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Synthesis and Structure of [Tris(trimethylsilyl)silyl]-Substituted Gallanes and Gallates

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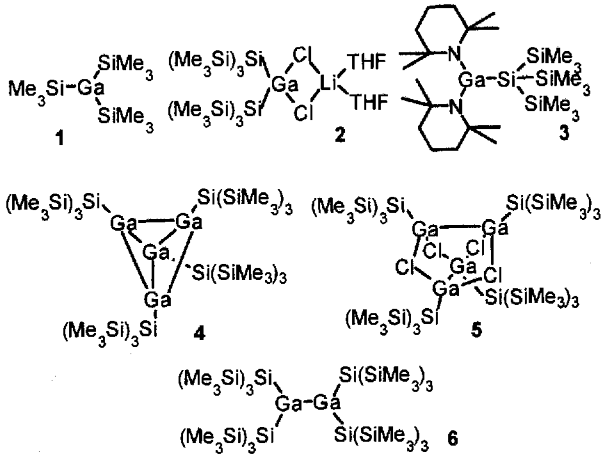
Reaction of lithium tris(trimethylsilyl)silanide · 3 THF with R_2GaCl (R = 2,2,6,6-tetramethylpiperidino, Me, Cl) yields $tmp_2GaSi(SiMe_3)_3$ (**3**) and $R_2Ga(THF)Si(SiMe_3)_3$ (R = Me, Cl) (**7**, **9**). Both gallium nitrogen bonds in **3** are cleaved by protic reagents. Depending on the acidity of these agents, either oligomeric gallanes $[(RO)_2GaSi(SiMe_3)_3]_n$ (R = Et, H, n = 2, 3) (**11**, **12**) or tetramethylpiperidinium gallates $[X_3GaSi(SiMe_3)_3]^-$ (X = OPh, Cl) (**13**, **14**) are formed. Hydroxide **11** adds lithium hydroxide to afford the mixed lithium gallium hydroxide **15**. Single-crystal X-ray diffraction studies confirm the suggested constitutions. The gallium-silicon bond can adopt values between 236 and 247 pm. Here electronic influences of the substituents on the gallium center are of great importance as well as their steric demand. This is underlined by quantum chemical calculations on the ab initio (SCF) level.

Organogallium compounds presently are being investigated intensively. In contrast, the chemistry of compounds with bonds between gallium and silicon has attracted less attention. Rösch et al.[2] synthesized tris(trimethylsilyl)gallane (**1**), the first compound with a gallium silicon bond, by dehalogenation of gallium chloride in the presence of chlorotrimethylsilane. The primary product was **1** · THF, which loses THF on sublimation. This silylgallane **1** is pyrophoric on contact with air and decomposes into gallium and hexamethyldisilane if heated above 50 °C. Gallane **1** possesses a planar $GaSi_3$ framework, as deduced from an analysis of its vibrational spectra. Compounds **2** to **6**[1,3–5] are the only compounds with gallium silicon bonds, which have been structurally characterized so far.

This work describes the synthesis of new silyl gallanes, mostly starting from the bis(amino)silylgallane **3**.

Scheme 1



Reactions

The reaction of lithium tris(trimethylsilyl)silanide · 3 THF[6] with bis(2,2,6,6-tetramethylpiperidino)gallium chloride[7] affords **3** (eq. 1). The analogous reaction of lithium tris(trimethylsilyl)silanide · 3 THF with dimethylgallium chloride yields the tetrahydrofuran adduct **7** (eq. 2). An attempt to prepare base-free $Me_2GaSi(SiMe_3)_3$ by sublimation gave a variety of unidentifiable decomposition products. It was however possible to replace THF by trimethylphosphane, leading to the formation of **8** (eq. 3). If lithium tris(trimethylsilyl)silanide · 3 THF is allowed to react with an excess of gallium(III) chloride, **9** crystallizes in good yields (eq. 2). If only a 1:1 or a 1:2 stoichiometry is applied the main product is **2**. Compound **9** is also formed as the only isolated product by addition of lithium tris(trimethylsilyl)silanide · 3 THF to a solution of gallium(I,III) chloride in toluene (eq. 4). With humid 2,6-dimethylpyridine it forms the hydrolysis product **10** (eq. 5).

3 and **7** dissolve readily in all common organic solvents. **3** decomposes above 150 °C into gallium and various unidentifiable organic products. **7** ignites on exposure to air, whereas **3** is even stable towards oxidation by oxygen and sulfur in boiling hexane. This may be attributed to the well-shielded gallium-silicon bond in **3**. The bis(amino)silylgal-

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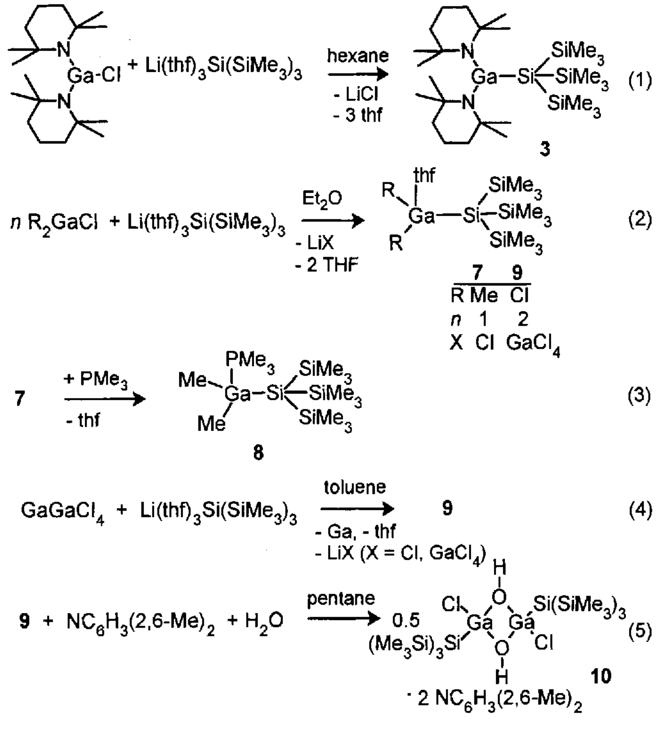
lane 3 is very sensitive to humidity. It hydrolyzes to **11** and 2,2,6,6-tetramethylpiperidine (Scheme 3), when it is dissolved in water or treated with stoichiometric amounts of water. Obviously, the gallium-silicon bond is not attacked but the gallium-nitrogen bonds are. Ethanol also cleaves the gallium-nitrogen bonds. Here dimeric **12** was isolated. The formation of trimeric **11** is not usual. Normally, hydrolysis of triorganylgallanes affords oligomeric diorganylhydroxygallanes like $[t\text{Bu}_2\text{Ga(OH)}]_3$[8] and $[\text{Me}_2\text{Ga(OH)}]_4$[9]. Organyldihydroxygallanes are rare, usually undergo partially condensation; examples are the hydrolysis products of dimesitylgallium fluoride and trimesitylgallane $[\text{Ga}_6\text{Mes}_6\text{O}_4\text{X}_4]$ (X = F[10], OH[11]) and $[\text{Ga}_{12}t\text{Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$[12]. The latter was obtained by oxidative hydrolysis of tri-*tert*-butylgallane. The formation of the first gallium-oxo cluster $[t\text{Bu}_2\text{GaO}]_9$ was achieved by heating of $[t\text{Bu}_2\text{Ga(OH)}]_3$ in xylene[8c]. $[2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Ga(OH)}_2]_3 \cdot 10\ \text{H}_2\text{O}$ is the only known dihydroxide of gallium[13].

