Bis-Catecholate, Bis-Dithiocatecholate, and Tetraalkoxy Diborane(4) Compounds: Aspects of Synthesis and Electronic Structure

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The synthesis and characterization of a series of bis-catecholate diborane(4) compounds, $B_2(1,2\text{-}O_2C_6H_4)_2$ (**3**), $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ (**6**), $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$ (**7**), $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**8**), $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$ (**9**), $B_2(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)_2$ (**10**), bis-dithiocatecholate diborane(4) compounds, $B_2(1,2\text{-}S_2C_6H_4)_2$ (**13**), $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ (**14**), and tetraalkoxy diborane(4) compounds, $B_2(OCH_2CMe_2CH_2O)_2$ (**11**) and $B_2(OCMe_2CMe_2O)_2$ (**12**) from $B_2(NMe_2)_4$ (**1**) is described, as are the bis($NHMe_2$) adducts of **3** and **9**, namely $[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2]$ (**4**) and $[B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2(NHMe_2)_2]$ (**5**). The latter two compounds are intermediates in the formation of **3** and **9** from **1**. Compound **1** is synthesized by reductive coupling of $BCl(NMe_2)_2$, which in turn is prepared from reaction of BCl_3 with $B(NMe_2)_3$ in a 1:2 stoichiometry. We have also characterized $[B_2Cl_4(NHMe_2)_2]$ (**15**) formed from addition of HCl to **1** prior to complete reaction with diols, and the salt, $[NH_2Me_2][B(1,2\text{-}O_2C_6H_4)_2]$ (**16**), which arises from addition of catechol to $B(NMe_2)_3$. Thus, any $B(NMe_2)_3$ impurity present after the preparation of **1** needs to be removed by distillation prior to reaction with alcohols. The dimer, $[BCl_2(\mu\text{-}NMe_2)]_2$ (**17**) has also been characterized. This is formed from reaction of BCl_3 with $B(NMe_2)_3$ if a 2:1 rather than 1:2 stoichiometry is used. Photoelectron spectra of **1**, **3**, **8**, **11**, and **12** are reported along with those of the corresponding diols, catechol, 4-Bu^t-catechol, 2,2-dimethyl-1,3-propanediol, and pinacol. The ionization energies of the $B_2(OR)_4$ compounds follow the series **8** < **3** < **12** < **11**. Replacement of O for N in the B_2N_4 framework increases the IE by ca. 1.65 eV, whereas the presence of an aromatic ring rather than an aliphatic chain decreases the IE by ca. 1.50 eV. The presence of electron donating Bu^t-groups also decreases the IE.

Derivatives of diborane(4)[1] are an important class of compound in boron chemistry, part of their interest deriving from the presence of an unsupported two-center, two-electron B−B bond. There are, however, many aspects of the chemistry of such species that have been developed only recently. Diborane(4) itself, B_2H_4, is only stable when complexed by Lewis base ligands such as amines or phosphines,[2] while the tetrahalides B_2X_4 (X = F, Cl, Br, I), although having a reasonably well-established chemistry,[3] suffer from low thermal stabilty (with the exception of B_2F_4) and preparative difficulties. Tetraorganodiborane(4) compounds, B_2R_4, are only stable with sterically demanding R groups such as Bu^t or CH_2Bu^t and mesityl, examples with the former two having been characterized for the first time in 1980 by Nöth and co-workers[4a] and Berndt et al.,[4b] and the latter much more recently by Power and co-workers.[5] By far the most stable derivatives are those in which good π-donor groups are present such as amido (NR_2) or alkoxy (OR), the prototypical examples being $B_2(NMe_2)_4$ (**1**)[6] and $B_2(OMe)_4$ (**2**);[7] the former compound **1** is the primary starting material for much of diborane(4) chemistry due to its thermal stability and the availability of high yield syntheses. More recently, as part of an interest in the oxidative addition chemistry[8,9] of the B−B bond and metal-catalyzed diborations[10] of alkenes[11] and alkynes,[9] we have characterized a series of

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(1) For a brief overview of the synthesis, structure and reactivity of diborane(4) compounds, see: Lesley, G.; Marder, T. B.; Norman, N. C.; Rice, C. R. *Main Group Chem. News* **1997**, *5*, 4.

(2) Kameda, M.; Driscoll, J. A.; Kodama, G. *Inorg. Chem.* **1990**, *29*, 3791 and references therein. See also: Parry, R. W. *Phosphorus Sulfur* **1994**, *87*, 177.

(3) See, for example: (a) Massey, A. G. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 1. (b) Coyle, T. D.; Ritter, J. J. *Adv. Organomet. Chem.* **1972**, *10*, 237.

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(5) (a) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715. (b) Moezzi, A.; Olmstead, M. M.; Bartlett, R. A.; Power, P. P. *Organometallics* **1992**, *11*, 2383.

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stable, crystalline bis-catecholate[8a] and bis-dithiocatecholate derivatives, and herein we describe full details of their syntheses, spectroscopic properties and aspects of bonding derived from photoelectron spectroscopic measurements and extended Hückel molecular orbital (EHMO) calculations. Also described is the tetraalkoxy compound $B_2(OCH_2CMe_2CH_2O)_2$. In a companion paper[12] we describe the solid-state structures of some of the diborane(4) compounds and related materials.

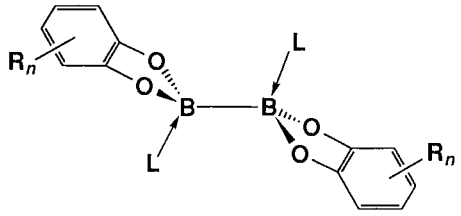
Results and Discussion

Syntheses. The starting compound for the preparation of all the diborane(4) compounds described herein was the tetraamido compound $B_2(NMe_2)_4$ (**1**).[6] A preparation of **1**, which is a modification of that reported by Brotherton and co-workers,[6] is represented as shown in eqs 1 and 2, the first being a redistribution reaction affording $BCl(NMe_2)_2$, and the second, a reductive coupling resulting in formation of the B−B bond.

$$BCl_3 + 2B(NMe_2)_3 \rightarrow 3BCl(NMe_2)_2 \quad (1)$$

$$2BCl(NMe_2)_2 + 2Na \rightarrow B_2(NMe_2)_4\ (\mathbf{1}) + 2NaCl \quad (2)$$

Treatment of **1** with 2 equiv of catechol in Et_2O solution resulted in the immediate formation of a white precipitate (both **1** and catechol are soluble in Et_2O) which we propose is the bis-dimethylamine adduct of $B_2(1,2\text{-}O_2C_6H_4)_2$, ($B_2cat_2$, **3**) i.e., $[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2]$ (**4**) as shown in eq 3. Support for the supposition that the initial precipiate is a bis-amine adduct comes from parallel studies on the reactivity of **3** which have resulted in a number of structurally characterized mono- and bis-4-picoline adducts of **3** (for a bis ligand adduct of **3**, see **A**; L = nitrogen base, e.g. amine or pyridine) in which the nitrogen



