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Synthesis of Fluorine-Containing Aryl(halo)boranes from Potassium Aryl(fluoro)borates

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Abstract—Fluorine-containing aryldihalogenoboranes have been obtained by the reaction of boron and aluminum chlorides and bromides with potassium aryltrifluoroborates K[$ArBF_3$] under mild conditions. In a similar way, bis(pentafluorophenyl)halogenoboranes have been synthesized by the reaction with K[$(C_6F_5)_2BF_2$]. The reaction of K[$C_6F_5BF_3$] with $AlBr_3$ affords a mixture of $C_6F_5BF_2$ and $C_6F_5BCl_2$ due to fast conversion of $AlBr_3$ to $AlBrCl_2$. The inductive and resonance parameters of BCl_2 and BBr_2 groups were calculated.

Keywords: aryldihaloboranes, aryltrifluoroborates, boron halides, aluminum halides

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Polyfluorinated aryl(halogeno)boranes are known since 1963, when $C_6F_5BF_2$ and $C_6F_5BCl_2$ have been first prepared [1, 2]. Till the end of 90-s, the main methods of their synthesis consisted in the replacement of the C–metal bond by the C–B bond, or in transformation of the BR_2 fragment into BX_2 (X = F, Cl, Br). In 2000, it was proposed to prepare aryldifluoroboranes by the reaction of potassium aryltrifluoroborates with fluorine-containing Lewis acids (BF_3, AsF_5) in an inert solvent (CH_2Cl_2, fluorochlorocarbons). The method is of general character and can be expanded to alkyl-, alkenyl- and alkynyldifluoroboranes. More general picture of the studies in this field is presented in review [3].

Until recently, generation of aryldifluoroboranes in solution using non-fluorinated fluoride ion acceptors was represented only by papers [4, 5]. Aryldifluoroboranes were obtained by the reaction of chlorotrimethylsilane with salts K[$ArBF_3$] (Ar = C_6H_5, 2-C_6FH_4, 2,6-$C_6Cl_2H_3$, 1-naphthyl) in acetonitrile or THF and they exist in equilibrium with the solvates $ArBF_2L$ [L = NCMe, $O(CH_2CH_2)_2$] (^{11}B NMR) [4]. According to [5], $C_6H_5BF_2$ was formed from K[$C_6H_5BF_3$], 18-crown-6 (cat.) and $SiCl_4$ in CH_2Cl_2, whereas in MeCN or MeCN–THF the solvate $C_6H_5BCl_2L$ was obtained. In neither case the yields of the products were reported.

The solutions of nonsolvated aryldifluoroboranes $C_6F_nH_{5-n}BF_2$ were obtained by us by defluorination of aryltrifluoroborates K[$C_6F_nH_{5-n}BF_3$] in the two-phase system [bmim][Al_2Cl_7]–hexane [6]. Despite of the fact that chloroaluminate was chosen as the acceptor of fluoride ion, no formation of chloro-containing arylboranes was observed. It is noteworthy, that we succeeded not only in the synthesis of compounds with the phenyl and fluorophenyl group, but also with electron withdrawing polyfluorinated aryl groups 4-$EtOC_6F_4$ and C_6F_5, because such aryldifluoroboranes are much more strong Lewis acids than their hydrocarbon analogues. The obtained solutions of arylboranes showed the properties of good homogeneous catalysts of alkylation of phenols with olefins [6]. These results open up perspectives for their use as mild acidic catalysts for selective transformations of polyfunctional compounds.

To develop this approach to aryl(halogeno)boranes we investigated defluorination of a series of easily accessible potassium aryl(fluoro)borates with some Lewis acids. As fluoride ion acceptors, boron and aluminum chlorides and bromides were used, as well as silicon chlorides.

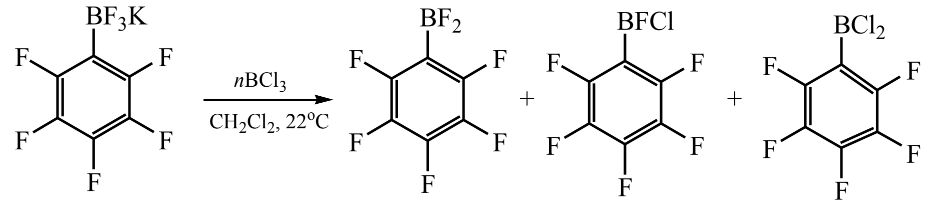
Earlier, we have described defluorination of K[$C_6H_5BF_3$] and fluorinated potassium phenyltrifluoroborates with boron fluoride in CH_2Cl_2 [7]. Boron chloride

Scheme 1.

$$\underset{\mathbf{1}}{K[3\text{-}FC_6H_4BF_3]} + BCl_3 \xrightarrow[22°C,\ 2\ h]{CH_2Cl_2} \underset{\mathbf{2}}{3\text{-}FC_6H_4BCl_2}$$

$$\underset{\mathbf{3}}{K[4\text{-}FC_6H_4BF_3]} + BCl_3 \xrightarrow[22°C,\ 2\ h]{CH_2Cl_2} \underset{\mathbf{4}}{4\text{-}FC_6H_4BCl_2}$$

Scheme 2.

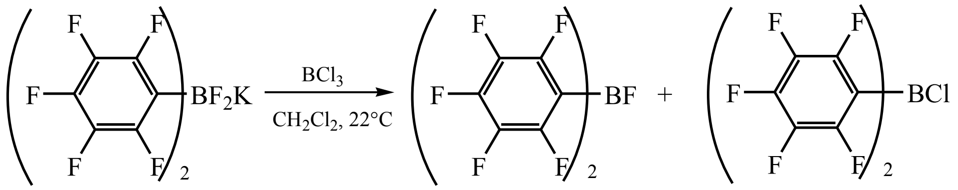


5 **6** **7** **8**

n = 1.2 : 0.2 : 0.2 : 1

n = 1.7 : 0 : 0 : 1

Scheme 3.



9 **10** **11**

is more strong Lewis acid (pF⁻ 9.40, 9.60) than BF_3 (pF⁻ 8.21) [8, 9]. Upon the action of BCl_3 in CH_2Cl_2 at room temperature, potassium 3-fluorophenyltrifluoroborate **1** is converted to 3-fluorophenyldichloroborane **2** with the absence of notable amounts of fluoroboranes $3\text{-}FC_6H_4BF_2$ and $3\text{-}FC_6H_4BFCl$. (Table 1, run 1). Potassium 4-fluorophenyltrifluoroborate **3** reacts similarly resulting in 4-fluorophenyldichloroborane **4** (Table 1, run 2). The yields of fluorophenylboranes in both cases exceed 80% (Scheme 1).

