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Compounds containing gallium–silicon bonding: syntheses and X-ray crystal structures of bis-[2(dimethylaminomethyl)phenyl]-[tris(trimethylsilyl)silyl]gallium, $Aryl_2GaSi(SiMe_3)_3$ and diphenyl-[tris(trimethylsilyl)silyl]gallium, $Ph_2GaSi(SiMe_3)_3 \cdot THF$[☆]

Nigel L. Pickett [a], Oliver Just [a,c], Xiaohua Li [a,c], Donald G. Vanderveer [a,c], William S. Rees Jr. [a,b,c,*]

[a] *School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA*
[b] *School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA*
[c] *Molecular Design Institute, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA*

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Abstract

The preparation and characterization of two new compounds with gallium–silicon interatomic interactions are described. The single crystal X-ray diffraction structure of bis-[(2-dimethylaminomethyl)phenyl]-[tris(trimethylsilyl)silyl]gallium, $Aryl_2GaSi(SiMe_3)_3$ (Aryl = (2-dimethylaminomethyl)phenyl) (**1**) and diphenyl-[tris(trimethylsilyl)silyl]gallium tetrahydrofuranate, $Ph_2GaSi(SiMe_3)_3 \cdot THF$ (**2**), are described. Each compound is obtained from the reaction between $LiSi(SiMe_3)_3 \cdot 3THF$ and R_2GaCl (R = Aryl for (**1**) and R = Ph for (**2**)). (**1**) crystallizes in the monoclinic space group $P2_1/m$, $Z = 4$, $a = 9.0283(2)$, $b = 30.8751(6)$, $c = 12.3403(3)$ Å, $\beta = 104.4160(10)°$. The gallium atom is four-coordinate, surrounded by two carbon atoms, a silicon atom and a nitrogen atom stemming from one of the amine 'arms' of one of the 2-(dimethylaminomethyl)phenyl ligands; **2** crystallizes in the triclinic space group $P\bar{1}$, $Z = 2$, $a = 9.51000(10)$, $b = 12.94050(10)$, $c = 13.1823(2)$ Å, $\alpha = 78.7750(10)°$, $\beta = 83.30°$, $\gamma = 79.4740(10)°$. The gallium atom is four-coordinate, bonding to two carbon atoms, a silicon atom and the THF-oxygen, in a near tetrahedral geometry. Both compounds, **1** and **2**, are monomeric in the solid state. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gallium; Silicon; X-ray structure; Intramolecular coordination

1. Introduction

The organometallic chemistry of Group 13 elements has experienced a renewed interest during the past decade, mainly based on their touted potential as precursors for materials used in the microelectronics industry [1]. As one component of this effort, interest has developed in compounds containing Group 13 elements and silicon, possessing direct interactions between the two elements, with the first compound reported containing a gallium–silicon bond, tris(trimethylsilyl)gallane, $Ga(SiMe_3)_3$ [2]. Compounds of the type GaR_2L, where L is the tris-coordinating 2,6-bis-(dimethylaminomethyl)phenyl ligand, have been reported by Cowley. We were interested in the comparison of the bonding exhibited in these molecules with that found in compounds $GaRL_2$, where L is the

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[☆] Dedicated with fondness to Professor Alan H. Cowley, on the wonderful occasion of his birthday.

* Corresponding author. Tel.: + 1-404-894-4049; fax: + 1-404-894-1144.

E-mail address: will.rees@chemistry.gatech.edu (W.S. Rees)

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bis-coordinating (2-dimethylaminomethyl)phenyl ligand, to determine what similarities and differences were observed when two 'one arm' ligands were employed, versus one 'two arm' ligand. In particular, the desire was present to determine if the trigonal bipyramidal coordination geometry displayed by the central metal atom in Cowley's compounds was retained in the case when using a one-arm ligand. To conduct a more thorough comparison, Ph_2GaR also was examined as an analog for interatomic distances and angles. This report focuses on this geometrical–metrical comparison, specifically involving cases with Ga–Si interactions.

