(Fluoroorgano)fluoroboranes and -borates. 16. Preparation of Bis(perfluoroalkyl)dimethoxyborate and Bis(perfluoroalkyl)difluoroborate Salts, $M[(C_nF_{2n+1})_2BX_2]$ ($M = K$, NMe_4; $X = OMe$, F)†

Nicolay Yu. Adonin and Hermann-Josef Frohn*

Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Lotharstrasse 1,
D-47048 Duisburg, Germany

Vadim V. Bardin

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Ave. 9,
630090 Novosibirsk, Russia

Received January 30, 2007

Potassium bis(perfluoroalkyl)dimethoxyborate salts, $K[(C_nF_{2n+1})_2B(OMe)_2]$ ($n = 3, 4, 6$), were prepared in 60−76% yield by the reaction of (perfluoroalkyl)lithium with chlorodimethoxyborane and subsequent metathesis of the cation with KF. Reactions of $K[(C_nF_{2n+1})_2B(OMe)_2]$ with 42−73% aqueous HF resulted in the salts $K[(C_nF_{2n+1})_2B(OR)F]$ ($R = H$, CH_3), which were converted into $K[(C_nF_{2n+1})_2BF_2]$ by the treatment with anhydrous HF. Metathesis of potassium salts with $[NMe_4]OH$ in water yielded the corresponding borates $[NMe_4][(C_nF_{2n+1})_2BF_2]$.

Introduction

During the past decade significant progress has been achieved in the syntheses of poly- and perfluorinated organoborates $M[R_FBX_3]$, where R_F represents a perfluoroaryl, perfluoroalkenyl, perfluoroalkynyl, or perfluoroalkyl group and X = OAlk, F.[1−5] Structurally related bis(perfluoroorgano)borates, $M[(R_F)_2BX_2]$, are a less investigated class of compounds.

The individual salt $[BrMg{\cdot}OEt_2][(C_6F_5)_2B(OEt)_2]$ was prepared from $B(OEt)_3$ and an excess of C_6F_5MgBr (2−4 equiv), but the yield was not reported.[6] The attempted metathesis of $Li[C_6F_5B(OMe)_3]$ with KF or $[NBu_4]Br$ in CH_2Cl_2 led to a mixture of $M[(C_6F_5)_2B(OMe)_2]$ and $M[C_6F_5B(OMe)_3]$ (byproduct) ($M = K$, $[NBu_4]$).[7] In the presence of coordinating solvents the salt $Li[C_6F_5B(OMe)_3]$ as well underwent dismutation to the diarylborate salt $[Li(L)_n][(C_6F_5)_2B(OMe)_2]$ ($L = Et_2O$, THF, DME, TMEDA) and $[Li(L)_n][B(OMe)_4]$.[7] In some reactions of perfluoroorgano nucleophiles R_FM with an excess of the electrophile $B(OMe)_3$, bis(perfluoroorganyl)dialkoxyborates were detected as minor admixtures by NMR spectroscopy ($R_FM = CF_3C{\equiv}CLi$,[5] C_6F_5MgBr,[8] $(4\text{-}C_5F_4N)Li$[9]). The reaction of $C_3F_7OCF{=}CFLi$ and $B(OMe)_3$ (>1 equiv) and the following substitution of OMe by F with $K[HF_2]$ in aqueous MeOH was accompanied by the formation of $K[(C_3F_7OCF{=}CF)_2BF_2]$ (7%) in addition to $K[C_3F_7OCF{=}CFBF_3]$ (main product).[10] However, the nucleophilic alkenylation of $B(OMe)_3$ (>1 equiv) with $RCF{=}CFLi$ (R = *trans*-Et_3Si,[11] *trans*-C_4H_9, *trans*-C_6H_5, *trans*-C_4F_9, *cis*-C_2F_5, *cis*-C_6F_{13}, *cis*- and *trans*-Cl[12]) or with $CF_2{=}CRLi$ (R = H, Cl, CF_3)[13] and subsequent workup with acidified $K[HF_2]$ gave no bis(alkenyl)difluoroborates. In the case of perfluoroalkyl nucleophiles even the reaction of an excess of $C_nF_{2n+1}Li$ with $B(OMe)_3$ (≤1 equiv) only led to $Li[C_nF_{2n+1}B(OMe)_3]$ ($n = 3, 4, 6$) in 92−98% yield, and no bis(perfluoroalkylated) boron compound was observed.[14]

A promising preparative approach to $M[(R_F)_2B(OMe)_2]$ consists of the nucleophilic addition of R_FM to boranes $R_FB(OMe)_2$. The latter can be obtained by demethoxylation of borates $M[R_FB(OMe)_3]$ with Me_3SiCl ($R_F = C_6F_5$,[7] $CF_2{=}CF$,[15] CF_3[16]), $CF_3SO_2OCH_3$, or CH_3SO_2Cl ($R_F = CF_3$, C_2F_5[16]) or generated in situ via the intermediate borate $[R_FBCl(OMe)_2]^-$. An important property of this anion is the better nucleofugality of the chloride anion relative to that of $[OAlk]^-$. The successful application of both methods was demonstrated in the synthesis of borates $M[(R_F)_2B(OMe)_2]$ ($M = Li$, K; $R_F = CF_2{=}CF$, C_2F_5), which were converted into salts $K[(R_F)_2BF_2]$ using an aqueous

---

* To whom correspondence should be addressed. E-mail: h-j.frohn@uni-due.de.

† Dedicated to Professor Neil Bartlett on the occasion of his 75th birthday.

(1) Bardin, V. V.; Frohn, H.-J. *Main Group Met. Chem.* **2002**, *25*, 589−613.

(2) Darses, S.; Genet, J.-P. *Eur. J. Org. Chem.* **2003**, 4313−4327.

(3) Pawelke, G.; Bürger, H. *Coord. Chem. Rev.* **2001**, *215*, 243−266.

