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Boron, Aluminum, and Gallium Silsesquioxane Compounds, Homogeneous Models for Group 13 Element-Containing Silicates and Zeolites

Gijsbert Gerritsen,[‡] Robbert Duchateau,*,[†] Rutger A. van Santen,[‡] and
Glenn P. A. Yap[§]

Department of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, Department of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and Chemistry Department, University of Ottawa, K1N 6N5, Ottawa, Ontario, Canada

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The incompletely condensed hydroxysilsesquioxanes $R_7Si_7O_9(OH)_3$ and $R_7Si_7O_9(OH)_2$-$OSiMePh_2$ (R = c-C_5H_9, c-C_6H_{11}) have been used to form Lewis and Brønsted acidic boron and gallium silsesquioxane compounds. Treatment of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with BI_3 in the presence of an amine yielded the dimeric $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]B\}_2$ (**1**). Compound **1** was also obtained when $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ was reacted with $LiBH_4$, eliminating LiH. On the other hand, treatment of $LiBH_4$ with 2 equiv of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ gave the solvent-free lithium borate salt $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{Li\}^+$ (**2**). Reaction of $GaCl_3$ with $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ in the presence of NEt_3 afforded the thermally robust amine adduct $[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga{\cdot}NEt_3$ (**3**). A similar reaction of $GaCl_3$ with 2 equiv of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2$-$OSiMePh_2$ gave the ammonium gallate $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga\}^-\{Et_3NH\}^+$ (**4**). Attempts to obtain the corresponding Brønsted acid of **4**, as could be obtained for aluminum, invariably failed. Nevertheless, ammonium salt **4** reacts as a masked Brønsted acid with the basic $GaMe_3$ to yield the dimethyl gallium gallate $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga(GaMe_2)$ (**5**). The equimolar reaction between $GaMe_3$ and $R_7Si_7O_9(OH)_3$ selectively yielded $\{[R_7Si_7O_{11}$-$(OH)]GaMe\}_2$ (R = c-C_5H_9 (**6a**), c-C_6H_{11} (**6b**)). The fact that in **6a/b** gallium methyl and silanol functionalities coexist clearly demonstrates the lower reactivity of gallium-alkyls compared to aluminum-alkyl groups. The equimolar reaction of $GaMe_3$ with the monosilylated $(c\text{-}C_5H_9)_7$-$Si_7O_9(OH)_2OSiMePh_2$ yielded $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]GaMe\}_2$ (**7**) as a 5:1:40 mixture of three conformational isomers, similar to what was observed for the corresponding methyl aluminum silsesquioxanes. The kinetic and thermodynamic stability of **7** and its chemical isomer **5** has been investigated. Isomerization experiments show that both **5** and the main conformer of **7** isomerize to a thermodynamic stable mixture of isomers of **7** with a 2:1:2 ratio. The dimethyl gallium silsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(GaMe_2)_4\}$ (**8**) was formed quantitatively upon treating $\{[(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ with 2 equiv of $GaMe_3$. Likewise, reacting $\{[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with 3 equiv of $GaMe_3$ yielded the dimerc $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2(GaMe_2)_6\}$ (**9**). The high tendency of gallium to obtain a tetrahedral coordination results in a crowded structure **9** with remarkable low fluxionality. Compounds **2**, **4**, **5**, **6b**, **8**, and **9** have been structurally characterized.

Introduction

Group 13 element-containing zeolites and silicates play an important role in heterogeneous catalysis, as either acidic catalysts or catalyst supports. A typical example of a process catalyzed by gallium-containing zeolites with Brønsted acid sites forms activation and aromatization of light gas molecules.[1] The heterogeneous nature of these systems clearly hampers detailed studies on reactions taking place during the catalytic processes. Recently, an increased number of complexes based on siloxanes[2] and incompletely condensed silsesquioxanes[3,4] have been reported that proved to be very suitable to mimic oxidic catalyst supports[3] and silica-supported catalyst systems.[4] It was shown that the catalytic activity of some of the homogeneous silsesquioxane-based systems resembles or even exceeds that of the heterogeneous systems they serve as a model for. As part of an ongoing study on the applicability of silsesquioxane-based systems as models for aluminosilicates and zeolitic materials, we recently reported the

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* Corresponding author. Tel: +31 (0)40 2474918. Fax: +31 (0)40 2463966. E-mail: R.Duchateau@tue.nl.

[‡] Department of Polymer Chemistry, Eindhoven University of Technology.

[†] Department of Inorganic Chemistry, Eindhoven University of Technology.

[§] University of Ottawa.

[1] For example see: (a) Frash, M. V.; Kazansky, V. B.; Rigby, A. M.; van Santen, R. A. *J. Phys. Chem.* **1998**, *102*, 2232. (b) Biscardi, J. A.; Meitzner, G. D.; Iglesia, E. *J. Catal.* **1998**, *179*, 192. (c) Frash, M. V.; van Santen, R. A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1085. (d) Frash, M. V.; van Santen, R. A. *J. Phys. Chem. A* **2000**, *104*, 2468.

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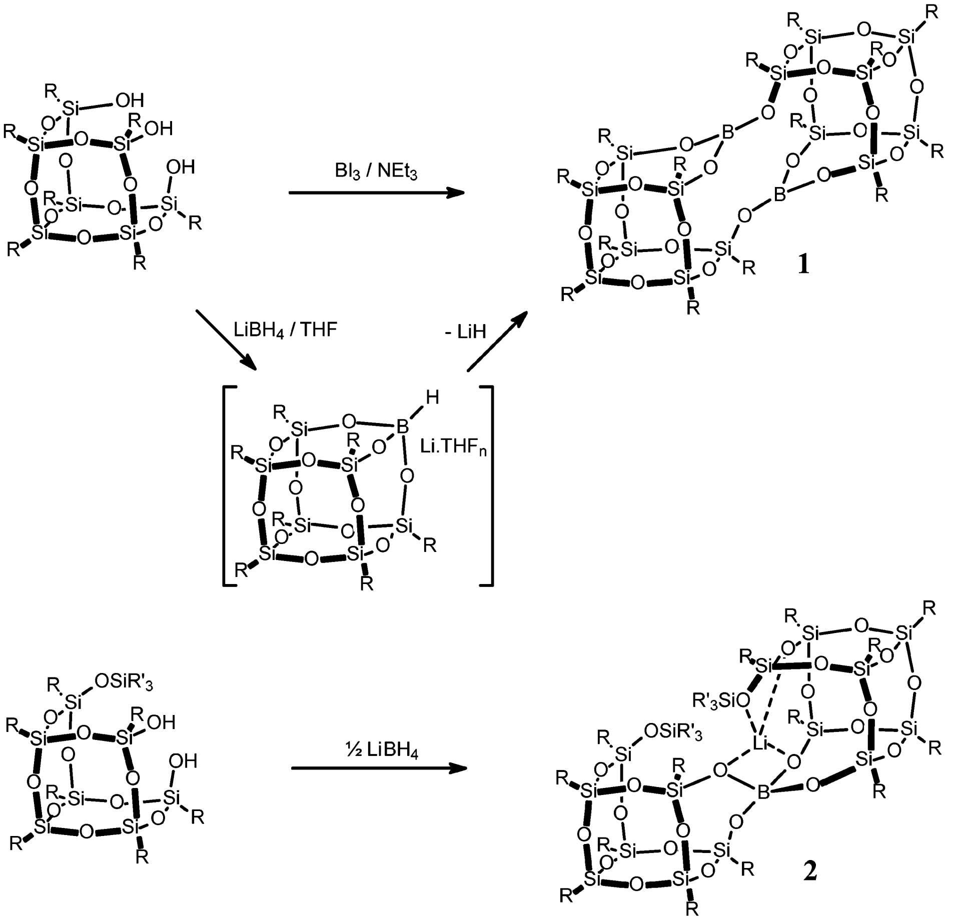
Scheme 1. Synthesis of Boron-Containing Silsesquioxanes



synthesis, stability, and reactivity of both Brønsted and Lewis acidic aluminosilsesquioxane species.[5] Two general routes to introduce aluminum to silsesquioxanes proved to be applicable: salt metathesis and protonolysis. Depending on the synthetic method applied, various Brønsted and Lewis acidic, mono-, di-, and polymeric structures have been obtained. For Lewis acidic aluminum silsesquioxanes simply changing the silyl hydrocarbon substituents from cyclohexyl to cyclopentyl proved to have a pronounced influence on the final structure (dimeric vs polymeric) of the product.[5a]

This contribution deals with the further development of silsesquioxane compounds containing group 13 elements that serve as model systems facilitating detailed mechanistic analysis of reactions taking place in the corresponding group 13 element-containing zeolites and silicates. Salt metathesis and protonolysis reactions between boron and gallium precursors and both cyclohexyl- and cyclopentyl-substituted silsesquioxanes will be discussed and compared with the chemistry of aluminum.