Compounds containing at least one gallium–silicon interaction, which to date have been structurally characterized, can be placed into three categories, (1) those consisting of a single gallium atom, bonded to one silyl group and additional ligands, (2) digallanes bonded exclusively to silyl ligands, and (3) clusters with a central core consisting of gallium atoms surrounded by silyl ligands. Compounds of the first type include $tmp_2GaSi(SiMe_3)_3$ **3** [3], which has the 2,2,6,6-tetramethylpiperidine ligand as shown in Fig. 1(a); the dichloro-gallium compound, $Cl_2GaSi(SiMe_3)_3 \cdot THF$, **4** [4] and the dimethyl-gallium compound, $Me_2GaSi(SiMe_3)_3 \cdot THF$, **5** [4]. This category also includes compounds containing chloride-bridged gallium dimers, $\{[(Me_3Si)_3Si]_2Ga\}_2(\mu\text{-}Cl)_2Li(THF)_2$, **6** [5], as well as μ-alkoxy-, $[\{(Me_3Si)_3Si\}(EtO)Ga]_2(\mu\text{-}OEt)_2$, **7** [4] and μ-hydroxo-bridged analogs, $[\{(Me_3Si)_3Si\}(Cl)Ga]_2(\mu\text{-}OH)_2 \cdot [NC_6H_3(2,6\text{-}Me_2)]$, **8** [4]. Additionally, an ionic complex has been reported containing the 2,2,6,6-tetramethylpiperidinium cation, $[tmpH_2][\{(Me_3Si)_3Si\}(PhO)_3Ga] \cdot PhOH$, **9** [4].

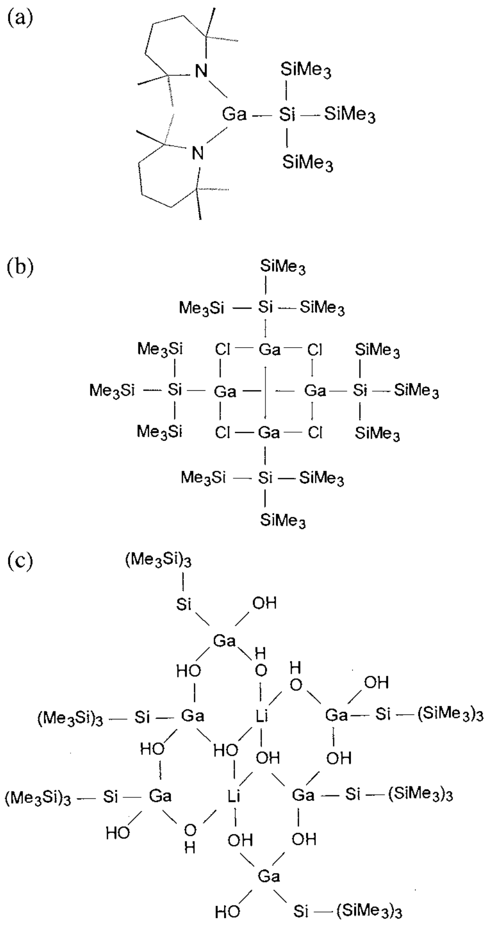

Fig. 1. Schematic representations of compounds (a) **3** (b) **13** (c) **14**.

Two structurally characterized complexes can be placed in the second category, containing unsupported gallium–gallium single bonds as well as gallium–silicon bonds: tetrakis[tris(trimethylsilyl)silyl]-digallane, $[\{(Me_3Si)_3Si\}_2Ga]_2$, **10** [6] and tris(tri-*t*-butylsilyl)digallane, $[(t\text{-}Bu_3Si)_3Si]_3Ga_2$, **11** [7]. In comparison with numerous structurally analyzed complexes containing the hypersilyl ligand, $(Me_3Si)_3Si^-$, the extremely bulky supersilyl ligand, $(t\text{-}Bu_3Si)_3Si^-$, is present only in complex **11**. The remaining known compounds (category 3) can be viewed as clusters displaying gallium–silicon interactions, as in the case of $[(Me_3Si)_3SiGa]_4$ **12**, which possesses a symmetrical tetrahedral core consisting of gallium atoms bonded to each other [8], or gallium–gallium and gallium–chloride interactions, as in the case of tetrakis(μ-chloro)-tetrakis[tris(trimethylsilyl)silyl]-gallium **13**, depicted in Fig. 1(b) [6]. Another Ga–Si cluster, structurally characterized by X-ray crystallography, is represented by the μ-hydroxo-gallium-silyl complex **14** [4] shown in Fig. 1(c).