Potassium pentafluorophenyltrifluoroborate **5** reacts with small excess of BCl_3 in CH_2Cl_2 at room temperature to give a mixture of pentafluorophenylfluorophenyldifluoroborane **6**, pentafluorophenylfluorochloroborane **7** and, mainly, pentafluorophenyldichloroborane **8** (Table 1, run 3). In a large excess of BCl_3, fluoroboranes **6** and **7** practically were not formed (Table 1, run 4) (Scheme 2).

Under similar conditions, potassium bis(pentafluorophenyl)difluoroborate **9** gives a small amount of bis(pentafluorophenyl)fluoroborane **10**, while the main product is bis(pentafluorophenyl)chloroborane **11** (1 : 14) (Scheme 3).

Using large excess of BCl_3 and increasing the duration of the reaction to 15 h, we tried to obtain 2-heptafluoronaphthyldichloroborane **12** from potassium heptafluoronaphthyltrifluoroborate **13**. Indeed, arylborane **12** was obtained in 50% yield but it contained notable amount of 2-heptafluoronaphthylfluorochloroborane **14** (2.6 : 1). Both arylhalogenoboranes are very sensitive to moisture and easily form 2-heptafluoronaphthylboronic acid **15** even with short-term exposure on wet air. The latter was characterized by ^{11}B and ^{19}F NMR spectra and the data of elemental analysis (Scheme 4).

Treatment of borate **5** with two-fold excess of boron bromide in CH_2Cl_2 gave equimolar amounts of difluoroborane **6** and pentafluorophenyldibromoborane **16** (Table 1, run 5) (Scheme 5).

Aluminum halides are more strong fluorine acceptors than the corresponding boron halides. For example, the fluoride ion affinity (pF⁻) of compounds

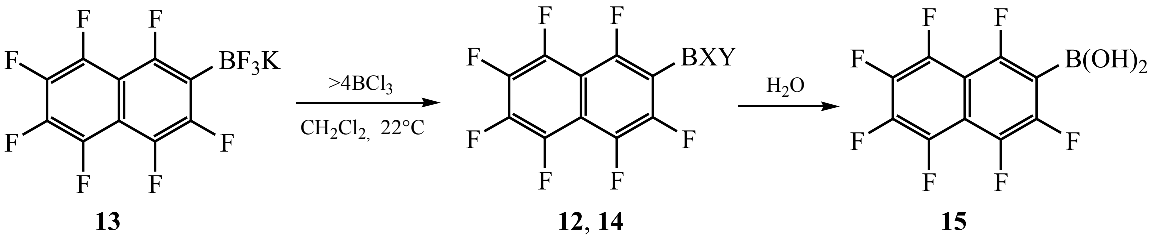
Table 1. Parameters of the reaction of K[$ArBF_3$] with boron and aluminum halogenides at 22°C

Run no.	Ar (mmol)	MX_3 (mmol)	Solvent (V, mL)	Time, h	Yield, mmol[a]		
					$ArBF_2$	ArBFX	$ArBX_2$
1	3-FC_6H_4 (1.7)	BCl_3 (2.8)	CH_2Cl_2 (7)	2			1.4
2	4-FC_6H_4 (3.2)	BCl_3 (4.4)	CH_2Cl_2 (11)	2			2.8
3	C_6F_5 (4.70)	BCl_3 (5.5)	CH_2Cl_2 (20)	2	0.48	0.54	3.24
4	C_6F_5 (0.9)	BCl_3 (1.5)	CH_2Cl_2 (4)	3			0.7
5	C_6F_5 (1.15)	BBr_3 (2.3)	CH_2Cl_2 (5)	2	0.44		0.56
6	C_6F_5 (0.78)	$AlCl_3$ (1.4)	CH_2Cl_2 (5)	4	0.41	0.09	0.21
7	C_6F_5 (1.2)	$AlCl_3$ (1.8)	Hexane (2)	4			0.3
8	C_6F_5 (1.2)	$AlCl_3$ (1.8)	Hexane (2)	24	0.1	0.09	0.4
9	C_6F_5 (0.89)	$AlCl_3$ (1.0)	Hexane (3)[b]	7	0.30	0.09	0.19
10	C_6F_5 (0.89)	$AlCl_3$ (1.0)	Hexane (3)[b]	14	0.67		
11	3-FC_6H_4 (1.24)	$AlBr_3$ (1.36)	Hexane (3)	3	0.78	0.08	0.26
12	3-FC_6H_4 (1.24)	$AlBr_3$ (1.36)	Hexane (3)[b]	9	0.78	0.08	0.26
13	3-FC_6H_4 (0.67)	$AlBr_3$ (1.70)	Hexane (3)	4			0.50
14	4-FC_6H_4 (0.56)	$AlBr_3$ (0.70)	Hexane (2)	4	0.19	0.04	0.22
15	4-FC_6H_4 (0.41)	$AlBr_3$ (0.76)	Hexane (2)	4	0.04	0.02	0.29
16	C_6F_5 (0.83)	$AlBr_3$ (0.86)	Hexane (3)	3	0.67		
17	C_6F_5 (0.83)	$AlBr_3$ (0.86)	Hexane (3)	24	0.67		
18	C_6F_5 (0.83)	$AlBr_3$ (0.86)	Hexane (3)[b]	6	0.67		
19	C_6F_5 (0.77)	$AlBr_3$ (1.51)	Hexane (3)	3	0.19	0.03	0.28
20	C_6F_5 (0.77)	$AlBr_3$ (1.51)	Hexane (3)	24	0.31	0.06	0.05
21	C_6F_5 (1.2)	$AlBr_3$ (1.2)	CH_2Cl_2 (10)	2	1.1		
22	C_6F_5 (1.00)	$AlBr_3$ (1.8)	CH_2Cl_2 (10)	1	0.84		0.14[c]
23	C_6F_5 (1.00)	$AlBr_3$ (3.4)	CH_2Cl_2 (20)	24			1.0[c]
24	4-C_5NF_4 (0.57)	BCl_3 (0.95)	CH_2Cl_2 (2)	5	0.03	0.07	0.40
25	4-C_5NF_4 (0.93)	$AlCl_3$ (2.1)	CH_2Cl_2 (3)	5	0.05	0.05	0.80

[a] From ^{19}F NMR.
[b] At 60–65°C.
[c] $C_6F_5BCl_2$.

