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Perfluoroalkyl borates and boronic esters: new promising partners for Suzuki and Petasis reactions

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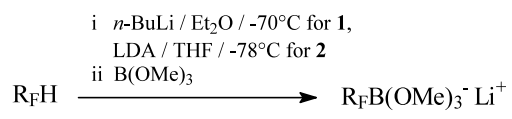
Abstract—Lithium and potassium trifluoromethyl-, pentafluoroethyl- and [(diethylphosphinyl)difluoromethyl]trialkoxyborates were synthesized by reaction of either perfluoroalkyllithium or (perfluoroalkyl)trimethylsilane/F^- with trialkoxyboranes. Treatment of perfluoroalkyltrialkoxyborates with methanesulfonyl chloride, methyl triflate or methyl tosylate furnished the hitherto unknown trifluoromethyl-, pentafluoroethyl- and [(diethylphosphinyl)difluoromethyl]boronic esters.

The Petasis (boronic acid Mannich) reaction of aryl- and vinylboronic acids with aldehydes and amines has recently become a very powerful tool for the one-pot synthesis of non-natural α-amino acids, β-amino alcohols and peptide mimetics.[1] There are also very useful examples of boronic esters as the boron component in this reaction.[2,3] For example, the first case of chiral induction in the reaction of glyoxylic acid, morpholine and a homochiral boronic ester as the chiral auxiliary has been reported.[3] Introduction of fluorine and perfluoroalkyl, especially trifluoromethyl, groups into organic molecules sometimes enhances or significantly changes their biological activities.[4] There are many examples demonstrating the unique biological properties of fluorinated α-amino acids.[5] Although many routes have been developed, there is still a need for concise and practical one-pot stereoselective syntheses of fluorinated amino acids. Prakash has recently reported a stereoselective synthesis of *anti*-α-(difluoromethyl)-β-amino alcohols by the boronic acid based three-component condensation and the stereoselective preparation of (2*S*,3*R*)-difluorothreonine.[6] To the best of our knowledge, the perfluoroalkyl boronic acids, $R_FB(OH)_2$, and their esters, $R_FB(OAlk)_2$, are unknown.

Boronic acids and esters, their perfluoroalkyl boronate precursors, $R_FB(OAlk)_3^-$ Q^+ and hence the easily synthesized perfluoroalkyltrifluoroborates, $R_FBF_3^-$ Q^+, could also be of interest as new reactive partners for Suzuki[7] cross-coupling reactions and for perfluoroalkylation of different types of organic compounds. Therefore, we reasoned that the development of simple synthetic routes to compounds of this type would hold potential for drug design and for material science.

In the course of our study of R_F-substituted lithium fluoroborates as electrolyte salts for lithium batteries



Scheme 1.

Keywords: perfluoroalkyl boronic acids and esters; perfluoroalkyl trialkoxyborates; perfluoroalkyllithium; (perfluoroalkyl)trimethylsilane.

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and double-layer capacitors, a range of salts $(R_F)_nBF_{3-n}^-$ Li^+ ($R_F = CF_3$, C_2F_5; $n = 1, 2$) were synthesized via the cation exchange reaction in the respective $(R_F)_nBF_{3-n}^-$ K^+ salts.[8] In continuation of this study and our ongoing systematic investigation[9] of anionic perfluoroalkylation of organic and organoelement derivatives, we disclose herein a new convenient method for the synthesis of perfluoroalkyltrialkoxyborates and, furthermore, their transformation into the hitherto unknown perfluoroalkyl boronic esters. The perfluoroalkyltrialkoxyborates were prepared via an anionic perfluoroalkylation of trialkoxyboranes. The first route included an addition of the perfluoroalkyllithiums generated from C_2F_5H (**1**) and $(EtO)_2P(O)CF_2H$ (**2**) to $B(OR)_3$. Thus, treating C_2F_5Li (**3**) with $(MeO)_3B$ in ether at −70°C for 1 h followed by warming to ambient temperature led, after a simple work-up, to the lithium (pentafluoroethyl)trimethoxyborate, $C_2F_5B(OMe)_3^-$ Li^+ (**4**)[10] as a colorless solid in 95% isolated yield (Scheme 1, Table 1). The pentafluoroethyl lithium (**3**) was conveniently generated by deprotonation of **1** with *n*-BuLi at −70°C in accordance with new 'green' technological method of R_FLi generation developed jointly with the Bayer AG.[11] A similar protocol has been used for the synthesis of lithium [(diethylphosphinyl)difluoromethyl]trimethoxyborate (**6**) (Scheme 1, Table 1) from [(diethylphosphinyl)difluoromethyl]-lithium (**5**), preformed from **2** either with LDA[4c] at −78°C or with *t*-BuLi at −85°C, and trimethoxyborane in THF or ether, respectively (Scheme 1, Table 1).