A

4, $R_n = H_4$, L = NMe_2H; **5**, R_n = 3,5-Bu^t_2-4,6-H_2, L = NMe_2H

donor atoms are bonded directly to the boron center(s); these results have been reported elsewhere.[13] In addition, a combination of elemental analysis and NMR spectroscopic results on $[B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2\text{-}C_6H_2)_2(NHMe_2)_2]$ (**5**) and elemental analysis of the insoluble parent compound $[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2]$ (**4**) are consistent with the proposed formulation.

$$B_2(NMe_2)_4 + 2(1,2\text{-}(HO)_2C_6H_4) \rightarrow [B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2] + 2NHMe_2 \quad (3)$$

After the reaction mixture containing the white precipiate had been stirred for several hours, 4 equiv of HCl, as a solution in Et_2O, were then added, resulting in the appearance of a further amount of white precipitate. This reaction is necessary to remove both complexed and uncomplexed amine as an ammonium salt, as shown in eq 4, to afford uncomplexed **3**. Subsequent removal of all volatiles followed by extraction into toluene and low-temperature crystallization yielded **3** as a colorless crystalline solid.

$$[B_2(1,2\text{-}O_2C_6H_4)_2(NHMe_2)_2]\ (\mathbf{4}) + 2NHMe_2 + 4HCl \rightarrow B_2(1,2\text{-}O_2C_6H_4)_2\ (\mathbf{3}) + 4[NH_2Me_2]Cl \quad (4)$$

The related catecholate compounds $B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ (**6**), $B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$ (**7**), $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**8**), $B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2C_6H_2)_2$ (**9**), and $B_2(1,2\text{-}O_2\text{-}3\text{-}MeOC_6H_3)_2$ (**10**) were prepared in a manner similar to **3**, the compounds becoming more soluble in toluene with increasing hydrocarbon side-group substitution (**3** itself is rather insoluble in most solvents). The tetraalkoxy compounds, $B_2(OCH_2CMe_2CH_2O)_2$ (B_2neop_2, **11**) and $B_2(OCMe_2CMe_2O)_2$ (B_2pin_2, **12**),[14] were

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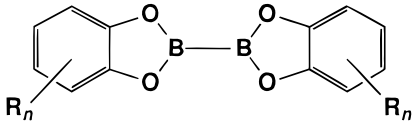
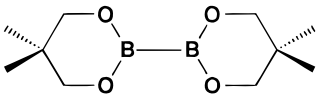
prepared similarly, as were the dithiocatecholate analogues of **3** and **7**, namely $B_2(1,2\text{-}S_2C_6H_4)$ (**13**) and $B_2(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)_2$ (**14**).



3, $R_n = H_4$; **6**, R_n = 3-Me-4,5,6-H_3; **7**, R_n = 4-Me-3,5,6-H_3;
8, R_n = 4-Bu^t-3,5,6-H_3; **9**, R_n = 3,5-Bu$^t_2$-4,6-H_2, **10**, R_n = 3-MeO-4,5,6-H_3



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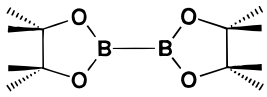

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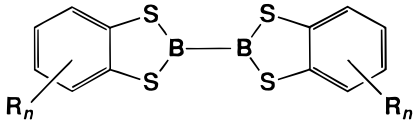
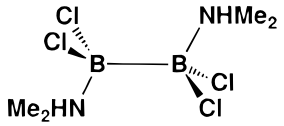


13, $R_n = H_4$; **14**, R_n = 4-Me-3,5,6-H_3;

In addition to the main reaction scheme described above, there are some secondary points which are important in the preparation of these diborane(4) compounds. First, in the case of **11**, the addition of HCl does not seem to be necessary as **11** does not appear to form any stable adducts with $NHMe_2$ and is therefore available directly after addition of the diol $HOCH_2CMe_2CH_2OH$ to **1**. Second, however, it is important when HCl addition is required to allow sufficient time for **1** to react with the catechol or diol. If HCl addition takes place before reaction 3 has gone nearly to completion, an alternative reaction pathway is followed in which the HCl reacts directly with **1** to give the complex $[B_2Cl_4(NHMe_2)_2]$ (**15**) as shown in eq 5. In fact, the reactivity of **1** toward HCl has been studied in some detail by Nöth and Meister[15] and by Malhotra,[16] the nature of the product depending on the relative amounts of **1** and HCl. Thus, Nöth and Meister observed the following: **1** and 2 equiv of HCl afforded $B_2Cl(NMe_2)_3$ and $[NH_2Me_2]Cl$; **1** and 4 equiv of HCl afforded $B_2Cl_2(NMe_2)_2$ and $2[NH_2Me_2]Cl$; **1** and 6 equiv of HCl afforded **15** and $2[NH_2Me_2]Cl$; while **15** and 2 equiv of HCl afforded the salt $[NH_2Me_2]_2[B_2Cl_6]$.

$$B_2(NMe_2)_4 + 4HCl \rightarrow [B_2Cl_4(NHMe_2)_2] + 2NHMe_2 \quad (5)$$



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Third, it is important to distill carefully the starting complex **1** as the crude product is usually contaminated with some $B(NMe_2)_3$ and this also reacts with catechols to give ammonium bis-catecholate borates as shown in eq 6 for catechol itself, i.e., $[NH_2Me_2][B(1,2\text{-}O_2C_6H_4)_2]$ (**16**).

$$B(NMe_2)_3 + 2(1,2\text{-}(HO)_2C_6H_4) \rightarrow [NH_2Me_2][B(1,2\text{-}O_2C_6H_4)_2] + 2NHMe_2 \quad (6)$$

Finally, careful control of the stoichiometry of eq 1 is required as an excess of BCl_3 leads to the complex $BCl_2(NMe_2)$ (**17**) which manifests itself as a colorless crystalline dimeric material after workup.