Results and Discussion

Boron-containing silsesquioxane species are rare. The only well-defined compound known to date is $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]B\}_2$, reported by Feher.[6]Reacting the cyclopentyl-substituted silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with BI_3 in the presence of an amine yielded the similar boron silsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]B\}_2$ (**1**, Scheme 1). Unlike the striking difference between the dimeric cyclohexyl-substituted $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Al\}_2$[3b] and the polymeric cyclopentyl-substituted aluminosilsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]Al\}_n$,[5a] both cyclohexyl-

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and cyclopentyl-substituted boron silsesquioxanes are dimeric and virtually identical. This might be due to the lower Lewis acidity of boron compared to aluminum, which leads to a lower tendency to reach a higher coordination number. A strong difference between boranes and allanes or gallanes is that alkylboranes are not readily protonolyzed. For example, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ does not react with BR_3 (R = H, Me), whereas $AlMe_3$ reacts violently with $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ to yield $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]Al\}_n$. Lithium tetrahydroborate is much more basic than BH_3 and therefore inclined to undergo protonolysis. Indeed, in THF $LiBH_4$ reacts with $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ selectively affording compound **1**. Unlike aluminum and gallium silsesquioxanes, for which stable anionic structures have been isolated (vide infra), the anionic silsesquioxane hydroborate $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]BH\}^-\{Li\cdot THF_n\}^+$ readily loses LiH under formation of **1** (Scheme 1). In contrast, when the disilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ was reacted with $LiBH_4$, the stable anionic borate $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{Li\}^+$ (**2**) was selectively formed (Scheme 1). In this compound the lithium cation is stabilized solely by coordination of silyl ether and Si−O−Ga oxygen functionalities of the silsesquioxane framework, whereas the corresponding lithium aluminate, formed by treating $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMe_3$ with $LiAlH_4$, was isolated as either a bis(THF) or a TMEDA adduct, $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Li\cdot L_2\}^+$ (L = THF, $^1/_2$ TMEDA).[5a] Attempts to protolyze **2** to yield the corresponding Brønsted acid $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{H\}^+$ invariably resulted in decomposition of the product and formation of the free ligand, $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$. Reaction of the disilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ with BI_3 under basic conditions did not result in well-defined species such as the Brønsted acid or its ammonium salt $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{X\}^+$ (X = H, HNR_3) either.

The X-ray crystal structure of **2** is shown in Figure 1. Four siloxy units tetrahedrally surround the boron atom. Interestingly, the lithium cation is tightly incorporated in the silsesquioxane framework structure without coordination of additional solvent molecules, which results in a distorted tetrahedrally coordinated lithium. This peculiar structure nicely shows how cations can be stabilized in a zeolite. As a consequence of the negative charge on boron, the average B−O distance (1.480(5) Å) of this anionic borate is 0.13 Å longer than the B−O bond distances in the neutral trigonal-planar boron silsesquioxane $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]B\}_2$ ($B-O_{av}$ = 1.351(23) Å)[6] and for example the boron siloxanes $[PhBO(Ph_2SiO)_2]$ (B−O, 1.3696(20) Å), $[PhBO(Ph_2SiO)_3]$ (B−O, 1.359(6) Å), and $[(t\text{-}Bu_2SiO_2)BPh]_2$ (B−O = 1.350(5) Å).[7] The coordination of O12 and O13 to lithium results in further elongation of the boron−oxygen bonds B−O12 (1.517(5) Å) and B−O13 (1.516(5) Å) compared to the noncoordinating boron−siloxy bonds (B−O10, 1.435(5) Å; B−O14, 1.453(5) Å). The presence of both an electron-rich and an electron-poor element in the structure also effects the Si−O bond distances. For example, the electron-rich Si−O bonds (av 1.610(3) Å) of the Si−O−B units are slightly shorter compared to the average Si−O distances of the silsesquioxane framework (1.624(3) Å). Likewise, the lower electron density in the silyl ether bonds coordinated to lithium is reflected in longer Si15−O24 (1.638(3) Å) and Si16−O24 (1.663(4) Å) bonds compared to the noncoordinated silyl ether functionalities (Si1−O1, 1.621(3) Å; Si2−O1, 1.618(4) Å). Other silyl oxygen distances and Si−O−Si angles are normal within the wide range known for silsesquioxane complexes. The NMR spectra (^{1}H, ^{13}C, ^{29}Si) of **2** show one single resonance for the two $SiMePh_2$ substituents and seven distinct resonances for the silsesquioxane methine carbon and framework silicon atoms, indicating fast fluxional behavior in solution at room temperature.

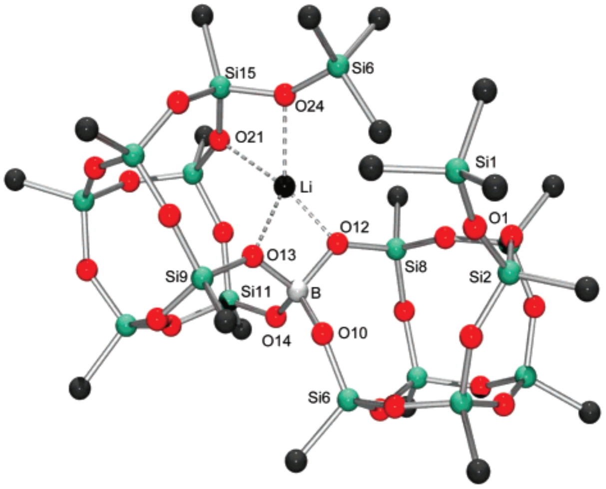

Figure 1. Molecular structure of $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2BLi$ (**2**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): B−O10, 1.435(5); B−O14, 1.453(5); B−O12, 1.517(5); B−O13, 1.516(5); Li−O12, 1.876(7); Li−O13, 1.925(8); Li−O21, 2.153(8); Li−O24, 2.177(7); Si6−O10, 1.605(3); Si8−O12, 1.614(3); Si9−O13, 1.623(3); Si11−O14, 1.598(3); Si1−O1, 1.621(3); Si16−O24, 1.663(3); Si2−O1, 1.618(4); Si15−O24, 1.638(3); Si15−O21, 1.639(3); $Si-O_{av}$, 1.624(3). Selected bond angles (deg): O10−B−O12, 111.5(3); O10−B−O13, 110.1(3); O10−B−O14, 112.9(3); O12−B−O13, 101.5(3); O12−B−O14, 109.6(3); O13−B−O14, 110.8(3); B−O12−Li, 90.5(3); B−O13−Li, 88.7(3); O12−LiO13, 76.3(3); O12−Li−O21, 143.3(5); O13−Li−O21, 107.0(3); O12−Li−O24, 135.9(4); O13−Li−O24, 130.6(4); O21−Li−O24, 70.1(2); Si1−O1−Si2, 164.8(3); Si15−O24−Si16, 146.15(18); $Si-O-Si_{av}$, 148.8 (2).

Like boron silsesquioxanes, gallium silsesquioxanes are rare, and only a few well-defined structures, formed either by salt elimination or protonolysis, have been reported.[8] $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ was reported to react with $GaCl_3$ in the presence of “Proton Sponge” to form the ionic $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]GaX\}^-\{C_{14}H_{19}N_2\}^+$ (X = Cl, I), which, upon refluxing in THF, yielded the dimeric $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\}_2$ (Scheme 2). This dimeric structure could readily be split by $Ph_3P{=}O$ to form the neutral Lewis base adduct $[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\cdot O{=}PPh_3$. Using similar conditions Feher reported for the synthesis of $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]GaCl\}^-\{C_{14}H_{19}N_2\}^+$ and $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\}_2$, we isolated a triethylamine-stabilized monomeric gallium silsesquioxane, $[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\cdot NEt_3$ (**3**, Scheme 2), instead. The 3:3:1 ratio

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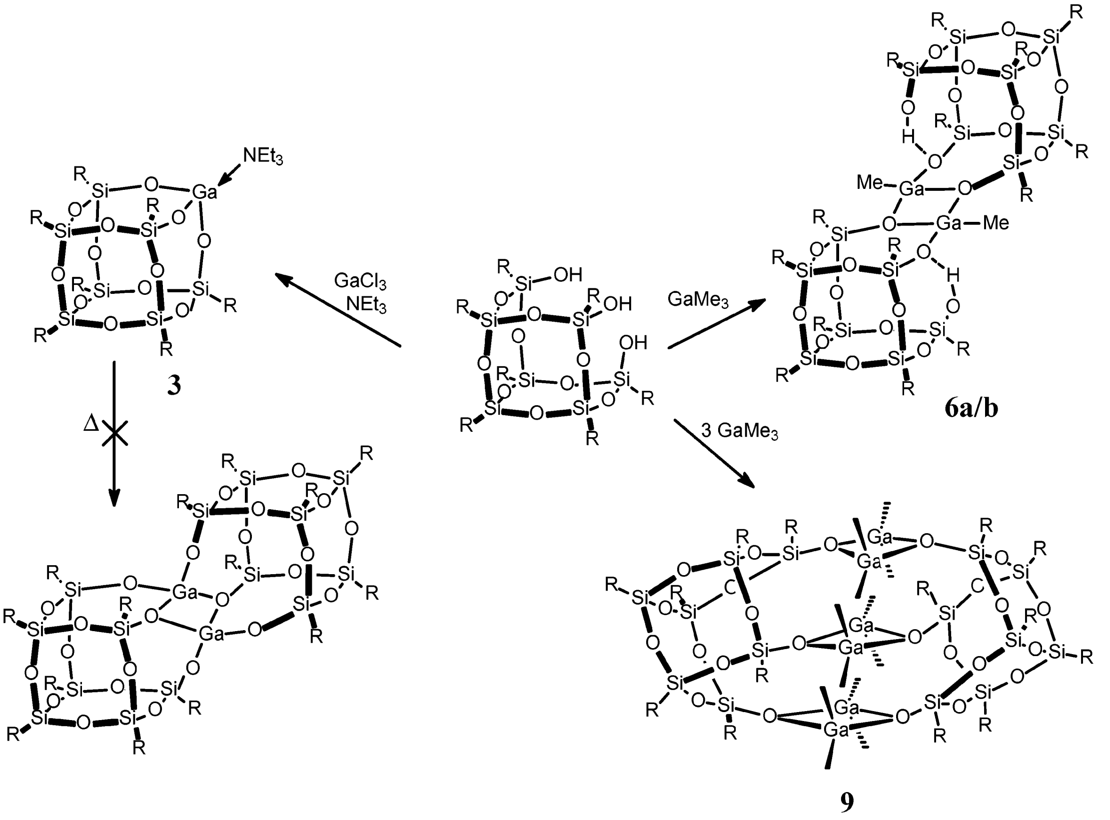
Scheme 2. Synthesis of Gallium Silsesquioxanes, Based on $R_7Si_7O_9(OH)_3$ (R = c-C_5H_9, c-C_6H_{11})



of the silsesquioxane methine carbon and silicon atoms, typical for a C_3-symmetric silsesquioxane structure, supported the monomeric nature of **3**, and the ^{13}C NMR spectrum of the crude reaction mixture showed that **3** was the major (~ 80%) silsesquioxane-containing product. Interestingly, the Lewis acidic gallium site prefers to coordinate the sterically hindered triethylamine rather than THF, which based on frontier- and back-strain is a better coordinating Lewis base.[9] The bulky triethylamine binds surprisingly strongly to the gallium, as attempts to form $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\}_2$ by heating **3** in toluene failed.

