Synthesis and Characterization of Novel Intramolecularly Base-stabilized Boron Halides. Molecular Structures of 1-$X_2BOCR^1R^2$-2-$NMe_2C_6H_4$ [$R^1 = R^2 = Ph$, X = Cl or F; $R^1 = R^2 = Cy$, X = Cl] and [1-LiN(Ph)C(H)Ph-2-$NMe_2C_6H_4]_2$

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Dedicated to Professor Arndt Simon on the Occasion of his 65th Birthday

Abstract. The lithium alkoxides [1-LiOCR^1R^2-2-$NMe_2C_6H_4]_2$ [$R^1 = R^2$ = Ph (**1**), Cy (**2**)] react with BCl_3 or $BF_3(Et_2O)$ to give 1-$X_2BOCR^1R^2$-2-$NMe_2C_6H_4$ [$R^1 = R^2$ = Ph, X = Cl (**4**); $R^1 = R^2$ = Cy, X = Cl (**5**); $R^1 = R^2$ = Ph, X = F (**6**); $R^1 = R^2$ = Cy, X = F (**7**)]. The lithium amide [1-LiN(Ph)C(H)Ph-2-$NMe_2C_6H_4]_2$ (**3**) reacts with BCl_3 to give 1-Cl_2BN(Ph)C(H)Ph-2-$NMe_2C_6H_4$ (**8**). Compounds **4** − **8** were characterized spectroscopically (NMR, IR, MS), and crystal structures were determined for **3** − **6**.

Keywords: Lithium alkoxide; Lithium amide; BCl_2 derivatives; BF_2 derivatives; Molecular structures

Synthese und Charakterisierung neuartiger intramolekular basen-stabilisierter Borhalogenide. Molekülstrukturen von 1-$X_2BOCR^1R^2$-2-$NMe_2C_6H_4$ [$R^1 = R^2 = Ph$, X = Cl, F; $R^1 = R^2 = Cy$, X = Cl] und [1-LiN(Ph)C(H)Ph-2-$NMe_2C_6H_4]_2$

Inhaltsübersicht. Die Lithiumalkoxide [1-LiOCR^1R^2-2-$NMe_2C_6H_4]_2$ [$R^1 = R^2$ = Ph (**1**), Cy (**2**)] reagieren mit BCl_3 oder $BF_3(Et_2O)$ zu 1-$X_2BOCR^1R^2$-2-$NMe_2C_6H_4$ [$R^1 = R^2$ = Ph, X = Cl (**4**); $R^1 = R^2$ = Cy, X = Cl (**5**); $R^1 = R^2$ = Ph, X = F (**6**); $R^1 = R^2$ = Cy, X = F (**7**)]. Das Lithiumamid [1-LiN(Ph)C(H)Ph-2-$NMe_2C_6H_4]_2$ (**3**) setzt sich mit BCl_3 zu 1-Cl_2BN(Ph)C(H)Ph-2-$NMe_2C_6H_4$ (**8**) um. Die Verbindungen **4** − **8** wurden spektroskopisch (NMR, IR, MS), **3** − **6** auch röntgenstrukturanalytisch charakterisiert.

Introduction

Boron reagents with reactive boron−substituent bonds are interesting starting materials for the preparation of transition metal−boron complexes [1] or compounds with multiple bonds between boron and main group elements, especially boron−boron bonds. Stable transition metal complexes with M−B bonds have been prepared with amido-substituted boron compounds by *Braunschweig* et al. [1] and *Nöth* et al. [2], while Power et al. [3] and *Nöth* et al. [4] reported the synthesis of $B_2Mes_3Ph^{2-}$ (Mes = 2,4,6-$Me_3C_6H_2$) [3a], $B_2Ph_2(NMe_2)_2^{2-}$ [3b] and $B_2(NMe_2)_2(NR'_2)_2^{2-}$ (NR'_2 = pyrrolyl, indolyl, carbazolyl) [4], which formally contain a boron−boron double bond.

In our ongoing studies on the synthesis and solid-state structures of boron reagents with reactive boron−substituent bonds [5, 6], we previously reported solvent-free chelated dimethylamino lithium alkoxide and lithium arylamide dimers with six- and seven-membered chelate rings [7, 8], which are obtained from the corresponding alcohols or amines [9]. These lithium salts are suitable starting materials for the synthesis of transition metal [10] or main group element complexes [11] with intramolecularly base-stabilized six- and seven-membered chelate rings which are more labile than the corresponding five-membered rings.

We now report the high-yield synthesis and spectroscopic properties of the BCl_2 and BF_2 derivatives 1-$X_2BOCR^1R^2$-2-$NMe_2C_6H_4$ [$R^1 = R^2$ = Ph, X = Cl (**4**); $R^1 = R^2$ = Cy, X = Cl (**5**); $R^1 = R^2$ = Ph, X = F (**6**); $R^1 = R^2$ = Cy, X = F (**7**)] and 1-Cl_2BN(Ph)C(H)Ph-2-$NMe_2C_6H_4$ (**8**). Compounds **4** − **8** were characterized spectroscopically (NMR, IR, MS), and crystal structures were determined for **4** − **6**.

