Organometallics **2001,** *20,* 4833−4839

Acac-Promoted Rearrangement of an Alkylaluminophosphonate Tetramer to a Decamer

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Received May 23, 2001

Reaction of $MeP(O)(OH)_2$ with $^tBu_3Al$ at low temperature and subsequent trimethylsilylation of the crude reaction product with Me_3SiNMe_2 yielded the cyclic dimer $[^tBu_2AlO_2P(OSiMe_3)Me]_2$ (**1**). In contrast, reaction of $MeP(O)(OH)_2$ with $^tBu_3Al$ in refluxing toluene/THF yielded a mixture of $[^tBuAlO_3PMe]_4$ (**2**), $[^tBuAlO_3PMe]_6$ (**3**), and $[^tBuAlO_3PMe]_{10}$ (**4**). Crystallization and sublimation of the crude mixture gave compound **2** in 54% yield. Small quantities of pure **3** were obtained by fractional crystallization of the remaining reaction products. Crystalline **3** was also obtained by slow diffusion of a $CHCl_3$ solution of acetylacetone into a solution of **2** in poly(ethylene oxide)/$CHCl_3$ gel. It was not possible to obtain reproducible yields of pure **4** by fractional crystallization of the crude mixture of **2**−**4**. Instead, compound **4** was obtained in 86% yield by an acetylacetone-promoted rearrangement of **2**. In the absence of acetylacetone, $CDCl_3$ solutions of **4** rearrange to a mixture of **2**, **3**, and **4** over a period of days. The role of acetylacetone in the rearrangement of **2** to **4** has not been elucidated. Compounds **1**−**4** were characterized by multinuclear (^1H, ^{13}C, ^{31}P) NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis. The molecular structures for compounds **2**−**4** were determined by X-ray crystallography.

Introduction

Investigations of molecular phosphates and phosphonates of the group 13 elements have thus far been driven by their potential use as models of, and potential precursors to, phosphate materials,[1−20] with particular attention focused on precursors to microporous alumino- and gallophosphate molecular sieves.[21,22] With this aim, organic-substituted derivatives of four-ring (4R),[4−9] six-ring (6R),[10] double-four-ring (D4R),[1,4−7,11−16] and double-six-ring (D6R)[11,17] secondary building units (SBUs) have been prepared using several synthetic approaches. Cage

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10.1021/om010432y CCC: $20.00
Publication on Web 09/20/2001

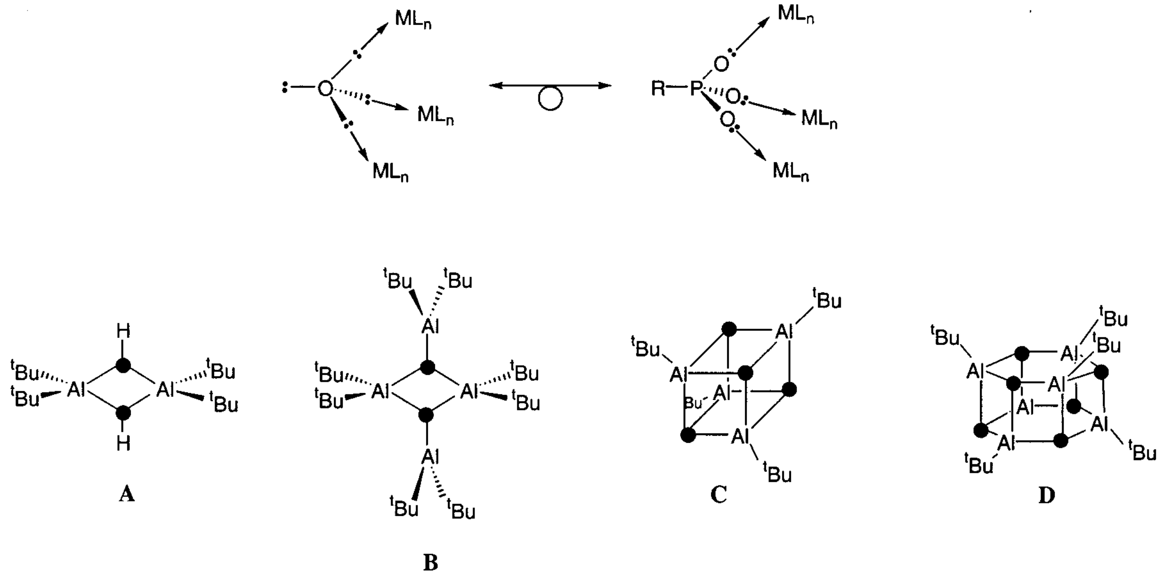

Figure 1. Structural relationship of alkylaluminophosphonates and *tert*-butylaluminoxanes; ● represents μ_3-R′PO_3^{2-} and μ_3-O^{2-}, respectively.

fragmentation and intermolecular rearrangements have been studied for molecular gallophosphonates,[6] and some unique clusters have been obtained when alkali metal salts are incorporated into the resulting phosphonate structures.[10,18] There have also been preliminary reports on conversion of these molecular precursors to phosphate and phosphonate materials.[11,19,20]

We previously suggested that alkylaluminophosphonates might alternatively be utilized as alkylaluminoxane analogues.[23] This suggestion was prompted by the structural similarity of alkylaluminophosphonates to well-studied *tert*-butylaluminoxanes[24] based on an isolobal relationship of μ_3-RPO_3^{2-} and μ_3-O^{2-} groups (Figure 1). The *tert*-butylaluminoxanes **A**, **B**, and **D** are known and have been structurally characterized, as are the phosphonate tetramers **C**, hexamers **D**, and trimethylsilyl derivatives of dimeric **A**.[1] The tetrameric (n = 4) aluminoxane **C** of formula $(^tBuAlO)_n$ is not known, presumably due to strain introduced by the 90° bond angles at oxygen,[25] but the tetramer may still be considered the parent compound of the series, three of which (n = 6, 8, 9) are stable and have been structurally characterized.[24] Phosphonate dimers **B**, believed to be formed in 2:1 reaction mixtures of aluminum alkyl and phosphonic acids, have not been isolated, but the analogous gallophosphonate $[(^tBu_2Ga)_2O_3PPh]_2$ has been isolated and fully characterized.[8]

