

POLYFLUOROORGANOBORON-OXYGEN COMPOUNDS.

7⁺. STUDIES OF CONVERSION OF $[(C_6H_nF_{5-n})B(OMe)_3]^-$ INTO $[(C_6H_nF_{5-n})_2B(OMe)_2]^-$ ($n = 0, 1$)Nicolai Yu. ADONIN^{a,*}, Vadim V. BARDIN^b and Hermann-Josef FROHN^c^a G. K. Borekov Institute of Catalysis, Siberian Branch Russian Academy of Sciences, Lavrentjev Ave. 5, 630090 Novosibirsk, Russia; e-mail: adonin@catalysis.ru^b N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch Russian Academy of Sciences, Lavrentjev Ave. 9, 630090 Novosibirsk, Russia; e-mail: bardin@nioch.nsc.ru^c Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany; e-mail: h-j.frohn@uni-due.de

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Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday in recognition of his outstanding contributions to organofluorine chemistry.

Conversion of salts $Li[(C_6H_nF_{5-n})B(OMe)_3]$ ($n = 0, 1$) into $(Li \cdot DME)[(C_6H_nF_{5-n})_2B(OMe)_2]$ was studied in dichloromethane–DME solution. The observed rate constants k decrease from $(21.4 \pm 0.9) \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ($Li[C_6F_5B(OMe)_3]$) over $(6.99 \pm 0.11) \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ($Li[(2,3,5,6-C_6HF_4)B(OMe)_3]$) to $(2.94 \pm 0.05) \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ($Li[(2,3,4,6-C_6HF_4)B(OMe)_3]$), while $Li[(2,3,4,5-C_6HF_4)B(OMe)_3]$ does not undergo any transformation. Hydrolysis of $(Li \cdot DME)[(C_6H_nF_{5-n})_2B(OMe)_2]$ leads to corresponding borinic acids, whereas treatment of them with aqueous solution of $M[HF_2]$ ($M = Bu_4N, K$) acidified with HF results in $M[(C_6H_nF_{5-n})_2BF_2]$ in high yields.

Keywords: Polyfluorophenyltrimethoxyborate; Bis(polyfluorophenyl)dimethoxyborate; Polyfluorobenzene derivatives; ¹⁹F NMR spectroscopy; Organoborate salts.

In preceding publications on polyfluoroorganoboron-oxygen compounds we demonstrated the dramatic qualitative and quantitative differences between polyfluorinated aryldihydroxyboranes (arylboronic acids) as well as (trialkoxy)arylborates and their non-fluorinated or less fluorinated analogues^{2–5}. For example, it is well known that arylboronic acids readily elimi-

+ For Part 6, see ref.¹

nate water giving corresponding anhydrides^{6,7}. This pattern is retained also for (3,4,5- $C_6H_2F_3$)B(OH)₂, (2,4- $C_6H_3F_2$)B(OH)₂ and (4- C_6H_4F)B(OH)₂, but fluorinated phenylboronic acids, ($C_6H_nF_{5-n}$)B(OH)₂ ($n = 0, 1$) and (2,4,6- $C_6H_2F_3$)B(OH)₂, containing fluorine atoms in both *ortho*-positions to boron can be crystallized from boiling toluene without water loss⁵. Furthermore, a series of borates M[ArB(OH)_n(OAlk)_{3-n}] ($n = 1-3$; M = Li, Na, K, Bu₄N; Ar = XC₆H₄) has been obtained in reactions of arylboronic acids, their esters or anhydrides with MOH or MOAlk in aqueous or alcoholic solutions⁷⁻¹⁰. However, all attempts to prepare analogous trihydroxy-(polyfluorophenyl)borates M[C₆H_nF_{5-n}B(OH)₃] ($n = 0-3$) failed owing to hydrodeboration (formal displacement of boron by hydrogen) of (polyfluorophenyl)boronic acids under alkaline conditions (KOH (1 equivalent)/33% H₂O-MeOH). Moreover, (pentafluorophenyl)boronic acid, C₆F₅B(OH)₂, decomposed to form C₆F₅H even in basic solvents (CH₃CN, MeOH, 33% H₂O-MeOH, pyridine and 9% D₂O-pyridine)⁴.

Earlier we have found optimal conditions for preparation and isolation of lithium trimethoxy(penta- and tetrafluorophenyl)borates, Li[(C₆H_nF_{5-n})B(OMe)₃] ($n = 0, 1$), and used these salts as reagents for palladium-catalyzed cross-coupling reactions². The other remarkable property of Li[C₆F₅B(OMe)₃] (**1a-Li**) is its ability to convert into dimethoxybis(pentafluorophenyl)borate salts, M[(C₆F₅)₂B(OMe)₂] (M = Bu₄N, K, Li-L_m; L = Et₂O, THF, DME, TMEDA), under substitution of Li⁺ cation with Bu₄N⁺ and K⁺ or complexation of Li⁺ with diethyl ether, THF, DME, or TMEDA³.