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1) Crystal structure determination

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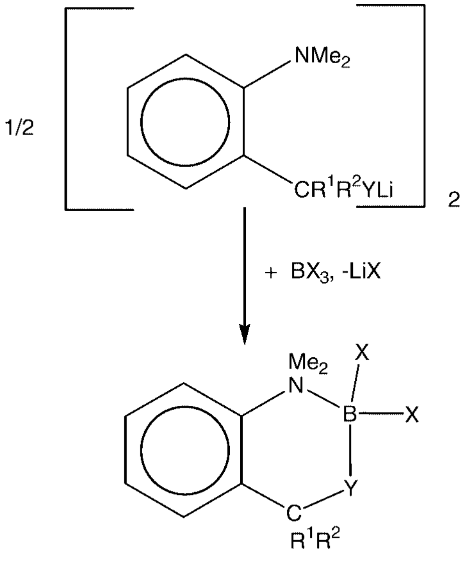


4: Y = O; $R^1 = R^2$ = Ph; X = Cl
5: Y = O; $R^1 = R^2$ = Cy; X = Cl
6: Y = O; $R^1 = R^2$ = Ph; X = F
7: Y = O; $R^1 = R^2$ = Cy; X = F
8: Y = NPh; R^1 = H, R^2 = Ph; X = Cl

Scheme 1 Preparation of **4** − **8**

Results and Discussion

Synthesis

The intramolecularly base-stabilized boron compounds **4** − **8** were prepared from the lithium alkoxides [1-LiOCR^1R^2-2-$NMe_2C_6H_4$]$_2$ [$R^1 = R^2$ = Ph (**1**), Cy (**2**)] [7] or the lithium amide [LiN(Ph)C(H)Ph-2-$NMe_2C_6H_4$]$_2$ (**3**) [8] and BCl_3 or $BF_3(Et_2O)$ as shown in Scheme 1. The BCl_2 and BF_2 derivatives **4** − **8** were obtained in 85-90 % yield; they are colorless, mostly air-stable solids.

Spectroscopic Properties

^1H NMR spectra

The $N(CH_3)_2$ protons appear as a singlet at 3.05 (**4**), 3.29 (**5**), 2.96 (**6**), 3.02 (**7**) and two singlets at 3.55 and 3.67 ppm (**8**), i.e. shifted downfield in comparison with the parent organic ligands [9], which suggests coordination of nitrogen to the boron atom. The CH proton appears as a singlet at 3.19 ppm (**8**). The resonances corresponding to the cyclohexyl (1.0-2.1 ppm) and aromatic protons (6.9-7.5 ppm) for each compound show the characteristic resonances in their expected chemical shift regions similar to those observed for the organic ligands [9].

^{13}C and ^{19}F NMR spectra

The $^{13}C\{^1H\}$ NMR signals of the $N(CH_3)_2$ carbon atoms appear as a singlet at 51.0 (**4**), 52.7 (**5**), 47.9 (**6**), 49.5 (**7**) and 49.0 ppm (**8**). Moreover, a singlet is observed for the CH carbon atom at 58.0 (**8**). The C−O carbon atoms appear as a singlet at 84.0 (**4**), 84.1 (**5**), 82.3 (**6**) and 82.4 ppm (**7**). The signals of the aromatic rings and cyclohexyl carbon atoms are in the expected range but slightly shifted compared to the organic ligands [9].

The ^{19}F NMR signal of the BF_2 group appears as a singlet at −156.9 (**6**) and −154.4 ppm (**7**).

^{11}B NMR spectra

The ^{11}B NMR spectra show that the ^{11}B signal moves to lower field in the BCl_2 derivatives [δ = 8.6 (**4**), 7.9 (**5**) and 9.8 ppm (**8**)] relative to the BF_2 derivatives [δ = 1.9 (**6**) and 1.3 ppm (**7**)]. These shifts appear in a region specific for an sp^3-coordinated boron atom (tetrahedral environment of the ^{11}B nucleus) [5, 6] with B−N interaction and are at higher field by ca. 69 ppm relative to three-coordinate boranes (cf. 9-phenyl-9-BBN, 9-BBN = 9-borabicyclo[3.3.1]nonyl; 80.4 ppm) [12]. It is of interest to note that the boron atom in the six-membered BF_2 chelate rings **6** and **7** are more shielded than in the the six-membered BCl_2 chelate rings **4** and **5**, which can be understood by taking electronic and steric factors into consideration. The F atom is more electronegative (more electron-withdrawing) and has a smaller size (less steric) than the Cl atom, consequently, the B−N bond is expected to be stronger and the boron atom becomes more shielded. However, this result is not in agreement with the B−N bond distances obtained from X-ray diffraction, the B−N bond of the six-membered BF_2 chelate ring in **6** [1.642(2) Å] being longer than those observed for the six-membered BCl_2 chelate rings in **4** [1.630(4) Å] and **5** [1.626(2) Å].

