Reactions of Trialkyl Phosphates with Trialkyls of Aluminum and Gallium: New Route to Alumino- and Gallophosphate Compounds via Dealkylsilylation[†]

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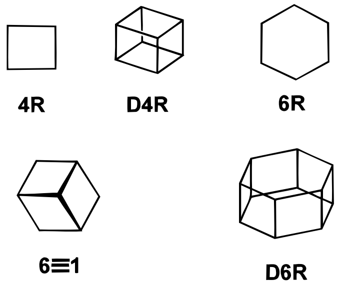
Received August 4, 1998

Trialkyl phosphates $OP(OR)_3$ (R = Me, Et, Ph, $SiMe_3$) react with $AlMe_3$, $AlEt_3$, and $GaMe_3$ in hydrocarbon solvents to form the adducts $Me_3Al{\cdot}OP(OR)_3$ (R = Me (**1**), Et (**2**), Ph (**3**), $SiMe_3$ (**4**)), $Et_3Al{\cdot}OP(OR)_3$ (R = $SiMe_3$ (**5**)), and $Me_3Ga{\cdot}OP(OR)_3$ (R = Me (**6**), $SiMe_3$ (**7**)). These products were characterized by ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR, infrared (IR), and mass (MS) spectroscopies and elemental analysis. The trimethylsilyl ester adducts **4**, **5**, and **7** further undergo a thermally induced dealkylsilylation with the formation of cyclic alumino- and gallophosphate dimers, $[R'_2M(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (R'_2M = Me_2Al (**8**), Et_2Al (**9**), and Me_2Ga (**10**)). The molecular structures of **8** and **9** were confirmed by X-ray crystallography.

Introduction

We are interested in developing rational synthetic techniques leading to microporous materials, such as alumino- and gallophosphates, using nonaqueous methods. In the pursuit of this goal, we followed the building block strategy and synthesized a series of molecular alumino- and gallophosphonates. These compounds represent organic-soluble models of the secondary building units (SBU,[1] Scheme 1[2]) found in extended three-dimensional structures of AlPO and GaPO materials.[3] To the previously known model compounds, mimicking a single four-ring[4−10] (4R) and a double four-ring [10−13] (D4R), we added a double six-ring[14] (D6R), a single six-ring[15] (6R), and a tricyclic unit (6≡1).[16]

Scheme 1



We also employed a complementary strategy for the preparation of these materials in which aluminum and gallium amides were reacted with trialkyl phosphates. These reactions of trifunctional moieties provide amorphous alumino- and gallophosphates under totally nonaqueous conditions via a dealkylamination route.[17] We surmised that species with structures analogous to 4R and D4R presumably are intermediates in these reactions (eq 1).

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[†] Dedicated to Professor Heinrich Marsmann on the occasion of his 60th birthday.

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10.1021/om9806702 CCC: $18.00

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\begin{aligned}
1/2[\mathrm{M(NMe_2)_3}]_2 + \mathrm{OP(OR)_3} &\rightarrow \mathrm{(Me_2N)_3M{\cdot}OP(OR)_3} \quad (1)\\
&\rightarrow [\mathrm{(Me_2N)_2M(\mu_2\text{-}O)_2P(OR)_2}]_n + \mathrm{RNMe_2}\\
&\rightarrow [\mathrm{(Me_2N)M(\mu_2\text{-}O)_3P(OR)}]_n + \mathrm{RNMe_2}\\
&\rightarrow \mathrm{MPO_4} + \mathrm{RNMe_2}
\end{aligned}
$$

$\mathrm{M = Al, Ga; R = Me, Et}$, n-Bu, $\mathrm{SiMe_3}$

To gain further insight into the mechanism of these reactions and to be able to analyze their individual steps, we prepared and fully characterized a series of adducts $\mathrm{Me_3Al{\cdot}OP(OR)_3}$ (R = Me (**1**), Et (**2**), Ph (**3**), $\mathrm{SiMe_3}$ (**4**)), $\mathrm{Et_3Al{\cdot}OP(OR)_3}$ (R = $\mathrm{SiMe_3}$ (**5**)), and $\mathrm{Me_3Ga{\cdot}OP(OR)_3}$ (R = Me (**6**), $\mathrm{SiMe_3}$ (**7**)). These compounds will serve as models for identification of nonisolable initial intermediates $\mathrm{(Me_2N)_3M{\cdot}OP(OR)_3}$ in the reaction mixture (eq 1) in the low-temperature NMR spectroscopic studies.

Interestingly, the tris(trimethylsilyl) phosphate adducts **4**, **5**, and **7** undergo a thermally induced dealkylsilylation and form cyclic phosphate dimers $[\mathrm{R'_2M(\mu_2\text{-}O)_2P(OSiMe_3)_2}]_2$ ($\mathrm{R'_2M = Me_2Al}$ (**8**), $\mathrm{Et_2Al}$ (**9**), and $\mathrm{Me_2Ga}$ (**10**)). Dealkylsilylation is a rare reaction which has been employed previously in the preparation of 12/16[18] and 13/15[19] materials. Compounds **8** and **9** were shown to possess the cyclic dimeric structure by NMR spectroscopy and X-ray crystallography and thus constitute additional examples of organic-soluble molecular models of the ubiquitous 4R SBU. Furthermore, these findings lend support to our mechanistic contention regarding the amide-phosphate systems[17] that four-ring units are one of the intermediates along the reaction pathway toward $\mathrm{MPO_4}$ (M = Al, Ga).

