, ^2J(B, F^1) = 20 Hz). ^{19}F NMR (CD_3CN): δ −80.0 (tt, $^4J(F^6, F^4)$ = 10 Hz, $^3J(F^6, F^5)$ = 3 Hz, 3F, F^6), −110.8 (md, $^2J(F^{3A}, F^{3B})$ = 293 Hz, 1F, F^{3A}), −112.2 (md, $^2J(F^{3B}, F^{3A})$ = 293 Hz, 1F, F^{3B}), −117.1 (md, $^2J(F^{4A}, F^{4B})$ = 296 Hz, 1F, F^{4A}), −119.4 (md, $^2J(F^{4B}, F^{4A})$ = 296 Hz, 1F, F^{4B}), −124.6 (ddddd, $^3J(F^{5A}, F^{4A})$ = 3 Hz, $^3J(F^{5A}, F^{4B})$ = 7 Hz, $^4J(F^{5A}, F^{3A})$ = 14 Hz, $^4J(F^{5A}, F^{3B})$ = 20 Hz, $^2J(F^{5A}, F^{5B})$ = 292 Hz, 1F, F^{5A}), −125.1 (ddddd, $^3J(F^{5B}, F^{4B})$ = 3 Hz, $^3J(F^{5B}, F^{4A})$ = 7 Hz, $^4J(F^{5B}, F^{3B})$ = 16 Hz, $^4J(F^{5B}, F^{3A})$ = 18 Hz, $^2J(F^{5B}, F^{5A})$ = 292 Hz, 1F, F^{5B}), −117.9 (br m, $\Delta\nu_{1/2}$ = 68 Hz, d, $^2J(F^{1A}, F^{1B})$ = 321 Hz, 1F, F^{1A}), −121.5 (br m, $\Delta\nu_{1/2}$ = 65 Hz, d, $^2J(F^{1B}, F^{1A})$ = 321 Hz, 1F, F^{1B}), −135.8 (m, 1F, F^2), −149.5 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3).

IR (KBr): 1358m, 1298m, 1234s, 1203s, 1167m, 1142s, 1099m, 1968m, 1038s, 1017s, 972m, 893w, 820m, 706w, 687m, 632w, 577w, 530w cm^{-1}.

Anal. Calcd for $C_6BBrF_{15}K$ (486.85): C, 14.80; Br, 16.41; F, 58.53. Found: C, 14.9; Br, 16.3; F, 58.6.

4.4.2. Reactions of K[$CF_3C{\equiv}CBF_3$]

A. NBS (83 mg, 0.47 mmol) was added in one portion to a cold (−15 °C) stirred solution of K[$CF_3C{\equiv}CBF_3$] (98 mg, 0.49 mmol) in aHF (0.5 mL). The yellow solution was stirred at ~20 °C for 2 h. The ^{11}B and ^{19}F NMR spectra of a probe showed the presence of [$CF_3C{\equiv}CBF_3$]$^-$, [$CF_3CBr{=}CFBF_3$]$^-$ ((*E*):(*Z*) = 5:1) and [CF_3CBr_2–CF_2BF_3]$^-$ in a molar ratio 45:4:51 besides a minor quantity of $CF_3C{\equiv}CH$. All volatiles were removed in vacuum. The residue was neutralized with KF (excess) and extracted with MeCN (1.5 mL). The MeCN solution was kept over KF overnight, filtered and MeCN was removed under reduced pressure to yield a mixture (133 mg) of K[$CF_3C{\equiv}CBF_3$], K[$CF_3CBr{=}CFBF_3$] ((*E*):(*Z*) = 2:1), and K[CF_3CBr_2–CF_2BF_3] in the molar ratio 37:5:58 (still contaminated with succinimide).

K[(*Z*)-$CF_3CBr{=}CFBF_3$]. ^{11}B NMR (aHF, 10 °C): δ −0.6 (m, overlapping). ^{11}B NMR (CH_3CN): δ −0.7 (m, overlapping). ^{19}F NMR (aHF, 10 °C): δ −68.0 (q, $^5J(F^3, BF_3)$ = 3 Hz, 3F, F^3), −69.0 (m, 1F, F^1), −143.2 (q (1:1:1:1), ^1J(F, B) = 35 Hz, 3F, BF_3). ^{19}F NMR (CH_3CN): δ −68.6 (q, $^5J(F^3, BF_3)$ = 3 Hz, 3F, F^3), −69.6 (m, 1F, F^1), −140.7 (q (1:1:1:1), ^1J(F, B) = 44 Hz, 3F, BF_3).

K[(*E*)-$CF_3CBr{=}CFBF_3$]. ^{11}B NMR (aHF, 10 °C): δ −0.6 (m, overlapping). ^{11}B NMR (CH_3CN): δ −0.7 (m, overlapping). ^{19}F NMR (aHF, 10 °C): δ −58.5 (d, $^4J(F^3, F^1)$ = 25 Hz, 3F, F^3), −94.0 (m, 1F, F^1), −139.0 (q (1:1:1:1), ^1J(F, B) = 34 Hz, 3F, BF_3). ^{19}F NMR (CH_3CN): δ −58.4 (dq, $^4J(F^3, F^1)$ = 25 Hz, $^5J(F^3, BF_3)$ = 1 Hz, 3F, F^3), −87.6 (q, $^4J(F^1, F^3)$ = 25 Hz, 1F, F^1), −143.1 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3).

B. NBS (397 mg, 2.23 mmol) was added in one portion to a cold (~0 °C) stirred solution of K[$CF_3C{\equiv}CBF_3$] (200 mg, 1 mmol) in aHF (1 mL). The yellow solution was stirred at ~0 °C for 1 h and at ~20 °C for 3 h. The ^{11}B and ^{19}F NMR spectra of a probe showed the complete conversion of K[$CF_3C{\equiv}CBF_3$]. All volatiles were removed in vacuum and the semi-solid was dissolved in water (2 mL) and stirred with charcoal (100 mg) at ~20 °C for 0.5 h. The filtrate was saturated with KF and extracted with acetonitrile (5× 1 mL). The combined extracts were treated with K_2CO_3 and the solvent was evaporated to yield K[CF_3CBr_2–CF_2BF_3] (400 mg) (still contaminated with succinimide). The solid was washed with CH_2Cl_2 (5× 1 mL) and stirred with 18-crown-6 (250 mg, 0.95 mmol) in CH_2Cl_2 (2 mL) for 1 h. After filtration the solution was evaporated at ~20 °C overnight. The solid was washed with pentane (5× 2 mL), ether (5× 2 mL), and dried in a vacuum desiccator over Sicapent®. The salt [K·18-crown-6][CF_3CBr_2–CF_2BF_3] (250 mg, 0.38 mmol, 38%) was isolated.

