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New Approach to the Synthesis of Tris(perfluoroalkyl)borane Adducts with Dialkylamines

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Abstract—A convenient synthetic approach to the adducts $(C_nF_{2n+1})_3BNHR_2$ (n = 2–4, 6; R = Me, Et) was developed, based on the reaction of lithium perfluoroalkyls with dichloro(dialkylamino)boranes at temperatures below –90°C. The target products can be synthesized with preparative yields of 50–90%.

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Perfluorinated organic derivatives of tri- and tetracoordinated boron are used in organoelemental and organic synthesis and as activators in the metallocene catalysts and postmetallocene catalyst of the olefins polymerization [1–5]. Many of the negatively charged polyfluorinated ions are weakly coordinating anions [6]. Several adducts of tris(perfluoroalkyl)-boranes with some nitrogen-containing compounds are known, which also are effective activators of the metallocene catalysts [7].

The tris(fluoroalkyl)boranes, which are much stronger Lewis acids, have not been obtained in free state, but the complexes $(C_nF_{2n+1})_3BNR_1R_2R_3$ (n = 1, 2) with some amines [8–13] have been described. There is no data on the complexes with long perfluoroalkyl groups ($n \geq 3$), due to the lack of a suitable method for preparation of such compounds. To date are known trifluoromethyl and pentafluoroethyl derivatives synthesized by nucleophilic perfluoroalkylation of the boranes Br_2BNAlk_2 with the Ruppert reagent $[C_nF_{2n+1}Hlg + P(NAlk_2)_3]$ (Hlg = Br, I; Alk = Me, Et) [14, 15] or the Pawelke reagent $[C_nF_{2n+1}I + (Me_2N)_2C{=}C(NMe_2)_2]$ [16]. This method is convenient for tris(trifluoromethyl) derivatives, but with the elongation of perfluorocarbon chain the yield of target products falls down sharply, and even in the case of $(C_2F_5)_3BNHAlk_2$ not exceeds 12% [12]. When Br_2BNAlk_2 is replaced with the borane $(CF_3)_2BNAlk_2$, the complexes $(C_nF_{2n+1})(CF_3)_2BNHAlk_2$ (n = 2, 4) could be synthesized [12], but the original bis(trifluoromethyl)dialkylaminoboranes themselves are the products of multistep synthesis and therefore not readily available. The main drawback of both methods is time-consuming purification of target products from the organic side products.

Previously we developed a method of perfluoroalkylation of trimetoxyborane and chlorodimetoxyborane with lithium perfluoroalkyl derivatives, and obtained a number of salts of general formula $M[C_nF_{2n+1}B(OMe)_3]$ and $M[(C_nF_{2n+1})_2B(OMe)_2]$, respectively, with yield above 90 % [17–20]. In this study, we investigated a possibility of using this method for the synthesis of complexes of tris(perfluoroalkyl) boranes with dialkylamines by perfluoroalkylation of available dichloro(dialkylamino) boranes.

Synthesis of aminoboranes. A reaction of boranes BX_nY_{3-n} with R^- nucleophiles is known to lead to the derivatives of tetracoordinated boron anions $[RBX_nY_{3-n}]^-$, and with the bases (Base) are formed neutral complexes $X_nY_{3-n}B{\cdot}Base$, whose fate is determined by the nature of the ligands R, X, and Y. Usually, the M $[RBX_nY_{3-n}]$ salts with organic ligands (R = X = Y) or

with one or more organic ligands R and strong electron-withdrawing ligands X, Y = F, OR' are stable under normal conditions, and the degree of dissociation to the borane RBX_nY_{2-n} and anion Y^- is low [21]. The situation is different in the case of the anions $[RBHlg_2NAlk_2]^-$ (Hlg = Cl, Br) obtained by the action of an organic nucleophile R^- on the borane $BHlg_2NAlk_2$. Since the chloride or bromide anion is a good leaving group, the solution contains the borane $RBHlgNAlk_2$ in a substantial equilibrium concentration. The presence of the dialkylamino group reduces the Lewis acidity of the borane due to the donor–acceptor interaction between the nitrogen lone electron pair and the boron vacant *p*-orbital. This impedes the complexation of the borane with the ether solvent, and the borane remains available for adding the second equivalent of nucleophile R^-.

