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(Fluoroorgano)fluoroboranes and -fluoroborates I: synthesis and spectroscopic characterization of potassium fluoroaryltrifluoroborates and fluoroaryldifluoroboranes

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Abstract

A convenient preparation of K[$ArBF_3$] (Ar = 2-C_6H_4F, 3-C_6H_4F, 4-C_6H_4F, 2,6-$C_6H_3F_2$, 3,5-$C_6H_3F_2$, 2,4,6-$C_6H_2F_3$, 3,4,5-$C_6H_2F_3$, 2,3,4,5-C_6HF_4 and C_6F_5) is offered and the IR and multinuclear NMR spectra of these salts are reported. Treatment of the trifluoroborate salts with BF_3 in chlorocarbon solvents provides an easy synthetic route to the corresponding aryldifluoroboranes $ArBF_2$. The multinuclear NMR spectra of $ArBF_2$ are presented. The electron substituent effect of the $[-BF_3]^-$-group shows this substituent as one of the strongest σ-electron donors, while its π-electron influence is negligible ($\sigma_I = -0.32$, $\sigma_R = -0.07$).

Keywords: Boranes; Borates; Boronic acid; Fluorophenyl boron compounds; NMR

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1. Introduction

The chemistry of aryldihalogenoboranes $ArBX_2$ (X = F, Cl, Br, I) is generally well established. Surprisingly, there are only a few communications concerning preparations and reactivity of the fluoro-containing aryldifluoroboranes $C_6H_nF_{5-n}BF_2$ and of the corresponding fluoroaryltrifluoroborates M[$C_6H_nF_{5-n}BF_3$]. Brownlee and Taft [1] used 3- and 4-fluorophenyldifluoroboranes to determine the electronic effects of the BF_2-group but did not describe neither the preparation nor the spectra of those boranes. The first synthesis of pentafluorophenyldifluoroborane $C_6F_5BF_2$ by reaction of $C_6F_5BCl_2$ with SbF_3 or $C_6F_5SnMe_3$ with BF_3 was reported by Chambers and Chivers [2,3]. Vedejs et al. have prepared potassium 5-R-2-fluorophenyltrifluoroborates (R = H, Me, CH=CMe$_2$, menthyloxy) and used some of those borates for in situ generation of the corresponding adducts $ArBF_2$·Base (Base = THF, MeCN) by reaction with $ClSiMe_3$ in THF or MeCN [4]. To our knowledge, no further attempts were undertaken neither to offer alternative routes to fluorophenyldifluoroboranes nor -trifluoroborates nor to optimize the reported preparations.

We are interested in fluorinated aryldifluoroboranes as potentially useful precursors for arylxenon(II) tetrafluoroborates and have studied some preparative routes to those compounds.

2. Results and discussion

One of the possible routes to fluoro-containing aryldifluoroboranes is the borondemetalation of substrates $ArMR_n$ with BX_3 followed by fluoridation of the intermediate $ArBX_2$ (X = Cl, Br). Haubold et al. have prepared some mono-substituted phenyldihalogenoboranes in good yields by reaction of $RC_6H_4SiMe_3$ with either boron trichloride or tribromide [5]. However, we found that under the same conditions boron tribromide did not react with the electron-poor aryl group in the substrate $C_6F_5SiMe_3$. This is not surprising taking into account the significantly decreased nucleophilicity of the aryl group in trimethylsilylpentafluorobenzene with respect to its hydrocarbon analogue [6].

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The borane $C_6F_5BCl_2$ was obtained by reaction of $C_6F_5SnMe_3$ or C_6F_5HgMe with boron trichloride in a good yield [3], whereas the reported yield of $C_6F_5BBr_2$ from $C_6F_5SnMe_3$ and boron tribromide was only 22% [7a]. We were able to optimize the yield of that dibromoborane up to 82% by using ethylmercuriopentafluorobenzene as substrate.

$$C_6F_5HgEt + BBr_3 \xrightarrow[-50°\text{C to r.t.}]{CH_2Cl_2} \underset{82\%}{C_6F_5BBr_2} + EtHgBr$$

$C_6F_5BBr_2$ can also be prepared from C_6F_5HgBr and BBr_3 [7b].

Using pentafluorophenyldihalogenoboranes as starting materials in halogen–fluorine substitution reactions, we attempted to prepare $C_6F_5BF_2$ from $C_6F_5BCl_2$ and SbF_3. But we were unable to reproduce the described procedure [3]. Pentafluorophenylantimony derivatives and BF_3 were obtained at -25 to -20°C. Pentafluorophenyldifluoroborane (**1**) was prepared successfully on an alternative route from the corresponding dichloroborane (**2**) and dibromoborane (**3**) in the two-phase fluoridation system, anhydrous HF (aHF)–dichloromethane or CCl_3F, which had previously been used for the synthesis of trifluorosilylpentafluorobenzene from $C_6F_5SiCl_3$ or $C_6F_5Si(OEt)_3$ [8,9].

$$\underset{\mathbf{2}}{C_6F_5BCl_2} + 2HF \xrightarrow[-50°\text{C to r.t.}]{CCl_3F} \underset{\mathbf{1}}{C_6F_5BF_2} + 2HCl$$

$$\underset{\mathbf{3}}{C_6F_5BBr_2} + 2HF \xrightarrow[-50\text{ to }-5°\text{C.}]{CH_2Cl_2} \underset{\mathbf{1}}{C_6F_5BF_2} + 2HBr$$

Despite of the appropriate yields of product **1**, we decided to evaluate alternative routes to $C_6F_5BF_2$ and other fluoroaryldifluoroboranes which avoid toxic organomercurials and highly moisture-sensitive boranes **2** and **3** as substrates. A general route consists in the defluoridation of fluoroaryltrifluoroborate anions with a suitable fluoride acceptor which was principally known from the following examples [10]:

$$\underset{X = 3\text{-F, }4\text{-F}}{[X-C_6H_4Xe][X-C_6H_4BF_3]} + BF_3$$
$$\xrightarrow{CH_2Cl_2} [X-C_6H_4Xe][BF_4] + X-C_6H_4BF_2$$

However, until recently the only known alkali fluoroaryltrifluoroborate $K[C_6F_5BF_3]$ was prepared from KF and aryldifluoroborane (**1**) in aqueous solution [11] and there was no alternative pathway to fluoroaryltrifluoroborates till 1995 when Vedejs et al. elaborated a convenient synthesis of potassium aryltrifluoroborates from arylboronic acids and $K[HF_2]$ in aqueous methanol [4]. We have found that this procedure is also available for the preparation of mono- and polyfluorinated phenyltrifluoroborates. Starting with the arylation of alkoxyboranes we got the products 18 $K[ArBF_3]$ without the isolation of the intermediate fluoroaryldialkoxyboranes and -boronic acids [12].