K[CF_3CBr_2–CF_2BF_3]. ^{11}B NMR (aHF, 0 °C): δ −1.0 (m). ^{11}B NMR (CD_3CN): δ −0.7 (tq, ^2J(B, F^1) = 21 Hz, ^1J(B, F) = 41 Hz). ^{13}C NMR (CD_3CN): δ 122.6 (qt, ^1J(C-3, F^3) = 280 Hz, ^3J(C-3, F^1) = 4 Hz, C-3), 63.8 (q, ^2J(C-2, F^3) = 31 Hz, C-2); the resonance of C-1 was not observed. ^{13}C{^{19}F} NMR (CD_3CN): δ 122.7 (q (1:1:1:1), ^1J(C-1, B) = 88 Hz, C-1), 122.6 (m, C-3), 63.8 (m, C-2). ^{19}F NMR (aHF, 0 °C): δ −68.0 (m, 3F, F^3), −106.7 (m, 2F, F^1), −144.0 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3). ^{19}F NMR (CD_3CN): δ −68.9 (tq, $^4J(F^3, F^1)$ = 9 Hz, $^5J(F^3, BF_3)$ = 6 Hz, 3F, F^3), −107.2 (m, 2F, F^1), −147.5 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3).

[K·18-crown-6][CF_3CBr_2–CF_2BF_3]. Anal. Calcd for $C_{15}H_{24}BBr_2F_8KO_6$ (662.05): C, 27.21; H, 3.65. Found: C, 27.7; H, 4.1.

4.4.3. Reaction of K[$C_3F_7C{\equiv}CBF_3$]

N-bromosuccinimide (397 mg, 2.23 mmol) was added in one portion to a cold (~0 °C) stirred solution of K[$C_3F_7C{\equiv}CBF_3$] (150 mg, 0.5 mmol) in aHF (1 mL). The yellow solution was stirred for 1 h at ~0 °C and at ~20 °C for 20 h. The ^{11}B and ^{19}F NMR spectra of a probe showed the complete conversion of K[$C_3F_7C{\equiv}CBF_3$] under formation of K[$C_3F_7CBr_2$–CF_2BF_3]. All volatiles were evaporated in vacuum and the semi-solid was dissolved in water (2 mL). The solution was stirred at ~20 °C for 0.5 h with charcoal (100 mg). The solid was filtered off, the filtrate was saturated with KF and extracted with acetonitrile (5× 1 mL). The combined extracts were treated with K_2CO_3. The solvent was evaporated to yield crude K[$C_3F_7CBr_2$–CF_2BF_3] (210 mg) (still contaminated with succinimide). The solid was washed with CH_2Cl_2 (5× 1 mL) and stirred with 18-crown-6 (200 mg, 0.76 mmol) in CH_2Cl_2 (2 mL) for 1 h. After filtration, the solution was evaporated at ~20 °C overnight. The solid was washed with pentane (5× 2 mL) and ether (5× 2 mL) and was dried in a vacuum desiccator over Sicapent®. The salt [K·18-crown-6][$C_3F_7CBr_2$–CF_2BF_3] (145 mg, 0.19 mmol) was isolated.

K[$C_3F_7CBr_2$–CF_2BF_3]. ^{11}B NMR (aHF, 0 °C): δ −0.7 (m). ^{19}F NMR (aHF, 0 °C): δ −78.9 (t, $^4J(F^5, F^3)$ = 13 Hz, 3F, F^5), −100.2 (m, 2F, F^3), −105.7 (m, 2F, F^1), −116.0 (m, 2F, F^4), −143.0 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3).

[K·18-crown-6][$C_3F_7CBr_2$–CF_2BF_3]. ^{1}H NMR (CD_3CN): δ 3.57 (s, 24H, $C_{12}H_{24}O_6$). ^{11}B NMR (CD_3CN): δ −0.7 (tq, ^2J(B, F^1) = 20 Hz, ^1J(B, F) = 41 Hz). ^{19}F NMR (CD_3CN): δ −80.1 (t, $^4J(F^5, F^3)$ = 13 Hz, 3F, F^5), −101.0 (m, 2F, F^3), −106.2 (m, 2F, F^1), −117.5 (m, 2F, F^4), −146.8 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3).

Anal. Calcd for $C_{17}H_{24}BBr_2F_{12}KO_6$ (762.07): C, 26.79; H, 3.17. Found: C, 27.5; H, 3.7.

4.5. Reaction of K[trans-$CF_3CF{=}CFBF_3$] with bromine in aHF

Bromine (0.12 mL, 2.25 mmol) was added to a cold (−20 °C) solution of K[*trans*-$CF_3CF{=}CFBF_3$] (512 mg, 2.15 mmol) in aHF (2 mL) and the red emulsion was stirred at ~20 °C for 1 h till

discoloration. The volatiles were removed under reduced pressure and the white solid was dissolved in water (1.5 mL). The solution was neutralized with solid K_2CO_3, evaporated to dryness and the residue was extracted with acetone (10 mL). The extract was dried with $MgSO_4$ and the solvent was evaporated to give the white solid $K[CF_3CFBr–CF_2BF_3]$ (655 mg, 1.94 mmol, 90%).

$K[CF_3CFBr–CF_2BF_3]$. ^{11}B NMR (CD_3CN): δ −0.7 (qt, ^1J(B, F) = 41 Hz, ^2J(B, F^1) = 21 Hz). ^{19}F NMR (CD_3CN): δ −74.6 (m, 3F, F^3), −118.6 (qdq (1:1:1:1), $^4J(F^{1A}, F^3)$ = 9 Hz, $^2J(F^{1A}, F^{1B})$ = 322 Hz, $^2J(F^{1A}$, B) = 22 Hz, 1F, F^{1A}), −121.0 (m, 1F, F^{1B}), −136.8 (m, 1F, F^2), −150.3 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3).

IR (KBr): 1621br w, 1297m, 1236s, 1213s, 1194s, 1168s, 1081s, 1028s, 976m, 935m, 910m, 858w, 822m, 786m, 733m, 715w, 649m, 605w, 548w cm^{-1}.

Anal. Calcd for C_3BBrF_9K (336.83): C, 10.70; Br, 23.72; F, 50.76. Found: C, 10.8; Br, 23.7; F, 50.6.

4.6. Reaction of $K[CF_3C{\equiv}CBF_3]$ with bromine in aHF

$K[CF_3C{\equiv}CBF_3]$ (300 mg, 1.5 mmol) was dissolved in aHF (3 mL) at 0 °C and bromine (0.116 mL, 2.2 mmol) was added drop-wise at ∼0 °C. After stirring at ∼20 °C for 3 h salt $K[CF_3C{\equiv}CBF_3]$ was consumed and the borates $K[CF_3CBr{=}CBrBF_3]$ (*cis*:*trans* = 94:6) and $K[BF_4]$ (60:40) were formed besides minor amounts of unknown products. The borates $K[CF_3CBr_2–CF_2BF_3]$, $K[CF_3CBr{=}CFBF_3]$, and $K[CF_3CFBr–CF_2BF_3]$ were not found (^{11}B, ^{19}F NMR). All volatiles were removed under reduced pressure. The residue was washed with CH_2Cl_2 and extracted with MeCN. The extract was evaporated to dryness to yield $K[CF_3CBr{=}CBrBF_3]$ (200 mg, 0.56 mmol, 37%) (*cis*:*trans* = 94:6). The solid product was stirred with 18-crown-6 (160 mg, 0.61 mmol) in CH_2Cl_2 (1 mL) for 1 h, filtered and the solvent was evaporated from the mother liquor at ∼20 °C overnight. The solid residue was washed with pentane (5× 1 mL) and ether (5× 1 mL) and dried in a vacuum desiccator over Sicapent® to give [K·18-crown-6][$CF_3CBr{=}CBrBF_3$] (300 mg, 0.48 mmol, 86% based on $K[CF_3CBr{=}CBrBF_3]$).

