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Synthesis and Characterization of Gallium-Containing Silsesquioxanes

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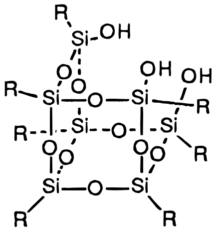
The reaction of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1a**) with GaX_3 (X = Cl or I) in the presence of Proton Sponge ($C_{14}H_{18}N_2$) affords $[(c\text{-}C_6H_{11})_7Si_7O_{12}GaX]^-$ $[C_{14}H_{18}N_2{\cdot}H]^+$ (**2a**, R = Cl; **2b**, R = I). A single-crystal X-ray diffraction study of **2a** reveals discrete ions with no significant interactions. Upon thermolysis both **2a** and **2b** liberate an equivalent of $[C_{14}H_{18}N_2{\cdot}H]^+X^-$ to produce quantitative yields of $[(c\text{-}C_6H_{11})_7Si_7O_{12}Ga]_2$ (**3**), a siloxy-bridged dimer which is isomorphous with previously characterized dimers containing Ti^{3+} and V^{3+}. The reaction of **3** with Ph_3PO affords $[(c\text{-}C_6H_{11})_7Si_7O_{12}Ga(OPPh_3)]$ (**5**), which was characterized by a single-crystal X-ray diffraction study. The reaction of trisilanol **1a** with $Ga(CH_2SiMe_3)_3$ affords **6**, an interesting cluster derived from the reaction of two molecules of **1a** with six molecules of $Ga(CH_2SiMe_3)_3$ and six molecules of water.

Introduction

Over the past few years we[1−3] and others[4−16] have described the synthesis, characterization, and reactivity of a large number of metallasilsesquioxanes derived from the reactions of incompletely-condensed silsesquioxanes with both main-group and transition-metal complexes.[17] Of particular interest have been reactions of trisilanols **1a** and **1b** with ligand-deficient trivalent metal complexes because the inability of these trisilanols to support trigonal planar coordination environments is expected to produce more complex structures. We have previously reported results concerning the reactions of **1a** with trivalent complexes of boron,[18] aluminum,[19] titanium,[20] and vanadium.[21] More recently, Herrmann et al.[6] have reported the synthesis of yttrium- and neodymium-containing silsesquioxanes derived from **1b**, and Roesky et al.[22] have reported the synthesis of gallium-containing silsesquioxanes from $[ArNSiMe_3]Si(OH)_3$ (Ar = 2,6-*i*-$Pr_2C_6H_3$ and 2,4,6-*i*-$Pr_3C_6H_2$). In this paper we describe the synthesis, characterization, and reactivity of several gallium-containing silsesquioxanes prepared from **1a**.



1a R = c-C_6H_{11}
b c-C_5H_9

The chemistry of gallium in its trivalent state, while very similar to that of aluminum, differs in several important respects.[23] For example, the complete protonolysis of alkyl−gallium bonds by weak acids (e.g., alcohols and silanols) occurs only with difficulty,[24] and the reaction of gallium halide complexes with alkali metal alkoxides proceeds more slowly and has been known to stop before complete metathesis occurs.[25] Trivalent complexes of gallium can also be powerful Lewis acids.[24] These characteristics of gallium chemistry are manifested in a number of interesting ways when trivalent gallium complexes are reacted with trisilanol **1a**.

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Experimental Section

A general experimental protocol for the synthesis and purification of **1a** appears elsewhere.[26] $GaCl_3$ was purchased from Aldrich Chemical Company and used without further purification. Ph_3PO (Aldrich) was purified by chromatography (silica gel, $CHCl_3/EtOH$) and subsequent recrystallization from $EtOH/Et_2O$. Proton Sponge (1,8-bis(dimethylamino)naphthalene, Aldrich) was sublimed in vacuo (60 °C, 0.01 Torr) and stored in a nitrogen-filled glovebox prior to use. GaI_3[27] and $Ga(CH_2SiMe_3)_3$[28] were prepared according to the literature procedures. Except where noted, all operations were performed under a nitrogen atmosphere either on a high-vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-lab. All NMR spectra were recorded on a General Electric GN-500 (^1H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{29}Si, 99.36 MHz) spectrometer. The CH_2 and CH resonances in the ^{13}C NMR spectra were assigned by using standard DEPT pulse sequences.

