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Synthesis and Structures of Salen-Supported Borates Containing Siloxides

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The ligand *N,N″*-bis(2-hydroxybenzylidene)diethylenetriamine (SalenN$_3$H$_3$) was used to prepare the compound SalenN$_3$H{B(OMe$_2$)}$_2$ (**1**) which could, in turn, be used in the formation of SalenN$_3$H{B(OSiPh$_3$)$_2$}$_2$ (**2**). For comparative purposes, the compounds Salben{B(OSiPh$_3$)$_2$}$_2$ (**3**) (Salben = *N,N′*-butylenebis(2-hydroxybenzylideneamine), Salen(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**4**) (Salen(^{t}Bu) = *N,N′*-ethylenebis(3,5-di-*tert*-butyl-2-hydroxybenzylideneamine) and Salben(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**5**) (Salben(^{t}Bu) = *N,N′*-butylenebis(3,5-di-*tert*-butyl-2-hydroxybenzylideneamine) were prepared. In reactions where the siloxide is (HO)$_2$SiPh$_2$, unique dimeric siloxide-bridged compounds result, [Salpten(^{t}Bu){B(O$_2$SiPh$_2$}]$_2$ (**6**) and [SalenN$_3$H{B(O$_2$SiPh$_2$)}]$_2$ (**7**). Compound **6** possesses a zeolite-like cavity having a volume of 157 Å^3. All of the compounds were characterized by physical (mp, analyses) and spectroscopic techniques (^{1}H and ^{11}B NMR, IR) and, in the case of **1**, **3**, **4**, and **6**, by X-ray crystallography.

Introduction

The potentially tetradentate Salen ligands (Figure 1a,b) incorporate a wide range of unique structures and reactivity with transition and main group metals.[1,2] For the group 13 elements these most often are monometallic and incorporating aluminum. Examples include cations,[3−5] five-coordinate alkyls,[6,7] alkoxides,[8] amides,[9] and siloxides.[7] Relatively few monometallic gallium[10] and indium[11] derivatives are known although they are clearly accessible. A few bimetallic aluminum,[12] gallium,[13,14] and indium[15] complexes are also known. By comparison to its heavier congeners the Salen chemistry of boron remains relatively unexplored. The one report describing Salen−boron combinations reveals the resulting complexes to be bimetallic with four-coordinate boron atoms.[16] They are formed through alcoholysis, and the resulting complexes have consequently contained alkoxide groups. The oxygens of these alkoxides partake in both intra- and intermolecular hydrogen bonding, leading to unusual extended structures. The impetus for the present work is to explore the supramolecular chemistry that might be associated with combinations between the Salen ligands and boron. This will involve varying the hydrogen-bonding potential of the ligand as well as the type of alkoxide on the boron atom.

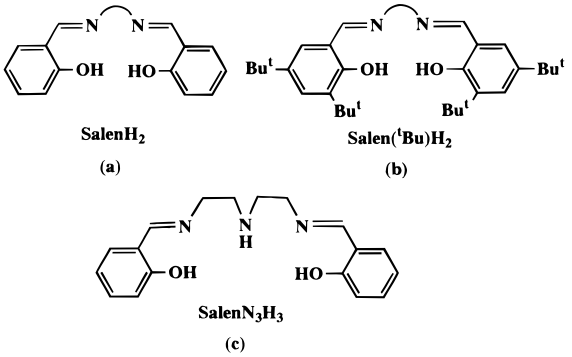

Figure 1. General depiction of the types of Salen ligands mentioned in the text: Salen (a); Salen(^{t}Bu) (b); SalenN$_3$H$_3$ (c).

The ligand, *N,N″*-bis(2-hydroxybenzylidene)diethylenetriamine (SalenN$_3$H$_3$) (Figure 1c) appeared useful in this context since it contained a central NH group capable of hydrogen bonding (or protonation). It is used to prepare the compound SalenN$_3$H{B(OMe$_2$)}$_2$ (**1**) which could, in turn, be used in the formation of SalenN$_3$H{B(OSiPh$_3$)$_2$}$_2$ (**2**). For comparison, the compounds Salben{B(OSiPh$_3$)$_2$}$_2$ (**3**) (Salben = *N,N′*-butylenebis(2-hydroxybenzylideneamine), Salen(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**4**) (Salen(^{t}Bu) = *N,N′*-ethylenebis(3,5-di-*tert*-butyl-2-hydroxybenzylideneamine), and Salben(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**5**) (Salben(^{t}Bu) = *N,N′*-butylenebis(3,5-di-*tert*-butyl-2-hydroxybenzylideneamine) were prepared. In reactions where the siloxide is (HO)$_2$SiPh$_2$, unique dimeric siloxide-bridged compounds result, [Salpten(^{t}Bu){B(O$_2$SiPh$_2$}]$_2$ (**6**) and [SalpenN$_3$H{B(O$_2$SiPh$_2$)}]$_2$ (**7**).