Herein we describe the syntheses and X-ray crystal structures of two compounds that contain a gallium–silicon bond, bis-[2-(dimethylaminomethyl)-phenyl]-[tris(trimethylsilyl)silyl]-gallium, $Aryl_2GaSi(SiMe_3)_3$ (**1**) and diphenyl-[tris(trimethylsilyl)silyl]gallium tetrahydrofuranate, $Ph_2GaSi(SiMe_3)_3 \cdot THF$ (**2**).

2. Results and discussion

The reaction between $(Me_3Si)_3SiLi(THF)_3$ and $Aryl_2GaCl$ in toluene afforded after work-up the intramolecularly mono-coordinated Lewis base-free complex **1**. Results of the X-ray diffraction analysis, performed on a suitable single crystal of compound **1**, are shown in Fig. 2 with interatomic distances and angles listed in Table 2. The molecular structure of compound **1** consists of a gallium atom surrounded by a carbon atom from each aromatic ring, the central silicon atom of the tris(trimethylsilyl)silyl ligand and a nitrogen atom belonging to the dimethylaminomethyl 'arm' of one of the aryl ligands, stabilizing, in an intramolecular donor–acceptor interaction, the otherwise electronically unsaturated metal center. In con-

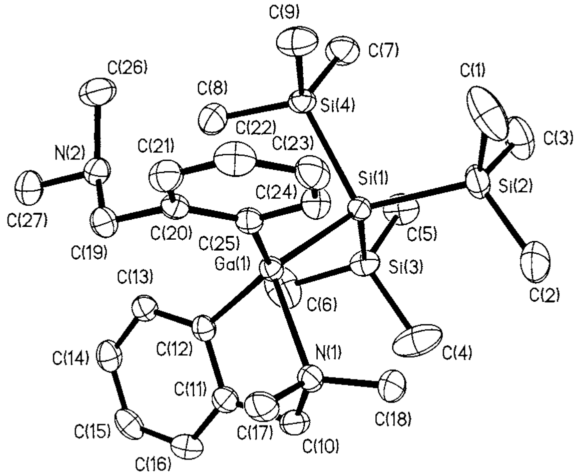

Fig. 2. ORTEP representation (30% probability level for thermal ellipsoids) of the solid state structure of compound **1**, as determined by single crystal X-ray diffraction analysis. All hydrogen atoms have been omitted from the representation for clarity of viewing.

trast, the nitrogen atom located on the second amine 'arm' of the remaining aryl ligand is uninvolved in either an intra- or an intermolecular interaction. The coordination sphere exhibited by the gallium atom deviates considerably from an ideal tetrahedron, due to angular distortion induced by geometric constraints associated with the five membered ring of the bidentate aryl ligand, which also gives rise to the chiral nature of the complex in the solid state.

Table 1
Crystal and data collection parameters for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{27}H_{51}N_2Si_4Ga$	$C_{25}H_{45}OSi_4Ga$
Formula weight (g mol^{-1})	764.261	543.69
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/m$	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.028(2)	9.510(10)
b (Å)	30.875(6)	12.941(10)
c (Å)	12.340(3)	13.182(2)
α (°)		78.78(10)
β (°)	104.41(10)	83.30(10)
γ (°)		79.47(10)
Volume (Å^3)	3331.55(13)	1558.92(4)
Z	4	2
Density (calc.) (g cm^{-3})	1.168	1.158
$F(000)$	1256	580
Crystal size (mm)	0.39 × 0.10 × 0.10	0.36 × 0.14 × 0.12
Reflections collected	17 135	14 016
Independent reflections	5857 [R(int) = 0.0452]	7117 [R(int) = 0.0267]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 3.11\%$, $wR_2 = 4.36\%$	$R_1 = 3.78\%$, $wR_2 = 6.22\%$