Syntheses of 2a and 2b. Solid $GaCl_3$ (75 mg, 0.43 mmol) was added to a solution of trisilanol **1a** (402 mg, 0.412 mmol) and Proton Sponge (265 mg, 1.24 mmol) in C_6H_6 (~20 mL). After stirring for 36 h, the solution was filtered, and the solvent was evaporated from the filtrate in vacuo (25 °C, 0.01 Torr) to afford **2a** as the only silsesquioxane-containing product. Residual amine hydrochloride salt was removed from this material by thin-pad chromatography (silica gel, $CHCl_3$) followed by recrystallization from hot hexanes (~25 mL). Yield: 310 mg, 58%. For **2a**, ^1H NMR (500.1 MHz, $CDCl_3$ 25 °C): δ 7.98 (d, 2H, $J = 8$ Hz), 7.82 (d, 2H, $J = 8$ Hz), 7.70 (dd, 2H, $J_1 = J_2 = 8$ Hz) for aromatic H; δ 3.29 (s, 12H) $N(CH_3)_2$; δ 2.79 (s, 1H) NH; δ 1.68 (br m, 35H), 1.21 (br m, 35H), 0.716 (tt, 1H, $J_1 = 11.9$ Hz, $J_2 = 2.4$ Hz), 0.655 (tt, 3H, $J_1 = 11.8$ Hz, $J_2 = 3.1$ Hz), 0.547 (tt, 3H, $J_1 = 12.2$ Hz, $J_2 = 2.8$ Hz). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 144.44, 135.51, 129.48, 127.17, 121.23, 118.80 for aromatic C; δ 47.18 ($N(CH_3)_2$); δ 27.92, 27.72, 27.67, 27.58, 27.13, 27.08, 27.04, 26.96, 26.80 (CH_2); δ 24.88, 23.82, 23.47 (3:3:1 for CH). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6H_6, 25 °C): δ 25.77, 24.60, 24.13 (3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −65.64, −68.66, −70.24 (3:1:3). MS (70 eV, 200 °C; relative intensity): *m/e* 958 ($M^+ - C_{14}H_{19}N_2$, − Cl, − C_6H_{11}; 40%, v weak), 1994 (dimer **2a** $M^+ - C_6H_{11}$, 100%, v weak). Anal. Calcd for $C_{56}H_{96}GaN_2O_{12}Si_7Cl$ (found): C, 52.10 (52.37); H, 7.49 (7.31). Mp: 125−7 °C. The iodide analogue, **2b**, may be synthesized in a similar manner. For **2b**, $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6H_6, 25 °C): δ 28.31, 28.19, 28.00, 27.94, 27.70, 27.63, 27.49, 27.46 (CH_2); δ 25.16, 24.37, 24.11 (3:3:1 for CH).

Synthesis of 3. Solid **2a** (200 mg, 0.156 mmol) was dissolved in ~5 mL of THF and heated at reflux for 4 h. The solvent was then evaporated in vacuo (~25 °C, 0.01 Torr) and the solid residue extracted with 4 × 2 mL of hexanes. The extract solvent was then removed in vacuo to afford 162 mg (quantitative) of **3** as an amorphous white powder. Complex **3** may be recrystallized from a minimum amount of hexanes (25 to −34 °C). Yield: 110 mg, 70%. For **3**, ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 1.9−1.6 (br m, 35H), δ 1.3−1.1 (br m, 35H), δ 0.8−0.6 (m, 7H). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 27.65, 27.60, 27.50, 27.41, 27.15, 27.03, 26.97, 26.88, 26.68, 26.36 (CH_2), δ 24.30, 24.11, 23.56, 23.11, 23.02, (1:2:1:1:2 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −62.10, −63.92, −67.34, −67.48, −71.56 (1:2:1:2:1). MS (70 eV, 200 °C; relative intensity): *m/e* 1994 ($M^+ - C_6H_{11}$, 100%, v weak), 957 ($M^+/2 - C_6H_{11}$, 88%, v weak). Anal. Calcd for $C_{84}H_{154}O_{24}Si_{14}Ga_2$ (found): C, 48.49 (48.44); H, 7.46 (7.24). Mp: 280−5 °C.

Fifteen well-centered reflections (10° ≤ 2θ ≤ 20°) obtained from a single crystal of **3** grown from hexanes gave the following unit cell parameters: monoclinic (C-centered), $a = 27.088(8)$ Å, $b = 15.961(6)$ Å, $c = 29.550(10)$ Å, $\beta = 107.56(3)°$; $V = 12177(7)$ Å^3. These values are in excellent agreement with those obtained for the Ti^{3+} and V^{3+} analogues whose structures were determined previously.

