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Hydrodeboration of potassium polyfluoroaryl(fluoro)borates with alcohols☆

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ABSTRACT

Potassium polyfluoroaryltrifluoroborates, $K[Ar_FBF_3]$ ($Ar_F = C_6F_5$, HC_6F_4, MeC_6F_4, 4-$MeOC_6F_4$, 4-indol-1-ylC_6F_4, 4-imidazol-1-ylC_6F_4, 4-pyrazol-1-ylC_6F_4, 2,4,6-$C_6F_3H_2$ and 4-tetrafluoropyridyl), and $K[(C_6F_5)_2BF_2]$ undergo hydrodeboration to Ar_FH in aliphatic alcohols at elevated temperature. At the same conditions, borates $K[3,4,5\text{-}C_6F_3H_2BF_3]$, $K[4\text{-}FC_6H_4BF_3]$ and $K[C_6H_5BF_3]$ remain intact. The presence of base (Et_3N, K_2CO_3 and NaOMe) retards or prevents conversion of $K[C_6F_5BF_3]$. Attempted hydrodeboration of $K[C_6F_5BF_3]$ in MeCN failed.

1. Introduction

The carbon–carbon bond formation based on transition metal-catalyzed cross-coupling reactions of organoboron compounds with appropriate carbon electrophiles is one of the most effective and intensively studied modern preparative methods [1–6]. The matter of importance is the nature of key reactive boron-containing species and their role within catalytic cycle. In general, two sorts of organoboron compounds are used as partners for cross-coupling: borane derivatives, $OrgBX_2$ and borate derivatives, $K[OrgBX_3]$ [4,7]. Both of them have advantages and disadvantages in preparation and efficiency in application, but the latter are moisture-resistant and thermally stable substances and thus they are more convenient for routine syntheses [4,8].

Several researches described detailed evaluation of the hydrolysis of potassium aryltrifluoroborates in aqueous buffer (pH∼7), aqueous THF or aqueous MeCN under conditions of cross-coupling reactions (without the Pd catalyst) [9–14]. Despite of distinction in substrates and reaction conditions, the common conclusion was consisted in conversion of $K[ArBF_3]$ to $ArB(OH)_2$ and then to ArH. The rate of consumption of aryltrifluoroborates diminished with increase of electron-withdrawing character of aryl groups.

In course of systematic research of the low-reactive polyfluorinated organoboron compounds as partners in the Pd-catalyzed cross-coupling reactions, we explored reactivity of $K[C_6F_5BF_3]$ and related borates towards alcohols (alcoholysis/hydrodeboration under basic conditions) as a part of mechanistic aspect of cross-coupling. It is important that in contrast to organo(fluoro)borates, their polyfluorinated analogs are the less investigated although significant progress in this field was achieved in last two decades [15–27]. Salts $K[C_6F_5BF_3]$ and $K[CF_2=CFBF_3]$ can be involved in cross-coupling but underwent fast hydrodeboration under reaction conditions typical for hydrocarbon organotrifluoroborates [28–31] (detail discussion see [5,16]). Hydrodeboration of polyfluorinated organoboranes are better described. Polyfluorophenylboronic acids, $C_6F_nH_{5-n}B(OH)_2$ ($n \geq 2$), (except $3,4,5\text{-}C_6F_3H_2B(OH)_2$) were converted to the corresponding arenes in MeOH, aqueous MeOH, aqueous pyridine and by action of KOH in aqueous MeOH [32]. Heating of $(C_6F_5)_2BOH$ in CD_2Cl_2 in the presence of 1,8-bis(dimethylamino)naphthalene [33] as well as in methanol [34] gave C_6F_5H. Tris(pentafluorophenyl)borane is slowly decomposed with water under rather drastic conditions (water–toluene, 100 °C) [35]. The formation of C_6F_5H (90%) from $C_6F_5B(OH)_2$ and diethylamine in DMF (25 °C, 24 h) was well documented [36]. Arylboronic acids bearing the more electron-rich aryl moiety are tolerant towards hydrodeboration

☆ Dedicated to Prof. Hermann-Josef Frohn (Germany) on the occasion of his 70th birthday.

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under basic conditions [37]. It should be noted that the rate of hydrodeboration of potassium organotrifluoroborates under acidic conditions increases in opposite mode [16,38]. Hydrodeboration of $K[C_6F_5BF_3]$ in refluxed water (1 h) was assumed to produce KHF_2 and H_3BO_3 although the formation of pentafluorobenzene was not proved [39]. Reaction of $K[C_6F_5BF_3]$ with MeOH at 70–90 °C [40] or with secondary amines in DMF, diglyme or DMSO at higher temperature (150 °C) [41] leads to total or partial hydrodeboration to C_6F_5H. Hydrodeboration of $Li[C_6F_5B(OMe)_3]$ to C_6F_5H in MeOH, $HOCH_2CH_2OH$, acetone and MeCN should be mentioned too [42,43].

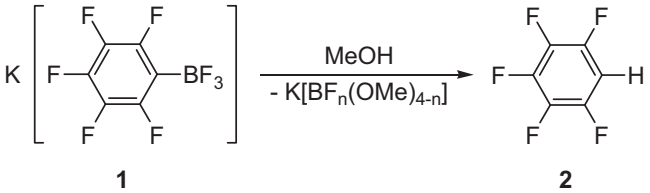
The picture presented above demonstrates the peculiar reactivity of perfluoroorganoboranes and borates towards their hydrocarbon analogues and requires clear experimental data for unambiguous interpretation of the observed phenomena.

2. Results

2.1. Effect of solvent

Potassium pentafluorophenyltrifluoroborate (**1**) does not react with methanol at 20–25 °C over a period of 30 h [40] but undergoes hydrodeboration to pentafluorobenzene (**2**) at elevated temperature (Scheme 1). At 50–55 °C the reaction is slow: conversion of **1** is 17% and 62% after 4 h and 11 h, respectively. At 90–95 °C **1** disappears within less than 4 h. Formation of $K[BF_4]$, $K[BF_3OMe]$ and in some cases $K[BF_2(OMe)_2]$ was detected by ^{19}FNMR spectroscopy (Table 1). It is important to note that reaction in a glass ampoule and in a FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) made trap gives the equal result, e.g. glass wall does not affect on the mode and rate of the process (cf. [9]).

Hydrodeboration of **1** under the action of other alcohols proceeds similarly although there are distinctions in the rate (Scheme 2). Thus, heating **1** in ethylene glycol at 90–95 °C results in consumption of **1** within 4 h. Conversion of **1** to C_6F_5H in 2-methoxyethanol is 7% and 29% after 1 h and 4 h, respectively. The use of propanol, *iso*-propanol or *tert*-butanol leads to the further decreasing of the hydrodeboration rate: conversion of **1** in these alcohols does not exceed 7%. In $(CF_3)_2CHOH$ borate **1** remains intact after stirring at 90–95 °C over a period of 4 h (Table 2).

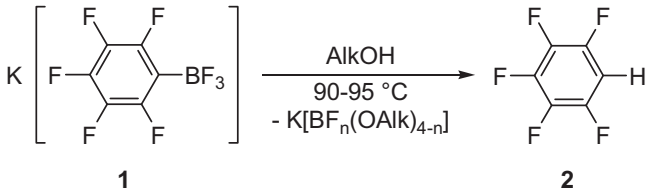


Scheme 1. Hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in MeOH.

Table 1
Results on hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in MeOH (Scheme 1).

Run	Temperature, °C	Time, h	Conversion of **1**, %	Notes
1	50–55	4	17	This work
2	50–55	11	62	This work
3[a]	50–55	4	21	This work
4[a]	50–55	6	29	This work
5	70	4	80	See [40]
6	90–95	1	81	See [40]
7	90–95	4	100	See [40]

[a] The reaction is performed in a FEP made trap.



Scheme 2. Hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in different alcohols.

Table 2
Results on hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in different alcohols after 4 h at 90–95 °C (Scheme 2).

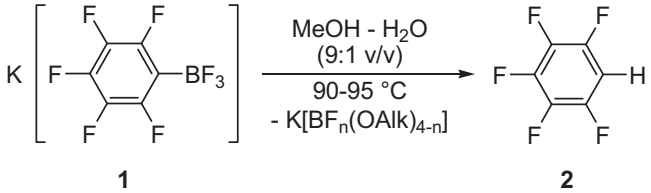
Run	Alk	Conversion of **1**, %
1	CH_3OH	100
2	$HOCH_2CH_2$	93
3	$CH_3OCH_2CH_2$	29
4	$CH_3CH_2CH_2$	6–7
5	$(CH_3)_2CH$	29
6	$(CH_3)_3C$	4
7	$(CF_3)_2CH$	<1

2.2. Effect of additives

We explored the effect of some additives on the relative hydrodeboration rate of **1** in methanol (Scheme 3). In aqueous methanol conversion of **1** at 90–95 °C is less than in the anhydrous solvent although difference is small (Table 3).

An additive of base stronger than MeOH tends to slow down the hydrodeboration rate of $K[C_6F_5BF_3]$. Borate **1** remains intact towards triethylamine in methanol at 50–55 °C within 11 h. At higher temperature pentafluorobenzene is formed although conversion is lower than in the absence of the base (27% vs. 100%, Table 1). Stirring of **1** with K_2CO_3 in MeOH or in neat MeCN at 90–95 °C does not affect this borate (Scheme 4).

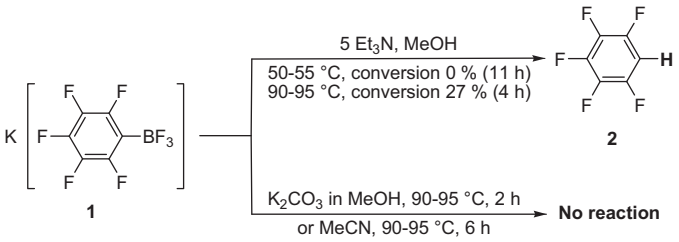
An additive of lithium chloride accelerates the consumption of **1** (Scheme 5). This is demonstrated by reactions at temperatures lower than 90–95 °C at which the above mentioned reactions do not proceed. Conversion of **1** in the presence of hydrate $LiCl{\cdot}H_2O$ at 50–55 °C (Table 4, run 2) is closely related to that in neat MeOH (Table 1, run 1), but besides of pentafluorobenzene (the hydrodeboration product), significant amounts of pentafluorophenyldifluoro(methoxy)borate (**3**) form in this case. Prolongation of heating up to 6 h causes disappearance of **3** and production of **2** at 86% conversion of **1** (Table 4, run 4; cf. Table 1, run 2). Anhydrous



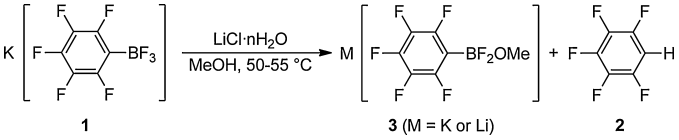
Scheme 3. Hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in aqueous MeOH.