(4) Chivers, T. *J. Fluorine Chem.* **2002**, *115*, 1−8.

(5) Bardin, V. V.; Adonin, N. Yu.; Frohn, H.-J. *Organometallics* **2005**, *24*, 5311−5317.

(6) Anulewicz-Ostrowska, R.; Klis, T.; Serwatowski, J. *Main Group Met. Chem.* **2002**, *25*, 501−504.

(7) Adonin, N. Yu.; Bardin, V. V.; Flörke, U.; Frohn, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2638−2646.

(8) Frohn, H.-J.; Franke, H.; Fritzen, P.; Bardin, V. V. *J. Organomet. Chem.* **2000**, *598*, 127−135.

(9) Abo-Amer, A.; Adonin, N. Yu.; Bardin, V. V.; Fritzen, P.; Frohn, H.-J.; Steinberg, C. *J. Fluorine Chem.* **2004**, *125*, 1771−1778.

(10) Frohn, H.-J.; Bardin, V. V. *J. Fluorine Chem.* **2003**, *123*, 43−49.

(11) Frohn, H.-J.; Adonin, N. Yu.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2499−2508.

(12) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2499−2505.

(13) Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2465−2469.

(14) Adonin, N. Yu.; Bardin, V. V.; Frohn, H.-J. *Z. Anorg. Allg. Chem.*, in press.

(15) Adonin, N. Yu.; Bardin, V. V.; Frohn, H.-J. *Organometallics* **2004**, *23*, 535−539.

(16) Kolomeitsev, A. A.; Kadyrov, A. A.; Szczepkowska-Sztolcman, J.; Milewska, M.; Koroniak, H.; Bissky, G.; Barten, J. A.; Röschenthaler, G.-V. *Tetrahedron Lett.* **2003**, *44*, 8273−8277.

10.1021/om070090h CCC: $37.00

solution of $K[HF_2]$ ($R_F = CF_2{=}CF$)[15] or anhydrous HF ($R_F = C_2F_5$).[9] The salt $K[(CF_3)_2BF_2]$ had already been obtained in 1979 by the reaction of CF_3SnMe_3 with BF_3 and a subsequent treatment with KF,[17] but the attempted extension of this approach to longer chain bis(perfluoroalkyl)difluoroborates later failed.[1]

In addition to fundamental aspects, the application potential of $M[(C_nF_{2n+1})_2B(OMe)_2]$ salts as counterions in ionic liquids or in lithium ion batteries and supercapacitors motivated us to study synthetic routes to the previously unknown bis(perfluoroalkyl)dimethoxyborates $M[(C_nF_{2n+1})_2B(OMe)_2]$ ($n > 2$) via perfluoroalkylation of chlorodimethoxyborane and to develop convenient conditions for the preparation of bis(perfluoroalkyl)difluoroborates $M[(C_nF_{2n+1})_2BF_2]$ (M = K, NBu_4).

Results and Discussion

Preparation of $K[(C_nF_{2n+1})_2B(OMe)_2]$ and $M[(C_nF_{2n+1})_2BF_2]$. Initially we investigated the perfluoroalkylation of $BCl(OMe)_2$ with $C_nF_{2n+1}MgBr$. (Perfluoropropyl)magnesium bromide (more than 3 equiv) was generated from perfluoropropyl iodide and MeMgBr in ether−THF (10/1 v/v) at −78 °C. After the addition of $BCl(OMe)_2$ the reaction mixture was warmed to 20 °C. The ^{11}B and ^{19}F NMR spectra showed the formation of a mixture of (perfluoropropyl)trimethoxyborate and bis(perfluoropropyl)dimethoxyborate salts (3/1) (Scheme 1). The alkylation of $BCl(OMe)_2$ with (perfluorobutyl)magnesium bromide in ether−THF (1/1 v/v) and the subsequent fluorodemethoxylation of the primary formed borates gave a mixture of potassium (perfluorobutyl)trifluoroborate and potassium bis(perfluorobutyl)methoxyfluoroborate in only 11 and 22% yield, respectively (Schemes 1 and 2). These experiments corroborate an insufficient reactivity of $C_nF_{2n+1}MgBr$ toward $BCl(OMe)_2$ under the examined reaction conditions.

Scheme 1

$$3C_nF_{2n+1}MgBr + BCl(OMe)_2 \xrightarrow[-78\text{ to }20\ ^\circ C]{\text{ether}-\text{THF}} 3[BrMg][(C_nF_{2n+1})_mB(OMe)_{4-m}]$$

$$n = 3, 4;\ m = 1, 2$$

Scheme 2

$$[BrMg][(C_4F_9)_mB(OMe)_{4-m}] \xrightarrow[2.\ K_2CO_3]{1.\ \text{aq HF}} K[C_4F_9BF_3] + K[(C_4F_9)_2BF(OMe)]$$

Recently we studied the perfluoroalkylation of $B(OMe)_3$ with longer chain (perfluoroalkyl)lithium reagents $C_nF_{2n+1}Li$ ($n = 3, 4, 6$) generated under different conditions.[14] The best results were obtained when $C_nF_{2n+1}Li$ had been prepared from 1H-perfluoroalkane and t-BuLi below −110 °C and was reacted with $B(OMe)_3$ at −110 °C with subsequent warming to 20 °C. Other approaches to $C_nF_{2n+1}Li$ (C_3F_7I + BuLi at −90 or −78 °C; C_3F_7I + MeLi at −90 °C; C_3F_7H + BuLi at −90 °C) gave poorer results.[14] The results with perfluoropropyl iodide differed from such with a shorter perfluoroalkyl chain. Thus, lithium (pentafluoroethyl)trimethoxyborate can be prepared from C_2F_5I, MeLi, and $B(OMe)_3$ at −80 °C in 43% yield.[18] On the basis of this experience, we generated (perfluoropropyl)lithium from 1H-perfluoropropane and t-BuLi under optimized conditions and allowed it to react with $BCl(OMe)_2$ at −110 °C and subsequently warmed it to 20 °C gradually. Lithium bis(perfluoropropyl)dimethoxyborate (**1a**) was converted into the corresponding potassium bis(perfluoropropyl)dimethoxyborate (**2a**) (69% isolated yield) by metathesis with KF in the presence of a small amount of water. Potassium bis(perfluorobutyl)dimethoxyborate (**2b**) and potassium bis(perfluorohexyl)dimethoxyborate (**2c**) were prepared in 60−76% yield using an analogous procedure (Scheme 3).