On the basis of this relationship, and cognizant that Vandenberg claimed in a patent that reaction products of methylphosphonic acid and aluminum alkyls affect epoxide polymerization,[26] we investigated alkylaluminophosphonate solutions as catalysts for the homopolymerization of epichlorohydrin (ECH) to high-molecular-weight polyether elastomers.[23] Indeed, reaction solutions of methylphosphonic acid and $^tBu_3Al$ were found to be active catalysts, capable of polymerizing ECH to polyether elastomers with M_n of 1.3×10^5 within 15 min. The catalytically active components of these mixtures were not isolated or identified in our previous study, so an investigation into the reaction of $^tBu_3Al$ with methylphosphonic acid was warranted.

Herein, we report that reactions of methylphosphonic acid with $^tBu_3Al$ give the 4R, D4R, and D6R derivatives $[^tBu_2AlO_2P(OSiMe_3)Me]_2$ (**1**), $[^tBuAlO_3PMe]_4$ (**2**), and $[^tBuAlO_3PMe]_6$ (**3**), respectively. Furthermore, we report that acetylacetone, which is a key component of Vandenberg's aluminoxane-based epoxide polymerization catalysts,[27] promotes rearrangement of **2** to the unprecedented decameric cluster $[^tBuAlO_3PMe]_{10}$ (**4**). The synthesis, characterization, and stability of **1**−**4** are discussed.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Pentane, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from sodium. Acetylacetone was

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purified by fractional distillation. Benzene-d_6 and $CDCl_3$ were dried by storage over activated molecular sieves. $^tBu_3Al$ was prepared as previously described.[28] Methylphosphonic acid, Me_2NSiMe_3, ^tBuLi, $AlCl_3$, and poly(ethylene oxide) (MW = 100 000) were purchased from Aldrich Chemical and used without further purification. Solution NMR spectra were recorded on Bruker AMX-500, Varian Unity 400, and Varian Inova 300 spectrometers using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Mattson Galaxy 5000 Series FTIR spectrometer on KBr pellets. High-resolution mass spectrometric analyses were provided by the Nebraska Center for Mass Spectrometry. Elemental analyses and solution molecular weight measurements were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of $[^tBu_2AlO_2P(OSiMe_3)Me]_2$ (1). A solution of methylphosphonic acid (0.882 g, 9.19 mmol) in 7 mL of THF was added dropwise at −40 °C to a stirred toluene solution (10 mL) of $^tBu_3Al$ (1.77 g, 8.95 mmol). The resulting solution was stirred at −30 °C for 30 min and then at room temperature for an additional 45 min. Dimethyl(trimethylsilyl)amine (1.5 mL, 9.4 mmol) was added dropwise, and the reaction solution was stirred for 30 min. Volatiles were removed in vacuo, and the remaining residue was dissolved in a minimum amount of toluene. Cooling at −20 °C overnight yielded clear, colorless crystals that were isolated by filtration and dried in vacuo. A second crop of **1** was similarly obtained by concentration of the filtrate and cooling to −20 °C. Yield: 1.29 g, 1.91 mmol, 43%. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.52 (d, $^2J_{PH} = 18.3$ Hz, 3H, PCH_3), 0.83 (s, 18H, ^tBu), 0.29 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz): δ 29.91 (s, $C(CH_3)_3$), 14.30 (d, $^1J_{PC} = 158.1$ Hz, PCH_3), 13.96 (br s, $C(CH_3)_3$), 0.93 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz): δ 3.4 (s). MS (EI) *m/z* (assignment, relative intensity): 601 ($M^+ - CH_3$, 2), 559 ($M^+ - {}^tBu$, 47), 503 ($M^+ - {}^tBu - C_4H_8$, 73), 178 (100). HRMS (EI) *m/z* for $C_{20}H_{51}O_6Al_2Si_2P_2$ ($M^+ - {}^tBu$): calcd, 559.2330; found, 559.2336. Anal. Calcd for $C_{24}H_{60}O_6Al_2Si_2P_2$: C, 46.73; H, 9.80; Al, 8.75; P, 10.04. Found: C, 46.10; H, 10.35; Al, 9.34; P, 10.03.

Preparation of $[^tBuAlO_3PMe]_4$ (2). A solution of methylphosphonic acid (1.25 g, 13.0 mmol) in 7 mL of THF was added dropwise at 0 °C to a stirred toluene (60 mL) and THF (10 mL) solution of $^tBu_3Al$ (2.56 g, 12.9 mmol). After warming to room temperature, THF was removed by concentration of the cloudy solution in vacuo. Refluxing the concentrate for 45 h yielded a small quantity of precipitate (mainly **2**, but contaminated with **3**, **4**, and unidentified products), which was isolated by filtration and fractionally recrystallized to effect separation of **2**, **3**, and samples enriched in **4**. Repeated concentration of the original filtrate and storage at −20 °C yielded several crops of crystalline **2**. The product was purified by sublimation at 240 °C/0.1 mmHg. Yield of **2**: 1.25 g, 1.75 mmol, 54%. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.41 (d, $^2J_{PH} = 19.0$ Hz, 3H, PCH_3), 0.85 (s, 9H, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ 30.93 (br, $C(CH_3)_3$), 28.87 (s, $C(CH_3)_3$), 11.90 (d, $^1J_{PC} = 165.4$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 10.8 (s). MS (EI) *m/z* (assignment, relative intensity): 655.1 ($M^+ - {}^tBu$, 100). HRMS (EI) *m/z* for $C_{16}H_{39}O_{12}Al_4P_4$ ($M^+ - {}^tBu$): calcd, 655.0654; found, 655.0652. Anal. Calcd for $C_{20}H_{48}O_{12}Al_4P_4$: C, 33.72; H, 6.74; Al, 15.16; P, 17.40. Found: C, 32.48; H, 7.10; Al, 15.58; P, 16.52.