Results and Discussion

Due to the strong, covalent nature of the B−C bond alkane eliminations (with BR$_3$, for instance) are not useful in preparing chelated boron complexes. However, alcohol eliminations work

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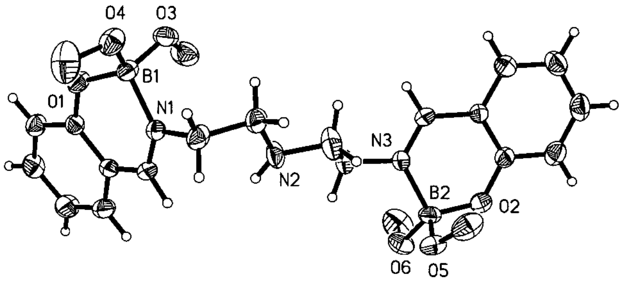
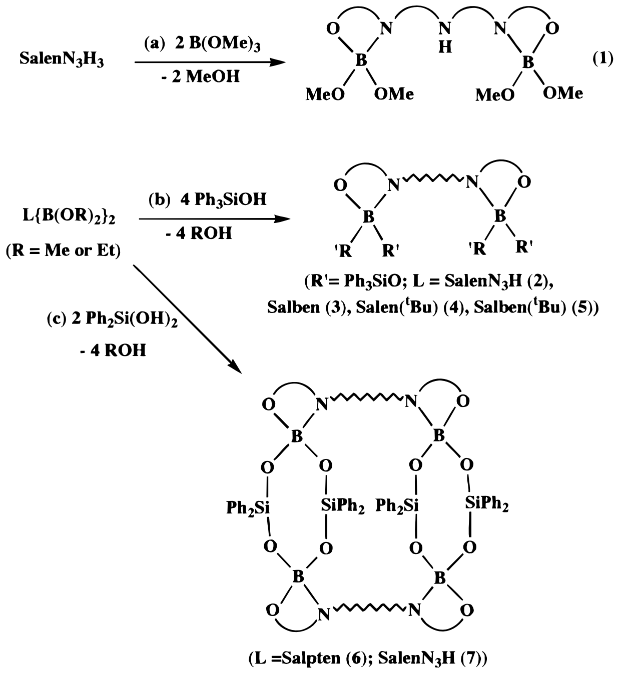


Figure 2. Molecular structure and atom numbering for SalenN$_3$H{B(OMe)$_2$}$_2$ (**1**).

Scheme 1. General Synthesis of the Bimetallic Borate Derivatives **1**−**7**



well provided the reaction is heated for a reasonable period of time. This was the route used to prepare a range of bimetallic borates supported by the Salen[16] and related Schiff base[17] ligands. The choice of alkyl group on the borate (whether Me, Et, ^{n}Pr, or ^{n}Bu) apparently has no influence on the outcome of the reaction. Good yields of **1** are isolated in this manner (Scheme 1a). The ^{1}H NMR spectrum reveals a symmetric solution state geometry with singlets for the OMe (δ 3.01 ppm) and N=CH (δ 8.26 ppm) groups. The NH is silent in the NMR but apparent in the IR (ν 3200 cm^{-1}).

A crystal structure of **1** reveals its arrangement in the solid (Figure 2). The boron atoms are chelated by the ligand and two alkoxides in an overall T_d geometry. The B−O(ligand) distance (1.496(5) Å) is marginally longer than the B−OMe distances (average 1.417(8) Å). The Salen-supported bimetallics usually adopt trans geometries in which the two B(OR)$_2$ groups are oriented away from one another.[16] Often these structures contain a center of inversion. Why **1** takes a less symmetric geometry without a center of inversion can be attributed to hydrogen-bonding interactions. Structurally characterized Salen{B(OR)$_2$} complexes have been shown to possess a wide range of hydrogen bonding involving predominantly the imine groups (N=CH) in contact with an oxygen of the B(OR)$_2$ group.[16] The distances for these contacts ranged from 2.4 to 2.6 Å. They were occasionally intramolecular for ligands containing short alkylene "backbones" (with Salen(^{t}Bu){B(OEt)$_2$}$_2$ for example) but were predominantly intermolecular, especially with longer alkylene groups in the ligand backbone (for (CH$_2$)$_n$ with n = 4−6). These hydrogen-bonding contacts produced interesting extended structures, most often in the form of infinite sheets. The SalenN$_3$H$_3$ ligand was chosen for the present study in order to explore what effect the additional NH group might have on the resulting structure. The NH group of **1** does form intermolecular hydrogen bonds (Figure 3). There is one to the OMe group (2.52 Å), which also has the expected imine contact (2.50 Å). This latter contact is also observed at the other end of the molecule (2.38 Å). The extended structure of **1** consists of infinite sheets organized by these three hydrogen-bonding contacts (see unit cell view in the Supporting Information). This arrangement is exactly what had been observed for the Salen ligands (without the extra NH)[12] so the effect of the NH is not significant in this structure.

