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Synthesis and characterization of novel intramolecularly base-stabilized BEt_2 and BEt derivatives: molecular structures of 1-Et_2BOCPh_2-2-$NMe_2C_6H_4$, 1-$(CH_3COO)EtBOCCy_2$-2-$NMe_2C_6H_4$ and $BEt(1\text{-}OCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4)_2$

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Abstract

The reaction of BEt_3 with the (2-dimethylaminophenyl)alcohols 1-HOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**1**), CCy_2 (**2**), CPh_2CH_2 (**3**)] [1:1 (for **1**–**3**) or 1:2 (for **3**)] in the presence of $^tBuCO_2H$ as catalyst gave the BEt_2 or BEt derivatives 1-Et_2BOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**4**), CCy_2 (**5**), CPh_2CH_2 (**7**)] and $BEt(1\text{-}OCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4)_2$ (**8**). Treatment of **5** with acetic acid gave 1-$(CH_3COO)EtBOCCy_2$-2-$NMe_2C_6H_4$ (**6**). Compounds **4**–**8** were characterized spectroscopically (NMR, IR, MS). Crystal structure determinations were carried out on **4**, **6** and **8**. For the chiral compound **6**, both enantiomers are present in the unit cell.

Keywords: Boranes; Ethylboranes; Boronalkoxides; Crystal structure

1. Introduction

Boron reagents with reactive boron-substituent bonds [1–4] 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 [5,6]. 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 (**3**)] [7], which are suitable for the formation of intramolecularly base-stabilized transition metal [8] and main group compounds [1,2,9] with six- and seven-membered chelate rings.

We now report the high-yield synthesis and spectroscopic properties of the novel intramolecularly base-stabilized ethylborane compounds 1-Et_2BOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**4**), CCy_2 (**5**), CPh_2CH_2 (**7**)], 1-$(CH_3COO)Et$-BOCCy$_2$-2-$NMe_2C_6H_4$ (**6**) and $BEt(1\text{-}OCPh_2CH_2\text{-}2\text{-}NMe_2C_6H_4)_2$ (**8**) with six- and seven-membered chelate rings and crystal structures of **4**, **6** and **8**.

2. Results and discussion

2.1. Synthesis

BEt_3 reacts with the alcohols 1-HOX-2-$NMe_2C_6H_4$ [X = CPh_2 (**1**), CCy_2 (**2**), CPh_2CH_2 (**3**)] [7] in refluxing

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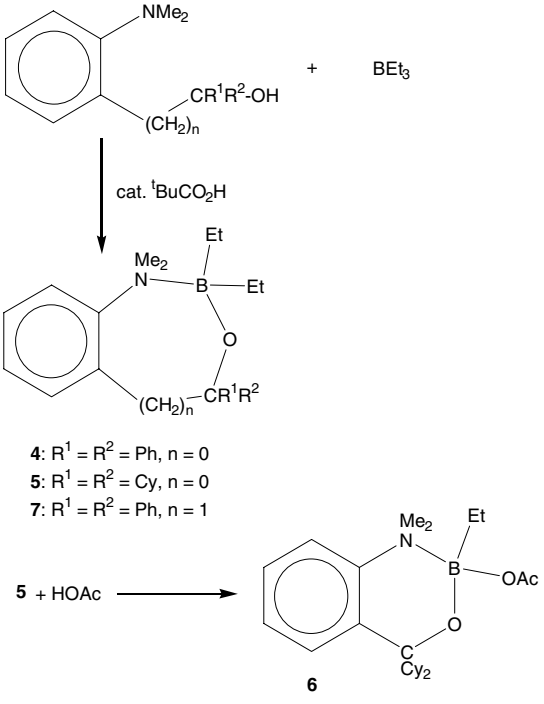
toluene in the presence of $^{t}BuCO_2H$ as catalyst [10] to give the boron heterocycles **4**, **5**, and **7** or **8**, as illustrated in Schemes 1 and 2. The BEt_2 derivative **5** reacts with acetic acid to afford **6** (Scheme 1). Compounds **4**–**8** were obtained in 70–80% yield. The by-product in all reactions is ethane gas, which does not interfere in subsequent reactions.