Preparation of $[^tBuAlO_3PMe]_6$ (3). Poly(ethylene oxide) (500 mg) and 2.0 mL of chloroform were stirred for 10 min. To this was added a chloroform solution (3.3 mL) of **2** (100 mg, 0.140 mmol), and the resulting mixture was stirred for 15 min to give a slightly yellow, turbid gel. A chloroform solution of acetylacetone (0.20 mL, 1.95 mmol) was layered onto the gel, and the reaction mixture was allowed to stand without interruption for two months. Crystals that formed just below the gel/solution interface were isolated by decantation. Spectroscopic data for these crystals were identical to those for samples of **3** obtained as a minor product in the preparation of **2**. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.46 (d, $^2J_{PH} = 18.9$ Hz, PCH_3), 0.83 (s, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 29.70 (br, $C(CH_3)_3$), 28.76 (s, $C(CH_3)_3$), 12.84 (d, $^1J_{PC} = 163.6$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 6.6 (s).

Preparation of $[^tBuAlO_3PMe]_{10}$ (4). To a solution of **2** (0.503 g, 0.706 mmol) in 15 mL of toluene was added acetylacetone (0.75 mL, 7.31 mmol). The resulting solution was stirred at room temperature for 5 h. In many cases, a small quantity of precipitate was removed by filtration and discarded. Storage of the filtrate at −20 °C resulted in a white precipitate that was isolated by filtration and dried briefly in vacuo. A second and third crop were similarly obtained by concentration of the filtrate and cooling to −20 °C. Yield: 0.435 g, 0.244 mmol, 86%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.458 (d, $^2J_{PH} = 19.2$ Hz, PCH_3), 1.450 (d, $^2J_{PH} = 19.0$ Hz, PCH_3), 1.440 (d, $^2J_{PH} = 18.3$ Hz, PCH_3), 1.426 (d, $^2J_{PH} = 18.9$ Hz, PCH_3), 1.421 (d, $^2J_{PH} = 18.9$ Hz, PCH_3), 0.858 (s, ^tBu), 0.847 (s, ^tBu), 0.832 (s, ^tBu), 0.827 (s, ^tBu), 0.809 (s, ^tBu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ 29.04 (s, $C(CH_3)_3$), 28.87 (s, $C(CH_3)_3$), 28.80 (s, $C(CH_3)_3$), 28.78 (s, $C(CH_3)_3$), 13.70 (d, $^1J_{PC} = 158.5$ Hz, PCH_3), 13.36 (d, $^1J_{PC} = 158.6$ Hz, PCH_3), 12.56 (d, $^1J_{PC} = 164.3$ Hz, PCH_3), 12.45 (d, $^1J_{PC} = 164.8$ Hz, PCH_3), 11.88 (d, $^1J_{PC} = 165.9$ Hz, PCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): δ 11.9 (s), 8.3 (s), 8.2 (s), 5.3 (s), 4.7 (s). MS (EI) *m/z* (assignment, relative intensity): 1011.3 ($6M^+ - {}^tBu$, 37), 833.3 ($5M^+ - {}^tBu$, 23), 655.1 ($4M^+ - {}^tBu$, 100). HRMS (EI) *m/z* for $C_{21}H_{51}O_{15}Al_5P_5$ ($5M^+ - {}^tBu$): calcd, 833.0993; found, 833.1011. Anal. Calcd for $C_{25}H_{60}O_{15}Al_5P_5 \cdot C_7H_8$: C, 39.11; H, 6.98; Al, 13.73; P, 15.76. Found: C, 38.83; H, 7.11; Al, 14.63; P, 15.44.

X-ray Crystallography for 2−4. Crystals of **2** were grown from a toluene solution at −20 °C. The crystal of **3** was obtained by slow diffusion of a chloroform solution of acetylacetone into a poly(ethylene oxide)/chloroform gel solution of **2** over a period of two months. Vapor-phase diffusion of acetylacetone into a toluene solution of **2** yielded crystals of **4** as a toluene disolvate within 6 days. The X-ray diffraction data for **2**−**4** were collected on a Siemens three-circle platform diffractometer equipped with a CCD detector maintained near −54 °C and the χ axis fixed at 54.74°. The frame data were acquired with the SMART[29] software using Mo Kα radiation ($\lambda = 0.710\ 73$ Å) from a fine-focus tube. Cell constants were determined from sixty 30 s frames. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 30 s/frame at the detector resolution of 512 × 512 pixels. A total of 1271 frames were collected for the data set. Additional frames (50 for **2**, **3**; 100 for **4**) were collected to determine crystal decay. The frames were processed on an SGI-Indy/Indigo 2 workstation by using the SAINT[30] software to give the *hkl* file corrected for decay and for Lorentz and polarization effects. For each compound, an absorption correction was performed using SADABS.[31] The structures were solved by direct methods using SHELXS-90 (**2**, **3**) or SHELXS-86 (**4**).[32] All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods on F^2, using all unique data and SHELXL-93.[33] Hydrogens were placed in their geometrically generated positions and refined as a riding model. In compound **2**, the methyl carbons of the *tert*-butyl groups on Al(1)

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Table 1. Summary of X-ray Crystallographic Data

