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Oligomerization of dialkylazidogallium compounds: a structural and solution-phase study †

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Dialkylazidogallium compounds R_2GaN_3 ($R = {}^t$Bu (**1**), Me_3SiCH_2 (**3**), ^{i}Pr (**5**)) are prepared by reaction of the dialkylmethoxy gallium precursors with trimethylsilylazide. The reactions produce the target compounds in high purity and yield. All compounds are low-melting solids or liquids, which have no tendency to thermally decompose near their melting/boiling points. The compounds display variable degrees of oligomerization in different physical states. Compound **3** is a solid-state trimer, but exhibits a monomer–dimer equilibrium in solution. Compound **1** is a waxy solid, and appears to be composed of dimeric molecules on the basis of mass spectral, Raman and PM3 computational analyses.

Introduction

The large body of work on the formation of III–V semiconductor materials from single-source or molecular precursor routes blossomed from an extensive effort occurring over the past fifteen years by several research groups. The number of molecules containing one or more bonds between group-13 atoms (B, Al, Ga, In) and group-15 atoms (N, P, As, Sb) synthesized and characterized for their physical properties, structure, and utility as MOCVD precursors grew enormously over that time period.[1] Of the family of III–V materials, gallium and indium nitride (GaN and InN) are of special interest. These materials are employed in InGaN/AlGaN double-heterostructure blue light-emitting diodes (LEDs)[2] and violet-emitting multi-quantum-well LEDs.[3]

Several authors report MOCVD of GaN films from azidogallium (R_2GaN_3) compounds as precursors. Reactivity within this class of compounds varies considerably with differences in the R ligands. The dialkylazido gallanes, where R = Et or Me, are thermally stable at room temperature and require high temperatures (>500 °C) for thermolysis, and the presence of ammonia for high-quality film formation. When R = H or Cl, the compounds are quite labile to thermolysis and form high-quality GaN films.[4] When R is an amido or hydrazino[5] ligand, film quality is improved without the need for ammonia. Base-chelating ligands, such as those shown in the work of Fisher,[6] provide azidogallium compounds with stability toward thermal and mechanical shock and greatly increase their volatility for MOCVD applications. Recently, a thorough review of group-13 azides has appeared that details the synthesis and structure of a number of gallium monoazides, including their synthesis, structures and applications.[7]

More recent work has focused on synthetic routes to nanostructured nitride materials.[8] Our group has made progress in the chemical synthesis of several III–V nanostructured materials. We found that azidoindium dialkyls (R_2InN_3) can be employed as precursors to prepare indium nitride nanowires and nanoparticles.[9] We further observed that the choice of alkyl ligand has a significant effect on the final InN morphology. Thus, our interest in the target azidogallium compounds (**1**, **3** and **5**) described in this work was directed at employing them in the solution-phase synthesis of gallium nitride wires.

We found the target compounds to be very stable toward thermal decomposition in the temperature range of 190–250 °C, even when co-reagents like hydrazine were employed. In our hands, the target compounds have not afforded nanostructured GaN materials to date. However, the target compounds are structurally intriguing and displayed a tendency to form various oligomers with a change in physical state. This work expands the body of knowledge of Group-13 azide chemistry cited above. The only report of dialkyl azidogallium compounds bearing bulky, noncoordinating ligands is from Schulz and Nieger.[10] We report the synthesis and characterization of a series of dialkylazido gallium compounds, including X-ray crystallography of **3** and vibrational characterization of **1** assisted by computational vibrational analysis. This work also reports the characterization of two alkylmethoxy gallium compounds isolated as intermediates in the synthesis of the azide compounds.