Scheme 2

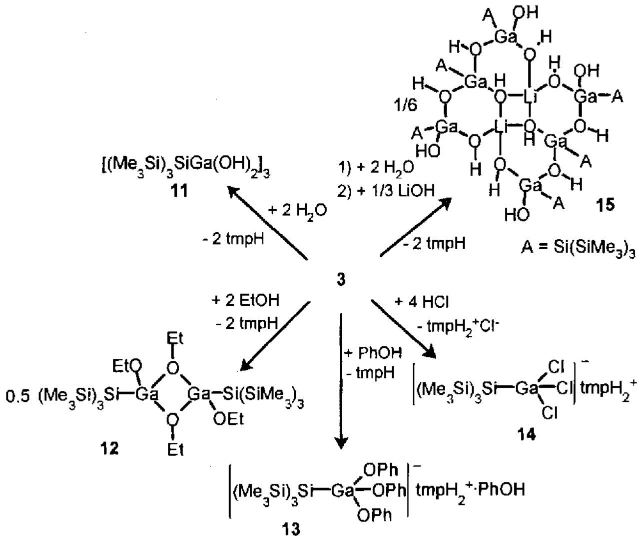


Thus, the hydrolytic (alcoholytic) elimination of amine from **3** is a useful route to dihydroxygallium(III) compounds. Similarly, tris(amino)alanes are cleaved by alcohols to give mixed aminoalkoxyalanes[14]. Partially hydrolyzed alkylaluminium[15a] and alkylgallium compounds[15b] are highly active cocatalysts for titanium and zirconium metallocenes in polymerization reactions. At present, their structures are the subject of intensive research[16], and derivatives bearing bulky substituents may serve as models.

Phenol reacts with **3**, but in a manner differing from that of ethanol. Formally, a 2,2,6,6-tetramethylpiperidinium phenolate adds to [tris(trimethylsilyl)silyl]gallium diphenoxide to afford the [tris(trimethylsilyl)silyl]triphenoxygallate as the tetramethylpiperidinium salt **13**. This behavior was expected on the basis of the pK_a value of phenol. Hydrogen chloride behaves analogously, thus allowing the isolation of **14**.

If a solution of **11** in diethyl ether is stirred with lithium hydroxide the mixed metal hydroxide **15** is isolated as colorless crystals.

Scheme 3



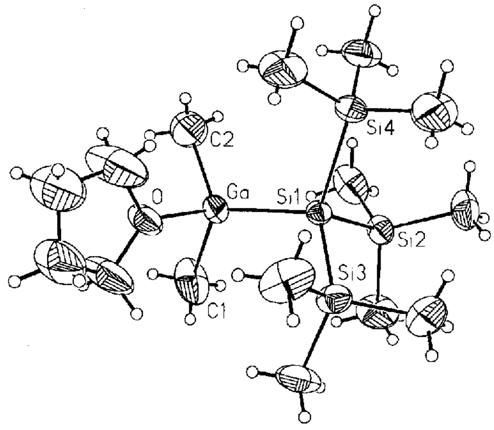
Spectroscopic Data

In the ^{1}H- and ^{13}C-NMR spectra of compounds **3** to **15** the signals of the trimethylsilyl groups appear at low field compared to those of tetrakis(trimethylsilyl)silane. In the ^{29}Si-NMR spectra the signal of the silicon atom bound to gallium is observed between $\delta = -115$ (**3**) and -142 (**15**). In general, the chemical shift of the central silicon atom in compounds $(\text{Me}_3\text{Si})_3\text{SiX}$ is very sensitive to a change in polarity of the SiX bond[17]. For example, in the spectrum of $(\text{Me}_3\text{Si})_3\text{SiF}$ the relevant silicon atom's signal appears at $\delta = -33.4$, in that of $(\text{Me}_3\text{Si})_3\text{SiAlCl}_3\text{Li(THF)}_4$[18] at $\delta = -108$ and in those of $(\text{Me}_3\text{Si})_4\text{Si}$[6c] and $(\text{Me}_3\text{Si})_3\text{SiSi(SiMe}_3)_3$[6c] at $\delta = -135.5$ and -130.0. The spectrum of $(\text{Me}_3\text{Si})_3\text{SiLi(THF)}_3$, which contains a more ionic lithium-silicon bond, exhibits a signal at $\delta = -189.4$[6c]. The observed shifts of the gallium compounds are therefore an indication of a non-polar gallium-silicon bond, which is also expected from the electronegativities of the two elements.

Crystal-Structure Analysis

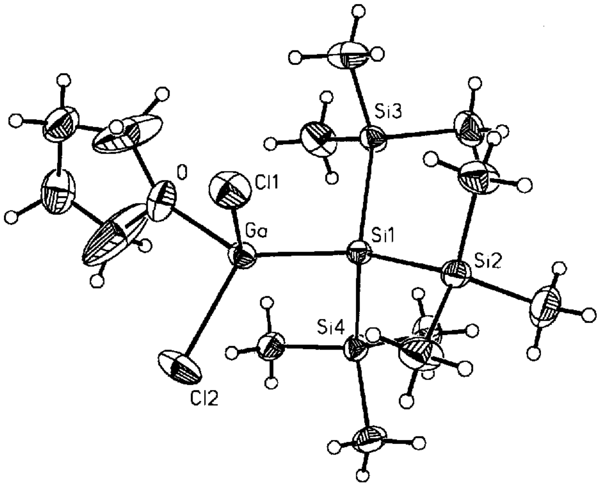
7 crystallizes in the orthorhombic crystal system, space group $Pna2_1$. Single, not mirrorsymmetric molecules are found in the crystal, incorporating a gallium atom which is tetracoordinated by a silicon atom, two carbon atoms, and one oxygen atom (Figure 1). The gallium-silicon distance is 240.8 pm, which is nearly the sum of covalent radii of these elements. The Shomaker-Stevenson formula, adapted by Blom and Haaland[19], predicts a gallium-silicon bond length of 242 pm, if standard covalent radii are used for gallium and silicon[20]. Compound **3** containing bulky substituents and a tricoordinated gallium atom, has a remarkably longer gallium-silicon bond of 246.8(2) pm[4]. **2** also has a longer gallium-silicon bond (d = 243.9 pm)[3]. The bond angles between the silicon atoms at the central silicon atom are nearly tetrahedral. Although the Ga–Si–Si angles are on an average 109.6°, they are different from one another. The smallest is the Ga–Si(1)–Si(2) angle, the Si(1)Si(2) bond being *anti* to the gallium-oxygen bond. This shows the tendency of the molecule to release steric strain caused by the tris(trimethylsilyl)silyl group. More bulky substituents than the $Me_2Ga(THF)$ group like R = tmp_2Ga, $(THF)_3Li$, and $(Me_3Si)_3Si$ give rise to Si–Si(1)–Si angles as small as 102° and RSi(1)Si angles as wide as 116°. The coordination tetrahedron of the gallium atom is distorted. Thus, the gallium atom lies only 40 pm above the C(1)/C(2)/Si(1) plane. In an ideally tetrahedral coordination sphere this should be about 80 pm. Consequently, bond angles of 115 to 118° between these carbon and silicon atoms and O–Ga–X angles [X = C(1), C(2), Si(1)] of approx. 100° are found. The gallium carbon distances are in the normal range.

