

## POLYFLUOROORGANOBORON-OXYGEN COMPOUNDS.

7<sup>+</sup>. 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<sup>a,\*</sup>, Vadim V. BARDIN<sup>b</sup> and Hermann-Josef FROHN<sup>c</sup><sup>a</sup> G. K. Borekov Institute of Catalysis, Siberian Branch Russian Academy of Sciences, Lavrentjev Ave. 5, 630090 Novosibirsk, Russia; e-mail: adonin@catalysis.ru<sup>b</sup> 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<sup>c</sup> Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany; e-mail: h-j.frohn@uni-due.de

Received April 25, 2008

Accepted August 10, 2008

Published online December 15, 2008

*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; <sup>19</sup>F 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<sup>2–5</sup>. For example, it is well known that arylboronic acids readily elimi-

+ For Part 6, see ref.<sup>1</sup>

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

Earlier we have found optimal conditions for preparation and isolation of lithium trimethoxy(penta- and tetrafluorophenyl)borates, Li[(C<sub>6</sub>H<sub>n</sub>F<sub>5-n</sub>)B(OMe)<sub>3</sub>] ( $n = 0, 1$ ), and used these salts as reagents for palladium-catalyzed cross-coupling reactions<sup>2</sup>. The other remarkable property of Li[C<sub>6</sub>F<sub>5</sub>B(OMe)<sub>3</sub>] (**1a-Li**) is its ability to convert into dimethoxybis(pentafluorophenyl)borate salts, M[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B(OMe)<sub>2</sub>] (M = Bu<sub>4</sub>N, K, Li-L<sub>m</sub>; L = Et<sub>2</sub>O, THF, DME, TMEDA), under substitution of Li<sup>+</sup> cation with Bu<sub>4</sub>N<sup>+</sup> and K<sup>+</sup> or complexation of Li<sup>+</sup> with diethyl ether, THF, DME, or TMEDA<sup>3</sup>.

Such conversion of [(C<sub>6</sub>F<sub>5</sub>)B(OMe)<sub>3</sub>]<sup>-</sup> into [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B(OMe)<sub>2</sub>]<sup>-</sup> provides a new synthetic approach to compounds containing two C<sub>6</sub>F<sub>5</sub> 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 derivatives<sup>11</sup> or elimination of C<sub>6</sub>F<sub>5</sub> group from B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> under the action of water<sup>12</sup>, xenon difluoride<sup>13</sup>, IF<sub>3</sub><sup>14</sup>, etc. To our knowledge, such conversion has not been previously reported for any other individual trialkoxy(aryl)borates M[ArB(OAlk)<sub>3</sub>] (Ar ≠ C<sub>6</sub>F<sub>5</sub>), although the formation of (MgBr)[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B(OEt)<sub>2</sub>] as the main product in the reaction of C<sub>6</sub>F<sub>5</sub>MgBr with B(OEt)<sub>3</sub> was described by Servatowski et al.<sup>15</sup>. An admixture (≤15%) of dialkoxydiarylborate salts, M[Ar<sub>F2</sub>B(OAlk)<sub>2</sub>] (Ar<sub>F</sub> = C<sub>6</sub>F<sub>5</sub>, 4-C<sub>5</sub>NF<sub>4</sub>; M = Li, MgBr), was detected in the reaction of Ar<sub>F</sub>M with B(OAlk)<sub>3</sub><sup>16,17</sup>.

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  $\text{CH}_2\text{Cl}_2$ . The resulting organic phase is analysed by  $^{19}\text{F}$  NMR<sup>3</sup>. 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 ratio<sup>3</sup>. 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  $\text{CH}_2\text{Cl}_2$ -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  $^{19}\text{F}$  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-Bu<sub>4</sub>N**) and  $[\text{Bu}_4\text{N}][(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{BF}_2]$  (**4b-Bu<sub>4</sub>N**) (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-Bu<sub>4</sub>N**) and  $(\text{Bu}_4\text{N})[(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{BF}_2]$  (**4c-Bu<sub>4</sub>N**) (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-Bu<sub>4</sub>N**) was the only product ( $^{19}\text{F}$  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-Bu<sub>4</sub>N**) and  $(\text{Bu}_4\text{N})[(\text{C}_6\text{F}_5)_2\text{BF}_2]$  (**4a-Bu<sub>4</sub>N**) in molar ratio 1:4.0<sup>3</sup>.

