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Synthesis and Characterization of Gallium Silylamido Complexes

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The reaction between $GaCl_3$ and 1 equiv of $HN(SiMe_2Ph)_2$ in CH_2Cl_2 solution affords colorless crystals of $[Cl_2Ga\{\mu\text{-}N(H)SiMe_2Ph\}]_2$ (**1**). The related reaction between $GaCl_3$ and 1 equiv of $LiN(SiMe_2Ph)_2$ in hexane solution results in the isolation of colorless crystals of $[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ (**2**). In contrast, treatment of $GaCl_3$ with 1 equiv of $N(SiMe_3)_3$ in CH_2Cl_2 solutions affords colorless crystals of $[MeGaCl_2]_2$ (**4**). Compounds **2** and **4** are the result of monochloride substitution and transfer of a phenyl and methyl ligand, respectively, from the silyl group of the amine to the Ga center. All the complexes have been characterized by X-ray crystallography.

Introduction

Gallium nitride (GaN) is a technologically important material because of its semiconducting properties, thermal stability, and resistance to chemical attack.[1] GaN has a band gap of 3.4 eV and is therefore suitable for use in a range of optoelectronic devices, such as blue-light-emitting diodes.[2] Bulk GaN may be prepared via the reaction of either Ga_2O_3[3] or Ga[4] metal with ammonia at high temperatures. Alternatively, thin films of GaN can be prepared via dual-source chemical vapor deposition (CVD) of R_3Ga (R = Me, Et) and ammonia.[1] However, this route requires high reaction temperatures (>900 °C) and huge overpressures of ammonia (as great as 10^4). Single-source precursors, which contain preformed Ga−N bonds, offer several potential advantages over these traditional routes. Possible advantages include lower deposition temperatures, reduced contamination from carbon, and removal of the inefficient use of ammonia. A further advantage of single-source precursors is the possibility of forming unusual phases, for example, cubic GaN.[5] A number of single-source precursors to GaN have been reported previously.[1,6] The list includes $[Ga(N_3)_3(py)_3]$,[7] $[N_3\{Me_2N\}_2Ga\{\mu\text{-}NMe_2\}]_2$,[8] $[H_2GaNH_2]_3$,[5] $[Ga\{N(SiMe_3)_2\}(OSiMe_3)_2py]$,[9] $[(N_3)_2Ga\{(CH_2)_3NMe_2\}]$,[10] and $[H_2GaN_3]_n$.[11] However, there are problems associated with these compounds, including the stability of the precursor and the quality of the GaN produced. Consequently there is a need for new Ga−N compounds.

Dehalosilylation reactions (i.e., the elimination of Me_3SiX) have been employed in the synthesis of relatively pure samples of GaAs and InAs at low temperatures.[12] Recently, this method was extended to dehydrosilylation reactions (involving the elimination of Me_3SiH) for the preparation of GaP, GaAs, AlP, and AlAs nanoparticles.[13] We are interested in developing gallium silylamido complexes as CVD precursors to GaN. These complexes should reduce the possibility of contamination from species such as carbon in the resulting films and address some of the foregoing problems.

In this paper, we report the synthesis and structures of two gallium silylamido complexes, $[Cl_2Ga\{\mu\text{-}N(H)SiMe_2Ph\}]_2$ (**1**) and $[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ (**2**). The structure of $[MeGaCl_2]_2$ (**4**) is also described. The formation of compounds **2** and **4** is the result of a phenyl and methyl group transfer, respectively, from the silyl group of the amide to the gallium center.

Results and Discussion

The reaction between $GaCl_3$ and $HN(SiMe_2Ph)_2$ at −78 °C in CH_2Cl_2 resulted, after workup, in a 63% yield of colorless crystalline **1** (Scheme 1). Analytical and spectroscopic data for **1** were consistent with the formulation $[Cl_2Ga\{N(H)SiMe_2Ph\}]_2$. The dimeric nature of **1** was confirmed by an X-ray crystal-

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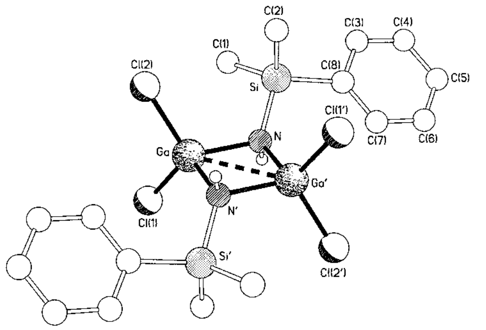

Figure 1. Molecular structure of **1**. The transannular Ga···Ga separation is 2.803(1) Å.