Scheme 3

$$C_nF_{2n+1}H \xrightarrow[\text{ether},\ -110\ ^\circ C]{t\text{-BuLi},\ -t\text{-BuH}} C_nF_{2n+1}Li \xrightarrow[-LiCl]{0.5BCl(OMe)_2} \underset{\mathbf{1a-c}}{Li[(C_nF_{2n+1})_2B(OMe)_2]}$$

$$\underset{\mathbf{1a-c}}{Li[(C_nF_{2n+1})_2B(OMe)_2]} + KF \xrightarrow[-LiF]{\text{ether},\ H_2O} \underset{\mathbf{2a-c}}{K[(C_nF_{2n+1})_2B(OMe)_2]}$$

$$n = 3, 4, 6$$

Previously we had described the synthesis of perfluoroalkyltrifluoroborates by fluorodemethoxylation of $K[C_nF_{2n+1}BF_2(OMe)]$ with 40% HF.[19] Later this method was employed for the conversion of $K[C_nF_{2n+1}BF_2(OH)]$ ($n = 2-4$)[20] and $M[C_nF_{2n+1}B(OMe)_3]$ (M = Li, K; $n = 1, 2$)[16] into the corresponding (perfluoroalkyl)trifluoroborates. However, the treatment of borates **2a−c** with 42−73% aqueous HF gave only a mixture of potassium bis(perfluoroalkyl)methoxyfluoroborates (**3a−c**) and bis(perfluoroalkyl)hydroxyfluoroborates (**4a−c**) (Scheme 4).

Scheme 4

$$\underset{\mathbf{2a-c}}{K[(C_nF_{2n+1})_2B(OMe)_2]} + HF_{aq} \rightarrow \underset{\mathbf{3a-c}}{K[(C_nF_{2n+1})_2B(OMe)F]} + \underset{\mathbf{4a-c}}{K[(C_nF_{2n+1})_2B(OH)F]}$$

The formation of the hydroxyborate anions **4a−c** indicates that the acidity of 42−73% aqueous HF ($-H_0 = 2-7$[21,22]) is high enough to form the intermediate **A** (Scheme 5), which is able to eliminate MeF, whereas the competitive elimination of MeOH is a reversible process. When the acidity of HF_{aq} is increased, MeOH becomes protonated and the highly acidic borane **B** will add fluoride instead of $[MeOH_2]^+$ (Scheme 5). A similar influence of the acidity was observed by Zhou et al. in the fluorodemethoxylation of $K[C_nF_{2n+1}B(OMe)_3]$ ($n = 2-4$) with $K[HF_2]$ in water or $K[HF_2]$ in aqueous HF, where the salts $K[C_nF_{2n+1}BF_2(OH)]$ were obtained.[20]

---

[17] Pawelke, G.; Heyder, F.; Bürger, H. *J. Organomet. Chem.* **1979**, *178*, 1−4.

[18] Frohn, H.-J.; Adonin, N. Yu.; Bardin, V. V. *Main Group Met. Chem.* **2001**, *24*, 845−846.

[19] Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2001**, *627*, 15−16.

[20] Zhou, Z.-B.; Takeda, M.; Ue, M. *J. Fluorine Chem.* **2003**, *123*, 127−131.

[21] Rochester, C. H. *Acidity Functions*; Academic Press: New York, 1970.

[22] Gillespie, R. J.; Liang, J. *J. Am. Chem. Soc.* **1989**, *110*, 6053−6057.

Scheme 5

$$\underset{\mathbf{3}}{[(C_nF_{2n+1})_2B(OMe)F]^-} \xrightleftharpoons{H^+_{aq}} \underset{\mathbf{A}}{<(C_nF_{2n+1})_2BF(OHMe)>}$$

$$\underset{\mathbf{5}}{[(C_nF_{2n+1})_2BF_2]^-} \xleftarrow{F^-} \underset{\mathbf{B}}{<(C_nF_{2n+1})_2BF>} \xrightleftharpoons[+MeOH]{+H^+} \mathbf{A} \xrightarrow[-MeF]{+F^-_{aq}} \underset{\mathbf{4}}{[(C_nF_{2n+1})_2BF(OH)]^-}$$

We found that the employment of the more highly acidic aHF ($-H_0 = 15$[23]) instead of 42−73% aqueous HF resulted in the protonation of eliminated ROH to $[ROH_2]^+$. Thus, potassium bis(perfluoroalkyl)difluoroborates (**5a**−**c**) were prepared in 37−48% overall isolated yield based on chlorodimethoxyborane (Schemes 3, 4, and 6).