	2	**3**	**4**
formula	$C_{20}H_{48}Al_4O_{12}P_4$	$C_{31}H_{72}Al_6Cl_3O_{18}P_6$	$C_{32}H_{68}Al_5O_{15}P_5$
fw	712.38	1186.94	982.61
cryst syst	triclinic	rhombohedral	monoclinic
space group	$P\bar{1}$	$R\bar{3}$	$P2(1)/n$
a, Å	9.9066(1)	22.4899(8)	12.1769(3)
b, Å	10.5862(2)	22.4899(8)	23.7660(6)
c, Å	19.3053(4)	10.5590(6)	19.0502(5)
α, deg	85.638(1)		
β, deg	88.96(1)		99.252(1)
γ, deg	79.744(1)		
V, Å^3	1986.47(6)	4625.2(4)	5441.3(2)
Z	2	3	4
D_{calcd}, g cm^{-3}	1.191	1.278	1.199
T, °C	27(2)	−60(2)	−123(2)
μ(Mo Kα), cm^{-1}	3.23	4.45	3.01
λ, Å	0.710 73	0.710 73	0.710 73
transm coeff	0.949−0.766	0.962−0.732	0.992−0.871
2θ limits, deg	4−50	4−50	4−54
total no. of data	9796	6954	34602
no. of unique data	6481	1480	11949
no. of obsd data[a]	5398	1480	7292
no. of params	418	105	599
R1[b]	0.0552	0.0691	0.0555
wR2[c]	0.1243	0.1215	0.1229
max., min. peaks, e/Å^3	0.419, −0.258	0.302, −0.448	0.494, −0.323

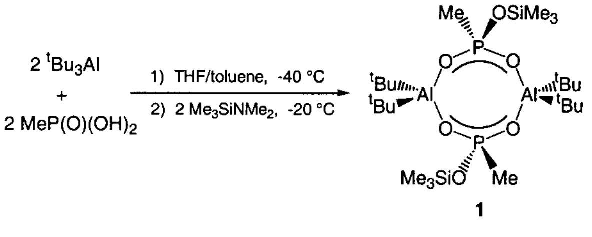
[a] $I > 2\sigma(I)$. [b] $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

and Al(4) were found to be disordered and were modeled with major methyl site occupancies of 64 and 73%, respectively. Similarly for **4**, the disordered methyl carbons of the *tert*-butyl groups on Al(1), Al(3), and Al(5) were modeled with major methyl group site occupancies of 75, 58, and 55%, respectively. The disordered $CHCl_3$ solvate in **3** was modeled adequately. Details of data collection, solution, and refinement are given in Table 1.

Results and Discussion

Reactions of $^tBu_3Ga$ with a phosphonic or phosphoric acid were previously shown to yield cyclic dimers of the formula $[^tBu_2GaO_2P(OH)R]_2$ (R = H, Me, ^{t}Bu, Ph, OH).[5,6] Although these dimers are isolable as solids, they are prone to further alkane elimination to form cuboidal tetramers $[^tBuGaO_3PR]_4$ (R = Me, ^{t}Bu, Ph). This reactivity complicates purification and spectroscopic characterization of the heterocycles. Similarly, previous work on reactions of $^tBu_3Al$ with a phosphonic acid at low temperature suggested the formation of heterocycles $[^tBu_2AlO_2P(OH)R]_2$ (R = ^{t}Bu, Ph), although only $[^tBu_2AlO_2P(OH)Ph]_2$ was isolated and spectroscopically characterized.[7] Compared to the cyclic gallophosphonates, the cyclic aluminophosphonates are more prone to alkane elimination under mild conditions. To aid characterization of these alumino- and gallophosphonate heterocycles, their hydroxyl substituents were treated with Me_3SiNMe_2 to give trimethylsilylated derivatives $[^tBu_2MO_2P(OSiMe_3)R]_2$ (M = Al, R = Ph; M = Ga, R = H, Me, ^{t}Bu, Ph, $OSiMe_3$) of greater stability and more amenable to spectroscopic and crystallographic characterization.[5−7] The same approach was utilized here.

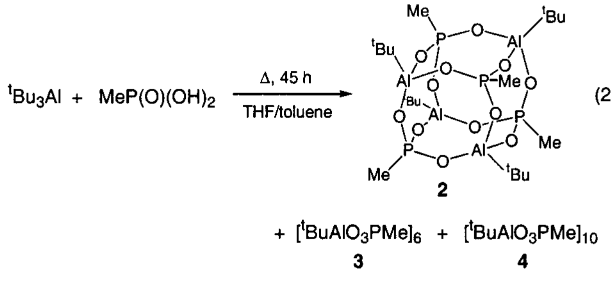
Reaction of $^tBu_3Al$ with an equimolar amount of MeP(O)(OH)$_2$ in THF/toluene at −40 °C, followed by addition of Me_3SiNMe_2 at room temperature, yielded $[^tBu_2AlO_2P(OSiMe_3)Me]_2$ (**1**) in 43% yield (eq 1). The ^{1}H NMR spectrum of **1** exhibits a doublet at 1.52 ppm ($^2J_{PH}$ = 18.3 Hz) for the methyl substituent on phosphorus and singlet resonances at 0.83 and 0.29 ppm assigned to ^{t}Bu and $SiMe_3$ substituents, respectively. Integration of the resonances reveals a 1:2:1 ratio of Me, ^{t}Bu, and $SiMe_3$ substituents, which is consistent with the proposed structure. Although cyclic gallophosphonates were shown to exist as a mixture of cis and trans isomers in solution,[5,6] single ^{t}Bu, $SiMe_3$, and Me resonances in the ^{1}H NMR spectrum and the singlet resonance at 3.4 ppm in the ^{31}P NMR spectrum of **1** are consistent only with the trans isomer. Spectroscopic and crystallographic data previously confirmed that $[^tBu_2AlO_2P(OSiMe_3)Ph]_2$ similarly adopts the trans configuration in solution and in the solid state.[7] The electron-impact mass spectrum of **1** shows fragments at m/z 601 and 559 assignable to loss of Me and ^{t}Bu, respectively, from the molecular ion. The elemental composition of the $M^+ - {}^tBu$ fragment was confirmed by high-resolution mass measurement.