Scheme 1

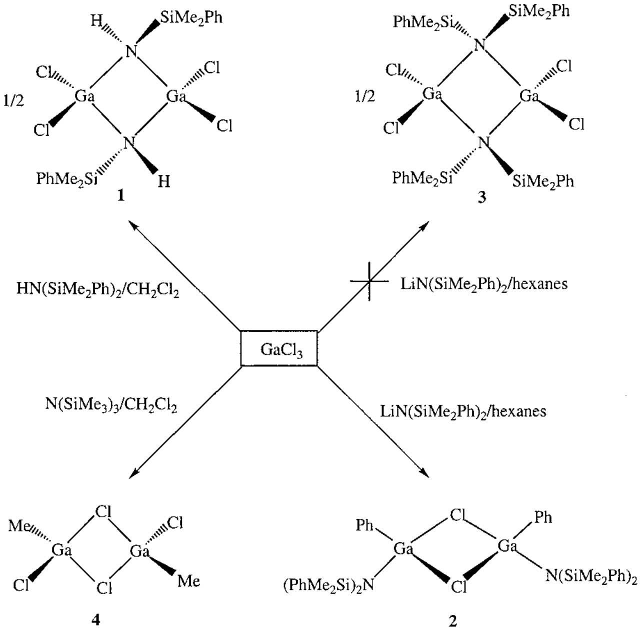

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ga−Cl(1)	2.1380(13)	Ga−Cl(2)	2.1540(14)
Ga−N	1.988(4)	Ga−N′	1.968(3)
Si−N	1.801(4)		
N−Ga−N′	89.74(14)	N−Ga−Cl(1)	110.55(11)
N′−Ga−Cl(1)	115.86(11)	N−Ga−Cl(2)	114.88(11)
N′−Ga−Cl(2)	110.73(11)	Cl(1)−Ga−Cl(2)	113.12(6)
Si−N−Ga	120.1(2)	Si−N−Ga′	127.2(2)
Ga−N−Ga′	90.26(14)		

lographic study which shows it to be centrosymmetric with a planar Ga_2N_2 ring and *trans* dimethylphenylsilyl groups (Figure 1). The bond lengths and angles within the $Ga_2N_2Cl_4$ core (Table 1) and to the silyl substituents are virtually identical to those seen in $[Cl_2Ga\{\mu\text{-}N(H)SiMe_3\}]_2$.[14] The Ga_2N_2 ring is very nearly square, with the Ga−N−Ga and N−Ga−N angles being, within statistical significance, 90°, though there is a small asymmetry in the nitrogen bridge, with the Ga−N distances being 1.968(3) and 1.988(4) Å (there is a similar asymmetry in the structure of $[Cl_2Ga\{\mu\text{-}N(H)SiMe_3\}]_2$). The transannular Ga···Ga separation [2.803(1) Å] lies at the short end of Ga···Ga separations in similarly bridged species (the separation in the trimethyl species is 2.810 Å[14]). The N−Si bond [1.801(4) Å] is the same as in $[Cl_2Ga\{\mu\text{-}N(H)SiMe_3\}]_2$, but significantly longer than observed in, for example, $[Me(Cl)Ga\{\mu\text{-}N(H)SiMe_3\}]_2$[15] [1.744 Å] and $[Me_2Ga\{\mu\text{-}N(Si(H)Me_2)_2\}]_2$[16] [av 1.770 Å]. There are no major intermolecular packing interactions of note, though there is evidence for a weak stacking interaction between the phenyl rings of symmetry-related molecules which have a mean interplanar separation of 3.75 Å and a centroid···centroid distance of 4.35 Å. The shortest intermolecular Cl···Cl distance is 3.45 Å.

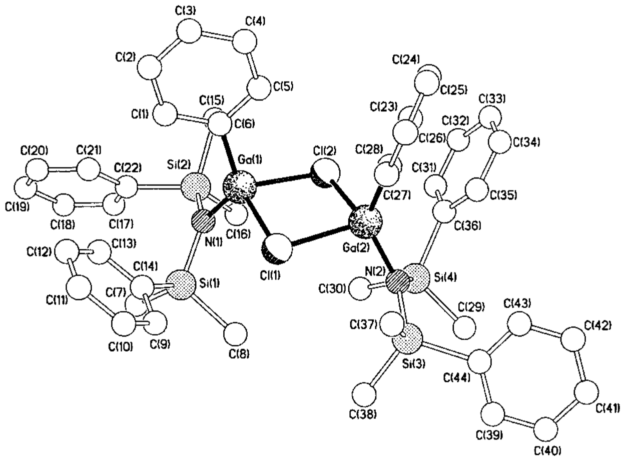

Figure 2. Molecular structure of **2**. The transannular Ga···Ga separation is 3.411(1) Å.

