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Dealkylation with boron bromide chelates

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Abstract

Potential two-point Lewis acid compounds can be formed by combining the salen(^{t}Bu)H_2 (*N*,*N*′-alkylenenebis(3,5-di-tertbutyl(2-hydroxy)benzylidenimine) class of ligands and its derivatives with boron tribromide. In the present study compounds having the formula, L(BBr_2)$_2$ (L = salen(^{t}Bu) (**1**), salhen(^{t}Bu) (**2**), L([^{p}tolyl]BBr) (L = salen(^{t}Bu) (**3**), salpen(^{t}Bu) (**4**), salben(^{t}Bu) (**5**), salhen(^{t}Bu) (**6**), and ^{t}Bu-sal(^{t}Bu)BBr_2 (**7**) were prepared. These compounds are active towards the dealkylation of alkyl phosphates and are catalytic when stoichiometric amounts of BBr_3 and trimethylphosphate are introduced to the chelate ligand. 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.

Keywords: Boron; Chelates; Dealkyation; Nerve gas agents

1. Introduction

By comparison to multidentate Lewis base compounds (for example, crown ethers), the chemistry of compounds having multiple Lewis acid sites remains relatively unexplored [1,2]. The majority of the compounds that have been reported have been bimetallic, 'two-point' Lewis acids [3]. These have featured two atoms of either boron, [4] aluminum, [5] indium, [6] or tin [7]. Perhaps the best established theme is the placement of two mercury atoms ortho to one another on an aryl ring [8].

Two-point Lewis acid compounds have tremendous potential for applications in catalysis, synthesis, and molecular recognition. For example, multidentate Lewis acids may be useful in the development of anion binding agents [9]. Additionally, there are a number of biologically important reactions that are mediated by two Lewis acidic metals in close proximity. This is an important characteristic in the hydrolysis of phosphate ester bonds, for instance [10]. Other applications will clearly be found once synthetic routes to these important compounds are established.

The incorporation of boron into two-point Lewis acidic frameworks has not been examined in recent times despite the early precedents with this element [5]. The Salen ligands are of proven utility in preparing bimetallic boron and aluminum compounds [11]. Furthermore, the separation between the two metals is easily controlled by the choice of Salen ligand 'backbone'. The present study will explore how boron-containing Salen compounds may be fashioned into useful bimetallic Lewis acids. The utility of these compounds in cleaving phosphate ester bonds will be examined. This will provide a measure of their future potential in other Lewis acid applications.

2. Results and discussion

2.1. Synthesis and characterization

The Salen-supported [12] binuclear boron bromide compounds (**1** and **2**) were prepared in high yields by combining the appropriate borate, salen(^{t}Bu)[$B(OMe)_2$]$_2$, with a stoichiometric amount of BBr_3 (Scheme 1). The Salen ^{p}tolyl boron bromide compounds (**3**–**6**) were synthesized in the same manner using salen(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ (Scheme 1). These syntheses were similar to the boron chloride compounds

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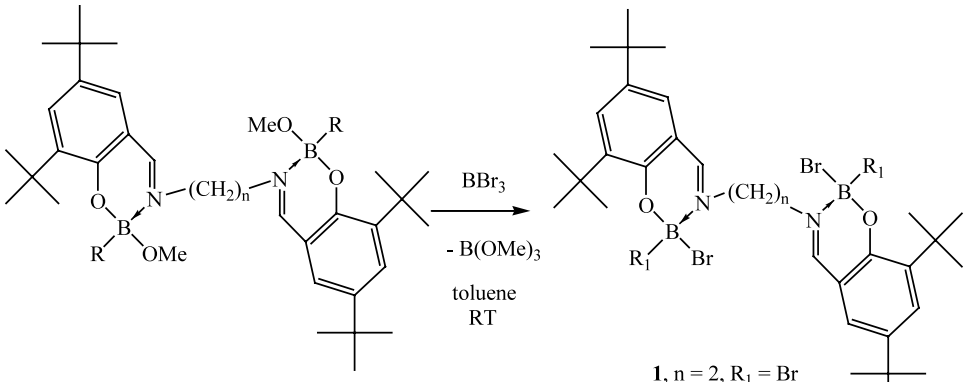


R = OMe (precusor for **1** and **2**)
R = ^{p}tolyl (precusor for **3 - 6**)

1, n = 2, R_1 = Br
2, n = 6, R_1 = Br
3, n = 2, R_1 = ^{p}tolyl
4, n = 3, R_1 = ^{p}tolyl
5, n = 4, R_1 = ^{p}tolyl
6, n = 6, R_1 = ^{p}tolyl

Scheme 1. Synthesis of Salen binuclear boron bromide compounds (**1**–**6**).

