On the Chemistry of Gallium, 14[◇]

Synthesis and Structure of Gallium/Silicon Heterocycles with a Ga_2Si_2 and a Ga_3Si Framework☆

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The reaction of $Ga_2X_4 \cdot 2$ dioxane with four equivalents of $(Me_3Si)_3SiLi(thf)_3$ (= hypersilyllithium) affords for X = Br a 1,3,2,4-disiladigalletane together with tetrahedral hypersilylgallium(I). For X = Cl an anionic 1,2,3,4-silatrigalletanate, a four-membered heterocycle with a Ga_3 unit, is isolated. These primary examples of gallium/group-14 heterocycles have been investigated by NMR spectroscopy as well as by X-ray single-crystal structure analysis. In addition, the synthesis and structure of bis(hypersilyl)gallium chloride is described. This monomeric molecule has a nearly T-shaped Si_2GaCl framework.

The tris(trimethylsilyl)silyl (= hypersilyl) group has proved to be a very useful substituent in gallium chemistry. Not only trivalent gallanes like $tmp_2GaSi(SiMe_3)_3$,[1] $Y_2GaSi(SiMe_3)_3 \cdot$ thf (Y = Me, Cl),[2] $Cl_2Ga[Si(SiMe_3)_3]_2 \cdot Li(thf)_2$[3], and $[(EtO)_2GaSi(SiMe_3)_3]_2$[2] are accessible but the hypersilyl group is also excellently capable of stabilizing a number of low-valent gallium compounds with gallium−gallium bonds. This includes hypersilyl-substituted digallanes $[(Me_3Si)_3Si]_2Ga-Ga[Si(SiMe_3)_3]_2$ and $[(Me_3Si)_3SiGa(Cl)-Ga(Cl)Si(SiMe_3)_3]_2$[4] as well as an anionic tetragallane $[(Me_3Si)_3SiGa\{Ga(I)Si(SiMe_3)_3\}_3]^-$ and the polyhedral nonagallane $[\{(Me_3Si)_3Si\}_6Ga_9]^-$.[5] The hypersilyl-substituted tetrahedral gallium(I) cluster $[(Me_3Si)_3SiGa]_4$ proved to be very stable towards dissociation into monomeric units.[6] In all these cases the hypersilyl group remained unaffected. Consequently, the central silicon atom is bonded to only one gallium atom and no cyclic compounds are known with gallium and silicon atoms as ring-building elements. In the following we describe results, where the inherent capability of the hypersilyl ligand for Si−Si bond cleavage is used for the synthesis of gallium−silicon heterocycles, which feature a tetracoordinate silicon atom bonded to two gallium atoms.

Reactions

By treating $[(Me_3Si)_3SiGa(Cl)-Ga(Cl)Si(SiMe_3)_3]_2$ (**1**) with two equivalents of $Li(thf)_3Si(SiMe_3)_3$ (Eq. 1) disproportionation of the gallium(II) species is achieved. Accompanying $[(Me_3Si)_3SiGa]_4$ (**2**), bis(hypersilyl)gallium chloride (**3**) is isolated in this reaction. Recently, we have described the synthesis of **2**[6] together with $Cl_2Ga[Si(SiMe_3)_3]_2 \cdot Li(thf)_2$ (**4**) and several not further characterized byproducts by reaction of $Ga_2Cl_4 \cdot 2$ dioxane with three equivalents $Li(thf)_3Si(SiMe_3)_3$ (Eq. 2). Another reaction course is observed, if $Ga_2Cl_4 \cdot 2$ dioxane, dissolved in tetrahydrofuran, is treated with four equivalents of $Li(thf)_3Si(SiMe_3)_3$ (Eq. 3). In this reaction the disproportionation of the gallium(II) species leads again to several hypersilylgallium compounds in oxidation state III, but no **2** is observed. Instead, black crystals of the unprecedented gallium/silicon heterocycle **5** are isolated. On the other hand, the analogous reaction of $Ga_2Br_4 \cdot 2$ dioxane with four equivalents of $Li(thf)_3Si(SiMe_3)_3$ affords **6** together with **2** (Eq. 4). The latter cocrystallizes with $Si(SiMe_3)_4$, which is formed during the reaction course. It is plausible, that **2** and bis(hypersilyl) gallium bromide are formed by disproportionation at first. **6** forms formally by elimination of bromotrimethylsilane from the sterically crowded $[(Me_3Si)_3Si]_2GaBr$. This takes place in the presence of excess $Li(thf)_3Si(SiMe_3)_3$, consequently the halosilane reacts further to produce $Si(SiMe_3)_4$ (Scheme 1). The pathway leading to **5** obviously also includes a step of disproportionation, but now an oligomeric hypersilylgallium(I) reacts with $Li(thf)_3Si(SiMe_3)_3$. Thus, a possible intermediate might be the three-membered gallacycle $[Ga_3\{Si(SiMe_3)_3\}_4]^-$. Migration of a trimethylsilyl group from an $Si(SiMe_3)_3$ group at the four-coordinate gallium center to a three-coordinate one and insertion of the remaining $Si(SiMe_3)_2$ unit into a Ga−Ga bond affords **5**.