Table 1. Vertical Ionization Energies of the Bands in the Photoelectron Spectra for the Diborane(4) Compounds **1**, **3**, **8**, **11**, and **12** and also for Catechol, 4-Bu^t-catechol, Pinacol, and 2,2-Dimethyl-1,3-propanediol

compound	vertical ionization energy (eV)
$B_2(NMe_2)_4$ (**1**)	7.16, 7.54, 8.94, 9.64, 12.25, 13.15, 14.67
catechol	8.43, 9.26, 11.42, 12.96, 14.36, 15.88, 17.92
B_2cat_2 (**3**)	8.81, 9.39, 12.13, 13.02, 14.02, 15.12, 16.84
4-Bu^t−catechol	8.17, 8.88, 12.70, 14.80, 15.82
$B_2Bu^tcat_2$ (**8**)	8.43, 8.94, 10.85, 12.70, 14.61, 16.46
pinacol	9.89, 10.66, 12.63, 13.78
B_2pin_2 (**12**)	9.74, 10.74, 11.88, 12.19, 13.50, 14.34, 15.68
2,2-dimethyl-1,3-propanediol	10.09, 10.73, 13.27, 15.57
B_2neop_2 (**11**)	10.38, 11.25, 11.59, 12.79−13.73, 15.18,16.23

The structures of the complexes **3**, **8**, **9**, **11**, and **13**−**17** have all been determined by X-ray crystallography, and these results are presented in the companion paper.[12]

Photoelectron Spectroscopy. Prior to this work, PES studies had only been carried out on B_2Cl_4 and B_2F_4[17] and on **1**.[18] Vertical ionization energy data for **1**, **3**, **8**, **11**, and **12** and also for catechol, 4-Bu^t-catechol, pinacol, and 2,2-dimethyl-1,3-propanediol are presented in Table 1, and the He I and He II spectra for **1**, **3**, and **12** are shown in Figures 1−3. The other PE spectra have been deposited as Supporting Information.

The spectrum of **1** (Fig. 1a,b) consists of four bands, which appear as two overlapping pairs between 7 and 10 eV, and a number of overlapping peaks above 11 eV. The He I spectrum is identical to that obtained in the previous study,[18] although the higher resolution obtained here shows fine structure on the broader band. The previous assignment of the PE spectrum of **1**[18] assumed D_{2h} symmetry; the first four bands were assigned to the π_4, π_3, π_2, and π_1 orbitals principally N pπ in character (these are labeled a_u, b_{1g}, b_{3g}, and b_{2u} respectively in the D_{2h} point group). However, following the most recent structure determination,[19] reassignment within D_2 symmetry is given in Table 2. The dimethylamido groups are twisted out of the BN_2 plane so that the N pπ electron pairs are not oriented to gain maximum overlap with the B pπ orbital. The B pπ orbitals transform as b_2 and b_3 in the D_2 group while the N pπ orbitals give a, b_1, b_2, and b_3 symmetry-adapted linear combinations. The a and b_1 linear combinations have the N pπ orbitals out of phase with one another and no stabilizing interaction with the boron. These orbitals are expected to lie at higher energy and give rise to the two lower IE bands at 7.16 and 7.54 eV. The sharpness of these bands indicates their nonbonding character. The b_2 and b_3 orbitals have boron 2p contributions and are bonding and antibonding across the B−B bond, respectively. They give rise to the broader bands at 8.94 and 9.64 eV. The broader band shape of the b_2 ionization at 9.64 eV is indicative

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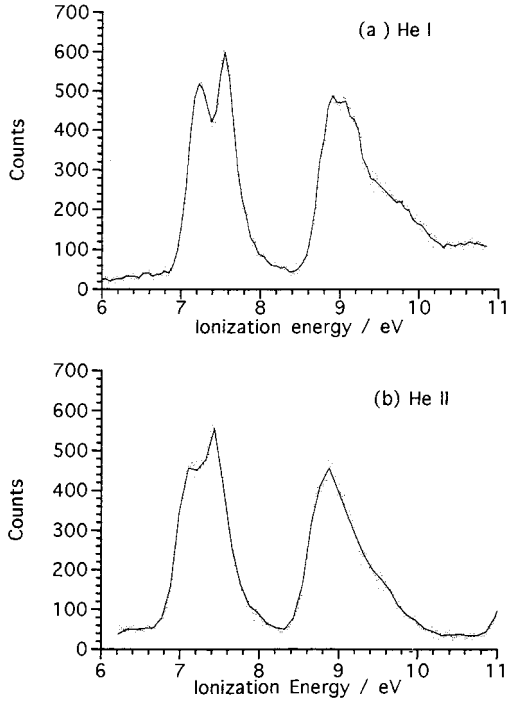


Figure 1. Short-range He I spectrum (a) and He II spectrum (b) for **1**.

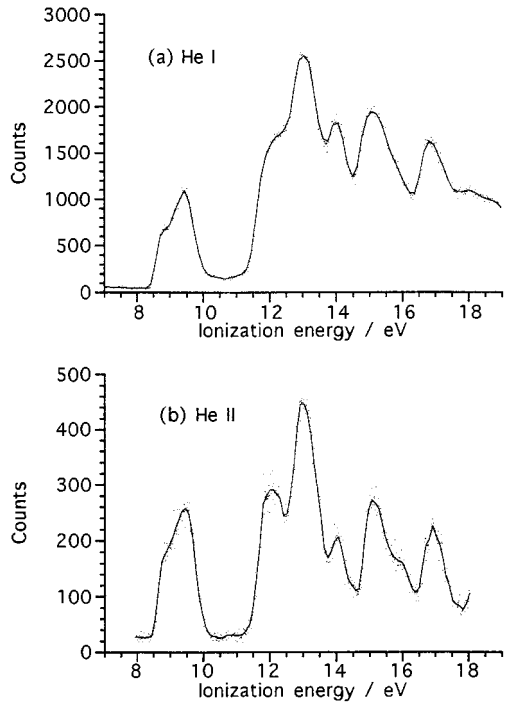


Figure 2. He I spectrum (a) and He II spectrum (b) for **3**.

of significant bonding character. The separations of the first and second bands (0.4 eV) and the third and fourth band (0.7 eV) give the size of interaction across the B−B bond, the separation of the average of the first and second bands and the average of the third and fourth bands of 2 eV is a measure of the N−B π donation.

