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# Aluminum Phosphinate and Phosphates of Salen Ligands

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A new dealkylation reaction between organophosphate esters and Salen aluminum bromide compounds has been used to prepare three new aluminum salen compounds salen($^t$Bu)AlOP(O)$Ph_2$ (**1**) (salen = *N,N′*-ethylenebis(3,5-di-*tert*-butylsalicylideneimine)), [(MeOH)Alsalen($^t$Bu){OMe$PO_2$(O)}Alsalen($^t$Bu){OMe$PO_2$(O)}Alsalen($^t$Bu)]Br (**2**), and [salpen($^t$Bu)AlO]$_2$[(BuO)$_2$PO]$_2$ (**3**) (salpen = *N,N′*-propylenebis(3,5-di-*tert*-butylsalicylideneimine)). Compounds **1·MeOH**, **2**, and **3** were characterized by single-crystal X-ray diffraction. Compound **1** is the first example of a monomeric aluminum Schiff base phosphinate. Compound **2** is a cationic Salen aluminum phosphate, and compound **3** contains an aluminophosphate ring. This work is the first example of the intentional use of an aluminum-based dealkylation reaction to form new compounds.

## Introduction

Group 13 phosphates and phosphonates are of potential utility in areas such as catalysis, molecular sieves, ion-exchange resins, and adsorption media.[1−3] Aluminophosphate molecular sieves[4] have traditionally been prepared by hydrothermal synthetic methods at temperatures between 100 and 200 °C where a source of aluminum, e.g., Al(O$^i$Pr)$_3$, is combined with aqueous $H_3PO_4$.[5,6] The nonaqueous preparation of aluminum phosphate molecules and materials has recently been discovered.[7−10]

The syntheses of molecular aluminophosphates by a dealkylation reaction between aluminum amides and phosphoric acid triesters, and also by a dealkylsilylation reaction between aluminum chloride and OP(OSiMe$_3$)$_3$ have been reported.[7] Also, aluminum trialkyls undergo adduct formation and subsequent dealkylsilylation to produce molecular aluminophosphates.[8] Most of the aluminophosphate molecules and materials contain four-coordinate aluminum.[11] There are relatively few higher-coordinate aluminum compounds bound to either a phosphate, phosphonate, or phosphinate. One such example is [Al(O$^i$Pr)$_2$O$_2$P(O$^t$Bu)$_2$]$_4$ where the aluminum atom is five-coordinate.[12] Group 13 molecular phosphates and phosphinates are predominantly dimeric, and almost all of them have four-coordinate aluminum.

Previously, we reported that six-coordinate aluminum phosphinates may be readily obtained in combinations with the tetradentate Salen class of ligand.[13,14] In these chelated phosphinates, [Salen($^t$Bu)AlO$_2$P(H)Ph]$_n$, the degree of aggregation may be manipulated by changing the length of the ligand "backbone". Some of the compounds revealed unique coupling of the Salen ligand with THF. Recently, our group has been studying the cleavage of organophosphate esters with group 13 Schiff base chelates,[15−18] and one of our goals has been to elucidate the structures of the dealkylated

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products resulting from the dealkylation reaction. This paper reveals for the first time the use of Salen aluminum compounds for the dealkylation of phosphinates and phosphates at room temperature in an organic solvent to prepare soluble monomeric aluminum phosphates and phosphinates with five- and six-coordinate aluminum.

## Experimental Section

All air-sensitive manipulations were conducted using standard benchtop Schlenk line techniques in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. All glassware was cleaned and dried in an oven at 130 °C for at least 12 h prior to use. The compounds salen($^t$Bu)AlBr and salpen($^t$Bu)AlBr were prepared according to the literature method.[18] All other chemicals were purchased from Sigma-Aldrich. NMR data were obtained on Varian Gemini-200 and Varian VXR-400 instruments. Chemical shifts are reported relative to $SiMe_4$ for $^1H$ and $^{13}C$, 85% $H_3PO_4$ for $^{31}P$, 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. Thermogravimetric analyses were performed on a TA Instruments Hi-Res TGA 2950 Analyzer. Elemental analyses were performed on a LECO CHN-2000 Analyzer.

X-ray data were collected on either a Bruker-Nonius X8 Proteum diffractometer (**1**; Cu K$\alpha$ radiation) or a Nonius Kappa-CCD (**2** and **3**; Mo K$\alpha$ radiation). All calculations were performed using the software package SHELXTL-Plus.[19,20] 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 with anisotropic thermal parameters. The hydrogen atoms were included using a riding model with isotropic parameters tied to the parent atom. Crystallographic data for **1**, **2**, and **3** were deposited with the Cambridge Crystallographic Data Center (CCDC reference numbers: 267092, 269612, and 290877, respectively) and copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