Table 2
Interatomic distances (Å) and angles (°) for compound **1**

Interatomic distances			
Ga(1)–C(12)	1.999(3)	N(1)–C(17)	1.488(4)
Ga(1)–C(25)	2.005(3)	N(1)–C(10)	1.492(4)
Ga(1)–N(1)	2.186(2)	N(2)–C(26)	1.462(4)
Ga(1)–Si(1)	2.4501(8)	N(2)–C(27)	1.468(4)
Si(1)–Si(3)	2.3651(11)	N(2)–C(19)	1.474(4)
Si(1)–Si(4)	2.3685(12)	C(10)–C(11)	1.509(4)
Si(1)–Si(2)	2.3717(12)	C(11)–C(12)	1.404(4)
		N(1)–C(18)	1.480(4)
Interatomic angles			
C(12)–Ga(1)–C(25)	124.70(12)	Si(4)–Si(1)–Si(2)	106.49(4)
C(12)–Ga(1)–N(1)	82.80(10)	Si(3)–Si(1)–Ga(1)	111.37(4)
C(25)–Ga(1)–N(1)	98.19(10)	Si(4)–Si(1)–Ga(1)	100.40(4)
C(12)–Ga(1)–Si(1)	113.88(8)	Si(2)–Si(1)–Ga(1)	122.78(4)
C(25)–Ga(1)–Si(1)	116.32(8)	C(10)–N(1)–Ga(1)	102.5(2)
N(1)–Ga(1)–Si(1)	112.37(7)	N(1)–C(10)–C(11)	110.2(2)
Si(3)–Si(1)–Si(4)	107.21(4)	C(12)–C(11)–C(10)	117.7(3)
Si(3)–Si(1)–Si(2)	107.35(5)	C(11)–C(12)–Ga(1)	112.0(2)

Compound **1** displays a slightly longer gallium–silicon interatomic distance of 2.45 Å than the corresponding distance in **2** (2.41 Å, see later) and negligibly deviates from the Ga–Si distance manifested by the three-coordinate and sterically strained complex **3**, $tmp_2GaSi(SiMe_3)_3$, (2.46 Å). This elongation may be considered a result of a decrease in electron density located at the gallium center, caused by a substantially weaker intramolecular Lewis base coordination through the lone pair on the nitrogen atom, as opposed to similar interactions with the more electronegative oxygen, as well as an increase in steric interactions between ligands situated on the gallium and the central silicon atom. The gallium–nitrogen distance of 2.18 Å can be arranged in the domain of rather short interactions [9a–f], pointing towards a relatively strong donor–acceptor relationship. Structurally characterized gallium compounds possessing 'two armed' 2,6-bis-(dimethylaminomethyl)phenyl aryl ligands, reported by the groups of Cowley and Schumann, include $ArylGaCl_2$ **15** [10,11] and $ArylGaH_2$ **16** [12]. Related gallium complexes containing 'one armed' 2-(dimethylaminomethyl)phenyl ligands, encompass $ArylGaCl_2$ **17** [13]; $ArylGaH_2$ **18** [13]; $Aryl_2GaH$ **19** [13]; $Aryl_2GaCl$ **20** [14a,b] and $Aryl_3Ga$ **21** [14a,b]. Gallium–nitrogen interatomic distances and coordination numbers around the gallium center for the above compounds are presented in Table 3.

In compounds **15** and **16** both amine 'arms' are coordinated intramolecularly to the central gallium atom, resulting in an approximately trigonal bipyramidal geometry for the gallium center, with the two nitrogen atoms from the same ligand occupying axial positions. A similar coordination sphere around the metal atom is portrayed by complexes **19**–**21**; however, the axial positions are coordinated by two nitrogen atoms belonging to independent ligands. The Ga–N interatomic distances in these complexes are, expectedly, longer than those reported in **1**, **17** and **18**, in which only one amine arm binds to the four-coordinate gallium center. The observed Ga–N interatomic distance elongation can be explained by both available dimethylamino arms, which are available for coordination, becoming competitively involved in an intramolecular Lewis base interaction at the electron deficient gallium center. The Ga–N bond in **1** is longer than those reported in the complexes **17** or **18**, which can be attributed to stronger electron withdrawing properties of groups bonded to gallium in **17** and **18**, creating a concomitant electron-deficient environment at the metal center in **1**. The gallium–carbon interatomic distances for both species **1** [1.99 and 2.00 Å] and **2** [1.99 Å] fall within earlier published values [15a,b].

