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A facile high-yield synthesis of the tetrahedral gallium(I) compounds $Ga_4[C(SiMe_2R)_3]_4$—crystal structure of $Ga_4[C(SiMe_2Et)_3]_4$

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Abstract

Alkyl gallium(I) derivatives with gallium in an unusual low oxidation state of +I are important starting materials for the synthesis of novel organo gallium compounds of main group or transition metal elements. Up to now, they were synthesized by a disproportionation reaction with yields below 15% with respect to the alkyl substituents. We succeeded now in synthesizing these compounds on a very simple route by the reduction of the chloro complexes $Li[Cl_3Ga-C(SiMe_2R)_3]$ (R = Me: **1**; R = Et: **2**) in toluene at 70–80°C by the two-electron donor Rieke magnesium in a yield of more than 70%. While the crystal structure of $[GaC(SiMe_3)_3]_4$ **3** showed a severe disorder of the whole molecule, $[GaC(SiMe_2Et)_3]_4$ **4** gives a clearly resolved crystal structure with an almost undistorted Ga_4 tetrahedron in the molecular center and a Ga–Ga distance of 271.0 pm on average. **4** gradually monomerizes in benzene with increasing dilution of the solutions to give the monomeric fragment $Ga-C(SiMe_2Et)_3$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gallium; Cluster; Low oxidation state

1. Introduction

The synthesis of tetrahedral cluster compounds with the heavier elements of the third main-group aluminium [1–3], gallium [4,5], indium [6,7] and thallium [8] in an unusual low oxidation state of +I was extensively studied in several groups in the last 5 years. Besides their singular structure and bonding situation [9] they are of particular interest as starting compounds for the synthesis of novel derivatives, and some remarkable articles in recent literature verify their outstanding importance. While the Tl–C bond of $Tl_4[C(SiMe_3)_3]_4$ [8] is much to unstable for carrying out any reaction successfully [10], several reactions of $Al_4Cp^*_4$ [1,2] or $In_4[C(SiMe_3)_3]_4$ [6,7] were recently reported. New cage or cluster compounds were synthesized by the treatment with the elements of the pnicogen or chalcogen groups [2,6,11]. The monomeric fragments E–R could be structurally characterized by electron diffraction experiments in the gas-phase for E = aluminium, gallium, indium and thallium bearing cyclopentadienyl substituents [12] or for the alkyl derivative $Ga-C(SiMe_3)_3$ [13]. Owing to its lower thermal stability the structure of monomeric $In-C(SiMe_3)_3$ could not be determined in the gas phase [13], but it was observed as the highest mass in the conventional mass spectrum of the tetramer [6]. Those monomeric alkylelement(I) derivatives have two empty p orbitals and a lone electron-pair at the gallium or indium atoms and are thus isolobal to carbon monoxide. Following this idea, some compounds were isolated, which are analogues of transition metal carbonyl complexes with some or all CO groups replaced by E–R. But these ligands mostly occupy bridging positions between two metal centers [14] and only one example with a terminal coordinated AlCp* group was published up to now [15], in which the back-donation of electron density from the metal atom to the ligand

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similar to the bonding situation in the carbonyls was verified by theoretical calculations.

$Al_4Cp^*_4$ is synthesized either by the treatment of reactive aluminium(I) chloride with bis(pentamethylcyclopentadienyl)magnesium [1] or by the reduction of the corresponding pentamethylcyclopentadienyl aluminium dichloride with potassium [2]. The alkyl derivatives $In_4[C(SiMe_3)_3]_4$ and $Tl_4[C(SiMe_3)_3]_4$ are both easily accessible in high yields by the reaction of $LiC(SiMe_3)_3 \cdot 2THF$ [16] with In(I) halides [6,7] or thallium(I) cyclopentadienide [8]. In contrast to these compounds, no facile method for the synthesis of the alkyl–Ga(I) derivatives is described in the literature, and their chemical properties are therefore almost unknown. $Ga_4[C(SiMe_3)_3]_4$ (**3**) [4] is obtained by the reaction of the Ga(II) halide $Ga_2Br_4 \cdot 2$dioxane with three equivalents of solvent free $LiC(SiMe_3)_3$, which can be synthesized using a mercury intermediate [17]. The reaction proceeds via a disproportionation, and the yield of the finally isolated crystalline product amounts to only about 15% with respect to the lithium compound. A similar method was subsequently used for the synthesis of the $Ga_4[Si(SiMe_3)_3]_4$ analog [5]. The great importance of these Ga_4 derivatives for the systematic investigation of the chemical properties of this new class of cluster compounds led us to intensive efforts to find an easy route for their synthesis, which is reported in this article. Derivatives of the alkyl compound **3** were further of particular interest, because the crystal structure of **3** showed a severe disorder across a pseudo mirror plane [4], and the molecular structure was determined with some uncertainty. A second structure determination of a related alkyl compound would thus be very helpful to verify the bond lengths and angles in the Ga_4 center given in the original paper about **3**.

