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Binuclear Salan borate compounds with three-coordinate boron atoms

Amitabha Mitra, Melanie J. Harvey, Mary K. Proffitt, Lauren J. DePue, Sean Parkin, David A. Atwood *

Department of Chemistry, University of Kentucky, Lexington, KY 40406-0055, United States

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Abstract

A series of binuclear boron compounds supported by Salan(^{t}Bu)H_4 ligands have been prepared. They are of the general formula Salan(^{t}Bu)[B(OR)]$_2$. The compounds are Salean(^{t}Bu)(BOR)$_2$ [Salean(^{t}Bu) = (*N*,*N*′-ethylenebis(3,5-di-*tert*-butyl-salicylamine)), R = Me (**1**), $SiMe_3$ (**4**)], Salban(^{t}Bu)(BOR)$_2$[Salban(^{t}Bu) = (*N*,*N*′-butylenebis(3,5-di-*tert*-butyl-salicylamine)), R = Me (**2**), $SiMe_3$ (**5**)], and Salhan(^{t}Bu)(BOR)$_2$ [Salhan(^{t}Bu) = (*N*,*N*′-hexylenebis(3,5-di-*tert*-butyl-salicylamine)), R = Me (**3**)]. All of the compounds were characterized by spectroscopic (^{1}H NMR, ^{11}B NMR, IR) and physical (mp, EA) techniques. Also, **1**, **2** and **4** were structurally characterized by single crystal X-ray diffraction studies.
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Keywords: Three-coordinate; Salan ligand; Binuclear; Boron

1. Introduction

There are a number of biologically important reactions that are mediated by two Lewis acidic sites in close proximity. This is an important feature in the hydrolysis of phosphate esters, for example [1–8]. Additionally, chiral binuclear boron compounds have been used as reaction templates in the asymmetric reduction of unsymmetric ketones [9]. Chiral borates have also been used as Lewis acidic catalysts for stereoselective Diels–Alder reactions [10]. Furthermore, two-point Lewis acidic compounds also find utility as anion binding agents [11,12].

Recently, our group has been interested in the synthesis of two-point Lewis acid boron compounds supported by SalenH_2 (*N*,*N*′-alkylenebis(salicylideneimine)) ligands. These were of somewhat limited utility as Lewis acid catalysts or anion binding agents because the boron atoms were four-coordinate [13,14]. However, in the Salen binuclear boron halide compounds the halide ligands are sufficiently labile that these compounds become cationic after Lewis base addition and catalytic for the dealkylation of phosphates [15].

The hydrogenated form of the Salen ligands, the so-called SalanH_4 (*N*,*N*′-alkylenebis(salicylamine)) ligands (Fig. 1) have been explored to a lesser extent with main group elements. Main group combinations are limited to compounds of zinc, [16] tin, [17–19] aluminum [18,20–23] and gallium [23,24]. This is despite the possibility that the presence of an amine rather than an imine functionality in these ligands could give rise to different structural, electronic and catalytic properties of their metal derivatives.

This paper focuses on the synthesis of binuclear boron compounds supported by Salan ligands which feature three-coordinate boron atoms.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

Previously, the synthesis of binuclear boron alkoxides and siloxides with Salen ligands were reported [25,26]. The borates containing alkoxides were prepared by refluxing

* Corresponding author. Tel.: +1 859 257 7304; fax: +1 859 323 1069.
E-mail address: datwood@uky.edu (D.A. Atwood).

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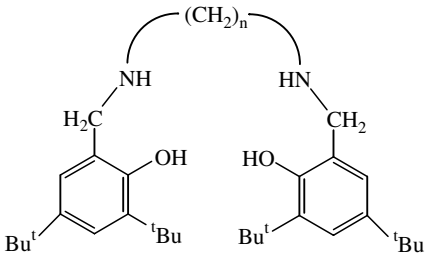


