

## Salen Supported Molecular Borosilicates

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Various Salen ligands (Salen(<sup>t</sup>Bu)H<sub>2</sub> = *N*, *N'*-ethylenebis(3,5-di-*t*erbutyl(2-hydroxy)benzylideneimine) were used to prepare borosilyl and  $\mu$ -O bridged borosilyl compounds having the formula, L{B(OSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (L = Salen(<sup>t</sup>Bu) (1), Salpen(<sup>t</sup>Bu) (2), Salben(<sup>t</sup>Bu) (3), Salhen(<sup>t</sup>Bu) (4) and L(BOSiMe<sub>3</sub>)<sub>2</sub>( $\mu$ -O) (L = Salen(<sup>t</sup>Bu) (5) and Salben(<sup>t</sup>Bu) (6)). In the case of 5 and 6 the formation of the B–O–B linkage takes precedence over the formation of a B–O–Si linkage. All of the compounds were characterized by Mp, elemental analysis, <sup>1</sup>H and <sup>11</sup>B NMR, IR, MS and in the case of 1, 2, and 6 by X-ray crystallography.

**KEY WORDS:** Borosilicate; salen; heterocycle.

### INTRODUCTION

Borosilicates are important solid state materials [1]. They are one of the key components in various glasses, and appear as components in many other materials, such as zeolites. In these compounds the B–O–Si linkages combine to form linear one-dimensional and cyclic two- and three-dimensional sub-structures. For this reason molecular compounds containing borosilicate rings are important research targets. Molecular models that successfully incorporate one- [2], two- [2], and three-dimensional [3–6] borosilicate structures have been recently reported. However there are still relatively few examples of this important type of compound.

The Salen class of ligand has been used to form many group 13 monometallic [7–14] and bimetallic compounds [15–21]. In a study of binuclear Salen borates, one-, two-, and three-dimensional molecular Salen borosilicate structures were formed and structurally characterized (Fig. 1) [2]. These compounds are attractive because they are soluble borosilicates,

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\* This is submitted to congratulate Prof. Richard Wells on the occasion of his retirement and to thank him for his many years of leadership in main group chemistry.

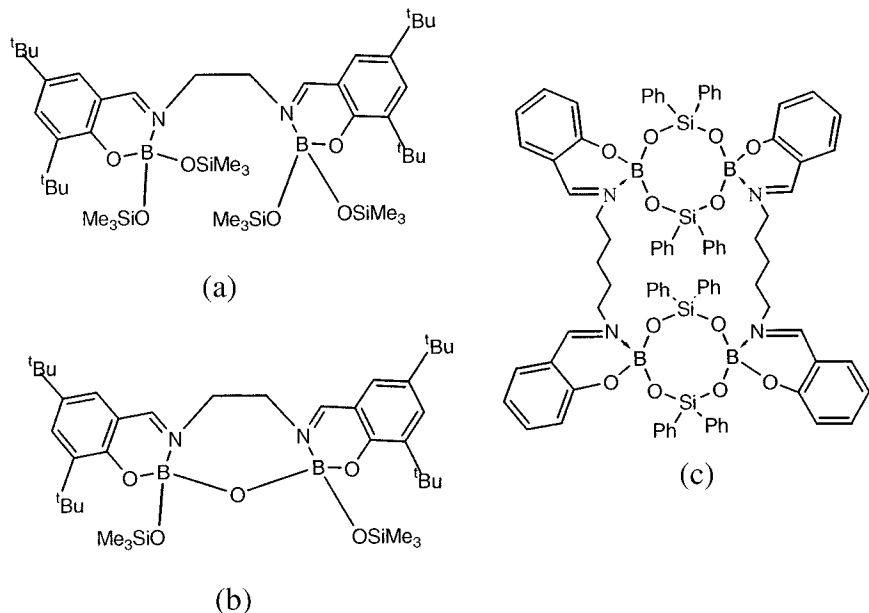
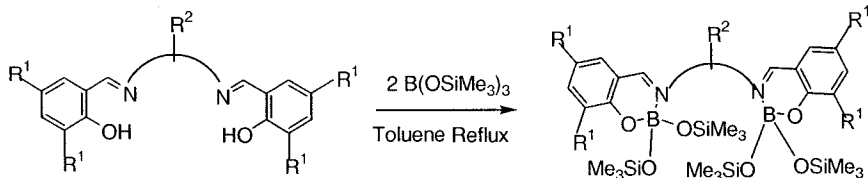


Fig. 1. Molecular structures of Salen(<sup>t</sup>Bu){B(OSiPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (a), Salben(<sup>t</sup>Bu){B(OSiMe<sub>3</sub>)<sub>2</sub>(μ-O)}<sub>2</sub> (b) (6), [Salpten{B(O<sub>2</sub>SiPh<sub>2</sub>)<sub>2</sub>}]<sub>2</sub> (c).

and therefore, can be fully characterized using techniques such as NMR spectroscopy and single crystal X-ray diffraction. The framework for the three-dimensional compound contains two 8-membered B–O–Si rings tethered together by two alkyl chains (the backbone of the Salen ligand). To continue the study of molecular borosilicates, herein we report the synthesis and characterization of Salen borosilicate compounds incorporating the moderately bulky siloxy group, –OSiMe<sub>3</sub>.