Reactions of pentafluorophenylmagnesium bromide with $B(OAlk)_3$ (2–2.3 equivalents) in ether at -40 to 0°C showed a decreasing reactivity of trialkoxyboranes in the series $B(OCH_3)_3 > B(OC_3H_7)_3 > B(O\text{-}i\text{-}C_3H_7)_3$. Immediately precipitation took place when the Grignard reagent was added to the solution of $B(OCH_3)_3$ at -40°C. After 1 h the resonances of C_6F_5MgBr had disappeared (^{19}F-NMR), whereas tripropoxyborane did not react with C_6F_5MgBr under the same conditions. Here the reaction began at -5 to 0°C and was completed within 1 h. Triisopropoxyborane was the less reactive alkoxyborane and C_6F_5MgBr was still present in the solution after 4 h at 0°C. The total consumption of C_6F_5MgBr was achieved at room temperature after 3–4 h.

After consumption of the Grignard reagent the ^{19}F-NMR spectra of the mother liquor, contained in all cases, the resonances of pentafluorophenyldialkoxyboranes at ca. -132.9 (F-2,6), -153.4 (F-4) and -162.4 (F-3,5) ppm, of an admixture of pentafluorobenzene and, presumably, of anions $[(C_6F_5)_nB(OAlk)_{4-n}]^-$ ($n = 1, 2$) with broad resonances which were located at lower frequencies [ca. -133, -157 and -165 ppm] than those of the boranes $C_6F_5B(OAlk)_2$. Hydrolysis of the reaction suspensions with diluted HCl and the subsequent treatment of the crude product with $K[HF_2]$ in water–methanol gave $K[C_6F_5BF_3]$ (**4**) [14a] and $K[(C_6F_5)_2BF_2]$ [14b] in the ratio 85:15%, respectively. The pure salt **4** was obtained in 60–70% yield after washing the crude product with water saturated ether and subsequent drying over P_4O_{10} in vacuum.

In one experiment with C_6F_5MgBr and $B(OCH_3)_3$, the reaction suspension was separated into mother liquor and solid phase and both phases were hydrolyzed and treated with $K[HF_2]$ in aqueous methanol, separately. The ^{19}F-NMR spectra showed the admixture of $K[(C_6F_5)_2BF_2]$ mainly in the product obtained from the solid phase while only traces were detected in the product produced from the mother liquor.

Similar results were obtained in the reaction of C_6F_5Li with excess of $B(OC_3H_7)_3$ in ether–hexane and subsequent hydrolysis and fluoridation of the crude product with $K[HF_2]$.

$$C_6F_5M \xrightarrow{B(OAlk)_3} C_6F_5B(OAlk)_2 + M[(C_6F_5)_nB(OAlk)_{4-n}]$$
$$\xrightarrow[]{\substack{1.\ \text{aq. HCl}\\ 2.\ K[HF_2]}} \underset{\mathbf{4}}{K[C_6F_5BF_3]} + K[(C_6F_5)_2BF_2]$$

$M = Li, MgBr; Alk = Me, Pr, i\text{-}Pr; n = 1, 2$

Based on the above results, we tried to generalize our procedure for electron-poor fluorinated aryl systems. A series of potassium fluoroaryltrifluoroborates were prepared in good yields.

$$ArM \xrightarrow[\substack{1.\ B(OAlk)_3\\ 2.\ \text{aq. HCl}\\ 3.\ K[HF_2]}]{} \underset{\mathbf{5-12}}{K[ArBF_3]}$$

M = MgX, Li; Ar = 2-C_6H_4F (**5**), 3-C_6H_4F (**6**), 4-C_6H_4F (**7**), 2,6-$C_6H_3F_2$ (**8**), 3,5 − $C_6H_3F_2$ (**9**), 2,4,6-$C_6H_2F_3$ (**10**), 3,4,5-$C_6H_2F_3$ (**11**), 2,3,4,5-C_6HF_4 (**12**).

Fluoroaryltrifluoroborates $K[ArBF_3]$ are soluble in MeOH, aq. MeOH, MeCN, acetone, DMF, slightly soluble in water and insoluble in ether, CH_2Cl_2 and CF_3CH_2OH.

Treatment of a chlorocarbon (CH_2Cl_2, CCl_3F) suspension of $K[ArBF_3]$ with BF_3 gas led to the formation of the corresponding aryldifluoroboranes and $K[BF_4]$. For aryl-fluorine substitution reactions with element fluorides $ArBF_2$ can be used directly after degassing in the chlorocarbon solution of known concentration. However, they can be also isolated easily by distillation in thoroughly dried glass equipment, which was demonstrated for pentafluorophenyldifluoroborane.

$$K[ArBF_3] + BF_3 \xrightarrow[-40\ \text{to}\ -50°C]{CH_2Cl_2} \underset{\mathbf{1},\ \mathbf{13-20}}{ArBF_2} + K[BF_4]$$

Ar = 2-C_6H_4F (**13**), 3-C_6H_4F (**14**), 4-C_6H_4F (**15**),

2,6-$C_6H_3F_2$ (**16**), 3,5-$C_6H_3F_2$ (**17**), 2,4,6-$C_6H_2F_3$ (**18**),

3,4,5-$C_6H_2F_3$ (**19**), 2,3,4,5-C_6HF_4 (**20**), C_6F_5 (**1**)

Aryldifluoroborane (**1**) is a colorless liquid which fumes on air (fast hydrolysis). Compound **1** is thermally stable at r.t. in a dry atmosphere. Chambers and Chivers have reported the slow conversion of $C_6F_5BF_2$ to $(C_6F_5)_2BF$ and BF_3 at r.t. (40% conversion within one month) [2] or at higher temperatures (77% conversion of **1** after 16 h at 95°C followed by 18 h at 195°C) [3]. In a dichloromethane solution of **1**, we did not detect such dismutation reaction over 1 month at 20°C.