The corresponding tetracoordinate BH_2 [δ = −2.5 to 4.4] [11a] derivatives with six- and seven-membered chelate rings exhibit chemical shifts in the same range as the tetracoordinate species in **4** − **8**. In contrast, while the BEt_2 derivatives of **1** and **2** 1-Et_2BOCR_2-2-$NMe_2C_6H_4$ (R = Ph, Cy), with six-membered rings exhibit similar chemical shifts (7.6 and 6.9 ppm), two major signals with different intensities are observed in the ^{11}B NMR spectra of 1-$Et_2BOCPh_2CH_2$-2-$NMe_2C_6H_4$ (7.9, 32.0 ppm, ca. 2:1), which demonstrates the existence of an equilibrium between two types of boron compounds, presumably in tricoordinate (sp^2) and tetracoordinate (sp^3) environments [13], in this larger seven-membered heterocycle, which is derived from the organic compound 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ [9].

Mass spectrometry

The mass spectra gave parent ion peaks at *m*/*z* = 382.8 (**4**) and 351.3 (**6**), or fragments due to the elimination of Cl (359.9 [M^+-Cl] (**5**)), Cy (280.3 [M^+-Cy] (**7**)), or BCl_2 (302.3 [M^+-BCl_2] (**8**)), which agree with the calculated isotopic distribution pattern. There are many fragments, which are either analogous or identical in these closely related compounds (see experimental part).

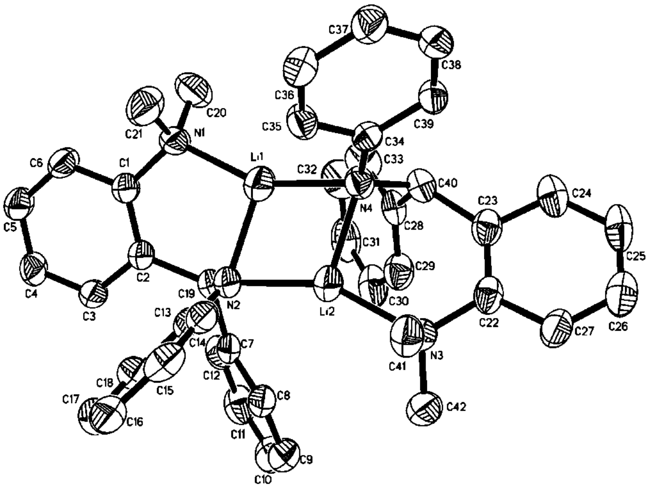


Figure 1 Molecular structure of **3** (hydrogen atoms and toluene omitted for clarity)

Table 1 Selected bond lengths /Å and bond angles /deg. for **3**

Li(1)-N(2)	1.975(8)	Li(2)-N(2)	1.986(7)
Li(2)-N(4)	1.972(8)	Li(1)-N(4)	2.038(8)
Li(1)-N(1)	2.053(8)	Li(2)-N(3)	2.034(8)
Sum of angles at Li(1)	360.0	Sum of angles at Li(2)	359.9
Li(1)-N(2)-Li(2)	74.1(3)	Li(2)-N(4)-Li(1)	73.0(3)
N(2)-Li(2)-N(4)	107.1(3)	N(4)-Li(1)-N(2)	105.0(3)

IR spectra

The infrared spectra of compounds **4** − **8** afford a means of determining the B−N stretching vibration, which usually appears as one of the strongest bands of the spectra between 1500 and 1444 cm^{-1} [14]. For **4** − **7**, the band which appears in the range of 1445-1321 cm^{-1} is attributed to the B−O stretching frequency [15]. For **4**, **5** and **8**, the medium-strong bands which appear in the range of 965-993 and 520-570 cm^{-1} are tentatively assigned to the asymmetric and the symmetric BCl_2 stretching vibration, for **6** and **7**, the strong or medium bands which appear in the range of 1445 and 1260 cm^{-1} are tentatively assigned to the asymmetric and the symmetric BF_2 stretching vibration [16].

Molecular Structures of 3 − 6

Compound **3** was prepared as described previously [8]. Colorless crystals of **3** were obtained from toluene at 20 °C. Compound **3** crystallizes in the triclinic space group $P\bar{1}$.

Compound **3** (Fig. 1, Table 1) forms a centrosymmetric dimer in the solid state. Due to the presence of an inversion center, only the *meso* isomer (*R,S*) is observed in the solid state. The central four-membered Li_2N_2 ring is planar with smaller Li-N-Li and larger N-Li-N bond angles. The dimethylamino groups are coordinated to the lithium atoms [Li(1)-N(1) 2.053(8) Å; Li(2)-N(3) 2.034(8) Å]. The Li-NMe_2 bond lengths, Li-N-Li and N-Li-N angles are similar to those reported previously for [1-LiNPhCHPhCH$_2$-2-$NMe_2C_6H_4$]$_2$ [8]. The bond lengths and angles of the organic fragment are similar to those observed for the corresponding organic compound [9].