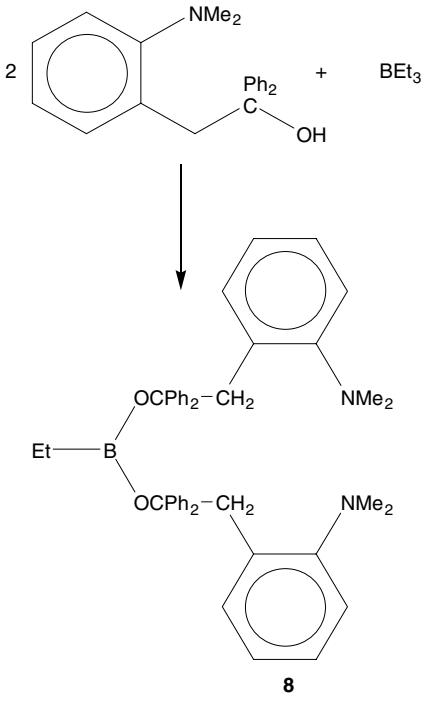
2.2. Spectroscopic properties

2.2.1. ^{1}H and ^{13}C NMR spectra

In the ^{1}H NMR spectra of the compounds **4**–**8** the most prominent signal is that due to the $N(CH_3)_2$ protons, which give rise to one (for **7** and **8**) or two singlets (for **4**, **5** and **6**) at 2.56, 3.03 (**4**), 2.87, 3.01 (**5**), 2.75, 2.96 (**6**), 2.49 (**7**) and 2.75 ppm (**8**). One (for **7** and **8**) or two (for **4**, **5** and **6**) ^{13}C NMR signals appear for the $N(CH_3)_2$ groups at 46.9, 50.0 (**4**), 50.6, 51.5 (**5**), 49.5, 51.6 (**6**), 45.4 (**7**) and 46.5 ppm (**8**). In the ^{1}H NMR spectra of **7** and **8** the benzylic methylene protons give rise to a singlet at 3.91 (**7**) and 3.74 ppm (**8**). Also, in the ^{13}C NMR spectra, the CH_2 carbon atoms appear as a singlet at 39.8 (**7**) and 46.0 ppm (**8**). The ^{13}C and ^{1}H NMR signals of $N(CH_3)_2$ and the benzylic group are shifted up- and downfield, respectively, in comparison with the parent organic ligands **1**–**3** [7]. The C–O carbon atoms appear as a singlet at 80.2 (**4**), 79.0 (**5**), 81.2 (**6**), 82.0 (**7**) and 78.8 ppm (**8**). The signals corresponding to the cyclohexyl and aromatic carbon atoms show the characteristic resonances in the expected chemical shift regions, similar to that observed for the organic ligands **1**–**3** [7].



Scheme 1. Preparation of **4**–**7**.



Scheme 2. Preparation of **8**.

2.2.2. ^{11}B NMR spectra

While **4**, **5** and **8** exhibit one signal in the ^{11}B NMR spectrum at 7.6 (**4**), 6.9 (**5**), and 33.4 ppm (**8**), two major signals with different intensities are observed in the ^{11}B NMR spectra of **6** and **7** at 7.7, 31.3 (ca. 2:1) (**6**) and 7.9, 32.0 ppm (ca. 2:1) (**7**). This demonstrates the presence of two types of boron compounds, presumably with tricoordinate (sp^2) and tetracoordinate (sp^3) environments [11]. The chemical shifts of around 32 ppm are indicative of a tricoordinate (sp^2) boron atom, although this value is shifted to high field compared with those reported in the literature [12]; on the other hand, the signals at ca. 7 ppm indicate the presence of intramolecular N–B coordination [tetracoordinate (sp^3) boron atom] [4]. This interaction appears to be absent in **8**, presumably due to steric hindrance. In the tricoordinate borane compound 9-phenyl-9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonyl), the signal is observed at 80.4 ppm [13]. The corresponding tetracoordinate BH_2 [$\delta = -2.5$ to 4.4 ppm] [2] and BX_2 [X = Cl ($\delta = 7.9-8.6$ ppm), X = F (1.3–1.9 ppm)] [1] derivatives of **1**–**3** exhibit chemical shifts in the same range as the tetracoordinate species in **4**–**7**.

2.2.3. IR spectra

In the infrared spectra of compounds **4**–**7** the B–N stretching vibration is observed as one of the strongest

bands between 1500 and 1444 cm^{-1} [14]. For **4**–**8**, a strong band, which appears in the range of 1400–1300 cm^{-1}, is attributed to the symmetric B–O stretching frequency [15]. A strong band at 1695 cm^{-1}, characteristic of a carbonyl stretching frequency, is present in the infrared spectrum of **6**.

2.2.4. Mass spectrometry

The mass spectra gave parent ion peaks at m/z = 370.9 (**4**), 383.9 (**5**), and 671.8 (**8**) or a fragment due to elimination of Et [385.0 ($M^+ - Et$)] for **6** or BEt_2 [317.1 ($M^+ - BEt_2$)] for **7**, which agree with the corresponding calculated isotopic distribution patterns. There are many fragments, which are either similar or identical for these closely related compounds (see Section 3).

2.3. Molecular structures of *4*, *6* and *8*

Colorless crystals of **4**, **6** and **8** were obtained as described in the experimental section. Selected interatomic distances and angles are given in Tables 1 and 2, the molecular structures are depicted in Figs. 1–3.

The common feature of the molecular structures of **4** and **6** is the intramolecular stabilization of the boron compounds by interaction with one amino group. The structural data of the O–C–phenylene–NC_2 fragments are similar for **4** (Fig. 1, Table 1) and **6** (Fig. 2, Table 1). The coordination of the amino group results in a puckered six-membered BOC_3N ring. The mean deviation of the atoms N(1), O(1), C(3), C(8), and C(9) from the mean plane is 0.044 Å for **4** and 0.0266 Å for **6**. The deviation of the B(1) atom from this plane is 0.75 Å for **4** and 0.59 Å for **6**. The puckering parameters according to Pople and Cremer [16] were determined for **4** and **6** and are in agreement with an envelope conformation (θ = 56.8° and 46.1°, ϕ = 10.95° and 2.26°, respectively). This leads to a distorted tetrahedral environment at B(1) [small O–B–N bite angle [**4**: 101.9(1); **6**: 106.7(2)°], one large and one small O–B–C_{Et} bond angle [**4**: 116.6(1), 108.3(1)°], or small bond angles for **6** [O–B–C_{Et} 108.3(2), O(1)–B–O(2) 109.7(2)°].