The ^{19}F chemical shifts of the *meta*- and *para*-fluorine atoms of $K[C_6F_5BF_3]$ in basic solvents (MeCN, MeOH, acetone, DMF) appeared substantially shielded which is typical for pentafluorobenzenes C_6F_5X bearing an electron-donating substituent X [15] (Table 1). It is a general feature, that the positions of ^{19}F resonances of the fluorine atoms bonded to boron depend from the presence of *ortho*-fluorine atoms in fluoroaryltrifluoroborates $K[C_6H_nF_{5-n}BF_3]$ and -difluoroboranes $C_6H_nF_{5-n}BF_2$ as well. In the ^{19}F-NMR spectra of potassium phenyltrifluoroborate [4] and fluoroaryltrifluoroborates **6**, **7**, **9** and **11** (no *ortho*-fluorine atoms) the signal of the BF_3^--group is located at −141 to −142 ppm. In aryltrifluoroborates **5** and **12** (one *ortho*-fluorine) the BF_3^--signal is shifted to -139.06 ± 0.36 ppm. When both *ortho*-positions were occupied by fluorine atoms (trifluoroborates **4**, **8** and **10**) the resonance of the BF_3^--group is placed at -133.30 ± 0.30 ppm. A similar effect was observed in the ^{19}F-NMR spectra of aryldifluoroboranes where the position of the BF_2-group changed from -91.43 ± 1.24 ppm (boranes **14**, **15**, **17** and **19**) to -75.58 ± 1.15 ppm (boranes **1**, **16** and **18**) (Table 2). However, those significant changes in the $\delta(F)$ values of BF_3^-- as well as BF_2-group are not accompanied by remarkable changes in the ^{11}B-NMR spectra of the aryltrifluoroborates and aryldifluoroboranes, respectively (Tables 3 and 4). The trifluoroborates show 1:1:1:1-quartets at 2.76 ± 0.95 ppm and the

Table 1
^{19}F-NMR spectra of potassium fluorophenyltrifluoroborates $K[ArBF_3]$ (35°C)

Ar	Solvent	Chemical shifts (ppm)						*J* (Hz)
		F-2	F-3	F-4	F-5	F-6	$[–BF_2]^-$	
C_6F_5	Acetone	−133.97	−165.70	−161.43	−165.70	−133.97	−133.62	(3,4) 19.5, (2, B*F*) 11
C_6F_5	CD_3CN	−135.17	−165.26	−160.74	−165.26	−135.17	−133.43	(3,4) 19.4, (2, B*F*) 12.0
C_6F_5 [14a] [a]	CH_3CN	−135.3	−164.9	−160.5	−164.9	−135.3	−132.2	
C_6F_5	CD_3OD	−134.70	−165.57	−160.65	−165.57	−134.70	−134.84	(3,4) 19.2
C_6F_5 [11]	aq. EtOH	−134.7	−165.6	−160.7	−165.6	−134.7	−134.7	
C_6F_5	DMF	−133.74	−165.67	−161.52	−165.67	−133.74	−132.79	(3,4) 20.0, (2, B*F*) 12.0
C_6F_5	40% aq. HF	−136.63	−164.06	−157.69	−164.06	−136.63	−131.65	(3,4) 19.5
C_6F_5	aHF [b]	−136.20	−163.22	−155.28	−163.22	−136.20	−131.88	(3,4) 18.3
2,3,4,5-C_6HF_4	Acetone	−135.20	−160.19	−162.76	−143.34		−139.40	(2,3) 20, (2,4) 9.5, (3,4) 20, (4,5) 19
2,3,4,5-C_6HF_4	CD_3CN	−136.25	−159.72	−162.04	−143.01		−139.16	(2,3) 22, (2,4) 9, (3,4) 19, (4,5) 19
2,4,6-$C_6H_2F_3$	DMF	−99.75		−114.94		−99.75	−133.00	(2,3) 9.4, (2,4) 10.2, (3,4) 7.0
3,4,5-$C_6H_2F_3$	Acetone		−139.40	−168.10	−139.40		−142.10	(2,3) 9.7, (2,4) 7.6, (3,4) 19.4
3,4,5-$C_6H_2F_3$	CD_3CN		−138.96	−167.26	−138.96		−141.88	(2,3) 9.7, (2,4) 7.4, (3,4) 19.0
2,6-$C_6H_3F_2$	Acetone	−103.23				−103.23	−133.60	(2, B*F*) 11
2,6-$C_6H_3F_2$	CD_3CN	−104.26				−104.26	−133.54	(2, B*F*) 11
3,5-$C_6H_3F_2$	Acetone		−113.71		−113.71		−142.12	(2,3) 6.0, (3,4) 9.0
3,5-$C_6H_3F_2$	CH_3CN		−113.24		−113.24		−141.81	
2-C_6H_4F	Acetone	−108.32					−138.72	
3-C_6H_4F	Acetone		−116.50				−143.37	
3-C_6H_4F	CD_3CN		−116.16				−141.63	
4-C_6H_4F	CD_3CN			−117.73			−140.99	(2,4) 6.6, (3,4) 9.8

[a] Cation $[C_6F_5Xe]^+$, at −30°C.
[b] At −40°C, see text.

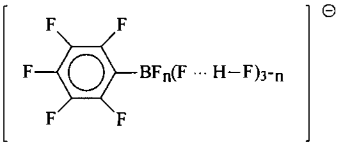
Table 2
^{19}F-NMR spectra of fluorophenyldifluoroboranes $ArBF_2$ (CH_2Cl_2, 35°C)

Ar	Chemical shifts (ppm)						J (Hz)
	F-2	F-3	F-4	F-5	F-6	$-BF_2$	
C_6F_5	−128.97	−161.26	−143.82	−161.26	−128.97	−74.43	(2,4) 6.5, (3,4) 19.3
C_6F_5 [3] [a]	−127.8	−160.4	−143.0	−160.4	−127.8	[b]	
2,3,4,5-C_6HF_4	−128.34	−155.19	−145.85	−138.53		−83.04	(2,3) 20, (2,4) 9, (2,5) 3, (3,4) 19, (3,5) 9, (4,5) 19, (4,6) 9, (5,6) 15
2,4,6-$C_6H_2F_3$	−96.30		−97.52		−96.30	−76.72	(2,4) 9, (3,4) 11
3,4,5-$C_6H_2F_3$		−134.22	−152.04	−134.22		−90.38	(2,3) 7, (2,4) 7, (3,4) 20
2,6-$C_6H_3F_2$	−99.99				−99.99	−75.65	
3,5-$C_6H_3F_2$		−109.65		−109.65		−90.19	
2-C_6H_4F	−102.50					−84.69	
3-C_6H_4F		−113.49				−91.11	
4-C_6H_4F			−104.01			−92.66	

[a] In CCl_4.
[b] No data.

difluoroboranes broad signals at 23.77 ± 0.92 ppm. In both classes of compounds, the ^{19}F shift values for fluorine bonded to boron are influenced by the re-distribution of partial negative charge from the aryl group to the fluorine atoms at boron parallel to the decreasing number of electron-withdrawing fluorine substituents in the *ortho*-positions.