2. Syntheses of the starting compounds $HC(SiMe_2R)_3$, $LiC(SiMe_2R)_3 \cdot xTHF$ and $Li[Cl_3Ga–C(SiMe_2R)_3] \cdot xTHF$

The synthesis of the compound $HC(SiMe_3)_3$ starting with chloroform, elemental lithium and chlorotrimethylsilane has been published by Cowley et al. several years ago [16]. The ethyl derivative $HC(SiMe_2Et)_3$ was obtained by our group using a method described by Eaborn et al. for the synthesis of the phenyl [18] or isopropyl [19] analogs; a mixture of bromoform and chloro dimethyl(ethyl)silane was treated with *n*-butyllithium in THF at low temperature (−78°C) and the product formed by successive metal to halogen exchange reactions in a yield of 71% (Eq. (1)). The methane derivatives were subsequently metalated by the treatment with an excess of methyllithium (Eq. (2)) [16,19,20]. $LiC(SiMe_3)_3 \cdot 2THF$ has been isolated before [16], $LiC(SiMe_2Et)_3$ was recrystallized from diisopropyl ether, isolated in a yield of 65% and contains 1.5 molecules of THF in each formula unit.

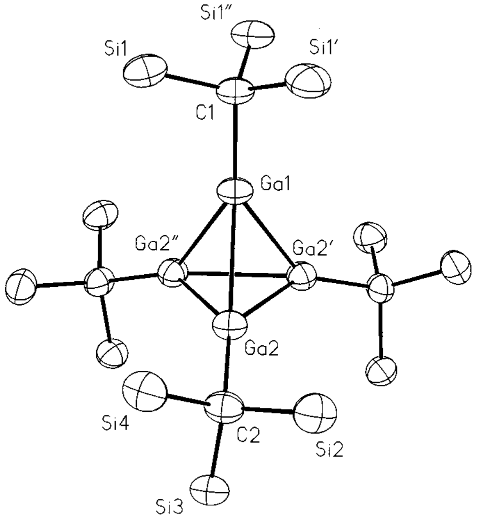


Fig. 1. Molecular structure of **4**; the ellipsoids are drawn at the 50% probability level; methyl groups are omitted for clarity; the atoms Ga′ and Si1′ are generated by the symmetry operation −*y*, *x*−*y*, *z*; Ga″ and Si1″ by −*x*+*y*, −*x*, *z*.

$$HCBr_3 + 3\ n\text{-BuLi} + 3\ ClSiMe_2Et \longrightarrow HC(SiMe_2Et)_3 + 3\ n\text{-BuBr} + 3\ LiCl \qquad (1)$$

$$HC(SiMe_2R)_3 + MeLi \xrightarrow{THF} LiC(SiMe_2R)_3 \cdot xTHF + CH_4 \qquad (2)$$

(R = Me [16], Et)

Due to the experience gained in our laboratory it is quite difficult to use these lithium compounds as starting materials for the synthesis of organo gallium derivatives, and we could not obtain a pure and isolable product by their reactions with $GaCl_3$ in pentane, hexane, toluene or diethyl ether. We suppose that instead ether cleavage products were formed, which showed very broad resonances in their NMR spectra. The

Table 1
Selected bond lengths (pm) and angles (°) for **4**

Ga1–Ga2	270.9(1)	C1–Si1	190.2(3)
Ga2–Ga2′[a]	271.2(1)	C2–Si2	189.6(7)
Ga1–C1	210.2(8)	C2–Si3	190.5(5)
Ga2–C2	209.8(6)	C2–Si4	189.3(6)
Ga1–Ga2–Ga2′[a]	59.96(2)	C1–Ga1–Ga2	144.69(2)
Ga2–Ga1–Ga2′[a]	60.07(3)	C2–Ga2–Ga1	145.4(2)
Ga2′[a]–Ga2–Ga2″[a]	60.0	C2–Ga2–Ga2′[a]	143.9(2)
		C2–Ga2–Ga2″[a]	145.0(2)

[a] The atom Ga2′ was generated by the symmetry operation −*y*, +*x*−*y*, +*z*; Ga2″ by −*x*+*y*, −*x*, +*z*.

groups of Atwood, Eaborn and Smith succeeded 1987 in synthesizing adducts of the type $Li[Cl_3Ga-C(SiMe_2R)_3]\cdot x THF$ ($R = -CH_3$, $-C_6H_5$) by the reaction of $GaCl_3$ with such Li compounds, when they used THF as a solvent (Eq. (3)) [21]. The different behavior may be explained by the formation of very stable THF adducts of $GaCl_3$, which results in a reduced Lewis acidity of the gallium halide and prevent the catalysis of the ether cleavage reaction. $[Li(THF)_3][Cl_3Ga-C(SiMe_3)_3]$ **1** was already published by Eaborn et al. [21]; our synthesis of $Li[Cl_3Ga-C(SiMe_2Et)_3]$ **2** followed exactly the same route. **2** contains 0.75 molecules THF in each formula unit after recrystallization from toluene and thorough drying in vacuo and was isolated in a yield of about 50%.

$$GaCl_3 + LiC(SiMe_2R)_3 \cdot xTHF \longrightarrow Li[Cl_3GaC(SiMe_2R)_3] \cdot xTHF \qquad (3)$$

(R = Me [21] **1**, R = Et **2**)