Experimental Section

All preparative procedures were performed under a dry nitrogen atmosphere using Schlenk and drybox techniques. Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated solvents were dried over and distilled from Na/K alloy and degassed prior to use. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments. Mass spectra were obtained on a Finnigan MAT 8230 or MAT 95 mass spectrometer (EI, 70 eV or FI). IR spectra (4000−400 cm^{-1}) were recorded on Bio Rad FTS-7. Samples of solids were prepared as KBr pellets, while neat liquids were spread between KBr disks. Elemental analyses were carried out by the Analytisches Labor des Anorganischen Instituts, Göttingen. Poor analysis results for compounds **1** and **3** are due in part to metal carbide formation and also to the pyrophoric nature of the adducts. Melting points were measured in sealed capillaries and are uncorrected.

General Procedure for the Reactions of Trialkyl Phosphates with Trimethylaluminum and Trimethylgallium. The phosphate ester (10 mmol) was dissolved in dry hexane (50 mL) or, in the case of $\mathrm{OP(OPh)_3}$, in toluene, and $\mathrm{AlMe_3}$ (2.0 M in hexane, 10% excess over the equimolar amount) was added slowly via syringe to the stirred and ice-cooled solution. The reaction mixture was left to warm slowly to ambient temperature. After solvent volume reduction under vacuum, a white solid (**1** and **4**) formed on storing at −24 °C. The products were cold filtered and dried under vacuum for 2 h. Compounds **2**, **3**, and **5**, on the other hand, were obtained as pure colorless liquids upon removing all volatile components under vacuum. A colorless liquid **6** and a white solid **7** were obtained by adding a phosphate ester to the solution of $\mathrm{GaMe_3}$ (6 mmol, 7% excess over the equimolar amount) in hexane at room temperature.

$\mathrm{Me_3Al{\cdot}OP(OMe)_3}$ (1). Yield: 74%. Mp: 34.5−35.0 °C. ^{1}H NMR (benzene-d_6): δ −0.398 (s, $\mathrm{AlCH_3}$, 9 H), 3.166 (d, $^3J_{\mathrm{PH}} = 11.5$ Hz, $\mathrm{POCH_3}$, 9 H). ^{13}C NMR (benzene-d_6): δ −6.76 (br s, $\mathrm{AlCH_3}$), 55.53 (d, $^2J_{\mathrm{PC}} = 6.2$ Hz, $\mathrm{POCH_3}$). ^{31}P NMR (benzene-d_6): δ −3.19 (s). MS (FI): m/z (%) 197 (M − $\mathrm{CH_3}$, 100), 155 (30), 140 ($\mathrm{OP(OMe)_3}$, 55). Anal. Calcd for $\mathrm{C_6H_{18}AlO_4P}$: C, 33.97; H, 8.55; Al, 12.72. Found: C, 32.84; H, 7.95; Al, 12.7.

$\mathrm{Me_3Al{\cdot}OP(OEt)_3}$ (2). Yield: 86%. ^{1}H NMR (benzene-d_6): δ −0.597 (s, $\mathrm{AlCH_3}$, 9 H), 0.964 (dt, $^4J_{\mathrm{PH}} = 1.3$ Hz, $^3J_{\mathrm{HH}} = 7.1$ Hz, $\mathrm{POCH_2C}H_3$, 9 H), 3.786 (dq, $^3J_{\mathrm{PH}} = 8.3$ Hz, $^3J_{\mathrm{HH}} = 7.1$ Hz, $\mathrm{POC}H_2\mathrm{CH_3}$, 6 H). ^{13}C NMR (benzene-d_6): δ −6.98 (br s, $\mathrm{AlCH_3}$), 15.57 (d, $^3J_{\mathrm{POCC}} = 6.7$ Hz, $\mathrm{POCH_2}C\mathrm{H_3}$), 66.25 (d, $^2J_{\mathrm{PC}} = 6.4$ Hz, $\mathrm{PO}C\mathrm{H_2CH_3}$). ^{31}P NMR (benzene-$d_6$): δ −6.91 (s). MS (EI): m/z (%) 239 (M − $\mathrm{CH_3}$, 17), 155 ($\mathrm{P(OEt)_2(OH)_2}$, 100). MS (FI): m/z (%) 239 (M − $\mathrm{CH_3}$, 100). IR (neat, KBr disks, cm^{-1}): ν 2988 s, 2918 s, 2884 s, 2817 m, 1480 m, 1445 m, 1398 m, 1373 m, 1294 m, 1224 vs (ν P═O), 1177 s, 1103 w, 1044 vs, 994 w, 825 s, 808 s, 697 vs, 615s, 518 m, 487 w. Anal. Calcd for $\mathrm{C_9H_{24}AlO_4P}$: C, 42.52; H, 9.51; Al, 10.61. Found: C, 42.26; H, 8.89; Al, 10.3.