Spectroscopic Characterization

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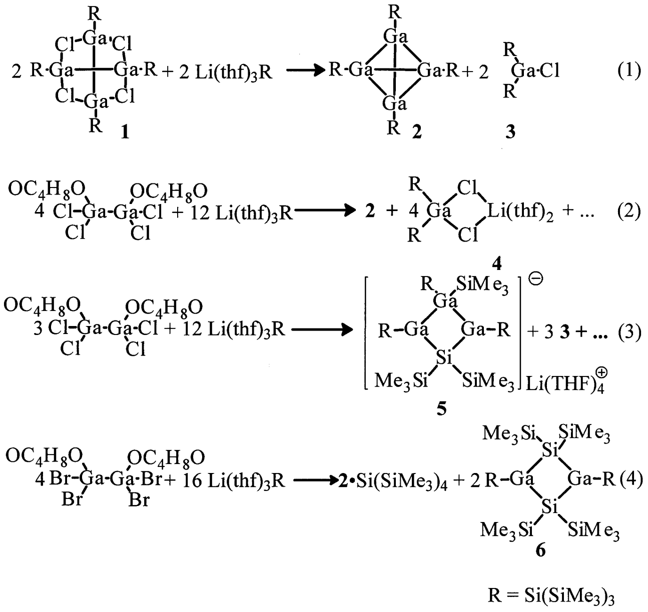
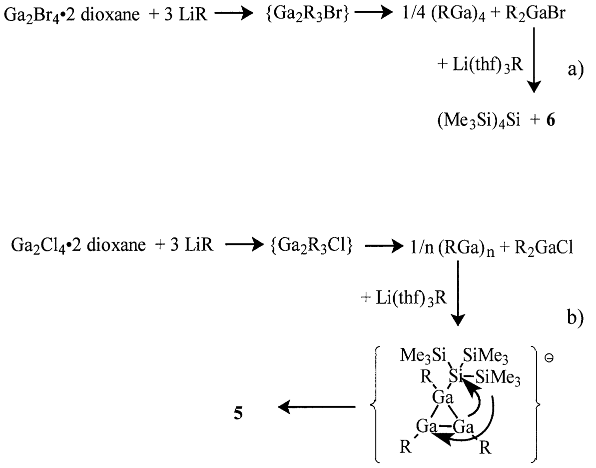


Scheme 1. Proposed reaction pathways to **6** (a) and **5** (b)