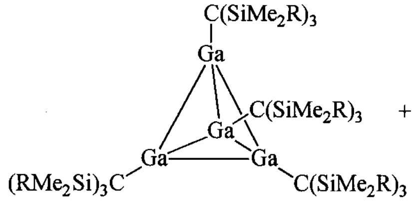
3. Synthesis of Ga_4 derivatives

The chlorogallate **1** with the $C(SiMe_3)_3$ substituent was first of all treated with the alkali metals lithium or potassium in toluene to synthesize the well-known Ga(I) derivative $Ga_4[C(SiMe_3)_3]_4$ **3** [4]. **1** was completely consumed after 12 h of vigorous stirring at room temperature (r.t.). After filtration, evaporation and recrystallization from different solvents (pentane, toluene, diisopropyl ether or THF) a solid mixture was isolated, which consists of the Ga_4 derivative **3** and the four-membered Si_2C_2 heterocycle $[Me_2Si-C(SiMe_3)_2]_2$ [22] in similar concentrations. The heterocycle was isolated before as a byproduct in the synthesis of **3** by the disproportionation method described above. It is probably formed via an intermediate with a Si=C double bond, which may be originate from an elimination of a Ga–Me fragment out of a $Ga-C(SiMe_3)_3$ group. The obtained mixture could not be separated by repeated recrystallization from different solvents. However, the carbosilane is volatile and could be removed by sublimation in vacuo at a bath temperature of 110°C. Although the Ga_4 derivative does not sublime or decompose at this temperature, the yield of the isolated compound **3** after recrystallization of the residue from toluene amounts to only about 10%. Similar results were obtained by the reduction of the ethyl derivative **2** with potassium in toluene; the red Ga_4 cluster **4** and probably a Si_2C_2 heterocycle $[(EtMe_2Si)_2C-SiMeEt]_2$ [^1H-NMR (C_6D_6): $\delta = 0.33$ (s, 12H, Me), 0.58 (s, 3H, Me), 0.79 (q, 4H, Et–CH_2), 0.97 (t, 6H, Et–CH_3), 1.01 (m, 5H, Et)] were isolated in a low yield, which in contrast to the $SiMe_3$ derivatives could be separated by recrystallization from pentane.

In further experiments, we employed the two-electron reductant elemental magnesium. Although we tested several commercially available magnesium samples and the very reactive Mg/Ni alloy reproducible results were only observed with freshly prepared and finely divided Rieke magnesium, which is easily obtained by the treatment of magnesium chloride with potassium in THF [23]. The mixture of chlorogallate **1** and Rieke magnesium suspended in toluene was heated for 20 h to 70°C, and the originally colorless suspension adopted a deep red color characteristic for **3**. The mixture was filtrated, evaporated and the residue recrystallized from *n*-pentane to give $Ga_4[C(SiMe_3)_3]_4$ (**3**) as red crystals in an excellent yield of 76%; the Si–C heterocycle could not be detected as a byproduct by NMR spectroscopy. A similar route (Eq. (4)) was used for the reduction of the ethyl derivative **2**, the reaction time is, however, lengthened to 3 days.

$$4\ Li[Cl_3GaC(SiMe_2R)_3] \cdot xTHF + 4\ Mg \xrightarrow[-THF]{}$$

(4)



$+ 4\ MgCl_2 + 4\ LiCl$

(R = Me **3**, Et **4**)

$Ga_4[C(SiMe_2Et)_3]_4$ (**4**) shows a singlet for the methyl groups bound to Si in the ^1H-NMR spectrum, and remarkably the protons of the ethyl groups coincide to give only one singlet. The ethyl carbon atoms are, however, clearly resolved in the ^{13}C-NMR spectrum. The α carbon atoms of the $C(SiMe_3)_3$ substituents of **3** could not be detected in our former investigations probably caused by the quadrupole moment of the Ga nucleus. Due to our experience with the characterization of In_4R_4 clusters we were able now to detect these resonances, which lie in a quite unusual range at 61.7 (**3**) and 64.2 (**4**) ppm, more than 30 ppm down-field to the resonances usually observed in alkyl derivatives of trivalent gallium [24]. The In_4 compounds show similar shifts of the α carbon atoms to 73 ppm on average, they are caused by the delocalized molecular orbitals of the clusters [25]. An absorption in the UV–vis spectrum of **4** at 440 nm is characteristic for the Ga_4 derivatives (**3**: 435 nm), while the In_4 analogues show bathochromically shifted absorptions at about 490 nm [6,7,25]. An absorption at 571 cm^{-1} in the IR spectrum is attributed to the Ga_4C_4 vibration of the molecular center.

Mass spectroscopy give the monomeric formula mass with a very weak intensity for a dimer. Similar to **3**, the ethyl derivative **4** is tetrameric in the solid state (see below), but as shown by cryoscopically determined molar masses **4** gradually dissociates in benzene solutions with decreasing concentration to finally give the monomeric formula mass of Ga–C($SiMe_2Et$)$_3$ in high dilution.