The structural data of the O–B–N bond angles in **4** and **6** differ remarkably from those of the strained

Table 1
Selected bond lengths (Å) and bond angles (°) for **4** and **6**

	4	**6**
Bond lengths		
B(1)–O(1)	1.458(2)	1.423(3)
B(1)–N(1)	1.726(2)	1.663(3)
B(1)–C_{Et}	1.624(2), 1.632(2)	1.604(3)
Bond angles		
C(9)–O(1)–B(1)	123.7(1)	124.9(2)
O(1)–B(1)–N(1)	101.9(1)	106.7(2)
O(1)–B(1)–C_{Et}	116.6(1), 108.3(1)	108.3(2)

Table 2
Selected bond lengths (Å) and bond angles (°) for **8**

Bond lengths	
B(1)–O(1)	1.357(4)
O(2)–B(1)	1.362(4)
B(1)–C(45)	1.573(5)
Bond angles	
O(1)–B(1)–O(2)	117.8(3)
O(1)–B(1)–C(45)	127.5(3)
O(2)–B(1)–C(45)	114.6(3)

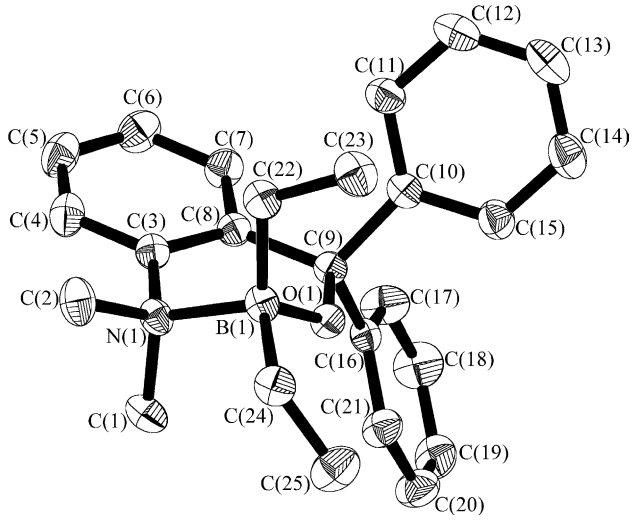


Fig. 1. Molecular structure of **4** (ORTEP, 50% probability, SHELXTL PLUS; XP [26], hydrogen atoms and toluene omitted for clarity).

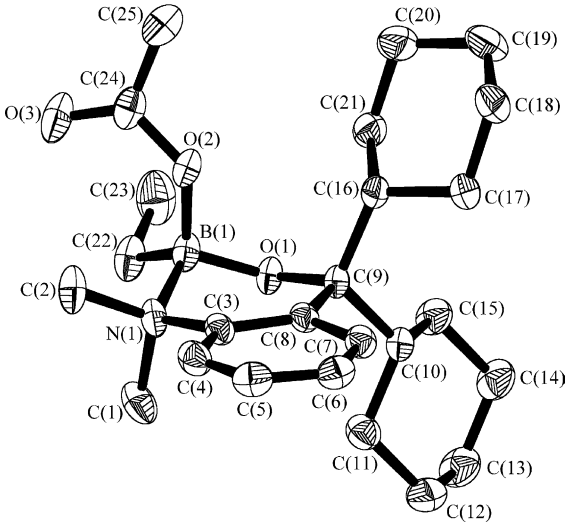


Fig. 2. Molecular structure of **6** (ORTEP, 50% probability, SHELXTL PLUS; XP [26], hydrogen atoms omitted for clarity; only the *R* enantiomer is shown).

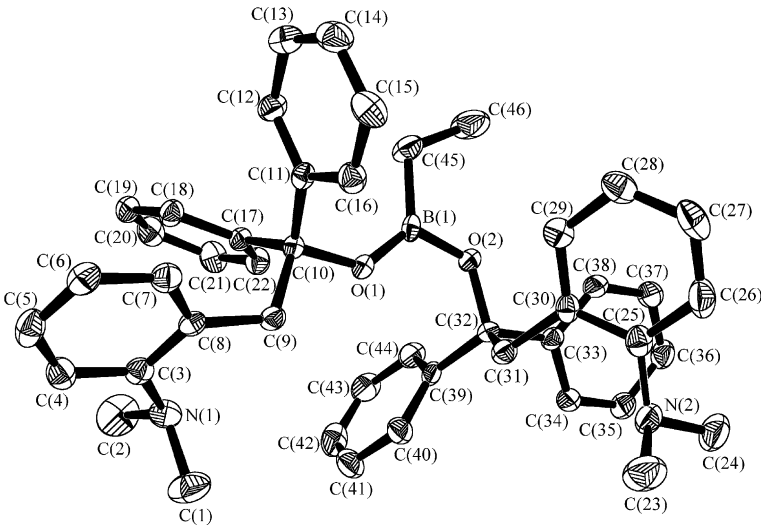


Fig. 3. Molecular structure of **8** (ORTEP, 50% probability, SHELXTL PLUS; XP [26], hydrogen atoms omitted for clarity).

