Boron halide chelate compounds and their activity towards the demethylation of trimethylphosphate

Timothy S. Keizer, Lauren J. De Pue, Sean Parkin, and David A. Atwood

Abstract: Salen(*t*-Bu)H_2 (*N*,*N*′-ethylenebis(3,5-di-*tert*-butyl(2-hydroxy)benzylidenimine) and its derivatives were used to prepare boron compounds having the formula L$(BCl_2)_2$ (L = salen(*t*-Bu) (**1**), salpen(*t*-Bu) (**2**), salben(*t*-Bu) (**3**), salpten(*t*-Bu) (**4**), salhen(*t*-Bu) (**5**)). These are formed from the reaction of the corresponding L$[B(OMe)_2]_2$ with BCl_3. In addition to being a new type of boron compound, they are also potential two-point Lewis acids. Indeed, they demonstrate Lewis acidic behavior in the dealkylation of trimethylphosphate. All of the compounds were characterized by mp, elemental analysis, ^{1}H and ^{11}B NMR, IR, MS, and in the case of **2** by X-ray crystallography.

Key words: boron, salen, dealkylation.

Résumé : On a utilisé le salen(*t*-Bu)H_2 (*N*,*N*′-éthylènebis(3,5-di-*tert*-butyl(2-hydroxy)benzylidènimide) et ses dérivés pour préparer des composés du bore de formules L$(BCl_2)_2$ (L = salen(*t*-Bu) (**1**), salpen(*t*-Bu) (**2**), salben(*t*-Bu) (**3**), salpten(*t*-Bu) (**4**) et salhen(*t*-Bu) (**5**) qui se forment par réaction du L$[B(OMe)_2]_2$ avec du BCl_3. En plus de correspondre à un nouveau type de composé du bore, ces produits sont potentiellement des acides de Lewis en deux points. Ils démontrent effectivement un comportement d'acide de Lewis dans la désalkylation du phosphate de triméthyle. Tous les composés ont été caractérisés par leurs points de fusion, une analyse élémentaire, par RMN du ^{1}H et du ^{11}B, par infrarouge et spectrométrie de masse et, dans le cas du produit **2**, par diffraction des rayons X.

Mots clés : bore, salen, désalkylation.

[Traduit par la Rédaction]

Introduction

Over the years, the dianionic Salen ligands (salen(*t*-Bu) = *N*,*N*′-ethylenebis(3,5-di-*tert*-butyl(2-oxo)benzylidenimine)) (Fig. 1) have been used in many applications (1, 2). The versatility of the ligand allows for the isolation of both monometallic and bimetallic derivatives usually involving the group 13 elements. For example, many compounds have been reported for aluminum (3–5), gallium (5, 6), and indium (7, 8). However, boron compounds of this type have been studied less extensively (9–11). Examples of Salen (L) boron compounds include alkoxide (L$[B(OR)_2]_2$, *R* = Me, Et) (9), siloxide (L$[B(OSiOPh_3)_2]_2$ (10), fluoride (L$[BF_2]_2$) (12), and acetate (L$[B(OAc)_2]_2$) (11) derivatives. Although these compounds are interesting from a fundamental standpoint, they are limited in usefulness because of their lack of reactivity or Lewis acid potential. In this paper we report the high-yield syntheses of new Salen-supported boron chloride derivatives, L$[BCl_2]_2$ (**1**–**5**). Preliminary work indicates that these chloride compounds will undergo salt elimination reactions, allowing for further derivatization of the boron atoms and thereby increasing their potential utility (13).

For instance, boron compounds could be useful as two-point Lewis acids. Many biological systems use a bis-metal complex to promote the binding and hydrolysis of phosphate esters (14). In recent years, synthetic derivatives containing *d*-block metals such as cobalt (15, 16), zinc (17–20), and copper (21, 22) have been used as catalysts for this reaction. A potentially important development in this area is the recent demonstration that boron bromide compounds such as salpen(*t*-Bu)$[BBr_2]_2$ can catalytically dealkylate a wide variety of phosphate esters (23). Herein, the boron chloride compounds L$[BCl_2]_2$ (**1**–**5**) will be synthesized, characterized, and examined as dealkylation agents for trimethylphosphate.