Table 3
Results on hydrodeboration of $K[C_6F_5BF_3]$ (**1**) in aqueous MeOH at 90–95 °C (Scheme 3).

Run	Time, h	Conversion of **1**, %
1	1	72
2	4	100



Scheme 4. Hydrodeboration of K[$C_6F_5BF_3$] (**1**) in the presence of base.



Scheme 5. Reactions of K[$C_6F_5BF_3$] (**1**) with MeOH in the presence of LiCl·$n$$H_2O$.

Table 4
Results of reactions of K[$C_6F_5BF_3$] (**1**) with MeOH in the presence of LiCl·nH_2O at 50–55 °C (Scheme 5).

Run	n	Time, h	Conversion of **1**, %[a]	Molar ratio	
				3	**2**
1	0	3	60	0.16	1
2	1	3	14	0.75	1
3	0	6	100	0	1
4	1	6	86	0	1

[a] Conversion on both routes.

LiCl proved to be the much more effective reagent than LiCl·H_2O. In this case at 50–55 °C conversion of **1** to **2** and **3** is 60% for 3 h and the latter borate is formed in low yield (Table 4, run 1). After 6 h both borates **1** and **3** disappear and pentafluorobenzene was obtained in quantitative yield (Table 4, run 3).

2.3. Effect of aryl group in K[$ArBF_3$]

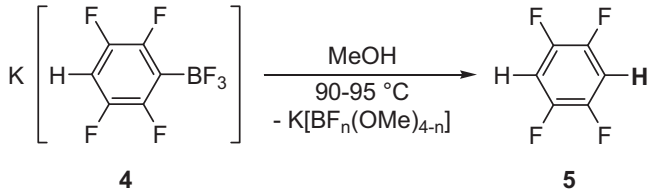
Preliminary experiments displayed the remarkable effect of substituent X in K[$XC_6F_4BF_3$] on the reactivity of these borates relating to parent K[$C_6F_5BF_3$]. Heating of potassium 2,3,5,6-tetrafluorophenyltrifluoroborate (**4**) in MeOH for 1 h leads to the less conversion of **4** to 1,2,4,5-tetrafluorobenzene (**5**) than in the case of the related reaction of **1** (Scheme 6). Nevertheless, after 4 h complete conversion of **4** to **5** was observed (Table 5).

Potassium 2,3,4,5-tetrafluorophenyltrifluoroborate (**6**) is more tolerant towards MeOH than **4** (Scheme 7). The reaction is very slow and leads to 2,3,4,5-tetrafluorophenyldifluoro(methoxy)borate (**7**) and 1,2,3,4-tetrafluorobenzene (**8**) (Table 6).

When a mixture of potassium 4-imidazol-1-yltetrafluorophenyltrifluoroborate (**9**), K[$C_6F_5BF_3$] and potassium 3,4-bis(imidazol-1-yl)trifluorophenyltrifluoroborate (**10**) was involved in the reaction with MeOH at 100 °C complete hydrodeboration of all borates to 1-(2′,3′,5′,6′-tetrafluorophenyl)imidazole (**11**), C_6F_5H and 1,2-bis(1-imidazolino)-3,5,6-trifluorobenzene (**12**) was observed after 6 h (Scheme 8).

These examples demonstrate the common transformation route of potassium polyfluoroaryltrifluoroborates but do not display the quantitative distinctions in their reactivity relative to K[$C_6F_5BF_3$]. To obtain this information we performed hydrodeboration of binary mixtures of K[$C_6F_5BF_3$] and salts from a series of different borates in MeOH at 90–95 °C and compared conversion of each borate to C_6F_5H and ArH, respectively, using ^{19}FNMR spectroscopy with quantitative internal standard (Scheme 9).

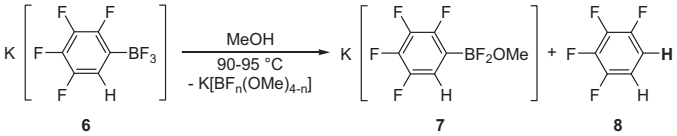
Potassium 4-methoxytetrafluorophenyltrifluoroborate (**13**) is the more reactive than K[$C_6F_5BF_3$] and forms 2,3,5,6-tetrafluoroanisole (**14**) in a quantitative yield within 2 h whereas **1** is still present under these conditions. K[$C_6F_5BF_3$] and potassium



Scheme 6. Hydrodeboration of K[2,3,5,6-$C_6F_4HBF_3$] (**4**) in MeOH.

Table 5
Results on hydrodeboration of K[2,3,5,6-$C_6F_4HBF_3$] (**4**) in MeOH at 90–95 °C (Scheme 6).

Run	Time, h	Conversion of **4**, %
1	1	40
2	4	100

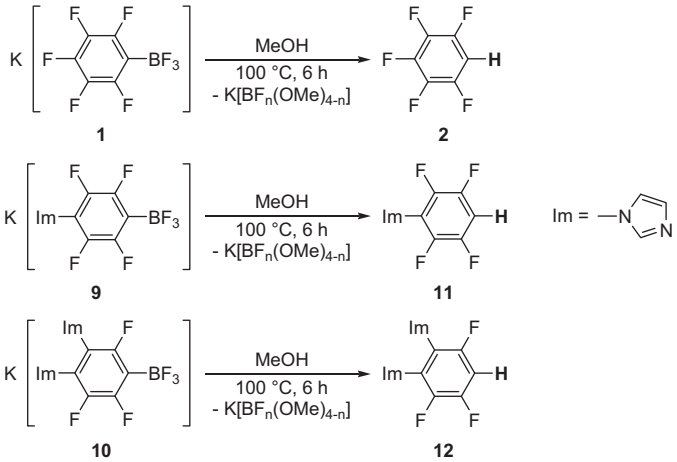


Scheme 7. Reaction of K[2,3,4,5-$C_6F_4HBF_3$] (**6**) in MeOH.

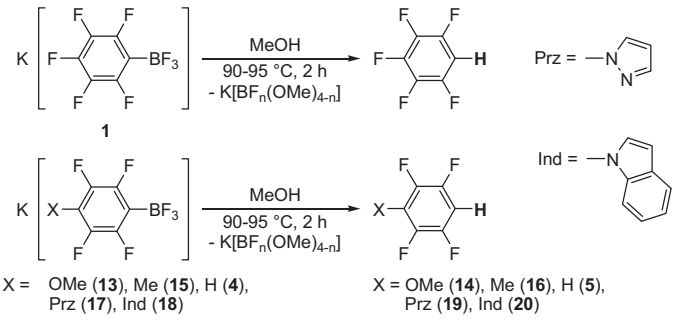
Table 6
Results of reaction of K[2,3,4,5-$C_6F_4HBF_3$] (**7**) with MeOH at 90–95 °C (Scheme 7).

Run	Time, h	Conversion of **6**, %	Molar ratio	
			7	**8**
1	1	<1	1	0
2	11	32[a]	0.6	1
3	30	100	0	1

[a] Conversion on both routes.



Scheme 8. Hydrodeboration of a mixture of K[4-$XC_6F_4BF_3$] (X = F, imidazol-1-yl) and K[3,4-$Im_2C_6F_3BF_3$] in MeOH.



Scheme 9. Hydrodeboration of a mixture of **1** and K[4-XC$_6$F$_4$BF$_3$] (X = OMe, Me, H, pyrazol-1-yl and indol-1-yl) in MeOH.

4-methyltetrafluorophenyltrifluoroborate (**15**) shows the equal reactivity towards MeOH producing pentafluorobenzene and 2,3,5,6-tetrafluorotoluene (**16**). Potassium 2,3,5,6-tetrafluorophenyltrifluoroborate (**4**), potassium 4-pyrazol-1-yltetrafluorophenyltrifluoroborate (**17**) and potassium 4-indol-1-yltetrafluorophenyltrifluoroborate (**18**) are the less reactive than **1**. Difference in the reactivity of **1** and **4** is not significant, but both borates **17** and **18** undergo hydrodeboration much more slowly relative to **1** and give 1-(2,3,5,6-tetrafluorophenyl)pyrazole (**19**) and 1-(2,3,5,6-tetrafluorophenyl)indole (**20**), respectively (Table 7).

To estimate the reactivity of K[5-XC$_6$F$_4$BF$_3$] relative to reactivity of K[4-XC$_6$F$_4$BF$_3$] and K[C$_6$F$_5$BF$_3$], a mixture of these borates was heated in MeOH at 90–95 °C for 40 min (Scheme 10). When X = Me, conversion of borates diminishes in the following order: from **1** to **15** and to K[5-MeC$_6$F$_4$BF$_3$] (**21**). The closed similarity was found for the structurally related borates K[4-HC$_6$F$_4$BF$_3$] and K[5-HC$_6$F$_4$BF$_3$] (**22**) (Table 8).

Borates with the less fluorinated phenyl groups, K[C$_6$F$_n$H$_{5-n}$BF$_3$] ($n \leq 3$), react with methanol more slowly than K[C$_6$F$_5$BF$_3$], and the rate of their consumption depends on the number and mutual disposition of fluorine atoms. Thus, heating of potassium 2,4,6-trifluorophenyltrifluoroborate (**23**) at 90–95 °C for 2 h results in mainly 2,4,6-trifluorophenyl(fluoro)(methoxy)borates **24** and **25** besides traces of 1,3,5-trifluorobenzene (**26**) (Scheme 11). Complete conversion of **23** to **26** was achieved over a period of 6 h (Table 9).

Potassium 3,4,5-trifluorophenyltrifluoroborate (**27**) does not react with MeOH over 12 h (Scheme 12).