$K[CF_3CBr{=}CBrBF_3]$. ^{11}B NMR (aHF, 0 °C): δ 0.6 (br s). ^{11}B NMR (CH_3CN): δ 0.2 (q, ^1J(B, F) = 38 Hz) (*cis*-isomer); −0.1 (q, ^1J(B, F) = 38 Hz) (*trans*-isomer). $^{13}C\{^{19}F$ selective decoupling of $BF_3\}$ NMR (CD_3CN): δ 154.1 (q (1:1:1:1), ^1J(C-1, B) = 86 Hz, C-1), 121.8 (q, ^1J(C-3, F^3) = 271 Hz, C-3), 115.7 (q, ^2J(C-2, F^3) = 27 Hz, C-2). ^{19}F NMR (aHF, 0 °C): δ −56.2 (s, 3F, F^3), −132 (br s, 3F, BF_3) (*cis*-isomer); −56.6 (s, 3F, F^3), −132 (br s, 3F, BF_3) (*trans*-isomer). ^{19}F NMR (CH_3CN): δ −56.9 (q, $^5J(F^3, BF_3)$ = 11 Hz, 3F, F^3), −136.1 (qq (1:1:1:1), $^5J(BF_3, F^3)$ = 11 Hz, ^1J(F, B) = 38 Hz, 3F, BF_3) (*cis*-isomer); −57.1 (q, $^5J(F^3, BF_3)$ = 1 Hz, 3F, F^3), −138.8 (q (1:1:1:1), ^1J(F, B) = 39 Hz, 3F, BF_3) (*trans*-isomer).

[K·18-crown-6][$CF_3CBr{=}CBrBF_3$]. Anal. Calcd for $C_{15}H_{24}BBr_2F_6KO_6$ (624.06): C, 28.87; H, 3.88. Found: C, 29.0; H, 4.1.

4.7. Reactions of $K[RCF{=}CFBF_3]$ (R = F, *trans*-CF_3, and C_4F_9) and $K[CF_3C{\equiv}CBF_3]$ with fluorine

A 11.7-mm i.d. PFA trap equipped with a Teflon-coated magnetic stir bar was charged with KF (10–15 M excess) in the glove box before a solution of $K[R_FBF_3]$ in MeCN was added. The suspension was stirred at ∼0 °C under an atmosphere of dry argon. Fluorine in nitrogen (5% v/v) (5–10 M excess) was bubbled slowly through the suspension using a FEP tube (0.7 mm i.d.). Residual fluorine was removed by flushing with nitrogen at ∼0 °C over a period of 0.5 h. The suspension was filtered. The filtrate was evaporated under reduced pressure to yield potassium perfluoroalkyltrifluoroborate (Table 1). The solid residue of the filtration consisted of $K[BF_4]$, KF, and $K[HF_2]$ (^{19}F NMR, aqueous solution).

4.8. Reactions of fluorinated alkenyltrifluoroborates with chlorine

4.8.1. Reaction of $K[trans\text{-}C_4H_9CF{=}CFBF_3]$ in MeCN

When chlorine (2.5 mmol) in argon was bubbled through the stirred solution of $K[trans\text{-}C_4H_9CF{=}CFBF_3]$ (231 mg, 1.02 mmol) in MeCN (3.5 mL) at ∼20 °C for 1 h a white suspension was formed. The suspension was centrifuged. A probe of the mother liquor showed resonances of *trans*-$C_4H_9CF{=}CFCl$ (0.43 mmol), $C_4H_9CFCl–CFCl_2$ (0.03 mmol), and $K[C_4H_9CFCl–CFClBF_3]$ (0.04 mmol). In order to isolate $K[C_4H_9CFCl–CFClBF_3]$, the reaction mixtures from repeated experiments were combined, the volatiles were removed under reduced pressure. The residue was washed with CCl_4 and dried in vacuum to give $K[C_4H_9CFCl–CFClBF_3]$.

$K[C_4H_9CFCl–CFClBF_3]$. ^1H NMR (CD_3CN): δ 2.1 (m, CH_2), 1.41 (m, CH_2), 1.26 (m, CH_2), 0.81 (t, $^3J(H^6, H^5)$ = 7 Hz, CH_3). ^{11}B NMR (CD_3CN): δ 0.4 (dq, ^2J(B, F^1) = 17 Hz, ^1J(B, F) = 41 Hz). ^{19}F NMR (CD_3CN): δ −109.7 (m, 1F, F^2), −136.8, −137.9, and −138.3 (m, 1F, F^1), −146.9 (q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3) (relative intensities 100:86:12:12:300 (≥3 diastereomeres).

4.8.2. Reaction of $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ in MeCN

A solution of $[Bu_4N][trans\text{-}C_4H_9CF{=}CFBF_3]$ (399 mg, 0.93 mmol) in MeCN (5 mL) was cooled to ∼0 °C under an atmosphere of dry argon. Chlorine (1.2 mmol) in argon was bubbled during 15 min through the stirred solution and a white suspension was formed. Residual chlorine was removed by bubbling of argon during 45 min at ∼0 °C. The suspension was stirred at ∼20 °C for additional 10 min and then centrifuged. The colorless mother liquor contained *trans*-$C_4H_9CF{=}CFCl$ (major product), $[Bu_4N][BF_4]$, and $[Bu_4N][C_4H_9CFCl–CFClBF_3]$ (resonances at −110 (m, 1F, F^2), −137 (m, 1F, F^1), and −147 (q (1:1:1:1), ^1J(F, B) = 39 Hz, 3F, BF_3) ppm (^{19}F NMR) (minor). The volatiles were distilled off. The residue was suspended in benzene (2 mL) and the volatiles were distilled off again. The combined distillates were washed with water (3× 10 mL) and dried with $MgSO_4$. NMR spectroscopy showed resonances of *trans*-$C_4H_9CF{=}CFCl$ (0.71 mmol, 76% yield), besides traces of *cis*-$C_4H_9CF{=}CFCl$ and *trans*-$C_3H_7CHClCF{=}CFCl$.

cis-$C_4H_9CF{=}CFCl$. ^{19}F NMR (benzene): δ −110.2 (d, $^3J(F^1, F^2)$ = 12 Hz, 1F, F^1), −133.1 (td, $^3J(F^2, H^3)$ = 23 Hz, $^3J(F^2, F^1)$ = 12 Hz, 1F, F^2).

trans-$C_4H_9CF{=}CFCl$. ^{19}F NMR (benzene): δ −127.6 (td, $^4J(F^1, H^3)$ = 5 Hz, $^3J(F^1, F^2)$ = 128 Hz, 1F, F^1), −143.9 (td, $^3J(F^2, H^3)$ = 22 Hz, $^3J(F^2, F^1)$ = 128 Hz, 1F, F^2).