Figure 1. ORTEP plot of a molecule of **7**; the thermal ellipsoids represent 50% probability. Selected bond lengths [pm] and angles [°]: Ga–Si(1) 240.8(2), Ga–C(1) 198.7(6), Ga–C(2) 198.2(8), Ga–O 211.7(6), Si(1)–Si(2) 234.9(3), Si(1)–Si(3) 232.8(3), Si(1)–Si(4) 234.4(2); Si(1)–Ga–C(1) 117.9(3), Si(1)–Ga–C(2) 117.6(3), C(1)–Ga–C(2) 114.7(5), Si(1)–Ga–O 106.2(2), C(1)–Ga–O 98.3(3), C(2)–Ga–O 98.3(4), Ga–Si(1)–Si(2) 102.6(1), Ga–Si(1)–Si(3) 114.3(1), Ga–Si(1)–Si(4) 112.1(1), Si(2)–Si(1)–Si(3) 110.1(1), Si(2)–Si(1)–Si(4) 106.9(1), Si(3)–Si(1)–Si(4) 110.4(1)



9 crystallizes orthorhombic, space group *Pccn*. This compound, too, has a distorted tetrahedrally coordinated gallium atom (Figure 2). The bond angles centered at the gallium atom resemble those of **7**. Only the bond angle Cl(1)–Ga–Cl(2) (106.1°) is more acute than the comparable C(1)–Ga–C(2) angle in **7**. The gallium-oxygen distance [201.0(3) pm] in **9** is 10 pm shorter than in **7**. This is a consequence of the higher Lewis acidity of $Cl_2GaSi(SiMe_3)_3$ than that of $Me_2GaSi(SiMe_3)_3$. The gallium-silicon bond length [236.2(1) pm] is shortened by 5 pm compared to that in **7**. The Ga–Si(1)–Si(2) angle is again the only one at Si(1) that differs markedly from the tetrahedral angle. The gallium-oxygen and gallium-chlorine bond lengths in **9** are similar to those in tripGaCl$_2$ · THF[21]. The

Figure 2. ORTEP plot of a molecule of **9**; thermal ellipsoids represent 50% probability. Selected bond lengths [pm] and angles [°]: Ga–Si(1) 236.2(1), Ga–Cl(1) 219.8(1), Ga–Cl(2) 220.3(1), Ga–O 201.0(3), Si(1)–Si(2) 234.6(2), Si(1)–Si(3) 233.9(2), Si(1)–Si(4) 234.2(2); Si(1)–Ga–Cl(1) 118.45(5), Si(1)–Ga–Cl(2) 119.87(5), Cl(1)–Ga–Cl(2) 106.15(5), Si(1)–Ga–O 112.98(11), Cl(1)–Ga–O 98.5(1), Cl(2)–Ga–O 96.8(1), Ga–Si(1)–Si(2) 103.23(5), Ga–Si(1)–Si(3) 110.05(5), Ga–Si(1)–Si(4) 112.70(6), Si(2)–Si(1)–Si(3) 111.97(6), Si(2)–Si(1)–Si(4) 110.85(6), Si(3)–Si(1)–Si(4) 112.70(6)



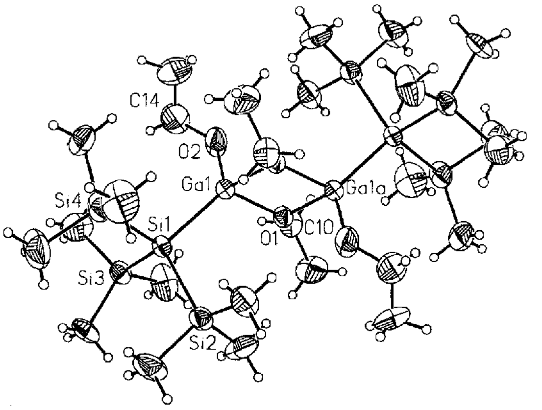
gallium-chlorine bonds are longer than the terminal ones in Ga_2Cl_6 (d_{Ga-Cl} = 210 pm)[22].

12, crystallizing in the monoclinic crystal system, space group *P2$_1$/c*, is a centrosymmetric dimer. One of the ethoxy groups at the gallium atom occupies a bridging position (Figure 3). The planar Ga_2O_2 ring has acute angles at the gallium atoms and wide ones at the oxygen atoms. The gallium-oxygen distances in the Ga_2O_2 four-membered ring are slightly different, but are in the typical range [193.9 pm (average)], which was found for other dimeric gallium ethoxides[23,24]. The tricoordinated oxygen atoms are pyramidal (sum of angles: 349.5°). The gallium-oxygen bonds to the terminal ethoxy ligands are 15 pm shorter. Even the bonds in monomeric diorganylgallium aryl oxides are longer by 4 pm. Comparably short is the gallium-oxygen bond in a known digalloxane[25]. The short gallium-oxygen bond of **12** featuring a tetracoordinated gallium atom suggests that π interactions do not play a major role in the formation of gallium-oxygen bonds (for a discussion of possible $(p,\sigma^*)\pi$ interactions see ref.[26]).

The gallium-silicon bond in **12** is shorter than in **3** and **7**, but comparable to that in **9**. This is understandable in terms of contraction of the effective covalent radius of gallium by electronegative bonding partners (chlorine, oxygen).

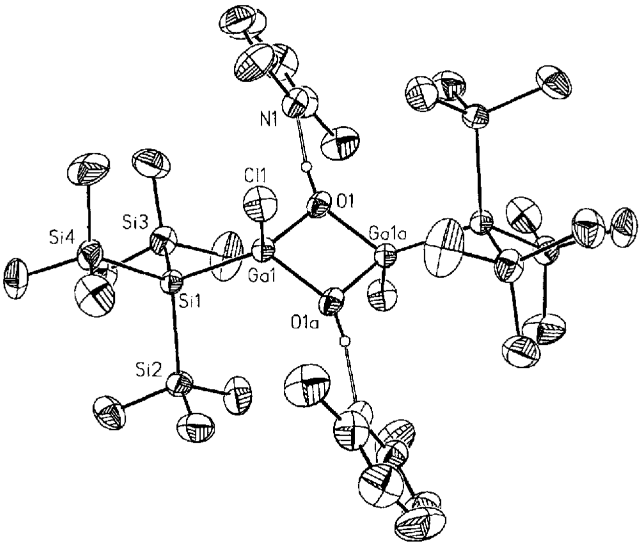
The structure of **10** is similar to that of **12**. It crystallizes as a centrosymmetric dimer with bridging hydroxy groups in the triclinic system, space group $P\bar{1}$. The diamond-shaped Ga_2O_2 ring has inner ring angles of approx. 80° at the gallium atoms and approx. 100° at the oxygen atoms (Figure 4). The gallium-oxygen bond lengths are 189.4 pm (average). This is shorter than in **12** and in diorganylgallium hydroxides (d_{Ga-O} = 194–200 pm)[8,9]. The coordination tetrahedra of the gallium atoms are distorted. Thus, the bond angles at the gallium atom with participation of Si(1) are the largest (117.3−123.7°). The gallium-silicon bond length (238 pm) is comparable to that in **12** and the silicon-silicon bond lengths in both compounds are nearly equal. The gallium-chlorine bond is longer than usual for terminal gallium-chlorine bonds in dimeric gallium compounds[21,24,27]. This structural description of **10** is not complete. A 2,6-dimethylpyridine unit is bound via a nearly linear N···H−O hydrogen bond (angle N−H−O 168.2°, d_{N-O} = 283 pm) to each hydroxy group. $[Mes^{F}Ga(Cl)OH]_2 \cdot 2\,OEt_2$ [$Mes^{F} = 2,4,6\text{-}(CF_3)_3C_6H_2$][28] has similar gallium-oxygen bond lengths, but a folded Ga_2O_2 ring and shorter gallium-chlorine bonds [214.3(2) pm].

