(Fluoroorgano)fluoroboranes and -borates. 6 [1]

The Reactivity of Potassium Polyfluoroaryl-, Polyfluoroalkenyl-, and Perfluoroalkyltrifluoroborates and their Hydrocarbon Analogues towards Acids of Different Strength: A Systematic Study of the Hydrodeboration

V. V. Bardin[a], S. G. Idemskaya[a], and H.-J. Frohn[b]*

[a] Novosibirsk/Russia, N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS
[b] Duisburg, Fachgebiet Anorganische Chemie, Gerhard-Mercator-Universität

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Abstract. The hydrodeboration of the (fluoroorgano)trifluoroborates K [R_FBF_3] [R_F = C_6F_5, XCF=CF (X = F, *cis*- and *trans*-Cl, -C_3F_7O, *cis*-C_2F_5, *trans*-C_4F_9, -C_4H_9) and C_6F_{13}] and of the organotrifluoroborates K [RBF_3] (R = C_6H_5, *cis*- and *trans*-C_4H_9CH=CH, C_4H_9 and C_8H_{17}) with CH_3CO_2H (100 %), CF_3CO_2H (100 %), aqueous HF and anhydrous HF was investigated. In the alkenyltrifluoroborates K [R′CF=$CFBF_3$] the formal replacement of BF_3 by a proton occurred stereospecifically under retention of the configuration. The ^{19}F NMR spectra of K [R_FBF_3] in acids indicate strong interactions of the BF_3 group with protons or acid molecules.

Keywords: Borates; Fluoroborates; Hydrodeboration; NMR spectroscopy

(Fluororgano)fluorborane und -fluoroborate. 6 [1] Die Reaktivität von Kaliumpolyfluoraryl-, polyfluoralkenyl- und perfluoralkyltrifluoroboraten und deren Kohlenwasserstoff Analoga gegenüber Säuren unterschiedlicher Stärke: Eine systematische Studie zur Hydrodeborierung

Inhaltsübersicht. Die Hydrodeborierung der (Fluororgano)trifluoroborate K [R_FBF_3] [R_F = C_6F_5, XCF=CF (X = F, *cis*- and *trans*-Cl, -C_3F_7O, *cis*-C_2F_5, *trans*-C_4F_9, -C_4H_9) und C_6F_{13}] und der Organotrifluoroborate K [RBF_3] (R = C_6H_5, *cis*- und *trans*-C_4H_9CH=CH, C_4H_9 und C_8H_{17}) mit CH_3CO_2H (100 %), CF_3CO_2H (100 %), wässeriger HF und wasserfreier HF wurde untersucht. In den Alkenyltrifluoroboratsalzen K [R′CF=$CFBF_3$] erfolgte formal die stereospezifische Substitution von BF_3 durch ein Proton. Die ^{19}F-NMR Spektren der Lösungen von K [R_FBF_3] Salzen in Säuren weisen auf starke Wechselwirkungen der BF_3-Gruppe mit Protonen oder Säuremolekülen hin.

Introduction

Recently we have elaborated simple and convenient preparative approaches to the new classes of organoboron compounds: the potassium salts of polyfluoroaryl-, polyfluoroalk-1-enyl- and perfluoroalkyltrifluoroborates [2−4] and the polyfluorinated aryl-, alk-1-enyl and alkyldifluoroboranes [2, 3, 5]. The latter were obtained from the corresponding salts K [R_FBF_3] by fluoride abstraction using Lewis acids (BF_3, AsF_5) as fluoride acceptors. The synthesis and some reactivities of their non-fluorinated analogues are well known [6−9]. It should be expected that the replacement of the hydrocarbon group R in organotrifluoroborates M [RBF_3] or in organodifluoroboranes RBF_2 by the highly electron-withdrawing poly- or perfluoroorgano group R_F will result in significant changes of the reactivity of the borates M [R_FBF_3] and boranes R_FBF_2. These changes are caused by the highly increased Lewis acidity of the three-coordinated boron atom in R_FBF_2 and the better leaving ability of the perfluorocarbanion $[R_F]^-$ in $[R_FBF_3]^-$ compared with the hydrocarbon analogues. This unique property of fluorinated aryl- and alkenyldifluoroboranes can be used for synthetic applications, e.g. the introduction of fluoroorgano groups into XeF_2 should be mentioned which is based on the interaction of the electrophilic boron centre with the highly nucleophilic fluorine atom in XeF_2 [10].

The σ-electron-withdrawing effect of the R_F groups requires an appropriate Brønsted acidic medium for the preparation of $[R_FBF_3]^-$ salts from the corresponding (fluoroorgano)trialkoxyborates or boronic acids [2−4].

* Prof. Dr. H.-J. Frohn
Fachgebiet Anorganische Chemie der Universität
Lotharstr. 1
D-47048 Duisburg
Fax: (+49)2 03-3 79 22 31
e-mail: frohn@uni-duisburg.de

$$[R_FBX_3]^- \overset{H^+}{\rightleftharpoons} R_FBX_2 + HX$$

$$R_FBX_2 + F^- \rightleftharpoons [R_FBFX_2]^- \overset{H^+}{\rightleftharpoons} R_FBFX + HX$$

$$R_FBFX + F^- \rightleftharpoons [R_FBF_2X]^- \overset{H^+}{\rightleftharpoons} R_FBF_2 + HX$$

$$R_FBF_2 + F^- \rightleftharpoons [R_FBF_3]^-$$

X = OAlk, OH

However, in highly Brønsted acidic solutions the $[R_FBF_3]^-$ anion can undergo hydrodeboration. Therefore, we decided to start a systematic study on (polyfluoroorgano)fluoroboron derivatives and investigated the reactions of (polyfluoroaryl)-, (polyfluoroalk-1-enyl)- and (perfluoroalkyl)trifluoroborates with some selected protic acids. In addition, the hydrodeboration of potassium phenyl-, hex-1-enyl, butyl- and octyltrifluoroborates was studied and the results in the series of $[RBF_3]^-$ were compared with those of the $[R_FBF_3]^-$ salts.

Results and Discussion

Potassium *trans*-1,2-difluorohex-1-enyltrifluoroborate **1** is slightly soluble in 100 % acetic acid ($-H_0$ ca. 0 [11]) and does not react at 20 °C within 24 h. Stronger acids like HF_{aq}. (25 % HF^{aq}: $-H_0 = 0.88$; 40 % HF_{aq}: $-H_0 = 2.08$; 50 % HF_{aq}: $-H_0 = 3.84$ [11]), 100 % CF_3CO_2H ($-H_0$ 3.0 [11]), or anhydrous HF (aHF) ($-H_0$ 15 [12]) caused a fast carbon-boron bond cleavage to form *trans*-1,2-difluorohex-1-ene **2** in a quantitative yield.

$$\underset{\mathbf{1}}{K\,[trans\text{-}C_4H_9CF{=}CFBF_3]} \xrightarrow[-K\,[BF4]]{+HX} \underset{\mathbf{2}}{trans\text{-}C_4H_9CF{=}CFH}$$

HX = 27 % $HF_{aq.}$ (20 °C, 1 h), 100 % CF_3CO_2H (20 °C, 1−3 h), aHF (−20 °C, ≤1 h)