$C_4H_9CF{=}CFCl$. ^1H NMR (benzene): δ 2.12 (tdd, $^3J(H^3, H^4)$ = 7 Hz, $^4J(H^3, F^1)$ = 5 Hz, $^3J(H^3, F^2)$ = 22 Hz, 2H, H^3), 1.31 (m, CH_2), 1.16 (m, CH_2), 0.81 (t, $^3J(H^4, H^3)$ = 7 Hz, 3H, H^4) (both *cis* and *trans* isomers). HRMS (EI) Calcd for $C_6H_9ClF_2$: 154.035536 (^{35}Cl). Found: 154.0356 (^{35}Cl).

Table 1
Reaction with elemental fluorine in MeCN.

Starting salt (mmol)	F_2 (mmol)	MeCN (mL)	KF (mg/mmol)	Product (% yield)
$K[CF_2{=}CFBF_3]$ (0.51)	4.8	6	480/8.3	$K[C_2F_5BF_3]$ (22)
$K[trans\text{-}CF_3CF{=}CFBF_3]$ (0.35)	3.5	4	330/5.7	$K[C_3F_7BF_3]$ (29)
$K[trans\text{-}C_4F_9CF{=}CFBF_3]$ (0.26)	2.6	3	240/4.1	$K[C_6F_{13}BF_3]$ (25)
$K[CF_3C{\equiv}CBF_3]$ (0.50)	2.5	3	580/10	$K[C_3F_7BF_3]$ (16)

trans-$C_3H_7CHClCF{=}CFCl$. ^{19}F NMR (benzene): δ −119.1 (dd, $^4J(F^1, H^3)$ = 3 Hz, $^3J(F^1, F^2)$ = 128 Hz, 1F, F^1), −157.0 (dd, $^3J(F^2, H^3)$ = 27 Hz, $^3J(F^2, F^1)$ = 128 Hz, 1F, F^2).

4.8.3. Reaction of K[*trans*-$C_4H_9CF{=}CFBF_3$] in sulfolane

Chlorine (2.5 mmol) in argon was bubbled through the stirred solution of K[*trans*-$C_4H_9CF{=}CFBF_3$] (226 mg, 1.0 mmol) in sulfolane (2 mL) at ~20 °C for 2 h to form a white suspension. The suspension was diluted with acetone (1 mL) and centrifuged. A probe of the mother liquor showed resonances of $C_4H_9CFCl{-}CFCl_2$ (0.16 mmol), *trans*-$C_3H_7CHClCF{=}CFCl$ (0.14 mmol), $C_4H_9CFCl{-}CFClH$ (0.10 mmol), and K[$C_4H_9CFCl{-}CFClBF_3$] (0.25 mmol) (^{19}F NMR).

K[$C_4H_9CFCl{-}CFClBF_3$]. ^{19}F NMR (sulfolane + acetone): δ −110.2 (m, 1F, F^2), −137.5 (m, 1F, F^1), −148.3 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3) (diastereomer A); −111.3 (m, 1F, F^2), −138.6 (m, 1F, F^1), −148.3 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 3F, BF_3) (diastereomer B) (ratio A:B = 83:17).

$C_4H_9CFCl{-}CFCl_2$. ^{19}F NMR (sulfolane + acetone): δ −66.5 (d, $^3J(F^1, F^2)$ = 16 Hz, 1F, F^1), −114.6 (ddd, $^3J(F^2, H^{3A})$ = 9 Hz, $^3J(F^2, H^{3B})$ = 31 Hz, $^3J(F^2, F^1)$ = 16 Hz, 1F, F^2).

$C_3H_7CHClCFCl{-}CFClH$. ^{19}F NMR (sulfolane + acetone): δ −125.7 (ddd $^3J(F^2, H^1)$ = 8 Hz, $^3J(F^2, H^3)$ = 18 Hz, $^3J(F^2, F^1)$ = 20 Hz, 1F, F^2), −145.4 (dd, $^2J(F^1, H^1)$ = 47 Hz, $^3J(F^1, F^2)$ = 20 Hz, 1F, F^1) (diastereomer A); δ −124.6 (m, 1F, F^2), −147.3 (dd, $^2J(F^1, H^1)$ = 47 Hz, $^3J(F^1, F^2)$ = 19 Hz, 1F, F^1) (diastereomer B) (ratio A:B = 60:40).

4.8.4. Reaction of K[*trans*-$C_4H_9CF{=}CFBF_3$] in MeOH

A solution of K[*trans*-$C_4H_9CF{=}CFBF_3$] (156 mg, 0.69 mmol) in MeOH (4 mL) was cooled to ~0 °C under an atmosphere of dry argon. Chlorine (1.0 mmol) in argon was bubbled through the stirred solution for 15 min and formed a white suspension. Residual chlorine was removed by flushing with argon for 45 min at ~0 °C. The suspension was stirred at ~20 °C for additional 10 min and centrifuged. A probe of the mother liquor showed resonances of *trans*-$C_4H_9CF{=}CFCl$ (0.43 mmol), $C_4H_9CFCl{-}CFCl_2$ (0.10 mmol), and *trans*-$C_3H_7CHClCF{=}CFCl$ (0.04 mmol) (^{19}F NMR). The resonances of [*trans*-$C_4H_9CF{=}CFBF_3]^-$, *cis*-$C_4H_9CF{=}CFCl$, $C_4H_9CF{=}CFH$, and [$C_4H_9CFCl{-}CFClBF_3]^-$ were not detected.

4.8.5. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] in MeOH

Chlorine (2 mmol) diluted by argon was bubbled through a stirred solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (186 mg, 0.48 mmol) in MeOH (3 mL) for 1 h. A small amount of white precipitate was formed. A probe of the mother liquor showed resonances of HF, K[$C_4F_9CFCl{-}C(O)BF_3$] (0.41 mmol), and K[$C_4F_9CFCl{-}CFClBF_3$] (0.03 mmol) besides minor quantities of unknown products. The reaction mixture was neutralized with KF (in excess), centrifuged and the mother liquor was evaporated to dryness under reduced pressure. The residue was extracted with MeCN (4 mL). The solvent was removed and the residue was dried in vacuum (~20 °C at 133 hPa) to yield a white semi-solid (190 mg) which consisted of K[$C_4F_9CFCl{-}C(O)BF_3$], K[$C_4F_9CFCl{-}CFClBF_3$], and K[$C_4F_9CFCl{-}C(O)BF_2OMe$] (molar ratio 82:7:11). The semi-solid was dissolved in CD_3OD and stored at ~20 °C. The ^{19}F and ^{11}B NMR spectra showed the signals of HF (−155 ppm) and of the transformation products of K[$C_4F_9CFCl{-}C(O)BF_3$] to K[$C_4F_9CFCl{-}C(O)BF_n(OCD_3)_{3-n}$] {principal NMR signals: δ(F) −132.2 (t, $^4J(F^2, F^4)$ = 18 Hz, 1F, F^2), −152.9 (br q (1:1:1:1), 1F, $BF(OCD_3)_2$), −137.2 (m, 1F, F^2), −149.3 (q (1:1:1:1), $^1J(F, B)$ = 40 Hz, 2F, $BF_2(OCD_3)$); δ(B) 0.3 ($BF(OCD_3)_2$, overlapping with the signal of [$C_4F_9CFCl{-}CFClBF_3]^-$), −1.2 (t, $^1J(B, F)$ = 48 Hz, $BF_2(OCD_3)$]}, K[$C_4F_9CFCl{-}C(O)B(OCD_3)_3$] {principal NMR signals: δ(F) −131.0 (t, $^4J(F^2, F^4)$ = 18 Hz, 1F, F^2); δ(B) 5.8 (s, $B(OCD_3)_3$)}, and probably $C_4F_9CFCl{-}C(O)B(OCD_3)_2$ {principal NMR signals: δ(F) −129.0 (t, $^4J(F^2, F^4)$ = 18 Hz, 1F, F^2); δ(B) 18.7 (s, $B(OCD_3)_2$)}. The molar ratio K[$C_4F_9CFCl{-}C(O)BF_3$]:K[$C_4F_9CFCl{-}C(O)BF_2(OCD_3)$]:K[$C_4F_9CFCl{-}C(O)BF(OCD_3)_2$]:K[$C_4F_9CFCl{-}C(O)B(OCD_3)_3$]:$C_4F_9CFCl{-}C(O)B(OCD_3)_2$ was 37:24:9:13:17 (~20 °C, 2 d) and 22:3:19:25:31 (~20 °C, 7 d). The solution of the transformation products was evaporated. The residue was dissolved in 33% aq HF (0.7 mL) and stirred at ~20 °C for 4 h. KF was added in excess and the slurry was extracted with MeCN (4 mL). The extract was dried with KF and the solvent was removed under reduced pressure to yield a low-melting solid (146 mg) which consisted of K[$C_4F_9CFCl{-}C(O)BF_3$] and K[$C_4F_9CFCl{-}CFClBF_3$] (molar ratio 90:10) (^{19}F, ^{11}B NMR).

