(Fluoroorgano)fluoroboranes and -fluoroborates. 2 [1]

Synthesis and Spectroscopic Characterization of Potassium Polyfluoroalken-1-yltrifluoroborates

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

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

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Abstract. The potassium fluoroborates K[RCF=CFBF$_3$] (R = F, Cl (*cis*-/*trans*-mixture), *trans*-C_4F_9, *cis*-C_2F_5, *cis*-C_6F_{13}, *trans*-C_4H_9, *trans*-C_6H_5) were prepared by fluoridation (methoxide-fluoride substitution with K[HF$_2$]) of RCF=CFB(OMe)$_2$ and Li[RCF=CFB(OMe)$_3$] which were obtained from RCF=CFLi and B(OMe)$_3$. The K[RCF=CFBF$_3$] salts were characterized by their ^{1}H, ^{11}B, ^{19}F NMR and IR spectra.

Keywords: Borates; Polyfluoroalken-1-yl; NMR spectroscopy

(Fluororgano)fluorborane und -fluoroborate. 2 [1] Synthese und spektroskopische Charakterisierung von Kalium Polyfluoralken-1-yltrifluoroboraten

Inhaltsübersicht. Die Kalium Fluoroborate K[RCF=CFBF$_3$] (R = F, Cl (*cis*-/*trans*-Gemisch), *trans*-C_4F_9, *cis*-C_2F_5, *cis*-C_6F_{13}, *trans*-C_4H_9, *trans*-C_6H_5) werden durch Fluoridierung (Methoxid-Fluorid-Substitution mit K[HF$_2$]) von RCF=CFB(OMe)$_2$ und Li[RCF=CFB(OMe)$_3$] dargestellt. Letztere resultieren aus der Umsetzung von RCF=CFLi mit B(OMe)$_3$. Die K[RCF=CFBF$_3$] Salze werden durch ihre ^{1}H, ^{11}B, ^{19}F NMR und IR Spektren charakterisiert.

Introduction

Recently we have reported a simple and convenient synthesis of potassium salts of polyfluoroaryltrifluoroborates K[$C_6H_{5-n}F_nBF_3$] (n = 1–5) and of perfluoroalkyltrifluoroborates K[$C_nF_{2n+1}BF_3$] (n = 3, 6) by the fluoridation of the corresponding dialkoxyboranes $Org_FB(OMe)_2$ and trialkoxyborates M[$Org_FB(OMe)_3$] using K[HF$_2$] [1, 2]. Those intermediate boranes and borates were obtained by the reaction of fluoro-containing organomagnesium or lithium reagents with B(OAlk)$_3$ and used in the further synthetic route without isolation.

Fluorinated alkenyltrifluoroborates are a still unknown class of organoelement compounds despite their high synthetic potential. In the course of systematic investigations of fluoro-containing organoboron compounds as precursors for the synthesis of organoxenonium salts $[Org_FXe]^+Y^-$, we elaborated a general route to potassium fluoroalken-1-yltrifluoroborates [3]. The reactivity of the corresponding boranes in fluoro-alkenyl substitution reactions will be discussed in forthcoming papers.

* 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

Results and Discussion

The preparation of potassium fluoroalken-1-yltrifluoroborates was performed analogously to the general scheme for the synthesis of fluoroaryl- and fluoroalkyltrifluoroborates.

$$RCF{=}CFLi \xrightarrow{B(OMe)_3} RCF{=}CFB(OMe)_2 + Li[RCF{=}CFB(OMe)_3] \xrightarrow[\text{aq. MeOH}]{K[HF_2]} K[RCF{=}CFBF_n(OMe)_{3-n}] \xrightarrow{40\%\ HF,\ aq.\ MeOH} K[RCF{=}CFBF_3]$$

R = F (**1**), *cis*-, *trans*-Cl (**2**), *cis*-C_2F_5 (**3**), *cis*-C_6F_{13} (**4**), *trans*-C_4F_9 (**5**), *trans*-C_4H_9 (**6**), *trans*-C_6H_5 (**7**). The position of substituent R is related to the BF_3 group.

We were very interested in the pure *cis*- and/or *trans*-2-R-1,2-difluoroethen-1-yltrifluoroborate salts. Taking into account that our favoured route consists of several steps it was therefore useful to generate the organolithium nucleophiles as substrates by the most simple and reliable procedure. Hence we had to apply different routes to the desired alkenyllithium substrates. One of them is based on the metallation of

polyfluorinated alkenes RCF=CFH with BuLi. The *trans*-RCF=CFH substrates (R = C_4H_9, C_6H_5) were prepared using the method of *Normant* et al [4, 5] from the corresponding trifluorovinyltrimethylsilane.

$$CF_2{=}CFSiMe_3 + RLi \rightarrow \textit{trans}\text{-}RCF{=}CFSiMe_3 \xrightarrow{KF+H_2O} \textit{trans}\text{-}RCF{=}CFH \xrightarrow{BuLi} \textit{trans}\text{-}RCF{=}CFLi$$

R = C_4H_9, C_6H_5

However, this pathway is not available for the stereoselective preparation of *trans*-$C_nF_{2n+1}CF{=}CFH$ because perfluoroalkylllithium reagents have too low nucleophilicity and insufficient thermal stability. The required *trans*-1 H-perfluoro-1-hexene was obtained by *Burton*'s method [6] via the stereospecific nucleophilic phosphodefluoridation of the easily available perfluoro-1-hexene.

$$C_4F_9CF{=}CF_2 \xrightarrow[2.\ H_2O]{1.\ PBu_3} \textit{trans}\text{-}C_4F_9CF{=}CFH \xrightarrow{BuLi} \textit{trans}\text{-}C_4F_9CF{=}CFLi$$

