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Synthesis, Characterization, and Crystal Structures of Novel Intramolecularly Base-Stabilized Borane Derivatives with Six- and Seven-Membered Chelate Rings

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The reaction of (2-dimethylaminophenyl)alcohols 1-HOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**1**), X = CCy_2 (**2**), X = CPh_2CH_2 (**4**)] and 1-phenylaminoalkyl-2-dimethylaminobenzene 1-HN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**3**), C(H)$PhCH_2$ (**5**)] with BH_3(THF) yielded the BH_2 derivatives 1-H_2BOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**6**), CCy_2 (**7**), CPh_2CH_2 (**9**)] and 1-H_2BN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**8**), C(H)$PhCH_2$ (**10**)]. Treatment of 1-H_2BOCPh_2-2-$NMe_2C_6H_4$ (**6**) with acetic acid gave 1-(CH_3COO)$HBOCPh_2$-2-$NMe_2C_6H_4$ (**11**). Compounds **6**–**11** were characterized spectroscopically (NMR, IR, MS). Crystal structure determinations were carried out on **6**–**11**, which are novel examples of structurally characterized BH_2 derivatives containing six- or seven-membered chelate rings. For the chiral compounds **8**, **10**, and **11**, both enantiomers are present in the unit cell.

Introduction

Boron reagents with reactive boron-substituent bonds,[1−3] especially boranes with reactive B−H bonds, are of interest as starting materials for the preparation of transition metal−boron complexes, in medicinal chemistry, catalysis, and hydroboration reactions, and as precursors for polymers.[4,5] Borane (BH_3) alone is not stable but exists as either diborane (B_2H_6) or as complexes with Lewis bases. Diborane is a highly reactive gas that burns spontaneously when exposed to air and is rapidly hydrolyzed by water. Despite the vast array of useful organic reactions that diborane is able to perform, it is not frequently used as a gaseous reagent but instead as a base-stabilized complex.[6] Some of these amine−borane complexes are quite stable and available as neat liquids or pure solids. The stability, solubility, and ease of handling of amine boranes make them attractive sources in many organic reductions.[7] Furthermore, the wide variety of amines available to form borane complexes allows their chemical reactivity to be tuned according to the subtle differences in the structure and properties of the specific amine used.[7]

We recently described the (2-dimethylaminophenyl)alcohols 1-HOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**1**), X = CCy_2 (**2**), X = CPh_2CH_2 (**4**)] and 1-phenylaminoalkyl-2-dimethylaminobenzene 1-HN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**3**),

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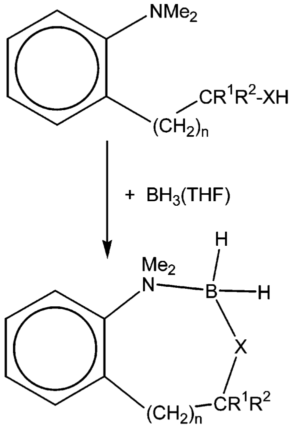
Scheme 1



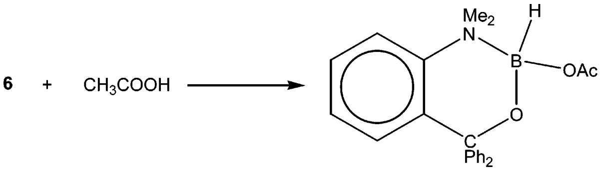
6: X = O; $R^1 = R^2$ = Ph; n = 0
7: X = O; $R^1 = R^2$ = Cy; n = 0
8: X = NPh; R^1 = H, R^2 = Ph; n = 0
9: X = O; $R^1 = R^2$ = Ph; n = 1
10: X = NPh; R^1 = H, R^2 = Ph; n = 1

C(H)PhCH$_2$ (**5**)],[8] which are useful for the formation of intramolecularly base-stabilized transition metal[9] and main group element compounds[1] with six- and seven-membered chelate rings.

We now report the high-yield synthesis, spectroscopic properties, and crystal structures of novel intramolecularly base-stabilized borane compounds 1-H_2BOX-2-$NMe_2C_6H_4$ [X = CPh$_2$ (**6**), CCy$_2$ (**7**), CPh$_2$CH$_2$ (**9**)], 1-H_2BN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**8**), C(H)PhCH$_2$ (**10**)], and 1-(CH$_3$-COO)HBOCPh$_2$-2-$NMe_2C_6H_4$ (**11**) with six- and seven-membered chelate rings.

Results and Discussion

Synthesis. The organic ligands 1-HOX-2-$NMe_2C_6H_4$ [X = CPh$_2$ (**1**), CCy$_2$ (**2**), CPh$_2$CH$_2$ (**4**)] and 1-HN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**3**), C(H)PhCH$_2$ (**5**)][8] react smoothly with BH$_3$(THF) in tetrahydrofuran and quantitatively at room temperature over 12 h to give the borane derivatives **6**−**10**, as illustrated in Scheme 1. The BH bond in these compounds is still reactive. Thus, borane **6** reacts with acetic acid in tetrahydrofuran to afford **11** (eq 1). The byproduct in all reactions is H$_2$ gas, which does not interfere in subsequent reactions. The colorless compounds **6**−**11** were obtained in 60−90% yield.



(**11**)

An alternative synthetic approach is the reaction of dihaloborane derivatives with LiAlH$_4$. Thus, compounds **6**−**8** are readily obtained from 1-Cl_2BOCR_2-2-$NMe_2C_6H_4$ (R = Ph, Cy)[1a] or 1-Cl_2BN(Ph)C(H)Ph-2-$NMe_2C_6H_4$[1a] and LiAlH$_4$ in 50−60% yield.

Spectroscopic Properties. ^{1}H NMR Spectra. The ^{1}H NMR spectra have the expected pattern characteristic for the organic ligands **1**−**5**. The N(CH$_3$)$_2$ protons appear as a singlet at 3.07 (**6**), 2.94 (**7**), 2.62 (**8**), 3.01 (**9**), and 2.81 ppm (**10**), while for **11**, which contains a chiral boron center, the diastereotopic methyl groups appear as two singlets at 3.00 and 3.04 ppm, i.e., shifted downfield in comparison with the parent organic ligands [2.38 (**1**), 2.65 (**2**), 2.61 (**3**), 2.74 (**4**), and 2.78 ppm (**5**)],[8] which is indicative of coordination of nitrogen to the boron atom. Moreover, the CH$_2$ protons appear as a broad singlet at 4.1 ppm (**9**), while in **10** these protons are diastereotopic and are observed as two doublets at 2.94 and 4.42 ppm, i.e., shifted downfield in comparison with the parent organic ligands [3.74 (**4**) and 2.93, 4.32 ppm (**5**)]. The CH protons appear as a singlet at 4.40 (**8**) and a doublet of doublets at 3.26 ppm (**10**), i.e., shifted downfield in comparison with the parent organic ligands [4.39 (**3**) and 3.20 ppm (**5**)]. The signals corresponding to the cyclohexyl (1.09−2.05 ppm) and aromatic protons (6.16−7.48 ppm) of each compound show the characteristic resonances in their expected chemical shift regions, similar to those observed for the organic ligands **1**−**5**. The CH$_3$ protons of the acetate group in **11** show a singlet at 1.83 ppm. The BH protons, if observed, show a broad signal in the range 1−3 ppm.