K[$C_4F_9CFCl{-}C(O)BF_3$]. ^{11}B NMR (CD_3OD): δ −2.0 (q, $^1J(B, F)$ = 43 Hz). ^{13}C NMR (CD_3OD): δ 224.1 (md, ^2J(C-1, F^2) = 33 Hz, C-1), 118.7 (td, ^2J(C-6, F^5) = 33 Hz, ^1J(C-6, F^6) = 287 Hz, C-6), 113.6 (mt, $^1J(C, F)$ = 268 Hz, CF_2), 112.2 (mt, $^1J(C, F)$ = 270 Hz, CF_2), 110.1 (mt, $^1J(C, F)$ = 270 Hz, CF_2), 104.8 (md, ^1J(C-2, F^2) = 265 Hz, C-2). ^{19}F NMR (CD_3OD): δ −80.1 (tt, $^3J(F^6, F^5)$ = 2 Hz, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6), −114.1 (md, $^2J(F^{3A}, F^{3B})$ = 289 Hz, 1F, F^{3A}), −115.0 (md, $^2J(F^{3B}, F^{3A})$ = 289 Hz, 1F, F^{3B}), −117.7 (md, $^2J(F^{4A}, F^{4B})$ = 300 Hz, 1F, F^{4A}), −119.0 (dqddd, $^3J(F^{4B}, F^{5B})$ = 7 Hz, $^4J(F^{4B}, F^6)$ = 10 Hz, $^3J(F^{4B}, F^{5A})$ = 13 Hz, $^3J(F^{4B}, F^{3A})$ = 19 Hz, $^2J(F^{4B}, F^{4A})$ = 300 Hz, 1F, F^{4B}), −124.9 (dddd, $^3J(F^{5A}, F^{4B})$ = 6 Hz, $^3J(F^{5A}, F^{4A})$ = 13 Hz, $^4J(F^{5A}, F^{3B})$ = 18 Hz, $^2J(F^{5A}, F^{5B})$ = 296 Hz, 1F, F^{5A}), −125.4 (dddd, $^3J(F^{5B}, F^{4B})$ = 6 Hz, $^3J(F^{5B}, F^{4A})$ = 14 Hz, $^4J(F^{5B}, F^{3A})$ = 17 Hz, $^2J(F^{5B}, F^{5A})$ = 296 Hz, 1F, F^{5B}), −136.6 (m, 1F, F^2), −146.6 (q (1:1:1:1), $^1J(F, B)$ = 44 Hz, 3F, BF_3) (the assignments $^3J(F^{4B}, F^{3A})$, $^4J(F^{5A}, F^{3B})$ and $^4J(F^{5B}, F^{3A})$ are tentitive). The ^{19}F NMR spectrum of K[$C_4F_9CFCl{-}C(O)BF_3$] in CD_3CN coincided with the one in CD_3OD.

K[$C_4F_9CFCl{-}C(O)BF_2OMe$]. ^{13}C NMR (CD_3OD): δ 220.6 (m, C-1), 118.6 (td, ^2J(C-6, F^5) = 33 Hz, ^1J(C-6, F^6) = 287 Hz, C-6), 113.4 (mt, $^1J(C, F)$ = 268 Hz, CF_2), 112.6 (mt, $^1J(C, F)$ = 270 Hz, CF_2), 110.8 (mt, $^1J(C, F)$ = 270 Hz, CF_2), 104.8 (md, ^1J(C-2, F^2) = 265 Hz, C-2).

4.8.6. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] in sulfolane

Chlorine (3 mmol) diluted with argon was bubbled through a stirred solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (248 mg, 0.64 mmol) in sulfolane (3 mL) for 1 h. The colorless solution was poured into water (20 mL) and the precipitate was filtered off and washed with water (3× 1 mL). After drying on air and in a vacuum desiccator over Sicapent® a white powder of K[$C_4F_9CFCl{-}CFXBF_3$] (244 mg) was obtained. The dissolution in MeOH led to its conversion into K[$C_4F_9CFCl{-}C(O)BF_3$] and HF (42% conversion after 4 h and 100% conversion after 24 h).

K[$C_4F_9CFCl{-}CFXBF_3$]. ^1H NMR (DMSO-d_6): δ 4.48 (m, CH_2), 3.63 (m, CH_2), 2.66 (m, CH_2), 2.47 (m, CH_2). ^{19}F NMR (sulfolane): δ −80.3 (t, $^4J(F^6, F^4)$ = 9 Hz, 3F, F^6), −113.3 (md, $^2J(F^{3A}, F^{3B})$ = 293 Hz, 1F, F^{3A}), −115.0 (md, $^2J(F^{3B}, F^{3A})$ = 293 Hz, 1F, F^{3B}), −118.4 (md, $^2J(F^{4A}, F^{4B})$ = 301 Hz, 1F, F^{4A}), −120.1 (md, $^2J(F^{4B}, F^{4A})$ = 301 Hz, 1F, F^{4B}), −121.5 (m, 1F, F^1), −125.5 (t, $^4J(F^5, F^3)$ = 15 Hz, 2F, F^5), −135.3 (m, 1F, F^2), −146.3 (broadened q, 3F, BF_3) (diastereomer A); −80.3 (t, $^4J(F^6, F^4)$ = 9 Hz, 3F, F^6), −114.2 (m, 2F, F^3), −117.8 (md, $^2J(F^{4A}, F^{4B})$ = 300 Hz, 1F, F^{4A}), −120.3 (md, $^2J(F^{4B}, F^{4A})$ = 300 Hz, 1F, F^{4B}), −119.8 (m, 1F, F^1), −125.5 (t, $^4J(F^5, F^3)$ = 15 Hz, 2F, F^5), −133.1 (m, 1F, F^2), −145.8 (broadened q, 3F, BF_3) (diastereomer B) (ratio A:B = 82:18). The ^{19}F NMR spectrum in DMSO-d_6 coincided with the above reported spectrum.