The replacement of the alkyl group at C(2) in borate **1** by the higher electron-withdrawing fluorine or chlorine atom results in a decreased rate of hydrodeboration. Potassium trifluoroethenyltrifluoroborate **3** did not react with 100 % HOAc (20 °C, 24 h), but evolved trifluoroethene **4** with the stronger acids. Monitoring by ^{19}F NMR spectroscopy showed, that the degree of conversion of salt **3** was ca. 20 % in 27 % $HF_{aq.}$ (20 °C, 26 h) and total in 100 % CF_3CO_2H (20 °C, 18 h). In aHF the complete cleavage of the C-B bond occurred at −30 °C within ≤ 3 h.

$$\underset{\mathbf{3}}{K\,[CF_2{=}CFBF_3]} \xrightarrow[-K\,[BF4]]{+HX} \underset{\mathbf{4}}{CF_2{=}CFH}$$

HX = 27 % $HF_{aq.}$ (20 °C, 26 h, 20 % conversion), 100 % CF_3CO_2H (20 °C, 18 h), aHF (−30 °C, ≤ 3 h)

The lower reactivity of borate **3** with respect to borate **1** towards hydrodeboration was confirmed by a competitive reaction with trifluoroacetic acid. After 40 minutes borate **1** was completely consumed whereas borate **3** underwent only a partial conversion into trifluoroethene.

$$\mathbf{1} + \mathbf{3}\,(1:1) \xrightarrow[20\,°C,\,40\,minutes]{+CF_3CO_2H,\,-K\,[BF4]} \mathbf{2}\,(100\,\%) + \mathbf{3} + \mathbf{4}$$

Both of the *cis*- and *trans*-isomers of potassium 2-chlorodifluoroethenyltrifluoroborate **5** are less reactive than salt **3**. The solution of salt **5** in aHF (−20 °C) displayed after 3 h still the ^{19}F resonances of the starting compound while salt **3** had already reacted under these conditions. Warming to room temperature resulted in the fast conversion of borate **5** into 2-chlorodifluoroethene **6**.

$$\underset{\mathbf{5}}{K\,[cis\text{- and }trans\text{-}ClCF{=}CFBF_3]} + aHF \xrightarrow[20\,°C]{}$$

$$\underset{\mathbf{6}}{cis\text{- and }trans\text{-}ClCF{=}CFH} + K\,[BF_4]$$

A slow hydrodeboration occurred in the solution of potassium 1,2-difluoro-2-(heptafluoropropoxy)ethenyltrifluoroborate **7** (*cis*/*trans* = 1 : 3) in 48 % $HF_{aq.}$. After 3 days at 20 °C ca. 50 % of the initial amount of borate **7** was decomposed with an equal rate of reaction for both *cis*- and *trans*-isomers. Under the action of aHF (20 °C) the borate **7** rapidly formed 1*H*-2-(heptafluoropropoxy)-1,2-difluoroethene **8** (*cis*/*trans* = 1 : 3).

Potassium perfluoro-*trans*-hex-1-enyltrifluoroborate **9** and potassium perfluoro-*cis*-but-1-enyltrifluoroborate *11* are well soluble in aHF at −50 to 20 °C. No hydrodeboration of **9** was detected at 20 °C within 3 days. However, after 30 days the partial hydrodeboration of borate **9** led to 1*H*-*trans*-undecafluorohexene-1 **10** (**9** : **10** = 2.5 : 1). The hydrodeboration of borate **11** proceeded relatively faster and after 3 days traces of 1*H*-*cis*-heptafluorobutene-1 **12** were observed in the solution.

$$\underset{\mathbf{9},\,\mathbf{11}}{K\,[R_FCF{=}CFBF_3]} + aHF \xrightarrow[20\,°C]{} \underset{\mathbf{10},\,\mathbf{12}}{R_FCF{=}CFH} + K\,[BF_4]$$

R_F = *trans*-C_4F_9 (**9, 10**) 3 days, no reaction; 30 days, 28 % conversion;
cis-C_2F_5 (**11, 12**) 3 days, ≤ 10 % conversion.

It should be emphasized that the hydrodeboration of the salts **1, 5, 7, 9** and **11** proceeds stereospecifically: the borates K [*trans*-$C_4H_9CF{=}CFBF_3$], K [*trans*-$C_4F_9CF{=}CFBF_3$] and K [*cis*-$C_2F_5CF{=}CFBF_3$] gave exclusively the alkenes *trans*-$C_4H_9CF{=}CFH$, *trans*-$C_4F_9CF{=}CFH$ and *cis*-$C_2F_5CF{=}CFH$, respectively. The *cis*/*trans* ratio of the alkenes RCF=CFH was the same as in the corresponding borates K [*cis*- and *trans*-$RCF{=}CFBF_3$] (R = Cl, C_3F_7O).

Potassium pentafluorophenyltrifluoroborate **13** is practically insoluble in 100 % CF_3CO_2H and showed no reaction at 60−70 °C (5 h). Salt **13** did not react with 40 % $HF_{aq.}$ at 20 °C within 4 days but in hot solution (85−95 °C) it underwent a slow hydrodeboration with a half of life of ca. 1 h. The total decomposition of borate **13** under those

conditions was completed within 6 h to yield pentafluorobenzene **14** and K [BF_4]. The solution of borate **13** in aHF at −40 °C displayed a graduate broadening of the ^{19}F resonance of the fluorine atoms bonded to boron and after 15−30 minutes the signal disappeared finally [3]. At 20 °C the conversion of borate **13** into C_6F_5H and K [BF_4] was completed within ≤ 18 h. It is interesting that the addition of K [HF_2] to the aHF solution („basic HF“) of **13** has no effect on the ^{19}F NMR spectrum of **13**, but it accelerated strongly the hydrodeboration.

$$\underset{\mathbf{10}}{K\,[C_6F_5BF_3]} \xrightarrow[20\,^\circ C,\ \leq 18\ h]{+\ aHF,\ -\ K\,[BF_4]} \underset{\mathbf{11}}{C_6F_5H}$$

$$\underset{\mathbf{10}}{K\,[C_6F_5BF_3]} \xrightarrow[20\,^\circ C,\ 0.5\ h]{+\ aHF\ +\ K\,[HF_2],\ -\ K\,[BF_4]} \underset{\mathbf{11}}{C_6F_5H}$$

Potassium perfluoroalkyltrifluoroborates are the most stable borates towards the hydrodeboration. No changes were found in the solution of potassium perfluorohexyltrifluoroborate **15** in aHF after 10 days at 20 °C as well as in K [HF_2]-aHF solutions (20 °C, 7 days).

$$\underset{\mathbf{15}}{K\,[C_6F_{13}BF_3]} + aHF\ \textit{or}\ K\,[HF_2]\text{-}aHF \xrightarrow[20\,^\circ C,\ 10\ \textit{or}\ 7\ days]{} \text{no reaction}$$

To complete the picture of reactivities of potassium organotrifluoroborates with protic acids, we studied the reactivity of some hydrocarbon analogues with the same protic acids.