n = 2 : Salean(^{t}Bu)H_4

n = 4 : Salban(^{t}Bu)H_4

n = 6 : Salhan(^{t}Bu)H_4

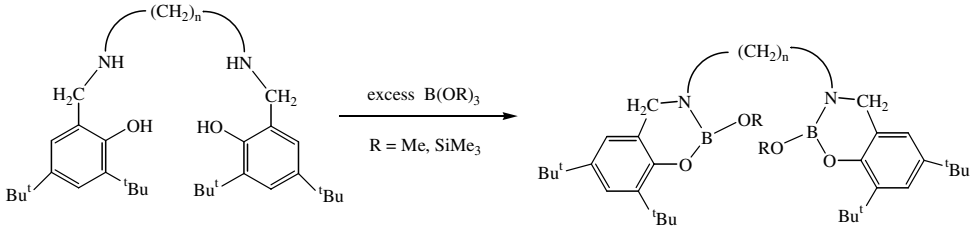
Fig. 1. Salan(^{t}Bu)H_4 ligands.

the ligands with excess trialkyl borate. Borates containing siloxides were prepared by further derivatization of the alkoxides with triphenyl silanol. In the present work, the Salan binuclear boron compounds were prepared by direct reaction of excess trimethylborate or tris(trimethylsiloxy)boron with various Salan(^{t}Bu)H_4 ligands in toluene (Scheme 1) under reflux. The Salan ligands used were salean(^{t}Bu), salban(^{t}Bu), and salhan(^{t}Bu) (Fig. 1). The compounds can be easily isolated by evaporating the volatiles under vacuum.

The ^{1}H NMR data for the five compounds (Scheme 1) show two singlets for the ^{t}Bu groups on the phenyl rings of each compound in the range δ 1.27–1.46 ppm. There are multiple CH_2 peaks corresponding to the alkylene backbone protons from the ligand ranging from 1.52 to 3.12 ppm. For compounds **1**–**3**, the methoxy groups attached to the boron show singlets in the range 3.51–3.74 ppm. The silyloxy groups attached to the boron in compounds **4** and **5** show singlets at 0.34 and 0.31 ppm. The presence of only one singlet for each type of ^{t}Bu (3- or 5-position on the phenyl rings) groups and one set of methoxy or silyloxy peaks indicates a C_2 symmetric solution state structure for each of the compounds. The ^{11}B NMR for compounds **1**–**5** shows peaks at δ 21.0, 20.7, 20.0, 19.8, 19.6 ppm. These correspond to the presence of three-coordinate boron atoms [27]. The mass spectra (EI, positive, direct probe) show the molecular ion peaks in low relative abundance (11% and 25%, respectively), for **1** and **2**. However, for **3** and **5** the molecular ion is the most abundant ion, and for **4**, it is present in 62% relative abundance. Thus, the compounds are rather robust under the MS conditions.

2.2. Structural characterization of *1*, *2* and *4*

Compounds **1**, **2** and **4** have been structurally characterized by single crystal X-ray diffraction studies. Figs. 2–4 show their molecular structures. The data collection parameters are located in Table 1 and selected bond distances and angles are located in Table 2. Compounds **1** and **4** crystallize in the triclinic space group $P\bar{1}$ while **2** crystallizes monoclinic in space group $P2_{1/n}$. Unlike their Salen counterparts [25] these compounds do not show any hydrogen bonding since there is no imine hydrogen present. In each of the compounds the boron atom adopts a three-coordinate trigonal planar geometry with bond angles close to 120°. The O–B–O angle (116.0–117.3°) is smaller than the O–B–N angles (121.8–121.9 and 120.4–122.1°). This is consistent with the higher electronegativity of oxygen compared to nitrogen leading to less s-character in the O–B bond. The B–O (ligand) bond distances range from ~1.37 to ~1.41 Å and B–N distances range from ~1.37 to ~1.39 Å. These distances are close to B–O and B–N distances in other three-coordinate boron chelate compounds. For example, in a boronato-functionalized ferrocenylphosphine ligand *rac*-BPPFAP-BMe these distances are 1.415(6) and 1.428(6) Å [28]. However, the distances are shorter than the B–O and B–N distances in the binuclear Salen borate compounds. For example, in salen[$B(OMe)_2$]$_2$ the B–O bond length is ~1.50 Å and B–N distance is ~1.61 Å [25]. This can be attributed to more s-character in sp^2 hybridized Salan boron compounds compared to sp^3 hybridized salen boron compounds.



n = 2, R = Me : Salean(^{t}Bu)[BOMe]$_2$ (**1**)

n = 4, R = Me : (Salban(^{t}Bu)[BOMe]$_2$, (**2**)

n = 6, R = Me : (Salhan(^{t}Bu)[BOMe]$_2$) (**3**)

n = 2, R = $SiMe_3$: (Salean(^{t}Bu)[BOSiMe_3]$_2$ (**4**)

n = 2, R = $SiMe_3$: (Salban(^{t}Bu)[BOSiMe_3]$_2$ (**5**)

Scheme 1. Synthesis of compounds **1**–**5**.