The comparison of the ^{19}F-NMR spectrum of a freshly prepared solution of borate (**4**) in acidic media (aHF or 40% HF) with that in basic solvents (Table 1) showed a significant deshielding of the *para* fluorine atom parallel to a smaller shielding of the *ortho*-fluorine atoms in acid solutions. Nevertheless, these changes cannot be interpreted as abstraction of the fluoride anion from $[C_6F_5BF_3]^-$ by H^+ because for the formation of $C_6F_5BF_2$ the resonances of the *para*- as well as *ortho*- fluorine atoms should be shifted to high frequency (cf. ^{19}F-NMR spectrum of pentafluorophenyldifluoroborane, Table 2). A possible rationalization consists in the partial protonation (or addition of HF) of (on) the fluorine atoms bonded to boron which causes reduction of the effective negative charge of the three fluorine atoms and consequently of the C_6F_5-group as well. Additionally, this process is not accompanied by a remarkable change of the steric requirement of the $-BF_3$-substituent. The combination of electronic (deshielding of *p*-F) and steric (shielding of *o*-F) effects may explain the unexpected shift behaviour of the *p*- and *o*-F atoms.



Moreover it should be noted that in aHF solution at −20 to −40°C, the resonances of the fluorine atoms bonded to boron became broad and disappeared within 15–30 min while the resonances of the ring bonded fluorine atoms did not change. Probably, the increase of the electric quadrupole of the boron atom caused by the lower symmetry of the coordination sphere of **4** in aHF solution in comparison to basic solutions is a reasonable explanation.

The availability of potassium fluorophenyltrifluoroborates (**6** and **7**) allowed us to determine the electron substituent parameters of the BF_3^--group based on the Taft's method (^{19}F-NMR) [1,16–18]. The calculated values $\sigma_I = -0.32$, $\sigma_R = -0.07$, $\sigma_m = -0.35$ and $\sigma_p = -0.39$ (in MeCN) showed the closed similarity to that of the $B(OH)_3^-$-group [$\sigma_I = -0.36$ (in MeOH)] [16]. This result displays both substituents as strongest σ-electron donors while their π-electron effects are negligible.

Additionally we re-investigated the electron substituent effects of the BF_2-group based on the ^{19}F-NMR spectra of fluorophenyldifluoroboranes (**14** and **15**) in dichloromethane and determined σ_I (BF_2) = 0.15, σ_R (BF_2) = 0.30, σ_m (BF_2) = 0.45 and σ_p (BF_2) = 0.37. For comparison, we compile the literature data obtained with different methods: σ_I (BF_2) = 0.16 [1], 0.26 [18b], σ_R (BF_2) = 0.24 [18b], 0.28 [18a], 0.35 [1]; σ_I $[B(OH)_2]$ = −0.05 (in CD_3OD) [18b], −0.09 [16], σ_R $[B(OH)_2]$ = 0.08 [17], 0.13 (in CD_3OD) [18b]; σ_I $[B(OMe)_2]$ = −0.27 [18b], σ_R $[B(OMe)_2]$ = 0.07 [18a], 0.12 [18b].

3. Experimental

NMR spectra were measured on Bruker spectrometers WP 80 SY (^{1}H at 80.13 MHz and ^{19}F at 75.39 MHz)

Table 3
^{1}H- and ^{11}B-NMR spectra of potassium fluorophenyltrifluoroborates K[$ArBF_3$] (35°C)

Ar	Solvent	δ(H) (ppm)	δ(B) (ppm)	^{1}J (B,F) (Hz)
C_6F_5	Acetone		1.82	43
C_6F_5	CD_3CN		1.81	43
C_6F_5	CD_3OD		2.06	43
C_6F_5	DMF		1.26	43
2,3,4,5-C_6HF_4	Acetone	6.91	2.07	46
2,3,4,5-C_6HF_4	CD_3CN	7.25		
2,4,6-$C_6H_2F_3$	DMF	6.56	2.67	49
3,4,5-$C_6H_2F_3$	Acetone	7.03	2.67	49
3,4,5-$C_6H_2F_3$	CD_3CN	7.09		
2,6-$C_6H_3F_2$	Acetone	6.92	2.36	47
2,6-$C_6H_3F_2$	CD_3CN	7.10, 6.70		
3,5-$C_6H_3F_2$	Acetone	6.97 (H-2,6), 6.56 (H-4)	2.77	50
2-C_6H_4F	Acetone	7.38, 6.99, 6.84, 6.70	3.01	50
2-C_6H_4F [4]	CD_3CN	7.55–7.42, 7.07, 6.91, 6.80–6.70	3.42	49
3-C_6H_4F	Acetone	7.19, 7.04, 6.67	3.25	52
3-C_6H_4F	CD_3CN	7.24–7.12, 6.83	3.26	52
4-C_6H_4F	CD_3CN	7.45, 6.90	3.70	45

and Avance DRX 500 (^{1}H at 500.13 MHz, ^{11}B at 160.46 MHz, ^{13}C at 125.76 MHz and ^{19}F at 470.59 MHz). Shift values were reported with respect to TMS (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B) and CCl_3F (^{19}F). The IR spectra were recorded on Bruker instruments IFS 66 and Vector 22 in KBr pellets.

1,2,3,4-Tetrafluorobenzene (Fluorochem), 1-bromo-2,4,6-trifluorobenzene (ABCR), 1-bromo-3,4,5-trifluorobenzene (ABCR), 1-bromo-2,6-difluorobenzene (ABCR), 1-bromo-3,5-difluorobenzene (ABCR), 1-iodo-2-fluorobenzene (Fluka), 1-bromo-3-fluorobenzene and 1-bromo-4-fluorobenzene (Riedel-de Haën), 1.6 M BuLi in hexane (Fluka), 2.5 M BuLi in hexanes (Aldrich), K[HF_2] (Fluka), BCl_3 (Merck) and BBr_3 (Mallinckrodt) were used as supplied. Bromopentafluorobenzene was produced in the Institute of Organic Chemistry Novosibirsk.

$B(OCH_3)_3$ (Merck) and B(O-*i*-C_3H_7)$_3$ (Aldrich) were distilled over Na before use. $B(OC_3H_7)_3$ was prepared from boric acid and propanol by azeotropic distillation of water with benzene and distilled over sodium before use. Dichloromethane and acetonitrile were purified by standard procedures.

All manipulations with aryldihalogenoboranes were performed under a dry argon atmosphere in FEP equipment.

3.1. Attempted reaction of $C_6F_5SiMe_3$ with BBr_3

A solution of $C_6F_5SiMe_3$ (138 mg, 0.55 mmol) in CH_2Cl_2 (0.1 ml) was treated with a solution of BBr_3 (142 mg, 0.56 mmol) in CH_2Cl_2 (0.05 ml) at −20°C. The solvent was distilled-off and the reaction mixture was maintained 1 h at 85–90°C followed by 3 days at r.t.. No reaction was detected (^{19}F-NMR).