Potassium 4-fluorophenyltrifluoroborate (**28**) and potassium phenyltrifluoroborate (**29**) do not react with MeOH at 90–95 °C over a period of 10–12 h, although the former gives traces of the corresponding aryldifluoro(methoxy)borate (**30**) (Scheme 13).

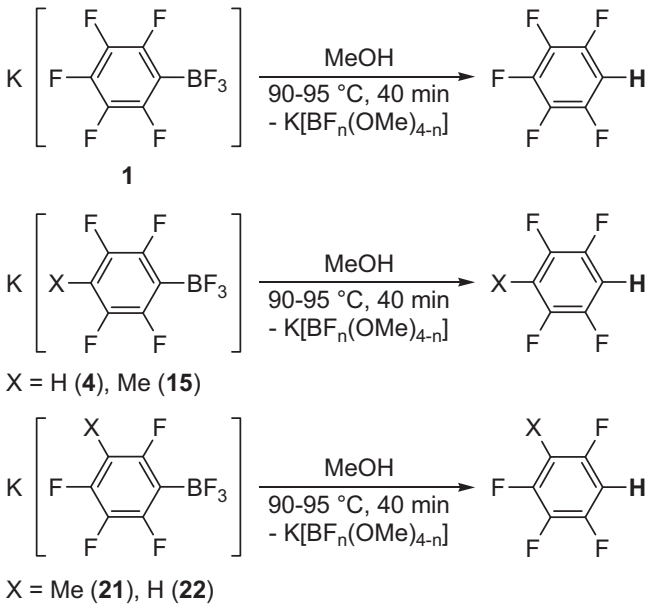
3. Discussion

The obtained results allow us to distinguish two routes of consumption of K[ArBF$_3$] in alcohols: (a) hydrodeboration to ArH and (b) alcoholysis to K[ArBF$_n$(OAlk)$_{3-n}$]$^-$. We assume that in both routes the initial step is dissociation of [ArBF$_3$]$^-$ to aryldifluoroborane and fluoride anion assisted by AlkOH (Scheme 14, Eq. (1)). Then ArBF$_2$ and AlkOH form adduct **A** (Scheme 14, Eq. (2)). The subsequent intramolecular substitution of boron atom by hydrogen (hydrodeboration) gives ArH (Scheme 14, Eq. (3)). Alternatively, elimination of H$^+$ from adduct **A** leads to aryldifluoro(alkoxy)borate (alcoholysis) (Scheme 14, Eq. (4)). The products of alcoholysis can be also involved in the above reactions forming ArH and BF(OAlk)$_2$ (these routes are not presented on Scheme 14 because closed similarity with conversions of [ArBF$_3$]$^-$). Attachment of a fluoride anion to BF$_n$(OAlk)$_{3-n}$ gives [BF$_{n+1}$(OAlk)$_{3-n}$]$^-$ (Scheme 14, Eq. (5)).

In the presence of species able to bind the fluoride anion equilibrium (Scheme 14, Eq. (1)) is shifted to right and thereby subsequent reactions facilitates. This is illustrated by the significant acceleration of the K[C$_6$F$_5$BF$_3$] consumption in the presence of anhydrous LiCl (Tables 1 and 4). Here LiCl acts as a scavenger of the fluoride anion because the large crystal lattice energy of formed LiF (1027 kJ mol^{-1}) [44] and its low solubility. Hydrate LiCl·H$_2$O is the less effective and initially produces much more M[C$_6$F$_5$BF$_2$OMe] than anhydrous LiCl (Table 4, runs 1, 2). The role of water (3–4 equivalents) in this phenomenon is not clear. If aryl(fluoro)borate is a very weak fluoride donor, concentration of the corresponding aryl(fluoro)borane (very strong Lewis acid) is too low for the subsequent conversions with the remarkable rate. Thus, heating of a mixture of **1** with potassium bis(pentafluorophenyl)difluoroborate (**31**) at 90–95 °C for 6 h leads to quantitative hydrodeboration of K[C$_6$F$_5$BF$_3$] (**1**) while K[(C$_6$F$_5$)$_2$BF$_2$] (**31**) remains intact (Scheme 15). Formation of **2** from **31** in MeOH occurs slowly at 120 °C and after 6 h conversion does not exceed 17% (Scheme 16).

Table 7
Results on hydrodeboration of K[4-XC$_6$F$_4$BF$_3$] (X = F, OMe, Me, H, pyrazol-1-yl and indol-1-yl) in MeOH after 2 h at 90–95 °C (Scheme 9).

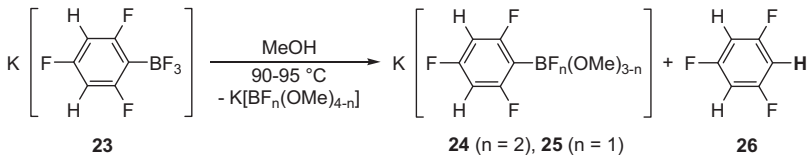
Run	X	K[4-XC$_6$F$_4$BF$_3$]	4-XC$_6$F$_4$H	Conversion, %	
				1	K[4-XC$_6$F$_4$BF$_3$]
1	OMe	**13**	**14**	80	100
2	Me	**15**	**16**	87	87
3	H	**4**	**5**	82	73
4	Prz	**17**	**19**	41	19
5	Ind	**18**	**20**	89	61



Scheme 10. Hydrodeboration of a mixture of **1** and salts K[XC$_6$F$_4$BF$_3$] (X = H and Me) in MeOH.

Table 8
Results on hydrodeboration of K[XC$_6$F$_4$BF$_3$] (X = F, H and Me) in MeOH after 40 min at 90–95 °C (Scheme 10).

Run	X	Conversion, %		
		1	K[4-XC$_6$F$_4$BF$_3$]	K[5-XC$_6$F$_4$BF$_3$]
1	H	83	43	36
2	Me	93	67	42

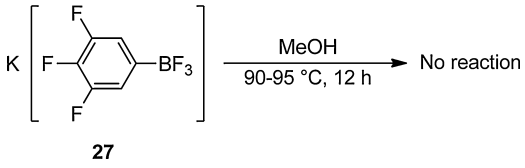


Scheme 11. Reaction of K[2,4,6-$C_6F_3H_2BF_3$] (**23**) with MeOH.

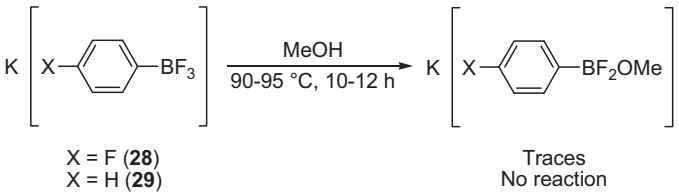
Table 9
Results of reaction of K[2,4,6-$C_6F_3H_2BF_3$] (**23**) with MeOH at 90–95 °C (Scheme 11).

Run	Time, h	Conversion of **23**, %[a]	Molar ratio, %	
			24 and **25**	**26**
1	2	21	4 (n = 1–3)	1
2	6	100	~0	1

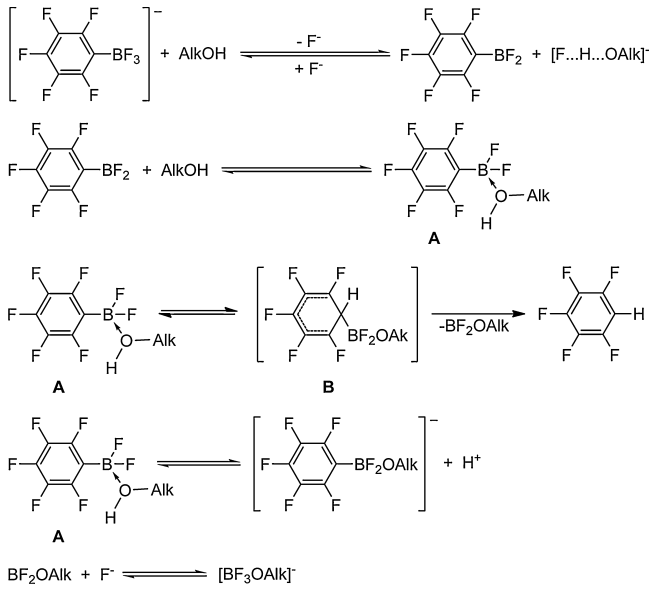
[a] Conversion on both routes.



Scheme 12. Attempted reaction of K[3,4,5-$C_6F_3H_2BF_3$] (**27**) with MeOH.



Scheme 13. Attempted reaction of K[4-$C_6H_4FBF_3$] (**29**) and K[$C_6H_5BF_3$] (**28**) with MeOH.

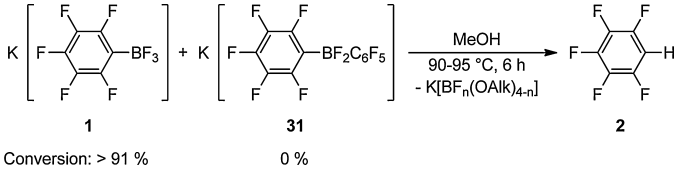


Scheme 14. Mechanism of the K[$C_6F_5BF_3$] hydrodeboration.

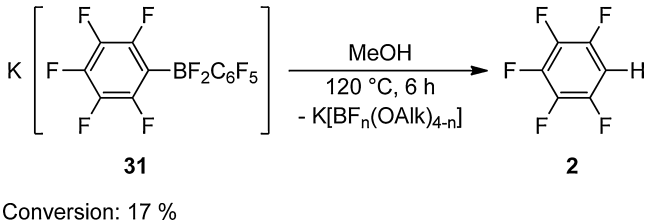
Analogously, hydrodeboration of potassium 2,3,5,6-tetrafluoropyridyltrifluoroborate (**32**) proceeds at 90–95 °C much more slowly than hydrodeboration of **1** (cf. Table 1 and Scheme 17).

Here elimination of fluoride anion from both [$(C_6F_5)_2BF_2$]$^-$and [2,3,5,6-$C_5NF_4BF_3$]$^-$aryl(fluoro)borates is the rate-determining step. These borates are much weaker fluoride donors than [$C_6F_5BF_3$]$^-$ [45]), and the negligible concentration of the corresponding perfluoroaryl(fluoro)borane is the key factor hindering the subsequent transformations (Scheme 14).

