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Five-Coordinate Aluminum Bromides: Synthesis, Structure, Cation Formation, and Cleavage of Phosphate Ester Bonds

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Abstract: The alkane elimination reaction between Salen(^{t}Bu)H_2 ligands and diethylaluminum bromide was used to prepare three Salen aluminum bromide compounds salen(^{t}Bu)AlBr (**1**) (salen = *N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylideneimine)), salpen(^{t}Bu)AlBr (**2**) (salpen = *N*,*N*′-propylenebis(3,5-di-*tert*-butylsalicylideneimine)), and salophen(^{t}Bu)AlBr (**3**) (salophen = *N*,*N*′-*o*-phenylenenebis(3,5-di-*tert*-butylsalicylideneimine)). The compounds contain five-coordinate aluminum either in a distorted square pyramidal or a trigonal bipyramidal environment. The bromide group in these compounds could be displaced by triphenylphosphine oxide or triphenyl phosphate to produce the six-coordinate cationic aluminum compounds [salen(^{t}Bu)Al($Ph_3PO)_2$]Br (**4**), [salpen(^{t}Bu)Al($Ph_3PO)_2$]Br (**5**), [salophen(^{t}Bu)Al($Ph_3PO)_2$]Br (**6**), and [salophen(^{t}Bu)Al{$(PhO)_3PO)\}_2$]Br (**7**). All the compounds were characterized by ^{1}H, ^{13}C, ^{27}Al, and ^{31}P NMR, IR, mass spectrometry, and melting point. Furthermore, compounds **1**−**3** and **5**−**7** were structurally characterized by single-crystal X-ray diffraction. Compounds **1**−**3** dealkylated a series of organophosphates in stoichiometric reactions by breaking the ester C−O bond. Also, they were catalytic in the dealkylation reaction between trimethyl phosphate and added boron tribromide.

Introduction

Examples of five-coordinate group 13 bromide compounds reported so far have been limited to indium.[1] This is despite the fact that the chloride compounds have been quite popular for synthetic and catalytic applications.[2−6] Specifically, Salen aluminum chloride (Salen = *N*,*N*′-alkylene(or arylene)bis(salicylideneimine)) compounds have been the subject of interest recently for their ease of synthesis and cation formation and subsequent catalysis. The compounds contain five-coordinate aluminum with a single ^{27}Al NMR peak in the range δ 43−57 ppm. The coordination environment around the central aluminum is either trigonal bipyramidal or square pyramidal depending on the "backbone" (the connection between the nitrogens) of the ligand. With three or more methylene units in the backbone (e.g., salpen) a tbp geometry is obtained whereas for two methylene units (e.g., salen) or 1,2-arylene (e.g., salophen) a sqp geometry is observed.[7]

SalenAlCl compounds have been used in oxirane polymerization,[2] phospho-transfer reactions,[3] conjugate addition of nucleophiles to unsaturated imides,[4−6] and an inverse electron demand Diels−Alder reaction.[8] The chloride group in Salen(^{t}Bu)AlCl can be displaced by strong donors, such as, H_2O, MeOH, THF, or HMPA to give cationic aluminum compounds (Scheme 1).[9−11] Also, solvent-free cations can be achieved by removing the chloride of SalenAlCl with $GaCl_3$ (Scheme 1).[12] In general, the utility of the SalenAlCl compounds has relied on their ability to produce the cation [SalenAl(base)$_2$]$^+$. It is likely that the bromide derivatives will have greater utility on the basis of the weaker Al−Br bond strength (bond energy: 511 kJ mol^{-1} for Al−Cl vs 430 kJ mol^{-1} for Al−Br).[13] Thus, it is anticipated that cation formation may occur for the bromide derivatives with less strong bases, thereby broadening the potential applicability of the compounds.

This article will detail the synthesis of five-coordinate Salen aluminum bromides and the formation of six-coordinate aluminum cations in combination with a Lewis base. Also, the ability of these compounds to dealkylate organophosphate compounds will be demonstrated.

Experimental Section

General Remarks. All air-sensitive manipulations were conducted using standard benchtop Schlenk line technique in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior

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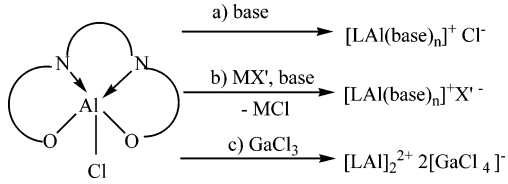
Scheme 1. Formation of Cationic Aluminum Compounds with Salen Ligands



to use. All glassware was cleaned with a base and an acid wash and dried in an oven at 130 °C overnight. The ligands salen(^{t}Bu)H_2, salpen(^{t}Bu)H_2, and salophen(^{t}Bu)H_2 were synthesized according to the literature procedure.[14] NMR data were obtained on Varian Gemini-200 and Varian VXR-400 instruments. Chemical shifts are reported relative to $SiMe_4$ for ^{1}H and ^{13}C and $AlCl_3$ in D_2O for ^{27}Al and are reported in ppm. Infrared transmission spectra were recorded at room temperature in a potassium bromide pellet on a Fourier transform Magna-IR ESP 560 spectrometer. The elemental analyses of the compounds were within acceptable limits.

X-ray data were collected on either a Nonius Kappa-CCD (compounds **2**, **5**−**7**; Mo Kα radiation) or a Bruker-Nonius X8 Proteum (compounds **1** and **3**; Cu Kα radiation) diffractometer. All calculations were performed using the software package SHELXTL-Plus.[15−18] The structures were solved by direct methods and successive interpretation of difference Fourier maps followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included using a riding model with isotropic parameters tied to the parent atom. Crystallographic data were deposited with the Cambridge Crystallographic Data Center (CCDC reference nos.: 276666 (**1**); 276668 (**2**); 276667 (**3**); 276669 (**5**); 276670 (**6**); 276671-(**7**)), and copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223-336033; E-mail deposit@ccdc.cam.ac.uk).