3.2. Pentafluorophenyldibromoborane (**3**)

A solution of C_6F_5HgEt (1.25 g, 3.15 mmol) in CH_2Cl_2 (1 ml) was added dropwise to a solution of BBr_3 (1.03 g, 4.10 mmol) in CH_2Cl_2 (4 ml) at −50°C. Immediately a white precipitate was formed. During 0.5 h, the reaction mixture was warmed to r.t. under stirring and after centrifugation the mother liquor was separated. The formation of borane $C_6F_5BBr_2$ (82% yield) and $(C_6F_5)_2Hg$ (6% yield) was detected in the mother liquor by ^{19}F-NMR spectrometry. Without isolation of dibromoborane (**3**) the solution was used for the preparation of $C_6F_5BF_2$.

3.3. Potassium pentafluorophenyltrifluoroborate (**4**)

BuLi (1.33 M in hexane; 38 ml, 50.5 mmol) was added dropwise to a solution of C_6F_5Br (11 g, 44.5 mmol) in ether (60 ml) at −70 to −60°C and stirred for 30 min. This solution was added gradually under stirring to the pre-cooled solution (−60°C) of $B(OPr)_3$

Table 4
^{1}H- and ^{11}B-NMR spectra of fluorophenyldifluoroboranes $ArBF_2$ (CH_2Cl_2, 35°C)

Ar	δ (H) (ppm)	δ (B) (ppm)
C_6F_5		22.84
2,3,4,5-C_6HF_4	7.41	23.33
2,4,6-$C_6H_2F_3$	6.74	23.26
3,4,5-$C_6H_2F_3$	7.53	23.88
2,6-$C_6H_3F_2$	7.61, 6.96	23.53
3,5-$C_6H_3F_2$	7.40, 7.10	24.04
2-C_6H_4F	7.82, 7.65, 7.27, 7.14	24.23
3-C_6H_4F	7.69, 7.55, 7.48, 7.34	24.52
4-C_6H_4F	7.91, 7.16	24.69

(9 g, 47.8 mmol) in ether (30 ml). After 1.5 h at −50 to −60°C the reaction mixture was warmed to −10 to −5°C within 30 min. The resulting suspension was stirred additionally for 30 min at r.t. before hydrolysis with 20 ml 10% HCl. The organic phase was separated, the aqueous one was extracted with CH_2Cl_2 (30 ml) and the combined organic phases were dried with $MgSO_4$. Evaporation of the solvent gave the crude pentafluorophenylboronic acid with an admixture of its propylate as yellow oil, which displayed broad resonances at −132.2 (F-2,6), −154.3 (F-4) and −162.6 (F-3,5) ppm (^{19}F-NMR, in ether). This crude material was dissolved in MeOH (100 ml) and added to the stirred solution of $K[HF_2]$ (11 g, 141 mmol) in water (50 ml). After stirring at r.t. for 16 h and concentration at reduced pressure the residual oil was extracted with acetonitrile (2 × 60 ml), the extract was dried with $MgSO_4$ and the solvent removed. After drying in vacuum over P_4O_{10} borate (**4**) was obtained in 62% yield (7.0 g). Anal. Calc. for C_6BF_8K: C, 26.3; F, 55.4%; found: C, 25.9; F, 54.6%. IR ν (cm^{-1}): 1656, 1532, 1466, 1388, 1312, 1144, 1004, 956, 816, 760, 636.

A solution of C_6F_5MgBr prepared from C_6F_5Br (4.9 g, 19.8 mmol) and magnesium (0.50 g, 20.5 mmol) in ether (40 ml) was cooled to 0°C and added gradually to the solution of $B(OCH_3)_3$ (4.20 g, 40 mmol) in ether (20 ml) at 0°C. After stirring at 0°C for 1 h, the suspension was poured into 5% HCl (50 ml), the organic layer was separated, the aqueous one was extracted with ether (2 × 10 ml) and the combined extracts were dried with $MgSO_4$. The solvent was removed in vacuum to give the crude pentafluorophenylboronic acid with a small admixture of bis(pentafluorophenyl)borinic acid (3.8 g) (^{19}F-NMR). The crude product was dissolved in MeOH (5 ml) and added to the solution of $K[HF_2]$ (4.7 g, 60 mmol) in water (30 ml). After stirring for 4 h, the precipitate was filtered-off, washed with water and ether and dried to give borate (**4**) (3.8 g, 70%).

In a similar manner, a solution of C_6F_5MgBr prepared from C_6F_5Br (4.9 g, 19.8 mmol) and magnesium (0.50 g, 20.5 mmol) in ether (40 ml) reacted with $B(OC_3H_7)_3$ (7.40 g, 39.3 mmol) in ether (20 ml) to give a mixture (1:1) of $C_6F_5B(OH)_2$ and $C_6F_5B(OC_3H_7)_2$ (brown oil, 5.0 g).

^{19}F-NMR (acetone): −131.8 (F-2,6), −154.2 (F-4), −162.1 (F-3,5) {$C_6F_5B(OH)_2$} and −131.8 (F-2,6), −153.7 (F-4), −162.1 (F-3,5) {$C_6F_5B(OPr)_2$} ppm.

The oil was dissolved in MeOH (8 ml), added to a solution of $K[HF_2]$ (6.3 g, 80 mmol) in water (30 ml) and stirred overnight. The precipitate was filtered-off, washed with water and ether and dried to give borate (**4**) (4.4 g, 81%).

A cold solution (−5°C) of C_6F_5MgBr prepared from C_6F_5Br (4.8 g, 19.4 mmol) and magnesium (0.50 g, 20.5 mmol) in ether (40 ml) reacted slowly with $B(O\text{-}i\text{-}C_3H_7)_3$ (7.50 g, 40 mmol) in ether (20 ml) at −5°C. After 4 h the mother liquor showed only a low conversion of the Grignard reagent (^{19}F-NMR). The conversion of C_6F_5MgBr increased to ca. 80% after 3 h at 20°C. After further stirring overnight, the ^{19}F-NMR spectrum of the mother liquor showed the presence of $C_6F_5B(O\text{-}i\text{-}C_3H_7)_2$ [resonances at −132.91 (F-2,6), −154.59 (F-4), −162.48 (F-3,5) ppm] and $[C_6F_5B(O\text{-}i\text{-}C_3H_7)_3]^-$ [resonances at −131.05 (F-2,6), −158.08 (F-4), −164.18 (F-3,5) ppm] (4.7:1). After hydrolysis of the suspension with 5% HCl (50 ml) and working-up as described above the crude reaction product in MeOH (8 ml) was reacted with $K[HF_2]$ (6.5 g, 83 mmol) in water (30 ml) for 5 h. The precipitate was filtered off, washed with water and dried over Sicapent to give $K[C_6F_5BF_3]$ and $K[(C_6F_5)_2BF_2]$ (4.0 g) (11:1) (^{19}F-NMR). Pure borate (**4**) (3.3 g, 61%) was obtained after washing of the crude product with water-saturated ether (20 ml) and drying over Sicapent.