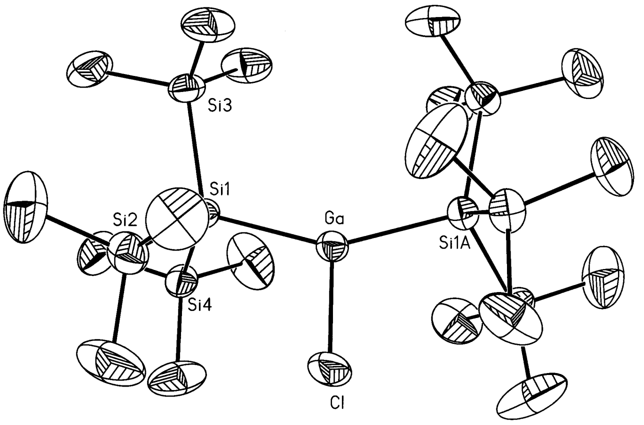
The ^{1}H- and ^{13}C-NMR spectra for **5** show two signals for the hypersilyl groups, one for the Ga−SiMe$_3$ group and two for the Si(SiMe$_3$)$_2$ unit, as is expected. In the ^{29}Si-NMR spectrum for the eight chemical different silicon atoms eight signals are observed. All trimethylsilyl groups, including the gallium-bonded one, resonate in the typical range between δ = −8.8 and −14.2. The central silicon atoms of the hypersilyl groups give rise to two signals at δ = −120.2 and −131.4. The signal for the ring silicon atom is identified at δ = −4.3. In **6** the signal for the ring silicon atoms is observed at δ = −3.3, that for the central atom of the hypersilyl group at δ = −103.8. Whereas there are no comparable data available for silicon atoms bonded to two gallium atoms, the chemical shifts for the hypersilyl silicon atoms are in the typical range known for other hypersilylgallium derivatives.[2] For example, the central silicon atom in tmp$_2$GaSi(SiMe$_3$)$_3$[1] resonates at δ = −115.3, in Cl$_2$GaSi(SiMe$_3$)$_3$ · thf[2] at δ = −127.8, and in [(PhO)$_3$GaSi(SiMe$_3$)$_3$]$^-$[2] at δ = −141.7. Electron-precise compounds with Ga−Ga bonds like [(Me$_3$Si)$_3$SiGa(Cl)−Ga(Cl)Si(SiMe$_3$)$_3$]$_2$[4] have signals in this range (δ = −112.2), too. This is only a small variation compared to other hypersilyl derivatives; here chemical shifts from δ = −33.4 for (Me$_3$Si)$_3$SiF[7] to −189.4 for Li(thf)$_3$Si(SiMe$_3$)$_3$[15c] are known. The chemical shifts of the gallium compounds seem to be affected by the electron-withdrawing properties of the ligands at and the coordination number of the gallium center. But the bonding situation at the gallium center obviously has the largest impact. In the electron-deficient tetrahedral cluster **1**, the signal for the hypersilyl silicon atom is observed at δ = −68.7. This shift to higher frequencies compared to other gallium compounds must be due to the multicenter-bonding situation the gallium atoms are involved in.

In the mass spectrum (70 eV) of **6** not only the molecular peak at m/z = 980 and the typical fragmentation pathway, i.e. loss of CH$_3$, SiMe$_3$, and Si(SiMe$_3$)$_3$ are observed, but in addition at m/z = 490 the radical cation [(Me$_3$Si)$_3$SiGaSi(SiMe$_3$)$_2$]$^{+\cdot}$ and consequent fragmentation occurs.

X-ray Structure Analysis

3 crystallizes in the hexagonal space group $P6_122$ with Z = 6. The crystal consists of well-separated monomeric molecules of **3** with a severely distorted trigonal-planar coordinated gallium center (Figure 1). The Ga−Si distance is 240.3(2) pm, which is comparable to the one in Me$_2$Ga(thf)−Si(SiMe$_3$)$_3$ [d_{GaSi} = 241.1(3) pm],[2] but shorter than in tmp$_2$Ga−Si(SiMe$_3$)$_3$ [d_{GaSi} = 246.8(1) pm].[1] Here, due to the three versus only two space-filling substituents the hypersilyl groups must minimize their steric interactions by bond elongation. In **3** this is achieved by a wide SiGaSi bond angle [150.3(1)°]. This is very wide, compared to other monomeric R$_2$GaCl compounds like [(Me$_3$Si)$_2$N]$_2$GaCl[8] [N−Ga−N = 128.5(2)°], (2,4,6-iPr$_3$C$_6$H$_2$)$_2$GaCl[9] [C−Ga−C = 133.8(7)°], and (2,4,6-tBu$_3$C$_6$H$_2$)$_2$GaCl[10] [C−Ga−C = 135.6(2)°]. Only (Mes$_2$C$_6$H$_3$)$_2$GaCl [C−Ga−C = 153.5(5)°] is even more T-shaped.[11]

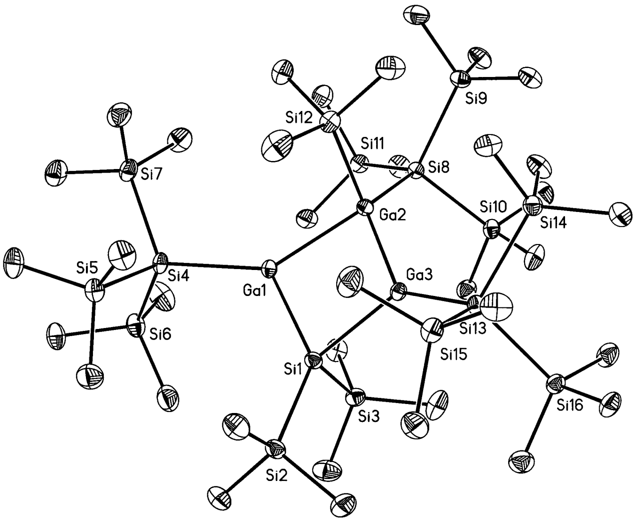
Figure 1. View of a molecule of **3**[a]