1

(1)

Reaction of $^tBu_3Al$ with MeP(O)(OH)$_2$ in refluxing toluene/THF yields crude $[^tBuAlO_3PMe]_4$ (**2**), contaminated with trace quantities of $[^tBuAlO_3PMe]_6$ (**3**) and $[^tBuAlO_3PMe]_{10}$ (**4**) (eq 2). Formation of **2** is favored by



(2)

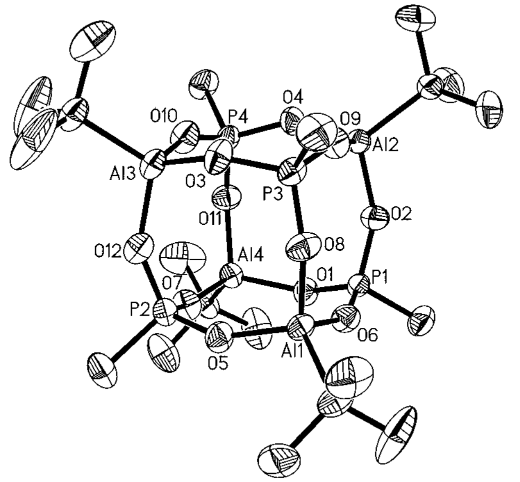


Figure 2. ORTEP drawing of [^{t}BuAlO$_3$PMe]$_4$ (**2**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

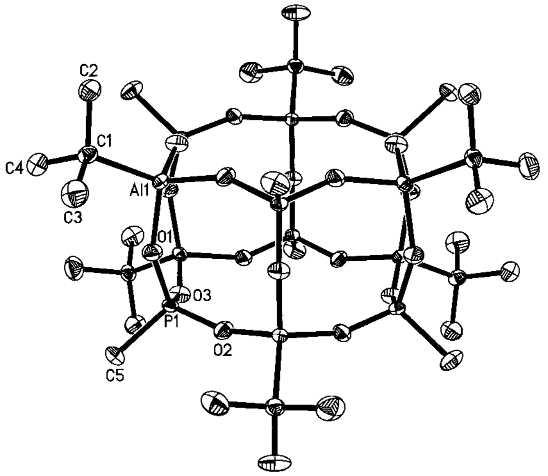


Figure 3. ORTEP drawing of [^{t}BuAlO$_3$PMe]$_6$ (**3**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [^{t}BuAlO$_3$PMe]$_4$ (2)

Distances			
Al(1)−O(5)	1.763(3)	P(1)−O(1)	1.512(3)
Al(1)−O(6)	1.762(3)	P(1)−O(2)	1.513(3)
Al(1)−O(8)	1.756(3)	P(1)−O(6)	1.513(3)
Angles			
O(8)−Al(1)−O(6)	106.1(2)	O(8)−Al(1)−O(5)	105.3(2)
O(6)−Al(1)−O(5)	105.1(2)	O(8)−Al(1)−C(1)	111.6(2)
O(6)−Al(1)−C(1)	113.0(2)	O(5)−Al(1)−C(1)	115.0(2)
O(1)−P(1)−O(2)	111.0(2)	O(1)−P(1)−O(6)	111.5(2)
O(2)−P(1)−O(6)	110.9(2)	O(1)−P(1)−C(17)	107.4(2)
O(2)−P(1)−C(17)	107.8(2)	O(6)−P(1)−C(17)	108.0(2)
P(1)−O(2)−Al(2)	151.8(2)	P(4)−O(4)−Al(2)	144.6(2)
P(1)−O(6)−Al(1)	151.1(2)	P(3)−O(8)−Al(1)	152.3(2)
P(4)−O(10)−Al(3)	155.0(2)	P(2)−O(12)−Al(3)	147.7(2)

high reaction temperature and long reaction time, whereas greater quantities of **3** and **4** are obtained under milder conditions. For example, refluxing in toluene for 45 h yields a product mixture with minimal quantities of **3** and **4**, whereas stirring at room temperature for 2 days yields a mixture of **2**−**4** that is moderately enriched in **3** and **4**. In our hands, compound **2** is always the major product of this reaction. Crystallization from toluene and sublimation at 240 °C/0.1 mmHg gave pure **2** in 54% yield. The ^{1}H NMR spectrum of **2** features a singlet ^{t}Bu resonance at 0.85 ppm and a doublet resonance at 1.41 ppm ($^2J_{PH}$ = 19.0 Hz) for the methyl substituent on phosphorus. The simplicity of the ^{1}H NMR spectrum and the singlet resonance at 10.8 ppm in the ^{31}P NMR spectrum suggest that **2** is highly symmetric. ^{1}H NMR and IR spectroscopic data indicate no hydroxyl substituents are present in **2**. Elemental analysis is consistent with the formula [^{t}BuAlO$_3$PMe]$_n$, but it is the base peak at *m/z* 655 (M$^+$ − ^{t}Bu) in the electron-impact mass spectrum that confirms **2** to be a tetramer (n = 4) in the gas phase. Elemental composition of the M$^+$ − ^{t}Bu fragment was verified by high-resolution mass measurement. X-ray crystallography confirmed **2** to be a tetramer in the solid state.

The molecular structure of **2** is shown in Figure 2. Selected bond distances and angles are given in Table 2. The structure of **2** is composed of a cuboidal Al$_4$P$_4$O$_{12}$ core in which distorted tetrahedral aluminum and phosphorus atoms alternately occupy vertex positions and oxygen atoms bridge each edge. Aluminum−oxygen distances (1.756(3)−1.773(4) Å; av 1.763 Å), phosphorus−oxygen distances (1.503(3)−1.515(3) Å; av 1.511 Å), and Al−O−P angles (144.6(2)−155.0(2)°; av 150.2°) are comparable with those reported for the Al$_4$P$_4$O$_{12}$ cores of [^{t}BuAlO$_3$PR]$_4$ (R = ^{t}Bu, Ph, C$_6$H$_4$CN),[1,7,11] [MeAlO$_3$-PMe]$_4$,[1,7] and [^{i}BuAlO$_3$P^{t}Bu]$_4$.[13]

Separation of **3** and **4** from crude mixtures of **2**−**4** (eq 2) by fractional crystallization proved considerably more difficult. After many attempts, we noted that compound **3** is less soluble in THF than are tetramer **2** and decamer **4**. Thus, dissolution of the crude mixture of **2**−**4** in minimal THF, followed by rapid filtration, afforded pure samples of the less soluble **3**. This separation method is tedious and yields were low, but it did provide milligram quantities of pure **3** for spectroscopic characterization.