**Synthesis of salen($^t$Bu)AlOP(O)Ph$_2$ (1).** To a rapidly stirred solution of salen($^t$Bu)AlBr (0.50 g, 1.77 mmol) in toluene $Ph_2P(O)OMe$ (0.197 g, 0.85 mmol) was added. The reaction mixture was stirred for 24 h and then refluxed for 17 h. It was then cannula filtered, and the resulting pale yellow residue was dried under vacuum. Yield: 0.400 g (65.0%). mp: 302−304 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.29 (s,18H, C(C$H_3$)$_3$), 1.59 (s,18H, C(C$H_3$)$_3$), 3.64 (m, 2H, NC$H_2$), 4.40 (m, 2H, NC$H_2$), 6.90 (d, 2H, Ph−$H$), 6.99 (m, 5H, Ph−$H$)7.26 (d, 2H, Ph-$H$), 7.52 (m, 5H, Ph-$H$) 8.17 (s, 2H, N=C$H$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 29.7 (C($C$H$_3$)$_3$), 31.3 (C($C$H$_3$)$_3$), 33.9 ($C$CH$_3$)$_3$), 35.6 ($C$CH$_3$)$_3$), 54.7 (N$C$H$_2$), 118.3 (Ph), 127.2 (Ph), 127.4 (Ph), 127.5 (Ph), 129.9 (Ph), 130.8 (Ph), 130.9 (Ph), 131.1 (Ph), 138.4 (Ph), 140.5 (Ph), 162.8 (Ph), 170.3 (N = $C$H); $^{27}Al$ NMR ($CDCl_3$): $\delta$ 30 ($W_{1/2}$ = 1951 Hz). $^{31}P\{^1H\}$ NMR($CDCl_3$): $\delta$ 35. IR (cm$^{-1}$): 3053 (w), 2955s, 2905m, 2858w, 1643s, 1625s, 1547w, 1536w, 1478m, 1468m, 1441m, 1390m, 1359m, 1259m, 1176s, 1131m, 1071w, 1025, 857w, 847m, 786w, 753m, 726m, 700m, 605m, 555m. MS (EI, positive): 734(M$^+$, 17%), 677 (M$^+$ − $^t$Bu, 100%), 517 (M$^+$ − Ph$_2$P(O)O, 8%). Anal. Calcd for $C_{44}H_{56}O_4N_2Al$: C 71.91, H 7.68, N 3.81. Found: C 71.40, H 8.18, N 3.57.

**Synthesis of [(MeOH)Alsalen($^t$Bu){OMePO$_2$(O)}Alsalen($^t$Bu)-{OMePO$_2$(O)}Alsalen($^t$Bu)]Br (2).** To a rapidly stirred solution of salen($^t$Bu)AlBr (0.62 g, 1.05 mmol) in toluene $(MeO)_3PO$ (0.062 g, 0.44 mmol) was added. The reaction mixture was stirred for 7 d. After concentration to about one-third of its volume and cooling for several days at −30 °C, yellow crystals precipitated which were filtered, washed with hexane, and dried under vacuum. Yield: 0.34 g (54.3%). mp: 284 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.30 (s, C(C$H_3$)$_3$), 1.43 (s, C(C$H_3$)$_3$), 2.1 (d, $^3J_{PH}$ = 12.2 Hz, OC$H_3$), 2.91 (d, $^3J_{PH}$ = 11.6 Hz, OC$H_3$), 3.76 (m, NC$H_2$), 7.11−7.18 (m, Ph−$H$), 7.48 (s, br, Ph−$H$) 8.35 (s, br, N=C$H$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 29.6 (C($C$H$_3$)$_3$), 30.0 (C($C$H$_3$)$_3$), 31.3 (C($C$H$_3$)$_3$), 31.4 (C($C$H$_3$)$_3$), 34.0 ($C$CH$_3$)$_3$), 35.5 ($C$CH$_3$)$_3$), 53.1 (O$C$H$_3$, $^2J_{POC}$ = 27.4 Hz), 53.9 (O$C$H$_3$), 54.4 (N$C$H$_2$), 118.3 (Ph), 127.5 (Ph), 127.8 (Ph), 130.4 (Ph), 130.6 (Ph), 130.9 (Ph), 131.1 (Ph), 138.9 (Ph), 139.9 (Ph) 140.5 (Ph), 162.6 (Ph), 171.5 (N = $C$H); $^{27}Al$ NMR ($CDCl_3$): $\delta$ −1 ($W_{1/2}$ = 8701 Hz). $^{31}P\{^1H\}$ NMR($CDCl_3$): $\delta$ −13 (s), −21 (s). IR (cm$^{-1}$): 3053w, 2956s, 2909m, 2869w, 1642s, 1625vs, 1547w, 1537w, 1478w, 1469w, 1444m, 1391m, 1360s, 1257m, 1236w, 1178m, 1139w, 1058w, 1025, 861w, 843m, 788w,756m, 726m, 607m, 587vw. MS (MALDI-TOF): 1644 (M$^+$ − Br − $^t$Bu, 17%), 1608 (M$^+$ − Br − 2$^t$Bu, 10%), 1160 (M$^+$ − salen($^t$Bu)Al − 3CH$_2$, 100%). Anal. Calcd for $C_{101}H_{153}O_{16}N_6Al_3P_2Br$: C 62.85, H 7.99, N 4.35. Found: C 64.12, H 6.36, N 4. 50.