An alternative method elaborated by us for the addition of 'R_F^-' to $B(OR)_3$ (R = Me, Et, *i*-Pr, *t*-Bu, Ph) used fluorinated silanes[12] and includes some of the most useful to date anionic perfluoroalkylating reagents, CF_3SiMe_3 (**7**), $C_2F_5SiMe_3$ (**8**), $(EtO)_2P(O)CF_2SiMe_3$ (**9**) with KF or Me_4NF. When this manuscript was under preparation, an ASAP communication on an improved synthesis of $CF_3BF_3^-$ K^+ via treatment of trimethoxyborate with (trifluoromethyl)trimethylsilane/KF followed by the fluorination of the $CF_3B(OMe)_3^-$ K^+ formed was published,[13] but with no characterization data for potassium (trifluoromethyl)trimethoxyborate. Similarly, Frohn and Bardin have pregenerated C_3F_7MgBr and $C_6F_{13}MgBr$ and reacted these species with $B(OMe)_3$ to afford ethereal solutions of the respective perfluoroalkyl-trialkoxyborate salts.[14,15] These authors also considered these salts as precursors for (perfluoroalkyl)-fluoroborates.[15] We have found that **7** and **8** based boron perfluoroalkylation is a convenient route to trifluoromethyl- and pentafluoroethyltrialkoxyborate salts derived from trialkoxyboranes containing primary alkyl groups. Reactions 1.05 equiv. of silanes **7** and **8** with 1 equiv. of KF and 1 equiv. of trimethoxy- and triethoxyboranes proceeded in monoglyme or THF at ambient temperature for 24–36 h (for Me_4NF: 0°C for 0.5 h, then 20°C for 3 h) to afford the tetramethylammonium (trifluoromethyl)trimethoxy- (**10**), potassium (trifluoromethyl)trimethoxy- (**11**), (trifluoromethyl)triethoxy- (**12**), (pentafluoroethyl)trimethoxy- (**13**) and (pentafluoroethyl)triethoxy- (**14**) borates. Gentle heating (40–50°C) accelerated these reactions. After the fluoride salts had been dissolved, the solvent and trimethylfluorosilane were removed in vacuo and the residual solid (for reactions in THF) or an oil (monoglyme) were washed with pentane and dried in vacuo to give the salts (**10**–**14**) with yields given in Scheme 2 and

$$B(OR)_3 + R_FSiMe_3 \xrightarrow[Q^+F^-]{\text{THF or monoglyme}} R_FB(OR)_3^- Q^+$$

10 - 15

R = Me, Et
R_F = CF_3, C_2F_5, $(EtO)_2P(O)CF_2$
Q^+ = K^+, Me_4N^+

Scheme 2.

Table 1.