Compound **3** is highly symmetric based on a single ^{31}P NMR resonance at 6.6 ppm, as well as a single ^{t}Bu resonance at 0.83 ppm and a doublet methyl resonance ($^2J_{PH}$ = 18.9 Hz) at 1.46 ppm in the ^{1}H NMR spectrum. Integration of the ^{1}H NMR resonances shows a 1:1 ratio of ^{t}Bu and Me substituents, consistent with the formula [^{t}BuAlO$_3$PMe]$_n$. Furthermore, no hydroxyl groups are present based on NMR and IR data. The mass spectrum of a mixture of **2** and **3** shows a peak at *m/z* 1011.3 assignable to the M$^+$ − ^{t}Bu fragment of a hexamer (n = 6). A hexameric structure is precedented by crystallographic characterization of [MeAlO$_3$P^{t}Bu]$_6$ and [^{t}BuAlO$_3$P(C$_6$H$_4$CN)]$_6$.[10,11] A hexameric structure for **3** is consistent not only with the symmetry suggested by the NMR data but also with the 4.2 ppm upfield shift of the ^{31}P NMR resonance for **3** compared with that for **2**. Roesky similarly observed a 4.1 ppm upfield shift of the ^{31}P NMR resonance for [MeAlO$_3$P^{t}Bu]$_6$ compared with that for [MeAlO$_3$P^{t}Bu]$_4$.[10] In fact, [MeAlO$_3$P^{t}Bu]$_4$ and [MeAlO$_3$P^{t}Bu]$_6$ are isosteric with **2** and **3**, respectively, with the only difference being the substitution at phosphorus and aluminum are interchanged between the two sets of compounds. X-ray crystallography confirmed **3** to be a hexamer in the solid state.

Compound **3** crystallizes in the rhombohedral space group $R\bar{3}$. The unique portion of the unit cell contains one ^{t}BuAlO$_3$PMe unit, which, upon symmetry expansion, yields a drum-like structure (Figure 3) with an

Table 3. Selected Bond Distances (Å) and Angles (deg) for [^{t}BuAlO$_3$PMe]$_6$ (3)

Distances			
P(1)−O(1)	1.516(3)	P(1)−O(2)	1.507(3)
P(1)−O(3)	1.511(3)	Al(1)−O(1)	1.759(3)
Al(1)−O(2B)[a]	1.755(3)	Al(1)−O(3A)[a]	1.752(3)
Angles			
O(2B)−Al(1)−O(1)[a]	107.4(2)	O(2B)−Al(1)−O(3A)[a]	104.3(2)
O(1)−Al(1)−O(3A)[a]	107.7(2)	O(2B)−Al(1)−C(1)[a]	114.0(2)
O(1)−Al(1)−C(1)	108.8(2)	O(3A)−Al(1)−C(1)[a]	114.3(2)
O(3)−P(1)−O(2)	110.3(2)	O(3)−P(1)−O(1)	111.2(2)
O(2)−P(1)−O(1)	111.2(2)	O(3)−P(1)−C(5)	107.8(2)
O(2)−P(1)−C(5)	108.0(2)	O(1)−P(1)−C(5)	108.3(2)
P(1)−O(1)−Al(1)	154.9(2)	P(1)−O(2)−Al(1A)[a]	153.2(2)
P(1)−O(3)−Al(1B)[a]	153.3(2)		

[a] A and B indicate symmetry-related atoms.

Al$_6$P$_6$O$_{18}$ core analogous to that reported for [MeAlO$_3$P^{t}Bu]$_6$ and [^{t}BuAlO$_3$P(C$_6$H$_4$CN)]$_6$.[10,11] This Al$_6$P$_6$O$_{18}$ core is also analogous to the D6R SBUs found in the aluminophosphate molecular sieves AlPO$_4$-5, AlPO$_4$-18, and their silicon- and metal-substituted derivatives.[21q,34] The inorganic core of **3** is comprised of two approximately parallel 12-membered Al$_3$P$_3$O$_6$ rings connected via six oxygen bridges. These latter Al−O−P linkages form six eight-membered rings along the edge of the drum-like core. Aluminum−oxygen (1.752(3)−1.759(3) Å; av 1.755 Å) and P−O (1.507(3)−1.516(3) Å; av 1.511 Å) distances (Table 3) are comparable with those for D4R derivatives, such as **2**, and previously reported D6R derivatives [MeAlO$_3$P^{t}Bu]$_6$ and [^{t}BuAlO$_3$P(C$_6$H$_4$CN)]$_6$.[10,11] Similarly, Al−O−P angles (153.2(2)−154.9(2)°; av 153.8°) are comparable with those observed in **2**, [MeAlO$_3$P^{t}Bu]$_6$, and [^{t}BuAlO$_3$P(C$_6$H$_4$CN)]$_6$. There is no variation between Al−O−P angles for oxygen atoms O(2) and O(3) which lie in the 12-membered rings compared with Al−O−P angles for oxygen atoms O(1) which bridge the two 12-membered ring. In the molecular structure of [MeAlO$_3$P^{t}Bu]$_6$, Al−O−P angles are smaller in the 12-membered rings and average 149.8°, whereas the six Al−O−P bridges that connect the 12-membered rings average 164.0°.