4.8.7. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] in acetonitrile

Chlorine (2.5 mmol) diluted in argon was bubbled through a stirred solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (200 mg, 0.52 mmol) in MeCN (3 mL) for 3 h. The suspension was centrifuged, the precipitate was washed with CH_2Cl_2 and dried to yield a white solid (45 mg), which consisted of KCl (tested with aqueous $AgNO_3$) and K[BF_4] (IR spectrum). The mother liquor was evaporated to dryness and the residue (150 mg) was extracted with CH_2Cl_2. The extract was combined with the dichloromethane washing and evaporated under reduced pressure to yield a yellow oil (93 mg). The ^{19}F NMR spectrum (in CH_2Cl_2) showed signals at −81.2 (t, $^4J(F^6,$

F^4) = 10 Hz, 3F, F^6) and −81.3 (t, $^4J(F^6, F^4)$ = 10 Hz, 3F, F^6), −126.6 (m, 2F, F^5) ppm and several AB-systems at −105 to −121 ($^2J(F^A, F^B)$ = 280–300 Hz) ppm, which belonged at least to two polyfluoroalkanes in the molar ratio 4:1. Signals of the BF_3 groups (expected: q (1:1:1:1) at −140 to −150 ppm), terminal $CFCl_2$ groups (expected: −60 to −65 ppm), or CFClH groups (expected: d, ^2J(F, H) = 45–50 Hz at −130 to −150 ppm) were not detected.

After extraction the residue was dried in vacuum (~20 °C at 133 hPa) to give a semi-solid (54 mg). The ^{19}F NMR spectrum showed resonances of K[*trans*-$C_4F_9CF{=}CFBF_3$] (trace) and K[$C_4F_9CFCl–CFYBF_3$]. Dissolution of this mixture in MeOH was accompanied by the conversion to K[$C_4F_9CFCl–C(O)BF_3$] and HF (~20 °C, 2 d) (^{19}F NMR).

K[$C_4F_9CFCl–CFYBF_3$]. ^{19}F NMR (CH_3CN): δ −80.0 (t, $^4J(F^6, F^4)$ = 9 Hz, 3F, F^6), −114.6 (m, 2F, F^3), −118.1 (md, $^2J(F^{4A}, F^{4B})$ = 300 Hz, 1F, F^{4A}), −119.3 (md, $^2J(F^{4B}, F^{4A})$ = 300 Hz, 1F, F^{4B}), −124.9 (m, 1F, F^1), −125.5 (m, 2F, F^5), −136.9 (m, 1F, F^2), −145.3 (q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3) (diastereomer A); −80.3 (t, $^4J(F^6, F^4)$ = 9 Hz, 3F, F^6), −111.5 (md, $^2J(F^{3A}, F^{3B})$ = 283 Hz, 1F, F^{3A}), −113.5 (md, $^2J(F^{3B}, F^{3A})$ = 283 Hz, 1F, F^{3B}), −117.3 (md, $^2J(F^{4A}, F^{4B})$ = 285 Hz, 1F, F^{4A}), −120.0 (md, $^2J(F^{4B}, F^{4A})$ = 285 Hz, 1F, F^{4B}), −123.7 (m, 1F, F^1), −125.3 (m, 2F, F^5), −135.2 (m, 1F, F^2), −148.3 (q (1:1:1:1), ^1J(F, B) = 38 Hz, 3F, BF_3) (diastereomer B) (ratio A:B = 83:17).

4.9. Reactions of fluorinated alkenyl- and alkynyltrifluoroborates with bromine

4.9.1. Reaction of K[*trans*-$C_6H_5CF{=}CFBF_3$] in MeCN

Bromine (71 mg, 0.44 mmol) in MeCN (0.3 mL) was added to a stirred suspension of K[*trans*-$C_6H_5CF{=}CFBF_3$] (82 mg, 0.33 mmol) in MeCN (3 mL) at ~20 °C. The suspension was stirred for 13 h and filtered. After concentration under reduced pressure the filtrate contained *trans*-$C_6H_5CF{=}CFBr$ (0.28 mmol), *threo*-$C_6H_5CFBr–CFBrH$ (0.03 mmol), and $BF_3{\cdot}NCCH_3$ (0.06 mmol) (^{19}F NMR).

trans-$C_6H_5CF{=}CFBr$. ^{19}F NMR (CH_3CN): δ −116.7 (d, $^3J(F^2, F^1)$ = 133 Hz, 1F, F^2), −140.5 (d, $^3J(F^1, F^2)$ = 133 Hz, 1F, F^1). {lit. δ −117.3 (d, $^3J(F^2, F^1)$ = 133.5 Hz, 1F, F^2), −142.5 (d, $^3J(F^1, F^2)$ = 133.4 Hz, 1F, F^1) [25]}.

threo-1,2-Dibromo-1,2-difluoro-2-phenylethane, $C_6H_5CFBr–CFBrH$. ^{19}F NMR (CH_3CN): δ −118.2 (dd, $^3J(F^2, F^1)$ = 30 Hz, $^3J(F^2, H^1)$ = 9 Hz, 1F, F^2), −139.8 (dd, $^3J(F^1, F^2)$ = 30 Hz, $^2J(F^1, H^1)$ = 46 Hz, 1F, F^1). {lit. ^{19}F NMR ($CDCl_3$): δ −118.3 (dd, $^3J(F^2, F^1)$ = 33 Hz, $^3J(F^2, H^1)$ = 3 Hz, 1F, F^2), −140.8 (dd, $^3J(F^1, F^2)$ = 35.7 Hz, $^2J(F^1, H^1)$ = 46.7 Hz, 1F, F^1) [17]}.

4.9.2. Reaction of K[*trans*-$C_4H_9CF{=}CFBF_3$] in MeCN

Bromine (113 mg, 0.70 mmol) in MeCN (0.4 mL) was added to a stirred solution of K[*trans*-$C_4H_9CF{=}CFBF_3$] (119 mg, 0.53 mmol) at ~20 °C. Discoloration occurred within ~1 min and a suspension was formed. Stirring was continued for 1 h before the mother liquor was decanted. It contained *trans*-$C_4H_9CF{=}CFBr$ (0.38 mmol), *trans*-$C_4H_9CF{=}CFH$ (0.05 mmol), and $BF_3{\cdot}NCCH_3$ (0.40 mmol) (^{19}F NMR). The precipitate was washed with CH_2Cl_2 (3 mL) and dried to give KBr (58 mg, 0.49 mmol) (determined by titration of an aqueous solution with 0.1 N $AgNO_3$).

trans-$C_4H_9CF{=}CFBr$. ^{19}F NMR (CH_3CN): δ −126.0 (td, $^4J(F^1, H^3)$ = 5 Hz, $^3J(F^1, F^2)$ = 133 Hz, 1F, F^1), −138.0 (td, $^3J(F^2, H^3)$ = 23 Hz, $^3J(F^2, F^1)$ = 133 Hz, 1F, F^2) {lit. ^{19}F NMR ($CDCl_3$ + CCl_4): δ −127.3 (td, $^3J(F^1, H^3)$ = 5 Hz, $^3J(F^1, F^2)$ = 134 Hz, 1F, F^1), −140.0 (td, $^3J(F^2, H^3)$ = 22 Hz, $^3J(F^2, F^1)$ = 134 Hz, 1F, F^2) [1]).

