Synthesis and Characterization of Dimeric, Trimeric, and Tetrameric Gallophosphonates and Gallophosphates⊥

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THF/toluene solutions of phosphonic or phosphoric acids were reacted with $^tBu_3Ga$ at low temperature to yield the cyclic dimers $[^tBu_2GaO_2P(OH)R]_2$ (R = Ph, Me, ^{t}Bu, H, OH; **1**−**5**). Poor crystallinity and variable thermal stabilities of **1**−**5** necessitated derivatization with Me_3SiNMe_2 to yield $[^tBu_2GaO_2P(OSiMe_3)R]_2$ (R = Ph, Me, ^{t}Bu, H, $OSiMe_3$; **6**−**10**), which were more amenable to purification and characterization. In solution, trans isomers were predominant for **6** and **7** at ambient temperature, whereas the cis isomer of **8** was predominant. NMR spectroscopy demonstrated cis−trans interconversion for **6**−**8** and crossover experiments showed interconversion to occur by, or be accompanied with, an intermolecular exchange process. Thermolysis of **3** in refluxing toluene yielded the cluster $[(^tBuGa)_2(^tBu_2Ga)(O_3P^tBu)_2\{O_2P(OH)^tBu\}]$ (**11**), which was converted to $[(^tBuGa)_2(^tBu_2Ga)(O_3P^tBu)_2\{O_2P(OSiMe_3)^tBu\}]$ (**12**) with Me_3SiNMe_2. Thermolysis of **1**−**3** in refluxing diglyme, or solid-state pyrolysis at 250 °C in vacuo, yielded $[^tBuGaO_3PR]_4$ (R = Ph, ^{t}Bu, Me; **13**−**15**). The gallophosphate $[^tBuGaO_3P(OSiMe_3)]_4$ (**16**) was similarly obtained by reaction of $^tBu_3Ga$ with H_3PO_4 in refluxing diglyme, followed by trimethylsilylation with Me_3SiNMe_2. Compounds **13**−**16** possess cuboidal $Ga_4P_4O_{12}$ cores analogous to double-four-ring secondary building units in the gallophosphates cloverite, gallophosphate-A, and ULM-5. The thermal, hydrolytic, and oxidative stabilities of **13**−**16** are discussed, as are observed intermolecular exchange processes. In addition to characterization of **1**−**16** by multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy, infrared spectroscopy, mass spectrometry, and elemental analysis, molecular structures for compounds **6**, **8**, **10**, **12**, **14**, **15**, and **16** were determined by X-ray crystallography.

Introduction

The large pores present in the gallophosphate cloverite[1] and in the aluminophosphates VPI-5[2] and JDF-20[3] have prompted an extensive search for additional large-pore aluminophosphate[4] ($AlPO_4$) and gallophosphate[5] ($GaPO_4$) materials for use as catalysts, catalyst supports, and sorbents.[6] This continuing search is primarily focused on the use of surfactants[7] and other templates in hydrothermal syntheses, but the synthesis of new large-pore phosphate materials via a molecular precursor approach has been proposed.[8−17] Despite the recent popularity

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⊥ Dedicated to Jean'ne M. Shreeve on her 65th birthday.

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of the molecular precursor approach to materials synthesis,[18] the successful synthesis of $AlPO_4$ and $GaPO_4$ materials from preformed molecular building blocks has not been reported and is presently limited by the paucity of suitable precursors.

To address this problem, we are developing synthetic routes to organic-soluble cyclic and cage phosphates and phosphonates which may act as molecular models of, and precursors to, secondary building units (SBUs) in phosphate materials of the group 13 elements. In this regard, we previously reported the synthesis and characterization of cyclic and cage alkylaluminophosphates via a trimethylsilyl chloride elimination route,[8] the synthesis and characterization of alkylaluminophosphonates via reaction of aluminum alkyls and phosphonic acids,[9−11] and the synthesis and characterization of the first cubic gallophosphonate[12] with a $Ga_4P_4O_{12}$ core analogous to the double-four-ring (D4R) SBU found in cloverite,[1] ULM-5[19] and gallophosphate-A.[20] Roesky has similarly reported several cubic phosphonates of the group 13 elements,[14−17] including the first tetrameric phosphonates of indium.[17] In addition, the Barron group and Kuchen and co-workers have reported a cyclic gallophosphonate[21] and a cubic borophosphonate,[22] respectively.

Thus far, research has been limited to phosphonate derivatives, but we envision difficulty in achieving P−C bond cleavage under mild conditions, a prerequisite for use of these precursors for the synthesis of phosphate materials. Improved precursors should contain hydrolytically sensitive P−E bonds (E = O, N) which would allow facile cage linkage via hydrolysis. Target precursors might include tetrameric phosphates of the group 13 elements, examples of which are limited to $[^tBuAlO_3P(OSiMe_3)]_4$ and $[Al(PO_4)(HCl)(EtOH)_4]_4$.[8,23] Described herein is a detailed accounting of our initial results on molecular gallophosphonates,[12] including the synthesis and characterization of several dimeric, trimeric, and tetrameric derivatives, as well as the synthesis and characterization of the first organic-soluble cyclic and cubic gallophosphates.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert-atmosphere techniques. Diethyl ether, diglyme, pentane, and tetrahydrofuran were distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from sodium. C_6D_6 and $CDCl_3$ were dried by storage over activated molecular sieves. $^tBu_3Ga$,[24] $[^tBu_2GaO_2P(OH)Ph]_2$ (**1**),[12] and $[^tBuGaO_3PPh]_4$ (**13**),[12] were prepared as previously described. Gallium trichloride was purchased from Strem Chemicals and was used without further purification. Phenylphosphonic acid, *tert*-butylphosphonic acid, methylphosphonic acid, phosphonic acid, 100% phosphoric acid and dimethyl(trimethylsilyl)amine were purchased from Aldrich and used as received. Solution NMR spectra were recorded on Bruker AMX-500 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 Series FTIR 5000 infrared spectrometer on KBr pellets. High-resolution mass spectrometric analyses were provided by the Nebraska Center for Mass Spectrometry. Low-resolution mass spectral *m*/*z* values are reported for the predominant peak in the isotope pattern. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of $[^tBu_2GaO_2P(OH)Me]_2$ (2). A solution of methylphosphonic acid (4.85 g, 50.5 mmol) in 60 mL of THF was added dropwise to a stirred solution of $^tBu_3Ga$ (12.1 g, 50.3 mmol) in 100 mL of toluene and 40 mL of THF. The resulting solution was refluxed for 2 h. Removal of volatiles in vacuo yielded a viscous white residue, spectroscopic data for which were consistent with the cyclic dimer **2** as the major component. It should be noted, however, that spectroscopic data sometimes varied considerably for seemingly identical preparations. Although impure, this material was suitable for the preparation of compounds **7** and **15**. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.78 (m, THF), 1.87 (m, THF), 1.58 (br d, $^2J_{PH}$ = 17.1 Hz, 3H, PCH_3), 1.49 (d, $^2J_{PH}$ = 18.1 Hz, 3H, PCH_3), 1.01 (s, 36H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 24.0−20.0 (br), 18.8 (s).

Preparation of $[^tBu_2GaO_2P(OH)^tBu]_2$ (3). A solution of *tert*-butylphosphonic acid (0.570 g, 4.15 mmol) in 15 mL of THF was added dropwise to a stirred solution of $^tBu_3Ga$ (1.00 g, 4.15 mmol) in 15 mL of THF at −50 °C. After 2 h of stirring, the solution volume was reduced in vacuo. Clear and colorless crystals were obtained by cooling the concentrate at −30 °C overnight. Yield: 0.760 g, 1.30 mmol, 58%. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.76 (br, OH), 4.76 (m, 4H, THF), 2.87 (m, 4H, THF), 2.22 (d, $^3J_{PH}$ = 16.8 Hz, 9H, ^{t}BuP), 2.03 (s, 18H, ^{t}BuGa). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 25.1 (s, major), 24.3 (s, minor). IR (KBr, cm^{-1}): 3606 (vs, ν_{OH}), 2949 (vs), 2843 (vs), 1479 (m), 1461 (m), 1218 (s), 1092 (s), 881 (m), 859 (m), 492 (m). MS (EI) *m*/*z* (assignment, relative intensity): 585.1 ($M^+ - {}^t$Bu, 7), 527.1 ($M^+ - {}^t$Bu − ^{t}BuH, 40), 471.0 ($M^+ - 3{}^t$Bu, 5). HRMS (EI) *m*/*z* for $C_{20}H_{47}O_6P_2{}^{69}Ga^{71}Ga$ ($M^+ - {}^t$Bu): calcd, 585.1351; found, 585.1341.

Preparation of $[^tBu_2GaO_2P(OH)H]_2$ (4). A solution of 100% H_3PO_3 (1.36 g, 16.6 mmol) in 20 mL of THF was added dropwise to a stirred solution of $^tBu_3Ga$ (4.00 g, 16.6 mmol) in 15 mL of THF. The resulting solution was gradually warmed to 0 °C and then stirred an additional 15 min at 0 °C. The solution was concentrated in vacuo to a volume of 10 mL. Clear cubelike crystals were obtained by cooling the concentrate at −20 °C for 3 days. Yield: 0.66 g, 1.25 mmol, 15%. ^1H NMR (C_6D_6, 500 MHz): δ 9.52 (s, 2H, OH), 7.03 (d, $^1J_{PH}$ = 685 Hz, 1H, PH), 6.98 (d, $^1J_{PH}$ = 686 Hz, 1H, PH), 6.82 (br d, $^1J_{PH}$ = 701 Hz, PH), 3.40 (m, 8H, THF), 1.35 (s, 36H, ^{t}Bu), 1.23 (m, 8H, THF). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 67.93 (s, THF), 30.09 (s, $C(CH_3)_3$), 29.96 (s, $C(CH_3)_3$), 25.25 (s, THF), 23.2 (br, $C(CH_3)_3$), 22.9 (br, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 4.0 (br), −0.7 (br), −2.2 (s), −2.5 (s). IR (KBr, cm^{-1}): 3200 (br, ν_{OH}), 2952 (s), 2930 (s), 2849 (s), 2441 (m, ν_{PH}), 1467 (m), 1364 (m), 1224 (br, s), 1011 (s), 816 (m).

Preparation of $[^tBu_2GaO_2P(OH)_2]_2\cdot 2THF$ (5). A solution of 100% H_3PO_4 (0.810 g, 8.29 mmol) in 20 mL of THF was added to a cooled (−40 °C) solution of $^tBu_3Ga$ (2.00 g, 8.29 mmol) in 10 mL of THF and 15 mL of toluene over a 15 min period. The resulting solution was stirred at −40 °C for 15 min and was then slowly warmed to room temperature. After 12 h of stirring at room temperature, half of the solvent was removed under reduced pressure and the concentrate was cooled at −20 °C for 12 h. The sheetlike crystals of **5** were isolated by filtration and dried in vacuo. Yield: 1.01 g, 1.32 mmol, 32%. ^1H

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NMR (C_6D_6, 300 MHz): δ 8.96 (br s, 2H, OH), 3.54 (m, 4H, THF), 1.45 (s, 18H, ^{t}Bu), 1.32 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 68.16 (s, THF), 30.07 (s, C(CH_3)$_3$), 25.36 (s, THF), 24.02 (br, s, *C* (CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −6.3 (s). IR (KBr, cm^{-1}): 3200 (br, vs, ν_{OH}), 2954 (s), 2844 (s), 1467 (m), 1365 (m), 1203 (vs), 1099 (vs), 1012 (m), 941 (m), 817 (m), 538 (s).