Table 1
Crystallographic data and refinement details for compounds **1**, **2** and **4**

	Salean(^{t}Bu)[BOMe]$_2$ (**1**)	Salban(^{t}Bu)[BOMe]$_2$ (**2**)	Salean(^{t}Bu)[BOSiMe$_3$]$_2$ (**4**)
Empirical formula	$C_{41}H_{62}B_2N_2O_4$	$C_{36}H_{58}B_2N_2O_4$	$C_{38}H_{66}B_2N_2O_4Si_2$
M (g mol^{-1})	668.55	604.46	692.73
Color	Pale yellow	Colorless	Colorless
Crystal size (mm)	$0.20 \times 0.16 \times 0.12$	$0.25 \times 0.20 \times 0.05$	$0.45 \times 0.22 \times 0.10$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_{1/n}$	$P\bar{1}$
a (Å)	10.592(2)	10.222(2)	12.5860(5)
b (Å)	11.431(2)	8.415(2)	13.7730(6)
c (Å)	17.454(3)	20.925(5)	14.1910(6)
α (°)	71.66(2)	90	90.835(2)
β (°)	81.70(2)	93.320(10)	92.723(2)
γ (°)	87.34(2)	90	116.568(2)
V (Å^3)	1985.0(6)	1796.9(7)	2195.95(16)
ρ_{calc} (g cm^{-3})	1.119	1.117	1.048
Z	2	2	2
$F(000)$	728	660	756
μ (Mo Kα) (mm^{-1})	0.070	0.070	0.117
T (K)	173(1)	88.5(2)	160.0(2)
hkl range	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 18$	$-10 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 8$, $-21 \leqslant l \leqslant 21$	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 18$
θ Range (°)	1.94–22.50	1.95–21.00	1.44–22.50
Reflections measured	10274	6628	11475
Unique reflections (R_{int})	5192 (0.0530)	1939 (0.1239)	5738 (0.0653)
Obsd reflections, $n[F \geqslant 4(F)]$	3495	1305	4322
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Refined parameters/restraints	507/975	199/0	443/456
R_1 [$I > 2$]	$R_1 = 0.0631$, $wR_2 = 0.1375$	$R_1 = 0.1002$, $wR_2 = 0.1388$	$R_1 = 0.1399$, $wR_2 = 0.3678$
R_1 (all data)	$R_1 = 0.1040$, $wR_2 = 0.1521$	$R_1 = 0.1504$, $wR_2 = 0.1543$	$R_1 = 0.1668$, $wR_2 = 0.3778$
Goodness-of-fit on F^2	1.061	1.179	1.146
Largest diff. peak and hole (e Å^{-3})	0.215 and −0.216	0.210 and −0.178	0.597 and −0.444

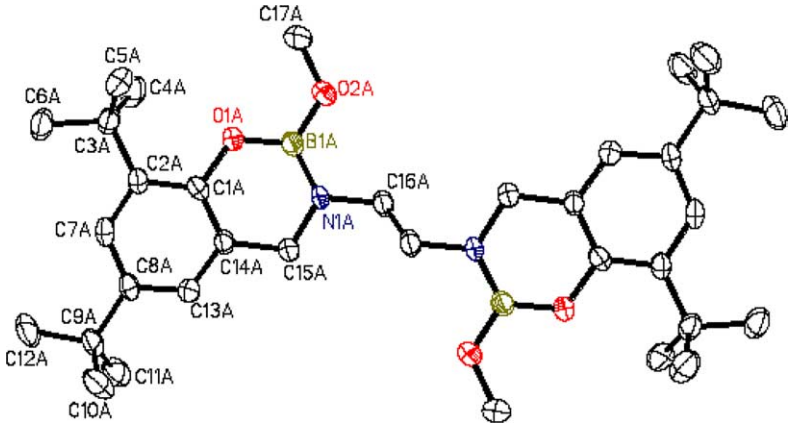


Fig. 2. Crystal structure of Salean(^{t}Bu)[BOMe]$_2$ (**1**). There are two molecules in the asymmetric unit. Only one of them is shown in the figure. Hydrogen atoms are omitted for clarity.

