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Mononuclear Schiff Base Boron Halides: Synthesis, Characterization, and Dealkylation of Trimethyl Phosphate

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A series of mononuclear boron halides of the type LBX_2 [LH = *N*-phenyl-3,5-di-*tert*-butylsalicylaldimine, X = Cl (**2**), Br (**3**)] and LBX [LH_2 = *N*-(2-hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine, X = Cl (**7**), Br (**8**); LH_2 = *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine, X = Cl (**9**), Br (**10**); and LH_2= *N*-(3-hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine, X = Cl (**11**), Br (**12**)] were synthesized from their borate precursors $LB(OMe)_2$ (**1**) (LH = *N*-phenyl-3,5-di-*tert*-butylsalicylaldimine) and LB(OMe) [LH_2 = *N*-(2-hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine (**4**), *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine (**5**), *N*-(3-hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine (**6**)]. The boron halide compounds were air and moisture sensitive, and upon hydrolysis, compound **7** resulted in the oxo-bridged compound **13** that contained two seven-membered boron heterocycles. The boron halide compounds dealkylated trimethyl phosphate in stoichiometric reactions to produce methyl halide and unidentified phosphate materials. Compounds **8** and **12** were found to be the most effective dealkylating agents. On reaction with *tert*-butyl diphenyl phosphinate, compound **8** produced a unique boron phosphinate compound $LB(O)OPPh_2$ (**14**) containing a terminal phosphinate group. Compounds **1**–**14** were characterized by ^{1}H, ^{13}C, ^{11}B, ^{31}P NMR, IR, MS, EA, and MP. Compounds **5**, **6**, and **11**–**14** also were characterized by single-crystal X-ray diffraction.

Introduction

Boron halides have been used extensively over the years in various organic syntheses, such as ester ring closure[1] and Friedel−Crafts alkylations.[2] However, boron trihalides are very reactive and are difficult to handle. The use of chelated boron compounds could help overcome this problem. One advantage of using chelated boron complexes rather than simple boron Lewis acids (e.g., BCl_3) is in the ability to tune their structure and properties by varying the constituents in the ligand environments, for example the size of the chelate rings and their substituents. Schiff base boron compounds have been studied recently for their possible applications in catalysis. Some of the recent examples of mononuclear Schiff base compounds include β-diketonates,[3] β-diketiminate,[4] substituted anthracene,[5] polysaccharides,[6] L-cysteine,[7] nitroles,[8,9] tropolonates,[10] and salicylaldimines.[11]

Organophosphate esters are active components of nerve agents and pesticides. Decontamination of organophosphate nerve gases is required in battle fields, laboratories, storage, and destruction sites. Examples of some nerve gas agents and pesticides are shown in Figure 1. All of these compounds possess a P−O−C linkage (the phosphate−ester linkage) in their structure. Although extensive research is being carried out on phosphate ester cleavage using various metal compounds in models of the biological phosphate hydrolysis,[12−14]

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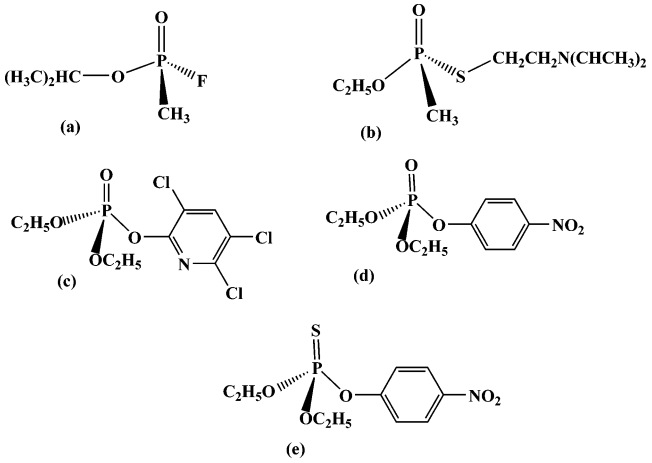

Figure 1. Structures of various organophosphate nerve gases and pesticides: (a) sarin gas, (b) VX gas, (c) chloropyrifos, (d) paraoxon, and (e) parathion.

the use of group 13 compounds in this field is limited. For example, some phosphate cleavage has been achieved with organoaluminum reagents[15] and aluminum or gallium amides.[16−18] However, these reagents have not been considered as potential nerve agent or as pesticide decontamination reagents, probably because of their limited scope or the high temperature and the long reaction time required. Our research has focused on using boron and aluminum chelates as possible organophosphate cleavage agents.[19−22] Binuclear boron halide chelate compounds based on Salen ligands (Salen = *N*,*N*′-alkylene(or arylene)bis(salicylideneimine)) were shown to dealkylate a wide range of organophosphates at ambient temperature.[19−21] For example, salpen(^{t}Bu)$[BBr_2]_2$ (salpen(^{t}Bu) = *N*,*N*′-propylenebis(3,5-di-*tert*-butylsalicylideneimine)) dealkylates $(MeO)_3P(O)$ and $(^n BuO)_3P(O)$ by 89 and 99%, respectively, in only 30 min.[21] This is significant considering that BCl_3 or BBr_3 alone is not effective compounds for phosphate dealkylation. In the dealkylation reaction, RCl or RBr (R = hydrocarbon residue of the phosphate) is produced along with a yet unidentified phosphate material. The active species in this type of reaction is thought to be a cation formed through the heterolytic cleavage of a B−X bond (Figure 2a). The cation then coordinates to the phosphate thereby activating the ester carbon. This is supported by the ease of formation of this type of cation by the simple addition of a Lewis base to $L[BX_2]_2$.[19] The coordination of the P═O bond to the boron atom makes the P−O−R bonds susceptible to nucleophilic attack by the halide anion (Figure 2b). The process could be made catalytic by conducting the reaction in the presence of excess BBr_3.[19,21]

The effectiveness of binuclear boron Schiff base halide compounds for the dealkylation of organophosphate esters opened up the possibility of a mild soft route for dealkylation of organophosphates. This finding was significant in the wake of recent concern for organophosphate nerve agent and pesticide destruction and decontamination.[23−25] To understand the full utility and scope of this discovery, it is necessary to study other similar and comparable systems. One preliminary step is to investigate the use of mononuclear boron Schiff base compounds in similar reactions. Mononuclear cationic boron complexes with *N*-salicylidene-*o*-aminophenol have been found to catalyze the polymerization of oxiranes.[11] However, these compounds have not been examined in detail for the dealkylation of phosphates. Previous work indicated that stoichiometric combinations of LBX_2 (LH = *N*-(*tert*-butyl-3,5-di-*tert*-butylsalicylaldimine, X = Br) and trimethyl phosphate leads to phosphate cleavage.[21] A detailed study of a series of mononuclear boron complexes for phosphate dealkylation would determine if the presence of two boron centers in the same compound is necessary for the dealkylation.

In this article, the synthesis and full characterization of a series of mononuclear boron halides of the type LBX and LBX_2 (L = various Schiff base N,O and N,O,O ligands; X = Cl, Br) are described. These compounds are shown to be useful in the dealkylation of organophosphates.

Experimental

General Remarks. All air-sensitive manipulations were conducted using standard benchtop Schlenk line techniques in conjunction with an inert atmosphere glovebox. All solvents were thoroughly dried prior to use. All glassware was cleaned with a base and an acid wash and then dried in an oven at 130 °C overnight. The Schiff base ligands *N*-phenyl-3,5-di-*tert*-butylsalicylaldimine, *N*-(2-hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine, *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine), and *N*-(3-hydroxpropyl)-3,5-di-*tert*-butylsalicylaldimine) were synthesized according to the literature procedure.[26] Nuclear magnetic resonance (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 ^{13}C, $BF_3{\cdot}Et_2O$ for ^{11}B, and 85% H_3PO4 for ^{31}P and are reported in ppm. Infrared (IR) transmission spectra were recorded at room temperature in a potassium bromide pellet on a Fourier Transform Magna-IR ESP 560 spectrometer. Elemental analyses were performed on either a Perkin-Elmer 2400 carbon−hydrogen−nitrogen (CHN) analyzer or a LECO CHN-2000 analyzer.

X-ray data were collected on either a Nonius Kappa-charge-coupled device (CCD) (compounds **1**, **6**, **11**, **12**, and **14**; Mo Kα radiation) or a Bruker-Nonius x8 Proteum (compound **13**; Cu Kα radiation) diffractometer. All calculations were performed using the software package SHELXTL-Plus.[27−30] The structures were

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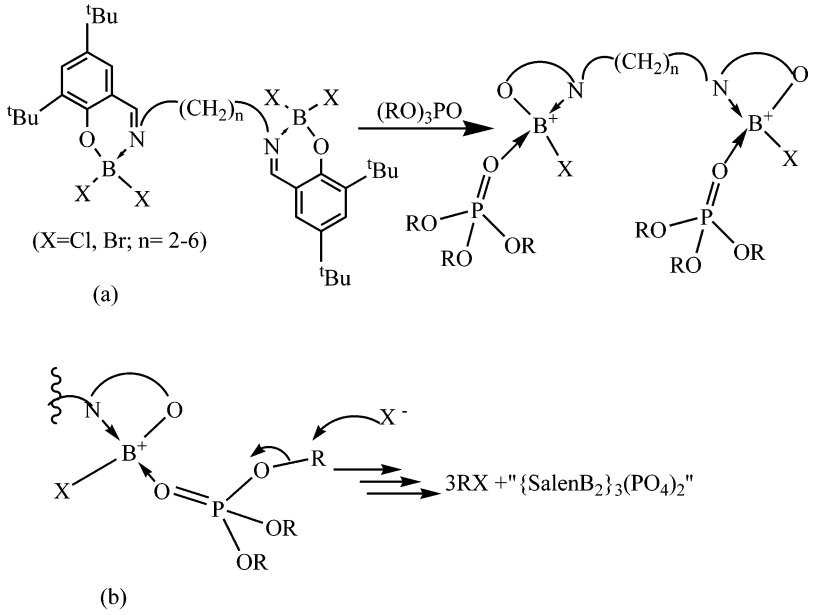

Figure 2. (a) Formation of a phosphate-coordinated boron cation. (b) Attack on P−O−R bond by a halide anion.