Figure 3. ORTEP plot of a molecule of **12**; thermal ellipsoids represent 50% probability. Selected bond lengths [pm] and angles [°]: Ga(1)−Si(1) 238.8(2), Ga(1)−O(2) 178.6(6), Ga(1)−O(1) 192.7(5), Ga(1)−O(1)a 195.0(5), Si(1)−Si(2) 235.3(3), Si(1)−Si(3) 235.9(3), Si(1)−Si(4) 234.5(4), O(1)−C(10) 143.3(9), O(2)−C(14) 135.1(11); O(2)−Ga(1)−O(1) 98.4(3), O(2)−Ga(1)−O(1)a 104.7(3), O(1)−Ga(1)−O(1)a 80.1(2), O(2)−Ga(1)−Si(1) 125.9(2), O(1)−Ga(1)−Si(1) 118.5(2), O(1)a−Ga(1)−Si(1) 118.8(2), Si(4)−Si(1)−Si(2) 111.07(13), Si(4)−Si(1)−Si(3) 107.65(13), Si(2)−Si(1)−Si(3) 109.16(13), Si(4)−Si(1)−Ga(1) 113.20(12), Si(2)−Si(1)−Ga(1) 108.62(11), Si(3)−Si(1)−Ga(1) 106.99(10), C(10)−O(1)−Ga(1) 126.4(5), C(10)−O(1)−Ga(1)a 123.2(5), Ga(1)−O(1)−Ga(1)a 99.9(2), C(14)−O(2)−Ga(1) 128.4(7)



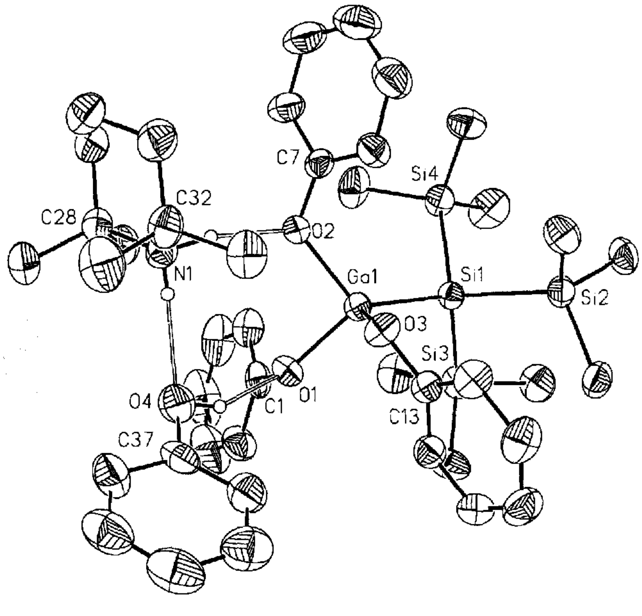
Comparably short gallium-silicon bonds as in **9**, **10**, and **12** were also found for **13**. This triphenoxy[tris(trimethylsilyl)silyl]gallate crystallizes in the triclinic space group $P\bar{1}$. In addition, the lattice contains a disordered, half-occupied toluene molecule. The gallium atom of **13** (Figure 5) is coordinated by three phenoxy ligands and a tris(trimethylsilyl)silyl group. Thus, a distorted tetrahedron is obtained. The O−Ga−O angles are small (100°), and the O−Ga−Si angles are wider than the tetrahedral angle, due to the bulky silyl substituent. The bond angles at the central silicon atom deviate from a tetrahedral angle by only ±4°. The three phenoxy groups are not equivalent in the crystal. Two of them are involved in the formation of hydrogen bonds between the 2,2,6,6-tetramethylpiperidinium counter ion and a phenol molecule. Together with the hydrogen bond between this ion and the phenol molecule an eight-membered ring results. The N−H···O and O−H···O distances are typical of hydrogen bonds of these types[29]. The gallium-oxygen bonds differ from one another, whereby the bonds between the phenoxy groups involved in hydrogen bonds and gallium are longer. Their average distance ($\bar{d}_{Ga-O}$ = 185.8 pm) is shorter than gallium-oxygen bonds in dimeric alkoxygallanes but longer than the terminal bonds in **12** and monomeric aryloxygallanes. In solution this hydrogen-bonded molecular cluster is not maintained as revealed by NMR data.

Figure 4. ORTEP plot of a molecule of **10**; thermal ellipsoids represent 50% probability; hydrogen atoms (except hydroxylic ones) omitted for clarity in the plot. Selected bond lengths [pm] and angles [°]: Ga(1)−Si(1) 238.4(3), Ga(1)−O(1) 189.0(8), Ga(1)−O(1)a 189.7(6), Ga(1)−Cl(1) 222.3(2), Si(1)−Si(2) 234.0(4), Si(1)−Si(4) 235.1(4), Si(1)−Si(3) 235.3(4); O(1)−Ga(1)−O(1)a 78.8(3), Ga(1)−O(1)−Ga(1)a 101.2(3), O(1)−Ga(1)−Cl(1) 104.1(2), O(1)a−Ga(1)−Cl(1) 104.6(2), O(1)−Ga(1)−Si(1) 123.7(2), O(1)a−Ga(1)−Si(1) 121.2(2), Cl(1)−Ga(1)−Si(1) 117.3(1), Si(2)−Si(1)−Si(4) 112.4(2), Si(2)−Si(1)−Si(3) 108.1(2), Si(4)−Si(1)−Si(3) 112.4(2), Si(2)−Si(1)−Ga(1) 106.6(1), Si(4)−Si(1)−Ga(1) 107.0(1), Si(3)−Si(1)−Ga(1) 110.3(1)