## RESULTS AND DISCUSSION

Compounds 1–4 are prepared by refluxing the Salen ligand and tris(trimethylsilyl)borate in toluene (Scheme 1). They are both moderately air and moisture stable. Unlike previously employed alcohol elimination reactions the by-product in this reaction, Me<sub>3</sub>SiOH, is not very volatile. However, after condensation to (Me<sub>3</sub>Si)<sub>2</sub>O it remains soluble in the solvent when 1–4 precipitate. Therefore an easy separation can be effected. The <sup>1</sup>H NMR spectra of these compounds contains a sharp singlet for the Si–Me and N=CH groups, indicating that these compounds are symmetric in solution. Additionally, the <sup>11</sup>B NMR (≈ 0 ppm) spectra of 1–4 is

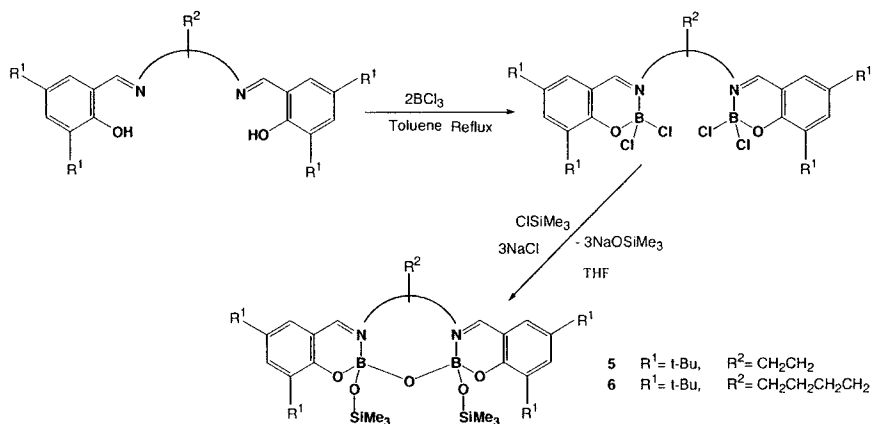


- 1**  $R^1 = {}^t\text{Bu}$ ,  $R^2 = \text{CH}_2\text{CH}_2$   
**2**  $R^1 = {}^t\text{Bu}$ ,  $R^2 = \text{CH}_2\text{CH}_2\text{CH}_2$   
**3**  $R^1 = {}^t\text{Bu}$ ,  $R^2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$   
**4**  $R^1 = {}^t\text{Bu}$ ,  $R^2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$

**Scheme 1.** Synthesis of compounds 1–4.

consistent with the presence of four-coordinate boron atoms [22]. The MS data shows both the parent ion (10–35% abundance) and the base ion peak for 1–4, which is the parent ion without a methyl group. A small amount (15–25% abundance) of the parent ion  $-\text{OSiMe}_3$  fragment is also present.

Compounds 5 and 6 are prepared by refluxing  $\text{L}(\text{BCl}_2)_2$  ( $\text{L} = \text{Salen}({}^t\text{Bu})$ ,  $\text{Salben}({}^t\text{Bu})$ ) and  $\text{NaOSiMe}_3$  in THF (Scheme 2). The expected products (1 and 3) did not form, instead the more interesting  $\mu\text{-O}$  bridged compounds formed instead. The reaction may produce the products through salt elimination followed by hydrolysis. However, compounds 1–4 do not form  $\mu\text{-O}$  bridged compounds in the presence of water. This demonstrates that the the  $\text{B-O-Si}$  linkages are favored over the formation



**Scheme 2.** Synthesis of compounds 5 and 6.

of B–O–B and Si–O–Si linkages in these systems [23]. Consequently, the intramolecular elimination of Me<sub>3</sub>SiCl is a more plausible mechanism for the formation of a  $\mu$ -oxo bridge in **5** and **6**. The compounds contain a 7- (**5**) and 9-membered (**6**) heterocyclic ring, with one –OSiMe<sub>3</sub> group on each boron atom. Similar compounds containing only 7- and 8-membered heterocyclic rings have previously been reported (Salen{(PhB)<sub>2</sub>( $\mu$ -O)})