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 using a riding model with isotropic parameters tied to the parent atom. Crystallographic data were deposited with the Cambridge Crystallographic Data Center (CCDC reference numbers: 606640 (**1**), 606642 (**6**), 606644 (**11**), 606643 (**12**), 606645 (**13**), and 606641 (**14**)) 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).

Synthesis of LB(OMe)$_2$ (LH = *N*-Phenyl-3,5-di-*tert*-butylsalicylaldimine) (1). To a rapidly stirred solution of *N*-phenyl-3,5-di-*tert*-butylsalicylaldimine (3.00 g, 9.71 mmol) in toluene, B(OMe)$_3$ (6.00 g, 57.69 mmol) was added and refluxed for 16 h. The volatiles were removed under vacuum and a yellow solid was obtained that was washed with 20 mL of hexane and dried under vacuum. Yield: 3.42 g (92%). X-ray quality crystals were grown from a concentrated toluene solution after slow cooling to −30 °C. mp: 98 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 3.22 (s, 6H, OC*H*$_3$), 7.25 (m, 1H, Ph-*H*), 7.27 (m, 2H, Ph-*H*), 7.44 (m, 3H, Ph-*H*), 7.62 (m, 1H, Ph-*H*), 7.78 (m, 1H, Ph-*H*), 8.63 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.7 (C(*C*H$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 34.4 (*C*(CH$_3$)$_3$), 35.3 (*C*(CH$_3$)$_3$), 49.9 (O*C*H$_3$), 118.5 (Ph), 121.4 (Ph), 123.9 (Ph), 126.1 (Ph), 126.7 (Ph), 128.5 (Ph), 129.5 (Ph), 133.5(Ph), 137.2 (Ph), 140.8 (Ph), 148.9 (Ph), 158.5 (Ph), 164.0 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.33 ($W_{1/2}$ = 58 Hz). IR (KBr) ν/ cm^{-1}: 3064w, 2962s, 2903m, 2860m, 1614s, 1575s, 1555w, 1478m, 1464m, 1437m, 1390w, 1360m, 1319w, 1273w, 1248m, 1196m, 1171s, 1130w, 1074w, 1025w, 973w, 903w, 878m, 865s, 823w, 801w, 759s, 728w, 688m. MS electron impact (EI), positive): 321 (M$^+$, 5%), 350 (M$^+$ − OCH$_3$, 45%), 319 (M$^+$ − 2 OCH$_3$, 10%), 264 (M$^+$ − OCH$_3$ − ^{t}Bu, 100%). Anal. Calcd for $C_{23}H_{32}O_3NB$: C 72.44, H 8.46, N 3.67. Found: C 73.61, H 8.72, N 3.51.

Synthesis of LBCl$_2$ (LH = *N*-Phenyl-3,5-di-*tert*-butylsalicylaldimine) (2). To a rapidly stirred solution of **1** (0.71 g, 1.87 mmol) in toluene, 1 M BCl_3 in heptane (0.68 mL, 0.68 mmol) was added. The yellow, cloudy mixture was stirred for 13 h. The volatiles were removed under vacuum. The yellow solid was washed with hexane and dried under vacuum. Yield: 0.45 g (62%). mp: 255−257 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 7.27 (m, 1H, Ph-*H*), 7.36 (m, 1H, Ph-*H*), 7.47 (m, 2H, Ph-*H*), 7.66 (m, 2H, Ph-*H*), 7.78 (m, 1H, Ph-*H*), 8.29 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.6 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 34.6 (*C*(CH$_3$)$_3$), 35.4 (*C*(CH$_3$)$_3$), 125.2 (Ph), 126.5 (Ph), 129.5 (Ph), 129.7 (Ph), 136.0 (Ph), 144.2 (Ph), 164.2 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.48 ($W_{1/2}$ = 57 Hz). IR (KBr) ν/cm^{-1}: 2961s, 2905w, 2869w, 1619s, 1566s, 1555m, 1492w, 1468w, 1392w, 1380w, 1363w, 1254m, 1200m, 1132w, 1015m, 1005m, 918w, 904w, 849m, 762w, 720w, 692m. MS (EI, positive): 390 (M$^+$, 0.5%), 355 (M$^+$ − Cl, 2%), 320 (M$^+$ − 2 Cl, 5%), 309 (M$^+$ − BCl_2, 45%), 294 (M$^+$ − BCl_2 − CH_3, 100%). Anal. Calcd for $C_{21}H_{26}ONBCl_2$: C 64.65, H 6.72, N 3.59. Found: C 66.11, H 8.44, N 3.51.

Synthesis of LBBr$_2$ (LH = *N*-Phenyl-3,5-di-*tert*-butylsalicylaldimine) (3). To a rapidly stirred solution of **1** (0.48 g, 1.26 mmol) in toluene, 1 M BBr_3 in heptane (0.42 mL, 0.42 mmol) was added with a syringe. The yellow reaction mixture was stirred for 20 h. The volatiles were removed under vacuum and the yellow residue was washed with hexane and dried under vacuum. Yield: 0.45 g (75%). mp: 284−288 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 9H, C(C*H*$_3$)$_3$), 1.38 (s, 9H, C(C*H*$_3$)$_3$), 6.95 (d, 2H, Ph-*H*), 7.17−7.30 (m, 3H, Ph-*H*), 7.85 (d, 1H, Ph-*H*), 7.98 (d, 1H, Ph-*H*), 9.38 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.7 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 34.9 (*C*(CH$_3$)$_3$), 35.3 (*C*(CH$_3$)$_3$), 123.4 (Ph), 125.5 (Ph), 128.4 (Ph), 129.3 (Ph), 129.8 (Ph), 130.2 (Ph), 132.8 (Ph), 137.0 (Ph), 138.9 (Ph), 141.6 (Ph), 145.0 (Ph), 153.6 (Ph), 167.7 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.38 ($W_{1/2}$ = 60 Hz). IR (KBr) ν/ cm^{-1}: 2959s, 2901w, 2870w, 1625m, 1594w, 1563s, 1493w, 1469m, 1442w, 1414w, 1381m, 1363w, 1255m, 1203m, 1134w, 1067w, 1030m, 774w, 757w, 690w. MS (EI, positive): 309 (M$^+$ − BBr_2, 33%), 294 (M$^+$

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− BBr_2 − CH_3, 100%). Anal. Calcd for $C_{21}H_{26}ONBBr_2$: C 52.65, H 5.47, N 2.92. Found: C 53.00, H 5.15, N 2.85.

Synthesis of L[B(OMe)] (LH_2 = *N*-(2-Hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine) (4). To a rapidly stirred solution of *N*-(2-hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine) (3.31 g, 10.21 mmol) in toluene, excess $B(OMe)_3$ (6.50 g, 62.50 mmol) was added and refluxed for 8 h. The volatiles were removed under vacuum to yield an orange solid. Yield: 3.06 g (82%). mp: 210 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 9H, C(CH_3)$_3$), 1.49 (s, 9H, C(CH_3)$_3$), 3.15 (s, 3H, OCH_3), 6.86−7.66 (m, 6H, Ph-*H*), 8.52 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.5 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 34.2 (*C*(CH_3)$_3$), 35.4 (*C*(CH_3)$_3$), 49.7 (O*C*H_3), 114.3 (Ph), 114.7 (Ph), 119.1 (Ph), 125.3 (Ph), 128.2 (Ph), 129.0 (Ph), 131.3 (Ph), 133.0(Ph), 139.8 (Ph), 142.2 (Ph), 150.5 (Ph), 154.6 (Ph), 157.3 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 5.09. IR (KBr) ν/ cm^{-1}: 2959s, 2905w, 2868w, 1628s, 1556m, 1545m, 1480s, 1419m, 1390m, 1380m, 1362m, 1324s, 1259m, 1202m, 1181s, 1108s, 1039w, 1018m, 1007m, 987m, 886w, 752s. MS (EI, positive): 365 (M^+, 11%), 334 (M^+ − OCH_3, 100%). Anal. Calcd for $C_{22}H_{28}O_3NB$: C 72.34, H 7.73, N 3.83. Found: C 73.20, H 8.33, N 3.60.

Synthesis of L[B(OMe)] (LH_2 = *N*-(2-Hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine) (5). To a rapidly stirred solution of *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine (3.5 g, 12.6 mmol) in toluene, $B(OMe)_3$ (4.2 g, 40.8 mmol) was added and refluxed for 18 h. The volatiles were removed under vacuum, and the yellow residue was washed with hexane. Yield: 3.2 g (81%). mp: 302−306 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 3.17 (s, 3H, OCH_3), 3.30−3.48 (m, 2H, NCH_2), 3.63−3.86 (m, 2H, OCH_2). 7.04 (d, 1H, Ph-*H*), 7.52 (d, 1H, Ph-*H*), 8.30 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.3 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 34.1 (*C*(CH_3)$_3$), 35.0 (*C*(CH_3)$_3$), 49.5 (O*C*H_3), 58.9 (N*C*H_2), 59.8 (O*C*H_2), 114.7 (Ph), 125.3 (Ph), 131.9 (Ph), 138.2 (Ph), 140.4, (Ph),157.8 (Ph), 166.8 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.38. IR (KBr) ν/ cm^{-1}: 2954s, 2905w, 2863w, 1644s, 1567w, 1479w, 1462w, 1444w, 1384w, 1360w, 1309w, 1254m, 1210m, 1149s, 1132m, 1017s, 989m, 805w, 774w. MS (EI, positive): 286 (M^+ − OCH_3, 100%). Anal. Calcd for $C_{18}H_{28}O_3NB$: C 68.15, H 8.90, N 4.42. Found: C 68.25, H 9.18, N 4.23.