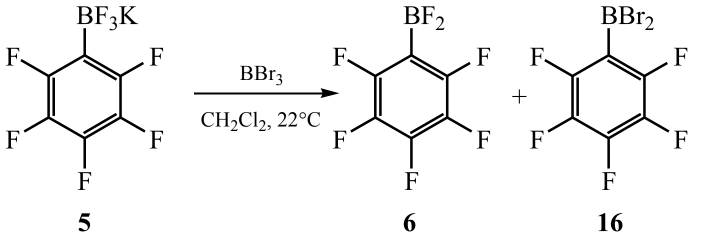
$AlCl_3$, $AlCl_2F$, $AlClF_2$, and AlF_3 is 11.46, 11.50, 11.47, and 11.50, respectively [10]. Indeed, upon stirring the suspension of borate **5** and $AlCl_3$ in CH_2Cl_2 (22°C, 4 h) we obtained the solution of $C_6F_5BF_2$, C_6F_5BFCl, and $C_6F_5BCl_2$ in the ratio 4 : 1 : 2 (Table 1, run 6). The reaction in hexane proceeds slower. After 4 h, only dichloroborane **8** was presented in the solution (yield 25%) (Table 1, run 7). Further stirring of the reaction suspension for 24 h leads to the increase of the yield of **8** to 33% and the formation of difluoroborane **6** (8%) and small amount of C_6F_5BClF (Table 1, run 8). Reflux in hexane for 7 h increases the conversion of borate **5** to 65% and is accompanied by conversion of dichloroborane **8** to fluorochloroborane **7** and difluoroborane **6** (Table 1,

Scheme 4.

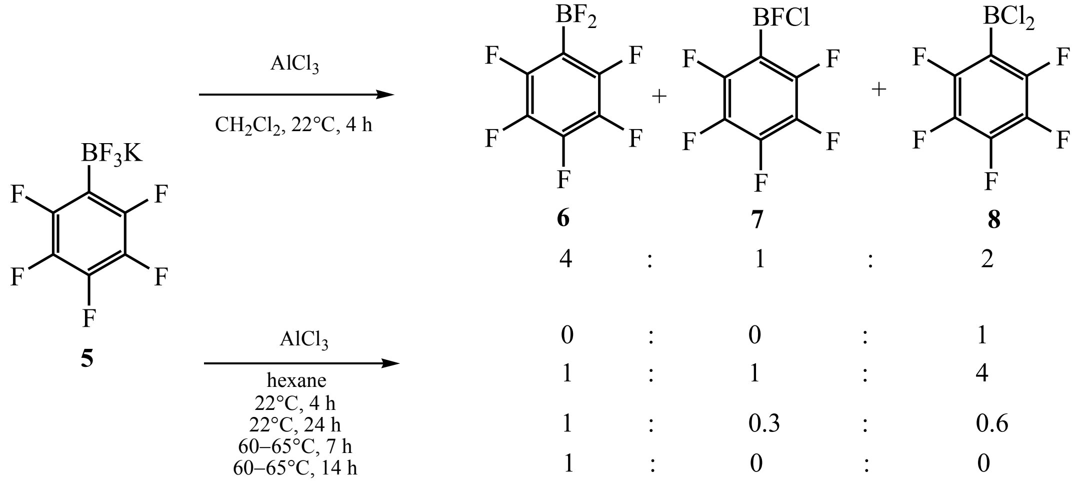


X = Y = Cl (**12**); X= F, Y = Cl (**14**).

Scheme 5.



Scheme 6.

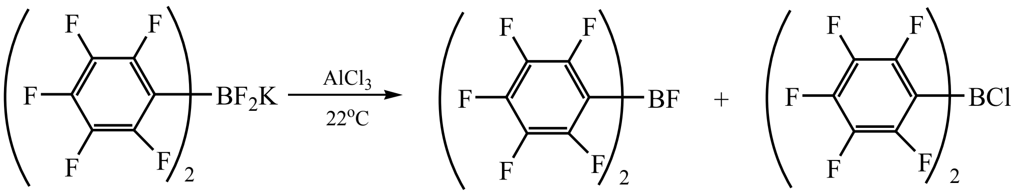


run 9). After 14 h reflux, the latter becomes the only product of the reaction (yield 75%) (Table 1, run 10) (Scheme 6). Apparently, the lower reaction rate in hexane as compared to that in dichloromethane is due to low solubility of the substrate and the reagent in hydrocarbons.

Similar changes in the rate of defluorination were observed in the reaction of K[(C$_6$F$_5$)$_2$BF$_2$] with AlCl$_3$ in dichloromethane and hexane. In CH$_2$Cl$_2$ solution at 22°C, this substrate was almost completely converted into the equimolar mixture of boranes **10** and **11** in 4 h. In hexane, the conversion of borate **9** was 40% after 5 h, and the main product was chloroborane **11**. Prolonged stirring (55 h) of heterogeneous mixture increased the conversion of **9** to 76%, but, a small amount of [(C$_6$F$_5$)$_2$B]$_2$O **17** was formed because of the contact with wet air (Scheme 7).

Although the affinity of aluminum bromide to fluoride ion is unknown, it can be assumed to be higher than that of aluminum chloride. The reaction of borate **1** with AlBr$_3$ (1 equiv.) in hexane at room temperature affords 3-fluorophenyldifluoroborane **18** (major product), 3-fluorophenylfluorobromoborane **19** and 3-fluorophenyldibromoborane **20** (Table 1, run 11). Heating at 60°C for 9 h did not change the composition and the ratio of the products (Table 1, run 12). With excess of

Scheme 7.



9 **10** **11**

	10		11
CH$_2$Cl$_2$, 4 h:	1	:	1
hexane, 5 h:	1	:	20
hexane, 55 h:	1	:	4

Scheme 8.

$$\underset{\mathbf{1}}{K[3\text{-}FC_6H_4BF_3]} + nAlBr_3 \xrightarrow[22°C]{\text{hexane}} \underset{\mathbf{18}}{3\text{-}FC_6H_4BF_2} + \underset{\mathbf{19}}{3\text{-}FC_6H_4BFBr} + \underset{\mathbf{20}}{3\text{-}FC_6H_4BBr_2}$$

	18		19		20
n = 1 (3 h):	3	:	0.3	:	1
n = 2.5 (4 h):	0	:	0	:	1

Scheme 9.

$$\underset{\mathbf{3}}{K[4\text{-}FC_6H_4BF_3]} + nAlBr_3 \xrightarrow[22°C,\ 4\ h]{\text{hexane}} \underset{\mathbf{21}}{4\text{-}FC_6H_4BF_2} + \underset{\mathbf{23}}{4\text{-}FC_6H_4BFBr} + \underset{\mathbf{22}}{4\text{-}FC_6H_4BBr_2}$$