The pure *cis*-1,2-difluoroalkenes RCF=CFH are less convenient available than the *trans*-isomers. With R = CF_3 or C_2F_5, they can be obtained by the isomerisation of *trans*-$CF_3CF{=}CFH$ or $CF_2{=}CFCF_2CF_2H$ with SbF_5 [6, 7]. This procedure can not be applied to hydroperfluoroalkenes with longer chains because they give a mixture of internal isomers in addition to the desired products [8]. We assumed that the formation of $CF_2{=}CFLi$ from CF_3CFH_2 via CF_3CFHLi developed by different English groups [9] may have a general character, and that the elimination of LiF from the related intermediate RCF_2CFHLi may lead to *cis*-olefins RCF=CFH rather than to *trans*-olefins. Indeed, the treatment of 1 H,1 H-perfluorooctane with two equivalents of BuLi resulted in the formation of *cis*-perfluorooctenyllithium with a negligible impurity of the *trans*-isomer (< 5%).

$$C_6F_{13}CF_2CFH_2 \xrightarrow{2\,BuLi} \textit{cis}\text{-}C_6F_{13}CF{=}CFLi$$

A mixture of *cis*-, *trans*-ClCF=CFLi was prepared from 1,2-dichlorodifluoroethene and *t*-BuLi in pentane-ether at –90 °C.

The reactions of all above mentioned organolithium reagents RCF=CFLi with $B(OMe)_3$ led to the formation of organyldimethoxyboranes and lithium organyltrimethoxyborates. Those organoboron derivatives were observed in the reaction mixture by ^{19}F-NMR spectroscopy but for the current purpose they were used without isolation. However, the preparation and characterization of the individual compounds $RCF{=}CFB(OR')_2$ and $M[RCF{=}CFB(OR')_3]$ (R′ = alkyl, H; M = countercation) will be described elsewhere.

Although the preparation of $K[RCF{=}CFBF_3]$ looks at first sight like the earlier described synthesis of $K[C_6H_{5-n}F_nBF_3]$ [1], nevertheless there are two distinctions between them. In contrast to the polyfluoroaryl-trialkoxyborane system [1], no diorganyl-(methoxy)boranes as well as diorganyldimethoxyborates were found in the polyfluoroalkenyl-$B(OMe)_3$ system. Furthermore, the fluoridation of $RCF{=}CFB(OMe)_2$ and Li $[RCF{=}CFB(OMe)_3]$ with $K[HF_2]$ in aqueous MeOH proceeds incompletely and gives a mixture of $K[RCF{=}CFBF_n(OMe)_{3-n}]$ while the previously investigated fluorodealkoxylation of both $ArB(OR')_2$ and $[ArB(OR')_3]^-$ [1, 10, 11] or of the acids $ArCH{=}CHB(OH)_2$ [12, 11] ends with the corresponding potassium organyltrifluoroborates. We assume that the replacement of the substituent Org in the borane $OrgB(OR')_2$ (Org = Ar, ArCH=CH) by higher electron-withdrawing Org-groups increases the Lewis acidity of the borane and hinders the elimination of the anion $[OR']^-$ from the corresponding borate $[OrgBF_n(OR')_{3-n}]^-$. However, the protonation of the oxygen atom by acidification with HF_{aq} facilitates the leaving of the oxygen-containing group from the boron atom as R′OH (or its protonated form) and allows to obtain the desired salts $K[RCF{=}CFBF_3]$ in good yields. The influence of acidity on the fluorodealkoxylation of alkoxyboranes is well demonstrated by a model reaction of $K[HF_2]$ with $B(OMe)_3$ in aqueous MeOH. Even in excess of $K[HF_2]$ the salt $K[BF_3(OMe)]$ is the predominant product and $K[BF_4]$ only the minor one.

$$> 3\,K[HF_2] + B(OMe)_3 \xrightarrow{MeOH,\ H_2O} K[BF_4] + K[BF_3(OMe)] + K[BF_n(OMe)_{4-n}]$$

n = 2, 1 — 4 : 96 — minor

Potassium polyfluoroalken-1-yltrifluoroborates **1**–**7** are air- and moisture-stable colourless solids which are soluble in polar organic solvents (acetone, MeCN, MeOH, DMF, diglyme). Salts **1**–**3** are soluble in water while the other ones only show a poor solubility.

The ^{11}B NMR spectra of salts $K[RCF{=}CFBF_3]$ display the weak influence of the substituent R on the shielding of the boron atom. All ^{11}B resonances of salts **1**–**7** are located at 0.3 ± 0.5 ppm (Table 1). Similar values were found for the salts $K[C_6H_{5-n}F_nBF_3]$ (n = 1–5) [δ(B) 2.76 ± 0.95] [1] and for the perfluoroalkyltrifluoroborates $K[C_nF_{2n+1}BF_3]$ [δ(B) –1.7 (n = 1) [13], –0.64 (n = 3), –0.53 (n = 6)] [2]. The recently reported ^{11}B NMR data of Cs $[CF_2{=}CFB(CF_3)_2F]$ showed a more shielded boron atom (Table 1) caused by the replacement of the fluorine atoms at boron by less electronegative trifluoromethyl groups [14]. In the case of K[*trans*-$RCH{=}CHBF_3$] with R = Ph, C_4H_9 and H the resonances are found at 3.8 (R = Ph), 3.6 (R = C_4H_9) and 3.4 (R = H) ppm and the ^1J(BF) coupling constants are 46, 52 and 56 Hz, respectively [11], which are significantly larger than in the 1,2-difluoroalken-1-yltrifluoroborate series.

The ^{19}F resonances of the BF_3 groups of the salts $K[RCF{=}CFBF_3]$ are located at –142 to –144 ppm (Ta-

ble 2). It is noteworthy that the boron-bonded fluorine atoms in the anions [*cis*-RCF=CFBF$_3$] (R = Cl, C_4F_9, C_6F_{13}) are slightly deshielded with respect to the corresponding *trans*-isomers. Deshielding also takes place after replacement of the electron-withdrawing substituents R = F, C_4F_9, C_6F_{13} by chlorine or C_4H_9, C_6H_5 groups (in acetonitrile solution).