Scheme 6

$$\underset{\mathbf{3a-c},\ \mathbf{4a-c}}{K[(C_nF_{2n+1})_2B(OR)F]} \xrightarrow[-[ROH_2]^+]{aHF} \underset{\mathbf{5a-c}}{K[(C_nF_{2n+1})_2BF_2]}$$

$$R = H, Me$$

Salts **5a**−**c** are soluble in polar organic solvents (acetone, CH_3CN, ether, THF, DME, etc.). In contrast to $K[C_nF_{2n+1}BF_3]$ ($n = 2$−4, 6),[19,24] salts **5a**,**b** are hygroscopic substances and are readily soluble in water. Metathesis with $[NMe_4]OH$ in aqueous solution gave the corresponding tetramethylammonium salts **6a**−**c** (eq 1).

$$\underset{\mathbf{5a-c}}{K[(C_nF_{2n+1})_2BF_2]} + [NMe_4]OH \xrightarrow[-KOH]{} \underset{\mathbf{6a-c}}{[NMe_4][(C_nF_{2n+1})_2BF_2]} \quad (1)$$

NMR Spectra of $K[(C_nF_{2n+1})_2BXY]$ (X, Y = F, OH, OMe). The constitution of the $K[(C_nF_{2n+1})_2BXY]$ salts (with correct elemental analysis) was unambiguously proved by multi-NMR spectroscopy (Tables 1 and 2). It is worth noting that the elongation of the perfluoroalkyl chain in $K[(C_nF_{2n+1})_2BF_2]$ (Table 1) and $K[C_nF_{2n+1}BF_3]$[26] ($n = 1$−6) salts caused a remarkable deshielding of both types of fluorine atoms *F* in the $C_{n-1}F_{2n-1}CF_2BF$ fragment in the ^{19}F NMR spectra and of the boron atom in the ^{11}B NMR spectra. A closely related phenomenon occurred in the ^{19}F and ^{11}B NMR spectra of borates $K[(C_nF_{2n+1})_2B(OMe)_2]$ (Table 1) and $K[C_nF_{2n+1}B(OMe)_3]$.[14,16] The deshielding of the boron-bonded F atoms reflects the inductive effect of the individual perfluoroalkyl groups.[27] A comparable influence of linear and branched perfluoroalkyl chains with the same number of C atoms was observed in the case of the ^{19}F NMR chemical shift of the BF_3 group of the $[CF_3CF_2CF_2CF_2BF_3]^-$ anion (δ −152.1 ppm) and of its isomer $[CF_3CF_2CF(CF_3)BF_3]^-$ (δ −147.1 ppm).[28] In the ^{19}F NMR spectra of the $[(C_nF_{2n+1})_2BXY]^-$ anions no AB spin system was found for the CF_2B fragment.

Conclusion

The reaction of (perfluoroalkyl)lithium, generated from 1*H*-perfluoroalkane and *t*-BuLi below −110 °C, with chlorodimethoxyborane and the subsequent cation exchange with aqueous KF is a convenient and general preparative route to potassium bis(perfluoroalkyl)dimethoxyborates $K[(C_nF_{2n+1})_2B(OMe)_2]$. The nucleophilic perfluoroalkylation of $BCl(OMe)_2$ with (perfluoroalkyl)magnesium bromides is less effective and results in a mixture of $M[(C_nF_{2n+1})_mB(OMe)_{4-m}]$ salts ($m = 1, 2$). In 42−73% aqueous HF, borates $K[(C_nF_{2n+1})_2B(OMe)_2]$ were converted into $K[(C_nF_{2n+1})_2B(OMe)F]$ and $K[(C_nF_{2n+1})_2B(OH)F]$, while the exhaustive conversion of $K[(C_nF_{2n+1})_2B(OR)F]$ to $K[(C_nF_{2n+1})_2BF_2]$ was achieved by treatment with highly acidic anhydrous HF.

Experimental Section

Materials and Methods. C_3F_7I (ABCR), C_4F_9I (ABCR), $C_6F_{13}H$ (Clariant), 1.7 M *t*-BuLi in pentane (Aldrich), boron trichloride (Merck), Sicapent (Merck), KF (spray dried) (Aldrich), 26% aqueous tetramethylammonium hydroxide (Riedel-de Haën), 73% aqueous HF (Fluka), anhydrous THF (Baker), and anhydrous ether (Baker) were used as supplied. $B(OMe)_3$ (Fluka) was distilled over sodium before use. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni electrodes). C_3F_7H and C_4F_9H were obtained by decarboxylation of $NaO_2CC_3F_7$ and $NaO_2CC_4F_9$, respectively, in diethylene glycol at 180−190 °C.[30] Chlorodimethoxyborane, $BCl(OMe)_2$ (bp 72.5−73 °C, lit.[31] bp 74.7 °C), was prepared from a 1/2 molar mixture of BCl_3 and $B(OMe)_3$. All manipulations with aqueous and anhydrous HF were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment.

Caution! Proper precaution must be used when handling anhydrous hydrogen fluoride (aHF).[32]

Physical and Analytical Measurements. NMR spectra were recorded on a Bruker AVANCE 300 (300.13 MHz, ^1H; 96.29 MHz, ^{11}B; 75.47 MHz, ^{13}C; 282.40 MHz, ^{19}F) FT spectrometer. The chemical shifts 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 a secondary reference (−162.9 ppm)), respectively. Elemental analyses were performed with a HEKAtech EA3000 analyzer. The compositions of the reaction mixtures and the yields of products in solution were determined by ^1H or ^{19}F NMR spectroscopy using the quantitative standard $C_6H_5CF_3$.

Reaction of C_3F_7MgBr with $BCl(OMe)_2$ in Ether−THF (10/1 v/v). A white suspension of C_3F_7MgBr was prepared by the addition of MeMgBr (3.0 M in ether, 0.2 mL, 0.6 mmol) to a solution of C_3F_7I (270 mg, 0.91 mmol) in ether (10 mL) and THF (1 mL) at −78 °C and stirring for an additional 1 h. $BCl(OMe)_2$ (27 mg, 0.25 mmol) was added by syringe, the reaction mixture was stirred at −78 °C for 1 h and warmed to 20 °C within 3 h to yield a suspension. The ^{19}F and ^{11}B NMR spectra of the mother liquor showed the presence of the anions $[C_3F_7B(OMe)_3]^-$ and $[(C_3F_7)_2B(OMe)_2]^-$ (3:1).

---

[23] O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; VCH: New York, 1993; p 14.

[24] Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1853−1856.

[25] Brauer, D. J.; Bürger, H.; Chebude, Y.; Pawelke, G. *Inorg. Chem.* **1999**, *38*, 3972−3977.