4. Crystal structure of 4

The molecular structure of **4** is depicted in Fig. 1, it possesses a nearly undistorted tetrahedron of four Ga atoms. The Ga–Ga–Ga angles inside the cluster deviate scarcely from the ideal value of 60° (59.96–60.07°, Table 1), and the Ga–Ga distances are almost equidistant (270.9(1)–271.2(1) pm). They are quite similar to that found for **3** (268.8(4) pm on average) [4], but much lengthened compared to the second known Ga_4 cluster $Ga_4[Si(SiMe_3)_3]_4$ [5] with Ga–Ga = 258.2 pm on average. The longer Ga–Si bonds of this compound compared to the shorter Ga–C bonds in **3** and **4** result in smaller steric interactions between the bulky substituents and may account thus for the shorter Ga–Ga distances; an electronic stabilization may give a further contribution to the enhanced stability against dissociation of those clusters bearing silyl substituents [5]. The larger steric stress in compounds **3** and **4** with the enlarged clusters in the molecular center may cause the easy monomerization in solution, while the In_4 analogues with longer In–C and In–In distances remain tetrameric in solution [6,25]. As expected for the delocalized bonding description, the Ga–Ga distances in the cluster are longer than the bond length of Ga–Ga single bonds in organoelement derivatives, which show values below 254 pm [26]. The Ga–C bond lengths (Ga(1)–C(1) 210.2(8), Ga(2)–C(2) 209.8(6) pm) are elongated compared to alkyl derivatives of the three-valent element [24,26]. The monomeric Ga(I) fragment Ga–C($SiMe_3$)$_3$ showed a Ga–C bond length of 206.4(17) pm, as determined by an electron diffraction experiment in the gas phase [13].

5. Experimental section

All procedures were carried out under purified argon in dried solvents (*n*-pentane with $LiAlH_4$, benzene, toluene, diisopropyl ether and THF with Na/benzophenone). $HC(SiMe_3)_3$ [16], $LiC(SiMe_3)_3 \cdot 2THF$ [16] and $[Li(THF)_3][Cl_3GaC(SiMe_3)_3]$ **1** [21] were synthesized according to literature procedures; the NMR spectroscopically detected THF content of **1** depends on the conditions of drying and decreases to two molecules for each formula unit in high-vacuum. Rieke magnesium was prepared from $MgCl_2$ (Fluka, 98%, water content < 0.5%) and potassium in THF [23], the black suspension was filtrated and the residue dried in vacuo. The pyrophoric powder contains two equivalents of KCl with respect to one equivalent of Mg. Commercial bromoform is stabilized by ethanol, which was removed by the repeated extraction with water. The organic layer was separated, dried with calcium chloride and distilled in vacuo. The pure bromoform was stored under argon at 4°C. Chlorodimethyl(ethyl)silane and a solution of methyllithium in diethyl ether from Aldrich were used without further purification.

Table 2
Crystal data and data collection parameters for **4**

Formula	$C_{52}H_{132}Ga_4Si_{12}$
Molecular weight	1373.54
Crystal system	Trigonal
Space group	R3; no.:146 [27]
Z	3
Unit cell dimensions	
a (pm)	2175.9(3)
b (pm)	2175.9(3)
c (pm)	1379.7(3)
α (°)	90
β (°)	90
γ (°)	120
V (10^{-30} m^3)	5657(2)
$D_{calc.}$ (g cm^{-3})	1.207
T (K)	293(2)
μ (mm^{-1})	1.633
Crystal dimensions (mm)	$0.42 \times 0.30 \times 0.17$
Diffractometer	STOE STADI4
Radiation: Mo–K_α (graphite-monochromated)	
2θ range	$3.6 \leq 2\theta \leq 50°$
Index ranges	$-25 \leq h \leq 12$
	$0 \leq k \leq 25$
	$-16 \leq l \leq 16$
Scan mode	$\omega - 2\theta$
Independent reflections	3753
Number of reflections $F > 4\sigma(F)$	3359
Program: SHELXTL, SHELXL-93 [28]; solutions by direct methods; full matrix refinement with all independent structure factors	
Parameters	226
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ ($F > 4\sigma(F)$)	0.044
$wR^2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.085
Max. residual (10^{30} e m^{-3})	0.497
Min. residual (10^{30} e m^{-3})	−0.246

5.1. *Tris[dimethyl(ethyl)silyl]methane*

A solution 24.48 g (0.20 mol) of chloro dimethyl(ethyl)silane and 5.9 ml (17.07 g, 0.068 mol) of purified bromoform in 100 ml of THF was cooled to − 78°C and dropwise treated with 141 ml of a cooled

(−78°C) 1.6 M solution of *n*-butyllithium in hexane (0.225 mol) under vigorous stirring. The mixture is warmed to r.t. over night and filtrated. The pale-yellow residue is washed with THF, and the solvent of the pale-yellow filtrate completely removed in vacuo. The product is isolated as the third fraction of a fractional distillation as a colorless liquid. Yield: 13.28 g (71%). B.p. 96–103°C (4 Torr). ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 0.95$ (t, 9H, Et–CH_3, $^3J_{HH} = 7.9$ Hz), 0.60 (q, 6 H, CH_2, $^3J_{HH} = 7.9$ Hz), 0.12 (s, 18 H, SiMe), −0.67 (1H, $HCSi_3$). ^{13}C-NMR (75 MHz,C_6D_6): $\delta = 10.9$ (CH_2), 7.9 (Et–CH_3), 0.9 (SiMe), −0.6 (CSi_3). IR (neat, CsBr plates, cm^{-1}): 2951 s, 2909 m, 2874 m, 2822 w νCH; 1464 m, 1420 w, 1377 w, 1254 vs δCH_3; 1117 vw, 1011 vs, 957 s νCC, δCH; 837 vs, 826 sh, 779 vs, 725 w ρCH_3(Si); 692 sh, 681 s ν_{as}SiC; 650 w, 596 w ν_sSiC, 525 w, 355 vw δSiC. MS *m*/*z* (%) (CI, isobutane): 259 (17) [$M^+ - CH_3$].

