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Synthesis and Structural Characterization of Homoleptic Gallium Amides

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The homoleptic Ga(III) amides $[(t\text{-Bu(H)N})_2\text{Ga}(\mu\text{-N(H)}t\text{-Bu})]_2$ (1) and $\text{Ga(N}(t\text{-Bu})\text{SiMe}_3)_3$ (2) have been synthesized via the reaction of $GaCl_3$ with 3 equiv of the appropriate lithium amide. A third tris(amide), Ga(tmp)_3 (3) (tmp = 2,2,6,6-tetramethylpiperidide), was prepared by the thermal reaction of $GaCl_3$ with 3 equiv of Htmp. The structures of 1 and $\text{Ga(N(SiMe}_3)_2)_3$ (4) have been determined by single-crystal X-ray diffraction methods. Compound 1 crystallizes in the monoclinic space group *C*2/*m* (No. 12) with $a = 9.879(2)$ Å, $b = 17.427(7)$ Å, $c = 19.742(1)$ Å, $\beta = 101.38(3)°$, $V = 3332(23)$ Å^3, and $Z = 4$. Compound 4 crystallizes in the trigonal space group $P\bar{3}1c$ (No. 163) with $a = 16.050(1)$ Å, $c = 8.6063(7)$ Å, $V = 1920(5)$ Å^3, and $Z = 2$. Compound 1 exists in the crystalline state as discrete dimeric units with two bridging and four terminal amido groups. The crystalline state of 4 comprises discrete monomers with D_3 symmetry. The structure of 2 is disordered.

Introduction

The recent surge of interest in compounds with group 13–15 bonds is attributable to their use as single-source precursors to important electronic materials such as semiconductors (e.g. GaAs) and lasers (e.g. GaN).[2] Initial work on GaAs precursors tended to be based on the assumption that the ideal precursor stoichiometry is 1:1. Indeed, several compounds of this genre have proved to be quite successful for the deposition of thin films of GaAs. However, subsequently it has become clear that the 1:1 combining ratio of the precursor is not necessarily preserved in the films due to the facile discharge of smaller molecules such as diarsines. Recalling that the formation of thin films from single-source precursors is under kinetic control,[3] ligand fragmentation and/or reorganization can play a key role in the conversion of molecules to materials by vapor deposition methods. In this vein, we have found that the 1:3 stoichiometry compound $\text{Ga(As-}t\text{-Bu}_2)_3$ is superior to any of the 1:1 precursors. The majority of the known gallium–nitrogen compounds feature a 1:1 stoichiometry, typical examples being amine adducts,[4] $R_3Ga{\leftarrow}NR'_3$, and gallium amides with various degrees of oligomerization,[5] $(R_2GaNR'_2)_n$. With the foregoing considerations in mind, we decided to prepare some gallium(III) amides with 1:3 stoichiometry. Such homoleptic compounds are, in fact, quite rare, being confined to $[\text{Ga(NMe}_2)_3]_2$[6] and $\text{Ga(N(SiMe}_3)_2)_3$.[7] Only the former derivative has been the subject of a detailed X-ray analysis; however, it was noted that $\text{Ga(N(SiMe}_3)_2)_3$ is isomorphous with $\text{Fe(N(SiMe}_3)_2)_3$[7,8] and thus possesses a similar structure. The present work is concerned with the synthesis and spectroscopic characterization of $[(t\text{-Bu(H)N})_2\text{Ga}(\mu\text{-N(H)-}t\text{-Bu})]_2$ (1), $\text{Ga(N}(t\text{-Bu})\text{SiMe}_3)_3$ (2), and Ga(tmp)_3 (3) (tmp = 2,2,6,6-tetramethylpiperidide). The X-ray crystal structures of 1 and $\text{Ga(N(SiMe}_3)_2)_3$ (4) are also reported.