Preparation of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)Ph]$_2$ (6). Phenylphosphonic acid (2.18 g, 138.8 mmol), ^{t}Bu$_3$Ga (3.26 g, 13.5 mmol), and Me$_3$SiNMe$_2$ (1.61 g, 13.7 mmol) were reacted using a procedure analogous to that described for the preparation of **8**. Concentration of the resulting reaction solution and cooling (−20 °C) overnight yielded a crystalline white product, which was isolated by filtration and dried in vacuo. Yield: 4.61 g, 5.59 mmol, 83%. ^{1}H, ^{13}C, and ^{31}P NMR spectra showed the presence of trans and cis isomers (20:1 ratio) in $CDCl_3$ solutions. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (m, 4H, Ph-ortho), 7.48 (m, 2H, Ph-para), 7.42 (m, 4H, Ph-meta), 1.15 (s, 1H, ^{t}Bu, cis), 1.00 (s, 36H, ^{t}Bu, trans), 0.84 (s, 1H, ^{t}Bu, cis), −0.02 (s, 18H, SiMe$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ 133.11 (d, $^1J_{PC}$ = 202.0 Hz, Ph-ipso, trans), 133.01 (d, $^1J_{PC}$ = 202.0 Hz, Ph-ipso, cis), 131.38 (d, $^4J_{PC}$ = 3.0 Hz, Ph-para), 131.30 (d, $^2J_{PC}$ = 10.2 Hz, Ph-ortho, trans), 131.25 (d, $^2J_{PC}$ = 10.2 Hz, Ph-ortho, cis), 128.08 (d, $^3J_{PC}$ = 15.2 Hz, Ph-meta), 29.84 (s, C(CH_3)$_3$, cis), 29.73 (s, C(CH_3)$_3$, cis), 29.70 (s, C(CH_3)$_3$, trans), 22.80 (s, *C*(CH_3)$_3$), 22.78 (s, *C*(CH_3)$_3$), 0.86 (s, Si(CH_3)$_3$, cis), 0.85 (s, Si(CH_3)$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −3.4 (s, trans), −3.7 (s, cis). MS (EI) *m*/*z* (assignment, relative intensity): 769 (M$^+$ − ^{t}Bu, 100), 713 (M$^+$ − ^{t}Bu − C_4H_8, 8), 655 (M$^+$ − 3^{t}Bu, 18). HRMS (EI) *m*/*z* for $C_{30}H_{55}O_6Si_2P_2{}^{69}Ga_2$ (M$^+$ − ^{t}Bu): calcd, 767.1524; found, 767.1520. Anal. Calcd for $C_{34}H_{64}O_6Si_2P_2Ga_2$: C, 49.41; H, 7.81; P, 7.49; Ga, 16.87. Found: C, 49.16; H, 8.46; P, 7.13; Ga, 17.28.

Preparation of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)Me]$_2$ (7). Methylphosphonic acid (0.860 g, 8.93 mmol), ^{t}Bu$_3$Ga (2.12 g, 8.80 mmol), and Me$_3$SiNMe$_2$ (1.10 g, 9.36 mmol) were reacted using a procedure analogous to that described for the preparation of **8**. Concentration of the resulting reaction solution and cooling (−20 °C) overnight yielded a crystalline white product, which was isolated by filtration and dried in vacuo. Concentration of the reaction filtrate yielded a second crop of product. Yield: 1.08 g, 1.54 mmol, 35%. ^{1}H, ^{13}C, and ^{31}P NMR spectra showed the presence of trans and cis isomers (12:1 ratio) in $CDCl_3$ solutions. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.42 (d, 6H, $^2J_{PH}$ = 18.1 Hz, PCH_3, trans), 1.41 (d, 0.5 H, $^2J_{PH}$ = 18.0 Hz, PCH_3, cis), 0.98 (s, 1.5H, ^{t}Bu, cis), 0.97 (s, 36H, ^{t}Bu, trans), 0.95 (s, 1.5H, ^{t}Bu, cis), 0.24 (s, 19H, SiMe$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ 29.93 (s, C(CH_3)$_3$, cis), 29.78 (s, C(CH_3)$_3$, trans), 29.59 (s, C(CH_3)$_3$, cis), 22.26 (s *C*(CH_3)$_3$, trans), 15.08 (d, $^1J_{PC}$ = 155.7 Hz, PCH_3, trans), 15.06 (d, $^1J_{PC}$ = 155.7 Hz, PCH_3, cis), 0.99 (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 7.0 (s, trans), 6.8 (s, cis). MS (EI) *m*/*z* (assignment, relative intensity): 643 (M$^+$ − ^{t}Bu, 100), 585 (M$^+$ − ^{t}Bu − ^{t}BuH, 6), 529 (M$^+$ − 3^{t}Bu, 11). HRMS (EI) *m*/*z* for $C_{20}H_{51}O_6Si_2P_2{}^{69}Ga^{71}Ga$ (M$^+$ − ^{t}Bu): calcd, 645.1202; found, 645.1201. Anal. Calcd for $C_{24}H_{60}O_6Si_2P_2Ga_2$: C, 41.05; H, 8.61; P, 8.82; Ga, 19.85. Found: C, 40.34; H, 9.13; P, 7.89; Ga, 19.06.

Preparation of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)^{t}Bu]$_2$ (8). A solution of *tert*-butylphosphonic acid (1.15 g, 8.34 mmol) in 15 mL of THF was added dropwise to a stirred solution of ^{t}Bu$_3$Ga (2.01 g, 8.34 mmol) in 10 mL of toluene. The resulting solution was stirred for 1 h and was gently heated for an additional hour. After the solution was cooled to room temperature, a solution of Me$_3$SiNMe$_2$ (1.01 g, 9.36 mmol) in 2 mL of toluene was added dropwise and the reaction solution was heated at reflux for 1 h. Precipitation of the white product occurred upon cooling to room temperature. The product was isolated by filtration and was recrystallized from hot THF. Yield: 2.13 g, 2.71 mmol, 65%. NMR spectra showed the presence of cis and trans isomers (20:1 ratio). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.19 (d, $^3J_{PH}$ = 17.1 Hz, 18H, ^{t}BuP, cis), 1.18 (d, $^3J_{PH}$ = 17.1 Hz, ^{t}BuP, trans), 1.02 (s, 18H, ^{t}BuGa), 1.01 (s, 18H, ^{t}BuGa), 0.29 (s, 6H, SiMe$_3$, cis), 0.27 (s, SiMe$_3$, trans). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.3 MHz): δ 32.04 (d, $^1J_{PC}$ = 159.3 Hz, P*C*(CH_3)$_3$), 30.41 (s, GaC(CH_3)$_3$, trans), 30.20 (s, GaC(CH_3)$_3$, cis), 30.07 (s, GaC-(CH_3)$_3$, cis), 25.97 (s, PC(CH_3)$_3$), 22.82 (br s, Ga*C*(CH_3)$_3$), 2.18 (s, SiMe$_3$, trans), 2.09 (s, SiMe$_3$, cis). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 13.4 (s, cis), 12.7 (s, trans). MS (EI) *m*/*z* (assignment, relative intensity): 729 (M$^+$ − ^{t}Bu, 100), 671 (M$^+$ − ^{t}Bu − ^{t}BuH, 6), 615 (M$^+$ − 3^{t}Bu, 12). HRMS (EI) *m*/*z* for $C_{26}H_{63}O_6Si_2P_2{}^{69}Ga_2$ (M$^+$ − ^{t}Bu): calcd, 727.2150; found, 727.2160. Anal. Calcd for $C_{30}H_{72}O_6Si_2P_2Ga_2$: C, 45.82; H, 9.23; P, 7.88; Ga, 17.73. Found: C, 45.70; H, 9.66; P, 7.62; Ga, 17.81.

Preparation of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)H]$_2$ (9). To a cooled (0 °C) solution of ^{t}Bu$_3$Ga (1.00 g, 4.15 mmol) in 40 mL of toluene was added a solution of 100% H_3PO_3 (0.340 g, 4.15 mmol) in 25 mL of THF over a period of 10 min. The resulting solution was heated at 40 °C for 6 h. The solution was then cooled to 0 °C and Me$_3$SiNMe$_2$ (0.500 g, 4.25 mmol) was added. The reaction solution was heated at 40 °C for an additional 6 h. The resulting solution was cooled, and volatiles were removed in vacuo. The remaining residue was dissolved in a minimum volume of pentane, and the resulting solution was subsequently cooled at −20 °C overnight to yield a white precipitate. The product was isolated by filtration and dried in vacuo. A second crop was similarly obtained from the mother liquor. Yield: 2.37 g, 3.53 mmol, 85%. NMR spectra showed the presence of trans and cis isomers (6:5 ratio). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.01 (d, $^1J_{PH}$ = 693 Hz, 1H, trans isomer), 6.94 (d, $^1J_{PH}$ = 693 Hz, 1H, cis), 1.35 (s, 9H, ^{t}Bu, cis), 1.31 (s, 18H, ^{t}Bu, trans), 1.27 (s, 9H, ^{t}Bu, cis), 0.13 (s, 18H, SiMe$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.5 MHz): δ 30.26 (s, C(*C*(CH_3)$_3$, cis), 30.11 (s, C(*C*(CH_3)$_3$, trans), 29.90 (s, C(*C*(CH_3)$_3$, cis), 23.18 (s, *C*(CH_3)$_3$, cis), 22.98 (s, *C*(CH_3)$_3$, trans), 22.71 (s, *C*(CH_3)$_3$, cis), 0.82 (s, SiMe$_3$, trans), 0.79 (s, SiMe$_3$, cis). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ −9.8 (s, trans), −10.5 (s, cis). MS (EI) *m*/*z* (assignment, relative intensity): 617 (M$^+$ − ^{t}Bu, 100), 561 (M$^+$ − ^{t}Bu − C_4H_8, 15), 503 (M$^+$ − 3^{t}Bu, 30). HRMS (EI) *m*/*z* for $C_{18}H_{47}O_6Si_2P_2{}^{69}Ga^{71}Ga$ (M$^+$ − ^{t}Bu): calcd, 617.0889; found, 617.0883. Anal. Calcd for $C_{22}H_{56}O_6Si_2P_2Ga_2$: C, 39.19; H, 8.37; P, 9.19; Ga, 20.68. Found: C, 39.35; H, 8.95; P, 9.10; Ga, 21.18.

Preparation of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)$_2$]$_2$ (10). A solution of 100% H_3PO_4 (0.810 g, 8.29 mmol) in 20 mL of THF was added dropwise to a cooled (−40 °C) solution of ^{t}Bu$_3$Ga (2.00 g, 8.29 mmol) in 10 mL of THF and 15 mL of toluene over a period of 15 min. After the addition was complete, the solution was slowly warmed to room temperature and was then refluxed for 4 h. The solution was cooled to room temperature, and Me$_3$SiNMe$_2$ (1.95 g, 16.6 mmol) was added dropwise. The reaction solution was warmed briefly to reflux to ensure complete reaction. The volume of the reaction solution was reduced by half in vacuo, and the concentrate was cooled at −20 °C overnight to afford clear crystals of **10**. The product was isolated by filtration. An additional crop of product was similarly obtained from the filtrate. Yield: 2.48 g, 2.92 mmol, 70%. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.38 (s, 18H, ^{t}Bu), 0.25 (s, 18H, SiMe$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 30.31 (s, C(*C*(CH_3)$_3$), 22.97 (s, *C*(CH_3)$_3$), 0.88 (s, SiMe$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −23.8 (s). MS (EI) *m*/*z* (assignment, relative intensity): 793 (M$^+$ − ^{t}Bu, 100), 735 (M$^+$ − ^{t}Bu − ^{t}BuH, 6), 679 (M$^+$ − 3^{t}Bu, 10). HRMS (EI) *m*/*z* for $C_{24}H_{63}O_8Si_4P_2{}^{69}Ga_2$ (M$^+$ − ^{t}Bu): calcd, 791.1587; found, 791.1575. Anal. Calcd for $C_{28}H_{72}O_8Si_4P_2Ga_2$: C, 39.54; H, 8.53; P, 7.28; Ga, 16.39. Found: C, 39.11; H, 8.57; P, 7.08; Ga, 16.22.

Preparation of [(^{t}BuGa)$_2$(^{t}Bu$_2$Ga)(μ_3-O$_3$P^{t}Bu)$_2$(μ_2-O$_2$P(OH)^{t}Bu)] (11). A solution of *tert*-butylphosphonic acid (0.848 g, 6.14 mmol) in 10 mL of THF was added dropwise to a stirred solution of ^{t}Bu$_3$Ga (1.48 g, 6.14 mmol) in 20 mL of toluene at 0 °C. After the addition was complete, the solution was warmed to room temperature and stirred at room temperature for 15 h. The more volatile THF was removed in vacuo to yield a clear solution rich in toluene. This solution was heated at reflux for 15 h. Solvent was removed in vacuo to give a white solid. Crystallization from a concentrated solution in THF at −20 °C yielded clear colorless crystals which were isolated by filtration and turned white upon drying in vacuo. Yield: 1.24 g, 1.46 mmol, 72%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.6 (br, OH), 3.74 (m, 3H, THF), 1.84 (m, 3H, THF), 1.18 (d, $^3J_{PH}$ = 17.7 Hz, 9H, ^{t}BuP), 1.16 (d, $^3J_{PH}$ = 16.5 Hz, 9H, ^{t}BuP), 1.12 (d, $^3J_{PH}$ = 16.5 Hz, 9H, ^{t}BuP), 1.05 (s, 18H, ^{t}BuGa), 0.99 (s, 18H, ^{t}BuGa). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 68.05 (s, THF), 31.38 (d, $^1J_{PC}$ = 156.9 Hz, P*C*(CH_3)$_3$), 31.35 (d, $^1J_{PC}$ = 156.8 Hz, P*C*(CH_3)$_3$), 30.95 (d, $^1J_{PC}$ = 149.0 Hz, P*C*(CH_3)$_3$), 30.24 (s, GaC-(CH_3)$_3$), 29.15 (s, GaC(CH_3)$_3$), 25.53 (s, PC(CH_3)$_3$), 25.49 (s, PC-(CH_3)$_3$), 24.60 (s, PC(CH_3)$_3$), 22.33 (br s, Ga*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 33.2 (s), 23.8 (s), 23.3 (s). IR (KBr, cm^{-1}): 3200 (br,

s, ν_{OH}), 2952 (s), 2874 (s), 2834 (s), 1479 (m), 1393 (m), 1364 (m), 1131 (vs), 1082 (vs), 1029 (vs), 959 (s), 896 (m), 834 (m), 661 (s), 486 (s). MS (EI) *m*/*z* (assignment, relative intensity): 789 ($M^+ - {}^t$Bu, 100), 733 ($M^+ - {}^t$Bu $- C_4H_8$, 8), 675 ($M^+ - 3^t$Bu, 33). HRMS (EI) *m*/*z* for $C_{24}H_{55}O_9P_3{}^{69}Ga_2{}^{71}Ga$ ($M^+ - {}^t$Bu): calcd, 789.0818; found, 789.0839. Anal. Calcd for $C_{28}H_{64}O_9P_3Ga_3 \cdot C_4H_8O$: C, 41.82; H, 7.90; P, 10.11; Ga, 22.76. Found: C, 41.65; H, 8.11; P, 8.97; Ga, 22.59.