15 crystallizes together with a highly disordered diethyl ether molecule in the triclinic space group $P\bar{1}$. The centrosymmetric molecule of a mixed gallium lithium hydroxide can be described by a $(LiOH)_2$ four-membered ring fused with four six-membered rings consisting of gallium and oxygen atoms (Figure 6). If one considers only the metal-containing skeleton, molecule **15** may be described as two distorted trigonal bipyramids, which are linked by a common lithium-lithium edge. The hydroxy groups are bridging the edges of these polyhedrons or lie above the Li_2Ga faces. Metal-metal interactions are not expected, although the shortest lithium-lithium (286.8 pm), lithium-gallium (321.8 pm) and gallium-gallium distances (342.9 pm) are smaller than the sum of van der Waals radii. In an alternative view this polycyclic molecule is represented by a cluster of corner-connected GaO_3Si and LiO_4 tetrahedra (Figure 7). Selected bond lengths and angles are compiled in Table 1. Compound **15** contains four different kinds of hydroxy groups with different gallium-oxygen bond lengths. The presence of different hydroxy groups was already inferred from the infrared spectrum, which shows four sharp and one broad band in the region typical of vOH. The oxygen-bound hydrogen atoms were taken from a difference Fourier map and refined with fixed thermal parameters. Nevertheless, their positions are afflicted with slight precariousness. An isomeric constitution with terminal water molecules and partial oxo bridges can be excluded on the basis of the gallium-oxygen and lithium-oxygen distances. The terminal gallium-oxygen distances average 187.4 pm. The Ga(μ_2-OH)Ga subunits have longer gallium-oxygen bond lengths [194 pm (aver.)]. For comparison, the gallium oxygen distances in $[t\text{Bu}_2\text{Ga(OH)}]_3$[8] and $[\text{Me}_2\text{Ga(OH)}]_4$[9] are very similar to the latter. Structural data of terminal GaOH groups are rare. To our knowledge $[2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Ga(OH)}_2]_3 \cdot 10\ \text{H}_2\text{O}$[13] is the only example [d_{GaO} = 182.4 pm (average)]. The terminal gallium-oxygen distances in **13** resemble the values found for **15**. Both other kinds of hydroxy groups are additionally coordinated to one or two lithium atoms. Here the averaged gallium-oxygen distance is 184.4 pm. This is intermediate between the gallium-oxygen bond lengths of dimeric and monomeric gallium alkoxides.

Figure 5. ORTEP plot of a molecule of **13**; thermal ellipsoids represent 50% probability; hydrogen atoms (except those participating in hydrogen bonding) omitted for clarity in the plot. Selected bond lengths [pm] and angles [°]: Ga(1)–Si(1) 237.0(2), Ga(1)–O(1) 185.3(4), Ga(1)–O(2) 189.2(4), Ga(1)–O(3) 182.9(4), Si(1)–Si(2) 236.2(3), Si(1)–Si(3) 235.0(3), Si(1)–Si(4) 226.8(3), N(1)–H(01) 79(7), N(1)–H(02) 94(7), O(4)–H(03) 76(7), N(1)–O(2) 286, N(1)–O(4) 276, O(1)–O(4) 267; O(1)–Ga(1)–O(2) 96.5(7), O(1)–Ga(1)–O(3) 97.0(6), O(2)–Ga(1)–O(3) 103.2(7), O(1)–Ga(1)–Si(1) 121.4(5), O(2)–Ga(1)–Si(1) 120.7(5), O(3)–Ga(1)–Si(1) 114.0(5), Ga(1)–Si(1)–Si(2) 110.2(3), Ga(1)–Si(1)–Si(3) 113.1(3), Ga(1)–Si(1)–Si(4) 111.3(3), Si(2)–Si(1)–Si(3) 107.7(4), Si(2)–Si(1)–Si(4) 108.9(4), Si(3)–Si(1)–Si(4) 105.5(4)



The lithium-oxygen distances of the μ_3-hydroxy groups are longer by 10 pm than those of the μ_2-hydroxy groups. The latter are comparable to lithium-oxygen distances in ether adducts of lithium compounds[30] [193 pm (average)]. In lithium hydroxide itself ($d_{\text{Li-O}}$ = 197 pm)[22] and its hydrate ($d_{\text{Li-OH}}$ = 195.5 pm, $d_{\text{Li-OH}_2}$ = 197.4 pm)[31] similar distances are observed. The lithium-oxygen distances of

Figure 6. ORTEP plot of a molecule of **15**; thermal ellipsoids represent 50% probability; methyl groups have been omitted for clarity in the plot

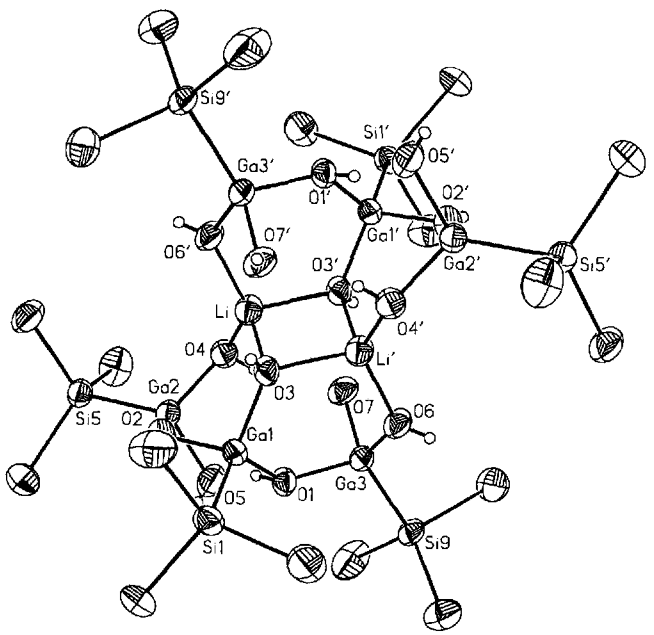


Figure 7. Linking of MO_3X tetrahedra (M = Ga, Li; X = O, Si) in **15**

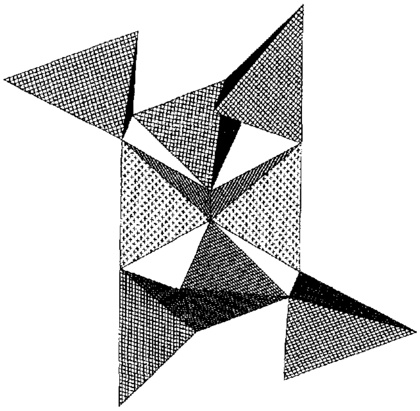


Table 1. Selected bond lengths [pm] and angles [°] for **15**

Bond lengths	**[pm]**		
O(1)-Ga(1)	189.3(6)	O(4)-Li(1)	193(2)
O(1)-Ga(3)	192.6(6)	O(5)-Ga(2)	188.8(7)
O(2)-Ga(1)	195.0(7)	O(6)-Ga(3)	184.3(7)
O(2)-Ga(2)	195.4(7)	O(6)-Li(1)'	189(2)
O(3)-Ga(1)	184.8(6)	O(7)-Ga(3)	185.9(7)
O(3)-Li(1)	202(2)	Ga(1)-Si(1)	237.8(3)
O(3)-Li(1)'	202(2)	Ga(2)-Si(5)	237.7(3)
O(4)-Ga(2)	184.0(8)	Ga(3)-Si(9)	239.9(3)
Bond angles	**[°]**		
Ga(1)-O(1)-Ga(3)	134.5(3)	Li(1)-O(3)-Li(1)'	90.6(7)
Ga(1)-O(2)-Ga(2)	122.8(3)	Ga(2)-O(4)-Li(1)	126.9(6)
Ga(1)-O(3)-Li(1)	117.8(5)	Ga(3)-O(6)-Li(1)'	118.8(6)
Ga(1)-O(3)-Li(1)'	121.9(6)		

oxygen atoms coordinated by three metal atoms are longer, pointing to weak lithium-oxygen interactions. For oxidic oxygen atoms shorter lithium-oxygen (≈ 160 pm in Li_2O)[22] and gallium-oxygen bond lengths would be expected. The Ga−O−M bond angles are between 118 and 135°, which is near the values observed in $[t\mathrm{Bu}_2\mathrm{GaOH}]_3$[8b] and in compounds with terminal alkoxy and phenoxy ligands. The gallium-silicon bonds are as short as in **12**, the silicon-silicon bonds are normal for the tris(trimethylsilyl)silyl ligand [234 pm (average)]. The bond angles at the silicon atoms bound to gallium are near 109°.