Results and discussion

The dialkylazido gallium compounds described in this work were synthesized by a "one-pot" alkoxide–azide metathesis chemistry developed in our laboratory and previously reported for dialkylazido indium compounds.[9] Addition of one equivalent of methanol to a hexane or pentane solution of the appropriate trialkylgallane yielded the dialkylmethoxy gallium after 10 min at room temperature. Subsequent addition of one equivalent of trimethylsilylazide yielded the desired dialkylazido gallium compound as shown in eqn. (1).

$$R_3Ga \xrightarrow[2)\ N_3SiMe_3:\ RT\ 1\text{-}2\ h]{1)\ MeOH:\ RT\ 10\ min} R_2GaN_3 + RH + (CH_3)_3SiOCH_3$$
$$R = {}^tBu\ (\mathbf{1}),\ (CH_3)_3SiCH_2\ (\mathbf{3}),\ {}^iPr\ (\mathbf{5}) \qquad (1)$$

In two cases we isolated and characterized the intermediate dialkylgallium methoxides produced from reaction (1). Bis[trimethylsilylmethyl]gallium methoxide (compound **2**) was not described in the literature, while diisopropylgallium methoxide (compound **4**) was previously described,[11] although it is prepared and characterized differently here.

We found the alkoxide–azide metathesis to be a convenient method for the preparation of dialkylazido gallium compounds in comparison to other methods described previously.[5–7] Most synthetic routes described start with gallium trichloride, construct the molecules *via* Grignard or alkali-metal reagent addition followed by reaction with sodium azide in a multi-step sequence. Some routes describe reaction of the trialkylgallanes

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† Electronic supplementary information (ESI) available: Fig. S1: Mass spectrum of **1** with M^+ peak at 225 and higher oligomers present in the vapor phase. See http://www.rsc.org/suppdata/dt/b3/b307813b/

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with hydrazoic acid, which must be prepared and handled with extreme caution. Here the target azide compounds were readily prepared in a “one-pot” method from the corresponding trialkylgallanes. Reaction (1) was rapid and resulted in high yields (>95%) of the respective targets. The by-products of the reaction and the solvents are volatile and were effectively removed *in vacuo*. The starting materials were easily prepared or purchased in high purity. The reactions did not employ NaN_3, so the products were free of sodium impurities and chloride, and no handling of hydrazoic acid was necessary. While each of the target azide compounds was purified by sublimation or distillation for full characterization, this was unnecessary for routine use. The unpurified compounds contained no detectable impurities by proton NMR.

The target azides were isolated as low-melting solids or oils that are readily soluble in common organic solvents such as hexane, benzene or acetone. The compounds displayed no tendency to spontaneously decompose upon heating or mechanical shock. Heating the compounds under reduced pressure resulted in sublimation or distillation with no observable decomposition. The thermal stability of this class of azides was unusual, and was unexpected given the thermal lability of the related indium analogs.[9] In an effort to understand the origin of the thermal stability, a structural study of these compounds was undertaken.

Variable-temperature NMR study of 3

Compounds **1**, **2**, **4** and **5** displayed the expected proton and carbon NMR signals. Compound **3**, however, displayed more complex NMR behavior. Fig. 1 shows the ^1H NMR spectrum of **3**. Two signals at 0.194 and 0.139 ppm were assigned to methyl protons on the trimethylsilylmethyl ligand and two signals at −0.008 and −0.129 ppm were assigned to methylene protons. The additional signals present were not due to an off-stoichiometric impurity as established by elemental analysis of **3**. Variable-temperature ^1H and ^{29}Si NMR experiments were conducted to gain further insights.

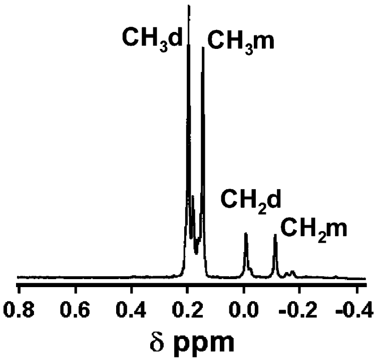


Fig. 1 ^1H NMR spectrum of **3** at 25 °C. The signals are labeled as follows: CH_3 = ^{t}Bu protons, CH_2 = methylene protons, m = monomer, d = dimer.