five-membered BC_3N rings in $B(OCH_2CPh_2O)\{2,6\text{-}(NMe_2CH_2)_2C_6H_3\}$ [17], $BCl_2\{2,6\text{-}(NEt_2CH_2)_2C_6H_3\}$, $BCl_2\{2\text{-}N(BCl_3)Et_2CH_2\text{-}6\text{-}(NEt_2CH_2)C_6H_3\}$, $BCl_2\{2\text{-}(NMe_2CH_2)C_6H_4\}$ [3] 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) [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 X–B–N [X = O(1), N(2)] bond angles of **4** and **6**, 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 $[BCl_2\{2\text{-}NHEt_2CH_2\text{-}6\text{-}(NEt_2CH_2)OC_6H_3\}]Cl$ [4] are larger than the X–B–N [X = O(1), N(2)] bond angles of **4** and **6**.

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: 109.9(2)°; X = CCy_2, Y = Cl: 109.2(1)°; X = CPh_2, Y = F: 108.4(1)°] [1] with those of the six-membered BOC_3N rings of the dialkylborane **4** and the monoalkylborane **6** shows that the O–B–N bite angles in the dihaloboranes are much larger than those observed for **4** and **6**.

A comparison of the structural data of the O–B–N bond angles in **4** and **6** with those of the six-membered BXC_3N [X = O(1), N(2)] rings in $1\text{-}H_2BOX\text{-}2\text{-}NMe_2C_6H_4$ [X = CPh_2: 106.1(1)°, CCy_2: 107.6(2)°], $1\text{-}H_2BN(Ph)C(H)Ph\text{-}2\text{-}NMe_2C_6H_4$ [106.2(3)°] and $1\text{-}(CH_3COO)HBOCPh_2\text{-}2\text{-}NMe_2C_6H_4$ [106.8(1)°] [2] shows that the O–B–N bond angle in **4** is much smaller than the X–B–N [X = O(1), N(2)] bond angles observed for the BH derivatives, while the O–B–N bond angle in **6** is similar to those observed for the borane derivatives. The range of bond angles about N(1) for **4** and **6** is smaller than those in the BH derivatives, which range from 107.1(3) to 113.4(2)°.

The C–X–B [X = O(1), N(2)] bond angles in the BH derivatives [113.7(1)–117.6(2)°] are much smaller than those observed for the dihaloborane derivatives [122.5(1)–124.0(2)°], **4** [123.7(1)°] and **6** [124.9(2)°].

The range of bond angles about B(1) in **4** and **6** is larger than those in the BH_2 derivatives [from 105(1) to 115.5(8)°]. The B–O bond in the dihaloborane derivatives [1.391(2)–1.409(2) Å] is shorter than those in the BH derivatives [1.432(2) to 1.511(4) Å] and the (di)alkylboranes **4** [1.458(2) Å] and **6** [1.423(3) Å], and the B–N bond in the dihaloborane derivatives [1.626(2)–1.642(2) Å] is shorter than that in the ethyl boron derivatives **4** [1.726(2) Å] and **6** [1.663(3) Å].

The above data of the six-membered BXC_3N [X = O(1), N(2)] rings in **4** and **6** are comparable with those of the BOC_3N six-membered rings in $BCl_2\{2\text{-}(NEt_2CH_2)OC_6H_4\}$ and $[BCl_2\{2\text{-}NHEt_2CH_2\text{-}6\text{-}(NEt_2CH_2)OC_6H_3\}]Cl$ [4]. The C–O–B bond angles [119.9(1) and 122.8(1)°] are smaller than those for **4** and **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** and **6**, the bond angles about N(1) [bond angles range from 104.8(1) to 116.0(1) and from 104.9(1) to 116.2(1)°] are more distorted than those observed for **4** and **6** and the B–O [1.425(2) and 1.420(2) Å] and B–N bond lengths [1.633(2) and 1.627(2) Å] are similar to those observed for **4** and **6**.

Other structurally characterized examples of intramolecularly base-stabilized six-membered boron-containing rings are $B(cat)\{2\text{-}(NHPhCH_2)OC_6H_4\}$ (cat = $O_2C_6H_4$) [19] and $BPh_2\{2\text{-}(CHO)OC_6H_4\}$ [20]. Here, the NHPh or C=O group is coordinated to the boron atom [B–N 1.636(4); B–O 1.496(4) Å], which exhibits a distorted tetrahedral environment about B(1). The bond angles range from 106.0(2)° to 114.9(3)° and thus lie in the range found in **4** and **6**, while the B–O bond is longer than those observed for **4** and **6**.

The B–N bond lengths of **4** and **6** are comparable to those of related dichloroborane derivatives [4] and those of dialkyl- or dialkoxyborane compounds with BC_3N rings [17,18]. Also, the B–N bond lengths in **4** and **6** are larger than those of the adducts $BCl_3(NMe_3)$ [B–N 1.575(10) Å] [21], BCl_3(py) [B–N 1.592(3) Å] [22], and BCl_3(NCMe) [B–N 1.562(8) Å] [23].