An interesting solvent-dependence was found for δ(F-1). Going from the polar aprotic solvents (acetone, acetonitrile) to the protic ones like water and methanol, the resonance of the F-1 fluorine atom shifts 3–5 ppm to higher frequency (R = F, *cis*-, *trans*-Cl). Simultaneously the resonance of the F-2 *trans* atom (R = F, *cis*-Cl) undergoes a smaller but still remarkable opposite shift. This effect cannot be assigned to differences in the dielectric constants of MeOH and MeCN because they are similar. Probably, the observed solvent-dependence arises from the formation of hydrogen bonds between the solvent molecules and the fluorine atoms bonded to boron. Unfortunately, the solubility of the other salts **3**–**7** is not high enough to examine the validity of our assumption

Table 1 The ^{11}B NMR spectra of K[RCF=CFBF$_3$][a),b)]

R	δ(B)	^1J(B,F)	^2J(B,F-1)
F[c),d)]	0.66	42	25
Cl	0.2–0.4[e)]		
cis-C_2F_5[c)]	–0.07	37	23
cis-C_6F_{13}	–0.17	36	23
trans-C_4F_9	–0.17	39	26
trans-C_4H_9	0.68	43	31
trans-C_6H_5	0.65	42	28
F[f)]	–6.4	56.9	23

a) The position of substituent R is given with respect to the boron atom.
b) In MeCN.
c) ^3J(B,F-2*trans*) 7 Hz.
d) In acetone.
e) Resonances are overlapping.
f) Salt Cs [CF_2=CFBF$(CF_3)_2$] [14].

Table 2 The ^{19}F NMR spectra of K[RCF=CFBF$_3$][a)]

R	Solvent	δ(F)				*J*, Hz					
		F-1	F-2*cis*	F-2*trans*	BF_3	1,B	1,2*trans*	1,2*cis*	2*cis*,BF	2*cis*,2*trans*	BF
F[b)]	acetone	–194.46	–124.41	–102.24	–143.36	24	25	110	8	92	41
F[c)]	MeCN	–195.65	–124.00	–101.16	–143.35	25	25	110	7	92	41
F	H_2O	–199.87	–123.36	–98.71	–143.46	25	25	110	9	87	40
F[d)]	MeOH	–198.49	–122.94	–99.02	–143.79		24	108	9	90	
F	acetone	Cl	–92.27	–82.17	–141.46	–	–	–	10	52	
F	MeCN	Cl	–92.71	–82.45	–141.32	–	–	–	9	54	40
F[e)]	MeCN	–195.7	–124.3	–99.5	–229.9	23	25.5	110.9	17.8	87.7	56.9
trans-Cl	acetone	–157.59	–126.20	–	–143.10	30	–	127	9	–	
trans-Cl	MeCN	–157.14	–126.51	–	–142.89	26	–	129	8	–	40
trans-Cl	D_2O	–162.37	–126.09	–	–142.84	26	–	128	9	–	40
trans-C_4F_9	acetone	–151.74	–177.33	–[f),g)]	–143.87		–	128		–	42
trans-C_4F_9	MeCN	–153.06	–177.16	–[h),g)]	–144.03	26	–	130		–	39
trans-C_6F_{13}	MeCN	–153.34	–177.08	–[i),g)]	–144.17		–	125		–	
trans-C_6H_5	acetone	–158.53	–162.81	–[j)]	–142.16	28	–	117	9	–	
trans-C_6H_5	MeCN	–160.32	–161.83	–	–142.13	28	–	118	10	–	42
trans-C_4H_9	acetone	–170.57	–157.11	–[k)]	–141.93		–	119	9	–	
trans-C_4H_9	MeCN	–170.74	–156.82	–[l)]	–142.00	31	–	118	9	–	43
cis-Cl	acetone	–147.26	–	–102.50	–143.10	24		–	–	–	
cis-Cl	MeCN	–146.93	–	–103.11	–142.58	25		–	–	–	39
cis-Cl	D_2O	–151.53	–	–100.94	–142.25	24		–	–	–	40
cis-C_2F_5	acetone	–131.73	–[m)]	–156.81	–142.30	23		–	–	–	37
cis-C_2F_5	MeCN	–131.73	–[n)]	–157.47	–142.47	23		–	–	–	37
cis-C_4F_9	MeCN	–130.82	–[o)]	–156.37	–142.50	25		–	–	–	37
cis-C_6F_{13}	acetone	–128.98	–[q)]	–157.15[p)]	–142.45			–	–	–	
cis-C_6F_{13}	MeCN	–131.19	–[r)]	–156.23	–142.61	23		–	–	–	34

a) The fluorine atoms F-2 are marked by *cis* or *trans* relative to the position of the BF_3 group.
b) ^3J(1,BF) 5.4, ^4J(2*trans*,BF) 9, ^3J(2*trans*,B) 7.4.
c) ^4J(2*trans*,BF) 8.
d) ^4J(2*trans*,BF) 9.
e) Salt Cs [CF_2=CFBF$(CF_3)_2$] [14].
f) δ(F): –80.17 (3 F-6), –115.28 (2 F-3), –123.63, –125.23 (2 CF_2).
g) Tentative assignment of the F-1 and F-2 resonances.
h) δ(F): –80.41 (3 F-6), –115.95 (2 F-3), –124.12, –125.60 (2 CF_2); ^4J(4,6) 10.
i) δ(F): –115.91 (2 F-3); the other signals overlap with resonances of the *trans*-isomer.
j) δ(H): 7.88.
k) δ(H): 2.21 (2 H-3), 1.39 (4 H-4,5), 0.88 (3 H-6); ^4J(H-3,H-5) 6, ^4J(F-1,H-3) 6, ^3J(F-2,H-3) 23.
l) δ(H): 2.29 (2 H-3), 1.41 (4 H-4,5), 0.90 (3 H-6); ^4J(H-3,H-5) 7, ^4J(F-1,H-3) 6, ^3J(F-2,H-3) 23.
m) δ(F): –83.24 (3 F-4), –117.62 (2 F-3).
n) δ(F): –83.52 (3 F-4), –117.79 (2 F-3); ^3J(2,3) 12, ^4J(2,4) 8, ^5J(3,BF) 12.
o) δ(F): –114.58 (2 F-3); the other signals overlap with resonances of the *trans*-isomer.
p) ^4J(F-2,BF) 10.
q) δ(F): –79.96 (3 F-8), –113.65 (2 F-3), –121.42, –124.98 (4 CF_2).
r) δ(F): –80.37 (3 F-8), –114.54 (2 F-3), –121.42, –121.97, –125.40 (4 CF_2).

as a general property in the class of alkenyltrifluoroborates.