^{13}C NMR Spectra. The ^{13}C NMR spectra also have the expected pattern characteristic for the organic ligands **1**−**5**. The N(CH$_3$)$_2$ carbon atoms appear as singlets at 51.9 (**6**), 51.9 (**7**), 45.6 (**8**), 47.8 (**9**), and 45.4 ppm (**10**), while for **11**, the diastereotopic methyl groups are observed at 45.6 and 48.6 ppm, i.e., shifted slightly downfield for **6**−**9**, but slightly upfield for **10** in comparison with the parent organic ligands [46.3 (**1**), 47.3 (**2**), 45.5 (**3**), 45.4 (**4**), and 46.1 ppm (**5**)].[8] Moreover, the CH$_2$ carbon atoms appear as a singlet at 46.1 (**9**) and 41.0 ppm (**10**), i.e., shifted down- and upfield in comparison with the parent organic ligands [45.0 (**4**) and 42.0 ppm (**5**)].[8] The CH carbon atoms appear as a singlet at 46.2 (**8**) and 61.4 ppm (**10**) and are thus shifted upfield in comparison with the parent organic ligands [56.2 (**3**) and 62.1 ppm (**5**)].[8] The C−O carbon atoms are observed as singlets at 84.3 (**6**), 82.0 (**7**), 79.3 (**9**), and 82.7 ppm (**11**), i.e., shifted only slightly upfield (**7**, **11**) and downfield (**6**, **9**) in comparison with the parent organic ligands [83.6 (**1**), 84.6 (**2**), and 78.6 ppm (**4**)],[8] while the resonance at 52.8 ppm (**11**) is characteristic for the CH$_3$ carbon atom of the acetate group. The signals of the aromatic rings and the cyclohexyl carbon atoms are in the expected ranges, similar to those observed for the organic ligands **1**−**5**.

^{11}B NMR Spectra. The ^{11}B NMR chemical shifts of compounds **6**−**11** indicate that the geometric constraints play a major role in addition to the strength of the B−N interaction.[10] It is apparent that the ^{11}B chemical shift of the

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Table 1. Selected Bond Angles (deg) and Bond Lengths (Å) for **6**−**11**

	6	**7**	**8**	**9**	**10**	**11**
C(9)(or C(10))−O(1)(or N(2))−B	113.7(1)	117.6(2)	116.6(2)	123.6(1)	117.4(2)	115.2(1)
O(1)(or N(2))−B(1)−N(1)	106.1(1)	106.7(2)	106.2(3)	110.2(1)	110.3(2)	106.8(1)
O(1)−B−O(2)						110.3(1)
O(1)(or N(2))−B−H	115.8(8), 111.5(7)	110(1), 105(1)	114(1), 113(1)	119.0(6), 109.0(6)	113.9(9), 112(1)	118.4(7)
B(1)−O(1)(or N(2))	1.446(2)	1.443(3)	1.511(4)	1.433(2)	1.508(3)	1.432(2)
B(1)−N(1)	1.648(2)	1.638(3)	1.642(4)	1.672(2)	1.698(3)	1.638(2)
B(1)−O(2)						1.472(2)
B(1)−H	1.19(2), 1.10(2)	1.17(2), 1.12(3)	1.10(2), 1.15(2)	1.14(1), 1.14(1)	1.13(2), 1.15(2)	1.15(2)

borane complexes is primarily determined by the ring size. In the six-membered rings (**6**−**8**), δ values range from −2.5 to 2.3 ppm, while in the seven-membered rings (**9** and **10**), δ values range from 2.9 to 4.4 ppm (in $CDCl_3$). For **11**, a broad signal is observed at 3.2 ppm. All shifts are in a region specific for tetrahedrally coordinated boron atoms[1,3] with B−N interactions and lie to higher field by ca. 77 ppm relative to three-coordinate boranes (cf. 9-phenyl-9-borabicyclo[3.3.1]nonane, 80.4 ppm).[11] The corresponding tetracoordinate BX_2 [X = Cl (δ = 7.9−9.8 ppm), X = F (1.3−1.9 ppm)][1a] derivatives of **1**−**3** exhibit chemical shifts in the same range as **6**−**11**. 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,[12] in this larger seven-membered heterocycle, which is derived from **4**.

The ^{11}B NMR spectrum of the seven-membered ring compounds **9** and **10** are solvent-dependent; thus, in $CDCl_3$ the signal is observed at δ = 4.4 (**9**) or 2.9 ppm (**10**), while in THF-d_8 two additional weaker broad signals are observed at ca. 20 and ca. 30 ppm for **9**. The solubility of **10** in THF is very low, so no meaningful NMR spectra could be obtained. However, both compounds **9** and **10** are soluble (**10** less than **9**) in a 1:1 mixture of $CDCl_3$ and THF-d_8, and the ^{11}B NMR spectrum of **9** therein shows the same pattern as in THF-d_8 alone, while for **10** an additional intensive signal is observed at ca. 19 ppm. We assume that due to the competition of THF and the NMe_2 group in these seven-membered ring compounds the B−N bond is cleaved by THF and the signal of the resulting boron species is observed (in the range of ca. 20 ppm). In contrast, compound **6**, which has a six-membered ring, does not show any solvent dependency in $CDCl_3$, THF-d_8, or 1:1 mixtures thereof.

IR Spectra. The IR spectra of **6**−**11** show the B−N stretching vibration as one of the strongest bands between 1500 and 1444 cm^{-1}.[13] Two bands in the range 2379−2260 cm^{-1} can be assigned to the symmetric (2320−2260 cm^{-1}) and antisymmetric (2379−2317 cm^{-1}) BH_2 stretching vibrations in **6**−**10**.[14] Compound **11** shows a medium B−H stretching vibration at 2370 cm^{-1}.[3] A strong band at 1702 cm^{-1} characteristic of the carbonyl stretching frequency was present in the infrared spectrum of compound **11**. For **6**, **7**, **9**, and **11**, the band which appears in the range 1394−1321 cm^{-1} is attributed to the symmetric B−O stretching vibration.[15]

Mass Spectrometry. The mass spectra showed parent ion peaks at *m*/*z* 313.9 (**6**), 326.1 (**7**), 313.0 (**8**), 329.0 (**9**), 328.2 (**10**), and 371.5 (**11**), which agree with the calculated distribution pattern. There are many fragments, which are either comparable or identical for these closely related compounds.