[26] For a compilation of ^{11}B and ^{19}F NMR spectra of $K[RBF_3]$ (R = polyfluoroalkyl), see the Supporting Information for ref 5 (Table S1).

[27] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

[28] NMR data of $[C_2F_5CF(CF_3)BF_3]^-$: $\delta(^{11}B)$ 0.1 ppm; $\delta(^{19}F)$ −80.4 (CF_3CF_2), −118.6 and −119.4 ($CF_3CF^aF^b$), −70.5 (CF_3CF), −209.8 (CFB), −147.1 (BF_3) ppm.[29]

[29] Finze, M.; Bernhardt, E.; Zaehres, M.; Willner, H. *Inorg. Chem.* **2004**, *43*, 490−505.

[30] LaZerte, J. D.; Hals, L. J.; Reid, T. S.; Smith, G. H. *J. Am. Chem. Soc.* **1953**, *75*, 4525−4528.

[31] Wiberg, E.; Sütterlin, W. *Z. Anorg. Allg. Chem.* **1931**, *202*, 31−36.

[32] For first aid, see: Finkel, A. J. *Adv. Fluorine Chem.* **1973**, *7*, 199−203.

Table 1. ^{11}B and ^{19}F NMR Spectra of $M[(C_nF_{2n+1})_2BXY]$ Salts (M = K, NMe_4; X = OMe, OH, F; Y = OMe, F) (CD_3CN, 24 °C)

	^{19}F NMR chem shift, ppm						
compd	CF_3	CF_3CF_2	CF_2	CF_2B	BF	^{11}B NMR chem shift, ppm	coupling constant $^nJ_{BF}$, Hz
$K[(CF_3)_2BF_2]$[25]	−73.9				−180.5	−2.2	$^1J = 57$; $^2J = 31$
$K[(C_2F_5)_2B(OMe)_2]$[9]	−82.5			−125.6		−2.1	$^2J = 15$
$K[(C_2F_5)_2B(OMe)F]$[a]	−81.4			−130.5	−188.7	−0.8	$^1J = 69$; $^2J = 20$
$K[(C_2F_5)_2B(OH)F]$[a]	−81.7			−132.3	−176.4	0.1	$^1J = 67$; $^2J = 21$
$K[(C_2F_5)_2BF_2]$[9]	−82.2			−133.9	−175.1	−0.2	$^1J = 63$; $^2J = 21$
$K[(C_3F_7)_2B(OMe)_2]$	−79.3	−124.4		−123.1		−1.3	$^2J = 17$
$K[(C_3F_7)_2B(OMe)F]$	−79.5	−125.3		−128.1	−187.2	*c*	$^1J = 66$; $^2J = 19$
$K[(C_3F_7)_2B(OH)F]$	−79.5	−125.0		−129.6	−175.0	−0.2	$^1J = 62$; $^2J = 21$
$K[(C_3F_7)_2BF_2]$	−79.8	−126.2		−131.3	−173.1	0.1	$^1J = 63$; $^2J = 21$
$[NMe_4][(C_3F_7)_2BF_2]$[b]	−79.8	−126.2		−131.2	−173.1	0.1	$^1J = 63$; $^2J = 21$
$K[(C_4F_9)_2B(OMe)_2]$	−80.2	−124.7	−120.9	−122.7		−1.2	$^2J = 17$
$K[(C_4F_9)_2B(OMe)F]$	−80.2	−124.8	−121.6	−127.5	−186.6	*c*	$^1J = 65$
$K[(C_4F_9)_2B(OH)F]$	−80.2	−124.9	−121.4	−129.0	−174.4	−0.2	$^1J = 65$; $^2J = 20$
$K[(C_4F_9)_2BF_2]$	−80.2	−125.0	−122.5	−130.6	−172.6	0.2	$^1J = 62$; $^2J = 22$
$[NMe_4][(C_4F_9)_2BF_2]$[b]	−80.2	−125.0	−122.5	−130.6	−172.7	0.2	$^1J = 62$; $^2J = 22$
$K[(C_6F_{13})_2B(OMe)_2]$	−79.9	−124.9	−119.5, −120.5, −121.5	−122.6		−1.0	$^2J = 17$
$K[(C_6F_{13})_2B(OMe)F]$	−80.0	−125.0	−120.4, −120.7, −121.6	−127.3	−186.4	−0.1	$^1J = 61$; $^2J = 15$
$K[(C_6F_{13})_2B(OH)F]$	−80.0	−125.0	−120.4, −120.7, −121.6	−128.8	−174.5	−0.1	$^1J = 61$; $^2J = 15$
$K[(C_6F_{13})_2BF_2]$	−79.9	−124.9	−120.7, −120.9, −121.6	−130.3	−172.5	0.2	$^1J = 62$; $^2J = 22$
$[NMe_4][(C_6F_{13})_2BF_2]$[b]	−79.9	−124.9	−120.7, −120.9, −121.6	−130.3	−172.4	0.3	

[a] This work. [b] δ(H) 3.03−3.07 (CH_3N) ppm. [c] The ^{11}B NMR spectrum was not measured, and $^nJ_{BF}$ values were taken from the ^{19}F NMR spectrum.