Experimental

NMR spectra were measured on Bruker spectrometers WP 80 SY (^{1}H at 80.13 MHz and ^{19}F at 75.39 MHz) and Avance DRX 500 (^{1}H at 500.13 MHz, ^{11}B at 160.46 MHz and ^{19}F at 470.59 MHz). Chemical shifts were reported with respect to TMS (^{1}H), $BF_3 \cdot OEt_2$ (^{11}B) and CCl_3F (^{19}F). IR spectra were recorded on a Bruker Vector 22 instrument as KBr pellets. Elemental analysis was performed in the N. N. Vorozhtsov Institute of Organic Chemistry, Novosibirsk.

1 H,1 H-Perfluorooctanol-1 (Clariant), 1 H,1 H,5 H-octafluoropentanol-1 (Acros), 1.6 M and 2.5 M BuLi in hexanes, 1.7 M *t*-BuLi in pentane, 1.8 M PhLi in cyclohexane-ether (Aldrich), KF (spray-dried) (Morita), K[HF_2] (Fluka), tributylphosphane (Fluka), 40% HF (Riedel-deHaen), perfluorobutanesulfonyl fluoride (Merck), 1,2-dichlorodifluoroethene (Bristol Organics) (contains 9% of 1,1-dichlorodifluoroethene) were used as supplied.

$B(OCH_3)_3$ (Aldrich) was distilled over Na before use. Antimony pentafluoride (N. N. Vorozhtsov Institute of Organic Chemistry, Novosibirsk) was distilled in a dry argon atmosphere. Diglyme (Merck), triglyme (Merck), THF (Baker), dichloromethane, ether, triethylamine, chlorotrimethylsilane were purified and dried using standard procedures. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni-electrodes).

Fluoroalkenes *trans*-RCF=CFH (R = C_4H_9 [4], C_6H_5 [5]) were prepared from trimethylsilyldifluoroalkenes *trans*-RCF=$CFSiMe_3$ and KF in aqueous DMSO using the literature procedures and distilled before use.

All manipulations with moisture-sensitive compounds were performed under dry argon atmosphere.

Preparation of starting compounds

Perfluoro-1-hexene. $C_6F_{13}COONa$ (87 g, 225 mmol) was heated at 200–300 °C under reduced pressure (40–60 hPa). The gaseous products were collected in two traps cooled at –70 to –80 °C and later warmed to room temperature, washed with water and dried with $MgSO_4$ and P_4O_{10}. After distillation perfluoro-1-hexene was obtained in 89% yield (60 g) (b. p. 55–56 °C, lit. 57 °C [15], 50–51 °C [16]) (The product contained ca. 6% of *trans*-$C_3F_7CF=CFCF_3$ (^{19}F-NMR)).

trans-1 H-Perfluoro-1-hexene. Tributylphosphane (19.9 g, 98 mmol) was added drop by drop into a stirred emulsion of perfluoro-1-hexene (29.6 g, 98 mmol) in diglyme (150 ml) at –50 °C within 30 min. The reaction mixture was slowly warmed to room temperature and showed the formation of *trans*-$C_4F_9CF=CFPFBu_3$ [δ(F): –15.8 (d, PF, ^{1}J(FP) 611), –81.8 (CF_3), –116.7 (2 F-3), –125.7 and –127.4 (2 CF_2), –138.0 and –166.7 (F-1 and F-2) ppm]. After addition of water (2 ml) the volatile products were distilled from the stirred solution at 120 to 130 °C (bath) during 3 h. The distillate was washed with water, dried with $MgSO_4$ and P_4O_{10} and re-distilled to yield 16.7 g (60%) of *trans*-1 H-perfluoro-1-hexene, b. p. 55–58 °C.

C_6HF_{11} (282,06): calculated C 25.55, H 0.36, F 74.09; found C 26.0, H 0.42, F 73.8%.

^{1}H-NMR ($CDCl_3$): 7.41; *J*, Hz: (H,F-1) 70.4, (H,F-2) 4.6.

^{19}F-NMR ($CDCl_3$): –82.03 (F-6), –119.75 (F-3), –125.80 (F-4), –127.42 (F-5), –164.32 (F-1), –176.82 (F-2); *J*, Hz: (1,H) 71, (1,2) 135, (1,3) 23, (1,4) 5, (3,5) 10, (4,6) 9.

IR (neat) $\tilde{\nu}$(cm^{-1}): 2984 m, 2876 m, 1774 w, 1718 m, 1688 w, 1448 w, 1383 m, 1352 s, 1296 m, 1241 vs, 1207 vs, 1190 vs, 1140 vs, 1022 m, 927 w, 877 s, 837 s, 792 m, 745 s, 714 m, 678 w, 628 w, 594 w, 519 w.

1 H,1 H-Perfluorooctyl nonaflate. A solution of 1 H,1 H-perfluorooctanol-1 (10.0 g, 25 mmol) and triethylamine (2.6 g, 26 mmol) in dichloromethane was cooled to 0 °C and perfluorobutanesulfonyl fluoride (10.0 g, 33 mmol) was added drop by drop under stirring. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 1 h. The volatile products were removed (evaporator) and the residual oil was dissolved in ether (80 ml). The etherial solution was washed with water and dried with $MgSO_4$. After removal of the solvent under reduced pressure 1 H,1 H-perfluorooctyl nonaflate (16.2 g, 95%) was obtained.