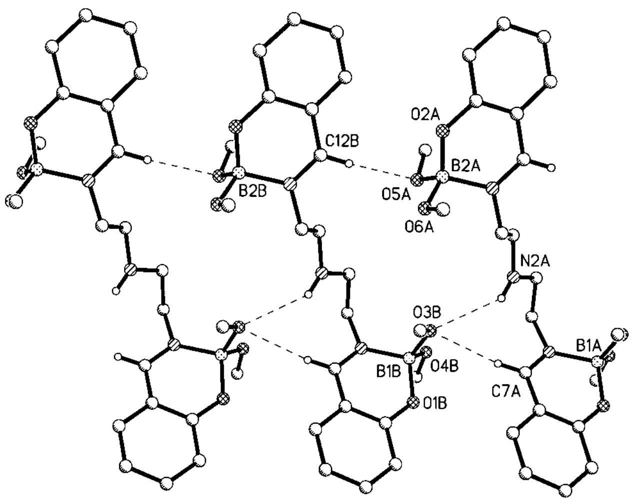


Figure 3. View of the hydrogen bonding for SalenN$_3$H{B(OMe)$_2$}$_2$ (**1**).

In previous work involving the Saltren ligand (tris(((2-hydroxybenzyl)amino)ethyl)amine) attempts to synthesize the bis(siloxide)s (Saltren{B(OSiPh$_3$)$_2$}$_2$ were unsuccessful.[18] Rather, the reactions led to the isolation of a complex, SaltrenH$_3${B(OSiPh$_3$)$_3$}$_3$, where the ligand acts as a Lewis base toward the neutral B(OSiPh$_3$)$_3$ group. Thus, it was interesting to find that high yields of the bis(siloxide)s **2**−**5** were readily available for various Salen ligands (Scheme 1b). For these compounds the N=CH groups appear as sharp singlets in the ^{1}H NMR in the region expected (~7.8 ppm). The PhH resonances were somewhat complicated and appeared as a mass of mutiplets in the range 6.5−7.5 ppm. By comparison, the Si−Ph protons of the monomeric SalenAl(OSiPh$_3$) compounds were easily discerned as equivalent with the appropriate coupling.[7] The difference may be attributed to the fact that there are six of these groups to consider in **2**−**5**. There are single broad resonances in the ^{11}B spectra of all of the compounds. For **2**−**5** these resonances occur in the narrow window, δ 0.08−0.72 ppm, in the region for T_d boron.[19]

Supporting the solution data, the crystal structures of **3** and **4** show that the two chelate-B(OSiPh$_3$)$_2$ units are related by a center of symmetry (Figures 4 and 5, respectively). This gives each of the complexes a trans orientation. By comparison to **1**

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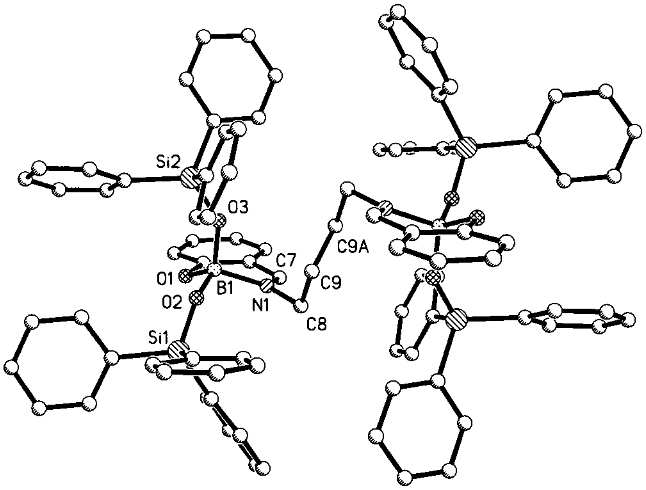

Figure 4. Molecular structure and atom numbering for Salben{B(OSiPh$_3$)$_2$}$_2$ (**3**).

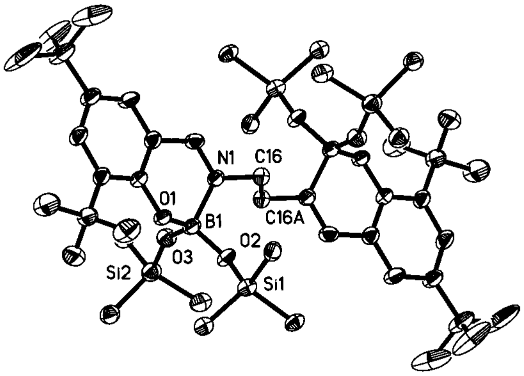

Figure 5. Molecular structure and atom numbering for Salen(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**4**).