Thus, the rates of conversion of salts **1-Li** to **2-Li** in  $\text{CH}_2\text{Cl}_2$ -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  $^{19}\text{F}$  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  $\text{CH}_2\text{Cl}_2$ -DME<sup>3</sup>. 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  $^{19}\text{F}$  NMR spectra of dichloro-



TABLE I  
 $^{19}\text{F}$  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    |  |
| $\text{Li}[(\text{C}_6\text{F}_5\text{B}(\text{OMe})_3)]^{\text{a}}$ <b>1a-Li</b>                            | $\text{CD}_2\text{Cl}_2$ | -143.9               | -163.9 | -159.2 | -163.9 | -143.9 |        |  |
| $\text{Li}[(2,3,5,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ <b>1b-Li</b>                   | $\text{CD}_2\text{Cl}_2$ | -144.7               | -141.1 |        | -141.1 | -144.7 |        |  |
| $\text{Li}[(2,3,4,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ <b>1c-Li</b>                   | $\text{CD}_2\text{Cl}_2$ | -135.0               | -168.0 | -137.7 |        | -119.3 |        |  |
| $\text{Li}[(2,3,4,5\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]^{\text{a}}$ <b>1d-Li</b>                   | $\text{CD}_2\text{Cl}_2$ | -148.2               | -160.2 | -158.9 | -140.8 |        |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[\text{C}_6\text{F}_5\text{B}(\text{OMe})_3]$                             | $\text{CH}_2\text{Cl}_2$ | -138.4               | -165.4 | -160.9 | -165.4 | -138.4 |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(2,3,5,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$                  | $\text{CH}_2\text{Cl}_2$ | -140.7               | -142.5 |        | -142.5 | -140.7 |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(2,3,4,6\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$                  | $\text{CH}_2\text{Cl}_2$ | -131.5               | -168.9 | -139.0 |        | -113.9 |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(2,3,4,5\text{-C}_6\text{HF}_4\text{B}(\text{OMe})_3)]$                  | $\text{CH}_2\text{Cl}_2$ | -141.7               | -163.3 | -161.4 | -144.1 |        |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(\text{C}_6\text{F}_5)_2\text{B}(\text{OMe})_2]^{\text{b}}$ <b>2a-Li</b> | $\text{CH}_2\text{Cl}_2$ | -136.3               | -165.7 | -161.3 | -165.7 | -136.3 |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{B}(\text{OMe})_2]$ <b>2b-Li</b>   | $\text{CH}_2\text{Cl}_2$ | -137.7               | -143.1 |        | -143.1 | -137.7 |        |  |
| $(\text{Li}(\text{DME})_{\text{m}})[(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{B}(\text{OMe})_2]$ <b>2c-Li</b>   | $\text{CH}_2\text{Cl}_2$ | -129.9               | -169.8 | -140.1 |        | -109.4 |        |  |
| $(\text{Bu}_4\text{N})[\text{C}_6\text{F}_5\text{BF}_3]^{\text{b}}$ <b>3a-Bu<sub>4</sub>N</b>                | $\text{CH}_2\text{Cl}_2$ | -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 <sub>4</sub> N)[(2,3,5,6-C <sub>6</sub> HF <sub>4</sub> )BF <sub>3</sub> ] <b>3b-Bu<sub>4</sub>N</b>               | CH <sub>2</sub> Cl <sub>2</sub> | -136.4               | -143.1 |        | -143.1 | -136.4 | -134.5 |  |
| (Bu <sub>4</sub> N)[(2,3,4,6-C <sub>6</sub> HF <sub>4</sub> )BF <sub>3</sub> ] <b>3c-Bu<sub>4</sub>N</b>               | CH <sub>2</sub> Cl <sub>2</sub> | -128.7               | -170.5 | -139.8 |        | -108.2 | -134.1 |  |
| (Bu <sub>4</sub> N)[(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4a-Bu<sub>4</sub>N</b>          | CH <sub>2</sub> Cl <sub>2</sub> | -136.7               | -166.5 | -161.9 | -166.5 | -136.7 | -139.0 |  |
| (Bu <sub>4</sub> N)[(2,3,5,6-C <sub>6</sub> HF <sub>4</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4b-Bu<sub>4</sub>N</b> | CH <sub>2</sub> Cl <sub>2</sub> | -137.2               | -143.4 |        | -143.4 | -137.2 | -147.2 |  |
| (Bu <sub>4</sub> N)[(2,3,4,6-C <sub>6</sub> HF <sub>4</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4c-Bu<sub>4</sub>N</b> | CH <sub>2</sub> Cl <sub>2</sub> | -129.6               | -170.8 | -140.6 |        | -109.0 | -146.7 |  |
| K[(C <sub>6</sub> F <sub>5</sub> BF <sub>3</sub> )] <sup>c</sup> <b>3a-K</b>   | CD <sub>3</sub> CN              | -135.2               | -165.3 | -160.7 | -165.3 | -135.2 | -133.4 |  |
| K[(2,3,5,6-C <sub>6</sub> HF <sub>4</sub> )BF <sub>3</sub> ] <sup>d</sup> <b>3b-K</b>                                  | CD <sub>3</sub> CN              | -135.8               | -142.2 |        | -142.2 | -135.8 | -133.8 |  |
| K[(2,3,4,6-C <sub>6</sub> HF <sub>4</sub> )BF <sub>3</sub> ] <sup>d</sup> <b>3c-K</b>                                  | CD <sub>3</sub> CN              | -128.4               | -169.6 | -139.3 |        | -107.5 | -133.7 |  |
| K[(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> BF <sub>2</sub> ] <sup>c</sup> <b>4a-K</b>                             | MeOH                            | -135.5               | -165.5 | -160.7 | -165.5 | -135.5 | -145.8 |  |
| K[(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4a-K</b>  | CD <sub>3</sub> CN              | -136.3               | -165.3 | -160.5 | -165.3 | -136.3 | -146.1 |  |
| K[(2,3,5,6-C <sub>6</sub> HF <sub>4</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4b-K</b>                                 | CD <sub>3</sub> CN              | -136.4               | -143.1 |        | -143.1 | -136.4 | -134.5 |  |
| K[(2,3,4,6-C <sub>6</sub> HF <sub>4</sub> ) <sub>2</sub> BF <sub>2</sub> ] <b>4c-K</b>                                 | CD <sub>3</sub> CN              | -128.7               | -170.5 | -139.8 |        | -108.2 | -134.1 |  |