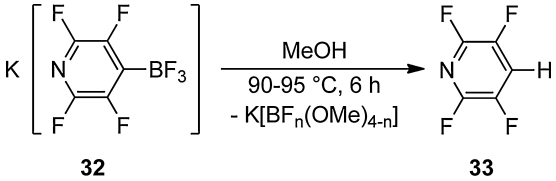
Tolerance of **31** and **32** towards MeOH is in agreement with the published data on hydrolysis of aryltrifluoroborates to arylboronic acids. Perrin et al. presented kinetics of hydrolysis of K[$ArBF_3$] in aqueous phosphate buffer (pH 6.9–7.0) (22 °C): Ar (half-life) = C_6H_5 (2 min) < 3,4-$C_6F_2H_3$ (9 min) < 4-$CF_3C_6H_4$ (29 min) = 4-CNC_6H_4 (29 min) < 4-$O_2NC_6H_4$ (42 min) < 2,4-$C_6F_2H_3$ (43 min) < 2-FC_6H_4 (50 min) < 2,4,6-$C_6F_3H_2$ (280 min) [10] < 4-C_5NH_4 (346 min) < 2-FC_5NH_3 (364 min) < 2,6-$C_5NCl_2H_2$ (866 min) < 2,6-$C_5NF_2H_2$ (1155 min) [11]. The strong tolerance against hydrolysis is attributed to zwitterionic aryltrifluoroborates, 2-$XC_6H_4BF_3$ (X is positively charged substituent (Me_3N, $MePh_2P$, and Me_2S) (phosphate buffer in 80% aqueous acetonitrile, pH 7.5) (20 °C) [12] and (1-methylpyridinium-4-yl)trifluoroborate (pH 6.9–7.0) (22 °C) [11]. Hydrolysis products [$ArBF_{3-n}(OH)_n$]$^-$ (n = 1, 2) are better fluoride anion donors than [$ArBF_3$]$^-$ and they



Scheme 15. Hydrodeboration of K[$(C_6F_5)_nBF_{4-n}$] (n = 1 and 2) in MeOH.



Scheme 16. Hydrodeboration of K[$(C_6F_5)_2BF_2$] in MeOH.



Scheme 17. Hydrodeboration of K[2,3,5,6-$C_5NF_4BF_3$] (**32**) in MeOH.

were not detected by the ^{19}FNMR spectroscopy. Thus, the loss of the first fluoride anion was outlined as a single rate-determining step. Under basic conditions (D_2O, ≥3 equivalents of K_2CO_3, Cs_2CO_3 or ≥6 equivalents of KOH), borate M[4-$FC_6H_4BF_3$] undergoes hydrolysis and such intermediates M[4-$FC_6H_4BF_n(OH)_{3-n}$] (n = 0–2) were detected [13]. Closely related conversion of K[$ArBF_3$] (Ar = C_6H_5, 2-XC_6H_4 (X = Cl, OH, OMe, OTs and CHO), 4-XC_6H_4 (X = F, Me and OMe) to the arylboronic acid occurs under the action of MOH, $MHCO_3$ and M_2CO_3 (M = Li, Na and K) in aqueous acetonitrile at room temperature while no hydrodeboration was observed [46]. More detailed evaluation of the hydrolysis with Cs_2CO_3 (three equivalents) in aqueous THF (THF:H_2O = 10:1) (55 °C) revealed the following order of the half-life of K[$ArBF_3$]: Ar (half-life) = 4-$MeOC_6H_4$ (19 min) < 4-MeC_6H_4 (51 min) < C_6H_5 (100 min) < 4-FC_6H_4 (200 min) < 4-$CF_3C_6H_4$ (2 d 18 h) < 3-$O_2NC_6H_4$ (5 d) < 3,5-$(CF_3)_2C_6H_3$ (54 d) [9]. Thus, electron-withdrawing aryl groups slow down hydrolysis of K[$ArBF_3$] relative to K[$C_6H_5BF_3$] while electron-donating groups accelerate hydrolysis. If transformation of fluoro-containing borates K[$C_6F_nH_{4-n}BF_3$] to $C_6F_nH_{5-n}$ in alcohols followed this way, K[$C_6H_5BF_3$] would be the most reactive compound while lowest reactivity would be attributed to K[$C_6F_5BF_3$]. However, the real picture is another: borates **29**, **28** and **27** do not react with MeOH at 90–95 °C, and the relative rate of consumption of other borates are graded in order: Ar = C_6H_5–4-FC_6H_4–3,4,5-$C_6F_3H_2$ << 2,4,6-$C_6F_3H_2$ < XC_6F_4.

This paradox arises from two factors which determine the observed rate of consumption of K[$ArBF_3$] in AlkOH. They act opposite to each other, and final result depends on balance of them. The first one is the *reversible* conversion of $[ArBF_3]^-$ to $ArBF_2$·OHAlk (adduct **A**) (Scheme 14, Eqs. (1) and (2)) and to $[ArBF_2(OAlk)]^-$ (Scheme 14, Eq. (4)). Some of species like $ArBF_2$·OHAlk or $[ArBF_2(OAlk)]^-$ were detected by ^{19}FNMR spectroscopy (Ar = 2,3,4,6-C_6F_4H; 2,3,4,5-C_6F_4H, 2,4,6-$C_6F_3H_2$, 4-FC_6H_4; OAlk = -OMe). The following cascade of dissociative exchanges of F for OR would yield the aryl(dialkoxy)borane or aryl(trialkoxy)borate, and rate of the reaction would rise from Ar = C_6F_5 to Ar = C_6H_5 as suggested above.

The second factor deals with rearrangement of adduct **A** to species **B** (or structurally related transition state) which loss BF_2OMe giving ArH (Scheme 14, Eq. (3)). The driving forces of the reversible conversion of electrically neutral adduct **A** to zwitter-ion **B** is necessity of sufficiently large negative charge at carbon atom C–1. If it is too small, contribution of **B** in equilibrium is too low and the *irreversible* formation of ArH from **B** occurs very slowly. Unfortunately, the charge distribution in adducts $ArBF_2$·OHAlk has not been reported so far. We assume that the presence of 1–2 fluorine atom(s) at the *ortho* position to boron atom in **A** increases the negative charge at carbon atom C–1. This consideration is based on experimental facts. Indeed, substituent X in borates like K[4-X-2,3,5,6-$C_6F_4BF_3$] is located far from reaction site C–1 and the effect of different X on the rate of hydrodeboration is weak relative to the effect of fluorine in K[$C_6F_5BF_3$] (Table 7). The consumption rate of borates K[5-X-2,3,5,6-$C_6F_4BF_3$] (X = H or Me) diminishes relative to that for **1** (Table 8), whereas K[2,3,4,5-$C_6F_4HBF_3$] (one fluorine atom at *ortho*-position) is the least reactive (Table 6). K[2,4,6-$C_6F_3H_2BF_3$] (two electron-acceptors at *ortho*-position) reacts with MeOH much faster than isomer K[3,4,5-$C_6F_3H_2BF_3$] (no electron-acceptors at *ortho*-position) (Schemes 11 and 12). It should be mentioned the kinetic investigation of hydrodeboration of fluoro-containing phenylboronic acids, $ArB(OH)_2$, in 9% D_2O–pyridine [32] that revealed the same order of reactivity of substrates {Ar = 3,4,5-$C_6F_3H_2$ << 2,4,6-$C_6F_3H_2$ < 2,3,4,5-C_6F_4H < 2,3,5,6-C_6F_4H < C_6F_5} as one obtained in this paper. The similar hydrodeboration of arylboronic acids, $ArB(OH)_2$, with K_3PO_4 in aqueous THF occurs with the rates ranked in the following order: Ar (half-life) = 2,6-$C_6F_2H_3$ (28 min) > 2,4,6-$C_6F_3H_2$ (10 min) > 3-Bu-2,6-$C_6F_2H_2$ (6 min) > 2,3,6-$C_6F_3H_2$ (2 min) [14]. The fast hydrodeboration of both $C_6F_5B(OH)_2$ and Li[$C_6F_5B(OMe)_3$] in methanol [32,42] as well as both 2,3,5,6-$C_5NF_4B(OH)_2$, and Li[2,3,5,6-$C_5NF_4B(OMe)_3$] in cold (−40 °C) aqueous MeOH acidified with HCl [47] proceeds by the similar pathways. In contrast, 3,5-$C_6F_2H_3B(OH)_2$ (no fluorine atoms at *ortho*-position) reacts with hot *iso*-propanol to give 3,5-$C_6F_2H_3B(OCHMe_2)_2$ that is converted to Na[3,5-$C_6F_2H_3B(OCHMe_2)_3$] in 79% yield by reflux with $NaOCHMe_2$ in *iso*-propanol without hydrodeboration [48]. Moreover, many arylboronic acids bearing electron-rich aryl group are resistant towards hydrodeboration in saturated aqueous NaOH or KOH in a water–toluene mixture producing aryltrihydroxyborates in preparative yields, and these borates are stable in aqueous alkali [49].