$C_{12}H_2F_{24}O_3S$ (682,17): calculated C 21.13, H 0.30, F 66.84, S 4.70; found C 21.3, H 0.30, F 66.9, S 5.20%.

^{1}H-NMR ($CF_2ClCFCl_2$): 4.86 ppm. ^{19}F-NMR ($CF_2ClCFCl_2$): –80.88 (2 CF_3), –109.58 (CF_2), –119.56 (CF_2), –120.71, –121.41, –122.38 (5 CF_2), –125.69 (2 CF_2) ppm.

IR $\tilde{\nu}$ (cm^{-1}): 3057 w, 3002 w, 2970 w, 2924 w, 2851 w, 1630 w, 1419 s, 1358 m, 1328 m, 1299 m, 1264 sh, 1237 vs, 1204 vs, 1146 vs, 1109 m, 1043 s, 1010 s, 958 m, 880 w, 839 w, 803 m, 773 m, 736 m, 701 m, 664 m, 647 m, 620 w, 596 m, 574 w, 533 m, 505 w, 482 m, 455 w.

1 H,1 H-Perfluorooctane. 1 H,1 H-Perfluorooctyl nonaflate (17.8 g, 27 mmol) and KF (7.6 g, 131 mmol) were stirred in triglyme (150 ml) at 170–200 °C. During 5 h the volatile products distilled off. The distillate was washed with water (3×5 ml) and dried with $MgSO_4$. The yield of 1 H,1 H-perfluorooctane was 8.2 g (75%). ^{1}H-NMR (neat): 4.69 ppm. ^{19}F-NMR (neat): –82.1 (CF_3), –123.2, –124.4, –126.9 (6 CF_2), –244.3 (CH_2F) ppm; *J*, Hz: (H,F-1) 46, (H,F-2) 11.

trans-1,2-Difluorohexen-1-yltrimethylsilane. CF_3CH_2F (12.3 g, 121 mmol) was condensed into cold ether (100 ml, –55 °C). 2.5 M BuLi (100 ml, 250 mmol) was added drop by drop to the –75 °C solution within 15 min. The solution was stirred at –60 °C for an additional hour. Chlorotrimethylsilane (14.2 g, 129 mmol) was added to the solution within 5 min. After 30 min of stirring at –60 °C a solution of trifluorovinyltrimethylsilane (^{19}F-NMR) was obtained.

A further portion of 2.5 M BuLi (50 ml, 125 mmol) was added at ≤ –50 °C and the resulting solution was warmed to room temperature. After washing with 10% HCl (300 ml) the organic phase was dried with $MgSO_4$ before the solvent was removed. *Trans*-1,2-difluorohexen-1-yltrimethylsilane (16.5 g, 71%) was isolated by vacuum-distillation, b. p. 60–62 °C (33 hPa) (lit. 50–52 °C (15 hPa) [4]).

$C_9H_{18}F_2Si$ (192,32): calculated C 56.21, H 9.43, F 19.76; found C 56.5, H 9.43, F 19.9%.

^{1}H-NMR ($CDCl_3$): 2.36 (2 H-3), 1.46 (4 H-4,5), 0.92 (3 H-6), 0.20 (SiCH_3) ppm; *J*(H-3,H-5) 7. ^{19}F-NMR ($CDCl_3$): –146.64 (F-2), –175.00 (F-1) ppm; *J*, Hz: (F-1,F-2) 126, (F-1,H-3) 6, (F-2,H-3) 23.

trans-1,2-Difluoro-2-phenylethen-1-yltrimethylsilane. A solution of $CF_2=CFSiMe_3$ prepared from CF_3CH_2F (12.6 g, 124 mmol), 2.5 M BuLi (100 ml, 250 mmol) and $ClSiMe_3$ (14.5 g, 132 mmol) in ether (250 ml) (see above) was reacted with 1.8 M PhLi in cyclohexane-ether (69 ml, 124 mmol) as described before. After removal of the solvent crude *trans*-1,2-difluoro-3-phenylethen-1-yltrimethylsilane (23 g) which

contained 16% of *trans*-BuCF=CFSiMe$_3$ was obtained and used for the preparation of *trans*-C_6H_5CF=CFH without purification.

5 H-Octafluoropentanoic acid. A three-necked 0.5 l flask was charged in sequence with water (110 ml), H_2SO_4 (52 ml) and $Na_2Cr_2O_7$ (35 g, 0.13 mol). Then 1 H,1 H,5 H-octafluoropentanol-1 (30.3 g, 0.13 mol) was added drop by drop at 95–98 °C under stirring within 15 min. The reaction mixture was refluxed for 4 h, cooled to 25 °C and extracted with ether (3×150 ml). The extracts were dried with $MgSO_4$ before the solvent was removed (evaporator). Conc. H_2SO_4 (100 ml) was added to the residual dark oil and the resulting solution was heated to 180–190 °C (bath) under stirring. Simultaneously 5 H-octafluoropentanoic acid (28 g, 87%), b. p. 155–158 °C distilled off.

cis-1 H-Heptafluoro-1-butene. Sodium 5 H-octafluoropentanoate (50 g) was prepared by neutralization of 5 H-octafluoropentanoic acid with aqueous NaOH, evaporation of water and drying in vacuum at 150 °C for 4 h. The salt was pyrolysed at 250–280 °C for 1.5 h. Volatile 4 H-heptafluoro-1-butene (29 g) was collected in a trap at –50 °C. For isomerization into *cis*-1 H-heptafluoro-1-butene [7] it was condensed on frozen SbF_5 at –40 °C (4 g) placed in a flask equipped with magnetic bar, reflux condenser (–78 °C) and inlet tube (Warning! The contact of 4 H-heptafluoro-1-butene with antimony pentafluoride causes an intensive heat evolution). At the end of the isomerization the stirred mixture was carefully warmed to 20–25 °C. *Cis*-1 H-heptafluoro-1-butene [23 g, 68% based on $H(CF_2)_4COONa$] distilled off and was collected at –50 °C.