**Synthesis of [salpen($^t$Bu)AlO]$_2$[(BuO)$_2$PO]$_2$ (3).** To a rapidly stirred solution of salpen($^t$Bu)AlBr (0.83 g, 1.35 mmol) in toluene $(BuO)_3PO$ (0.13 g, 0.47 mmol) was added. The yellow reaction mixture was stirred for 48 h. After filtration and concentration to about one-third of its volume and cooling for several days at −30 °C, yellow crystals precipitated which were filtered, washed with ether (twice) and hexane, and dried under vacuum. Yield: 0.35 g (100%). mp: softens at 196 °C and melts at 236−238 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 0.65 (m, phosphate CH$_2$CH$_2$CH$_2$C$H_3$), 0.89 (m, phosphate CH$_2$CH$_2$CH$_2$C$H_3$), 1.30 (s, C(C$H_3$)$_3$), $\delta$ 1.32 (s, br, phosphate CH$_2$CH$_2$C$H_2$CH$_3$ and C(C$H_3$)$_3$), 1.41 (s, C(C$H_3$)$_3$), 1.46 (s, br, phosphate CH$_2$C$H_2$CH$_2$CH$_3$ and C(C$H_3$)$_3$), 2.1 (m, CH$_2$C$H_2$-CH$_2$), 3.4 (m, phosphate C$H_2$CH$_2$CH$_2$CH$_3$), 3.72 (m, NC$H_2$), 7.20−7.54 (m, Ph−$H$), 8.41 (s, br, N=C$H$), 8.50 (s, br, N=C$H$); $^{13}C$ NMR ($CDCl_3$, 200 MHz): $\delta$ 13.6 (phosphate CH$_2$CH$_2$CH$_2$$C$H$_3$), 18.3 (phosphate CH$_2$CH$_2$$C$H$_2$CH$_3$), 27.2 ($C$H$_2$), 29.6 (C($C$H$_3$)$_3$), (29.8 (C($C$H$_3$)$_3$), 31.5 (C($C$H$_3$)$_3$), 31.6(C($C$H$_3$)$_3$), 31.9 (phosphate CH$_2$$C$H$_2$CH$_2$$C$H$_3$), 34.2 ($C$CH$_3$)$_3$), 34.3 ($C$CH$_3$)$_3$), 35.5 ($C$CH$_3$)$_3$), 55.1 (N$C$H$_2$), 67.8 ($C$H$_2$CH$_2$CH$_2$$C$H$_3$), 118.4 (Ph), 125.6 (Ph), 126 (Ph), 128.1 (Ph), 128.5 (Ph), 129.3 (Ph), 131.4 (Ph),139.4 (Ph), 140.6 (Ph), 166.9 (Ph), 172.0 (N = $C$H);$^{27}Al$ NMR ($CDCl_3$): $\delta$ −5 ($W_{1/2}$ = 997 Hz), 40 ($W_{1/2}$ = 3704 Hz). $^{31}P\{^1H\}$ NMR-($CDCl_3$): $\delta$ −18 (s). IR $\nu$/cm$^{-1}$: IR $\nu$/cm$^{-1}$: 2957s, 2906s, 2870m, 1620s, 1547m, 1479s, 1467s, 1442s, 1418s, 1391m, 1361m, 1342w, 1326w, 1312w, 1271s, 1259s, 1236m, 1201m, 1174s, 1091w, 1068w, 1028w, 860w, 847m, 786w, 751w, 599w, 568w. MS (MALDI-TOF): 1272 (M$^+$ − (BuO)$_2$PO$_2$, 1.9%), 531 (M$^+$ − 2(BuO)$_2$PO$_2$, 100%). Anal. Calcd for $C_{82}H_{132}O_{12}N_4Al_2P_2$: C 66.46, H 8.98, N 3.78. Found:C 65.85, H 9.66, N 4.15.

## Results and Discussion

Compound **1** was prepared by dealkylation by salen($^t$Bu)-AlBr of methyl diphenyl phosphinate by stirring in toluene at room temperature (Figure 1). Compound **1** was soluble in the organic solvents toluene and chloroform. It was fully

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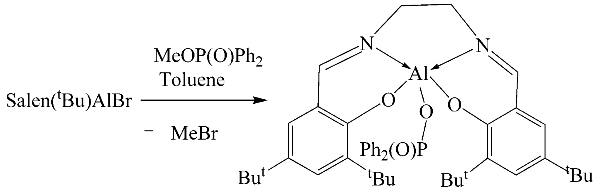