Results and Discussion

Syntheses of Homoleptic Gallium Amides. The gallium(III) amides $[(t\text{-Bu(H)N})_2\text{Ga}(\mu\text{-N(H)-}t\text{-Bu})]_2$ (1) and $\text{Ga(N(SiMe}_3)\text{-}t\text{-Bu})_3$ (2) were prepared in >90% yields by treatment of $GaCl_3$ with 3 equiv of the appropriate lithium amide in Et_2O solution at −78 °C (eq 1). The homoleptic piperidide derivative Ga(tmp)_3

$$\text{GaCl}_3 + 3\text{LiNR}_1\text{R}_2 \rightarrow (1/n)[\text{Ga(NR}_1\text{R}_2)_3]_n + 3\text{LiCl} \qquad (1)$$

$$\begin{aligned} \mathbf{1}:\ & R_1 = \text{H};\\ & R_2 = t\text{-Bu};\ n = 2\\ \mathbf{2}:\ & R_1 = \text{SiMe}_3;\\ & R_2 = t\text{-Bu};\ n = 1 \end{aligned}$$

(3; tmp = 2,2,6,6-tetramethylpiperidide) can also be prepared by the metathetical route summarized in eq 1. However, it was discovered that higher yields of 3 (>80%) can be realized via the reaction of $GaCl_3$ with 3 equiv of Htmp in refluxing toluene solution (eq 2). The synthesis of the bis(trimethylsilyl)amido

$$\text{GaCl}_3 + 3\text{Htmp} \rightarrow \text{Ga(tmp)}_3 + 3\text{HCl} \qquad (2)$$

compound $\text{Ga(N(SiMe}_3)_2)_3$ (4) was reported several years ago by Bürger, Wannagat, et al.[7] Compounds 1, 2, and 4 are colorless, crystalline solids; 3 is a yellow, microcrystalline solid.

The proposed compositions for 1–3 are in accord with elemental analysis data. Furthermore, peaks corresponding to monomers with these compositions were detected in the CI mass spectra of these compounds. In the case of 1, a peak was detected at *m*/*e* 572, suggesting the existence of a dimer in the vapor phase.

The ^{1}H NMR of 1 exhibits a broad multiplet resonance in the *t*-Bu region, suggesting dynamic behavior (dimer or higher oligomer formation?) in solution. In contrast, the ^{1}H resonances

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Table 1. Crystal Data, Details of Intensity Measurements, and Structure Refinement for [*t*-Bu(H)NGa(μ-N(H)-*t*-Bu)]$_2$ (**1**) and Ga(N(SiMe$_3$)$_2$)$_3$ (**4**)

	1	**4**
formula	$C_{24}H_{60}Ga_2N_6$	$C_{22}H_{62}GaN_3OSi_6$
fw	572.21	622.99
cryst dimens, mm^3	0.25 × 0.31 × 0.51	0.19 × 0.28 × 0.45
cryst syst	monoclinic	trigonal
space group	$C2/m$	$P\bar{3}1c$
a, Å	9.879(2)	16.050(1)
b, Å	17.427(7)	16.050(1)
c, Å	19.742(1)	8.6063(7)
α (=γ), deg	90	90
β, deg	101.38(3)	90
V, Å^3	3332(23)	1920(5)
d(calc), g cm^{-3}	1.160	1.165
Z	4	2
radiation	Mo Kα	Mo Kα
no. of unique refls	2735	563
no. of tot. obs refls	2132	525
σ test	$F_o > 6\sigma(F_o)$	$F_o > 6\sigma(F_o)$
no. of params	145	50
weighting scheme: g in $[(\sigma(F))^2 + gF^2]^{-1}$	0.0001	0.000 625
R^a	0.0958	0.0441
$R_w{}^b$	0.0960	0.0540

[a] $R = \sum||F_o| - |F_c|\sum|F_o|$. [b] $R_w = [w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Atomic Positional Parameters for (*t*-Bu(H)N)$_2$Ga(μ-N(H)-*t*-Bu)]$_2$ (**1**)