$\mathrm{Me_3Al{\cdot}OP(OPh)_3}$ (3). Yield: 92%. ^{1}H NMR (benzene-d_6): δ −0.420 (s, $\mathrm{AlCH_3}$, 9 H), 6.8−7.1 (m, Ph, 15 H). ^{13}C NMR (benzene-d_6): δ −6.77 (br s, $\mathrm{AlCH_3}$), 120.04 (d, $^3J_{\mathrm{PC}} = 4.9$ Hz, *o*-C), 126.89 (d, $^5J_{\mathrm{PC}} = 1.4$ Hz, *p*-C), 130.42 (d, $^4J_{\mathrm{PC}} = 1.0$ Hz, *m*-C), 149.81 (d, $^2J_{\mathrm{PC}} = 8.3$ Hz, *ipso*-C). ^{31}P NMR (benzene-d_6): δ −21.89 (s). MS (EI): m/z (%) 383 (M − $\mathrm{CH_3}$, 16), 326 ($\mathrm{OP(OPh)_3}$, 78), 281 (30), 249 ($\mathrm{O_2P(OPh)_2}$, 45), 177 (26), 161 (100). IR (neat, KBr disks, cm^{-1}): ν 3062 w, 3045 w, 2919 s, 2884 m, 2816 w, 1589 s, 1489 vs, 1458 m, 1266 s (ν P═O), 1219 m, 1180 vs, 1160 vs, 1072 m, 1029 vs, 992 vs, 953 w, 905 m, 779 m, 753 s, 704 vs, 685 vs, 617 m, 580 w, 519 m. Anal. Calcd for $\mathrm{C_{21}H_{24}AlO_4P}$: C, 63.32; H, 6.07; Al, 6.77. Found: C, 62.23; H, 6.02; Al, 6.5.

$\mathrm{Me_3Al{\cdot}OP(OSiMe_3)_3}$ (4). Yield: 74%. Mp: 86−88 °C. ^{1}H NMR (benzene-d_6): δ −0.327 (s, $\mathrm{AlCH_3}$, 9 H), 0.148 (s, $^1J_{\mathrm{CH}} = 120.0$ Hz, ^{13}C satellites, $^2J_{\mathrm{SiH}} = 7.0$ Hz, ^{29}Si satellites, $\mathrm{SiCH_3}$, 27 H). ^{13}C NMR (benzene-d_6): δ −6.2 (br s, $\mathrm{AlCH_3}$), 0.31 (d, $^3J_{\mathrm{PC}} = 2.0$ Hz, $^1J_{\mathrm{SiC}} = 60.3$ Hz, ^{29}Si satellites, $\mathrm{SiCH_3}$). ^{29}Si NMR (benzene-d_6): δ 26.7 (d, $^2J_{\mathrm{PSi}} = 5.8$ Hz, $^1J_{\mathrm{SiC}} = 60.4$ Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −31.7 (s, $^2J_{\mathrm{PSi}} = 5.7$ Hz, ^{29}Si satellites). MS (EI): m/z (%) 655 (5), 581 (**8** − $\mathrm{CH_3}$, 100). MS (FI): m/z (%) 581 (**8** − $\mathrm{CH_3}$, 10), 371 (M − $\mathrm{CH_3}$, 100). IR (KBr pellet, cm^{-1}): ν 2963 m, 2927 w, 1422 w, 1260 s, 1221 s (ν P═O), 1130 m, 1082 vs, 853 vs, 764 m, 687 s, 615 m, 557 w, 467 m. Anal. Calcd for $\mathrm{C_{12}H_{36}AlO_4PSi_3}$: C, 37.28; H, 9.38; Al, 6.98; P, 8.01. Found: C, 36.70; H, 9.20; Al, 7.02; P, 8.17.

$\mathrm{Et_3Al{\cdot}OP(OSiMe_3)_3}$ (5). Yield: 87%. ^{1}H NMR (benzene-d_6): δ 0.135 (d, $^4J_{\mathrm{PH}} = 0.4$ Hz, $^1J_{\mathrm{CH}} = 120.0$ Hz, ^{13}C satellites, $^2J_{\mathrm{SiH}} = 6.9$ Hz, ^{29}Si satellites, $\mathrm{SiCH_3}$, 27 H), 0.295 (q, $^3J_{\mathrm{HH}} = 8.1$ Hz, $\mathrm{CH_2}$, 6 H), 1.555 (t, $^3J_{\mathrm{HH}} = 8.1$ Hz, $\mathrm{CH_3}$, 9 H). ^{13}C NMR (benzene-d_6): δ 0.23 (d, $^3J_{\mathrm{PC}} = 1.8$ Hz, $^1J_{\mathrm{SiC}} = 60.4$ Hz, ^{29}Si satellites, $\mathrm{SiCH_3}$), 1.78 (br s, $\mathrm{AlCH_2}$), 10.86 (s, $\mathrm{CH_3}$). ^{29}Si NMR (benzene-d_6): δ 26.6 (d, $^2J_{\mathrm{PSi}} = 6.1$ Hz, $^1J_{\mathrm{SiC}} = 60.4$ Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −31.7 (s, $^2J_{\mathrm{PSi}} = 6.1$ Hz, ^{29}Si satellites). MS (EI): m/z (%) 623 (**9** − $\mathrm{C_2H_5}$, 20), 399 (M − $\mathrm{C_2H_5}$, 68), 299 ($\mathrm{OP(OSiMe_3)_3}$ − $\mathrm{CH_3}$, 100). MS (FI): m/z (%) 623 (**9** − $\mathrm{C_2H_5}$, 14), 399 (M − $\mathrm{C_2H_5}$, 100). IR (neat, KBr disks, cm^{-1}): ν 2963 s, 2932 s, 2897 vs, 2888 vs, 2853 vs, 2789 m, 1463 w, 1410 m, 1260 vs, 1215 vs (ν P═O), 1080 vs, 985 s, 943 m, 852 vs, 764s, 700 w, 646 s, 616 s, 475 w.