Synthesis of L[B(OMe)] (LH_2 = *N*-(3-Hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine) (6). To a rapidly stirred solution of *N*-(3-hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine (4.28 g, 14.71 mmol) in toluene, $B(OMe)_3$ (2.00 g, 19.23 mmol) was added and refluxed for 16 h. The volatiles were removed under vacuum, and a pale yellow solid was obtained, which was dried under vacuum. Yield: 4.50 g (92%). mp: 190−192 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H, C(CH_3)$_3$), 1.43 (s, 9H, C(CH_3)$_3$), 1.68−1.86 (m, 1H, CH_2), 2.00−2.24 (m, 1H, CH_2), 3.23 (s, 3H, OCH_3), 3.56−3.66 (m, 1H, NCH_2), 3.92−3.99 (m, 1H, NCH_2), 4.09−4.31 (m, 2H, OCH_2), 7.03 (d, 1H, Ph-*H*), 7.53 (d, 1H, Ph-*H*), 7.99 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.4 (C(*C*H_3)$_3$), 30.4 (*C*H_2), 31.2 (C(*C*H_3)$_3$), 34.0 (*C*(CH_3)$_3$), 35.1 (*C*(CH_3)$_3$), 49.7 (O*C*H_3), 54.5 (N*C*H_2), 61.2 (O*C*H_2), 114.8 (Ph), 125.0 (Ph), 132.1 (Ph), 138.7 (Ph), 140.5 (Ph), 157.2 (Ph), 160.7 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.00 ($W_{1/2}$ = 140 Hz). IR (KBR) ν/ cm^{-1}: 2955s, 2901m, 2867m, 1661s, 1567m, 1478m, 1448m, 1452m, 1429m, 1392w, 1361m, 1344m, 1307m, 1283w, 1265m, 1244m, 1202m, 1186m, 1153m, 1105s, 1082m, 1039m, 989m, 970m, 923m, 884m, 776w. MS (EI, positive): 331 (M^+, 1%), 300 (M^+ − OCH_3, 100%). Anal. Calcd for $C_{19}H_{30}O_3NB$: C 68.89, H 9.13, N 4.23. Found: C 69.55, H 9.28, N 4.31.

Synthesis of L[BCl] (LH_2 = *N*-(2-Hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine) (7). To a rapidly stirred solution of **4** (1.00 g, 2.74 mmol) in toluene, excess 1 M BCl_3 in heptane (2.75 mL, 2.75 mmol) was added. The reaction mixture was stirred for 13 h. The golden yellow solution was cannula filtered, and the volatiles were removed from the filtrate under vacuum to give a yellow solid. Yield: 0.96 g (95.0%). mp: 298 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 9H, C(CH_3)$_3$), 1.54 (s, 9H, C(CH_3)$_3$), 6.97−7.81 (m, 6H, Ph-*H*), 8.58 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.6 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 34.4 (*C*(CH_3)$_3$), 35.4 (*C*(CH_3)$_3$), 115.0 (Ph), 115.3 (Ph), 120.6 (Ph), 125.8 (Ph), 128.2 (Ph), 129.0 (Ph), 132.0 (Ph), 134.1 (Ph), 140.6 (Ph), 144.1 (Ph), 150.3 (Ph), 153.2 (Ph), 156.3 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 7.28. IR (KBr) ν/cm^{-1}: 2960s, 2901w, 2869w, 1631s, 1563m, 1549w, 1479s, 1467m, 1424m, 1392m, 1382m, 1363m, 1327m, 1254m, 1202m, 1190s, 1111w, 1031w, 1747m. MS (EI, positive): 286 (M^+ − Cl, 100%, 319 (M^+ − Cl − O, 15%). Anal. Calcd for $C_{21}H_{25}O_2NBCl$: C 68.23, H 6.82, N 3.79. Found: C 68.75, H 7.65, N 4.04.

Synthesis of L[BBr] (LH_2 = *N*-(2-Hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine) (8). To a rapidly stirred solution of **4** (1.00 g, 2.74 mmol) in toluene, excess 1 M BBr_3 in heptane (2.78 mL, 2.78 mmol) was added. The reaction mixture was stirred for 13 h. The solution was concentrated to about one-third of its volume. The yellow precipitate was cannula filtered and dried under vacuum. Yield: 0.73 g (64.6%). mp: 234−238 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 9H, C(CH_3)$_3$), 1.52 (s, 9H, C(CH_3)$_3$), 7.00−7.83 (m, 6H, Ph-*H*), 8.81 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.6 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 34.4 (*C*(CH_3)$_3$), 35.4 (*C*(CH_3)$_3$), 115.3 (Ph), 118.3 (Ph), 121.3 (Ph), 126.3 (Ph), 128.6 (Ph), 129.0 (Ph), 132.1 (Ph), 134.8 (Ph), 140.7 (Ph), 144.9 (Ph), 150.9 (Ph), 152.8 (Ph), 155.4 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 6.47 (four-coordinate boron). IR (KBr) ν/cm^{-1}: 2960s, 2905w, 2869w, 1629s, 1564m, 1549m, 1479s, 1424m, 1392m, 1380m, 1363m, 1328s, 1253m, 1203w, 1189w, 1103w, 1014w, 864w, 769w, 747m, 694w, 664w. MS (EI, positive): 414 (M^+, 3%), 334 (M^+ − Br, 100%), 318 (M^+ − Br − O, 20%). Anal. Calcd for $C_{21}H_{25}O_2NBBr$: C 60.90, H 6.08, N 3.38. Found: C 61.58, H 6.07, N 3.16.

Synthesis of L[BCl] (LH_2 = *N*-(2-hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine) (9). To a rapidly stirred solution of **5** (0.97 g, 3.05 mmol) in toluene, 1 M BCl_3 in heptane (1.10 mL, 1.10 mmol) was added. The reaction mixture was stirred for 24 h. Then, it was cannula filtered and the pale yellow residue was dried under vacuum. mp: >320 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H, C(CH_3)$_3$), 1.42 (s, 9H, C(CH_3)$_3$), 3.44−3.55 (m, 2H, NCH_2), 3.33−3.44 (m, 2H, OCH_2), 7.07 (d, 1H, Ph-*H*), 7.56 (d, 1H, Ph-*H*), 8.11 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.86 (C(*C*H_3)$_3$), 31.4 (C(*C*H_3)$_3$), 34.3 (*C*(CH_3)$_3$), 35.2 (*C*(CH_3)$_3$), 60.5 (N*C*H_2), 61.2 (O*C*H_2), 115.0 (Ph), 125.8 (Ph), 133.7 (Ph), 139.0 (Ph), 141.4 (Ph), 157.2 (Ph), 164.9 (N*C*H). ^{11}B NMR ($CDCl_3$): δ 2.05 ($W_{1/2}$ = 360 Hz). IR (KBr) ν/cm^{-1}: 2960s, 2905w, 2870w, 1640s, 1573m, 1479s, 1444s, 1395m, 1378s, 1363s, 1334m, 1302m, 1283m, 1261m, 1243m, 1214m, 1202m, 1190m, 1138m, 1085m, 1027m, 913w, 879w, 851w, 818w, 802w, 774w. MS (EI, positive): 322 (M^+, 1%), (M^+ − Cl, 90%). Anal. Calcd for $C_{17}H_{25}O_2NBCl$: C 63.48, H 7.83, N 4.36. Found: C 63.37, H 8.78, N 4.15.

Synthesis of L[BBr] (LH_2 = *N*-(2-Hydroxyethyl)-3,5-di-*tert*-butylsalicylaldimine) (10). To a rapidly stirred solution of **5** (0.54 g, 1.70 mmol) in toluene, 1 M BBr_3 in heptane (0.60 mL, 0.60 mmol) was added with a syringe. The clear yellow solution was stirred for 17 h. The volatiles were removed under vacuum, and the off-white residue was washed with hexane and dried under vacuum. Yield: 0.47 g (75%). mp: 228−232 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 9H, C(CH_3)$_3$), 1.47 (s, 9H, C(CH_3)$_3$), 3.94 (m, 4H, NCH_2 and OCH_2); 7.17 (d, 1H, Ph-*H*), 7.59 (d, 1H, Ph-*H*), 8.25 (s, 1H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.4 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 33.2 (*C*(CH_3)$_3$), 35.0 (*C*(CH_3)$_3$), 50.8 (N*C*H_2), 55.0

(O*C*H$_2$), 115.4 (Ph), 125.6 (Ph), 132.2 (Ph), 138.3 (Ph), 140.6, (Ph), 157.8 (Ph), 164.9 (N*C*H). ^{11}B NMR (CDCl$_3$): δ 2.00 ($W_{1/2}$ = 122 Hz). IR (KBr) ν/cm^{-1}: 2958s, 2901w, 2869w, 1644s, 1566m, 1479m, 1469m, 1441m, 1391m, 1378s, 1360m, 1336m, 1304m, 1259m, 1240w, 1203w, 1188m, 1135s, 1042m, 975m, 931w, 877w, 827w, 811w, 775w, 762w. MS (EI, positive): 366 (M$^+$, 30%), 286 (M$^+$ − Br, 55%), 270 (M$^+$ − Br − O, 45%). Anal. Calcd for $C_{17}H_{25}O_2NBBr$: C 55.77, H 6.88, N 3.83. Found: C 54.98, H 7.36, N 3.96.