Salt metathesis between the monosilylated disilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ and half an equivalent of $GaCl_3$ in the presence of triethylamine yielded the ammonium gallate $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga\}^-\{Et_3NH\}^+$ (**4**, Scheme 3), similar to what was obtained when the disilanol was reacted with $AlCl_3$ in the presence of triethylamine.[5,10] The seven equi-intense resonances in the ^{13}C (methine-C) and ^{29}Si (silsesquioxane framework-Si) NMR spectra indicate that **4** is symmetric at room temperature in solution.

As can be seen from its molecular structure (Figure 2), **4** forms a contact ion pair in the solid state in which the ammonium fragment is hydrogen bonded to one of the Ga–O–Si oxygens. The same feature was also observed for the cyclopentyl-substituted $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiR'_3)]_2Al\}^-\{Et_3NH\}^+$ (SiR'_3 = $SiMe_3$, $SiMePh_2$),[5] while the sterically more crowded cyclohexyl-substituted analogue $\{[(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)]_2Al\}^-\{Et_3NH\}^+$ was isolated as a separated ion pair.[10] The coordination of the ammonium ion is accompanied by elongation of the Ga–O14 (1.841(4) Å) bond compared to the other three Ga–O (average: 1.807(4) Å) bonds. The average length of the four Ga–O bonds (Ga–O_{av} 1.816(5) Å) in the ammonium salt **4** is comparable

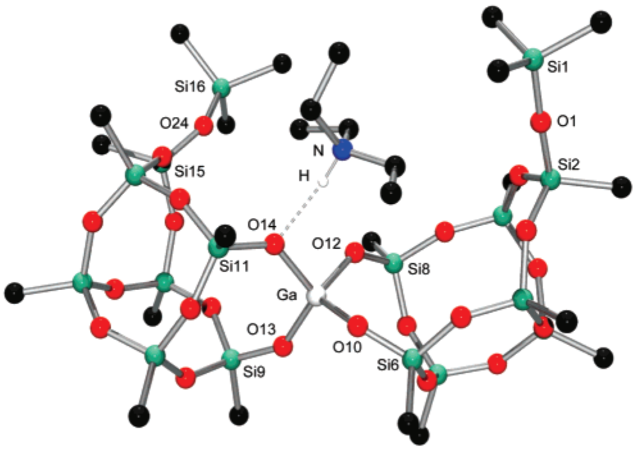


Figure 2. Molecular structure of $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga\}^+\{Et_3NH\}^-$ (**4**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Ga–O10, 1.802(4); Ga–O12, 1.830(4); Ga–O13, 1.790(4); Ga–O14, 1.841(4); Si6–O10, 1.588(4); Si8–O12, 1.584(4); Si9–O13, 1.590(4); Si11–O14, 1.604(4); Si–O_{av}, 1.618(4); N···O14, 2.862(6). Selected bond angles (deg): Ga–O10–Si6, 137.4(2); Ga–O12–Si8, 134.9(3); Ga–O13–Si9, 143.7(3); Ga–O14–Si11, 134.0(2); O10–Ga–O12, 109.15(17); O10–Ga–O13, 111.84(19); O10–Ga–O14, 106,26(17); O12–Ga–O13, 112.22(18); O12–Ga–O14, 101.55(17); O13–Ga–O14, 115.15(17); Si–O1–Si2, 175.9(3); Si15–O24–Si16, 149.0(3); Si–O–Si_{av}, 148.8(3).

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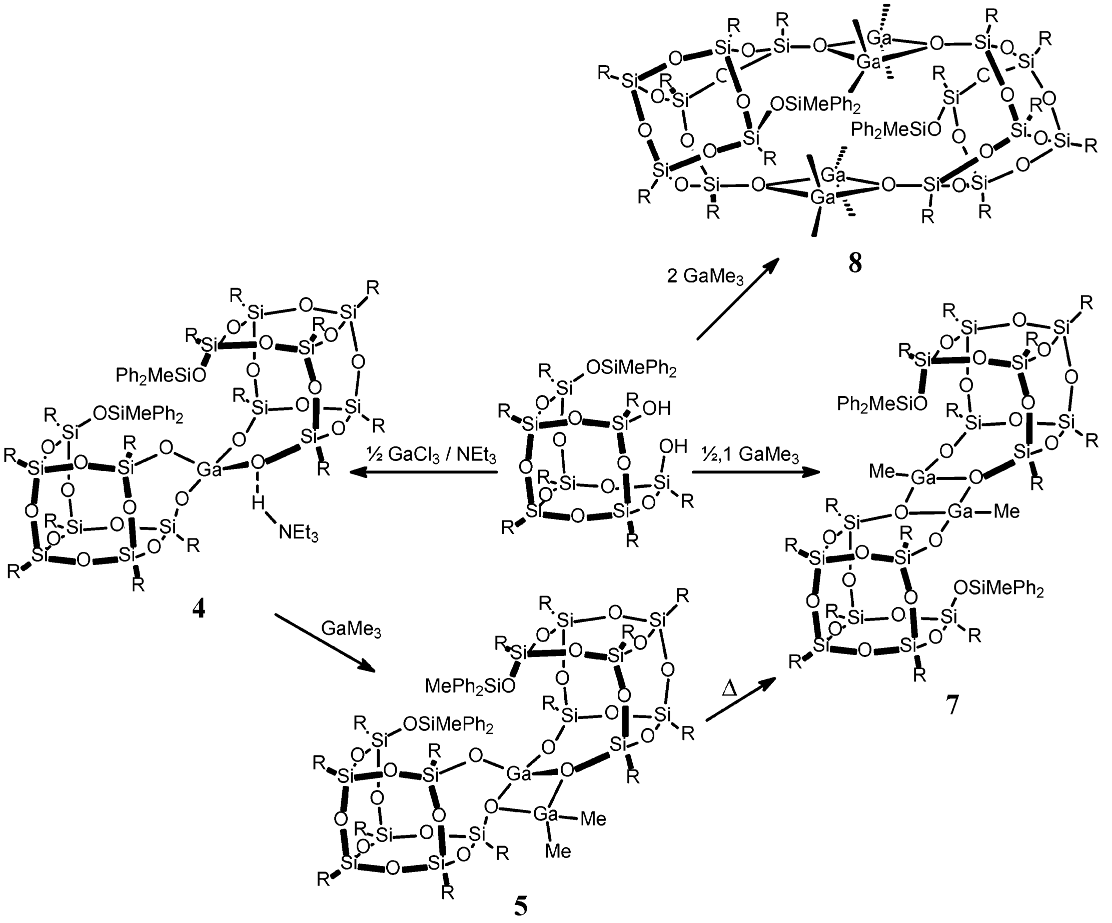
Scheme 3. Synthesis of Gallium Silsesquioxanes, Based on $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$



to the Ga–O bond distances in the chloro-gallate $\{[(c\text{-}C_6H_{11})_7Si_7O_{12}]GaCl\}^-\{C_{14}H_{19}N_2\}^+$ ($Ga{-}O_{av} = 1.806(5)$ Å) and are slightly elongated compared to the average $Ga{-}O_{av}$ distances in the neutral $[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\cdot O{=}PPh_3$ ($Ga{-}O_{av} = 1.795(3)$ Å).[8] Although the Si–O bond distances and Si–O–Si bond angles span a wide range, they are not exceptional for (metalla)silsesquioxane compounds.

Attempts to prepare the corresponding Brønsted acid of **4** by controlled protonolysis failed. Nevertheless, compound **4** is a masked form of the Brønsted acid and reacts with various Brønsted bases. For example when treated with another equivalent of $GaMe_3$, **4** is readily deprotonated to afford free triethylamine and the dimethyl gallium gallate $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga(GaMe_2)$ (**5**, Scheme 3), the molecular structure of which is shown in Figure 3. Compound **5** strongly resembles its aluminum analogue $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Al(AlMe_2)$ reported earlier.[11] Taking the difference in ionic radii of Al^{3+} and Ga^{3+} into account ($\Delta = 0.08$ Å),[9] most of the bond distances in **5** are very similar to those in the aluminum analogue. Only the Ga1–C1 is shorter and the Ga1–O1 is longer than in its aluminum counterpart, emphasizing the lower oxophilicity of gallium compared to aluminum. The various bond angles in the aluminum and gallium species differ only slightly.