[13], but a few differences were noticeable. In the synthesis of the boron chloride compounds, the amount of BCl_3 added was not important, provided at least 4/3 equivalent were added. However, if excess BBr_3 was added in the synthesis of the bromide compounds, an additional product formed. The excess BBr_3 extracted a bromide from the boron bromide compound forming $L[BBr_2(BBr)]^+$ BBr_4^- [14]. This was an early indication that the boron-bromide bonds could be heterolytically cleaved. This can also be accomplished by addition of a Lewis base [14].

The ^{1}H-NMR data for **1**–**7** contained two singlets for the ^{t}Bu–Ph groups in the range δ 1.27–1.46 ppm. There were multiple CH_2 peaks corresponding to the backbone protons from the ligand ranging from δ 1.01 to 4.70 ppm, depending on the ligand type. For **1** and **2**, there was one imine singlet for each compound at 8.56 and 8.22 ppm, respectively. Like the chloride analogue, these values decreased with increasing backbone length. In compounds **3**–**6**, the imine proton appeared between 8.06 and 8.15 ppm with no apparent relationship between the shift and change in backbone length. Only in the case of the Salen boron dihalide compounds did the imine proton resonance shift with the change in backbone length.

The ^{11}B-NMR showed a broad singlet for **1** and **2** (−0.42 and 2.02 ppm), upfield from the related chloride analogue, salen(^{t}Bu)$[BCl_2]_2$ (6.21 ppm) [13]. This is also upfield by comparison to the methoxide starting materials, as expected [15]. When one bromide was replaced with a tolyl group, as in **3**–**6**, the ^{11}B-NMR resonance shifts downfield 6–8 ppm (6.40–9.04 ppm) by comparison to **1** and **2**. These were similar to the starting materials for **3**–**6**, Salen(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ which had a ^{11}B resonance of $\sim$5 ppm.

In the mass spectra of compounds **1** and **2** no parent ion peaks were present. The most abundant peak for compound **1** was the parent ion minus three bromides (with the correct isotope pattern for one bromide atom and two boron atoms. The base peak for **2** was the parent ion minus one bromide atom and parent minus two bromide atoms. In the case of both compounds, an ion peak was present for the loss of one, two and three bromide ions.

The structure of **2** consists of the salhen ligand chelating two boron dibromide units (Fig. 1). Each boron is in a distorted tetrahedral environment, coordinated by a nitrogen atom and an oxygen atom from the salhen ligand. The boron atoms are *trans* to one another in the solid state, consistent with most structurally characterized Salen boron compounds [11]. The bite angle of the ligand on the boron atom (N–B–O) is 112.8(6)° (Table 1). The angle is slightly larger than other Salen binuclear boron compounds, such as the N–

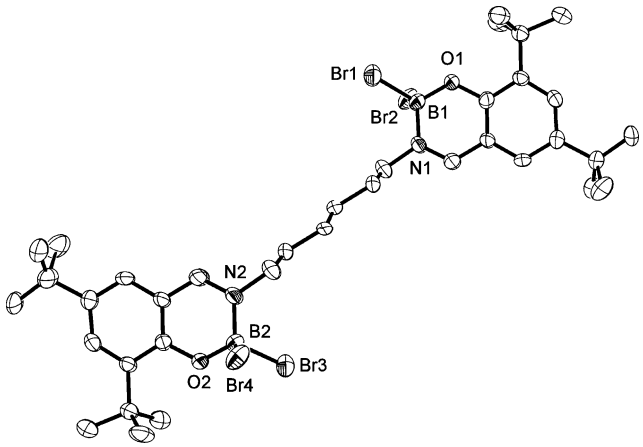


Fig. 1. Molecular structure of salhen(^{t}Bu)$[BBr_2]_2$ (**2**).Hydrogen atoms are omitted for clarity.

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

Bond lengths	
B–O	1.418(9)
B–N	1.517(9)
B–Br(1)	2.023(8)
B–Br(2)	2.077(9)
Bond angles	
O–B–N	112.8(6)
O–B–Br(1)	108.6(5)
N–B–Br(1)	112.2(5)
O–B–Br(2)	110.1(5)
N–B–Br(2)	105.2(5)
Br(1)–B–Br(2)	107.7(3)