trans-$C_4H_9CF{=}CFH$. ^{19}F NMR (CH_3CN): δ −159.7 (ttd, $^4J(F^2, H^4)$ = 1 Hz, $^3J(F^2, H^3)$ = 23 Hz, $^3J(F^2, F^1)$ = 127 Hz, 1F, F^2), −183.3 (tdd, $^4J(F^1, H^3)$ = 3 Hz, $^2J(F^1, H^1)$ = 76 Hz, $^3J(F^1, F^2)$ = 127 Hz, 1F, F^1). ^{19}F NMR ($CDCl_3$): δ −161.3 (td, $^3J(F^2, H^3)$ = 24 Hz, $^3J(F^2, F^1)$ = 127 Hz, 1F, F^2), −185.1 (tdd, $^4J(F^1, H^3)$ = 5 Hz, $^2J(F^1, H^1)$ = 77 Hz, $^3J(F^1, F^2)$ = 127 Hz, 1F, F^1) {lit. ^{1}H NMR: δ 2.35 (2H), 7.05 (H); ^2J(H, F) = 77 Hz, ^3J(H, F) = 4 Hz, ^3J(H, F) = 23 Hz, ^4J(H, F) = 5 Hz. ^{19}F NMR: δ −161.2 (F-2), −184.9 (F-1); ^3J(F, F) = 128 Hz) [26]}.

4.9.3. Reaction of K[*trans*-$C_4H_9CF{=}CFBF_3$] with Br_2 and AgF in MeCN

Silver fluoride (82 mg, 0.65 mmol) was added to a stirred solution of K[*trans*-$C_4H_9CF{=}CFBF_3$] (112 mg, 0.49 mmol) in MeCN (2.5 mL) and formed a fine suspension. Then bromine (80 mg, 0.50 mmol) in MeCN (0.5 mL) was added drop-wise within 5 min. Discoloration occurred immediately after each drop and the reaction was accompanied by a voluminous precipitation. The suspension was stirred at ~20 °C for 1 h and filtered. The mother liquor contained *trans*-$C_4H_9CF{=}CFBr$ (0.41 mmol) and *cis*-$C_4H_9CF{=}CFBr$ (0.06 mmol) (^{19}F NMR).

4.9.4. Reaction of K[*cis*-$C_2F_5CF{=}CFBF_3$] in MeCN

A solution of K[*cis*-$C_2F_5CF{=}CFBF_3$] (101 mg, 0.35 mmol) and bromine (62 mg, 0.38 mmol) in MeCN (2.3 mL) was heated in a sealed tube in a boiling water bath for 4 h. After cooling to ~20 °C the yellow mother liquor was separated from the white precipitate after centrifugation. The ^{19}F NMR spectrum showed the presence of residual K[*cis*-$C_2F_5CF{=}CFBF_3$] (0.02 mmol), *cis*-$C_2F_5CF{=}CFBr$ (0.07 mmol), *cis*-$C_2F_5CF{=}CFH$ (0.15 mmol), *trans*-$C_2F_5CF{=}CFBr$ (0.02 mmol), *trans*-$C_2F_5CF{=}CFH$ (0.05 mmol), and $BF_3{\cdot}NCCH_3$ (0.20 mmol). The precipitate was washed with ether (2× 2 mL) and dried in vacuum to yield KBr (35 mg, 0.29 mmol) which was determined by the quantitative reaction with $AgNO_3$ in water.

4.9.5. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] in MeCN

A solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (85 mg, 0.22 mmol) and bromine (40 mg, 0.25 mmol) in MeCN (2 mL) was heated in a sealed tube for 6 h at 50 °C. No reaction occurred (^{19}F NMR). When this solution was heated in a boiling water bath for 2 h, it became yellow and a white precipitate was formed. After cooling to ~20 °C, the yellow mother liquor was separated from white precipitate after centrifugation. The ^{19}F NMR spectrum showed the presence of K[$C_4F_9CF{=}CFBF_3$] (0.02 mmol) (*cis*:*trans* = 50:50), $C_4F_9CF{=}CFBr$ (0.04 mmol) (*cis*:*trans* = 25:75), $C_4F_9CF{=}CFH$ (0.12 mmol) (*cis*:*trans* = 67:33), and $BF_3{\cdot}NCCH_3$ (0.02 mmol).

4.9.6. Reaction of K[*trans*-$C_4F_9CF{=}CFBF_3$] in MeOH

A. A solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (41 mg, 0.10 mmol), bromine (19 mg, 0.12 mmol), and C_6F_6 (11 mg, 0.06 mmol) (internal integral standard) in MeOH (0.5 mL) was kept in a sealed tube at ~20 °C for 80 h. The yellow solution contained K[$C_4F_9CF{=}CFBF_3$] (0.09 mmol) (*cis*:*trans* = 58:42) (^{19}F NMR).

B. A solution of K[*trans*-$C_4F_9CF{=}CFBF_3$] (41 mg, 0.11 mmol), bromine (19 mg, 0.12 mmol), and C_6F_6 (11 mg, 0.06 mmol) (internal integral standard) in MeOH (0.5 mL) was kept at 90 °C for 1 h. The yellow solution contained K[$C_4F_9CF{=}CFBF_3$] (0.05 mmol) (*cis*:*trans* = 42:58), *trans*-$C_4F_9CF{=}CFBr$ (0.02 mmol), and *trans*-$C_2F_5CF{=}CFH$ (0.02 mmol) besides traces of *cis*-$C_4F_9CF{=}CFBr$ and *cis*-$C_4F_9CF{=}CFH$ (^{19}F NMR).

4.9.7. Reaction of K[$CF_3C{\equiv}CBF_3$] in MeCN

A solution of K[$CF_3C{\equiv}CBF_3$] (50 mg, 0.25 mmol) and bromine (48 mg, 0.30 mmol) in MeCN (0.6 mL) was heated in a sealed tube at 50 °C for 5 h and formed a white precipitate and a yellow mother liquor. The ^{19}F NMR spectrum of the latter showed resonances of $CF_3C{\equiv}CBr$ (0.03 mol), $CF_3C{\equiv}CH$ (0.02 mmol), $CF_3CBr{=}CBr_2$ (0.05 mmol) besides many resonances of weak intensity at −49 to −65 ppm. Signals of $[CF_3C{\equiv}CBF_3]^-$ and $[CF_3CBr{=}CBrBF_3]^-$ as well as signals of any $[RBF_3]^-$ anion at −130 to −160 ppm were not detected.

4.10. Attempted reaction of $K[C_6F_{13}BF_3]$ with bromine in MeCN

A solution of $K[C_6F_{13}BF_3]$ (61 mg, 0.14 mmol) and bromine (30 mg, 0.18 mmol) in MeCN (0.7 mL) was stirred at ~20 °C for 40 h. No reaction was detected (^{19}F NMR).