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Results and discussion

Synthesis and characterization of 1–5

The boron chlorides (**1**–**5**) were prepared in nearly quantitative yield by combining the corresponding salen(*t*-Bu)$[B(OMe)_2]_2$ reagent with BCl_3 (Scheme 1). The resulting compounds have two four-coordinate boron atoms held in a bidentate manner by the Salen ligand. Each boron atom is bound by two chlorides, a nitrogen, and an oxygen from the Salen ligand. This reaction is unique and unusual in that all of the methoxide groups are replaced with chloride groups. It is known that boron trichloride mixed with trimethylborate (eq. [1]) undergoes a ligand redistribution to form $BCl(OMe)_2$ and BCl_2(Ome) (24). Thus, the reaction described in Scheme 1 is expected to produce compounds with various combinations of chlorides and methoxides on the boron

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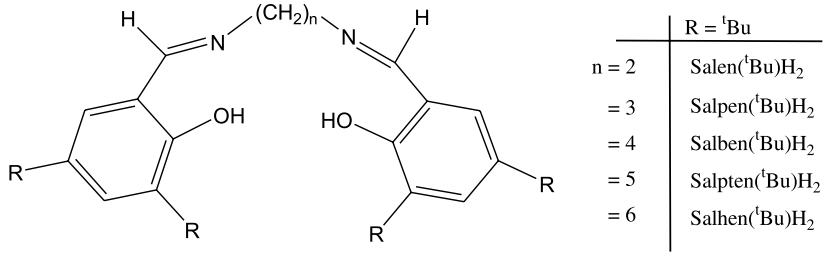
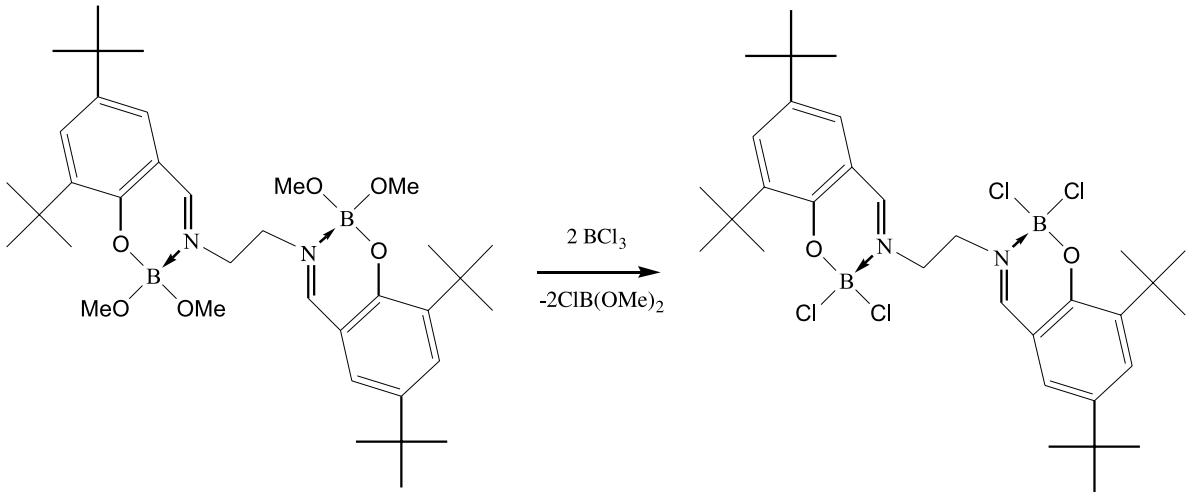
Fig. 1. Nomenclature of the Salen ligand precursors used herein.