The mutually *trans* arrangement of the bridging $N(H)SiMe_2Ph$ groups we observe in **1** is also seen in the solid-state structures of all other known dimeric silylamidogallanes.[14−18] However, the NMR data for compound **1** indicated that in solution, mixtures of *trans*-$[Cl_2Ga\{\mu\text{-}N(H)SiMe_2Ph\}]_2$ and *cis*-$[Cl_2Ga\{\mu\text{-}N(H)SiMe_2Ph\}]_2$ were present (*trans:cis* = 1:1). A similar *trans−cis* isomerization was reported for the dimeric silylamidogallanes described previously.[14−18]

With a view to preparing a gallium silylamide, of the type $[Cl_2Ga\{N(SiR_3)_2\}]_n$, the reaction of $GaCl_3$ with a lithiated silylamine was carried out. Accordingly, $GaCl_3$ was reacted with 1 equiv of $LiN(SiMe_2Ph)_2$ at −78 °C in hexanes (Scheme 1). A colorless crystalline product was obtained by cooling a hexane solution of **2** to −20 °C. Analytical and spectroscopic data for **2** were consistent with the formation of $[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ rather than the expected product $[Cl_2Ga\{N(SiMe_2Ph)_2\}]_2$ (**3**). The structure of **2** was confirmed by X-ray crystallography and is seen to have approximate molecular C_2 symmetry (about an axis perpendicular to the Ga_2Cl_2 plane) that is broken only by the differently skewed orientations of the gallium-bound phenyl rings (Figure 2). The $[N(SiMe_2Ph)_2]$ groups are oriented *cis* with respect to the Ga_2Cl_2 ring, which has a nonplanar geometry, being slightly folded (by ca. 13°) about the Cl···Cl vector. This structure is, to the best of our knowledge, the only reported example of a bis(amino)-substituted Ga_2Cl_2 ring system, the closest related structure being that of an indium complex,[19] where the amino groups are *trans*. The dimensions of the Ga_2Cl_2 core (Table 2) are very similar to those observed in $[Cy_2Ga(\mu\text{-}Cl)]_2$[20] (Cy = cyclohexyl), having a transannular Ga···Ga separation of 3.411(1) Å (cf. 3.38 Å in

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ga(1)−Cl(1)	2.3587(9)	Ga(1)−Cl(2)	2.3813(8)
Ga(1)−N(1)	1.850(3)	Ga(1)−C(6)	1.952(2)
Ga(2)−Cl(1)	2.4025(8)	Ga(2)−Cl(2)	2.3651(9)
Ga(2)−N(2)	1.846(2)	Ga(2)−C(28)	1.957(2)
Si(1)−N(1)	1.739(3)	Si(2)−N(1)	1.738(3)
Si(3)−N(2)	1.738(3)	Si(4)−N(2)	1.740(3)
N(1)−Ga(1)−C(6)	130.04(11)	N(1)−Ga(1)−Cl(1)	111.27(9)
C(6)−Ga(1)−Cl(1)	105.73(9)	N(1)−Ga(1)−Cl(2)	106.62(8)
C(6)−Ga(1)−Cl(2)	107.12(7)	Cl(1)−Ga(1)−Cl(2)	87.89(3)
N(2)−Ga(2)−C(28)	132.93(11)	N(2)−Ga(2)−Cl(2)	109.80(9)
C(28)−Ga(2)−Cl(2)	103.97(7)	N(2)−Ga(2)−Cl(1)	106.68(8)
C(28)−Ga(2)−Cl(1)	106.76(7)	Cl(2)−Ga(2)−Cl(1)	87.25(3)
Ga(1)−Cl(1)−Ga(2)	91.50(3)	Ga(2)−Cl(2)−Ga(1)	91.87(3)

the cyclohexyl species). In both complexes the N−Ga−C angles are substantially enlarged from tetrahedral, being 130.0(1)° and 132.9(1)° at Ga(1) and Ga(2), respectively, in **2**, and 132.4° in $[Cy_2Ga(\mu\text{-}Cl)]_2$,[20] enlargements that are very much greater than those observed in, for example, **1**, where the Cl(1)−Ga−Cl(2) angle is only 113.1(1)°. The Ga−N distances [Ga(1)−N(1) = 1.850(3) Å, Ga(2)−N(2) = 1.846(2) Å] are both significantly shorter than those seen in, for example, $[(\eta^1\text{-}Cp^*)Ga\{N(SiMe_3)_2\}(\mu\text{-}N_3)]_2$[21] (Cp* = pentamethylcyclopentadienyl), where the Ga−N distance is 1.872 Å. There are no noteworthy intermolecular packing interactions.