The cyclic six-membered ring compound, $B(CF_3)_2NMe_2CH(Me)CMe{=}CHO$ [24] has similar B–N [1.64(1) Å] and B–O bond lengths [1.45(1) Å] to **4** and **6**.

The bond lengths and angles of the organic fragment of **4** and **6** are similar to those observed for the corresponding organic compounds **1** and **2** [7].

The X-ray crystal structure of **8** (Fig. 3, Table 2) shows a trigonal-planar three-coordinate boron atom [sum of angles at boron 360.2(3)°]. The boron atom is coordinated by two oxygen atoms [B(1)–O(1) 1.357(1) and B(1)–O(2) 1.362(4) Å] and by one ethyl group [B(1)–C(45) 1.573(5) Å]. The B–O bonds in **8** are shorter than those observed for the BH derivatives [1.432(2) to 1.511(4) Å] [2] and the (di)alkylboranes **4** [1.458(2) Å] and **6** [1.423(3) Å]. The $B–C_{Et}$ bond in **8** [1.573(5) Å] is slightly shorter than those observed for **4** and **6**. The bond lengths and angles of **8** are normal and in agreement with those observed for the corresponding organic ligand **3** [7].

3. Experimental

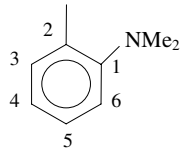
3.1. General remarks

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) with tetramethylsilane as external standard. ^{11}B NMR spectra (128.38 MHz) 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). The chemicals BEt_3 and $^tBuCO_2H$ were 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 (**3**)] were prepared according to the literature [7].

3.2. [(2-Dimethylaminophenyl)diphenylmethoxy]diethylborane (4)

1 g (3.2 mmol) of 1-HOCPh$_2$-2-$NMe_2C_6H_4$ (**1**) was treated with a solution of 0.32 g (3.2 mmol) of BEt_3 (1 M) in toluene in the presence of $^tBuCO_2H$ (0.1 g) as catalyst. The solution was stirred for 3 h at −10 °C and then at 50 °C for 12 h. The mixture was cooled to r.t. and the solvent was removed under vacuum. The residual oil was dissolved in 20 ml of CH_2Cl_2, and the solution filtered. After evaporation of the solvent and recrystallization of the residue from toluene/hexane (1/3) colorless crystals were obtained at −20 °C in 80% yield (0.95 g). M.p. 160–162 °C. ^1H NMR (δ/ppm): 0.80 (s, 6H, BCH_2CH_3), 1.1 (m, 4H, BCH_2CH_3), 2.56 (s, 3H, $N(CH_3)_2$), 3.03 (s, 3H, $N(CH_3)_2$), 7.19–7.42 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 9.3 (s, BCH_2CH_3), 27.1 (s, BCH_2CH_3), 46.9 (s, $N(CH_3)_2$), 50.0 (s, $N(CH_3)_2$), 80.2 (s, CO), 119.0 (s, C6 in C_6H_4), 126.4 (s, C4 in C_6H_4), 127.7 (s, C3 in C_6H_4), 127.9 (s, C5 in C_6H_4), 128.9 (s, *p*-C in C_6H_5), 131.0 (s, *o*-C in C_6H_5), 137.0 (s, *m*-C in C_6H_5), 145.1 (s, C2 in C_6H_4), 148.5 (s, C1 in C_6H_4), 150.0 (s, *ipso*-C in C_6H_5). ^{11}B NMR (δ/ppm): 7.6 (br. s). IR: 3084 w, 3059 w, 3023 w, 2978 w-m, 2947 m, 2867 w, 2837 w, 2791 w-m, 2636 w, 1954 w, 1597 w, 1486 vs, 1459 vs, 1446 vs, 1398 m-s, 1282 m-s, 1267 m, 1205 m, 1178 s, 1166 m, 1155 m, 1134 w-m, 1098 s, 1051 w, 1035 s, 1022 vs, 1001 w-m, 940 m, 930 m-s, 896 m-s, 771 vs, 703 vs, 637 s, 565 m-s, 524 w cm^{-1}. MS: *m*/*z* = 370.9 (5%, M^+), 342.1 (60%, $M^+ - Et$), 303.0 (19%, $M^+ - BEt_2$), 286.0 (65%, $M^+ - OBEt_2$), 249.9 (13%, $M^+ - Ph - N(CH_3)_2$), 193.9 (18%, $M^+ - Ph - N(CH_3)_2 - 2Et$), 164.9 (18%, CPh_2^+), 119.9 (15%, $C_6H_4NMe_2^+$), 104.9 (18%, $C_6H_4NMe^+$), 90.9 (100%, $C_7H_7^+$), 76.9 (35%, $C_6H_5^+$), 55.1 (15%, $C_4H_7^+$), and fragmentation products thereof. Calc. for $C_{25}H_{30}BNO$: M = 371.33. Found: C, 79.50; H, 6.99; N, 4.39%. Calc. for $C_{25}H_{30}BNO$: C 80.87; H, 8.14; N, 3.77%.