The choice of the perfluoroalkyl nucleophile source is the key factor. Since the magnesium perfluoroalkyl derivatives were ineffective even toward chlorometoxyboranes [20], we used the corresponding lithium compounds as the nucleophiles. In contrast to the lithium alkyl derivatives, the nucleophilicity of their perfluorinated analogs is much lower due to the electronic effect of the fluorine atoms. In addition, they are thermally instable in ether or ether–pentane (hexane), and are limitedly soluble, the solubility decreases sharply with increasing the carbon chain length. Thus, there is no reliable information in the literature about trifluoromethyllithium, and it is known that pentafluoroethyllithium is stable in an ether–hexane mixture to a temperature of ~ –70°C [22], while the higher homologues $C_nF_{2n+1}Li$ decompose at the same or lower temperature [23]. Perfluoroalkylating ability of the reagents $C_nF_{2n+1}Li$ ($n > 2$) is largely determined by the method of their generation. For example, perfluoroalkyliodides $C_nF_{2n+1}I$ ($n > 2$) react with butyllithium to give a poorly reactive complex $Li[(C_nF_{2n+1})_2I]$ [24]. To overcome the problems associated with the formation of such a complex at the perfluoroalkylation of carbonyl compounds, the nucleophilic reagents typically are generated by the action of BuLi or PhLi on $C_nF_{2n+1}I$ in the presence of the substrate [24]. However, this approach is unacceptable in the case of the boron-containing substrates since the latter interact with butyl- or methyllithium [18].

$$C_nF_{2n+1}X + AlkLi \xrightarrow[\text{or ether–pentane}]{\text{Ether}} C_nF_{2n+1}Li + AlkX,$$

$n = 2$; X = I; Alk = Me; from –95 to –90°C; $n = 3, 4, 6$; X = H; Alk = *t*-Bu, from –105 to –100°C.

During the research on the preparation of the perfluoroalkyl trimethoxyborates and bis(perfluoroalkyl) dimetoxyborates, we determined the optimal conditions for the generation of the nucleophiles $C_nF_{2n+1}Li$ [18, 20, 25, 26] used in this study. So, perfluoroethyllithium is formed at the action of methyllithium on the perfluoroethyl iodide, and the homologues $C_nF_{2n+1}Li$ are generated from 1*H*-perfluoroalkanes and *tert*-butyllithium.

When a suspension of perfluorohexyllitium was treated with dichloro(dimethylamino)borane dimer at a temperature below –100°C and the reaction mixture was slowly heated to 24°C, we found only the products of $C_6F_{13}Li$ decomposition and the parent $(Cl_2BNMe_2)_2$ (^{11}B, ^{19}F NMR). This happened because of the low electrophilicity of the dimer [27] and therefore in the further experiments we used 20% solution of dichloro(dimethylamino)borane in benzene. Thus we succeeded to synthesize complexes $(C_nF_{2n+1})_3BNHMe_2$ (**I**, $n = 4$; **II**, $n = 6$) in a good yield.

$$3\ C_nF_{2n+1}Li + Cl_2BNMe_2$$

(1) Ether–pentane from –105 to –100°C; (2) 5% HCl

$$(C_nF_{2n+1})_3BNHMe_2 + 3\ LiCl,$$

$n = 4$ (**I**, 50%); $n = 6$ (**II**, 59%).

Interaction of Cl_2BNEt_2 with pentafluoroethyllithium or heptafluoropropyllithium excess followed by hydrolysis gave the related complexes of tris(perfluoroalkyl)boranes with diethylamine, **III** and **IV**, respectively.

$$3\ C_nF_{2n+1}Li + Cl_2BNEt_2$$

(1) Ether–pentane from –105 to –100°C; (2) 5% HCl

$$(C_nF_{2n+1})_3BNHEt_2 + 3\ LiCl,$$

$n = 2$ (**III**, 90%); $n = 3$ (**IV**, 75%).

The results of the interaction of three equivalents of perfluorobutillithium and perfluorohexyllithium with one equivalent of Cl_2BNEt_2 were unexpected. In the

first case after hydrolysis of the reaction mixture with dilute HCl we detected the adduct $(C_4F_9)_2ClBNHEt_2$ (**V**), which was isolated as a yellow oil in a preparative yield 92–95% and was identified by comparing its ^{11}B and ^{19}F NMR spectra with those of the known compound $(CF_3)_2ClBNHEt_2$ [28].

$$3\ C_4F_9Li + Cl_2BNEt_2$$

(1) Ether–pentane, from –105 to –100°C; (2) 5% HCl

$$(C_4F_9)_2ClBNHEt_2,$$

V (92–95%)