Such conversion of [(C₆F₅)B(OMe)₃]⁻ into [(C₆F₅)₂B(OMe)₂]⁻ provides a new synthetic approach to compounds containing two C₆F₅ groups bonded to boron, whereas the existing methods of their preparation are based on direct introduction of both pentafluorophenyl substituents with the use of corresponding tin derivatives¹¹ or elimination of C₆F₅ group from B(C₆F₅)₃ under the action of water¹², xenon difluoride¹³, IF₃¹⁴, etc. To our knowledge, such conversion has not been previously reported for any other individual trialkoxy(aryl)borates M[ArB(OAlk)₃] (Ar ≠ C₆F₅), although the formation of (MgBr)[(C₆F₅)₂B(OEt)₂] as the main product in the reaction of C₆F₅MgBr with B(OEt)₃ was described by Servatowski et al.¹⁵. An admixture (≤15%) of dialkoxydiarylborate salts, M[Ar_{F2}B(OAlk)₂] (Ar_F = C₆F₅, 4-C₅NF₄; M = Li, MgBr), was detected in the reaction of Ar_FM with B(OAlk)₃^{16,17}.

In continuation of our systematic research on chemistry of polyfluoro-organoboron-oxygen compounds, we studied kinetic features of transformation of lithium trimethoxy(pentafluorophenyl)borate (**1a-Li**), trimethoxy(2,3,5,6-tetrafluorophenyl)borate (**1b-Li**), trimethoxy(2,3,4,6-tetrafluorophenyl)borate (**1c-Li**), and trimethoxy(2,3,4,5-tetrafluorophenyl)borate

(**1d-Li**) into corresponding salts $(\text{Li}\cdot\text{DME})[(\text{C}_6\text{H}_n\text{F}_{5-n})_2\text{B}(\text{OMe})_2]$ (**2a-2d**) in dichloromethane in the presence of DME. Using the kinetic data we developed a synthetic approach to bis(2,3,4,6- and 2,3,5,6-tetrafluorophenyl)-borinic acids, $(\text{C}_6\text{HF}_4)_2\text{BOH}$, and potassium difluorobis(tetrafluoro- or pentafluorophenyl)borates, $\text{K}[(\text{C}_6\text{H}_n\text{F}_{5-n})_2\text{BF}_2]$ ($n = 0, 1$).

RESULTS AND DISCUSSION

Earlier we elaborated a simple and representative method for analysis of the reaction mixtures containing $[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3]^-$ (**1a**) and $[(\text{C}_6\text{F}_5)_2\text{B}(\text{OMe})_2]^-$ (**2a**) anions. This method is based on fast conversion of salts of **1a** and **2a** into corresponding fluoroborates, $[\text{C}_6\text{F}_5\text{BF}_3]^-$ (**3a**) and $[(\text{C}_6\text{F}_5)_2\text{BF}_2]^-$ (**4a**), with a mixture of $(\text{Bu}_4\text{N})\text{HF}_2$ and aqueous HF followed by extraction with CH_2Cl_2 . The resulting organic phase is analysed by ^{19}F NMR³. As a rule, fluorodemethoxylation of lithium methoxy(polyfluorophenyl)borates with $(\text{Bu}_4\text{N})\text{HF}_2$ in aqueous HF does not affect the monoarylborate:diarylborate molar ratio³. Using this method we tested the ability of isomeric lithium trimethoxy(tetrafluorophenyl)borates (**1b-Li-1d-Li**) to transform into corresponding salts $(\text{Li}\cdot\text{DME})[(\text{C}_6\text{HF}_4)_2\text{B}(\text{OMe})_2]$ (**2b-Li-2d-Li**). Starting lithium trimethoxy(tetrafluorophenyl)borates **1b-Li-1d-Li** were dissolved in CH_2Cl_2 -DME (5:1 v/v) and after 15 min the solutions were treated with $(\text{Bu}_4\text{N})\text{HF}_2$ in aqueous HF. The ^{19}F NMR spectra of the organic phases showed the formation of $(\text{Bu}_4\text{N})[(2,3,5,6\text{-C}_6\text{HF}_4)\text{BF}_3]$ (**3b-Bu₄N**) and $[\text{Bu}_4\text{N}][(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{BF}_2]$ (**4b-Bu₄N**) (molar ratio 1.5:1) from **1b-Li** and the corresponding tetrabutylammonium salts, $(\text{Bu}_4\text{N})[(2,3,4,6\text{-C}_6\text{HF}_4)\text{BF}_3]$ (**3c-Bu₄N**) and $(\text{Bu}_4\text{N})[(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{BF}_2]$ (**4c-Bu₄N**) (molar ratio 3.8:1), from salt **1c-Li**. Under the above conditions, no changes were observed for the solution of **1d-Li**. After the work-up, salt $(\text{Bu}_4\text{N})[(2,3,4,5\text{-C}_6\text{HF}_4)\text{BF}_3]$ (**3d-Bu₄N**) was the only product (^{19}F NMR) (Scheme 1). It should be noted that under the mentioned conditions salt **1a-Li** gave $(\text{Bu}_4\text{N})[\text{C}_6\text{F}_5\text{BF}_3]$ (**3a-Bu₄N**) and $(\text{Bu}_4\text{N})[(\text{C}_6\text{F}_5)_2\text{BF}_2]$ (**4a-Bu₄N**) in molar ratio 1:4.0³.