**Table I.** Crystallographic Data and Collection Parameters for **1**, **2**, and **6**

Crystal data	<b>1</b>	<b>2</b>	<b>6</b>
CCDC #	176382	176381	176383
Formula	C <sub>44</sub> H <sub>82</sub> B <sub>2</sub> N <sub>2</sub> O <sub>6</sub> Si <sub>4</sub>	C <sub>45</sub> H <sub>84</sub> B <sub>2</sub> N <sub>2</sub> O <sub>6</sub> Si <sub>4</sub>	C <sub>47</sub> H <sub>76</sub> B <sub>2</sub> N <sub>2</sub> O <sub>5</sub> Si <sub>2</sub>
Crystal size (mm)	0.40 × 0.40 × 0.15	0.30 × 0.20 × 0.15	0.50 × 0.38 × 0.24
Formula weight	869.10	883.12	826.90
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
Crystal system	Monoclinic	Monoclinic	Triclinic
<i>T</i> (°C)	–100	–100	–100
<i>a</i> (Å)	11.872 (2)	14.431(1)	9.964 (1)
<i>b</i> (Å)	10.330 (2)	21.565(2)	15.742(1)
<i>c</i> (Å)	45.637 (6)	18.110(1)	16.403(1)
$\alpha$ (°)	90	90	80.416(10)
$\beta$ (°)	93.342 (10)	99.290(10)	85.352(10)
$\gamma$ (°)	90	90	77.615(10)
<i>V</i> (Å <sup>3</sup> )	5587.3 (16)	5562.0(7)	2475(3)
<i>Z</i>	4	4	2
$\mu$ (mm <sup>–1</sup> )	0.146	0.148	0.115
$\rho_{\text{calcd}}$ (g · cm <sup>–3</sup> )	1.033	1.055	1.109
<i>F</i> (000)	1860	1928	900
$\theta$ limits (°)	2.02 < $\theta$ < 24.00	1.48 < $\theta$ < 25.00	1.69 < $\theta$ < 25.00
<i>hkl</i> limits	–13, 13; –11, 11; –52, 52	–17, 17; –25, 25; –21, 21	–11, 11; –18, 18; –19, 16
No. reflns collected	28084	36055	13906
No. independent reflns	8726	9805	8718
<i>R</i> <sub>int</sub>	0.0498	0.0884	0.0353
No. data	8726	9805	8716
No. params	549	566	580
No. restraints	116	8	22
GOF on <i>F</i> <sup>2</sup>	0.960	1.119	1.040
<i>R</i> 1 <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0549	0.0721	0.0602
<i>wR</i> 2 <sup>b</sup> (all data)	0.1424	0.1315	0.1656
Largest diff peak and hole (e <sup>–</sup> · Å <sup>–3</sup> )	0.241, –0.259	0.374, –0.260	0.553, –0.607

<sup>a</sup>  $R1 = \sum (||F_o| - |F_c||) / \sum |F_o|$ .

<sup>b</sup>  $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w |F_o^2|]^{1/2}$ .

**Table II.** Bond Lengths (Å) and Angles (°) for Compounds 1, 2, and 6

Distances (1)			
B(1)–O(4)	1.418(3)	B(1)–O(3)	1.424(4)
B(1)–O(1)	1.481(4)	B(1)–N(1)	1.618(4)
B(2)–O(5)	1.418(4)	B(2)–O(6)	1.423(4)
B(2)–O(2)	1.490(4)	B(2)–N(2)	1.603(4)
N(1)–C(15)	1.304(3)	N(2)–C(18)	1.295(3)
Angles (1)			
O(4)–B(1)–O(3)	113.1(2)	O(4)–B(1)–O(1)	111.6(2)
O(3)–B(1)–O(1)	110.5(2)	O(4)–B(1)–N(1)	107.5(2)
O(3)–B(1)–N(1)	106.5(2)	O(1)–B(1)–N(1)	107.2(2)
O(5)–B(2)–O(6)	113.6(3)	O(5)–B(2)–O(2)	110.2(3)
O(6)–B(2)–O(2)	110.1(3)	O(5)–B(2)–N(2)	106.5(2)
O(6)–B(2)–N(2)	109.1(3)	O(2)–B(2)–N(2)	107.2(2)
Distances (2)			
B(1)–O(4)	1.413(3)	B(1)–O(3)	1.437(3)
B(1)–O(1)	1.481(4)	B(1)–N(1)	1.620(4)
B(2)–O(6)	1.413(3)	B(2)–O(5)	1.436(3)
B(2)–O(2)	1.487(4)	B(2)–N(2)	1.623(4)
N(1)–C(15)	1.287(3)	N(2)–C(19)	1.287(3)
Angles (2)			
O(4)–B(1)–O(3)	113.2(2)	O(4)–B(1)–O(1)	111.0(2)
O(3)–B(1)–O(1)	112.3(2)	O(4)–B(1)–N(1)	109.6(2)
O(3)–B(1)–N(1)	104.8(2)	O(1)–B(1)–N(1)	105.5(2)
O(6)–B(2)–O(5)	113.5(2)	O(6)–B(2)–O(2)	110.3(2)
O(5)–B(2)–O(2)	112.0(2)	O(6)–B(2)–N(2)	110.1(2)
O(5)–B(2)–N(2)	104.6(2)	O(2)–B(2)–N(2)	105.9(2)
Distances (6)			
B(1)–N(1)	1.633(4)	B(2)–N(2)	1.622(4)
B(1)–O(1)	1.501(3)	B(2)–O(2)	1.488(3)
B(1)–O(4)	1.420(3)	B(2)–O(3)	1.415(3)
B(1)–O(3)	1.409(4)	B(2)–O(5)	1.439(4)
C(15)–N(1)	1.283(3)	C(20)–N(2)	1.291(3)
Angles (6)			
O(2)–B2–N(2)	106.5(2)	O(1)–B1–N(1)	105.3(2)
O(2)–B2–O(3)	112.2(2)	O(1)–B1–O(3)	111.1(2)
O(2)–B2–O(5)	107.8(2)	O(1)–B1–O(4)	109.7(2)
O(3)–B2–O(5)	112.1(2)	O(3)–B1–O(4)	116.2(2)
O(3)–B2–N(2)	111.2(2)	O(3)–B1–N(1)	105.8(2)
N(2)–B2–O(5)	106.7(2)	N(1)–B1–O(4)	108.1(2)
B(1)–O3–B(2)	131.5(2)		