Synthesis of Salen(^{t}Bu)AlBr (1). A rapidly stirred solution of Et_2AlBr in toluene, prepared in situ by the redistribution of triethylaluminum (0.42 g, 3.60 mmol) and aluminum(III) bromide (1 M solution in dibromomethane, 1.8 mL, 1.80 mmol), was combined with a solution of salen(^{t}Bu)H_2 (2.69 g, 5.46 mmol) in toluene by cannula. The reaction mixture was refluxed for 8 h and filtered. The volatiles were removed under vacuum from the clear yellow filtrate to give a yellow microcrystalline solid which was purified by recrystallization from toluene. Single crystals suitable for X-ray analysis were grown from slow diffusion of hexane vapor into a concentrated CH_2Cl_2 solution. Yield: 2.69 g (73.8%). Mp: 330−332 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18H, C(CH_3)$_3$), 1.57 (s, 18H, C(CH_3)$_3$), 3.97 (m, 4H, NCH_2), 7.08 (d, 2H, Ph*H*), 7.60 (d, 2H, Ph*H*), 8.40 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.7 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 34.0 (*C*CH$_3$)$_3$), 35.5 (*C*CH$_3$)$_3$), 54.5 (NCH$_2$), 118.2 (Ph), 127.3 (Ph), 131.6 (Ph), 139.1 (Ph), 141.3 (Ph), 162.7 (Ph), 170.4 (NCH). ^{27}Al NMR ($CDCl_3$): δ 38 ($W_{1/2}$ = 5183 Hz). IR (KBr; ν in cm^{-1}): 2962 m, 2905 w, 2866 w, 1648 s, 1628 s, 1544 m, 1475 m, 1444 m, 1421 w, 1390 w, 1361 w, 1310 w, 1257 w, 1180 w, 867 w, 845 m, 816 w, 786 w, 756 w, 608 m, 586 w. MS (EI, positive): *m*/*z* 597 (M^+, 8%), 517 (M^+ − Br, 100%), 501 (M^+ − Br − O, 44%).

Synthesis of Salpen(^{t}Bu)AlBr (2). A rapidly stirred solution of Et_2AlBr in toluene, prepared in situ by the redistribution of triethylaluminum (0.24 g, 2.08 mmol) and aluminum(III) bromide (1 M solution in dibromomethane, 1.0 mL, 1.00 mmol), was combined with a solution of salpen(^{t}Bu)H_2 (1.57 g, 3.10 mmol) in toluene by cannula. The reaction mixture was refluxed for 17 h. The cloudy yellow solution was concentrated under vacuum to about one-third of its volume. The yellow precipitate was isolated by cannula filtration, washed with ∼15 mL of hexane, dried under vacuum, and recrystallized from toluene. X-ray-quality crystals were grown from slow diffusion of hexane vapor into a concentrated CH_2Cl_2 solution. Yield: 1.04 g (55%). Mp: 333−334 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 18H, C(CH_3)$_3$), 1.50 (s, 18H, C(CH_3)$_3$), 2.23 (m, 2H, $CH_2CH_2CH_2$), 3.85 (m, 4H, NCH_2), 7.07 (d, 2H, Ph-*H*), 7.56 (d, 2H, Ph-*H*), 8.29 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 27.2 (*C*H$_2$), 29.7 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 33.9 (*C*CH$_3$)$_3$), 35.4 (*C*CH$_3$)$_3$), 55.1 (NCH$_2$), 118.1 (Ph), 127.2 (Ph), 131.4 (Ph),138.9 (Ph), 141.0 (Ph), 162.5 (Ph), 172.0 (N=*C*H). ^{27}Al NMR ($CDCl_3$): δ 36 ($W_{1/2}$ = 3339 Hz). IR (KBr; ν in cm^{-1}): 2956 m, 2906 w, 2866 w, 1642 s, 1624 s, 1548 m, 1463 s, 1418 m, 1390 w, 1361 m, 1312 m, 1259 m, 1180 m, 1097 w, 863 m, 847 m, 784 w, 755 w, 601 m. MS (EI, positive): *m*/*z* 531 (M^+ − Br, 100%).

Synthesis of Salophen(^{t}Bu)AlBr (3). A rapidly stirred solution of Et_2AlBr in toluene, prepared in situ by the redistribution of triethylaluminum (0.21 g, 1.80 mmol) and aluminum(III) bromide (1 M solution in dibromomethane 0.90 mL, 0.90 mmol), was combined with a solution of salophen(^{t}Bu)H_2 (1.46 g, 2.70 mmol) in toluene by cannula. The golden yellow solution was refluxed for 15 h. Then it was concentrated under vacuum to about one-third of its volume. Yellow crystals precipitated after cooling at −30 °C for 24 h. The crystals were isolated by cannula filtration, washed with hexane, and dried under vacuum. Yield: 1.54 g (88%). Mp: 320 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 18H, C(CH_3)$_3$), 1.63 (s, 18H, C(CH_3)$_3$), 7.24 (d, 2H, Ph-*H*), 7.35 (m, 2H, Ph-*H*), 7.66 (m, 2H, Ph-*H*), 7.71 (d, 2H, Ph-*H*), 8.94 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.8 (C(*C*H$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 34.1 (C(*C*H$_3$)$_3$), 35.6 (C(*C*H$_3$)$_3$), 115.4 (Ph), 115.7 (Ph), 118.5 (Ph), 126.7 (Ph), 127.5 (Ph), 128.2 (Ph), 129.1 (Ph), 133.2 (Ph), 137.5 (Ph), 139.8 (Ph), 141.6 (Ph), 161.2 (Ph), 162.4 (Ph), 164.1 (N=*C*H). ^{27}Al NMR ($CDCl_3$): δ 32 ($W_{1/2}$ = 5183 Hz). IR (KBR; ν in cm^{-1}): 2961 s, 2905 w, 2868 w, 1621 s, 1554 m, 1542 s, 1469 s, 1474 m, 1445 m, 1420 m, 1391 m, 1361 s, 1311 m, 1255 m, 1202 w, 1179 w, 865 w, 847 m, 786 w, 757 w, 610 m. MS (EI, positive): *m*/*z* 646 (M^+, 13%), 565 (M^+ − Br, 95%), 549 (M^+ − Br − O, 100%).