It was found that the potassium salts of hex-1-enyltrifluoroborate **16**, phenyltrifluoroborate **17**, butyltrifluoroborate **18** and octyltrifluoroborate **19** did not react with 100 % HOAc at 20 °C. The C-B bond of **16** was cleaved completely by 27 % $HF_{aq.}$ within 1 h (20 °C) to form hex-1-ene. The hydrodeboration of K [$C_6H_5BF_3$] **17** with 27 % $HF_{aq.}$ proceeded slowly at 20 °C, whereas **17** was converted into benzene at 50 °C within 2 h. The alkylborate **19** formed octane and K [BF_4] (27 % $HF_{aq.}$, 65−70 °C) in a slow reaction (43 % conversion of **19** after 2.5 h). In aHF **19** was cleaved quantitatively within a few minutes.

$$K\,[RBF_3] + 100\,\%\ HOAc \xrightarrow{20\,^\circ C} \text{no reaction}$$

R = *cis*- and *trans*-$C_4H_9CH{=}CH$ **16** (1 h), C_6H_5 **17** (60 h), C_4H_9 **18** (3 h), C_8H_{17} **19** (3 h)

$$K\,[RBF_3] \xrightarrow{+\ 27\%\ HF_{aq.},\ -\ K\,[BF_4]} RH$$

R = *cis*- and *trans*-$C_4H_9CH{=}CH$ (20 °C, 1 h), C_6H_5 (20 °C, 48 h or 50 °C, 2 h), C_8H_{17} (65 − 70 °C, 2.5 h; 43 % conversion of **19**)

$$\underset{\mathbf{19}}{K\,[C_8H_{17}BF_3]} \xrightarrow[20\,^\circ C,\ few\ minutes]{+\ aHF,\ -\ K\,[BF_4]} C_8H_{18}$$

The higher stability of alkyltrifluoroborates with respect to aryltrifluoroborates was confirmed by a competitive reaction of an equimolar mixture of borates **17** and **18** with 27 % $HF_{aq.}$ at 70 °C. After 40 minutes salt K [$C_6H_5BF_3$] was consumed while borate K [$C_4H_9BF_3$] was still present.

These results allow to build the following sequences of reactivity of organotrifluoroborate salts towards hydrodeboration: K [*trans*-$C_4H_9CF{=}CFBF_3$] > K [*cis*- and *trans*-$C_3F_7OCF{=}CFBF_3$] ≈ K [$CF_2{=}CFBF_3$] ≥ K [*cis*- and *trans*-$ClCF{=}CFBF_3$] ≈ K [$C_6F_5BF_3$] > K [*cis*-$C_2F_5CF{=}CFBF_3$] ≥ K [*trans*-$C_4F_9CF{=}CFBF_3$] > K [$C_6F_{13}BF_3$] and K [*cis*- and *trans*-$C_4H_9CH{=}CHBF_3$] > K [$C_6H_5BF_3$] > K [$C_4H_9BF_3$] ≈ K [$C_8H_{17}BF_3$].

The comparison of the ^{19}F NMR spectra of K [RBF_3] and K [R_FBF_3] in acids and in basic solvents like MeCN, MeOH or acetone displays remarkable differences caused by the interaction of the organotrifluoroborate anion with the acid. Generally, the dissolution of K [RBF_3] and K [R_FBF_3] salts in acids leads to a deshielding of the BF_3 resonances in the ^{19}F NMR spectra. The broadening of the BF_3 signal can be moderate (for example, **1** in 100 % HOAc, $\tau_{1/2}$ 100 Hz; **9** in aHF (−30 °C), $\tau_{1/2}$ 153 Hz or **17** in 27 % $HF_{aq.}$, $\tau_{1/2}$ 302 Hz) or extreme (K [$C_4H_9BF_3$] **18** and K [$C_8H_{17}BF_3$] **19** both in 27 % $HF_{aq.}$: in both cases no BF_3 signals were observed).

The ^{19}F NMR spectral data of the K [RBF_3] and K [R_FBF_3] salts in 100 % HOAc are presented in Table 1. The fluorine atoms bonded to boron are deshielded in the series of alkenyl- and alkyltrifluoroborates when the perfluorocarbon group R_F was replaced by the hydrocarbon group R. In the series of alkenyl borates [$R'CF{=}CFBF_3$], the fluorine atoms in *cis*-position to the BF_3 group, (borates **1, 3** and **9**) are deshielded when going from MeCN to HOAc solutions and the Δδ(F) values are diminished from R′ = C_4F_9 to R′ = F and R′ = C_4H_9 (borate **7** is only very purely soluble in 100 % HOAc, therefore its ^{19}F NMR spectrum was not analysed). In contrast, the resonances of the fluorine atoms F^1 at C-1 are shifted to low frequencies and the Δδ value becomes a minimum in the case of the perfluorohexyltrifluoroborate anion. The solution of K [$C_6F_5BF_3$] in HOAc (100 %) displayed slightly deshielded Δδ(F) values of the *para*-fluorine atom and of the BF_3 group, whereas the *ortho*- and *meta*-positions were not changed.

Solutions of potassium (polyfluoroorgano)trifluoroborates in anhydrous HF, the strongest acid which we investigated, are characterized by significantly higher differences in chemical shifts with respect to those in basic solvents or in aqueous HF (Table 2). For instance, the Δδ(F) values of both vinylic fluorine atoms of the anions [$R'CF{=}CFBF_3$] (R′ = Cl, C_2F_5, C_4F_9) changed up to ±9 ppm. In the pentafluorophenyltrifluoroborate anion a large deshielding is observed for the *meta*- and especially for the *para*-fluorine atoms [3].

We explain the observed changes of ^{19}F NMR shift values in acids of different protonation ability by the protonation of the fluorine atoms bonded to boron, which bear the majority of the negative charge or as a strong donor-acceptor interaction of these fluorine atoms with an acid molecule (Scheme 1).

Path 1
In media of high acidity:

$$[RBF_3]^- + H^+ \rightleftharpoons \underset{\mathbf{A}}{[RBF_2(F\text{-}H)]} \rightleftharpoons RBF_2 + HF$$

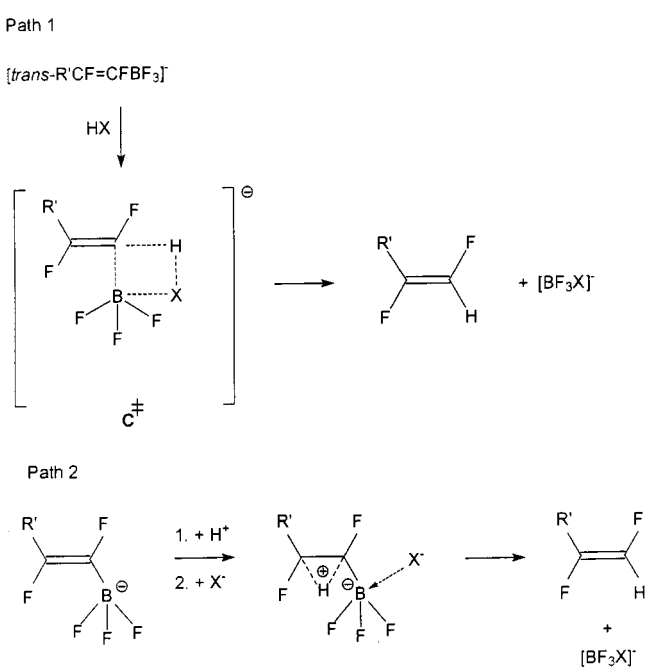
Path 2
In media of low acidity:

$$[RBF_3]^- + HX \rightleftharpoons \underset{\mathbf{B}}{[RBF_2(F\cdots H\text{-}X)]^-}$$

Scheme 1

In order to simplify the interaction of fluoroborates with acids we distinguish only two borderline cases of high and low acidity. In a highly protonating medium (path 1) the organotrifluoroborate anion is in equilibrium with the corresponding − not significantly solvated − organodifluoroborane via the intermediately formed neutral species **A**. In a medium of low acidity (path 2) the formation of the adduct **B** is predominant without a significant conversion into the corresponding organodifluoroborane. The formation of **A** as well as of **B** have principally in common the increase of the positive charge on the boron atom which causes a charge redistribution as well in the residual non-protonated B-F fragment as in the organo group R or R_F. The lower symmetry of the borate anion in the protonated species **A** or in the adduct **B** increases the electric quadrupole of the boron atom. The observed broadening of the B-F resonances may be caused by the electric quadrupole and/or by intermolecular exchange processes.