Obviously, the adduct **V** is formed at adding HCl to the intermediate borane $(C_4F_9)_2BNEt_2$, which does not react with the third equivalent of C_4F_9Li. This is confirmed by the analysis of the ^{11}B NMR spectrum of the reaction mixture obtained by the action of $C_6F_{13}Li$ (3 eq.) on Cl_2BNEt_2. The spectrum contains a signal of the borane $(C_6F_{13})_2BNEt_2$ **VI** at 33.3 ppm, whose position is close to that in the spectra of related compounds $(CF_3)_2BNR_2$ (R = Me, Et, and *i*-Pr) [28, 29].

$$3\ C_6F_{13}Li + Cl_2BNEt_2$$

(1) Ether–pentane, from –105 to –100°C; (2) 5% HCl

$$(C_6F_{13})_2BNEt_2,$$

VI

Another proof of the formation of bis(perfluoroalkyl)boron fragment is the conversion of the reaction products **V** and **VI** into the previously described salt $K[(C_nF_{2n+1})_2B(OH)F]$ (n = 4, 6) [20].

$$(C_4F_9)_2ClBNHEt_2 + 2\ KOH \xrightarrow{H_2O} K[(C_4F_9)_2B(OH)_2] + KCl + NHEt_2,$$

$$K[(C_4F_9)_2B(OH)_2] + HF(aq) \rightarrow K[(C_4F_9)_2BF(OH)] + H_2O,$$

$$(C_6F_{13})_2BNEt_2 + KOH \xrightarrow{H_2O} K[(C_6F_{13})_2B(OH)_2] + NHEt_2,$$

$$K[(C_6F_{13})_2B(OH)_2] + HF(aq) \rightarrow K[(C_6F_{13})_2BF(OH)] + H_2O.$$

The reaction stops after the formation of $(C_nF_{2n+1})_2BNEt_2$ (n = 4, 6) apparently due to the steric shielding of the boron atom with two perfluoroalkyl and one diethylamino groups, whereas a smaller volume of dimethylamino group in $(C_nF_{2n+1})_2BNMe_2$ leaves a possibility of adding the third perfluoroalkyl group C_nF_{2n+1} (n = 4, 6).

Table 1 lists the ^{11}B and ^{19}F NMR data of the obtained compounds.

Crystal structure of $(C_2F_5)_3BNHEt_2$ (III). Adduct **III** was characterized additionally by XRD. Crystals of $(C_2F_5)_3BNHEt_2$ suitable for X-ray diffraction were obtained by crystallization of complex **III** melt at the room temperature. Analyzing the structure of $(C_2F_5)_3BNHEt_2$, it was interesting to compare its geometric parameters with those of the structurally similar complexes $(C_2F_5)_3BNMe_3$ (**VII**) [30], $(CF_3)_3BNHEt_2$ (**VIII**) [31], and anion $[(C_2F_5)_3BNO_2]^-$ (**IX**) [12].

The coordination polyhedron of the boron atom in the $(C_2F_5)_3BNHEt_2$ crystal is a distorted tetrahedron formed by three carbon atoms of the pentafluoroethyl groups and the nitrogen atom of diethylamino group (see the figure). Geometric characteristics of the pentafluoroethyl groups and the lengths of all C–B bonds are not equivalent. The latter value varies in the range of 1.658–1.675 Å and differs substantially from the corresponding bond lengths of the complex $(C_2F_5)_3 \cdot BNMe_3$ (**VII**) (1.666–1.688 Å) [30]. Similar difference is observed in the bond lengths of B–N and $C(CF_3)$–$C(CF_3)$. Thus, in the adduct **VII** the length of B–N bond is 1.674 Å, while the corresponding value in compound **III** is 1.618 Å, which is close to the same bond length in $(CF_3)_3BNHEt_2$ [1.596 (8) Å] [31]. The $C(CF_3)$–$C(CF_3)$ bonds in compound **III** are also shorter than the analogous bonds in compound **VII** [30], but are comparable by the length with the carbon–carbon bonds in the pentafluoroethyl groups of the anion $[(C_2F_5)_3BNO_2]^-$ [12]. The NBC angles vary from 106.6° to 110.3°, the angles CBC, from 107.7° to 111.6°. The scatter in the NBC and CBC angles in the adduct **III** is larger than in compounds **VII**, **VIII** and anion **IX** [12, 30, 31].

Crystallographic parameters, the values of the main bond lengths and angles for the adduct **III** are listed in Tables 2–5.