Protonolysis of the trialkyl gallium $Ga(CH_2SiMe_3)_3$ with $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ has been reported to yield ill-

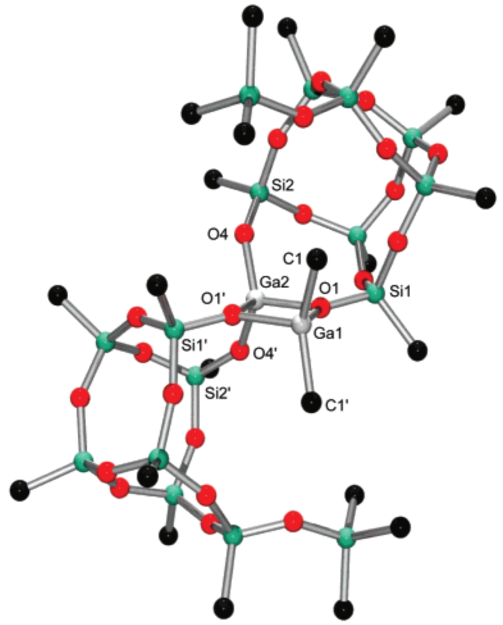


Figure 3. Molecular structure of $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga(GaMe_2)$ (**5**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Ga1–C1, 1.918(5); Ga1–O1, 1.990(3); Ga2–O1, 1.887(3); Ga2–O4, 1.770(3); Si1–O1, 1.636(3); Si2–O4, 1.598(3); $Si{-}O_{av}$, 1.617(3). Selected bond angles (deg): C1–Ga1–C1′, 132.1(5); C1–Ga1–O1, 107.7(2); C1–Ga1–O1′, 108.7(3); O1–Ga1–O1′, 79.5(2); C1–Ga1–Ga2, 113.9(2); O1–Ga2–O1′, 84.8(2); O4–Ga2–O4′, 117.9(2); O4–Ga2–O1, 121.1(1); O4–Ga2–O1′,113.2(1).

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[11] Skowronska-Ptasinska, M. D.; Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2001**, *20*, 3519.

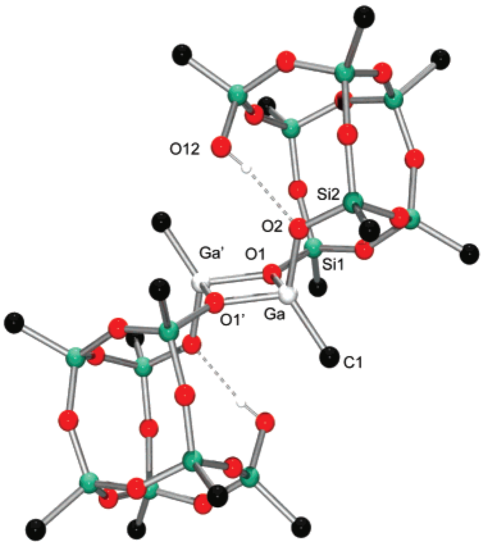

Figure 4. Molecular structure of {[(*c*-C_6H_{11})$_7Si_7O_{11}$(OH)]GaMe}$_2$ (**6b**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Ga−C1, 1.898(8); Ga−O1, 1.930(6); Ga−O1′, 1.924(5); Ga−O2, 1.790(6); Si1−O1, 1.667(5); Si2−O2, 1.628(6); Si−O$_{av}$, 1.620(6); O2···O12, 2.85(2). Selected bond angles (deg): C1−Ga−O1, 117.0(4); C1−Ga−O1′, 118.2(3); C1−Ga−O2, 124.4(4); O1−GaO1′, 81.9(2); O1−Ga−O2, 103.1(2); O1′-Ga-O2, 103.6(2); Ga−O1−Ga′, 98.1(2); Ga−O1−Si1, 121.7(3); Ga′−O1−Si1, 139.0(3); Ga−O2−Si2, 129.6(3).

defined products that upon controlled hydrolysis resulted in a cluster compound {[(*c*-C_6H_{11})$_7Si_7O_{12}$]$_2$[Ga(CH_2SiMe_3)(μ-OH)]$_6$}.[8] Although trialkyl gallium compounds are very reactive, after substitution of one of the alkyls by a heteroatom, the thus formed gallium dialkyls are considerably more stable than corresponding aluminum dialkyl species. Whereas protonolysis of the second gallium carbon bond is still relatively easy, protonolysis of the final alkyl is known to be quite difficult.[12] This phenomenon was nicely illustrated by the reaction of $R_7Si_7O_9(OH)_3$ (R = *c*-C_5H_9, *c*-C_6H_{11}) with an equimolar amount of $GaMe_3$, which cleanly afforded {[$R_7Si_7O_{11}$(OH)]GaMe}$_2$ (R = *c*-C_5H_9 (**6a**), *c*-C_6H_{11}(**6b**), Scheme 2), in which gallium alkyl and silanol functionalities coexist.

Compound **6b** (Figure 4) consists of a dimeric structure in which both gallium atoms are linked by two bridging siloxy functionalities. The siloxy groups that are σ-bonded to the gallium atoms also form hydrogen bonds with the adjacent silanol functionalities (O2···O12 = 2.85(2) Å). Unlike observed in **4**, the hydrogen bonding in **6b** has no notable effect on the Ga−O2 and Si2−O2 bond distances. The IR (Nujol) OH stretching vibrations (**6a**, $\nu_{OH} = 3317$ cm^{-1}; **6b**, $\nu_{OH} = 3289$ cm^{-1}) are shifted to higher frequency compared to that of the strongly hydrogen bonded silanol in {[(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMe_3$)]$_2$Al}$^-${H}$^+$ ($\nu = 3150$ cm^{-1}) and resemble that of the silanols in the Brønsted acid {[(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]$_2$Al}$^-${H}$^+$ ($\nu_{OH} = 3366$ cm^{-1}). Furthermore, the ^{1}H NMR spectra of **6a/b** show sharp resonances (**6a**, δ 5.79 ppm; **6b**, δ 5.82 ppm) for the hydroxyl groups, suggesting that the hydrogen bonding is essentially nonexistent in solution.[5,13] Heating NMR tubes with benzene-d_6 solutions of **6a/b** did not result in protonolysis of the final gallium methyl substituent and formation of {[$R_7Si_7O_{12}$]Ga}$_2$, emphasizing the remarkable thermal stability of **6a/b**. The structure of **6b** gives insight into the protonolysis reactions of the trisilanol $R_7Si_7O_9(OH)_3$ (R = *c*-C_5H_9, *c*-C_6H_{11}). A similar structure is feasible as an intermediate during the synthesis of {[(*c*-C_6H_{11})$_7$-Si_7O_{12}]Al}$_2$ and {[(*c*-C_5H_9)$_7Si_7O_{12}$]Al}$_n$, respectively.[5a] Intra- or intermolecular protonolysis of the final Al−Me in the putative intermediate {[$R_7Si_7O_{11}$(OH)]AlMe}$_2$ then determines whether a dimeric or a polymeric structure is formed.

When, instead of (*c*-C_5H_9)$_7Si_7O_9(OH)_3$, the monosilylated disilanol (*c*-C_5H_9)$_7Si_7O_9(OH)_2OSiMePh_2$ was treated with an equimolar amount of $GaMe_3$, the silylated analogue of **6a**, {[(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]GaMe}$_2$ (**7**, Scheme 3), was formed. As was observed for the corresponding methyl aluminum silsesquioxane species {[(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]AlMe}$_2$,[11] **7** consists of three conformational structures. Purification by fractional crystallization yielded one of the conformers in 85% purity (remaining 15% consist of a 5:1 ratio of the other two conformers). As for the corresponding aluminum isomers, two of the gallium isomers show a single GaCH_3 resonance, while the third isomer shows two equi-intense singlets for the GaCH_3.[11] The ^{13}C and ^{29}Si NMR spectra of the major isomer were also consistent with the analogous methyl aluminum silsesquioxane and the proposed structure with the gallium methyl group trans to each other. While the ratio of the three isomers upon isolation directly after the reaction was found to be approximately 5:1:40, after heating for 3 h at 90 °C, this ratio changed to the thermodynamic stable equilibrium of 2:1:2. These gallium conformers isomerize in a fashion similar to what was observed for the corresponding methyl aluminum silsesquioxane system.[11] However, the fact that isomerization of **7** was completed after only 3 h at 90 °C compared to the 400 h at 76 °C for the analogous methyl aluminum silsesquioxanes indicates that the methyl gallium silsesquioxane system shows a significantly higher fluxional behavior than the aluminum system. Further proof for the analogy between methyl aluminum and methyl gallium silsesquioxane species was provided by the thermolysis of the chemical isomer of **7**, [(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]$_2$Ga($GaMe_2$) (**5**). Heating a benzene-d_6 solution of **5** for 1100 h at 60 °C resulted in complete conversion of **5** in a 2:1:2 ratio of the three isomers of **7**. The rate constant for this isomerization of $k_{60\,°C} = 4.7 \times 10^{-7}$ s^{-1} corresponds well with the rate constant of $k_{66\,°C} = 6.9 \times 10^{-7}$ s^{-1} for the isomerization of the analogous dimethylaluminum aluminate [(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]$_2$Al($AlMe_2$) to its methyl aluminum silsesquioxane isomers {[(*c*-C_5H_9)$_7Si_7O_{11}$($OSiMePh_2$)]AlMe}$_2$. Hence, isomerization of **5** to **7** is considerably more difficult than for the isomers **7** to reach their thermodynamic equilibrium.