[a] Selected bond lengths [pm] and angles [°]: Ga−Cl 222.4(3), Ga−Si1 240.3(2), Si1−Si4 235.8(3), Si1−Si3 235.(3), Si1−Si2 236.1(3); Cl−Ga−Si1 104.83(5), Si1−Ga−Si1 150.33(10), Si4−Si1−Si3 110.1(1), Si4−Si1−Si2 113.96(10), Si3−Si1−Si2 110.9(1), Si4−Si1−Ga 102.42(8), Si3−Si1−Ga 113.79(9), Si2−Si1−Ga 105.36(9).

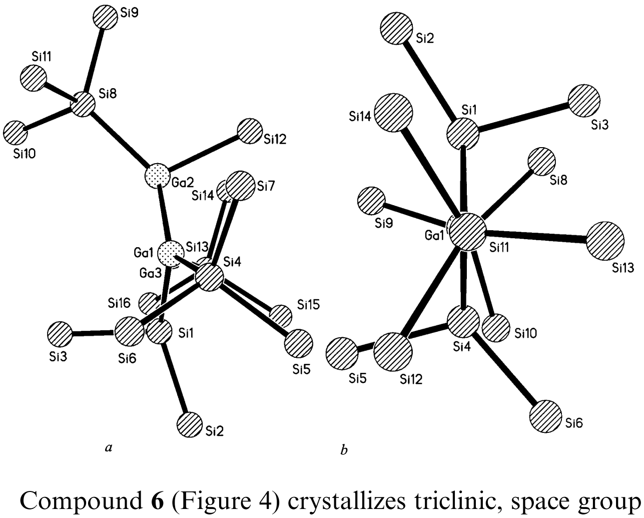
5 crystallizes monoclinic, space group $P2_1/n$, and consists of anionic Ga_3Si heterocycles (Figure 2) and isolated $Li(thf)_4$ cations. The heterocycle **5** is diamond-shaped with acute angles of 84.52(5)° at the ring silicon atom and of 81.39(3)° at the tetracoordinated gallium center. The wide angles [97.78(4), 95.96(4)°] are as expected at the three-coordinate gallium atoms. As is indicated by the sum of angles the ring adopts a flat butterfly structure; the Si1Ga1Ga2 and Si1Ga3Ga2 plane orthogonals intersect at 20.6°. Consequently, the two hypersilyl groups at Ga1 and Ga3 are on the same side of the ring, the hypersilyl group at Ga2 is in *trans* position to them. Nevertheless, the attachment of so many bulky substituents to that four-membered ring results in a considerable distortion of the bond angles and the coordination spheres around Ga2 and Ga3 (Figure 3a). Inspecting the ring silicon atom, at first, the Si2−Si1−Si3 angle, namely the angle between the trimethylsilyl groups is near the tetrahedral angle, but the trimethylsilyl group (Si2) on the inner side of the butterfly has very wide Si2−Si1−Ga2,3 angles. This means the Si1−Si2 bond has only an angle of 26.5° with the Si1Ga2Ga3 plane. In contrast, the Si1−Si3 bond is nearly perpendicular to this plane (Si3Si1//Si1Ga2Ga3: 100.5°). At the tetracoordinated gallium atom Ga2 the situation is similar. The Si8−Ga2−Si12 angle [110.37(6)°] is near the tetrahedral angle, too. The bond Ga2−Si8, involving the central atom of the attached hypersilyl group, has wide angles with the Ga2−Ga1,3 bonds [Si8−Ga2−Ga1 126.64(4)°; Si8−Ga2−Ga3 128.57(4)°], but, in contrast, the corresponding angles involving the trimethylsilyl silicon atom Si12 have values of only 105.67(5)° and 98.09(5)°. This means angles between the Ga2Ga1Ga3 plane and the Si8−Ga2 and Si12−Ga2 bonds of 36.4° and 106.8°, respectively. Furthermore, the steric crowding in **5** causes a no longer exactly planar arrangement around Ga1 and Ga3. Both atoms are 16 pm above the plane through their neighboring atoms. The Ga−Ga bond lengths in the trigallane unit of **5** [255.27(9), 252.88(9) pm] are in the typical range for other hypersilyl-substituted oligogallanes like $[(Me_3Si)_3SiGa(Cl)-Ga(Cl)Si(SiMe_3)_3]_2$ (d_{GaGa} = 250.5 pm),[4] $[(Me_3Si)_3SiGa\{Ga(I)Si(SiMe_3)_3\}_3]^-$ (d_{GaGa} = 253.3 pm)[5] and $[(Me_3Si)_3Si]_2Ga-Ga[Si(SiMe_3)_3]_2$ (d_{GaGa} = 259.9 pm).[4] Only one structurally investigated compound with a trigallane unit is known so far, $Ga_3I_5 \cdot 3\ PEt_3$.[12] In this gallium subhalide shorter Ga−Ga bond lengths [d_{GaGa} = 245.1(1), 246.0(1) pm] are observed. The $Ga-Si(SiMe_3)$ distances in **5** [d_{GaSi} = 248.4 pm] are very long compared to other hypersilylgallium compounds, as is discussed above. There is no difference between the Ga−Si bond lengths involving three- or four-coordinate gallium atoms in **5**. In contrast, the $Ga-SiMe_3$ bond length is 5 pm shorter. As we have noted earlier,[2] the Ga−Si bond lengths are very sensitive to steric requirements. In this sense, the shorter bond length to the trimethylsilyl group is expected, but further structural data on molecules with $Ga-SiMe_3$ bonds are not available, yet. The ring silicon atom is also in a novel environment. For this atom bonded to two gallium atoms Ga−Si bond lengths of 247.5(2) and 245.2(2) pm are observed, thus in the range of long Ga−Si bonds. The Si−Si and Si−C bond lengths are in the normal range for these bond types.