The important role plays the nature of solvent or reaction media as whole. Basicity of alcohols (pK_{BH^+}) increases with elongation and branching of hydrocarbon chain from methanol to *tert*-butanol, CH_3OH (−4.86) < $(CH_3)_2CHOH$ (−4.72) < $(CH_3)_3COH$ (−3.80) (water, 25 °C) [50], and the rate of hydrodeboration of K[$C_6F_5BF_3$] diminishes in parallel way giving decrease of conversion from 81% to 4% (Table 2). Steric requirements around the three-coordinated boron atom (Scheme 14, eq. 2) are not so strong to discriminate CH_3OH vs. RCH_2CH_2OH (R = H, CH_3 and CH_3O) on their coordination ability, although the steric factor can be decisive for coordination of $ArBF_2$ with $(CH_3)_2CHOH$, $(CH_3)_3COH$ and $(CF_3)_2CHOH$. An additive of base stronger than MeOH retards reaction. In the presence of Et_3N (pK_{BH^+} 10.6 [50]) the rate of hydrodeboration diminishes in three times, while in the presence of NaOMe (24 °C, 28 h and 68 °C, 4 h) [40], K_2CO_3 or in neat MeCN (pK_{BH^+} 0.80 [50]) consumption of **1** was not observed. Presumably, these bases form the hydrogen bond with AlkOH + Base = Alk-O...H...Base, and a competition with F^- inhibits dissociation of K[$C_6F_5BF_3$] to $C_6F_5BF_2$ and F^- (Scheme 14, Eq. (1)). This elucidates moderate conversion of **1** and **17** during hydrodeboration (Table 7, run 4) as a consequence of increased basicity of reaction media by borate **17** as well as arylated heterocycle **19** [51]. On the other side, reaction of K[4-$FC_6H_4BF_3$] with Et_3N in CD_3OH (rt, 1 h) results in only [Et_3NH][4-$FC_6H_4BF_2OCD_3$] [52], e.g. the fluoride anion donor stronger than K[$C_6F_nH_{4-n}BF_3$] ($n \geq 3$) does not require the hydrogen bond assistance (Scheme 14, run 1) and the corresponding adduct **A** undergoes deprotonation rather than rearrangement to **B**. The formation of strong adduct $C_6F_5BF_2$·Base (Base = NEt_3, $NCCH_3$) as a reason of tolerance of **1** was rejected on the basis of the ^{19}FNMR data [16,53].

4. Conclusion

Despite on apparent similarity with reported hydrolysis/hydrodeboration of K[$ArBF_3$] (Ar is aryl or hetaryl group) in H_2O, aqueous THF or aqueous MeCN [9–14], reaction of fluorinated potassium aryl(fluoro)borates with alcohols proceeds in more complex way. The highest rate of hydrodeboration of K[$C_6F_5BF_3$] was observed for reactions carried out in MeOH. The reaction rate slightly reduces in aqueous 90% MeOH and in $HOCH_2CH_2OH$ whereas hydrodeboration in $MeOCH_2CH_2OH$, $CH_3CH_2CH_2OH$, $(Me)_2CHOH$, $(Me)_3COH$ and $(CF_3)_2CHOH$ proceeds slowly. The presence of LiCl (fluoride anion scavenger) accelerates the reaction while in the more basic media (MeCN) or with additives like Et_3N, K_2CO_3, and NaOMe hydrodeboration retards or does not occur. Reactivity of borates K[$C_6F_nH_{5-n}BF_3$] increases with number of fluorine atoms n. In a series of isomers, the borate with maximum number of fluorine atoms at positions 2,3,5,6 is the most reactive. However, K[2,3,5,6-$C_5NF_4BF_3$] and K[$(C_6F_5)_2BF_2$] are more resistant than K[$C_6F_5BF_3$] due to the high fluoride affinity of the corresponding perfluoroaryl(fluoro)boranes.

5. Experimental

5.1. General

The NMR spectra were recorded using a Bruker AVANCE 300 spectrometer (^{1}H at 300.13 MHz, ^{19}F at 282.40 MHz, and ^{11}B at 96.29 MHz). The chemical shifts are referenced to TMS (^{1}H), CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), and $BF_3{\cdot}OEt_2/CDCl_3$ (15% v/v) (^{11}B), respectively. The high resolution mass spectra were recorded using a Thermo Scientific DFS spectrometer in EI mode (70 eV). These analyses as well as elemental analysis were performed in the Collective Service Center of SB RAS (Novosibirsk).

Methanol, ethylene glycol, propanol, *iso*-propanol, *tert*-butanol, and triethylamine were refluxed with CaO and distilled. 2-Methoxyethanol (Acros) and $(CF_3)_2CHOH$ (ABCR) were used as supplied. LiCl was prepared by calcination of $LiCl{\cdot}H_2O$ at 200–250 °C over 4 h $K[C_6F_5BF_3]$ [54], $K[2,3,5,6\text{-}C_5NF_4BF_3]$ [47], $K[2,3,4,5\text{-}C_6F_4HBF_3]$ [30], $K[2,3,4,6\text{-}C_6F_4HBF_3]$ [30], $K[2,3,5,6\text{-}C_6F_4HBF_3]$ [55], $K[2,4,6\text{-}C_6F_3H_2BF_3]$ [55], $K[3,4,5\text{-}C_6F_3H_2BF_3]$ [55], $K[4\text{-}C_6FH_4BF_3]$ [55], $K[C_6H_5BF_3]$ [38], $K[4\text{-PrzC}_6F_4BF_3]$ [41], $K[4\text{-ImC}_6F_4BF_3]$ [41], $K[4\text{-IndC}_6F_4BF_3]$ [41], $K[4\text{-CH}_3OC_6F_4BF_3]$ [40], $K[(C_6F_5)_2BF_2]$ [56] and a mixture of $n\text{-HC}_6F_4CF_3$ (n = 4, 5 and 6 in molar ratio 23:70:7) [57] were prepared as described. Known products $2,3,5,6\text{-}C_6F_4HOCH_3$ (**14**) [58], 1-(2,3,5,6-tetrafluorophenyl)pyrazole (**19**) [59], $1,2,4,5\text{-}C_6F_4H_2$ (**5**), $1,2,3,5\text{-}C_6F_4H_2$ (**34**), $1,2,3,4\text{-}C_6F_4H_2$ (**8**), $1,3,5\text{-}C_6F_3H_3$ (**26**), $2,3,5,6\text{-}C_5NF_4H$ (**33**) [60] were identified by their ^{19}FNMR spectra. Synthesis of $K[n\text{-}CH_3C_6F_4BF_3]$ (n = 5, 6) described below. Quantitative analysis of products in reaction mixtures were performed by the ^{19}FNMR with C_6F_6 or C_6H_5F as an internal reference. Because of limited solubility of some $K[ArBF_3]$ in AlkOH, conversion of borate to ArH was calculated from a ratio $\{ArH\}/\{K[ArBF_3]_0\}$ where {ArH} is quantity of produced ArH (^{19}FNMR) and $\{K[ArBF_3]_0\}$ is initial quantity of borate (in mmol).

Solubility of $K[C_6F_5BF_3]$ (mg {mmol}) per mL of alcohol: 1 {0.004} in PrOH, 0.8 {0.003} in $(CH_3)_2CHOH$, 0.3 {0.001} in *tert*-BuOH, >80 {>0.29} in $MeOCH_2CH_2OH$).

5.2. Reaction of $K[C_6F_5BF_3]$ with MeOH at 50–55 °C

5.2.1. In a glass tube

Suspension of $K[C_6F_5BF_3]$ (24 mg, 0.087 mmol) in MeOH (0.83 mL) was kept at 50–55 °C for 4 h in a sealed tube. The ^{19}FNMR spectrum of resulted solution showed the resonances of C_6F_5H (0.015 mmol) and $K[C_6F_5BF_3]$ (0.072 mmol). Heating for the next 7 h (total 11 h) gave C_6F_5H (0.054 mmol) and $K[C_6F_5BF_3]$ (0.033 mmol). In both cases, the ^{19}FNMR signals of $K[BF_3OMe]$ and $K[BF_2(OMe)_2]$ were present.

5.3. In a FEP made trap

$K[C_6F_5BF_3]$ (58 mg, 0.211 mmol) and MeOH (1.5 mL) were loaded into a FEP made trap (o.d. = 9.0 mm, i.d = 8.0 mm) equipped with a Teflon-coated magnetic bar and the trap was deposited in a bath (50–55 °C). The suspension was stirred for 4 h, cooled to 22 °C and a probe of the mother liquid was taken. The ^{19}FNMR spectrum displayed the resonances of C_6F_5H (0.044 mmol) beside the signals of $K[C_6F_5BF_3]$, $K[BF_4]$ and $K[BF_3OMe]$. After 6 h at 50–55 °C, 0.062 mmol of C_6F_5H were formed.

5.4. Reaction of $K[C_6F_5BF_3]$ with alcohols at 90–95 °C

5.4.1. With MeOH

Suspension of $K[C_6F_5BF_3]$ (31 mg, 0.11 mmol) in MeOH (0.76 mL) was kept for 4 h in a sealed tube. The ^{19}FNMR spectrum of the resulted solution showed the resonances of C_6F_5H (0.11 mmol) beside the signals of $K[BF_3OMe]$, $K[BF_2(OMe)_2]$ and traces of $K[C_6F_5BF_3]$.

5.5. With ethylene glycol

Solution of $K[C_6F_5BF_3]$ (89 mg, 0.32 mmol) in ethylene glycol (1.3 mL) was kept for 4 h in a sealed tube to give C_6F_5H (0.30 mmol) (^{19}FNMR).

5.5.1. With 2-methoxyethanol for 1 h

Solution of $K[C_6F_5BF_3]$ (40 mg, 0.15 mmol) in 2-methoxyethanol (0.9 mL) was kept for 1 h in a sealed tube. Conversion of **1** to C_6F_5H (0.010 mmol) was 7%.

5.5.2. With 2-methoxyethanol for 4 h

Solution of $K[C_6F_5BF_3]$ (38 mg, 0.14 mmol) in 2-methoxyethanol (0.9 mL) was kept for 4 h in a sealed tube. Conversion of **1** to C_6F_5H (0.040 mmol) was 29%.

5.6. With n-propanol

Suspension of $K[C_6F_5BF_3]$ (41 mg, 0.150 mmol) in PrOH (1 mL) was stirred for 4 h in a sealed tube forming C_6F_5H (0.009 mmol) (^{19}FNMR).

5.7. With iso-propanol

Suspension of $K[C_6F_5BF_3]$ (48 mg, 0.175 mmol) in $(Me)_2CHOH$ (1 mL) was stirred for 4 h in a sealed tube forming C_6F_5H (0.012 mmol) (^{19}FNMR).

5.8. With tert-BuOH

Suspension of $K[C_6F_5BF_3]$ (30 mg, 0.109 mmol) in *tert*-BuOH (0.8 mL) was stirred for 4 h in a sealed tube forming C_6F_5H (0.004 mmol) (^{19}FNMR).

5.9. With $(CF_3)_2CHOH$

Suspension of $K[C_6F_5BF_3]$ (41 mg, 0.150 mmol) in $(CF_3)_2CHOH$ (1 mL) was stirred for 4 h in a sealed tube. After cooling, trace of C_6F_5H was detected (^{19}FNMR).