[18, 24]. However, all prior attempts to increase the size of the ring to greater than eight have resulted in the formation of insoluble polymers [24]. Therefore, compound **6** contains the largest heterocyclic ring synthesized with Salen ligands. Like compounds **1–4**, the  $^1\text{H}$  NMR spectra of compounds **5** and **6** show one singlet for both the Si–Me and N=CH groups, indicating that only one of the possible isomers formed. The crystal structure of **6** revealed that the trans isomer (with regards to the  $\text{Me}_3\text{SiO}$  groups) formed in this particular reaction. Either the cis or trans isomer may have formed in the synthesis of compound **5**, for which no crystal structure was obtained.

## STRUCTURAL CHARACTERIZATION OF **1**, **2**, AND **6**

Details of the crystal data and a summary of data collection parameters for the compounds are given in Table I. Selected bond distances and angles are listed in Table II. Figures 2–4 show the molecular structures of **1**, **2**, and **6**, respectively. Each of the three structures contains two boron atoms that have a distorted tetrahedral geometry. Most Salen-supported

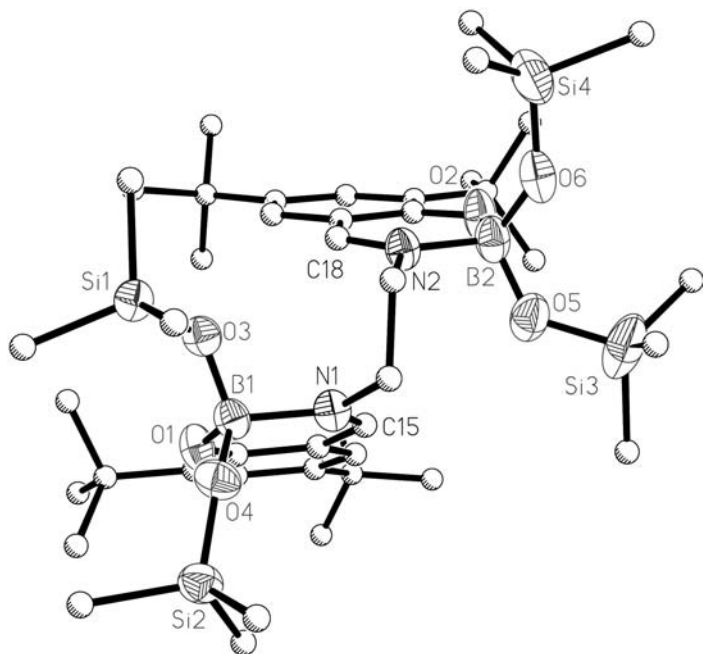


Fig. 2. Molecular structure of Salen('Bu) $\{\text{B}(\text{OSiMe}_3)_2\}_2$  (**1**).

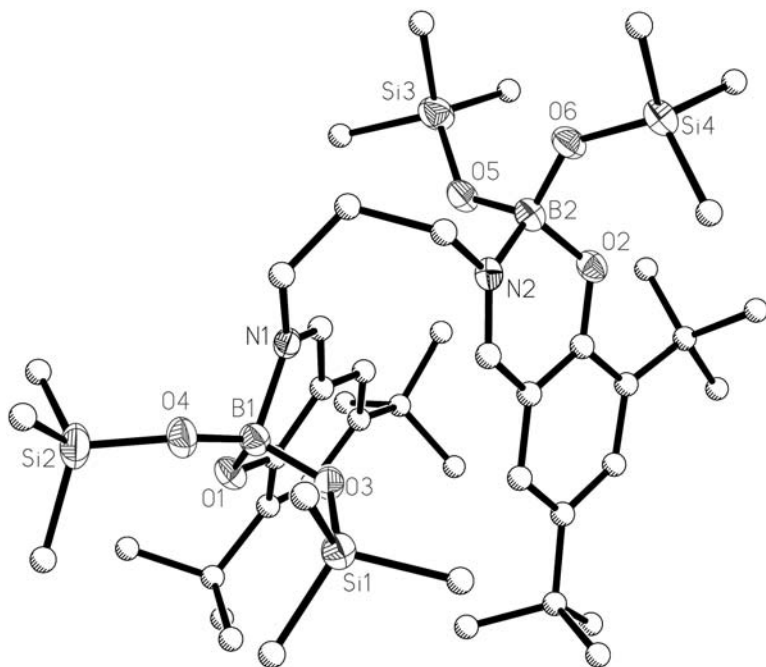


Fig. 3. Molecular structure of Salpen(*t*-Bu){B(OSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (2).