B–O angle of 105.9(3)° in salenN_3H[B(OMe)$_2$]$_2$ (as a representative borate compound) [11a]. This deviation is in keeping with decreased *p* character in the B–Br bonds by comparison to a B–OMe bond. [16] This was also similar to other Salen binuclear compounds, such as the salben(^{t}Bu)[BBr_2]$_2$ (112.3(4) and 112.9(4)°) [14] and slightly larger than the chloride analogue, salpen(^{t}Bu)[BCl_2]$_2$ (110.1(4)° and 111.8(4)°) [13]. A noticeable trend in the length of the N→B dative bond occurs with the exchange of the substituents on the boron atoms [17]. The N→B length for **2** is 1.517(5) Å; this was shorter than the N→B bond length of salen[B(OMe)$_2$]$_2$ (1.615(2) Å). [11a] An inverse relationship existed between the lengths of the C=N and N→B bonds; the N→B bond was shorter in **2** than in the borate compound and the C=N bond lengthens for **2** (1.304(8) Å) compared with the borate (1.288(2) Å). The C=N and N→B bond lengths of **2**, however, were consistent with bromide and chloride derivatives, salben(^{t}Bu)[BBr_2]$_2$ (1.295(4) Å and 1.539(5) Å, respectively) and salpen(^{t}Bu)[BCl_2]$_2$ (1.295(4) Å and 1.548(5) Å, respectively). The B–Br bond lengths are 2.023(8) Å and 2.077(9) Å for **2,** similar to salben(^{t}Bu)[BBr_2]$_2$ (2.038(4) Å, 2.058(4) Å, 2.031(4) Å and 2.068(4) Å). These were marginally longer than those observed in other bidentate chelate four-coordinate boron dibromide compounds, such as [2-Me_2NCH_2)C_6H_4]BBr_2 which had B–Br bond distances of 2.01(1) and 2.02(1) Å [18].

2.2. Dealkylation of alkyl phosphate esters

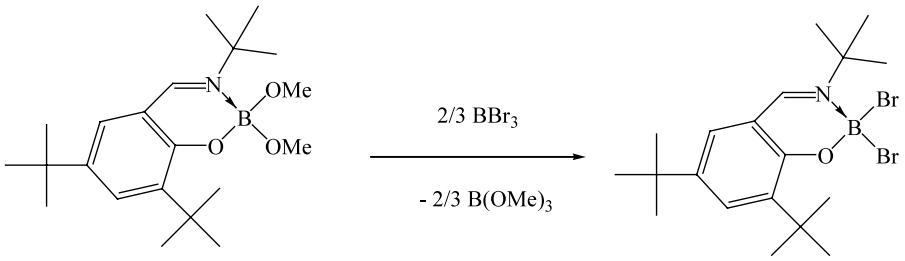
BBr_3 is known to be able to cleave the O–C bond of alkyl[19], and silyl ethers [20]. However, BBr_3 does not effect the dealkylation of phosphates (less than 2% dealkylation of trimethylphosphate in 24 h). Other reagents, such as AlCl_3 [21] or CyBCl_2 [22] can dealkylate phosphates and phosphonates but require long reaction times (12 h–2 days) and heat (70 °C). Only in the case of [Al(NMe_2)$_3$]$_2$ with trimethylphosphate will dealkylation occur at room temperature, but with ethyl or larger alkyl groups in the phosphate, the reaction requires more time and heat [21]. Moreover, no reaction occurred when bulky groups such as $SiMe_3$ were present on the amine.

It was found that the bimetallic boron compounds **1**–**6** readily dealkylated a wide variety of phosphate esters containing primary and secondary sp^3 α-carbons (Tables 3 and 4). For most of the compounds, dealkylation progressed more than 50% within 30 min at ambient temperature. The bromide derivatives were more efficient than the chloride analogues, which demethylated trimethylphosphate only 7–42% [16]. With most phosphate esters, **1** and **3** were the least efficient compounds of the series. The shorter backbone presumably leads to unfavorable interactions between the two boron sites. As a further indication of this, the ^{p}tolyl bromide compounds with longer backbones (**5** and **6**) were more efficient than the compounds with shorter backbones (**3** and **4**). For the dibromide compounds, the intermediate-length backbones salpen(^{t}Bu)[BBr_2]$_2$ and salpen(^{t}Bu)[BBr_2]$_2$ [14] were more efficient than **1** and **2**. However, all the Salen boron bromide compounds showed a slight decrease in activity with the branched phosphates such as (PhO)$_2$((2-Et)hexylO)P(O). In general both the ^{p}tolyl bromide and dibromide boron compounds were comparatively active towards the dealkylation of a broad range of phosphate esters.

To test the possibility that a bimetallic compound was not required in the dealkylations a mononuclear boron halide compound was synthesized. ^{t}BuSal(^{t}Bu)[BBr_2] (**7**) was prepared in the same fashion as the binuclear boron compounds (Scheme 2). Compound **7** does dealkylate trimethylphosphate at 92% conversion within 30 min. Therefore, the chelated boron compound did not need to be tethered together by a ligand in order for the dealkylation to occur. The synthesis of the binuclear compounds (**1**–**6**) were produced in a significantly higher yield (68–98%) than the mononuclear compound (**7**) (38%). However, it has not been determined if two mononuclear compounds were needed to work jointly in order for the dealkylation to proceed.