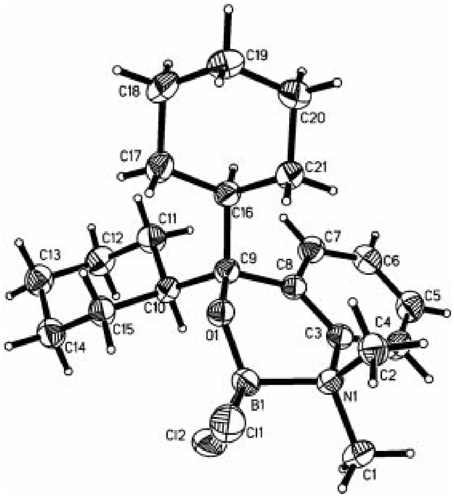


Figure 2 Molecular structure of **4** (toluene omitted for clarity)

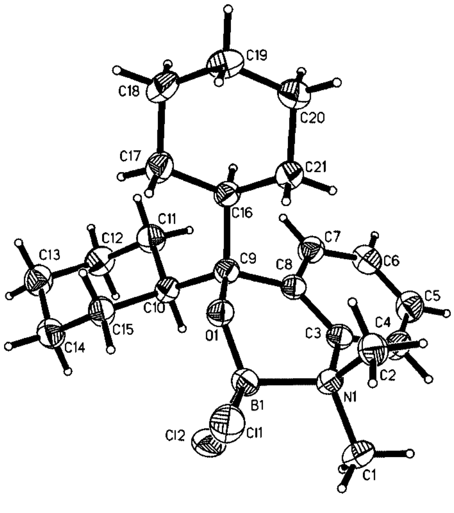


Figure 3 Molecular structure of **5**

A planar environment would be expected for the three-coordinate lithium atoms, and the sums of bond angles are indeed close to 360°. The *anti* arrangement of the two NMe_2 methyl groups with respect to the Li_2N_2 core is similar to the *anti* alignment of the two NMe_2 methyl groups with respect to the Li_2O_2 core in [1-LiOCCy$_2$-2-$NMe_2C_6H_4$]$_2$ and [1-LiOCPh$_2$CH$_2$-2-$NMe_2C_6H_4$]$_2$ [7]. The Li-N amide bond lengths [Li(1)-N(2) 1.975(8) Å; Li(1)-N(4) 2.038(8) Å; Li(2)-N(2) 1.986(7) Å; Li(2)-N(4) 1.972(8) Å] are similar to other lithium amides, which also contain a three-coordinate lithium atom [8].

Colorless crystals of **4** − **6** were obtained as described in the experimental section. Selected bond lengths and angles are collected in Table 2. The molecular structures are depicted in Figures 2-4.

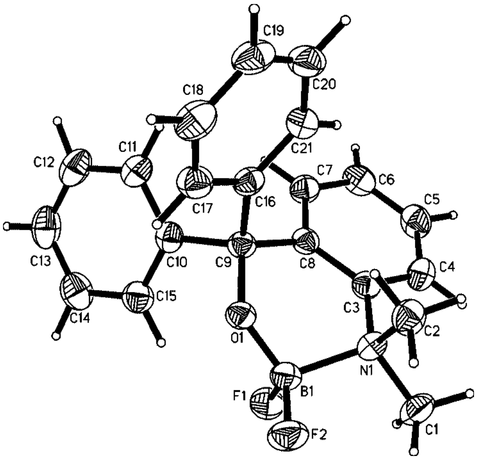


Figure 4 Molecular structure of **6**

Table 2 Selected bond lengths /Å and bond angles /deg. for **4** − **6**

	4	5	6
B(1)-O(1)	1.394(3)	1.391(2)	1.409(2)
B(1)-N(1)	1.630(4)	1.626(2)	1.642(2)
B(1)-Cl(or F)	1.881(3)	1.860(2)	1.389(2)
	1.859(3)	1.891(2)	1.384(2)
C(3)-N(1)	1.493(3)	1.496(2)	1.484(2)
C(3)-C(8)	1.405(3)	1.401(2)	1.394(2)
C(8)-C(9)	1.540(3)	1.536(2)	1.537(2)
C(9)-O(1)	1.437(3)	1.438(2)	1.432(1)
C(9)-O(1)-B(1)	124.0(2)	122.5(1)	122.73(9)
O(1)-B(1)-N(1)	109.9(2)	109.2(1)	108.4(1)
O(1)-B(1)-Cl(or F)	114.6(2)	117.5(1)	115.8(1)
	108.8(2)	107.8(1)	110.0(1)
N(1)-C(3)-C(8)	118.4(2)	121.5(2)	118.9(1)
C(3)-C(8)-C(9)	122.5(2)	124.0(1)	123.3(1)
C(8)-C(9)-O(1)	110.4(2)	108.9(1)	111.41(9)

The common feature of the molecular structures of **4** − **6** is the intramolecular stabilization of the boron compounds by interaction with the dimethylamino group. The structural data of the O-C-phenylene-NC$_2$ fragments are similar for **4** (Fig. 2, Table 2), **5** (Fig. 3, Table 2) and **6** (Fig. 4, Table 2). The coordination of the amino group results in a puckered six-membered BOC$_3$N ring in **4** − **6**: the C(9)-C(8)-C(3)-N(1) fragment is coplanar, and in **4** and **6**, both the boron and oxygen atom lie above this plane [**4**: B(1) 0.995 Å, O(1) 0.510 Å; **6**: B(1) 0.923 Å, O(1) 0.351 Å], while in **5**, B(1) lies 0.567 Å below and O(1) lies 0.071 Å above this plane. This leads to a distorted tetrahedral environment at B(1) [small O-B-N bite angle [**4**: 109.9(2); **5**: 109.2(1); **6**: 108.4(1)°], one large and one small O-B-X (X = F, Cl) bond angle [**4**: 114.6(2), 108.8(2); **5**: 117.5(1), 107.8(1); **6**: 115.8(1), 110.0(1)°].