Preparation of [(^{t}BuGa)$_2$(^{t}Bu$_2$Ga)(μ_3-O$_3$P^{t}Bu)$_2$(μ_2-O$_2$P(OSiMe$_3$)^{t}Bu)] (12). A solution of Me_3SiNMe_2 (0.20 mL, 1.25 mmol) in 10 mL of THF was added dropwise to a stirred solution of **11** (0.807 g, 0.953 mmol) in THF, and the resulting clear solution was stirred for 15 h. The volume of the solution was reduced in vacuo, and the concentrate was cooled (−20 °C) overnight to produce clear crystals of **12**. The product was isolated by filtration and dried in vacuo. Yield: 0.606 g, 0.659 mmol, 69%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15 (d, $^3J_{PH}$ = 16.2 Hz, 9H, ^{t}BuP), 1.13 (d, $^3J_{PH}$ = 17.7 Hz, 9H, ^{t}BuP), 1.11 (d, $^3J_{PH}$ = 16.8 Hz, 9H, ^{t}BuP), 1.03 (s, 18H, ^{t}BuGa), 0.98 (s, 18H, ^{t}BuGa), 0.27 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 31.58 (d, $^1J_{PC}$ = 158.1 Hz, P*C*(CH$_3$)$_3$), 31.40 (d, $^1J_{PC}$ = 151.9 Hz, P*C*(CH$_3$)$_3$), 31.30 (d, $^1J_{PC}$ = 152.6 Hz, P*C*(CH$_3$)$_3$), 30.29 (s, GaC(*C*H$_3$)$_3$), 29.23 (s, GaC(*C*H$_3$)$_3$), 25.93 (s, PC(*C*H$_3$)$_3$), 25.20 (s, PC(*C*H$_3$)$_3$), 22.22 (br s, GaC), 1.43 (s, $SiMe_3$). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 23.4 (s), 23.1 (s), 18.9 (s). MS (EI) *m*/*z* (assignment, relative intensity): 903 (M^+ − Me, 3), 861 ($M^+ - {}^t$Bu, 100), 804 ($M^+ - 2^t$Bu, 3), 747 ($M^+ - 3^t$Bu, 13). HRMS (EI) *m*/*z* for $C_{27}H_{63}O_9SiP_3{}^{69}Ga_2{}^{71}Ga$ ($M^+ - {}^t$Bu): calcd, 861.1213; found, 861.1230. Anal. Calcd for $C_{31}H_{72}O_9SiP_3Ga_3$: C, 40.51; H, 7.90; P, 10.11; Ga, 22.76. Found: C, 39.77; H, 8.22; P, 9.78; Ga, 22.63.

Preparation of [^{t}BuGaO$_3$P^{t}Bu]$_4$ (14). A solution of *tert*-butylphosphonic acid (0.830 g, 3.46 mmol) in 15 mL of diglyme was added dropwise to a stirred solution of ^{t}Bu$_3$Ga (0.475 g, 3.96 mmol) in 15 mL of diglyme. The resulting solution was heated under reflux for 2 h to yield a white precipitate. The mixture was cooled (−20 °C) overnight to complete precipitation, and the product was isolated by filtration. Recrystallization from hot diglyme yielded **14** as clear colorless crystals. Yield of **14**: 0.57 g, 0.52 mmol, 63%. The compound can also be purified by sublimation at 175 °C, 0.1 mmHg. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.15 (d, $^3J_{PH}$ = 17.0 Hz, 36H, ^{t}BuP), 1.06 (s, 36H, ^{t}BuGa). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 19.5 (s). MS (EI) *m*/*z* (assignment, relative intensity): 995 ($M^+ - {}^t$Bu, 100), 937 ($M^+ - {}^t$Bu $- {}^t$BuH, 9), 881 ($M^+ - 3^t$Bu, 15). HRMS (EI) *m*/*z* for $C_{28}H_{63}O_{12}P_4{}^{69}Ga_2{}^{71}Ga_2$ ($M^+ - {}^t$Bu): calcd, 995.0276; found, 995.0262. Anal. Calcd for $C_{32}H_{72}O_{12}Ga_4P_4$: C, 36.55; H, 6.90; P, 11.78; Ga, 26.52. Found: C, 37.22; H, 7.46; P, 11.35; Ga, 25.25.

Preparation of [^{t}BuGaO$_3$PMe]$_4$ (15). Method 1. Compound **2** (8.47 g, 15.2 mmol) was refluxed in 200 mL of diglyme for 24 h. Concentration of the solution in vacuo and cooling overnight (−20 °C) yielded **15** as a white solid. A second crop of product was similarly obtained from the filtrate. Yield: 5.80 g, 6.60 mmol, 86%.

Method 2. Pyrolysis of **2** (1.95 g, 3.50 mmol) at 250 °C/0.1 mmHg formed compound **15** as a white sublimate. Sublimation of crude **15** at 150 °C/0.1 mmHg over a period of 24 h yielded pure crystalline product. Yield: 1.24 g, 1.40 mmol, 80%. ^{1}H NMR (C_6D_6, 500 MHz): δ 1.38 (d, $^2J_{PH}$ = 18.5 Hz, 3H, PCH_3), 1.19 (s, 9H, ^{t}Bu). ^{13}C-{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 29.01 (s, C(*C*H$_3$)$_3$), 21.27 (br s, *C*(CH$_3$)$_3$), 13.45 (d, $^1J_{PC}$ = 162.1 Hz, PCH_3). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 15.7 (s). MS (EI) *m*/*z* (assignment, relative intensity): 869 ($M^+ - CH_3$, 1), 827 ($M^+ - {}^t$Bu, 85), 769 ($M^+ - {}^t$Bu $- {}^t$BuH, 6), 713 ($M^+ - 3^t$Bu, 15), 129 (100). HRMS (EI) *m*/*z* for $C_{16}H_{39}O_{12}P_4{}^{69}Ga_2{}^{71}Ga_2$ ($M^+ - {}^t$Bu): calcd, 826.8398; found, 826.8397. Anal. Calcd for $C_{20}H_{48}O_{12}P_4Ga_4$: C, 27.19; H, 5.48; P, 14.02; Ga, 31.57. Found: C, 26.37; H, 5.52; P, 13.73; Ga, 32.82.

Preparation of [^{t}BuGaO$_3$P(OSiMe$_3$)]$_4$ (16). A solution of 100% H_3PO_4 (0.810 g, 8.29 mmol) in 20 mL of diglyme was added dropwise to a cooled (−40 °C) solution of ^{t}Bu$_3$Ga (2.00 g, 8.29 mmol) in 20 mL of diglyme over a period of 15 min. The reaction solution was slowly warmed to room temperature and was then refluxed for 4 h. The resulting solution was cooled to 0 °C and treated dropwise with Me_3SiNMe_2 (2.45 g, 8.29 mmol). This solution was refluxed briefly to ensure complete reaction and concentrated in vacuo to a viscous oil. Addition of pentane (20 mL) and cooling to −20 °C resulted in precipitation. The solid was isolated by filtration and dried in vacuo. Yield: 1.61 g, 0.926 mmol, 66%. Crystalline **16** can be obtained by concentrating the reaction solution under reduced pressure, followed by cooling, but yields are lower than when precipitation is induced by pentane. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.28 (s, 9H, ^{t}Bu), 0.28 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125.5 MHz): δ 29.06 (s, C(*C*H$_3$)$_3$), 21.42 (*C*(CH$_3$)$_3$), 0.75 (s, $SiMe_3$). ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ −20.3 (s). MS (EI) *m*/*z* (assignment, relative intensity): 1123 ($M^+ - {}^t$Bu, 100), 1009 ($M^+ - 3^t$Bu, 15). Anal. Calcd for $C_{28}H_{72}O_{16}Si_4P_4Ga_4$: C, 28.50; H, 6.15; P, 10.50; Ga, 23.63. Found: C, 28.61; H, 6.33; P, 9.81; Ga, 22.93.

X-ray Crystallography for 6, 8, 10, 12, 14, and 15. Crystals of **6**, **8**, **10**, and **12** suitable for diffraction studies were obtained by crystallization from THF, either at room temperature or at −20 °C. The crystal of **14** was obtained from a slowly cooled hot diglyme solution, and the crystal of **15** was obtained by sublimation in a tube furnace at 150 °C/0.1 mmHg. The X-ray diffraction data 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[25] software using Mo Kα radiation (λ = 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 dataset. An additional 50 frames were collected to determine crystal decay. The frames were processed on an SGI-Indy/Indigo 2 workstation by using the SAINT[26] software to give the *hkl* file corrected for decay and for Lorentz and polarization effects. For each compound, an absorption correction was performed using the SADABS program.[27] The structures were solved by direct methods using SHELXS-90[28] and refined by least-squares methods on F^2, using SHELXL-93[29] incorporated in SHELXTL-PC V 5.03.[30] All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in their geometrically generated positions and refined as a riding model. Compound **12** contained a disordered THF molecule which was modeled with a flipping conformation as the minor component. Also in **12**, the methyl carbons of the *tert*-butyl groups on Ga(1) and Ga(2) were found to be disordered and were modeled with major methyl group site occupancies of 57 and 66%, respectively. Similarly for **15**, the disordered methyl carbons of the *tert*-butyl groups on Ga(2), Ga(3), and Ga(4) were modeled with major methyl group site occupancies of 70, 70, and 60%, respectively. Gallium and phosphorus positions were disordered at the vertexes of the cuboidal $Ga_4P_4O_{12}$ core of **14**. All vertex sites were refined with gallium and phosphorus occupying similar sites with a partial occupancy of 50% for each of the atoms using similar thermal values. Details of data collection, solution, and refinement are given in Table 1.

X-ray Crystallography for 16. A colorless plate of **16** with dimensions of 0.33 × 0.33 × 0.17 mm was mounted on a glass fiber in a random orientation. Data were collected using Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident-beam monochromator. Three representative check reflections measured after every 60 min of X-ray exposure showed a gradual loss of intensity which totaled 5.2% during the course of data collection. A linear decay correction was applied, as were Lorentz and polarization corrections. The structure was solved by direct methods and refined using the teXsan crystallographic software package.[31] All non-hydrogen atoms except for the methyl carbons were refined anisotropically. Disordered methyl carbons of the *tert*-butyl

(25) *SMART, Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
(26) *SAINT, Software for the CCD Detector System*; Siemens Analytical Instruments Division: Madison, WI, 1995.
(27) *SADABS*; Siemens Analytical Instruments Division: Madison, WI, 1996.
(28) Sheldrick, G. M. SHELXS-90. *Acta Crystallogr.* **1990**, *A46*, 467.
(29) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.
(30) *SHELXTL 5.03, Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.
(31) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1993.