Table 2. ^{1}H and ^{13}C NMR Spectra of $K[(C_nF_{2n+1})_2BXY]$ Salts (n = 3, 4, 6; X = OMe, OH, F; Y = OMe, F) (CD_3CN, 24 °C)

	^{13}C NMR chem shift, ppm				
compd	CF_3	CF_3CF_2	CF_2	CF_2B	coupling constant, Hz[a]
$K[(C_2F_5)_2BF_2]$[b]	122.6			120.5	^1J(C-2,F-2) = 285; ^2J(C-2,F-1) = 32
$K[(C_3F_7)_2B(OMe)_2]$[c,d]	120.4	112.7		126.2	^1J(C-1,B) = 66; ^1J(C-1,F-1) = 268; ^1J(C-2,F-2) = 260; ^2J(C-2,F-1) = 35; ^2J(C-2,F-3) = 42
$K[(C_3F_7)_2B(OH)F]$[e]	120.1	112.7		123.4	^1J(C-1,B) = 70; ^1J(C-2,F-2) = 259; ^2J(C-2,F-1) = 35
$K[(C_3F_7)_2BF_2]$	120.0	112.3		121.9	^1J(C-1,B) = 76; ^1J(C-1,F-1) = 258; ^1J(C-2,F-2) = 259; ^2J(C-2,F-1) = 35
$K[(C_4F_9)_2B(OMe)_2]$[c,d]	119.3	111.2	114.8	127.0	^1J(C-1,B) = 66; ^1J(C-1,F-1) = 269; ^2J(C-1,F-2) = 41; ^1J(C-2,F-2) = 264; ^2J(C-2,F-1) = 36; ^2J(C-2,F-3) = 37; ^1J(C-3,F-3) = 268; ^2J(C-3,F-2) = 38; ^2J(C-3,F-4) = 37
$K[(C_4F_9)_2B(OMe)F]$[c,d]	118.4	110.1	114.1	123.9	^1J(C-1,B) = 67; ^1J(C-3,F-3) = 267; ^2J(C-3,F-4) = 38
$K[(C_4F_9)_2B(OH)F]$[e]	118.4	110.0	114.3	124.4	^1J(C-1,B) = 71; ^1J(C-3,F-3) = 266; ^2J(C-3,F-4) = 37
$K[(C_4F_9)_2BF_2]$	119.1	110.7	114.0	122.6	^1J(C-1,B) = 76; ^1J(C-3,F-3) = 266; ^2J(C-3,F-4) = 38
$K[(C_6F_{13})_2B(OMe)_2]$[c,d]	118.5	109.9	114.8, 113.4, 111.8	127.1	^1J(C-1,B) = 66
$K[(C_6F_{13})_2B(OMe)F]$[c,d]	118.5	109.9	114.7, 113.2, 111.8	124.6	
$K[(C_6F_{13})_2B(OH)F]$[e]	118.5	109.9	114.8, 113.1, 111.8	124.6	
$K[(C_6F_{13})_2BF_2]$	118.4	109.8	114.4, 112.8, 111.7	122.8	^1J(C-1,B) = 70

[a] In all cases, $^1J(CF_3)$ = 287−289 Hz and $^2J(CF_3,CF_2)$ = 33−35 Hz. [b] In D_2O.[14] [c] $\delta(^{13}C)$ 49.0−50.1 (OCH_3) ppm; q, $^1J_{CH}$ = 138−140 Hz. [d] $\delta(^1H)$ 3.23−3.26 ppm. [e] ^{1}H NMR spectrum was not measured.

$[C_3F_7B(OMe)_3]^-$. ^{19}F NMR (ether−THF): δ −80.5 (t $^4J_{FF}$ = 11 Hz, 3F, F^3), −125.5 (s, 2F, F^2), −128.4 (bs, 2F, F^1) ppm. ^{11}B NMR (ether−THF): δ −0.1 (s) ppm.

$[(C_3F_7)_2B(OMe)_2]^-$. ^{19}F NMR (ether−THF): δ −80.1 (t $^4J_{FF}$ = 9 Hz, 3F, F^3), −122.4 (bs, 2F, F^1), −124.3 (bs, 2F, F^2). ^{11}B NMR (ether−THF): δ −2.1 (s) ppm.

Reaction of C_4F_9MgBr with $BCl(OMe)_2$ in Ether−THF (1/1 v/v). A white suspension of C_4F_9MgBr was prepared from C_4F_9I (2.99 g, 8.64 mmol) and MeMgBr (3.0 M in ether, 2 mL, 6 mmol) in ether (30 mL) and THF (30 mL) at −78 °C within 1 h. A solution of $BCl(OMe)_2$ (325 mg, 3 mmol) in pentane (1 mL) was added by syringe. The mixture was stirred at −78 °C for 1 h and gradually warmed to 20 °C within 2 h. The solvents were evaporated under reduced pressure. The residue was mixed with $K[HF_2]$ (3 g), water (20 mL), and charcoal (0.5 g) and stirred at 20 °C for 1 h. After filtration the filtrate was treated with K_2CO_3 (adjustment of the pH to 8−9), saturated with KF, and extracted with acetonitrile (5 × 10 mL). The combined extracts were evaporated to dryness under reduced pressure. The residue was dissolved in 73% HF (10 mL). After 1 h, the solution was treated with charcoal, neutralized, saturated with KF, and extracted with CH_3CN (5 × 10 mL), as mentioned above. The ^{19}F and ^{11}B NMR spectra of the extract showed the formation of $K[C_4F_9BF_3]$ (0.32 mmol, 11%) and $K[(C_4F_9)_2B(OH)F]$ (0.63 mmol, 21%).

Preparation of $K[(C_3F_7)_2B(OMe)_2]$ (2a). A three-necked round-bottomed flask was equipped with a low-temperature thermometer, a magnetic stir bar, a gas inlet tubing, and a reflux condenser (−78 °C) topped with a bubbler. The device was flushed with dry argon and charged with ether (120 mL). After cooling below −80 °C, C_3F_7H (7.82 g, 46.0 mmol) was condensed. The inlet tubing was replaced by a septum. The solution was cooled below −110 °C before a solution of *t*-BuLi in pentane (24 mL, 40.8 mmol) was added by syringe within ca. 30 min (an increase of temperature above −110 °C must be avoided). The resulting fine white suspension was stirred at −120 to −110 °C for 40 min before $BCl(OMe)_2$ (2.17 g, 20 mmol) was added by syringe in one portion. The mixture was stirred at −110 to −90 °C for 3 h, warmed to −78 °C within 1 h, and finally to 20 °C within 1 h. Subsequently

KF (6 g) and water (6 mL) were added into the flask and the mixture was stirred for an additional 0.5 h at 20 °C. The organic phase was separated, and the aqueous phase was extracted with ether (20 mL). The combined extracts were evaporated under reduced pressure to give the white salt **2a** (6.18 g, 69%).