5.2. Tris[dimethyl(ethyl)silyl]methyllithium · 1.5THF

A solution of methyllithium in diethyl ether (1.6 M, 28.6 ml, 45.76 mmol) is added to a solution of 11.96 g (43.65 mmol) tris[dimethyl(ethyl)silyl]methane in 100 ml of THF. The mixture is stirred at r.t. for 20 h. The gold brown solution is treated with an additional portion of the 1.6 M solution of methyllithium (10.0 ml, 16.0 mmol), and the mixture stirred at r.t. for further 3 h. Diethyl ether is distilled off by a fractional distillation and the remaining THF solution heated under reflux for 2 h. All volatile components are removed in vacuo, the brown residue is treated with 50 ml of diisopropyl ether and filtrated. After concentration to about 15 ml the product crystallizes at −30°C. Yield: 11.02 g (65%), yellowish crystals. M.p. (closed capillary, argon) 82–83°C. ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 3.24$ (m, 6 H, OCH_2-THF), 1.22 (t, 9 H, Et–CH_3), 1.18 (m, 6H, CH_2-THF), 0.85 (q, 6H, Et–CH_2), 0.36 (18H, $SiMe_2$). ^{13}C-NMR (75 MHz, C_6D_6): $\delta = 68.4$ (CO-THF), 25.1 (CC-THF), 23.0 (LiC), 15.2 (CH_2), 9.6 (CH_3), 4.8 ($SiMe_2$). IR (paraffin, CsBr plates, cm^{-1}): 1344 w, 1319 w, 1294 w, 1244 s δCH_3; 1044 s, 1003 s; 955 vs, 901 vs νCC, νCO; 835 s, 820 vs, 793 s, 764 s ρCH_3(Si); 665 s ν_{as}SiC; 638 w, 625 w ν_sSiC; 586 m, 540 w, 419 w,br. νLiC, νLiO; 359 w δSiC.

5.3. $Li[Cl_3GaC(SiMe_2Et)_3] \cdot 0.75THF$ 2

A solution of 5.28 g (13.62 mmol) $LiC(SiMe_2Et)_3 \cdot 1.5THF$ in 50 ml of THF is dropwise added to a solution of 2.40 g (13.62 mmol) $GaCl_3$ in 75 ml of THF cooled to 0°C. The mixture is stirred for 30 min at 0°C and for 4 h at r.t. The yellow solution is evaporated and the pale-yellow residue dried in vacuo at r.t. and over night at 85°C. Treatment of the product with 50 ml of toluene, filtration, concentration and cooling to −50°C yields compound **2** as a colorless solid. Yield: 3.38 g (49%). M.p. (closed capillary, argon) 130°C. ^{1}H-NMR (300 MHz, C_6D_6): $\delta = 3.53$ (br, 3H, OCH_2-THF), 1.22 (br, 3H, CH_2-THF), 1.13 (br, 6H, Et–CH_2), 1.02 (t, 9H, Et–CH_3), 0.53 (s, 18H, $SiMe_2$). ^{13}C-NMR (75 MHz, C_6D_6): $\delta = 68.4$ (CO-THF), 25.3 (CC-THF), 11.9 (Et–CH_2), 8.5 (Et–CH_3), 2.0 ($SiMe_2$). IR (paraffin, CsBr plates, cm^{-1}): 1296 w, 1258 s δCH_3; 1171 vw, 1155 vw, 1034 m, 1003 s, 961 m, 916 w νCO, νCC; 885 w, 843 vs, 818 vs, 723 s, 706 m δCH_3(Si); 681 m ν_{as}SiC; 598 vw ν_sSiC; 536 vw νGaC; 415 vw, 359 m, 330 s νGaCl, δSiC_3, νLiO.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (10^{-22} m^2) for the atoms of the asymmetric unit in **4** (excluding H atoms)

	x	*y*	*z*	*U*(eq)
Ga1	0.0000	0.0000	0.5010	4.52(3)
Ga2	0.08295(3)	0.03726(4)	0.34077(8)	4.13(2)
C1	0.0000	0.0000	0.6533(6)	4.7(3)
Si1	0.0309(1)	−0.0632(1)	0.6966(1)	6.32(6)
C11	0.1061(4)	−0.0571(5)	0.6230(5)	7.9(2)
C12	−0.0392(5)	−0.1589(4)	0.6874(5)	8.5(3)
C14A[a]	−0.015(1)	−0.2134(8)	0.717(1)	13.0(6)
C13	0.0616(5)	−0.0483(5)	0.8259(5)	8.3(3)
C14B[a]	0.089(2)	−0.096(2)	0.845(2)	18.0(2)
C2	0.1874(3)	0.0852(3)	0.2 886(4)	4.4(2)
Si2	0.2325(1)	0.1838(1)	0.3151(2)	5.62(5)
C21	0.2043(4)	0.2322(4)	0.2319(5)	7.8(2)
C22	0.2119(4)	0.2042(5)	0.4388(5)	8.0(2)
C23	0.3311(4)	0.2288(4)	0.3053(6)	7.9(2)
C24	0.3670(8)	0.3081(8)	0.301(1)	21.5(8)
Si3	0.1833(1)	0.0700(1)	0.1522(1)	4.85(5)
C31	0.1103(4)	0.0791(4)	0.0936(4)	6.0(2)
C32	0.1644(4)	−0.0210(4)	0.1180(5)	6.7(2)
C33	0.2676(4)	0.1320(4)	0.0854(5)	7.2(2)
C34	0.2621(5)	0.1188(5)	−0.0235(5)	10.9(4)
Si4	0.2360(1)	0.0443(1)	0.3507(1)	5.61(5)
C41	0.3173(4)	0.0577(5)	0.2853(5)	7.5(2)
C42	0.2688(4)	0.0817(5)	0.4764(4)	7.7(2)
C43	0.1786(4)	−0.0533(4)	0.3640(5)	7.1(2)
C44	0.2135(7)	−0.0935(6)	0.4083(7)	11.7(4)

[a] Disordered methyl group.