Table 1. Summary of X-ray Crystallographic Data

	6	**8**	**10**	**12**
formula	$C_{17}H_{32}GaO_3PSi$	$C_{30}H_{72}Ga_2O_6P_2Si_2$	$C_{28}H_{72}Ga_2O_8P_2Si_4$	$C_{35}H_{80}Ga_3O_{10}P_3Si$
fw	413.21	786.44	850.60	991.15
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/n$
a, Å	9.485(2)	35.1763(13)	21.1348(11)	12.8965(3)
b, Å	11.085(3)	13.0340(5)	12.6241(5)	26.7499(7)
c, Å	11.730(3)	19.2322(7)	20.4695(8)	14.7946(2)
α, deg	89.10(2)			
β, deg	75.82(2)	91.761(1)	119.263(1)	90.26
γ, deg	71.60(2)			
V, Å^3	1132.2(4)	8813.6(6)	4764.5(4)	5103.8(2)
Z	2	8	4	4
D_{calcd}, g cm^{-3}	1.212	1.185	1.186	1.290
T, °C	20(2)	−60(2)	27(2)	−60(2)
μ(Mo Kα), cm^{-1}	13.48	13.82	13.34	17.33
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
transm coeff	0.571−0.828	0.670−0.949	0.770−0.949	0.782−0.949
2θ limits, deg	4−50	2−56	4−56	3−56
total no. of data	2776	26 448	13 922	31 912
no. of unique data	2770	10 387	5609	12 128
no. of obsd data[a]	1884	7968	4173	12 126
no. of params	209	380	200	539
$R1$[b]	0.0616	0.0368	0.0375	0.0572
w$R2$[c]	0.179	0.0932	0.0780	0.0887
max, min peaks, e/Å^3	0.625, −0.455	0.721, −0.567	0.273, −0.294	0.450, −0.444

	14	**15**	**16**
formula	$C_{32}H_{72}Ga_4O_{12}P_4$	$C_{20}H_{48}Ga_4O_{12}P_4$	$C_{28}H_{72}Ga_4P_4Si_4O_{16}$
fw	1051.66	883.34	1179.98
crystal system	triclinic	orthorhombic	tetragonal
space group	$P1$	$Pbca$	$I4_1/a$
a, Å	10.6709(7)	19.261(2)	20.904(3)
b, Å	10.9726(7)	19.530(3)	20.904(3)
c, Å	11.9742(8)	19.840(3)	13.199(3)
α, deg	69.572(1)		
β, deg	72.226(1)		
γ, deg	84.498(1)		
V, Å^3	1251.1(1)	7463(2)	5768(1)
Z	1	8	4
D_{calcd}, g cm^{-3}	1.396	1.572	1.359
T, °C	20(2)	27(2)	23(3)
μ(Mo $K\alpha$), cm^{-1}	23.05	30.75	20.91
λ, Å	0.710 73	0.710 73	0.710 73
transm coeff	0.378−0.694	0.602−0.962	0.80−1.00
2θ limits, deg	4−46	4−50	2−50
total no. of data	5472	34 097	2807
no. of unique data	4341	6385	2664
no. of obsd data[a]	4341	5356	1010[d]
no. of params	471	393	145
$R1$[b]	0.0368	0.0443	0.045
w$R2$[c]	0.1008	0.0837	0.045[e]
max, min peaks, e/Å^3	0.478, −0.421	0.529, −0.392	0.27, −0.27

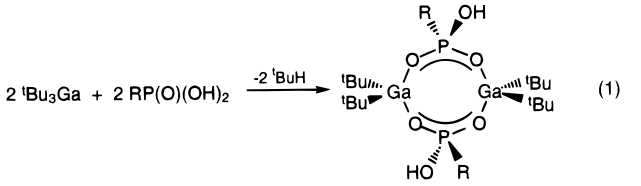
[a] $I > 2\sigma(I)$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [d] $I > 3\sigma(I)$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2]/\sum w(F_o^2)]^{1/2}$.

and trimethylsilyl substituents were adequately modeled as three tetrahedral groups of atoms (a, b, and c) with site occupancies of 33% and were refined isotropically. Hydrogen atoms were located by difference maps and added to the structure factor calculations, but their positions were not refined. Thermal parameters for hydrogen atoms were set to 1.3 × B_{eq} of the carbon atoms to which they were bound. Details of data collection, solution, and refinement are given in Table 1.

Results and Discussion

Synthesis and Characterization of Cyclic Compounds. We previously reported that equimolar quantities of phenylphosphonic acid and ^{t}Bu$_3$Ga react in THF and toluene to form [^{t}Bu$_2$GaO$_2$P(OH)Ph]$_2$ (**1**).[12] Multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) demonstrated **1** to exist as a 50:50 mixture of cis and trans isomers in solution, while the trans orientation of hydroxyl substituents on phosphorus was confirmed in the solid state by X-ray crystallography.

Isolation and characterization of reaction products of ^{t}Bu$_3$Ga with additional acids of phosphorus proved more troublesome. Methylphosphonic acid, *tert*-butylphosphonic acid, phosphorous acid, and phosphoric acid each react with 1 equiv of ^{t}Bu$_3$Ga at low temperature to yield products tentatively formulated as [^{t}Bu$_2$GaO$_2$P(OH)Me]$_2$ (**2**), [^{t}Bu$_2$GaO$_2$P(OH)^{t}Bu]$_2$ (**3**), [^{t}Bu$_2$GaO$_2$P(OH)H]$_2$ (**4**), and [^{t}Bu$_2$GaO$_2$P(OH)$_2$]$_2$ (**5**), respectively (eq 1). Compound **2** is isolated as a viscous residue, whereas **3**−**5** crystallize as disolvates from THF at −20 °C, although with considerable difficulty for **4**. All attempts at purification of **2** by recrystallization from a variety of solvents proved unsuccessful. This is unfortunate, since spectroscopic data for **2** sometimes varied considerably for seemingly identical

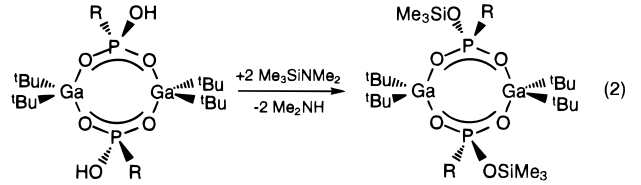


(1)

preparations. The complexity of **2** is undoubtedly greater than that suggested by the given formula.

Aside from poor reproducibility in the preparation of **2**, spectroscopic data for **2**−**5** are generally consistent with cyclic dimers analogous to **1**. The presence of unreacted hydroxyl substituents in these compounds is indicated by broad and intense hydroxyl absorptions (3600−3200 cm^{-1}) in their infrared spectra, as well as broad hydroxyl proton resonances in the corresponding ^1H NMR spectra. For **2**−**4**, where the presence of isomeric dimers is possible, solution NMR spectroscopic data (^1H, ^{31}P) are consistent with predominantly trans isomers, with evidence for small quantities of the cis isomer in each case. Satisfactory elemental analyses for **2**−**5** were thwarted by compound degradation via further alkane elimination which was facile over a period of hours to days, even at room temperature. For example, fresh solutions of $[^tBu_2GaO_2P(OH)_2]_2$ (**5**) showed clean ^1H NMR spectra, although somewhat broadened presumably due to a dynamic exchange process. Over a period of hours at room temperature, isobutane formation was indicated by the appearance of a doublet resonance at 0.85 ppm and a multiplet at 1.65 ppm, both of which increased in intensity over time. Isobutane formation was accompanied by new ^{t}Bu resonances in the ^1H and ^{13}C NMR spectra at 1.41 and 28.9 ppm, respectively. In addition to the prominent singlet at −6.3 ppm in the ^{31}P NMR spectrum of **5**, numerous additional resonances were often observed in the region −6 to −7 ppm, especially for older samples, or for NMR solutions stored at room temperature for more than an hour. Similar observations confirmed isobutane formation in solutions of **2**, **3**, and **4**. The poor thermal stability of **2**−**5** also hindered mass spectrometric characterization except in the case of **3**. High-resolution mass measurements on fragments at *m*/*z* 585.1 ($M^+ - {}^t$Bu, 7%) and 527.1 ($M^+ - {}^t$Bu − C_4H_8, 40%) in the electron impact mass spectrum of **3** support the dimeric formulation in the gas phase. The observation of low-intensity fragments at higher mass suggested the presence of a trimeric component in the sample. The nature of the trimeric impurity in **3** will be elaborated upon below.

To further aid characterization of compounds **1**−**5**, hydroxyl substituents on phosphorus were derivatized using Me_3SiNMe_2 to give 65−85% yields of $[^tBu_2GaO_2P(OSiMe_3)Ph]_2$ (**6**), $[^tBu_2GaO_2P(OSiMe_3)Me]_2$ (**7**), $[^tBu_2GaO_2P(OSiMe_3)^tBu]_2$ (**8**), $[^tBu_2GaO_2P(OSiMe_3)H]_2$ (**9**), and $[^tBu_2GaO_2P(OSiMe_3)_2]_2$ (**10**), respectively (eq 2). The silylated derivatives readily crystallize



(2)

in analytical purity from THF or THF/toluene solutions at −20 °C. Electron impact mass spectra and exact mass measurements

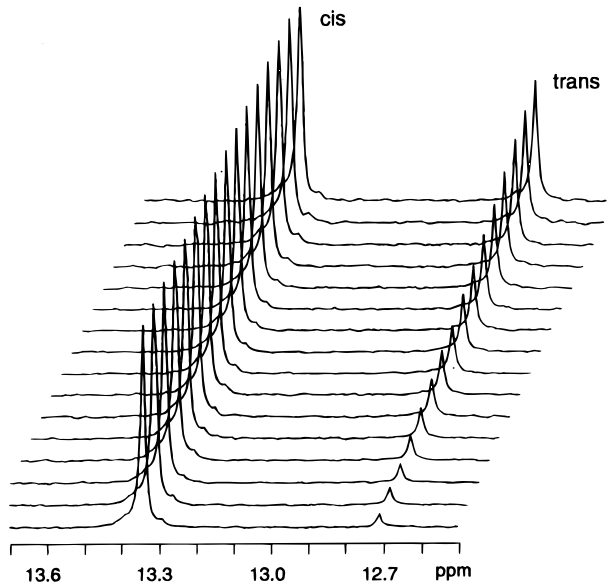
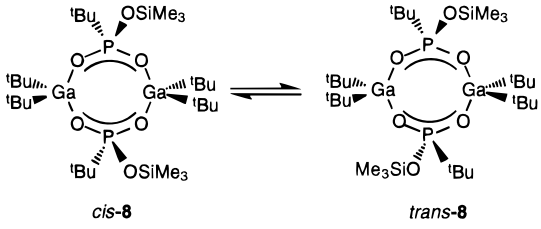


Figure 1. Cis−trans isomerization of **8** as monitored over 12 h by ^{31}P NMR spectroscopy.

demonstrate that **6**−**10** are cyclic dimers in the gas phase, and NMR spectroscopic data are consistent with dimeric structures in solution. Although primary and secondary phosphines often react with gallium alkyls via elimination of alkane and the formation of gallium phosphido compounds,[32] the retention of the P−H bond in **9**, as well as in **4**, is unambiguous on the basis of a large one-bond coupling ($^1J_{PH}$ = 693 Hz) in the ^1H NMR spectrum.

NMR spectra show the presence of cis and trans isomers for **6**−**9**. Of these, the trans isomers predominate in freshly prepared solutions with trans:cis ratios of 20:1, 12:1, and 6:5 for **6**, **7**, and **9**, respectively. The trans isomers are identified by a single ^{t}BuGa resonance in the ^1H NMR spectra. In contrast, there are two ^{t}BuGa resonances of equal intensity in the ^1H NMR spectrum for **8**, suggesting that the cis isomer is the major species (>95%). Over a period of 12 h, however, the trans:cis ratio for **8** changes to 1:2 (eq 3; Figure 1). Similarly, $CDCl_3$



(3)

solutions of **6** or **7** slowly equilibrate to trans:cis ratios of 1:1. Cis−trans interconversion is also observed for **1**, as well as for the related gallophosphonate $[^tBu_2GaO_2P(OGa^tBu_2)Ph]_2$.[21]

Cis−trans interconversion in **6**−**8** could proceed via several pathways, including (1) Ga−O bond cleavage followed by an oxygen to oxygen trimethylsilyl migration and recoordination to gallium, (2) Ga−O bond cleavage followed by an intermolecular exchange of phosphonate groups, and (3) complete dissociation into $^tBu_2GaO_2P(OSiMe_3)R$ monomers followed by reassociation of monomers with either opposite or like configurations at phosphorus to give trans or cis isomers, respectively. The last pathway could include a trimethylsilyl migration, but this is not required to account for our observations.

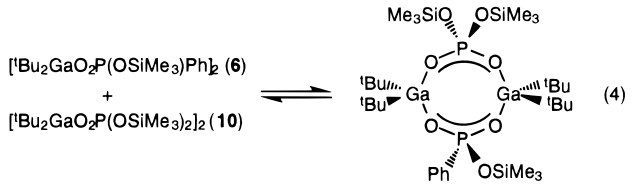
(32) Cowley, A. H.; Harris, P. R.; Jones, A. R.; Nunn, C. M. *Organometallics* **1991**, *10*, 652 and references therein.