**Figure 1.** Synthesis of Salen aluminum phosphinate (**1**).

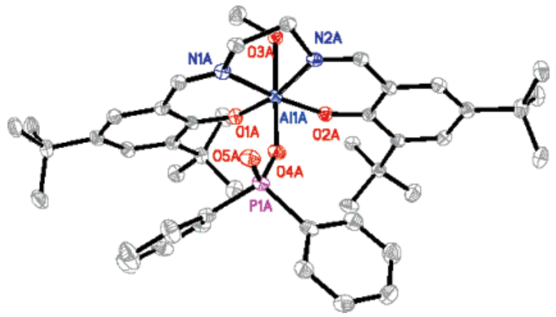

**Figure 2.** Crystal structure of **1·MeOH** (hydrogen atoms are omitted for clarity).

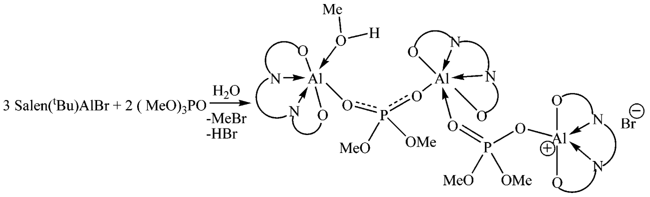

**Figure 3.** Synthesis of compound **2**.

characterized using $^1$H, $^{13}$C, $^{27}$Al, and $^{31}$P NMR, IR, and MS (EI, positive). The $^1$H NMR spectrum of **1** was very close to the corresponding chloride analogues reported in the literature[21] and also the bromide starting materials.[18] There are two singlets for the $^t$Bu−Ph groups at $\delta$ 1.29 and 1.58. Two methylene peaks corresponding to the ethylene backbone protons from the ligand appear at $\delta$ 3.64 and 4.40. There is only one imine singlet at $\delta$ 8.17. The $^{27}$Al NMR showed a broad peak centered at $\delta$ 30 for five-coordinate aluminum, which is similar to the shift observed in many other five-coordinate aluminum Salen compounds (e.g., Salen($^t$Bu)AlOSiMe$_3$ ($\delta$ 30.5) and Salen($^t$Bu)AlN$_3$ ($\delta$ 31.9)).[22] However, this is upfield from the related chloride analogue ($\delta$ 57).[21] The $^{31}$P{H} NMR of **1** contained a single peak at $\delta$ 35. Interestingly, this is considerably downfield compared to dimeric or polymeric Salen aluminum phosphinates ($\delta$ 7.08−9.16).[14]

Compound **1** was recrystallized by slow evaporation of a methanol solution at room temperature under atmospheric conditions to produce **1·MeOH**. The compound was stable in the atmosphere, and no nucleophilic displacement of the phosphinate group by methanol or atmospheric moisture was observed. The molecular structure is shown in Figure 2. There are two molecules in the asymmetric unit; only one is shown in the figure. Previously, the only structurally characterized examples of Salen aluminum phosphinate compounds were polymeric [Salen($^t$Bu)Al{O$_2$P(H)Ph}]$_n$ ($n = \infty$) for salen, salophen, and salomphen and dimeric ($n$ = 2) for salpen and salben.[13,14] In these compounds, two phosphinate groups bridge between the Salen($^t$Bu)Al units. They were synthesized by alkane elimination between Salen($^t$Bu)Me and phenyl phosphinic acid, Ph(H)P(O)OH, and some of the compounds revealed unique coupling of the Salen ligand with THF. Typically, the Salen ligands are not so readily derivatized. Compound **1·MeOH** is the first example of a structurally characterized monomeric aluminum phosphinate compound bound by a Salen ligand. The aluminum atom has a six-coordinate distorted octahedral environment with MeOH and the phosphinate group at the axial positions. The O3−Al−O4 angle is nearly linear (~175°). The Al−O−P linkage is bent with a bond angle of 151°, which is considerably narrower than the Al−O−P angle (~159°) in [Salen($^t$Bu)Al{O$_2$P(H)Ph}]$_\infty$.[14] The Al−O (ligand) bond distances (~1.80−1.81 Å) are marginally shorter than the Al−O(P) bond distance (~1.87 Å).

The reaction of salen($^t$Bu)AlBr and trimethyl phosphate after stirring in toluene for 7 days at room temperature gave **2** (Figure 3), which could be isolated as yellow crystals after concentration and filtration of the reaction mixture followed by cooling. Compound **2** is a trimetallic cation with three salenAl units connected by phosphate linkages. It is soluble in the organic solvents toluene and chloroform. It was characterized by IR, $^1$H NMR, $^{27}$Al NMR, $^{31}$P NMR, mp, and MS. The $^1$H and $^{13}$C NMR contain peaks corresponding to salen($^t$Bu) units and phosphate methoxy groups. Interestingly, there are two $^{31}$P peaks at $\delta$ −13 and −21. These shifts are close to that of other bridging phosphate compounds. For example, the $^{31}$P shift in Mg$_2$(XDK)DPP(CH$_3$OH)$_3$(H$_2$O)(NO$_3$) (H$_2$XDK = *m*-xylenediaminebis (Kemp's triacid imide), HDPP = diphenyl phosphate) is $\delta$ −15.46[23] and in Me$_2$AlO$_2$P(O$^t$Bu)$_2$]$_2$ is $\delta$ −22.57.[12] The two $^{31}$P peaks imply different shielding environments for the two phosphorus atoms. There is only one very broad $^{27}$Al NMR peak at $\delta$ −1, which confirms the presence of a six-coordinate aluminum atom. Surprisingly, another aluminum peak for the five-coordinate aluminum was not observed in the $^{27}$Al NMR. It is possible that it was overshadowed by the broad six-coordinate aluminum peak. Interestingly, one methanol molecule was coordinated to one of the aluminum atoms. The formation of methanol in the reaction system could occur by adventitious hydrolysis of the reaction byproduct methyl bromide.