Synthesis of [Salen(^{t}Bu)Al(Ph$_3$PO)$_2$]Br (4). A rapidly stirred solution of salen(^{t}Bu)AlBr (0.41 g, 0.69 mmol) in toluene was combined with triphenylphosphine oxide (0.38 g, 1.38 mmol). The cloudy yellow slurry became clear greenish yellow with heating. The solution was refluxed for 16 h. A pale yellow precipitate formed after cooling to room temperature. The precipitate was isolated by cannula filtration and dried under vacuum. Yield: 0.77 g (97%). Mp: 260 °C. ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 18H, C(CH_3)$_3$), 1.42 (s, 18H, C(CH_3)$_3$), 3.67 (s, br, 4H, NCH_2), 6.86 (d, 2H, Ph-*H*), 7.29−7.54 (m, 32H, Ph-*H*), 8.04 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 29.8 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 33.9 (C(*C*H$_3$)$_3$), 35.5 (C(*C*H$_3$)$_3$), 53.3 (NCH$_2$), 118.6 (Ph), 127.3 (Ph), 128.1 (Ph), 128.6 (Ph), 128.9 (Ph), 128.1 (Ph), 129.5 (Ph), 128.1 (Ph), 130.4 (Ph), 132.0 (Ph), 132.3 (Ph), 132.8 (Ph), 132.9 (Ph), 137.5 (Ph), 139.9 (Ph), 162.7 (Ph), 168.7 (NCH). ^{27}Al NMR ($CDCl_3$): δ −6 ($W_{1/2}$ = 7859 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 34 (s). IR (KBr; ν in cm^{-1}): 2951 s, 2901 w, 2862 w, 1621 s, 1547 w, 1439 m, 1422 w, 1391 w, 1358 w, 1258 w, 1173 s ($\nu_{P=O}$), 1121 m, 856 w, 787 w, 757 w, 724 s, 694 m, 610 m, 539 s. MS (MALDI-TOF): *m*/*z* 795 (M^+ − Br − Ph$_3$PO, 100%), 517 (M^+ − Br − 2Ph$_3$PO, 36%).

Synthesis of [Salpen(^{t}Bu)Al(Ph$_3$PO)$_2$]Br (5). A rapidly stirred solution of salpen(^{t}Bu)AlBr (0.32 g, 0.53 mmol) in toluene was combined with triphenylphosphine oxide (0.29 g, 1.05 mmol). The cloudy yellow slurry became clear yellow with heating. The solution was refluxed for 10 h. A yellow precipitate formed after cooling to room temperature and concentrating the solution. The precipitate was isolated by cannula filtration and dried under vacuum. Yield: 0.42 g (69%). Mp: 246 °C. ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 36H, C(CH_3)$_3$), 2.08 (m, 2H, $CH_2CH_2CH_2$), 3.56 (m, 4H, NCH_2), 7.05 (d, 2H, Ph-*H*),

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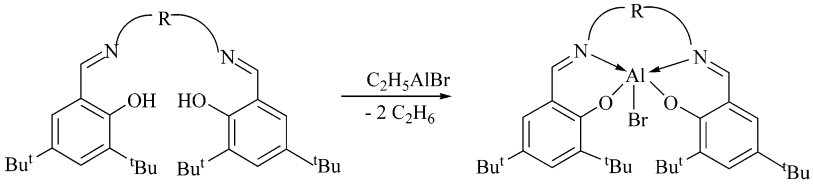
Scheme 2. Formation of Salen(ᵗBu)AlBr Compounds



R=$(CH_2)_2$, salen(ᵗBu)AlBr (**1**)
R=$(CH_2)_3$, salpen(ᵗBu)AlBr (**2**)
R=*o*-Ph , salophen(ᵗBu)AlBr (**3**)

7.27−7.59 (m, 32H, Ph-*H*), 8.29 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 27.2 (CH_2), 29.9 (C(CH_3)$_3$), 31.6 (C(CH_3)$_3$), 34.2 (C(CH_3)$_3$), 35.5 (C(CH_3)$_3$), 56.6 (NCH_2), 118.8 (Ph), 128.1 (Ph), 128.4 (Ph), 129.0 (Ph), 129.2 (Ph), 130.3 (Ph), 131.3 (Ph), 132.4 (Ph), 132.6 (Ph), 133.1 (Ph), 133.2 (Ph), 139.2 (Ph), 140.2 (Ph), 162.6 (Ph), 172.8 (N=*C*H). ^{27}Al NMR ($CDCl_3$): δ 0 ($W_{1/2}$ = 4835 Hz). ^{31}P{^{1}H} NMR($CDCl_3$): δ 35 (s). IR (KBr; ν in cm^{-1}): 2950 s, 2905 w, 2866 w, 1632 s, 1620 s, 1548 m, 1478 m 1461 m, 1439 s, 1426 s, 1391 w, 1358 m, 1316 m, 1279 w, 1255 m, 1200 w, 1162 s ($\nu_{P=O}$), 1120 s, 1094 w, 999 w, 841 m, 786 w, 753 m, 726 s, 693 s, 537 s. MS (MALDI-TOF): *m*/*z* 809 (M^+ − Br − Ph_3PO, 11%), 531 (M^+ − Br − 2Ph_3PO, 100%).