The structural data of the O-B-N bond angles in **4** − **6** differ remarkably from those of the strained five-membered BC$_3$N rings in B(OCH$_2$CPh$_2$O){2,6-(NMe$_2$CH$_2$)$_2$C$_6$H$_3$} [17], BCl$_2${2,6-(NEt$_2$CH$_2$)$_2$C$_6$H$_3$} and BCl$_2${2-N(BCl$_3$)Et$_2$CH$_2$-6-(NEt$_2$CH$_2$)C$_6$H$_3$} and BX$_2${2-(NR$_2$CH$_2$)C$_6$H$_4$} (X = Cl, R = Me [5]; BX$_2$ = 9-borabicyclo[3.3.1]nonane [18], R = Me, Et; X$_2$ = OCH$_2$CPh$_2$O, R = Me [18]). Thus, the C-B-N bond angles in the latter [94.7(2), 95.2(1) and 95.7(2)°] are much smaller than the O-B-N bond angles of **4** − **6**, while the O-B-N bond angles [109.2(1) and 110.0(1)°] of the BOC$_3$N six-membered rings in BCl$_2${2-(NEt$_2$CH$_2$)OC$_6$H$_4$} and [BCl$_2${2-NHEt$_2$CH$_2$-6-(NEt$_2$CH$_2$)OC$_6$H$_3$}]Cl [6] are larger than the O-B-N bond angle of **6** and similar to those observed for **4** and **5**.

The data of the six-membered BOC$_3$N rings in **4** − **6** are, however, similar with those of the BOC$_3$N six-membered rings in BCl$_2${2-(NEt$_2$CH$_2$)OC$_6$H$_4$} and [BCl$_2${2-NHEt$_2$CH$_2$-6-(NEt$_2$CH$_2$)OC$_6$H$_3$}]Cl [6]. The C-O-B bond angles [119.9(1) and 122.8(1)°] are smaller than those for **4** − **6**, the bond angles about B(1) [bond angles range from 108.0(1) to 111.6(1) and from 106.4(1) to 112.1(1)°] are less distorted than those observed for **4** − **6**, the bond angle about N(1) [bond angles range from 104.8(1) to 116.0(1) and from 104.9(1) to 116.2(1)°] is more distorted than those observed for **4** − **6**, and the B−O [1.425(2) and 1.420(2) Å] and the B−N bond lengths [1.633(2) and 1.627(2) Å] are similar to those observed for **4** − **6**.

Other structurally characterized examples of intramolecularly base-stabilized six-membered boron-containing rings include B(cat){2-(NHPhCH$_2$)OC$_6$H$_4$} (cat = O$_2$C$_6$H$_4$) [19], BPh$_2${2-(CHO)OC$_6$H$_4$} [20] and B(CF$_3$)$_2$NMe$_2$CH(Me)CMe=CHO [21]. Here, the NHPh or C=O [B−N 1.636(4); B−O 1.496(4) or 1.45(1) Å] group is coordinated to the boron atom, which exhibits a distorted tetrahedral environment [bond angles range from 106.0(2) to 114.9(3)°] in the range found in **4** − **6**, while the B−O bond is longer than those observed in **4** − **6** [1.394(3), 1.391(2) and 1.409(2) Å].

The B−N bond lengths of **4** − **6** are similar to those of related dichloroboron derivatives [5] and those of dialkyl- or dialkoxyboron compounds with BC$_3$N rings [17, 18]. Also, the B−N bond lengths in **4** − **6** are larger than those of the adducts BCl$_3$(NMe$_3$) [B−N 1.575(10) Å] [22], BCl$_3$(py) [B−N 1.592(3) Å] [23] and BCl$_3$(NCMe) [B−N 1.562(8) Å] [24].

The bond lengths and angles of the organic fragment of **4** − **6** are similar to those observed for the corresponding organic compounds [9].

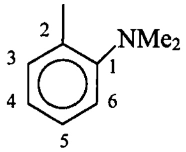
Experimental Section

General Remarks: All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen. The NMR spectra were recorded in CDCl$_3$ with an AVANCE DRX 400 spectrometer (Bruker): ^{1}H (400.1 MHz) and ^{13}C NMR (100.6 MHz) with tetramethylsilane as external standard; ^{11}B NMR spectra (128.4 MHz) with BF$_3$(Et$_2$O) as external standard; ^{19}F NMR spectra (228.3 MHz) with CFCl$_3$ as external standard. Infrared spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrometer between 4000 and 400 cm^{-1} using KBr disks. Elemental analyses were determined with a VARIO EL (Heraeus). Melting points (Gallenkamp) are uncorrected. Mass spectra were recorded with a MAT-8230 (EI-MS, 70 eV). BCl$_3$ and BF$_3$(Et$_2$O) were used as purchased. **1** − **3** were prepared according to the literature [7, 8].

2-(Dimethylaminophenyl)diphenylmethanolatoborondichloride (4): A 100 ml Schlenk flask containing **1** (6.64 g, 10.7 mmol) was cooled to −78 °C and 50 ml of toluene was added. BCl_3 in pentane (1 M solution, 21.4 ml, 21.4 mmol) was added dropwise to this solution while stirring. The reaction mixture was stirred at r.t. for 4 h. The resulting suspension was filtered through celite to remove LiCl, the filtrate was concentrated to about 20 ml and cooled to −30 °C giving the product as colorless crystals in 90 % yield (3.69 g). Mp 170-175 °C.