From the existence of **6a/b** it is clear that the methyl functionality in (≡SiO)$_2$GaMe is considerably less reactive than the corresponding methyl group in (≡SiO)$_2$AlMe. In analogy, dimethyl gallium siloxane species of

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[12] Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Williamson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford 1982; Vol. 1, Chapter 7.

[13] Koller, H.; Engelhardt, G.; van Santen, R. A. *Top. Catal.* **1999**, *9*, 163.

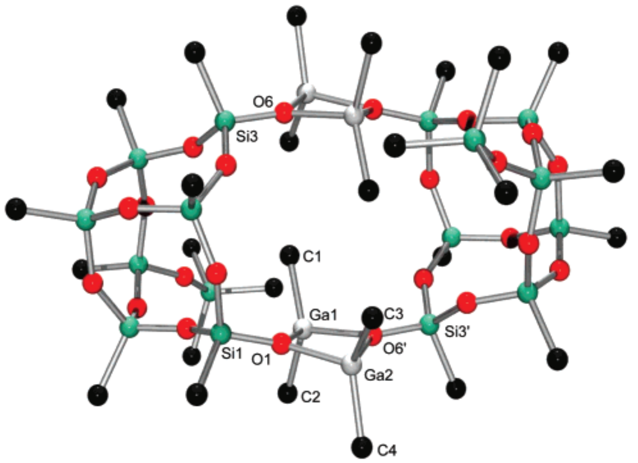

Figure 5. Molecular structure of $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(GaMe_2)_4\}$ (**8**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Ga1−C1, 1.932(3); Ga1−C2, 1.951(3); Ga1−O1, 1.985(2); Ga1−O6′, 1.985(2); Ga2−C3, 1.949(3); Ga2−C4, 1.957(3); Ga2−O1, 1.961(2); Ga2−O6′, 1.964(2); Si1−O1, 1.622(2); Si3′−O6′, 1.628(2); Si−O_{av}, 1.619(2). Selected bond angles (deg): C1−Ga1−C2, 127.18(14), C1−Ga1−O1, 111.30(11); C2−Ga1−O1, 107.01(11); C1−Ga1−O6′, 110.57(11); C2−Ga1−O6′, 110.57(11); O1−Ga1−O6′, 80.28(7); C1−Ga1−Ga2, 124.55(10); C2−Ga1−Ga2, 108.23(10); O1−Ga1−Ga2, 40.55(4); O6′-Ga1-Ga2, 40.65(5); C3−Ga2−C4, 124.22(13); C3−Ga2−O1, 111.86(10); C4−Ga2−O1, 110.07(11); C3−Ga2−O6′, 116.42(10); C4−Ga2−O6, 104.67(10); O1−Ga2−O6′, 81.38(7), C3−Ga2−Ga1, 129.42(9); C4−Ga2−Ga1, 106.35(10); O1−Ga2−Ga1, 41.16(5); O6′-Ga2-Ga1, 41.16(5); Si1−O1−Ga1, 123.14(9); Si1−O1−Ga2, 138.37(10); Si3′−O6′-Ga1, 133.12(10); Si3′−O6′-Ga2, 128.63(10).

the type ≡SiOGaMe$_2$ are expected to be considerably more stable than their aluminum congeners in ≡SiOAlMe$_2$. When $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ was treated with 2 equiv of $GaMe_3$, $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(GaMe_2)_4\}$ (**8**, Scheme 3) was formed nearly quantitatively (NMR) and was isolated in good yield. Due to the high reactivity of its remaining alkyl substituents, the corresponding aluminum silsesquioxane $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(AlMe_2)_4\}$,[11] formed after an equimolar reaction between $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ and $AlMe_3$, could be isolated only as a side product in low yield. Treating the trisilanol $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ with 3 equiv of $GaMe_3$ afforded an interesting hexa(dimethylgallium) product, $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2(GaMe_2)_6\}$ (**9**), in moderate isolated yield (Scheme 2).

The molecular structure of **8** as shown in Figure 5 corresponds well with the solid-state structure of the analogous aluminum compound, though small differences are notable. Taking the effective radii of a tetrahedral Ga^{3+} (0.61 Å) and Al^{3+} (0.53 Å) into account,[9] the average Ga−O bond length in **8** of 1.974(2) Å is virtually identical to the average Al−O distance of 1.868(2) Å in the corresponding aluminum species, while the effective Ga−C_{av} distances (1.947(3) Å) in **8** is approximately 0.08 Å shorter than the Al−C bond length (av: 1.946(4) Å) in $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(AlMe_2)_4\}$. In Lewis acidic metallasilsesquioxane complexes, the distance between the silicon and the oxygen bonded to the Lewis acidic metal site often gives a qualitative indication of the oxophilicity of the metal center.[4f,5,11] Hence, the shorter Si1−O1 (1.622(2) Å) and Si3′−O6′ (1.628(2) Å) distances in **8** compared to the same Si−O bond lengths (1.641(2), 1.646(2) Å) in the corresponding aluminum compound support the higher oxophilicity of aluminum compared to gallium.

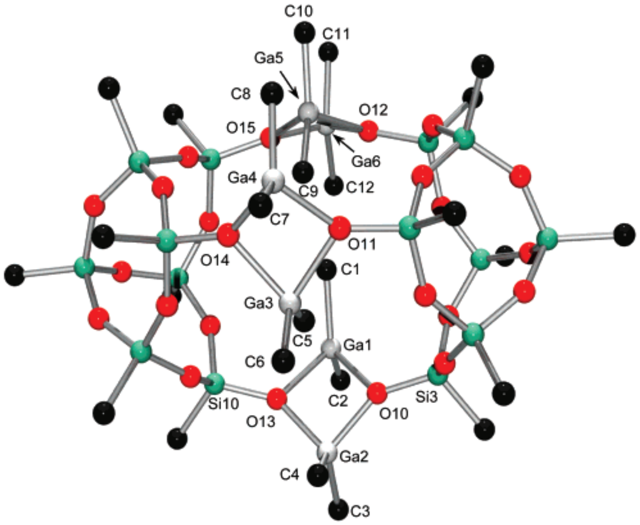

Figure 6. Molecular structure of $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2(GaMe_2)_6\}$ (**9**). For clarity reasons, only the α-carbons of the silicon substituents are shown. Selected bond distances (Å): Ga1−C1, 1.959(5); Ga1−C2, 1.913(5); Ga1−O10, 2.074(3); Ga1−O13, 2.082(3); Ga2−C3, 1.971(5); Ga2−C4, 2.017(6); Ga2−O10, 1.892(3); Ga2−O13, 1.892(3); Ga−C_{av}, 1.957(6); Ga−O_{av}, 1.99(3); Si−O_{av}, 1.618(3). Selected bond angles (deg): C1−Ga1−C2, 129.5(3); C1−Ga1−O10, 111.8(2); C2−Ga1−O10, 106.8(2); C1−Ga1−O13, 114.0(2); C2−Ga1−O13, 105.6(2); O10−Ga1−O13, 76.4(1); C1−Ga1−Ga2, 131.9(2); C2−Ga1−Ga2, 98.6(2); O10−Ga1−Ga2, 39.85(8); O13−Ga1−Ga2, 39.75(8); C3−Ga2−C4, 120.8(2); C3−Ga2−O10, 109.7(2); C4−Ga2−O10, 111.6(2); C3−Ga2−O13, 110.7(2); C4−Ga2−O13, 113.1(2); O10−Ga2−O13, 85.4(1); C3−Ga2−Ga1, 103.6(2); C4−Ga2−Ga1, 135.5(2); O10−Ga2−Ga1, 44.5(1); O13−Ga2−Ga1, 44.72(9); Si3−O10−Ga1, 122.6(2); Si3−O10−Ga2, 141.7(2); Si10−O13−Ga1, 120.8(2); Si10−O13−Ga2, 143.7(2).

The solid-state structure of **9** is shown in Figure 6. In each of the three $[\mu\text{-}(\equiv SiO)GaMe_2]_2$ fragments, one of the two gallium atoms forms considerably shorter Ga−C and longer Ga−O bonds (Ga1, Ga3, Ga5) than the other gallium atoms (Ga2, Ga4, Ga6). The deviations in the Ga−C (Δ_{Ga-C} = 0.160 Å) and Ga−O (Δ_{Ga-O} = 0.209 Å) bond distances are quite dramatic. Furthermore, the tetrahedral geometry of the Ga1, Ga3, and Ga5 is also more distorted than of the other gallium atoms, which is most probably caused by the large steric strain within the molecule. The structure of **9** shows four inequivalent methyl groups per gallium center. Three of the total of 12 methyl groups are pointing into the cavity formed by the silsesquioxane structures (C1, C5, C9), while the other nine point outward. On the basis of a fluxional C_3 symmetric structure one would expect two or even only one gallium methyl resonance. However, the ^1H and ^{13}C NMR spectra show four distinct resonances corresponding to four inequivalent methyl groups. This indicates that this molecule is rather crowded, which dramatically limits its fluxional behavior. The methyl groups that are pointing into the cavity of the silsesquioxane structure give relative lowfield resonances in the ^1H (δ 1.04 ppm) and ^{13}C (δ 5.99 ppm) NMR. The other methyl groups show normal high-field resonances (^{1}H, δ 0.47, 0.41, 0.28 ppm; ^{13}C, δ −1.99, −2.75, −3.47 ppm). Two of the high-field methyl resonances coalescent at 95 °C in benzene-d_6, corresponding with a Gibbs free energy of rotation of $\Delta G^{\ddagger}_{Tc} = 78$ kJ.[14] At even higher temperatures, **9** gradually starts to thermolyze. Consequently, coalescence of other gallium methyl resonances could not be observed.[15]