(106.0(3)°) the angles between the ligands are somewhat widened in **3** and **4** (average 114(1)°). This reflects the mild steric effect of the Ph$_3$Si group. However, the B−O(ligand) distances are comparable for all of the compounds (**1**, **3**, and **4**) (Table 1). In keeping with the electronegativity difference between oxygen and nitrogen, the B−N distances are lengthened (average for the three compounds, 1.623(5) Å). Overall the bond distances are similar to those for other four-coordinate borates.[16,17] For instance, these distances in two diarylboroxazolidines average 1.65(5) and 1.477(4) Å, respectively.[20] There is no inter- or intramolecular hydrogen bonding in compounds **3** and **4**. The three phenyl groups of the Ph$_3$SiO− unit effectively shield the oxygen atom and prevent any contact. On the basis of the similarity of these two compounds, it is clear that the Ph−^{t}Bu groups of **4** do not have a significant effect on how the ligand coordinates the boron atom. However, these groups do significantly improve the solubility of this complex in nonpolar solvents.

The combination of Ph$_2$Si(OH)$_2$ with Salpten(^{t}Bu)[B(OMe)$_2$]$_2$ (reported in ref 12) and **1** leads to **6** and **7**, respectively (Scheme 1c). The solution ^{1}H NMR data show that the N=CH groups of both compounds are equivalent. For **7** the NCH$_2$ groups appeared as a multiplet. Notably, ν_{N-H} is not observed in the IR spectrum of **6** and **7** perhaps due to hydrogen bonding involving this group. From these data it is uncertain whether the BO$_2$ unit is attached to one ligand or bridged across two. In aluminum derivatives containing the RSi(OH)$_3$ group the (OH)SiO$_2$ unit bridges two metals[21,22] rather than chelating just one.[23] Likewise, this type of bonding is observed in phosphonate RPO(OH)$_2$ derivatives of the group 13 elements.[24−26] In these compounds eight-membered rings form that contain the group 13 element, two oxygens, and the heteroatom (either Si or P) (Figure 6a). This arrangement is important in that it is also found in group 13 silicate and phosphate solid-state materials. This type of bonding is revealed in the crystal structure of **6** (Figure 7). However, unlike the previously reported examples, the eight-membered, (BO$_2$Si)$_2$ units in **6** are connected to one another by the length of the ligand backbone rather than an oxygen (Figure 6b). The O−B−O angles (107.6(9)−115.7(8)°) and B−O distances (1.394(13)−1.512(11) Å) are close to the values observed in [^{t}BuPO$_3$B^{s}Bu]$_4$ (~108° and ~1.48 Å).[26] For the six-membered ring [(PhBO)(Ph$_2$SiO)$_2$],[27] the distance is similar (1.3696(2) Å) but the angles are wider (120.79(21)°). The angles and distances for eight-membered ring compounds incorporating