Figure 2. View of the heterocyclic anion in **5**; the methyl groups have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga1−Ga2 255.27(9), Ga2−Ga3 252.88(9), Ga1−Si1 247.5(2), Ga3−Si1 245.2(2), Ga1−Si4 248.4(2), Ga2−Si8 248.4(2), Ga2−Si12 243.6(2), Ga3−Si13 248.3(2), Si1−Si2 235.4(2), Si1−Si3 236.5(2), $Si-SiMe_3$ 235.5; Si1−Ga1−Ga2 94.78(4), Ga3−Ga2−Ga1 81.39(3), Si1−Ga3−Ga2 95.96(4), Ga3−Si1−Ga1 84.52(5), Si1−Ga1−Si4 119.60(6), Si4−Ga1−Ga2 144.07(5), Si12−Ga2−Si8 110.37(6), Si12−Ga2−Ga3 105.67(5), Si8−Ga2−Ga3 128.57(4), Si12−Ga2−Ga1 98.09(5), Si8−Ga2−Ga1 126.64(4), Si1−Ga3−Si13 125.63(5), Si13−Ga3−Ga2 136.59(5), Si2−Si1−Si3 106.12(8), Si2−Si1−Ga3 127.03(7), Si3−Si1−Ga3 98.00(7), Si2−Si1−Ga1 135.74(7), Si3−Si1−Ga1 97.47(7).

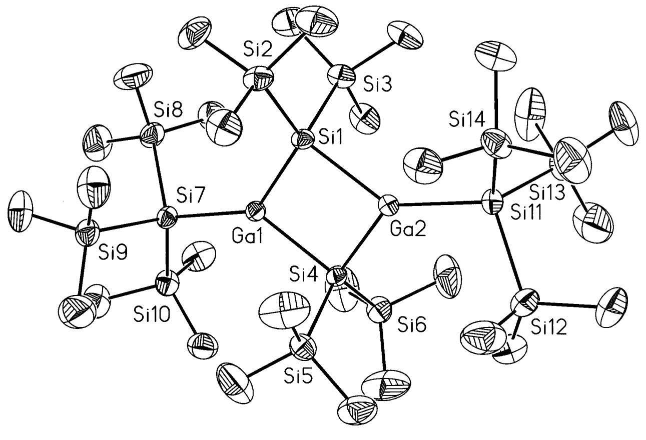
Figure 3. Side-on view of a) anionic **5**, b) one of the two independent molecules of **6**; the methyl groups have been omitted for clarity