Entry	$B(OR)_3$	R_F	Product $R_FB(OR)_3^-$ Q^+	Yield[a] (%)
1	$B(OMe)_3$	**3**	$C_2F_5B(OMe)_3^-Li^+$ **4**	95
2	$B(OMe)_3$	**5**	$(EtO)_2P(O)CF_2B(OMe)_3^-Li^+$ **6**	98
3	$B(OMe)_3$	**7**/Me_4NF[b]	$CF_3B(OMe)_3^-Me_4N^+$ **10**	98
4	$B(OMe)_3$	**7**/KF[c]	$CF_3B(OMe)_3^-K^+$ **11**	98
5	$B(OEt)_3$	**7**/KF[c]	$CF_3B(OEt)_3^-K^+$ **12**	95
6	$B(OMe)_3$	**8**/KF[d]	$C_2F_5B(OMe)_3^-K^+$ **13**	98
7	$B(OEt)_3$	**8**/KF[d]	$C_2F_5B(OEt)_3^-K^+$ **14**	96
8	$B(OPr\text{-}i)_3$	**7**/KF[e]	–	–
9	$B(OPr\text{-}i)_3$	**8**/KF[e]	–	–
10	$B(OBu\text{-}t)_3$	**7**/KF[e]	–	–
11	$B(OPh)_3$	**8**/KF[e]	–	–
12	$B(OMe)_3$	**9**/Me_4NF[f]	$(EtO)_2P(O)CF_2B(OMe)_3^-Me_4N^+$ **15**	40

[a] All yields refer to pure, isolated salts. All compounds have been characterized by elemental analysis (C, H, F) and NMR data.
[b] Reaction conditions for entry 3: 0°C for 0.5 h, then 20°C for 3 h.
[c] Reaction conditions for entries 4, 5: THF (or monoglyme), 20°C, 24–36 h.
[d] Conditions for 6, 7: THF (or monoglyme), 20°C, 4 h, then 50°C for 4 h.
[e] Reaction conditions for entries 8–11: THF (or monoglyme), 20°C, 36 h, then reflux for 12 h.
[f] For entry 12: monoglyme, −30°C, 5 h, then 20°C for 1 h.

Table 1.† Surprisingly, the only new fluorinated products from the $B(OPr\text{-}i)_3$ and $B(OBu\text{-}t)_3$ reactions with **7**/KF and **8**/KF were fluoroform and pentafluoroethane, respectively. Our attempts to prepare the borates via triphenoxyborane reaction with CF_3SiMe_3/KF and $C_2F_5SiMe_3$/KF also failed. In both cases no reaction was observed. The reaction of **9** with trimethoxyborane was more complex compared to the reactions of **7** or **8** with the $(MeO)_3B/F^-$ system.

The isolated yield of Me_4N^+ $(EtO)_2P(O)CF_2B(OMe)_3^-$ (**15**) was only 40% (Scheme 2, Table 2).

After revealing the scope and limitations of the B-perfluoroalkylation procedures, the perfluoroalkyltrialkoxyborates **6**, **11** and **14** were dealkoxylated to produce the hitherto unknown [(diethylphosphinyl)-difluoromethyl] (**16**), trifluoromethyl (**17**)[16] and pentafluoroethyl (**18**) boronic esters. The dealkoxylation was performed by treating of **6**, **11** and **14** with methyl triflate, methyl tosylate, methanesulfonyl chloride and trimethylchlorosilane in petrol ether, monoglyme, xylene or neat (Scheme 3, Table 2).†

$$R_FB(OAlk)_3^-Q^+ \quad (\mathbf{6, 11, 14}) \quad + \quad E \longrightarrow R_FB(OAlk)_2 \quad (\mathbf{16\text{-}18})$$

Q = Li, K
R_F = $(EtO)_2P(O)CF_2$ (**6**), CF_3 (**11**), C_2F_5 (**14**)
E = CF_3SO_2OMe, $MeSO_2Cl$, Me_3SiCl, 4-$MeC_6H_4SO_2OMe$
Alk = Me, Et

Scheme 3.

The solutions of **16**–**18** in monoglyme were conveniently generated by addition of 1 equiv. of methyl triflate to the respective borates solution in monoglyme and stirring the mixture for 4–6 h at ambient temperature (Table 2). To separate potassium trifluoromethanesulfonate, the solvent and the boronic esters **17** and **18** were distilled off in vacuo (0.05 Torr) resulting in easy to handle colorless monoglyme solutions of these compounds. There is only one precedent for conversion of an organyl borate into a boronic ester via an alkylation sequence. In DMF at 70°C alkylation of sodium *cis*,*cis*-phenyl(cyclohexane-1,3,5-trihydroxy)borate with

Table 2.