Coordination about the gallium center for compound **1** is distorted greatly from that of an ideal tetrahedron, with bond angles ranging from 82.80(10)° to 124.70(12)°. This distortion is similar to that seen in **17** and **18**, and can be attributed, in the case of **1**, not only to the steric bulkiness of the ligands, but also to the geometric constraints associated with the acute bite angle of the five membered ring of the bidentate aryl ligand. The interatomic angles about the four-coordinate silicon atom bonded to the gallium atom are closer to those of an ideal tetrahedron, ranging from 100.40(4)° to 122.78(4)°.

Reaction between Ph_2GaCl and one equivalent of $(Me_3Si)_3SiLi(THF)_3$ in toluene afforded, after work-up, colorless crystals of **2**. Results of a single crystal X-ray analysis are shown in Fig. 3, with interatomic distances and angles listed in Table 4. Compound **2** consists of a gallium atom bonded to two carbon atoms, each from a Ph ligand, an oxygen atom, from a coordinated THF molecule, and a silicon atom from a tris(trimethylsilyl)silyl ligand, with a coordination geometry around the gallium center closer to that of an ideal tetrahedral than in compound **1**. The gallium–silicon interatomic distance of 2.41 Å appears to be close to the sum of the covalent radii for gallium and silicon (2.38 Å; Ga = 1.20 Å and Si = 1.18 Å). Presently, the longest structurally characterized Ga–Si interatomic distance is found in the three-coordinate sterically bulky compound **3**, $tmp_2GaSi(SiMe_3)_3$ [2.46 Å]. However, the observed Ga–Si distances in both **1** and **2** are longer than any other documented distance in non-bridged four-coordinate compounds (**4**, **5** and **9**), see Table 5. This elongation of the observed gallium–silicon interatomic distance presumably is due to the greater degree of steric interaction between the trisilyl ligand on the central silicon and the two aromatic rings on the gallium. The gallium–oxygen interatomic distance of 2.08 Å for compound **2** lies between the values of coordinated THF molecules reported for **4** and **5** (2.01 and 2.11 Å, respectively), with that of **4** being shorter (due to the enhanced Lewis acidity of the gallium center, where the gallium is bonded to two chlorine atoms, which are more electron withdrawing than the two Ph groups present in the case of **2**). The two gallium–carbon bonds in **2** (1.99 Å) are comparable with those seen in **5** (1.98 Å).

The four-coordinate geometry about the gallium center depicted for compound **2** is somewhat distorted from an ideal tetrahedron, with the bond angles ranging from 95.53(6)° to 120.48(5)°. This distortion is enhanced, relative to that seen in **4** or **5**, and, once more, is attributed to the steric bulk differentiation between the two species. Interatomic angles about the central four-coordinate silicon atom, bonded to the gallium, are closer to an ideal tetrahedron, ranging from 103.06(2)° to 117.39(2)°, with all three Ga–Si–Si angles being larger than 109.7°, due to steric interactions between both phenyl rings, the THF molecule and the bulky silyl ligand. Such manifestation is typically seen in other tris(silyl)silyl species [16].