Although it has yet to be determined whether two activate boron sites are necessary for the dealkylation, the binuclear compounds had some advantages over the mononuclear compound. Both the borate and halide compounds were isolated in a considerably higher yield and the mononuclear compound did not dealkylate trimethylphosphate.

Previously, salpen(^{t}Bu)[B(OMe)$_2$ was shown to catalytically dealkylate trimethylphosphate in the presence of BBr_3 [14]. The catalytic dealkylation of trimethylphosphate with **1** and **2** occurred within 5 min through the addition of **1** and **2** to a BBr_3 to trimethylphosphate ratio of 20:1. The catalytic dealkylation may also occur by using the precursors to **1** and **2** (salen(^{t}Bu)[B(OMe)$_2$ and salhen(^{t}Bu)[B(OMe)$_2$) with BBr_3. Addition of BBr_3



(7)

Scheme 2. Synthesis of ^{t}BuSal(^{t}Bu)[BBr_2] (**7**).

or the borate alone did not dealkylate trimethylphosphate within 24 h.

During the catalytic reaction, a white precipitate formed which is likely to be some type of boron phosphate (BPO_4). The ^{1}H-NMR of the precipitate did not contain ligand resonances but did have some peaks which could be attributed to trimethylphosphate. ^{11}B MAS-NMR indicated the presence of three- (24.73 ppm) and four-coordinate (6.99 ppm) boron. The IR was similar to BPO_4 and showed strong P–OH (1051 cm^{-1}) and B–OH (3216 cm^{-1}) stretches [23]. The precipitate was insoluble in non-polar organic solvents, partially soluble in polar organic solvents and water, and reacted with alcohols.

3. Conclusion

Binuclear boron bromide compounds formed with the Salen ligands were readily synthesized from the corresponding borate compounds with a stoichiometric amount of BBr_3. These compounds may be utilized as Lewis acid activators or as binuclear catalysts. This was demonstrated in the dealkylation of a wide range of phosphate esters, a process that was made catalytic by addition of excess BBr_3.

The phosphates dealkylated with the boron bromide compounds are reagents that may be viewed as models for the nerve gas agents, Sarin and VX, since they have similar P–O–C units. Thus, chelated boron bromide compounds are promising candidates for the decomposition of chemical warfare agents under non-aqueous conditions.

4. Experimental

4.1. 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 [24] salen(^{t}Bu)H_2, salpen(^{t}Bu)H_2, salben(^{t}Bu)H_2, salhen(^{t}Bu)H_2, and ^{t}BuSal(^{t}Bu)H were synthesized according to the literature procedure. Salen(^{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 [24]. NMR data (^{1}H, ^{11}B, ^{31}P) were obtained on JEOL-GSX-400 and 200 MHz instruments. Chemical shifts are reported relative to $SiMe_4$ for ^{1}H, BF_3Et_2O in $CDCl_3$ for ^{11}B, H_3PO_4 for ^{31}P and are in ppm. ^{31}P-NMR was decoupled. ^{11}B and ^{31}PMAS-NMR spectra were recorded on a Varian 400 spectrometer. Infrared data were recorded as KBr pellets on a Mattson 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** was taken on a Nonius CCD unit employing Mo–K_α radiation. The structure(s) was solved by direct methods (SHELXS97) [25] and difference Fourier (SHELXL97). Refinement was carried out against F^2 by weighted full-matrix least-squares (SHELXL97). 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 analysis are given in Table 2.

4.2. Salen(^{t}Bu)[BBr_2]$_2$ (**1**)

To a stirring solution of salen(^{t}Bu)[$B(OMe)_2$]$_2$ (0.50 g, 0.78 mmol) in toluene (30 ml) was added 1 M BBr_3 in heptane (1.17 ml, 1.17 mmol). The reaction mixture was stirred for 3 h. The solution was concentrated to 5 ml, precipitate was filtered, and dried. Yield: 0.51 g (80%). melting point (decomposition) (m.p. (dec.)): 291–292 °C. ^{1}H-NMR ($CDCl_3$): δ 1.27 [s, 18H, C(CH_3)$_3$], 1.45 [s, 18H, C(CH_3)$_3$], 4.70 [s, 4H, NCH_2], 7.20 [d, 2H, C_6H_2], 7.78 [d, 2H, C_6H_2], 8.56 [s, 2H, C*H*N]. ^{11}B-NMR ($CDCl_3$): δ −0.42 ($w_{1/2}$ = 77.89 Hz). IR(cm^{-1}): 2965(s), 2905(w), 2866(w), 1623(s), 1575(s), 1472(m), 1457(m), 1442(m), 1365(m), 1311(w), 1257(m), 1228(m), 1199(w), 1100(w), 1038(w), 865(w), 766(w), 651 (m), 636(m). MS:

Table 2
Crystal data and structure refinement for salhen(^{t}Bu)[BBr_2]$_2$ (**2**)

Compound	**2**
Color/shape	Yellow/plates
Chemical formula	$C_{20}H_{27}BBr_2Cl_6NO_{1.55}$
Formula weight	689.60
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.378(2)
b (Å)	13.851(2)
c (Å)	14.752(2)
α (°)	90.00
β (°)	101.08(2)
γ (°)	90.00
V (Å^3)	2883.1(7)
Z	4
D_{calc} (mg m^{-3})	1.589
Absorption coefficient (mm^{-1})	3.384
Crystal size (mm)	0.40 × 0.32 × 0.08
$F(000)$	1374
θ Range for data collection (°)	1.81–25.00
Index ranges	$-17 \le h \le 17; -14 \le k \le 16; -17 \le l \le 17$
Reflections measured	9419
Independent reflections	5074 [$R_{int} = 0.0643$]
Data/restraints/parameters	5074/650/382
Goodness-of-fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0692$, $wR_2 = 0.1714$
R indices (all data)	$R_1 = 0.1207$, wR_2 0.1988
Largest difference peak and hole (e Å^{-3})	1.196 and −0.706

752(M ⊕ −Br, 25%), 672(M ⊕ −2Br, 10%), 592(M ⊕ −3Br, 100%). Anal. Calc. for $B_2C_{32}H_{46}N_2O_2Br_4$: C, 46.37(47.11), H, 5.60(5.07), N 3.38(3.34)%.

4.3. Salhen(^{t}Bu)[BBr_2]$_2$ (**2**)

To a stirring solution of salhen(^{t}Bu)[$B(OMe)_2$]$_2$ (3.00 g, 4.34 mmol) in toluene (50 ml) was added 1 M BBr_3 in heptane (5.78 ml, 5.78 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 10 ml, precipitate was filtered and dried. Yield: 2.76 g (72%). m.p. (dec.): 267–269 °C. ^{1}H-NMR ($CDCl_3$): δ 1.28 [s, 18H, C(CH_3)$_3$], 1.41 [s, 18H, C(CH_3)$_3$], 1.59 [m, 4H, CH_2], 2.05 [m, 4H, CH_2], 3.99 [m, 4H, NCH_2], 7.22 [d, 2H, C_6H_2], 7.73 [d, 2H, C_6H_2], 8.22 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ 2.02 ($w_{1/2} = 176.6$ Hz). IR(cm^{-1}): 2954(s), 2862(w), 1623(s), 1572(s), 1458(s), 1432(m), 1432(w), 1363(m), 1284(w), 1251(m), 1219(w), 1192(w), 1130(w), 1015(w), 842(m), 769(w), 668(m). MS: 808(M ⊕ −Br, 30%), 728 (M ⊕ −2Br, 100%), 671(M ⊕ −3Br-^{t}Bu, 40%). Anal. Calc. for $B_2C_{36}H_{54}N_2O_2Br_4$: C, 48.86(49.14), H, 6.16(5.89), N 3.17(2.58)%.

4.4. Salen(^{t}Bu)[(^{p}tolyl)BBr]$_2$ (**3**)

To a stirring solution of salen(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ (4.00 g, 5.29 mmol) in toluene (70 ml) was added 1 M BBr_3 in heptane (3.88 ml, 3.88 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 30 ml, precipitate was filtered and dried. Yield: 3.06 g (68%). m.p. (dec.): 225–230 °C. ^{1}H-NMR ($CDCl_3$): δ 1.28 [s, 18H, C(CH_3)$_3$], 1.44 [s, 18H, C(CH_3)$_3$], 2.42 [s, 6H, Ph-CH_3], 3.59 [s, 4H, NCH_2], 7.08 [d, 2H, C_6H_2], 7.22–7.42 [m, 4H, C_6H_4], 7.78 [d, 2H, C_6H_2], 7.73 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ 9.04 ($w_{1/2} = 481.0$ Hz). IR(cm^{-1}): 2959(s), 2869(m), 2820(w), 1632(s), 1565(s), 1477(m), 1430(w), 13691(m), 1312(m), 1262(w), 1221(m), 1198(s), 1183(m), 1091(m), 961(s), 914(m), 879(w), 790(m), 767(m), 744(w). Anal. Calc. for $B_2C_{46}H_{60}N_2O_2Br_2$: C, 64.66(65.01), H, 7.08(7.54), N 3.28(3.12)%.