atom	x	y	z	U, Å^2
Ga(1)	0.38217(12)	0.48291(7)	0.69071(6)	0.0408(4)
N(1)	0.5861(8)	0.5032(3)	0.7071(4)	0.028(3)
N(2)	0.3492(10)	0.3763(5)	0.6739(5)	0.055(4)
N(3)	0.2699(10)	0.5466(6)	0.6324(5)	0.064(4)
C(1)	0.6856(14)	0.4811(7)	0.6604(7)	0.060(5)
C(2)	0.2420(14)	0.3396(9)	0.6235(7)	0.066(6)
C(3)	0.627(2)	0.5105(9)	0.5866(7)	0.107(8)
C(4)	0.2530(14)	0.6278(6)	0.6243(7)	0.056(5)
C(5)	0.8236(14)	0.5149(9)	0.6873(8)	0.094(7)
C(6)	0.101(2)	0.3611(10)	0.6306(10)	0.111(9)
C(7)	0.688(2)	0.3949(7)	0.6557(8)	0.082(7)
C(8)	0.262(2)	0.3563(10)	0.5514(7)	0.115(9)
C(9)	0.259(2)	0.2508(6)	0.6351(9)	0.100(8)
C(10)	0.345(2)	0.6707(11)	0.6731(14)	0.25(2)
C(11)	0.126(2)	0.6517(10)	0.632(2)	0.43(4)
C(12)	0.274(3)	0.6562(14)	0.5635(13)	0.221(13)

for **2** and **4** comprise sharp singlets and are thus consistent with the existence of monomers in solution. Assignment of the Me$_3$Si (d, 0.49 ppm) and *t*-Bu (d, 1.50 ppm) resonances in **2** is based on the chemical shifts of the Me$_3$Si (d, 0.36 ppm)[9] and *t*-Bu (d, 1.35 ppm) groups in **4** and **1**, respectively. The equivalence of all the Me groups in the ^{1}H NMR spectrum of **3** is also indicative of monomer formation.

X-ray Crystallography. Single crystals of **1**, **2**, and **4** suitable for X-ray analysis were grown by recrystallization at −30 °C. Unfortunately **3** could only be obtained in microcrystalline form. Moreover, in the case of **2** the structure was highly disordered and could not be refined satisfactorily. A summary of the crystal data for **1** and **4** is presented in Table 1, and the fractional coordinates for these compounds are given in Tables 2 and 3, respectively.

The solid state of **1** comprises dimers of composition [(*t*-Bu-(H)N)$_2$Ga(μ-N(H)-*t*-Bu)]$_2$. There are no unusually short intermolecular contacts. Individual molecules of **1** reside on a C_2 crystallographic axis which is perpendicular to and passes through the center of the Ga$_2$N$_2$ four-membered ring. The molecular structure and atom-numbering scheme for **1** are illustrated in Figure 1. As shown in Figure 2, the Ga$_2$N$_2$ ring adopts a nonplanar "butterfly" type of conformation in which the endocyclic angle at nitrogen (Ga(1)–N(1)–Ga(1)′ = 94.8(4)°) is larger than that at gallium (N(1)–Ga(1)–N(1)′ = 81.6(3)°). A similar trend in M$_2$E$_2$ core bond angles is evident in virtually all group 13/15 dimers.[2] The puckering of the Ga$_2$N$_2$ ring is similar to that observed in the homoleptic dimer [{(Me$_3$SiCH$_2$)$_2$-As}$_2$Ga(μ-As(CH$_2$SiMe$_3$)$_2$]$_2$.[10] The overall conformation of **1** (Figure 2) is presumably governed by the minimization of steric repulsions between the *t*-Bu groups. It is interesting to note, however, that the *t*-Bu groups of the bridging amido substituents adopt a mutually cis disposition. The Ga–N bond distance for the bridging amide groups in **1** (2.008(8) Å) is similar to those measured for other dimers with this structural feature, e.g. [Me$_2$-Ga(μ-N(H)-*t*-Bu]$_2$ (2.012(4) Å),[4c] [(Me$_2$N)$_2$Ga(μ-NMe$_2$)]$_2$