Entry	$R_FB(OR)_3^-$ Q^+	Electrophile E	Solvent	Borane $R_FB(OR)_2$	Yield (%)
1	$(EtO)_2PO)CF_2B(OMe)_3^-$ Li^+ **6**	CF_3SO_2OMe	Monoglyme	$(EtO)_2P(O)CF_2B(OMe)_2$ **16**	93[a]
2	$CF_3B(OMe)_3^-$ K^+ **11**	CF_3SO_2OMe	Monoglyme	$CF_3B(OMe)_2$ **17**	89[b]
3	$CF_3B(OMe)_3^-$ K^+ **11**	$MeSO_2Cl$	Xylene	$CF_3B(OMe)_2$ **17**	95[a]
4	$CF_3B(OMe)_3^-$ K^+ **11**	$MeSO_2Cl$	Pentane	$CF_3B(OMe)_2$ **17**	50[b]
5	$CF_3B(OMe)_3^-$ K^+ **11**	$MeSO_2Cl$	Hexane	$CF_3B(OMe)_2$ **17**	60[b]
6	$CF_3B(OMe)_3^-$ K^+ **11**	$MeSO_2Cl$	Neat	$CF_3B(OMe)_2$ **17**	60[c]
7	$CF_3B(OMe)_3^-$ K^+ **11**	Me_3SiCl	Pentane	$CF_3B(OMe)_2$ **17**	90[b]
8	$CF_3B(OMe)_3^-$ K^+ **11**	$TolSO_2OMe$	Monoglyme	$CF_3B(OMe)_2$ **17**	85[b]
9	$C_2F_5B(OEt)_3$ K^+ **14**	CF_3SO_2OMe	Monoglyme	$C_2F_5B(OEt)_2$ **18**	92[b]

[a] NMR yields estimated with internal $PhCF_3$ in the reaction mixture.
[b] NMR yields estimated with internal $PhCF_3$ for the distillate $R_FB(OR)_2$/solvent.
[c] Isolated yield; **17** has been characterized by elemental analysis (C, H, F) and NMR data.