3. Conclusion

Salan(^{t}Bu)H$_4$ ligands in combination with boron alkoxides or siloxides form a series of bimetallic boron alkoxides and siloxides containing three-coordinate boron atoms. These compounds are more air and moisture sensitive compared to the bimetallic Salen-boron compounds. This is due to the lower coordination number of boron in the Salan compounds compared to the Salen compounds. The presence of three-coordinate boron in these compounds makes them suitable for potential Lewis acidic applications. For example, these compounds could be used for binding Lewis bases such as organophosphates. This and other potential applications of these compounds as Lewis acidic catalysts are currently being explored.

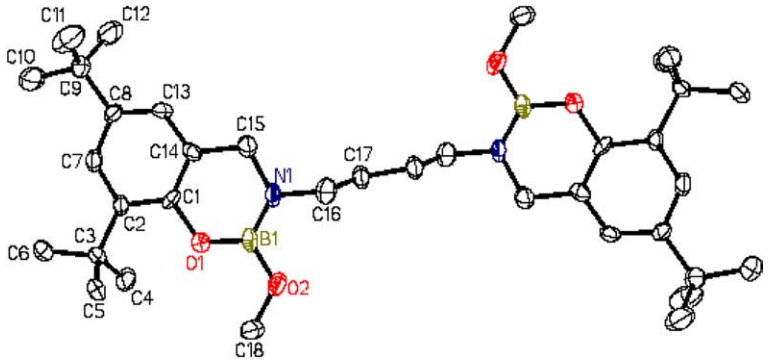


Fig. 3. Crystal structure of Salban(^{t}Bu)[BOMe]$_2$ (**2**). Hydrogen atoms are omitted for clarity.

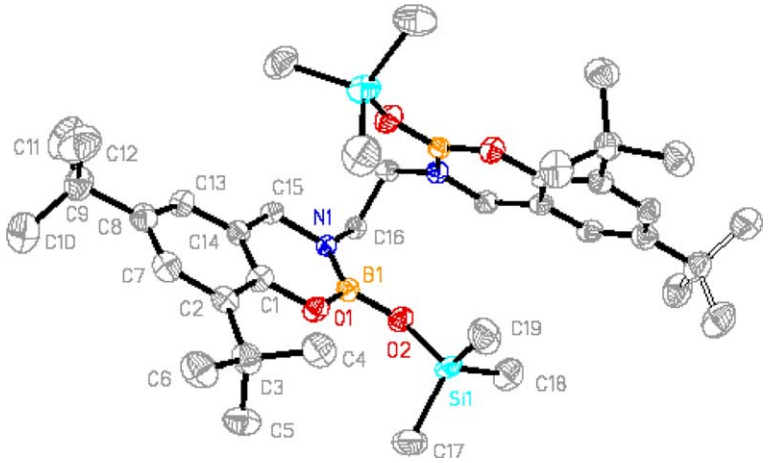


Fig. 4. Crystal structure of Salean(^{t}Bu)[BOSiMe$_3$]$_2$ (**4**). Hydrogen atoms are omitted for clarity.

4. Experimental

4.1. General

All air-sensitive manipulations were conducted using standard bench-top Schlenk line technique in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. All glassware was cleaned with a base and an acid wash and dried in an oven at 130 °C overnight prior to use. The ligands salean(^{t}Bu)H$_2$, salban(^{t}Bu)H$_2$ and salhan(^{t}Bu)H$_2$ were synthesized according to the literature procedure [16]. NMR data were obtained on Varian Gemini-200 and Varian VXR-400 instruments. Chemical shifts were reported relative to $SiMe_4$ for ^{1}H and $BF_3 \cdot Et_2O$ for ^{11}B and are reported in ppm. Infrared transmission spectra were recorded at room temperature using the potassium bromide pellet technique on a Fourier-transform Magna-IR ESP 560 spectrometer. Elemental analyses were obtained on a Perkin–Elmer 2400 analyzer.