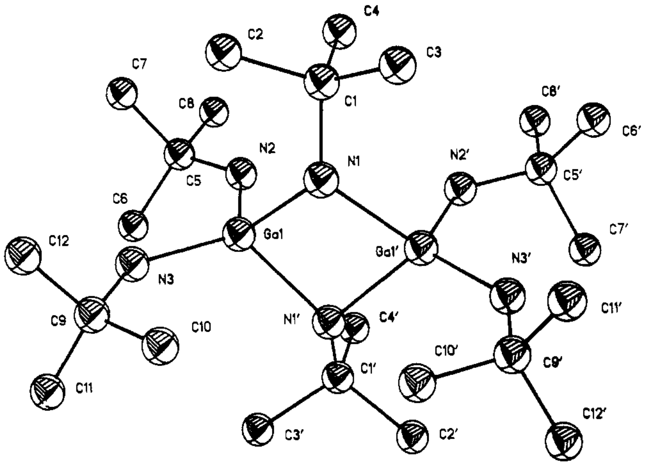

Figure 1. View (ORTEP) of **1** showing the atom-numbering scheme. The hydrogen atoms are omitted for clarity.

Table 3. Atomic Positional Parameters for Ga(N(SiMe$_3$)$_2$)$_3$ (**4**)

atom	x	y	z	U, Å^2
Ga	−0.3333	0.3333	0.2500	0.037(5)
Si	−0.1736(1)	0.2966(1)	0.3832(2)	0.055(6)
N	−0.2660(2)	0.2660(2)	0.2500	0.043(3)
Me(1)	−0.0523(5)	0.3583(6)	0.2918(9)	0.083(24)
Me(2)	−0.1845(7)	0.1889(6)	0.4850(9)	0.090(8)
Me(3)	−0.1765(6)	0.3752(6)	0.5382(7)	0.077(11)
O(1)S	0.0000	0.0000	0.684(3)	0.123(10)
C(1)S	−0.057(2)	0.057(2)	0.7500	0.162(20)
C(2)S	0.045(3)	−0.045(3)	0.7500	0.254(38)

Table 4. Selected Bond Distances (Å) and Angles (deg) for [(*t*-Bu(H)N)$_2$Ga(μ-N(H)-*t*-Bu)]$_2$ (**1**)

	Bond Distances		
Ga(1)–N(1)	2.008(8)	N(1)–C(1)	1.52(2)
Ga(1)–N(2)	1.904(9)	N(2)–C(5)	1.45(2)
Ga(1)–N(3)	1.813(10)	N(3)–C(9)	1.429(15)
	Bond Angles		
N(1)–Ga(1)–N(1)′	81.6(3)	Ga(1)–N(1)–Ga(1)′	94.8(4)
N(1)–Ga(1)–N(2)	109.4(3)	Ga(1)–N(1)–C(1)	127.2(6)
N(1)–Ga(1)–N(3)	117.6(4)	Ga(1)–N(2)–C(5)	128.8(8)
N(2)–Ga(1)–N(3)	115.1(4)	Ga(1)–N(3)–C(9)	136.1(8)

Table 5. Selected Bond Distances (Å) and Angles (deg) for Ga(N(SiMe$_3$)$_2$)$_3$ (**4**)

	Bond Distances		
Ga–N	1.870(6)	Si–Me(2)	1.867(7)
N–Si	1.740(4)	Si–Me(3)	1.853(7)
Si–Me(1)	1.861(7)		
	Bond Angles		
N–Ga–N′	120.0	N–Si–Me(3)	111.0(3)
Ga–N–Si	119.6(2)	Me(1)–Si–Me(2)	106.3(4)
Ga–N–Si′	120.7(3)	Me(1)–Si–Me(3)	108.5(4)
N–Si–Me(1)	112.9(3)	Me(2)–Si–Me(3)	105.7(4)
N–Si–Me(2)	112.1(3)		

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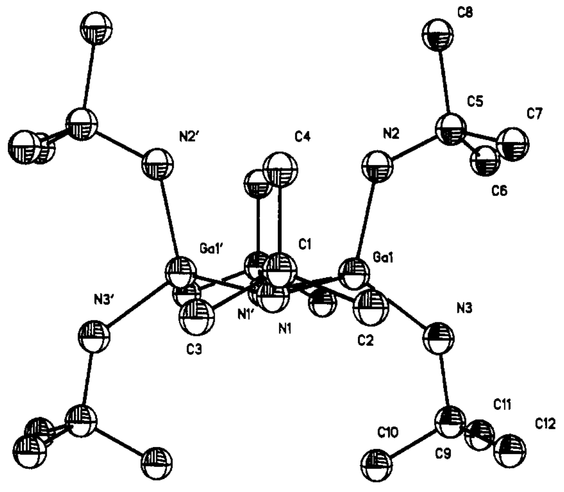

Figure 2. Side view of **1** showing the arrangement of *t*-Bu groups. The hydrogen atoms are omitted for clarity.