Thus, the rates of conversion of salts **1-Li** to **2-Li** in CH_2Cl_2 -DME solution decrease in the order $\text{Li}[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3] > \text{Li}[(2,3,5,6\text{-C}_6\text{HF}_4)\text{B}(\text{OMe})_3] > \text{Li}[(2,3,4,6\text{-C}_6\text{HF}_4)\text{B}(\text{OMe})_3] > \text{Li}[(2,3,4,5\text{-C}_6\text{HF}_4)\text{B}(\text{OMe})_3]$.

Recently we have reported the remarkable difference between the ^{19}F NMR spectrum of $\text{Li}[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3]$ in dichloromethane and the spectrum of freshly prepared solution of **1a-Li** in CH_2Cl_2 -DME³. This difference consists in deshielding of fluorine atoms in *ortho*-position to boron and less meaningful shielding of fluorine atoms in the *meta*- and *para*-positions in the presence of DME. Similar changes in the ^{19}F NMR spectra of dichloro-

TABLE I
 ^{19}F NMR spectra of $\text{M}[(\text{C}_6\text{F}_5)_n\text{BX}_{4-n}]$ and $\text{M}[(\text{C}_6\text{HF}_4)_n\text{BX}_{4-n}]$ (X = OMe, F; n = 1, 2)

Compound	Solvent	Chemical shifts, ppm						
		F-2	F-3	F-4	F-5	F-6	B-F	
$\text{Li}[(\text{C}_6\text{F}_5\text{B}(\text{OMe})_3)]^{\text{a}}$ 1a-Li	CD_2Cl_2	-143.9	-163.9	-159.2	-163.9	-143.9		
$\text{Li}[(2,3,5,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ 1b-Li	CD_2Cl_2	-144.7	-141.1		-141.1	-144.7		
$\text{Li}[(2,3,4,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ 1c-Li	CD_2Cl_2	-135.0	-168.0	-137.7		-119.3		
$\text{Li}[(2,3,4,5\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ 1d-Li	CD_2Cl_2	-148.2	-160.2	-158.9	-140.8			
$(\text{Li}(\text{DME})_m)[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3]$	CH_2Cl_2	-138.4	-165.4	-160.9	-165.4	-138.4		
$(\text{Li}(\text{DME})_m)[(2,3,5,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$	CH_2Cl_2	-140.7	-142.5		-142.5	-140.7		
$(\text{Li}(\text{DME})_m)[(2,3,4,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$	CH_2Cl_2	-131.5	-168.9	-139.0		-113.9		
$(\text{Li}(\text{DME})_m)[(2,3,4,5\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$	CH_2Cl_2	-141.7	-163.3	-161.4	-144.1			
$(\text{Li}(\text{DME})_m)[(\text{C}_6\text{F}_5)_2\text{B}(\text{OMe})_2]^{\text{b}}$ 2a-Li	CH_2Cl_2	-136.3	-165.7	-161.3	-165.7	-136.3		
$(\text{Li}(\text{DME})_m)[(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{B}(\text{OMe})_2]$ 2b-Li	CH_2Cl_2	-137.7	-143.1		-143.1	-137.7		
$(\text{Li}(\text{DME})_m)[(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{B}(\text{OMe})_2]$ 2c-Li	CH_2Cl_2	-129.9	-169.8	-140.1		-109.4		
$(\text{Bu}_4\text{N})[\text{C}_6\text{F}_5\text{BF}_3]^{\text{b}}$ 3a-Bu₄N	CH_2Cl_2	-135.7	-166.2	-161.5	-166.2	-135.7	-131.1	

TABLE I
(Continued)