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$Me_3Ga{\cdot}OP(OMe)_3$ (6). Yield: 75%. ^1H NMR (benzene-d_6): δ 0.007 (s, $GaCH_3$, $^1J_{CH}$ = 118 Hz, ^{13}C satellites, 9 H), 3.185 (d, $^3J_{PH}$ = 11.3 Hz, $^1J_{CH}$ = 149 Hz, ^{13}C satellites, $POCH_3$, 9 H). ^{13}C NMR (benzene-d_6): δ −2.88 (s, $GaCH_3$), 54.67 (d, $^2J_{PC}$ = 6.1 Hz, $POCH_3$).^{31}P NMR (benzene-d_6): δ −0.05 (s). MS (FI): m/z (%) 239 (M − CH_3, 100).

$Me_3Ga{\cdot}OP(OSiMe_3)_3$ (7). Yield: 95%. Mp: 37−38 °C. ^1H NMR (benzene-d_6): δ 0.122 (s, $GaCH_3$, 9 H), 0.146 (d, $^4J_{PH}$ = 0.6 Hz, $^2J_{SiH}$ = 6.8 Hz, ^{29}Si satellites, $SiCH_3$, 27 H). ^{13}C NMR (benzene-d_6): δ −2.70 (br s, $GaCH_3$), 0.40 (d, $^3J_{PC}$ = 1.8 Hz, $^1J_{SiC}$ = 60.3 Hz, ^{29}Si satellites, $SiCH_3$). ^{29}Si NMR (benzene-d_6): δ +24.23 (d, $^2J_{PSi}$ = 5.4 Hz, $^1J_{SiC}$ = 60.3 Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −28.5 (s, $^2J_{PSi}$ = 5.3 Hz, ^{29}Si satellites). MS (EI): m/z (%) 667 (**10** − CH_3, 100). MS (FI): m/z (%) 667 (**10** − CH_3, 100). IR (neat, KBr disks, cm^{-1}): ν 2964 vs, 2906 m, 2840 w, 1420 w, 1259 s, 1213 vs (ν P=O), 1197 s, 1099 vs, 1065 vs, 849 vs, 763 s, 736 m, 612 m, 596 sh, 546 m, 481 w. Anal. Calcd for $C_{12}H_{36}GaO_4PSi_3$: C, 33.57; H, 8.45; Ga, 16.24; P, 7.21. Found: C, 33.36; H, 8.10; Ga, 16.70; P, 7.27.

Preparation of the Dimeric Four-Ring Compounds 8−10. $[Me_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (8). Method A. Compound **4** (12.41 g, 32.10 mmol) was heated in a sublimation apparatus under dry nitrogen at atmospheric pressure to 200 °C for 4 h. It underwent a dealkylsilylation and gave a white crystalline solid which condensed on the coldfinger. This product was subsequently resublimed at 120 °C/0.007 mm, affording 8.57 g (90%) of **8**. The outlet of the sublimation apparatus was connected to a cold trap held at −70 °C. A colorless liquid which collected in the cold trap (1.70 g) was shown by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy to consist of mainly $SiMe_4$ with traces of $MeOSiMe_3$ (<1%) and $(Me_3Si)_2O$ (1%).

Method B. Me_2AlCl (0.46 g, 5.0 mmol) was added slowly to $OP(OSiMe_3)_3$ (1.57 g, 5.0 mmol) in THF (40 mL). The reaction mixture was heated at reflux for 5 h, and then all volatile components were removed under vacuum. The solid residue was recrystallized from cold hexane yielding 2.4 g (81%) of **8**. Characterization data were identical for both methods. Mp: 95−98 °C. ^1H NMR (benzene-d_6): δ −0.32 (s, $AlCH_3$, 6 H), 0.18 (d, $^4J_{PH}$ = 0.3 Hz, $^1J_{CH}$ = 119.7 Hz, ^{13}C satellites, $^2J_{SiH}$ = 7.0 Hz, ^{29}Si satellites, $SiCH_3$, 18 H). ^{13}C NMR (benzene-d_6): δ −9.4 (br s, $AlCH_3$), 0.43 (X of AA′X, $^3J_{PC}$ = 1.9 Hz, $^1J_{SiC}$ = 60.4 Hz, ^{29}Si satellites). ^{29}Si NMR (benzene-d_6): δ +23.4 (X of AA′X, $^2J_{POSi}$ = 4.7 Hz, $^1J_{SiC}$ = 60.6 Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −29.3 (s). MS (EI): m/z (%) 581 (M − CH_3, 100). IR (KBr pellet, cm^{-1}): ν 2967 m, 2929 m, 2892 w, 1422 w, 1259 s, 1219 s (ν P=O), 1189 w, 1130 s, 1065 vs, 852 vs, 763 m, 684 vs, 613 m, 555 w, 464 w. Anal. Calcd for $C_{16}H_{48}Al_2O_8P_2Si_4$: C, 32.20; H, 8.11; Al, 9.04; P, 10.38; Si, 18.82. Found: C, 31.90; H, 7.70; Al, 8.50; P, 9.48; Si, 18.72.