a Ref.<sup>2</sup>; b ref.<sup>3</sup>; c ref.<sup>16</sup>; d ref.<sup>19</sup>

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 results<sup>3</sup> 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 pyridine<sup>4</sup> 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  $(2,3,4,5-C_6HF_4)B(OH)_2$  [ $k(32\text{ }^\circ\text{C}) = 0.009 \times 10^{-2}$ ]

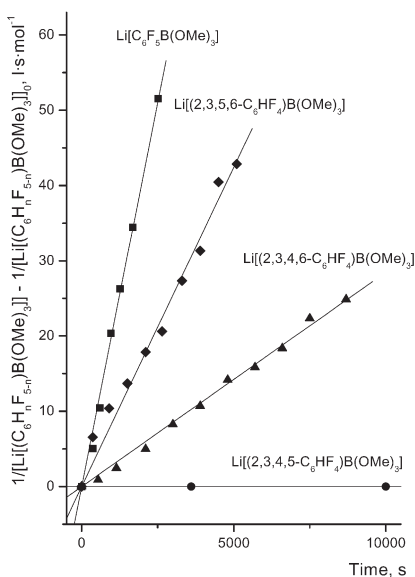
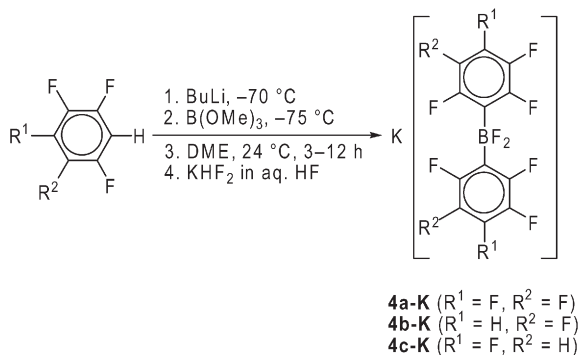


FIG. 1

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<sup>-1</sup>]. In both cases, the driving force of the processes can be associated with qualitative changes in Lewis acidity of arylboranes (C<sub>6</sub>H<sub>n</sub>F<sub>5-n</sub>)B(OR)<sub>2</sub> (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[(C<sub>6</sub>H<sub>n</sub>F<sub>5-n</sub>)<sub>2</sub>BF<sub>2</sub>] (*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 KHF<sub>2</sub> 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 <sup>19</sup>F NMR data, see Table I) and elemental analysis.