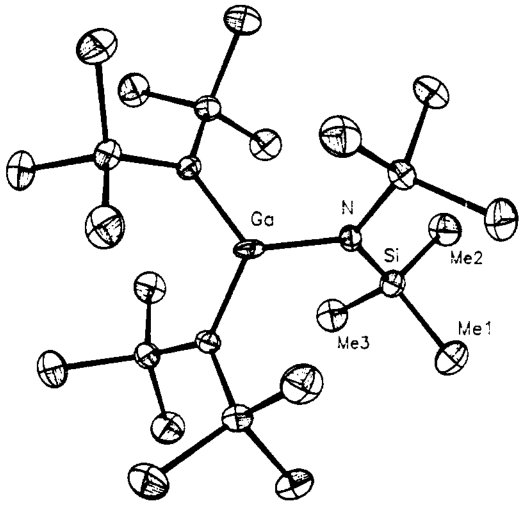

Figure 3. View (ORTEP) of **4** showing the atom-numbering scheme.

(2.005(2) Å),[6] and $(Me_2NGaH_2)_2$ (2.027(4) Å).[11] In a recent study,[5c] it was shown that terminal Ga–N bond distances in amido complexes span the range 1.85–1.92 Å. This distance is 1.813(10) Å in **1** and thus falls close to the established experimental range and to the estimated single-bond value of 1.84 Å if adjustment is made for ionic contributions.

As pointed out above, the unit cell dimensions, space group, and Ga–N bond distance of $Ga(N(SiMe_3)_2)_3$ (**4**) have been determined previously.[7] However, no further structural details are available. Discrete monomers of **4** crystallize in the trigonal space group $P\bar{3}1c$. There are two molecules of **4** and two molecules of THF of crystallization in the asymmetric unit. The molecular symmetry D_3 is imposed crystallographically, and consequently the GaN_3 skeleton possesses a rigorous trigonal planar geometry (Figure 3). The $(Me_3Si)_2N$ groups are arranged in a propeller fashion with a dihedral angle of 50° between the Si_2N and GaN_3 planes. Although the nitrogen atoms adopt a trigonal planar geometry (sum of angles = 359.9(3)°), the Ga–N bond distance falls within the range 1.85–1.92 Å, which has been observed for a bond order of unity.[5c] Taken together with the observation of a dihedral angle of 50°, there is therefore little evidence of dative π bonding from nitrogen lone pairs to the formally vacant 4p orbital on gallium. A previously reported photoelectron study of **4** supports this view.[12] Additionally, the overall similarity of the solid state structures of **4** and $M(N(SiMe_3)_2)_3$ (M = Al,[13] In,[14] Fe[8]) implies that the observed conformation is determined by the packing of the Me groups.

Unfortunately, it was not possible to solve the X-ray crystal structure of $Ga(N(t\text{-}Bu)SiMe_3)_3$ (**2**) satisfactorily because of disorder among the *t*-Bu and Me_3Si groups. However, since individual molecules of **2** reside on sites of C_3 symmetry, it is likely that the solid state structure is very similar to that of **4**.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. The solvents toluene, hexane, tetrahydrofuran, and diethyl ether were distilled freshly from sodium/benzophenone prior to use. Aniline and *tert*-butylamine were dried over 4-Å molecular sieves and then distilled from calcium hydride. ^1H NMR spectra were recorded on a General Electric QE 300 instrument operating at 300.17 MHz and are referenced to Me_4Si (0.0 ppm). The C_6D_6 solvent was dried over 4-Å molecular sieves prior to use. Mass spectra (EI and CI) were recorded on a Bell and Howell 21-491 instrument. IR spectra were run as Nujol mulls on a Digilab FTS-40 spectrometer, and elemental analyses were determined on a Perkin-Elmer 2400 analyzer. Melting points were determined in sealed capillaries under argon (1 atm) and are uncorrected. Bis(trimethylsilyl)amine, *tert*-butyl(trimethylsilyl)amine, and 2,2,6,6-tetramethylpiperidine were procured commercially (Aldrich) and used as supplied.