Unlike **3**, samples of **4** could not be adequately obtained by fractional crystallization of crude reaction mixtures containing **2**, **3**, and **4**. Heating compound **2** to 70 °C in toluene occasionally resulted in precipitation of pure **4**, and in one instance a yield of 70% was obtained. Yields were highly variable, and in many instances only traces of **4** were produced. Isolation of **4** might be explained by cage rearrangement of **2** to the less soluble kinetic product **4**, which precipitates under these conditions. Cage rearrangement for cuboidal gallophosphonates has been confirmed by observing intermolecular exchange in crossover experiments.[6] Nonetheless, this procedure did produce samples of pure **4** for characterization.

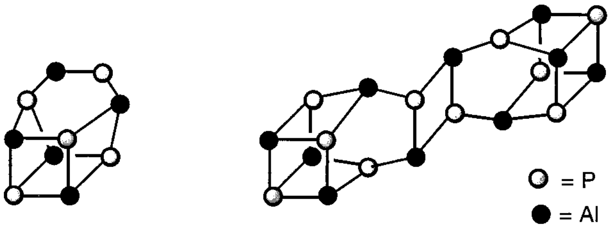


Figure 4. Ball and stick models for possible pentameric (left) and decameric (right) alkylaluminophosphonates [^{t}BuAlO$_3$PMe]$_5$ and [^{t}BuAlO$_3$PMe]$_{10}$. All organic substituents and edge-bridging oxygen atoms are omitted for clarity. Aluminum and phosphorus atoms alternate at vertexes.

Elemental analysis shows that compound **4** has the same composition as **2**, suggesting that **4** is an oligomer of [^{t}BuAlO$_3$PMe]$_n$. In agreement with this proposal, the ^{1}H NMR spectrum of **4** confirms the expected 1:1 ratio of ^{t}Bu and Me substituents. The ^{1}H NMR spectrum also indicates low molecular symmetry. There are five equally intense singlets from 0.858 to 0.809 ppm assigned to ^{t}Bu substituents and 10 peaks of equal intensity from 1.5 to 1.38 ppm assigned to doublets for the methyl substituents on phosphorus. Comparison of ^{1}H NMR spectra obtained on 300, 400, and 500 MHz spectrometers allowed reasonable assignments of chemical shifts (1.458 ≥ δ ≥ 1.421 ppm) and coupling constants (19.2 Hz ≥ $^2J_{\mathrm{PH}}$ ≥ 18.3 Hz) for the five methyl resonances. The molecular symmetry of **4** is also clearly reflected in the ^{13}C and ^{31}P NMR spectra. For example, the ^{31}P NMR spectrum of **4** exhibits five equally intense singlets at 11.9, 8.3, 8.2, 5.3, and 4.7 ppm, consistent with the five methyl resonances observed in the ^{1}H and ^{13}C NMR spectra. These data argue for either a pentameric (n = 5) or decameric (n = 10) structure as suggested in Figure 4. It is, however, difficult to envision a pentameric structure with five distinct phosphorus environments without invoking the presence of either a three-coordinate aluminum center or a coordinated THF, the latter of which is precluded by the ^{1}H and ^{13}C NMR data. Thus, a decameric structure is more likely based on the NMR data. The electron-impact mass spectrum of **4** shows only three major fragments corresponding to loss of a *tert*-butyl substituent from each of [^{t}BuAlO$_3$PMe]$_4$ (m/z 655.1; 100%), [^{t}BuAlO$_3$PMe]$_5$ (m/z 833.3; 23%), and [^{t}BuAlO$_3$PMe]$_6$ (m/z 1011.3; 37%). The elemental composition of the ^{t}Bu$_4$Al$_5$O$_{15}$P$_5$Me$_5^+$ fragment was confirmed by high-resolution mass measurement. No fragments with m/z greater than 1011 were observed. This mass spectrometric data could indicate that **4** is a pentamer, [^{t}BuAlO$_3$PMe]$_5$, which rearranges to the tetramer, [^{t}BuAlO$_3$PMe]$_4$, and hexamer, [^{t}BuAlO$_3$PMe]$_6$, under EI MS conditions. Alternatively, the mass spectrometric data could indicate that **4** is a decamer of low volatility that cleaves into two equivalent pentameric units or a tetrameric and a hexameric unit during volatilization and ionization. A solution molecular weight measurement for **4** in chloroform was obtained by vapor pressure osmometry. The experimentally determined molecular weight of 1589 is more consistent with a decamer (MW = 1780) rather than a pentamer (MW = 890), although the 10% error is higher than desired. On the basis of all of the data presented, we hypothesized that the decameric structure was most probable.[1a] Unfortunately, crystal growth was thwarted by rearrangement of **4** in solution to give a mixture of **2** and **3**. Monitoring a CDCl$_3$ solution of **4** by ^{1}H and ^{31}P NMR spectroscopy showed clean, but incomplete, conversion to **2** and **3** in 6 days (eq 3). No additional products were observed. Hence, it appeared that growing crystals of **4** to substantiate the structure in the solid

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(34) (a) Simmen, A.; McCusker, L. B.; Baerlocher, Ch.; Meier, W. M. *Zeolites* **1991**, *11*, 654. (b) McGuire, N. K.; Bateman, C. A.; Blackwell, C. S.; Wilson, S. T.; Kirchner, R. M. *Zeolites* **1995**, *15*, 460.

$$\underset{\mathbf{4}}{[{}^{t}BuAlO_3PMe]_{10}} \xrightarrow[20\ °C,\ 6\ d]{CDCl_3} \underset{\mathbf{2}}{[{}^{t}BuAlO_3PMe]_4} + \underset{\mathbf{3}}{[{}^{t}BuAlO_3PMe]_6} \quad (3)$$

state by X-ray crystallography would be a challenging task. Fortunately, we were aided in this effort by an unanticipated result.