The catechol and 4-Bu^t-catechol spectra give two sharp peaks in the region 8−10 eV. These highest occupied orbitals are those with the oxygen lone pairs out of phase with the C pπ orbitals six-carbon ring (Figure 4 shows a schematic diagram of the electron density for these orbitals derived from the EHMO calculations). EHMO calculation gives the energy of the 3a″ orbital as the lower of the two so the first band at 8.43 eV is assigned to the 4a″ orbital and the second at 9.26 eV is assigned to the 3a″ orbital. An analogous assignment has been made for phenol[20] on the basis of an SCF calculation. The increase in intensity of those two bands, on moving from the He I to the He II spectrum, probably reflects both the smaller decrease of the photoionization cross section of oxygen in comparison to carbon and also the increase commonly found for C pπ orbitals relative to C−H σ bonding orbitals.[21]

Comparison of the catechol spectrum with the 4-Bu^t-catechol spectrum shows a shift of the two bands to lower ionization energy in the spectrum of the latter. This reflects the inductive effect of the Bu^t group through the σ system and the delocal-

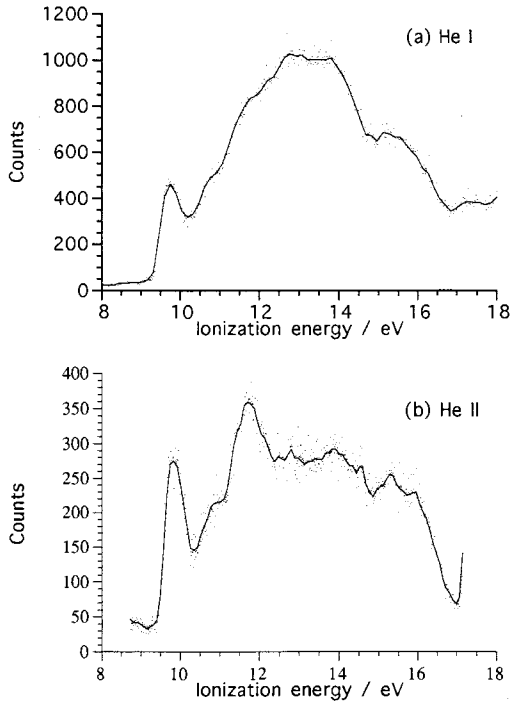


Figure 3. He I spectrum (a) and He II spectrum (b) for **12**.

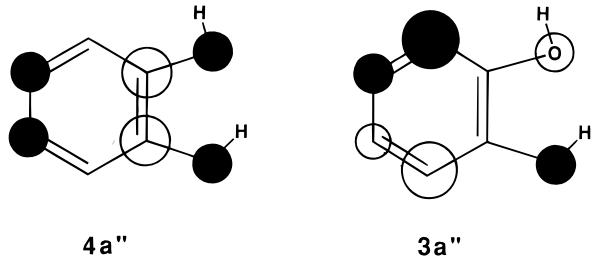


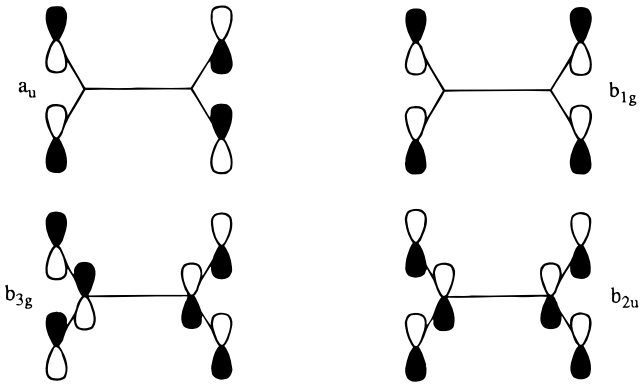
Figure 4. Schematic representations of the 4a″ and 3a″ nonbonding oxygen orbitals in catechol as dervied from EHMO calculations.

Table 2. Assignment of the Bands in the PES Spectrum of $B_2(NMe_2)_4$ (**1**)

band	IE (eV)	orbital
1	7.16	a
2	7.54	b_1
3	8.94	b_3
4	9.64	b_2

(20) Kimura, K.; Katsumatra, S.; Achiba, Y.; Yamazaki, T.; Iwata, S.; *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981.
(21) Yeh, J.-J. *Atomic Calculation of Photoionisation Cross-Sections and Asymmetry Parameters*; Gordon and Breach Science Publishers S.A.: Newark, NJ, 1993.

Chart 1



ization of electron density through the phenyl group and oxygen atoms. It should be noted that the first IE of both the catechols occurs at a lower energy than either parent function, that is either the corresponding arene or O lone pair. This is a strong indication that the associated electron is delocalized over both the oxygens and the ring.

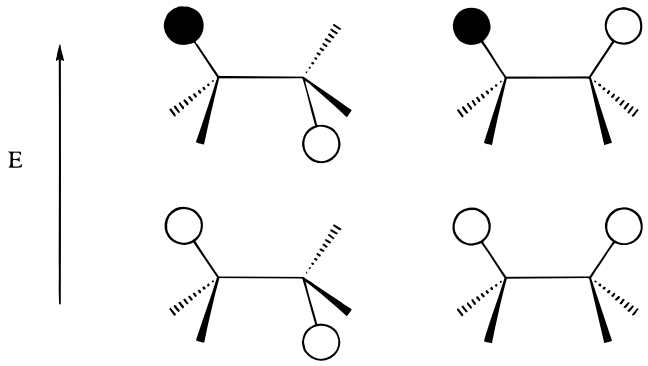
In **3**, which has a planar structure, four ionization bands are expected in the low IE region, two arising from the catechol pπ orbitals (a_u and b_{1g}) and two from the interactions with the in-phase and out-of-phase boron p orbitals (b_{3g} and b_{2u}). All four orbitals are shown in Chart 1; for clarity only the O pπ orbitals of the catechol function are included.

In the spectrum (Figure 2) the four associated ionization bands are ill-defined but appear between 8.5 and 10 eV. This assignment is supported by their increase in relative intensity in moving from He I to He II photon energies, as was found for the parent catechol. The separation of the four bands is less distinct than for **1** even though the planar structure should favor increased π bonding. One reason is that π donation from the catechol to the B pπ orbital is confined to the 4a″ orbital of catechol. The IE difference found between the first two bands in catechol should therefore decrease in **3** as is found. Second, as the electrons are now to a significant extent localized on the arene rings, the interaction across the B−B bond is less. As a consequence, the low lying bands only spread across ca. 1.5 eV whereas the highest and the lowest in **1** are separated by 2.5 eV. The band at 12.13 eV must correspond to ionization from the B−O σ bonds, as there is no analogous peak in the catechol spectrum. Again, this is supported by the increase in relative intensity of the band in the He II spectrum.

The spectrum of **8** may be assigned in an identical manner, with the four bands between 8 and 10 eV corresponding to the a_u, b_{1g}, b_{3g}, and b_{2u} orbitals, respectively. However, the relative intensity change of the band at 10.85 eV, assigned to the B−O σ orbital is not nearly so marked as in the spectrum of **3**. The magnitude of the shift of the four bands to lower ionization energy from **3** to **8** is approximately 0.4 eV, compared with the analogous shift with an approximate magnitude of 0.34 eV from catechol to 4-Bu^t-catechol. This larger shift for the diboron compounds indicates the greater extent of the π framework in these compounds, compared to the more limited π framework in the free catechols.