Based on our results we propose in Scheme 2 two paths for the hydrodeboration reaction of K [R′CF=CFBF$_3$] salts with acids. For simplification we neglect in both paths the solvation of the alkenyltrifluoroborate anion.



Scheme 2

Path 1 includes the dipolar conjugated addition of HX to the carbon-boron bond. The transition state **C** favours the stereospecific cleavage of the alkenyl-boron bond. In the alternativ path 2 the negative charge of a boron-bonded fluorine atom orientates the (3c−2e) addition product of the proton to the C=C double bond and leads to the stereospecific hydrodeboration product. The primary protonation of carbon C-1 (path 3) can be neglected, because it leads to the betaine R′C$^+$F-CHF-BF$_3^-$ with a planar carbocationic centre, which gives rise to a non-stereospecific cleavage of the carbon-boron bond.

In the case of the hydrodeboration of K [$C_6F_5BF_3$] in aHF all three paths are reasonable. At first glance the hydrodeboration of K [$C_6F_5BF_3$] in aHF presents a paradox, because in "basic" HF (in the presence of K [HF_2]) the C-B cleavage is significantly accelerated under less acidic conditions. Path 1 (Scheme 1) helps to understand this paradox: in "basic" HF the [$C_6F_5BF_3$]$^-$/$C_6F_5BF_2$ equilibrium is shifted towards the borate species. Additionally, it should be mentioned that the borane $C_6F_5BF_2$ does not undergo hydrodeboration in aHF [3].

Experimental

The NMR spectra were measured on Bruker spectrometers WP 200 (^{1}H at 200.13 MHz, ^{19}F at 188.28 MHz), AM 400 (^{13}C{H} at 100.61 MHz, ^{19}F at 376.50 MHz), AVANCE 300 (^{1}H at 300.13 MHz, ^{11}B at 96.29 MHz, ^{19}F at 282.40 MHz), DRX 500 (^{1}H at 500.13 MHz, ^{11}B at 160.46 MHz, ^{13}C{H} at 125.76 MHz). The chemical shifts are referred to TMS (^{1}H, ^{13}C), $BF_3 \cdot OEt_2$/$CDCl_3$ 15 % v/v (^{11}B) and $CFCl_3$ (^{19}F) [with C_6F_6 or CF_3CO_2H as secondary references (−162.9 ppm or (−76.53 ppm, respectively)]. The composition of the reaction mixtures and the yields of products were determined by ^{1}H or ^{19}F NMR spectroscopy. The fluorine atoms F^2 at C-2 in alkenyltrifluoroborates are specified by *cis* or *trans* relative to the position of the BF_3 group. The IR spectra were recorded on a Bruker Vector 22 FT-spectrometer using KBr pellets. The elemental analysis was performed in the *N. N. Vorozhtsov* Novosibirsk Institute of Organic Chemistry (Novosibirsk).

All manipulations with aqueous and anhydrous HF were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment.

Potassium (polyfluoroorgano)trifluoroborates **1, 3, 5, 9, 11, 13** and **15** were prepared as described recently [2, 3, 4]. The synthesis of K [*cis*- and *trans*-C_3F_7OCF=$CFBF_3$] will be presented elsewhere.

Potassium phenyltrifluoroborate K [$C_6H_5BF_3$] 17

Phenylmagnesium bromide prepared from PhBr (31 g, 0.2 mol), Mg (5 g, 0.2 mol) in ether (200 ml) was added drop by drop to the solution of $B(OMe)_3$ (22 g, 0.2 mol) in ether (100 ml) at −65 to −70 °C within 2 h. The resulting suspension was stirred for 1 h and then warmed to 20 °C. The reaction mixture was hydrolysed with 5 % aqueous HCl, the organic phase was separated, the aqueous one was extracted with ether and the combined ether phases were dried with $MgSO_4$. Ether was removed at reduced pressure, the residue was dissolved in MeOH (40 ml) and poured into the stirred solution of K [HF_2] (60 g, 0.77 mol) in water (150 ml). After 5 minutes the precipitate was filtered off, dried and extracted with hot

Table 1 The ^{19}F NMR spectra of K [RBF_3] and K [R_FBF_3] in HOAc (100 %)[a]

R	*trans*-BuCH=CH *trans*-**16**	*cis*-BuCH=CH *cis*-**16**	C_4H_9 **18**	C_6H_5 **17**	*trans*-BuCF=CF **1**[d]	CF_2=CF **3**[e]	*trans*-C_4F_9CF=CF **9**[f]	C_6F_{13} **15**[g]	C_6F_5 **13**[h]
δ(F) (BF_3)	−135.70	−130.66	−135.33	−137.32	−139.89	−141.86	−142.54	−150.46	−132.24
Δδ (BF_3)[b]	4.38	4.12							
Δδ (BF_3)[c]			3.76	3.44	2.11	1.51	1.49	1.36	1.19
Δδ (F^1)[c]					−2.40	−1.83	−1.66	−0.79	0.78[i]
Δδ (F^2-*cis*)[c]					0.53	0.71	0.89		

[a] The fluorine atoms F-2 are specified by *cis* or *trans* relative to the position of the BF_3 group.
[b] Δδ = δ(in 100 % HOAc) − δ(in CD_3OD).
[c] Δδ = δ(in 100 % HOAc) − δ(in CD_3CN).
[d] δ(F): −156.29 (dtq, $^3J(F^2,F^1)$ 120 Hz, $^3J(F^2,H^3)$ 24 Hz, $^4J(F^2,BF)$ 9 Hz, 1F, F^2), −173.14 (d, 1F, F^1).
[e] δ(F): −99.90 (d, 1F, F^2-trans), −123.29 (ddq, $^3J(F^2$-cis,$F^1)$ 111 Hz, $^2J(F^2$-cis,F^2-trans) 88 Hz, $^4J(F^2$-cis,B*F*) 10 Hz, 1F, F^2-cis), −197.48 (d, 1F, F^1); ^1J(F,B) 45 Hz.
[f] δ(F): −80.85 (3F, F^6), −116.60 (2F, F^3), −124.54 (2F, F^4), −126.03 (2F, F^5), −154.72 (1F, F^1), −176.27 (d, $^3J(F^2,F^1)$ 131 Hz 1F, F^2).
[g] δ(F): −80.67 (3F, F^6), −121.78, −122.45, −123.09 (6F, F^2,F^3,F^4), −125.73 (2F, F^5), −133.37 (2F, F^1).
[h] δ(F): −135.42 (2F, F^2,F^6), −159.96 (1F, F^4), −165.26 (2F, F^3,F^5).
[i] Δδ(F^4).