^{19}F-NMR (ether): –84.42 (3 F-4), –122.88 (2 F-3), –151.23 (F-1), –157.16 (F-2) ppm (lit. [7] ^{19}F-NMR (neat liquid): –85.6, –124.1, –155.2, –157.3 ppm, respectively).

Preparation of potassium fluoroalken-1-yltrifluoroborates

*Potassium trifluorovinyltrifluoroborate (**1**).* 1 H,1 H-Tetrafluoroethane (8.6 g, 84 mmol) was condensed into THF (100 ml) at –75 °C and 2.5 M BuLi in hexane (63 ml, 157 mmol) was added drop by drop within 1 h. The reaction mixture was stirred for 40 min at –75 °C and then transferred into the pre-cooled (–90 °C) and stirred solution of $B(OCH_3)_3$ (16.4 g, 157 mmol) in THF (40 ml). The resulting suspension was additionally stirred for 30 min at –80 °C before it was warmed to room temperature within 4.5 h. The mother liquor was decanted. The solid residue was dissolved in THF-MeOH. After filtration and evaporation of the solvent crude lithium trifluorovinyltrimethoxyborate was obtained (white powder, 13.3 g) [δ(F) (THF): –100.6 (dd, F-2*trans*), –123.4 (dd, F-2*cis*), –192.9 (br. d, F-1) ppm). It was suspended in 1,1,2,2-tetrachloroethane (50 ml) and $ClSiMe_3$ (15 ml) was added. After stirring at room temperature for 1 h its ^{19}F NMR spectrum showed the formation of borane CF_2=CFB$(OCH_3)_2$ [δ(F) (THF-CH_2Cl_2): –86.27 (dd, F-2*trans*), –106.92 (dd, F-2*cis*), –199.30 (br. d, F-1) ppm; *J*(FF), Hz: (1,2*cis*) 112.1, (1,2*trans*) 24.8, (2*cis*,2*trans*) 44.5.]. Heating of the reaction mixture to 135–140 °C (bath) resulted in the simultaneous distillation of the volatile products (b. p. 40–72 °C). The products were distilled into a receiver which contained a stirred solution of K[HF_2] (20 g, 256 mmol) in water (50 ml) and MeOH (10 ml). The reaction mixture was stirred overnight before it was saturated with KF and extracted with MeCN (3×40 ml). The combined extracts were dried with Na_2SO_4 and evaporated to dryness. After washing with dry ether potassium trifluorovinyltrifluoroborate was obtained (9.3 g, 59% based on CF_3CFH_2).

C_2BF_6K (187,92): calculated C 12.78, F 60.66, found C 13.2, F 60.1%.

IR $\tilde{\nu}$ (cm^{-1}): 1761 vs, 1626 w, 1441 w, 1316 vs, 1293 s, 1233 vs, 1090 s, 1024 vs, 972 vs, 939 vs, 915 vs, 615 s.

Potassium trans-perfluorohexen-1-yldifluoro(methoxy)borate. A solution of *trans*-1 H-perfluoro-1-hexene (3.1 g, 11 mmol) in ether (30 ml) was cooled to –80 °C and 1.6 M BuLi in hexane (6 ml, 9.6 mmol) was added drop by drop within 15 min. The reaction mixture was stirred for 1 h at –60 to –65 °C and then transferred into the pre-cooled (–90 °C) and stirred solution of $B(OCH_3)_3$ (1.8 g, 17 mmol) in ether (20 ml). The resulting suspension was stirred for an additional hour at –70 to –55 °C before it was warmed to room temperature within 1 h. The obtained solution was evaporated under reduced pressure. The residue was dissolved in MeOH (10 ml) and poured into a solution of K[HF_2] (7 g, 90 mmol) in water (50 ml). After stirring overnight the solution was saturated with KF and extracted with acetone (2×20 ml). The combined extracts were dried with $MgSO_4$. After evaporation of the solvent the yellow product was washed with dichloromethane (10 ml) and dried in vacuum to yield solid potassium *trans*-perfluorohexen-1-yldifluoro-(methoxy)borate (1.7 g, 45%).

$C_7H_3BF_{13}KO$ (399,99): calculated C 21.02, H 0.76, F 61.75; found C 21.9, H 0.99, F 61.3%.

^{1}H-NMR (acetone-d_6): 2.96 ppm. ^{19}F-NMR (acetone-d_6): –80.27 (CF_3), –115.30 (2 F-3), –123.70 (2 F-4), –125.36 (2 F-5), –151.55 and –177.54 (F-1 and F-2), –144.00 (BF_2) ppm; *J*, Hz: (1,2) 130, (F,B) 36.

*Potassium trans-perfluorohexen-1-yltrifluoroborate (**5**).* A solution of *trans*-1 H-perfluorohexene (15.2 g, 54 mmol) in ether (140 ml) was cooled to –80 °C and 1.6 M BuLi in hexane (35 ml, 56 mmol) was added drop by drop within 20 min. The reaction mixture was stirred for 1 h at –75 to –80 °C before it was transferred into the pre-cooled (–90 °C) and stirred solution of $B(OCH_3)_3$ (11.3 g, 108 mmol) in ether (50 ml). Following the solution was stirred for 1 h at –70 to –75 °C and finally warmed to room temperature within 2 h. The solution was concentrated to ca. 60 ml volume under reduced pressure and poured into a solution of K[HF_2] (35 g, 449 mmol) in water (75 ml) and 40% HF (40 ml). After stirring overnight the reaction mixture was saturated with KF and extracted with ether (5×50 ml). The combined extracts were dried with K_2CO_3. The solvent was evaporated and potassium *trans*-perfluorohexen-1-yltrifluoroborate was dried in vacuum (15.1 g, 72%).

$C_6BF_{14}K$ (387,95): calculated C 18.58, F 68.56; found C 18.6, F 69.2%.

IR $\tilde{\nu}$ (cm^{-1}): 1363 m, 1332 m, 1264 s, 1240 vs, 1210 vs, 1137 vs, 1081 w, 1063 m, 1045 m, 1010 vs, 981 s, 878 m, 863 s, 770 m, 752 s, 734 vs, 702 w, 656 w, 624 m, 598 s, 569 w, 534 m, 472 m, 409 w.