Compound	Solvent	Chemical shifts, ppm						
		F-2	F-3	F-4	F-5	F-6	B-F	
(Bu ₄ N)[(2,3,5,6-C ₆ HF ₄)BF ₃] 3b-Bu₄N	CH ₂ Cl ₂	-136.4	-143.1		-143.1	-136.4	-134.5	
(Bu ₄ N)[(2,3,4,6-C ₆ HF ₄)BF ₃] 3c-Bu₄N	CH ₂ Cl ₂	-128.7	-170.5	-139.8		-108.2	-134.1	
(Bu ₄ N)[(C ₆ F ₅) ₂ BF ₂] 4a-Bu₄N	CH ₂ Cl ₂	-136.7	-166.5	-161.9	-166.5	-136.7	-139.0	
(Bu ₄ N)[(2,3,5,6-C ₆ HF ₄) ₂ BF ₂] 4b-Bu₄N	CH ₂ Cl ₂	-137.2	-143.4		-143.4	-137.2	-147.2	
(Bu ₄ N)[(2,3,4,6-C ₆ HF ₄) ₂ BF ₂] 4c-Bu₄N	CH ₂ Cl ₂	-129.6	-170.8	-140.6		-109.0	-146.7	
K[(C ₆ F ₅ BF ₃)] ^c 3a-K	CD ₃ CN	-135.2	-165.3	-160.7	-165.3	-135.2	-133.4	
K[(2,3,5,6-C ₆ HF ₄)BF ₃] ^d 3b-K	CD ₃ CN	-135.8	-142.2		-142.2	-135.8	-133.8	
K[(2,3,4,6-C ₆ HF ₄)BF ₃] ^d 3c-K	CD ₃ CN	-128.4	-169.6	-139.3		-107.5	-133.7	
K[(C ₆ F ₅) ₂ BF ₂] ^c 4a-K	MeOH	-135.5	-165.5	-160.7	-165.5	-135.5	-145.8	
K[(C ₆ F ₅) ₂ BF ₂] 4a-K	CD ₃ CN	-136.3	-165.3	-160.5	-165.3	-136.3	-146.1	
K[(2,3,5,6-C ₆ HF ₄) ₂ BF ₂] 4b-K	CD ₃ CN	-136.4	-143.1		-143.1	-136.4	-134.5	
K[(2,3,4,6-C ₆ HF ₄) ₂ BF ₂] 4c-K	CD ₃ CN	-128.7	-170.5	-139.8		-108.2	-134.1	

a Ref.²; b ref.³; c ref.¹⁶; d ref.¹⁹

dict the previously assumed scheme for the conversion of **1a-Li** to **2a-Li** via dissociation of the former to $C_6F_5B(OMe)_2$ and MeO^- and subsequent formation of key dinuclear methoxy-bridged borate intermediate such as $[C_6F_5B(OMe)_2(\mu-O)B(OMe)_2C_6F_5]^-$. The migration of both the aryl and methoxy group in the latter species results³ in $[(C_6F_5)_2B(OMe)_2]^-$ and $B(OMe)_3$. The dramatic decrease in the transformation rate of anions $[(2,3,5,6-C_6HF_4)B(OMe)_3]^-$ (two *ortho* and two *meta* fluorines), $[(2,3,4,6-C_6HF_4)B(OMe)_3]^-$ (two *ortho* and one *meta* fluorines) and $[(2,3,4,5-C_6HF_4)B(OMe)_3]^-$ (one *ortho* and two *meta* fluorine atoms) can be elucidated by the decreasing Lewis acidity of the corresponding boranes $C_6HF_4B(OMe)_2$ because of the weakening of joint inductive effect of fluorine atoms in the same order. It should be noted that the observed first-order rate constants of hydrodeborylation of fluoro-containing dihydroxy-(phenyl)boranes in aqueous pyridine⁴ change from $(2,3,5,6-C_6HF_4)B(OH)_2$ [$k(32\text{ }^\circ\text{C}) = (6.0 \pm 0.6) \times 10^{-2} \text{ min}^{-1}$] over $(2,3,4,6-C_6HF_4)B(OH)_2$ [$k(32\text{ }^\circ\text{C}) = (0.83 \pm 1) \times 10^{-2} \text{ min}^{-1}$] to $(2,3,4,5-C_6HF_4)B(OH)_2$ [$k(32\text{ }^\circ\text{C}) = 0.009 \times 10^{-2}$]