Phenyl ring numbering scheme:



3.3. [(2-Dimethylaminophenyl)dicyclohexylmethoxy]diethylborane (5)

A similar procedure to that described for **4** was used here, except that 1-HOCCy$_2$-2-$NMe_2C_6H_4$ (**2**) (0.32 g, 1.01 mmol) was used instead of **1**. Colorless crystals were obtained from a CH_2Cl_2/hexane solution (1/3) at 20 °C. Yield: 0.27 g (70%). M.p. 165–170 °C. ^1H NMR (δ/ppm): 0.65–2.0 (m, 32H, BCH_2CH_3 and C_6H_{11}), 2.87 (s, 3H, $N(CH_3)_2$), 3.01 (s, 3H, $N(CH_3)_2$), 7.24–7.42 (m, 4H, C_6H_4). ^{13}C NMR (δ/ppm): 9.7 (s, BCH_2CH_3), 26.5 (C4 in C_6H_{11}), 26.7 (s, BCH_2CH_3), 27.5 (s, C3/C5 in C_6H_{11}), 28.0 (s, C3/C5 in C_6H_{11}), 29.0 (s, C2/C6 in C_6H_{11}), 29.7 (s, C2/C6 in C_6H_{11}),

48.8 (s, C1 in C_6H_{11}), 50.6 (s, $N(CH_3)_2$), 51.5 (s, $N(CH_3)_2$), 79.0 (s, CO), 119.6 (s, C6 in C_6H_4), 126.7 (s, C4 in C_6H_4), 127.1 (s, C3 in C_6H_4), 141.7 (s, C5 in C_6H_4), 145.1 (s, C2 in C_6H_4), 153.2 (s, C1 in C_6H_4). ^{11}B NMR (δ/ppm): 6.9 ppm (br.). IR: 2931 vs, 2851 vs, 2785 s, 1703 vs, 1574 w, 1482 vs, 1457 vs, 1366 s, 1284 s, 1185 vs, 1102 m-s, 1084 m, 1071 m, 1044 s, 993 m, 932 m-s, 894 m, 865 m, 816 m, 762 s, 717 m-s, 674 m, 635 w, 566 m, 520 w, 484 w cm^{-1}. MS: *m/z* = 383.9 (75%, M^+), 354.0 (28%, $M^+ - Et$), 298.9 (15%, $M^+ - OBEt_2$), 270.0 (90%, $M^+ - OBEt_2 - 2CH_3$), 256.0 (28%, $M^+ - OBEt_2 - N(CH_3)_2$), 243.9 (30%, $M^+ - 2Et - C_6H_{11}$), 213.9 (35%, $M^+ - OBEt_2 - C_6H_{11}$), 199.9 (10%, $M^+ - OBEt_2 - C_6H_{11} - CH_3$), 173.9 (12%, $M^+ - OBEt_2 - N(CH_3)_2 - C_6H_{11}$), 83.0 (48%, C_6H_{11}), 55.0 (98%, $C_4H_7^+$), and fragmentation products thereof. Calc. for $C_{25}H_{42}BNO$: M = 383.42. Found: C, 74.1; H, 9.32; N, 3.58%. Calc. for $C_{25}H_{42}BNO \cdot 0.25\ CH_2Cl_2$: C, 74.95; H, 10.59; N, 3.46%.

3.4. [(2-Dimethylaminophenyl)dicyclohexylmethoxy](acetoxy)ethylborane (6)