Pinacol exists in the trans form in all phases (with free rotation around the C−C bond), meaning that it is not ideal for comparison with **12**, where the pinacolate is locked into the cis form. The nonbonding, in phase π_+ (stabilized by long-range interactions) and the out of phase π_- orbitals for pinacol are shown in Chart 2 together with the analogous orbitals for the less stable cis form.

Chart 2



π_- and π_+ orbitals of *trans* and *cis* pinacol

Table 3. Assignment of the PES Spectrum of B_2pin_2 (**12**)

IE (eV)	orbital
9.74	a_u
9.74	b_{1g}
10.74	b_{3g}
10.74	b_{2u}

Table 4. Assignment of the PES Spectrum of B_2neop_2 (**11**)

IE (eV)	orbital
10.38	a_u
10.38	b_{1g}
11.25	b_{3g}
11.59	b_{2u}

The two bands at 9.89 and 10.66 eV can be assigned to these π_+ and π_- orbitals, respectively. This assignment is supported by the equal intensities of the two bands in the He II spectrum, indicating equal oxygen character. The first two IE for pinacol are higher than those of catechol, the expectation being that they are more O localized.

The assignment for **12** is given in Table 3. The assignment of the 10.74 eV band to the b_{3g} and b_{2u} orbitals is supported by the smaller relative intensity of this band compared with those from the a_u and b_{1g} orbitals in the He II spectrum, which indicates smaller oxygen character and greater boron character. The separation between the two bands of ca.1 eV is less than that of the average of the first two and the third and fourth band of **1**, which is ca. 2 eV. This indicates that in these alcohol derivatives, B−O π interaction is less than the B−N π interaction found in **1**, again despite the more favorable planar geometry. The B−O σ bond is assigned to the band at 11.88 eV.

The compound 2,2-dimethyl-1,3-propanediol shows the two bands associated with the nonbonding oxygen orbitals at 10.09 and 10.73 eV, overlapping slightly. The remainder of the spectrum, as expected, shows a similar shape to that of pinacol.

The assignment for **11** is given in Table 4. The b_{3g} and b_{2u} have smaller relative intensity in the He I spectrum and a decrease in photoionization cross section in the He II spectrum. These effects reflect the decrease in oxygen character and increase in boron character in comparison with the a_u and b_{1g} orbitals. The band due to the ionization from the B−O σ bond does not show the usual dominance in the He II spectrum and is consequently not assigned.

In considering the whole series of compounds, the following trends may be identified. First, the replacement of oxygen for nitrogen in the N_2BBN_2 framework leads to an increase in IE of ca. 1.65 eV; second, the presence of an aromatic ring rather than an aliphatic chain bonded to the oxygens in the O_2BBO_2

framework decreases the IE by ca. 1.50 eV; and third, the presence of electron-donating groups such as Bu^t or methyl groups decrease the IE by ca. 0.40 eV. The first effect is a consequence of the greater electronegativity of oxygen compared with nitrogen such that the electrons are more difficult to ionize. The second and third effects are linked to electron donation from delocalization and inductive effects, which destabilize the orbitals.

The ionization energies of the orbitals of the $B_2(OR)_4$ series follow the trend **8** < **3** < **12** < **11**, such that ionizations from the orbitals in **8** occur at lowest IE. This is a consequence of the effects mentioned above.

Separation in the π type orbitals indicate less π donation to the boron in the alkoxide than the amido derivatives. In **1** there is evidence of interaction between the π orbitals across the B−B bond.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry dinitrogen using standard Schlenk or glovebox techniques. All solvents were dried and distilled prior to use according to established procedures. Pinacol, 2,2-Me$_2$-1,3-propanediol (neopentyl glycol), catechol, 3-Me-catechol, 4-Me-catechol, 4-Bu^t-catechol, 3,5-Bu$^t_2$-catechol, 1,2-dithiocatechol, and 1,2-dithio-4-Me-catechol were purchased from Aldrich, and their purity was checked by GC/MS and/or NMR spectroscopy prior to use.

Nuclear magnetic resonance experiments were performed on Bruker AC200, WP200, WM300, AM500, and AMX500 spectrometers at the following frequencies: ^{1}H, 200, 300, or 500 MHz; ^{13}C{^{1}H}, 50, 75, or 125 MHz; and ^{11}B{^{1}H}, 64 or 160 MHz. ^{1}H chemical shifts were referenced either to the internal standard tetramethylsilane (TMS) or to residual ^{1}H resonances in the deuterated solvents, all ^{13}C chemical shifts were referenced to the solvent resonances and are relative to the external standard TMS, and ^{11}B chemical shifts were referenced to external BF$_3$•(OEt$_2$). All spectra were recorded in $CDCl_3$ unless otherwise stated. Elemental analyses were obtained either from M-H-W Laboratories (Phoenix, AZ) or the University of Newcastle upon Tyne. GC/MS analyses were performed on a Hewlett-Packard 5890 series II/5971A MSD instrument equipped with an HP 7673A autosampler and a fused silica column (30 m × 0.25 mm × 0.25 mm, cross-linked 5% phenylmethyl silicone). The following operating conditions were used: injector, 260 °C; transfer line, 280 °C; oven temperature was ramped from 70 °C to 260 °C at the rate of 20 °C/min. UHP grade helium was used as the carrier gas. Hrms spectra were recorded on a Kratos MS-80 instrument. Extended Hückel molecular orbital (EHMO) calculations were performed on idealized B_2cat_2 and on the simplified model compounds $B_2(NH_2)_4$ and $B_2(OCH_2CH_2O)_2$ using standard parameters and charge iteration sequences.[22]

Photoelectron Spectra. The photoelectron (PE) spectra were measured using a PES Laboratories 0078 photoelectron spectrophotometer which has a hollow cathode He discharge lamp capable of providing both He I and He II radiation. The samples were held at a constant temperature in the ranges given below, giving a vapor pressure of ca. 4×10^{-2} mmHg, and data were collected on the gas-phase molecules by repeated scans using an Atari microprocessor. The spectra were calibrated with reference to N_2, Xe and He. Recording temperatures (°C) were as follows: $B_2(NMe_2)_4$ (**1**), room temperature; $B_2(1,2\text{-}O_2C_6H_4)_2$ (**3**), 118−140; B_2pin_2 (**12**), 20−40; $B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (**8**), 120−148; $B_2(OCH_2CMe_2CH_2O)_2$ (**11**), 85−100; catechol, 35−50; 4-Bu^{t}catechol, 55−60; pinacol, 25−40; and 2,2-dimethyl-1,3-propanediol, 35−40.