A solution of C_6F_5MgBr prepared from C_6F_5Br (2.46 g, 10.0 mmol) and magnesium (0.25 g, 10.3 mmol) in ether (25 ml) was cooled to 3°C and added gradually to a solution of $B(OCH_3)_3$ (2.10 g, 20.2 mmol) in ether (25 ml) at 3°C. After stirring for 4 h at 3°C, the mother liquor was decanted from the solid phase under argon. Each phase was treated as mentioned above. Aryltrifluoroborate (**4**) (0.42 g from the mother liquor) and a mixture of **4** and $K[(C_6F_5)_2BF_2]$ (0.94 g, 86:14, from the solid phase) were obtained.

$K[C_6F_5BF_3]$: $^{13}C\{^{19}F\}$-NMR (CH_3CN–CD_3CN): 148.11 (C-2,6), 139.23 (C-4), 136.82 (C-3,5) ppm. ^{13}C-NMR (CH_3CN–CD_3CN): ^1J(C-2) (F-2) 238.8 Hz, ^1J(C-3) (F-3) 245.6 Hz, ^1J(C-4) (F-4) 244.4 Hz, ^2J(C-4) (F-3,5) 13.9 Hz, ^3J(C-4) (F-2,6) 5.8 Hz. ^{13}C-NMR (CD_3OD): 149.66 (C-2,6), 140.74 (C-4), 138.12 (C-3,5), 118.36 (C-1, br) ppm; ^1J(C-2) (F-2) 244.3 Hz, ^1J(C-3) (F-3) 249.8 Hz, ^1J(C-4) (F-4) 246.3 Hz.

$K[(C_6F_5)_2BF_2]$: ^{19}F-NMR (CD_3CN): −135.10 (F-2,6), −145.40 (BF_2^-, br), −161.49 (F-4), −165.24 (F-3,5) ppm.

*3.4. Potassium 2,3,4,5-tetrafluorophenyltrifluoroborate (**12**)*

Crude 2,3,4,5-$C_6HF_4B(OH)_2$ was prepared in steps by the metalation of 1,2,3,4-tetrafluorobenzene (4.6 g, 30 mmol) with BuLi (1.6 M in hexane; 20 ml, 32 mmol) in ether (60 ml) at −60°C followed by arylation of $B(O\text{-}i\text{-}C_3H_7)_3$ (8.0 g, 42 mmol) in ether (60 ml) at −70°C and finally hydrolysis of the reaction mixture with 10% HCl (120 ml). Treatment with $K[HF_2]$ (9.8 g, 125 mmol) in 60% aqueous methanol (60 ml) at r.t. for 22 h resulted in a suspension. After extraction with acetonitrile followed by evaporation of the solvent borate (**12**) was obtained in 56% yield (4.3 g). An analytically pure sample resulted after crystallization from MeCN–water (9:1). Anal. Calc. for C_6HBF_7K: C, 28.1; H, 0.39: F, 52.0%; found:

C, 28.2; H, 0.44; F, 52.2%. IR ν (cm^{-1}): 3084, 1761, 1647, 1608, 1526, 1460, 1383, 1340, 1302, 1284, 1252, 1194, 1107, 1072, 1018, 976, 879, 845, 812, 744, 710, 625, 572, 534, 523, 484.

3.5. *Potassium 2,4,6-trifluorophenyltrifluoroborate* (**10**)

2,4,6-$C_6H_2F_3Li$ was prepared from 1-bromo-2,4,6-trifluorobenzene (4.20 g, 20 mmol) and BuLi (2.5 M in hexane; 8 ml, 20 mmol) in ether (30 ml) at −75°C and added gradually to a cold solution of $B(OCH_3)_3$ (5.5 g, 53 mmol) in ether (40 ml) at −70°C. After stirring for 1 h the reaction mixture was warmed to 10°C within 3 h followed by hydrolysis with 10% HCl (60 ml). The organic layer was separated, the aqueous one was extracted with ether (2 × 10 ml) and the combined extracts were dried with $MgSO_4$. The solvent was removed to give the crude arylboronic acid (3.4 g).

^{19}F-NMR (acetone): −99.6 (F-2,6), −106.6 (F-4) ppm; ^{1}H-NMR (acetone): 7.41 (OH), 6.78 (H-3,5) ppm.

A solution of the arylboronic acid in MeOH (10 ml) was added to the solution of K[HF_2] (5.6 g, 72 mmol) in water (45 ml). After stirring overnight the precipitate was filtered off, washed with water and dried over Sicapent to give borate (**10**) (3.6 g, 76%). Anal. Calc. for $C_6H_2BF_6K$: C, 30.3; H, 0.85; F, 47.9%; found: C, 30.0; H, 0.90; F, 48.2%. IR ν (cm^{-1}): 3106, 1644, 1617, 1595, 1520, 1490, 1412, 1293, 1221, 1176, 1159, 1115, 1005, 970, 837, 727, 614, 575, 550, 519.

3.6. *Potassium 3,4,5-trifluorophenyltrifluoroborate* (**11**)

3,4,5-Trifluorophenylmagnesium bromide was prepared from 1-bromo-3,4,5-trifluorobenzene (4.34 g, 20.5 mmol) and magnesium (0.51 g, 21.0 mmol) in ether (35 ml) and added dropwise to the solution of B(O-*i*-C_3H_7)$_3$ (4.17 g, 22.1 mmol) in ether (30 ml) at −30°C. The white suspension was warmed to 10°C within 30 min. The ^{19}F-NMR spectrum displayed resonances at −135.9 (F-3,5) and −160.4 (F-4) ppm which were assigned to 3,4,5-$C_6H_2F_3$B(O-*i*-Pr)$_2$. The reaction mixture was poured into 10% HCl (90 ml) and stirred at r.t. for 1 h. The organic phase was separated, the aqueous one extracted with ether (40 ml) and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent at reduced pressure the crude arylboronic acid (4.3 g) was obtained.

^{19}F-NMR (ether): −137.1 (F-3,5), −160.4 (F-4) ppm {3,4,5-$C_6H_2F_3B(OH)_2$} and −135.3 (F-3,5), −162.0 (F-4) ppm {probably 3,4,5-$C_6H_2F_3$B(O-*i*-Pr)$_2$} (7:1).