Concluding Remarks

The boron and gallium species described here show many similarities with the corresponding aluminum silsesquioxane compounds, although compounds formed by salt metathesis show some peculiar differences as well. Compound **1** is dimeric with trigonal planar boron centers, whereas the corresponding aluminum silsesquioxane forms a dimer (cyclohexyl substituted) or polymer (cyclopentyl substituted) with tetrahedrally coordinated aluminum centers. Under identical conditions the gallium silsesquioxane was isolated as the monomeric triethylamine adduct **3**, although it has to be noted that the corner-capped gallium silsesquioxane has also been isolated as a Lewis base-free dimeric species with tetrahedrally coordinated gallium centers, isomorphic to its aluminum congener. For B, Al, and Ga anionic species of the type $\{[c\text{-}C_5H_9Si_7O_{11}(OSiMePh_2)]_2M\}^-\{X\}^+$ are known, either as ammonium (M = Al, Ga), lithium (M = B, Al), or MMe_2^+ (M, M′ = Al, Ga) salts. Only for aluminum is the corresponding Brønsted acid $\{[c\text{-}C_5H_9Si_7O_{11}(OSiR'_3)]_2Al\}^-\{H\}^+$ stable enough to be isolated. Due to the much lower tendency of boranes to undergo protonolysis, deprotonation reactions of silsesquioxanes with boranes are not possible. On the other hand, both $AlMe_3$ and $GaMe_3$ readily undergo protonolysis with incompletely condensed silsesquioxanes, and their chemistry is qualitatively similar albeit that the reactivity observed for gallium is considerably milder and more selective than for aluminum. Hence, the mild chemistry of gallium alkyl species provides insight into the analogous but more violent reactivity of aluminum alkyl species. Not surprisingly, both aluminum and gallium tend to form stable tetrahedrally surrounded metal centers, which in the case of **9** results in a very crowded species.

Experimental Section

General Comments. All manipulations were performed under an argon atmosphere using glovebox (Braun MB-150 GI) and Schlenk techniques. Solvents were distilled from Na (toluene) or Na/K alloy (hexanes) and stored under argon. NMR solvents were dried over Na/K alloy (benzene-d_6) or 4 Å molecular sieves (CDCl$_3$, toluene-d_8). NMR spectra were recorded on a Varian Mercury 400 (^{1}H, ^{13}C NMR, 25 °C) and Varian Indigo 500 (^{29}Si NMR, 25 °C) spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C NMR) or external standards (^{29}Si: SiMe$_4$ = 0 ppm). Elemental analyses were carried out at the Analytical Departments of the University of Groningen (The Netherlands) and the Eindhoven University of Technology (The Netherlands). To reduce the often-observed silicon carbide formation, in some cases V_2O_5 was added to improve the combustion. Silsesquioxanes $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$, $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiR'_3$ (SiR'_3 = SiMe$_3$, SiMePh$_2$) were prepared following literature procedures.[3,5b]

$\{[(c\text{-}C_5H_9)_7Si_7O_{12}]B\}_2$ (1). To a solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (1.68 g, 1.92 mmol) in THF (20 mL) was added LiBH$_4$ (0.96 mL, 2 M in THF, 1.92 mmol) at 0 °C. The solution was allowed to warm to room temperature and was stirred overnight. All volatiles were evaporated, and the product was redissolved in THF (10 mL) and filtered. Slow cooling of a hot, saturated THF solution yielded colorless crystals of **1** (1.09 g, 1.23 mmol, 64%). ^{1}H NMR (CDCl$_3$, δ): 1.75 (m, 28H, CH_2-C$_5$H$_9$), 1.61 (m, 28H, CH_2-C$_5$H$_9$), 1.51 (m, 56H, CH_2-C$_5$H$_9$), 0.90 (m, 14H, CH-C$_5$H$_9$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 27.80, 27.65, 27.49, 2738, 27.30, 27.10, 26.93, 26.83 (s, CH$_2$-C$_5$H$_9$), 23.60, 22.98, 22.79, 22.34, 22.29 (s, CH-C$_5$H$_9$, 2:2:1:1:1 ratio). Anal. Calcd for $(C_{35}H_{63}BO_{12}Si_7)_2$: C, 47.59; H, 7.19. Found: C, 47.34; H, 7.03.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{Li\}^+$ (2). To a cooled (−80 °C) solution of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ (2.10 g, 2.0 mmol) in THF (20 mL) was added LiBH$_4$ (0.49 mL, 2 M in THF, 0.98 mmol). The reaction mixture was allowed to reach room temperature, upon which hydrogen started to evolve. The mixture was heated to reflux for 5 min and left overnight at room temperature. After evaporation of the volatiles, the residue was crystallized from hexane to give **2** as microcrystalline material (1.56 g, 0.72 mmol, 74%). Single crystals of **2**·hexane, suitable for X-ray diffraction, were obtained by recrystallization from hexane (0.26 g, 0.116 mmol, 12%). ^{1}H NMR (CDCl$_3$, δ): 7.15−7.50 (m, 10H, Ph), 1.50 (m, 56H, CH_2-C$_5$H$_9$), 0.95 (m, 7H, CH-C$_5$H$_9$), 0.70 (s, 3H, Si-Me). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 136.62, 135.84, 134.59, 134.25, 129.71, 129.68, 127.58, 127.56 (Ph), 28.39, 28.31, 28.18, 27.79, 27.65, 27.61, 27.58, 27.50, 27.40, 27.37, 27.33, 27,25, 27.19, 27.09, 27.05, 27.03, 27.00, 26.93, 26.90, 26.81, 26.71 (CH$_2$-C$_5$H$_9$), 24.59, 24.04, 23.92, 23.62, 22.89, 22.51 (CH-C_5H$_9$, 1:1:1:1:1:2 ratio), −0.07 (Si(CH$_3$)$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −7.05 (SiMePh$_2$), −61.37, −63.40, −63.61, −64.68, −64.88, −66.15, −67.32 ((≡O)$_3$$SiC_5H_9$). Anal. Calcd for $C_{96}H_{152}BLiO_{24}Si_{16}$: C, 53.45; H, 7.10. Found: C, 52.98; H, 7.38.

$[(c\text{-}C_6H_{11})_7Si_7O_{12}]Ga\cdot NEt_3$ (3). Gallium trichloride (1.33 g, 7.55 mmol) was carefully suspended in cooled (−80 °C) THF (30 mL), and at room temperature $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (7.36 g, 7.56 mmol) and triethylamine (3.05 g, 30 mmol, 4 equiv) were added. The brown suspension was stirred at 60 °C for 5 h. The mixture was filtered, and the filtrate was evaporated. Traces of toluene were removed by adding hexane (5 mL) to the residue, which was subsequently evaporated. Chloroform (40 mL) was added, and the solution was filtered over Celite. The filtrate was evaporated to half its original volume, and hexane (20 mL) was added to give a precipitate. Heating redissolved the precipitate, and solid **3** (3.28 g, 2.87 mmol, 38%) was obtained by cooling to −30 °C. Crystals, suitable for X-ray diffraction, were obtained by recrystallization from chlorobenzene. ^{1}H NMR (CDCl$_3$, δ): 2.94 (q, 6H, N-CH_2-CH$_3$, $^3J_{HH}$ = 7.3 Hz), 1.73 (m, 35H, CH_2-C$_6$H$_{11}$), 1.26 (t+m, 44H, N-CH$_2$-CH_3 + CH_2-C$_6$H$_{11}$), 0.78 (m, 7H, CH-C$_6$H$_{11}$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 48.77 (NCH$_2$CH$_3$), 28.09, 27.94, 27.89, 27.62, 27.45, 27.32, 27.11, 27.04 (CH$_2$-C$_6$H$_{11}$), 24.58, 23.91, 23.69 (3:3:1, CH-C$_6$H$_{11}$), 9.65 (NCH$_2$$CH_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −64.32, −68.60, −70.08 (3:1:3). Anal. Calcd for $C_{48}H_{92}Si_7O_{12}GaN$: C, 50.50; H, 8.12; N, 1.23. Found: C, 50.67; H, 7.92; N, 1.24.

$\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga\}^-\{Et_3NH\}^+$ (4). To a solution of GaCl$_3$ (0.38 g, 2.18 mmol) and $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$ (4.40 g, 4.10 mmol) in toluene (40 mL) was added Et$_3$N (0.89 g, 8.80 mmol) at room temperature. The mixture gradually gave a precipitate of Et$_3$NHCl. After stirring overnight at 65 °C, the reaction mixture was filtered. The filtrate was evaporated, and traces of toluene were removed by

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(14) T_c = 368 K, $\Delta\nu$ = 38.4 Hz, $\Delta G^{\ddagger}_{Tc} = -RT_c \ln(\pi\Delta\nu h/2k_bT_c)$: Kessler, H. *Angew. Chem.* **1970**, *82*, 237.