$K[(C_3F_7)_2B(OMe)_2]$. Anal. Calcd for $C_8H_6BF_{14}KO_2$ (450.02): C, 21.35; H, 1.34. Found: C, 20.25; H, 1.10.

Preparation of $K[(C_3F_7)_2B(OH)F]$ (4a). $K[(C_3F_7)_2B(OMe)_2]$ (4 g, 8.9 mmol) was dissolved in 42% HF (50 mL), and the solution was stirred at 20 °C for 1 h. Charcoal (0.5 g) was added, and after additional stirring for 0.5 h the suspension was filtered. The charcoal was washed with water (10 mL), and the washing was combined with the filtrate. The aqueous solution was treated with K_2CO_3, the pH value adjusted to 8−9, and the solution extracted with ether (5 × 10 mL). The combined extracts were dried over anhydrous KF and evaporated to dryness. Borate **4a** (2.9 g, 77%) was contaminated with traces of $K[(C_3F_7)_2B(OMe)F]$ (**3a**) (^1H, ^{19}F NMR).

$K[(C_3F_7)_2B(OH)F]$. Anal. Calcd for $C_6HBF_{15}KO$ (423.96): C, 17.00; H, 0.24. Found: C, 17.60; H, 0.30.

Preparation of $K[(C_3F_7)_2BF_2]$ (5a). $K[(C_3F_7)_2B(OH)F]$ (2.50 g, 5.70 mmol) and aHF (8 mL) were stirred at 20 °C for 24 h. Excess aHF was removed under reduced pressure. The semisolid residue was dissolved in water (20 mL), and the solution was stirred with charcoal (0.5 g) for 0.5 h at 20 °C. The charcoal was filtered off and washed with water (10 mL), and the washing was combined with the filtrate. The solution was treated with K_2CO_3 to adjust the pH value to 8−9. After extraction with ether (5 × 10 mL) the combined extracts were dried with KF and evaporated to dryness. An additional drying overnight in a vacuum desiccator over Sicapent gave **5a** (2.2 g, 91%).

Preparation of $[Me_4N][(C_3F_7)_2BF_2]$ (6a). An aqueous solution of tetramethylammonium hydroxide (1 mL, 2.7 mmol) was added to a solution of $K[(C_3F_7)_2BF_2]$ (100 mg, 0.23 mmol) in water (0.5 mL) with stirring. The white precipitate was filtered off, washed with water (5 mL), and dried over Sicapent in a vacuum desiccator overnight to yield **6a** (95 mg, 91%).

$[Me_4N][(C_3F_7)_2BF_2]$. Anal. Calcd for $C_{10}H_{12}BF_{16}N$ (461.00): C, 26.05; H, 2.62; N, 3.04. Found: C, 25.55; H, 2.76; N, 3.05.

Preparation of $K[(C_4F_9)_2B(OMe)_2]$ (2b). (Nonafluorobutyl)-lithium was prepared from C_4F_9H (3.75 g, 17 mmol) and *t*-BuLi (9 mL, 15.3 mmol) in ether (60 mL) at −120 to −110 °C (see preparation of **2a**) and treated with a solution of $BCl(OMe)_2$ (758 mg, 7 mmol) in hexane (2 mL). The mixture was stirred at −110 to −90 °C for 2 h and warmed stepwise from −90 to −78 °C (1 h) and finally to 20 °C (1 h). The addition of KF (3 g) and water (5 mL) to the solution caused a white suspension. After stirring for 1 h the solid dissolved. The organic phase was decanted, and the aqueous phase was extracted with ether (3 × 10 mL). The combined ethereal extracts were evaporated under reduced pressure. After drying overnight in a vacuum desiccator over Sicapent, the white salt **2b** (2.92 g, 76%), was obtained. The purity of the product was satisfactory for further reactions. An analytically pure sample was prepared by additional washing of **2b** (100 mg) with pentane (5 × 10 mL) and drying at 2.6 hPa for 4 h.

$K[(C_4F_9)_2B(OMe)_2]$. Anal. Calcd for $C_{10}H_6BF_{18}KO_2$ (550.04): C, 21.84; H, 1.10. Found: C, 21.68; H, 1.03.

Preparation of $K[(C_4F_9)_2B(OMe)F]$ (3b) and $K[(C_4F_9)_2B(OH)F]$ (4b). A solution of $K[(C_4F_9)_2B(OMe)_2]$ (2.04 g, 3.71 mmol) in 73% HF (10 mL) was stirred at 20 °C for 1 h. After addition of charcoal (0.5 g) the mixture was stirred for an additional 0.5 h. The slurry was filtered, and the solid was washed with 20 mL of water. The colorless filtrate was treated with K_2CO_3, adjusted to pH 8−9, and extracted with ether (5 × 10 mL). The combined extracts were dried with K_2CO_3 and evaporated under reduced pressure. The product was dried over Sicapent in a vacuum desiccator overnight to give a white solid mixture (1.56 g) of $K[(C_4F_9)_2B(OH)F]$ and $K[(C_4F_9)_2B(OMe)F]$ (2/1) (^{19}F NMR).

$K[(C_4F_9)_2B(OH)F]$ ($C_8HBF_{19}KO$ (523.97)) and $K[(C_4F_9)_2B(OMe)F]$ ($C_9H_3BF_{19}KO$ (538.00)) (Molar Ratio 2/1). Anal. Calcd for the 2:1 mixture: C, 18.93; H, 0.32. Found: C,18.88; H, 0.30.