Compound **IV** also gave single crystals of good quality, but attempts to determine the structure of this compound by XRD failed due to disordering of the perfluoroalkyl groups in the crystals.

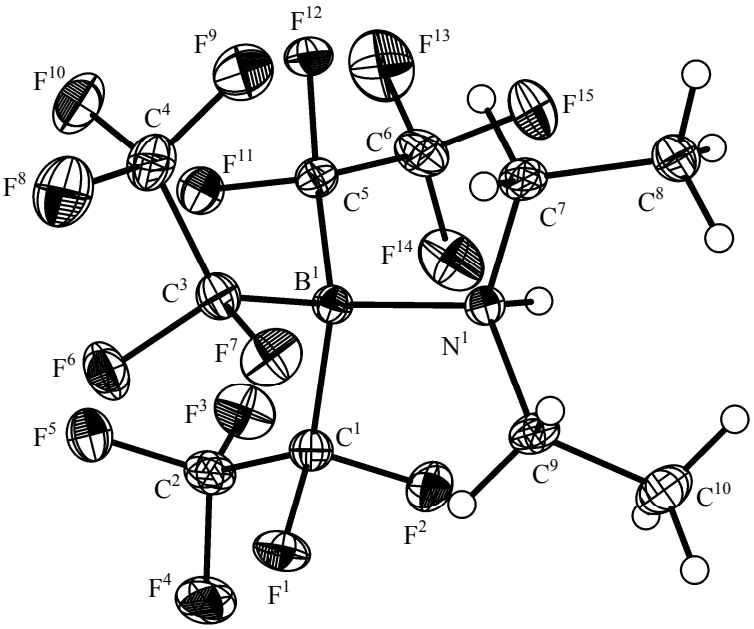
Thus, we have developed a convenient synthetic approach to the adducts of tris(perfluoroalkyl)boranes

Table 1. ^{11}B, ^{19}F NMR parameters of adducts **II–V** and aminoborane **VI**

Compound	Solvent	^{19}F NMR, δ_F, ppm				^{11}B NMR, δ_B, ppm (J, Hz)
		CF_3	CF_3CF_2	CF_2	CF_2B	
$(C_2F_5)_3BNHEt_2$ (**III**)	Ether	–80.6			–114.5	–8.4 ($^2J_{BF}$ 15.4)
$(C_2F_5)_3BNHEt_2$ (**III**)	Methanol	–79.5			–116.1	–10.6 ($^2J_{BF}$ 18.1)
$(C_2F_5)_3BNHMe_2$[a]	$CDCl_3$	–81.8			–117.1	–9.1
$(C_3F_7)_3BNHEt_2$[b] (**IV**)	$CDCl_3$	–79.2	–121.6		–111.5	–10.0
$(C_4F_9)_3BNHMe_2$[c] (**I**)	$CDCl_3$	–79.9	–124.0	–117.5	–111.2	–11.0 ($^4J_{FF}$ 15.1)
$(C_4F_9)_3BNHMe_2$ (**I**)	Ether	–80.5	–124.5	–117.8	–111.4	–10.9
$(C_4F_9)_2BClNHEt_2$ (**V**)	$CHCl_3$	–81.4	–126.4	–123.2	–131.4	–3.9
$(C_6F_{13})_3BNHMe_2$[d] (**II**)	$CDCl_3$	–79.8	–125.1	–116.8 –120.7 –121.8	–111.7	–11.7 ($^4J_{FF}$ 10.0, $^5J_{FF}$ 2.4)
$(C_6F_{13})_2BNMe_2$ (**VI**)	Ether	–77.6	–122.6	–115.3 –115.6 –118.2 –118.3 –119.0	114.5	33.3

[a] ^1H NMR: δ(CH_3) 3.03 ppm [13]. [b] ^1H NMR: δ(CH_2) 3.86, δ(NH) 3.50, δ(CH_2) 3.06, δ(CH_3) 1.43 ppm. [c] ^1H NMR: δ(CH_3) 3.07 ppm. [d] ^1H NMR: δ(CH_3) 2.88, δ(NH) 4.25 ppm.

with the dialkylamines $(C_nF_{2n+1})_3BNHR_2$ (n = 2–4, 6; R = Me, Et), based on the interaction between perfluoroalkyllithium reagents with dichloro(dialkylamino)boranes at temperatures below –90°C. This method allowed us providing the target products with preparative yields of 50–90%. Because of steric requirements, a synthesis of boron complexes $(C_nF_{2n+1})_3BNHR_2$ (n = 4, 6) by nucleophilic perfluoroalkylation with $C_nF_{2n+1}Li$



Molecular structure of adduct **III**.