Preparation of $[(t\text{-}Bu(H)N)_2Ga(\mu\text{-}N(H)\text{-}t\text{-}Bu)]_2$ (1). A 2.05 M *n*-hexane solution of *t*-BuLi (21.1 mL, 43.28 mmol) was added via cannula to a stirred solution of $t\text{-}BuNH_2$ (4.55 mL, 43.28 mmol) in 50 mL of Et_2O at −78 °C. The resulting clear solution was allowed to warm to 25 °C, following which it was added to a stirred solution of $GaCl_3$ (2.54 g, 14.43 mmol) in 20 mL of Et_2O at −78 °C. The reaction mixture was allowed to warm slowly to 25 °C and was stirred at this temperature for 12 h. The solvent and volatiles were removed under reduced pressure, and the resulting white residue was extracted with 100 mL of *n*-hexane. The white precipitate of LiCl was filtered off, and the solvent was removed from the filtrate to afford 3.8 g (92.7% yield) of white, microcrystalline **1**. Mp: 162–165 °C dec. Colorless, X-ray-quality crystals of **1** were grown from a concentrated Et_2O solution which was maintained at −30 °C for 2 weeks. ^1H NMR (C_6D_6, 25 °C, 300.15 MHz): d 1.35 ppm (60 H, broad m, *t*-BuN). IR (Nujol mull): 3201 cm^{-1} (s, broad, ν_{N-H}). Anal. Calcd for $C_{24}H_{60}Ga_2N_6$: C, 50.38; H, 10.57; N, 14.69. Found: C, 52.86; H, 12.03; N, 14.57. MS (CI, (CH_4): *m/e* 572 (M^+).

Preparation of $Ga(N(t\text{-}Bu)SiMe_3)_3$ (2). A 2.09 M *n*-hexane solution of *t*-BuLi (24.6 mL, 51.45 mmol) was added via cannula to a stirred solution of $t\text{-}Bu(Me_3Si)NH$ (9.8 mL, 51.45 mmol), in 50 mL of Et_2O at −78 °C. The resulting clear solution was allowed to warm to 25 °C, following which it was added to a stirred solution $GaCl_3$ (3.02 g, 17.15 mmol) in 20 mL of Et_2O at −78 °C. The reaction mixture was allowed to warm slowly to 25 °C and was stirred at this temperature for 24 h. The solvent and volatiles were removed under reduced pressure, and the resulting white residue was extracted with 100 mL of *n*-hexane. The white precipitate of LiCl was filtered off, and the solvent was removed to afford 8.21 g (95.3% yield) of white, microcrystalline **2**. Mp: 174–176 °C dec. Colorless, X-ray-quality crystals of **2** were grown from a saturated toluene solution at −30 °C. ^1H NMR (C_6D_6, 25 °C, 300.15 MHz): d 0.49 (27 H, s, Me_3SiN), 1.50 ppm (27 H, s, *t*-BuN). Anal. Calcd for $C_{21}H_{54}GaN_3Si_3$: C, 50.18; H, 10.83; N, 8.36. Found: C, 50.36; H, 10.53; N, 8.70. MS (EI, 70 eV): *m/e* 501 (M^+), 357 ($M^+ - t\text{-}Bu(Me_3Si)N$).