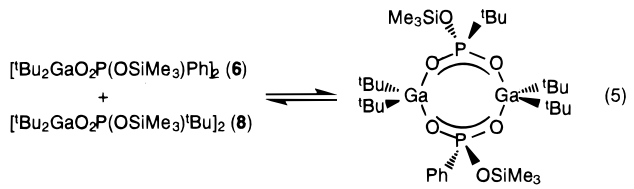
Table 2. ^{31}P NMR Data for Crossover Products [(^{t}Bu$_2$Ga)$_2${O$_2$P(OSiMe$_3$)R}{O$_2$P(OSiMe$_3$)R′}]

	R/R′					
	Ph/OTMS	Me/OTMS	^{t}Bu/OTMS	Ph/Me	Ph/^{t}Bu	Me/^{t}Bu
^{31}P δ, ppm	−3.59 (Ph) −24.43 (OTMS)	7.20 (Me) −24.40 (OTMS)	13.61 (^{t}Bu) −24.02 (OTMS)	7.81 (Me) *a* −2.77 (Ph) −3.22 (Ph)	13.93 (^{t}Bu) 13.84 (^{t}Bu) −3.07 (Ph) −3.39 (Ph)	13.87 (^{t}Bu) 13.69 (^{t}Bu) 7.40 (Me) 7.04 (Me)
solvent	$CDCl_3$	$CDCl_3$	C_6D_6	C_6D_6	C_6D_6	C_6D_6
reactants	**6, 10**	**7, 10**	**8, 10**	**6, 7**	**6, 8**	**7, 8**

[a] Unresolved from resonances in **7**.

Although we have not elucidated all details of the isomerization mechanism, results of crossover experiments monitored by ^{1}H and ^{31}P NMR spectroscopy demonstrate that heterocycle fragmentation and an intermolecular exchange process account for, or at least accompany, isomerization. For example, a nearly equimolar $CDCl_3$ solution of **6** and **10** shows evidence of reaction within 2 h, and equilibrium is achieved within 24 h. In the ^{1}H NMR spectra, two new ^{t}Bu resonances of equal intensity appear at 1.07 and 0.91 ppm as the four ^{t}Bu resonances for **6** and **10** decrease in intensity. In addition, three new $SiMe_3$ resonances of equal intensity appear at 0.28, 0.23, and 0.03 ppm. The number and intensities of the new ^{t}Bu and $SiMe_3$ resonances are consistent with the formation of the mixed cyclic dimer [(^{t}Bu$_2$Ga)$_2${O$_2$P(OSiMe$_3$)$_2$}{O$_2$P(OSiMe$_3$)Ph}] (eq 4). In addition to the resonances for **6** and **10**, the ^{31}P NMR spectrum exhibits two new resonances at −3.59 and −24.43 ppm assignable to the phosphonate and phosphate groups, respectively, in the mixed cyclic dimer. The ^{31}P NMR data for several crossover experiments conducted in two different solvents demonstrate the formation of mixed cyclic dimers in every case (Table 2). Combination of the phosphate **10** with phosphonate **6**, **7**, or **8** gives in each case one mixed dimer with two ^{31}P NMR resonances. Combinations of two phosphonates (**6**, **7**, or **8**) give four ^{31}P NMR resonances, two resonances assignable to a cis isomer and two assignable to a trans isomer (eq 5). ^{1}H NMR data are consistent with mixed dimer formation in all experiments conducted, although overlapping resonances make some assignments difficult. We have made no attempt to isolate these mixed products for structural characterization.





The molecular structures of **6**, **8**, and **10** are shown in Figures 2−4. Selected bond distances and angles are given in Tables 3−5. Each structure consists of an eight-membered $Ga_2P_2O_4$ ring composed of two μ_2-η^2-O$_2$P(OSiMe$_3$)R (R = Ph, ^{t}Bu, OSiMe$_3$) bridges between distorted tetrahedral gallium centers. In **8** and **10**, the two ^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)R monomer units which comprise the heterocycles are related by a crystallographically imposed inversion center. Gallium−oxygen distances range from a minimum of 1.901(7) Å in **6** to a maximum of 1.947(2) Å in **8**. In all three compounds, endocyclic P−O distances fall in the narrow range 1.494(8)−1.513(2) Å. A large range of P−O−Ga angles is observed in the three structures, with a minimum angle of 144.5(1)° in **10** and a maximum value of 161.9(1)° in **8**. All Ga−O distances, P−O distances, and P−O−Ga angles lie within the ranges observed for other gallophosphonate and gallophosphinate heterocycles. Comparison of average bond distances and angles for **6**, **8**, and **10** to those for **1**,[12] [Me$_2$GaO$_2$PPh$_2$]$_2$,[33] [^{t}Bu$_2$GaO$_2$PPh$_2$]$_2$,[34] and [^{t}Bu$_2$GaO$_2$P(OGa^{t}Bu$_2$)Ph]$_2$[21] is provided in Table 6. Noteworthy are the trans orientation of trimethylsiloxide substituents in the molecular structure of **6** and the cis orientation of trimethyl-

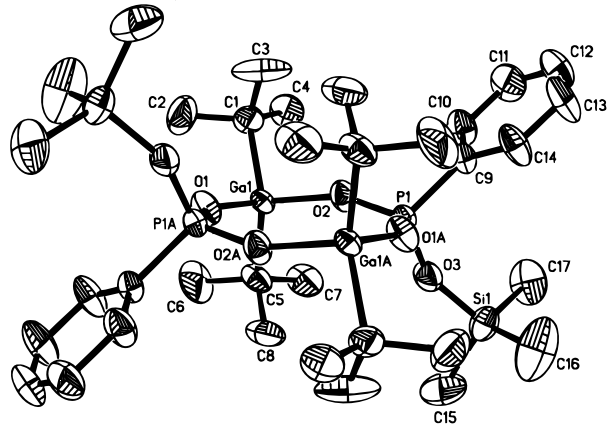


Figure 2. ORTEP drawing of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)Ph]$_2$ (**6**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

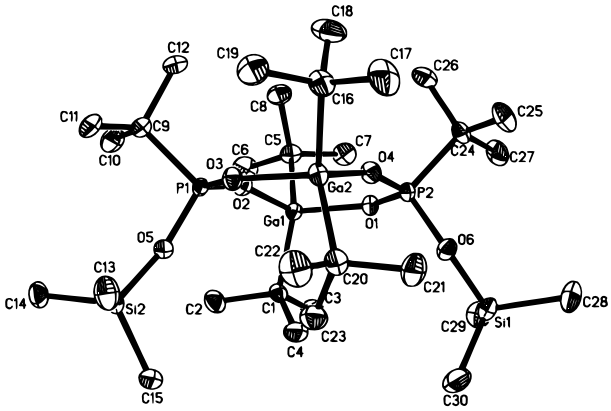


Figure 3. ORTEP drawing of [^{t}Bu$_2$GaO$_2$P(OSiMe$_3$)^{t}Bu]$_2$ (**8**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

(33) Hahn, F. E.; Schneider, B.; Reier, F.-W. *Z. Naturforsch.* **1990**, *45B*, 134.

(34) Landry, C. C.; Hynes, A.; Barron, A. R.; Haiduc, I.; Silvestru, C. *Polyhedron* **1996**, *15*, 391.

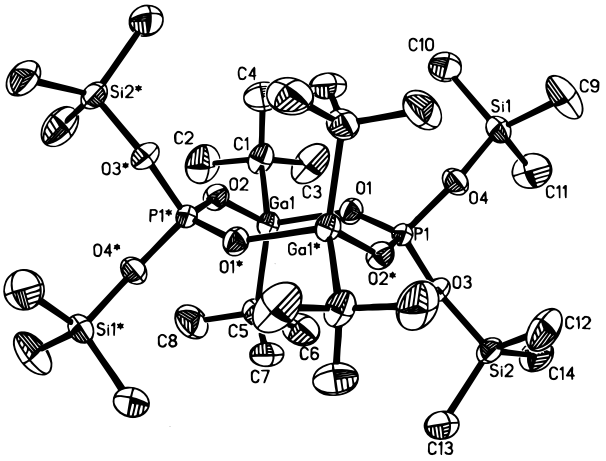


Figure 4. ORTEP drawing of $[^tBu_2GaO_2P(OSiMe_3)_2]_2$ (**10**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[^tBu_2GaO_2P(OSiMe_3)Ph]_2$ (**6**)

Distances			
Ga(1)−O(1)	1.916(7)	P(1)−O(1A)[a]	1.494(8)
Ga(1)−O(2)	1.901(7)	P(1)−O(2)	1.496(8)
Si(1)−O(3)	1.637(8)	P(1)−O(3)	1.549(8)
Angles			
O(2)−Ga(1)−O(1)	101.0(4)	O(1A)−P(1)−O(2)[a]	115.7(5)
O(2)−Ga(1)−C(1)	103.3(4)	O(1A)−P(1)−O(3)[a]	110.0(5)
O(1)−Ga(1)−C(1)	104.2(4)	O(2)−P(1)−O(3)	108.8(5)
O(2)−Ga(1)−C(5)	109.2(5)	O(1A)−P(1)−C(9)[a]	108.4(5)
O(1)−Ga(1)−C(5)	106.1(4)	O(2)−P(1)−C(9)	107.9(5)
C(1)−Ga(1)−C(5)	129.6(6)	O(3)−P(1)−C(9)	105.4(5)
P(1A)−O(1)−Ga(1)[a]	148.7(5)	P(1)−O(3)−Si(1)	149.7(6)
P(1)−O(2)−Ga(1)	157.7(5)		

[a] A indicates a symmetry-related atom.

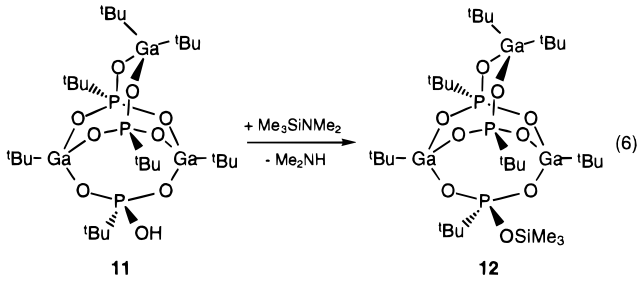
Table 4. Selected Bond Distances (Å) and Angles (deg) for $[^tBu_2GaO_2P(OSiMe_3)^tBu]_2$ (**8**)

Distances			
Ga(1)−O(1)	1.947(2)	P(1)−O(2)	1.509(2)
Ga(1)−O(2)	1.928(2)	P(1)−O(3)	1.513(2)
Ga(2)−O(3)	1.945(2)	P(1)−O(5)	1.567(2)
Ga(2)−O(4)	1.934(2)	P(2)−O(4)	1.505(2)
Si(1)−O(6)	1.672(2)	P(2)−O(6)	1.571(2)
Si(2)−O(5)	1.676(2)		
Angles			
O(2)−Ga(1)−O(1)	99.8(1)	O(2)−Ga(1)−C(1)	107.8(1)
O(1)−Ga(1)−C(1)	107.7(1)	O(2)−Ga(1)−C(5)	107.5(1)
O(1)−Ga(1)−C(5)	106.9(1)	C(1)−Ga(1)−C(5)	124.4(1)
O(4)−Ga(2)−O(3)	100.2(1)	O(4)−Ga(2)−C(16)	108.3(1)
O(3)−Ga(2)−C(16)	105.0(1)	O(4)−Ga(2)−C(20)	107.6(1)
O(3)−Ga(2)−C(20)	108.6(1)	C(16)−Ga(2)−C(20)	124.6(1)
O(2)−P(1)−O(3)	115.0(1)	O(2)−P(1)−O(5)	108.4(1)
O(3)−P(1)−O(5)	109.5(1)	O(2)−P(1)−C(9)	108.2(1)
O(3)−P(1)−C(9)	109.6(1)	O(5)−P(1)−C(9)	105.6(1)
O(4)−P(2)−O(1)	115.2(1)	O(4)−P(2)−O(6)	108.5(1)
O(1)−P(2)−O(6)	109.2(1)	O(4)−P(2)−C(24)	108.2(1)
O(1)−P(2)−C(24)	109.5(1)	O(6)−P(2)−C(24)	105.9(1)
P(2)−O(1)−Ga(1)	145.9(1)	P(1)−O(2)−Ga(1)	160.0(1)
P(1)−O(3)−Ga(2)	145.6(1)	P(2)−O(4)−Ga(2)	161.9(1)
P(1)−O(5)−Si(2)	149.8(1)	P(2)−O(6)−Si(1)	151.2(1)

siloxide substituents in **8**. These solid-state orientations are in agreement with the preferred isomers at low temperature in solution as determined by NMR spectroscopy.