The X-ray crystal structure of **2** (Figure 4) reveals three aluminum salen units connected by two phosphate groups. The compound is monocationic with two six-coordinate and one five-coordinate aluminum atom. The phosphate groups are monodealkylated with two methoxy groups attached to each phosphorus atom. It is interesting to note that out of the four P−O bonds around P1P, P1P−O1P (1.476(3) Å) and P1P−O2P (1.480(3) Å), have bond lengths close to a phosphorus−oxygen double bond; the other two P−O bonds, P1P−O3P and P1P−O4P, are longer and their bond lengths

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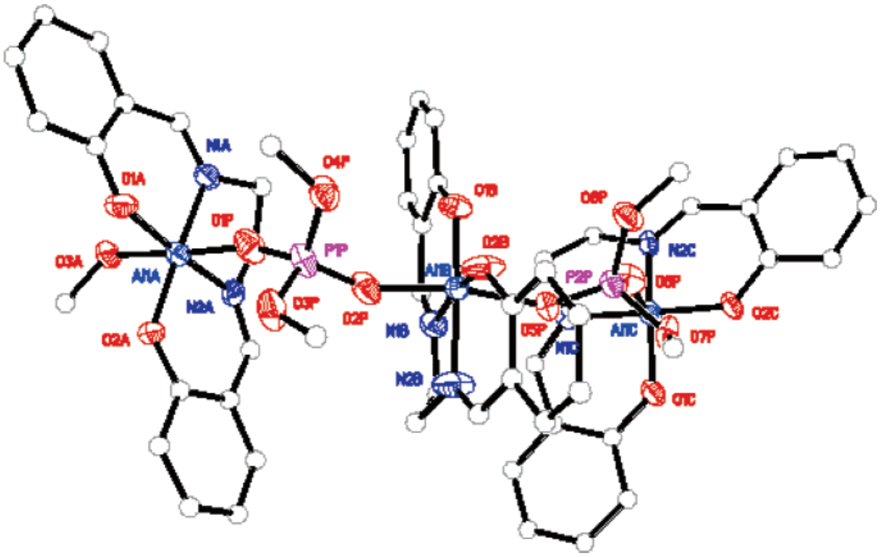

**Figure 4.** Molecular structure of **2**. The $^{t}$Bu groups on the phenyl rings, the disordered atoms, and the hydrogen atoms are omitted for clarity.

**Table 1.** Crystallographic Data and Refinement Details for Compounds **1**−**3**

| | compound **1** | compound **2** | compound **3** |
|---|---|---|---|
| empirical formula | $C_{45}H_{60}AlN_2O_5P_2$ | $C_{115}H_{169}Al_3BrN_6O_{15}P_2$ | $C_{96}H_{148}Al_2N_4O_{12}P_2$ |
| M/g mol$^{-1}$ | 766.90 | 2098.35 | 1666.08 |
| color | yellow | pale yellow | pale yellow |
| cryst size/mm$^3$ | 0.22 × 0.10 × 0.10 | 0.35 × 0.10 × 0.10 | 0.20 × 0.20 × 0.08 |
| cryst syst | orthorhombic | triclinic | monoclinic |
| space group | $P2_12_12_1$ | $P\bar{1}$ | $P2_{1/c}$ |
| $a$/Å | 11.6850(2) | 15.02320(10) | 10.6546(2) |
| $b$/Å | 26.1840(5) | 18.8031(2) | 17.6944(3) |
| $c$/Å | 28.1148(5) | 21.9993(3) | 24.9473(5) |
| α/° | 90.00 | 89.9924(4)) | 90.00 |
| $\beta$/° | 90.00 | 71.8021(4) | 95.9921(7) |
| $\gamma$/° | 90.00 | 82.2916(4) | 90.00 |
| $V$/Å$^3$ | 8602.0(3) | 5844.49(11) | 4677.54(15) |
| $\rho_{calc}$/g cm$^{-3}$ | 1.184 | 1.191 | 1.183 |
| $Z$ | 8 | 2 | 2 |
| $F$(000) | 3296 | 2244 | 1808 |
| radiation used | Cu $K_\alpha$ | Mo $K_\alpha$ | Mo $K_\alpha$ |
| $\mu$/mm$^{-1}$ | 1.121 | 0.463 | 0.126 |
| $T$/K | 90.0(2) | 90.0(2) | 90.0(2) |
| $hkl$ range | $-14 \le h \le 13$,<br>$-11 \le k \le 31$,<br>$-33 \le l \le 32$ | $-17 \le h \le 17$,<br>$-21 \le k \le 21$,<br>$-25 \le l \le 25$ | $-12 \le h \le 12$,<br>$-21 \le k \le 21$,<br>$-29 \le l \le 29$ |
| Θ range/° | 2.31−68.22 | 1.46−24.00 | 1.41−25.00 |
| reflns measured | 48 842 | 36 627 | 91 792 |
| unique reflns ($R_{int}$) | 15 283 (0.0524) | 18337 (0.0604) | 8238 (0.1476) |
| obsd reflns, $n$ [$I \ge 2\sigma(I)$] | 14 037 | 11 102 | 4803 |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| refined params/restraints | 1018/120 | 1315/235 | 538/0 |
| R1 [$I > 2\sigma$] | R1 = 0.0408, wR2 = 0.0996 | R1 = 0.0720, wR2 = 0.1783 | R1 = 0.0566, wR2 = 0.1079 |
| R1 (all data) | R1 = 0.0457, wR2 = 0.1030 | R1 = 0.1426, wR2 = 0.2108 | R1 = 0.1236, wR2 = 0.1307 |
| GOF on $F^2$ | 1.050 | 1.032 | 0.998 |
| largest diff. peak and hole/e·Å$^{-3}$ | 0.415 and −0.277 | 0.713 and −0.600 | 0.314 and −0.559 |