	R = ^{t}Bu
n = 2	Salen(^{t}Bu)H_2
= 3	Salpen(^{t}Bu)H_2
= 4	Salben(^{t}Bu)H_2
= 5	Salpten(^{t}Bu)H_2
= 6	Salhen(^{t}Bu)H_2

[1] $BCl_3 + B(OMe)_3 \rightleftharpoons BCl_2OMe + BCl(OMe)_2$

Scheme 1.



atoms. However, only the desired products $L[BCl_2]_2$ (**1**–**5**) were formed. The presence of the chelate apparently stabilizes the dihalide derivative relative to the other possibilities.

The ^{1}H NMR data for **1**–**5** contain two singlets for the *t*-Bu-Ph groups in the range δ: 1.22–1.45 ppm. There are multiple CH_2 peaks corresponding to the backbone protons from the ligand ranging from δ: 1.55–4.62 ppm depending on ligand type. There is one imine singlet for each compound in the range δ: 8.19–8.52 ppm. These values decrease with increasing backbone length. Thus, the most shielded shift (8.2 ppm) is associated with **4** and **5** and the less shielded shift at 8.5 ppm is associated with **1**. This might indicate a slight increase in nitrogen basicity for electron releasing "carbon rich" ligands and a moderate decrease in basicity for the "carbon poor" **1**, with a comparatively lower inductive effect. The ^{13}C NMR data also supports this trend. The chemical shift for the C=N group for **1**–**5** (166.7–163.4 ppm) decreases with the increase in the backbone length. The effect is more distinct between **1** (166.7 ppm) and **2** (164.9 ppm) than between **4** (163.7 ppm) and **5** (163.4 ppm). Thus, the inductive effect on the C=N is further evident when the backbone is increased from two carbons to three carbons rather than five carbons to six carbons. The ^{11}B NMR shows broad single peaks ranging from δ: 5.99–6.39 ppm with $w_{1/2}$ ranging from 28.2–56.7 Hz, which are in the region for tetrahedral boron (25). The IR data shows strong B-Cl stretches between 697–743 cm^{-1}. In the mass spectrum, the compounds show the parent ion with the isotope pattern appropriate for four chlorines and two borons. The most abundant peak for the compounds is the parent ion minus chlorine with the correct isotope pattern for three chlorines and two borons.

The structure of **2** (Fig. 2) was determined by X-ray crystallography. The geometry around the two boron atoms is slightly distorted from a tetrahedral geometry. Other Salen boron derivatives also show this distortion (9). The bite angles of the ligand on the boron atoms (N-B-O) are 110.1(4)° and 111.8(4)° (Table 1). These are slightly larger than other Salen-supported boron systems such as $salenN_3H[B(OMe)_2]_2$, which has an angle of 105.9(3)° (10). This deviation is in keeping with an increased *sp* hybridization in the N,O bonds and more obtuse angles with these atoms for **2** resulting from an increase in *p* character for the B—Cl bonds by comparison to B—OMe bonds (26). The (N-B-O) angles are significantly larger than the (N-Al-O) angle in salben(*t*-Bu)$[AlMeCl]_2$ (96.0(4)°) and the (N-Ga-O) angle in salphen(*t*-Bu)$[Ga(Et)_2]_2$ (92.5(2)°) (5). Thus, the angle decreases as the atoms increase in size, and displaces further "out" of the chelate. The B—Cl bond lengths are 1.849(5) Å, 1.855(5) Å, 1.841(5) Å, and 1.907(5) Å. These are comparable to a similar Schiff base compound, dichloro-[2-(1-imino-2,2,2-trichloroethyl)-4-methoxyphenoxido-O,N]boron, which

Fig. 2. Crystal structure of salpen(*t*-Bu)[BCl_2]$_2$ (**2**).