binuclear boron compounds have a trans configuration with the siloxide groups oriented away from each other [2]. In **1** and **2**, however, the cis configuration is obtained despite the steric influence of the *t*-Bu groups. In previous cases a cis configuration was attributed to intramolecular hydrogen bonding, but there is no evidence for this type of interaction in the structures of either **1** or **2** [2]. Compound **1** contains a larger bite angle (N1–B1–O1 = 107.5(2)°) than **2** (105.5(2)°) and **6** (105.3(2)°) and related compounds such as Salen(*t*-Bu){B(OSiPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (104.9(4)°) [2]. The average N→B bond is shorter in **1** (1.611(4) Å) than in **2** (1.622(4) Å) and **6** (1.628(4) Å). Thus the average C=N bond is shorter for **2** (1.287(3) Å) and **6** (1.287(3) Å) than **1** (1.300(3) Å). The B–O–B angle for **6** (131.5(2)°) is smaller than similar heterocyclic compounds such as Salpen(*t*-Bu){(PhB)<sub>2</sub>(μ-O)} (137.5(3)°) [24]. Compound **6** has a trans configuration (with regards to the Me<sub>3</sub>SiO groups) whereas previous Salen boron heterocyclic compounds adopt the cis configuration [24].

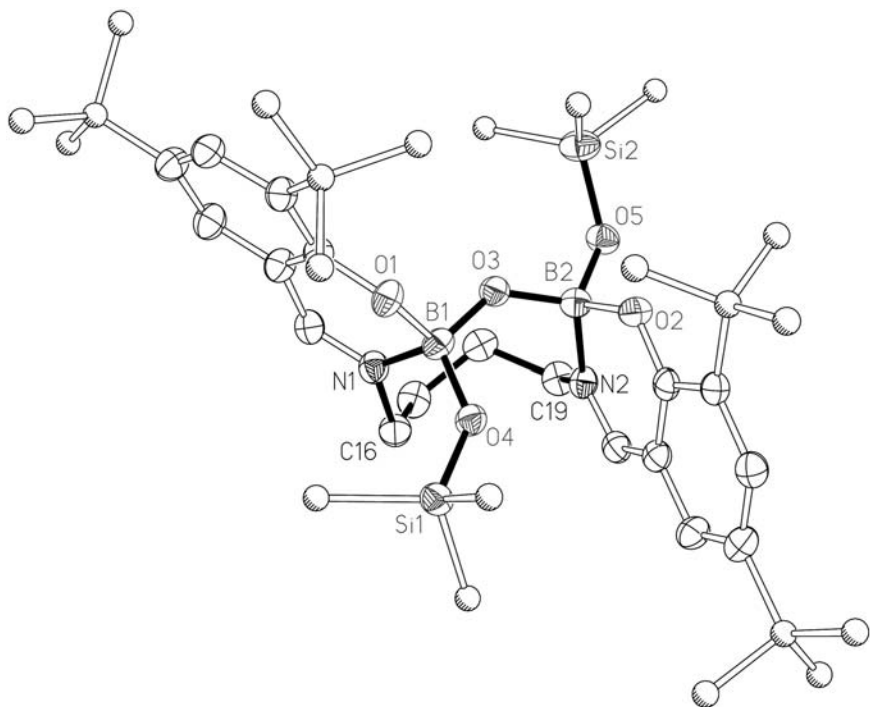


Fig. 4. Molecular structure of Salben(*t*-Bu){B(OSiMe<sub>3</sub>)<sub>2</sub>}(μ-O) (6).

## CONCLUSION

These borosilicate compounds provide insight into the reactivity and structural configuration of B–O–Si and B–O–B linkages. The Salen ligand allows access to borosilicates with a range of heterocyclic rings, including the first 9-membered heterocyclic ring in a Salen boron compound. It is interesting that the formation of the B–O–B bridge takes preference over the formation of the B–O–Si linkage in the formation of the nine-membered heterocyclic ring. However, the B–O–Si linkage may be formed exclusively under the appropriate conditions (Scheme 1). We are currently pursuing three-dimensional structures with these systems by attempting to link the heterocyclic rings. This should allow for the formation of cage systems incorporating rings of various sizes.