Molecular Structures of 6−**11.** Colorless crystals of **6**−**11** were obtained as described in the Experimental Section. Selected interatomic distances and angles are collected in Table 1. The molecular structures are depicted in Figures 1−6.

The common feature of the molecular structures of **6**−**11** is intramolecular stabilization of the boron compounds by interaction with one amino group. The structural data (Table 1) of the X-C-aryl-NC_2 [X = O(1), N(2)] fragments are similar for **6** (Figure 1), **7** (Figure 2), **8** (Figure 3a), and **11** (Figure 6), and the structural data of the X-C-C-aryl-NC_2 [X = O(1), N(2)] fragments are similar for **9** (Figure 4) and **10** (Figure 5a).

Boranes **8** and **10** have a chiral C center [C(9) in **8**, C(10) in **10**]. They crystallize in noncentrosymmetric space groups ($P2_12_12_1$ for **8**, $P2_1$ for **10**). As the data sets were obtained with Mo Kα radiation, which has only little effect on the anomalous scattering, the absolute configuration could not be determined. Here, the *R* enantiomer was assumed to be present in the unit cell.[16] In compound **11**, there is a chiral B center; however, due to the centrosymmetric space group $P2_1/n$, both enantiomers are present in the unit cell.

The coordination of the amino group results in a puckered six-membered BXC_3N [X = O(1), N(2)] ring for **6**−**8** and **11**, with the C_3N fragment [C(9)−C(8)−C(3)−N(1)] being coplanar and B(1) and O(1) or N(2) lying above and below this plane [**6**, B(1) 0.521 Å, O(1) −0.293 Å; **7**, B(1) 0.551 Å, O(1) −0.184 Å; **8**, B(1) 0.849 Å, N(2) −0.134 Å; **11**, B(1) 0.532 Å, O(1) −0.234 Å]. The puckered seven-

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(16) Presumably, the crystalline material contains both enantiomeric forms.

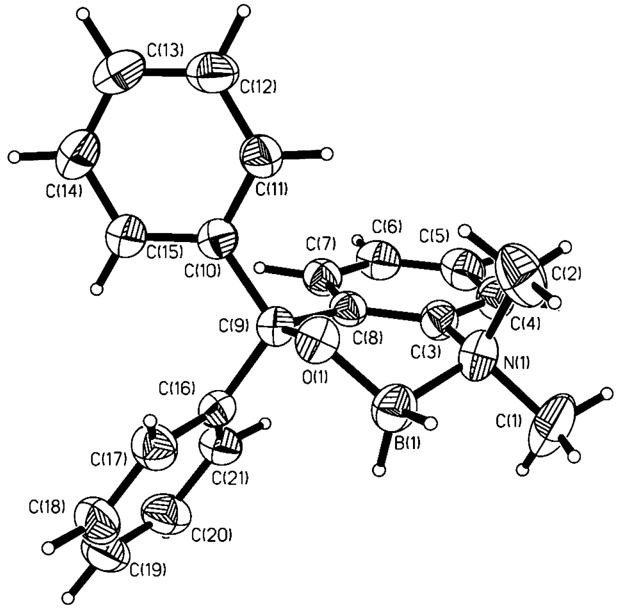

Figure 1. Molecular structure of **6** (ORTEP, 50% probability, SHELXTL PLUS, XP;[30] THF omitted for clarity).

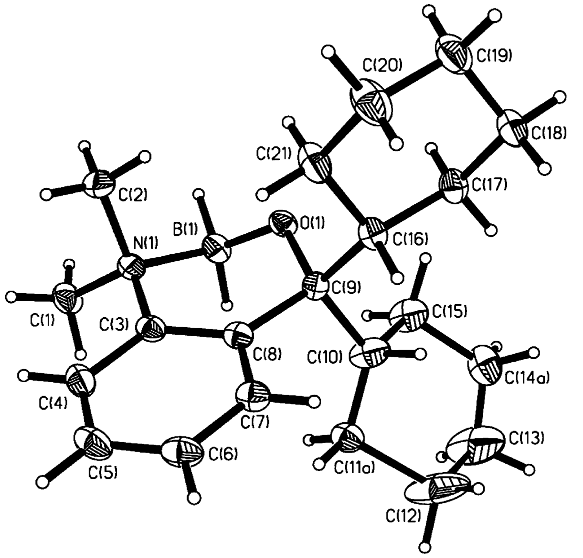

Figure 2. Molecular structure of **7** (ORTEP, 50% probability, SHELXTL PLUS, XP[30]).

membered BXC_4N [X = O(1), N(2)] rings in **9** and **10** have different conformations; in both compounds, the C_3N fragment [C(9)−C(8)-C(3)−N(1)] is coplanar, but in **9**, B(1) (0.343 Å) lies above this plane, and O(1) (−0.740 Å) and C(10) (−0.968 Å) lie below this plane, while in **10** all three atoms B(1) (0.367 Å), N(2) (1.544 Å), and C(10) (1.264 Å) lie above this plane. Representative examples of the central six- and seven-membered rings (compounds **8** and **10**) are given in Figures 3b and 5b. The puckering parameters according to Pople and Cremer[17] were determined and are in agreement with a half-boat conformation of the six-membered rings (Table 3) and a twist-boat conformation of the seven-membered rings (puckering parameters for **9** are $\Phi_2 = 13.0°$, $\Phi_3 = -42.6°$, $\Theta_2 = 65.68°$; for **10**, $\Phi_2 = 38.8°$, $\Phi_3 = -37.8°$, $\Theta_2 = 72.0°$).

This leads to a distorted tetrahedral environment at B(1) with a small X−B−N [X = O(1), N(2)] bite angle [**6**, 106.1(1)°; **7**, 106.7(2)°; **8**, 106.2(3)°; **9**, 110.2(1)°; **10**, 110.3(2)°; **11**, 106.8(1)°], large X−B−H [X = O(1), N(2)] bond angle [**6**, 115.0(8)°, 111.5(7)°; **8**, 114(1)°, 113(1)°; **10**, 113.9(9)°, 112(1)°], or one large and one small O−B−H bond angle [**7**, 110(1)°, 105(1)°; **9**, 119.0(6)°, 109.0(6)°; **11**, O(1)−B−H 118.4(7)°, O(1)−B−O(2) 110.3(1)°].