Compound **6** (Figure 4) crystallizes triclinic, space group $P\bar{1}$, with two independent molecules in the asymmetric unit. The nearly planar four-membered gallium/silicon heterocycles have an approximately quadratic alternating Ga_2Si_2 framework of distorted trigonal-planar coordinated gallium and tetrahedrally coordinated silicon centers. Thus, the inner ring angles at the gallium atoms are 91.6°, those at the silicon atoms 88.4°, on an average. The Ga−Si bond lengths in the ring (d_{GaSi} = 242.1 pm on an average) vary only by

2 pm. The exocyclic gallium−silicon bond lengths are similar to the innercyclic, too. But, if **5** and **6** are compared, it has to be noted, that all Ga−Si bonds are shortened by more than 5 pm. This is, at least in part, a consequence of the replacement of a $[Ga(SiMe_3)Si(SiMe_3)_3]^-$ unit by the less bulky $Si(SiMe_3)_2$ group. In spite of the reduction of steric crowding, the *anti*-standing trimethylsilyl groups are bonded either in a flat or nearly perpendicular manner to the heterocycle (Figure 3b). The corresponding angle pairs between Si−Si bonds and the Ga_2Si planes are 31 and 104.3° or 42.3 and 115.9°, respectively. It has to be noted, that the two independent molecules differ only a little in the orientation of the approximately staggered hypersilyl groups to one another.

Figure 4. View of a molecule of **6**[a]



[a] Selected bond lengths [pm] and angles [°]: Ga1−Si1 242.89(9), Ga1−Si4 241.2(1), Ga1−Si7 241.5(1), Ga2−Si1 242.5(1), Ga2−Si4 241.68(9), Ga2−Si11 242.5(1), Si1−Si2 232.8(1), Si1−Si3 233.9(1), Si4−Si5 233.7(2), Si4−Si6 232.4(1), Si−SiMe$_3$ 234.0; Si4−Ga1−Si1 91.59(4), Si4−Ga2−Si1 91.57(4), Ga2−Si1−Ga1 88.11(3), Ga1−Si4−Ga2 88.68(3), Si4−Ga1−Si7 132.66(3), Si7−Ga1−Si1 135.74(3), Si4−Ga2−Si11 132.77(4), Si11−Ga2−Si1 135.64(3), Si2−Si1−Si3 107.27(5), Si2−Si1−Ga2 128.62(5), Si3−Si1−Ga2 96.78(5), Si2−Si1−Ga1 127.47(5), Si3−Si1−Ga1 102.77(5), Si6−Si4−Si5 116.52(5), Si6−Si4−Ga1 123.73(5), Si5−Si4−Ga1 100.53(5), Si6−Si4−Ga2 120.08(5), Si5−Si4−Ga2 101.97(5).

Conclusions

With **5** and **6** we have described two novel gallium- and silicon-containing heterocycles, which have both been prepared starting from gallium(II) halides, showing that the hypersilyl ligand is not only useful as a bulky substituent, but is also a valuable source for $Si(SiMe_3)_2$ units. **6** is formally a dimer of a hypothetical silagallene $RGa{=}SiR'_2$, **5** is a novel substituted trigallane derivative. Obviously, in all reactions described in this work disproportionation takes place. The different product distributions reflect the sensitivity of low-valent gallium halide reaction chemistry. Only small variations in the reaction conditions may either proceed in retention or cleavage of the initial Ga−Ga bond. In the latter case gallium(III) compounds and new oligogallanes are formed; in the worst case elemental gallium precipitates.

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Experimental Section

General: All handling was performed under purified nitrogen or in vacuo using Schlenk techniques. − NMR: Bruker ACP 200 and 250. − MS: Varian MAT 711 with direct inlet. − Gallium halides were prepared from the elements,[14] $(Me_3Si)_3SiLi(thf)_3$[15] as described in the literature. Other chemicals were used as purchased. − X-ray Crystallographic Study:[13] Suitable crystals were mounted with a perfluorated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collections were performed in ω-scan with Mo-K_α radiation (graphite monochromator) on a Stoe STADI4 (**3**, **5**) or Stoe IPDS (**6**) diffractometer using the commercial software. Structures were solved using 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 bonded to carbon atoms were included as riding model with fixed isotropic U's in the final refinement. For further details see Table 1.