Preparations. $B_2(1,2\text{-}O_2C_6H_4)_2$ [2,2′-Bis(1,3,2-benzodioxaborole)] (3). Catechol (7.3 g, 66.6 mmol) was added to a stirred solution of **1** (6.0 g, 30.3 mmol) in Et$_2$O (250 mL) at room temperature. After stirring for several hours, the reaction flask was placed in an ice/water bath and 152 mL of a 1 M solution of HCl in Et$_2$O was added dropwise over a period of 30 min. The resulting reaction mixture was then allowed to stir at room temperature for an additional 10 h. After this time, the solvent was removed in vacuo and the product was extracted into toluene and filtered through Celite. After removal of the toluene in vacuo, and subsequent washing with MeCN, 4.3 g of white solid **3** was obtained. The MeCN washings were concentrated and cooled (−30 °C) to give an additional 0.9 g of **3**. The overall yield of **3** was 5.2 g (72%). Spectroscopic data for **3**. NMR (CD_2Cl_2): ^{1}H δ 7.38 (m, 4H, 3,6-C*H*), 7.20 (m, 4H, 4,5-C-*H*); ^{13}C{^{1}H} δ 147.8 (s, 1,2-*C*O), 123.5 (s, 3,6-*C*H), 113.2 (s, 4,5-*C*H); ^{11}B{^{1}H} δ 31.6. Anal. Calcd for $C_{12}H_8B_2O_4$: C, 60.60; H, 3.40. Found: C, 60.80; H, 3.20. MS (EI): 238 (M^+, 100), 237 (50), 209 (4), 162 (28), 119 (9), 76 (13), 63 (12).

$[B_2(1,2\text{-}O_2\text{-}C_6H_4)_2(NHMe_2)_2]$ (4). A solution of catechol (0.220 g, 2 mmol) in 5 mL of Et$_2$O was added to a stirred solution of **1** (0.198 g, 1 mmol) in 2 mL of Et$_2$O at room temperature. The resulting reaction mixture was allowed to stir for 30 min, then the solvent was removed in vacuo affording the bis-amine adduct (**4**) as an insoluble white solid (0.292 g, 89%). Anal. Calcd for $C_{16}H_{22}B_2N_2O_4$: C, 58.59; H, 6.76. Found: C, 58.57; H, 6.51.

$[B_2(1,2\text{-}O_2\text{-}3,5\text{-}Bu^t_2\text{-}C_6H_2)_2(NHMe_2)_2]$ (5). A solution of 3,5-di-*tert*-butylcatechol (0.888 g, 4.0 mmol) in Et$_2$O (5 mL) was added to a solution of **1** (0.396 g, 2.0 mmol) in Et$_2$O (5 mL) at 0 °C which gave a white precipitate. The solvent was removed by syringe, and the solid was washed with Et$_2$O (10 mL) before being dried in vacuo (0.75 g, 68%). Spectroscopic data for **5**. NMR ($CDCl_3$): ^{1}H δ 6.70 (d, 2H, 6-C*H*, $^4J_{HH}$ = 2.1 Hz), 6.55 (d, 2H, 4-C*H*, $^4J_{HH}$ = 2.1 Hz), 6.27 (v br s, 2H, N*H*), 2.45 (br s, 12H, N*Me*), 1.34 (s, 18H, Bu^t), 1.22 (s, 18H, Bu^t); ^{11}B{^{1}H} δ 11.8. Anal. Calcd for $C_{32}H_{54}N_2O_4B_2$: C, 69.58; H, 9.85; N, 5.07. Found: C, 69.93; H, 10.40; N, 4.87.

$B_2(1,2\text{-}O_2\text{-}3\text{-}MeC_6H_3)_2$ (6). Compound **1** (1.00 g, 5.0 mmol) was dissolved in Et$_2$O (10 mL) at 0 °C and a solution of 3-methylcatechol (1.24 g, 10 mmol) in Et$_2$O (10 mL) was then added slowly. A white precipitate formed immediately, and after 30 min, a solution of 1.0 M HCl in Et$_2$O (25 mL, 25 mmol) was added dropwise and the reaction mixture allowed to warm to room temperature and stir overnight. The solvent was then partially removed in vacuo, and the white solid was extracted into toluene (40 mL) and filtered through Celite, affording a colorless solution from which white crystals of **6** were obtained over 24 h at −30 °C (0.93 g, 70%). Spectroscopic data for **6**. NMR ($CDCl_3$): ^{1}H δ 7.14 (d, 2H, 6-C*H*, $^3J_{HH}$ = 7.5 Hz), 7.01 (t, 2H, 5-C*H*, $^3J_{HH}$ = 7.5 Hz), 6.94 (d, 2H, 4-C*H*, $^3J_{HH}$ = 7.5 Hz), 2.43 (s, 6H, *Me*); ^{13}C{^{1}H} δ 147.3 and 146.4 (s, 1 and 2-*C*O), 124.7 (s, 6-*C*H), 123.5 (s, 3-*C*Me), 123.0 and 110.4 (s, 4 and 5-*C*H), 14.8 (s, *Me*); ^{11}B{^{1}H} δ 30.5. Anal. Calcd for $C_{14}H_{12}B_2O_4$: C, 63.25; H, 4.55. Found: C, 63.25; H, 4.50. HRMS calcd for $C_{14}H_{12}B_2O_4$: 266.0922. Found: 266.0919.

$B_2(1,2\text{-}O_2\text{-}4\text{-}MeC_6H_3)_2$ (7). Using the same method as that for **6**, a solution of 4-methylcatechol (1.24 g, 10 mmol) in Et$_2$O (10 mL) was added to a solution of **1** (1.00 g, 5.0 mmol) in Et$_2$O (10 mL) at 0 °C giving a white precipitate. A 1.0 M solution of HCl in Et$_2$O (25 mL, 25 mmol) was added dropwise and the reaction mixture was allowed to stir overnight. Reduction of the solvent volume, extraction into toluene and filtration through Celite afforded white crystals of **7** (0.89 g, 67%). Spectroscopic data for **7**. NMR ($CDCl_3$): ^{1}H δ 7.28 (d, 2H, 6-C*H*, $^3J_{HH}$ = 8.1 Hz), 7.23 (s, 2H, 3-C*H*), 7.02 (d, 2H, 5-C*H*, $^3J_{HH}$ = 8.1 Hz), 2.45 (s, 6H, *Me*); ^{13}C{^{1}H} δ 147.8 and 145.6 (s, 1 and 2-*C*O), 133.5 (s, 4-*C*Me), 123.9 (s, 5-*C*H), 113.5 and 112.3 (s, 3 and 6-*C*H), 21.4 (s, *Me*); ^{11}B{^{1}H} δ 30.6. Anal. Calcd for $C_{14}H_{12}B_2O_4$: C, 63.25; H, 4.55. Found: C, 63.70; H, 4.40. HRMS calcd for $C_{14}H_{12}B_2O_4$: 266.0922. Found: 266.0923.