Fig. 2 shows the variable-temperature ^{29}Si spectrum of **3** in toluene-d_8. As the solution temperature was increased from 20 to 70 °C, a gradual disappearance of the downfield resonance relative to the upfield resonance occurred. By 70 °C the upfield resonance (at 0.85 ppm) was the only signal present, and no new signal evolved as the temperature was raised to 90 °C. Lowering the temperature of the solution from 20 to −15 °C showed the opposite effect, an increase in the downfield resonance peak with a decrease in temperature. The process described was completely reversible.

^1H NMR VT spectra showed similar trends, but were complicated by the evolution of overlapping proton signals. The behavior described was consistent with a temperature-dependent oligomerization of **3** in solution. Evidence to support this hypothesis was also found in the cryoscopic molecular weight determination of **3**. A 0.04 M solution of **3** in benzene gave a molecular weight of 410 ± 30 g mol^{-1}, or a molecularity of 1.4, intermediate to that of a dimer and a monomer of **3**. Since no additional ^{29}Si NMR signals appear at temperatures greater than 70 °C, the single resonance most likely represents a monomer in solution at this temperature. Reduction of the solution temperature to below 70 °C likely initiated a monomer–dimer equilibrium as shown in eqn. (2).

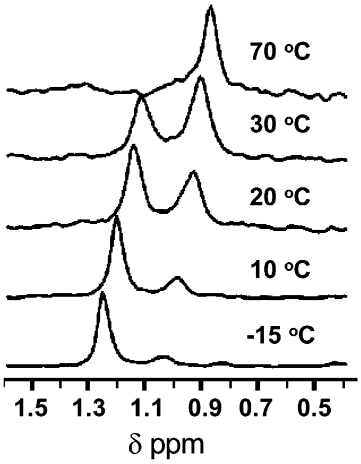
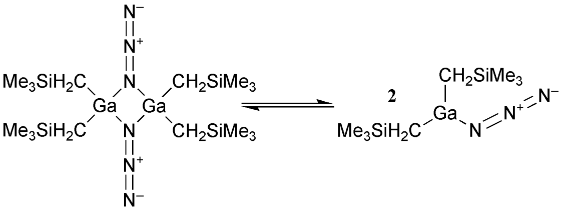


Fig. 2 VT ^{29}Si NMR spectrum of **3** in toluene-d_8. Upfield and downfield signals correspond, respectively, to a dimer and monomer.



(2)

The relative ratios of the separate methyl and methylene peaks in the NMR spectra of **3** changed with variations in the concentration. The downfield-to-upfield ratio of methyl protons of trimethylsilylmethyl changed from 0.97 : 1 at a concentration of 2.92×10^{-5} M to 1.38 : 1 at a concentration of 7.79×10^{-5} M. Based on the proton assignments, higher concentrations favored dimer formation.

The thermodynamic parameters of the solution-phase dissociation process was calculated by from the VT ^1H NMR data by a Bayesian analysis[12] to extract accurate areas from under the various resonances. The ratio of the concentrations gave the equilibrium constant for reaction (2) at the temperature of the NMR experiment (eqn. (3)).

$$K_{dissoc} = [monomer]^2/[dimer] \qquad (3)$$

A plot of the dependence of $\ln K$ *vs.* $1/T$ yielded the thermodynamics of the equilibrium process. The calculated values for the process are $\Delta H = 66 \pm 9$ kJ mol^{-1} and $\Delta S = 300 \pm 10$ J mol^{-1} K^{-1}. The equilibrium is driven by both a weak bond enthalpy and a significant entropy term.