(15) When the same reaction was carried out with AlMe$_3$ instead, a much more complex reaction pattern was observed in which not only protonolysis of the Al−C bonds but also Si−O and Al−C bond breaking accompanied by Si−C and Al−O bond formation was observed. Although the ^{1}H, ^{13}C, and ^{29}Si NMR of the thus formed reaction product are characteristic for a single aluminosilsesquioxane species, the exact structure is as yet unknown.

dissolving the product in hexane (10 mL) followed by evaporation of the volatiles. Pure product was obtained by recrystallization from hexane (40 mL) at −30 °C, yielding **4** as colorless crystals (2.23 g, 0.96 mmol, 47%), containing hexane in the lattice. ^{1}H NMR (CDCl$_3$, δ): 9.38 (s, 1H, NH), 7.64 (dd, 4H, Ph), 7.56 (dd, 4H, Ph) 7.40 (m, 12H, Ph), 2.56 (dm, 6H, HN(CH_2CH$_3$)$_3$, $^{3}J_{\mathrm{HH}} = 58$ Hz), 1.50 (m, 112H, CH_2-C$_5$H$_9$), 0.90 (m, 14H, CH-C$_5$H$_9$) 0.80 (t, HN(CH$_2$CH_3)$_3$, $J_{\mathrm{HH}} = 7.2$ Hz) 0.66 (s, 6H, Si-CH_3). ^{13}C{^{1}H} NMR ([D$_1$]chloroform): δ 137.88, 137.38, 134.17, 134.10, 129.50, 127.71, 127.64 (Ph), 45.25 (NCH$_2$CH$_3$), 28.34, 28.06, 27.85, 27.80, 27.64, 27.61, 27.52, 27.46, 27.34, 27.21, 27.14, 27.09, 26.99, 26.93, 26.86, 26.80, 26.70 (CH$_2$-C$_5$H$_9$), 25.54, 24.95, 24.34, 23.98, 23.82, 22.80, 22.40 (1:1:1:1:1:1:1 CH-C_5H$_9$), 8.58 (NCH$_2$$CH_3$), −0.02 (Si-$CH_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −12.83 (SiMePh$_2$), −63.93, −63.59, −64.42, −65.08, −65.79, −67.34, −67.8 (1:1:1:1:1:1:1). Anal. Calcd for C$_{102}$H$_{168}$O$_{24}$Si$_{16}$GaN: C, 53.00; H, 7.33; N, 0.61. Found: C, 53.24; H, 7.62; N, 0.63.

[(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)]$_2$Ga(GaMe$_2$) (5). To a cooled (−80 °C) solution of **3** (1.08 g, 0.45 mmol) in toluene (10 mL) was added GaMe$_3$ (0.90 mL, 0.5 M in toluene, 0.45 mmol). The mixture was allowed to warm to room temperature and was heated to reflux for 5 min. The mixture was pumped to dryness, and by adding hexane (5 mL) and subsequently evaporating the volatiles, final traces of toluene were removed. The dry residue was dissolved in hot hexane (10 mL) and cooled to −30 °C to give crystalline **5** (0.23 g, 0.10 mmol, 22%). ^{1}H NMR (CDCl$_3$, δ): 7.63 (m, 8H, Ph), 7.35 (m, 12H, Ph), 1.55 (m, 112H, CH_2-C$_5$H$_9$), 0.90 (m, 14H, CH-C$_5$H$_9$), 0.65 (s, 6H, Si-CH_3), −0.22 (s, 6H, GaMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 138.13, 137.64, 134.51, 134.43, 129.39, 129.32, 127.85, 127.52 (Ph), 28.89, 28.39, 28.26, 27.94, 27.82, 27.73, 27.69, 27.56, 27.37, 27.34, 27.31, 27.27, 27.15, 27.10, 27.00, 26.93, 26.66 (CH$_2$-C$_5$H$_9$), 25.32, 24.79, 23.99, 23.17, 22.78, 22.73, 22.65 (C_5H$_9$, 1:1:1:1:1:1:1 ratio), 0.01 (Si-CH$_3$) −2.44 (Ga-CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −11.91 (SiMePh$_2$), −61.19, −61.93, −65.12, −65.78, −66.21, −67.83, −68.07 ((≡O)$_3$$SiC_5H_9$, 1:1:1:1:1:1 ratio). Variable-temperature ^{1}H NMR experiments of **7** were carried out in toluene-d_8. Anal. Calcd for C$_{98}$H$_{158}$Ga$_2$O$_{24}$Si$_{16}$: C, 50.97; H, 6.90. Found: C, 50.82; H, 7.01.

{[R$_7$Si$_7$O$_{11}$OH]GaMe}$_2$ (R = *c*-C$_5$H$_9$ (6a), *c*-C$_6$H$_{11}$ (6b)). **6a**: To a cooled (−80 °C) suspension of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (0.88 g, 1.0 mmol) in toluene (35 mL) was added GaMe$_3$ (2.0 mL, 0.5 M in toluene, 1.0 mmol). The mixture was allowed to warm to room temperature and turned clear after standing for 5 days. After evaporation of the volatiles, hexane (ca 5 mL) was added to the residue. Evaporation of the hexane gave **6a** as the only silsesquioxane-containing product. Recrystallization from hot hexanes (40 mL) gave 0.47 g (0.25 mmol, 49%), and 0.13 g (0.068 mmol, 14%) as a second crop after concentration of the mother liquor. ^{1}H NMR (CDCl$_3$, δ): 5.79 (sharp s, 2H, OH), 1.70 (m, 112H, CH_2-C$_5$H$_9$), 1.02 (m, 14H, CH-C$_5$H$_9$), 0.31 (s, 6H, GaMe). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 28.04, 27.65, 27.49, 27.42, 27.36, 27.30, 27.28, 27.24, 27.19, 27.06, 27.04, 26.98, 26.92, 26.87 (CH$_2$−C$_5$H$_9$), 23.91, 22.78, 22.50, 22.37, 22.19 (CH-C$_5$H$_9$, 1:2:1:2:1 ratio), −6.99 (Ga-CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −56.42, −57.95, −60.56, −65.65, −65.85, −65.97, −69.12. IR (CCl$_4$): $\nu = 3317$ cm^{-1} (br). Anal. Calcd for C$_{72}$H$_{134}$O$_{24}$Si$_{14}$Ga$_2$: C, 45.12; H, 7.05. Found: C, 45.31; H, 6.65. **6b**: The general procedure as for **6a** was used starting from (c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$ (0.98 g, 1.0 mmol) and GaMe$_3$ (2.0 mL, 0.5 M in toluene, 1.0 mmol), crystals of **6b**·C$_6$H$_{14}$ (0.41 g, 0.19 mmol, 37%) formed upon cooling a saturated hexane solution. A second crop (0.25 g, 0.11 mmol, 23%) was obtained at −30 °C after evaporating half of the volume of the mother liquor. Crystals suitable for diffraction were obtained by recrystallization from hexane. ^{1}H NMR (CDCl$_3$, δ): 5.82 (sharp s, 2H, OH), 1.76 (m, 70H, CH_2-C$_6$H$_{11}$), 1.30 (m, 70H, CH_2-C$_6$H$_{11}$), 0.93 (m, 14H, CH-C$_6$H$_{11}$), 0.27 (s, 6H, GaMe). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 27.77, 27.74, 27.53, 27.51, 27.46, 27.40, 27.05, 26.89, 26.83, 26.67, 26.60, 26.11, 25.98 (CH$_2$-C$_6$H$_{11}$), 24.95, 23.81, 23.67, 22.31, 22.26, 23.11, 23.06 (CH-C$_6$H$_{11}$, 1:1:1:1:1:1:1:1 ratio), −6.61 (Ga-CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −58.52, −59.94, −62.82, −67.70, −67.86, −68.14, −71.28. IR (CCl$_4$): $\nu = 3289$ cm^{-1} (br). Anal. Calcd for C$_{86}$H$_{162}$O$_{24}$Si$_{14}$Ga$_2$·(C$_6$H$_{14}$)$_{0.8}$: C, 51.02; H, 8.26. Found: C, 51.09; H, 8.23 (about 0.2 equiv of the lattice hexane was evaporated).

{[(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)]GaMe}$_2$ (7). To a cooled (−80 °C) toluene solution (20 mL) of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_2$-OSiMePh$_2$ (2.14 g, 2.0 mmol) was added GaMe$_3$ (4.0 mL, 0.5 M in toluene, 2.0 mmol). The mixture was warmed to room temperature and refluxed overnight. The volatiles were evaporated, and the crude product was dissolved in hexane (70 mL). After filtering traces of impurities, the clear solution was concentrated (30 mL), and slow cooling of a saturated, hot solution gave **7** as microcrystalline material (0.46 g, 0.2 mmol, 20%). The product consisted of a mixture of three conformers of **7** in a 5:1:40 ratio. Major isomer (85% pure): ^{1}H NMR (CDCl$_3$, δ): 7.58 (m, 4H, Ph), 7.30 (m, 6H, Ph), 1.78 (m, 14H, CH_2-C$_5$H$_9$), 1.47 (m, 42H, CH_2-C$_5$H$_9$), 0.90 (m, 7H, CH-C$_5$H$_9$), 0.64 (s, 3H, SiCH_3), −0.30 (s, 3H, GaCH_3). ^{13}C NMR (CDCl$_3$, δ): 137.29 (*ipso*-C, Ph), 134.14 (Ph), 129.29 (Ph), 127.42 (Ph), 28.15, 28.09, 28.04, 27.30. 27.20, 27.06, 27.03, 26.98, 26.92, 26.87 (CH$_2$-C$_5$H$_9$), 24.52, 24.48, 23.72, 22.98, 22.84, 22.42, 22.31 (CH-C$_5$H$_9$, 1:1:1:1:1:1:1 ratio), −0.44 (SiCH$_3$), −6.70 (GaCH$_3$). Anal. Calcd for (C$_{49}$H$_{79}$GaO$_{12}$Si$_8$)$_2$: C, 50.97; H, 6.90. Found: C, 50.67; H, 6.64. Variable-temperature ^{1}H NMR experiments of **7** were carried out in toluene-d_8.