As part of our previous work on the polymerization of ECH using alkylaluminophosphonates, we tested the polymerization activity of **2**. Compound **2** showed little catalytic activity and was not the active catalyst in reaction solutions of ${}^{t}Bu_3Al$ and $MeP(O)(OH)_2$. Since Vandenberg discovered that addition of acetylacetone to alkylaluminoxane solutions dramatically increases epoxide polymerization activity, we treated compound **2** with acetylacetone to see if increased catalytic activity could be obtained. Although no increase was observed, we were surprised to find that addition of acetylacetone to toluene solutions of **2** led to an 86% yield of **4** (eq 4).

$$5\,\underset{\mathbf{2}}{[{}^{t}BuAlO_3PMe]_4} \xrightarrow[70\ °C]{THF/toluene/acacH} 2\,\underset{\mathbf{4}}{[{}^{t}BuAlO_3PMe]_{10}} \quad (4)$$

The reaction was monitored by ${}^{1}H$ and ${}^{31}P$ NMR spectroscopy at room temperature, and only unreacted acetylacetone was observed in solution. There was no evidence for acac-containing aluminum complexes. The role of acetylacetone in this rearrangement is unclear, and a complete understanding of this reaction will require further study.

Initial attempts at growing crystals of **4** using this reaction focused on slow diffusion of a $CHCl_3$ solution of acetylacetone into a poly(ethylene oxide)/$CHCl_3$ gel that contained **2**.[35] After two months, crystalline **3**, not **4**, was isolated and subjected to X-ray analysis. With hindsight, the isolation of **3** under these conditions is attributable to the conversion of **4** to **2** and the less soluble **3** (eq 3). Vapor diffusion of acetylacetone into a toluene solution of **2** gave crystalline **4** within a few days. Evaporation of toluene during this process left crystals of **4** on the wall of the container and minimized the conversion of **4** to a mixture of **2** and **3**, as would have occurred with prolonged exposure of **4** to the growth solution. X-ray crystallography confirmed **4** to be a decamer in the solid state.

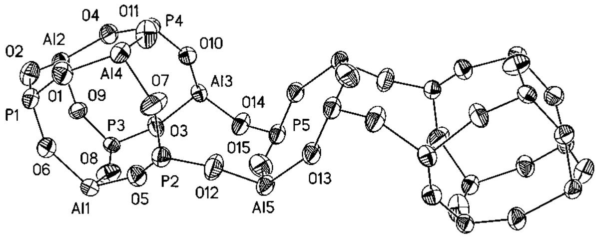

Figure 5. ORTEP drawing of the $Al_{10}P_{10}O_{30}$ core of $[{}^{t}BuAlO_3PMe]_{10}$ (**4**). Methyl and *tert*-butyl substituents on phosphorus and aluminum, respectively, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[{}^{t}BuAlO_3PMe]_{10}$ (4)

Distances			
P(1)−O(1)	1.516(2)	Al(1)−O(5)	1.762(2)
P(1)−O(2)	1.516(2)	Al(1)−O(6)	1.762(2)
P(1)−O(6)	1.515(2)	Al(1)−O(8)	1.748(2)
P(5)−O(13A)	1.520(2)	Al(5)−O(12)	1.748(2)
P(5)−O(14)	1.516(2)	Al(5)−O(13)	1.757(2)
P(5)−O(15)	1.510(3)	Al(5)−O(15)	1.766(3)
Angles			
O(6)−P(1)−O(2)	111.32(13)	O(8)−Al(1)−O(5)	106.10(11)
O(6)−P(1)−O(1)	110.59(13)	O(8)−Al(1)−O(6)	106.90(11)
O(2)−P(1)−O(1)	110.73(13)	O(5)−Al(1)−O(6)	105.25(11)
P(1)−O(2)−Al(2)	144.20(15)	P(4)−O(10)−Al(3)	145.01(13)
P(4)−O(4)−Al(2)	155.47(16)	P(2)−O(12)−Al(5)	156.35(17)
P(1)−O(6)−Al(1)	151.36(14)	P(5)−O(14)−Al(3)	150.71(14)
P(3)−O(8)−Al(1)	153.88(15)		

[a] A indicates symmetry-related atom.

The molecular structure of **4** (Figure 5) consists of two symmetry-related cuboidal $Al_4P_4O_{11}$ units that lack an Al−O−P linkage between P(2) and Al(3). These edge-opened cubes are each linked via two Al−O−P bridges to an eight-membered $Al_2P_2O_4$ heterocycle. The trans arrangement of Me substituents on P(5) and P(5A) and ${}^{t}Bu$ substituents on Al(5) and Al(5A) of the $Al_2P_2O_4$ heterocycle is consistent with the trans orientation of substituents in heterocyclic **1** and $[{}^{t}Bu_2AlO_2P(OSiMe_3)Ph]_2$. Aluminum−oxygen distances (1.745(2)−1.769 (2) Å; av 1.758 Å), phosphorus−oxygen distances (1.495(2)−1.520(2) Å; av 1.512 Å), and Al−O−P angles (144.20(15)−159.22(16)°; av 151.6°) in **4** (Table 4) are comparable with those observed for **2** and **3**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grants 29723-G3 and 34890-AC3), for support of this research. Zeon Chemicals L.P. is acknowledged for partial support of A.M.P. We thank Kristin Kirschbaum for instruction on the operation of the Siemens CCD diffractometer at the University of Toledo. The CCD facility of the Ohio Crystallography Consortium located at the University of Toledo was established with grants from the Ohio Board of Regents and ONR. The single-crystal CCD X-ray facility at the University of Idaho was established with the support of the NSF-Idaho EPSCoR Program (Grant OSR-9350539) and the M.J. Murdock Charitable Trust, Vancouver, WA.

Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, complete bond distances and angles, and fully labeled ORTEP diagrams for **2**−**4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM010432Y

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[35] Yaghi, O. M.; Li, G.; Li, H. *Chem. Mater.* **1997**, *9*, 1074.