Solid-state structure of 3

Compound **3** was the only azide of the series that gave well-formed crystals upon sublimation. It exhibited the structure shown in Fig. 3 and selected bond lengths and bond angles are given in Table 1. The compound was found to be a trimer in the solid state with a Ga_3N_3 core. The N–Ga–N bond angles are close to 90° while the Ga–N–Ga bond angles are near 130°. The Ga_3N_3 core is not planer as the sum of the bond angles is 660°. The bonds about the gallium atom conformed to a distorted

Table 1 Selected bond lengths (Å) and angles (°) of **3**

Ga(1)–C(1)	1.951(6)	Si(1)–C(1)	1.871(6)
Ga(1)–N(1)	2.064(5)	N(7)–N(8)	1.233(8)
Ga(1)–N(7)	2.043(5)	N(8)–N(9)	1.119(8)
C(2)–Ga(1)–C(1)	129.6(3)	N(2)–N(1)–Ga(2)	115.3(4)
C(1)–Ga(1)–N(7)	107.9(3)	Ga(2)–N(1)–Ga(1)	128.4(3)
C(6)–Ga(3)–N(7)	112.3(2)	N(3)–N(2)–N(1)	179.0(8)
N(7)–Ga(1)–N(1)	93.6(2)	Si(1)–C(1)–Ga(1)	118.2(3)
N(4)–Ga(3)–N(7)	90.0(2)		

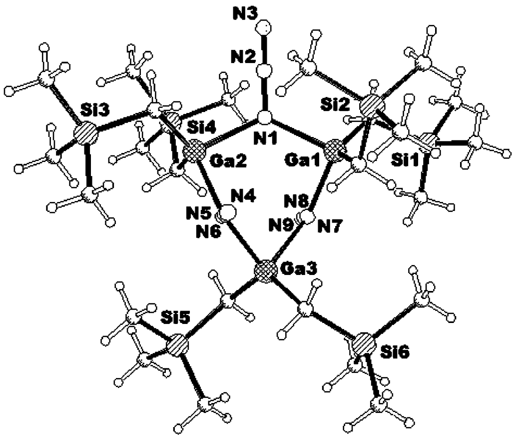


Fig. 3 Ball-and-stick representation of the crystal structure of **3** showing the 90° bond angle of N4–Ga–N7.

tetrahedron, while the bridging nitrogen atoms were trigonal planer. The N–N bonds on the azide moiety displayed unequal bond distances, typical for covalently bound azides. The bond distance from the gallium-bound nitrogen to the central nitrogen is on the order of 1.13 Å, while the bond distance from the center to the terminal nitrogen is 1.23 Å. All of the Ga–N bond lengths were essentially equivalent, displaying distances of 2.04–2.06 Å. All other bond distances and angles were typical for carbon, hydrogen and silicon bonds.

The behavior of **3** is similar to $(Me_3CCH_2)_2InPPh_2$,[13] which also adopts a trimeric solid-state structure while exhibiting a monomer–dimer distribution in solution. In the solid state both **3** and the indium phosphide adopt an approximate C_{3v} cyclohexane chair conformation of the M_3E_3 core (M = Ga or In, E = N or P). Group III–V organometallic compounds with ligands bearing Me_3SiCH_2 and neopentyl moieties have come under extensive study in recent years.[14] These compounds, termed amphoteric due to the presence of both Lewis acidic (group III) and Lewis basic (group V) sites, often show variable degrees of association for which no reliable method for predicting the degree of oligomerization is known. Steric effects, valency angle strain, ring size, and conformation have been shown to play a role in oligomerization of group III amphoteric molecules.[15] However, it is thought that oligomerization primarily occurs to minimize the number of filled energetically similar molecular orbitals.[16]

Other compounds similar to **3**, but which do not appear to exhibit variable oligomerization, include $(Me_3SiCH_2)_2GaCl$,[17] a linear polymer, and the bromide analog, which is a solid-state dimer. The phosphides $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$[18] also exhibit solution-phase monomer–dimer equilibria but are solid-state dimers.