X-ray data for **1**, **2** and **4** were collected on a Nonius Kappa-CCD unit using Mo Kα radiation. Crystal data are summarized in Table 1. All calculations were performed using the Siemens software package SHELXTL-Plus [29–32]. The structures were solved by direct methods and successive interpretation of difference Fourier maps followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in refinement in calculated positions using fixed isotropic parameters.

4.1.1. Synthesis of salean(^{t}Bu)[BOMe]$_2$ (**1**)

Salean(^{t}Bu)H$_4$ (0.530 g, 1.1 mmol) and B(OMe)$_3$ (0.520 g, 5.0 mmol) were refluxed together in 35 mL of toluene for 18 h. The solvent was evaporated under reduced pressure to get a pale yellow solid which was washed a few times with hexane to yield 0.460 g of **1** as a pale yellow powder (73% yield). Single crystals of **1** for X-ray analysis were grown from a saturated toluene solution at 15 °C. Mp: 95–97 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.27 (s, 18H, C(CH_3)$_3$), 1.39 (s, 18H, C(CH_3)$_3$), 3.09 (s, br, 4H, CH_2CH_2), 3.51 (s, 6H, OCH_3), 4.24 (s, 4H, NCH_2), 7.14–7.24 (m, 4H, PhH). ^{11}B NMR ($CDCl_3$, 64.1 MHz): δ 21.0 ($W_{1/2} = 1680$ Hz); IR (KBr; ν, cm^{-1}): 2956 (s), 2864 (m), 1603 (w), 1562 (w), 1513 (s), 1470 (s), 1415 (w), 1375 (s), 1352 (m), 1333 (s), 1311 (m), 1259 (s), 1238 (m), 1208 (m), 1184 (m), 1107 (m), 1011 (m), 960 (w), 878 (m), 847 (w), 804 (w), 755 (w), 731 (m), 697 (w), 639 (m). MS (EI, positive): 576 (11%, Salean(^{t}Bu)-[BOMe]$_2$), 545 (6%, (Salean(^{t}Bu)[BOMe]$_2$) – OCH_3), 515

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **4**

*Salean(^{t}Bu)[BOMe]$_2$ (**1**)*	
B1A–N1A	1.388(4)
B1A–O1A	1.395(4)
B1A–O2A	1.367(4)
O2A–C17A	1.422(3)
O1A–B1A–O2A	117.7(3)
O1A–B1A–N1A	121.8(3)
O2A–B1A–N1A	120.4(3)
B1A–O2A–C17A	122.2(2)
B1A–N1A–C16A	122.3(2)
C15A–N1A–C16A	113.8(2)
*Salban(^{t}Bu)[BOMe]$_2$ (**2**)*	
B1–N1	1.390(7)
B1–O1	1.384(7)
B1–O2	1.381(7)
O2–C18	1.440(5)
O1–B1–O2	117.6(6)
O1–B1–N1	121.8(6)
O2–B1–N1	120.6(6)
B1–O2–C18	119.5(4)
B1–N1–C16	123.5(5)
C15–N1–C16	114.5(4)
*Salean(^{t}Bu)[BOSiMe$_3$]$_2$ (**4**)*	
B1–N1	1.373(13)
B1–O1	1.406(13)
B1–O2	1.386(13)
O2–Si1	1.627(7)
O1–B1–O2	116.0(9)
O1–B1–N1	121.9(9)
O2–B1–N1	122.1(9)
B1–O2–Si1	139.9(7)
B1–N1–C16	123.4(8)
C15–N1–C16	114.2(7)

(100%, (Salean(^{t}Bu)[BOMe]$_2$) − 2 OMe). Anal. Calc. for $C_{34}H_{54}O_4N_2B_2$: C, 70.84; H, 9.44; N, 4.86. Found: C, 73.86, H, 9.61, N, 4.23.