(1.568(3) and 1.559(3) Å) fall in the range of P−O single bonds (Table 2).

For the phosphorus atom P2P, the P2P−O5P bond length 1.469(4) Å indicates double-bond character but the other three P−O bonds (P2P−O6P = 1.531(4), P2P−O7P = 1.575(5), and P2P−O8P = 1.554(4) Å) show normal P−O single bond lengths. The variation of the P−O bond lengths around the two phosphorus atoms P1P and P2P could partly explain the presence of two different $^{31}$P chemical shifts. Each phosphorus atom has a distorted tetrahedral geometry and is connected to the aluminum atoms through the oxygen atoms. The largest deviation from the ideal tetrahedral angle of 109.5° is shown for P1P by O1P−P1P−O2P (116.48(19)° and for P2P by O5P−P2P−O6P (120.1(2)°). Al1A and Al1B have distorted octahedral geometries, whereas Al1C has a distorted geometry between trigonal bipyramidal and square pyramidal. The compound is cationic with bromide (not shown in the crystal structure) present as the counteranion.

A quantitative measure has been proposed to describe the distortion from perfectly sqare pyramidal or trigonal bipyramidal geometry in five-coordinate compounds. The amount of this distortion is expressed by a value "$\tau$". (For a description of the calculation of the "$\tau$ value" see Supporting