$[Et_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (9). Method A. Compound **5** (2.576 g, 6.009 mmol) was treated analogously as described above for the transformation of **4** to **8**. The dealkylsilylation product was resublimed at 100 °C/0.02 mm and afforded 1.57 g (80%) of **9**. A colorless liquid which collected in the cold trap (0.34 g) was analyzed by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as $EtSiMe_3$ with traces of $EtOSiMe_3$ and $(Me_3Si)_2O$.

Method B. Et_2AlCl (1.30 g, 10.8 mmol) and $OP(OSiMe_3)_3$ (3.39 g, 10.8 mmol) were reacted analogously as described above for **8**, yielding 5.8 g (82%) of **9**. Characterization data were identical for both methods. Mp: 82−84 °C. ^1H NMR (benzene-d_6): δ 0.204 (d, $^4J_{PH}$ = 0.3 Hz, $^1J_{CH}$ = 120.0 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.9 Hz, ^{29}Si satellites, $SiCH_3$, 18 H), 0.28 (q, $^3J_{HH}$ = 8.2 Hz, $AlCH_2$, 4 H), 1.47 (t, $^3J_{HH}$ = 8.2 Hz, CH_3, 6 H). ^{13}C NMR (benzene-d_6): δ 0.38 (X of AA′X, $^3J_{PC}$ = 1.9 Hz, $^1J_{SiC}$ = 60.4 Hz, ^{29}Si satellites, $SiMe_3$), 0.2 (br s, $AlCH_2$), 9.46 (s, CH_3). ^{29}Si NMR (benzene-d_6): δ 23.3 (X of AA′X, $^2J_{PSi}$ = 5.0 Hz, $^1J_{SiC}$ = 60.4 Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −28.8 (s). MS (EI): m/z (%) 623 (M − C_2H_5, 100). IR (KBr pellet, cm^{-1}): ν 2963 m, 2938 m, 2899 m, 2861 s, 2792 w, 1458 w, 1411 w, 1370 vw, 1259 s, 1221 s (ν P=O), 1128 m, 1067 vs, 989 w, 948 w, 852 vs, 763 m, 696 w, 648 s, 613 w, 531 w, 467 w. Anal. Calcd for $C_{20}H_{56}Al_2O_8P_2Si_4$: C, 36.79; H, 8.65. Found: C, 36.27; H, 8.60.

Table 1. Crystal and Structure Refinement Data for $[R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$, R = Me (8), Et (9)

	8	**9**
empirical formula	$C_{16}H_{48}Al_2O_8P_2Si_4$	$C_{20}H_{56}Al_2O_8P_2Si_4$
fw	596.80	652.91
a, Å	19.309(4)	18.581(5)
b, Å	9.757(2)	11.016(4)
c, Å	19.846(4)	21.442(6)
β, deg	109.41(3)	115.22(2)
volume, $Å^3$	3526.6(12)	3971(2)
Z	4	4
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
T, °C	−123(2)	−93(2)
wavelength, Å	0.710 73	0.710 73
d_{calcd}, $g{\cdot}cm^{-3}$	1.124	1.092
cryst dimens, mm	0.90 × 0.70 × 0.30	0.70 × 0.60 × 0.60
μ, cm^{-1}	3.39	3.07
no. of rflns collctd	4711	12707
no. of unique rflns	2306	6877
R_{int}	0.0215	0.0553
$R1$, $[I > 2\sigma(I)]$[a]	0.0360	0.0850
wR2 (all data)[b]	0.0961	0.2701
GOF on F^2	1.032	1.024

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

$[Me_2Ga(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (10). A benzene-d_6 solution of **7** was heated to 110 °C in a screw-cap NMR tube for 136 h. Approximately 50% of **7** was converted to **10**. Byproducts included $(Me_3Si)_2O$ and $MeOSiMe_3$. ^1H NMR (benzene-d_6): δ 0.09 (s, $GaCH_3$, 6 H), 0.229 (s, $^1J_{CH}$ = 119 Hz, ^{13}C satellites, $^2J_{SiH}$ = 6.9 Hz, ^{29}Si satellites, $SiCH_3$, 18 H). ^{13}C NMR (benzene-d_6): δ −5.40 (t, $^3J_{PC}$ = 2.6 Hz, $GaCH_3$), 0.64 (d, $^3J_{PC}$ = 1.8 Hz, $^1J_{SiC}$ = 60 Hz, ^{29}Si satellites). ^{29}Si NMR (benzene-d_6): δ 20.45 (d, $^2J_{PSi}$ = 5.0 Hz, $^1J_{SiC}$ = 60 Hz, ^{13}C satellites). ^{31}P NMR (benzene-d_6): δ −21.5 (s).