^{1}H- and ^{13}C-NMR spectra of **1** and **2** in C_6D_6 show single peaks just up field of TMS, $\delta = 0.28$ ^{1}H (4.12 ^{13}C) for **1** and $\delta = 0.34$ ^{1}H (3.97 ^{13}C) for **2**. For the ^{29}Si-NMR spectra, the signal for the central silicon atom bound to the gallium is very broad for both compounds **1** and **2**, $\delta = -112.4$ and -113.1, respectively, with the terminal $SiMe_3$ signals being much sharper at $\delta = -9.13$ for **1** and $\delta = -9.46$ for **2**. The location of the ^{29}Si-NMR signals in related compounds containing the $GaSi(SiMe_3)_3$ moiety (accommodating essentially unpolarized gallium–silicon bonds) varies be-

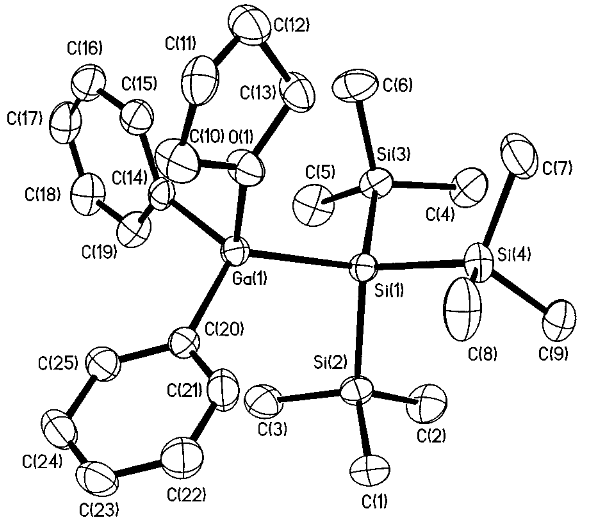

Fig. 3. ORTEP representation (30% probability level for thermal ellipsoids) of the solid state structure of compound 2, as determined by single crystal X-ray diffraction analysis. All hydrogen atoms have been omitted from the representation for clarity of viewing.

Table 3
Gallium–nitrogen interatomic distances and coordination number about the gallium center for crystallographically characterized compounds containing a gallium–nitrogen acceptor–donor bond

Compound	Gallium–nitrogen interatomic distances (Å)	Coordination number	Reference
17	2.071(2)	4	[13]
18	2.087(7)	4	[13]
1	2.186(2)	4	Herein
20	2.304(6), 2.385(6)	5	[14a]
	2.301(2), 2.394(2)	5	[14b]
19	2.324(7), 2.457(8)	5	[13]
15	2.351(4), 2.359(4)	5	[11]
16	2.380(6), 2.398(6)	5	[12]
21	2.551(2), 2.399(2)	5	[14a]
	2.531(3), 2.377(4)	5	[14b]

tween $\delta = -115$ [5] and $\delta = -142$ [17]. This value is between both extremes of polarity, thus, when the silicon atom is attached to a highly electronegative element ($Si^{\delta+}$–$F^{\delta-}$), the resonance shifts to lower field values ($\delta = -33$ in $FSi(SiMe_3)_3$ [4]), whereas when attached to a highly electropositive element ($Si^{\delta-}$–$Li^{\delta+}$), the resonance shifts to higher field values ($\delta = -185$ in $LiSi(SiMe_3)_3$ [18a]).

3. Summary

Examples of compounds containing gallium–silicon bonding interactions have been prepared and characterized by single crystal X-ray diffraction analyses. Comparison has been drawn between the presence of two mono-intramolecular ligand coordination environments in the present work, and one bi-intramolecular ligand coordination environment in earlier work of Cowley and Schumann. For thorough metrical and geometrical comparison of local geometry around the central gallium atom in these species, a comparable steric environment was designed, prepared and characterized, compound **2**.

The gallium–silicon interatomic distances presented here (Table 5) are on the long side (2.418 and 2.450 Å) for the range of other available data (2.362–2.503 Å). The intramolecularly coordinated gallium–nitrogen interatomic distance observed for compound **1** (2.186 Å) is on the short end of the corresponding values of previous explorations (2.071–2.551 Å). Likewise, the geometry correlates well in these species. The five-coordinate gallium environments are at the upper end of this range (2.301–2.551 Å), while four-coordinate examples are at the lower end of the scale (2.071–2.186 Å). It is noteworthy that among the four-coordinate examples, compound **1** (2.186 Å) is somewhat longer than other reported data (2.071–2.087 Å). The origin of these metrical deviations, and the corresponding interatomic angles, are explained by a combination of electronic and steric impacts on the molecules.