5.9.1. Reaction in aqueous MeOH for 1 h

Suspension of $K[C_6F_5BF_3]$ (31 mg, 0.11 mmol) in aqueous MeOH (H_2O:MeOH = 1:9, v/v) (0.83 mL) was kept for 1 h in a sealed tube. The ^{19}FNMR spectrum of resulted solution showed resonances of C_6F_5H (0.080 mmol) beside the signals of $K[C_6F_5BF_3]$, $K[BF_3OMe]$, $K[BF_2(OMe)_2]$ and traces of $K[BF_3OH]$.

5.9.2. Reaction in aqueous MeOH for 4 h

Suspension of $K[C_6F_5BF_3]$ (28 mg, 0.10 mmol) in aqueous MeOH (H_2O:MeOH = 1:9, v/v) (0.83 mL) was kept for 4 h in a sealed tube. The ^{19}FNMR spectrum of the resulted solution showed the resonances of C_6F_5H (0.10 mmol) beside the signals of $K[BF_3OMe]$, $K[BF_2(OMe)_2]$ and traces of $K[BF_3OH]$ [δ −144.4 (q (1:1:1:1), ^1J(F, B) = 15 Hz] [61,62].

5.10. Reaction of $K[C_6F_5BF_3]$ with Et_3N in MeOH

$K[C_6F_5BF_3]$ (61 mg, 0.22 mmol) and Et_3N (122 mg, 1.20 mmol) in MeOH (1.5 mL) was kept in a sealed tube at 50–55 °C for 11 h (no reaction) and 4 h at 90–95 °C to produce C_6F_5H (0.06 mmol) (^{19}FNMR).

5.11. Attempted reaction of K[$C_6F_5BF_3$] and K_2CO_3 with MeOH

Suspension of K[$C_6F_5BF_3$] (28 mg, 0.10 mmol) and K_2CO_3 (21 mg, 0.15 mmol) in MeOH (0.8 mL) was magnetically stirred at 90–95 °C for 2 h in a sealed tube. The ^{19}FNMR spectrum of the mother liquor showed the resonances of K[$C_6F_5BF_3$] and C_6F_5H (trace).

5.12. Attempted reaction of K[$C_6F_5BF_3$] with MeCN

Suspension of K[$C_6F_5BF_3$] (22 mg, 0.08 mmol) in anhydrous MeCN (0.8 mL) was kept in a sealed tube at 90–95 °C for 6 h (no reaction) (^{19}FNMR).

5.13. Reaction of K[$C_6F_5BF_3$] with LiCl in MeOH at 50–55 °C

5.13.1. Reaction with anhydrous LiCl

K[$C_6F_5BF_3$] (56 mg, 0.20 mmol), LiCl (35 mg, 0.83 mmol) and MeOH (1 mL) were loaded into a glass ampoule. The ampoule was sealed by flame and kept at 50–55 °C. After 3 h, a probe of the mother liquor showed the resonances of $[C_6F_5BF_3]^-$ (0.06 mmol), $[C_6F_5BF_2(OMe)]^-$ (0.02 mmol) and C_6F_5H (0.12 mmol). After 6 h signals of C_6F_5H (0.19 mmol) beside the signals of traces of $[C_6F_5BF_3]^-$ were present.

5.14. Reaction with LiCl·H_2O

LiCl·H_2O (162 mg, 2.7 mmol) was dissolved in MeOH (3 mL) and K[$C_6F_5BF_3$] (230 mg, 0.83 mmol) was added. The suspension was stirred at 50–55 °C. A probe of the mother liquor showed the resonances of $[C_6F_5BF_3]^-$ (0.57 mmol), $[C_6F_5BF_2(OMe)]^-$ (0.09 mmol), C_6F_5H (0.12 mmol) after 3 h and C_6F_5H (0.72 mmol) beside the signals of traces of $[C_6F_5BF(OMe)_2]^-$ after 6 h, respectively.

M[$C_6F_5BF_2OMe$] (**3**). ^{19}FNMR (MeOH): δ −133.8 (m, 2F, $F^{2,6}$), −141.9 (q (1:1:1:1), ^1J(F, B) = 47 Hz, 2F, BF_2OMe), −161.0 (t, $^3J(F^4, F^{3,5})$ = 20 Hz, 1F, F^4), −165.7 (m, 2F, $F^{3,5}$).

5.15. Reaction of potassium polyfluoroaryl(fluoro)borates with MeOH at 90–95 °C

*5.15.1. Reaction of K[2,3,5,6-$C_6F_4HBF_3$] (**4**)*

A mixture of K[2,3,5,6-$C_6F_4HBF_3$] (34 mg, 0.13 mmol) and MeOH (0.8 mL) was heated for 1 h in a sealed tube. Cooling the colorless solution resulted in formation of white crystals. The ^{19}FNMR spectrum of the mother liquor showed the resonances of 1,2,4,5-$C_6F_4H_2$ (0.052 mmol) beside the signals of K[2,3,5,6-$C_6F_4HBF_3$], K[BF_3OMe] and K[$BF_2(OMe)_2$]. After 4 h, reaction of **4** (29 mg, 0.11 mmol) and MeOH (0.8 mL) gave the colorless solution of 1,2,4,5-$C_6F_4H_2$ (0.11 mmol), K[BF_3OMe] and K[$BF_2(OMe)_2$] (^{19}FNMR).

*5.15.2. Reaction of K[2,3,4,5-$C_6F_4HBF_3$] (**6**)*

Solution of **6** (0.19 mmol) (10 mg, 0.05 mmol) in MeOH (0.7 mL) was heated in a sealed tube The solution contained **6** (0.18 mmol) and K[2,3,4,5-$C_6F_4HBF_2(OMe)$] **7** (0.01 mmol) after 1 h, and **6** (0.09 mmol), **7** (0.04 mmol), and 1,2,3,4-$C_6F_4H_2$ (0.06 mmol) besides K[BF_3OMe] and K[$BF_2(OMe)_2$] after 11 h. Heating for 30 h led to complete conversion of **6** to 1,2,3,4-$C_6F_4H_2$ (0.19 mmol).

K[2,3,4,5-$C_6F_4HBF_2OMe$] (**7**). ^{19}FNMR (MeOH): δ −135.1 (m, 1F, F^2), −143.1 (m, 1F, F^5), −146.8 (q (1:1:1:1), ^1J(F, B) = 47 Hz, 2F, BF_2OMe), −160.0 (m, 1F, F^3), −162.3 (ddd, $^4J(F^4, F^2)$ = 9 Hz, $^3J(F^4, F^3)$ = 19 Hz, $^3J(F^4, F^5)$ = 19 Hz, 1F, F^4).

*5.15.3. Reaction of K[$C_6F_5BF_3$] and K[4-$MeOC_6F_4BF_3$] (**13**)*

Suspension of **1** (27 mg, 0.10 mmol) and **16** (30 mg, 0.10 mmol) in MeOH (1 mL) was kept for 2 h in a sealed tube to produce solution. This contained C_6F_5H (0.08 mmol) and 2,3,5,6-C_6F_4HOMe (**14**) (0.10 mmol) besides K[BF_3OMe] and K[$BF_2(OMe)_2$] (^{19}FNMR).

5.15.4. Reactions of K[$RC_6F_4BF_3$] (R = F and Me)

Solution of K[$C_6F_5BF_3$] (0.030 mmol) and K[4-$MeC_6F_4BF_3$] (0.070 mmol) in MeOH (1.5 mL) was stirred in a sealed tube for 2 h. The ^{19}FNMR spectroscopy showed the resonances of C_6F_5H (0.026 mmol) and 2,3,5,6-C_6F_4HMe (0.061 mmol) beside the signals of traces of K[$C_6F_5BF_3$], K[4-$MeC_6F_4BF_3$], K[4-$MeC_6F_4BF_2(OMe)$], K[BF_4] and K[BF_3OMe].

K[4-$MeC_6F_4BF_2OMe$]. ^{19}FNMR (MeOH): δ −136.1 (m, 2F, $F^{2,6}$), −147.4 (dd, $^3J(F^3, F^2)$ = 23 Hz, $^3J(F^3, F^6)$ = 14 Hz, 2F, $F^{3,5}$), −142 (br m, 2F, BF_2OMe).

*5.15.5. Reaction of K[$C_6F_5BF_3$] and K[2,3,5,6-$C_6F_4HBF_3$] (**4**)*

Suspension of **1** (34 mg, 0.126 mmol) and **4** (17 mg, 0.066 mmol) in MeOH (1 mL) was kept for 1 h in a sealed tube. The formed solution contained **1**, **2**, **4** and **5** in molar ratio 1.0:4.5:0.8:2.1 (conversion of **1** to **2** and **4** to **5** was 82% and 73%, respectively) besides K[BF_4] and K[BF_3OMe].

*5.15.6. Reaction of K[$C_6F_5BF_3$] and potassium 4-pyrazol-1-yltetrafluorophenyltrifluoroborate (**17**)*

Suspension of **1** (28 mg, 0.102 mmol) and **17** (24 mg, 0.075 mmol) in MeOH (1 mL) was heated for 2 h to produce colorless solution. The ^{19}FNMR spectrum showed the resonances of C_6F_5H (0.042 mmol), 1-(2,3,5,6-tetrafluorophenyl)pyrazole **035** (0.014 mmol) beside the signals of **1**, **17**, K[BF_4] and K[BF_3OMe]. Admixture of K[3,4-$Prz_2C_6F_3BF_3$] (0.008 mmol) in initial borate **17** did not react.

*5.15.7. Reaction of K[$C_6F_5BF_3$] and potassium 4-indol-1-yltetrafluorophenyltrifluoroborate (**18**)*

Suspension of **1** (51 mg, 0.18 mmol) and **18** (103 mg, 0.28 mmol) in MeOH (8 mL) was heated for 12 h. A probe of the mother liquor contained C_6F_5H (0.16 mmol), 1-(2,3,5,6-tetrafluorophenyl)indol **20** (0.17 mmol) besides **18**, K[BF_4] (0.021 mmol) and K[BF_3OMe].