Gallium dimer **3** may also be synthesized directly from trisilanol **1a** and $GaCl_3$ or GaI_3 in toluene (115 °C, 12 h) or THF (65 °C, 4 h) containing Et_3N (≥3 equiv).

Synthesis of 5. Triphenylphosphine oxide (278 mg, 1.00 mmol) was added to a solution of **3** (208 mg, 0.010 mmol) in $CHCl_3$ (~2 mL) and heated to 65 °C. After 4 h, the solvent was removed in vacuo (~25 °C, 0.01 Torr) to afford a virtually quantitative yield of **5** as the only silsesquioxane-containing product (by NMR spectroscopy). Recrystallization was performed by allowing acetonitrile to slowly diffuse into a saturated C_6H_6 solution of **5** over several days. Yield: 1.19 g, 90%. For **5**, ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 7.77 (m, 6H), 7.52 (m, 3H), 7.46 (m, 6H); δ 1.70 (br m, 35H), 1.20 (br m, 35H), 0.71 (m, 4H), 0.60 (m, 3H). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 133.60 (d, $J_{CP} = 3.9$ Hz), 132.88 (d, $J_{CP} = 11.6$ Hz), 128.91 (d, $J_{CP} = 13.6$ Hz), 126.97 (d, $J_{CP} = 110.5$ Hz) for aromatic C; δ 27.91, 27.70, 27.65, 27.13, 27.08, 27.03, 26.91, 26.78 (CH_2); δ 24.39, 23.70, 23.45 (3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −64.26, −68.65, −70.20 (3:1:3). MS (70 eV, 200 °C; relative intensity): *m/e* 1318 (M^+; 1%), 1235 ($M^+ - C_6H_{11}$; 100%), 957 ($M^+ - C_6H_{11}$, $- OPPh_3$; 90%).

Synthesis of 6. $Ga(CH_2SiMe_3)_3$ (0.510 g, 1.54 mmol) was added to a suspension of trisilanol **1a** (0.500 g, 0.513 mmol) in C_6H_6 (~25 mL). After all of the solid material dissolved, H_2O (27 mg, 1.5 mmol) was added and the reaction mixture heated at 80 °C for 5 h. After standing at room temperature overnight, the microcrystalline solid which formed was collected by vacuum filtration, washed with additional C_6H_6, and dried in vacuo at 60 °C overnight. Astonishingly, the complex is so insoluble that NMR spectroscopic characterization was not possible. (A saturated $CDCl_3$ solution of **6** did not produce an interpretable ^{13}C NMR spectrum after 20 000 scans!) Anal. Calcd for **6** $C_{108}H_{226}O_{30}Ga_6Si_{20}$ (found): C, 43.46 (43.62); H, 7.63 (7.34). Mp: 240−5 °C (dec without melting).

Collection of X-ray Diffraction Data for the Halide "ate" Complex 2a. Crystals suitable for X-ray diffraction were grown from a toluene solution of **2a** by slow evaporation. Crystal data for **2a** [$C_{56}H_{96}ClGaN_2O_{12}Si_7 \cdot 3C_7H_8$ (fw 1567.5)] are as follows: triclinic $P\bar{1}$, $a = 15.059(4)$ Å, $b = 15.853(3)$ Å, $c = 19.033(4)$ Å, $\alpha = 81.51(2)°$, $\beta = 69.60(2)°$, $\gamma = 85.37(2)°$; $V = 3558(2)$ Å^3; $D_{calc} = 1.237$ g/cm^3 ($Z = 2$). A total of 8132 unique reflections with 4.0° < 2θ ≤ 42.0° were collected on a Syntex P2$_1$ diffractometer at −90 °C with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL-PLUS). Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for all Si, O, Cl, N, and nondisordered C) led to convergence with $R_F = 7.4\%$, $R_{wF} = 8.2\%$, and GOF = 1.57 for 862 variables refined against those 7364 data with $|F_o| > 2.\sigma|F_o|$. All other details regarding the crystal structure appear in the Supporting Information.