*Potassium trans-1,2-difluorohexen-1-yltrifluoroborate (**6**).* A solution of *trans*-1,2-difluoro-1-hexene (10.0 g, 83 mmol) in THF (100 ml) was cooled to –60 °C and 2.5 M BuLi in hexane (33 ml, 83 mmol) was added drop by drop within 20 min. The reaction mixture was stirred for 0.5 h at –60 °C and then

transferred into the pre-cooled (–65 °C) and stirred solution of $B(OCH_3)_3$ (15 g, 144 mmol) in THF (70 ml). After 15 min at –60 °C it was warmed to room temperature within 1.5 h. The ^{19}F-NMR spectra of the resulting suspension showed the presence of *trans*-$C_4H_9CF{=}CFB(OMe)_2$ [δ(F): –145.14 (F-2), –173.27 (F-1) ppm; *J*, Hz: (F-1,F-2) 127, (F-2,H-3) 23] and Li [*trans*-$C_4H_9CF{=}CFB(OMe)_3$] [δ(F): –159.53 (F-2), –170.60 (F-1) ppm; *J*, Hz: (F-1,F-2) 115, (F-2,H-3) 24]. The suspension was concentrated under reduced pressure and poured into a solution of $K[HF_2]$ (50 g, 641 mmol) in water (100 ml), MeOH (20 ml) and 40% HF (50 ml). After stirring for 6 h the reaction mixture was saturated with KF and extracted with MeCN (3×100 ml). The combined extracts were dried with K_2CO_3 and evaporated in vacuum to yield potassium *trans*-1,2-difluorohexen-1-yltrifluoroborate (9.5 g, 51%).

$C_6H_9BF_5K$ (226,04): calculated C 31.88, H 4.01, F 42.02; found C 31.5, H 4.25, F 41.9%.

IR $\tilde{\nu}$ (cm^{-1}): 2961 s, 2932 s, 2875 s, 1707 s, 1626 w, 1468 m, 1434 m, 1374 w, 1315 m, 1292 m, 1266 s, 1207 s, 1156 vs, 1016 vs, 969 vs, 903 m, 880 s, 838 m, 751 m, 627 m, 581 m, 560 m, 491 w, 455 w.

*Potassium trans-1,2-difluoro-2-phenylethen-1-yltrifluoroborate (**7**).* A solution of *trans*-1,2-difluoro-2-phenylethene (6.3 g, 45 mmol) in ether (100 ml) was cooled to –70 °C and 2.5 M BuLi in hexane (18 ml, 45 mmol) was added drop by drop within 5 min. The reaction mixture was stirred for 1 h at –60 °C before $B(OCH_3)_3$ (6.2 g, 59 mmol) was added. After 15 min at –60 °C the stirred solution was warmed to room temperature within 1 h. The ^{19}F NMR spectrum showed the presence of *trans*-$C_6H_5CF{=}CFB(OMe)_2$ [δ(F): –150.57 (F-1), –164.38 (F-2) ppm; *J*, Hz: (F-1,F-2) 109] and Li[*trans*-$C_6H_5CF{=}CFB(OMe)_3$] [δ(F): –160.16 (F-1), –164.05 (F-2) ppm; *J*, Hz: (F-1,F-2) 113]. The solution was concentrated under reduced pressure and poured into a solution of $K[HF_2]$ (23 g, 396 mmol) in water (40 ml), MeOH (10 ml) and 40% HF (20 ml). After stirring for 5 h the reaction mixture was saturated with KF and extracted with MeCN (2×100 ml). The combined extracts were dried with K_2CO_3 and $MgSO_4$ and evaporated under vacuum to yield potassium *trans*-1,2-difluoro-2-phenylethen-1-yltrifluoroborate (5.2 g, 47%).

$C_8H_5BF_5K$ (246,03): calculated C 39.06, H 2.05, F 38.61; found C 39.7, H 2.23, F 38.7%.

IR $\tilde{\nu}$ (cm^{-1}): 3065 m, 3031 w, 1666 w, 1495 m, 1447 m, 1339 m, 1320 m, 1303 m, 1276 m, 1237 m, 1202 vs, 1188 m, 1114 m, 1091 s, 1068 vs, 1026 vs, 990 vs, 812 s, 762 s, 691 s, 633 m, 608 s, 592 m, 530 m.

*Potassium cis-perfluoroocten-1-yltrifluoroborate (**4**).* A solution of 1 H,1 H-perfluorooctane (8.2 g, 20 mmol) in THF (190 ml) was cooled to –75 °C and 1.6 M BuLi in hexane (27 ml, 43 mmol) was added drop by drop within 15 min. The reaction mixture was stirred for 1 h at this temperature and then transferred into the pre-cooled (–75 °C) and stirred solution of $B(OCH_3)_3$ (4.0 g, 38.4 mmol) in THF (40 ml). The resulting suspension was stirred for an additional hour at –70 °C before it was warmed to room temperature within 3 h. The obtained solution was concentrated to ca. 80 ml volume under reduced pressure and poured into a solution of $K[HF_2]$ (18.5 g, 237 mmol) in water (50 ml) and 40% HF (20 ml). After stirring overnight it was saturated with KF and extracted with ether (3×50 ml). The combined extracts were treated with K_2CO_3 and dried with $MgSO_4$. After evaporation of the solvent the brownish viscous oil was washed with benzene (3×5 ml) and with $CFCl_3$ (5×10 ml) and dried in vacuum to yield potassium *cis*-perfluoroocten-1-yltrifluoroborate (4.8 g, 49%).

$C_8BF_{18}K$ (487,97): calculated C 19.69, F 70.08; found C 19.6, F 69.9%.