Reaction of 2 with Dimethylamine. A solution of **2** (0.230 g, 0.905 mmol) in C_6D_6 (0.6 mL) was placed in a 200 mL ampule fitted with a Teflon valve. An excess of Me_2NH (10 mL, dried over Na) was condensed into the ampule, and the reaction mixture was degassed by three freeze−pump−thaw cycles. Overnight heating to 80 °C yielded a white solid (88 mg). The excess of Me_2NH was vented at room temperature, and all the remaining volatile components were vacuum transferred to an NMR tube and flame-sealed. $EtNMe_2$ was identified by ^1H and ^{13}C NMR spectroscopy.

Single-Crystal X-ray Diffraction Study of 8 and 9. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer. The cell parameters were determined from randomly chosen and well-centered high-angle reflections. The structure solution by direct methods and refinement by full-matrix least-squares on F^2 were carried out using SHELXS-90 and SHELXL-93 programs. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were found and refined isotropically. Crystal data and solution and refinement parameters are listed in Table 1.

Results and Discussion

Adducts. Compounds **1**−**7** were obtained in high yield by direct reactions of their components in hydrocarbon solvents (eq 2) as liquids or low-melting solids. Their ester/metal alkyl composition (1:1) was confirmed by elemental analyses and a correct intensity ratio of the ^1H NMR signals.

$$\mathrm{R'_3M + OP(OR)_3 \rightarrow R'_3M{\cdot}OP(OR)_3} \qquad (2)$$

M = Al; R′ = Me; R = Me (**1**), Et (**2**), Ph (**3**), $SiMe_3$ (**4**);

M = Al; R′ = Et; R = $SiMe_3$ (**5**);

M = Ga; R′ = Me; R = Me (**6**), $SiMe_3$ (**7**)

The NMR spectra show that these adducts are stable in solution at room temperature. The ^{31}P NMR chemical shifts of the $AlMe_3$ adducts are shielded with respect to the free phosphate esters by 5−7 ppm, while the $GaMe_3$ adducts only by 3−4 ppm. The smaller upfield shift of the latter derivatives reflects the lower acidity of the gallium center. The magnitudes of $\Delta\delta$ values in the AlR'_3 series correspond well with the published shielding (6.7 ppm) of the $Cl_3Al{\cdot}OP(OPh)_3$ signal upon adduct formation.[20] The nature of the alkyl group on Al (Me or Et) induced no detectable change of the ^{31}P NMR chemical shifts of **4** and **5**. The coordination of a metal moiety to the phosphoryl group decreases its stretching frequency by 33−54 cm^{-1}. These values agree well with the shifts reported for a series of $AlMe_3$ adducts with phosphine oxides.[21] However, we found little correlation between changes in the ^{31}P NMR chemical shifts and the P═O vibrations.

Some adducts were of limited stability under electron impact (EI-MS) conditions. The trimethyl phosphate adducts **1** and **6** showed no molecular peaks, while ethyl and phenyl ester adducts **2** and **3** showed them in low intensity (<20%). When a milder field ionization technique (FI) was used, we observed the molecular peaks for **1**−**6** ($M - R^+$, R = CH_3, C_2H_5) with 100% intensity. However, the mass spectra of the tris(trimethylsilyl) phosphate adducts **4**, **5**, and **7** contained also relatively intensive high mass signals, which corresponded to loss of an alkyl group (CH_3 or C_2H_5) from the dimers **8**, **9**, and **10**, respectively. This indicated that reactions similar to the ones in eq 1 may take place in these systems, formally via a dealkylsilylation of the adducts and subsequent dimerization.

Four-Rings. To study the dealkylsilylation reactions on a larger preparative scale, **4** and **5** were heated at atmospheric pressure at 200 °C. The resulting white solids were characterized by elemental analysis and spectroscopic methods as pure **8** and **9**, respectively (eq 3). Evolved volatile components were trapped at −70 °C and were subsequently characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as $RSiMe_3$ (R = Me, Et) with trace amounts of $ROSiMe_3$ and $(Me_3Si)_2O$. When these elimination reactions were carried out with **4**, **5**, and **7** in C_6D_6 solution, $ROSiMe_3$ was observed as the major byproduct, with $(Me_3Si)_2O$ and $RSiMe_3$ as minor components.

$$\begin{aligned}&\mathrm{2R_3Al{\cdot}OP(OSiMe_3)_3 \rightarrow}\\&\quad \mathrm{R = Me\ (\mathbf{4}),\ Et\ (\mathbf{5})}\\&\qquad\qquad \mathrm{2RSiMe_3 + [R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2} \qquad (3)\\&\qquad\qquad\qquad \mathrm{R = Me\ (\mathbf{8}),\ Et\ (\mathbf{9})}\end{aligned}$$