4.1.2. Synthesis of salban(^{t}Bu)[BOMe]$_2$ (2)

Salban(^{t}Bu)H$_4$ (0.825 g, 1.57 mmol) and B(OMe)$_3$ (0.660 g, 6.35 mmol) were refluxed together in 60 mL of toluene for 18 h. The solvent was evaporated under reduced pressure and the solid was washed a few times with hexane to yield 0.750 g of **2** as a white powder (79% yield). Single crystals of **2** for X-ray analysis were grown from a saturated toluene solution at 15 °C. Mp: 154–156 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.31 (s, 18H, C(CH_3)$_3$), 1.46 (s, 18H, C(CH_3)$_3$), 1.52 (s, br, 4H, CH$_2$CH_2CH_2CH$_2$), 3.05 (s, br, 4H, CH_2CH$_2$CH$_2$$CH_2$), 3.74 (s, 6H, OC$H_3$), 4.19 (s, 4H, NC$H_2$), 6.87–7.20 (m, 4H, Ph$H$). ^{11}B NMR ($CDCl_3$, 64.1 MHz): δ 20.7 ($W_{1/2} = 572$ Hz); IR (KBr; ν, cm^{-1}): 2961 (m), 2866 (w), 2835 (w), 1560 (w), 1545 (vs), 1484 (s), 1363 (vs), 1349 (m), 1319 (m), 1295 (m), 1251 (m), 1181 (m), 1104 (m), 1016 (m), 802 (w), 636 (w). MS (EI, positive): 604.5 (25%, Salban(^{t}Bu)[BOMe]$_2$), 589.5 (4%, (Salban(^{t}Bu)[BOMe]$_2$) − CH$_3$), 573.4 (2%, (Salban(^{t}Bu)[BOMe]$_2$) − OCH$_3$), 557.5 (100%, (Salban(^{t}Bu)[BOMe]$_2$) − OCH$_3$ − CH$_3$), 543.5 (40%, (Salban(^{t}Bu)[BOMe]$_2$) − 2 OMe), 529.5 (92%, (Salban(^{t}Bu)[BOMe]$_2$) − BOMe − OMe). Anal. Calc. for $C_{36}H_{58}O_4N_2B_2$: C, 71.53; H, 9.67; N, 4.63. Found: C, 70.52, H, 11.07, N, 4.22.

4.1.3. Synthesis of salhan(^{t}Bu)[BOMe]$_2$ (3)

Salhan(^{t}Bu)H$_4$ (1.48, 2.68 mmol) and B(OMe)$_3$ (1.11 g, 10.7 mmol) were refluxed together in 50 mL of toluene for 18 h. The solvent was evaporated under reduced pressure and the solid was washed a few times with hexane to yield 1.18 g of **3** as a sticky colorless solid (70% yield). Mp: 82–86 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.29 (s, 18H, C(CH_3)$_3$), 1.35 (m, 8H, CH$_2$(CH_2)$_4$CH$_2$), 1.45 (s, 18H, C(CH_3)$_3$), 3.00 (t, 4H, CH_2(CH$_2$)$_4$$CH_2$), 3.72 (s, 6H, OC$H_3$), 4.17 (s, 4H, NC$H_2$), 6.86–7.19 (m, 4H, Ph$H$). ^{11}B NMR ($CDCl_3$, 64.1 MHz): δ 20.0 ($W_{1/2} = 446$ Hz); IR (KBr; ν, cm^{-1}): 2960 (s), 2863 (m), 1561 (s), 1547 (s), 1523 (vs), 1453 (m), 1390 (vs), 1351 (s), 1314 (s), 1288 (vs), 1203 (s), 1175 (s), 1130 (s), 1094 (s), 1019 (s), 959 (m), 873 (m), 846 (w), 803 (m), 755 (w), 729 (w), 641 (m). MS (EI, positive): 632 (100%, Salhan(^{t}Bu)[BOMe]$_2$), 618 (15%, (Salhan(^{t}Bu)[BOMe]$_2$) − CH$_3$), 602 (2%, (Salhan(^{t}Bu)-[BOMe]$_2$) − OCH$_3$), 586 (87%, (Salhan(^{t}Bu)[BOMe]$_2$) − OMe − Me), 576 (100%, (Salhan(^{t}Bu)[BOMe]$_2$) − BOMe − Me), 560 (4%, (Salhan(^{t}Bu)[BOMe]$_2$) − BOMe − OMe). Anal. Calc. for $C_{38}H_{62}O_4N_2B_2$: C, 72.16; H, 9.88, N, 4.43. Found: C, 72.59; H, 11.36, N, 4.13.