Synthesis of L[BCl] (LH$_2$ = *N*-(3-hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine) (11). To a rapidly stirred solution of **6** (1.07 g, 3.23 mmol) in toluene, 1 M BBr_3 in heptane (1.10 mL, 1.10 mmol) was added. The clear golden-yellow solution was stirred for 14 h. The volatiles were removed under vacuum, and the yellow residue was washed with hexane and dried under vacuum. Yield: 0.88 g (81%). X-ray quality crystals were isolated after cooling a concentrated toluene solution to −30 °C. mp: 192−194 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 1.29 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 2.02 (q, 2H, C*H*$_2$), 4.06 (t, 2H, NC*H*$_2$), 4.24 (t, 2H, OC*H*$_2$), 7.13 (d, 1H, Ph-*H*), 7.66 (d, 1H, Ph-*H*), 7.93 (s, 1H, N=C*H*). ^{13}C NMR (CDCl$_3$): δ 28.8 (*C*H$_2$), 29.4 (C(*C*H$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 35.1 (*C*(CH$_3$)$_3$), 53.8 (N*C*H$_2$), 61.3 (O*C*H$_2$), 115.4 (Ph), 125.4 (Ph), 133.1 (Ph), 139.2 (Ph), 142.0 (Ph), 155.9 (Ph), 161.3 (N*C*H). ^{11}B NMR (CDCl$_3$): δ 3.3 ($W_{1/2}$ = 166 Hz). IR (KBr) ν/cm^{-1}: 2960s, 2866w, 1649s, 1572m, 1479m, 1461m, 1441m, 1432w, 1384m, 1365m, 1345m, 1285w, 1265m, 1246w, 1193m, 1164m, 1125w, 1093w, 1024w, 959w, 930w, 872w, 831w, 773w, 758w. MS (EI, positive): 336 (M$^+$, 1%), 300 (M$^+$ − Cl, 100%). Anal. Calcd for $C_{18}H_{27}O_2NBCl$: C 64.41, H 8.11, N 4.17. Found: C 65.72, H 6.86, N 4.06.

Synthesis of L[BBr] (LH$_2$ = *N*-(3-hydroxypropyl)-3,5-di-*tert*-butylsalicylaldimine) (12). To a rapidly stirred solution of **6** (0.69 g, 2.09 mmol) in toluene, 1 M BBr_3 in heptane (0.75 mL, 0.75 mmol) was added. The clear yellow solution was stirred for 6 h. Then, it was concentrated to about one-third of its volume, and yellow crystals were obtained after cooling at −30 °C overnight. The crystals were isolated by cannula filtration and dried under vacuum. Yield: 0.50 g (63% based on the borate). mp: softens at 174 °C and melts at 178−181 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 1.27 (s, 9H, C(C*H*$_3$)$_3$), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 2.11 (m, 2H, C*H*$_2$), 4.31 (s, br, 4H, NC*H*$_2$ and OC*H*$_2$), 7.48 (d, 1H, Ph-*H*), 7.78 (s, br, 1H, Ph-*H*), 8.97 (s, 1H, N=C*H*). ^{13}C NMR (CDCl$_3$): δ 26.3 (*C*H$_2$), 29.8 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 35.4 (*C*(CH$_3$)$_3$), 52.3 (N*C*H$_2$), 63.0 (O*C*H$_2$), 116.9 (Ph), 127.2 (Ph), 135.9 (Ph), 140.0 (Ph), 145.5 (Ph), 154.5 (Ph), 166.6 (N*C*H). ^{11}B NMR (CDCl$_3$): δ 9.7 ($W_{1/2}$ = 383 Hz). IR (KBr) ν/ cm^{-1}: 2962s, 2869w, 1638s, 1573s, 1471m, 1459m, 1452m, 1437w, 1386w, 1365m, 1347m, 1285m, 1265m, 1247s, 1196s, 1180m, 1135m, 1097m, 1084m, 1046w, 1000w, 961w, 931w, 874w, 831m, 772m, 755w, 661m, 623m, 607m, 545m. MS (EI, positive): 380 (M$^+$, 5%), 300 (M$^+$ − Br, 100%). Anal. Calcd for $C_{18}H_{27}O_2NBBr$: C 56.87, H 7.16, N 3.69. Found: C 56.04, H 5.91, 3.36.

Hydrolyzed Product (13). Compound **13** was obtained during the preparation of the halide **7** from the borate **4** by adventitious exposure to moisture. To a rapidly stirred solution of **4** (1.00 g, 2.74 mmol) in toluene, 1 M BCl_3 in heptane (1.00 mL, 1.00 mmol) was added. The deep brown solution was stirred for 18 h. The volatiles were removed under vacuum to obtain a yellow solid. The solid was recrystallized from dichloromethane to give yellow X-ray quality crystals of **13**. Yield: 0.61 g (33%). mp: 303−305 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 1.24 (s, 9H, C(C*H*$_3$)$_3$), 1.29 (s, 9H, C(C*H*$_3$)$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 6.52−7.73 (m, 12H, Ph-*H*), 8.51 (s, 2H, N=C*H*). ^{13}C NMR (CDCl$_3$): δ 29.5 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 34.3 (*C*(CH$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 38.1 (*C*(CH$_3$)$_3$), 114.9 (Ph), 120.6 (Ph), 121.8 (Ph), 122.0 (Ph), 125.6 (Ph), 126.2 (Ph), 129.6 (Ph), 132.0 (Ph), 133.0 (Ph), 134.2 (Ph), 139.4 (Ph), 141.3 (Ph), 144.9 (Ph), 151.6 (Ph), 159.4 (N*C*H). ^{11}B NMR (CDCl$_3$): δ 3.19 ($W_{1/2}$ = 720 Hz), 7.33 ($W_{1/2}$ = 320 Hz). IR (KBr) ν/ cm^{-1}: 2959s, 2909w, 2869w, 1620m, 1586m, 1563m, 1548m, 1486m, 1468m, 1441m, 1414m, 1391m, 1378w, 1362m, 1324w, 1293m, 1263s, 1255s, 1204s, 1187m, 1155m, 1110w, 1016w, 944m, 905m, 749m. MS (EI, positive): 684 (M$^+$, 5%), 334 (M$^+$ − $C_{21}H_{25}O_3NB$, 100%). Anal. Calcd for $C_{42}H_{50}O_5NB2$: C 73.70, H 7.36, N 4.09. Found: C 73.77, H 7.11, N 3.62.

Dealkylation of Phosphates. In a typical experiment, the chelate compound (for **8**, 30 mg, 0.07 mmol) was dissolved in 1 mL of $CDCl_3$ in a glass vial. The solution was transferred to an NMR tube and trimethyl phosphate (2.83 μL, 0.024 mmol, density 1.197 g/mL) was added with a microsyringe. The mixture was shaken and monitored by ^{1}H NMR. The percent dealkylation was calculated from the peak integrations of MeBr produced and the unchanged phosphate.

Synthesis of 14. To a rapidly stirred solution of **8** (0.57 g, 1.56 mmol) in toluene, *tert*-butyl-diphenylphosphinate (0.41 g, 1.57 mmol) was added. The golden-yellow reaction mixture was refluxed for 7 h. The volatiles were removed under vacuum, and a yellow solid was obtained, which was dried under vacuum and washed with hexane. Yield: 0.59 g (68%). mp: 239−240 °C (dec.). ^{1}H NMR (CDCl$_3$): δ 1.31 (s, 9H, C(C*H*$_3$)$_3$), 1.50 (s, 9H, C(C*H*$_3$)$_3$), 6.64 (m, 1H, Ph-*H*), 6.86 (m, 1H, Ph-*H*), 7.14−7.23 (m, 4H, Ph-*H*), 7.25−7.39 (m, 4H, Ph-*H*), 7.44−7.54 (m, 4H, Ph-*H*), 7.66−7.79 (m, 2H, Ph-*H*), 8.57 (s, 1H, N=C*H*). ^{13}C NMR (CDCl$_3$): δ 29.7 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 35.7 (*C*(CH$_3$)$_3$), 38.0 (*C*(CH$_3$)$_3$), 120.2 (Ph), 128.0 (Ph), 128.2 (Ph), 129.2 (Ph), 131.4 (Ph), 132.8 (Ph), 143.3 (Ph), 157.6 (N*C*H). ^{11}B NMR (CDCl$_3$): δ 3.57 ($W_{1/2}$ = 47 Hz). ^{31}P{H} NMR (CDCl$_3$): δ 28.90 (s), δ 33.97 (s). IR (KBR) ν/cm^{-1}: 2959m, 2909w, 2867w, 1640s, 1564w, 1548w, 1482m, 1440m, 1391m, 1384m, 1365w, 1327m, 1259m, 1212s, 1184m, 1127m, 1082m, 1014s, 994s, 966m, 888w, 750m, 725m, 694m, 544m. MS (EI, positive): 331 (M$^+$, 15%), 334 (M$^+$ − Ph_2-PO_2, 45)%), 333 (M$^+$ − Ph_2PO_2 − H, 100%). Anal. Calcd for $C_{33}H_{35}O_4NBP$: C 71.88, H 6.40, N: 2.54. Found: C 70.78, H 6.73, N 1.84.