† Selected data for compounds (**4**, **10**, **11**, **14**, **16**, **18**).
4: Yield 98%, hydroscopic colorless solid, mp 136–138°C. ^1H NMR (200.13 MHz, THF-d_8): δ 1.29 (t, $^3J_{HH}=7.1$ Hz, 6H, CH_3), 3.23 (s, 9H, CH_3), 4.19 (m, 4H, CH_2). ^{19}F NMR (188.31 MHz, THF-d_8): δ −128.3 (br.d, $^2J_{PF}=107.0$ Hz, 2F, CF_2). ^{11}B NMR (64.21 MHz, THF-d_8): δ 0.6 (br.s, $\delta=57.1$ Hz). ^{31}P NMR (81.00 MHz, THF-d_8): δ 19.6 (br.t, $^2J_{PF}=106.7$ Hz). ^{13}C NMR (90.56 MHz, THF-d_8): δ 16.48 (d, $^3J_{CP}=5.0$ Hz, CH_3), 49.6 (s, OCH_3), 65.4 (d, $^2J_{CP}=7.4$ Hz, CH_2), 113.9 (m, CF_2). **10**: Yield 98%, hygroscopic colorless powder, mp 110–112°C (dec.). ^1H NMR (200.13 MHz, D_2O): δ 3.04 (s, 12H, H_3C-N), 3.21 (br.s, CH_3, 9H). ^{19}F NMR (188.31 MHz, D_2O): δ −76.0 (m, 3F, CF_3). ^{11}B NMR (64.21 MHz, D_2O): δ −1.1 (q, $^2J_{BF}=30.2$ Hz). ^{13}C NMR (50.33 MHz, D_2O): δ 49.1 (s, CH_3, OCH_3), 55.5 (s, CH_3, N-CH_3), CF_3 is not observed. **11**: Yield 98%, hydroscopic colorless powder, mp >360°C. ^1H NMR (200.13 MHz, D_2O): δ 3.21 (s, CH_3, 9H). ^{19}F NMR (188.31 MHz, D_2O): δ −75.9 (m, 3F, CF_3). ^{11}B NMR (64.21 MHz, D_2O): δ −0.9 (q, $^2J_{BF}=29.5$ Hz). ^{13}C NMR (90.56 MHz, $CDCl_3$): δ 49.6 (s, CH_3), CF_3 is not observed. **14**: $[C_2F_5B(OEt)_3^-$ $K^+]\cdot CH_3OCH_2CH_2OCH_3$: Yield 98%, mp 63–65°C. ^1H NMR (200.13 MHz, D_2O): δ 1.04 (t, $^3J_{HH}=7.1$ Hz, 9H, CH_3), 3.24 (s, 6H, CH_3), 3.47 (s, 4H, CH_2), 3.5 (q, $^3J_{HH}=7.1$ Hz, 6H, CH_3). ^{19}F NMR (188.31 MHz, D_2O): δ −83.4 (s, 3F, CF_3), −134.8 (m, 2F, CF_2). ^{11}B NMR (64.21 MHz, D_2O): δ −0.3 (t, $^2J_{BF}=18.9$ Hz). ^{13}C NMR (90.56 MHz, D_2O): δ 17.6, 58.1, 58.8, 71.6, 122.5 (qt, $^1J_{CF}=285.3$ Hz, $^2J_{CF}=31.6$ Hz, CF_3), CF_2 is not observed. **16**: Yield 93% (from ^{19}F NMR with internal $PhCF_3$). ^{19}F NMR (188.31 MHz, THF-d_8): two species, (A) and (B), in the ratio A:B = 2:1 were observed: (A), δ −129.8 (br.d, $^2J_{PF}=91.4$ Hz 2F, CF_2), (B), δ −131.7 (br.d, $^2J_{PF}=95.4$ Hz 2F, CF_2). ^{11}B NMR (64.21 MHz, monoglyme/$CDCl_3$): two species, (A) and (B), were found: (A), δ 17.8 (br.s, $\delta=40.2$ Hz), (B), δ 21.6 (br.s, $\delta=91.5$ Hz). ^{31}P NMR (81.00 MHz, monoglyme/$CDCl_3$): two species, (A) and (B), in the ratio A:B = 2:1 were observed: (A), δ 8.3 (br.t, $^2J_{PF}=91.2$ Hz), (B), δ 13.8 (br.t, $^2J_{PF}=95.7$ Hz). **18**: for $C_2F_5B(OEt)_2$/monoglyme distillate. ^{19}F NMR (188.31 MHz, monoglyme/$CDCl_3$): two species, (A) and (B), in the ratio A:B = 8:1 were observed: (A) δ −85.3 (s, 3F, CF_3), −131.0 (br.s, $\delta=53.9$ Hz, 2F, CF_2), (B) δ −85.3 (s, 3F, CF_3), −134.0 (br.s, $\delta=53.9$ Hz, 2F, CF_2). ^{11}B NMR (64.21 MHz, monoglyme/$CDCl_3$): two species, (A) and (B), were found, (A), δ 17.8 (bs, $\delta=40.2$ Hz), (B), 21.58 (bs, $\delta=91.5$ Hz). ^{13}C NMR (90.56 MHz, monoglyme/$CDCl_3$): δ: 17.7 (s, CH_3), 58.1 (s, OCH_2), 120.1 (m, CF_3), CF_2 is not observed.