Table 2 The ^{19}F NMR spectra of K [R_FBF_3] in aHF (−20 °C)[a].

R	C_6F_{13} **15**[c]	*trans*-C_4F_9CF=CF **9**[d]	*cis*-C_2F_5CF=CF **11**[e]	*trans*-ClCF=CF *trans*-**5**[f, g]	*cis*-ClCF=CF *cis*-**5**[g, h]	C_6F_5 **13** [4]
δ(F) (BF_3)	−148.67	−141.18	−139.70			−131.88
Δδ (BF_3)[b]	3.15	2.85	2.77			1.55
Δδ (F^1)[b]	0.38	−5.95	−7.94	−7.64	−7.14	Δδ (F^2,F^6) −1.03,
Δδ (F^2)[b]		6.93	9.23	5.28	7.34	Δδ (F^3,F^5) 2.04, Δδ (F^4) 5.45

[a] The fluorine atoms F-2 are specified by *cis* or *trans* relative to the position of the BF_3 group.
[b] Δδ = δ(in aHF) − δ(in CH_3CN).
[c] δ(F): −79.37 (3F, F^6), −120.04, −120.45, −121.23, −124.17 (4 CF_2), −132.20 (2F, F^1).
[d] δ(F): −79.49 (t, $^4J(F^6,F^4)$ 9 Hz, 3F, F^6), −115.89 (2F, F^3), −122.84, −124.44 (2F, F^4 and 2F, F^5), −170.23 (d, $^3J(F^2,F^1)$ 133 Hz, 1F, F^2), −159.01 (d, 1F, F^1).
[e] δ(F): −82.76 (3F, F^4), −119.03 (2F, F^3), −148.24 (1F, F^2), −139.70 (1F, F^1).
[f] δ(F): −121.23 (d, $^3J(F^1,F^2)$ 129 Hz, 1F, F^2), −164.78 (d, 1F, F^1).
[g] The shift value of the BF_3 group cannot be determined because of the strong broadening of the signal.
[h] δ(F): −95.77 (s,1F, F^2), −154.07 (br,1F, F^1).

acetone (270 ml). Acetone was removed under reduced pressure and the product was dried over P_4O_{10} to yield 21 g (57 %) of salt **17**.

^{19}F NMR (CD_3CN): δ = −140.76 (q, ^1J(F,B) 51 Hz) {lit. δ = −142 (^1J(F,B) 57 Hz) [13]}.
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3072 w, 3052 w, 3013 w, 1597 w, 1434 s, 1265 w, 1244 s, 1226 s, 1181 w, 1080 m, 1030 s, 991 vs, 975 vs, 937 vs, 906 vs, 752 vs, 700 s, 607 m, 540 w.

*Potassium butyltrifluoroborate K [$C_4H_9BF_3$] **18***

Butylmagnesium bromide prepared from BuBr (13.7 g, 0.1 mol), Mg (2.4 g, 0.1 mol) in ether (100 ml) was added drop by drop to the solution of $B(OMe)_3$ (10 g, 0.1 mol) in ether (100 ml) at −65 to −70 °C within 90 minutes The resulting suspension was warmed to 20 °C within 3 h. The reaction mixture was hydrolysed with 5 % $HCl_{aq.}$, the organic phase was separated and dried with $MgSO_4$. The solvent was removed at reduced pressure. The residue was dissolved in MeOH (60 ml) and poured into the stirred solution of K [HF_2] (31 g, 0.4 mol) in water (100 ml). After 30 minutes the precipitate was filtered off, dried and continuously (5 h) extracted with hot acetone (700 ml). The solvent was removed under reduced pressure and the product was dried over P_4O_{10} to yield 5.7 g (35 %) of salt **18**.

$C_4H_9BF_3K$ (164,02): calculated C 29.29, H 5.53, F 34.75; found C 29.7, H 5.66, F 34.7 %.

^1H NMR (acetone-d_6): δ = 1.23 (4H, H^2, H^3), 0.84 (t, $^3J(H^4,H^3)$ 6.5 Hz, 3H, H^4), 0.16 (2H, H^1). ^{19}F NMR (acetone-d_6): δ = −139.09 (apparent doublet). ^{11}B NMR (acetone-d_6): δ = 5.61 (q, ^1J(B,F) 52 Hz).
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2961 s, 2920 s, 2874 m, 2855 s, 1466 w, 1377 w, 1345 w, 1321 m, 1300 w, 1283 w, 1243 s, 1210 w, 1126 s, 1103 vs, 1088 vs, 1069 s, 957 vs, 933 vs, 920 s, 866 s, 844 s, 754 w, 721 w, 571 w.

*Potassium octyltrifluoroborate K [$C_8H_{17}BF_3$] **19***

Borate **19** was prepared similar to **18** by reacting $C_8H_{17}MgBr$ [from $C_8H_{17}Br$ (19 g, 0.09 mol), Mg (2.4 g, 0.1 mol) and ether (100 ml)] with $B(OMe)_3$ (22 g, 0.2 mol) in ether (100 ml) at −55 °C followed by hydrolysis and treatment of the crude octylboronic acid with K [HF_2] (42 g, 0.92 mol) in water (100 ml) and MeOH (30 ml). Crystallization from MeOH gave 7.5 g (30 % based on $C_8H_{17}Br$) of salt **19**.

^1H NMR (acetone-d_6): δ = 1.28 − 1.24 (12H, $6CH_2$), 0.86 (3H, H^8), 0.10 (2H, H^1). ^{19}F NMR (acetone-d_6): δ = −139.26 (apparent doublet). ^{11}B NMR (acetone-d_6): δ = 5.31 (q, ^1J(B,F) 62 Hz) {lit. δ(^1H, DMSO-d_6) = 1.30 − 1.05 (12H, $6CH_2$), 0.81 (3H, H^8), −0.08 (2H, H^1); δ(^{19}F, DMSO-d_6) = −137.5 (^1J(F,B) not reported) [6]}.

IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2954 m, 2917 s, 2873 m, 2850 s, 1632 w, 1468 w, 1352 vw, 1329 m, 1293 m, 1250 m, 1205 m, 1100 s, 1071 s, 1040 m, 1010 m, 988 w, 941 s, 920 s, 888 s, 826 m, 771 w, 723 w, 708 w, 573 w.

*Potassium hex-1-enyltrifluoroborate K [C_4H_9CH=$CHBF_3$] **16***

This borate was prepared similar to the alkylborates by the reaction of *cis*- and *trans*-C_4H_9CH=CHMgBr [from *cis*- and *trans*-C_4H_9CH=CHBr (16.3 g, 0.1 mol), Mg (2.4 g, 0.1 mol) and THF (60 ml)] with $B(OMe)_3$ (11 g, 0.1 mol) in ether (40 ml) at −70 °C and following treatment of the reaction mixture with K [HF_2] (32 g, 0.41 mol) in water (100 ml) and MeOH (25 ml). The organic phase was separated, the aqueous one was extracted with acetone (100 ml), the combined acetone extracts were dried with Na_2SO_4 and the solvent was removed under reduced pressure to yield 8.8 g (46 % based on $C_6H_{11}Br$) of the white product **16**.

K [cis-C_4H_9CH=$CHBF_3$].