Bis[tris(trimethylsilyl)silyl]gallium Chloride (**3**): Into a solution of $[(Me_3Si)_3Si]_4Ga_4Cl_4$ (**1**) (0.51 g, 0.36 mmol) in 20 ml of tetrahydrofuran a solution of $LiSi(SiMe_3)_3 \cdot 3$ thf (0.34 g, 0.73 mmol) in 15 ml of tetrahydrofuran was added dropwise at 60°C (at room temperature no reaction was observed). After stirring the resulting red solution for additional 12 h at room temperature all volatiles were removed in vacuo. The residue was suspended in 10 ml of pentane. Upon filtration the solution was reduced to a volume of 2 ml and cooled to −25°C. Yellow prisms of **3** crystallized followed by black violet plates of **2**.

Lithium 2,4,4-Tris(trimethylsilyl)-1,2,3-tris[tris(trimethylsilyl)silyl]-1,3-digalla-2-gallata-4-silacyclobutane · 4 THF (**5**): A solution of $Ga_2Cl_4 \cdot 2$ dioxane (0.49 g, 1.07 mmol) in 15 ml of tetrahydrofuran was added dropwise at −78°C to a solution of $LiSi(SiMe_3)_3 \cdot 3$ thf (2.00 g, 4.25 mmol) in 20 ml of tetrahydrofuran. After slowly warming to ambient temperature, the mixture was stirred for another 12 h, then all volatiles were removed in vacuo and the residue was extracted three times with 20 ml of pentane, each. The insoluble residue was treated with 15 ml of toluene and sonicated for 5 min. The red solution was filtered. Upon standing a dark red oil separated, which was redissolved in methylcyclohexane/tetrahydrofuran (25:1). At 0°C 0.15 g of **5** (14%) crystallized as black-red prisms. From the pentane fraction bis(hypersilyl)gallium chloride could be identified as one of the gallium(III) products. − ^{1}H NMR ([D$_8$]THF): δ = 0.30 [54 H, 1,3-Si(SiMe$_3$)$_3$], 0.25 (9 H, 2-SiMe$_3$), 0.20 [27 H, 2-Si(SiMe$_3$)$_3$], 0.17, 0.13 (9 H each, 4-SiMe$_3$). − ^{13}C NMR ([D$_8$]THF): δ = 11.8, 8.2 (4-SiMe$_3$), 5.8 [1,3-Si(SiMe$_3$)$_3$], 5.6 [2-Si(SiMe$_3$)$_3$], 3.6 (2-SiMe$_3$). − ^{29}Si NMR ([D$_8$]THF): δ = −4.3 (Si-4), −8.8 [2-Si(*Si*Me$_3$)$_3$], −9.4 [1,3-Si(*Si*Me$_3$)$_3$], −11.8 (4-SiMe$_3$), −12.7 (GaSiMe$_3$), −14.2 (4-SiMe$_3$), −120.2 [1,3-*Si*(SiMe$_3$)$_3$], −131.4 [2-*Si*(SiMe$_3$)$_3$]. − MS (70 eV, EI, ^{69}Ga): *m/z* (%) = 536 (5) $[Ga\{Si(SiMe_3)_3\}_2]^+$, 389 (16) $[Me_3SiGaSi(SiMe_3)_3]^+$, 316 (10) $[GaSi(SiMe_3)_3]^+$, 248 (94) $[HSi(SiMe_3)_3]^+$, 174 (83) $[Si(SiMe_3)_2]^+$, 160 (100) $[HSi(SiMe_3)(SiMe_2)]^+$, 73 (76) $[SiMe_3]^+$. − $C_{52}H_{140}Ga_3LiO_4Si_{16}$ (1495.2): calcd. C 41.77, H 9.44; found C 42.15, H 10.16.

1,1,3,3-Tetrakis(trimethylsilyl)-2,4-bis[tris(trimethylsilyl)silyl]-1,3,2,4-disiladigalletane (**6**): A solution of $LiSi(SiMe_3)_3 \cdot 3$ thf (4.66 g, 9.89 mmol) in 30 ml of tetrahydrofuran was treated at room temperature dropwise with a solution of $Ga_2Cl_4 \cdot 2$ dioxane (1.59 g, 2.50 mmol) in 40 ml of tetrahydrofuran. After stirring for an-