5.4. Tetrahedro-tetrakis[tris(trimethylsilyl)-methylgallium(I)] 3

A suspension of 0.43 g Rieke-Mg/2 KCl (2.46 mmol) in 10 ml of toluene is treated with 1.18 g (2.11

mmol) of $LiGaCl_3C(SiMe_3)_3 \cdot 2THF$ (**1**) dissolved in 20 ml of toluene. After ultrasonic treatment for 30 min the mixture is vigorously stirred at 70°C for 20 h. The color changes over yellow and orange to dark red. The reaction mixture is filtrated and the solvent evaporated in vacuo. The residue is thoroughly dried in vacuo, treated with 20 ml of *n*-pentane and filtrated. The residue is washed twice with 10 ml of *n*-pentane, the filtrate concentrated until the beginning of crystallization and cooled to 0°C to yield dark red crystals of **3**. Yield: 0.48 g (76%). The characterization has been published before [4] with the exception of a complete ^{13}C-NMR spectrum. ^{13}C-NMR (75 MHz, C_6D_6): $\delta = 61.7$ (GaC), 7.7 ppm ($SiMe_3$).

5.5. *Tetrahedro-tetrakis-{tris[dimethyl(ethyl)silyl]-methylgallium(I)}* **4**

A suspension of 0.38 g Rieke-Mg/2 KCl (2.20 mmol) in 10 ml of toluene is treated with 0.99 g (1.93 mmol) $LiGaCl_3C(SiMe_2Et)_3 \cdot 0.75THF$ (**2**) dissolved in 25 ml of toluene. After ultrasonic treatment for 30 min the mixture is vigorously stirred at 70–80°C for 3 days. The color changes to dark red. The mixture is filtrated and the residue washed with 10 ml of toluene. The filtrate is evaporated in vacuo, the brown–red residue thoroughly dried in vacuo, treated with 20 ml of *n*-pentane and the precipitated colorless dust filtered off. The dark red filtrate is concentrated up to the beginning of crystallization and cooled to −30°C to obtain compound **4** as dark red crystals. Yield: 0.47 g (71%). Dec. p. (closed capillary, argon) 211°C. Molar mass (cryoscopically in benzene) [$g \cdot mol^{-1}$]: experimental 1045 (concentration 0.0079 mol l^{-1}, red solution), 475 (0.0013 mol l^{-1}, orange solution), 356 ($8.2 \cdot 10^{-4}$ mol l^{-1}, yellow-orange solution); calculated 1030.2 (trimer), 343.4 (monomer). MS (EI) *m*/*z* (%): 686 (0.8), 689 (0.8), 691 (0.5) all [M^+] of the dimer, 342 (32), 344 (26) all [M^+] of the monomer, 313 (100) [M^+-C_2H_5]. ^1H-NMR (300 MHz, C_6D_6): $\delta = 1.06$ (s, 5H, Et–CH_2 and Et–CH_3), 0.50 (s, 6H, $SiMe_2$). ^{13}C-NMR (75 MHz, C_6D_6): $\delta = 64.2$ (GaC), 14.3 (Et–CH_2), 8.4 (Et–CH_3), 3.9 ($SiMe_2$). IR (paraffin, CsBr plates, cm^{-1}): 1304 w, 1254 s δCH_3; 1169 vw, 1155 vw, 1078 vw, 1001 m, 959 w νCC; 918 vw, 887 vw, 835 vs, 822 vs, 721 m $\delta CH_3(Si)$; 692 m, 685 w $\nu_{as}SiC$; 633 m, 602 vw $\nu_{s}SiC$; 571 m νGa_4C_4; 465 vw, 415 vw, 357 vw, 330 vw δSiC, δCC. UV–vis (*n*-hexane): λ_{max} [nm] (lgε) = 224 (4.9), 258 (4.8), 283 (4.9), 440 (3.8).

5.6. *Crystal structure determination of* **4**

Dark red single crystals of **4** were obtained by recrystallization from *n*-pentane, it crystallizes as a racemic twin with BAS factors [28] of 0.63 and 0.37. Details of the crystal data, data collection parameters and structure determination are given in Table 2, atomic coordinates and isotropic displacement parameters in Table 3. The molecule is located on a crystallographic threefold rotational axis with Ga1 and C1 on the axis and three symmetrically equivalent Ga2 atoms. The silyl groups at C1 are also equivalent by symmetry; they show a disorder of the ethyl substituent, of which the methyl group (C14) occupies two positions at different carbon atoms (C12 and C13). The occupancy factors are 0.67 and 0.33; the bond length C13–C14B of the less occupied position was fixed to an ideal value. Due to the disorder of the ethyl groups at Si1 one hydrogen atom was not included in the refinement of the structure.