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compouds

SalenN$_3$H[B(OMe)$_2$]$_2$ (**1**)			
B(1)−O(3)	1.422(5)	B(1)−O(4)	1.411(5)
B(1)−O(1)	1.496(5)	B(1)−N(1)	1.614(5)
B(2)−O(6)	1.416(5)	B(2)−O(5)	1.425(5)
B(2)−O(2)	1.480(5)	B(2)−N(3)	1.610(5)
O(3)−B(1)−O(4)	106.0(3)	O(3)−B(1)−O(1)	112.7(3)
O(4)−B(1)−O(1)	110.9(3)	O(3)−B(1)−N(1)	109.8(3)
O(4)−B(1)−N(1)	111.7(3)	(1)-B(1)−N(1)	105.9(3)
O(6)−B(2)−O(5)	106.8(3)	O(6)−B(2)−O(2)	111.1(3)
O(5)−B(2)−O(2)	112.6(3)	O(6)−B(2)−N(3)	110.5(3)
O(5)−B(2)−N(3)	108.8(3)	O(2)−B(2)−N(3)	107.0(3)
Salben[B(OSiPh$_3$)$_2$]$_2$ (**3**)			
B(1)−O(2)	1.418(4)	B(1)−O(3)	1.429(4)
B(1)−O(1)	1.481(4)	B(1)−N(1)	1.618(5)
O(2)−B(1)−O(3)	113.3(3)	O(2)−B(1)−O(1)	110.8(3)
O(3)−B(1)−O(1)	111.3(3)	O(2)−B(1)−N(1)	110.4(3)
O(3)−B(1)−N(1)	105.0(3)	O(1)−B(1)−N(1)	105.5(3)
Salen(^{t}Bu)[B(OSiPh$_3$)$_2$]$_2$ (**4**)			
B(1)−O(2)	1.411(6)	B(1)−O(3)	1.431(6)
B(1)−O(1)	1.479(6)	B(1)−N(1)	1.635(6)
O(2)−B(1)−O(3)	114.8(4)	O(2)−B(1)−O(1)	110.9(4)
O(3)−B(1)−O(1)	112.3(4)	O(2)−B(1)−N(1)	107.6(4)
O(3)−B(1)−N(1)	105.7(4)	O(1)−B(1)−N(1)	104.9(4)
[Salpten(^{t}Bu){B(O$_2$SiPh$_2$)}$_2$]$_2$ (**6**)			
B(1)−O(3)	1.424(11)	B(1)−O(5)	1.418(11)
B(1)−O(1)	1.474(12)	B(1)−N(1)	1.641(12)
B(2)−O(6)	1.394(13)	B(2)−O(4)	1.449(11)
B(2)−O(2)	1.512(11)	B(2)−N(2)	1.609(11)
O(3)−B(1)−O(5)	115.7(8)	O(3)−B(1)−O(1)	110.3(8)
O(5)−B(1)−O(1)	109.5(9)	O(3)−B(1)−N(1)	107.2(8)
O(5)−B(1)−N(1)	108.6(8)	O(1)−B(1)−N(1)	105.0(7)
O(6)−B(2)−O(4)	116.9(8)	O(6)−B(2)−O(2)	114.3(9)
O(4)−B(2)−O(2)	107.6(9)	O(6)−B(2)−N(2)	105.4(8)
O(4)−B(2)−N(2)	106.7(8)	O(2)−B(2)−N(2)	104.9(7)

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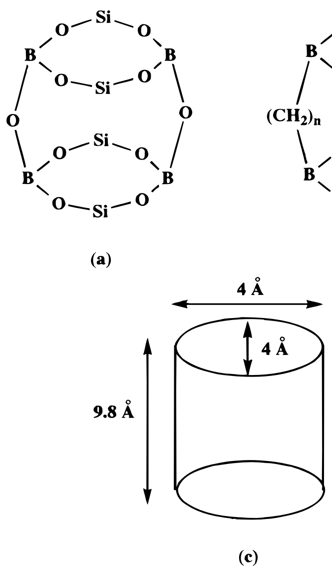

Figure 6. Frameworks of borosilicate molecules (a and b) and the cylinder represented by compound **6** (c).

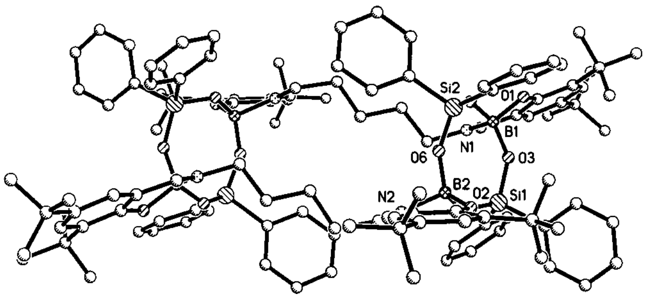

Figure 7. Molecular structure and atom numbering scheme for [Salpten{B(O$_2$SiPh$_2$)}]$_2$ (**6**).

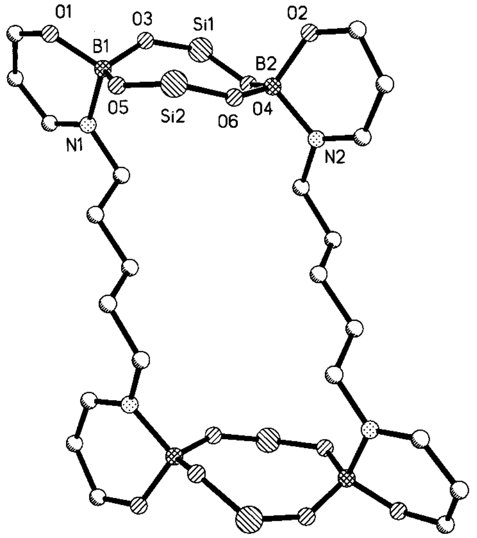

Figure 8. Molecular framework for [Salpten{B(O$_2$SiPh$_2$)}]$_2$ (**6**).

aluminum ([^{t}BuPO$_3$Al^{i}Bu]$_4$)[25] are 105.2(1)−114.2(2)° and 1.762(4) Å, and those for gallium ([PhPO$_3$Ga^{t}Bu]$_4$)[24] are 103.9(1)° and 1.835(7) Å.