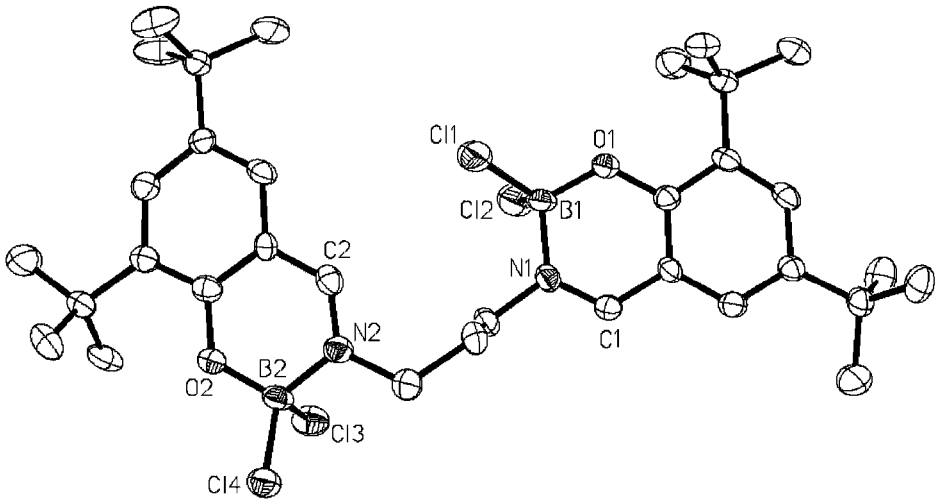
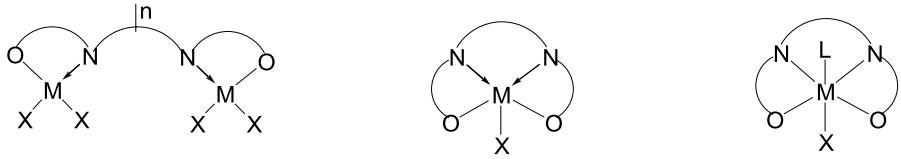


Fig. 3. Bimetallic (*a*) and monometallic (*b* and *c*) metal compounds with Salen ligands.



(*a*) (*b*) (*c*)

Table 1. Selected bond lengths (Å) and angles (°) for compound **2**.

Bond lengths	(Å)	**Bond angles**	(°)
B(1)—O(1)	1.422(5)	O(1)-B(1)-N(1)	110.1(4)
B(1)—N(1)	1.561(5)	O(1)-B(1)-Cl(1)	108.2(3)
B(1)—Cl(1)	1.849(5)	N(1)-B(1)-Cl(1)	109.7(3)
B(1)—Cl(2)	1.855(5)	O(1)-B(1)-Cl(2)	111.7(3)
C(1)—N(1)	1.295(4)	N(1)-B(1)-Cl(2)	106.5(3)
B(2)—O(2)	1.418(5)	Cl(1)-B(1)-Cl(2)	110.6(3)
B(2)—N(4)	1.548(5)	O(2)-B(2)-N(2)	111.8(4)
B(2)—Cl(3)	1.907(5)	O(2)-B(2)-Cl(4)	109.1(3)
B(2)—Cl(4)	1.841(5)	N(2)-B(2)-Cl(4)	111.0(3)
C(2)—N(2)	1.294(4)	O(2)-B(2)-Cl(3)	110.5(3)
		N(2)-B(2)-Cl(3)	104.9(3)
		Cl(4)-B(2)-Cl(3)	109.4(2)

has B—Cl bonds lengths of 1.855(7) Å and 1.841(7) Å (27). A noticeable trend in the length of the N→B dative bond occurs with the exchange of the substituents on the boron atom (28). The N→B lengths for **2** are 1.561(5) Å and 1.548(5) Å. These are shorter than the N→B bond length of salen[$B(OMe)_2$]$_2$ (1.615(2) Å) (9). An inverse relationship exists between the lengths of the C=N and N→B bonds. Where the N→B bond shortens the C=N bond lengthens. The C=N bond for 2 is 1.295(4) Å which is longer than that of the borate C=N bond (1.288(2) Å). The C=N and N→B bond lengths of **2** compare closely to those in the boron bromine derivative salben(*t*-Bu)[BBr_2]$_2$ (1.295(4) Å and 1.539(5) Å, respectively) (23).

Table 2. Percent dealkylation of trimethylphosphate.