4.5. Salpen(^{t}Bu)[(^{p}tolyl)BBr]$_2$ (**4**)

To a stirring solution of salpen(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ (2.00 g, 2.60 mmol) in toluene (50 ml) was added 1 M BBr_3 in heptane (1.90 ml, 1.90 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)[(^{p}tolyl)BBr]$_2$. Yield: 2.22 g (98%). m.p. (dec.): 150–156 °C. ^{1}H-NMR ($CDCl_3$): δ 1.32 [s, 18H, C(CH_3)$_3$], 1.42 [s, 18H, C(CH_3)$_3$], 1.64 [m, 2H, CH_2], 2.32 [s, 6H, PhCH_3], 3.42 [m, 4H, NCH_2], 7.18 [d, 2H, C_6H_2], 7.23 [d, 2H, C_6H_4], 7.70 [d, 2H, C_6H_4], 7.78 [d, 2H, C_6H_2], 8.15 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ 7.85 ($w_{1/2} = 570$ Hz). IR(cm^{-1}): 2960(s), 2913(m), 2867(w). 1629(s), 1572(s), 1468(m), 1436(w), 1394(w), 1362(m), 1300(m),1255 (s), 1221(m), 1201(m), 1184(m), 1029(w), 1016(w), 914(w), 806(m), 771(w), 729(m), 676(m), 636(w). Anal. Calc. for $B_2C_{47}H_{62}N_2O_2Br_2$: C, 72.45(72.50), H, 8.03(7.75), N 3.60(2.77)%.

4.6. Salben(^{t}Bu)[(^{p}tolyl)BBr]$_2$ (**5**)

To a stirring solution of salben(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ (3.00 g, 3.83 mmol) in toluene (50 ml) was added 1 M BBr_3 in heptane (2.80 ml, 2.80 mmol). The reaction mixture was stirred for 18 h at room temperature (r.t.). The solution was concentrated to 10 ml, filtered, and dried. Yield: 3.08 g (91%). m.p (dec.): 216–218 °C. ^{1}H-NMR ($CDCl_3$): δ 1.29 [m, 4H, CH_2], 1.35 [s, 18H, C(CH_3)$_3$], 1.44 [s, 18H, C(CH_3)$_3$], 2.28 [s, 6H, PhCH_3], 3.41 [m, 4H, NCH_2], 7.15 [d, 2H, C_6H_2], 7.25 [d, 2H, C_6H_4], 7.69 [d, 2H, C_6H_4], 7.75 [d, 2H, C_6H_2], 8.06 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ 6.40 ($w_{1/2} = 1328.0$ Hz). IR(cm^{-1}): 2960(s), 2912(m), 2868(w), 1627(s),

1571(s), 1462(m), 1394(w), 1362(m), 1255(m), 1221(m), 1200(s), 1185(m), 1030(w), 1016(m), 911(w), 885(w), 805(m), 773(w), 738(w), 674(m), 636(m). Anal. Calc. for $B_2C_{48}H_{64}N_2O_2Br_2$: C, 65.43(65.33), H, 7.33(6.87), N 3.18(2.77)%.

4.7. Salhen(^{t}Bu)[(^{p}tolyl)Br]$_2$ (6)

To a stirring solution of salhen(^{t}Bu)[(^{p}tolyl)B(OMe)]$_2$ (0.50 g, 0.62 mmol) in toluene (25 ml) was added 1 M BBr_3 in heptane (0.42 ml, 0.42 mmol). The reaction mixture was stirred for 24 h. The solution was concentrated to 5 ml, precipitate was filtered and dried. Yield: 0.49 g (88%). m.p. (dec.): 213–217 °C. ^{1}H-NMR ($CDCl_3$): δ 1.01 [m, 4H, CH_2], 1.33 [m, 4H, CH_2], 1.37 [s, 18H, C(CH_3)$_3$], 1.43 [s, 18H, C(CH_3)$_3$], 2.33 [s, 6H, PhCH_3], 3.53 [m, 4H, NCH_2], 7.19–7.25 [m, 4H, C_6H_4], 7.73 [d, 2H, C_6H_2], 7.78 [d, 2H, C_6H_2], 8.15 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ 7.23 ($w_{1/2} = 769.3$ Hz). IR(cm^{-1}): 2958(s), 2915(m), 2865(w), 1632(s), 1570(m), 1460(m), 1433(w), 1395(w), 1363(w), 1250(m), 1223(m), 1202(m), 1186(m), 1028(w), 1014(w), 982(w), 915(w), 884(w), 805(w), 772(w), 735(m), 668(m), 636(w). MS: (M $\oplus$ −Br, 30%), (M $\oplus$ −2Br, 100%), (M $\oplus$ −2Br-^{t}Bu, 40%). Anal. Calc. for $B_2C_{50}H_{68}N_2O_2Br_2$: C, 66.05(66.45), H, 7.54(7.70), N 3.08(2.55)%.