6. Supplementary material available

Further details of the crystal structure determination are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407275.

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References

[1] (a) C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. 103 (1991) 594; Angew. Chem. Int. Ed. Engl. 30 (1991) 564. (b) Review: C. Dohmeier, D. Loos, H. Schnöckel, Angew. Chem. 108 (1996) 141; Angew. Chem. Int. Ed. Engl. 35 (1996) 129.

[2] S. Schulz, H.W. Roesky, H.J. Koch, G.M. Sheldrick, D. Stalke, A. Kuhn, Angew. Chem. 105 (1993) 1828; Angew. Chem. Int. Ed. Engl. 32 (1993) 1729.

[3] (a) N. Wiberg, K. Amelunxen, H. Nöth, M. Schmidt, H. Schwenk, Angew. Chem. 108 (1996) 110; Angew. Chem. Int. Ed. Engl. 35 (1996) 65. (b) See also: E.P. Schram, N. Sudha, Inorg. Chim. Acta 183 (1991) 213.

[4] W. Uhl, W. Hiller, M. Layh, W. Schwarz, Angew. Chem. 104 (1992) 1378; Angew. Chem. Int. Ed. Engl. 31 (1992) 1364.

[5] G. Linti, J. Organomet. Chem. 520 (1996) 107.

[6] W. Uhl, R. Graupner, M. Layh, U. Schüz, J. Organomet. Chem. 493 (1995) C1.

[7] R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, J.L. Atwood, J. Coord. Chem. 30 (1993) 25.

[8] W. Uhl, S.U. Keimling, K.W. Klinkhammer, W. Schwarz, Angew. Chem. 109 (1997) 64; Angew. Chem. Int. Ed. Engl. 36 (1997) 64.

[9] (a) R. Ahlrichs, M. Ehrig, H. Horn, Chem. Phys. Lett. 183 (1991) 227. (b) U. Schneider, R. Ahlrichs, H. Horn, A. Schäfer, Angew. Chem. 104 (1992) 327; Angew. Chem. Int. Ed. Engl. 31 (1992) 353.

[10] W. Uhl, S.U. Keimling, unpublished.

[11] (a) C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. 106 (1994) 225; Angew. Chem. Int. Ed. Engl. 33 (1994) 199. (b) S. Schulz, T. Schoop, H.W. Roesky, L. Häming, A. Steiner, R. Herbst-Irmer, Angew. Chem. 107 (1995) 1015; Angew. Chem. Int. Ed. Engl. 34 (1995) 919. (c) S. Schulz, L. Häming, R. Herbst-Irmer, H.W. Roesky, G.M. Sheldrick, Angew. Chem. 106 (1994) 1052; Angew. Chem. Int. Ed. Engl. 33 (1994) 969. (d) S. Schulz, A. Voigt, H.W. Roesky, L. Häming, R. Herbst-Irmer, Organometallics 15 (1996) 5252. (e) C.K.F. von Hänisch, C. Üffing, M.A. Junker, A. Ecker, B.O. Kneisel, H. Schnöckel, Angew. Chem. 108 (1996) 3003; Angew. Chem. Int. Ed. Engl. 35 (1996) 2875. (f) W. Uhl, R. Graupner, M. Pohlmann, S. Pohl, W. Saak, Chem. Ber. 129 (1996) 143. (g) W. Uhl, R. Graupner, W. Hiller, M. Neumayer, Angew. Chem. 109 (1997) 62; Angew. Chem. Int. Ed. Engl. 36 (1997) 62.

[12] (a) A. Haaland, K.-G. Martinsen, S.A. Shlykov, H.V. Volden, C. Dohmeier, H. Schnöckel, Organometallics 14 (1995) 3116. (b) A. Haaland, K.G. Martinsen, H.V. Volden, D. Loos, H. Schnöckel, Acta Chem. Scand. 48 (1994) 172. (c) O.T. Beachley, Jr., R. Blom, M.R. Churchill, K. Faegri, Jr., J.C. Fettinger, J.C. Pazik, L. Victoriano, Organometallics 8 (1989) 346. (d) R. Blom, H. Werner, J. Wolf, J. Organomet. Chem. 354 (1988) 293. Cited literature.

[13] A. Haaland, K.-G. Martinsen, H.V. Volden, W. Kaim, E. Waldhör, W. Uhl, U. Schütz, Organometallics 15 (1996) 1146.

[14] (a) C. Dohmeier, H. Krautscheid, H. Schnöckel, Angew. Chem. 106 (1994) 2570; Angew. Chem. Int. Ed. Engl. 33 (1994) 2482. (b) W. Uhl, S.U. Keimling, W. Hiller, M. Neumayer, Chem. Ber. 128 (1995) 1137. (c) W. Uhl, S.U. Keimling, W. Hiller, M. Neumayer, Chem. Ber. 129 (1996) 397. (d) W. Uhl, M. Pohlmann, Organometallics 16 (1997) 2478.

[15] J. Weiß, D. Stetzkamp, B. Nuber, R.A. Fischer, C. Boehme, G. Frenking, Angew. Chem. 109 (1997) 95; Angew. Chem. Int. Ed. Engl. 36 (1997) 70.