The isolation of compound **2** is surprising and is a result of a monochloride substitution and transfer of a phenyl ligand from the $[N(SiMe_2Ph)_2]$ group to the Ga center. The mechanism for the formation of **2** is not known. However, related methyl group transfers have been observed previously for indium and antimony compounds.[22,23] If the reaction between $GaCl_3$ and 2 equiv of $LiN(SiMe_2Ph)_2$ is carried out, the result is the same; however, compound **2** was formed in a higher yield. It is interesting to note that a phenyl ligand rather than a methyl ligand transfers from the $[N(SiMe_2Ph)_2]$ group in the reaction described herein. The NMR data for compound **2** indicated that in solution, mixtures of *cis*-$[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ and *trans*-$[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ were present.

The reaction between $GaCl_3$ and 1 equiv of $N(SiMe_3)_3$ in CH_2Cl_2 at −78 °C resulted, after workup, in a light brown oil. Cooling of this oil to −20 °C overnight afforded colorless crystalline **4** (Scheme 1). Spectroscopic and analytical data indicated, however, that a product of, or similar to, the anticipated formula $[Cl_xGaN(SiMe_3)_{3-x}]_n$ ($x = 1-3$) had not been formed. The nature of the crystalline material was established by X-ray crystallography and found to be dimeric with the formula $[MeGaCl_2]_2$ (**4**). The structure of **4** revealed that individual $[MeGaCl_2]$ units are associated into centrosymmetric dimers via bridging chlorine interactions (Figure 3), the molecule having (excluding the methyl hydrogen atoms) both molecular and crystallographic C_{2h} symmetry. Each gallium is four-coordinate with a severely distorted tetrahedral geometry. The Ga_2Cl_2 core is planar, and the internal ring angles at gallium and chlorine are 88.89(6)° and 91.11(6)°, respectively (Table 3). As expected, the terminal Ga−Cl bond distance of 2.1547(9) Å is shorter than the bridging Ga−Cl bond distance [2.3324(12) Å]. The Cl(1)−Ga−C(1) angle is significantly enlarged from tetrahedral at 127.0(3)°, a value closer to the analogous angle observed in **2** than that seen in **1**. The structure of **4** is related to the aluminum analogue $[MeAlCl_2]_2$, which has a similar dimeric structure.[24] The packing of molecules of **4** is a classic cubic close-packed arrangement with hexagonal layers of molecules lying in the crystallographic *ab* plane stacked in an ABCABC fashion (Figure 4); the interlayer separation is 5.82 Å. The isolation of compound **4** was surprising and is a result of a monochloride substitution and transfer of a methyl group from the amine $[N(SiMe_3)_3]$ to the gallium center. This is similar to the phenyl transfer observed in the formation of compound **2**, although in this reaction a chloride was not substituted for an amide ligand. Interestingly, the formation of $[MeGaCl_2]_2$ from the reaction of $GaCl_3$ with $[Me_2SiO]_4$, $(Me_3Si)_2O$, Me_3SiOLi, or Me_4Si has been described previously.[25] The colorless crystals were difficult to isolate from the light brown oil, and so the NMR spectrum of **4** shows a number of peaks in the region 0.42−0.62 ppm. However, a number of peaks are also expected due to the possible formation of isomers in solution (e.g., *trans*-$[MeGaCl_2]_2$ and *cis*-$[MeGaCl_2]_2$).

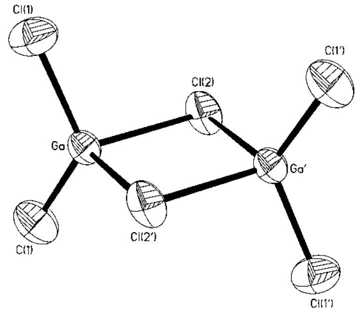

Figure 3. Molecular structure of **4** (90% probability ellipsoids). The transannular Ga···Ga separation is 3.3304(15) Å.