## CONCLUSIONS

The rates of conversion of Li[C<sub>6</sub>F<sub>5</sub>B(OMe)<sub>3</sub>], Li[(2,3,5,6-C<sub>6</sub>HF<sub>4</sub>)B(OMe)<sub>3</sub>] and Li[(2,3,4,6-C<sub>6</sub>HF<sub>4</sub>)B(OMe)<sub>3</sub>] to the corresponding salts (Li·DME)[(C<sub>6</sub>H<sub>n</sub>F<sub>5-n</sub>)<sub>2</sub>-



$B(OMe)_2]$  ( $n = 0, 1$ ) 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 ( $\delta$ , 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 method<sup>2</sup>. Borates  $K[C_6F_5BF_3]$ <sup>16</sup>,  $K[(2,3,4,5-C_6HF_4)BF_3]$ <sup>16</sup>,  $K[(2,3,5,6-C_6HF_4)BF_3]$ <sup>19</sup> and  $K[(2,3,4,6-C_6HF_4)BF_3]$ <sup>19</sup> 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  $\mu$ 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  $\mu$ l, 0.041 mmol) and  $(\text{Bu}_4\text{N})\text{HF}_2$  (prepared from 48% HF (1 ml, 28 mmol) and 40%  $\text{Bu}_4\text{NOH}$  (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  $^{19}\text{F}$  NMR spectra of the separated organic phase showed the formation of **3b-Bu<sub>4</sub>N**, **4b-Bu<sub>4</sub>N** (1.5:1), **3c-Bu<sub>4</sub>N**, **4c-Bu<sub>4</sub>N** (3.8:1), and **3d-Bu<sub>4</sub>N** 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 ( $5 \times 2$  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  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR spectra<sup>5</sup>.

$(2,3,4,6\text{-C}_6\text{HF}_4)_2\text{BOH}$ .  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{CH}_2\text{Cl}_2$ ): 40.00 bs.  $^{19}\text{F}$  NMR (282.40 MHz,  $\text{CH}_2\text{Cl}_2$ ): -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.

$(2,3,5,6\text{-C}_6\text{HF}_4)_2\text{BOH}$ .  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{CH}_2\text{Cl}_2$ ): 37.56 bs.  $^{19}\text{F}$  NMR (282.40 MHz,  $\text{CH}_2\text{Cl}_2$ ): -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 ( $^{19}\text{F}$  NMR, Table I). The reaction mixture was poured out into a solution of  $\text{KHF}_2$  (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  $\text{K}_2\text{CO}_3$  to pH 8–9. A white precipitate was filtered off, washed with water, dried in air, and extracted with acetonitrile ( $5 \times 10$  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  $\text{P}_4\text{O}_{10}$  overnight, pure  $\text{K}[(\text{C}_6\text{F}_5)_2\text{BF}_2]$  (7.2 g, 68%) was obtained.

$^{11}\text{B}$  NMR (96.29 MHz,  $\text{CD}_3\text{CN}$ ): 4.34 t, 1 B,  $^1J(\text{BF})$  59.  $^{13}\text{C}\{^{19}\text{F}\}$  NMR (75.47 MHz,  $\text{CD}_3\text{CN}$ ): 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  $\text{KHF}_2$  (16 g, 0.2 mol) in water (100 ml) acidified with 48% HF (10 ml), and an impurity of  $\text{K}[(2,3,5,6\text{-C}_6\text{HF}_4)\text{BF}_3]$  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  $\text{P}_4\text{O}_{10}$  overnight gave pure salt **4b-K** (6.0 g, 62%).

$^1\text{H}$  NMR (300.13 MHz,  $\text{CD}_3\text{CN}$ ): 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).  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{CD}_3\text{CN}$ ): 4.33 1 B,  $^1\text{J}(\text{BF}) = 63$ .  $^{13}\text{C}\{^{19}\text{F}\}$  NMR (75.47 MHz,  $\text{CD}_3\text{CN}$ ): 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  $\text{KHF}_2$  (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  $\text{P}_4\text{O}_{10}$  overnight.

$^1\text{H}$  NMR (300.13 MHz,  $\text{CD}_3\text{CN}$ ): 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).  $^{11}\text{B}$  NMR (96.29 MHz,  $\text{CD}_3\text{CN}$ ): 4.45 t, 1 B,  $^1\text{J}(\text{BF}) = 66$ .  $^{13}\text{C}\{^{19}\text{F}\}$  NMR (75.47 MHz,  $\text{CD}_3\text{CN}$ ): 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.

*We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.*

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