The framework of **6** (Figure 8) can be represented by a cylinder that is 9.8 Å long (the average of the Si1−Si2a and Si2−Si1a distances), 4 Å wide (the Si1−Si2 distance), and 4 Å deep (the B1−B2 distance) (Figure 6c). A crude estimate of the volume within this cavity would then be 157 Å^3, large enough to accommodate solvent molecules or a couple of group 1 or 2 cations. Realistically, however, the potential for forming soluble molecular inclusion complexes with **6** may be impeded by the steric requirements of the Ph$_2$Si group. A more likely cage would be one in which the silicon contains smaller groups such as Me. Further efforts to accomplish this are in progress, as are efforts to deprotonate the NH groups of **7** with large atoms such as Rb and Cs.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 MHz (^{1}H) and 32.08 MHz (^{11}B) and are reported relative to SiMe$_4$ and BF$_3$·OEt$_2$, respectively (in ppm). Samples were run in CDCl$_3$ for all compounds except **7** which was run in C$_6$D$_6$. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde[28] was prepared according to the literature. X-ray data ($2\theta = 45°$) for **1**, **3**, **4**, and **6** were collected on a Siemens SMART-CCD unit (Table 2). The hydrogen atoms in these complexes were placed in ideal positions with a C−H distance of 0.90 Å. Being involved in hydrogen bonding, these distances could conceivably be somewhat longer, but in the absence of neutron diffraction data they cannot be quantitatively determined. However, they are clearly within the sum of the van der Waals radii for hydrogen (1.20 Å) and oxygen (1.50 Å)[29] and in keeping with distances observed in other systems containing such hydrogen bonds.[30]

SalenN$_3$H[B(OMe)$_2$]$_2$ (1). To a solution of SalenN$_3$H$_3$ (1.00 g, 3.21 mmol) in toluene (30 mL) was added trimethylborate (1.34 g, 12.84 mmol). The resulting solution was refluxed for 6 h. After filtration and concentration, yellow crystals were grown at 25 °C (1.10 g, 76%): Mp 116 °C (dec); ^{1}H NMR δ 3.01 (m, 4H, CH$_2$CH$_2$), 3.22 (s, 12H, OCH$_3$), 3.67 (m, 4H, CH$_2$CH$_2$), 6.65 (m, 2H, PhH), 6.94 (m, 4H, PhH), 7.43 (m, 2H, PhH), 8.26 (s, 2H, NCH); ^{11}B NMR δ 2.45 ($W_{1/2}$, 238.63 Hz); IR ν 3283 (m), 3067 (w), 2960 (m), 2823 (m), 1977 (w), 1892 (w), 1807 (w), 1641 (s), 1612 (w), 1562 (m), 1483 (m), 1467 (m), 1419 (w), 1371 (w), 1317 (m), 1211 (m), 1130 (m), 977 (m), 833 (w), 783 (w), 756 (m), 549 (w), 468 (w). Anal. Calcd for C$_{22}$H$_{31}$N$_3$O$_6$B$_2$: C, 40.67; H, 4.77. Found: C, 40.38; H, 4.65.

SalenN$_3$H[B(OSiPh$_3$)$_2$]$_2$ (2). To a solution of SalenN$_3$H[B(OMe)$_2$]$_2$ (0.75 g, 1.65 mmol) in toluene (30 mL) was added triphenylsilanol (1.82 g, 6.60 mmol). The resulting solution was refluxed for 5 h. After filtration and concentration, a pale yellow solid was obtained from a toluene/hexane (1/5) solution (1.80 g, 78%): Mp 63 °C (dec); ^{1}H NMR δ 2.49 (m, 4H, CH$_2$CH$_2$), 3.10 (m, 4H, CH$_2$CH$_2$), 6.45 (m, 2H, PhH), 6.62 (m, 2H, PhH), 7.01 (m, 2H, PhH), 7.14 (m, 32H, SiPhH, PhH), 7.50 (m, 30H, SiPhH), 7.72 (d, 2H, NCH); ^{11}B NMR δ 0.72 ($W_{1/2}$, 356.41 Hz); IR ν 3065 (m), 3047 (m), 2998 (w), 2849 (w), 1959 (w), 1892 (w), 1828 (w), 1643 (s), 1610 (w), 1560 (m), 1483 (m), 1427 (m), 1315 (w), 1234 (w), 1116 (br s), 1026 (w), 964 (m), 891 (w), 798 (w), 742 (w), 702 (m), 513 (m), 426 (w). Anal. Calcd for C$_{90}$H$_{79}$N$_3$O$_6$B$_2$Si$_4$: C, 75.49; H, 5.52. Found: C, 75.36; H, 5.48.