The structural data of the X−B−N [X = O(1), N(2)] bond angles in **6**−**11** differ remarkably from those of the strained five-membered BC_3N rings in $B(OCH_2CPh_2O)\{2,6\text{-}(NMe_2CH_2)_2C_6H_3\}$,[18] $BCl_2\{2,6\text{-}(NEt_2CH_2)_2C_6H_3\}$, $BCl_2\{2\text{-}N(BCl_3)Et_2CH_2\text{-}6\text{-}(NEt_2CH_2)C_6H_3\}$, $BCl_2\{2\text{-}(NMe_2CH_2)C_6H_4\}$,[2] and $BX_2\{2\text{-}(NR_2CH_2)C_6H_4\}$ (R = Me, Et, BX_2 = 9-borabicyclo-[3.3.1]nonane; R = Me, X = OCH_2CPh_2O),[19] the C−B−N bond angles of which [94.7(2)°, 95.2(1)°, and 95.7(2)°] are much smaller than the X−B−N [X = O(1), N(2)] bond angles of **6**−**11**, while the O−B−N bond angles [109.2(1)° and 110.0(1)°] of the BOC_3N six-membered rings in $BCl_2\{2\text{-}(NEt_2CH_2)OC_6H_4\}$ and $[BCl_2\{2\text{-}NHEt_2CH_2\text{-}6\text{-}(NEt_2CH_2)\text{-}OC_6H_3\}]Cl$[3] are larger than the X−B−N [X = O(1), N(2)] bond angles of **6**−**8** and **11** and comparable to those of **9** [110.2(1)°] and **10** [110.3(2)°]. The seven-membered rings show highly distorted bond angles about N(1) [bond angles range for **9** from 105.1(1)° to 115.27(9)°, and for **10** from 105.3(1)° to 117.3(1)°].

A comparison of the structural data of the O−B−N bond angles in $1\text{-}Y_2BOX\text{-}2\text{-}NMe_2C_6H_4$ [X = CPh_2, Y = Cl (**12**), 109.9(2)°; X = CCy_2, Y = Cl (**13**), 109.2(1)°; X = CPh_2, Y = F (**14**), 108.4(1)°][1a] with those of the six-membered BXC_3N [X = O(1), N(2)] rings in **6** [106.1(1)°], **7** [106.7(2)°], **8** [106.2(3)°], and **11** [106.8(1)°] shows that the O−B−N bond angles in **12**−**14** are much larger than the X−B−N [X = O(1), N(2)] bond angles observed for **6**−**8** and **11**, while the O−B−N bond angles in **9** and **10** are much larger than the X−B−N [X = O(1), N(2)] bond angles observed for **6**−**8** and **11**, and only slightly larger than those in **12**−**14**.

These data for the six-membered BOC_3N rings in **12**−**14** are comparable with those of the six-membered BXC_3N [X = O(1), N(2)] rings in the borane complexes **6**−**8** and **11** and the seven-membered BXC_4N [X = O(1), N(2)] rings in **9** and **10**. The C−X−B [X = O(1), N(2)] bond angles in **6** [113.7(1)°], **7** [117.6(2)°], **8** [116.6(2)°], and **11** [115.2(1)°] are much smaller than those observed for **12**−**14** [122.5(1)−124.0(2)°] and **9** [123.6(1)°] and similar to those observed for **10** [117.4(2)°].

The range of bond angles about B(1) in **9** [from 102.0(6)° to 119.0(6)°] is larger than those in **6** [from 103.8(8)° to 115.5(8)°], **7** [from 104.5(9)° to 115(1)°], **8** [from 102.9(1)° to 113.0(1)°], **10** [from 103.1(8)° to 113.9(9)°], **12** [from 108.8(2)° to 114.6(2)°], **13** [from 107.8(1)° to 117.5(1)°], and **14** [from 108.4(1)° to 115.8(1)°].

The B−O bonds in **12**−**14** [1.391(2)−1.409(2) Å] are shorter than those in the borane complexes **6** [1.446(2) Å],

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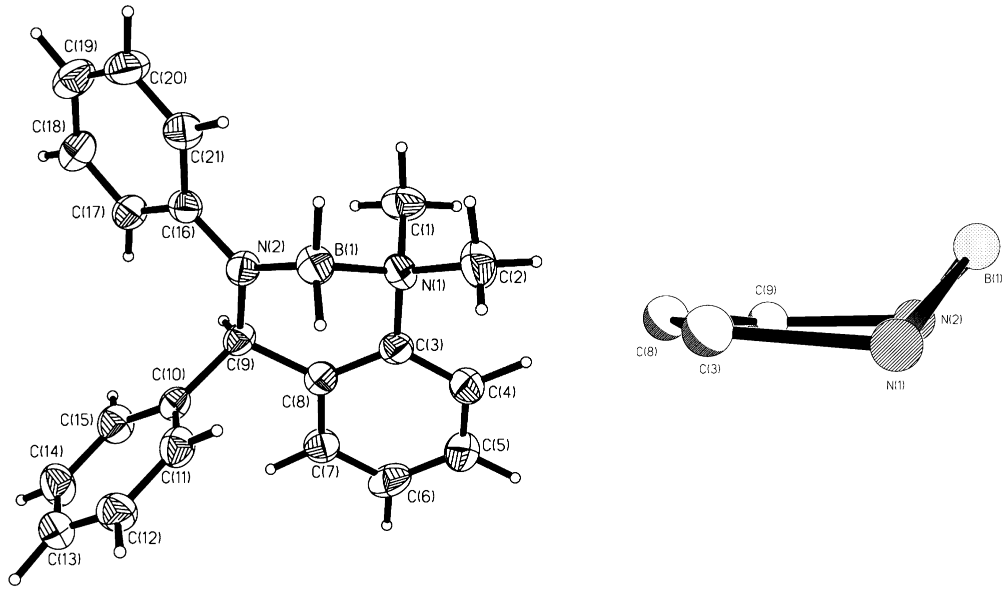

(a) (b)

Figure 3. (a) Molecular structure of **8** (ORTEP, 50% probability, SHELXTL PLUS, XP[30]) and (b) half-boat conformation of the six-membered ring in **8**.