[16] A.H. Cowley, N.C. Norman, M. Pakulski, G. Becker, M. Layh, E. Kirchner, M. Schmidt, Inorg. Synth. 27 (1990) 235.

[17] (a) W. Hiller, M. Layh, W. Uhl, Angew. Chem. 103 (1991) 339; Angew. Chem. Int. Ed. Engl. 30 (1991) 324. (b) An improved method in: F. Schaller, W. Schwarz, H.-D. Hausen, K.W. Klinkhammer, J. Weidlein, Z. Anorg. Allg. Chem. 623 (1997) 1455.

[18] S.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, K. Tavakkoli, A.D. Webb, J. Organomet. Chem. 462 (1993) 45.

[19] (a) A.I. Almansour, C. Eaborn, J. Organomet. Chem. 489 (1995) 181. (b) See also: A.G. Avent, C. Eaborn, P.B. Hitchcock, G.A. Lawless, P.D. Lickiss, M. Mallien, J.D. Smith, A.D. Webb, B. Wrackmeyer, J. Chem. Soc. Dalton Trans. (1993) 3259.

[20] C. Eaborn, A.I. Mansour, J. Chem. Soc. Perkin Trans. II (1985) 729.

[21] J.L. Atwood, S.G. Bott, P.B. Hitchcock, C. Eaborn, R.S. Shariffudin, J. D. Smith, A.C. Sullivan, J. Chem. Soc. Dalton Trans. (1987) 747.

[22] (a) N. Wiberg, G. Preiner, O. Schieda, Chem. Ber. 114 (1981) 2087. (b) D. Seyferth, J.L. Lefferts, J. Organomet. Chem. 116 (1976) 257.

[23] (a) R.D. Rieke, S.E. Bales, J. Am. Chem. Soc. 96 (1974) 1775. (b) R.D. Rieke, Acc. Chem. Res. 10 (1977) 301.

[24] (a) W. Uhl, K.-W. Klinkhammer, M. Layh, W. Massa, Chem. Ber. 124 (1991) 279. (b) W. Uhl, U. Schütz, W. Hiller, M. Heckel, Organometallics 14 (1995) 1073. (c) W. Uhl, I. Hahn, M. Koch, M. Layh, Inorg. Chim. Acta 249 (1996) 33. (d) W. Uhl, I. Hahn, U. Schütz, S. Pohl, W. Saak, J. Martens, J. Manikowski, Chem. Ber. 129 (1996) 897. (e) W. Uhl, R. Gerding, I. Hahn, S. Pohl, W. Saak, H. Reuter, Polyhedron 15 (1996) 3987. (f) W. Uhl, R. Graupner, I. Hahn, Z. Anorg. Allg. Chem. 623 (1997) 565. (g) T. Kräuter, B. Werner, B. Neumüller, Z. Naturforsch. B, Chem. Sci. 51 (1996) 637. (h) See also ref. [26].

[25] W. Uhl, A. Jantschak, M. Kaupp, unpublished.

[26] (a) W. Uhl, M. Layh, T. Hildenbrand, J. Organomet. Chem. 364 (1989) 289. W. Uhl, I. Hahn, H. Reuter, Chem. Ber. 129 (1996) 1425. (b) W. Uhl, I. Hahn, R. Wartchow, Chem. Ber. 130 (1997) 417. (c) X. He, R.A. Bartlett, M.M. Olmstead, K. Ruhlandt-Senge, B.E. Sturgeon, P.P. Power, Angew. Chem. 105 (1993) 761; Angew. Chem. Int. Ed. Engl. 32 (1993) 717. (d) G. Linti, W. Köstler, Angew. Chem. 108 (1996) 593; Angew. Chem. Int. Ed. Engl. 35 (1996) 550. (e) G. Linti, R. Frey, M. Schmidt, Z. Naturforsch., B. Chem. Sci. 49 (1994) 958. (f) D.S. Brown, A. Decken, A. H. Cowley, J. Am. Chem. Soc. 117 (1995) 5421. (g) A.K. Saxena, H. Zhang, J.A. Maguire, N.S. Hosmane, A.H. Cowley, Angew. Chem. 107 (1995) 378; Angew. Chem. Int. Ed. Engl. 34 (1995) 332. (h) X.-W. Li, W.T. Pennington, G.H. Robinson, J. Am. Chem. Soc. 117 (1995) 7578. (i) X.-W. Li, Y. Xie, P.R. Schreiner, K.D. Gripper, R.C. Crittendon, C.F. Campana, H.F. Schaefer, G.H. Robinson, Organometallics 15 (1996) 3798. (j) B. Beagley, S.M. Godfrey, K.J. Kelly, S. Kungwankunakorn, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Chem. Commun. (1996) 2179. (k) M.C. Kuchta, J.B. Bonanno, G. Parkin, J. Am. Chem. Soc. 118 (1996) 10914. (l) A.H. Cowley, A. Decken, C.A. Olazabal, J. Organomet. Chem. 524 (1996) 271.

[27] T. Hahn (Ed.), International Tables for Crystallography, Space Group Symmetry, vol. A, Kluwer Academic, Dordrecht-Boston-London, 1989.

[28] SHELXTL-Plus REL. 4.1, Siemens Analytical X-RAY Instruments Inc., Madison, USA, 1990; G. M. Sheldrick, SHELXL-93, Program for the Refinement of Structures, Universität Göttingen, 1993.