Synthesis of [Salophen(ᵗBu)Al(Ph$_3$PO)$_2$]Br (6). A rapidly stirred solution of salophen(ᵗBu)AlBr (0.51 g, 0.79 mmol) in toluene was combined with triphenylphosphine oxide (0.44 g, 1.58 mmol). The yellow slurry was refluxed for 14 h and then cooled to room temperature and concentrated. Yellow crystals precipitated, which were isolated by cannula filtration and dried under vacuum. Yield: 0.58 g (61%). Mp: 304−305 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18H, C(CH_3)$_3$), 1.50 (s, 18H, C(CH_3)$_3$), 6.92 (d, 2H, Ph-*H*), 7.06−7.40 (m, 34H, Ph-*H*), 7.62 (d, 2H, Ph-*H*), 8.11 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 30.1 (C(CH_3)$_3$), 31.6 (C(CH_3)$_3$), 34.3 (C(CH_3)$_3$), 35.9 (C(CH_3)$_3$), 116.2 (Ph), 119.1 (Ph), 125.6 (Ph), 126.7 (Ph), 128.5 (Ph), 128.6 (Ph), 128.8 (Ph), 128.9 (Ph), 129.3 (Ph), 129.8 (Ph), 132.2 (Ph), 132.4 (Ph), 133.0 (Ph), 133.1 (Ph), 137.6 (Ph), 138.2 (Ph), 140.8 (Ph), 159.9 (Ph), 164.9 (N=*C*H); ^{27}Al NMR ($CDCl_3$): δ 42 ($W_{1/2}$ = 5078 Hz). ^{31}P{^{1}H} NMR-($CDCl_3$): δ 33 (s). IR (KBr; ν in cm^{-1}): 2954 s, 2901 w, 2862 w, 1614 s, 1586 s, 1547 m, 1536 s, 1469 m, 1440 m, 1413 w, 1391 m, 1357 w, 1266 w, 1199 m, 1172 s ($\nu_{P=O}$), 1121 s, 847 w, 787 w, 757 w, 756 w, 726 s, 693 m, 602 w, 538 s. MS (MALDI-TOF): *m*/*z* 43 (M^+ − Br − Ph_3PO, 100%).

Synthesis of [Salophen(ᵗBu)Al{(PhO)$_3$PO)}$_2$]Br (7). To a rapidly stirred solution of salophen(ᵗBu)AlBr (0.68 g, 1.05 mmol) in toluene was added triphenyl phosphate (0.69 g, 2.11 mmol). The clear golden yellow solution was stirred at room temperature for 17 h. Concentration followed by slow evaporation at room temperature gave yellow crystals which were cannula filtered, washed with hexane, and dried under vacuum. Yield: 1.08 g (79%). Mp: 120−122 °C (dec). ^{1}H NMR ($CDCl_3$): δ 140 (s, 18H, C(CH_3)$_3$), 6.81−7.60 (m, 38H, Ph-*H*), 7.62 (d, 2H, Ph-*H*), 8.43 (s, 2H, N=C*H*). ^{13}C NMR ($CDCl_3$): δ 30.0 (C(CH_3)$_3$), 31.6 (C(CH_3)$_3$), 34.4 (C(CH_3)$_3$), 35.9 (C(CH_3)$_3$), 116.0 (Ph), 118.6 (Ph), 119.7 (Ph), 119.8 (Ph), 125.5 (Ph), 126.2 (Ph), 128.4 (Ph), 128.6 (Ph), 129.2 (Ph), 130.1 (Ph), 132.8 (Ph), 137.5 (Ph), 139.0 (Ph), 141.3 (Ph), 149.9 (Ph), 150.0 (Ph), 161.5 (Ph), 164.3 (N=*C*H). ^{27}Al NMR ($CDCl_3$): δ 12 ($W_{1/2}$ = 15053 Hz). ^{31}P{^{1}H} NMR($CDCl_3$): δ −21 (s). IR (KBR; ν in cm^{-1}): 2953 m, 2901 w, 2866 w, 1614 s, 1587 s, 1547 m, 1536 m, 1487 s, 1392 w, 1359 w, 1278 s ($\nu_{P=O}$), 1266 m, 1220 w, 1184 vs, 1163 s, 1029 s ((ν_{P-O}), 1078 m, 983 s, 848 w, 783 w, 753 m, 726 s, 686 w, 610 w, 523 w. MS (MALDI-TOF): *m*/*z* 843 (M^+ − Br − 2(PhO)$_3$PO, 100%).

Dealkylation of Phosphates. In a typical experiment salen(ᵗBu)-AlBr (30 mg, 0.05 mmol) was dissolved in 1 mL of $CDCl_3$ in a glass vial. The solution was transferred to an NMR tube in which trimethyl phosphate (1.96 μL, 0.017 mmol, density 1.197 g/mL) was added with a syringe. The mixture was shaken and monitored by ^{1}H NMR. The % dealkylation was calculated from the peak integrations of methyl bromide produced and unchanged phosphate.

Catalytic Dealkylation of Phosphate. In a typical experiment 15 mg (0.025 mmol) salen(ᵗBu)AlBr was dissolved in 1 mL of $CDCl_3$ in a glass vial. The solution was transferred to an NMR tube in which trimethyl phosphate (28.65 μL, 0.25 mmol, density 1.197 g/mL) and boron tribromide (0.25 mL, 0.25 mmol, 1 M solution in hexane) were added with a syringe. The mixture was shaken and monitored by ^{1}H NMR. The % dealkylation was calculated from the peak integrations of methyl bromide produced and unchanged phosphate.

Results and Discussion

Salen Aluminum Bromides. Compounds **1**−**3** were prepared by alkane elimination between diethyl aluminum bromide and Salen(ᵗBu)H_2 under reflux (Scheme 2). The compounds were isolated by removing the solvent under vacuum or by precipitation after concentration and cooling to −30 °C**.** All three compounds were soluble in chloroform. The ^{1}H NMR data were very close to the corresponding chloride analogues reported in the literature.[14] For example, the ^{1}H NMR data for all three compounds show two singlets for the ᵗBu−Ph groups in the range δ 1.30−1.63 ppm. For **1** and **2** there are multiple CH_2 peaks corresponding to the alkylene backbone protons from the ligand ranging from δ 2.23 to 3.97 ppm. There is only one imine singlet for each compound at δ 8.40, 8.29, and 8.94 ppm, respectively. Like their chloride analogues, these values decrease slightly with increasing backbone length from **1** to **2** and increase in **3** because of the greater electronegativity and deshielding effect of the aryl backbone compared to an alkyl backbone. The presence of only one set of ᵗBu peaks and one imine peak for each compound suggests a symmetric solution state structure.