Quantum-Chemical Results

X-ray crystallographic studies indicate a range of 10 pm for the gallium-silicon bonds between 236.2 and 247.8 pm. Table 2 summarizes the results of ab initio calculations on the SCF level for the model compounds $(H_2N)_2GaSiH_3$, $R_2GaSi(SiH_3)_3$, and $R_2Ga(OH_2)Si(SiH_3)_3$ (R = NH_2, Me, Cl). For molecules with a tricoordinated gallium atom the gallium-silicon bond lengths vary from 239.7 to 245.7 pm. Here more polar gallium-R bonds are parallel to shorter gallium-silicon bonds. Adduct formation with water results in a lengthening of the gallium-silicon bond, as expected from the effects of a change in the coordination number. The dimethylgallyl derivative gives a weaker Lewis base adduct than the chloride. The calculated enthalpies of adduct formation of these compounds are $\Delta H = -77$ and -121 kJ/mol, respectively. This is also obvious from the gallium-oxygen distances, which are shorter by 10 pm in the chlorine derivative than in the methyl derivative, which is similar to the experimental values for **7** and **9**. A shorter gallium-silicon bond for **9** compared to **7** was predicted by calculations, but the absolute calculated values are larger than the experimental ones. **3** has the longest observed gallium-silicon bond, in contrast to $(H_2N)_2GaSi(SiH_3)_3$ for which a gallium-silicon bond length shorter than in the methyl derivative was predicted. This reflects the influence of steric factors on the gallium-silicon bond length. The same conclusion may be drawn from simple MM+ force-field calculations. Thus, for **3** a gallium-silicon bond length of 246 pm was calculated, for $(H_2N)_2GaSi(SiMe_3)_3$ only 243 pm. By similar calculations on **7** and **9** gallium-silicon distances of 238 and 237 pm were found. These values are in good accordance with the X-ray data. The steric demand can influence the gallium-silicon bond to a great extent, because this bond seems to be "elastic". The change in energy for $(H_2N)_2GaSi(SiH_3)_3$, as derived from single-point ab initio calculations, is only 2 kJ/mol if the gallium-silicon bond is elongated between 236 and 247 pm. This is the known range for gallium-silicon bonds. Obviously, very small changes in the bulkiness or electronegativity of the substituents result in large changes of the gallium-silicon distances.

Conclusions

The bis(amino)silylgallane **3** proved to be a valuable compound for the preparation of various silylgallanes and gallates by reaction with protic reagents. In this reaction the gallium-nitrogen bonds are cleaved, but the gallium-silicon bond is not affected. From X-ray crystallographic data and quantum-chemical calculations it was concluded that the gallium-silicon bond is sensitive to electronic and steric influences. **9** will be a versatile starting material for the synthesis of new compounds containing gallium-silicon bonds.

Table 2. Bond lengths [pm] as results of ab initio (SCF) calculations on silyl gallium compounds

Compound	d_{Ga-Si}	d_{Ga-X}	d_{Ga-O}	d_{Si-Si}
$(H_2N)Ga-SiH_3$	242.9	179.5		
$(H_2N)Ga-Si(SiH_3)_3$	242.2	179.5		235.1
$Cl_2Ga-Si(SiH_3)_3$	239.7	220.0		235.3
$Cl_2Ga(OH_2)-Si(SiH_3)_3$	239.9	223.8	202.6	235.0
$Me_2Ga-Si(SiH_3)_3$	245.7	198.2		235.0
$Me_2Ga(OH_2)-Si(SiH_3)_3$	248.1	199.0	212.6	235.0

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Experimental

All handling was performed under purified nitrogen or in vacuo by using Schlenk techniques. – NMR: Bruker ACP 200 and 250. – MS: Atlas CH7 or Varian MAT 711. – Elemental analyses: Microanalytic laboratory of the Institut für Anorganische Chemie (München). – Melting points (uncorrected): In sealed capillaries. – Single-crystal X-ray diffraction: Suitable crystals were mounted with a perfluorated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head or were sealed under argon in a Lindemann capillary. Data were collected with Mo-K_α radiation in the ω scan mode with Syntex P3 (**13**), Siemens P4 (**7**, **12**, **15**), and Stoe STADI4 (**9**, **10**) diffractometers by using commercial software. Structures were solved with the program XS from Siemens SHELXTL (PC) and refined against F^2 (full matrix) with SHELXL93. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon atoms were included as riding model with fixed isotropic U values in the final refinement. OH and NH hydrogen atoms were taken from a difference Fourier map and refined isotropically (partially with fixed isotropic U). For further details see Table 3 and ref.[32]. – Quantum-chemical calculations: The program GAUSSIAN94 (Windows PC version)[33] installed on a Pentium 90 PC was used with the base set LANL2DZ[34] for all atoms. – Gallium halides were prepared from the elements[35], $Li(THF)_3Si(SiMe_3)_3$[6], tmp_2GaCl[7], $tmp_2GaSi(SiMe_3)_3$[4] as described in the literature. Other chemicals were used as purchased.

Dimethyl[tris(trimethylsilyl)silyl]gallium–Tetrahydrofuran (**7**): 4.0 ml of a solution of methyllithium in diethyl ether (c = 1.64 mol/l) was added slowly at −78 °C to a solution of $GaCl_3$ (0.58 g, 3.28 mmol) in 20 ml of diethyl ether. After careful warming to ambient temp. and stirring for 4 h a solution of $LiSi(SiMe_3) \cdot 3$ THF (1.54 g, 3.28 mmol) in 10 ml of diethyl ether was added between −78 and −30 °C. After stirring for 20 h at room temp. and subsequent filtration, from the reduced solution (5 ml) colorless prisms of **7** crystallized; yield: 0.85 g (62%), m.p. 75–77 °C. – ^1H NMR