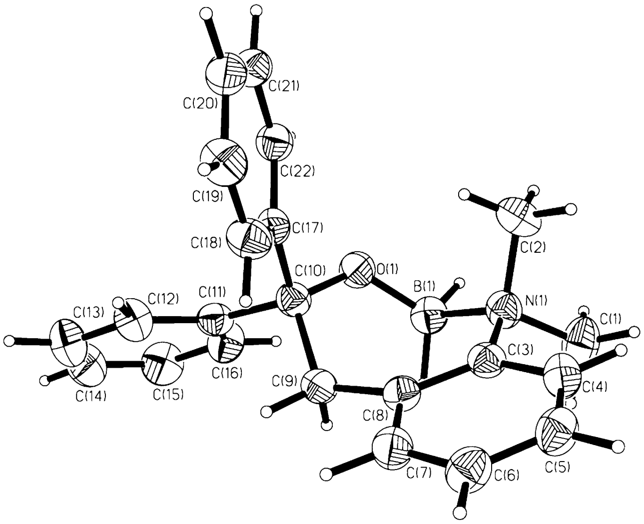

Figure 4. Molecular structure of **9** (ORTEP, 50% probability, SHELXTL PLUS, XP[30])

7 [1.443(3) Å], **8** [1.511(4) Å], **11** [1.432(2) Å], and the B−N bonds in **12**−**14** [1.626(2)−1.642(2) Å], **6** [1.648(2) Å], **7** [1.638(3) Å], **8** [1.642(4) Å], and **11** [1.638(2) Å] are shorter than those in the borane complexes **9** [1.672(2) Å] and **10** [1.698(3) Å].

The B−N bond lengths of **6**−**8** and **11** are comparable to those of related dichloroborane derivatives[2] and those of dialkyl- or dialkoxyborane compounds with BC_3N rings.[18,19] Also, the B−N bond lengths in **6**−**11** are longer than those of the adducts $BCl_3(NMe_3)$ [B−N 1.575(10) Å],[20] $BCl_3(py)$ [B−N 1.592(3) Å],[21] and $BCl_3(NCMe)$ [B−N 1.562(8) Å].[22]

These data for the six-membered BXC_3N [X = O(1), N(2)] rings in **6**−**8** and **11** are comparable with those of the BOC_3N six-membered rings in $BCl_2\{2\text{-}(NEt_2CH_2)OC_6H_4\}$ and $[BCl_2\{2\text{-}NHEt_2CH_2\text{-}6\text{-}(NEt_2CH_2)OC_6H_3\}]Cl$.[3] The C−O−B bond angles [119.9(1)° and 122.8(1)°] are larger, 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 **6**−**11**, and the B−O [1.425(2) and 1.420(2) Å] and the B−N bonds [1.633(2) and 1.627(2) Å] are similar to those observed for **6**−**8** and **11**, but shorter than those for **9** and **10**.

The cyclic six-membered ring compound $B(CF_3)_2NMe_2\text{-}CH(Me)CMe{=}C(H)O$[23] has similar B−N [1.64(1) Å] and B−O bond lengths [1.45(1) Å] to **6**−**8** and **11**. Other structurally characterized examples of intramolecularly base-stabilized six-membered boron-containing rings are B(cat)-$\{2\text{-}(NHPhCH_2)OC_6H_4\}$[24] and $BPh_2\{2\text{-}(CHO)OC_6H_4\}$.[25] Here, the NHPh or C═O group is coordinated to the boron atom [B−N 1.636(4) Å; B−O 1.496(4) Å], which exhibits a distorted tetrahedral environment. The bond angles range from 106.0(2)° to 114.9(3)°, which is in the range found in **6**−**8** and **11**, while the B−O bond is longer than those observed for **6**, **7**, and **11**.

Only a few boron compounds containing seven-membered chelate rings involving bidentate ligands have been reported in the literature,[26−28] and the structural data show that the C−O−B bond angles [124.5(2)°, 125.8(2)°, and 126.2(2)°] are larger than those observed for C−X−B [X = O(1), N(2)] in **9** and **10**. The B−O bonds [1.494(4), 1.481(4), and 1.449(3) Å] are slightly longer than the B−O bond in **9**, and the

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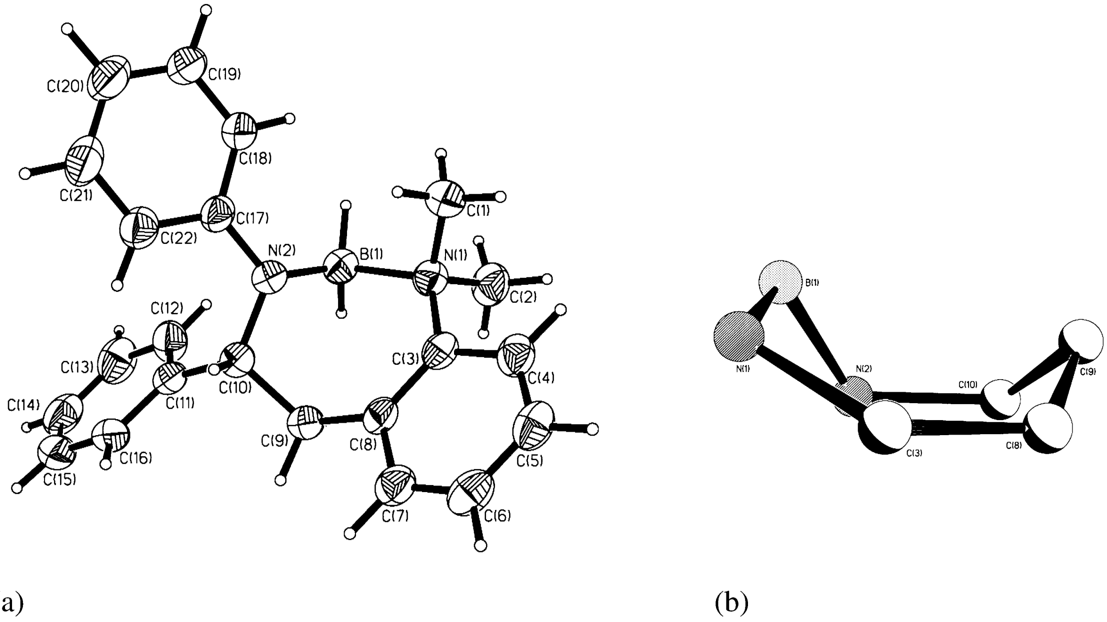

Figure 5. (a) Molecular structure of **10** (ORTEP, 50% probability, SHELXTL PLUS, XP[30]) and (b) twist-boat conformation of the seven-membered ring in **10**.