Table 2. Crystallographic parameters of adduct **III**

Parameter	Value
Empirical formula	$C_{10}H_{11}BF_{15}N$
Crystal system	Orthorombic
Molecular weight, g mol^{-1}	441.01 441.01
Space group	*Pca*2(1)
a, Å	13.361(2)
b, Å	11.054(1)
c, Å	10.425(1)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	1539.7(3)
Z	4
$d_{calc.}$, g cm^{-3}	1.902
Radiation	MoK_α (λ 0.71073 Å)
Region of θ–2θ scan, deg	1.84–28.19
Number of measured reflections	14834
Number of reflections with $I \geq 2\sigma(I)$	3774
R_1 0.0350	0.0350
wR_2 0.0783	0.0783

proceeded successfully only when R = CH_3. From the borane Cl_2BNEt_2 the complexes $(C_nF_{2n+1})_3BNHEt_2$ (n = 2, 3) can readily be obtained, but at the action of perfluorobutillithium or perfluorohexyllithium, the perfluoroalkylation is limited to the introduction of only two perfluoroalkyl groups.

EXPERIMENTAL

NMR spectra were registered on a Bruker Avance 300 instrument (^{1}H 300.13 MHz, ^{11}B 96.29 MHz, ^{19}F 282.40 MHz). Chemical shifts are given in ppm relative to TMS (^{1}H), 15% $BF_3{\cdot}OEt_2$ in $CDCl_3$ (^{11}B), and CCl_3F (^{19}F) respectively, C_6F_6 (–162.9 ppm) was used as a secondary reference. Elemental CHN-analysis was performed on an Elementaranalysator EA3000 instrument.

Boron trichloride (Merck), KF (spray drying, Aldrich), $C_6F_{13}H$ (Clariant), anhydrous ether (Baker), the solutions of 1.6 M of MeLi in ether (Fluka) and 1.7 M of *t*-BuLi in pentane (Aldrich) were used without further purification. Dichloro(diethylamino)-borane [27], 1*H*-heptafluoropropane, and 1*H*-nona-fluorobutane [32] were prepared along the described procedures. Dichloro(dimethylamino)borane was synthesized according to [33], isolated and used as a 20 wt % solution in benzene, the solution was stored at 0°C.

Table 3. Interatomic distances in adduct **III**

Bond	*d*, Å	Bond	*d*, Å
F^1–C^1	1.370(2)	F^{14}–C^6	1.320(3)
F^2–C^1	1.376(2)	F^{15}–C^6	1.331(2)
F^3–C^2	1.324(3)	N^1–C^7	1.524(2)
F^4–C^2	1.332(2)	N^1–C^9	1.534(2)
F^5–C^2	1.317(3)	N^1–B^1	1.618(2)
F^6–C^3	1.366(2)	B^1–C^5	1.658(3)
F^7–C^3	1.371(2)	B^1–C^3	1.666(3)
F^8–C^4	1.339(2)	B^1–C^1	1.675(3)
F^9–C^4	1.324(3)	C^1–C^2	1.550(3)
F^{10}–C^4	1.327(3)	C^3–C^4	1.547(3)
F^{11}–C^5	1.365(2)	C^5–C^6	1.537(3)
F^{12}–C^5	1.371(2)	C^7–C^8	1.505(3)
F^{13}–C^6	1.316(3)	C^9–C^{10}	1.510(3)

Synthesis of $(C_2F_5)_3BNHEt_2$ (III). Pentafluoro-ethyl iodide (9.4 g, 38 mmol) was dissolved in cold (–78°C) ether (120 ml) under an atmosphere of dry argon, and the solution was cooled to –95°C in an acetone–liquid nitrogen bath. Then 1.6 M solution of MeLi in ether (20 ml, 32 mmol) was added with stirring at a rate maintaining the reaction mixture temperature below –90°C. The mixture was stirred for 20 min at –95 to –90°C, and dichloro(diethylamino)-borane (1.4 g, 9.1 mmol) was added with a syringe in one portion. The reaction mixture was stirred for 2 h at –95 to –90°C and warmed to –78°C within 4 h and then to 20°C in 2 h. Then 20 ml of 5% HCl was added, the organic layer was separated, the aqueous layer was extracted with ether (2 × 10 ml). The combined extract was dried over magnesium sulfate and evaporated on a rotary evaporator. The distillation of the residue (a dark brown oil) in a vacuum afforded a colorless oil, bp 80–90°C (0.02 mm Hg), 3.61 g, 90%, which on standing became colorless crystals. Found, %: C 27.23, H 2.48, N 3.18. $C_{10}H_{11}BF_{15}N$. Calculated, %: C 27.24, H 2.51, N 3.18.