^{1}H NMR (δ/ppm): 3.05 (s, 6H, $N(CH_3)_2$), 7.17-7.31 (m, 14H, C_6H_4 and C_6H_5). **^{13}C{^{1}H} NMR** (δ/ppm): 51.0 (s, $N(CH_3)_2$), 84.0 (s, CO), 119.9 (s, C6 in C_6H_4), 128.1 (s, C4 in C_6H_4), 128.6 (s, C3 in C_6H_4), 128.9 (s, C5 in C_6H_4), 129.1 (s, *p*-C in C_6H_5), 129.8 (s, *o*-C in C_6H_5), 132.4 (s, *m*-C in C_6H_5), 136.9 (s, C2 in C_6H_4), 143.8 (s, C1 in C_6H_4), 147.2 (s, *ipso*-C in C_6H_5). **^{11}B NMR** (δ/ppm): 8.6 (s). **IR** (KBr): 3053 w, 1603 m, 1583 m, 1491 s, 1470 s, 1445 s, 1430 m, 1207 m, 1171 vs, 1150 vs, 1130 vs, 1107 m, 1093 m, 1084 m, 1060 m, 1035 m, 1007 m, 993 m, 955 m, 930 m, 922 m-s, 897 m-s, 812 s, 789 vs, 761 vs, 742 s, 704 vs, 645 m, 637 s, 612 s, 599 m, 554 m cm^{-1}. **MS** found: *m/z* 382.8 (12 %, M^+), 347.9 (100 %, M^+-Cl), 305.8 (15 %, M^+-Ph), 285.9 (68 %, M^+-OBCl_2), 255.8 (18 %, $M^+-BCl_2-N(CH_3)_2$), 207.8 (35 %, M^+-OBCl_2-Ph), 164.8 (23 %, $M^+-OBCl_2-Ph-N(CH_3)_2$), 90.9 (93 %, $C_7H_7^+$), 76.9 (28 %, $C_6H_5^+$), 55.1 (18 %, $C_4H_7^+$), calc. for $C_{21}H_{20}BCl_2NO$: M = 383.1. Found: C 62.40; H 5.37; N 2.69 %. Calc. for $C_{21}H_{20}BCl_2NO{\cdot}H_2O$: C 62.72; H 5.51; N 3.48 %.

Phenyl ring numbering scheme:



2-(Dimethylaminophenyl)dicyclohexylmethanolatoborondichloride (5): The reaction was carried out as described for **4** except that **2** (6.88 g, 10.7 mmol) was used instead of **1**. Colorless crystals were obtained from diethyl ether at −10 °C in 90 % yield (3.81 g). Mp 180-185 °C.

^{1}H NMR (δ/ppm): 1.08-2.11 (m, 22H, C_6H_{11}), 3.29 (s, 6H, $N(CH_3)_2$), 7.34-7.48 (m, 4H, C_6H_4). **^{13}C{^{1}H} NMR** (δ/ppm): 27.2, 28.0, 28.3, 29.2, 30.8 (all s, C in C_6H_{11}), 49.3 (s, C1 in C_6H_{11}), 52.7 (s, $N(CH_3)_2$), 84.1 (s, CO), 120.7 (s, C6 in C_6H_4), 127.7 (s, C4 in C_6H_4), 128.7 (s, C3 in C_6H_4), 128.9 (s, C5 in C_6H_4), 141.2 (s, C2 in C_6H_4), 143.8 (C1 in C_6H_4). **^{11}B NMR** (δ/ppm): 7.9 (s). **IR** (KBr): 3019 m, 2985 m-s, 2919 vs, 2852 vs, 2669 w, 1488 vs, 1467 vs, 1447 vs, 1404 vs, 1328 m, 1308 m-s, 1278 m, 1233 m, 1205 m-s, 1168 vs, 1154 vs, 1130 vs, 1049 m, 1084 m, 1075 m, 1048 m-s, 987 s, 961 m-s, 951 m, 914 vs, 895 m-s, 871 m-s, 822 s, 789 vs, 767 vs, 745 m-s, 722 s, 701 vs, 677 m, 647 m-s, 608 s, 564 m-s, 558 m-s, 519 m cm^{-1}. **MS** found: *m/z* 359.9 (10 %, M^+-Cl), 311.9 (100 %, M^+-Cy), 275.9 (28 %, $M^+-Cy-Cl$), 232.0 (18 %, $M^+-Cy-Cl-N(CH_3)_2$), 213.9 (30 %, $M^+-Cy-OBCl_2$), 83.0 (30 %, $C_6H_{11}^+$), 55.1 (80 %, $C_4H_7^+$), calc. for $C_{21}H_{32}BCl_2NO$: M = 396.2. Found: C 63.50; H 9.28; N 3.59 %. Calc. for $C_{21}H_{32}BCl_2NO$: C 63.66; H 8.14; N 3.54 %.