L[BCl_2]$_2$	% Conversion[a] 30 min	% Conversion[a] 24 h
1	14	45
2	20	32
3	11	53
4	42	62
5	7	47

[a]Yields were calculated from the amount of MeCl produced to the amount of trimethylphosphate remaining in the ^{1}H NMR.

One unique aspect of these compounds (Fig. 3(*a*)) is that there are no corresponding transition metal derivatives. Rather, transition metals adopt fully chelated five-coordinate and more often six-coordinate complexes with the Salen ligands (Figs. 3(*b*) and 3(*c*)) (1). These ligands are very versatile in the fact that the "backbone" of the ligand may be altered. For instance, the length of the backbone may be increased to the point that binding to a single metal is ineffectual. Thus, the existence of **1**–**5** may indicate the possibility of isolating transition metals of the form L[MX_2]$_2$.

Demethylation of trimethylphosphate with compounds 1–5

It is known that boron trichloride will demethylate aryl ethers (29). Nevertheless, it has been found that BCl_3 alone is ineffective towards the demethylation of trimethylphosphate. Compounds (**1**–**5**), however, are capable of demethylating trimethylphosphate (Table 2). When compounds **1**–**5**

Table 3. Crystal structure data.

	Salpen(*t*-Bu)$[BCl_2]_2$ (**2**)
Color, shape	Pale yellow, plate
Chemical formula	$C_{33}H_{48}B_2Cl_4N_2O_2\cdot(1/2)C_7H_8$
Formula weight	714.22
Temperature (K)	145(1)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	9.086(3)
b (Å)	14.604(4)
c (Å)	14.947(4)
α (°)	84.29(2)
β (°)	81.62(2)
γ (°)	89.24(2)
Volume (Å^3)	1952.4(10)
Z	2
$D_{calcd.}$ (mg m^{-3})	1.215
Absorption coefficient (mm^{-1})	0.336
Crystal size (mm)	0.12 × 0.10 × 0.04
Diffractometer, scan	Nonius CCD
θ range for data collection (°)	1.38–22.50
Reflections measured	10 240
Independent reflections	5122 (R_{int} = 0.0984)
Data/restraints/parameters	5122/414/424
Goodness of fit on F^2	1.046
Final *R* indices [I > 2σ(I)]	R_1 = 0.0700, wR_2 = 0.1006
R indices (all data)	R_1 = 0.1409, wR_2 = 0.1172

are added to a stoichiometric amount of trimethylphosphate, methyl chloride is produced. However, these species are less reactive than the boron bromide analogue, salpen(*t*-Bu)$[BBr_2]_2$ (23). For example, compound **2** demethylates 20% of the trimethylphosphate within 30 min whereas salpen(*t*-Bu)$[BBr_2]_2$ demethylates 89% of the trimethylphosphate within 30 min. This heightened activity may be explained by the fact that the B—Cl bond is less labile than the B—Br bond. In demonstration of this, it has been found that THF does not displace the chloride from **2** as readily as in the boron bromide compound, which forms an in situ cation (23). By analogy then, trimethylphosphate does not displace the chloride as well as bromide resulting in a decrease in dealkylation efficiency of the boron chloride compared with the boron bromide chelate. The bromide derivative can be made catalytic for the dealkylation of a wide range of phosphate esters, including trimethylphosphate, by the addition of BBr_3 (23). In this process it was not necessary to have two connected sites. This was confirmed by using a monometallic boron compound under the same conditions.