Table 4
Interatomic distances (Å) and angles (°) for compound **2**

Interatomic distances			
Ga(1)–C(20)	1.996(2)	Si(1)–Si(3)	2.3482(7)
Ga(1)–C(14)	1.998(2)	Si(1)–Si(2)	2.3489(7)
Ga(1)–O(1)	2.0859(12)	Si(1)–Si(4)	2.3517(7)
Ga(1)–Si(1)	2.4184(5)		
Interatomic angles			
C(20)–Ga(1)–C(14)	112.52(7)	Si(3)–Si(1)–Si(2)	109.74(3)
C(20)–Ga(1)–O(1)	95.53(6)	Si(3)–Si(1)–Si(4)	108.87(3)
C(14)–Ga(1)–O(1)	100.13(6)	Si(2)–Si(1)–Si(4)	106.80(3)
C(20)–Ga(1)–Si(1)	120.48(5)	Si(3)–Si(1)–Ga(1)	110.61(2)
C(14)–Ga(1)–Si(1)	116.21(5)	Si(2)–Si(1)–Ga(1)	103.06(2)
O(1)–Ga(1)–Si(1)	107.14(4)	Si(4)–Si(1)–Ga(1)	117.39(2)

Table 5
Gallium–silicon interatomic distances for crystalographically characterized compounds

Compound	Gallium–silicon interatomic distance (Å)	Ref.
4	2.362(1)	[4]
9	2.370(2)	[4]
14	2.384[a]	[4]
8	2.384(3)	[4]
7	2.388(2)	[4]
13	2.398[a]	[6]
12	2.406(2)	[9]
5	2.408(2)	[4]
2	2.418(5)	Herein
6	2.439(5)	[5]
1	2.450(8)	Herein
3	2.468(1)	[3]
11	2.503[a]	[7]

[a] Average interatomic distance.

4. Experimental

4.1. General comments

All syntheses and manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk or glove box techniques. All solvents were distilled from appropriate drying agents prior to use (sodium/benzophenone for THF, Et_2O, toluene and hexanes). $GaCl_3$, $Si(SiMe_3)_4$ and MeLi were procured commercially and used without further purification. $(Me_3Si)_3SiLi(THF)_3$ [18a,b], Ar_3Ga [14a,b] and Ph_2GaCl [19] were prepared as described in the literature. All NMR spectra were recorded in benzene-d_6 with $SiMe_4$ as an external reference. Microanalytical data were obtained on a Perkin–Elmer CHNS/O 2400 Analyzer.

4.2. Preparation of $Aryl_2GaCl$

$Aryl_2GaCl$ was prepared by a different method to that described in the literature [14b] to avoid the formation of a $Aryl_2GaCl/Aryl_3Ga$ mixture [14a]. Instead, $Aryl_3Ga$ (7.00 g, 14.82 mmol) and $GaCl_3$ (1.31 g, 7.41 mmol) were refluxed in toluene (80 ml) for 24 h. The resulting pale yellow solution was reduced in solvent volume by 50%. Storing at −35°C for several days afforded after work-up $Aryl_2GaCl$ as a crystalline white solid. Typical yields: 93%. $C_{18}H_{24}N_2ClGa$. ^1H-NMR (500 MHz, C_6D_6): δ 2.15 (s, 12H, CH_3), 2.95 (vbr, 2H, CH_2), 4.05 (vbr, 2H, CH_2), 7.04, 7.19 (8H, m, C_6H_4).