The crude product was treated with K[HF_2] (5.19 g, 65 mmol) in 70% aqueous methanol (120 ml) overnight. The mother liquor was decanted, the residue was extracted with MeCN (10 ml) and the combined extracts were evaporated to dryness under reduced pressure. Extraction with MeCN (2 × 15 ml) followed by drying with $MgSO_4$ and removal of the solvent gave a colorless solid. Pure borate (**11**) was obtained in 83% yield (4.08 g) after drying over P_4O_{10} in vacuum. Anal. Calc. for $C_6H_2BF_6K$: C, 30.3; H, 0.85; F, 47.9%; found: C, 29.7; H, 0.83; F, 48.5%. IR ν (cm^{-1}): 3078, 1614, 1529, 1412, 1331, 1283, 1232, 1213, 1136, 1034, 999, 889, 750, 737, 625, 532.

3.7. *Potassium 2,6-difluorophenyltrifluoroborate* (**8**)

2,6-$C_6H_3F_2Li$ was prepared from 1-bromo-2,6-difluorobenzene (3.86 g, 20 mmol) and BuLi (2.5 M in hexane; 8 ml, 20 mmol) in ether (30 ml) at −78°C and added gradually to the cold solution of $B(OCH_3)_3$ (4.20 g, 40 mmol) in ether (20 ml) at −70°C. After stirring at −70°C for 1 h the reaction mixture was warmed to 10°C within 20 min followed by hydrolysis with 5% HCl (20 ml). The organic layer was separated, the aqueous one was extracted with ether (2 × 10 ml) and the combined extracts were dried with $MgSO_4$. After removal of the solvent the crude arylboronic acid (3.0 g) was obtained. ^{19}F-NMR (acetone): −102.59 (F-2,6) ppm; ^{1}H-NMR (acetone): 7.07 (H-4), 6.61 (H-3,5) ppm.

A solution of the arylboronic acid in MeOH (5 ml) was added to the solution of K[HF_2] (4.7 g, 60 mmol) in water (40 ml). After stirring for 1 h, the precipitate was filtered off, washed with water and with dry ether (2 × 10 ml) and dried over Sicapent to give compound **8** (3.6 g, 82%). The product was slightly soluble in acetone, MeCN, MeOH. Anal. Calc. for $C_6H_3BF_5K$: C, 32.8; H, 1.37; F, 43.2%; found: C, 33.2; H, 1.56; F, 43.0%. IR ν (cm^{-1}): 3089, 1626, 1587, 1570, 1446, 1290, 1264, 1218, 1176, 1005, 970, 775, 712, 547, 516.

3.8. *Potassium 3,5-difluorophenyltrifluoroborate* (**9**)

3,5-Difluorophenylmagnesium bromide was prepared from 1-bromo-3,5-difluorobenzene (3.80 g, 19.7 mmol) and magnesium (0.48 g, 19.7 mmol) in ether (40 ml) and added dropwise to the solution of $B(OCH_3)_3$ (5.5 g, 53 mmol) in ether (40 ml) at −25°C. The white suspension was warmed to 20°C overnight. The reaction mixture was poured into 5% HCl (110 ml). The organic phase was separated, the aqueous one extracted with ether (2 × 10 ml) and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent at reduced pressure the crude arylboronic acid (3.0 g) was obtained.

^{19}F-NMR (acetone): −111.0 (F-3,5) ppm {3,5-$C_6H_3F_2B(OH)_2$} and admixtures at −110.0 and −107.6 ppm. ^{1}H-NMR (acetone): 7.37 (H-2,6) and 6.90 (H-4) ppm.

The crude product was treated with K[HF_2] (5.6 g, 72 mmol) in water–methanol (4:1) (50 ml) overnight. The reaction solution was saturated with KF·2H_2O and extracted with MeCN (3 × 30 ml). The combined extracts were dried with Na_2SO_4 and solvent was removed. The product was washed with dry ether (10 ml) to yield borate (**9**) (2.5 g, 58%). Anal. Calc. for $C_6H_3BF_5K$: C, 32.8; H, 1.37; F, 43.2%; found: C, 33.0; H, 1.38; F, 43.3%. IR ν (cm^{-1}): 3101, 1626, 1592, 1418, 1295, 1155, 1108, 1037, 960, 857, 819, 687, 627, 551, 511.

3.9. Potassium 2-fluorophenyltrifluoroborate (5)

2-Fluorophenylmagnesium iodide was prepared from 1-iodo-2-fluorobenzene (8.6 g, 38.7 mmol) and magnesium (0.95 g, 38.6 mmol) in ether (45 ml) at −20°C and added dropwise to the solution of $B(OCH_3)_3$ (7.7 g, 74 mmol) in ether (40 ml) at < -30°C. The white suspension was stirred for 1 h at −20°C and warmed to 15°C within 1 h, before poured into 5% HCl (100 ml). The organic phase was separated, the aqueous one was extracted with ether (2 × 30 ml) and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent at reduced pressure and washing of the residue with hexane (3 × 15 ml) the crude arylboronic acid (3.5 g) was obtained.

The crude product was dissolved in MeOH (10 ml) and added portionwise to the stirred solution of $K[HF_2]$ (8.3 g, 106 mmol) in water (60 ml). The suspension was stirred for 4 h, the precipitate was filtered off, washed with water, dried over Sicapent and finally washed with dichloromethane (10 ml) to yield compound **5** (1.5 g). The filtrate was saturated with $KF{\cdot}2H_2O$ and extracted with MeCN (3 × 50 ml). The combined extracts were dried with $MgSO_4$ before the solvent was removed. The total yield of **5** was 3.1 g (41%). Anal. Calc. for $C_6H_4BF_4K$: C, 35.7; H, 2.00; F, 37.6%; found: C, 35.3; H, 2.11; F, 37.8%. IR ν (cm^{-1}) cf [4]: 3080, 3058, 3030, 1618, 1568, 1474, 1439, 1267, 1222, 1203, 1187, 1102, 977, 944, 925, 847, 809, 747, 725, 685, 612, 549, 508, 492, 442.