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 ligand precursors (30) salen(*t*-Bu)H_2, salpen(*t*-Bu)H_2, salben(*t*-Bu)H_2, salpten(*t*-Bu)H_2, and salhen(*t*-Bu)H_2 were synthesized according to the literature procedure. Salen(*t*-Bu)$[B(OMe)_2]_2$, salpen(*t*-Bu)$[B(OMe)_2]_2$, salben(*t*-Bu)$[B(OMe)_2]_2$, salpten(*t*-Bu)$[B(OMe)_2]_2$, and salhen(*t*-Bu)$[B(OMe)_2]_2$ were prepared as reported previously (9). NMR data (^{1}H, ^{11}B) were obtained on JEOL-GSX-400 and 200 MHz instruments. Chemical shifts are reported relative to $SiMe_4$ for ^{1}H and ^{13}C and relative to $BF_3\cdot Et_2O$ in $CDCl_3$ for ^{11}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^{-1}. EI (positive) (direct probe) spectra were acquired on a Kratos Concept IH at 70 eV. Elemental analyses were obtained on Vario EL III Elementar. X-ray data for **2** were obtained on a Nonius CCD unit employing Mo Kα radiation.[2] 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 3.

Salen(*t*-Bu)$[BCl_2]_2$ (1)

To a stirring solution of salen(*t*-Bu)$[B(OMe)_2]_2$ (2.5 g, 3.93 mmol) in toluene (75 mL) was added 1M BCl_3 in heptane (7.8 mL, 7.80 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 5 mL, filtered, and dried. Yield: 2.41g (94%); mp 314–320°C (decomposition temperature (dec.)). IR (KBr pellet) (cm^{-1}): 2962 (s), 2905 (m), 2862 (w), 1627 (s), 1622 (m), 1573 (m), 1456 (m), 1427 (w), 1359 (w), 1310 (w), 1258 (m), 1210 (w), 1138 (w), 1026 (s), 995 (w), 917 (m), 869 (m), 769 (w), 470 (m), 706 (vs). ^{1}H NMR ($CDCl_3$) δ: 1.22 (s, 18H, C(C*H*$_3$)$_3$), 1.45 (s, 18H, C(C*H*$_3$)$_3$), 4.62 (br s, 4H, NC*H*$_2$), 7.10 (d, 2H, C$_6$*H*$_2$), 7.73 (d, 2H, C$_6$*H*$_2$), 8.52 (s, 2H, N=C*H*) ^{13}C NMR ($CDCl_3$) δ: 29.3 (C(*C*H$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 34.4 (N*C*H$_2$), 35.1 (N*C*H$_2$), 54.5 (*C*(CH$_3$)$_3$), 115.6 (Ph), 126.2 (Ph), 135.7 (Ph), 139.7 (Ph), 144.2 (Ph), 154.7 (Ph), 166.7 (N=*C*H). ^{11}B NMR ($CDCl_3$) δ: 6.21 ($w_{1/2}$ = 43.9 Hz). MS (%): 654 ([M]$^+$, 5), 617 ([M – Cl], 100), 582 ([M – 2Cl], 15), 547 ([M – 3Cl], 55). Anal. calcd. for $B_2C_{32}H_{46}N_2O_2Cl_4$: C 58.87, H 7.11, N 4.29; found: C 58.52, H 7.18, N 4.20.

Salpen(*t*-Bu)$[BCl_2]_2$ (2)

To a stirring solution of salpen(*t*-Bu)$[B(OMe)_2]_2$ (1.0 g, 1.54 mmol) in toluene (50 mL) was added 1M BCl_3 in heptane (3.1 mL, 3.10 mmol). The reaction mixture was stirred for 24 h. The solvent was removed and washed with 5 mL of hexanes. Filtration and vacuum drying afforded salpen(*t*-Bu)$[BCl_2]_2$. Yield: 0.85g (83%); mp 234°C. IR (KBr pellet) (cm^{-1}): 2963 (s), 2862 (w), 1631 (s), 1569 (m), 1557 (m), 1454 (m), 1429 (w), 1394 (w), 1364 (m), 1346

[2] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 174675 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