Synthesis and Characterization of Trimeric and Tetrameric Cage Compounds. As discussed above, spectra of fresh solutions of **3** are consistent with a dimeric structure with trans orientation of hydroxyl substituents. However, NMR spectra of older samples routinely exhibit numerous additional resonances which we initially attributed to decomposition and/or interconversion between isomeric cyclic dimers and/or trimers. ^{31}P NMR spectra of freshly prepared solutions of **3** (δ 25.1 ppm) show gradual conversion over a period of a few days to a new compound with three equally intense singlet resonances at 33.2, 23.8, and 23.3 ppm. Monitoring the solution by ^1H NMR spectroscopy shows that this conversion is accompanied by isobutane formation, identified by a doublet at 0.85 ppm and a multiplet at 1.65 ppm. On a preparative scale, thermolysis of **3** in refluxing toluene for 15 h yields the trimeric gallophosphonate $[(^tBuGa)_2(^tBu_2Ga)(O_3P^tBu)_2\{O_2P(OH)^tBu\}]$ (**11**) as a white precipitate. The ^1H NMR spectrum of **11** reveals two equally intense singlets at 1.05 and 0.99 ppm assigned to *tert*-butyl substituents on gallium. The *tert*-butyl substituents on phosphorus give rise to three doublets at 1.18, 1.17, and 1.16 ppm, consistent with the three phosphorus environments indicated by ^{31}P NMR spectroscopy. Integration shows a 2:2:1:1:1 ratio of *tert*-butyl substituents on gallium and phosphorus. A broad singlet at 5.6 ppm in the ^1H NMR spectrum and an intense infrared absorption at 3200 cm^{-1} confirm the presence of a hydroxyl substituent on phosphorus. The electron impact mass spectrum of **11** shows very little fragmentation, limited to an intense cluster of peaks at *m*/*z* 789 (100%), assignable to the $M^+ - {}^t$Bu fragment, and fragments at *m*/*z* 733 and 675, resulting from loss of a second and a third *tert*-butyl substituent. Elemental analysis and exact mass measurements on the $M^+ - {}^t$Bu fragment confirm the elemental composition.

Further support for the proposed formula and structure is offered by complete characterization of the silylated derivative $[(^tBuGa)_2(^tBu_2Ga)(O_3P^tBu)_2\{O_2P(OSiMe_3)^tBu\}]$ (**12**), obtained in 69% yield by reaction of **11** with Me_3SiNMe_2 (eq 6). NMR



11 12 (6)

and mass spectra for **12** exhibit features similar to those described for **11**. Of particular note are the lack of a hydroxyl stretch in the infrared spectrum of **12** and the lack of a hydroxyl resonance in the corresponding ^1H NMR spectrum, both

Table 6. Comparison of Average Bond Distances and Angles for Gallophosphinate, Gallophosphonate, and Gallophosphate Heterocycles[a]

	Ga−O, Å (av)	P−O, Å (av)	P−O−Ga, deg (av)	P−O−Ga, deg (range)	ref
$[Me_2GaO_2PPh_2]_2$	1.93	1.52	132.6	128.7−136.5	33
$[^tBu_2GaO_2PPh_2]_2$	1.96	1.49	146.2	139.5−152.9	34
$[^tBu_2GaO_2P(OH)Ph]_2$ (**1**)	1.93	1.49	150.1	142.3−157.8	12
$[^tBu_2GaO_2P(OGa^tBu_2)Ph]_2$	1.90	1.50	153.1	146.0−160.2	21
$[^tBu_2GaO_2P(OSiMe_3)Ph]_2$ (**6**)	1.91	1.50	153.2	148.7−157.7	this work
$[^tBu_2GaO_2P(OSiMe_3)^tBu]_2$ (**8**)	1.94	1.51	153.5	145.6−161.9	this work
$[^tBu_2GaO_2P(OSiMe_3)_2]_2$ (**10**)	1.94	1.50	144.9	144.5−145.2	this work

[a] Endocyclic values only.

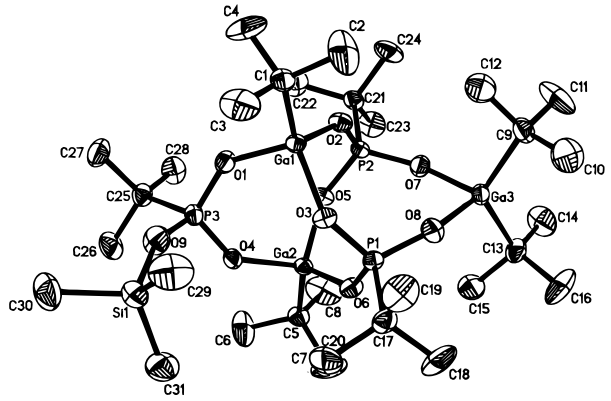


Figure 5. ORTEP drawing of **12**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

indicative of trimethylsilylation of the initial hydroxyl substituent in **11**. In addition, a singlet $SiMe_3$ resonance is observed at 0.27 ppm, the integration of which confirms the presence of one $SiMe_3$ group, four *tert*-butyl groups on gallium, and three *tert*-butyl substituents on phosphorus. As for **11**, the chemical inequivalence of the three phosphorus sites is confirmed by singlet ^{31}P NMR resonances at 23.4, 23.1, and 18.9 ppm. The resonances at 23.4 and 23.1 ppm are virtually unchanged from their respective values for **11**, but the resonance at 33.2 ppm for **11** shifts upfield to 18.9 ppm upon trimethylsilylation, allowing unambiguous assignment of these resonances to the hydroxyl-substituted and trimethylsiloxide-substituted phosphorus sites, respectively.

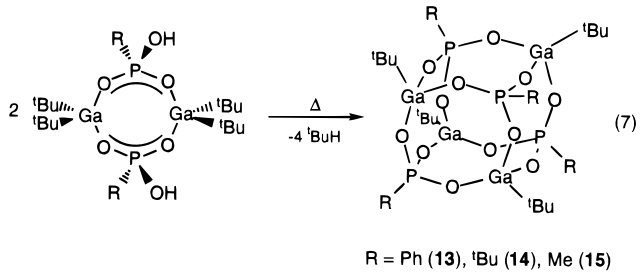
The molecular structure of **12** was further confirmed by X-ray crystallography (Figure 5, Table 7). The structure is composed of three phosphonate units bridging two ^tBuGa moieties. Two of the phosphonate units also bridge to a $^tBu_2Ga$ moiety, whereas the trimethylsilylated phosphonate group is only doubly bridging. Gallium−oxygen distances in **12** range from 1.852(2) to 1.925(2) Å. Of these, gallium distances to O(2), O(3), O(5), and O(6) range from 1.852(2) to 1.862(2) Å with an average value of 1.858 Å, significantly shorter than the Ga−O distances for the heterocycles in Table 6 but comparable to distances observed in tetrameric gallophosphonates (vide infra). These short Ga−O distances are all associated with ^tBuGa units and μ_3-phosphonate groups. Gallium−oxygen distances associated with the μ_2-phosphonate group or the $^tBu_2Ga$ moiety are considerably longer, averaging 1.891 and 1.921 Å, respectively. Whereas gallium distances to O(2), O(3), O(5), and O(6) are relatively short, phosphorus distances to these oxygens are elongated, ranging from 1.526(2) to 1.539(2) Å (average 1.532 Å). Phosphorus−oxygen distances associated with the μ_2-phosphonate group or the $^tBu_2Ga$ unit are significantly shorter (1.508(2)−1.512(2) Å; average 1.510 Å) and comparable to P−O distances observed in the gallophosphinate, gallophosphonate, and gallophosphate heterocycles. All other distances and angles are normal. The average for P−O−Ga angles is 139.6°, but the values range from 135.3(2) to 145.2(2)°.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[(^tBuGa)_2(^tBu_2Ga)(\mu_3\text{-}O_3P^tBu)_2(\mu_2\text{-}O_2P(OSiMe_3)^tBu)]$ (**12**)

Distances			
Ga(1)−O(1)	1.890(2)	Ga(1)−O(2)	1.852(2)
Ga(1)−O(3)	1.862(2)	Ga(2)−O(4)	1.891(2)
Ga(2)−O(5)	1.862(2)	Ga(2)−O(6)	1.855(2)
Ga(3)−O(7)	1.917(2)	Ga(3)−O(8)	1.925(2)
P(1)−O(3)	1.539(2)	P(1)−O(6)	1.530(2)
P(1)−O(8)	1.508(2)	P(2)−O(2)	1.526(2)
P(2)−O(5)	1.532(2)	P(2)−O(7)	1.509(2)
P(3)−O(1)	1.512(2)	P(3)−O(4)	1.512(2)
P(3)−O(9)	1.540(2)	Si(1)−O(9)	1.659(2)
Angles			
O(2)−Ga(1)−O(3)	105.54(8)	O(2)−Ga(1)−O(1)	101.4(1)
O(3)−Ga(1)−O(1)	102.5(1)	O(2)−Ga(1)−C(1)	116.7(1)
O(3)−Ga(1)−C(1)	117.8(1)	O(1)−Ga(1)−C(1)	110.8(1)
O(6)−Ga(2)−O(5)	105.1(1)	O(6)−Ga(2)−O(4)	103.6(1)
O(5)−Ga(2)−O(4)	103.3(1)	O(6)−Ga(2)−C(5)	115.8(1)
O(5)−Ga(2)−C(5)	117.7(1)	O(4)−Ga(2)−C(5)	109.7(1)
O(7)−Ga(3)−O(8)	98.6(1)	O(7)−Ga(3)−C(9)	110.7(1)
O(8)−Ga(3)−C(9)	104.2(1)	O(7)−Ga(3)−C(13)	104.1(2)
O(8)−Ga(3)−C(13)	110.8(2)	C(9)−Ga(3)−C(13)	125.4(2)
O(8)−P(1)−O(6)	112.4(2)	O(8)−P(1)−O(3)	112.3(2)
O(6)−P(1)−O(3)	109.8(2)	O(8)−P(1)−C(17)	107.4(2)
O(6)−P(1)−C(17)	107.6(2)	O(3)−P(1)−C(17)	107.2(2)
O(7)−P(2)−O(2)	111.9(2)	O(7)−P(2)−O(5)	112.3(1)
O(2)−P(2)−O(5)	110.5(1)	O(7)−P(2)−C(21)	107.3(2)
O(2)−P(2)−C(21)	107.1(2)	O(5)−P(2)−C(21)	107.4(2)
O(1)−P(3)−O(4)	113.7(2)	O(1)−P(3)−O(9)	108.5(2)
O(4)−P(3)−O(9)	110.3(2)	O(1)−P(3)−C(25)	108.9(2)
O(4)−P(3)−C(25)	110.1(2)	O(9)−P(3)−C(25)	104.9(2)
P(3)−O(1)−Ga(1)	137.1(2)	P(2)−O(2)−Ga(1)	137.3(2)
P(1)−O(3)−Ga(1)	137.9(2)	P(3)−O(4)−Ga(2)	141.2(1)
P(2)−O(5)−Ga(2)	140.9(1)	P(1)−O(6)−Ga(2)	135.3(2)
P(2)−O(7)−Ga(3)	141.6(2)	P(1)−O(8)−Ga(3)	145.2(2)
P(3)−O(9)−Si(1)	154.9(2)		

Although all gallium and phosphorus centers are crystallographically unique in the solid-state structure of **12**, the idealized molecular symmetry is C_s with a reflection plane incorporating P(1), P(2), P(3), and Ga(3). This reflection plane would relate Ga(1) with Ga(3), making them chemically equivalent for NMR spectroscopic purposes. However, the ^{t}Bu and Me_3SiO substituents on P(3) preclude a reflection plane through Ga(1), Ga(2), Ga(3), and P(3), consistent with the inequivalence of all phosphorus sites as demonstrated by ^1H and ^{31}P NMR spectroscopy.

Refluxing toluene solutions of **11** for longer than 15 h results in conversion to $[^tBuGaO_3P^tBu]_4$ (**14**). Compound **14** can more conveniently be obtained as a crystalline white solid in 60−70% yield by refluxing diglyme solutions of **3**, **11**, or $^tBu_3Ga$ and $^tBuP(O)(OH)_2$ for a period of 2 h. The methylphosphonate $[^tBuGaO_3PMe]_4$ (**15**) can be obtained in 86% yield in an analogous manner starting from **2** (eq 7) or starting directly from $^tBu_3Ga$ and $MeP(O)(OH)_2$. Both **14** and **15** lack hydroxyl substituents on the basis of infrared and ^1H NMR spectroscopic data. Their ^1H NMR spectra exhibit only a singlet ^{t}BuGa resonance, as well as a doublet resonance at 1.15 ppm ($^3J_{PH}$ = 17.0 Hz) for **14** and a doublet at 1.38 ppm ($^2J_{PH}$ = 18.5 Hz) for



15 assignable to *tert*-butyl and methyl substituents on phosphorus. Compounds **14** and **15** each exhibit only a single ^{31}P NMR resonance. Although elemental analyses and NMR spectroscopic data are consistent with symmetrical cage compounds of the formula $[^tBuGaO_3PR]_n$ (R = Me, ^{t}Bu), it is the observation of intense $M^+ - {}^t$Bu fragments in the electron impact mass spectra and the corresponding high-resolution mass measurements which confirm **14** and **15** to be tetramers ($n = 4$) in the gas phase. NMR spectroscopic data are consistent with retention of the $Ga_4P_4O_{12}$ cores in solution, and the tetrameric nature of **14** and **15** in the solid state was confirmed by X-ray crystallography.