	21		23		22
n = 1:	1	:	0.2	:	1
n = 1.9:	0.1	:	0.1	:	1

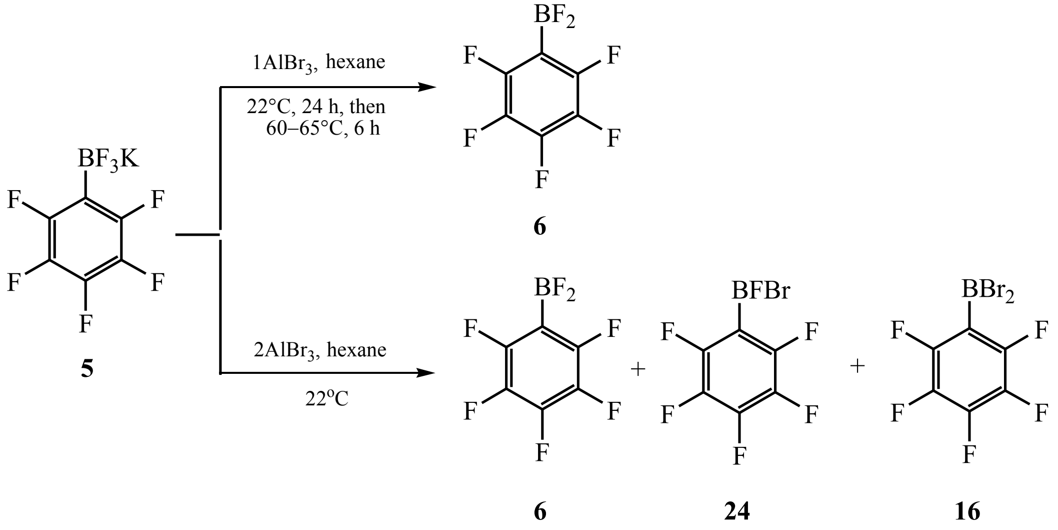
AlBr$_3$, only dibromoborane **20** is formed (Table 1, run 13) (Scheme 8).

Isomeric borate **3** reacts with AlBr$_3$ in hexane in a similar way. With small excess of aluminum bromide, approximately equal amounts of 4-fluorophenyldifluoroborane **21** and 4-fluorophenyldibromoborane **22** are formed besides a small amount of 4-fluorophenylfluorobromoborane **23** (Table 1, run 14). With two-fold excess of AlBr$_3$, the major product is dibromoborane **22**, while the total amount of fluorine-containing boranes **21** and **23** does not exceed 15–17% (Table, run 15) (Scheme 9).

The reaction of borate **5** with AlBr$_3$ (1 equiv.) at 22°C in hexane affords C$_6$F$_5$BF$_2$ in 80% yield (Table 1, run 16). The increase of duration of the reaction from 4 to 20 h, or heating at 60-65°C for 6 h did not lead to arylbromoboranes (Table 1, runs 17, 18). This means that the formed AlBr$_2$F does not exchange the fluorine atoms in **6** by bromine atoms under these conditions. Upon the action of two equiv. of AlBr$_3$ on borate **5**, dihaloboranes **6** and **16** were obtained in the ratio 1 : 1.5 and total yield of 60% after 3 h. Also, a small amount of pentafluorophenylbromofluoroborane **24** and unidentified compounds were found (Table 1, run 19). More protracted stirring led to partial transformation of aryldibromoborane **16** to the corresponding aryldifluoroborane (Table 1, run 20) (Scheme 10).

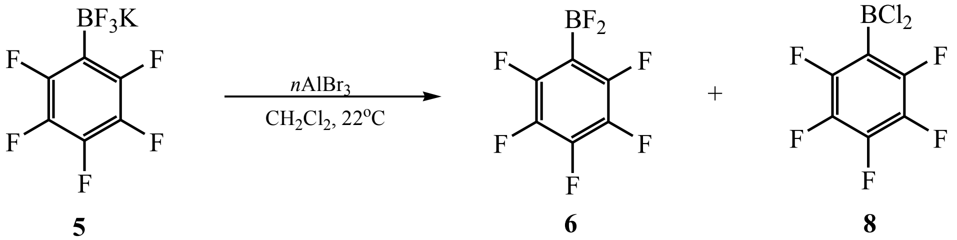
The reaction of **5** with AlBr$_3$ (1 equiv.) in CH$_2$Cl$_2$ proceeds faster than in hexane and after 2 h difluoroborane **6** is formed in almost quantitative yield (Table 1, run 21). However, when 1.8 equiv. of AlBr$_3$ was used, along with difluoroborane **6**, dichloroborane **8** was unexpectedly formed besides difluoroborane **6**. With larger excess of AlBr$_3$ it was the only product of the reaction (Table 1, runs 22, 23). We assumed that aluminum bromide is converted to the chloride or bromochloride, which are responsible for the formation of compound **8**. Special experiment has shown that dissolution of AlBr$_3$ (1 equiv.) in CH$_2$Cl$_2$ (22°C) gives rise to the formation of dark so-

Scheme 10.



	6		24		16
3 h:	10	:	2	:	15
24 h:	10	:	2	:	2

Scheme 11.



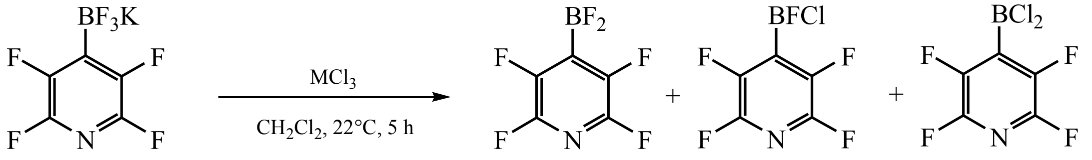
	6		8
n = 1 (2 h):	10	:	0
n = 1.8 (1 h):	10	:	1.6
n = 3.4 (24 h):	0	:	10

$$AlBr_3 + CH_2Cl_2 \xrightarrow[22^{\circ}C]{} \text{"}AlBrCl_2\text{"} + 2CH_2BrCl$$

lution, from which gray precipitate is sedimented. After 4 h, 2 equiv. of CH_2ClBr is formed and the composition is not changed during the next 20 h. Stoichiometrically, it corresponds to substitution of two bromine atoms in $AlBr_3$ by chlorine atoms and formation of $AlBrCl_2$, although we did not investigate the nature of the precipitate in detail (Scheme 11).

Since tetrafluoro-4-pyridyldifluoroborane **25** has the highest affinity to fluoride ion among aryldifluoroboranes (pF^- 9.08 [11]), defluorination of potassium tetrafluoro-4-pyridyltrifluoroborate **26** requires strong acceptor of fluoride ion. Thus, this borate did not react with boron fluoride (pF^- 7.88 [11], 8.21 [9]), but under the action of AsF_5 (pF^- 10.59 [10]) in CH_2Cl_2 tetrafluoro-4-pyridyldifluoroborane **25** was formed [12]. This compound along with tetrafluoro-4-pyridylfluorochloroborane **27** is formed from borate **26** by the action of boron chloride (pF^- 9.60 [9]) or aluminum chlorides (11.46 [10]), but the main product is tetrafluoro-4-pyridyldichloroborane **28**, whose yields exceed 70% (Table 1, runs 24, 25) (Scheme 12). In this connection, the inertness of arylborate **26** to boron bromide (pF^- 10.24 [9]) and aluminum bromide is surprising. For example, it does not react with BBr_3 in CH_2Cl_2 (22°C, 20 h), or with excess of $AlBr_3$ in hexane (22°C, 96 h) or with excess of BBr_3 in boiling 1,2-dichloroethane (^{11}B and ^{19}F NMR). The reasons for that are unclear.

Scheme 12.