Salben[B(OSiPh$_3$)$_2$]$_2$ (3). To a solution of Salben[B(OEt)$_2$]$_2$ (0.67 g, 1.35 mmol) in toluene (30 mL) was added triphenylsilanol (1.50 g, 5.40 mmol). The resulting solution was refluxed for 5 h. After filtration and concentration, yellow crystals were grown at 25 °C (1.70 g, 89%): Mp 153 °C (dec); ^{1}H NMR δ 1.45 (m, 4H, CH2CH2), 2.95 (m, 4H, NCH2), 6.45 (d, 2H, PhH), 6.56 (d, 2H, PhH), 7.11−7.52 (m, 60H, SiPhH), 7.73 (d, 2H, NCH); ^{11}B NMR δ 0.22 ($W_{1/2}$, 236.89 Hz); IR ν 3067 (w), 2984 (w), 2866 (w), 1959 (w), 1886 (w), 1820 (w), 1643 (s), 1612 (w), 1564 (m), 1483 (m), 1464 (w), 1427 (m), 1317 (m), 1261 (w), 1236 (w), 1113 (s), 1028 (m), 960 (m), 883 (w), 777 (w),

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Table 2. Data Collection and Processing Parameters for Compounds

	compounds			
	1	**3**	**4**	**6**
formula	$C_{22}H_{31}N_3O_{6B2}$	$C_{45}H_{39}NO_3BSi_2$	$C_{59}H_{56}NO_3BSi_2$	$C_{66}H_{80}N_2O_6B_2Si_2$
fw	455.12	708.76	894.04	1075.12
color, habit	yellow prism	yellow block	yellow block	yellow prism
cryst size (mm^3)	0.50 × 0.25 × 0.20	0.10 × 0.18 × 0.22	0.40 × 0.35 × 0.25	0.50 × 0.30 × 0.25
cryst system	monoclinic	triclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	27.997(2)	13.627(1)	13.862(1)	13.127(1)
b (Å)	6.200(1)	13.657(1)	14.045(1)	13.748(1)
c (Å)	31.071(2)	14.051(1)	15.249(1)	19.705(2)
α (deg)	90	65.83(1)	82.36(1)	78.26(1)
β (deg)	116.53(1)	61.10(1)	80.10(1)	80.96(1)
γ (deg)	90	64.21(1)	62.32(1)	68.00(1)
V (Å^3)	4825.3(6)	1994.9(2)	2585.4(3)	3216(2)
Z	8	2	2	2
F(000)	1936	746	948	1152
D(calcd) (g cm^{-3})	1.253	1.180	1.148	1.110
μ (mm^{-1})	0.089	0.129	0.113	0.104
unique data measd	2571	4100	4386	3635
obsd data, n [$F \geq 4\sigma(F)$]	2571	4100	4374	3594
no. of variables, p	298	469	595	650
R1^a	0.054	0.046	0.060	0.075
wR2^b	0.129	0.119	0.153	0.169
S (goodness of fit)^c	1.12	0.87	1.00	1.33

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$. [c] $S = [(\sum w(|F_o| - |F_c|)^2/n - m)]^{1/2}$.

711 (m), 584 (w), 520 (w), 493 (w). Anal. Calcd for $C_{90}H_{78}N_2O_6B_2Si_4$: C, 76.29; H, 5.51. Found: C, 76.15; H, 5.39.

Salen(^{t}Bu)[B(OSiPh$_3$)$_2$]$_2$ (4). To a solution of Salen(^{t}Bu)[B(OEt)$_2$]$_2$ (0.80 g, 1.15 mmol) in toluene (30 mL) was added triphenylsilanol (1.27 g, 4.60 mmol). The resulting solution was refluxed for 5 h. The filtrate was concentrated to incipient crystallization and let stand at 25 °C for 24 h to afford the product as yellow crystals (0.53 g, 30%): Mp >260 °C; ^{1}H NMR δ 1.13 (s, 18H, CCH$_3$), 1.26 (s, 18H, CCH$_3$), 3.55 (m, 2H, NCH$_2$), 3.79 (m, 2H, NCH$_2$), 6.24 (d, 2H, PhH), 6.66 (d, 2H, PhH), 7.21−7.50 (m, 60H, SiPhH), 7.82 (d, 2H, NCH); ^{11}B NMR δ 0.08 ($W_{1/2}$, 260.21 Hz); IR ν 3049 (w), 2957 (m), 2870 (w), 1959 (w), 1897 (w), 1828 (w), 1637 (s), 1566 (m), 1460 (w), 1427 (s), 1357 (m), 1313 (s), 1261 (w), 1166 (w), 1120 (s), 1028 (w), 958 (m), 740 (w), 709 (m), 513 (w), 451 (w). Anal. Calcd for $C_{104}H_{106}N_2O_6B_2Si_4$: C, 77.43; H, 6.57. Found: C, 77.58; H, 6.51.