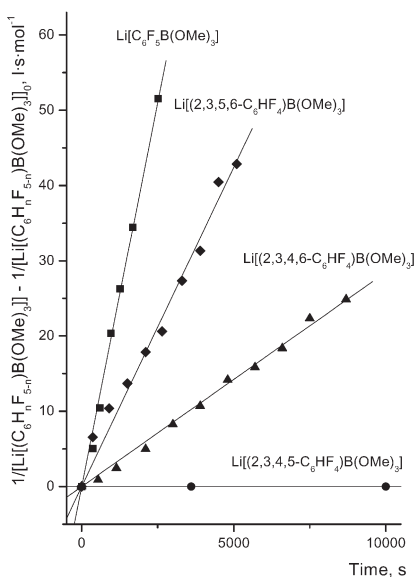
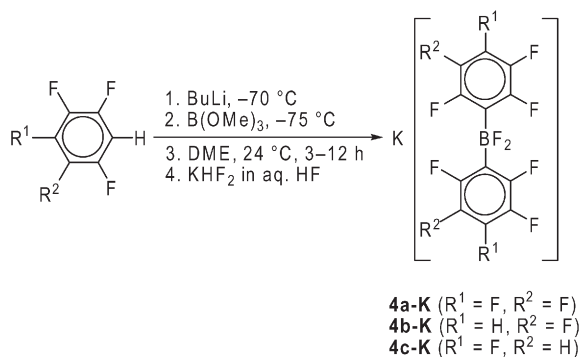


FIG. 1

Rates of transformations of lithium trimethoxy(tetrafluoro- and pentafluorophenyl)borates into corresponding dimethoxybis(penta- or tetrafluorophenyl)borates: ■ $Li[C_6F_5B(OMe)_3]$ (**1a-Li**), ◆ $Li[(2,3,5,6-C_6HF_4)B(OMe)_3]$ (**1b-Li**), ▲ $Li[(2,3,4,6-C_6HF_4)B(OMe)_3]$ (**1c-Li**), ● $Li[(2,3,4,5-C_6HF_4)B(OMe)_3]$ (**1d-Li**)

min⁻¹]. In both cases, the driving force of the processes can be associated with qualitative changes in Lewis acidity of arylboranes (C₆H_nF_{5-n})B(OR)₂ (R = H, Me) when *n* decreased from 5 to 0.

The kinetic measurements of **1a-Li-1c-Li** to **2a-Li-2c-Li** were utilized for development of synthetic approach to fluorinated diphenylborinic acids and K[(C₆H_nF_{5-n})₂BF₂] (*n* = 0, 1) salts. Salts **1a-Li-1c-Li** were generated by the reaction of corresponding polyfluorophenyllithium reagents with trimethoxyborane at -75 °C followed by in situ treatment of the resulting salts with excess of DME at 25 °C (Scheme 2).



SCHEME 2

The last procedure was performed for salt **1a-Li** within 3 h, and for salts **1b-Li** and **1c-Li** within 10 and 12 h, respectively. The estimation performed using the kinetic data showed that contamination of salts **2a-Li-2c-Li** with residual amounts of **1a-Li-1c-Li** must not be higher than 4%. The resulting solutions of salts **2a-Li-2c-Li** were treated with aqueous solution of KHF₂ and aqueous HF. After removing organic solvents and neutralization of the aqueous phase the desired products were isolated by mere filtration. For purification of compounds **4a-K-4c-K**, the salts were treated with 48% aqueous HF at 60 °C for 1 h.

Salts **4a-K-4c-K** were obtained as white solids in 62–74% overall yields calculated relative to BuLi used for generation the (polyfluorophenyl)lithium reagents. They were characterized by multinuclear NMR spectroscopy (for ¹⁹F NMR data, see Table I) and elemental analysis.

CONCLUSIONS

The rates of conversion of Li[C₆F₅B(OMe)₃], Li[(2,3,5,6-C₆HF₄)B(OMe)₃] and Li[(2,3,4,6-C₆HF₄)B(OMe)₃] to the corresponding salts (Li·DME)[(C₆H_nF_{5-n})₂-

$B(OMe)_2]$ ($n = 0, 1$) in the presence of the coordinating additive DME decrease in the above order. This can be elucidated by the related decrease in Lewis acidity of intermediate dimethoxy(polyfluorophenyl)boranes $(C_6H_nF_{5-n})B(OMe)_2$ because of the less cooperative inductive effect of fluorine atoms in this series. Consequently, the salt $Li[(2,3,4,5-C_6HF_4)B(OMe)_3]$ (one fluorine atom in *ortho*-position to B) did not form the corresponding dimethoxybis(tetrafluorophenyl)borate. This phenomenon was successfully used for preparation of diarylborinic acids, Ar_2BOH , and potassium diaryl-difluoroborates, $K[Ar_2BF_2]$ ($Ar = C_6F_5, 2,3,5,6-C_6HF_4$ and $2,3,4,6-C_6HF_4$).