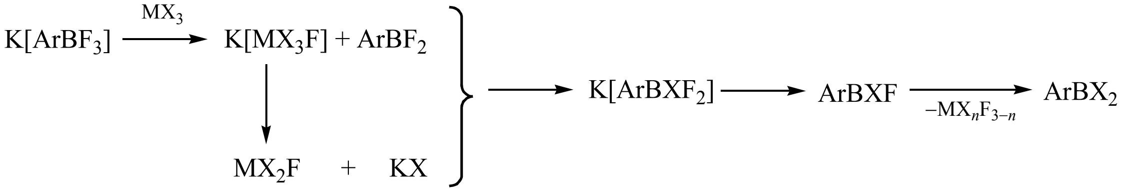


26 **25** **27** **28**

MCl$_3$ = BCl$_3$: 0.7 : 1.7 : 10

MCl$_3$ = AlCl$_3$: 0.6 : 0.6 : 10

Scheme 13.



X = Cl, Br.

Although silicon chlorides Me$_3$SiCl and SiCl$_4$ successfully defluorinate hydrocarbon potassium aryltrifluoroborates [4, 5], they do not react with K[C$_6$F$_5$BF$_3$] at reflux in CHCl$_3$ (weakly coordinating solvent) during 2–3 h. This is consistent with notable difference of the pF$^-$ values of aryldifluoroboranes C$_6$H$_5$BF$_2$ and C$_6$F$_5$BF$_2$ (ΔpF$^-$ = 1.74 [11]).

The reaction of potassium aryltrifluoroborates with boron and aluminum halides can be represented by Scheme 13. Although the final product here is ArBX$_2$, the ratio of boranes ArBF$_2$: ArBFX : ArBX$_2$ depends on the stoichiometry of the reagents, solubility or volatility of MF$_n$X$_{3–n}$ (n = 0–2), which can be removed from the reaction mixture as precipitate or gas, and possible interconversion of these boranes. It is known that in the mixture of phenyldihaloboranes C$_6$H$_5$BF$_2$ + C$_6$H$_5$BX$_2$ = 2 C$_6$H$_5$BFX (X = Cl, Br) the halogen atoms are exchanged and equilibrium is established [13], but there are no data on the behavior of their polyfluorinated analogues. Another determining factor is heterogeneity of the reaction mixture. Defluorination was carried out in weakly coordinating solvents (hexane, dichloromethane, 1,2-dichloroethane), in which borates K[ArBF$_3$] are insoluble and, most probably, the reaction occurs on the surface of the solid compound.

The products of defluorination, aryldihaloboranes, are very sensitive to air moisture, especially in pure form, and are easily converted to the mixtures of arylboronic acids and their anhydrides when exposed to air. This strongly complicates the determination of their elemental composition by classical methods. The structure of the earlier unknown aryldihaloboranes was established using multinuclear NMR spectroscopy, by comparing with the spectra of known aryldifluoroboranes (Table 2). In the ^{11}B NMR spectrum of the solution obtained from borate **5** and AlCl$_3$ (Scheme 6), apart from the signals of the known boranes C$_6$F$_5$BF$_2$ and C$_6$F$_5$BCl$_2$ (Table 2), a doublet with the spin-spin coupling constant CCB ^1J(B,F) 85 Hz appears at 38.2 ppm that was assigned to the boron atom in pentafluorophenylfluorochloroborane **7**. The ^{19}F NMR spectrum of this solution contain the signal of the BFCl group at –28.4 (q, $^1J_{BF}$ = 82 Hz) and the signals of pentafluorophenyl group at –129.2 (m, 2F, F^{2,6}), –144.9 (t. t, 1F, F^4, ^3J(F^4, F^{3,5}) 20.1 Hz, ^4J(F^4, F^{2,6}) 6.6 Hz) and –161.1 (m, 2F, F^{3,5}) ppm of the corresponding intensity. The ^{11}B NMR spectrum of tetrafluoro-4-pyridylflurochloroborane **27** contains a doublet at 37.3 ppm ($^1J_{BF}$ = 84 Hz) belonging to the boron atom in the BFCl group, whereas in the ^{19}F NMR spectrum the signal of the fluorine atom of this group appears at –23.6 ppm. The multiplets at –91.5 (2F, F^{2,6}) and –132.2 ppm (2F, F^{3,5}) correspond to the fluorine atoms of the tetrafluoropyridyl ring. The solution of pentafluorophenyldihaloboranes in hexane (Scheme 10)

Table 2. ^{11}B and ^{19}F NMR spectroscopy data for aryl(halogeno)boranes

Borane	Solvent	δ_B, ppm	δ_F, ppm			
			BF	2,6-F	4-F[a]	3,5-F
$C_6F_5BF_2$	CH_2Cl_2	22.4	–74.0	–128.6	–143.6	–161.1
$C_6F_5BF_2$ [17]	CH_2Cl_2	22.8	–74.4	–129.0	–143.8	–161.3
$C_6F_5BF_2$ [6]	Hexane	23.2	–73.0	–128.7	–144.5	–161.7
$C_6F_5BCl_2$	CH_2Cl_2	53.0		–128.8	–145.3	–161.2
$C_6F_5BCl_2$	Hexane	54.0		–128.6	–146.1	–161.2
$C_6F_5BCl_2$ [21]	C_6D_6	52.3		–129.9	–146.6	–162.4
$C_6F_5BCl_2$ [2]	CCl_4			–128.3	–145.3	–160.7
4-$C_5NF_4BCl_2$	CH_2Cl_2	53.9		–90.7		–132.9
$C_6F_5BBr_2$	CH_2Cl_2	53.6		–128.8	–146.5	–161.4
$C_6F_5BBr_2$	Hexane	54.8		–129.0	–147.2	–161.0
$C_6F_5BBr_2$ [21]	C_6D_6	53.3		–130.3	–147.4	–161.9
$(C_6F_5)_2BF$	CH_2Cl_2	43.3		–130.0	–144.7	–161.0
$(C_6F_5)_2BF$ [23]	$CDCl_3$	43.2	–26	–133	–146	–161
$(C_6F_5)_2BCl$	CH_2Cl_2	58.3		–129.0	–144.2	–161.0
$(C_6F_5)_2BCl$ [2]	–			–129.5	–145.4	–161.3
$(C_6F_5)_2BCl$ [22]	Toluene-d_8	58.8		–129.6	–144.0	–161.4
$(C_6F_5)_2BBr$ [24]	$CDCl_3$	61.2				
$(C_6F_5)_2BBr$	Hexane	61.6		–128.9	–145.3	–161.1
3-$FC_6H_4BF_2$ [17]	CH_2Cl_2	24.5	–91.1		–113.5	
3-$FC_6H_4BCl_2$	CH_2Cl_2	54.9			–113.8[b]	
3-$FC_6H_4BCl_2$ [25]	–	54.3				
3-$FC_6H_4BBr_2$	Hexane	57.6				–112.6[c]
4-$FC_6H_4BF_2$	CH_2Cl_2	26.2	–92		–105.7	
4-$FC_6H_4BF_2$ [17]	CH_2Cl_2	24.7	–92.7		–104.0	
4-$FC_6H_4BF_2$ [6]	Hexane	24.5	–93.6		–104.1	
4-$FC_6H_4BCl_2$	CH_2Cl_2	54.1			–102.2[d]	
4-$FC_6H_4BCl_2$ [25]	–	54.9				
4-$FC_6H_4BBr_2$	Hexane	56.7			–101.2[e]	

[a] $^3J_{F^4F^{3,5}}$ = 19–20 Hz.