X-ray Data Collection and Refinement for 5. Crystals suitable for X-ray diffraction were grown by allowing acetonitrile to slowly diffuse into a saturated C_6H_6 solution of **5** (containing excess Ph_3PO, 5 equiv) over a period of several days. Crystal data for **5** [$C_{60}H_{92}O_{13}Si_7PGa$ (fw 1318.7)] are as follows: triclinic $P\bar{1}$, $a = 13.338(4)$ Å, $b = 14.101(4)$ Å, $c = 21.179(6)$ Å, $\alpha = 91.18(3)°$, $\beta = 108.10(2)°$, $\gamma = 115.18(2)°$; $V = 3372(2)$ Å^3; $D_{calc} = 1.299$ g/cm^3 ($Z = 2$). A total of 11 029 unique reflections with 4.0° ≤ 2θ ≤ 40.0° were collected on a Syntex P2$_1$ diffractometer at −90 °C with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL-PLUS). Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for Si, O, Ga, C, P) led to convergence with $R_F = 4.5\%$, $R_{wF} = 5.4\%$, and GOF = 1.33 for 739 variables refined against those 9575 data with $|F_o| > 3.0\sigma\,|F_o|$. All other details regarding the crystal structure appear in the Supporting Information.

X-ray data Collection and Refinement for 6. Crystals suitable for X-ray diffraction grew spontaneously from the reaction mixture. Crystal data for the $CHCl_3$ solvate of **6** [$C_{110}H_{222}O_{30}Si_{20}Ga_6Cl_6$ (fw 3217.7)] are as follows: monoclinic $P2_1/n$, $a = 20.800(6)$ Å, $b = 15.777(5)$ Å, $c = 24.505(8)$ Å, $\beta = 99.25(3)°$; $\gamma = 7937(4)$ Å^3; $D_{calc} = 1.346$ g/cm^3 ($Z = 2$). A total of 9277 unique reflections with 4.0° ≤ 2θ ≤ 42.0° were collected on a Syntex P2$_1$ diffractometer at −115 °C with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL-PLUS). Full-matrix

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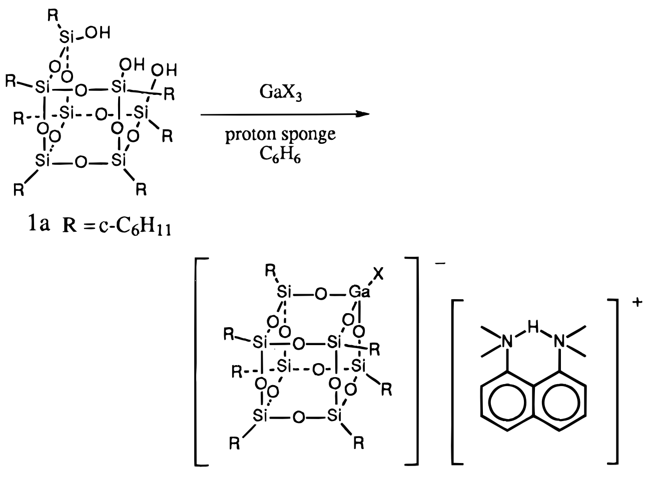
least-squares refinement of positional and thermal parameters (anisotropic for Ga, Si, O, Cl) led to convergence with $R_F = 11.2\%$, $R_{wF} = 12.4\%$, and GOF = 3.15 for 500 variables refined against those 4288 data with $|F_o| > 5.0\sigma|F_o|$. All other details regarding the crystal structure appear in the Supporting Information.

Results and Discussion

Reactions of 1a with Gallium Trihalides. The reaction of trisilanol **1a** with $GaCl_3$ or GaI_3 in C_6H_6 containing a stoichiometric amount of "Proton Sponge" (1,8-bis(dimethylamino)-naphthalene) produces a quantitative yield of the corresponding pseudo-C_3-symmetric halide "ate" complexes **3**, which were easily identified by NMR (^1H, ^{13}C, ^{29}Si) spectroscopy. ^1H NMR spectra indicate that the products contained elements of Proton Sponge and trisilanol **1a** in a 1:1 ratio, and both the ^{29}Si NMR spectrum and the methine (CH) region of the ^{13}C NMR spectrum exhibited characteristic sets of resonances with relative integrated intensities of 3:3:1.



1a R = c-C_6H_{11}

2a R = c-C_6H_{11} X = Cl
b X = I

Consistent with their ionic nature, **2a** and **2b** are insoluble in aliphatic solvents (e.g., alkanes). They are, however, soluble in many moderately polar organic solvents (e.g., $CHCl_3$), and well-formed X-ray quality crystals can be obtained by allowing toluene solutions of **2a** and **2b** to evaporate slowly at room temperature. The ORTEP plot from a single-crystal X-ray diffraction study of **2a** is shown in Figure 1. The complex crystallizes from toluene as discrete $[(c\text{-}C_6H_{11})_7Si_7O_{12}GaCl]^-$ and $[C_{14}H_{18}N_2{\cdot}H]^+$ ions in the triclinic space group $P\bar{1}$. The nitrogen atoms of the cation are directed toward the chlorine atom of the anion, suggesting that there is some dipolar interaction between the localized charges on the two species, but this interaction must be quite weak; the N1−Cl1 (4.43 Å) and N2−Cl1 (4.65 Å) distances are very long. Placement of a proton (not located during refinement of the structure) in an idealized tetrahedral position between the two nitrogen atoms of the cation gives d(H−Cl) = ∼4.15 Å, which is also insufficient for strong interaction.