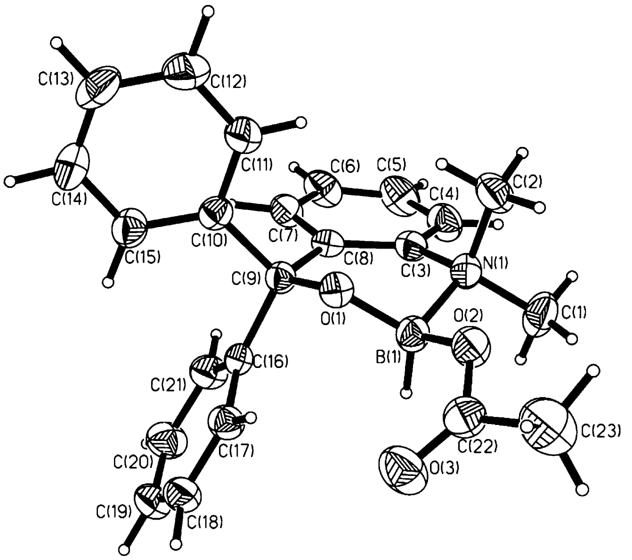

Figure 6. Molecular structure of **11** (ORTEP, 50% probability, SHELXTL PLUS, XP;[30] both enantiomers are present in the unit cell, only the *R* enantiomer is shown).

range of bond angles about B(1) [from 108.1(3)° to 117.4(3)°, from 106.0(2)° to 111.5(2)°, and from 103.7(2)° to 111.3(2)°] is in the range found in **9** and **10**.

The bond lengths and angles of the organic fragments of **6**−**11** are similar to those observed for the corresponding organic compounds **1**−**5**.[8]

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). ^1H (400.13 MHz) and ^{13}C NMR spectra (100.63 MHz) were measured with tetramethylsilane as external standard. ^{11}B NMR spectra (128.38 MHz) were measured with $BF_3(OEt_2)$ 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). $BH_3(THF)$ was used as purchased. The (2-dimethylaminophenyl)alcohols 1-HOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**1**), X = CCy_2 (**2**), X = CPh_2CH_2 (**4**)] and 2-phenylaminoalkyl-dimethylaminobenzene 1-HN(Ph)X-2-$NMe_2C_6H_4$ [X = C(H)Ph (**3**), C(H)$PhCH_2$ (**5**)] were prepared according to the literature.[8]

(2-Dimethylaminophenyl)diphenylmethoxyborane (6). A 16 mL portion of $BH_3(THF)$ in THF (1 M solution) was added dropwise at −20 °C to a solution of 1-$HOCPh_2$-2-$NMe_2C_6H_4$ (**1**) (5 g, 0.016 mol) in THF (100 mL). The reaction mixture was then warmed to room temperature and stirred for 12 h. The volume was reduced to 50 mL, the reaction mixture was cooled to −30 °C, and a colorless solid was obtained that was recrystallized from a THF/pentane solution (1/4) at −10 °C to give the product as colorless crystals. Yield: 4.54 g (90%). Mp 188−189 °C. ^1H NMR (δ/ppm): 1.85 (m, 2H, THF), 2−3 (v br, 2H, BH_2), 3.07 (s, 6H, $N(CH_3)_2$), 3.75 (m, 2H, THF), 7.15−7.33 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 26.3 (THF), 51.9 (s, $N(CH_3)_2$), 68.7 (s, THF), 84.3 (s, C−O), 121.3 (s, C6 in C_6H_4), 127.38 (s, C4 in C_6H_4), 127.44 (s, C3 in C_6H_4), 128.1 (s, C5 in C_6H_4), 128.3 (s, *p*-C in C_6H_5), 129.3 (s, *o*-C in C_6H_5), 133.3 (s, *m*-C in C_6H_5), 139.0 (s, C2 in C_6H_4), 146.7 (s, C1 in C_6H_4), 149.5 (s, *ipso*-C in C_6H_5). ^{11}B NMR (δ/ppm): 2.3 (br s). IR: 2379 vs ($\nu_{as}(BH_2)$), 2309 m ($\nu_s(BH_2)$) cm^{-1}. MS found: *m*/*z* 313.9 (42%, M^+ − H), and fragmentation products thereof; calcd for $C_{21}H_{22}BNO \cdot 1/2THF$: M = 351.24. Found: C 78.70; H 7.83; N 4.09%. Calcd for $C_{21}H_{22}BNO \cdot 1/2THF$: C 78.64; H 7.46; N 3.99%.

(2-Dimethylaminophenyl)dicyclohexylmethoxyborane (7). A similar procedure as that described for **6** was used here except that 5.04 g (0.016 mol) of 1-$HOCCy_2$-2-$NMe_2C_6H_4$ (**2**) was used instead of **1**. Colorless crystals were obtained from a CH_2Cl_2/hexane solution (1/3) at 20 °C. Yield: 3.67 g (70%). Mp 197−200 °C. ^1H NMR (δ/ppm): 1.09−1.3 (m, 6H, Cy), 1.3−1.39 (m, 6H, Cy), 1.58−1.65 (m, 4H, Cy), 1.77−1.79 (m, 2H, Cy), 1.88 (m, 2H, Cy), 2.05 (m, 2H, Cy), 2.94 (s, 6H, $N(CH_3)_2$), 7.24 (m, 3H, C_6H_4), 7.38 (m, 1H, C_6H_4), BH_2 is too broad to be observed. ^{13}C NMR

Table 2. Crystal Data and Structure Refinement for **6**−**11**

	6	**7**	**8**	**9**	**10**	**11**
formula	$C_{21}H_{22}BNO\cdot 0.5THF$	$C_{21}H_{34}BNO$	$C_{21}H_{23}BN_2$	$C_{22}H_{24}BNO$	$C_{22}H_{25}BN_2$	$C_{23}H_{24}BNO_3$
M_r	351.24	327.32	314.22	329.23	328.25	373.24
temp (K)	220(2)	223(2)	223(2)	220(2)	223(2)	220(2)
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P2_1$	$P2_1/n$
a (Å)	9.7634(5)	10.525(2)	6.2803(9)	9.6979(9)	11.079(2)	14.8691(8)
b (Å)	13.5487(7)	16.133(3)	13.385(2)	10.3428(9)	7.588(1)	9.3989(5)
c (Å)	15.3285(8)	11.463(2)	20.519(3)	18.351(2)	11.595(2)	15.3368(8)
α (deg)	90	90	90	90	90	90
β (deg)	107.6(1)	101.962(3)	90	104.083(2)	110.306(3)	113.102(1)
γ (deg)	90	90	90	90	90	90
V (Å^3)	1933.2(2)	1904.1(5)	1724.9(4)	1785.4(3)	914.2(2)	1971.5(2)
Z	4	4	4	4	2	4
ρ_{calcd} (Mg m^{-3})	1.207	1.142	1.21	1.225	1.192	1.257
F(000)	752	720	672	704	352	792
abs coeff (mm^{-1})	0.074	0.068	0.07	0.073	0.069	0.082
no. reflns collected	11651	12353	4784	10857	5540	11947
no. indep reflns	4215	4613	3054	3907	3780	4294
R_{int}	0.0261	0.0446	0.0413	0.0252	0.0214	0.0347
no. params	351	254	309	323	326	340
R1 ($I > 2\sigma(I)$)	0.0468	0.0708	0.0371	0.0387	0.0395	0.0433
wR2 (all data)	0.1377	0.2235	0.0821	0.113	0.096	0.1208
$(\Delta/\rho)_{min}$ (e Å^{-3})	0.296	0.6	0.129	0.163	0.116	0.236
$(\Delta/\rho)_{max}$ (e Å^{-3})	−0.213	−0.355	−0.147	−0.174	−0.149	−0.171