Results and Discussion

Synthesis of Compounds 1−12. Unlike Schiff base aluminum compounds (LAlR), the boron chelates (LBR) cannot be prepared by an alkyl elimination reaction between the ligand LH_2 and BR_3 because of the low polarity of the B−C bond. The common methods for creating boron−ligand compounds are water elimination using a boronic acid and alcohol elimination using a borate (represented in the equations below).[31]

$$LH_2 + RB(OH)_2 \rightarrow LBR + 2\ H_2O$$

$$LH_2 + B(OR)_3 \rightarrow LBOR + 2\ ROH$$

The boron alkyls arising from the boronic acid reaction are generally stable, whereas the boron alkoxides formed

(31) Vaultier, M.; Carboni, B. In *Comprehensive Organometallic Chemistry II: A Review of the Literature 1982−1994*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, England, 1995; Vol. 11, p 191.

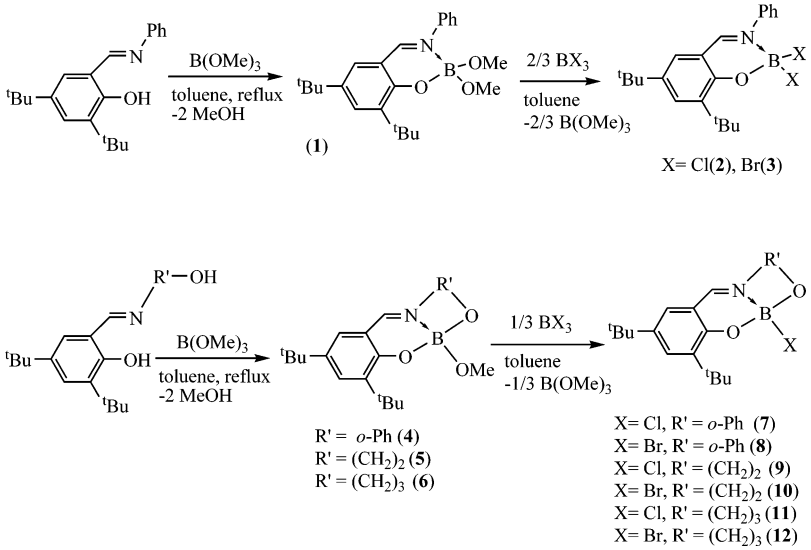

Figure 3. Preparation of compounds **1**−**12**.

from the reaction using a borate could be further derivatized (e.g., to boron siloxides).[32]

Binuclear boron halides of the type $L[BX_2]_2$ (X = Cl, Br) (L = salen ligands) can be prepared by the exchange reaction of the binuclear alkoxides $L[B(OMe)_2]_2$ with BX_3.[19−21] In the present work, similar reactions were employed to synthesize mononuclear Schiff base boron halide compounds from their borate precursors. The borate precursors were prepared in good yield by alcohol elimination between the Schiff base salicylidenimine ligand and excess trimethyl borate under reflux. The byproduct MeOH could be removed under vacuum to drive the reaction to completion. The salicylidenimine ligands could be prepared easily by the condensation reaction between 3,5-di-*tert*-butyl aldehyde and the corresponding amines according to the literature procedures.[26] The synthetic route used for the preparation of compounds **1**−**12** is depicted in Figure 3. Thus the halides **2**, **3**, and **7**−**12** were prepared from the corresponding borate precursors **1** and **4**−**6**. The borate precursors, in turn, were prepared by refluxing Schiff base ligands and excess trimethyl borate in toluene. The borates were converted to the boron halides by combination with BCl_3 or BBr_3 at room temperature. All compounds were isolated by removing the solvent under vacuum or by precipitation after concentration and cooling to −30 °C. The byproduct $B(OMe)_3$ was removed under vacuum. The compounds were pale white to orange in color.

Spectroscopy. Compounds **1**−**12** were characterized by ^{1}H, ^{13}C, and ^{11}B NMR, as well as mp, MS, and EA. The ^{1}H NMR data for all the compounds showed two singlets for the ^{t}Bu−Ph groups in the range of δ 1.24−1.54 ppm. The imine peaks appeared at δ 8.63, 8.52, 8.30, and 7.99 ppm for the borates **1**, **4**, **5**, and **6**, δ 8.29, 8.58, 8.11, and 7.93 ppm for the chlorides **2**, **7**, **9**, and **11**, and δ 9.38, 8.81, 8.25, and 8.97 ppm for the bromides **3**, **8**, **10**, and **12**, respectively. The imine peaks for the bromides appeared at a higher chemical shift compared to the chlorides. The presence of only one set of ^{t}Bu peaks and one imine peak for each compound suggested a symmetric solution state structure.

The ^{11}B NMR spectra showed single peaks at δ 2.33, 5.09, 2.38, and 2.00 ppm for the borate compounds, δ 2.48, 7.28, 2.05, and 3.33 ppm for the chlorides, and δ 2.38, 6.47, 2.00, and 9.7 ppm for the bromides. These shifts indicate the presence of four-coordinate boron[21] in all of the compounds. The IR spectra have a ν_{B-N} stretch in the region 1000−1042 cm^{-1} for all of the compounds. The mass spectra (EI) of the borates **1**, **4**, **5**, and **6** showed peaks corresponding to molecular ions minus methoxy groups, and this was the most abundant peak for **4**, **5**, and **6**. Compounds **4**, **5**, and **6** also showed molecular ions in low abundance. The chloride compounds **2**, **7**, **9**, and **11** showed molecular ions minus the chloride in high abundance. Additionally, **2**, **9**, and **11** showed molecular ion in low abundance. The bromide compounds **8**, **10**, and **12** had molecular ion as well as molecular ion minus bromide in their spectra. However, **3** showed molecular ion minus the BBr_2 group (33%) and also molecular ion minus BBr_2 and CH_3 (100%). This indicated that the EI ionization process was sufficiently strong to separate a boron fragment from the ligand. This was a rare occurrence for the Schiff base group 13 compounds, which are usually not observed to release the group 13 element from the ligand. The elemental analyses of the compounds were within acceptable limits. In some cases (e.g., **2**, **7**, **9**, and **11**), slightly different values from the calculated values could be due to the high air and moisture sensitivity of the compounds.

Structures. The borate compounds **1** and **6** and the halide compounds **11** and **12** were structurally characterized by single-crystal X-ray diffraction studies. The X-ray crystal structures confirmed the presence of four-coordinate boron atoms in these compounds (Figures 4−7). The crystal data collection parameters are shown in Table 1 and selected bond lengths and angles are shown in Table 2. The B−O bond

(32) Wei, P.; Keizer, T.; Atwood, D. A. *Inorg. Chem.* **1999**, *38*, 3914−3918.

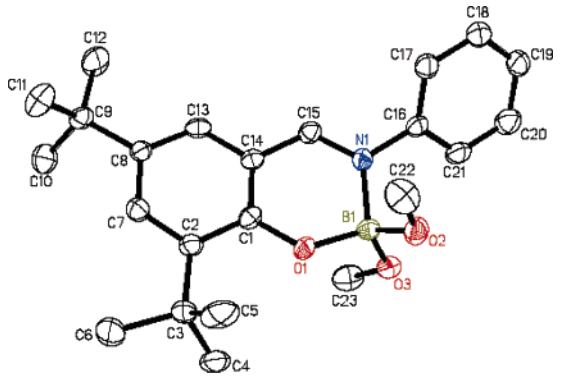

Figure 4. Structure of **1**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity.

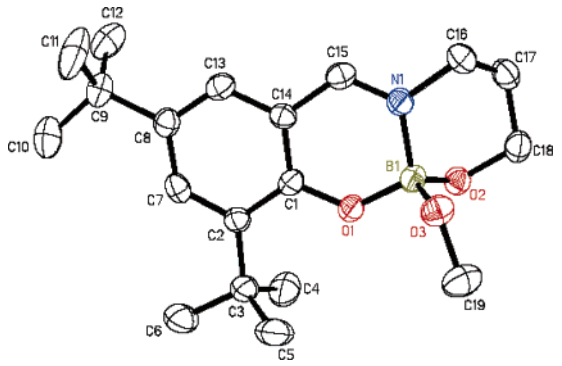

Figure 5. Structure of **6**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity.

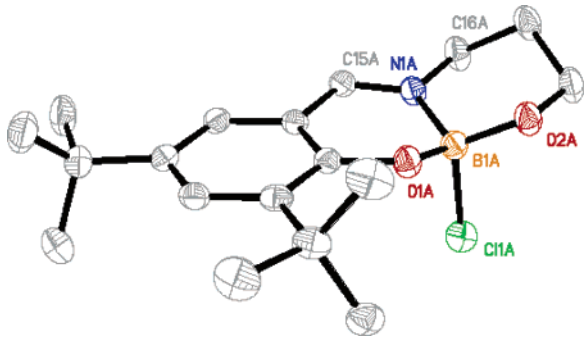

Figure 6. Structure of **11**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity. Only one molecule is shown out of two molecules in the unit cell.

lengths are in the range 1.414(4)−1.485(4) Å for the borates **1** and **6** and 1.394(2)−1.440(2) Å for the halides **11** and **12**. These distances are slightly shorter than the B−N distances (1.540(2)−1.628(4) Å), which is a reflection of the smaller covalent radius of oxygen and the coordinative character of B−N bonds. Nevertheless, the B−N distances reported are among the shortest known so far. The B−Br bond length (2.197(2) Å) in **12** is longer than the B−Cl bond length (1.966(2) Å) in **11**, which is a reflection of the greater covalent radii of Br compared to that of Cl. These distances are slightly larger compared to the binuclear boron halides reported previously. For example, in the binuclear Schiff base boron bromide salben(^{t}Bu)[BBr_2]$_2$,[19] the B−Br lengths are 2.023(8) and 2.077(9) Å, and in the binuclear Schiff base

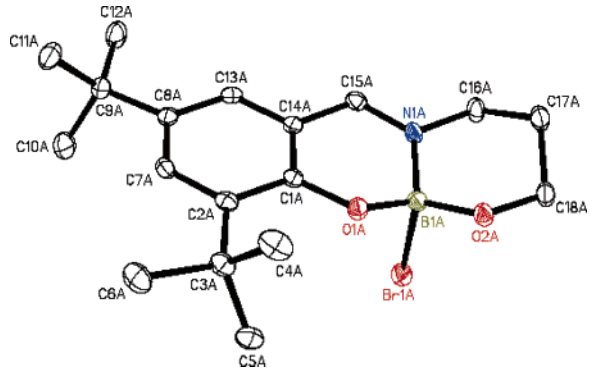

Figure 7. Structure of **12**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity. Only one molecule is shown out of two molecules in the unit cell.

boron chloride salpen(^{t}Bu)[Cl_2]$_2$,[20] the B−Cl bond lengths are 1.849(5) and 1.855(5) Å.