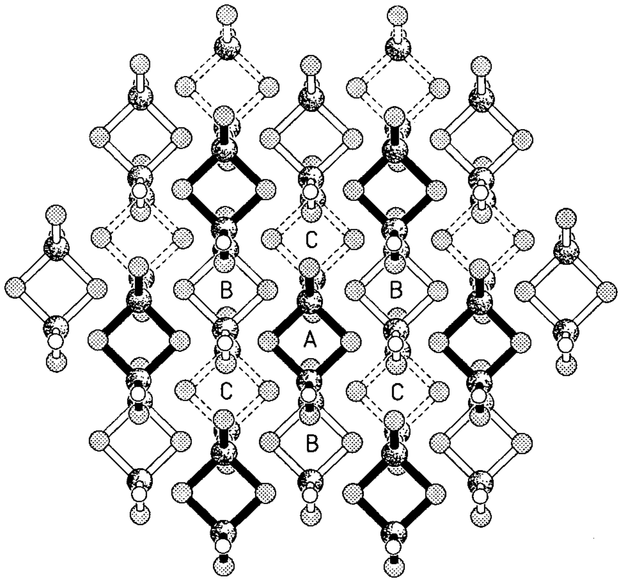

Figure 4. Part of the pseudo cubic close-packed array of molecules present in the crystals of **4**, showing the ABC sequence layers.

Table 3. Bond Lengths (Å) and Angles (°) for **4**

Ga−C(1)	1.928(7)	Ga−Cl(1)	2.1547(19)
Ga−Cl(2)	2.3324(12)		
C(1)−Ga−Cl(1)	127.0(3)	C(1)−Ga−Cl(2)	113.17(17)
Cl(1)−Ga−Cl(2)	103.83(4)	Cl(2′)−Ga−Cl(2)	88.89(6)
Ga′−Cl(2)−Ga(1)	91.11(6)		

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In summary, the gallium silylamido complexes $[Cl_2Ga\{N(SiMe_2Ph)_2\}]_2$ (**1**) and $[PhGa\{N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$ (**2**) have been synthesized and structurally characterized. In addition, the reaction of $GaCl_3$ with $N(SiMe_3)_3$ led to the formation of $[MeGaCl_2]_2$ (**4**), which was structurally characterized. The formation of **2** and **4** involved unusual transfer of phenyl and methyl groups, respectively, from the silyl ligand to the Ga center. Unfortunately, the low volatility of compound **2** and the presence of a Ga−C bond precluded thin film growth by CVD. However, preliminary investigations of compound **1** have shown that it can serve as a precursor to GaN, the details of which will be described in a future publication.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glovebox. All solvents were distilled from appropriate drying agents prior to use (sodium−ether and hexanes; CaH_2 for CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at the University College London (UCL).

Physical Measurements. NMR spectra were recorded on a Brüker AMX400 spectrometer at UCL, referenced to CD_2Cl_2, which was dried and degassed over molecular sieves prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (δ 0.00). Mass spectra (CI) were run on a micromass ZABSE instrument and IR spectra on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected.

Synthesis of 1. A solution of $HN(SiMe_2Ph)_2$ (1.64 mL, 5.68 mmol) in CH_2Cl_2 (10 mL) was added slowly to a stirred solution of $GaCl_3$ (1.00 g, 5.68 mmol) in CH_2Cl_2 (15 mL) at −78 °C. A white precipitate formed immediately, and the reaction mixture was allowed to warm slowly to room temperature over a 1 h period. The resulting colorless solution was reduced in vacuo to a volume of approximately 10 mL. Cooling of this solution to −20 °C afforded colorless crystals of **1** after a few days. These crystals were redissolved in ether (5 mL) and cooled to −20 °C. X-ray-quality crystals of **1** were obtained after a few weeks at this temperature (63% yield). Mp: 104−107 °C. ^{1}H NMR (CD_2Cl_2): δ 0.78 (s, SiCH_3), 0.82 (s, SiCH_3), 2.41 (s, NH), 7.00−7.39 (m, SiC_6H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 1.16 (s, SiCH_3), 3.10 (s, SiCH_3), 127.9, 128.4 (s, *m*-SiC_6H_5), 129.3, 131.0 (s, *p*-SiC_6H_5), 133.7, 133.9 (s, *o*-SiC_6H_5), 134.4 (s, *ipso*-SiC_6H_5). IR (KBr disk, cm^{-1}): 2957 m, 1428 s, 1258 s, 1180 m, 1116 vs, 1051 m, 998 w, 933 s, 831 vs, 800 vs, 748 m, 699 vs, 687 w, 594 w, 471 w.