2-(Dimethylaminophenyl)diphenylmethanolatoborondifluoride (6): A 100 ml Schlenk flask containing **1** (6.64 g, 10.7 mmol) was cooled to −78 °C and 50 ml of toluene was added. $BF_3(Et_2O)$ in diethyl ether (1 M solution, 21.4 ml, 21.4 mmol) was added dropwise to this solution. The reaction mixture was stirred at room temperature for 2 h. The resulting suspension was filtered through celite to remove LiF, the resulting filtrate was concentrated to about 20 ml and cooled to −20 °C to give the product as colorless crystals in 85 % yield (3.19 g). Mp 190-192 °C.

^{1}H NMR (δ/ppm): 2.96 (s, 6H, $N(CH_3)_2$), 7.14-7.50 (m, 14, C_6H_4 and C_6H_5). **^{13}C{^{1}H} NMR** (δ/ppm): 47.9 (s, $N(CH_3)_2$), 82.4 (CO), 119.7 (s, C6 in C_6H_4), 127.1 (s, C4 in C_6H_4), 127.7 (s, C3 in C_6H_4), 128.1 (s, C5 in C_6H_4), 128.6 (s, *p*-C in C_6H_5), 129.3 (s, *o*-C in C_6H_5), 132.0 (s, *m*-C in C_6H_5), 137.0 (s, C2 in C_6H_4), 144.6 (s, C1 in C_6H_4), 147.8 (s, *ipso*-C in C_6H_5). **^{11}B NMR** (δ/ppm): 1.9 (s). **^{19}F NMR** (δ/ppm): −156.9 (s). **IR** (KBr): 3033 w, 1583 m, 1488 m-s, 1474 s, 1445 s, 1283 w, 1260 m, 1203 vs, 1176 vs, 1124 vs, 1101 vs, 1086 s, 1060 m, 1047 m-s, 1034 m, 1004 m, 960 m-s, 926 m, 906 vs, 881 vs, 863 s, 785 vs, 778 vs, 770 vs, 746 m-s, 726 vs, 703 vs, 664 m, 651 w, 639 s, 566 w cm^{-1}. **MS** found: *m/z* 351.3 (10 %, M^+), 303.2 (55 %, M^+-BF_2), 287.2 (15 %, M^+-OBF_2), 274.1 (25 %, M^+-Ph), 258.1 (15 %, $M^+-BF_2-N(CH_3)_2$), 226.1 (58 %, M^+-BF_2-Ph), 210.1 (72 %, M^+-OBF_2-Ph), 180.0 (18 %, $M^+-BF_2-Ph-N(CH_3)_2$), 91.0 (100 %, $C_7H_7^+$), 77.0 (80 %, $C_6H_5^+$), 55.1 (45 %, $C_4H_7^+$), calc. for $C_{21}H_{20}BF_2NO$: M = 351.2. Found: C 71.00; H 4.99; N 3.70 %. Calc. for $C_{21}H_{20}BF_2NO$: C 71.82; H 5.74; N 3.99 %.

2-(Dimethylaminophenyl)dicyclohexylmethanolatoborondifluoride (7): The reaction was carried out as described for **6** except that **2** (6.88 g, 10.7 mmol) was used instead of **1**. Colorless crystals were

Table 3 Crystal data and structure refinement for **3** − **6**

	3	**4**	**5**	**6**
formula	$C_{42}H_{42}Li_2N_4{\cdot}C_7H_8$	$C_{21}H_{20}BCl_2NO{\cdot}0.5\ C_6H_5CH_3$	$C_{21}H_{32}BCl_2NO$	$C_{21}H_{20}BF_2NO$
M_r	708.81	430.16	396.19	351.19
temp /K	208(2)	220(2)	223(2)	210(2)
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a /Å	12.253(2)	8.6297(9)	7.328(2)	9.482(1)
b /Å	12.366(2)	13.376(1)	13.090(3)	10.065(1)
c /Å	14.593(2)	18.878(2)	21.199(5)	18.212(2)
α /°	78.285(4)	90	90	90
β /°	86.969(3)	95.781(2)	90.46(1)	90
γ /°	67.467(3)	90	90	90
V /Å^3	1998.9(5)	2168.1(4)	2033.5(8)	1738.1(3)
Z	2	4	4	4
$d_{calcd.}$ Mg m^{-3}	1.178	1.318	1.294	1.342
$F(000)$	756	900	848	736
crystal size /mm	0.20 x 0.20 x 0.05	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.30	0.80 x 0.40 x 0.20
abs coeff /mm^{-1}	0.068	0.316	0.33	0.096
no. of rflns collec.	13288	13348	13032	10721
no. of indep rflns	8158	4736	4833	4102
R_{int}	0.0651	0.0413	0.0351	0.0205
no. of params	696	300	237	315
$R1$ ($I > 2\sigma(I)$)	0.0786	0.0451	0.0431	0.0297
w$R2$ (all data)	0.2029	0.1204	0.106	0.0648
$(\Delta/\rho)_{min/max}$ /e Å^{-3}	0.216/−0.231	0.345/−0.267	0.292/−0.274	0.117/−0.219

obtained from diethyl ether at −10 °C in 90 % yield (3.49 g). Mp 178-180 °C.