4.1.4. Synthesis of salean(^{t}Bu)[BOSiMe$_3$]$_2$ (4)

Salean(^{t}Bu)H$_4$ (0.749 g, 1.51 mmol) and B(OSiMe$_3$)$_3$ (0.892 g, 3.20 mmol) were refluxed together in 30 mL of toluene for 18 h. The solvent was evaporated under reduced pressure and the solid was washed a few times with hexane to yield 0.720 g of **4** as a white powder (69% yield). Single crystals of **4** for X-ray analysis were grown from a saturated toluene solution at 15 °C. Mp: 138 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.34 (s, 18H, Si(CH_3)$_3$),1.28 (s, 18H, C(CH_3)$_3$), 1.39 (s, 18H, C(CH_3)$_3$), 3.12 (s, br, 4H, CH_2CH_2), 4.27 (s, 4H, NCH_2), 6.83–7.15 (m, 4H, PhH). ^{11}B NMR ($CDCl_3$, 64.1 MHz): δ 19.8 ($W_{1/2} =$ 736 Hz); MS (EI, positive): 693 (62%, Salean(^{t}Bu)[BOSiMe$_3$]$_2$), 678 (100%, (Salean(^{t}Bu)[BOSiMe$_3$]$_2$) − CH$_3$), 619 (5%, (Salean(^{t}Bu)[BOSiMe$_3$]$_2$) − SiMe$_3$), 603 (15%, (Salean(^{t}Bu)[BOSiMe$_3$]$_2$) − OSiMe$_3$). Anal. Calcd. for $C_{38}H_{66}O_4N_2Si_2B_2$: C, 65.89; H, 9.60, N, 4.04. Found: C, 64.28; H, 10.54, N, 3.71.

4.1.5. Synthesis of salban(^{t}Bu)[BOSiMe$_3$]$_2$ (5)

Salban(^{t}Bu)H$_4$ (0.971 g, 1.85 mmol) and B(OSiMe$_3$)$_3$ (1.087 g, 3.90 mmol) were refluxed together in 30 mL of toluene for 18 h. The solvent was evaporated under reduced pressure and the solid was washed a few times with hexane to yield 1.00 g of **5** as a pale yellow powder (75% yield). Mp: 112 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.21 (s, 18 H, Si(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 1.43 (s, 18H, C(CH_3)$_3$), 1.51 (s, br, 4H, CH$_2$CH_2CH_2CH$_2$), 3.04 (s, 4H, CH_2CH$_2$CH$_2$$CH_2$), 4.19 (s, 4H, NC$H_2$), 6.86–7.18 (m, 4H, Ph$H$).^{11}B NMR ($CDCl_3$, 64.1 MHz): δ 19.6

($W_{1/2} = 722$ Hz); MS (EI, positive): 720 (100%, Salban(^{t}Bu)[BOSiMe$_3$]$_2$), 705 (88%, (Salban(^{t}Bu)[BOSiMe$_3$]$_2$) − CH$_3$), 648 (3%, (Salban(^{t}Bu)[BOSiMe$_3$]$_2$) − SiMe$_3$), 633 (1%, (Salban(^{t}Bu)[BOSiMe$_3$]$_2$) − OSiMe$_3$), 622 (2%, (Salban(^{t}Bu)[BOSiMe$_3$]$_2$) − BOSiMe$_3$). Anal. Calcd. for $C_{40}H_{70}O_4N_2Si_2B_2$: C, 66.65; H, 9.79, N, 3.89. Found: C, 65.38; H, 10.60, N, 3.11.

5. Supplementary information

Crystallographic data for **1**, **2** and **4** have been deposited with the Cambridge Crystallographic Data Center (CCDC reference numbers: 276637, 276475 and 276474, respectively), and copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk).

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