Synthesis of 2. A solution of ^nBuLi (1.78 mL, 2.84 mmol; 1.6 M in hexane) was added dropwise to a cooled (−78 °C) solution of $HN(SiMe_2Ph)_2$ (0.82 mL, 2.84 mmol) in hexanes (10 mL) with stirring. A white precipitate formed after a few minutes, and the mixture was stirred for 2 h. The slurry was then added dropwise to a cooled (−78 °C) solution of $GaCl_3$ (0.5 g, 2.84 mmol) in hexanes (10 mL). The mixture was allowed to warm slowly to room temperature with stirring. After this time the reaction mixture was filtered through Celite to give a pale yellow solution. Cooling of this solution to −20 °C afforded colorless crystals of **2** after a few weeks (20% yield). The reaction between 2 equiv of $LiN(SiMe_2Ph)_2$ with $GaCl_3$ resulted in a 40% yield of compound **2**. ^{1}H NMR (CD_2Cl_2): δ 0.17 (s, SiCH_3), 0.25 (s, SiCH_3), 7.20−7.63 (m, SiC_6H_5 and GaC_6H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 1.6, 2.7 (s, SiCH_3), 126.1, 126.5 (s, *m*-SiC_6H_5), 131.9, 132.3 (s, *p*-SiC_6H_5), 140.8, 142.0 (s, *o*-SiC_6H_5), 128.3, 128.5 (s, *m*-GaC_6H_5), 131.4, 131.6 (s, *p*-GaC_6H_5), 140.2, (s, *o*-GaC_6H_5), *ipso*-carbon not detected. IR (KBr disk, cm^{-1}): 2957 m, 2899 w, 1483 w, 1427 s, 1406 w, 1302 w, 1258 vs, 1180 w, 1112 s, 1022 s, 999 w, 947 s, 868 vs, 798 vs, 729 s, 700 s, 648 w, 522 w, 472 w, 449 w, 407 w.

Table 4. Crystallographic Data for Compounds **1**, **2**, and **4**

	1	**2**	**4**
empirical formula	$C_{16}H_{24}N_2Si_2Cl_4Ga_2$	$C_{44}H_{54}N_2Si_4Cl_2Ga_2$	$C_2H_6Cl_4Ga_2$
fw	581.8	933.6	311.3
space group	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*C*2/*m* (no. 12)
T (°C)	−90	−100	−173
a (Å)	12.530(1)	10.296(1)	11.999(2)
b (Å)	14.472(2)	13.970(1)	6.737(1)
c (Å)	13.457(1)	17.756(1)	7.218(1)
α (deg)		73.50(1)	
β (deg)	93.85(1)	83.42(1)	126.20(1)
γ (deg)		75.59(1)	
V (Å^3)	2434.8(4)	2369.2(3)	470.8(1)
Z	4[a]	2	2[b]
ρ_{calcd} (g cm^{-3})	1.587	1.309	2.196
λ (Å)	0.71073	1.54178	0.71073
μ (mm^{-1})	2.76	3.64	6.77
R1[c]	0.040	0.037	0.054
wR2[d]	0.086	0.087	0.152

[a] The molecule has crystallographic C_i symmetry. [b] The molecule has crystallographic C_{2h} symmetry. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Synthesis of 4. A solution of $N(SiMe_3)_3$ (0.66 g, 2.84 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cooled (−78 °C) solution of $GaCl_3$ (0.50 g, 2.84 mmol) in 10 mL of CH_2Cl_2 with stirring. The reaction temperature was maintained at −78 °C for 1 h, and the mixture was allowed to warm slowly to room temperature. During this time a color change occurred from colorless to light straw, and the mixture was stirred at 40 °C for 30 min. The solvent was removed in vacuo, and the resulting light brown oil was dissolved in CH_2Cl_2 (2 mL). Cooling of this solution to −20 °C overnight afforded colorless crystals of **4**. Anal. Calcd for CH_3Cl_2Ga (carried out on oil): C, 7.72; H, 1.94; Cl, 45.55. Found: C, 9.39; H, 2.40; Cl, 41.32. ^{1}H NMR ($CDCl_3$): δ 0.416−0.624 (m, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 3.23, 2.91, 2.06, 1.78, 1.62.

X-ray Crystallography. Table 4 provides a summary of the crystallographic data for compounds **1**, **2**, and **4**. CCDC 171272 to 171274.

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Supporting Information Available: ORTEP diagrams and X-ray crystallographic files in CIF format for the structures of compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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