Table 3. Data of the crystal structure analyses

Compound	**7**	**9**	**10**	**12**	**13**	**15**
Formula	$C_{15}H_{41}GaOSi_4$	$C_{13}H_{35}Cl_2GaOSi_4$	$C_{16}H_{37}ClGaNOSi_4$	$C_{13}H_{37}GaO_2Si_4$	$C_{42}H_{68}GaO_4NSi_4 \cdot 0.25C_7H_8$	$C_{27}H_{88}Ga_3LiO_7Si_{12} \cdot 0.5\ C_4H_{10}O$
Mol. mass	419.6	460.39	477.0	407.5	855.8	1115.2
Temperature [K]	183	210	213	203	293	210
Crystal size [mm]	0.65 x 0.25 x 0.2	0.50 x 0.50 x 0.50	1.0 x 0.70 x 0.10	0.20 x 0.18 x 0.15	0.55 x 0.50 x 0.35	0.4 x 0.3 x 0.2
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	$Pna2_1$	$Pccn$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [pm]	1950.4(10)	1336.5(3)	1031.6(2)	925.7(3)	1258.6(3)	1517.5(3)
b [pm]	1307.2(5)	2814.2(6)	1069.7(2)	1725.4(7)	1434.8(3)	1606.3(10)
c [pm]	995.2(7)	1321.6(3)	1359.1(3)	1549.7(5)	1518.0(3)	1655.7(3)
α [°]	90	90	71.56(3)	90	70.04(3)	82.14(3)
β [°]	90	90	69.11(3)	107.18(2)	81.63(3)	69.97(3)
γ [°]	90	90	82.23(3)	90	76.36(3)	65.43(3)
V [nm^3]	2.537(3)	4.971(2)	1.3288(5)	2.365(1)	2.4976(9)	3.448(2)
Z	4	8	2	4	2	2
μ [mm^{-1}]	1.272	1.230	1.32	1.37	0.68	1.40
ρ_r [gcm^{-3}]	1.098	1.513	1.19	1.14	1.14	1.06
2Θ range	4 - 50	4 - 50	5 - 50	4 - 52	3 - 48	3 - 47
Refl. measured (in)	4586 ($h\pm kl$)	4815 ($-h$-kl)	6921 ($\pm h\pm k\pm l$)	4976 ($-h$-$k\pm l$)	7689 ($h\pm k\pm l$)	10374 ($\pm h\pm k\pm l$)
Unique reflections	2381	4371	4668	4635	7294	9636
Observed (with $F>n\sigma(F)$)	1996 (4)	3028 (4)	2853 (4)	2023 (4)	4602 (4)	6407 (4)
Structure solution with	Direct methods	Direct methods	Direct methods	Heavy-atom method	Heavy-atom method	Direct methods
R	0.047	0.041	0.096	0.076	0.065	0.075
$wR2$	0.105	0.110	0.230	0.117	0.160	0.204
Weighting scheme x/y [a]	0.0375/0.00	0.0687/3.4127	0.100/0.00	0.0331/0.00	0.0955/1.3012	0.0827/29.631
Data/parameters	11.9	22.0	20.2	24.1	14.2	18.4
Largest Δ/σ	0.000	0.000	0.001	0.000	0.000	0.036
largest residual electron density [eÅ^{-3}]	0.74	0.61	2.30 (near Ga)	0.57	0.72	0.82

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$

(C_6D_6): δ = 3.41 (m, 4H, OCH_2), 1.30 (m, 4H, CH_2), 0.47 (s, 27H, $SiMe_3$), −0.02 (s, 6H, GaMe). − ^{13}C NMR (C_6D_6): δ = 68.5 (OCH_2), 25.4 (CH_2), 4.2 ($SiMe_3$), −1.9 (br., GaMe). − $C_{15}H_{41}GaOSi_4$ (419.6): calcd. C 42.94, H 9.85; found 39.82, H 9.48.

Reaction of **7** *with Trimethylphosphane with Formation of* **8**: A solution of **7** (0.12 g, 0.26 mmol) in 23 ml of pentane was mixed with trimethylphosphane (0.05 ml, 0.5 mmol), and the mixture was stirred for 2 h. Then all volatile components were removed in vacuo. The residue was investigated by NMR spectroscopy. − ^1H NMR (C_6D_6): δ = 0.65 (d, $^2J_{PH}$ = 5 Hz, PMe_3), 0.44 (s, $SiMe_3$). − ^{31}P NMR (C_6D_6): δ = −40.6.

Dichloro[tris(trimethylsilyl)silyl]gallium−Tetrahydrofuran (**9**). − *Method 1:* To a solution of $LiSi(SiMe_3)_3 \cdot 3$ THF (0.40 g, 0.84 mmol) in 5 ml of diethyl ether a solution of gallium(III) chloride (0.30 g, 1.67 mmol) in 5 ml of diethyl ether was added at −78 °C. After warming to room temp. the mixture was stirred for 15 h. Then all volatile components were removed in vacuo, and the residue was taken up in 5 ml of hexane. After filtration of the solution 0.25 g of **9** (65%) crystallized from the filtrate as large colorless plates, m.p. >80 °C (dec.). − *Method 2:* $GaGaCl_4$ (0.19 g, 0.68 mmol) was dissolved in 40 ml of toluene. At room temp. a solution of $LiSi(SiMe_3)_3 \cdot 3$ THF (0.32 g, 0.68 mmol) in 15 ml of toluene was added dropwise such that the observed red color vanished before the next drop was added. After further stirring of the mixture for 8 h all volatile components were removed in vacuo, and the residue was taken up in hexane. After filtration the solution was reduced to 2 ml and cooled to −30 °C. 0.14 g of **9** (44%) crystallized. − ^1H NMR (C_6D_6): δ = 3.72 (m, 4H, OCH_2), 1.10 (m, 4H, CH_2), 0.38 (s, 27H, $SiMe_3$). − ^{13}C NMR (C_6D_6): δ = 69.1 (OCH_2), 25.8 (CH_2), 2.8 ($SiMe_3$). − ^{29}Si NMR (C_6D_6): δ = −8.6 ($SiMe_3$), −127.8 (Si). − MS (70 eV, EI, ^{69}Ga), *m/z* (%): 386 (0.5) [M − THF]$^{+\bullet}$, 371 (0.5) [M − THF − Me]$^+$, 351 (15) [M − THF − Cl]$^+$, 247 (90) $[Si(SiMe_3)_3]^+$, 73 (100) $[SiMe_3]^+$. − $C_{13}H_{35}Cl_2GaOSi_4$ (460.4): calcd. Cl 15.4; found Cl 15.3. − Mol. mass: calcd. 385.9823; found 385.9821 (MS, for M − THF).

Dichlorodi-μ-hydroxy-bis[tris(trimethylsilyl)silyl]digallium−Bis(2,6-dimethylpyridine) (**10**): A solution of **9** (0.01 g, 0.02 mmol) in 5 ml of pentane was treated with 0.5 ml of 2,6-dimethylpyridine. During several days 0.006 g of **10** (69%) crystallized as colorless plates. − MS (70 eV, EI, ^{69}Ga), *m/z* (%): 351 (2) $[ClGaSi(SiMe_3)_3]^+$, 316 (21) $[GaSi(SiMe_3)_3]^{+\bullet}$, 107 (17) $[NC_5H_3(CH_3)_2]^{+\bullet}$, 73 (100) $[SiMe_3]^+$.

[Tris(trimethylsilyl)silyl]gallium Dihydroxide (**11**): 0.13 ml (7.36 mmol) of water was added to a solution of **3** (2.20 g, 3.68 mmol) in 10 ml of pentane. After the solution had become colorless, it was reduced in vacuo to half of its volume. At −30 °C 1.12 g of **11** (87%) crystallized; m.p. >270 °C (dec.). − ^1H NMR (C_6D_6): δ = 0.41 ($SiMe_3$). − ^{13}C NMR (C_6D_6): δ = 3.4 ($SiMe_3$). − ^{29}Si NMR (C_6D_6): δ = −8.9 ($SiMe_3$), n.o. (Si). − MS (70 eV, EI, ^{69}Ga), *m/z* (%): 803 (1) $[M - Si(SiMe_3)_3]^+$, 787 (3) $[M - Si(SiMe_3)_3 - O]^+$, 771 (2) $[M - Si(SiMe_3)_3 - 2\ O]^+$, 73 (100) $[SiMe_3]^+$. − IR: $\tilde{\nu}$ [cm^{-1}] = 3683 (OH_{term}), 3638 ($OH_{bridg.}$), ..., 492 s, 477 s, 452 m, 417 s, 409 s. − $C_9H_{29}GaO_2Si_4$ (351.4): calcd. C 30.76, H 8.32; found C 31.48, H 8.63. − Mol. mass: 1050 (MS, ^{69}Ga).