(w), 1259 (m), 1223 (m), 1190 (w), 1115 (m), 1018 (s), 981 (w), 915 (w), 876 (m), 769 (m), 697 (s), 642 (m). ^{1}H NMR ($CDCl_3$) δ: 1.29 (s, 18H, C(CH_3)$_3$), 1.43 (s, 18H, C(CH_3)$_3$), 2.75 (m, 2H, CH_2), 4.09 (m, 4H, NCH_2), 7.12 (d, 2H, C$_6H_2$), 7.73 (d, 2H, C$_6H_2$), 8.38 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$) δ: 29.6 (C(*C*H$_3$)$_3$), 30.0 (*C*H$_2$), 31.4 (C(*C*H$_3$)$_3$), 34.6 (N*C*H$_2$), 35.3 (N*C*H$_2$), 54.8 (*C*(CH$_3$)$_3$), 115.7 (Ph), 126.2 (Ph), 135.4 (Ph), 139.8 (Ph), 144.2 (Ph), 154.7 (Ph), 164.9 (N=*C*H). ^{11}B NMR ($CDCl_3$) δ: 6.05 ($w_{1/2}$ = 46.7 Hz). MS (%): 668 ([M]$^+$, 2), 631 ([M – Cl], 100). Anal. calcd. for $B_2C_{33}H_{48}N_2O_2Cl_4$: C 59.44, H 7.26, N 4.20; found: C 60.08, H 7.82, N 3.96.

Salben(*t*-Bu)[BCl_2]$_2$ (3)

To a stirring solution of salben(*t*-Bu)[B(OMe)$_2$]$_2$ (0.5 g, 0.75 mmol) in toluene (50 mL) was added 1M BCl_3 in heptane (1.5 mL, 1.50 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 5 mL, filtered, and dried. Yield: 0.41g (81%); mp 316–318°C (dec.). IR (KBr pellet) (cm^{-1}): 2949 (s), 2893 (w), 2862 (w), 1631 (s), 1574 (m), 1470 (w), 1405 (w), 1361 (w), 1254 (m), 1219 (m), 1204 (w), 1095 (w), 1018 (m), 1008 (m), 872 (s), 771 (m), 743 (m), 705 (m), 641 (w). ^{1}H NMR ($CDCl_3$) δ: 1.22 (s, 18H, C(CH_3)$_3$), 1.41 (s, 18H, C(CH_3)$_3$), 2.17 (m, 4H, CH_2), 4.03 (m, 4H, NCH_2), 7.20 (d, 2H, C$_6H_2$), 7.70 (d, 2H, C$_6H_2$), 8.21 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$) δ: 26.7 (*C*H$_2$), 29.6 (C(*C*H$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 34.2 (N*C*H$_2$), 35.0 (N*C*H$_2$), 52.5 (*C*(CH$_3$)$_3$), 125.3 (Ph), 125.9 (Ph), 128.2 (Ph), 129.0 (Ph), 137.8 (Ph), 154.5 (Ph), 164.2 (N=*C*H). ^{11}B NMR ($CDCl_3$) δ: 5.99 ($w_{1/2}$ = 49.5 Hz). MS (%): 681 ([M]$^+$, 2), 645 ([M – Cl], 100), 610 ([M – 2Cl], 20). Anal. calcd. for $B_2C_{34}H_{50}N_2O_2Cl_4$: C 59.98, H 7.41, N 4.12; found: C 61.35, H 7.36, N 4.01.

Salpten(*t*-Bu)[BCl_2]$_2$ (4)