Salben(^{t}Bu)[B(OSiPh$_3$)$_2$]$_2$ (5). To a solution of Salben(^{t}Bu)-[B(OMe)$_2$]$_2$ (0.53 g, 0.80 mmol) in toluene (30 mL) was added triphenylsilanol (0.88 g, 3.20 mmol). The resulting solution was refluxed for 5 h. After filtration and concentration, yellow crystals were grown at 25 °C (0.80 g, 62%): Mp 230 °C (dec); ^{1}H NMR δ 1.12 (s, 18H, CCH3), 1.33 (s, 18H, CCH$_3$), 1.47 (m, 4H, CH$_2$CH$_2$), 2.76 (m, 4H, NCH$_2$), 6.50 (d, 2H, PhH), 6.58 (d, 2H, PhH), 7.17−7.52 (m, 60H, SiPhH), 7.72 (d, 2H, NCH); ^{11}B NMR δ 0.70 ($W_{1/2}$, 270.76 Hz); IR ν 3086 (w), 2962 (m), 2868 (w), 1961 (w), 1900 (w), 1822 (w), 1647 (s), 1464 (w), 1429 (m), 1361 (w), 1261 (m), 1153 (w), 1111 (s), 1026 (w), 952 (w), 891 (w), 806 (m), 702 (s), 570 (w), 513 (w), 422 (w). Anal. Calcd for $C_{106}H_{110}N_2O_6B_2Si_4$: C, 77.57; H, 6.70. Found: C, 77.65; H, 6.77.

[Salpten(^{t}Bu){B(O$_2$SiPh$_2$)}$_2$]$_2$ (6). To a solution of Salpten(^{t}Bu)-[B(OMe)$_2$]$_2$ (0.74 g, 1.09 mmol) in toluene (30 mL) was added diphenylsilanediol (0.47 g, 2.18 mmol). The resulting solution was refluxed for 5 h. The filtrate was concentrated to 5 mL and stand at 25 °C for 2 weeks to yield pale yellow crystals (0.85 g, 79%): Mp 160 °C (dec); ^{1}H NMR δ 1.29 (s, 18H, CCH$_3$), 1.37 (s, 18H, CCH$_3$), 1.42 (m, 12 H, CH$_2$CH$_2$), 1.55 (m, 4H, CH$_2$CH$_2$), 6.89 (d, 2H, PhH), 7.06 (d, 2H, PhH), 7.15−7.47 (m, 20H, SiPhH), 7.71 (d, 2H, NCH); ^{11}B NMR δ 0.60 ($W_{1/2}$, 243.06 Hz); IR ν 3045 (w), 2953 (w), 2868 (w), 1957 (w), 1894 (w), 1826 (w), 1645 (s), 1591 (w), 1566 (m), 1471 (m), 1429 (m), 1392 (w), 1361 (w), 1043 (m), 954 (m), 912 (w), 873 (w), 805 (m), 773 (w), 717 (m), 642 (w), 572 (w), 513 (w), 495 (w). Anal. Calcd for $C_{118}H_{144}N_4O_{12}B_4Si_4$: C, 72.12; H, 7.33. Found: C, 72.01; H, 7.28.

[SalenN$_3$H{B(O$_2$SiPh$_2$)}$_2$]$_2$ (7). To a solution of SalenN$_3$H-[B(OMe)$_2$]$_2$ (0.85 g, 1.87 mmol) in toluene (30 mL) was added diphenylsilanediol (0.81 g, 3.74 mmol). The resulting solution was refluxed for 5 h. After filtration and concentration, yellow solid was isolated from a toluene/hexane (1/5) solution (1.30 g, 77%): Mp 103 °C (dec); ^{1}H NMR δ 2.49 (m, 4H, CH$_2$CH$_2$), 2.53 (m, 4H, NCH$_2$), 3.30 (m, 4H, CH$_2$CH$_2$), 6.48 (m, 2H, PhH), 6.61 (m, 2H, PhH), 6.75 (m, 2H, PhH), 7.16 (m, 12H, SiPhH, PhH), 7.83 (m, 10H, SiPhH), 8.01 (d, 2H, NCH); ^{11}B NMR δ 0.98 ($W_{1/2}$, 277.86 Hz); IR ν 3067 (w), 3047 (w), 2968 (w), 2841 (w), 1957 (w), 1892 (w), 1830 (w), 1645 (s), 1610 (w), 1560 (m), 1481 (m), 1465 (w), 1429 (m), 1330 (m), 1261 (w), 1234 (w), 1116 (br, s), 1024 (w), 964 (w), 800 (w), 756 (w), 700 (m), 551 (w), 507 (m), 407 (w) cm^{-1}. Anal. Calcd for $C_{84}H_{78}N_6O_{12}B_4Si_4$: C, 66.43; H, 5.14. Found: C, 66.26; H, 5.05.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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