Diethoxydi-μ-ethoxy-bis[tris(trimethylsilyl)silyldigallium (**12**): A solution of **3** (0.30 g, 0.50 mmol) in 5 ml of pentane was treated with 1 ml of ethanol and stirred for 12 h. Afterwards all volatile components were removed in vacuo, and the residue was recrystallized from 3 ml of pentane. On cooling to 0°C 0.16 g of **12** (78%) crystallized as colorless prisms; m.p. 195–197°C. – ^{1}H NMR (C_6D_6): δ = 4.02 (q, $^3J_{HH}$ = 6.8 Hz, 2H, μ-OCH_2CH_3), 3.92 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OCH_2CH_3), 1.38 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH_2CH_3), 1.25 (t, $^3J_{HH}$ = 6.8 Hz, 3H, μ-OCH_2CH_3), 0.42 (s, 27H, $SiMe_3$). – MS (70 eV, EI, ^{69}Ga), *m/z* (%): 797 (10) $[M_2 - Me]^+$, 767 (6) $[M_2 - OEt]^+$, 752 (3) $[M_2 - MeOEt]^{+\bullet}$, 739 (3) $[M_2 - SiMe_3]^+$, 694 (23) $[M_2 - Me_3SiOEt]^{+\bullet}$, 565 $[M_2 - Si(SiMe_3)_3]^+$, 520 (39) $[M_2 - EtOSi(SiMe_3)_3]^{+\bullet}$, 505 (11) $[M_2 - EtOSi(SiMe_3)_3 - Me]^+$, 475 (28) $[M_2 - EtOSi(SiMe_3)_3 - OEt]^+$, 447 (32) $[M_2 - EtOSi(SiMe_3)_3 - SiMe_3]^+$, 406 (100) $[M]^{+\bullet}$, 391 (25) $[M - Me]^+$, 361 (53) $[M - OEt]^+$, 346 (21) $[M - MeOEt]^{+\bullet}$, 333 (49) $[M - SiMe_3]^+$. – $C_{13}H_{37}GaO_2Si_4$ (407.5): calcd. C 38.32, H 9.15; found C 38.57, H 9.27. – Mol. mass: 812 (MS, ^{69}Ga), 807 (cryoscopic in benzene).

2,2,6,6-Tetramethylpiperidinium Triphenoxy[tris(trimethylsilyl)silyl]gallate–Phenole–0.25 Toluene (**13**): A solution of phenol (0.28 g, 3.0 mmol) in 20 ml of a toluene/pentane mixture was added to a solution of **3** (0.59 g, 0.99 mmol) in 15 ml of pentane. After stirring for 16 h all volatile components were removed in vacuo, and the residue was dissolved in 5 ml of hexane. On cooling of the solution to –30°C 0.43 g of **13** (51%) precipitated as colorless crystals; m.p. 105–110°C. – ^{1}H NMR (C_6D_6): δ = 7.35 (t, 6H, *m*-H OPh), 7.03 (t, 3H, *p*-H OPh), 6.56 (d, 6H, *o*-H OPh), 7.32 (t, 2H, *m*-H HOPh), 6.86 (t, 1H, *p*-H HOPh), 6.76 (d, 2H, *o*-H HOPh), 2.1 (s, $C_6H_5CH_3$), 1.35 (m, 2H, 4-CH_2), 0.99 (s, 12H, CMe_2), 0.98 (m, 4H, 3,5-CH_2), 0.31 (s, 27H, $SiMe_3$). – ^{29}Si NMR (C_6D_6): δ = –141.7 (Si), –8.8 ($SiMe_3$). – MS (70 eV, EI, ^{69}Ga), *m/z* (%): 737 (5) $[M - PhOH]^{+\bullet}$, 612 (10) $[(PhO)_3GaSi(SiMe_3)_3 - Me]^+$. – $C_{43.75}H_{70}GaNO_4Si_4$ (855.8): [i.e. $C_{42}H_{68}GaNO_4Si_4 \cdot 0.25\ C_7H_8$]: calcd. C 61.39, H 8.18, N 1.63; found C 60.76, H 8.22, N 1.73. – Mol. mass (70 eV, EI, ^{69}Ga): 737 $[(PhO)_3GaSi(SiMe_3)_3H_2tmp]$.

2,2,6,6-Tetramethylpiperidinium Trichloro[tris(trimethylsilyl)silyl]gallate (**14**): A solution of **3** (0.38 g, 0.64 mmol) in 30 ml of hexane was treated at –78°C with 0.84 ml of a hydrogen chloride solution in Et_2O (*c* = 2.56 mol/l). A thick precipitate consisting of $tmpH_2^+Cl^-$ (0.11 g, 0.62 mmol) formed. The mixture was filtered and the solution reduced to a quarter of its volume. On cooling to –30°C 0.31 g of **15** (83%) crystallized in several portions; m.p. 290–295°C. – ^{1}H NMR (C_6D_6): δ = 1.05 (s, 12H, CMe_2), 1.30 (m, 2H, 4-CH_2), 0.76 (m, 4H, 3,5-CH_2), 0.59 (s, 27H, $SiMe_3$). – ^{13}C NMR (C_6D_6): δ = 58.6 (C-2,6), 34.7 (C-3,5), 27.9 (C-7 to -10), 17.3 (C-4), 2.9 ($SiMe_3$). – ^{29}Si NMR (C_6D_6): δ = –9.1 ($SiMe_3$), n.o. (Si). – $C_{18}H_{47}Cl_3GaNSi_4$ (566.0): calcd. C 38.20, H 8.37, N 2.47; found C 39.47, H 8.68, N 2.65. – Mol. mass (anion-FAB-MS, ^{69}Ga): 421 $[Cl_3GaSi(SiMe_3)_3^-]$.

Tetrahydroxy-tetra(μ_{2GaGa}-hydroxy)-tetra(μ_{2LiGa}-hydroxy)-di($\mu_{3LiLiGa}$-hydroxy)-hexakis[tris(trimethylsilyl)silyl]dilithiumhexagallium (**15**): A solution of **11** (0.24 g, 0.67 mmol of monomer) in 5 ml of diethyl ether was stirred with lithium hydroxide (0.005 g, 0.22 mmol) for 1 d. From the colorless solution 0.20 g of **15** (83%) crystallized at 0°C as colorless crystals. – ^{1}H NMR (C_6D_6): δ = 0.43 (s, 54H, $SiMe_3$), 0.41 (s, 27H, $SiMe_3$). – ^{13}C NMR (C_6D_6): δ = 3.7, 3.4 ($SiMe_3$). – ^{29}Si NMR (C_6D_6): δ = –142.1 (Si), –8.4, –7.9 ($SiMe_3$). – ^{7}Li NMR (C_6D_6): δ = 0.92. – IR: $\tilde{\nu}$ [cm^{-1}] = 3689 m, 3673 m, 3661 m, 3649 m (all sharp, OH), 3354 s (broad, OH), 2949 s, 2893 s (CH), 1244 s, 924 m, 834 s, 747 m, 688 s, 624 s, 588 s, 561 m, 551 m, 477 m, 449 m, 417 m, 394 m. – $C_{27}H_{88}Ga_3LiO_7Si_{12}$ (1078.1): calcd. C 30.08, H 8.23; found C 29.90, H 8.15.

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