Acetic acid (0.09 g, 1.57 mmol) in 10 ml of THF was added dropwise at room temperature to a solution of **5** (0.60 g, 1.57 mmol) in 40 ml of dry tetrahydrofuran over 20 minutes, and the mixture was refluxed for 2 hours. When the solvent and other volatile material were removed in vacuum a white compound remained, which was recrystallized from CH_2Cl_2/*n*-hexane (1:3). At −10 °C 0.45 g of a colorless crystalline compound was obtained (70% yield). M.p. 160–165 °C. ^{1}H NMR (δ/ppm): 0.78–2.16 (m, 27H, BCH_2CH_3 and C_6H_{11}), 2.58 (s, 3H, CH_3), 2.75 (s, 3H, $N(CH_3)_2$), 2.96 (s, 3H, $N(CH_3)_2$), 7.07–7.34 (m, 4H, C_6H_4). ^{13}C NMR (δ/ppm): 9.9 (s, BCH_2CH_3), 17.4 (s, BCH_2CH_3), 25.1 (s, C4 in C_6H_{11}), 27.4 (s, C3/C5 in C_6H_{11}), 28.6 (s, C2/C6 in C_6H_{11}), 47.3 (s, C1 in C_6H_{11}), 49.5 (s, $N(CH_3)_2$), 51.6 (s, $N(CH_3)_2$), 53.7 (s, CH_3), 81.2 (s, CO), 120.8 (s, C6 in C_6H_4), 123.7 (s, C4 in C_6H_4), 128.4 (s, C3 in C_6H_4), 142.2 (s, C5 in C_6H_4), 146.2 (s, C2 in C_6H_4), 154.0 (s, C1 in C_6H_4), 172.5 (s, CO_2). ^{11}B NMR (δ/ppm): 7.7, 31.3 (br. s, ca. 2:1). IR: 3373 m, 3063 m, 2946 vs, 2848 vs, 2786 m, 2662 m, 2588 m, 1950 m, 1752 s, 1695 vs, 1656 s, 1581 m, 1487 vs, 1447 vs, 1415 vs, 1401 vs, 1365 vs, 1287 vs, 1259 vs, 1219 m-s, 1205 m, 1185 s, 1174 vs, 1143 vs, 1019 vs, 976 m, 963 m, 935 vs, 894 s, 868 m-s, 856 s, 802 vs, 771 vs, 741 vs, 718 vs, 674 s, 659 m, 607 m, 566 vs, 551 m, 517 m-s, 484 m, 458 m cm^{-1}. MS: *m/z* = 385.0 (2%, $M^+ - Et$), 371.0 (1%, $M^+ - Et - CH_3$), 355.0 (1%, $M^+ - BEt-2CH_3$), 330.8 (5%, $M^+ - C_6H_{11}$), 297.8 (10%, $M^+ - OBEtOCOCH_3$), 270.7 (5%, $M^+ - C_6H_{11}$ –OCO-CH_3), 256.7 (28%, $M^+ - C_6H_{11} - OCOCH_3 - CH_3$), 232.7 (100%, $M^+ - C(C_6H_{11})_2$), 214.6 (15%, $M^+ - OBEtOCOCH_3 - C_6H_{11}$), 185.0 (10%, $M^+ - OBEtOCOCH_3 - C_6H_{11} - 2CH_3$), 83.0 (15%, C_6H_{11}), 54.7 (30%, $C_4H_7^+$), and fragmentation products thereof. Calc. for $C_{25}H_{40}BNO_3$: M = 413.39. Found: C 75.9; H 9.13; N 4.03%. Calc. for $C_{25}H_{40}BNO_3$: C 72.63; H 9.75; N 3.39%.

3.5. [2-(2-Dimethylaminophenyl)-1,1-diphenylethoxy]diethylborane (7)

A similar procedure to that described for **4** was used here, except that 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**4**) (0.32 g, 1.01 mmol) was used instead of **1**. Yield: 0.27 g (70%). M.p. dec. 120 °C. ^{1}H NMR (δ/ppm): 0.86 (br. s, 6H, BCH_2CH_3), 0.94 (m, 4H, BCH_2CH_3), 2.49 (s, 6H, $N(CH_3)_2$), 3.91 (s, 2H, CH_2), 6.38 (m, 1H, C_6H_4), 6.65 (m, 1H, C_6H_4), 7.02–7.32 (m, 12H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 8.1 (s, BCH_2CH_3), 26.4 (s, BCH_2CH_3), 39.8 (s, CH_2), 45.4 (s, $N(CH_3)_2$), 82.0 (s, CO), 118.8 (s, C6 in C_6H_4), 122.5 (s, C4 in C_6H_4), 126.3 (s, C3 in C_6H_4), 127.3 (s, C5 in C_6H_4), 127.7 (s, *p*-C in C_6H_5), 130.2 (s, *m*-C in C_6H_5), 130.9 (s, *o*-C in C_6H_5), 132.5 (s, C2 in C_6H_4), 147.4 (s, C1 in C_6H_4), 154.2 (s, *ipso*-C in C_6H_5). ^{11}B NMR (δ/ppm): 7.9, 32.0 (br. s). IR: 3084 m, 3059 m, 3023 m, 2978 m-s, 2947 s, 2867 m-s, 2837 m-s, 2791 m-s, 1597 w, 1582 w, 1486 vs, 1459 vs, 1446 vs, 1393 m-s, 1313 m, 1282 m-s, 1266 m, 1205 m, 1178 m-s, 1166 m, 1154 m, 1098 s, 1051 m, 1035 vs, 1021 vs, 1001 m, 987 w, 940 m, 930 m-s, 907 m, 896 m-s, 771 vs, 703 vs, 637 s, 587 w, 565 m-s, 524 w, 442 w cm^{-1}. MS: *m/z* = 317.1 (1%, $M^+ - BEt_2$), 299.0 (1%, $M^+ - OBEt_2$), 240.0 (2%, $M^+ - Ph - OBEt_2$), 134.9 (100%, $M^+ - 2Ph - CH_3 - OBEt_2$), 90.9 (20%, $C_7H_7^+$), 76.9 (25%, $C_6H_5^+$), and fragmentation products thereof. Calc. for $C_{26}H_{32}BNO$: M = 385.36. Found: C, 78.20; H, 7.16; N, 3.95%. Calc. for $C_{26}H_{32}BNO \cdot 0.25\ CH_2Cl_2$: C, 77.55; H, 8.06; N, 3.45%.