The Ga−O bonds in **2a** are well within their expected range and somewhat longer than the Si−O bonds, but the polyhedron defined by the nonbonded Si and Ga atoms is nearly cubic: interatomic distances between silicon atoms in Si−O−Si linkages average 3.12 Å, while Si−Ga distances for the Si−O−Ga moieties average 3.19 Å. The Si−O−Ga bond angles are therefore significantly more acute than their Si−O−Si counterparts. Given the soft bending potentials for most main-group Si−O−R heteroethers,[29] we are hesitant to provide a rationale for this observation, but it is interesting to note that most fully condensed heterosilsesquioxanes containing $[Si_7MO_{12}]$ units appear to prefer solid-state structures which place Si and M atoms at the vertices of a nearly regular cube.

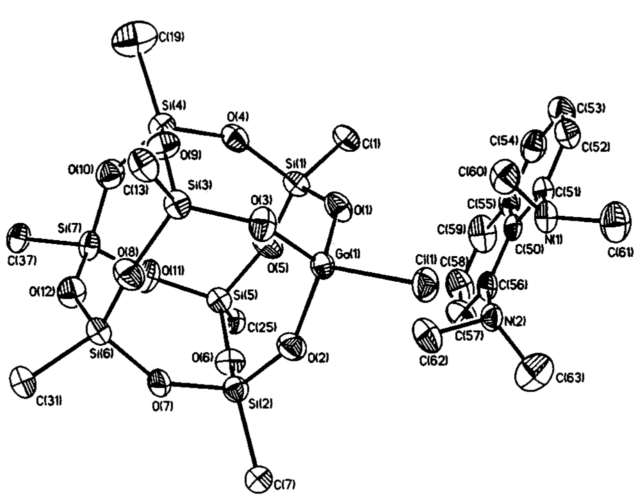
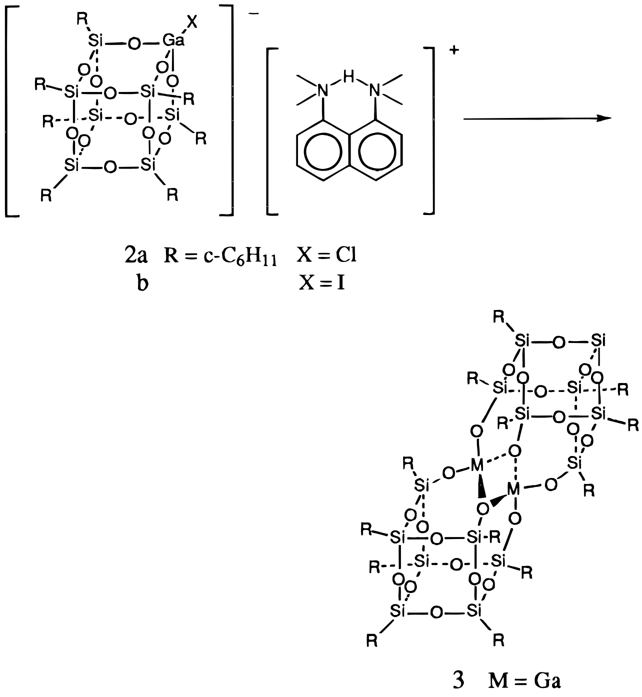


Figure 1. ORTEP drawing of **2a** with thermal ellipsoids plotted at the 50% probability level. For clarity, only the ipso carbon atoms (SiCH) of the cyclohexyl groups are shown. Selected interatomic distances (Å) and interbond angles (deg) are as follows: Ga−C1, 2.189(2); Ga−O1, 1.819(6); Ga−O2, 1.790(5); Ga−O3, 1.809(4); Si1−O1, 1.602(5); Si2−O2, 1.578(5); Si3−O3, 1.599(4); other Si−O, 1.605−1.634; N1−C1, 4.43; N2−C1, 4.65; C1−Ga−O1, 107.1(2); C1−Ga−O2, 107.1(1); C1−Ga−O3, 107.7(1); O1−Ga−O2, 113.0(2); O1−Ga−O3, 109.1(2); O2−Ga−O3, 112.5(2); Si1−O1−Ga, 134.3(3); Si2−O2−Ga, 150.3(3); Si3−O3−Ga, 136.0(3); Si−O−Si, 143−157; O−Si−O, 107−111.