[b] d. d. d, $^3J_{F^3H^2}$ = 9.0, $^3J_{F^3H^4}$ = 9.0, $^4J_{F^3H^5}$ = 5.4 Hz.

[c] t. t, $^3J_{F^3H^{3,5}}$ = 8.1, $^4J_{F^4H^{2,6}}$ = 6.6 Hz.

[d] d. d. d, $^3J_{F^3H^2}$ = 8.4, $^3J_{F^3H^4}$ = 8.4, $^4J_{F^3H^5}$ = 5.2 Hz.

[e] t. t, $^3J_{F^3H^{3,5}}$ = 7.9, $^4J_{F^4H^{2,6}}$ = 6.4 Hz.

contains the ^{11}B NMR signals of boranes **6**, **16** (Table 2) and pentafluorophenylbromofluoroborane **24** at δ_B = 39.4 ppm (d, ${}^{1}J_{BF}$ = 98 Hz). In the ^{19}F NMR spectrum the signals of pentafluorophenyl group appear at –128.0 (m, 2F, $F^{2,6}$), –144.8 (t. t. t, 1F, F^4, ${}^{3}J_{F4F3,5}$ = 19.8 Hz, ${}^{4}J_{F4F2,6}$ = 7.0 Hz, ${}^{6}J_{F4BF}$ = 2.8 Hz) and –161.0 (m, 2F, $F^{3,5}$) ppm, but a weak and broad resonance of the BBrF group cannot be seen. In both cases, the signals of the boron atoms and of the pentafluorophenyl group appear between the corresponding signals of boranes $C_6F_5BF_2$ and $C_6F_5BX_2$ (X = Cl, Br) (Table 2). The structure of 4-fluorophenylbromofluoroborane **23** (Scheme 9) follows from the presence of a doublet (${}^{1}J_{BF}$ = 100 Hz) at 42.1 ppm (^{11}B) and the ^{19}F NMR signal at –37.0 ppm (q 1 : 1 : 1 : 1, 1F, BFBr, ${}^{1}J_{BF}$ = 100 Hz) and –101.6 ppm (t. t. d, 1F, F^4, ${}^{3}J_{F4H3,5}$ = 8.6 Hz, ${}^{4}J_{F4H2,6}$ = 5.8 Hz, ${}^{6}J_{F4BF}$ = 3.2 Hz) ppm. The ^{1}H NMR spectrum, apart from signals of boranes **21** and **22**, contains the signals of borane **23**: doublet of doublets at 7.96 ppm (${}^{3}J_{H3,5F4}$ = 6.0 Hz, ${}^{3}J_{H3,5H2}$ = 8.1 Hz) and multiplet at 7.01 ppm of equal intensity. In the ^{11}B NMR spectrum of 3-fluorophenylbromofluoroborane **19** a doublet (${}^{1}J_{BF}$ = 100 Hz) appears at 42.4 ppm, and in the ^{19}F NMR spectrum, the signal of the BFBr group at –34.1 ppm (q 1 : 1 : 1 : 1, 1F, BFBr, ${}^{1}J_{BF}$ ~95 Hz), whereas fluorine atom F^3 resonates close to the corresponding signals of boranes **20** and **18** (δ_F = –112.7 ppm, 1F, t. d, ${}^{3}J_{F3H2,4}$ = 9.3 Hz, ${}^{4}J_{F3H5}$ = 5.8 Hz). In the ^{1}H NMR spectrum of the reaction mixture the signal of atom H^6 was identified at 7.72 ppm (d, ${}^{3}J_{H6H5}$ = 7.2 Hz), but the signals of other hydrogen atoms in compound **19** are overlapped with those of boranes **20** and **18**.

The picture can be completed by the spectral characteristics of the known boranes C_6H_5BFX. The ^{11}B NMR signal of phenylfluorochloroborane is a doublet at 41 ppm (${}^{1}J_{BF}$ = 80±10 Hz) [14] or 40.4 ppm (${}^{1}J_{BF}$ = 90 Hz) [13]. The corresponding ^{19}F NMR signal is very broaden and appears at –51 [13]) or –49.5 ppm [14]. The doublet signal of phenylbromofluoroborane in the ^{11}B NMR spectrum is found at 42.6 ppm (${}^{1}J_{BF}$ = 98 Hz), but the ^{19}F NMR signal was too broaden to be detected neither in the spectrum of neat borane nor in the solution in methylcyclohexane. Later, this compound was characterized by the following NMR parameters: δ_B = 34.2 ppm (d, ${}^{1}J_{BF}$ = 125 Hz) and δ_F = –31.5 ppm (br. s) [14].

The data for fluorophenyldihaloboranes $FC_6H_4BX_2$ (X = Cl, Br) allowed to calculate electronic parameters of BX_2 groups from the ^{19}F NMR spectra using the Taft method [15]. The obtained values of inductive and resonance constants are σ_I = 0.10 and σ_R^0 = 0.39 for BCl_2 and σ_I = 0.11 and σ_R^0 = 0.39 for BBr_2. According to the literature data, the dichloroboryl group is characterized by parameters σ_I = 0.04 [16] and σ_R^0 = 0.31 [16] and 0.34 [15]. For the BBr_2 group, the values of inductive and resonance constants were not determined. For comparison, the corresponding values for substituent BF_2 are σ_I = 0.15 [17], 0.16 [18], 0.23, 0.26 [15] and σ_R^0 = 0.22, 0.28 [15], 0.30 [17]. Despite of variation in the parameter values measured by different methods, there is an evident trend of the decrease of inductive effect and simultaneous enhancement of the resonance effect of substituents BX_2 with replacement of X = F by X = Cl and Br.

In the present study, the content and the yields of $ArBX_2$ were determined from ^{19}F NMR spectra. If only total concentration of aryldihaloboranes is required, the method described by us earlier can be used [6]. Thus, the aliquot of the $ArBX_2$ solution was added to the solution of methylpyridine in hexane of known concentration, the precipitate of the complex was filtered off and the amount of the residual base was determined by the method of GC or by titration with acid.

Therefore, we have developed a convenient method for preparation of solutions of fluorinated aryldihaloboranes and diarylhaloboranes, which can be used as homogeneous catalysts of electrophilic reactions, as well as precursors of arylboronic and arylborinic acids and their derivatives.