## EXPERIMENTAL

**General Remarks.** All glassware was rigorously cleaned and dried in an oven at 130°C for 24 h prior to use. They were assembled hot and



cooled under nitrogen. All air sensitive manipulations were conducted using standard bench top inert atmosphere techniques in conjunction with an inert-atmosphere glove box. The ligands Salen(<sup>t</sup>Bu)H<sub>2</sub>, Salpen(<sup>t</sup>Bu)H<sub>2</sub>, Salben(<sup>t</sup>Bu)H<sub>2</sub>, and Salhen(<sup>t</sup>Bu)H<sub>2</sub>, were synthesized according to the literature procedure [25]. NMR data (<sup>1</sup>H, <sup>11</sup>B) were obtained on JEOL-GSX-400 and 200 MHz instruments. Chemical shifts are reported relative to SiMe<sub>4</sub> for <sup>1</sup>H and <sup>13</sup>C and BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub> for <sup>11</sup>B and are in ppm. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series Spectrometer and are reported in cm<sup>-1</sup>. EI (positive) (direct probe) spectra were acquired on a Kratos Concept IH at 70 eV. Elemental analyses were obtained on a Vario EL III Elementar analyzer. X-ray Data was obtained on a Nonius CCD unit employing Mo<sub>kα</sub> radiation. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Further details of the structure analyses are given in Table III.

**Salen(<sup>t</sup>Bu){(BOSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (1).** To a stirring solution of Salen(<sup>t</sup>Bu)H<sub>2</sub> (1 g, 2.03 mmol) in toluene (50 ML) was added B(OSiMe<sub>3</sub>)<sub>3</sub> (1.24 g, 4.46 mmol) and then refluxed for 21 h. The solvent was removed and the resulting solid dissolved in 10 ML of hexanes. After cooling to -30°C for several hours **1** precipitated. The supernatant was removed by filtration and dried to yield a yellow solid, 1.25 g (71%). Mp: 170–174°C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.05 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.13 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.41 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 4.15 [m, 4H, NCH<sub>2</sub>], 7.0 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.49 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.93 [s, 2H, CHN]. <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ 1.19(w<sub>1/2</sub>, 88.8 Hz). IR(cm<sup>-1</sup>): 2955(s), 2903(w), 1640(s), 1566(m), 1464(w), 1440(w), 1363(w), 1248(s), 1204(m), 1189(m), 1130(s), 1084(s), 959(m), 958(w), 924(m), 903(m), 839(s), 798(m), 752(w), 682(w), 625(w), 472(w). MS(m/z): 868 (M<sup>+</sup>, 35%), 853 (M<sup>+</sup>-Me, 100%), 779 (M<sup>+</sup>-OSiMe<sub>3</sub>, 25%). EA: B<sub>2</sub>C<sub>44</sub>H<sub>82</sub>N<sub>2</sub>O<sub>6</sub>Si<sub>4</sub> C 60.79 (60.71), H 9.51 (10.25), N 3.22 (3.15).

**Salpen(<sup>t</sup>Bu){(BOSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (2).** To a stirring solution of Salpen(<sup>t</sup>Bu)H<sub>2</sub> (0.5 g, 0.99 mmol) in toluene (50 ML) was added B(OSiMe<sub>3</sub>)<sub>3</sub> (1.10 g, 3.95 mmol) and then refluxed for 4 h. The solvent was removed and the resulting solid dissolved in 10 ML of hexanes. After cooling to -30°C for several hours **2** precipitated. The supernatant was removed by filtration and dried to yield a yellow solid, 0.65 g (75%). Mp: 120.5°C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.05 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.25 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.43 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 2.44 [m, 2H, CH<sub>2</sub>], 3.66 [m, 4H, NCH<sub>2</sub>], 6.98 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.52 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 8.05 [s, 2H, CHN]. <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ

−0.19 ( $w_{1/2}$ , 113.15 Hz). IR( $\text{cm}^{-1}$ ): 2956(m), 2900(w), 2870(w), 1653(s), 1647(m), 1569(w), 1479(w), 1437(w), 1395(w), 1361(m), 1347(w), 1305(w), 1261(s), 1240(s), 1223(w), 1179(m), 1149(s), 1086(m), 1053(s), 1000(w), 962(w), 919(m), 835(s), 800(m), 766(w), 750(w), 680(vw), 619(vw). MS(m/z): 882 ( $\text{M}^+$ , 10%), 867 ( $\text{M}^+ - \text{Me}$ , 100%), 793 ( $\text{M}^+ - \text{OSiMe}_3$ , 15%). EA:  $\text{B}_2\text{C}_{45}\text{H}_{84}\text{N}_2\text{O}_6\text{Si}_4$  C 61.19 (61.30), H 9.59 (10.59), N 3.17 (3.15).