Structural studies of 1

Variable states of oligomerization were also found to occur in compound **1**. Several crystallization techniques failed to give X-ray quality crystals of **1**. The compound was extremely soluble in both polar and non-polar solvents such that concentration and cooling only yielded a polycrystalline solid while slow sublimation yielded a waxy substance. The cryoscopic molecular weight of **1** was 470 ± 30 g mol^{-1}, or a molecularity of 2.0, indicative of a solution-phase dimer. Low-resolution mass spectrometry of compound **1** (ESI †) yielded an M$^+$ peak for the monomer at *m*/*z* = 225. Also present was a peak assigned to the dimer of **1** less a ^{t}Bu ligand (calc. 394.4, found 395). Very high *m*/*z* signals were also observed with isotopic ratios consistent with gallium containing species. These species are probably formed in the mass-spectrometry experiment.

Since we were unable to obtain X-ray quality crystals of **1**, FT-Raman spectra were obtained of **1** and its precursor ^{t}Bu$_3$Ga, a clear oily liquid, for structural elucidation. The spectra are shown in Fig. 4. In order to assist in the assignment of Raman spectra, a semiemperical PM3 normal vibrational mode calculation was carried out on both **1** and ^{t}Bu$_3$Ga using SPARTAN.[19] Prior MO calculations using SPARTAN at the PM3 level have been successful in elucidating the photoluminescence spectra of Me_2GaN_3.[20] Calculations were carried out on monomeric, dimeric and trimeric aggregations of **1**. The best agreements between the observed and calculated vibrations for **1** were obtained for a dimeric structure with D_{2h} symmetry. This symmetrical structure was calculated to be the lowest-energy dimer arrangement at $\Delta H_f = -104$ kcal mol^{-1}. The alternative low-energy structures include the monomer, with C_s symmetry ($\Delta H_f = -37$ kcal mol^{-1}) and the trimer with C_1 symmetry ($\Delta H_f = -160$ kcal mol^{-1}). Both of these molecules should show much more complicated Raman spectra than observed due to their lower symmetry. ^{t}Bu$_3$Ga was calculated to have an energy minimum monomeric C_{3v} structure ($\Delta H_f = -118$ kcal mol^{-1}).

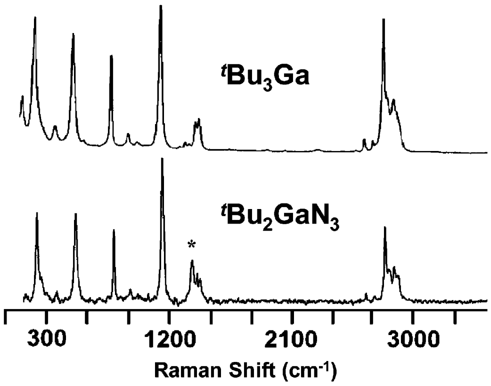


Fig. 4 Raman spectra of ^{t}Bu$_3$Ga and **1**. Note the presence of a symmetrical N_3 stretch at 1406 cm^{-1} (*) in the latter spectrum.

The calculated and observed Raman vibrational frequencies are compiled in Table 2 and show good agreement between the vibrational modes for both ^{t}Bu$_3$Ga and dimeric **1**, with a few exceptions. The Raman spectra of **1** and ^{t}Bu$_3$Ga are similar except for a vibration at 1406 cm^{-1} in **1**. This peak was assigned to the A_g vibration of azide in the dimer. SPARTAN calculated this vibration to occur at 1517 cm^{-1}. SPARTAN calculations indicated that a second Raman active A_g azide vibration should occur at 2424 cm^{-1}. No vibration near this energy was observed in the Raman spectrum. It should be noted that the IR spectrum of **1** did display all expected azide vibrations. The other discrepancy is the appearance of a strong Raman line near 810 cm^{-1}. This band was present in both **1** and ^{t}Bu$_3$Ga and was not predicted by SPARTAN to be a fundamental mode of either molecule. The nearest predicted normal modes to the observed frequency were C–C stretching vibrations at 940–975 cm,$^{-1}$ which are not expected to have large intensities.[21] The mode probably represents a combination of normal modes that could be determined by a full normal-coordinate analysis. We conclude that the Raman spectrum of **1** is consistent with a dimeric structure having D_{2h} symmetry.