^{1}H NMR (CD_3OD): δ = 5.77 − 5.32 (CH=CH), 2.18 (2H, H^3), 1.32 (4H, H^4,H^5), 0.89 (3H, H^6). ^{19}F NMR (CD_3OD): δ = (134.78 (q, ^1J(F,B) 50 Hz). ^{11}B NMR (CD_3OD): δ = 3.10; (q, ^1J(B,F) 56 Hz). ^{13}C{H} NMR (CD_3OD): δ = 140.51 (q, ^3J(C-2,F) 4.5 Hz, C-2), (C-1) *not observed*, 33.87 and 32.18 (C-4,5), 23.54 (C-3), 14.49 (C-6).
^{1}H NMR (DMF): δ = 5.58 − 5.34 (CH=CH), 2.20 (2H, H^3), 1.27 (4H, H^4,H^5), 0.86 (3H, H^6). ^{19}F NMR (DMF): δ = −133.24 (q, ^1J(F,B) 50 Hz).
^{1}H NMR (DMSO-d_6): δ = 5.77 (br, 1H, H^2), 5.30 (dqt, $^3J(H^1,H^2)$ 13.3 Hz, $^3J(H^1,BF)$ 6 Hz, $^4J(H^1,H^3)$ 1.3 Hz, 1H, H^1), 2.23 (2H, H^3), 1.35 (4H, H^4,H^5), 0.93 (t, $^3J(H^6,H^5)$ 7 Hz, 3H, H^6). ^{13}C{H} NMR (DMSO-d_6): δ = 136.27 (C-2), 54.54 (C-1), 32.39 and 30.54 (C-4,5), 22.09 (C-3), 14.11 (C-6).

K [trans-C_4H_9CH=$CHBF_3$].
^{1}H NMR (CD_3OD): δ = 5.77 − 5.32 (CH=CH), 2.00 (2H, H^3), 1.32 (4H, H^4 and H^5), 0.89 (3H, H^6). ^{19}F NMR (CD_3OD): δ = −140.08. ^{11}B NMR (CD_3OD): δ = 3.10 (q, ^1J(B,F) 56 Hz). ^{13}C{H} NMR (CD_3OD): δ = 138.32 (q, ^3J(C-2,F) 4.7 Hz, C-2), (C-1) *not observed*, 36.56 and 32.94 (C-4,5), 23.38 (C-3), 14.38 (C-6).
^{1}H NMR (DMF): δ = 5.58 − 5.34 (CH=CH), 1.99 (2H, H^3), 1.27 (4H, H^4 and H^5), 0.86 (3H, H^6). ^{19}F NMR(DMF): δ = −138.53.
^{1}H NMR (DMSO-d_6): δ = 5.83 (dt, $^3J(H^2,H^3)$ 7 Hz, 1H, H^2), 5.39 (dqt, $^3J(H^1,H^2)$ 17.5 Hz, $^3J(H^1,BF)$ 4 Hz, $^4J(H^1,H^3)$ 1.5 Hz, 1H, H^1), 2.02 (2H, H^3), 1.35 (4H, H^4 and H^5), 0.93 (t, $^3J(H^6,H^5)$ 7 Hz, 3H, H^6). ^{13}C{H} NMR (DMSO-d_6): δ = 134.24 (C-2), 53.53 (C-1), 35.09 and 31.52 (C-4,5), 21.92 (C-3), 14.00 (C-6).

The ratio *cis*-**16**/*trans*-**16** was 2.4 : 1. The reported ^{19}F NMR (acetone-d_6) data for K [*trans*-C_4H_9CH=$CHBF_3$]:
δ = 11.0 (relative to $BF_3 \cdot OEt_2$) with ^1J(F,B) of ∼52 Hz [7].
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 2959 s, 2928 s, 2873 m, 2860 m, 1645 m, 1632 m, 1466 m, 1404 m, 1379 m, 1109 vs, 1085 s, 995 vs, 944 vs, 919 vs, 744 w, 708 w, 623 vw, 594 vw, 484 w.

Product **16** contained additionally an admixture (ca. 10 mol %) of K [(*cis*- and *trans*-C_4H_9CH=$CH)_2BF_2$] (*cis*/*trans* = 2.4 : 1) which was identified by its ^{19}F and ^{11}B NMR spectra.
K [(cis-C_4H_9CH=$CH)_2BF_2$]. ^{19}F NMR (CD_3OD):
δ = −133.45. ^{11}B NMR (CD_3OD): δ = 27.87 (s, $\tau_{1/2}$ 53 Hz). ^{19}F NMR (DMF): δ = −131.76.

K [(trans-C_4H_9CH=$CH)_2BF_2$. ^{19}F NMR (CD_3OD):
δ = −137.37. ^{11}B NMR (CD_3OD): δ = 27.87 (s, $\tau_{1/2}$ 53 Hz). ^{19}F NMR (DMF): δ −136.36.

Reactions of potassium polyfluoroalk-1-enyltrifluoroborates with acids

The salt K [*trans*-C_4H_9CF=$CFBF_3$] (51 mg, 0.22 mmol) was suspended and stirred in 100 % CH_3CO_2H (1 ml) at 20 °C. After 24 h no reaction could be detected (^{19}F NMR).

A FEP trap was charged in sequence with hexane (0.5 ml), $PhCF_3$ (26 mg, 0.17 mmol, as quantitative reference), borate K [*trans*-C_4H_9CF=$CFBF_3$] (80 mg, 0.35 mmol) and 27 % $HF_{aq.}$ (0.5 ml) under stirring. After 70 minutes the quantitative formation of *trans*-C_4H_9CF=CFH was detected (^{19}F NMR).

The suspension of borate K [*trans*-C_4H_9CF=$CFBF_3$] (129 mg, 0.57 mmol) in 100 % CF_3CO_2H (0.5 ml) was stirred at 20 °C for 3 h and formed a turbid solution. Hexane (1 ml) and water (1 ml) were added. The upper organic phase was separated. The ^{19}F NMR spectrum showed the formation of *trans*-C_4H_9CF=CFH in 95 % yield.

A mixture of K [*trans*-C_4H_9CF=$CFBF_3$] **1** (100 mg, 0.44 mmol) and K [CF_2=$CFBF_3$] **3** (82 mg, 0.43 mmol) was stirred in 100 % CF_3CO_2H (1.5 ml) at 20 °C. The ^{19}F NMR spectrum showed the complete conversion of borate **1** into *trans*-C_4H_9CF=CFH within 40 minutes.
The resonances of the $[CF_2=CFBF_3]^-$ anion [−94.75 (dd, $^2J(F^2\text{-cis},F^2\text{-trans})$ 80 Hz, $^3J(F^2\text{-trans},F^1)$ 20 Hz, 1F, F^2-trans), −118.61 (dd, $^3J(F^2\text{-cis},F^1)$ 115 Hz, 1F, F^2-cis), −200.60 (dd, 1F, F^1) and −145.97 (br, BF_3) ppm] and, probably, of $[CF_2=CFBF_n(O_2CCF_3)_{3-n}]^-$ or $[CF_2=CFBF_n(F\cdots HO_2CCF_3)_{3-n}]^-$ [−95.63 (d, $^2J(F^2\text{-cis},F^2\text{-trans})$ 78 Hz, 1F, F-2trans), −120.35 (dd, $^3J(F^2\text{-cis},F^1)$ 109 Hz, 1F, F-2cis), −199.21 (d, 1F, F-1)] (the resonance of the BF_n group was not detected) were observed still after 3 h besides the resonances of CF_2=CFH [−101.30 (1F, F^2-trans), −127.96 (1F, F^2-cis) and −206.77 (1F, F^1) ppm].