The ^{27}Al NMR showed broad single peaks centered at δ 38, 36, and 32 ppm, respectively, for **1**−**3** which indicate the presence of five-coordinate aluminum. However, these are shifted upfield from the related chloride analogues (δ 57, 43, 52 ppm, respectively).[14] This is in accordance with the lower electronegativity of Br compared to Cl and hence more shielding of the Al center.

The mass spectra (EI) of **1** and **3** contained molecular ion peaks in low abundance. All three compounds had a peak corresponding to the molecular ion minus bromide, and for **1** and **2** this was the most abundant peak. Compounds **1** and **3** also had peaks corresponding to molecular ion minus bromide and one oxygen, and for **3** this was the most abundant peak. It was interesting to note that the loss of bromide occurred and not the loss of ᵗBu from the ligand. This might provide some indication of the relative weakness of the Al−Br bond in the compounds.

The X-ray crystal structures of **1**−**3** confirmed the presence of five-coordinate aluminum atoms (Figures 1−3). The crystal

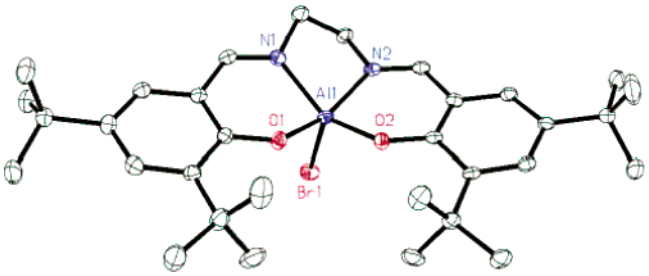


Figure 1. Crystal structure of salen(ᵗBu)AlBr **(1)**.

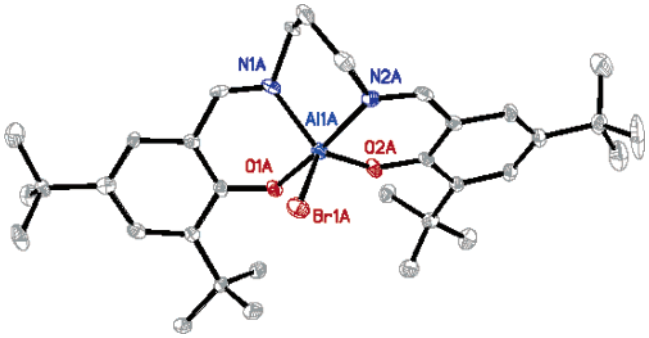


Figure 2. Crystal structure of salpen(ᵗBu)AlBr **(2)**. There are two molecules in the asymmetric unit; only one is shown.

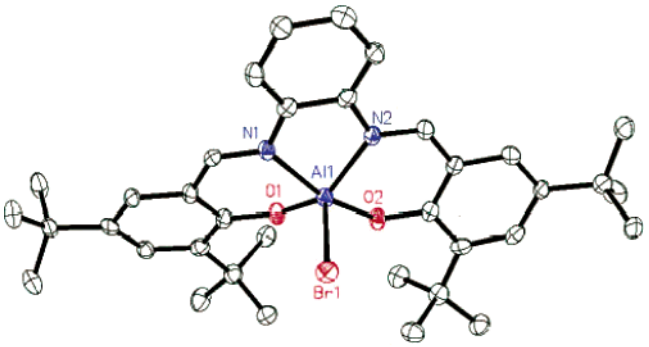


Figure 3. Crystal structure of salophen(ᵗBu)AlBr **(3)**.

data collection parameters are listed in Supporting Information Table S1, and selected bond lengths and angles in Table S2. The Al−Br bond lengths fall in the range 2.35−2.36 Å, which are longer than the Al−Cl bond length (∼2.18 Å) in Salen-(ᵗBu)AlCl compounds.[7] The Al−N bond lengths (∼1.96−2.02 Å) are marginally longer than the Al−O bond lengths (∼1.76−1.81 Å). The geometries of these compounds are close to either square pyramidal or trigonal bipyramidal depending on the ligand backbone. Salen and salophen have rigid backbones and favor a square pyramidal geometry, while salpen with a longer, flexible, propylene backbone favors a tbp geometry around the aluminum. A similar trend was observed previously in the case of Salen aluminum alkyl, chloride, and siloxide compounds.[7,19,20]

A quantitative measure, expressed as the "τ value", can be used to describe the distortion from perfectly sqp or tbp geometry in these compounds (Figure 4).[21] A perfectly sqp geometry has a τ value equal to zero whereas a perfectly tbp geometry has a τ value equal to 1. In Table 1 the calculated τ values for compounds **1**−**3**, along with some previously

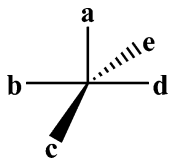
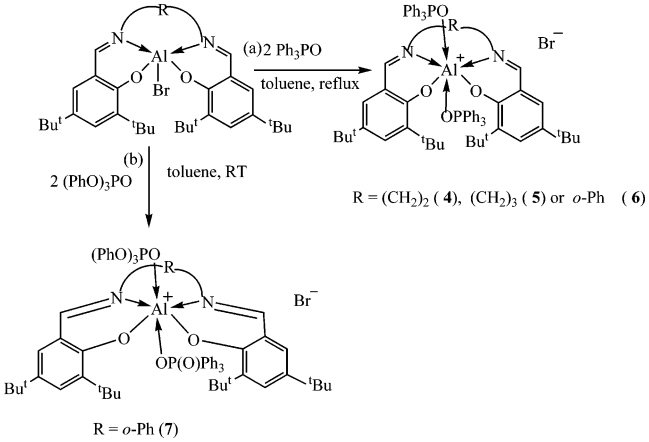


Figure 4. τ diagram. $\tau = (\alpha - \beta)/60$. α (c−e) and β (b−d) are the angles opposite to each other in the *xy* plane, where a is along the *z*-axis. By convention β is the most obtuse angle.