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Compounds **1**−**3**

| | | | |
|---|---|---|---|
| | **1** | | |
| Al1A−N1A | 2.0023(19) | Al1A−O2A | 1.8133(16) |
| Al1A−N2A | 1.9977(19) | Al1A−O3A | 2.0255(17) |
| Al1A−O1A | 1.8033(16) | Al1A−O4A | 1.8729(17) |
| | | O4A−P1A | 1.5052(17) |
| O1A−Al1−O2A | 95.97(7) | O3A−Al1A−N1A | 88.76(7) |
| O1A−Al1−O3A | 87.18(7) | O3A−Al1A−N2A | 82.36(7) |
| O1A−Al1A−N1A | 91.34(7) | O3A−Al1A−O4A | 175.39(7) |
| O2A−Al1A−N2A | 91.22(7) | N1A−Al1A−N2A | 81.27(8) |
| O2A−A1lA−O3A | 89.79(7) | Al1A−O4A−P1A | 151.12(11) |
| | **2** | | |
| Al1A−N1A | 1.988(4) | Al1C−N2C | 1.996(4) |
| Al1A−N2A | 2.008(4) | AlC−O1C | 1.758(3) |
| AlA−O1A | 1.808(3) | AlC−O2C | 1.797(3) |
| AlA−O2A | 1.795(3) | Al1C−O6P | 1.798(4) |
| Al1A−O3A | 2.038(3) | P1P−O1P | 1.476(3) |
| Al1A−O1P | 1.847(3) | P1P−O2P | 1.480(3) |
| Al1B−N1B | 1.997(4) | P1P−O3P | 1.568(3) |
| Al1B−N2B | 2.005(4) | P1P−O4P | 1.559(3) |
| AlB−O1B | 1.801(3) | P2P−O5P | 1.469(4) |
| AlB−O2B | 1.814(3) | P2P−O6P | 1.531(4) |
| Al1B−O2P | 1.883(3) | P2P−O7P | 1.575(5) |
| Al1B−O5P | 1.921(4) | P2P−O8P | 1.554(4) |
| Al1C−N1C | 1.977(4) | | |
| O1A−Al1A−O2A | 96.55(14) | O1B−Al1B−O2B | 97.70(15) |
| O1A−Al1A−O3A | 87.37(14) | O1B−Al1B−O2P | 93.39(15) |
| O1A−Al1A−N1A | 91.38(15) | O1B−Al1B−N1B | 91.87(15) |
| O1A−Al1A−N2A | 169.73(16) | O1B−Al1B−N2B | 172.19(16) |
| O2A−Al1A−N2A | 91.32(15) | O2B−Al1B−N2B | 89.97(16) |
| O2A−A1lA−O3A | 89.67(13) | O2B−A1lB−O2P | 93.30(17) |
| O3A−Al1A−N1A | 84.38(14) | O2P−Al1B−N1B | 87.58(15) |
| O3A−Al1A−N2A | 86.09(14) | O2P−Al1B−N2B | 84.64(17) |
| O3A−Al1A−O1P | 173.56(15) | O2P−Al1B−O5P | 169.04(17) |
| N1A−Al1A−N2A | 80.12(16) | N1B−Al1B−N2B | 80.50(16) |
| Al1A−O1P−P1P | 163.6(2) | Al1B−O5P−P2P | 151.2(3) |
| O1P−P1P−O2P | 116.48(19) | O5P−P2P−O6P | 120.1(2) |
| O1P−P1P−O3P | 105.60(18) | O5P−P2P−O7P | 111.1(3) |
| O1P−P1P−O4P | 110.28(19) | O5P−P2P−O8P | 108.8(2) |
| O2P−P1P−O3P | 111.2(2) | O6P−P2P−O7P | 100.7(2) |
| O2P−P1P−O4P | 106.98(18) | O6P−P2P−O8P | 108.3(3) |
| P1P−O2P−Al1B | 153.4(2) | O7P−P2P−O8P | 106.9(2) |
| O3P−P1P−O4P | 105.86(19) | P2P−O5P−Al1B | 151.2(3) |
| N1C−Al1C−N2C | 79.14(15) | O2C−Al1C−N2C | 88.55(15) |
| N1C−Al1C−O1C | 90.02(15) | N2C−Al1C−O1C | 143.45(17) |
| O1C−Al1C−O2C | 92.14(15) | N1C−Al1C−O2C | 161.90(17) |
| N1C−Al1C−O6P | 93.67(17) | O1C−Al1C−O6P | 111.64(16) |
| O2P−Al1B−O5P | 169.04(17) | | |
| P2P−O6P−Al1C | 151.6(3) | | |
| | **3** | | |
| Al1−N1 | 2.026(2) | P1−O3 | 1.4827(18) |
| Al1−N2 | 2.001(2 | P1−O4 | 1.4778(18) |
| Al1−O1 | 1.8274(19) | P1−O5 | 1.5750(19) |
| Al−O2 | 1.8597(19) | P1−O6 | 1.5836(18) |
| Al1−O3 | 1.8816(19) | | |
| Al1−O4 | 1.8611(19) | | |
| O1−Al1−N1 | 88.32(9) | O2−Al1−O4 | 91.34(8) |
| O1−Al1−N2 | 176.15(10) | O3−Al1−N1 | 86.60(9) |
| O1−Al1−O2 | 93.01(9) | O3−Al1−N2 | 87.23(9) |
| O1−Al1−O3 | 93.64(8) | O3−Al1−O4 | 91.40(8) |
| O1−Al1−O4 | 93.45(8) | N1−Al1−N2 | 87.98(9) |
| O2−Al1−N1 | 90.45(9) | Al1−O3−P1 | 150.46(12) |
| O2−Al1−N2 | 85.94(9) | Al1−O4−P1 | 165.22(12) |
| O2-A1l−O3 | 172.64(9) | O3−P1−O4 | 118.52(11) |
| O3−P1−O5 | 111.59(10) | O4−P1−O6 | 110.32(10) |
| O5−P1−O6 | 105.78(10) | | |

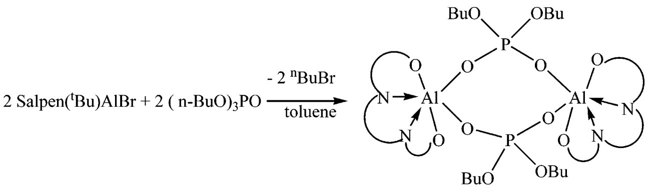

**Figure 5.** Synthesis of compound **3**.

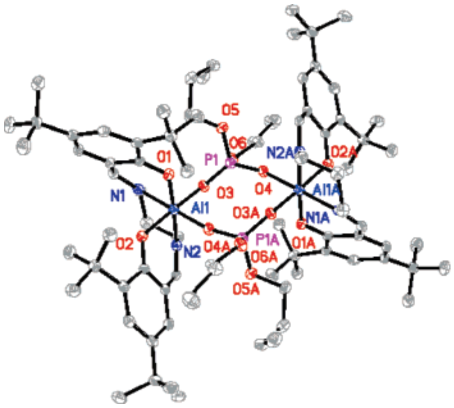

**Figure 6.** Molecular structure of **3**. Hydrogen atoms are not shown for clarity.

Information Figure S2).[24] A perfectly sqp geometry has a $\tau$ value equal to zero, whereas a perfectly trigonal bipyramidal geometry has a $\tau$ value equal to 1. This value may be important in determining the accessibility of a sixth coordination site. [25] For compound **2**, the calculated $\tau$ value was found to be 0.31. Thus, it cannot be reasonably defined as either of the geometries but is closer to square pyramidal.