*5.15.8. Reaction of K[$XC_6F_4BF_3$](X = F, 4-Me (**15**) and 5-Me (**21**))*

Suspension of K[$C_6F_5BF_3$] (21 mg, 0.076 mmol), K[4-$MeC_6F_4BF_3$] (13 mg, 0.048 mmol) and K[5-$MeC_6F_4BF_3$] (32 mg, 0.118 mmol) in MeOH (1 mL) was stirred in a sealed ampoule for 40 min. After cooling to 22 °C, white suspension formed. A probe of the mother liquor contained C_6F_5H (0.071 mmol), 2,3,5,6-C_6F_4HMe (**16**) (0.032 mmol) and 2,3,4,6-C_6F_4HMe (**34**) (0.049 mmol) besides K[$C_6F_5BF_3$], K[4-$MeC_6F_4BF_3$], K[5-$MeC_6F_4BF_3$], K[BF_4] and K[BF_3OMe] (^{19}FNMR). Conversion of **1** to **2**, **15** to **16** and **21** to **34** was 93%, 67% and 42%, respectively.

*5.15.9. Reaction of K[$XC_6F_4BF_3$](X = F, 4-H (**4**) and 5-H (**22**))*

Suspension of K[$C_6F_5BF_3$] (18 mg, 0.065 mmol), K[2,3,5,6-$C_6F_4HBF_3$] (32 mg, 0.125 mmol) and K[2,3,4,6-$MeC_6F_4BF_3$] (17 mg, 0.066 mmol) in MeOH (0.9 mL) was stirred in a sealed ampoule for 40 min. After cooling to 22 °C, white suspension formed. A probe of the mother liquor contained C_6F_5H (0.054 mmol), 1,2,4,5-$C_6F_4H_2$ (**5**) (0.054 mmol) and 1,2,3,5-$C_6F_4H_2$ (**34**) (0.024 mmol) besides the started borates, K[BF_4] and K[BF_3OMe] (^{19}FNMR). Conversion of **1** to **2**, **4** to **5** and **22** to **34** was 83%, 43% and 36%, respectively.

*5.15.10. Reaction of K[2,4,6-$C_6F_3H_2BF_3$] (**23**)*

Suspension of **23** (33 mg, 0.14 mmol) in MeOH (1.0 mL) was kept in a sealed tube. After 2 h, the ^{19}FNMR spectrum of the mother liquor showed resonances of **23**, K[2,4,6-$C_6F_3H_2BF_2(OMe)$] (**24**), K[2,4,6-$C_6F_3H_2BF(OMe)_2$] (**25**) (1:2:2), 1,3,5-$C_6F_3H_3$ (**26**) (0.03 mmol) beside the signals of K[BF_3OMe] and K[$BF_2(OMe)_2$]. After 6 h, the formed solution contained **26** (0.14 mmol) besides K[BF_3OMe], K[$BF_2(OMe)_2$] and traces of **23**, **24** and **25**.

K[2,4,6-$C_6F_3H_2BF_2OMe$] (**24**). ^{19}FNMR (MeOH): δ −100.5 (m, 2F, $F^{2,6}$), −113.8 (tt, $^4J(F^4, F^{2,6})$ = 9 Hz, $^3J(F^4,H^{3,5})$ = 8 Hz, 1F, F^4), −141.8 (q (1:1:1:1), ^1J(F, B) = 42 Hz, 2F, BF_2OMe).

K[2,4,6-$C_6F_3H_2BF(OMe)_2$] (**25**). ^{19}FNMR (MeOH): δ −101.8 (m, 2F, $F^{2,6}$), −114.6 (m, 1F, F^4), −146.5 (br, 1F, $BF(OMe)_2$).

*5.15.11. Attempted reaction of K[3,4,5-$C_6F_3H_2BF_3$] (**27**)*

Solution of **27** (0.25 mmol) in MeOH (1.0 mL) was kept for 12 h in a sealed tube. Borate **27** did not react (^{19}FNMR).

*5.15.12. Reaction of K[4-$C_6FH_4BF_3$] (**28**)*

Suspension of **28** (31 mg, 0.15 mmol) in MeOH (0.9 mL) was kept for 12 h in a sealed tube. Cooling the formed solution led to precipitation of white solid. The mother liquor contained **28**, K[4-$C_6FH_4BF_2(OMe)$] **30** (10:1), while C_6H_5F was not detected (^{19}FNMR).

K[4-$C_6FH_4BF_2OMe$] (**30**). ^{19}FNMR (MeOH): δ −117.9 (m, 1F, F^4), −148.5 (br q (1:1:1:1), ^1J(F, B)∼40 Hz, 2F, BF_2OMe).

*5.15.13. Attempted reaction of K[$C_6H_5BF_3$] (**29**)*

Suspension of **29** (15 mg, 0.08 mmol) in MeOH (0.8 mL) was kept for 10 h in a sealed tube. Borate **29** did not react (^{19}FNMR).

*5.15.14. Reaction of K[2,3,5,6-$C_5NF_4BF_3$] (**32**)*

Suspension of **32** (66 mg, 0.25 mmol) in MeOH (0.8 mL) was kept for 6 h in a sealed tube. The ^{19}FNMR spectrum of the mother liquor showed the resonances of 2,3,5,6-C_5NF_4H **33** (0.017 mmol) beside the signals of **32**, K[BF_3OMe] and K[$BF_2(OMe)_2$].

*5.15.15. Reaction of K[$C_6F_5BF_3$] and K[$(C_6F_5)_2BF_2$] (**31**)*

Suspension of K[$C_6F_5BF_3$] (0.066 mmol) and K[$(C_6F_5)_2BF_2$] (0.101 mmol) in MeOH (0.76 mL) was kept for 6 h in a sealed tube. The ^{19}FNMR spectrum of resulted solution showed the resonances of C_6F_5H (0.060 mmol) beside the signals of **31**, K[BF_3OMe] and K[$BF_2(OMe)_2$].

*5.16. Reaction of K[$C_6F_5BF_3$], K[4-Im$C_6F_4BF_3$] (**9**) and K[3,4-$Im_2C_6F_3BF_3$] (**10**) at 100 °C*

A mixture of K[4-Im$C_6F_4BF_3$], K[$C_6F_5BF_3$] and K[3,4-$Im_2C_6F_3BF_3$] (100:7:7) (110 mg) was dissolved in MeOH (1 mL) and heated in a sealed tube for 6 h. The ^{19}FNMR spectrum showed formation of 2,3,5,6-C_6F_4HIm **11**, C_6F_5H and 1,2-Im_2-3,5,6-C_6F_3H **12** (100:16:21), $[BF_4]^-$ and $[BF_3OMe]^-$. The solution was evaporated to dryness under reduced pressure, the residue was extracted with acetone. The solution contained **11** (73%) and **12** (23%) (GC–MS).

1-(2′,3′,5′,6′-Tetrafluorophenyl)imidazole (**11**). ^{19}FNMR (acetone): δ −137.5 (dddd, $^3J(F^{3'}, F^{2'})$ = 21 Hz, $^5J(F^{3'}, F^{6'})$ = 11 Hz, $^3J(F^{3'}, H^{4'})$ = 10 Hz, $^4J(F^{3'}, F^{5'})$ = 3 Hz, 2F, $F^{3',5'}$), −148.9 (m, 2F, $F^{2',6'}$) {lit. δ −136.5 (d 22 Hz, d 12 Hz, d 10 Hz, d 4 Hz, 2F, $F^{3',5'}$), −147.1 (d 22 Hz, d 12 Hz, d 4 Hz, 2F, $F^{2',6'}$) [63]}.

1,2-Bis(1-imidazolino)-3,5,6-trifluorobenzene (**12**). ^{19}FNMR (acetone): δ −121.6 (ddd, $^5J(F^{3'}, F^{6'})$ = 12 Hz, $^3J(F^{3'}, H^{4'})$ = 10 Hz, $^4J(F^{3'}, F^{5'})$ = 4 Hz, 1F, $F^{3'}$), −129.4 (ddd, $^3J(F^{5'}, F^{6'})$ = 22 Hz, $^4J(F^{5'}, F^{3'})$ = 4 Hz, $^3J(F^{5'}, H^{4'})$ = 10 Hz, 1F, $F^{5'}$),−148.0 (ddd, $^3J(F^{6'}, F^{5'})$ = 22 Hz, $^5J(F^{6'}, F^{3'})$ = 12 Hz, $^4J(F^{6'}, H^{4'})$ = 7 Hz, 1F, $F^{6'}$).

HRMS (ESI) (a mixture of **11** and **12**). Calcd. for $C_9H_4F_4N_2$: 216.0310; found 216.0321; Calcd. for $C_{12}H_7F_3N_4$: 264.0622; found 264.0617.

*5.17. Reaction of K[$(C_6F_5)_2BF_2$] (**31**) with MeOH at 120 °C*

Solution of **31** (67 mg, 0.158 mmol) in MeOH (1 mL) was stirred at 120 °C for 6 h in a sealed tube to yield C_6F_5H (0.055 mmol) besides **31**, K[BF_3OMe] and K[$BF_2(OMe)_2$].

5.18. Preparation of K[4-Me$C_6F_4BF_3$] and K[5-Me$C_6F_4BF_3$] (isomer mixture)

5.18.1. Preparation of $C_6F_4HCCl_3$ (isomer mixture)

A three-necked flask equipped with a reflux condenser topped with bubbler and gas inlet/outlet tube, dropping funnel, thermometer and a Teflon-coated magnetic bar was flushed with dry argon and charged with anhydrous $AlCl_3$ (14.5 g, 0.11 mol) and CH_2Cl_2 (60 mL). The stirred suspension was cooled with ice bath and a solution of *n*-$HC_6F_4CF_3$ (4-H:5-H:6-H = 23:70:7) (22 g, 0.10 mol) in CH_2Cl_2 (10 mL) was added dropwise within 30 min at <14 °C. The red reaction mixture was stirred at 20–22 °C for 2 h, cooled with ice bath, and water (100 mL) was added. The organic phase was separated, washed with water till neutral and dried with $MgSO_4$. The solvent was removed on rotary evaporator and the residue was evacuated at 95 °C for 1 h to give *n*-$HC_6F_4CCl_3$ (4-H:5-H:6-H = 24:69:7) (22 g, 0.08 mol).

2,3,5,6-$C_6F_4HCCl_3$. ^{19}FNMR ($CDCl_3$): δ −134.5 (m, 2F, $F^{2,6}$), −137.6 (m, 2F, $F^{3,5}$).