Preparation of $Ga(tmp)_3$ (3) (tmp = 2,2,6,6-Tetramethylpiperidide). Three equivalents of Htmp (3.38 mL, 20.04 mmol) was added to a stirred solution of $GaCl_3$ (1.18 g, 6.68 mmol) in 20 mL of toluene at −78 °C. The reaction mixture was allowed to warm slowly to 25 °C, during which time gas evolution took place and the solution assumed a yellow color. After refluxing the reaction mixture for 12 h, the solvent and volatiles were removed under reduced pressure to afford 2.76 g (84% yield) of yellow, microcrystalline **3**. Mp: 130–132 °C. ^1H NMR (C_6D_6, 25 °C, 300.15 MHz): d 1.13 (18 H, m, CH_2), 1.34 ppm (36 H, s, Me). Anal. Calcd for $C_{27}H_{54}GaN_3$: C, 66.12; H, 11.10. Found: C, 66.51; H, 10.77. MS (CI, CH_4): *m/e* 459 (M^+ − 2Me), 443 (M^+ − 3Me).

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Preparation of $Ga(N(SiMe_3)_2)_3$ (4). This compound was prepared in 93.1% yield via the reaction of 3 equiv of $LiN(SiMe_3)_2$ with $GaCl_3$ in Et_2O solution. The procedure was essentially that described by Bürger, Wannagat, et al.[7] Colorless, X-ray-quality crystals of **4** were grown from a saturated THF solution maintained at −30 °C. Anal. Calcd for $C_{22}H_{62}GaN_3OSi_6$: C, 42.42; H, 10.03; N, 6.75. Found: C, 42.12; H, 10.09; N, 6.85.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **1** and **4** are presented in Table 1. Both data crystals were mounted in thin-walled glass capillaries and sealed under argon. Unit cell parameters were obtained by centering 25 reflections having 2θ values between 22 and 26°. Data were collected on an Enraf-Nonius CAD-4 diffractometer at $2\theta = 2$–$50°$ using graphite-monochromated Mo Kα radiation. Intensity data were collected in the usual manner.[15] The intensity standards for **1** and **4** indicated a <2% decrease in intensity over the course of data collection, and no corrections were applied. For each structure, the data were corrected for Lorentz and polarization effects. Data with intensities less than $3.0\sigma(I)$ and $(\sin\theta)\lambda$ less than 0.10 Å^{-1} were excluded, and a weighting scheme ($[(\sigma(F))^2 + 0.000625F^2]^{-1}$) was used in the final stages of the refinement. The observed structure factors of equivalent reflections were averaged. All calculations were performed on a MICROVAX 3100 computer using the SHELX software package.[16]

$[(t\text{-Bu(H)N})_2Ga(\mu\text{-N(H)-}t\text{-Bu})]_2$ (1). Crystals of **1** suitable for X-ray diffraction were grown by cooling a diethyl ether solution to −30 °C. The monoclinic space group $C2/m$ was determined uniquely by the systematic absences hkl, $h + k = 2n + 1$, $h0l$, h, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. Data were collected in the $+h,+k,\pm l$ quadrant between 2θ values of 2 and 50°, A ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 89.0% and a maximum transmission of 98.8%. No empirical absorption correction was applied. The gallium atom was found by means of a Patterson search, and subsequent location of the other non-hydrogen atoms was achieved using difference Fourier maps. Due to the high thermal motion of the heavy atoms, the hydrogen atoms were not found or calculated and their contributions were not included in the final refinement. The structure was refined to final R and R_w values of 0.0958 and 0.0960, respectively.

$Ga(N(SiMe_3)_2)_3$ (4). Crystals of **4** suitable for X-ray diffraction were grown by cooling a THF solution to −30 °C. The trigonal space group $P\bar{3}1c$ was determined uniquely by the systematic absences $h,h,2h,l$, $l = 2n + 1$, and $000l$, $l = 2n + 1$. Data were collected in the $+h,+k,\pm l$ quadrant between 2θ values of 2 and 50°. A ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 58.0% and a maximum transmission of 100%. An empirical absorption correction was applied. The location of the gallium atom and the other non-hydrogen atoms was achieved using direct methods followed by successive cycles of difference Fourier maps. The non-hydrogen atoms were not located, but their contributions were included in the final refinements. A molecule of THF of crystallization was located and treated with isotropic thermal parameters. The structure was refined to final R and R_w values of 0.0441 and 0.0540, respectively.

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Supplementary Material Available: Tables of hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** and **4** and a view of the unit cell of **4** (11 pages). Ordering information is given on any current masthead page.

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