4.8. ^{t}BuSal(^{t}Bu)[BBr_2] (7)

To a stirring solution of ^{t}BuSal(^{t}Bu)[B(OMe)$_2$] (2.20 g, 4.79 mmol) in toluene (35 ml) was added 1 M BBr_3 in heptane (5.20 ml, 5.20 mmol). The reaction mixture was stirred for 3 h. The solution was concentrated to 15 ml, filtered, and dried. Yield: 1.06 g (38%). ^{1}H-NMR δ 1.30 [s, 9H, C(CH_3)$_3$], 1.46 [s, 9H, C(CH_3)$_3$], 1.58 [s, 9H, C(CH_3)$_3$], 7.08 [d, 2H, C_6H_2], 7.55 [d, 2H, C_6H_2], 8.31 [s, 2H, CHN]. ^{11}B-NMR ($CDCl_3$): δ −1.76 ($w_{1/2} = 325.0$ Hz).

4.9. Dealkylation of phosphates with the boron bromide compounds

In a NMR tube, phosphate was added to an equimolar solution of the compound (salen(^{t}Bu)[BBr_2]$_2$ or BBr_3) (**1**–**7**) in $CDCl_3$ and held at r.t. for 30 min. The reaction was monitored by ^{1}H-NMR (Tables 3 and 4).

4.10. Catalytic dealkylation of trimethylphosphate with the Salen boron bromide compound

In a NMR tube, equimolar amounts of $(MeO)_3P(O)$ and BBr_3 were added to a solution of catalytic amount of L[B(OMe)$_2$]$_2$ in $CDCl_3$ in the ratio of 20:1 of phosphate to borate and held at r.t. The reaction was monitored by ^{1}H-NMR. A white precipitate formed during the reaction and was a type of boron phosphate compound with no Salen ligand present. White precipitate: Yield: 1.06 g. m.p. (dec.) 320 °C . ^{11}B MAS-NMR: δ 24.73 ($w_{1/2} = 1482.7$ Hz), 6.99 ($w_{1/2} = 1125.7$ Hz). ^{31}P MAS-NMR: δ −2.98 (s), −3.90 (vbrs). IR(cm^{-1}): 3216(sbr), 2966(m), 2862(w), 1640(w), 1460(m), 1190(m), 1051(sbr), 884(mbr), 555(mbr).

Table 4
Percent dealkylation of different phosphates with Salen phenyl boron bromide compounds (**3**–**6**)

Compound	**3** (%) [a]	**4** (%) [a]	**5** (%) [a]	**6** (%) [a]
Carbons in backbone of ligand	2	3	4	6
Phosphate	30 min	30 min	30 min	30 min
$(MeO)_3P(O)$	45	52	92	80
$(EtO)_3P(O)$	40	50	71	56
(^{n}BuO)$_3$P(O)	31	58	70	47
$(MeO)_2P(O)H$	59	67	50	50
$(MeO)_2P(O)Me$	47	50	50	50
(^{i}PrO)$_2$P(O)H	42	32	37	26
$(PhO)_2$((2-Et)HexO)P(O)	12	46	52	42
$(Me_3SiO)_3P(O)$	43	48	69	89
$(PhO)_3P(O)$	0	0	0	0

[a] The percent conversion was determined by the amount of phosphate remaining to the amount of alkyl bromide produced in the ^{1}H-NMR. Rxn. run in $CDCl_3$ and at r.t.

Table 3
Percent dealkylation of phosphates with Salen boron bromide compounds (**1, 2, 7**)

Compound	**1**	**Salpen**[14] (%) [a]	**Salben**[14] (%) [a]	**2** (%) [a]	**7** (%) [a]
Carbons in backbone of ligand	2	3	4	6	
Phosphate	30 min	30 min	30 min	30 min	30 min
$(MeO)_3P(O)$	76	89	90	81	92
(^{n}BuO)$_3$P(O)	42	99	77	69	
$(MeO)_2P(O)Me$	61	98	87	47	
$(PhO)_2$((2-Et)HexO)P(O)	48	71	64	88	
$(Me_3SiO)_3P(O)$	88	98	90	79	
$(PhO)_3P(O)$	0	0	0	0	

[a] The percent conversion was determined by the amount of phosphate remaining to the amount of alkyl bromide produced in the ^{1}H-NMR. Rxn. run in $CDCl_3$ and at r.t.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 193681 for compound 2. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.).