2a R = c-C_6H_{11} X = Cl
b X = I

3 M = Ga

Upon thermolysis (THF, reflux, 4 h) both **2a** and **2b** liberate 1 equiv of ammonium salt $[C_{14}H_{18}N_2{\cdot}H]^+X^-$ to produce virtually quantitative yields of a new gallium-containing silsesquioxane. The ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum for this new compound exhibited five resonances with relative integrated intensities of 2:2:1:1:1. Our suspicions that this product was siloxy-bridged dimer **3**

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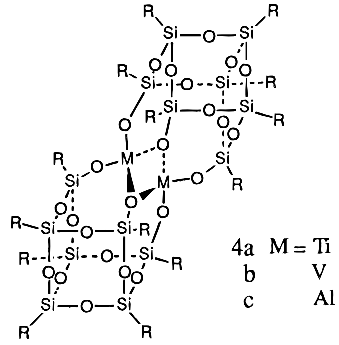
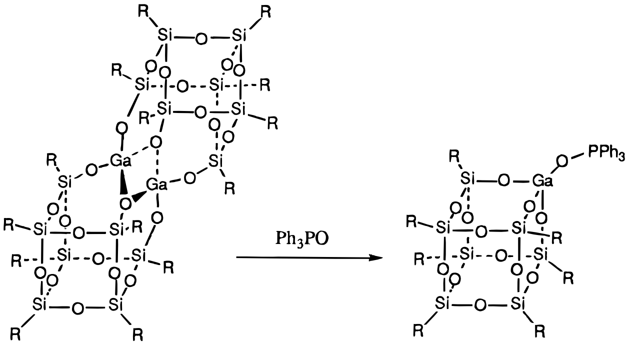
were confirmed by X-ray diffraction: crystals of **3** grown from hexane were isomorphous with the known Ti^{3+} and V^{3+} dimers, **4a** and **4b**.[20,21]



The edge-sharing bitetrahedral M_2O_2 core observed in **3** is a common structural motif in the chemistry of ligand-deficient $M(OR)_3$ complexes, including gallium alkoxides and siloxides.[30] It is also observed for a wide range of R_2GaOR^1 complexes.[31−33] The conformational flexibility of **1a** can accommodate a wide range of complex siloxy-bridged structures, but the dimeric structure adopted by **3** appears to be particularly stable. It has been observed for a number of trivalent metal ions.

Reaction of 3 with Ph_3PO: Synthesis and Crystal Structure of $[(c\text{-}C_6H_{11})_7Si_7O_{12}Ga(OPPh_3)]$ (5). Like aluminum dimer **4c**,[19] gallium dimer **3** can be dissociated by Ph_3PO to give a monomeric phosphine oxide complex **5**. The reaction is much slower, however, and prolonged reaction times and/or heating are required to drive the reaction to completion.



3 **5**

Complex **5** was unambiguously identified on the basis of analytical and NMR spectral data, but a single-crystal X-ray diffraction study was undertaken to determine metrical data for bond distances and angles involving gallium; an ORTEP plot of **5** is shown in Figure 2.

Large colorless "cubes" of **5** crystallize from benzene/acetonitrile in the space group $P\bar{1}$. As was the case for chloride complex **2a** and the analogous Ph_3PO adduct of **4c**, the polyhedron defined by the Ga and Si atoms is again nearly cubic [$d(Si{-}Si)_{av} = 3.12$ Å; $d(Ga{-}Si)_{av} = 3.15$ Å], and the Si−O−Ga bond angles (136.5° av) are significantly more acute than their Si−O−Si counterparts (148.6° av) to compensate for the somewhat larger ionic radius of Ga^{3+} (0.62 Å)[34] compared to Si^{4+} (0.41 Å). Bond angles for Si−O−Si range from 138° 172°.