2,3,4,6-$C_6F_4HCCl_3$. ^{19}FNMR ($CDCl_3$): δ −106.3 (dddd, $^5J(F^6, F^3)$ = 11 Hz, $^3J(F^6, H^5)$ = 11 Hz, $^4J(F^6, F^4)$ = 6 Hz, $^4J(F^6, F^2)$ = 5 Hz, 1F, F^6), −125.2 (dddd, $^3J(F^2, F^3)$ = 20 Hz, $^5J(F^2, H^5)$ = 2 Hz, $^4J(F^2, F^4)$ = 11 Hz, $^4J(F^2, F^6)$ = 5 Hz, 1F, F^2), −127.8 (dddd, $^3J(F^4, F^3)$ = 22 Hz, $^4J(F^4, H^5)$ = 11 Hz, $^4J(F^4,F^2)$ = 11 Hz, $^4J(F^4, F^6)$ = 6 Hz, 1F, F^4), −162.7 (dddd, $^3J(F^3, F^2)$ = 20 Hz, $^4J(F^3, H^5)$ = 6 Hz, $^3J(F^3, F^4)$ = 22 Hz, $^5J(F^3, F^6)$ = 11 Hz, 1F, F^3).

2,3,4,5-$C_6F_4HCCl_3$. ^{19}FNMR ($CDCl_3$): δ −130.2 (ddd, $^3J(F^5, F^4)$ = 20 Hz, $^3J(F^5, H^6)$ = 8 Hz, $^5J(F^5, F^2)$ = 12 Hz, 1F, F^5), −138.3 (dddd, $^3J(F^2, F^3)$ = 20 Hz, $^5J(F^2, F^5)$ = 12 Hz, $^4J(F^2, F^4)$ = 8 Hz, $^4J(F^2, H^6)$ = 3 Hz, 1F, F^2), −150.9 (dddd, $^3J(F^4, F^3)$ = 21 Hz, $^3J(F^4, F^5)$ = 20 Hz, $^4J(F^4, F^2)$ = 8 Hz, $^4J(F^4, H^6)$ = 8 Hz, 1F, F^4), −153.0 (dddd, $^3J(F^3, F^2)$ = 20 Hz, $^4J(F^3, F^5)$ = 3 Hz, $^3J(F^3, F^4)$ = 21 Hz, $^5J(F^3, H^6)$ = 3 Hz, 1F, F^3).

HRMS (ESI) (mixture of $C_6F_4HCCl_3$), *m/z*: calcd. for $C_7HCl_3F_4$ 265.9075 (^{35}Cl); found 265.9074.

5.18.2. Preparation of $C_6F_4HCH_3$ (isomer mixture)

A three-necked flask equipped with a reflux condenser topped with bubbler, dropping funnel, thermometer and Teflon-coated magnetic bar was charged with zinc powder (13 g, 0.20 mol) and glacial CH_3COOH (90 mL). The stirred suspension was cooled with ice bath and *n*-$HC_6F_4CCl_3$ (22 g, 0.08 mol) (4-H:5-H:6-H = 24:69:7) was added dropwise within 30 min at 15–22 °C. The suspension was stirred at 20–22 °C for 1 h, at 50–53 °C (bath) for 5 h and left overnight. Then water (100 mL) was added and products were steam distilled. The organic phase was separated, washed with water till neutral and dried with $MgSO_4$ to yield colorless liquid (11 g). The ^{1}H and ^{19}FNMR spectra showed the presence of $C_6F_4HCH_2Cl$ besides $C_6F_4HCH_3$. This mixture was reduced again with zinc powder (11 g, 0.17 mol) and glacial CH_3COOH (50 mL) as above to give n-$HC_6F_4CH_3$ (8 g, total yield 61%) (4-H:5-H:6-H = 32:64:4).

2,3,5,6-$C_6F_4HCH_3$ (**16**). ^{1}HNMR (neat): δ 6.72 (tt, $^3J(H^4, F^{3,5})$ = 10 Hz, $^4J(H^4, F^{3,5})$ = 8 Hz, 1H, H^4), 2.16 (t, $^4J(CH_3, F^{2,6})$ = 2 Hz, 3H, CH_3). ^{19}FNMR (neat): δ −140.5 (ddd, $^3J(F^3, F^2)$ = 21 Hz, $^3J(F^3, H^4)$ = 10 Hz, $^5J(F^3, F^6)$ = 13 Hz, 2F, $F^{3,5}$), −144.0 (dddq, $^3J(F^2, F^3)$ = 21 Hz, $^4J(F^2, H^4)$ = 8 Hz, $^5J(F^2, F^5)$ = 13 Hz, $^4J(F^2,CH_3)$ = 2 Hz, 2F, $F^{2,6}$) (cf. ^{19}FNMR (neat): δ −139.1 and −140.6) [64].

2,3,4,6-$C_6F_4HCH_3$ (**36**). ^{1}HNMR (neat): δ 6.54 (dddd, $^3J(H^5, F^4)$ = 9 Hz, $^3J(H^5, F^6)$ = 10 Hz, $^4J(H^5, F^3)$ = 6 Hz, $^5J(H^5, F^2)$ = 3 Hz, 1H, H^5), 2.07 (s, 3H, CH_3). ^{19}FNMR (neat): δ −118.5 (dd, $^3J(F^6, H^5)$ = 10 Hz, $^5J(F^6, F^3)$ = 10 Hz, 1F, F^6), −136.2 (d, $^3J(F^2, F^3)$ = 20 Hz, 1F, F^2), −137.0 (ddd, $^3J(F^4, F^3)$ = 20 Hz, $^4J(F^4, H^5)$ = 10 Hz, $^4J(F^4, F^6)$ = 4 Hz, 1F, F^4), −166.7 (dddd, $^3J(F^3,$

F^2) = 20 Hz, $^4J(F^3, H^5)$ = 6 Hz, $^3J(F^3, F^4)$ = 20 Hz, $^5J(F^3, F^6)$ = 10 Hz, 1F, F^3).

2,3,4,5-$C_6F_4HCH_3$. ^{1}H NMR (neat): δ 6.66 (m, 1H, H^6), 1.97 (s, 3H, CH_3) [65]. ^{19}FNMR (neat): δ −140.9 (dddd, $^3J(F^5, F^4)$ = 20 Hz, $^3J(F^5, H^6)$ = 11 Hz, $^4J(F^5, F^3)$ = 2 Hz, $^5J(F^5, F^2)$ = 12 Hz, 1F, F^5), −143.1 (m, 1F, F^2), −157.5 (dddd, $^3J(F^3, F^2)$ = 19 Hz, $^4J(F^3, F^5)$ = 2 Hz, $^3J(F^3, F^4)$ = 19 Hz, $^5J(F^3, H^6)$ = 2 Hz, 1F, F^3), −160.5 (ddd, $^3J(F^4, F^3)$ = 19 Hz, $^3J(F^4, F^5)$ = 20 Hz, $^4J(F^4, F^2)$ = 8 Hz, 1F, F^4) [65].

Anal. calcd for $C_7H_4F_4$ (164.10): C, 51.23; H, 2.46; F, 46.31; found: C, 51.9; H, 2.46; F, 45.9.

5.18.3. Preparation of K[4-MeC$_6$F$_4$BF$_3$] and K[5-MeC$_6$F$_4$BF$_3$] (isomer mixture)

A solution of *n*-$HC_6F_4CH_3$ (4-H:5-H:6-H = 32:64:4) (1.37 g, 8.4 mmol) in ether (17 mL) was cooled to −80 °C, and 2.0 M BuLi in hexanes (5 mL, 10 mmol) was added using a syringe within 20 min, ensuring that the internal temperature did not rise above −73 °C. The solution was stirred at −75 °C for 1 h and then transferred with a cannula into the cold (−75 °C) stirred solution of $B(OMe)_3$ (1.0 g, 10 mmol) in ether (20 mL). After additional stirring at −70 °C for 1 h, the solution was warmed to 0 °C within 2 h and poured out onto stirred solution of $K[HF_2]$ (6 g, 79 mmol) in water (15 mL) and MeOH (30 mL). The reaction mixture was stirred for 16 h, saturated with KF (5 g), and extracted with acetone (2 × 23 mL). The combined extracts were dried with $MgSO_4$ and evaporated to dryness. Subsequent drying in a vacuum desiccator over Sicapent® gave the white solid (2.0 g, 88%) consisted from K[4-MeC$_6$F$_4$BF$_3$] and K[5-MeC$_6$F$_4$BF$_3$] (3:7).

K[4-MeC$_6$F$_4$BF$_3$] (**15**). ^{19}FNMR (acetone): δ −133.8 (tq, $^4J(BF_3, F^{2,6})$ = 11 Hz, $^1J(F, B)$ = 44 Hz, BF_3), −136.0 (ddq, $^3J(F^2, F^3)$ = 23 Hz, $^5J(F^2, F^5)$ = 12 Hz, $^4J(F^2, BF_3)$ = 11 Hz, 2F, $F^{2,6}$), −147.2 (dd, $^3J(F^3, F^2)$ = 23 Hz, $^5J(F^3, F^6)$ = 12 Hz, 2F, $F^{3,5}$). ^{11}BNMR (acetone-d_6): δ 1.90 (q, $^1J(B, F)$ = 45 Hz, BF_3).

K[5-MeC$_6$F$_4$BF$_3$] (**21**). ^{19}FNMR (acetone): δ −111.7 (m, 1F, F^6), −132.5 (m, 1F, F^2), −133.8 (BF_3) (overlapped on signal of **15**), −143.4 (d, $^3J(F^4, F^3)$ = 20 Hz, 1F, F^4), −170.2 (ddd, $^3J(F^3, F^4)$ = 20 Hz, $^3J(F^3, F^2)$ = 22 Hz, 1F, F^3), $^5J(F^3, F^6)$ = 13 Hz, 2F, $F^{3,5}$). ^{11}BNMR (acetone-d_6): δ 1.97 (q, $^1J(B, F)$ = 45 Hz, BF_3).

Anal. calcd for $C_7H_3BF_7K$ (270.0) (a mixture of **15** and (**21**): C, 31.14; H, 1.12; F, 49.26; found: C, 31.7; H, 1.38; F, 48.8.[66,67]

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