The molecular structures of **14** and **15** are composed of a cuboidal $Ga_4P_4O_{12}$ core in which distorted tetrahedral gallium and phosphorus atoms alternately occupy vertex positions and oxygen atoms bridge along the edges. For **15** (Figure 6, Table 8), gallium−oxygen distances range from 1.833(4) to 1.868(4) Å (average 1.85 Å), comparable to the range 1.827(7)−1.858(7) Å found for $[^tBuGaO_3PPh]_4$ (**13**)[12] but significantly shorter than the corresponding distances for the heterocycles given in Table 6. Phosphorus−oxygen distances (1.491(4)−1.520(4) Å; average 1.51 Å) and Ga−O−P angles (131.6(2)−172.0(3)°; average 148.0°) are also comparable to those reported for **13**.

The molecular structure of **14** suffers a 50:50 disorder of phosphorus and gallium sites. This is evident in the Ga−O and P−O distances (see Supporting Information), which have similar ranges and each of which average to 1.68 Å. These distances are intermediate to those expected for Ga−O (1.85 Å) and P−O (1.50 Å) bonds by comparison to the molecular structures for **13** and **15**. Because of this disorder, no further discussion of the structure of **14** is warranted.

Attempts to form $[^tBuGaO_3PH]_4$ by methods analogous to those utilized for the preparation of **13**−**15** have thus far failed. Thermolysis of **4** or refluxing solutions of ^{t}Bu$_3$Ga and H_3PO_3 under a variety of reaction conditions yielded only complex mixtures. However, the use of phosphoric acid gave much better results. Equimolar reaction of ^{t}Bu$_3$Ga and H_3PO_4 in refluxing diglyme, followed by trimethylsilylation with Me_3SiNMe_2, yields **16** as a white crystalline solid in 66% yield. Elemental analysis confirms a formulation of $[^tBuGaO_3P(OSiMe_3)]_n$, and the mass spectrum of **16** verifies the existence of a tetramer ($n = 4$) in the gas phase. A cubic tetramer is also consistent with the symmetry suggested by a single resonance at −20.3 ppm in the ^{31}P NMR spectrum and a single ^{t}Bu resonance and an equally intense Me_3Si resonance in the ^1H NMR spectrum. Retention of a cubic tetrameric structure in the solid state was confirmed by X-ray crystallography.

Compound **16** crystallizes in the tetragonal space group $I4_1/a$. The unique portion of the unit cell contains one ^{t}BuGaO$_3$P(OSiMe$_3$) unit which, upon symmetry expansion, yields a cuboidal $Ga_4P_4O_{12}$ core (Figure 7) analogous to the cores in **13**−**15**. The large angles (Table 9) at the μ_2-oxygens (141.2(4), 145.4(4)°) are in the range observed for $[^tBuGaO_3PPh]_4$ (135.6(5)−175.2(6)°; average 150.3°) and $[^tBuGaO_3PMe]_4$ (131.7(2)−172.1(3)°; average 148.1°). Intra-cage P−O dis-

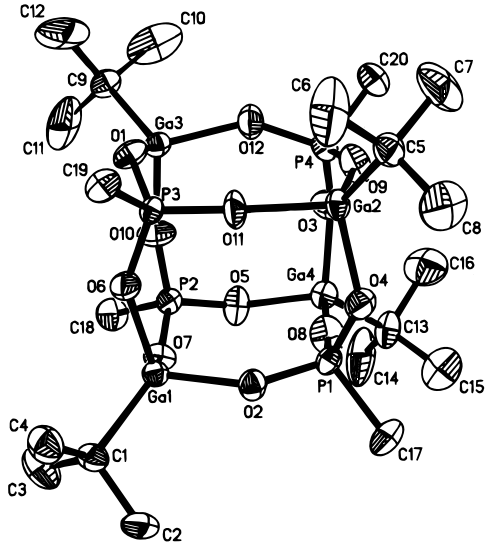


Figure 6. ORTEP drawing of $[^tBuGaO_3PMe]_4$ (**15**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 8. Selected Bond Distances (Å) and Angles (deg) for $[^tBuGaO_3PMe]_4$ (**15**)

		Distances	
Ga(1)−O(2)	1.860(4)	Ga(1)−O(6)	1.862(3)
Ga(1)−O(7)	1.869(3)	Ga(2)−O(11)	1.833(4)
Ga(2)−O(9)	1.853(4)	Ga(2)−O(4)	1.857(4)
Ga(3)−O(10)	1.850(4)	Ga(3)−O(12)	1.856(4)
Ga(3)−O(1)	1.860(3)	Ga(4)−O(8)	1.838(4)
Ga(4)−O(3)	1.847(4)	Ga(4)−O(5)	1.863(4)
P(1)−O(8)	1.501(4)	P(1)−O(4)	1.506(4)
P(1)−O(2)	1.519(4)	P(2)−O(10)	1.490(4)
P(2)−O(7)	1.514(4)	P(2)−O(5)	1.515(4)
P(3)−O(11)	1.502(4)	P(3)−O(6)	1.512(4)
P(3)−O(1)	1.521(4)	P(4)−O(12)	1.506(4)
P(4)−O(9)	1.506(4)	P(4)−O(3)	1.509(4)
		Angles	
O(2)−Ga(1)−O(6)	104.8(2)	O(2)−Ga(1)−O(7)	105.4(2)
O(6)−Ga(1)−O(7)	105.8(2)	O(2)−Ga(1)−C(1)	113.5(2)
O(6)−Ga(1)−C(1)	114.0(2)	O(7)−Ga(1)−C(1)	112.6(2)
O(11)−Ga(2)−O(9)	104.7(2)	O(11)−Ga(2)−O(4)	100.6(2)
O(9)−Ga(2)−O(4)	103.8(2)	O(11)−Ga(2)−C(5)	114.4(2)
O(9)−Ga(2)−C(5)	113.6(2)	O(4)−Ga(2)−C(5)	117.9(2)
O(10)−Ga(3)−O(12)	105.0(2)	O(10)−Ga(3)−O(1)	101.6(2)
O(12)−Ga(3)−O(1)	103.9(2)	O(10)−Ga(3)−C(9)	114.0(2)
O(12)−Ga(3)−C(9)	112.9(2)	O(1)−Ga(3)−C(9)	117.9(2)
O(8)−Ga(4)−O(3)	104.4(2)	O(8)−Ga(4)−O(5)	103.1(2)
O(3)−Ga(4)−O(5)	103.7(2)	O(8)−Ga(4)−C(13)	113.1(2)
O(3)−Ga(4)−C(13)	115.5(2)	O(5)−Ga(4)−C(13)	115.7(2)
O(8)−P(1)−O(4)	111.6(2)	O(8)−P(1)−O(2)	110.5(2)
O(4)−P(1)−O(2)	111.8(2)	O(8)−P(1)−C(17)	109.5(3)
O(4)−P(1)−C(17)	106.0(3)	O(2)−P(1)−C(17)	107.3(3)
O(10)−P(2)−O(7)	111.5(2)	O(10)−P(2)−O(5)	112.3(2)
O(7)−P(2)−O(5)	111.1(2)	O(10)−P(2)−C(18)	108.2(3)
O(7)−P(2)−C(18)	107.3(3)	O(5)−P(2)−C(18)	106.1(3)
O(11)−P(3)−O(6)	111.5(2)	O(11)−P(3)−O(1)	111.5(2)
O(6)−P(3)−O(1)	111.7(2)	O(11)−P(3)−C(19)	108.1(3)
O(6)−P(3)−C(19)	106.8(2)	O(1)−P(3)−C(19)	106.9(2)
O(12)−P(4)−O(9)	111.8(3)	O(12)−P(4)−O(3)	112.2(3)
O(9)−P(4)−O(3)	112.3(3)	O(12)−P(4)−C(20)	106.9(3)
O(9)−P(4)−C(20)	106.8(3)	O(3)−P(4)−C(20)	106.5(3)
P(3)−O(1)−Ga(3)	131.7(2)	P(1)−O(2)−Ga(1)	142.8(2)
P(4)−O(3)−Ga(4)	145.0(3)	P(1)−O(4)−Ga(2)	134.6(2)
P(2)−O(5)−Ga(4)	133.0(2)	P(3)−O(6)−Ga(1)	144.2(2)
P(2)−O(7)−Ga(1)	140.8(2)	P(1)−O(8)−Ga(4)	172.1(3)
P(4)−O(9)−Ga(2)	145.6(3)	P(2)−O(10)−Ga(3)	169.0(3)
P(3)−O(11)−Ga(2)	171.3(3)	P(4)−O(12)−Ga(3)	147.0(3)

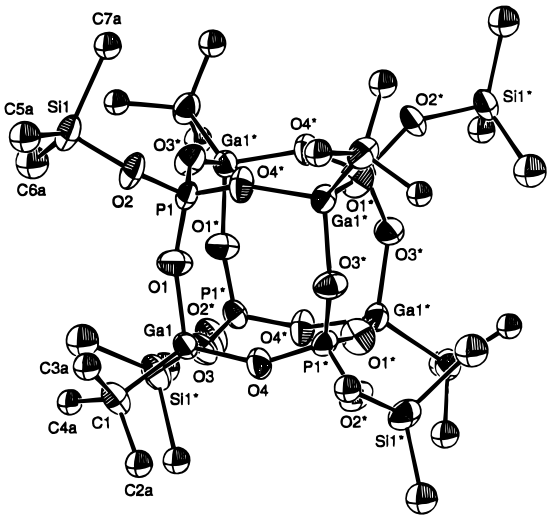


Figure 7. ORTEP drawing of $[^tBuGaO_3P(OSiMe_3)]_4$ (**16**). Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms are omitted for clarity.

Table 9. Selected Bond Distances (Å) and Angles (deg) for $[^tBuGaO_3P(OSiMe_3)]_4$ (**16**)

		Distances	
Ga(1)−O(1)	1.825(6)	Ga(1)−O(3)	1.849(5)
Ga(1)−O(4)	1.824(6)	Si(1)−O(2)	1.608(6)
P(1)−O(1)	1.474(6)	P(1)−O(2)	1.524(6)
P(1)−O(3*)[a]	1.498(6)	P(1)−O(4*)[a]	1.495(6)
		Angles	
O(1)−Ga(1)−O(3)	104.7(3)	O(1)−Ga(1)−O(4)	103.5(3)
O(1)−Ga(1)−C(1)	113.9(4)	O(3)−Ga(1)−O(4)	104.3(3)
O(3)−Ga(1)−C(1)	114.1(4)	O(4)−Ga(1)−C(1)	115.2(4)
O(1)−P(1)−O(2)	106.5(4)	O(1)−P(1)−O(3*)[a]	111.5(4)
O(1)−P(1)−O(4*)[a]	112.4(4)	O(2)−P(1)−O(3*)[a]	108.1(3)
O(2)−P(1)−O(4*)[a]	105.1(4)	O(3*)−P(1)−O(4*)[a]	112.7(4)
Ga(1)−O(1)−P(1)	162.4(5)	P(1)−O(2)−Si(1)	146.1(5)
Ga(1)−O(3)−P(1*)[a]	141.2(4)	Ga(1)−O(4)−P(1*)[a]	145.4(4)

[a] Asterisks indicate symmetry-related atoms.

tances (1.474(6) − 1.498(6) Å) and gallium−oxygen distances (1.825(6), 1.849(5), 1.824(6) Å; average 1.83 Å) are also normal by comparison to distances in **13** and **15**.

Reactivity of 13−16. Compounds **13−15** are remarkably stable to oxygen and a variety of protic reagents, including water. Similar stability was recently noted by Roesky for the methyl-substituted analogues $[MeGaO_3PR]_4$ (R = Me, Et, ^{t}Bu, Ph).[17] The thermal stabilities of **13−15** are also impressive, as each compound is stable to 300 °C in an inert atmosphere. Furthermore, these compounds sublime at 150−250 °C/0.1 mmHg, with $[^tBuGaO_3PMe]_4$ (**15**) being the most volatile and $[^tBuGaO_3PPh]_4$ (**13**) being the least. Solid-state pyrolysis of **1−3** in a tube furnace at 250 °C/0.1 mmHg is actually a convenient high-yield route to pure **13−15**, which sublime and condense at the cool end of the reaction tube.

In contrast to the hydrolytic stability of **13−15**, $[^tBuGaO_3P(OSiMe_3)]_4$ (**16**) is readily hydrolyzed by moisture with the formation of hexamethyldisiloxane. Trimethylsilyl substituents can also be removed with $^nBu_4NF$, analogous to the reactivity observed for $[^tBuAlO_3P(OSiMe_3)]_4$.[35] The metal- and phosphorus-containing products arising from hydrolysis of **16** and $[^tBuAlO_3P(OSiMe_3)]_4$ are presently under investigation.