4.3. Preparation of $Aryl_2GaSi(SiMe_3)_3$ (**1**)

A solution of $Aryl_2GaCl$ (0.708 g, 1.50 mmol) in toluene (20 ml) was added dropwise to a vigorously stirred solution of $(Me_3Si)_3SiLi(THF)_3$ (0.704 g, 1.50 mmol) in toluene (30 ml). The resulting cloudy reaction mixture was stirred for 18 h at ambient temperature. Removal of the toluene at reduced pressure afforded a white residue, which subsequently was extracted with pentane (ca. 20 ml). The resulting solution was filtered through Celite. Following reduction of the filtrate to ca. 2 ml, it was stored at −35°C for several days affording after work-up compound **1** as colorless crystals. Yield: 70%, m.p. = 103–104°C. Anal. Calc. for $C_{27}H_{51}N_2Si_4Ga$: C, 55.78; H, 8.09; N, 4.82%. Found: C, 55.24; H, 9.46; N, 4.33%. ^1H-NMR ([ppm], 500 MHz, C_6D_6): δ 0.28 [s, 27H, $Si(CH_3)_3$], 1.94 [s, 12H, $N(CH_3)_2$], 3.37 [m, 4H, CH_2], 7.17, 7.25, 7.93 [m, 8H, C_6H_4], 7.25; ^{13}C-NMR ([ppm], 500 MHz, C_6D_6): δ 4.12 [s, $Si(CH_3)_3$], 46.38, 67.14, 126.65, 126.91, 138.31, 144.15, [s, C_6H_4]; ^{29}Si-NMR ([ppm], 500 MHz, C_6D_6): δ −9.13 [s, $SiMe_3$], −112.41 [vbr s, $Si(SiMe_3)_3$].

4.4. Preparation of $Ph_2GaSi(SiMe_3)_3 \cdot THF$ (**2**)

A solution of Ph_2GaCl (0.65 g, 2.51 mmol) in toluene (25 ml) was added dropwise to a vigorously stirred solution of $(Me_3Si)_3SiLi(THF)_3$ (1.18 g, 2.51 mmol) in toluene (25 ml). The resulting bright yellow and cloudy reaction mixture was stirred for 18 h at ambient temperature. Removal of the toluene at reduced pressure yielded a yellowish residue, which was extracted with hexane (ca. 20 ml) and filtered through Celite. Reduction of the filtrate to ca. 2 ml and storing at −35°C afforded after work-up compound **2** as colorless crystals. Yield: 33%, m.p. = 138–141°C. Anal. Calc. for $C_{25}H_{45}OSi_4Ga$: C, 55.26; H, 8.28%. Found: C, 53.74; H, 8.83%. ^1H-NMR ([ppm], 500 MHz, C_6D_6): δ 0.34 [s, 27H, $Si(CH_3)_3$], 0.99 [m, 4H, THF], 3.44 [m, 4H, THF], 7.23, 7.34, 7.80 [m, 10H, C_6H_5]; ^{13}C-NMR ([ppm], 500 MHz, C_6D_6): δ 3.97 [s, $Si(CH_3)_3$], 25.04 [s, THF], 70.94 [s, THF], ^{29}Si-NMR (500 MHz, C_6D_6) δ −9.46 [s, $SiMe_3$], −113.15 [vbr s, $Si(SiMe_3)_3$].

4.5. Crystallographic investigations

Crystals of compounds **1** and **2** were selected and mounted on glass fibers while in a stream of cold argon gas and placed immediately on a Siemens SMART CCD diffractometer at 173 K under a stream of cold nitrogen gas. Graphite monochromatic Mo–K_α radiation was used ($\lambda = 0.71073$ Å). In both cases, reflections were collected with a frame width of 0.3° in ω scans and a counting time of 30 s per frame at a crystal-to-detector distance of 4.911 cm. The double-pass method of scanning was used to exclude any noise. The first 50 frames of data were recollected at the conclusion of data collection to monitor crystal decay. Insignificant (less than 0.5% in both cases) deterioration of the crystal quality was detected. Both structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares on F^2 procedures. Semi-empirical absorption corrections were applied. All non-hydrogen atoms were refined to convergence with anisotropic displacement coefficients. Hydrogen atoms were refined isotropically. All software sources are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). Additional crystal and data collection parameters for both compounds are given in Table 1.

5. Supplementary material

Full details of the data collection, atomic coordinates, complete interatomic distances and angles and thermal parameters have been deposited as supplementary material at the Cambridge Crystallographic Data Centre, CCDC No. 110247 for compound **1**, CCDC No. 110248 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax.: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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