Synthesis of $(C_3F_7)_3BNHEt_2$ (IV). The reaction was carried out in a three-neck flask equipped with the

Table 4. Main bond angles in adduct **III**

Angle	ω, deg	Angle	ω, deg
$C^7N^1C^9$	108.87(13)	$F^6C^3B^1$	109.66(14)
$C^7N^1B^1$	114.20(14)	$F^7C^3B^1$	109.09(14)
$C^9N^1B^1$	118.12(13)	$C^4C^3B^1$	125.34(15)
$N^1B^1C^5$	109.18(14)	$F^9C^4F^{10}$	108.72(17)
$N^1B^1C^3$	110.32(14)	$F^9C^4F^8$	107.30(17)
$C^5B^1C^3$	111.34(14)	$F^{10}C^4F^8$	106.94(16)
$N^1B^1C^1$	106.61(14)	$F^9C^4C^3$	112.79(17)
$C^5B^1C^1$	111.58(14)	$F^{10}C^4C^3$	111.42(17)
$C^3B^1C^1$	107.70(14)	$F^8C^4C^3$	109.42(16)
$F^1C^1F^2$	105.09(14)	$F^{11}C^5F^{12}$	105.31(14)
$F^1C^1C^2$	103.24(15)	$F^{11}C^5C^6$	105.89(15)
$F^2C^1C^2$	103.61(15)	$F^{12}C^5C^6$	102.61(14)
$F^1C^1B^1$	109.99(14)	$F^{11}C^5B^1$	109.12(14)
$F^2C^1B^1$	108.79(14)	$F^{12}C^5B^1$	112.34(14)
$C^2C^1B^1$	124.48(16)	$C^6C^5B^1$	120.38(15)
$F^5C^2F^3$	108.63(17)	$F^{13}C^6F^{14}$	108.35(17)
$F^5C^2F^4$	107.78(16)	$F^{13}C^6F^{15}$	108.07(18)
$F^3C^2F^4$	106.63(16)	$F^{14}C^6F^{15}$	106.85(17)
$F^5C^2C^1$	112.57(16)	$F^{13}C^6C^5$	111.06(17)
$F^3C^2C^1$	111.99(16)	$F^{14}C^6C^5$	112.24(17)
$F^4C^2C^1$	108.98(16)	$F^{15}C^6C^5$	110.09(16)
$F^6C^3F^7$	105.84(15)	$C^8C^7N^1$	112.92(16)
$F^6C^3C^4$	101.62(15)	$C^{10}C^9N^1$	112.50(14)
$F^7C^3C^4$	103.64(15)		