EXPERIMENTAL

NMR spectra were recorded on Bruker AVANCE 300 [300.13 (^{1}H), 282.40 MHz (^{19}F)] and DRX 500 [160.46 MHz (^{11}B)] spectrometers. Chemical shifts referenced to Me_4Si (^{1}H), CCl_3F (^{19}F, secondary standard C_6F_6, δ_F = –162.9 ppm) and BF_3OEt_2 (15% in $CDCl_3$, ^{11}B).

Dichloromethane, chloroform, 1,2-dichloroethane and hexane were distilled over P_2O_5. Me_3SiCl and $SiCl_4$ were distilled over CaH_2. Commercial $AlCl_3$, $AlBr_3$ (Acros), BCl_3 and BBr_3 were used. $K[C_6F_5BF_3]$ [19], $K[2,3,5,6\text{-}C_5NF_4BF_3]$ [12], $K[3\text{-}FC_6H_4BF_3]$, $K[4\text{-}FC_6H_4BF_3]$ [17], $K[(C_6F_5)_2BF_2]$ [20] were synthesized by the known methods. Aryldihaloboranes were identified by the NMR spectra (Table 2). Quantitative analysis of the reaction mixtures was performed by ^{19}F NMR spectroscopy (internal standard C_6F_6 or C_6H_5F). All operations were performed in dry argon atmosphere.

Defluorination of potassium aryltrifluoroborates with boron chloride (bromide). To the suspension of K[$ArBF_3$] in CH_2Cl_2 the 0.9–1.1 M. solution of BX_3 in CH_2Cl_2 was added and stirred at 22°C. The suspension was centrifuged and the solution of aryldihaloboranes separated by decantation (Table 1).

3-Fluorophenyldichloroborane (2). ^{1}H NMR spectrum (CH_2Cl_2), δ_H, ppm: 7.86 d (1H, H^6, $^3J_{H^6H^5}$ = 7.4 Hz), 7.72 d (1H, H^2, $^3J_{H^2F^3}$ = 9.4 Hz), 7.41 d. d. d (1H, H^5, $^3J_{H^5H^4}$ = 7.7, $^3J_{H^5H^6}$ = 7.4, $^4J_{H^5F^3}$ = 5.6 Hz), 7.29 d. d. d (1H, H^4, $^3J_{H^4F^3}$ = 9.0, $^3J_{H^5H^4}$ = 7.7, $^4J_{H^4H^2}$ = 2.1 Hz).

4-Fluorophenyldichloroborane (4). ^{1}H NMR spectrum (CH_2Cl_2), δ_H, ppm: 8.10 d. d (2H, $H^{2,6}$, $^3J_{H^3H^2}$ = 7.0, $^4J_{H^3H^2}$ = 7.0 Hz), 7.09 d. d (2H, $H^{3,5}$, $^3J_{H^3H^2}$ = 7.0, $^3J_{H^3F^4}$ = 9.0 Hz).

Defluorination of K[$(C_6F_5)_2BF_2$] with boron chloride. The solution of $(C_6F_5)_2BCl$ (0.85 mmol) and $(C_6F_5)_2BF$ (0.06 mmol) in CH_2Cl_2 was obtained from the suspension of K[$(C_6F_5)_2BF_2$] (433 mg, 1.0 mmol) in CH_2Cl_2 (6 mL) and 1.1 M BCl_3 in CH_2Cl_2 (1.2 mL, 1.3 mmol) by stirring for 1 h at 22°C.

Defluorination of K[$(C_6F_5)_2BF_2$] with aluminum chloride. *a.* To the suspension of $AlCl_3$ (118 mg, 0.88 mmol) in CH_2Cl_2 (3 mL) K[$(C_6F_5)_2BF_2$] (375 mg, 0.90 mmol) was added and stirred for 4 h at 22°C. The suspension was centrifuged to obtain the solution of $(C_6F_5)_2BF$ (0.40 mmol) and $(C_6F_5)_2BCl$ (0.43 mmol) (^{11}B, ^{19}F NMR).

b. The reaction was performed similarly using $AlCl_3$ (157 mg, 1.18 mmol), hexane (4 mL) and K[$(C_6F_5)_2BF_2$] (452 mg, 1.07 mmol). After 5 h the solution contained $(C_6F_5)_2BF$ (0.02 mmol) and $(C_6F_5)_2BCl$ (0.39 mmol). After 55 h: $(C_6F_5)_2BF$ (0.13 mmol), $(C_6F_5)_2BCl$ (0.56 mmol) and compound **17** (0.07 mmol) were present in the mixture (^{11}B, ^{19}F NMR).

Defluorination of K[2-$C_{10}F_7BF_3$] with boron chloride. 0.95 M solution of BCl_3 in CH_2Cl_2 (2 mL, 1.9 mmol) was added to the suspension of K[2-$C_{10}F_7BF_3$] (152 mg, 0.42 mmol) in CH_2Cl_2 (2.5 mL) and stirred for 15 h at 22°C. After centrifugation the solution was decanted and concentrated at a reduced pressure to ~2 mL to obtain the solution containing 2-$C_{10}F_7BFCl$ (0.08 mmol) and 2-$C_{10}F_7BCl_2$ (0.21 mmol) (^{11}B, ^{19}F NMR).

2-Heptafluoronaphthyldichloroborane (12). ^{11}B NMR spectrum (CH_2Cl_2), δ_B: 53.7 ppm. ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –103.4 d. d (1F, F^1, $^4J_{F^1F^8}$ = 75.0, $^5J_{F^1F^4}$ = 18.0 Hz), –128.8 d. m (1F, F^3, $^3J_{F^3F^4}$ = 14.0 Hz), –142.2 d. d. d (1F, F^8, $^4J_{F^1F^8}$ = 75.0, $^3J_{F^7F^8}$ = 17.0, $^5J_{F^5F^8}$ = 17.0 Hz), –146.2 d. d. d (1F, F^5, $^4J_{F^4F^5}$ = 59.0, $^3J_{F^5F^6}$ = 15.0, $^5J_{F^5F^8}$ = 15.0 Hz), –149.9 d. d. d (1F, F^4, $^4J_{F^4F^5}$ = 59.0, $^3J_{F^3F^4}$ = 18.0, $^5J_{F^1F^4}$ = 18.0 Hz), –150.3 d. d (1F, F^6, $^3J_{F^5F^6}$ = 18.0, $^3J_{F^6F^7}$ = 18.0 Hz), –155.3 d. d (1F, F^7, $^3J_{F^6F^7}$ = 18.0, $^3J_{F^7F^8}$ = 18.0 Hz).