In comparison with other elimination reactions, dealkylsilylations have been studied only rarely. Adducts of alkyls of group 12 and 13 metals and trialkylsilyl chalcogens and pnicogens eliminate tetraalkylsilane and form binary 12/16[18] and 13 /15[19] compounds, respectively. The reaction of $CdMe_2$ with $Se(SiMe_3)_2$ was proposed to proceed via a unimolecular 1,2-elimination of $SiMe_4$ from $Me_2Cd{\cdot}Se(SiMe_3)_2$.[18] However, dimeric intermediates were isolated in the reactions of gallium and indium trialkyls with $P(SiMe_3)_3$.[19] These findings are more consistent with an *inter*molecular alkylsilane elimination. Similarly, the elimination reactions from $R_3Al{\cdot}OP(OSiMe_3)_3$ provide ultimately the cyclic dimeric products, presumably through a bimolecular pathway. The formation of the aluminophosphate is clearly facilitated by the energy difference between Al−C (259 $kJ{\cdot}mol^{-1}$)[22] and Al−O (585 $kJ{\cdot}mol^{-1}$)[23] bonds. This large thermodynamic driving force easily overcomes an unfavorable transformation of an Si−O (439 $kJ{\cdot}mol^{-1}$)[24] into an Si−C bond (322 $kJ{\cdot}mol^{-1}$).[22] Interestingly, the stronger of the two bonds in the P−O−$SiMe_3$ moiety is cleaved, while the weaker, P−O (369 $kJ{\cdot}mol^{-1}$),[25] is retained. Its reaction would lead to an even weaker P−C bond (271 $kJ{\cdot}mol^{-1}$),[25] but more importantly, the additional gain from the P═O to P−O−Al transformation would be lost. The interactions of alkylaluminum compounds with SiO_2[26] and organosiloxanes[27] which result in products with newly formed Si−C bonds are well established.

The gallium analogue **7** was converted to the four-ring compound **10** only slowly on prolonged heating (136 h, 50%). This lower reactivity may be explained by the less exothermic transformation of the Ga−C (238 $kJ{\cdot}mol^{-1}$)[22] to Ga−O (430 $kJ{\cdot}mol^{-1}$)[23] bond and by a lower propensity of Ga to higher coordination numbers necessary for the transition state.

For comparison, **8** and **9** were prepared by a modification of the published method from R_2AlCl and $OP(OSiMe_3)_3$ by dechlorosilylation[10a] (eq 4).

$$\begin{aligned}&\mathrm{2R_2AlCl + 2OP(OSiMe_3)_3 \rightarrow}\\&\qquad \mathrm{[R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2 + 2Me_3SiCl} \qquad (4)\\&\qquad\qquad \mathrm{R = Me\ (\mathbf{8}),\ Et\ (\mathbf{9})}\end{aligned}$$

The ^{13}C and ^{29}Si NMR spectra of **8**, **9**, and **10** substantiated the cyclic dimeric formulation by displaying the X part of an AA′X pattern for the Me_3SiO groups. The signals appeared as doublets with an additional weak central line. A simulation showed that the $^4J_{PP}$ coupling constant is smaller than 0.5 Hz. ^{31}P NMR signals of the phosphate groups in these four-rings are shifted to lower field by nearly 3 ppm with respect to the parent adducts (7 ppm for the Ga compound **10**) and

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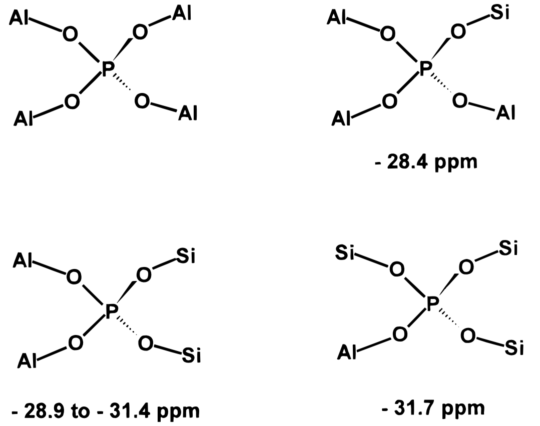
Scheme 2



display a ^{29}Si satellite pattern of the AA′ part of the AA′X system.

One can think of the adducts $R_3Al{\cdot}OP(OSiMe_3)_3$ (R = Me (**4**), Et (**5**)), the four-ring compounds $[R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (R = Me (**8**), Et (**9**), t-Bu (**11**)[10a]), and the cube $[t\text{-}BuAl(\mu_2\text{-}O)_3P(OSiMe_3)]_4$[10a] as a series of molecular models of the structural units shown in Scheme 2. Although these units have not been found in the four-connected networks of silicoaluminophosphate materials (SAPO)[28] due to the Si−O−P avoidance principle,[29] the ^{31}P NMR chemical shifts of the phosphate center in these models follow the order found in other networks containing $PO_4(M^n)_x(M^{n+1})_{4-x}$ structural moieties.[30] A higher shielding effect is produced by a progressive replacement of cations with a lower charge/radius ratio (M^n) by the cations with the higher ratio (M^{n+1}).

Finally, the identity of **8** and **9** was confirmed by single-crystal X-ray analyses. Crystallographic details are summarized in Table 1. The molecular structure of **8** is shown in Figure 1; the structure of **9** is not shown, as it is very similar to that of **8**. Important bond distances and angles of **8** and **9** are gathered in Table 2. For comparison, relevant data of a closely related derivative, $[t\text{-}Bu_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (**11**),[10a] are also listed. The centrosymmetric $Al_2P_2O_4$ core has a chair conformation. The two independent Al−O distances are identical (within 3σ), and they are very similar in **8** and **11**. Their values are also in agreement with the reference value of 1.85 Å for an Al−O bond with equal normal and dative bonding contributions.[31] The two independent intra-ring P−O bond distances in the $(\mu_2\text{-}O)_2P(OSiMe_3)_2$ group are also indistinguishable in **8** (av 1.503(3) Å), but they are slightly longer (by 0.03 Å) than the corresponding distances in the t-Bu analogue **11**. Similar values have been observed in $[t\text{-}BuNTi(O_2P(OSiMe_3)_2)_2]_2$ (av 1.50 Å).[32] The O−Al−O (approximately 102°) and O−P−O (approximately 114°) angles are comparable in all three compounds. However, these rings feature a set of two different Al−O−P angles.