**Salben('Bu){(BOSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (3).** To a stirring solution of Salben('Bu)H<sub>2</sub> (1 g, 1.92 mmol) in toluene (50 ML) was added B(OSiMe<sub>3</sub>)<sub>3</sub> (1.17 g, 4.23 mmol) and then refluxed for 24 h. The solvent was removed and the resulting solid dissolved in 10 ML of hexanes. After cooling to −30°C for several hours (3) precipitated. The supernatant was removed by filtration and dried to yield a yellow solid, 0.95 g (56%). Mp: °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  −0.05 [s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.25 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.42 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.8 [m, 2H, CH<sub>2</sub>], 1.85 [m, 2H, CH<sub>2</sub>], 3.65 [m, 4H, NCH<sub>2</sub>], 7.03 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.52 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.95 [s, 2H, CHN]. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  −0.25 ( $w_{1/2}$ , 129.5 Hz). IR( $\text{cm}^{-1}$ ): 2958(s), 2871(w), 1647(s), 1565(m), 1471(m), 1443(m), 1362(m), 1393(w), 1247(s), 1151(s), 1101(s), 979(w), 958(w), 921(m), 837(s), 801(m), 752(m), 677(w), 610(w). MS(m/z): ( $\text{M}^+$ , 4%), ( $\text{M}^+ - \text{Me}$ , 14%), EA:  $\text{B}_2\text{C}_{46}\text{H}_{86}\text{N}_2\text{O}_6\text{Si}_4$  C (61.59), H (9.66), N (3.12).

**Salhen('Bu){(BOSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (4).** To a stirring solution of Salhen('Bu)H<sub>2</sub> (1 g, 1.83 mmol) in toluene (50 ML) was added B(OSiMe<sub>3</sub>)<sub>3</sub> (1.11 g, 4.01 mmol) and then refluxed for 21 h. The solvent was removed and the resulting solid dissolved in 10 ML of hexanes. After cooling to −30°C for several hours (4) precipitated. The supernatant was removed by filtration and dried to yield a yellow solid. Yield: 1.10g (65%). Mp: 136–138°C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  −0.05[s, 36H, Si(CH<sub>3</sub>)<sub>3</sub>], 1.25 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.28[m, 4H, CH<sub>2</sub>], 1.41 [s, 18H, C(CH<sub>3</sub>)<sub>3</sub>], 1.85[m, 4H, CH<sub>2</sub>], 3.61 [m, 4H, NCH<sub>2</sub>], 7.0 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.49 [d, 2H, C<sub>6</sub>H<sub>2</sub>], 7.95 [s, 2H, CHN]. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  −0.285( $w_{1/2}$ , 120 Hz). IR( $\text{cm}^{-1}$ ): 2953(s), 2863(w), 1641(s), 1564(w), 1470(w), 1447(w), 1258(s), 1246(m), 1187(s), 1145(s), 1108(s), 1106(s), 1067(m), 958(m), 922(s), 836(s), 799(w), 751(m), 620(w). MS(m/z): 924 ( $\text{M}^+$ , 25%), 909 ( $\text{M}^+ - \text{Me}$ , 100%), 835 ( $\text{M}^+ - \text{OSiMe}_3$ , 20%). EA:  $\text{B}_2\text{C}_{48}\text{H}_{90}\text{N}_2\text{O}_6\text{Si}_4$  C 62.71 (62.31), H 10.38 (9.80), N 3.18 (3.03).

**Salen('Bu)(BOSiMe<sub>3</sub>)<sub>2</sub>( $\mu$ -O) (5).** To a stirring solution of Salen('Bu)(BCl<sub>2</sub>)<sub>2</sub> (0.5 g, 0.77 mmol) in THF (50 ML) was added NaOSiMe<sub>3</sub> (0.43 g, 3.85 mmol) and then refluxed for 4 h. The solvent was

removed and the resulting solid dissolved in 10 ML of hexanes. After cooling to  $-30^{\circ}\text{C}$  for several hours (**5**) precipitated. The supernatant was removed by filtration and dried to yield a yellow solid, 0.41g (61%). Mp:  $260 > ^{\circ}\text{C}$  (dec).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.33$  [s, 18H,  $\text{Si}(\text{CH}_3)_3$ ], 1.25 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ], 1.41 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ], 3.56 [m, 2H,  $\text{NCH}_2$ ], 4.15 [m, 2H,  $\text{NCH}_2$ ], 7.0 [d, 2H,  $\text{C}_6\text{H}_2$ ], 7.49 [d, 2H,  $\text{C}_6\text{H}_2$ ], 7.93 [s, 2H,  $\text{CHN}$ ].  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.42( $w_{1/2}$ , 99.3 Hz). IR( $\text{cm}^{-1}$ ): 3057(m), 2987(w), 2968(w), 1616(w), 1579(m), 1479(s), 1427(s), 1256(m), 1185(w), 1149(m), 1030(w), 852(m), 746(vs), 712(vs), 606(s). MS( $m/z$ ): 870( $\text{M}^+$ , 4%), 855 ( $\text{M}^+ - \text{Me}$ , 14%), EA:  $\text{B}_2\text{C}_{38}\text{H}_{64}\text{N}_2\text{O}_5\text{Si}_2$  C 66.30 (64.58), H 8.68 (8.86).