Table 1. τ Values of Salen Aluminum Halide Compounds

compd	τ value	ref
salpen(ᵗBu)AlCl	0.77	7
salomphen(ᵗBu)AlCl	0.18	7
salen(ᵗBu)AlBr (**1**)	0.20	this work
salpen(ᵗBu)AlBr (**2**)	0.77	this work
salophen(ᵗBu)AlBr (**3**)	0.32	this work

Scheme 3. Formation of Six-Coordinate Aluminum Cations from Salen(ᵗBu)AlBr Compounds



described five-coordinate Salen aluminum chloride compounds, are listed. Compounds **1** and **3** have τ values close to 0 indicative of a distorted sqp geometry, whereas **2** has a τ value close to 1 indicating a distorted tbp geometry. This value may be important in determining the accessibility of a sixth coordination site.[22]

Six-Coordinate Aluminum Cations. Four cationic compounds, [salen(ᵗBu)Al($Ph_3PO)_2$]Br (**4**), [salpen(ᵗBu)Al($Ph_3PO)_2$]Br (**5**), [salophen(ᵗBu)Al($Ph_3PO)_2$]Br (**6**), and [salophen(ᵗBu)Al{$(PhO)_3PO)\}_2$]Br (**7**), were formed by displacement of the bromide from compounds **1**−**3** with either triphenylphosphine oxide or triphenyl phosphate (Scheme 3). Similar cationic compounds were formed previously from Salen(ᵗBu)AlCl with H_2O, THF, or MeOH.[2,23] Salen aluminum chlorides do not form cations with triphenylphosphine oxide, which confirms the value of the SalenAlBr compounds in making new cations. Triphenylphosphine oxide was also found to form [Me_2Al-$(OPPh_3)_2$]Br from Me_2AlBr.[24] However, it was not a strong enough base to displace chloride from Me_2AlCl even under reflux. Instead, the adduct Me_2AlCl·$OPPh_3$ formed.

The ^{1}H NMR spectra of **4**, **6**, and **7** show two peaks for the ᵗBu groups of the ligand with each peak corresponding to 18 protons. Interestingly, for **5**, there is only one ᵗBu peak with 36 protons. This could be attributed to the shielding of the *ortho*-

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^{t}Bu group of the ligand due to the ring current of the phenyl groups of triphenylphosphine oxide. This shielding causes an upfield shift of the ^{t}Bu group thus superimposing it on the peak of the other.[25] In the aromatic regions there are overlapping peaks due to the phenyl groups from both the ligands and triphenylphosphine oxide or triphenyl phosphate. The ^{27}Al NMR shows very broad peaks at δ −6, 0, and 12 ppm for **4**, **5**, and **7**, respectively. These correspond to the presence of six-coordinate aluminum.[26] However, for **6** this value is δ 42 ppm, which is more likely to be the shift of a five-coordinate aluminum atom.[14] Thus, the solution product for **6** appears to be different from the solid-state structure found in the X-ray crystal studies where the aluminum atom is six-coordinate (see next paragraph). One possible explanation could be that one of the two loosely bound triphenylphosphine oxide ligands dissociates in the polar NMR solvent ($CDCl_3$) making the aluminum five-coordinate. The ^{31}P NMR spectra of **4**−**6** show peaks at δ 34, 35, and 33 ppm, respectively. These are downfield from the NMR shift of δ 29 ppm of free triphenylphosphine oxide[27] because of deshielding of the phosphorus due to coordination of the phosphoryl group with aluminum. However, for **7** this shift is δ −21 ppm which is slightly upfield from the shift of −18 ppm of free triphenyl phosphate.[27] The IR spectrum shows strong P═O absorption at 1173, 1162, 1172, and 1278 cm^{-1} for **4**−**7**, respectively. For **7**, the stretching of the P−O bond of the P−O−C linkage of the phosphate gives rise to a strong band at 1029 cm^{-1}. In the mass spectra (EI) of the six-coordinate aluminum compounds no parent ion or parent ion minus bromide ion was observed. However, all the compounds show peaks corresponding to parent ion minus the bromide and two triphenylphosphine oxide or triphenyl phosphate moieties in high abundance. This indicates the weak coordination between the Lewis base and the aluminum.

Compounds **5**−**7** were structurally characterized by single-crystal X-ray diffraction. The data collection parameters are contained in Supporting Information Table S3, while Table S4 lists selected bond lengths and angles. Their structures consist of a central six-coordinate aluminum atom in a distorted octahedral geometry (Figures 5−7). The ligand occupies four equatorial positions, and two phosphine oxide or phosphate molecules occupy the two axial positions. The equatorial bond angle is larger for O−Al−O (∼89.38−96.1°) compared to N−Al−N (∼80.7−90.85°). This is a reflection of the steric restrictions of the ligand creating a more "open" front for the compound. The axial O−Al−O bond angles are distorted (∼169.1−174.6°) from ideal linearity. The amount of distortion is more for the phosphine oxide compounds **5** and **6** compared to the phosphate compound **7**. This is probably due to the fact that the P−O−Ar linkage in **7** allows the bulky phenyl group to move away from the equatorial ligand atoms and thus avoid steric congestion. The axial Al−O distances (∼1.92−1.97 Å) are longer than the equatorial Al−O distances (∼1.79−1.84) due to the greater steric requirements of the axial groups.