EXPERIMENTAL

NMR spectra were recorded on a Bruker Avance 300 (FT 1H : 300.13 MHz, ^{11}B : 96.29 MHz, ^{13}C : 75.47 MHz, ^{19}F : 282.40 MHz) spectrometer. The chemical shifts (δ , ppm) are referenced to TMS (1H , ^{13}C), $BF_3 \cdot OEt_2/CDCl_3$ 15% v/v (^{11}B) and CCl_3F (^{19}F , with C_6F_6 as secondary reference (-162.9 ppm)). Coupling constants (J) are given in Hz. The C, H elemental analysis were performed with an EA3000. The F analysis was performed in the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry. High-resolution mass spectra were recorded on a Finigan MAT 8200 spectrometer (EI mode, 70 eV).

Pentafluorobenzene (ABCR), tetrafluorobenzenes 1,2,3,4- $C_6H_2F_4$ (ABCR), 1,2,3,5- $C_6H_2F_4$ (ABCR), 1,2,4,5- $C_6H_2F_4$ (ABCR), 2.5 M BuLi in hexanes (Aldrich), 48% aqueous HF (Fluka), KHF_2 (Riedel-de Haën), and anhydrous ether (Baker) were used as supplied. $B(OMe)_3$ (Fluka) was distilled over sodium. Dichloromethane (Baker) and 1,2-dimethoxyethane (DME) (Riedel-de Haën) were purified by standard procedures and stored over molecular sieve (3 Å). Salts $Li[C_6F_5B(OMe)_3]$ (**1a-Li**), $Li[(2,3,5,6-C_6HF_4)B(OMe)_3]$ (**1b-Li**), $Li[(2,3,4,6-C_6HF_4)B(OMe)_3]$ (**1c-Li**), and $Li[(2,3,4,5-C_6HF_4)B(OMe)_3]$ (**1d-Li**) were prepared using the literature method². Borates $K[C_6F_5BF_3]$ ¹⁶, $K[(2,3,4,5-C_6HF_4)BF_3]$ ¹⁶, $K[(2,3,5,6-C_6HF_4)BF_3]$ ¹⁹ and $K[(2,3,4,6-C_6HF_4)BF_3]$ ¹⁹ were identified in mixtures by ^{11}B and ^{19}F NMR spectra (see also Table I). All manipulations with lithium trimethoxy(polyfluorophenyl)borates were performed under dry argon.

Conversion of Lithium Trimethoxy(polyfluorophenyl)borates to Lithium Dimethoxybis(polyfluorophenyl)borates (Kinetic Measurements)

NMR tube was charged with $Li[(C_6H_nF_{5-n})B(OMe)_3]$ ($n = 0, 1$) (0.10 mmol) inside a glovebox. Then dichloromethane (0.500 ml), $C_6H_5CF_3$ (internal quantitative reference, 5 μ l, 0.041 mmol), and DME (0.100 ml, 0.86 mmol) were added in this order dry argon. A sample (transparent colourless solution) was immediately placed into a probehead of NMR spectrometer (24 °C), and the composition of the reaction solution was monitored quantitatively by ^{19}F NMR spectroscopy.

Reaction of $Li[(C_6HF_4)B(OMe)_3]$ **1b-Li-1d-Li** with DME in CH_2Cl_2 and Subsequent Substitution of a Methoxy Group by Fluorine

Salt $Li[(C_6HF_4)B(OMe)_3]$ (260 mg, 1.0 mmol) was dissolved in CH_2Cl_2 (1 ml) and DME (0.312 ml, 3 mmol) was added in one portion under atmosphere of dry argon. The colourless transparent solution was stirred at 24 °C for 15 min. Finally, $C_6H_5CF_3$ (quantitative

standard, 5 μ l, 0.041 mmol) and $(\text{Bu}_4\text{N})\text{HF}_2$ (prepared from 48% HF (1 ml, 28 mmol) and 40% Bu_4NOH (1 ml, 1.53 mmol)) were added successively. The two-phase system was stirred for 20 min and then kept without stirring for 15 min. The ^{19}F NMR spectra of the separated organic phase showed the formation of **3b-Bu₄N**, **4b-Bu₄N** (1.5:1), **3c-Bu₄N**, **4c-Bu₄N** (3.8:1), and **3d-Bu₄N** from lithium salts **1b-Li**, **1c-Li** and **1d-Li**, respectively.