2-Heptafluoronaphthylfluorochloroborane (14). ^{11}B NMR spectrum (CH_2Cl_2): δ_B 36.4 ppm. ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –102.8 d. d (1F, F^1, $^4J_{F^1F^8}$ = 74.0, $^5J_{F^1F^4}$ = 20.0 Hz), –129.1 m (1F, F^3), –142.2 m (1F, F^8), –146.5 d. d. d (1F, F^5, $^4J_{F^4F^5}$ = 59.0, $^3J_{F^5F^6}$ = 19.0, $^5J_{F^5F^8}$ = 19.0 Hz), –150.0 d. d (1F, F^6, $^3J_{F^5F^6}$ = 20.0, $^3J_{F^6F^7}$ = 20.0 Hz), –150.6 d. d (1F, F^4, $^4J_{F^4F^5}$ = 59.0, $^3J_{F^3F^4}$ = 19.0, $^5J_{F^1F^4}$ = 19.0 Hz), –156.1 d. d (1F, F^7, $^3J_{F^6F^7}$ = 20.0, $^3J_{F^7F^8}$ = 20.0 Hz).

2-Heptafluoronaphthylboronic acid (15). The obtained solution of naphthylhalogenoboranes in CH_2Cl_2 was kept in air for 2–3 h. After evaporation of solvent the residue was washed with cold diethyl ether (1 mL) Yield 80 mg (64%), white solid. ^{11}B NMR spectrum (Et_2O): δ_B 27.1 ppm. ^{19}F NMR spectrum (Et_2O), δ_F, ppm: –108.6 d. d (1F, F^1, $^4J_{F^1F^8}$ = 69.4, $^5J_{F^1F^4}$ = 19.5 Hz), –127.6 d. m (1F, F^3, $^3J_{F^3F^4}$ = 18.0 Hz), –144.7 d. d. d (1F, F^8, $^4J_{F^1F^8}$ = 69.4, $^3J_{F^7F^8}$ = 16.5, $^5J_{F^5F^8}$ = 16.5 Hz), –147.1 d. d. d. d (1F, F^5, $^4J_{F^4F^5}$ = 57.4, $^3J_{F^5F^6}$ = 16.5, $^5J_{F^5F^8}$ = 16.5, $^4J_{F^5F^7}$ = 3.6 Hz), –151.5 d. d. d. d. d (1F, F^4, $^4J_{F^4F^5}$ = 57.4, $^3J_{F^3F^4}$ = 19.2, $^5J_{F^1F^4}$ = 19.5, $^5J_{F^4F^6}$ = 4.0, $^6J_{F^4F^8}$ = 4.0 Hz), –155.1 d. d (1F, F^6, $^3J_{F^5F^6}$ = 16.4, $^3J_{F^6F^7}$ = 18.0 Hz),–158.0 d. d (1F, F^7, $^3J_{F^6F^7}$ = 18.0, $^3J_{F^7F^8}$ = 16.5 Hz). Found, %: C 39.5; H 1.02; F 44.2. $C_{10}H_2BF_7O_2$. Calculated, %: C 40.32; H 0.68; F 44.64.

Reaction of K[2,3,5,6-$C_5NF_4BF_3$] with boron bromide. *a.* 1.1 M. solution of BBr_3 in CH_2Cl_2 (1.5 mL, 1.27 mmol) was added to the suspension of K[2,3,5,6-$C_5NF_4BF_3$] (297 mg, 1.15 mmol) in CH_2Cl_2 (6 mL) and stirred for 20 h at 22°C. No organofluorine compounds were detected in the mother liquor (^{19}F NMR).

b. 1.1 M. solution of BBr_3 in CH_2Cl_2 (2 mL, 2.2 mmol) was added to the stirred suspension of K[2,3,5,6-$C_5NF_4BF_3$] (262 mg, 1.0 mmol) in dichloromethane (7 mL) and heated to distill off the solvent. The residue was refluxed for 3 h. No organofluorine compounds were detected in the mother liquor (^{19}F NMR). The suspension was treated with 2% HCl, the precipitate dried in air to obtain K[2,3,5,6-$C_5NF_4BF_3$] (234 mg).

Defluorination of potassium aryltrifluoroborates with aluminum chloride (bromide). Potassium aryltrifluoroborate was added to the suspension of aluminum halide in the solvent and stirred at a given temperature (Table 1). The obtained mixture was centrifuged and the solution of aryldihaloboranes decanted.

3-Fluorophenyldibromoborane (20). ^{1}H NMR spectrum (hexane), δ, ppm: 7.98 d (1H, H^6, $^3J_{H^6H^5}$ = 7.3 Hz), 7.86 d (1H, H^2, $^3J_{H^2F^3}$ = 8.4 Hz), 7.33 m (1H, H^5), 7.18 d. d. d (1H, H^4, $^3J_{H^2F^3}$ = 8.4, $^3J_{H^4H^5}$ = 8.4, $^4J_{H^2H^4}$ = 2.7 Hz).

4-Fluorophenyldibromoborane (22). ^{1}H NMR spectrum (CH_2Cl_2), δ, ppm: 8.24 d. d (2H, $H^{2,6}$, $^3J_{H^2H^3}$ = 8.3, $^4J_{H^2F^3}$ = 6.0 Hz), 7.02 d. d (2H, $H^{3,5}$, $^3J_{H^2H^3}$ = 8.3, $^3J_{H^3F^4}$ = 8.3 Hz).

Reaction of K[2,3,5,6-$C_5NF_4BF_3$] with $AlBr_3$ in hexane. Hexane (3 mL) and borate **26** (125 mg, 0.5 mmol) were added to $AlBr_3$ (388 mg, 1.4 mmol). The obtained suspension was stirred for 96 h at 22°C. No organofluorine compounds were detected in the mother liquor (^{19}F NMR). The precipitate was filtered, washed with CH_2Cl_2 and dried in air to give starting borate **26** (115 mg).

Reaction of $AlBr_3$ with dichloromethane. Dark solution of $AlBr_3$ (467 mg, 1.75 mmol) in CH_2Cl_2 (2.0 mL, 56 mmol) was stirred for 4 h at 22°C. Grey suspension was centrifuged. ^{1}H NMR spectrum of the solution contained the signals of CH_2Cl_2 (5.24 ppm) and CH_2ClBr (5.11 ppm) (100 : 18). No changes occurred in the next 20 h. The reaction mixture was poured on ice, organic phase was dried with $MgSO_4$ and benzene (quantitative internal standard) was added. Yield of CH_2ClBr was 3.5 mmol (^{1}H NMR).

Reaction of K[$C_6F_5BF_3$] with $ClSiMe_3$. Suspension of borate **5** (740 mg, 2.7 mmol) and $ClSiMe_3$ (880 mg, 8.0 mmol) in $CHCl_3$ (3 mL) was refluxed with stirring for 3 h. No organofluorine compounds were found in the solution (^{19}F NMR).

Reaction of K[$C_6F_5BF_3$] with $SiCl_4$.. Suspension of borate **5** (740 mg, 2,7 mmol) and $SiCl_4$ (1 mL) in $CHCl_3$ (3 mL) was refluxed with stirring for 2 h. No organofluorine compounds were found in the solution (^{19}F NMR).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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