3.10. Potassium 3-fluorophenyltrifluoroborate (6)

3-C_6H_4FLi was prepared from 1-bromo-3-fluorobenzene (6.3 g, 36 mmol) and BuLi (2.5 M in hexane; 13 ml, 33 mmol) in ether (25 ml) at −55°C, warmed slowly to 15°C and chilled again to −40°C. The reagent was added gradually to the cold solution of $B(OC_3H_7)_3$ (16 g, 85 mmol) in ether (25 ml) at −55°C. The reaction mixture was stirred for 0.5 h, warmed to 18°C within 1 h and additionally kept at this temperature for 1 h before it was poured into 5% HCl (100 ml). The organic layer was separated, the aqueous one was extracted with ether (2 × 10 ml) and the combined extracts were dried with $MgSO_4$. The solvent was removed to give the crude product. Its solution in MeOH (10 ml) was added to the stirred solution of $K[HF_2]$ (10.6 g, 136 mmol) in water (40 ml) and reacted for 6 h. The reaction solution was saturated with $KF{\cdot}2H_2O$ and extracted with MeCN (3 × 40 ml). The combined extracts were dried with $MgSO_4$ and the solvent was removed. The product was washed with dry dichloromethane (80 ml) to give borate (**6**) (3.3 g, 50%). Anal. Calc. for $C_6H_4BF_4K$: C, 35.7; H, 2.00; F, 37.6%; found: C, 35.9; H, 1.85; F, 37.6%. IR ν (cm^{-1}): 3074, 1614, 1578, 1484, 1423, 1265, 1244, 1166, 1152, 1085, 1046, 1014, 992, 951, 877, 841, 793, 751, 702, 604, 530, 483.

3-Fluorophenylmagnesium bromide was prepared from 1-bromo-3-fluorobenzene (2.58 g, 14.7 mmol) and magnesium (0.40 g, 16.5 mmol) in ether (30 ml), cooled to 3°C and added dropwise to the solution of $B(OCH_3)_3$ (4.67 g, 45.0 mmol) in ether (30 ml) at 3°C. The white suspension was stirred for 3 h at 3°C before poured into 5% HCl (50 ml). The organic phase was separated, the aqueous one was extracted with ether (2 × 20 ml) and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent at reduced pressure the crude arylboronic acid (1.87 g) was obtained.

The crude product was dissolved in MeOH (9 ml) and added portionwise to a stirred solution of $K[HF_2]$ (6.27 g, 80 mmol) in water (25 ml). The solution was stirred for 2 h, saturated with $KF{\cdot}2H_2O$ and extracted with MeCN (3 × 35 ml). The combined extracts were dried with Na_2SO_4 before the solvent was removed. The product was washed with dry ether (2 × 10 ml) and dichloromethane (20 ml). After drying over Sicapent borate (**6**) was obtained (1.03 g, 35%).

3.11. Potassium 4-fluorophenyltrifluoroborate (7)

4-Fluorophenylmagnesium bromide was prepared from 1-bromo-4-fluorobenzene (7.00 g, 40.0 mmol) and magnesium (1.01 g, 41.9 mmol) in ether (60 ml), cooled to 3°C and added dropwise to the solution of $B(OCH_3)_3$ (8.31 g, 80.0 mmol) in ether (50 ml) at 3°C. The white suspension was stirred for 2 h at 3°C and poured into 10% HCl (50 ml). The organic phase was separated, the aqueous one was extracted with ether (2 × 20 ml) and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent at reduced pressure the crude arylboronic acid (5.99 g) was obtained.

The crude product was dissolved in MeOH (14 ml) and added to the stirred solution of $K[HF_2]$ (10.0 g, 129 mmol) in water (39 ml). After 2 h the precipitate was filtered off and dried over Sicapent to yield compound **7** (1.47 g). The filtrate was saturated with $KF{\cdot}2H_2O$ and extracted with MeCN (3 × 35 ml). The combined extracts were dried with Na_2SO_4 before the solvent was removed. The product was washed with dry ether (2 × 10 ml) and dichloromethane (20 ml). After drying over Sicapent borate $K[4\text{-}C_6H_4FBF_3]$ was obtained (1.86 g). Total yield of **7** was 3.33 g (41%). Anal. Calc. for $C_6H_4BF_4K$: C, 35.7; H, 2.00; F, 37.6%; found: C, 36.2; H, 2.36; F, 37.9%. IR ν (cm^{-1}): 3030, 1682, 1608, 1515, 1396, 1230, 1160, 988, 973, 953, 919, 833, 723, 558.

Table 5
Preparation of aryldifluoroboranes

$K[ArBF_3]$	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
(mmol)	1.45	0.62	0.20	0.70	0.23	0.26	0.42	1.99	1.93
CH_2Cl_2 (ml)	3	1	1	1	1	1	1	2	1.8
Yield of $ArBF_2$	**1**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
(mmol [a])	1.45	0.55	0.16	0.46	0.19	0.24	0.38	1.99	1.79

[a] From ^{19}F-NMR spectrum, with quantitative internal reference.

*3.12. Pentafluorophenyldifluoroborane (**1**)*

A solution of $C_6F_5BBr_2$ (2.5 mmol) in CH_2Cl_2 (5 ml) was treated with aHF (5 ml) at −50°C under stirring. The stirred two-phase system was warmed gradually to −5°C within 20 min under a slow stream of argon to remove HBr. After dilution with CH_2Cl_2 (5 ml) the acidic phase was separated. The ^{19}F-NMR spectrum of the dichloromethane phase showed the formation of $C_6F_5BF_2$ besides C_6HF_5 in 62 and 13% yield, respectively.

C_6F_5HgEt (2.8 g, 7.1 mmol) was combined with BCl_3 (3 ml, 35.9 mmol) at −78°C and the mixture was warmed to r.t. The reaction mixture was kept at r.t. for 18 h, excess of BCl_3 was removed and the residue was extracted with CCl_3F (3 × 8 ml). The CCl_3F-solution was treated with aHF (10 ml) at −40 to −50°C under stirring for 1 h. The acidic phase was decanted. After centrifugation the dichloromethane mother liquor was separated and characterized by its ^{19}F-NMR spectrum: formation of $C_6F_5BF_2$ in 52% yield based on C_6F_5HgEt.

Borate (**4**) (2.74 g, 10.0 mmol) was suspended in CCl_3F (15 ml) at −45 to −50°C and an excess of BF_3 gas was bubbled under stirring for 50 min. Under argon atmosphere the reaction mixture was warmed to room temperature. After centrifugation the organic phase was decanted and the residual solid was washed with CCl_3F (20 ml). The solvent was distilled off and the borane was distilled in a flame-dried glass equipment to yield borane (**1**) (1.80 g, 83%) (b.p. 104–105°C).

$^{13}C\{^{19}F\}$-NMR ($C_6F_5BF_2$ in CH_2Cl_2): 151.82(C-2,6), 146.16 (C-4), 138.20 (C-3,5), 98.72 (C-1, br.) ppm.

3.13. Preparation of aryldifluoroboranes (general procedure)

Boron trifluoride was bubbled into the stirred suspension of potassium aryltrifluoroborate in dichloromethane at −40 to −50°C during 15–25 min and degassed in vacuum at −78°C. After centrifugation the mother liquor was decanted under argon at r.t., the solid was washed with dichloromethane (1–2 ml) and both extracts were combined. For details see Table 5.

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