The borate K [*trans*-C_4H_9CF=$CFBF_3$] (37 mg, 0.16 mmol) was placed in a FEP trap and pre-cooled aHF (−20 °C) (0.3 ml) was added. After shaking the white suspension for 1 h at −20 °C the quantitative conversion of borate **1** into *trans*-C_4H_9CF=CFH and K [BF_4] had proceeded (^{19}F NMR).

The salt K [CF_2=$CFBF_3$] (93 mg, 0.49 mmol) was stirred with 100 % CH_3CO_2H (1 ml) at 20 °C for 24 h without any reaction (^{19}F NMR).

The salt K [CF_2=$CFBF_3$] (83 mg, 0.44 mmol) was stirred with 27 % $HF_{aq.}$ (0.8 ml) at 20 °C. The ^{19}F NMR spectra showed the molar ratio of anions $[CF_2=CFBF_3]^-$ to $[BF_4]^-$ 9 : 1 (6 h) and 4 : 1 (26 h).
^{19}F NMR (27 % $HF_{aq.}$): δ = −98.97 (d, $^2J(F^2\text{-cis},F^2\text{-trans})$ 92 Hz, 1F, F^2-trans), −123.29 (dd, $^3J(F^2\text{-cis},F^1)$ 111 Hz, 1F, F^2-cis), −200.08 (d, 1F, F^1), −142.66 (q, ^2J(F,B) 38 Hz, 3F, BF_3).

The borate K [CF_2=$CFBF_3$] (106 mg, 0.56 mmol) was stirred with 100 % CF_3CO_2H (1 ml) in a sealed ampoule at 20 °C for 18 h. The probe was a fine suspension and showed the presence of CF_2=CFH while borate **3** was absent.

Anhydrous HF (0.25 ml) was added to the borate K [CF_2=$CFBF_3$] (27 mg, 0.14 mmol) at −50 °C and the suspension was kept at −30 °C for 3 h. The ^{19}F NMR spectrum showed the quantitative conversion of borate **3** into CF_2=CFH and K [BF_4].

The borate K [ClCF=$CFBF_3$] (*cis*/*trans* = 49 : 51) (37 mg, 0.18 mmol) was treated with aHF (0.25 ml) at −20 °C in a similar way as above. The ^{19}F NMR spectrum (−20 °C) showed the presence of the residual anions $[ClCF=CFBF_3]^-$ (Table 2) (*cis*/*trans* = 4 : 6), and of the olefins *cis*-ClCF=CFH [−104.35 (dd, $^2J(F^2\text{-trans},H)$ 11 Hz, $^3J(F^2\text{-trans},F^1)$ 10 Hz, 1F, F^2-trans), −156.31 (dd, $^2J(F^1,H)$ 73 Hz, 1F, F^1) ppm] and *trans*-ClCF=CFH [−129.46 (d, 1F, F^2-cis), −173.13 (dd, $^3J(F^1,F^2\text{-cis})$ 130 Hz, $^2J(F^1,H)$ 74 Hz, 1F, F^1) ppm]; besides $[BF_4]^-$ (−148.43 ppm). Warming to 20 °C led to the quantitative conversion of the borate isomers into *cis*- and *trans*-ClCF=CFH (*cis*/*trans* = 4 : 6).

Similarly, K [*cis*-C_2F_5CF=$CFBF_3$] (44 mg, 0.15 mmol) was dissolved in aHF (0.25 ml) at −50 °C and the solution was kept at −30 °C for 4 h but showed no reaction. After 3 days at 20 °C the ^{19}F NMR spectrum contained the resonances of the starting borate

11 (Table 2), *cis*-$C_2F_5CF{=}CFH$ (content was less than 10 %) and $[BF_4]^-$ (−148.24 ppm, only traces).

Similarly, K [*trans*-$C_4F_9CF{=}CFBF_3$] (45 mg, 0.11 mmol) was dissolved in aHF (0.25 ml) at −30 °C. The solution was maintained at 20 °C for 3 days to show only ^{19}F resonances of starting borate **9** (Table 2). After 30 days at 20 °C the formation of *trans*-$C_4F_9CF{=}CFH$ was detected (**9** : **10** = 2.5 : 1, ^{19}F NMR).

Similarly, K [*cis*- and *trans*-$C_3F_7OCF{=}CFBF_3$] **7** (*cis*/*trans* = 1 : 3; 33 mg, 0.09 mmol) was dissolved in aHF (0.3 ml) at −20 °C. After 3 d at 20 °C the ^{19}F NMR spectrum showed the resonances of *cis*- and *trans*-$C_3F_7OCF{=}CFH$ (ca. 1 : 2.5) and the $[BF_4]^-$ anion. The solution of borate **7** (44 mg, 0.12 mmol) in 48 % $HF_{aq.}$ (0.5 ml) was kept at 20 °C. After 3 d the concentration of salt **7** was reduced to ca. 50 %. Parallel a precipitation occurred and the resonance of the $[BF_4]^-$ anion appeared in the ^{19}F NMR spectrum. The signals of $C_3F_7OCF{=}CFH$ were not observed, probably caused by the low solubility of that polyfluoroalkene in $HF_{aq.}$.

K [cis-$C_3F_7OCF{=}CFBF_3$]. ^{19}F NMR (48 % $HF_{aq.}$): δ = −80.35 (t, ^4J($OCF_2CF_2CF_3$,$OCF_2CF_2CF_3$) 7 Hz, 3F, $OCF_2CF_2CF_3$), −84.76 (m, 2F, $OCF_2CF_2CF_3$), −99.45 (s, 1F, F^2), −128.43 (s, 2F, $OCF_2CF_2CF_3$), −141.22 (q, ^1J(F,B) 36 Hz, BF_3), −170.37 (s, 1F, F^1).

K [trans-$C_3F_7OCF{=}CFBF_3$]. ^{19}F NMR (48 % $HF_{aq.}$): δ = −80.40 (t, ^4J($OCF_2CF_2CF_3$,$OCF_2CF_2CF_3$) 7.5 Hz, 3F, $OCF_2CF_2CF_3$), −83.77 (dqt, ^4J($OCF_2CF_2CF_3$,F^2) 14.3 Hz, ^3J($OCF_2CF_2CF_3$,$OCF_2CF_2CF_3$) 2.5 Hz, 2F, $OCF_2CF_2CF_3$), −124.07 (dtq, ^3J(F^2,F^1) 118 Hz, ^3J(F^2,BF_3) 9 Hz, 1F, F^2), −128.43 (s, 2F, $OCF_2CF_2CF_3$), −141.22 (q, ^1J(F,B) 36 Hz, BF_3), −177.68 (d, 1F, F^1).

The reactions of potassium pentafluorophenyltrifluoroborate with acids

The suspension of K $[C_6F_5BF_3]$ (70 mg, 0.25 mmol) in 100 % CF_3CO_2H (1 ml) was stirred at 20 °C for 26 h. No ^{19}F resonances of borate **13** and C_6F_5H **14** were detected in the solution phase. The same result was obtained after stirring a suspension of borate **13** in 100 % CF_3CO_2H at 60 − 70 °C for 5 h.