Table 5. Main dihedral angles in adduct **III**

Angle	ω, deg	Angle	ω, deg
$C^7N^1B^1C^5$	62.42(18)	$C^1B^1C^3C^4$	–149.48(17)
$C^9N^1B^1C^5$	–167.63(14)	$F^6C^3C^4F^9$	176.66(16)
$C^7N^1B^1C^3$	–60.24(18)	$F^7C^3C^4F^9$	66.99(20)
$C^9N^1B^1C^3$	69.71(18)	$B^1C^3C^4F^9$	–58.80(24)
$C^7N^1B^1C^1$	–176.91(14)	$F^6C^3C^4F^{10}$	–60.73(19)
$C^9N^1B^1C^1$	–46.96(18)	$F^7C^3C^4F^{10}$	–170.40(15)
$N^1B^1C^1F^1$	80.19(17)	$B^1C^3C^4F^{10}$	63.81(24)
$C^5B^1C^1F^1$	–160.69(14)	$F^6C^3C^4F^8$	57.32(19)
$C^3B^1C^1F^1$	–38.21(19)	$F^7C^3C^4F^8$	–52.35(20)
$N^1B^1C^1F^2$	–34.42(18)	$B^1C^3C^4F^8$	–178.14(16)
$C^5B^1C^1F^2$	84.71(17)	$N^1B^1C^5F^{11}$	169.77(13)
$C^3B^1C^1F^2$	–152.81(14)	$C^3B^1C^5F^{11}$	–68.18(18)
$N^1B^1C^1C^2$	–156.76(16)	$C^1B^1C^5F^{11}$	52.18(18)
$C^5B^1C^1C^2$	–37.64(23)	$N^1B^1C^5F^{12}$	–73.83(17)
$C^3B^1C^1C^2$	84.84(20)	$C^3B^1C^5F^{12}$	48.22(19)
$F^1C^1C^2F^5$	74.50(19)	$C^1B^1C^5F^{12}$	168.58(14)
$F^2C^1C^2F^5$	–176.11(15)	$N^1B^1C^5C^6$	47.14(21)
$B^1C^1C^2F^5$	–51.49(24)	$C^3B^1C^5C^6$	169.19(16)
$F^1C^1C^2F^3$	–162.76(15)	$C^1B^1C^5C^6$	–70.45(20)
$F^2C^1C^2F^3$	–53.36(20)	$F^{11}C^5C^6F^{13}$	46.14(21)
$B^1C^1C^2F^3$	71.26(23)	$F^{12}C^5C^6F^{13}$	–64.05(19)
$F^1C^1C^2F^4$	–45.03(19)	$B^1C^5C^6F^{13}$	170.32(16)
$F^2C^1C^2F^4$	64.37(19)	$F^{11}C^5C^6F^{14}$	–75.32(19)
$B^1C^1C^2F^4$	–171.01(16)	$F^{12}C^5C^6F^{14}$	174.49(15)
$N^1B^1C^3F^6$	–144.43(14)	$B^1C^5C^6F^{14}$	48.85(23)
$C^5B^1C^3F^6$	94.18(17)	$F^{11}C^5C^6F^{15}$	165.80(15)
$C^1B^1C^3F^6$	–28.44(19)	$F^{12}C^5C^6F^{15}$	55.61(19)
$N^1B^1C^3F^7$	–28.94(19)	$B^1C^5C^6F^{15}$	–70.03(21)
$C^5B^1C^3F^7$	–150.32(14)	$C^9N^1C^7C^8$	65.58(19)
$C^1B^1C^3F^7$	87.05(17)	$B^1N^1C^7C^8$	–160.03(15)
$N^1B^1C^3C^4$	94.53(20)	$C^7N^1C^9C^{10}$	–101.53(17)
$C^5B^1C^3C^4$	–26.86(24)	$B^1N^1C^9C^{10}$	126.12(16)

inlet and outlet tubes for dry argon, magnetic stirrer, low temperature thermometer, and a reflux condenser cooled by a mixture of acetone with dry ice. The flask was charged with ether (120 ml), cooled to –78°C, and through the gas inlet tube 1*H*-heptafluoropropane (9.25 g, 54.4 mmol) was condensed. The solution was cooled to –105°C, and 1.7 M solution of *t*-BuLi in pentane (25 ml, 42.5 mmol) was entered with a syringe at a rate maintaining the reaction mixture temperature below –100°C. The mixture was stirred at –105 to –100°C for 30 min, and dichloro(diethylamino)borane (1.85 g, 12 mmol) was introduced with a syringe while keeping the temperature below –105°C. Then the stirred mixture was warmed to –90°C within 4 h, then to –78°C within 1 h and to 20°C within 30 min. The resulting suspension was hydrolyzed with 100 ml of 5% HCl, the organic layer was separated, the water layer was extracted with ether (2 × 10 ml). The combined extracts were dried over magnesium sulfate,

evaporated on the rotary evaporator to a volume of 20 ml, the concentrate was filtered through a layer of silica gel and evaporated. The recrystallization of the solid residue from chloroform gave 5.35 g (75%) of colorless crystals of compound **IV**. Found, %: C 26.54, H 1.86, N 2.39. $C_{13}H_{11}BF_{21}N$. Calculated, %: C 26.42, H 1.88, N 2.37.

Synthesis of $(C_4F_9)_3BNHMe_2$ (I). The synthesis was carried out as described above, using 1*H*-nonafluorobutane (4.13 g, 18.8 mmol), 1.7 M solution of *t*-BuLi in pentane (10 ml, 17 mmol), ether (50 ml), and 20 wt % solution of dichloro(dimethylamino)-borane (1.9 g, 3 mmol) in benzene. The yellow oil obtained after evaporation of combined extracts (2.5 g) was distilled in a vacuum. Complex $(C_4F_9)_3BNHMe_2$ **I** (1.06 g, 50%) was obtained, bp 110–115°C (0.02 mm Hg). Found, %: C 24.29, H 0.90, N 2.09. $C_{14}H_7BF_{27}N$. Calculated, %: C 23.58, H 0.99, N 1.96.