Table 2 Observed and computed Raman active vibrational modes of dimeric **1** and $^t\mathrm{Bu}_3\mathrm{Ga}$

Observed Raman modes/cm^{-1}		Assignment	Calculated/cm^{-1}	
$(^t\mathrm{Bu})_3\mathrm{Ga}$	$(^t\mathrm{Bu})_2\mathrm{GaN}_3$	Spartan '02 Platform	$(^t\mathrm{Bu})_3\mathrm{Ga}$	$[^t\mathrm{Bu}_2\mathrm{GaN}_3]_2$
140	Not obsd.	Ga–C(CH$_3$)$_3$ rocking	143	Not calc.
231	240	C–CH$_3$ torsions	251	245
390	386	Ga–C out of plane def.	375	371
516	530	Ga–C vib + C–Me rocking	508	544
806	818	Not assigned	Not calc.	Not calc.
1174	1188	Ga–C vibrations	1180	1189
N/A	1406	Sym. azide stretch	N/A	1517
1443	1445	C–CH$_3$ vibrations	1435	1446
1468	1468	C–CH$_3$ vibrations	1475	1460
N/A	Not obsd.	Sym. azide stretch	N/A	2424
2847	2857	C–H vibrations	3057	3016
2924	2928	C–H vibrations	3119	3131

A similar elucidation by Raman analysis was done by Müller and Dehnicke for the compound $\mathrm{Et_2GaN_3}$,[22] concluding that the compound is composed of $\mathrm{Et_2GaN_3}$ trimers. A solid-state and solution-phase Raman study of $\mathrm{Me_2GaN_3}$ was also done recently by Bittner and Zink,[20] who concluded that the dissolved species were structurally similar to the solid, which is a coiled polymer.

Conclusion

This paper describes the synthesis and characterization of a series of dialkylazido gallium compounds and their corresponding alkoxy intermediates. The azide compounds **1** and **3** display variable degrees of aggregation depending on their physical state. Compound **3** is a solid-state trimer, but displays a monomer–dimer equilibrium in solution. Compound **1** appears to be a dimer in the solid state and in solution, but is predominantly a monomer in the mass spectrometer. In our hands, the compounds did not make suitable precursors for the solution-phase synthesis of nanostructured GaN. They may be suitable for MOCVD of GaN films as they are easily synthesized in high purity and in high yield by the alkoxy–azide exchange route we describe.

Experimental

All manipulations were performed using standard dry-box or Schlenk techniques under dry nitrogen. Hydrocarbon solvents were dried with sodium benzophenone ketyl. MeOH was dried over Mg activated by $\mathrm{I_2}$. DIPHOS (1,2-Bis(diphenylphosphino)ethane) and trimethylsilylazide was used as received from Aldrich. $^t\mathrm{Bu_3Ga}$,[23] $^t\mathrm{Bu_2GaOMe}$[24] and $\mathrm{(Me_3SiCH_2)_3Ga}$,[25] were prepared by literature procedures. $^i\mathrm{Pr_3Ga}$ was prepared by adapting the method of Bradley *et al.*[26] for preparing trialkylgallium compounds from Grignard reagents and DIPHOS. Melting points were measured in grease-plugged glass capillary tubes with a Hakke melting point apparatus. Molecular weight determinations were carried out on 0.04 M benzene solutions of the compounds in a 7″ cryocell immersed in an ice–ethanol bath employing a calibrated benzene thermometer. NMR spectra were recorded at a field corresponding to 300 MHz for ^{1}H, variable-temperature information is given below. IR spectra were run on a Mattson FT-IR. Raman spectra were conducted with a Jobin Yvon S-3000 triple monochromator laser Raman microprobe using multi-channel detection. Samples were placed in a sealed borosilicate glass capillary. Analysis was performed with a laser excitation wavelength of 514.5 nm and power adjusted to 25 mW argon laser radiation. Raman spectral data were processed with ISA Raman data software. Low-resolution electrospray ionization mass spectrometry was provided by the Washington University Mass Spectrometry Resource. C, H and N analysis were performed by Oneida Research Services, Whitesboro, New York.