Preparation of $K[(C_4F_9)_2BF_2]$ (5b). A mixture of $K[(C_4F_9)_2B(OH)F]$ and $K[(C_4F_9)_2B(OMe)F]$ (2:1) (1.05 g, 1.99 mmol) was dissolved in aHF (5 mL) at 0 °C and stirred at 20 °C for 24 h. After removal of aHF under reduced pressure a semisolid resulted, which was dissolved in water (20 mL). Charcoal (0.5 g) was added, and the suspension was stirred at 20 °C for 0.5 h. The charcoal was filtered off and washed with water (10 mL). The combined aqueous solutions were treated with K_2CO_3 till pH 8−9 was reached. After extraction with ether (5 × 10 mL) the combined extracts were dried over K_2CO_3 before ether was removed on an evaporator. The product was dried over Sicapent in a vacuum desiccator overnight to give **5b** (720 mg, 69%).

Preparation of $[NMe_4][(C_4F_9)_2BF_2]$ (6b). Aqueous tetramethylammonium hydroxide (1 mL, 2.7 mmol) was added to the stirred solution of $K[(C_4F_9)_2BF_2]$ (100 mg, 0.19 mmol) in water (0.5 mL). The resulting white precipitate was filtered off, washed with water (5 mL), and dried over Sicapent in a vacuum desiccator overnight to yield **6b** (88 mg, 83%).

$[Me_4N][(C_4F_9)_2BF_2]$. Anal. Calcd for $C_{12}H_{12}BF_{20}N$ (561.01): C, 25.69; H, 2.16; N, 2.50. Found: C, 25.78; H, 2.12; N, 2.44.

Preparation of $K[(C_6F_{13})_2B(OMe)_2]$ (2c). (Perfluorohexyl)-lithium was prepared from $C_6F_{13}H$ (6.40 g, 20 mmol) and *t*-BuLi (10 mL, 17 mmol) in ether (60 mL) below −110 °C (see preparation of **2a**). A solution of $BCl(OMe)_2$ (867 mg, 8 mmol) in hexane (2 mL) was added by syringe, and the mixture was stirred at −110 to −90 °C for 2 h. The reaction mixture was warmed from −90 to −78 °C within 1 h and finally to 20 °C within 1 h. KF (3 g) and water (5 mL) were added to the solution. After the mixture was stirred for 1 h, the upper organic phase was decanted and the residue was extracted with ether (3 × 10 mL). The combined extracts were evaporated to give a white solid, which was dried over Sicapent in a vacuum desiccator overnight to yield **2c** (7.6 g, 60%). An analytically pure product was prepared by an additional washing of **2c** (100 mg) with pentane (5 × 10 mL) and drying under vacuum (2.6 hPa) for 4 h.

$K[(C_6F_{13})_2B(OMe)_2]$. Anal. Calcd for $C_{14}H_6BF_{26}KO_2$ (750.07): C, 22.42; H, 0.81. Found: C, 22.35; H, 0.80.

Preparation of $K[(C_6F_{13})_2B(OMe)F]$ (3c) and $K[(C_6F_{13})_2B(OH)F]$ (4c). A solution of $K[(C_6F_{13})_2B(OMe)_2]$ (2.25 g, 3 mmol) in a mixture of 73% HF (15 mL) and MeOH (5 mL) was stirred at 20 °C for 1 h, treated with charcoal (0.5 g), and stirred for an additional 0.5 h. The slurry was filtered, and the cake was washed with 20 mL of water. The colorless filtrate was treated with K_2CO_3 to adjust to a pH value of 8−9. After extraction with ether (5 × 10 mL) the combined extracts were dried with K_2CO_3 and evaporated under reduced pressure. The residue was dried over Sicapent in a vacuum desiccator overnight to yield the white solid mixture of $K[(C_6F_{13})_2B(OH)F]$ and $K[(C_6F_{13})_2B(OMe)F]$ (5/4) (1.82 g) (^{19}F NMR).

$K[(C_6F_{13})_2B(OH)F]$ ($C_{12}HBF_{27}KO$) (724.00) and $K[(C_6F_{13})_2B(OMe)F]$ ($C_{13}H_3BF_{27}KO$) (738.03) (Molar Ratio 5/4). Anal. Calcd for the 5/4 mixture: C, 20.47; H, 0.26. Found: C, 20.67; H, 0.26.

Preparation of $K[(C_6F_{13})_2BF_2]$ (5c). A solution of $K[(C_6F_{13})_2B(OH)F]$ and $K[(C_6F_{13})_2B(OMe)F]$ (5/4) (1.36 g, 2 mmol) in aHF (5 mL) was kept at 20 °C for 2 days before being poured onto ice (50 g). The resulting aqueous solution was neutralized with K_2CO_3. The precipitate was filtered off, washed with water (2 × 10 mL), and dried in the air. After an additional washing with hexane (3 × 10 mL) and drying in a vacuum desiccator over Sicapent, salt **5c** (1.09 g, 75%) was obtained.

Preparation of [NMe$_4$][(C$_6$F$_{13}$)$_2$BF$_2$] (6c). Aqueous tetramethylammonium hydroxide (1 mL, 2.7 mmol) was added to a stirred solution of K[(C$_6$F$_{13}$)$_2$BF$_2$] (100 mg, 0.14 mmol) in methanol (1 mL). After 24 h the white precipitate was filtered off, washed with 5 mL of water, and dried over Sicapent in a vacuum desiccator overnight to yield **6c** (100 mg, 94%).

[NMe$_4$][(C$_6$F$_{13}$)$_2$BF$_2$]. Anal. Calcd for $C_{16}H_{12}BF_{28}N$ (761.04): C, 25.25; H, 1.89; N, 1.84. Found: C, 24.73; H, 1.47; N, 1.66.

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

Supporting Information Available: Figures S1−S18, giving ^{11}B and ^{19}F NMR spectra of K[(C$_n$F$_{2n+1}$)$_2$B(OMe)$_2$], K[(C$_n$F$_{2n+1}$)$_2$B(OR)F] (R = H, CH$_3$), and K[(C$_n$F$_{2n+1}$)$_2$BF$_2$] (n = 3, 4, 6). This material is available free of charge via the Internet at http://pubs.acs.org.

OM070090H