Table 3. Puckering Parameter for the Six-Membered Chelate Rings According to Cremer and Pople,[17] Which Indicate an Envelope or Half-Boat Conformation

compd	q_2	q_3	Φ_2	Θ
6	0.428	0.333	20.54	52.12
7	0.358	0.342	12.26	46.34
8	0.470	0.295	7.81	57.92
11	0.357	0.373	15.24	43.78

(δ/ppm): 27.3 (s, C4 in Cy), 28.0 (s, C3/C5 in Cy), 28.5 (s, C3/C5 in Cy), 28.9 (s, C2/C6 in Cy), 30.8 (s, C2/C6 in Cy), 49.2 (s, C1 in Cy), 51.9 (s, $N(CH_3)_2$), 82.0 (s, C−O), 121.0 (s, C6 in C_6H_4), 127.5 (s, C4 in C_6H_4), 128.6 (s, C3 in C_6H_4), 129.0 (s, C5 in C_6H_4), 142.7 (s, C2 in C_6H_4), 147.1 (s, C1 in C_6H_4). ^{11}B NMR (δ/ppm): 2.0 (br s). IR: 2376 vs ($\nu_{as}(BH_2)$), 2320 vs ($\nu_s(BH_2)$) cm^{-1}. MS found: m/z 326.1 (10%, $M^+ - H$), and fragmentation products thereof; calcd for $C_{21}H_{34}BNO$: M = 327.32. Found: C 74.75; H 10.28; N 3.83%. Calcd for $C_{21}H_{34}BNO\cdot 0.5H_2O$: C 75.00; H 10.49; N 4.17%. Compound **7** is hygroscopic.

2-[(Phenylamidoboranyl)phenylmethyl]dimethylaminobenzene (8). The reaction was carried out as described for **6** except that 4.83 g (0.016 mol) of 1-HN(Ph)C(H)Ph-2-$NMe_2C_6H_4$ (**3**) was used instead of **1**. Colorless crystals were obtained from diethyl ether at −10 °C. Yield: 3.27 g (65%). Mp 230−234 °C. ^{1}H NMR (δ/ppm): 2.62 (s, 6H, $N(CH_3)_2$), 4.40 (s, 1H, CH), 6.16 (m, 1H, C_6H_4), 6.56 (m, 2H, C_6H_4), 6.7 (m, 1H, C_6H_4), 7.00−7.36 (m, 10H, C_6H_4 and C_6H_5), BH_2 too broad to be observed. ^{13}C NMR (δ/ppm): 45.6 (s, $N(CH_3)_2$), 46.2 (s, 1H, CH), 113.2 (s, C6 in C_6H_4), 117.2 (s, C4 in C_6H_4), 120.7 (s, C3 in C_6H_4), 126.7 (s, C5 in C_6H_4), 127.5 (s, *p*-C in C_6H_5), 128.3 (s, *o*-C in C_6H_5), 128.7 (s, *m*-C in C_6H_5), 129.1 (s, C2 in C_6H_4), 140.0 (s, C1 in C_6H_4), 147.2 (s, *ipso*-C in C_6H_5). ^{11}B NMR (δ/ppm): −2.5 (br s). IR: 2317 m ($\nu_{as}(BH_2)$), 2292 m ($\nu_s(BH_2)$) cm^{-1}. MS found: m/z 313.0 (100%, $M^+ - H$), and fragmentation products thereof; calcd for $C_{21}H_{23}N_2$: M = 314.22. Found: C 76.80; H 6.87; N 8.42%. Calcd for $C_{21}H_{23}BN_2\cdot H_2O$: C 75.92; H 7.58; N 8.43%. Compound **8** is hygroscopic.

2-(2-Dimethylaminophenyl)-1,1-diphenylethoxyborane (9). A similar procedure as that described for **6** was used here, except that 5.07 g (0.016 mol) of 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**4**) was used instead of **1**. Colorless crystals were obtained from THF at 20 °C. Yield: 3.69 g (70%). Mp 161−163 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): 3.01 (s, 6H, $N(CH_3)_2$), 4.1 (br s, 2H, CH_2), 6.55−7.48 (m, 14H, C_6H_4 and C_6H_5), BH_2 too broad to be observed. ^{13}C NMR ($CDCl_3$, δ/ppm): 46.1 (s, CH_2), 47.8 (s, $N(CH_3)_3$), 79.3 (s, C−O), 120.7 (s, C6 in C_6H_4), 123.3 (s, C4 in C_6H_4), 125.8 (s, C3 in C_6H_4), 127.2 (s, C5 in C_6H_4), 128.3 (s, *p*-C in C_6H_5), 128.5 (s, *o*-C in C_6H_5), 134.0 (s, *m*-C in C_6H_5), 134.2 (s, C2 in C_6H_4), 148.6 (s, C1 in C_6H_4), 152.5 (s, *ipso*-C in C_6H_5). ^{11}B NMR ($CDCl_3$, δ/ppm): 4.4 (br s). ^{1}H NMR (THF-d_8, δ/ppm): 2.67 (s, 6H, $N(CH_3)_2$), 3.72 (s, 2H, CH_2), 6.7 (m, 2H, C_6H_4 and C_6H_5), 7.03 (m, 3H, C_6H_4 and C_6H_5), 7.13 (m, 5H, C_6H_4 and C_6H_5), 7.45 (m, 4H, C_6H_4 and C_6H_5), BH_2 too broad to be observed. ^{13}C NMR (THF-d_8, δ/ppm): 45.7 (s, CH_2), 47.1 (s, $N(CH_3)_3$), 80.0 (s, C−O), 120.7 (s, C6 in C_6H_4), 125.2 (s, C4 in C_6H_4), 126.4 (s, C3 in C_6H_4), 127.1 (s, C5 in C_6H_4), 127.9 (s, *p*-C in C_6H_5), 128.1 (s, *o*-C in C_6H_5), 134.0 (s, *m*-C in C_6H_5), 134.3 (s, C2 in C_6H_4), 149.5 (s, C1 in C_6H_4), 153.3 (s, *ipso*-C in C_6H_5). ^{11}B NMR (THF-d_8, δ/ppm): 20.1 (br s). IR: 2354 m-s ($\nu_{as}(BH_2)$), 2262 m ($\nu_s(BH_2)$) cm^{-1}. MS found: m/z 329.0 (32%, M^+), and fragmentation products thereof; calcd for $C_{22}H_{24}BNO$: M = 329.23. Found: C 79.70; H 7.12; N 4.35%. Calcd for $C_{22}H_{24}BNO$: C 80.26; H 7.35; N 4.25%.