^{1}H NMR (δ/ppm): 1.11-2.04 (m, 22H, C_6H_{11}), 3.02 (s, 6H, $N(CH_3)_2$), 7.26-7.42 (m, 4H, C_6H_4). **^{13}C{^{1}H} NMR** (δ/ppm): 26.5, 27.2, 27.6, 28.2, 29.2 (all s, C in C_6H_{11}), 49.1 (s, C1 in C_6H_{11}), 49.5 (s, $N(CH_3)_2$), 82.3 (s, CO), 120.2 (s, C6 in C_6H_4), 127.2 (s, C4 in C_6H_4), 127.4 (s, C3 in C_6H_4), 128.1 (s, C5 in C_6H_4), 139.2 (s, C2 in C_6H_4), 144.7 (s, C1 in C_6H_4). **^{11}B NMR** (δ/ppm): 1.3 (s). **^{19}F NMR** (δ/ppm): −154.4 (s). **IR** (KBr): 2935 vs, 2855 vs, 2748 m-s, 2531 m, 1615 m, 1583 m, 1445-1370 vs, br., 1306 s, 1279 m, 1264 m, 1244 m-s, 1228 m-s, 1196 vs, 1172 m, 1125 m, 1097 m, 1085 m, 1074 m, 1046 m-s, 990 s, 947 m, 893 m, 817 s, 765 vs, 731 s, 677 s, 652 m, 584 w, 557 m-s, 547 m-s, 519 m-s, 482 m cm^{-1}. **MS** found: *m/z* 280.3 (100 %, $M^+-C_6H_{11}$), 260.3 (5 %, $M^+-F-C_6H_{11}$), 214.2 (15 %, $M^+-OBF_2-C_6H_{11}$), 132.1 (35 %, $M^+-OBF_2-2C_6H_{11}$), 91.1 (15 %, $C_7H_7^+$), 83.0 (30 %, $C_6H_{11}^+$), 77.1 (15 %, $C_6H_5^+$), 55.1 (80 %, $C_4H_7^+$), calc. for $C_{21}H_{32}BF_2NO$: M = 363.0. Found: C 64.40; H 7.32; N 3.17 %. Calc. for $C_{21}H_{32}BF_2NO \cdot H_2O$: C 66.15; H 8.99; N 3.67 %.

2-(Phenylamidoborondichloride-phenyl)methyl-dimethylaminobenzene (8): The reaction was carried out as described for **4** except that **3** (6.60 g, 10.7 mmol) was used instead of **1**. The product was obtained from toluene at 25 °C in 90 % yield (3.69 g). Mp 185-195 °C.

^{1}H NMR (δ/ppm): 3.19 (s, 1H, CH), 3.55 (br. s, 3H, $N(CH_3)_2$), 3.67 (s, 3H, $N(CH_3)_2$), 6.92-7.55 (m, 14H, C_6H_4 and C_6H_5). **^{13}C{^{1}H} NMR** (δ/ppm): 49.0 (s, $N(CH_3)_2$), 58.0 (s, CH), 115.0 (s, C6 in C_6H_4), 120.0 (s, C4 in C_6H_4), 127.8 (s, C3 in C_6H_4), 128.5 (s, C5 in C_6H_4), 128.9 (s, *p*-C in C_6H_5), 129.3 (s, *o*-C in C_6H_5), 129.7 (s, *m*-C in C_6H_5), 130.5 (s, C2 in C_6H_4), 131.8 (s, C1 in C_6H_4), 150.0 (s, *ipso*-C in C_6H_5). **^{11}B NMR** (δ/ppm): 9.8 (s). **IR** (KBr): 3064 w, 2922 vs, 2851 vs, 2671 w, 1633 m, 1582 w, 1490 m-s, 1475 s, 1447 vs, 1409 m, 1301 w, 1254 s, 1186 vs, 1146 vs, 1125 vs, 1093 vs, 1051 s, 965 m, 932 m, 895 s, 873 vs, 851 s, 802 m, 771 s, 760 s, 746 s, 702 m, 684 w, 661 w, 648 w, 612 m, 567 m, 547 w, 522 m cm^{-1}. **MS** found: *m/z* 302.3 (35 %, M^+-BCl_2), 287.3 (10 %, $M^+-BCl_2-CH_3$), 210.2 (87 %, $M^+-BCl_2-CH_3-Ph$), 195.0 (35 %, $M^+-BCl_2-2CH_3-Ph$), 91.1 (100 %, $C_7H_7^+$), 77.1 (30 %, $C_6H_5^+$), 55.1 (80 %, $C_4H_7^+$), calc. for $C_{21}H_{21}BCl_2N_2$: M = 383.0. Found: C 65.90; H 5.46; N 6.88 %. Calc. for $C_{21}H_{21}BCl_2N_2$: C 65.84; H 5.53; N 7.31 %.

X-ray Crystallographic Study: Crystallographic data are given in Table 3. Data [$\lambda(Mo_{K\alpha}) = 0.71073$ Å] were collected with a Siemens CCD (SMART) diffractometer. Empirical absorption correction with SADABS [25]. The structure was solved by direct methods (SHELXTL PLUS [26]). H atoms were located by difference maps and refined isotropically for compounds **3** and **6**; for **4** and **5** the hydrogen atoms were placed in calculated positions and refined isotropically in the riding mode.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 244737 for **3**, CCDC 244738 for **4**, CCDC 244739 for **5** and CCDC 244740 for **6**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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