Reaction of $\text{Li}[(2,3,5,6\text{-C}_6\text{HF}_4)\text{B}(\text{OMe})_3]$ (**1b-Li**) and $\text{Li}[(2,3,4,6\text{-C}_6\text{HF}_4)\text{B}(\text{OMe})_3]$ (**1c-Li**)
Dissolved in DME with Aqueous HCl

$\text{Li}[(\text{C}_6\text{HF}_4)\text{B}(\text{OMe})_3]$ (520 mg, 2 mmol) was placed into an one-neck flask supplied with a magnetic stir bar and inlet septum in a glovebox. DME (1 ml) was added with a syringe under dry argon, and the resulting transparent colourless solution was stirred at 20 °C within 18 h. The solution was hydrolysed with aqueous HCl and extracted with ether (5×2 ml). The extract was evaporated under reduced pressure, and concentrated aqueous HCl (2 ml) was added to the oil. The mixture was kept in air over a period of 1 week at 20 °C, and then a white precipitate was filtered off. After drying in air, a mixture of $(\text{C}_6\text{HF}_4)\text{B}(\text{OH})_2$ and $(\text{C}_6\text{HF}_4)_2\text{BOH}$ (220 and 230 mg starting from **1b-Li** and **1c-Li** salts, respectively) (molar ratio 18:82 in both cases) was obtained. Boronic acids, $(2,3,5,6\text{-C}_6\text{HF}_4)\text{B}(\text{OH})_2$ and $(2,3,4,6\text{-C}_6\text{HF}_4)\text{B}(\text{OH})_2$, were identified by their ^{11}B and ^{19}F NMR spectra⁵.

$(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{BOH}$. ^{11}B NMR (96.29 MHz, CH_2Cl_2): 40.00 bs. ^{19}F NMR (282.40 MHz, CH_2Cl_2): -107.2 bs, 1 F (F-6); -126.3 dd, 1 F, $^3J(\text{F-2},\text{F-3}) = 22$, $^4J(\text{F-2},\text{F-6}) = 8$ (F-2); -127.6 m, 1 F (F-4); -166.6 dddd, 1 F, $^3J(\text{F-2},\text{F-3}) = 21$, $^3J(\text{F-3},\text{F-4}) = 21$, $^5J(\text{F-3},\text{F-6}) = 12$, $^4J(\text{F-3},\text{H-5}) = 6$ (F-3). Calculated for $\text{C}_{12}\text{H}_3\text{BF}_8\text{O}$ 326.014923, found 326.01541.

$(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{BOH}$. ^{11}B NMR (96.29 MHz, CH_2Cl_2): 37.56 bs. ^{19}F NMR (282.40 MHz, CH_2Cl_2): -134.7 unresolved m, 2 F (F-2,6); -139.6 unresolved m, 2 F (F-3,5). Calculated for $\text{C}_{12}\text{H}_3\text{BF}_8\text{O}$ 326.014923, found: 326.01509.

Synthesis of Potassium Difluorobis(pentafluorophenyl)borate **4a-K**

(Pentafluorophenyl)lithium was prepared from pentafluorobenzene (10 g, 60 mmol) and 2.5 M BuLi in hexanes (20 ml, 50 mmol) in ether (100 ml) at -78 °C, and $\text{B}(\text{OMe})_3$ (5.7 g, 55 mmol) was gradually added with a syringe. The resulting solution was stirred at -78 °C for 1 h, and then DME (25 ml) was added dropwise keeping temperature below -70 °C. After additional stirring for 1 h, the solution was slowly warmed up to 20 °C. The conversion of $[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3]^-$ into $[(\text{C}_6\text{F}_5)_2\text{B}(\text{OMe})_2]^-$ was complete in 1 h (^{19}F NMR, Table I). The reaction mixture was poured out into a solution of KHF_2 (16 g, 0.2 mol), 48% aqueous HF (10 ml) in water (100 ml). Volatiles were removed by evaporation under reduced pressure, and the resulting white suspension was stirred at 20 °C for 4 h. The suspension was neutralised with solid K_2CO_3 to pH 8–9. A white precipitate was filtered off, washed with water, dried in air, and extracted with acetonitrile (5×10 ml). The combined extracts were filtered and evaporated to yield **4a-K** contaminated with $\text{K}[\text{C}_6\text{F}_5\text{BF}_3]$. The crude product was stirred with 48% aqueous HF (20 ml) at 60 °C for 1 h. The hot suspension was filtered, the filtration cake was washed with water and dried in air. After drying in a vacuum desiccator over P_4O_{10} overnight, pure $\text{K}[(\text{C}_6\text{F}_5)_2\text{BF}_2]$ (7.2 g, 68%) was obtained.

^{11}B NMR (96.29 MHz, CD_3CN): 4.34 t, 1 B, $^1J(\text{BF})$ 59. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (75.47 MHz, CD_3CN): 122.3 (C-1); 137.9 (C-3,5); 140.4 (C-4); 149.0 (C-2,6). For $\text{C}_{12}\text{BF}_{12}\text{K}$ (422.02) calculated: 34.15% C, 54.02% F; found: 34.64% C, 54.71% F.