[2-(2-Phenylamidoboranyl)-2-phenylethyl]dimethylaminobenzene (10). A similar procedure to that described for **6** was used here, except that 5.06 g (0.016 mol) of 1-HN(Ph)C(H)$PhCH_2$-2-$NMe_2C_6H_4$ (**5**) was used instead of **1**. Colorless crystals were obtained from a THF/hexane solution (1/1) at −10 °C. Yield: 3.15 g (60%). Mp 135−140 °C. ^{1}H NMR (δ/ppm): 1−2 (br, 2H, BH_2), 2.81 (s, 6H, $N(CH_3)_2$), 2.94 (dd, $^3J_{H-H} = 13.6$ Hz, $^2J_{H-H} = 3$ Hz, 1H, CH_2), 3.26 (dd, $^3J_{H-H} = 10$ Hz, $^3J_{H-H} = 13.6$ Hz, 1H, CH), 4.42 (dd, $^3J_{H-H} = 10$ Hz, $^2J_{H-H} = 3$ Hz, 1H, CH_2), 6.2−6.6 and 6.95−7.44 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 41.0 (s, CH_2), 45.4 (s, $N(CH_3)_2$), 61.4 (s, CH), 112.8 (s, C6 in C_6H_4), 116.0 (s, C4 in C_6H_4), 119.9 (s, C3 in C_6H_4), 126.3 (s, C5 in C_6H_4), 126.8 (s, *p*-C in C_6H_5), 128.9 (s, *o*-C in C_6H_5), 131.3 (s, *m*-C in C_6H_5), 144.5 (s, C2 in C_6H_4), 148.9 (s, C1 in C_6H_4), 152.8 (s, *ipso*-C in C_6H_5). ^{11}B NMR (δ/ppm): 2.9 (br s). IR: 2315 m ($\nu_{as}(BH_2)$), 2295 m ($\nu_s(BH_2)$) cm^{-1}. MS found: m/z 328.2 (11%, M^+), and fragmentation products thereof; calcd for $C_{22}H_{25}BN_2$: M = 328.25.

Found: C 80.51; H 7.67; N 8.52%. Calcd for $C_{22}H_{25}BN_2$: C 80.50; H 7.68; N 8.53%.

[(2-Dimethylaminophenyl)diphenylmethoxy]acetylborane (11). 1-H_2BOCPh_2-2-$NMe_2C_6H_4$ (**6**) (0.5 g, 1.57 mmol) in 40 mL of tetrahydrofuran was placed in a 50 mL flask. Acetic acid (0.09 g, 1.57 mmol) in 10 mL of THF was added dropwise at room temperature over 20 min to the stirred solution. The solution was refluxed for 2 h. After the solvent and other volatile materials had been removed in a vacuum, a white solid remained, which was recrystallized from a CH_2Cl_2/*n*-hexane solution (1/3) at −10 °C to give a colorless crystalline compound. Yield: 0.53 g (90%). Mp dec 197 °C. ^1H NMR (δ/ppm): 1.6 (br, 1H, BH), 1.83 (s, 3H, CH_3), 3.00 (s, 3H, $N(CH_3)_2$), 3.04 (s, 3H, $N(CH_3)_2$), 7.21−7.34 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 45.6 (s, $N(CH_3)_2$), 48.6 (s, $N(CH_3)_2$), 52.8 (s, CH_3), 82.7 (s, C−O), 120.6 (s, C6 in C_6H_4), 126.9 (s, C4 in C_6H_4), 127.4 (s, C3 in C_6H_4), 127.6 (s, C5 in C_6H_4), 128.5 (s, *p*-C in C_6H_5), 132.3 (s, *o*-C in C_6H_5), 138.0 (s, *m*-C in C_6H_5), 144.7 (s, C2 in C_6H_4), 147.5 (s, C1 in C_6H_4), 148.9 (s, *ipso*-C in C_6H_5), 173.4 (s, CO_2). ^{11}B NMR (δ/ppm): 3.2 (br s). IR: 2370 m (ν_s(BH)), 1702 vs (ν(CO)), cm^{-1}. MS found: *m*/*z* 371.5 (50%, $M^+ - 2H$), and fragmentation products thereof; calcd for $C_{23}H_{24}NBO_3$: M = 373.24. Found: C 70.7; H 5.06; N 3.88%. Calcd for $C_{23}H_{24}NBO_3 \cdot H_2O$: C 70.60; H 6.69; N 3.58%. Compound **11** is hygroscopic.

General Procedure for the Reaction of Dichloroboranes with Lithium Aluminum Hydride. 1-Cl_2BOCR_2-2-$NMe_2C_6H_4$ (R = Ph, Cy)[1a] or 1-$Cl_2BN(Ph)C(H)Ph$-2-$NMe_2C_6H_4$[1a] (1 mmol) was added slowly to a large excess of lithium aluminum hydride (3 mmol) in 50 mL of diethyl ether at −10 °C. The solution was stirred at 40 °C for 12 h. The resulting suspension was filtered (G3 frit). The solvent was removed in a vacuum, and the borane complexes **6**−**8** were obtained in 50−60% yield after recrystallization.

Data Collection and Structure Determination. Crystallographic data are given in Table 2. Data [λ(Mo Kα) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction was performed with SADABS.[29] The structure was solved by direct methods (SHELXTL PLUS[30]). H atoms were located by difference maps and refined isotropically.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 233512 for **6**, 233513 for **7**, 233514 for **8**, 233515 for **9**, 233516 for **10**, and 233517 for **11**. These data can be obtained from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: (internat) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available: Complete IR and MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Sheldrick, G. M. *SADABS—A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

(30) *SHELXTL PLUS*; Siemens Anal. X-ray Inst. Inc.: Madison WI, 1990 (XS, Program for Crystal Structure Solution; XL, Program for Crystal Structure Determination; XP, Interactiv Molecular Graphics).