IR $\tilde{\nu}$ (cm^{-1}): 1686 s, 1627 w, 1368 m, 1330 w, 1307 m, 1293 w, 1239 s, 1204 vs, 1146 vs, 1127 m, 1071 m, 1029 s, 1000 m, 922 s, 863 w, 846 s, 805 w, 774 m, 763 s, 745 m, 714 s, 670 s, 637 m, 624 w, 610 w, 585 w, 565 w, 533 m, 483 w, 417 w.

*Potassium cis-heptafluorobuten-1-yltrifluoroborate (**3**).* A solution of *cis*-1 H-heptafluoro-1-butene (13.9 g, 76 mmol) in ether (300 ml) was cooled to –85 °C and 2.5 M BuLi in hexane (32 ml, 80 mmol) was added drop by drop within 15 min at ≤ –85 °C. After stirring for 40 min, a solution of $B(OCH_3)_3$ (8.1 g, 78 mmol) in ether (8 ml) was added within 10 min via a septum using a syringe. The reaction mixture was additionally stirred for 40 min at –85 °C and then warmed to room temperature within 1.5 h. The obtained suspension was concentrated to ca. 70 ml volume under reduced pressure and formed a high viscous phase. The ^{19}F-NMR spectrum showed the presence of *cis*-1 H-heptafluoro-1-butene and presumably, Li[*cis*-$C_2F_5CF{=}CFB(OMe)_3$] [resonances at –83.63 (3 F), –119.98 (2 F), –134.62 (1 F), –153.57 (1 F) ppm] in the 1 : 4 ratio. The viscous phase was poured into a solution of $K[HF_2]$ (47 g, 602 mmol) in water (150 ml) and MeOH (30 ml). The resulting two-phase system was stirred for 1 h. The organic phase was separated, the aqueous one was acidified with a few drops of 40% HF and extracted with ether (3×100 ml). After drying with $MgSO_4$, the combined extracts showed the presence of K[*cis*-$C_2F_5CF{=}CFBF_n(OMe)_{3-n}$] [broadened resonances at –83.2 (3 F), –117.9 (2 F), –135.6 (1 F), –151.0 and 153.6 (total 1 F) and –140.2, –144.2 (B–F) ppm].

The extract was concentrated under reduced pressure, dissolved in MeOH (20 ml) before 40% HF (10 ml) was added. The solution was stirred for 1 h, diluted with water (40 ml) and neutralized with solid K_2CO_3. After evaporation to dryness, the white solid was extracted with acetone (3×50 ml) and the extracts were dried with $MgSO_4$. The solvent was removed, the residue was washed with anhydrous CH_2Cl_2 (50 ml) and dried in vacuum to yield K[*cis*-$C_2F_5CF{=}CFBF_3$] (9.5 g, 43% based on *cis*-$C_2F_5CF{=}CFH$).

$C_4BF_{10}K$ (287,94): calculated C 16.69, F 65.98, found C 16.7, F 66.0%.

IR $\tilde{\nu}$ (cm^{-1}): 1693 s, 1331 s, 1227 vs, 1167 m, 1135 s, 1058 s, 1006 vs, 959 s, 859 vs, 744 vs, 684 w, 643 s, 614 w, 543 m.

*Potassium cis-, trans-chlorodifluoroethen-1-yltrifluoroborate (**2**).* A solution of *cis*-, *trans*-1,2-dichlorodifluoroethene (9.2 g, 69 mmol) (*cis* : *trans* = 47 : 53) in ether (150 ml) was cooled to –90 °C and 1.7 M *t*-BuLi in pentane (41 ml, 69 mmol) was added drop by drop within 30 min. After stirring for 30 min at ≤ –83 °C, a solution of $B(OCH_3)_3$ (7.2 g, 69 mmol) in ether (10 ml) was added within 5 min via a septum using a syringe. The reaction mixture was additionally stirred for 40 min at –85 °C and then warmed to room temperature within 4 h. After concentration to ca. 70 ml volume under reduced pressure the resulting viscous phase was poured into a solution of $K[HF_2]$ (43 g, 551 mmol) in water (130 ml) and MeOH (30 ml). The two-phase system was stirred for 2 h. The organic phase was separated, the aqueous one was saturated with KF and extracted with acetone

(2×50 ml). The combined acetone extracts were dried with $MgSO_4$, before the solvent was removed.

The residue was dissolved in MeOH (45 ml) and 40% HF (4 ml) was added. The solution was stirred for 2 h, diluted with water (20 ml) and neutralized with solid K_2CO_3. After evaporation to dryness, the white solid was extracted with acetone (2×30 ml) and the extract was dried with $MgSO_4$. The solvent was removed and the solid dried in vacuum to yield K[*cis*-, *trans*-ClCF=CFBF_3] with an admixture of K[F_2C=CClBF_3] (ratio 44:46:9) (7.7 g, 54% based on ClCF=CFCl).

C_2BClF_5K (204,38): calculated C 11.75, Cl 17.35, F 46.48; found C 11.1, Cl 16.9, F 47.0%.

IR $\tilde{\nu}$ (cm^{-1}): 1724 w, 1683 s, 1635 w, 1300 w, 1246 s, 1224 s, 1134 vs, 1080 s, 1028 vs, 969 vs, 880 s, 813 s, 655 m, 589 m, 534 w, 522 m.

The reaction of $B(OCH_3)_3$ with K[HF_2]

K[HF_2] (234 mg, 3.0 mmol) was dissolved in water (0.93 ml) and MeOH (0.30 ml) and $B(OCH_3)_3$ (92 mg, 0.88 mmol) was added under stirring. After 1 h the mother liquor of the suspension was decanted and the precipitate was dissolved in water. The ^{19}F-NMR spectra of both solutions displayed the resonance of the aqueous fluoride anion (br, –138 to –145 ppm), of the $[BF_3OCH_3]^-$ anion (–148.8 ppm; 1:1:1:1 quartet, ^{1}J(FB) 15 Hz] [17], of $[BF_4]^-$ (small amounts) and a weak unrecognized resonance at –155 ppm (1:1:1:1 quartet) which disappeared within 4 days. The final molar ratio $[BF_3OCH_3]^-$ to $[BF_4]^-$ was 96:4.

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