**Salben('Bu)(BOSiMe<sub>3</sub>)<sub>2</sub>( $\mu$ -O) (6).** To a stirring solution of Salben('Bu)( $\text{BCl}_2$ )<sub>2</sub> (0.5 g, 0.735 mmol) in THF (50 ML) was added  $\text{NaOSiMe}_3$  (0.33 g, 2.94 mmol). The solution was refluxed for 4 h. The solvent was removed and the resulting solid dissolved in 10 ML of toluene. After a few days pale yellow crystals were grown at  $-30^{\circ}\text{C}$ . Yield: 0.31 g (48%). Mp:  $58-60^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.05$  [s, 18H,  $\text{Si}(\text{CH}_3)_3$ ], 1.19 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ], 1.44 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ], 1.9 [m, 2H,  $\text{CH}_2$ ], 1.97 [m, 2H,  $\text{CH}_2$ ], 3.65 [m, 4H,  $\text{NCH}_2$ ], 7.03 [d, 2H,  $\text{C}_6\text{H}_2$ ], 7.52 [d, 2H,  $\text{C}_6\text{H}_2$ ], 7.95 [s, 2H,  $\text{CHN}$ ].  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-0.04$  ( $w_{1/2}$ , 99.2 Hz). IR( $\text{cm}^{-1}$ ): 2959(s), 2863(w), 1655(m), 1557(w), 1471(m), 1442(m), 1392(w), 1361(m), 1249(m), 1132(s), 1097(s), 1005(s), 947(m), 922(w), 836(s). EA:  $\text{B}_2\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_5\text{Si}_2$  C (65.35), H (9.33), N (3.81).

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## REFERENCES

1. Kirk-Othmer (Wiley, New York, 1994).
2. P. Wei, D. A. Atwood, and T. S. Keizer (1999). *Inorg. Chem.* **38**, 3914.
3. L. A. Neville, T. R. Spalding, and G. Ferguson (2000). *Angew. Chem. Int. Ed. Engl.* **39**, 3598.
4. F. J. Feher, T. A. Budzichowski, and J. W. Ziller (1992). *Inorg. Chem.* **31**, 5100.
5. A. T. O'Dowd, T. R. Spalding, G. Ferguson, J. F. Gallagher, and D. Reed (1993). *J. Chem. Soc., Chem. Commun.* 1816.
6. B. O'Leary, D. M. Murphy, T. R. Spalding, and G. Ferguson (1996). *J. Organomet. Chem.* **526**, 195.

7. P. L. Gurian, L. K. Cheatham, J. W. Ziller, and A. R. Barron (1991). *J. Chem. Soc. Dalton Trans.*: 1449.
8. D. Rutherford and D. A. Atwood (1996). *Organometallics* **15**, 4417.
9. M.-A. Munoz-Hernandez, B. Sannigrahi, and D. A. Atwood (1999). *J. Am. Chem. Soc.* **121**, 6747.
10. M. Muñoz-Hernández, T. S. Keizer, S. Parkin, B. Patrick, and D. A. Atwood (2000). *Inorg. Chem.* **19**, 4416.
11. M. S. Hill and D. A. Atwood (1998). *Eur. J. Inorg. Chem.* 67.
12. K. Chong, S. J. Rettig, A. Storr, and J. Trotter (1981). *Can. J. Chem.* **59**, 94.
13. T. S. Keizer, M. Munoz-Hernandez, P. Wei, S. Parkin, and D. A. Atwood (2001). *Inorg. Chem.* **40**, 6782.
14. M. S. Hill and D. A. Atwood (1998). *Main Group Chem.* **2**, 191.
15. P. Wei and D. A. Atwood (1997). *Inorg. Chem.* **36**, 4060.
16. M. A. Van Aelstyn, T. S. Keizer, D. L. Klopotek, S. Liu, M. Munoz-Hernandez, P. Wei, and D. A. Atwood (2000). *Organometallics* **19**, 1796.
17. M. J. Harvey and D. A. Atwood (2001). *Chem. Rev.* **101**, 37.
18. M. Sanchez, H. Hopfl, M. Ochoa, N. Farfan, R. Santillan, and S. Rojas (2001). *Inorg. Chem.* **40**, 6405.
19. K. S. Chong, A. R. Storr, and J. S. J. Trotter (1977). *Can. J. Chem.* **55**, 2540.
20. T. S. Keizer, L. J. De Pue, S. Parkin, and D. A. Atwood (in press). *Can. J. Chem.*
21. T. S. Keizer, L. J. Depew, S. Parkin, and D. A. Atwood (2002). *J. Am. Chem. Soc.* **124**, 1864.
22. R. G. Kidd. *NMR of Newly Accessible Nuclei* (Academic Press, 1983).
23. M. G. Davidson, A. K. Hughes, T. B. Marder, and K. Wade. *Contemporary Boron Chemistry* (Royal Society of Chemistry Cambridge, United Kingdom, 2000).
24. M. Sanchez, T. S. Keizer, S. Parkin, H. Hopfl, and D. A. Atwood (submitted). *J. Organomet. Chem.*
25. L. Deng and E. N. Jacobsen (1992). *J. Org. Chem.* **57**, 4320.