Synthesis of $(C_6F_{13})_3BNHMe_2$ (II). The synthesis was carried out as described above, using 1*H*-perfluorohexane (7.04 g, 22 mmol), 1.7 M solution of *t*-BuLi in pentane (10 ml, 17 mmol), ether (60 ml) and a 20 wt % solution of dichloro(dimethylamino)borane (1.9 g, 3 mmol) in benzene. By a vacuum distillation complex $(C_6F_{13})_3BNHMe_2$ **II** was isolated (2.09 g, 59%), colorless viscous oil, bp 125–150°C (0.03 mm Hg). Adduct is insoluble in water and poorly soluble in organic solvents. Found, %: C 23.87, H 0.75, N 1.54. $C_{20}H_7BF_{39}N$. Calculated, %: C 23.71, H 0.70, N 1.38.

Reaction of nonafluorobutyllithium with dichloro-(diethylamino)borane. The synthesis was carried out as described above, using 1*H*-nonafluorobutane (8.97 g, 40.8 mmol), 1.7 M solution of *t*-BuLi in pentane (20 ml, 34 mmol), ether (100 ml) and dichloro-(diethylamino)borane (1.54 g, 10 mmol). By evaporation of the combined extracts adduct **V** was isolated, 3.5 g, light yellow oil. It was mixed with a solution of 2 g of KOH in 20 ml of water and stirred for 2 h at 25°C, the mixture was extracted with ether (5 × 10 ml). The combined extracts were dried over magnesium sulfate and evaporated. The solid residue was dissolved in 20 ml of 73% HF, stirred for 2 h at 25°C, and the solution was neutralized with a saturated solution of K_2CO_3. The solution was evaporated, the solid residue was extracted with acetonitrile (5 × 10 ml), and the solvent was distilled off on a rotary evaporator. 1.73 g of the salt $K[(C_4F_9)_2B(OH)F]$ was obtained [20].

Reaction of perfluorohexyllithium with dichloro-(diethylamino)borane. From 1*H*-perfluorohexane (2.1 g, 6.6 mmol) and *t*-BuLi in pentane (3.2 ml, 5.44 mmol) reacted in 25 ml of ether at –105 to –110°C a solution of $C_6F_{13}Li$ was obtained. To this reagent was added 231 mg (1.5 mmol) of dichloro(dimethylamino)-borane. The mixture was stirred for 1 h at a temperature below –105°C. Then the mixture was heated to –90°C for 4 h, then to –78°C for 1 h and to 20°C for 0.5 h. According to ^{11}B NMR data, the main component of the solution was $(C_6F_{13})_2BNEt_2$. The mixture was hydrolyzed with 20 ml of 5% HCl. The organic layer was separated and the aqueous layer was extracted with ether (2 × 10 ml). The combined extracts were dried over $MgSO_4$, ether was distilled off and to the oily residue a solution of 1 g of KOH in 10 ml of water was added. The mixture was stirred at room temperature for 2 h, extracted with ether (3 × 10 ml), and the ether extract was dried over magnesium sulfate. After evaporation of the solution we obtained 900 mg of a solid. The substance was dissolved in 5 ml of 73% HF, and the solution was stirred for 1 h at 20°C. To the solution was added 300 mg of activated carbon, the mixture was stirred for 30 min and filtered. The filtrate was neutralized with solid K_2CO_3 and extracted with acetonitrile (5 × 5 ml). The extract was dried over anhydrous potassium carbonate and evaporated. Salt $K[(C_6F_{13})_2B(OH)F]$ (780 mg) [20] was obtained.

The XRD analysis of adduct III. X-ray diffraction data for determining the crystal structure were obtained on a Smart Apex diffractometer (Bruker) (MoK_α radiation, 0.71073 Å, graphite monochromator) at 120(2) K. The extinction was taken into account semiempirically, based on the intensity of equivalent reflexes. The structure was solved by the direct method and refined by the full-matrix mean-square method on F^2 anisotropically for the non-hydrogen atoms using the program package SHELXTL [SADABS (Version 2.03) and SHELXTL (Version 6.10), Bruker AXS Inc., Madison (Wisconsin, USA), 2002]. The hydrogen atoms were localized geometrically and refined in the *rigid body* approximation.

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