4.11. Reactions of alkenyl- and alkynyltrifluoroborate salts with $[Bu_4N][Br_3]$

4.11.1. Reaction of $K[C_4H_9CH{=}CHBF_3]$

$K[C_4H_9CH{=}CHBF_3]$ (118 mg, 0.62 mmol) was dissolved in aq THF (1:1, v/v) (6 mL) and $[Bu_4N][Br_3]$ (307 mg, 0.64 mmol) was added in one portion. The pale-yellow solution was stirred at ~20 °C for 30 min and diluted with ether (3 mL). The organic phase was decanted and the aqueous one was extracted with ether (5 mL). The combined ether phases were dried with $MgSO_4$ and concentrated to ~1 mL at 60–65 °C (bath). The solution contained $C_4H_9CH{=}CHBr$ (0.18 mmol, internal integral standard C_6F_5H, ^1H NMR) and $[Bu_4N]^+$ (signals were overlapped by solvent signals).

4.11.2. Reaction of $K[trans\text{-}C_4H_9CF{=}CFBF_3]$

$K[trans\text{-}C_4H_9CF{=}CFBF_3]$ (159 mg, 0.70 mmol) was reacted with $[Bu_4N][Br_3]$ (365 mg, 0.76 mmol) in aq THF (1:1, v/v) (4 mL) as described above and yielded a solution of $trans\text{-}C_4H_9CF{=}CFBr$ (0.32 mmol) and $[Bu_4N][BF_4]$ (0.70 mmol) (^{19}F NMR).

4.11.3. Reaction of $K[trans\text{-}C_4F_9CF{=}CFBF_3]$

A solution of $K[trans\text{-}C_4F_9CF{=}CFBF_3]$ (130 mg, 0.34 mmol) and $[Bu_4N][Br_3]$ (161 mg, 0.33 mmol) in aq THF (1:1, v/v) (2 mL) was stirred at ~20 °C for 24 h and formed a yellow emulsion. After separation of the phases, the ^{19}F NMR spectrum of the upper organic phase showed the presence of $K[C_4F_9CF{=}CFBF_3]$ (*cis*:*trans* = 20:80) (0.30 mmol) ($C_6H_5CF_3$ as internal integral standard).

4.11.4. Reaction of $K[CF_3C{\equiv}CBF_3]$

A solution of $K[CF_3C{\equiv}CBF_3]$ (146 mg, 0.73 mmol) and $[Bu_4N][Br_3]$ (366 mg, 0.76 mmol) in aq THF (1:1, v/v) (4 mL) was stirred at ~20 °C for 6 h and formed a yellow emulsion. After phase separation, the ^{19}F NMR spectrum of upper (organic) phase showed the quantitative recovery of $K[CF_3C{\equiv}CBF_3]$.

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References

[1] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, Z. Anorg. Allg. Chem., in press.
[2] M.-L. Yao, M.S. Reddy, L. Yong, I. Walfish, D.W. Blevins, G.W. Kabalka, Org. Lett. 12 (2010) 700–703.
[3] G.W. Kabalka, A.R. Mereddy, J.F. Green, J. Label. Compd. Radiopharm. 49 (2006) 11–15.
[4] G.W. Kabalka, A.R. Mereddy, Organometallics 23 (2004) 4519–4521.
[5] G.W. Kabalka, A.R. Mereddy, Tetrahedron Lett. 45 (2004) 1417–1419.
[6] G.W. Kabalka, A.R. Mereddy, J. Label. Compd. Radiopharm. 48 (2005) 359–362.
[7] N.A. Petatis, A.K. Yudin, I.A. Zavialov, G.K.S. Prakash, G.A. Olah, Synlett (1997) 606–608.
[8] (a) Partially reported: H.-J. Frohn, V.V. Bardin, 13th European Symposium on Fluorine Chemistry, Bordeaux (France), July 15–20, 2001, 1-P61;
(b) N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, 18th International Symposium on Fluorine Chemistry, Bremen (Germany), July 30–August 4, (2006), p. 300.
[9] V.V. Bardin, S.G. Idemskaya, H.-J. Frohn, Z. Anorg. Allg. Chem. 628 (2002) 883–895.
[10] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 628 (2002) 1853–1856.
[11] L.M. Yagupolskii, in: B. Baasner, H. Hagemann, J.C. Tatlow (Eds.), 4th ed., Houben–Weyl Methods of Organic Chemistry. Organo-Fluorine Compounds, vol. E10a, Thieme, Stuttgart, 2000, pp. 234–264.
[12] F.L.M. Pattison, D.A.V. Peters, F.H. Dean, Can J. Chem. 43 (1965) 1689–1699.
[13] R.E.A. Dear, J. Org. Chem. 35 (1970) 1703–1705.
[14] A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, I.N. Krotovich, A.S. Tatarinov, O.V. Verenikin, Izv. Akad. Nauk. SSSR Ser. Khim. 229 (1985) 8–2302;
A.V. Fokin, Yu.N. Studnev, A.I. Rapkin, I.N. Krotovich, A.S. Tatarinov, O.V. Verenikin, Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.) 34 (1985) 2128–2131.
[15] V.V. Bardin, H.-J. Frohn, Z. Anorg. Allg. Chem. 628 (2002) 721–722.
[16] H.-J. Frohn, M. Giesen, V.V. Bardin, J. Fluorine Chem. 131 (2010) 969–974.
[17] D.F. Shellhamer, J.L. Allen, R.D. Allen, D.C. Gleason, C. O'Neil Schlosser, B.J. Powers, J.W. Probst, M.C. Rhodes, A.J. Ryan, P.K. Titterington, G.G. Vaughan, V.L. Heasley, J. Org. Chem. 68 (2003) 3932–3937.
[18] (a) H.-J. Frohn, M.E. Hirschberg, R. Boese, D. Bläser, U. Flörke, Z. Anorg. Allg. Chem. 634 (2008) 2539–2550;
(b) W.L.F. Armarego, C. Li Lin Chai, Purification of Laboratory Chemicals, 5th ed., Elsevier, 2003.
[19] (a) F. Tellier, R. Sauvêtre, J.-F. Normant, J. Organomet. Chem. 362 (1989) 23–29;
(b) G. Brauer (Ed.), Handbuch der Präparativen Anorganischen Chemie, 3rd ed., vol. 1, F. Enke Verlag, Stuttgart, 1975, p. 289.
[20] S. Kajigaeshi, T. Kakinami, T. Okamoto, S. Fujisaki, Bull. Chem. Soc. Jpn. 60 (1987) 1159–1160.
[21] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 627 (2001) 2499–2505.
[22] H.-J. Frohn, V.V. Bardin, Z. Anorg. Allg. Chem. 629 (2003) 2465–2469.
[23] V.V. Bardin, N.Yu. Adonin, H.-J. Frohn, Organometallics 24 (2005) 5311–5317.
[24] N.Yu. Adonin, V.V. Bardin, H.-J. Frohn, Main Group Met. Chem. 32 (2009) 153–159.
[25] T. Gouyon, R. Sauvêtre, J.-F. Normant, J. Organomet. Chem. 394 (1990) 37–44.
[26] S. Martin, R. Sauvêtre, J.-F. Normant, J. Organomet. Chem. 264 (1984) 155–161.