{[(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)]$_2$(GaMe$_2$)$_4$} (8). To a cooled (−80 °C) solution of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_2$OSiMePh$_2$ (2.14 g, 2.0 mmol) in toluene (20 mL) was added GaMe$_3$ (8.0 mL, 0.5 M in toluene, 4.0 mmol). The mixture was allowed to warm to room temperature, upon which evolution of gas was visible. After stirring for 30 min, the mixture was gently heated and, when gas evolution ceased, heated to reflux for 1 min. After evaporation of the volatiles, traces of toluene were removed by dissolving the product in hexane (5 mL) and subsequent evaporation of the volatiles. Pure **8** was obtained as a white powder. Recrystallization from hot hexane (40 mL) afforded air-stable, hexane-containing crystals suitable for diffraction (1.87 g, 0.71 mmol, 72%). ^{1}H NMR (CDCl$_3$, δ): 7.63 (d, 8H, Ph), 7.38 (m, 12H, Ph), 1.45 (m, 112H, CH_2-C$_5$H$_9$ + CH$_2$-hexane), 0.85 (t, 20H, $J_{\mathrm{HH}} = 5.2$ Hz, CH_3-hexane + m, CH-C$_5$H$_9$), 0.60 (s, 6H, Si-CH_3), −0.20 (s, 24H, GaMe$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 137.51, 134.52, 129.63, 127.74 (Ph), 28.25, 28.07, 28.00, 27.91, 27.86, 27.82, 27.52, 27.14, 27.00, 26.95, 26.71 (CH$_2$-C$_5$H$_9$), 25.53, 25.38, 24.30, 24.24, 22.90 (CH-C$_5$H$_9$, 1:2:2:1:1 ratio), 1.21 (Si-CH$_3$), −1.91 (Ga-CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −11.84 (SiMePh$_2$), −61.65, −66.86, −67.37, −68.16 ((≡O)$_3$$SiC_5H_9$, 2:3:1:1 ratio). Anal. Calcd for C$_{104}$H$_{176}$O$_{24}$Si$_{16}$-Ga$_4$·C$_6$H$_{14}$: C, 50.33; H, 7.30. Found: C, 50.23; H, 7.12.

{[(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$]$_2$(GaMe$_2$)$_6$} (9). To a cooled (−80 °C) suspension of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_3$ (1.75 g, 2.0 mmol) in toluene (20 mL) was added GaMe$_3$ (12.0 mL, 0.5 M in toluene, 6.0 mmol). The mixture was allowed to warm to room temperature, upon which the mixture turned clear and gas evolved. After gas evolution ceased, the mixture was heated to reflux for ca. 1 min. Pure **9** (1.20 g, 0.49 mmol, 49%) was obtained by crystallization from a concentrated reaction mixture as toluene-containing crystals. Recrystallization from a minimum amount of toluene at room temperature afforded toluene-containing crystals, suitable for diffraction. ^{1}H NMR (CDCl$_3$, δ): 1.50 (m, 112H, CH_2-C$_5$H$_9$), 0.87 (m, 14H, CH-C$_5$H$_9$), 0.58 (s, 9H, GaMe), −0.04 (s, 9H, GaMe), −0.19 (s, 9H, GaMe), −0.23 (s, 9H, GaMe). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 27.77, 27.65, 27.55, 27.42, 27.28, 27.24, 26.99, 26.90, 26.88, 26.80 (CH$_2$-C$_5$H$_9$), 25.43, 24.12, 22.51 (3:3:1, CH-C$_5$H$_9$), 5.99, −1.99, −2.75, −3.47 (1:1:1:1, Ga-CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$, δ): −62.17, −67.09, −68.13 (3:1:3). Anal. Calcd for C$_{82}$H$_{162}$O$_{24}$Si$_{14}$Ga$_6$: C, 42.02; H, 6.97. Found: C, 41.60; H, 6.90. Variable-temperature ^{1}H NMR (benzene-d_6) of **9** was carried out. The two most upfield GaCH_3 singlets ($\Delta = 0.13$ ppm) coalesce at 95 °C.

Table 1. Details of the X-ray Structure Determination of $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2B\}^-\{Li\}^+$ (2), $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga\}^-\{HNEt_3\}^+$ (4), $[('c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2Ga(GaMe_2)$ (5), $\{[(c\text{-}C_6H_{11})_7Si_7O_{11}(OH)]GaMe\}_2$ (6b), $\{[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)]_2(GaMe_2)_4\}$ (8), and $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2(GaMe_2)_6\}$ (9)

	2	4	5	6b	8	9
formula	$C_{102}H_{166}BLiO_{24}Si_{16}$	$C_{108}H_{180}GaNO_{24}Si_{16}$	$C_{98}H_{158}Ga_2O_{24}Si_{16}$	$C_{92}H_{176}Ga_2O_{24}Si_{14}$	$C_{110}H_{190}Ga_4O_{24}Si_{16}$	$C_{89}H_{170}Ga_6O_{24}Si_{14}$
fw	2243.54	2395.69	2309.12	2199.03	2624.94	2435.83
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group, no.	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	17.054(3)	24.9079(16)	34.125(3)	14.275(7)	14.1074(15)	18.165(3)
b, Å	18.506(4)	19.0745(12)	12.7336(10)	15.077(7)	20.841(2)	24.870(4)
c, Å	21.499(6)	28.6507(18)	27.676(2)	15.909(8)	22.718(2)	26.031(4)
α, deg	91.804(18)			97.374(9)		
β, deg	102.076(14)	111.5890(10)	105.2320(10)	99.935(9)	96.813(2)	100.971(3)
γ, deg	113.823(18)			112.552(8)		
V, Å^3	6019(2)	12657.2(14)	11603.6(16)	3043(3)	6632.1(12)	11545(3)
D_{calc}, g·cm^{-3}	1.238	1.257	1.322	1.200	1.314	1.401
Z	2	4	4	1	2	4
F(000), electrons	2404	5128	4896	1178	2780	5112
μ(Mo, Kα), cm^{-1}	2.33	4.33	6.96	6.40	10.11	15.89
cryst size, mm	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.05	0.2 × 0.1 × 0.1	0.4 × 0.2 × 0.1	0.3 × 0.3 × 0.3
T, K	203(2)	203(2)	203(2)	203(2)	203(2)	203(2)
θ range, deg: min., max.	0.98, 28.28	1.36, 23.26	1.24, 26.37	1.33, 20.82	1.33, 28.66	1.14, 28.71
λ(Mo, Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
monochromator	graphite	graphite	graphite	graphite	graphite	graphite
index ranges	h: −22→21 k: −23→23 l: 0→28	h: −27→25 k: 0→21 l: 0→31	h: −42→41 k: 0→15 l: 0→34	h: −14→13 k: −15→14 l: 0→15	h: −18→17 k: 0→28 l: 0→30	h: −23→23 k: 0→33 l: 0→34
total no. of data	34 649	99 146	101 348	27 012	51 429	89 433
no. of unique data	24 834	18 163	11 836	6369	15 722	27 277
$wR(F^2)$	0.1717	0.1612	0.1023	0.1839	0.1143	0.1561
$R(F)$	0.0677	0.0658	0.0487	0.0795	0.0399	0.0559
GooF	1.032	1.048	1.016	1.044	1.036	1.027
largest diff peak hole, e/Å^3	0.888, −0.536	0.913, −0.893	0.456, −0.547	0.722, −0.543	0.855, −0.495	0.926, −0.953

X-ray Structure Determination of 2, 4, 5, 6b, 8, and 9. Suitable crystals were selected, mounted on a thin, glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[16] The raw data were routinely processed with XPREP, which flags unit cells with possible higher symmetry settings or super lattices. The space group assignment was unique to the observed unit cells and systematic absences. No symmetry higher than triclinic was observed for **2** and **6b**. Systematic absences in the diffraction data were consistent with *Cc* and *C*2/*c* for **5** and, uniquely, for the reported space groups for **4**, **8**, and **9**. Solution in the centric options yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The compound molecules in **6b** and **8** were located at inversion centers. The compound molecule in **5** is located at a 2-fold axis. The gallium atoms in **9** were found disordered in two chemically equivalent positions with a 70/30 site occupancy. Two cyclopentyl, one cyclopentyl, and one cyclohexyl ring were found disordered in roughly 50/50 site occupancy distributions for **2**, **5**, and **6b**. Hexane molecules were found cocrystallized in the asymmetric units of **2** (one molecule), **4** (one molecule), **6b** (one-half molecule on inversion center), and **8** (one-half molecule on inversion center). A toluene molecule was found cocrystallized in the asymmetric unit of **9**. The crystal structure of **6b** suffers from its *R*-value as a result of a high degree of mosaicity. Thus the data quality was not as good as the others, and the maximum angle of diffraction was also lower than the other compounds. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[17] Detailed data are listed in Table 1.

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Supporting Information Available: Full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and bond distances and bond angles for **2**, **4**, **5**, **6b**, **8**, and **9** and ^{29}Si NMR spectra of compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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