3.6. Bis[2-(2-Dimethylaminophenyl)-1,1-diphenylethoxy]ethylborane (8)

A similar procedure to that described for **7** was used here, except that 2 equiv. of 1-$HOCPh_2CH_2$-2-$NMe_2C_6H_4$ (**4**) (0.64 g, 2.02 mmol) was used instead of 1 equiv. Colorless crystals were obtained from toluene at −20 °C, Yield: 0.48 g (70%). M.p. 150–154 °C. ^{1}H NMR (δ/ppm): 0.84–0.98 (br. m, 5H, BCH_2CH_3), 2.75 (s, 12H, $N(CH_3)_2$), 3.74 (s, 4H, CH_2), 6.5 (m, 2H, C_6H_5), 6.7 (m, 2H, C_6H_4), 7.1–7.3 (m, 16H, C_6H_4 and C_6H_5), 7.4–7.5 (m, 8H, C_6H_4 and C_6H_5). ^{13}C NMR (δ/ppm): 2.10 (s, BCH_2CH_3), 28.0 (s, BCH_2CH_3), 46.0 (s, CH_2), 46.5 (s, $N(CH_3)$), 78.8 (s, CO), 121.1 (s, C6 in C_6 H_4), 126.1 (s, C4 in C_6 H_4), 127.3 (s, C3 in C_6H_4), 127.5 (s, C5 in C_6H_4), 128.7 (s, C2 in C_6H_4), 128.8 (s, C1 in C_6H_4), 134.1 (s, *p*-C in C_6H_5), 134.5 (s, *o*-C in C_6H_5), 149.0 (s, *m*-C in C_6H_5), 152.0 (s, *ipso*-C

Table 3
Crystal data and structure refinement for **4**, **6** and **8**

	4	**6**	**8**
Formula	$C_{25}H_{30}BNO \cdot 0.5$ toluene	$C_{25}H_{40}BNO_3$	$C_{46}H_{49}BN_2O_2$
M_r	416.87	413.39	672.68
Temperature (K)	219(2)	223(2)	223(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.6416(8)	9.225(1)	9.077(1)
b (Å)	11.4800(9)	11.137(2)	13.712(2)
c (Å)	11.5716(9)	12.303(2)	16.361(2)
α (°)	105.945(1)	98.775(3)	73.348(3)
β (°)	116.561(1)	107.943(2)	85.774(3)
γ (°)	95.350(2)	96.740(3)	76.548(3)
V (Å^3)	1176.8(2)	1170.2(3)	1897.3(5)
Z	2	2	2
ρ_{calc} (Mg m^{-3})	1.176	1.173	1.177
F (000)	449	452	720
Absorption coefficient (mm^{-1})	0.069	0.075	0.071
No. of reflections collected	6853	5389	12722
No. of independent reflections	4554	3355	8766
R_{int}	0.0147	0.0191	0.0605
No. of parameters	298	275	465
$R_1(I > 2\sigma(I))$	0.0504	0.0489	0.0638
wR_2 (all data)	0.1549	0.1448	0.1655
$(\Delta/\rho)_{max}$ (e Å^{-3})	0.245	0.611	0.329
$(\Delta/\rho)_{min}$ (e Å^{-3})	−0.261	−0.21	−0.256

in C_6H_5). ^{11}B NMR (δ/ppm): 33.4 (br.). IR: 3084 m, 3059 m, 3022 m, 2987 m, 2962 m, 2946 m, 2932 m, 2862 m-s, 2831 s, 2801 m, 2784 m-s, 2664 w, 1731 m, 1703 m-s, 1667 m, 1645 w, 1598 m, 1580 w, 1492 vs, 1475 s, 1460 m-s, 1447 s, 1305 m-s, 1292 m-s, 1281 m-s, 1261 s, 1231 s, 1197 m, 1180 m-s, 1166 m, 1159 m, 1149 w-m, 1104 s, 1058 s, 1048 m, 1038 m-s, 1032 m-s, 1006 m-s, 955 m-s, 937 s, 872 m, 862 m-s, 818 m-s, 803 m-s, 786 s, 767 vs, 757 vs, 721 m, 701 vs, 647 m, 608 s, 566 m, 546 m, 534 m, 507 m, 467 m, 434 m cm^{-1}. MS: m/z = 671.8 (2%, M^+), 429.8 (2%, $M^+ - 2N(CH_3)_2$ –2Ph), 356.3 (78%, $M^+ - 2N(CH_3)_2 - 2Ph - EtBO_2$), 300.3 (95%, $CPh_2CH_2C_6H_4NMe_2^+$), 134.1 (100%, $CH_2C_6H_4NMe_2^+$), 91.0 (28%, $C_7H_7^+$), 77.0 (20%, $C_6H_5^+$), 55.1 (10%, $C_4H_7^+$), and fragmentation products thereof. Calc. for $C_{46}H_{49}BN_2O_2$: M = 672.68. Found: C, 73.4; H, 5.99; N, 3.53%. Calc. for $C_{46}H_{49}BN_2O_2 \cdot CH_2Cl_2$: C 74.51; H 6.79; N 3.70%.

4. Data collection and structure determination

Crystallographic data are listed in Table 3. 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 with SADABS [25]. The structures were solved by direct methods (SHELXTL PLUS [26]). H atoms were refined in a viding mode.

CCDC Nos. 237059 (**4**), 237060 (**6**) and 237061 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 11223-336-033; or deposit@ccdc.cam.uk).

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