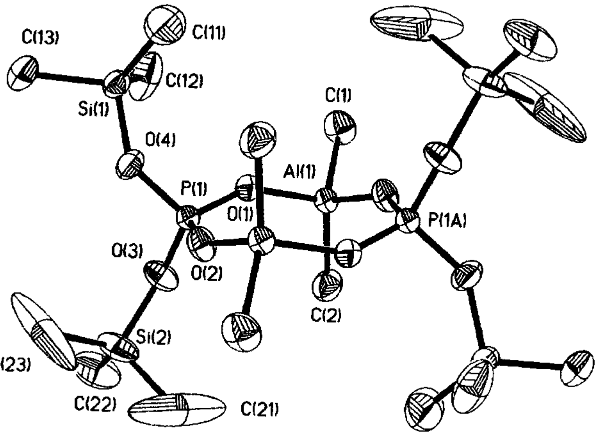


Figure 1. Molecular structure of $[Me_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (**8**).

Table 2. Selected Bond Distances (Å) and Angles (deg)[a] in $[R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$, R = Me (8), Et (9),[b] *t*-Bu (11)[c]

	8	**9A**	**9B**	**11**[c]
P−O intra-ring	1.503(3)	1.445(4) 1.486(4)	1.463(5) 1.491(5)	1.470(6)
P−O extra-ring	1.541(3)	1.496(6)	1.508(6)	1.504(6)
Al−O	1.811(3)	1.768(6)	1.776(7)	1.798(6)
Al−C	1.954(4)	1.98(2)	1.98(2)	1.972(7)
Si−O	1.672(3)	1.641(6)	1.627(5) 1.669(5)	1.650(4) 1.628(4)
Al−O−P	148.0(1) 146.5(1)	159.1(3) 152.4(3)	150.0(4) 147.1(3)	160.9(3) 151.4(2)
O−P−O intra-ring	114.7(1)	114.8(3)	115.0(3)	113.6(2)
O−Al−O	101.3(1)	103.2(2)	102.1(2)	102.3(2)

[a] Pairs of independent parameters within the molecules were averaged when their difference (Δ) was smaller than 3σ(Δ). [b] Two independent half-molecules, **9A** and **9B**. [c] Ref 10a.

Reaction of 2 with Me_2NH. Further relation of the trialkylaluminum adducts $R'_3M{\cdot}OP(OR)_3$ to the above-mentioned $(Me_2N)_3M{\cdot}OP(OR)_3$ systems[17] was revealed by the reaction of **2** with liquid Me_2NH. Adding an excess of the amine to **2** at room temperature caused no reaction even after 1 month. However, heating of the clear reaction solution to 80 °C overnight produced a white, insoluble precipitate of aluminophosphate and $EtNMe_2$, which was identified by ^1H and ^{13}C NMR spectroscopy. This suggests that the trialkylaluminum adduct **2** was converted by aminolysis to the intermediate aluminum amide adduct, which subsequently decomposed to $AlPO_4$ and tertiary amine according to eqs 5 and 6. Interestingly, related thermal oligomerization (at 175 °C) of an $AlEt_3/OP(OEt)_3$ mixture has been reported without further mechanistic details.[33] The resulting oligomeric oil was converted to an amorphous $AlPO_4$ material by introducing NH_3 gas or by calcination at 500 °C.

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$$Me_3Al{\cdot}OP(OEt)_3 + 3Me_2NH \rightarrow 3CH_4 + (Me_2N)_3Al{\cdot}OP(OEt)_3 \quad (5)$$

$$(Me_2N)_3Al{\cdot}OP(OEt)_3 \rightarrow AlPO_4 + 3EtNMe_2 \quad (6)$$

Conclusion

Aluminum and gallium alkyls form stable adducts with alkyl and aryl esters of phosphoric acid. On the other hand, the trimethylsilyl ester adducts undergo a thermally induced dealkylsilylation reaction, which provides cyclic aluminophosphates $[R_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$, R = Me (**8**), Et (**9**). These are easily synthesized in high purity and yields from commercially available starting materials and contain reactive Al−alkyl and P−O−SiMe$_3$ groups. Therefore, they will serve us as precursors for the studies of their transformation to three-dimensional aluminophosphate materials by nonaqueous routes.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. J.P. thanks the Alexander von Humboldt-Stiftung for a research fellowship.

Supporting Information Available: Tables (S1−S10) of crystallographic details, atomic coordinates, bond lengths and bond angles, thermal displacement parameters, and hydrogen position parameters for **8** and **9**, and ^{1}H NMR spectra (18 pages). Ordering information is give on any current masthead page.

OM9806702