The geometry around the boron atom is slightly distorted tetrahedral in all four compounds. For compound **1**, the largest deviations are shown by the angles O1−B1−N1 (106.8(3)°), O1−B1−O2 (112.1(3)°), and O1−B1−O3 (112.1(3)°), whereas for **6**, the largest deviation is shown in the angle O2−B1−O3 (115.3(2)°). The angle O1−B1−N1 is slightly larger for **6** (109.4(2)°) compared to **1**. This could be caused by the steric restriction that arises because the boron is part of a second six-membered ring in **6**.

For the halide compounds **11** and **12**, the largest deviation from the ideal tetrahedral angle is observed for the angle O2A−B1A−N1A, which is 112.59(15)° for **11** and 114.64(14)° for **12**. The angles O1A−B1A−Cl1A (107.83(13)°), O2A−B1A−Cl1A (113.18(14)°), and N1A−B1A−Cl1A (102.89(13)°) in **11** are larger than the corresponding angles O1A−B1A−Br1A (107.09(11)°), O2A−B1A−Br1A (108.82(12)°), and N1A−B1A−Br1A (102.00(11)°) in **12**. This is contrary to what would be expected from the Bent's Rule[33] when the higher electronegativity of chlorine compared to bromine and, thus, less *s*-character in the B−Cl bond are considered. The angle O1A−B1A−N1A (110.72(15)° for **11** and 112.48(14)° for **12**) is close to the angle found in the bimetallic boron halides, salpen(^{t}Bu)[Cl_2]$_2$ (110.1(4)°)[20] and salben(^{t}Bu)[BBr_2]$_2$ (112.8(6)°).[19]

A quantitative correlation called the tetrahedral character (THC) value (Figure 8) has been proposed to determine the deviation of the geometry around boron in compounds containing N→B bonds.[34] A THC value of 100% refers to a perfectly tetrahedral geometry and a value of 0% refers to a trigonal planar geometry around the boron. Compounds **1**, **6**, **11**, and **12** have THC values of 88, 83, 84, and 77%, respectively. According to the previous observation, the THC values should increase with increased N−B interaction (i.e., decrease in N→B bond length).[34] However, the N→B bond lengths in **1**, **6**, **11**, and **12** (1.628(4), 1.585(4), 1.560(2), and 1.540(2) Å, respectively) do not agree with this observation, which is possibly because of the restriction imposed by the ligand.

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Table 1. Crystallographic Data and Refinement Details for Compounds **1**, **6**, and **11**−**14**

	1	**6**	**11**	**12**	**13**	**14**
empirical formula	$C_{23}H_{32}BNO_3$	$C_{19}H_{30}BNO_3$	$C_{18.15}H_{27.46}BCl_{0.85}NO_{2.15}$	$C_{18}H_{27}BBrNO_2$	$C_{44}H_{54}B_2Cl_4N_2O_5$	$C_{36.50}H_{39}BNO_4P$
M/g mol^{-1}	381.31	331.25	335.00	380.13	854.31	597.47
crystal size/mm	0.90 × 0.15 × 0.03	0.20 × 0.10 × 0.08	0.45 × 0.35 × 0.25	0.30 × 0.20 × 0.08	0.12 × 0.08 × 0.05	0.15 × 0.15 × 0.05
crystal system	monoclinic	monoclinic	triclinic	triclinic	orthorhombic	triclinic
space group	*Cc*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a/Å	11.5730(4)	16.2045(3)	11.6315(10)	11.5811(1)	12.9606(2)	12.1241(2)
b/Å	26.0370(11)	11.2564(3)	11.8250(10)	11.9058(1)	19.6141(3)	12.3740(2)
c/Å	8.5110(3)	10.4662(5)	16.5808(2)	16.5674(1)	51.9064(7)	12.4470(2)
α/°	90.00	90.00	100.1133(4)	101.1731(3)	90.00	73.7525(6)
β/°	120.9071(19)	94.7290(11)	102.1617(5)	101.3603(4)	90.00	89.0625(7)
γ/°	90.00	90.00	115.9115(5)	115.8035(3)	90.00	62.5102(6)
V/Å^3	2200.42(14)	1902.58(11)	1910.10(3)	1912.52(3)	13195.2(3)	1576.34(4)
ρ_{calc}/g cm^{-3}	1.151	1.156	1.165	1.320	1.290	1.259
Z	4	4	4	4	12	2
μ/mm^{-1}	0.074	0.076	0.188	2.157	2.810	0.128
T/K	90.0(2)	90.0(2)	90.0(2)	90.0(2)	90.0(2)	90.0(2)
Θ range/°	1.56−25.00	1.26−25.00	1.32−27.49	1.32−27.50	2.41−67.99	1.72−27.45
reflections measured	3820	6477	17406	47040	93693	13929
unique reflections	3808	3359	8762	8775	23333	7183
R1 [$I > 2\sigma$]	R1 = 0.0512, wR2 = 0.0950	0.0556, wR2 = 0.1277	0.0523, wR2 = 0.1419	0.0267, wR2 = 0.0598	0.0718, wR2 = 0.1730	R1 = 0.0501, wR2 = 0.1109
R1 (all data)	R1 = 0.0980, wR2 = 0.1108	0.1418, wR2 = 0.1583	0.0834, wR2 = 0.1599	0.0388, wR2 = 0.0641	0.1066, wR2 = 0.1947	R1 = 0.1036, wR2 = 0.1318

Interestingly, the mononuclear borates **1** and **6** do not show any hydrogen bonding as was observed for binuclear Salen-[(BOMe)$_2$]$_2$ compounds.[35]

Hydrolysis of Boron Halide Compounds. The boron halide compounds are moisture sensitive. They are hydrolyzed by trace amounts of moisture present in the reaction medium. Binuclear compound **13**, which contains a B−O−B linkage, was obtained during the preparation of the halide **7** from the borate **4** by adventitious exposure to moisture (Figure 9). Similar Schiff base compounds with B−O−B bridges can be prepared intentionally from the combinations of various Salen ligands with phenylboronic acid (Figure 10)[36,37] or boric acid,[38] various salicylaldimine derivatives with boric acid,[39] or salicylaldehyde with 2-$H_2NC_6H_4$Bpin (pin = 1,2-$O_2C_2Me_4$).[40]

The ^{1}H NMR of **13** contained four ^{t}Bu peaks. The ^{11}B NMR showed two boron peaks at δ 3.19 and δ 7.33 ppm corresponding to two four-coordinate boron atoms. The presence of the second boron peak and two extra ^{t}Bu peaks could be caused by the presence of a hydrolyzed compound "LBOH" produced in the reaction. This hydrolyzed compound presumably condensed to the dinuclear oxo-bridged compound **13**. The IR shows a peak at 1620 cm^{-1} that is attributed to $\nu_{C=N}$ stretching. The mass spectra (EI) had a molecular ion peak in 5% relative abundance.

An X-ray structure (shown in Figure 11) confirmed the presence of two four-coordinate boron atoms in **13**. The crystal data collection parameters are shown in Table 1, and selected bond distances and angles are shown in Table 2. The boron atoms are part of two seven-membered BOBNCCO heterocycles. There is a B−O−B bridge between the two boron atoms. The bridging B−O bond lengths are 1.404(6) and 1.388(6) Å, whereas the B−O(Ph) bond lengths range from 1.462(6) to 1.481(6) Å. The bridging B−O lengths are close to those observed in previously reported binuclear Schiff base boron compounds containing B−O−B bridges although the B−O(Ph) lengths are slightly shorter. For example, in the compounds L[(PhB)$_2$(μ-O)] (L = salen-(^{t}Bu), salpen(^{t}Bu), and acpen (acpen = *N*,*N*′-propylenebis-((methyl)salicylineneimine)), the bridging B−O bond lengths range from 1.416(5) to 1.419(3) Å, and B−O(Ph) bond lengths range from 1.493(3) to 1.511(4) Å.[36] The B−N bond lengths for **13** are 1.607(6) and 1.610(6) Å. Each boron atom is in a distorted tetrahedral environment. The THC values for B1A and B2A are 75 and 76%, respectively. The most acute angle for B1A is O2A−B1A−N1A (101.3(3)°) and for B2A is O3A−B2A−N2A (101.8(3)°). The most obtuse angle is O2A−B1A−O5A (115.3(4)°) for B1A and O5A−B2A−O3A (115.2(4)°) for B2A. The B−O−B angle is 117.1(4)°. This angle is significantly smaller compared to the B−O−B bridged compounds L[(PhB)$_2$(μ-O)] (L = Salen(^{t}Bu) (131.4(3)°), salpen(^{t}Bu) (137.5(3)°), and acpen (128.6°).[36]

Dealkylation of Trimethyl Phosphate with Various Mononuclear Compounds. The mononuclear Schiff base boron halide compounds **2**, **3**, and **7**−**12** dealkylated tri-