Dealkylation of Organophosphates. Organophosphate esters are found in both nerve gas agents and pesticides. The breaking of the P−O−C linkages may be a means of deactivating these toxic agents.[28,29] Although extensive research is being carried out on phosphate ester cleavage using various metal compounds in models of biological phosphate hydrolysis,[30−32] the use of group 13 compounds in this field is limited. For example, some phosphate cleavage has been achieved with organo-aluminum reagents[33] and aluminum or gallium amides.[34−36] However, these reagents have not been considered as potential nerve agent or pesticide decontamination reagents, probably due to their limited scope or the high temperature and the long reaction time required. Recently the use of boron-Schiff base halides has shown promise for the catalytic cleavage of various organophosphates at room temperature, opening the possibility

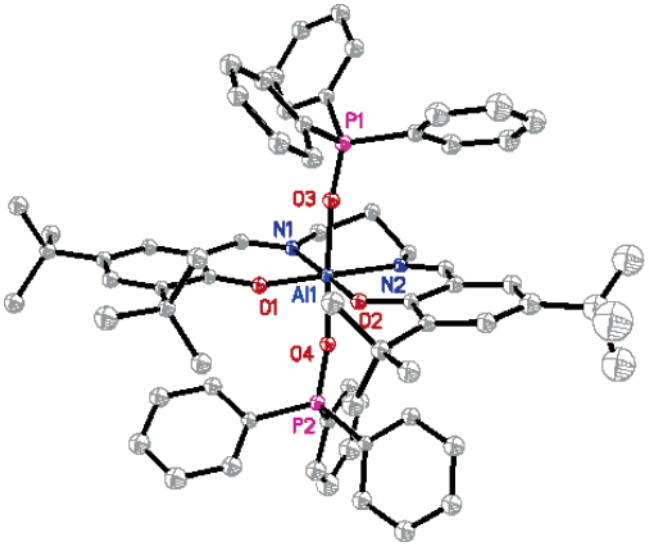

Figure 5. Crystal structure of [salpen(^{t}Bu)Al($Ph_3P(O)_2$]Br **(5)**.

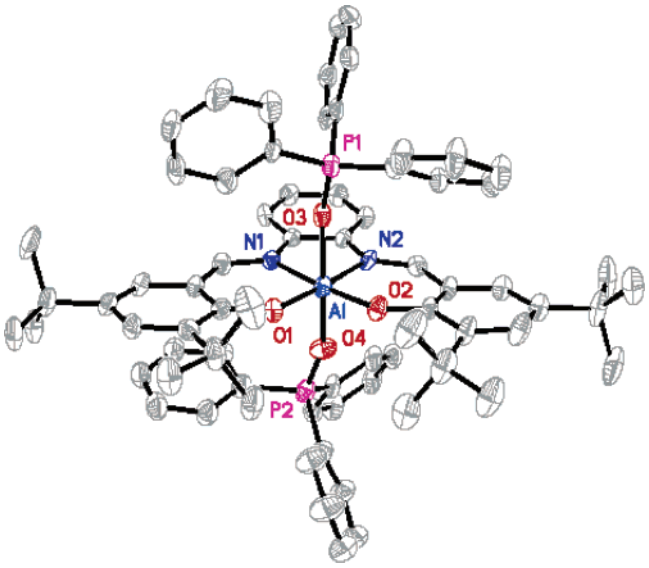

Figure 6. Crystal structure of [salophen(^{t}Bu)Al($Ph_3PO)_2$]Br **(6)**.

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(36) Pinkas, J.; Loebl, J.; Dastych, D.; Necas, M.; Roesky, H. W. *Inorg. Chem.* **2002**, *41*, 6914−6918.

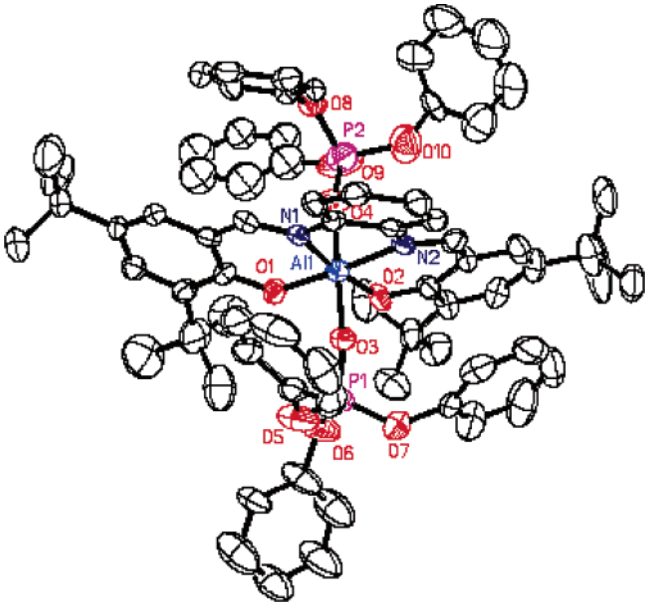
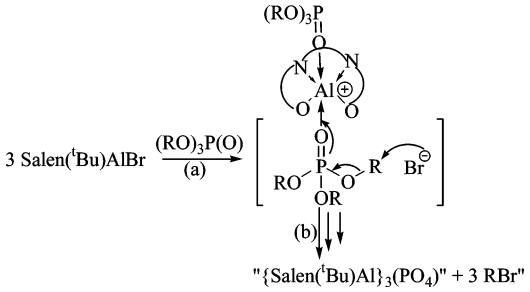


Figure 7. Crystal structure of [salophen(ᵗBu)Al{$(PhO)_3PO_2$}]Br **(7)**.

Scheme 4 Plausible Dealkylation Pathway of Organophosphates with Salen((ᵗBu)AlBr Compounds



of finding a soft, chemical, catalytic means of destroying nerve gas agents and pesticides.[37−39]

Compounds salen(ᵗBu)AlBr (**1**), salpen(ᵗBu)AlBr (**2**), and salophen(ᵗBu)AlBr (**3**) dealkylated a series of organophosphate compounds at room temperature to produce methyl bromide and an unidentified aluminum phosphate compound that remained in solution (Scheme 4). The dealkylation reaction was carried out in an NMR tube in $CDCl_3$. The percent conversion was calculated from the integration of the remaining phosphate and the methyl bromide produced (Table 2). The percent dealkylation was comparable to the binuclear boron Salen bromide compounds Salen(ᵗBu)$[BBr_2]_2$ reported before.[37−39] For trimethyl phosphate, compound **1**, having an ethylene backbone, showed greater dealkylation compared to **2** which has a propylene backbone and **3** which has an aromatic backbone. For example, with **1** the dealkylation was 89% complete in just 4 h and 96% complete after 12 h. However, the difference in Salen ligand backbone does not seem to affect the dealkylation of longer chain phosphates. Another interesting observation is that the percent dealkylation was greater for longer chain phosphates compared to those with shorter chains. For example, with **2**, dealkylation was complete in 2 h for triethyl phosphate and in 30 min for tributyl phosphate, as opposed to only 30% conversion for trimethyl phosphate after 2 h.