bromoacetic acid diisobutylamide gave the corresponding borane in 50% yield.[17] To the best of our knowledge, the second route using the nucleophilic substitution on sulfur or silicon has not been reported previously. The simplest representative of perfluoroalkyl boronic esters, the trifluoromethyl boronic acid dimethyl ester **17**, obtained as a liquid in 60% yield (not optimized) from potassium (trifluoromethyl)trimethoxyborate and methanesulfonyl chloride fumed when exposed to air. This ester is stable until ca. 95°C, however it cannot be distilled under normal pressure without decomposition. It is known, that perfluoroalkyltrialkoxyborates are the best precursors for perfluoroalkyltrifluoroborate salts.[14] The fluorination of $C_2F_5B(OMe)_3^-$ Li^+, $C_2F_5B(OMe)_3^-$ K^+ and $CF_3B(OMe)_3^-$ K^+ with 48% $HF_{aq.}$ for 16 h at 20°C followed by quenching the reaction mixture with an excess of solid KF and extraction with hot acetonitrile furnished the pure perfluoroalkyltrifluoroborate salts, $C_2F_5BF_3^-$ Li^+, $C_2F_5BF_3^-$ K^+ and $CF_3BF_3^-$ K^+ in 85–91% yield.

In summary, we have developed a synthesis of new perfluoroalkyltrialkoxyborates and perfluoroalkyl boronic esters of potential interest as new reactants for perfluoroalkylation processes. Among the perfluoroalkyl boron compounds synthesized, the salt $C_2F_5B(OMe)_3^-$ Li^+, being a precursor for $C_2F_5B(OMe)_2$, $C_2F_5BF_3^-$ Li^+ and $C_2F_5BF_3^-$ K^+, merits special attention since its forerunner, pentafluoroethane, is a cheap modern refrigerant. Studies on the synthesis of perfluoroalkyl boronic acids and the derived 1,2-diol boronic esters as well as the application of the new perfluoroalkyl boron derivatives for perfluoroalkylation of different classes of organic compounds are in progress.

Acknowledgements

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10. *Lithium (pentafluoroethyl)trimethoxyborate* (**4**). To a stirred solution of C_2F_5Li in ether/hexane, pregenerated from 12 mmol of pentafluoroethane in ether (40 mL) with 4.5 g of a 1.6 M solution of *n*-BuLi (10 mmol) in hexane accordingly to the patent[11] at −70°C, was added 1.04 g (10 mmol) of the commercial trimethoxyborane. The reaction mixture was kept at the indicated temperature for 1 h and then allowed to warm to 25°C. The solvent was pumped off in vacuo (0.05 Torr) and the residue was washed with pentane (2×5 mL) to leave a colorless solid, which was dried in vacuo 0.05 Torr at 50°C for 7 h to give 2.19 g (95%) of **4**, purity 99.5%, mp >360°C. ^{1}H NMR (200.13 MHz, D_2O): δ 3.20 (s, 9H, CH_3). ^{19}F NMR (188.31 MHz, D_2O): δ −85.0 (s, 3F, CF_3), −134.8 (m, 2F, CF_2). ^{11}B NMR (64.21 MHz, D_2O): δ −0.3 (t, J_{BF} = 18.8 Hz). ^{13}C NMR (90.56 MHz, D_2O): 49.6 (s, CH_3), C_2F_5 is not observed.
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16. *(Trifluoromethyl)dimethoxyborane* (**17**). A mixture of 3.5 g (16.51 mmol) of potassium trifluoromethyltrimethoxyborate (**11**) and 15 mL of methanesulfonyl chloride was stirred at ambient temperature under nitrogen for 12 h. The crude (**17**) was separated by distillation (water bath, ca. 50°C) in vacuo (20 Torr) in a cooled with a liquid nitrogen trap. The liquid obtained was distilled to give

1.41 g of **17** as a colorless liquid, fuming when exposed to air. Bp 35–36°C (165 Torr). The samples for the NMR investigations and elemental analysis were prepared in a dry box under nitrogen. ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.71 (s, 6H, CH_3). ^{19}F NMR (188.31 MHz, $CDCl_3$): δ −69.7 (m, 3F, CF_3). ^{11}B NMR (64.21 MHz, $CDCl_3$): δ 21.6 (q, $^{2}J_{BF} = 36.3$ Hz). ^{13}C NMR (90.56 MHz, $CDCl_3$): δ 52.7 (s, CH_3), 124.6 (m, CF_3).

17. Reany, O.; Blair, S.; Kataky, R.; Parker, D. *J. Chem. Soc., Perkin Trans. 2* **2000**, 623–630.