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1**, **6**, **11**,[a] **12**,[a] **13**,[b] and **14**

1			
B1−O1	1.485(4)	O3−C23	1.412(4)
B1−O2	1.414(4)	N1−C15	1.302(4)
B1−O3	1.426(4)	N1−C16	1.442(4)
B1−N1	1.628(4)		
O1−B1−N1	106.8(3)	O1−B1−O2	112.1(3)
O2−B1−N1	108.5(3)	O1−B1−O3	112.1(3)
O3−B1−N1	108.9(3)	O2−B1−O3	108.4(3)
6			
B1−O1	1.473(3)	O3−C19	1.428(3)
B1−O2	1.431(3)	N1−C15	1.286(3)
B1−O3	1.444(3)	N1−C16	1.466(3)
B1−N1	1.585(4)		
O1−B1−N1	109.4(2)	O1−B1−O2	107.6(2)
O2−B1−N1	108.2(2)	O1−B1−O3	111.2(2)
O3−B1−N1	105.0(2)	O2−B1−O3	115.3(2)
11			
B1−O1	1.440(2)	B1−N1	1.560(2)
B1−O2	1.401(2)	B1−Cl1	1.966(2)
O1−B1−N1	110.72(15)	O1−B1−Cl1	107.83(13)
O1−B1−O2	109.40(16)	O2−B1−Cl1	113.18(14)
O2−B1−N1	112.59(15)	N1−B1−Cl1	102.89(13)
12			
B1−O1	1.422(2)	B1−N1	1.540(2)
B1−O2	1.394(2)	B1−Br1	2.197(2)
O1−B1−N1	112.48(14)	O1−B1−Br1	107.09(11)
O1−B1−O2	110.61(15)	O2−B1−Br1	108.82(12)
O2−B1−N1	114.64(14)	N1−B1−Br1	102.00(11)
13			
B1−O1	1.467(6)	B2−O3	1.473(6)
B1−O2	1.478(6)	B2−O4	1.467(6)
B1−O5	1.398(6)	B2−O5	1.402(6)
B1−N1	1.610(6)	B2−N2	1.611(6)
O1−B1−N1	105.6(3)	O5−B2−N2	112.4(4)
O1−B1−O2	111.0(3)	O5−B2−O3	115.3(4)
O1−B1−O5	109.5(4)	O5−B2−O4	109.7(4)
O2−B1−N1	101.7(3)	O3−B2−N2	102.0(3)
O2−B1−O5	115.5(4)	O3−B2−O4	110.8(4)
O5−B1−N1	112.8(4)	O4−B2−N2	106.0(3)
B1−O5−B2	116.5(4)		
14			
B1−O1	1.432(2)	P1−O3	1.5633(13)
B1−O2	1.463(2)	P1−O4	1.4811(13)
B1−O3	1.476(2)	P1−C22	1.799(2)
B1−N1	1.568(3)	P1−C28	1.8004(19)
N1−C15	1.293(2)		
N1−C16	1.413(2)		
O1−B1−N1	109.97(16)	O3−P1−O4	116.50(7)
O2−B1−N1	102.22(15)	O3−P1−C22	107.33(8)
O3−B1−N1	110.45(16)	O3−P1−C28	112.93(8)
O1−B1−O2	114.49(16)	O4−P1−C22	111.30(8)
O1−B1−O3	107.91(15)	O4−P1−C28	112.93(8)
O2−B1−O3	111.71(16)	C22−P1−C28	106.26(9)
		P1−O3−B1	132.43(12)

[a] The values are the mean for the two independent molecules present in the asymmetric unit. [b] The values are the mean for the three independent molecules present in the asymmetric unit.

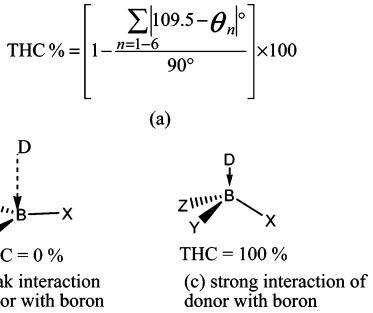

Figure 8. THC diagram. (a) Equation for calculating THC % [θ_n (n = 1−6) are the angles around the boron atom]. (b) Weak interaction between boron and the donor, which leads to three-coordinate trigonal boron. (c) Strong interaction between boron and the donor, which leads to tetrahedral four-coordinate boron.

methyl phosphate at room temperature in stoichiometric reactions to produce methyl halide and unidentified phosphate materials, which remained in solution (Figure 12 and Table 3). The dealkylation reaction was conducted in NMR tubes in $CDCl_3$, and the percent conversion was determined from the integration of the ^{1}H NMR peaks for the methyl halide produced and the unchanged methoxy groups of the phosphate. The reaction mixture stayed clear throughout the dealkylation reaction. The possible dealkylation pathway for the LBX compounds is shown in Figure 13. The best results were obtained from the monobromide compounds **8** (90% after 30 min) and **12** (64% after 30 min, 74% after 2 h, and 100% after 24 h). These results are comparable to the binuclear boron halides studied before.[19−21] In compounds **8** and **12** with an ONO environment, either an *o*-phenylene or a propylene backbone connects the N and O atoms. These compounds were far more active than the chloride analogues, **7** and **11**. This could be expected from the lower B−Br bond strength compared to the B−Cl bond strength (bond enthalpies for diatomic B−X: 396 kJ mol^{-1} for B−Br vs 511 kJ mol^{-1} for B−Cl) and the consequent ease of formation of the phosphate coordinated cations. Interestingly, the LBX (X = Cl, Br) compounds, **9** and **10**, with an ethylene backbone between the N and O atoms were almost inactive toward phosphate dealkylation. Compound **3**, the dibromide $LBBr_2$, also showed negligible activity. However, the dichloride compound, **2**, showed moderate activity (17% in 30 min, 61% in 2 h, and 85% in 24 h). The higher activity of chloride compared to bromide for LBX_2 could not be explained by the B−X bond strength. Thus, a correlation of higher reactivity and B−X bond strength occurs only for the monohalide compounds. The $LBCl_2$ compounds are more reactive than the $LBBr_2$ compounds could be because the inductive effect of the second chloride makes the formation of $LBCl^+$ easier to achieve.

Preparation of a Chelated Monomeric Boron Phosphinate (14) through Dealkylation. Although attempts to get the structure of the fully dealkylated phosphate triester was not successful, the dealkylated product, $LBOP(O)Ph_2$ (LH_2 = *N*-(2-hydroxyphenyl)-3,5-di-*tert*-butylsalicylaldimine) (**14**), which was produced from *tert*-butyl-diphenylphosphinate, $Ph_2P(O)O^tBu$, and the boron bromide compound **8**, was isolated and fully characterized. Molecular phosphates and phosphonates are interesting because of their possible use as precursors to solid-state materials.[41−44] Examples of

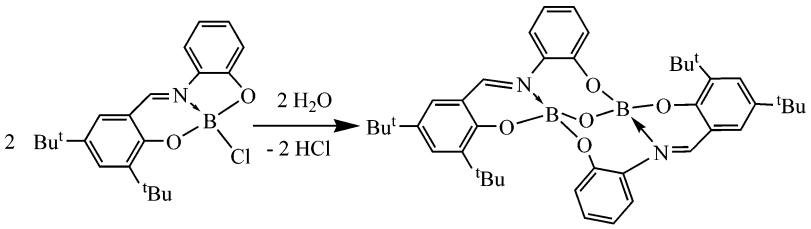

Figure 9. Formation of the hydrolyzed product **13** from the halide compound **7**.

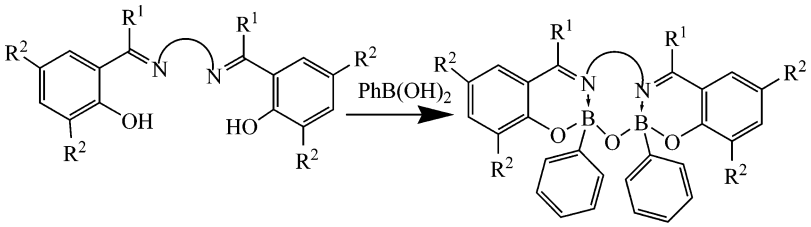

Figure 10. Formation of the binuclear oxo-bridged boron compounds from the Salen ligands.

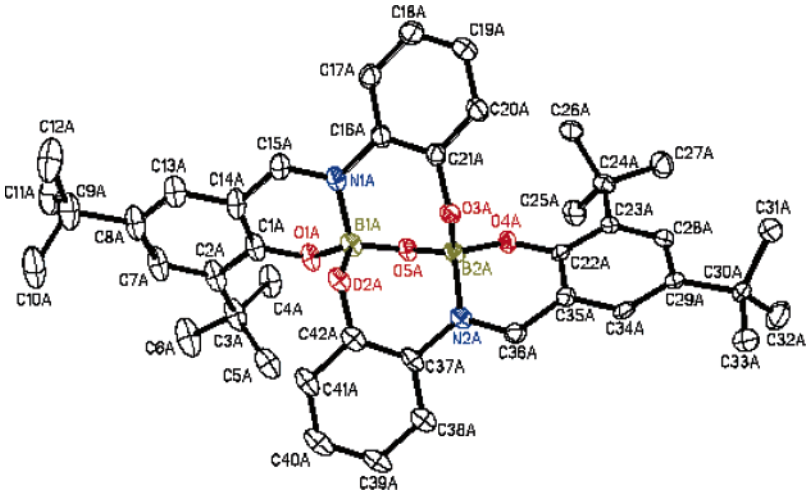

Figure 11. Structure of the hydrolyzed product **13**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity. Only one molecule is shown out of the three molecules in the asymmetric unit.