$B_2(1,2\text{-}O_2\text{-}4\text{-}Bu^tC_6H_3)_2$ (8). 4-Bu^{t}catechol (10.5 g, 63.3 mmol) was added to a stirred solution of **1** (5.7 g, 28.8 mmol) in hexane (300 mL) at room temperature. To this solution was then added 150 mL of a 1 M solution of HCl in Et$_2$O dropwise over a period of 30 min, and the resulting mixture was allowed to stir at room temperature for 5 h. After this time, the solvent was removed in vacuo and the product was extracted into hexane and filtered through Celite. Upon removal of hexane in vacuo, 8.8 g (88%) of **8** was obtained as a white solid. Spectroscopic data for **8**. NMR ($CDCl_3$): ^{1}H δ 7.36 (m, 2H, 6-C*H*), 7.17 (m, 4H, 3 and 5-C*H*), 1.29 (s, 18H, Bu^t); ^{13}C{^{1}H} δ 147.7 and 147.3 (s, 1 and 2-*C*O), 145.4 (s, 4-*C*Bu^t), 120.3 and 112.0 and 110.2 (s, 3 and 5 and 6-*C*H), 34.9 (s, *C*(CH$_3$)$_3$), 31.7 (s, C(*C*H$_3$)$_3$); ^{11}B{^{1}H}

(22) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

δ 31.9. Anal. Calcd for $C_{20}H_{24}B_2O_4$: C, 68.65; H, 6.90. Found: C, 68.80; H, 7.05. MS (EI): 350 (M^+, 18), 335 (100), 319 (3), 307 (8), 295 (2), 251 (4), 160 (8), 132 (11), 89 (3), 77 (3), 57 (4).

B_2(1,2-O_2-3,5-Bu^t_2-C_6H_2)$_2$ (9). Using the same method as for **8**, a solution of 3,5-di-*tert*-butylcatechol (2.22 g, 10 mmol) in Et_2O (10 mL) was added to a solution of **1** (1.00 g, 5.0 mmol) in Et_2O (10 mL) at 0 °C giving a white precipitate. A 1.0 M solution of HCl (25 mL, 25 mmol) was added dropwise and the reaction mixture was allowed to stir overnight at 0 °C. The product was extracted into toluene (40 mL) and after filtering through Celite, the volume was reduced by 50%. After 24 h at −30 °C, white crystals of B_2(1,2-O_2-3,5-Bu^t_2-C_6H_2)$_2$ were collected, washed with hexanes (40 mL), and dried in vacuo (1.45 g, 63%). Spectroscopic data for **9**. NMR ($CDCl_3$): ^{1}H δ 7.28 (d, 2H, 6-C*H*, $^4J_{HH}$ = 2 Hz), 7.13 (d, 2H, 4-C*H*, $^4J_{HH}$ = 2 Hz), 1.50 (s, 18H, Bu^t), 1.35 (s, 18H, Bu^t); ^{13}C{^{1}H} δ 148.3 and 145.6 (s, 1 and 2-*C*O), 144.0 and 134.9 (s, 3 and 5-*C*Bu^t), 116.4 and 107.6 (s, 4 and 6-*C*H), 35.0 (s, *C*$(CH_3)_3$), 34.5 (s, *C*$(CH_3)_3$), 31.9 (s, C(*C*$H_3)_3$), 29.9 (s, C(*C*$H_3)_3$); ^{11}B{^{1}H} δ 31.6. Anal. Calcd for $C_{28}H_{40}B_2O_4$: C, 72.75; H, 8.70. Found: C, 72.90; H, 8.75. MS (EI): 463 (M + 1^+, 19), 462 (M^+, 54), 461 (27), 448 (37), 447 (100), 446 (57), 445 (7), 233 (13), 216 (29), 86 (20), 84 (31), 57 (73).

B_2(1,2-O_2-3-MeOC_6H_3)$_2$ (10). A solution of 3-methoxycatechol (1.00 g, 7.135 mmol) was added to a solution of **1** (0.63 mL, 0.707 g, 3.57 mmol) in Et_2O (30 mL). A white precipitate formed immediately. The reaction mixture was allowed to stir for 4 h after which time a 1 M solution of HCl in Et_2O (14.14 mL, 14.14 mmol) was added. After the mixture had stirred for a further 12 h, the volatiles were removed in vacuo, and the remaining solid was redissolved in toluene (40 mL) and filtered through a small amount of Celite to afford a colorless solution over which hexanes (40 mL) were layered. Solvent diffusion over 48 h at −30 °C afforded a white solid. (0.771 g, 72%). Spectroscopic data for **10**. NMR ($CDCl_3$): ^{1}H δ 7.18 (t, 2H, 5-C*H*, $^3J_{HH}$ = 7.5 Hz), 7.02 and 6.80 (d, 4H, 4 and 6-C*H*, $^3J_{HH}$ = 7.5 Hz); ^{13}C{^{1}H} δ 149.2 and 146.3 (s, 1 and 2-*C*O), 137.5 (s, 3-*C*OMe), 123.6 and 108.0 and 105.9 (s, 4 and 5 and 6-*C*H), 56.7 (s, O*Me*); ^{11}B{^{1}H} δ 28.6. Anal. Calcd for $C_{14}H_{12}B_2O_6$: C, 56.45; H, 4.06. Found: C, 56.34; H, 4.30. MS (EI): 300 (M + 2^+, 3), 298 (M + 1^+, 17), 298 (M^+, 100), 297 (56), 296 (7), 283 (9), 282 (5), 255 (6), 149 (6), 107 (8), 79 (9).

B_2(OCH_2CMe_2CH_2O)$_2$ (11). Neopentyl glycol (2,2-dimethyl-1,3-propanediol) (2.1 g, 20.2 mmol) was added to a stirred solution of **1** (2.0 g, 10.1 mmol) in Et_2O (50 mL) at room temperature. The reaction mixture was stirred at ambient temperature for 5 h and was then cooled to −78 °C in a dry ice/acetone bath. To this cooled solution was added 50 mL of a 1 M solution of HCl in Et_2O dropwise via an addition funnel over a period of 2 h. After warming slowly to room temperature, the solvent was removed in vacuo and the product was extracted into hexane using a Soxhlet apparatus. Subsequent recrystallization from hexane/CH_2Cl_2 (90/10) afforded 1.45 g (64%) of **11** as a white solid. Spectroscopic data for **11**. NMR ($CDCl_3$): ^{1}H δ 3.35 (s, 8H, CH_2), 0.91 (s, 12H, CMe_2); ^{13}C{^{1}H} δ 71.6 (s, *C*H_2), 31.7 (s, *C*Me_2), 22.1 (s, CMe_2); ^{11}B{^{1}H} δ 28.4. Anal. Calcd for $C_{10}H_{20}B_2O_4$: C, 53.15; H, 8.90. Found: C, 52.95; H, 9.00. MS (EI): 226 (M^+, 1), 211 (5), 115 (20), 103 (8), 99 (8), 89 (13), 70 (78), 69 (100), 56 (53), 55 (72).