Synthesis of Potassium Difluorobis(2,3,5,6-tetrafluorophenyl)borate **4b-K**

(2,3,5,6-Tetrafluorophenyl)lithium was prepared from 1,2,4,5-tetrafluorobenzene (9.0 g, 60 mmol) and 2.5 M BuLi in hexanes (20 ml, 50 mmol) in ether (100 ml) at $-78\text{ }^{\circ}\text{C}$. After an addition of $\text{B}(\text{OMe})_3$ (5.7 g, 54.9 mmol) and stirring at $-70\text{ }^{\circ}\text{C}$ for 1 h, DME (25 ml) was added dropwise. The solution was kept at $-70\text{ }^{\circ}\text{C}$ for 1 h and left standing at $20\text{ }^{\circ}\text{C}$ over a period of 10 h. The reaction mixture was worked up with a solution of KHF_2 (16 g, 0.2 mol) in water (100 ml) acidified with 48% HF (10 ml), and an impurity of $\text{K}[(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{BF}_3]$ was removed with aqueous HF at $60\text{ }^{\circ}\text{C}$ as described above. Evaporation of the acetonitrile extract under reduced pressure and drying the residue in a vacuum desiccator over P_4O_{10} overnight gave pure salt **4b-K** (6.0 g, 62%).

^1H NMR (300.13 MHz, CD_3CN): 6.97 tt, 1 H, $^3\text{J}(\text{H-4,F-3};\text{H-4,F-5}) = 10$, $^4\text{J}(\text{H-4,F-2};\text{H-4,F-6}) = 7$ (H-4). ^{11}B NMR (96.29 MHz, CD_3CN): 4.33 1 B, $^1\text{J}(\text{BF}) = 63$. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (75.47 MHz, CD_3CN): 104.0 m, 1 C, $\text{J}(\text{C-4,H-4}) = 168.0$ (C-4); 130.0, 1 C (C-1); 146.6, 2 C (C-2, C-6); 148.9, 2 C (C-3,5). For $\text{C}_{12}\text{H}_2\text{BF}_{10}\text{K}$ (386.04) calculated: 37.34% C, 0.52% H, 49.21% F; found: 38.09% C, 0.83% H, 49.40% F.

Synthesis of Potassium Difluorobis(2,3,4,6-tetrafluorophenyl)borate **4c-K**

(2,3,4,6-Tetrafluorophenyl)lithium was prepared from 1,2,3,5-tetrafluorobenzene (9.0 g, 60 mmol) and 2.5 M BuLi in hexanes (20 ml, 50 mmol) in ether (100 ml) at $-78\text{ }^{\circ}\text{C}$. After addition of $\text{B}(\text{OMe})_3$ (5.7 g, 54.9 mmol) and stirring at $-70\text{ }^{\circ}\text{C}$ for 1 h, DME (25 ml) was added dropwise. The solution was kept at $-70\text{ }^{\circ}\text{C}$ for 1 h and left standing at $20\text{ }^{\circ}\text{C}$ overnight. The reaction mixture was worked up with a solution of KHF_2 (16 g, 0.2 mol) in water (100 ml) acidified with 48% HF (10 ml) and an impurity of $\text{K}[2,3,4,6\text{-C}_6\text{HF}_4\text{BF}_3]$ was removed with aqueous HF at $60\text{ }^{\circ}\text{C}$ as described above. Pure salt **4c-K** (7.18 g, 74%) was obtained after evaporation of acetonitrile extract under reduced pressure and drying in vacuum over P_4O_{10} overnight.

^1H NMR (300.13 MHz, CD_3CN): 6.64 dddd, $^3\text{J}(\text{H-5,F-4}) = 11$, $^3\text{J}(\text{H-5,F-6}) = 9$, $^4\text{J}(\text{H-5,F-3}) = 6$, $^5\text{J}(\text{H-5,F-2}) = 3$ (H-5). ^{11}B NMR (96.29 MHz, CD_3CN): 4.45 t, 1 B, $^1\text{J}(\text{BF}) = 66$. $^{13}\text{C}\{^{19}\text{F}\}$ NMR (75.47 MHz, CD_3CN): 100.8, 1 C, $^1\text{J}(\text{C-5,H-5}) = 167$ (C-5); 122.7, 1 C (C-1); 137.7, 1 C (C-6); 150.0, 1 C (C-2); 154.3, 1 C (C-3); 160.6, 1 C (C-4). For $\text{C}_{12}\text{H}_2\text{BF}_{10}\text{K}$ (386.04) calculated: 37.34% C, 0.52% H, 49.21% F; found: 38.41% C, 0.90% H, 49.29% F.

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