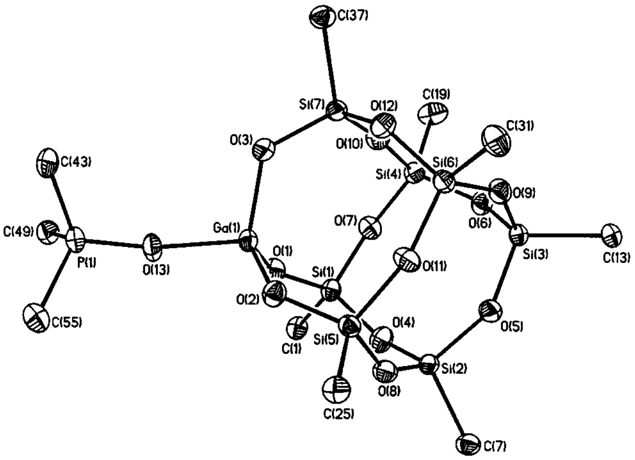


Figure 2. ORTEP drawing of **5** with thermal ellipsoids plotted at the 50% probability level. For clarity, only the ipso carbon atoms of the cyclohexyl and phenyl groups are shown. Selected interatomic distances (Å) and interbond angles (deg) are as follows: Ga−O1, 1.782(3); Ga−O2, 1.800(2); Ga−O3, 1.803(2); Ga−O13, 1.866(2); P−O13, 1.496(2); P−C, 1.789−1.796(4); Si1−O1, 1.600(3); Si5−O2, 1.601(2); Si7−O3, 1.609(2); other Si−O, 1.615−1.642(2); P−O13−Ga, 168.1(2); O1−Ga−O2, 115.1(1); O1−Ga−O3, 112.8(1); O1−Ga−O13, 104.6(1); O2−Ga−O3, 115.3(1); O2−Ga−O13, 103.9(1); O3−Ga−O13, 103.5(1); O13−P−C, 108.6−111.4(2); Ga−O1−Si1, 145.9(1); Ga−O2−Si5, 135.9(2); Ga−O3−Si7, 127.8(1); Si−O−Si, 138−172; O−Si−O, 107−111.

The observed Ga−O−P bond angle in **5** (168.1°), like the Al−O−P linkage in the analogous Al complex (160.4°), is quite obtuse. This would be consistent with strong π-bonding between oxygen (O13) and Ga and/or P, but the Ga1−O13 bond distance (1.866(2) Å) is only slightly longer than the Ga−O(P) distance (1.818(10) Å) observed in $Ph_3POGaCl_3$,[35] which possesses a linear Ga−O−P linkage. The Ga−O(P) distance is actually longer than the Ga−O(Si) distances in **2a** and **5**, which have more acute Ga−O−Si angles. There is clearly no dependence between the Ga−O bond lengths and the Ga−O−P bond angles, consistent with little or no $p\pi{-}d\pi$ bonding between O and Ga.[35,36]

Reactions of Trisilanol 1 with $Ga(CH_2SiMe_3)_3$. The reaction of equimolar mixtures of $Ga(CH_2SiMe_3)_3$[28] and trisilanol **1** in anhydrous refluxing benzene results in a complicated mixture of metallasilsesquioxane products. On one occasion, however, a $CDCl_3$ solution of a crude product mixture left standing in an NMR tube on the bench top for several days produced large, well-formed crystals. These crystals were totally insoluble in common organic solvents, so a single-crystal X-ray diffraction study was performed in order to identify this new compound. An ORTEP drawing from the results of this study is shown in Figure 3.

The $CDCl_3$ solvate of complex **6** crystallizes in the space group $P2_1/n$. The asymmetric unit consists of one half of the dimer shown; the other half of the molecule is generated by the crystallographically imposed center of inversion. The molecule is formally derived from the coordination of two silsesquioxane frameworks to a cyclic $[Ga(CH_2SiMe_3)(\mu\text{-}OH)]_6$ unit. Serious disorder problems with several cyclohexyl groups, the Me_3SiCH_2 groups, and clathrated solvent do not permit a