B_2(OCMe_2CMe_2O)$_2$ (12). Pinacol (2.7 g, 22.8 mmol) was added to a stirred solution of **1** (2.2 g, 11.1 mmol) in Et_2O (50 mL) at room temperature. The reaction mixture was allowed to stir at ambient temperature for 5 h and then cooled to −78 °C in a dry ice/acetone bath. To this was added 50 mL of a 1 M solution of HCl in Et_2O dropwise via an addition funnel over a period of 2 h. After warming slowly to room temperature, the solvent was removed in vacuo and the product was extracted into hexane and then filtered through Celite. Upon removal of hexane in vacuo, 2.2 g (76%) of **12** was obtained as a white solid. Spectroscopic data for **12**. NMR ($CDCl_3$): ^{1}H δ 1.27 (s, 24H, *Me*); ^{13}C{^{1}H} δ 83.4 (s, *C*Me), 24.9 (s, C*Me*); ^{11}B{^{1}H} δ 30.7. MS (EI): 254 (M^+, 1), 239 (39), 238 (19), 171 (3), 155 (7), 139 (6), 129 (7), 113 (10), 84 (100), 83 (37), 69 (26), 57 (8).

B_2(1,2-S_2-C_6H_4)$_2$ (13). Compound **1** (0.31 mL, 1.76 mmol) was dissolved in Et_2O (5.0 mL) and cooled to 0 °C. To this was added a solution of benzene-1,2-dithiol (0.500 g, 3.515 mmol) in Et_2O (5.0 mL). A white precipitate was observed immediately. After 5 min, a 1.0 M solution of HCl in Et_2O (8.80 mL, 8.80 mmol) was added dropwise. The reaction mixture was then stirred for 24 h, after which time the solvent was removed in vacuo. The remaining white solid was extracted into toluene (20 mL) and filtered through Celite to give a colorless solution from which white crystals of **13** formed over 12 h at 5 °C (0.402 g, 76%). Spectroscopic data for **13**. NMR ($CDCl_3$): ^{1}H δ 7.98 (m, 4H, 3,6-C*H*), 7.43 (m, 4H, 4,5-C*H*); ^{13}C{^{1}H} δ 143.6 (s, 1 and 2-*C*S), 126.7 and 125.6 (s, 4,5 and 3,6-*C*H); ^{11}B{^{1}H} δ 57.9. Anal. Calcd for $C_{12}H_8B_2S_4$: C, 47.70; H, 2.65. Found: C, 47.70; H, 4.57. HRMS Calcd for $C_{12}H_8B_2S_4$: 301.9695. Found: 301.9704.

B_2(1,2-S_2-4-MeOC_6H_4)$_2$ (14). Using a method similar to that above, a solution of 4-methyl-1,2-dithiocatechol (1.179 g, 7.545 mmol) in Et_2O (10 mL) was added to a solution of **1** (0.67 mL, 3.772 mmol) in Et_2O (10 mL) at 0 °C to give a white precipitate. A 1.0 M solution of HCl in Et_2O (18.86 mL, 18.86 mmol) was added and the reaction was stirred overnight. Reduction of the solvent volume was followed by extraction into toluene and filtration through Celite. The volume of filtrate was reduced and the solution was cooled, affording a white precipitate which was separated by decanting the solvent. White crystals of **14** were obtained by cooling a CH_2Cl_2 solution to 5 °C for 48 h (0.598 g, 48%). Spectroscopic data for **14**. NMR ($CDCl_3$): ^{1}H δ 7.72 (d, 2H, 6-C*H*, J_{HH} = 8.1 Hz), 7.66 (m, 2H, 3-C*H*), 7.12 (d m, 2H, 5-C*H*, J_{HH} = 8.1 Hz), 2.38 (s, 6H, *Me*); ^{13}C{^{1}H} δ 143.8 and 140.5 (s, 1 and 2-*C*S), 139.4 (s, 4-*C*Me), 127.0 and 126.7 and 126.0 (s, 3 and 5 and 6-*C*H), 21.1 (s, *Me*); ^{11}B{^{1}H} δ 58.1. Anal. Calcd for $C_{14}H_{12}B_2S_4$: C, 50.95; H, 3.65. Found: C, 51.20; H, 3.67. HRMS calcd for $C_{14}H_{12}B_2S_4$: 330.0008. Found: 330.0021.

[B_2Cl_4(NHMe_2)$_2$] (15). This compound was isolated when HCl was added to **1** before complete reaction with the diols (e.g. pinacol or neopentyl glycol) had taken place. Spectroscopic data for **15**. NMR ($CDCl_3$): ^{1}H δ 4.75 (br s, 1H, N*H*), 2.75 (d, 6H, N*Me*), $^3J_{HH}$ = 6 Hz); ^{13}C{^{1}H} δ 39.4 (s); ^{11}B{^{1}H} δ 9.5. Anal. Calcd for $C_4H_{14}N_2B_2Cl_4$: C, 19.30; H, 5.45; N, 10.80. Found: C, 19.05; H, 5.50; N, 10.85.

[NH_2Me_2][Bcat$_2$] (16). Neat B$(NMe_2)_3$ (0.143 g, 1 mmol) was added to a solution of catechol (0.222 g, 2 mmol) in Et_2O (3 mL). The resulting precipitate was collected and washed thoroughly with Et_2O (20 mL), followed by drying in vacuo to afford **16** (0.250 g, 91%) as an insoluble white solid. Spectroscopic data for **16**. NMR (CH_3CN/C_6D_6): ^{11}B{^{1}H} δ 14.0. Anal. Calcd for $C_{14}H_{16}NO_4B$: C, 61.57; H, 5.91. Found: C, 61.67; H, 5.93.

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Supporting Information Available: Photoelectron spectra for catechol, 4-Bu^t-catechol, **8**, pinacol, 2,2-dimethyl-1,3-propanediol, and **11**, Figures 5−10, are available (6 pages). Ordering information is given on any current masthead page.

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