Table 1. Crystal data and data-collection parameters

Compound	**3**	**5**	**6**
Chem. formula	$C_{18}H_{54}ClGaSi_8$	$C_{52}H_{140}Ga_3LiO_4Si_{16}$	$C_{30}H_{90}Ga_2Si_{14}$
Form. weight	600.50	1495.18	983.72
Cryst. size [mm]	0.30×0.40×0.50	0.25×0.28×0.30	0.20×0.20×0.25
Cryst. system	hexagonal	monoclinic	triclinic
Space group	$P6_122$	$P2_1/n$	$P\bar{1}$
a [Å]	9.604(4)	14.054(2)	24.113(3)
b [Å]	9.604(4)	24.232(6)	25.480(4)
c [Å]	68.530(40)	26.036(4)	9.6617(10)
α [°]	90	90	100.191(15
β [°]	90	97.56(3)	80.874(13)
γ [°]	120	90	98.330(15)
V [Å^3]	5474.1(45)	8790(3)	5726.7(12)
Z	6	4	4
ρ(calcd.) [Mg/m^3]	1.093	1.130	1.141
μ [mm^{-1}]	1.096	1.164	1.253
F(000)	1932	3216	2112
Index range	$\pm h \pm k \pm l$	$\pm hkl$	$\pm h \pm k \pm l$
$2\theta_{max}$ [°]	46.04	49.98	48.24
Temp. [K]	210	200	193(2)
Refl. collected	8624	15607	31672
Refl. unique	2554	14661	17028
Refl. observed (4σ)	1964	9521	10226
R_{int}	0.1393	0.0485	0.0322
Absorption corr.	n. a.	semi-empirical	semi-empirical
Min/max. transm.	–	0.7493/0.6647	0.6369/0.8580
No. variables	137	721	889
Weighting scheme[a] x/y	0.0448/5.5264	0.0232/2.7117	0.0303/0.0000
GOOF	1.139	1.130	0.794
Final R (4σ)	0.0476	0.0527	0.0308
Final $wR2$	0.1074	0.0884	0.0679
Largest resid. peak [e/Å^3]	0.716	0.439	0.345

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

other 12 h, the volatiles were removed in vacuo and the oily residue was suspended in 30 ml of pentane. After filtration, a dark red solution was obtained from which after separation of minor portions of **6** 0.43 g of **2** · $Si(SiMe_3)_4$ (43%) as blue-violet plates crystallized upon cooling to −30°C. The in pentane not soluble residue of filtration was extracted with 30 ml of toluene. From the solution obtained, 0.54 g of **6** (44%) crystallized as orange needles at −30°C. – **6**: ^{1}H NMR (C_6D_6): δ = 0.47. – ^{13}C NMR (C_6D_6): δ = 6.8 ($SiMe_3$), 5.5 [$Si(SiMe_3)_3$]. – ^{29}Si NMR (C_6D_6): δ = −3.3 ($Ga_2\mathit{Si}_2$), −7.1 ($SiMe_3$), −8.0 [$Si(\mathit{Si}Me_3)_3$], −103.8 [$\mathit{Si}(SiMe_3)_3$]. – MS (70 eV, EI, ^{69}Ga): m/z (%) = 980 (23) $[M]^{+\cdot}$, 965 (11) $[M - CH_3]^+$, 907 (2) $[M - SiMe_3]^+$, 733 (100) $[M - Si(SiMe_3)_3]^+$, 660 (1) $[M - Si(SiMe_3)_4]^{+\cdot}$, 645 (40) $[(660) - CH_3]^+$, 587 (28) $[(660) - SiMe_3]^+$, 490 (55) $[M/2]^{+\cdot}$, 475 (18) $[M/2 - CH_3]^+$, 417 (42) $[M/2 - SiMe_3]^+$, 316 (68) $[GaSi(SiMe_3)_3]^+$, 243 (40) $[M/2 - Si(SiMe_3)_3]^+$.– $C_{30}H_{90}Ga_2Si_{14}$ (983.7): calcd. C 36.63, H 9.22; found C 35.35, H 9.28. – **2** · $Si(SiMe_3)_4$: ^{1}H NMR (C_6D_6): δ = 0.47 [s, 27 H, $GaSi(SiMe_3)_3$], 0.27 [s, 9 H, $Si(SiMe_3)_4$]. – ^{13}C NMR (C_6D_6): δ = 4.4 [$GaSi(SiMe_3)_3$], 2.8 [$Si(SiMe_3)_4$]. – ^{29}Si NMR (C_6D_6): [= −8.3 ($GaSi(\mathit{Si}Me_3)_3$], −9.8 [$Si(\mathit{Si}Me_3)_4$], −68.7 [$Ga\mathit{Si}(SiMe_3)_3$], −135.5 [$\mathit{Si}(SiMe_3)_4$].

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[13] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100895. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int code +44(0)1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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