To a stirring solution of salpten(*t*-Bu)[B(OMe)$_2$]$_2$ (0.68 g, 1.00 mmol) in toluene (50 mL) was added 1M BCl_3 in heptane (2.0 mL, 2.0 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 5 mL, filtered, and dried. Yield: 0.64g (98%); mp 261–262°C (dec.). IR (KBr pellet) (cm^{-1}): 2961 (s), 2869 (w), 1630 (s), 1575 (m), 1474 (m), 1437 (m), 1395 (w), 1363 (m), 1251 (m), 1217 (w), 1190 (w), 1135 (w), 1078 (m), 1025 (m), 914 (m), 8749 (m), 771 (m), 731 (s), 644 (w). ^{1}H NMR ($CDCl_3$) δ: 1.28 (s, 18H, C(CH_3)$_3$), 1.45 (s, 18H, C(CH_3)$_3$), 1.59 (m, 2H, CH$_2$), 2.19 (m, 4H, CH_2), 3.98 (m, 4H, NCH_2), 7.19 (d, 2H, C$_6H_2$), 7.69 (d, 2H, C$_6H_2$), 8.19 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$) δ: 23.4 (*C*H$_2$), 29.2 (C(*C*H$_3$)$_3$), 29.5 (*C*H$_2$), 31.2 (C(*C*H$_3$)$_3$), 34.3 (N*C*H$_2$), 35.0 (N*C*H$_2$), 54.2 (*C*(CH$_3$)$_3$), 115.3 (Ph), 125.8 (Ph), 134.7 (Ph), 139.5 (Ph), 143.7 (Ph), 154.2 (Ph), 163.7 (N=*C*H). ^{11}B NMR ($CDCl_3$) δ: 5.90 ($w_{1/2}$ = 37.6 Hz). MS (%): 696 ([M]$^+$, 5), 659 ([M – Cl], 100), 624 ([M – 2Cl], 20). Anal. calcd. for $B_2C_{35}H_{52}N_2O_2Cl_4$: C 60.49, H 7.55, N 4.03; found: C 60.48, H 8.56, N 3.82.

Salhen(*t*-Bu)[BCl_2]$_2$ (5)

To a stirring solution of salhen(*t*-Bu)[B(OMe)$_2$]$_2$ (1.0 g, 1.46 mmol) in toluene (50 mL) was added 1M BCl_3 in heptane (2.9 mL, 2.92 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 5 mL, filtered, and dried. Yield: 0.91g (91%); mp 302–304°C (dec.). IR (KBr pellet) (cm^{-1}): 2952 (s), 2904 (w), 2862 (w), 1632 (s), 1573 (m), 1458 (m), 1433 (w), 1359 (w), 1295 (w), 1254 (m), 1215 (w), 1079 (w), 1010 (m), 974 (w), 847 (m), 771 (m), 712 (s), 641 (w). ^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 18H, C(CH_3)$_3$), 1.43 (s, 18H, C(CH_3)$_3$), 1.55 (m, 4H, CH_2), 2.02 (m, 4H, CH_2), 3.91 (m, 4H, NCH_2), 7.18 (d, 2H, C$_6H_2$), 7.68 (d, 2H, C$_6H_2$), 8.19 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$) δ: 25.7 (*C*H$_2$), 29.5 (C(*C*H$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 34.3 (N*C*H$_2$), 35.0 (N*C*H$_2$), 54.4 (*C*(CH$_3$)$_3$), 125.2 (Ph), 125.6 (Ph), 128.1 (Ph), 129.0 (Ph), 134.6 (Ph), 154.6 (Ph), 163.4 (N=*C*H). ^{11}B NMR ($CDCl_3$) δ: 6.39 ($w_{1/2}$ = 28.2 Hz). MS (%): 673 ([M – Cl], 100), 658 ([M – Cl – Me], 10), 638 ([M – 2Cl], 50). Anal. calcd. for $B_2C_{36}H_{54}N_2O_2Cl_4$: C 60.99, H 7.68, N 3.95; found: C 61.40, H 8.04, N 3.66.

Dealkylation of the trimethylphosphate

In an NMR tube, trimethylphosphate was added to an equimolar solution of the compound (**1**–**5**) in $CDCl_3$ and held at room temperature for 30 min and 24 h. The reaction was monitored by ^{1}H NMR (Table 2).

Addition of a Lewis base

In an NMR tube, 5 equiv of THF were added to a solution of **2** in $CDCl_3$. ^{11}B NMR ($CDCl_3$) δ: 6.04 ($w_{1/2}$ = 52.6 Hz).

Conclusion

A range of chelated boron compounds have been synthesized and fully characterized. They demonstrate that further derivatization of boron alkoxide compounds with Salen are possible and that some are active in the dealkylation of trimethylphosphate. It has been demonstrated that **1**–**5** are inefficient dealkylating compounds by comparison to the bromide analogues (23). Future work in this area entails increasing the activity of the boron chloride compounds and broadening their use as Lewis acid activators.

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