The Al−O−P linkages in **2** are bent. However, the angle Al1A−O1P−P1P (163.5(2)°) is considerably less bent than the other Al−O−P angles (151.1(3)−153.4(2)°) in the molecule.

Compound **3** was prepared by the reaction of salpen($^t$Bu)-AlBr with tributyl phosphate in toluene at room temperature (Figure 5). Only one of the three methoxy groups on each phosphate molecule undergoes dealkylation. The compound is soluble in toluene and chloroform. It was characterized by IR, $^1$H NMR, $^{27}$Al NMR, $^{31}$P NMR, mp, and MS. The $^1$H NMR has peaks corresponding to the ligand and the alkoxy groups of the mono-dealkylated phosphate. The $^{27}$Al NMR shows two peaks. The peak at $\delta$ −5 corresponds to six-coordinate aluminum. However, the peak at $\delta$ 40 falls in the region of five-coordinate aluminum. This does not correspond to the solid-state structure of the compound which shows the presence of six-coordinate aluminum only. It could be possible that in solution one phosphate linkage from one of the aluminum atoms dissociates, thus making it five-coordinate. The $^{31}$P NMR has a single peak at $\delta$ −18. The TGA curve (Supporting Information Figure S3) of **3** shows a weight loss of about 10% around 100−120 °C, which is probably due to the entrapped solvent. There is a second weight loss of about 90% in the temperature range 300−600 °C that is probably due to the thermal oxidation of the organic species leaving behind some inorganic aluminophosphate material.

The molecular structure of **3** (Figure 6) contains an aluminum−phosphate ring formed by two Salen aluminum units and two mono-dealkylated phosphate units. Two aluminum and two phosphorus atoms are part of an eight-membered Al−O−P ring. The ring P−O bond distances P1−O3 and P1−O4 (1.4827(18) and 1.4778(18) Å, respectively) are essentially equal and have double-bond character (Table 2). The other P−O distances, P1−O5 and P1−O6, are longer (1.5750(19) and 1.5836(18) Å, respectively) and in the range of P−O single bonds.

Each phosphorus atom is in a distorted tetrahedral geometry. The biggest distortion is found in the O−P−O bond angle (118.52(11) °) inside the aluminophosphate ring. Each aluminum atom is six-coordinate with a distorted octahedral geometry. The phosphate oxygen atoms occupy two of the equatorial positions. The other two equatorial positions are occupied by one nitrogen atom and one oxygen atom from the ligand. Another pair of nitrogen and oxygen from the ligand occupy the axial positions. The axial Al−O distance (1.8274(19)Å) is slightly shorter than the equatorial Al−O distances (1.8597(19), 1.8816(19) and 1.8611(19) Å). However, the axial Al−N2 distance (2.001(2) Å) is almost the same as the equatorial Al−N1 distance (2.026(2) Å). The longer Al−N distances compared to Al−O distances are a reflection of the larger atomic radius of nitrogen. The Al−O−P angles are not equal. Al1−O4−P1 (165.22(12) Å) is larger than Al1−O3−P1 (150.46(12) Å).

The crystal packing diagram of **3** (Supporting Information Figure S4) shows that the aluminophosphate rings stack on top of each other with alkyl chains on phosphorus and ligand groups on aluminum extending away from the ring. The distance between two aluminum atoms is 5.108 Å, which is comparable to the pore diameter (6.6 Å) of layered aluminphosphate templated by 2-methylpiperazine.[26]

## Conclusion

The dealkylation reaction between a Salen aluminum Schiff base halide and methyl diphenylphosphinate has been used to synthesize the first structurally characterized monomeric Salen aluminum phosphinate. Furthermore, the dealkylation reaction with alkyl phosphates has been used to prepare a cationic aluminum phosphate and an aluminophosphate ring. These compounds are the first examples of aluminum phosphates with Salen ligands. They contain five- and six-coordinate aluminum, which is rare for molecular aluminophosphate compounds. The reaction conditions for the preparation of all of the compounds are very mild. This method could be developed to prepare aluminophosphate cage and chain structures for potential application as molecular sieves and catalysts. This is the first example of the intentional use of an aluminum-based dealkylation reaction to form new compounds. The utility of this reaction in forming other unique products is currently being explored.

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**Supporting Information Available:** The crystal packing diagrams of **2**·MeOH and **3**; figure showing the calculation of $\tau$ value; TGA curve for **3**; figure of **3** showing the Al−O−P ring; and CIF files for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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