$(^t\mathrm{Bu})_2\mathrm{GaN}_3$ (1)

$(^t\mathrm{Bu})_2\mathrm{GaOMe}$ (3.92 g, 18.2 mmol) was dissolved in 10 ml of hexane. 2.60 ml of 95% $\mathrm{N_3SiMe_3}$ (2.14 g, 18.6 mmol) was added by syringe and the solution was refluxed for 2 h. The volatiles were removed *in vacuo* to yield a white solid that was sublimed (125 °C at 0.01 Torr) to yield 4.00 g (17.7 mmol, 97.2%) of **1**, a white waxy solid (mp 76.9 °C). FT-IR (cm^{-1}, KBr): 3494 w, 2931 s, 2851 s, 2097 vs (ν_{asym} $\mathrm{N_3}$), 1466 s, 1363 s, 1291 w, 1261 w, 1179 m, 1011 sh, 941 w, 814 s, 622 s. FT-Raman (cm^{-1}): 1406 m (ν_{sym} $\mathrm{N_3}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.20 (s, 9 H). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 37.98 (methyl CH$_3$), 41.96 (*C*(CH$_3$)$_3$). MS: *m*/*z* 225.1 (100%, $\mathrm{C_8H_{18}GaN_3}$ requires M$^+$ 225.9), 395.0 (80%, calc. dimer − ^{t}Bu = 394.8). Cryoscopic MW (benzene): 470 ± 30 g mol^{-1} (Found: C, 42.46; H, 7.94; N, 17.48. $\mathrm{C_8H_{18}GaN_3}$ requires C, 42.52; H 8.03; N, 18.60%).

$\mathrm{(Me_3SiCH_2)_2GaOMe}$ (2)

$\mathrm{(Me_3SiCH_2)_3Ga}$ (2.112 g, 6.27 mmol) was placed in 20 ml of hexane. Methanol (0.260 ml, 6.42 mmol) was added to the solution dropwise with a microsyringe. A very mild warming of the solution occurred. The solution was refluxed for 1 h and the volatiles removed *in vacuo* to yield a white crystalline solid that was purified by sublimation (100 °C at 0.01 Torr) to give 1.616 g (5.87 mmol, 93.6%) of **2**. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 3.207 (s, 3 H), 0.181 (s, 18 H), −0.395 (s, 4 H) (Found: C, 39.65; H, 9.30; Si, 20.77. $\mathrm{C_9H_{25}GaOSi_2}$ requires C, 39.28; H, 9.16; Si, 20.41%).

$\mathrm{(Me_3SiCH_2)_2GaN_3}$ (3)

Compound **2** (1.594 g, 5.79 mmol) was dissolved in 20 ml hexane and 0.801 ml (0.694 g, 5.79 mmol) of 95% $\mathrm{N_3SiMe_3}$ were added by microsyringe. The solution was refluxed overnight and the volatiles removed *in vacuo* to yield a white solid which sublimed at 120 °C (0.01 Torr) to yield 1.557 g (5.44 mmol, 93.9%) of **3** (mp 135 °C). FT-IR (cm^{-1}, KBr): 3329 m, 2954 s, 2895 m, 2475 m, 2105 vs (ν_{sym} $\mathrm{N_3}$), 1407 w, 1357 w, 1248 s, 1160 w, 1003 s, 855 s, 752–707 m, 571 m. ^{1}H and ^{29}Si NMR ($\mathrm{C_6D_6}$): complex, see Results section. MS: *m*/*z* 99.0 (100) 243.1 (47), 272.1 (20), 530 (100%). Cryoscopic MW (benzene): 430 ± 30 g mol^{-1} (Found: C, 33.62; H, 7.80; N, 14.34; Si, 19.44. $\mathrm{C_8H_{22}Si_2GaN_3}$ requires: C, 33.57; H, 7.75; N, 14.69; Si, 19.62%).