Considering the facile intermolecular cis−trans isomerization observed for **1** and for **6−9**, we were concerned about possible

(35) Matthews, R. M.; Mason, M. R. Unpublished result.

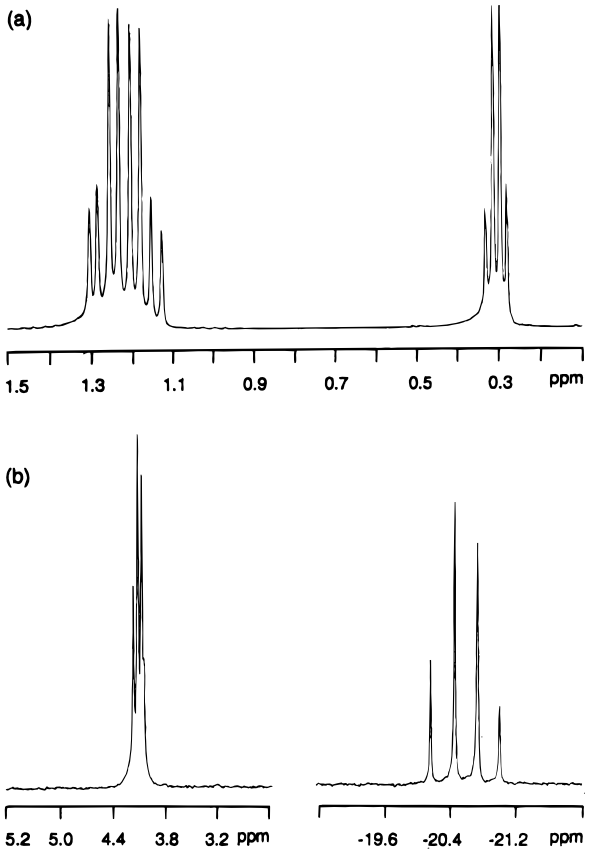


Figure 8. Selected spectra for C_6D_6 solutions of **13** and **16** after 2 days at 85 °C: (a) ^{1}H NMR spectrum, aliphatic region; (b) ^{31}P NMR spectrum.

fragmentation of the $Ga_4P_4O_{12}$ cores of **13−15** in solution. X-ray diffraction and mass spectrometric data presented here confirm tetrameric structures for **13−15** in the solid and gas phases, respectively. However, could the solution NMR data which indicate retention of a symmetric structure possibly result from rapid interconversion of different cage structures? Alternatively, could the tetramers slowly fragment and rapidly re-form? Crossover experiments indicate that fragmentation does occur in C_6D_6 or $CDCl_3$ as monitored by ^{1}H and ^{31}P NMR spectroscopy. Reaction of **13** with **16** in $CDCl_3$ at room temperature results in the appearance of six new ^{31}P NMR resonances over the course of 3 days, with a decrease in intensity of resonances for **13** and **16** (Figure 8). Resonances at 3.16, 3.10, and 3.05 ppm, adjacent to the resonance at 3.24 ppm for **13**, are assigned to $PhPO_3^{2-}$ units. Resonances at −21.15, −21.45, and −21.75 ppm are clearly assigned to $(Me_3SiO)PO_3^{2-}$ groups on the basis of their proximity to the resonance at −20.83 ppm for **16**. ^{31}P NMR spectra obtained to monitor reactions of **14** with **16**, **15** with **16**, and **13** with **15** similarly change over several days at room temperature, whereas reaction of **13** with **14** is indicated by the appearance of only two low-intensity ^{31}P NMR resonances after a week. There was no evidence of reaction between **14** and **15** under the same conditions. Heating these solutions at 85 °C for 1−2 days accelerates these reactions, but reaction of **13** with **14** and reaction of **14** with **16** are still slow even at 85 °C. Solutions of **14** and **15** show no evidence for reaction, even after heating at 85 °C for 2 days. More vigorous conditions, such as refluxing **13** with **14** in diglyme for 12 h, yield product mixtures similar to those obtained in the other experiments (Table 10).

These data can be explained by cage fragmentation and recombination to form a mixture of five tetramers of the formula

Table 10. ^{31}P NMR Data[a] for Crossover Products $[(^{t}BuGa)_4(RPO_3)_{4-x}(R'PO_3)_x]$

	R/R′					
	Ph/^{t}Bu[b]	Ph/Me	Ph/OTMS	^{t}Bu/Me	^{t}Bu/OTMS	Me/OTMS
^{31}P δ, ppm	21.19 (^{t}Bu)	16.10 (Me)	4.07 (Ph)*	21.72 (^{t}Bu)*	21.72 (^{t}Bu)*	15.85 (Me)
	21.10 (^{t}Bu)	15.98 (Me)	4.02 (Ph)	15.76 (Me)*	21.57 (^{t}Bu)	15.80 (Me)
	21.07 (^{t}Bu)*	15.86 (Me)	3.98 (Ph)		21.45 (^{t}Bu)	15.75 (Me)*
	3.24 (Ph)*	15.76 (Me)*	3.95 (Ph)		−20.30 (OTMS)*	−20.56 (OTMS)
	3.03 (Ph)	4.08 (Ph)*	−20.29 (OTMS)*		−20.64 (OTMS)	−20.83 (OTMS)
	2.89 (Ph)	3.98 (Ph)	−20.56 (OTMS)		−20.88 (OTMS)	−21.09 (OTMS)
	2.78 (Ph)	3.87 (Ph)	−20.83 (OTMS)		−21.02 (OTMS)	
		3.77 (Ph)	−21.07 (OTMS)			
*reactants	**13**, **14**	**13**, **15**	**13**, **16**	**14**, **15**	**14**, **16**	**15**, **16**

[a] C_6D_6; 30 h, 85 °C. [b] Diglyme; 12 h, 162 °C.

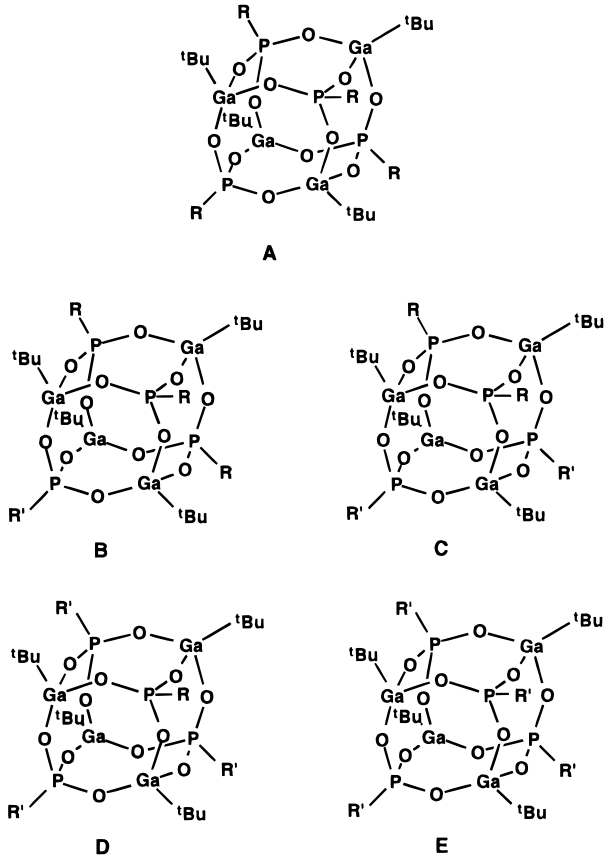


Figure 9. The five tetramers **A**−**E** present in crossover experiments involving two different phosphonate substituents (R, R′).

$[(^{t}BuGa)_4(RPO_3)_{4-x}(R'PO_3)_x]$ (x = 0−4, **A**−**E**; Figure 9). Tetramers **A**−**E** should exhibit one, two, two, two, and one ^{31}P NMR resonances, respectively. Thus a mixture of all five tetramers should exhibit eight ^{31}P NMR resonances, consistent with the data obtained upon reaction of **13** with **16**. ^{1}H NMR data are also consistent with the presence of the five tetramers in these reaction solutions. For example, the ^{1}H NMR spectrum for the reaction solution of **13** and **16** exhibits eight ^{t}BuGa resonances and four Me_3SiO resonances (Figure 8), the maximum expected for a mixture of tetramers **A**−**E**. Control experiments demonstrated solutions of individual tetramers **13**−**16** are stable under the reaction conditions employed here, with no evidence for decomposition or rearrangement to different cage structures. In summary, these data indicate that a slow, but significant, cage fragmentation process proceeds even under mild conditions in nonpolar solvents. Although we have not yet determined the exact mechanism at play, we speculate that exchange could proceed via dissociation to cyclic dimers which rapidly recombine or via an intermolecular exchange initiated by cage opening along one or two edges.

Relevance to Phosphate Materials. The gallophosphonates and gallophosphates reported above have a structural relationship to SBUs in phosphate materials. The cyclic $Ga_2P_2O_4$ cores in **1**−**10** and the cubic $Ga_4P_4O_{12}$ cores in **13**−**16** are analogous to four-ring (4R) and double-four-ring (D4R) SBUs common to numerous aluminophosphate and gallophosphate molecular sieves.[36] In particular, the $Ga_4P_4O_{12}$ cores in **13**−**16** have a structural relationship to the D4Rs in cloverite,[1] ULM-5,[19] and gallophosphate A.[20] Metric parameters for **13**−**16** are generally comparable to those for the D4Rs in cloverite, with the exception of larger O−Ga−O angles (114.7−121.3°) for cloverite compared to those for **13**−**16** (100.6(2)−105.8(2)°). The presence of an encapsulated fluoride ion and the resulting trigonal bipyramidal coordination at gallium in the D4Rs of cloverite account for these differences. Intracage diagonal Ga−P distances are also considerably shorter in cloverite (5.42 Å) than in **13**−**16** (5.56−5.61 Å), allowing plenty of room for encapsulation of fluoride in the latter. Efforts to effect encapsulation of fluoride in **13**−**15** and related phosphonate cage compounds are in progress.

In addition to comparison of **1**−**10** and **13**−**16** to 4R and D4R SBUs, the $Ga_3P_3O_8$ cores of **11** and **12** are common to the asymmetric unit in the open framework gallophosphate $Ga_9P_9O_{36}OH{\cdot}NHEt_3$.[5i] Although three phosphonate or phosphate groups bridging two gallium centers is rare, this motif is also observed in the $[Ga(H_2PO_4)(HPO_4)_2]^{2-}$ columns found in $[Cs_2Ga(H_2PO_4)(HPO_4)_2]$.[37]

Despite these structural relationships, numerous problems must be addressed before molecular building blocks as described here can be utilized for the rational preparation of phosphate materials. Among these are the ability to remove organic substituents under mild conditions and the assurance of retention of the inorganic core. The thermal, oxidative, and protolytic stabilities of **13**−**15** are too great for the facile cage linkage reactions necessary to make phosphate materials. The moisture-sensitive gallophosphate **16** is much superior in this regard, but increased reactivity at gallium is still necessary. More important are concerns over fragmentation of the inorganic core as observed in the crossover reactions involving **13**−**16** in nonpolar solvents at only 85 °C. Fragmentation would be exacerbated by the higher temperatures and increased solvent polarity of solvothermal syntheses, the present preparative route to phosphate molecular sieves. We are presently searching for solutions to these problems. We note here that the facility of cage

(36) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 3rd ed.; Butterworth-Heinemann: London, 1992.
(37) Anisimova, N.; Chudinova, N.; Hoppe, R.; Serafin, M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 39.

fragmentation in structurally related metallasiloxanes and its implication for the synthesis of zeolitic materials via molecular routes have not been addressed.[38] On the basis of our results, cage fragmentation might be anticipated in some of the related metallasiloxane systems.

Conclusions

The synthesis of dimeric, trimeric, and tetrameric gallophosphonates and gallophosphates has been achieved by reactions of $^tBu_3Ga$ and acids of phosphorus. As far as we are aware, the gallophosphates **10** and **16** are the first molecular products reported from reactions of a gallium alkyl and phosphoric acid. Although **1**−**16** have a structural relationship to SBUs in phosphate molecular sieves, the fragmentation and intermolecular exchange processes observed raise serious obstacles to the utilization of these compounds as precursors to phosphate materials. We are not only continuing our efforts to overcome these obstacles but also focusing on the use of these compounds as precursors to gallophosphonate materials via introduction of organic and metal linkers.

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Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, and complete bond distances and angles for **6**, **8**, **10**, **12**, **14**, **15**, and **16** and a fully labeled ORTEP diagram for **14** (52 pages). Ordering information is given on any current masthead page.

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(38) For a few examples, see: (a) Voigt, A.; Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Parisini, E.; Lubini, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2203. (b) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 748. (c) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183. (d) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205. (e) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918.