A solution of K $[C_6F_5BF_3]$ (56 mg, 0.20 mmol) in 40 % $HF_{aq.}$ (0.4 ml) was kept at 20 °C. After 4 days it showed no reaction (^{19}F NMR).

A solution of K $[C_6F_5BF_3]$ (38 mg, 0.13 mmol) in 40 % $HF_{aq.}$ (0.3 ml) was kept at 80 °C for 0.5 h. The ^{19}F NMR spectrum showed the signals of the starting borate **13**, $[BF_4]^-$ and $HF_{aq.}$ (−166.40 ppm) in a molar ratio of 90 : 10. When this solution was maintained at 90 − 95 °C, the ratio $[C_6F_5BF_3]^-/[BF_4]^-$ increased to 57 : 43 (50 minutes) and 16 : 84 (3 h). After 6 h the resonances of the anion $[C_6F_5BF_3]^-$ disappeared parallel to the formation of C_6F_5H (^{19}F NMR).

The borate K $[C_6F_5BF_3]$ (40 mg, 0.14 mmol) was suspended in precooled aHF (0.2 ml) at −78 °C. The suspension was warmed to 0 °C for 1 minute and a solution was formed. After cooling to −40 °C the ^{19}F NMR spectrum showed resonances at −136.20 (F^2,F^6), −155.28 (F^4), −163.22 (F^3,F^5), −131.88 (br, B*F*) with relative intensities of 2 : 1 : 2 : 2. At −10 °C the B-F signal became too broad for observation while the resonances of the C_6F_5 group were not changed. After 18 h at 20 °C the quantitative formation of C_6F_5H and K $[BF_4]$ (1 : 1) was found (^{19}F NMR).

The borate K $[C_6F_5BF_3]$ (105 mg, 0.38 mmol) was dissolved in the cold (−30 °C) solution of K $[HF_2]$ (38 mg, 0.48 mmol) in aHF (0.3 ml). The ^{19}F NMR spectrum (−30 °C) showed no difference to the spectrum of K $[C_6F_5BF_3]$ in aHF (see above). However, warming to 20 °C led to the fast and quantitative formation of C_6F_5H and K $[BF_4]$ (1 : 1) within 30 minutes (^{19}F NMR).

The reaction of potassium perfluorohexyltrifluoroborate with aHF

The borate K $[C_6F_{13}BF_3]$ (72 mg, 0.17 mmol) was suspended in aHF (0.6 ml) at −50 °C. Warming to 20 °C resulted in a solution. It was kept for 10 days at 20 °C but displayed no reaction (Table 2).

The solution of K $[C_6F_{13}BF_3]$ (64 mg, 0.15 mmol) in aHF (0.3 ml), which contained K $[HF_2]$ (30 mg, 0.38 mmol), was kept for 7 days at 20 °C and displayed no reaction (^{19}F NMR).

The reaction of potassium cis- and trans-hex-1-enyltrifluoroborate with 27 % $HF_{aq.}$

The borate K [*cis*- and *trans*-$C_4H_9CH{=}CHBF_3$] (300 mg, 1.58 mmol) was suspended in 27 % $HF_{aq.}$ (2.5 ml) and benzene (1 ml) and stirred at 20 °C for 1 h. The organic extract contained hex-1-ene [^1H NMR: δ = 5.84 (1H, H^1), 5.09 and 5.03 (2H, $H^{1,2}$), 2.04 (2H, H^3), 1.35 (4H, H^4 and H^5) and 0.92 (3H, H^6)] (quantitative yield).

The reactions of potassium phenyltrifluoroborate with acids

The solution of borate K $[C_6H_5BF_3]$ **17** (321 mg, 1.74 mmol) in 27 % $HF_{aq.}$ (3 ml) was stirred at 20 °C. The observed molar ratio of K $[C_6H_5BF_3]$ [^{19}F NMR: δ = −138.69, br] and K $[BF_4]$ [^{19}F NMR: δ = −150.67] changed from 7.7 : 1 (0.5 h) to 1.6 : 1 (6 h) and after 48 h the resonance of borate **17** disappeared (^{19}F NMR, in 27 % $HF_{aq.}$).

The borate K $[C_6H_5BF_3]$ (300 mg, 1.63 mmol) was stirred with 27 % $HF_{aq.}$ (2.5 ml) and CCl_4 (1 ml) at 50 °C for 2 h. After cooling to 20 °C the ^{19}F NMR spectrum of the acidic phase showed the resonances of K $[BF_4]$ (−150 ppm), aqueous HF (−166 ppm) and no signal of borate **17**. After washing with aq. $Na_2[CO_3]$ and drying, the CCl_4 extract displayed the presence of benzene (ca. 45 % yield, ^1H NMR).

The borate K $[C_6H_5BF_3]$ (353 mg, 1.91 mmol) was suspended in 100 % HOAc (3 ml) and stirred at 20 °C for 60 h. The solid was filtered off, washed with ether and dried to yield 280 mg of borate **17** [^{19}F NMR (DMF): δ = −140.30 (q, ^1J(F,B) 50 Hz], with traces (< 2 %) of K $[BF_4]$ [δ = −149.42]. The filtrate contained borate **17** (47 mg) (^{19}F NMR). The total recovery of borate **17** was 327 mg (93 %).

The reactions of potassium alkyltrifluoroborate with acids

The borate K $[C_8H_{17}BF_3]$ (378 mg, 1.71 mmol) was stirred with 27 % $HF_{aq.}$ (2 ml) at 65 − 70 °C for 2.5 h. The clear solution was cooled to 20 °C and the precipitate was filtered off, washed in sequence with water and ether and dried to give a white solid (205 mg), which consisted of K $[C_8H_{17}BF_3]$ (0.53 mmol) and K $[BF_4]$ (0.70 mmol) (^{19}F NMR). The filtrate was neutralized with solid K $[HCO_3]$ and extracted with DMF. The ^{19}F NMR spectrum showed the presence of K $[C_8H_{17}BF_3]$ (0.44 mmol) and K $[BF_4]$ (0.04 mmol).

The similar reaction of K $[C_8H_{17}BF_3]$ (317 mg, 1.44 mmol) with 27 % $HF_{aq.}$ (2 ml) at 65 − 70 °C for 2 h resulted in K $[C_8H_{17}BF_3]$ (0.90 mmol) and K $[BF_4]$ (0.54 mmol).

The borates K $[C_6H_5BF_3]$ (199 mg, 1.08 mmol) and K $[C_4H_9BF_3]$ (184 mg, 1.12 mmol) were stirred with 27 % $HF_{aq.}$ (1.5 ml) at 70 °C for 40 minutes. After cooling to 20 °C the reaction mixture was neutralized with solid K $[HCO_3]$ and extracted with DMF (2 ml). The ^{19}F NMR spectrum of the extract showed the resonances of K $[C_4H_9BF_3]$ (−137.52 ppm), K $[BF_4]$ (−149.69 ppm), aq. KF (−122.88 ppm) but no signal of K $[C_6H_5BF_3]$.

Cold (−20 °C) aHF (1 ml) was added to the pre-cooled (−25 °C) borate **19** (145 mg, 0.66 mmol) under stirring. Immediately an upper hydrocarbon phase was formed. The reaction mixture was stirred at 20 °C for 20 minutes and extracted with benzene. The extract was treated with NaF. The ^1H NMR spectrum showed the quantitative formation of octane.

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