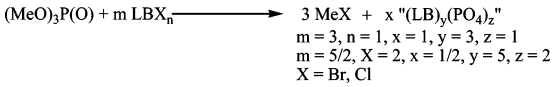

Figure 12. Reaction between trimethyl phosphate and the mononuclear Schiff base boron halides.

monomeric main group or transition metal chelate compounds with terminal phosphinates are rare. Previously reported metal phosphinate compounds of Ti,[45,46] Zr,[47] Ta,[46] Sn,[48,49] Pb,[48] Al,[50,51] Ga,[52,53] and In[52] contained bridging phosphinate groups, and almost all of the compounds were di- or polynuclear. A unique example of a mononuclear metal chelate phosphinate compound is $Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2$-

Table 3. Percent Dealkylation[a] of Trimethyl Phosphate with Schiff Base Boron Halides

compound	2	3	7	8	9	10	11	12
30 min	17	10	9	90	2	4	3	64
2 h	61	13	24	90	6	4	8	74
4 h			40	92	7			
6 h			52	94	7			
8 h			62	94	9			
10 h			68	94	11			
12 h			73	94	11			
24 h	85	18	84	94	13	4	57	100

[a] Calculated from the integration of ^{1}H NMR spectra of methyl halide produced and unchanged trimethyl phosphate at room temperature in $CDCl_3$.

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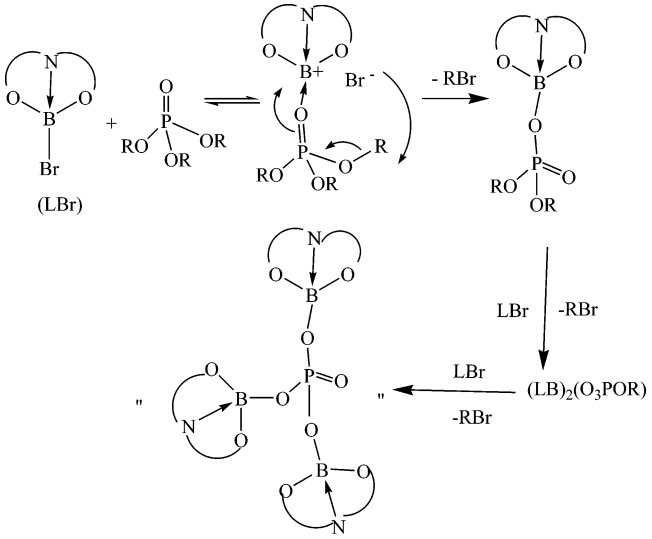

Figure 13. Possible dealkylation pathway for the boron compound LBX.

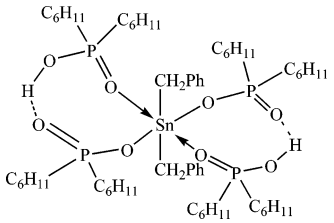

Figure 14. Monomeric tin phosphinate $Sn(CH_2Ph)_2[O_2P(C_6H_{11})_2]_2[HO_2P(C_6H_{11})_2]_2$.[49]

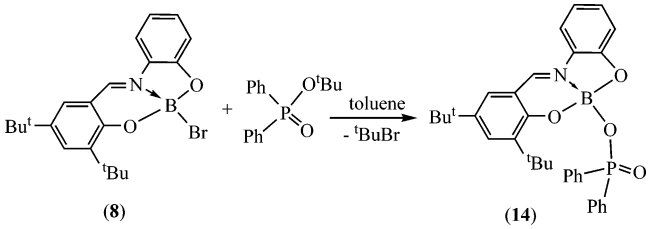

Figure 15. Synthesis of **14**.

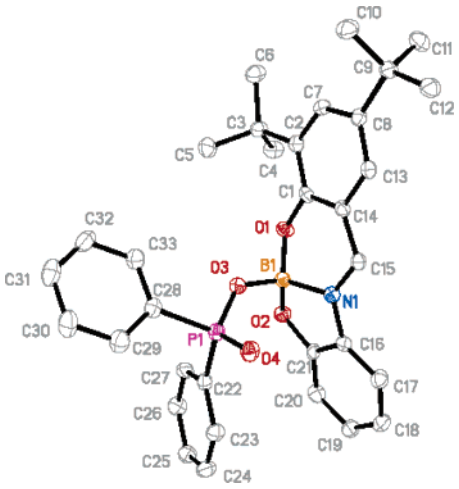

Figure 16. Crystal structure of compound **14**. Atoms are shown in 50% probability level. Hydrogen atoms are omitted for clarity.

$[HO_2P(C_6H_{11})_2]_2$ (Figure 14).[49] In this compound, the phosphinate groups participate in intramolecular hydrogen bonding. The aluminum phosphinate Salen chelate compounds, $[Salen(^tBu)Al\{O_2P(H)Ph\}]_n$ ($n = 2, \infty$), had bridging phosphinate groups, and they contained six-coordinate aluminum.[51] Recently, a Salen aluminum phosphinate compound (salenOP(O)Ph_2), which contained a terminal phosphinate group, was prepared through dealkylation.[54] The methanol coordinated structure of this compound was reported. Compound **14** is another rare example of a monomeric chelated compound with a terminal phosphinate group.

Compound **14** was prepared by refluxing **8** and $Ph_2P(O)$-O^{t}Bu in toluene (Figure 15). The byproduct ^{t}BuBr was removed under vacuum. The formation of this byproduct was confirmed by repeating the reaction in an NMR tube, which showed a ^{1}H peak corresponding to ^{t}BuBr. Compound **14** was soluble in organic solvents. The ^{1}H NMR showed ^{t}Bu peaks at δ 1.31 and δ 1.50 ppm, and an imine peak at δ 8.57 ppm. The ^{11}B NMR showed a single peak at δ 3.57 ppm, which is in the appropriate region for a four-coordinate boron atom. Interestingly, the ^{31}P NMR had two peaks at δ 28.90 and δ 33.97 ppm in the intensity ratio of 4:3. The presence of two peaks suggested that there might be some type of rearrangement in the solution state. One possibility could be the existence of a monomer−dimer equilibrium in the solution. A phosphinate-bridged dimer could form through the breakage of the B−N linkage, which previously has been postulated.[11] The chemical shift is close to some other phosphinate compounds. For example, in $[(\eta^5\text{-Cp})TiCl_2(\mu\text{-}Ph_2PO_2)_2]$ the ^{31}P shift was 34.5 ppm.[46] The IR for **14** showed strong ν_{B-N} absorption at 1014 cm^{-1}, $\nu_{(C=N)}$ at 1640 cm^{-1}, and $\nu_{(P=O)}$ at 1212 cm^{-1}. The MS (EI, positive) showed a molecular ion peak in 15% abundance and a $M^+ - PhPO_2$ peak in 45% abundance. The base peak (100%) was attributed to $M^+ - PhPO_2 - H$.

Structure of 14. The single-crystal X-ray structure of **14** is shown in Figure 16. Data collection parameters are given in Table 1, and selected bond lengths and angles are given in Table 2. The compound contained a four-coordinate boron and a four-coordinate phosphorus atom. The B−O bond lengths (1.432(2), 1.463(2), and 1.476(2) Å) were shorter than the B−N bond length (1.568(3) Å). The P1−O3 bond length (1.5633(13) Å) was in the single bond range (1.59−1.60 Å), and the P1−O4 bond (1.4811(13) Å) was close to the double bond range (1.45−1.46 Å).[55] In a previously reported molecular borophosphonate cage compound $[^tBuPO_3BEt]_4$, the average P−O bond length was 1.50 Å, which was between P−O and P═O.[56]

The geometry around the boron was distorted tetrahedral. The THC value[34] for **14** was 81%. The largest deviation from

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a perfect tetrahedral angle was in the O2−B1−N1 angle (102.22(15)°) caused by the constraints imposed by the chelate.

The phosphorus atom was in a distorted tetrahedral environment. The angle O3−P1−O4 (116.50(7))°) was the most obtuse angle, whereas the angle C22−P1−C28 (106.26-(9)°) was the least obtuse. The angle P1−O3−B1 (132.43-(12)°) was significantly narrower than the Al−O−P angle (138.8(3)°) in the dimeric aluminum phosphinate compound [salophen(thf)(^{t}Bu)AlO_2P(H)Ph]$_2$.[51]

Conclusion

A series of mononuclear Schiff base borates, LB$(OMe)_2$ and LB(OMe) based on N,O and N,O,O ligands, were prepared. The borates were further derivatized to mononuclear Schiff base boron halides, LBX_2 and LBX (X = Cl, Br). The boron halides are moisture sensitive, and one of them on reaction with trace water, produced a binuclear compound containing a B−O−B linkage and BOBNCCO heterocycles. Compounds **2**, **3**, and **7**−**12** dealkylated trimethyl phosphate to various extents at room temperature. The monobromide compounds **8** and **12** were the most effective, and their activity was comparable to the results obtained from binuclear Salen boron bromide compounds previously reported. However, it should be noted that the mononuclear compounds were less stable to air and moisture compared to their binuclear counterparts. For any useful application, this problem should be considered. Although the structure of the fully dealkylated product could not be determined, a monodealkylated product (compound **14)** was fully characterized. Compound **14** is the first example of a chelated boron phosphinate. Interestingly, the compound had a terminal phosphinate group, which contrasted with the bridging phosphinate groups that are found in many other metal chelates. The dealkylation reaction has the potential to produce novel structures when used with phosphate di- and triesters (i.e., phosphonates and phosphates).

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Supporting Information Available: CIF files for compounds **1**, **6**, and **11**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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