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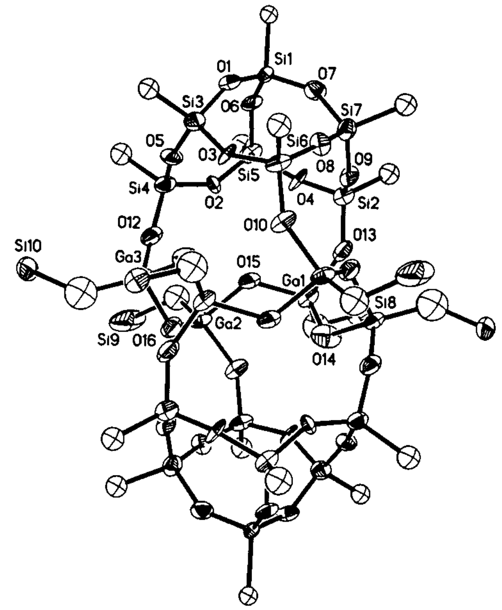
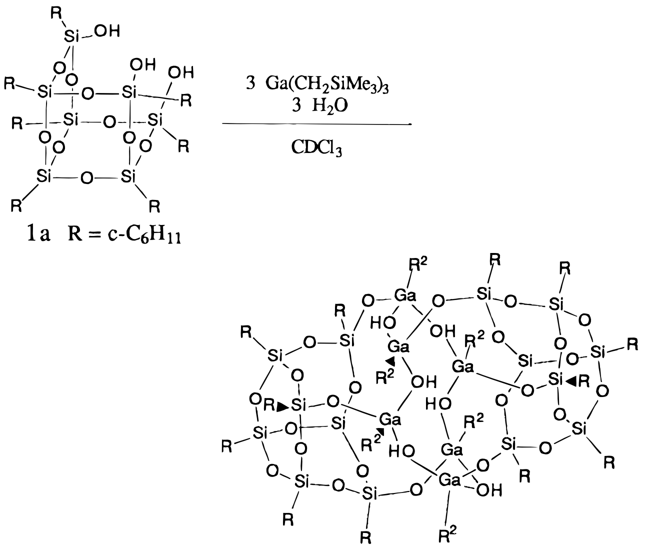


Figure 3. ORTEP figure of **6** with thermal ellipsoids plotted at the 50% probability level. For clarity only the methine carbons of the cyclohexyl groups are shown.

serious discussion of the bond distances and angles (current R_F = ~12%). Nevertheless, the core connectivity and structure of **6** are convincingly established from this experiment.



1a R = c-C_6H_{11}

6 R^2 = CH_2SiMe_3

The molecular formula of **6** suggests that **6** is derived from the reaction of **1a** with three molecules of $Ga(CH_2SiMe_3)_3$ and three molecules of water. Indeed, when the reaction between $Ga(CH_2SiMe_3)_3$, trisilanol **1a**, and H_2O is performed in refluxing C_6H_6 or $CDCl_3$ with this stoichiometry, **6** crystallizes from solution in ~90% yield. The crystals obtained from the C_6H_6 reaction were analyzed by X-ray diffraction and shown to be isomorphous with those obtained from $CHCl_3$. This impressive yield is apparently the result of the nearly total insolubility of this compound in common noncoordinating organic solvents.

Concluding Remarks

A common theme in the chemistry of metallasilsesquioxanes is the ability of silsesquioxane frameworks to accommodate a wide range of coordination geometries. This allows silsesquioxanes to chelate a wide variety of elements and adopt most common coordination geometries. The flexibility of silsesquioxanes also allows otherwise reactive metal complexes to find more stable alternative structures. In the case of trivalent transition-metal and main-group elements, siloxy-bridged dimeric structures with four-coordinate metal centers are clearly preferred over monomeric metallasilsesquioxanes with bare, three-coordinate metal atoms. These and structurally related dimeric structures appear to be quite stable when the metal ion is a transition-metal or lanthanide element, and they often remain intact when exposed to potential Lewis bases. In cases where expansion of the coordination sphere is not favorable, the coordination of Lewis bases (e.g., Ph_3PO) usually produces monomeric, four-coordinate metallasilsesquioxanes.

The work described here demonstrates that the chemistry of gallium-containing silsesquioxanes is qualitatively similar to the chemistry of aluminosilsesquioxanes. There is a strong preference for the formation of four-coordinate metal centers, but the stronger Lewis acidity of Ga^{3+} versus Al^{3+}, as well as the greater covalency of Ga−C bonds versus Al−C bonds, greatly slows the interconversion of Ga-containing silsesquioxanes.

Although the reaction chemistry of gallium is well established,[23,24,37−39] the structural chemistry of four-coordinate gallium alkoxides is relatively undeveloped, especially when complexes containing Ga−C bonds are excluded.[40] The work described here provides the first crystallographically characterized examples of four-coordinate gallium containing GaO_3-(halide) and $[Ga(\mu\text{-OH})(O)C]_6$ moieties, as well as one of the few crystallographically characterized examples of four-coordinate GaO_4 that are not part of an extended Ga/silicate[41] or Ga/phosphate[42−44] framework.

Acknowledgment. These studies were supported by the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supporting Information Available: X-ray crystal data for **2a**, **5**, and **6** including text detailing the experimental procedures and tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (39 pages). Ordering information is given on any current masthead page.

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