Table 2. Dealkylation (%)[a] of Organophosphates with Compounds **1**−**3**

	1			**2**			**3**		
time	TMP	TEP	TBP	TMP	TEP	TBP	TMP	TEP	TBP
30 min	64	14	12	35	75	7	18	7	100
2 h	79	100	100	44	100	100	30	100	
4 h	89			44			40		
6 h	91			56			46		
8 h	93			58			58		
10 h	95			62			64		
12 h	96			67			69		
24 h	96			69			85		

[a] Calculated from the integration of ^{1}H NMR spectra of methyl bromide produced and unchanged trimethyl phosphate at room temperature in $CDCl_3$. In CD_3OD after 24 h **1** showed no dealkylation while **2** and **3** had 4% and 3% dealkylation, respectively. Salen(ᵗBu)AlCl showed 55% dealkylation of TMP in $CDCl_3$ after 24 h. TMP = trimethyl phosphate, TEP = triethyl phosphate, and TBP = tributyl phosphate.

Table 3. Catalytic Dealkylation (%) of Trimethyl Phosphate (TMP) with Salen(ᵗBu)AlBr Compounds[a]

time	**1** + TMP + BBr_3 (1:10:10)	**2** + TMP + BBr_3 (1:10:10)	**3** + TMP + BBr_3 (1:10:10)	TMP + BBr_3 (1:1)
30 min	88	78	82	58
2 h	100	92	84	67
6 h	100	100	95	67
24 h	100	100	95	81

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

Previously, it was shown that Salen(ᵗBu)AlCl compounds readily formed cations through the replacement of chloride by a donor ligand like THF, MeOH, or H_2O.[2,9,11,23,40,41] Cation formation should be more favorable for the Salen bromide compounds because bromide is a better leaving group due to the weaker Al−Br bond (bond energy: 430 kJ mol^{-1} for Al−Br vs 511 kJ mol^{-1} for Al−Cl). As noted previously in this work, cations are readily formed when SalenAlBr compounds are combined with triphenylphosphine oxide and triphenyl phosphate. Cation formation was also observed for Salen boron bromide compounds with THF.[39] Thus, it is likely that compounds **1**−**3** form cations through coordination of the Lewis basic phosphate to the aluminum with displacement of the bromide anion. This activates the α-carbon of the phosphate for nucleophilic attack of the bromide (Scheme 4). A similar activation of an ester carbon due to coordination of the phosphoryl oxygen to a cationic center was reported before.[42] The cation formation is followed by attack of the bromide on the methyl group and elimination of methyl bromide. Ultimately, all three ester bonds are cleaved to produce an unidentified phosphate material "[$(SalenAlO)_3PO$]". This mechanism is supported by the following observations:

(i) There is little dealkylation in CD_3OD (Table 2). Methanol is a stronger Lewis base than trimethyl phosphate, and although a cation is formed,[23] the phosphate cannot replace the CD_3OD to become activated. (ii) The dealkylation with salen(ᵗBu)AlCl (55% after 24 h, Table 2) is much less compared to the bromide

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analogue. The Al−Cl bond is stronger than Al−Br bond, which impedes the replacement of chloride with the phosphate and hence the required cation formation. (iii) The triphenyl phosphate coordinated cationic compound **7** was structurally characterized. Salen aluminum halide compounds do not dealkylate triphenyl phosphate. No dealkylation was also found with Salen boron bromide compounds.[39] The reaction stops at the formation of the phosphate coordinated cation. (iv) The postulate that the bromide attacks the ester carbon instead of the phosphorus is in agreement with the previous findings that, for cleavage of phosphate esters in solution, nucleophiles with a high charge density, such as, hydroxides and alkoxides, preferentially attack the phosphorus whereas more polarizable nucleophiles such as bromide or iodides attack the carbon.[42,43]

The dealkylation reaction with the Salen(^{t}Bu)AlBr compounds was found to be catalytic in the presence of excess BBr_3 (Table 3). With BBr_3 only, the dealkylation of trimethyl phosphate is low. However, compounds **1**−**3** in only 10 mol % with BBr_3 dramatically increased the dealkylation. For example, with **1** the reaction was 100% complete within only 2 h. Although detailed mechanistic studies are still under progress, it is likely that BBr_3 regenerates the Salen aluminum bromide compound from the dealkylated phosphate material allowing the repetition of the catalytic cycle.

Conclusion

Three new five-coordinate aluminum bromides salen(^{t}Bu)-AlBr (**1**), salpen(^{t}Bu)AlBr (**2**), and salophen(^{t}Bu)AlBr (**3**) have been synthesized and fully characterized. These compounds readily formed six-coordinate aluminum cations when combined with triphenylphosphine oxide or triphenyl phosphate. The Salen(^{t}Bu)AlBr compounds dealkylated a series of trialkyl phosphates in high percent conversion, and the reaction was catalytic in the presence of excess boron tribromide. The phosphates used in this study could be envisioned as model compounds for organophosphate chemical warfare agents and pesticides. Thus, the compounds could be developed into potential nerve gas and pesticide decontamination agents. Attempts to experimentally prove the proposed mechanistic pathway and isolation and full characterization of the dealkylated products are in progress and will be published in due course.

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Supporting Information Available: Crystal data collection parameters (Tables S1 and S3), selected bond lengths and angles (Tables S2 and S4), and CIF files for compounds **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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