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References

[1] M. Tsunoda, F. Gabbai, J. Am. Chem. Soc. 122 (2000) 8335.
[2] H. Lee, M. Diaz, C.B. Knobler, M.F. Hawthorne, Angew. Chem. Int. Ed. Engl. 39 (2000) 776.
[3] (a) J. Vaugeois, M. Simard, J.D. Wuest, Coord. Chem. Rev. 145 (1995) 55;
(b) J.D. Wuest, Acc. Chem. Res. 21 (1999) 81.
[4] (a) M.J. Biallas, D.F. Shriver, J. Am. Chem. Soc. 88 (1966) 375;
(b) R. Koster, G. Seidel, K. Wagner, B. Wrackmeyer, Chem. Ber. 126 (1993) 305.
[5] (a) O. Saied, M. Simard, J.D. Wuest, Organometallics 17 (1998) 1128;
(b) T. Ooi, M. Takahashi, K. Maruoka, Angew. Chem. Int. Ed. Engl. 37 (1998) 835;
(c) W. Uhl, F. Hannemann, J. Organomet. Chem. 579 (1999) 18.
[6] (a) F.P. Gabbai, A. Schier, J. Riede, Angew. Chem. Int. Ed. Engl. 37 (1998) 622;
(b) A. Cotone, III, D. Morales, J.L. Lecuivre, M.J. Scott, Organometallics 21 (2002) 418;
(c) A. Cottone, III, M.J. Scott, Organometallics 21 (2002) 3610.
[7] (a) R. Altmann, O. Gausset, D. Horn, K. Jurkschat, M. Schurman, M. Fontani, P. Zanello, Organometallics 19 (2000) 430;
(b) M. Schulte, M. Schurmann, K. Jurkschat, Chem. Eur. J. 7 (2001) 347.
[8] (a) A.L. Beauchamp, M.J. Olivier, J.D. Wuest, B. Zacharie, Organometallics 6 (1987) 153;
(b) J. Vaugeois, J.D. Wuest, J. Am. Chem. Soc. 120 (1998) 13016;
(c) M. Tschinkl, A. Schier, J. Riede, F.P. Gabbai, Organometallics 18 (1999) 1747.
[9] J.L. Atwood, E.D. Davies, D.D. Machicol, F. Vogtle, Comprehensive Supramolecular Chemistry, vol. 2, Elsevier, New York, 1996.
[10] (a) M. Olivanen, S. Kuusela, H. Lonnberg, Chem. Rev. 98 (1998) 961;
(b) A. Blasko, T. Bruice, Acc. Chem. Res. 32 (1999) 475;
(c) C. Bazzicaluni, A. Bencini, E. Berni, A. Bianchi, V. Fedi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli, Inorg. Chem. 38 (1999) 4115.
[11] (a) M.S. Hill, P. Wei, D.A. Atwood, Polyhedron 17 (1998) 811;
(b) P. Wei, D.A. Atwood, T.S. Keizer, Inorg. Chem. 38 (1999) 3914;
(c) D. Agustin, G. Rima, H. Gornitzka, J. Barrau, J. Organomet. Chem. 592 (1999) 1;
(d) M.A. Van Aelstyn, T.S. Keizer, D.L. Klopotek, S. Liu, S.M. Munoz-Hernandez, P. Wei, D.A. Atwood, Organometallics 19 (2000) 1796;
(e) M. Sanchez, T.S. Keizer, S. Parkin, H. Hopfl, D.A. Atwood, J. Organomet. Chem. 654 (2002) 36.
[12] 'Salen' is a term used to designate the entire class of possible ligands. Written with a lower case 's' the 'salen' ligand in particular is *N*,*N*′-ethylenenebis(2-hydroxy)benzylidenimine).
[13] T.S. Keizer, L.J. De Pue, S. Parkin, D.A. Atwood, Can. J. Chem. 80 (2002), in press.
[14] T.S. Keizer, L.J. De Pue, S. Parkin, D.A. Atwood, J. Am. Chem. Soc. 124 (2002) 1864.
[15] R.G. Kidd, NMR of Newly Accessible Nuclei, vol. 2, Academic Press, 1983.
[16] H.A. Bent, J. Chem. Educ. 37 (1960) 616.
[17] H. Hopfl, J. Organomet. Chem. 581 (1999) 129.
[18] D.S. Brown, C.J. Carmalt, A.H. Cowley, A. Decken, H. Isom, Heteroat. Chem. 9 (1998) 79.
[19] F.L. Benton, T.E. Dillon, J. Am. Chem. Soc. 64 (1942) 1128.
[20] S. Kim, J.H. Park, J. Org. Chem. 53 (1988) 3111.
[21] J. Pinkas, H. Wessel, Y. Yang, M.L. Montero, M. Noltemeyer, M. Froba, H.W. Roesky, Inorg. Chem. 37 (1998) 2450.
[22] (a) J. Mortier, I.D. Gridnev, A. Fortineau, Org. Lett. 1 (1999) 981;
(b) J. Mortier, I.D. Gridnev, P. Guenot, Organometallics 19 (2000) 4266.
[23] J.B. Moffat, J.F. Neeleman, J. Catal. 34 (1974) 376.
[24] L. Deng, E.N. Jacobsen, J. Org. Chem. 57 (1992) 4320.
[25] G.M. Sheldrick, SHELX97-Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.