$(^i\mathrm{Pr})_2\mathrm{GaOMe}$ (4)

$^i\mathrm{Pr_3Ga}$ (1.457 g, 7.32 mmol) was dissolved in 15 mL of pentane and the solution was stirred for 10 min under nitrogen. 0.300 mL (0.237 g, 7.40 mmol) of MeOH was added with a microsyringe. The solution was brought to reflux for 1 h and the volatiles were removed *in vacuo* to yield 1.166 g (6.24 mmol, 85.2%) of **4**, as a thick clear oil, in the glove-box. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 3.281 (OCH$_3$, 3H), 1.314 (CH(C*H*$_3$)$_2$, d, *J* = 7.2 Hz, 12 H), 1.080 (C*H*(CH$_3$)$_2$, complex m, 2 H). ^{13}C{^{1}H} NMR: ($\mathrm{C_6D_6}$): δ 53.42 (OCH$_3$), 20.95 (CH$_3$), 15.32 (CH) (Found: C, 45.49; H, 9.30. $\mathrm{C_7H_{17}OGa}$ requires C, 45.46; H, 9.18%)

$(^i\text{Pr})_2\text{GaN}_3$ (5)

Compound **4** (1.062 g, 5.68 mmol) was dissolved in 15 ml of pentane. 0.800 ml of N_3SiMe_3 (0.694 g 5.72 mmol) was added and the solution brought to reflux for 2 h. The volatiles were removed *in vacuo* to yield a thick oil. The oil was distilled at 87–89 °C under vacuum (0.2 Torr) to yield 0.757 g (3.82 mmol, 67.34%) of **5** as a clear colorless oil. FT-IR (cm^{-1} neat): 3325 w, 2932 s, 2858 s, 2757 vw, 2724 vw, 2109 vs (ν_{sym} N_3), 1466 m, 1383 m, 1279 m, 1236 s, 1159 w, 1122 w, 1069 w, 990 m, 871 m, 708 m. ^{1}H NMR (C_6D_6): δ 1.280 (d, J = 4.2 Hz), methine proton appears as a broad signal at 1.280. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 20.669 (CH_3), 17.511 (CH) (Found: C, 36.28; H, 7.33; N, 20.97. $C_6H_{14}GaN_3$ requires: C, 36.41; H 7.13; N, 21.23%).

Variable-temperature NMR of 3

A 2.92×10^{-5} M solution of **3** in toluene was prepared in a 7″ NMR tube in a nitrogen drybox. The tube was sealed under nitrogen outside the drybox and examined by ^{1}H and ^{29}Si NMR using tetramethylsilane as an external standard. The tube was heated to 90 °C and the NMR spectrum was recorded. The NMR sample chamber and tube were cooled in several intervals to −15 °C. At each interval, the solution was allowed to equilibrate for 5 min before the spectra were recorded. ^{1}H data were analyzed by Bayesian[12] signal deconvolution analysis to extract accurate ^{1}H peak area counts for determination of relative concentrations of monomers and dimers of **3**. Relative concentrations were used to determine the monomer–dimer equilibrium constants at each interval and data was used to determine thermodynamic parameters of the solution-phase equilibrium.

X-Ray crystallography of 3

Crystals suitable for X-ray structure determination of **3** were grown from sublimation of the compound at 100 °C at 0.02 Torr over a period of 5 h. Preliminary examination and data collection was performed using a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). SMART and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 1998) were used for data collection and data integration. Final cell constants were determined by a global refinement of *xyz* centroids of 8192 reflections (θ < 25°). Structure solution and refinement were carried out using the SHELXTL-PLUS software package (G. M. Sheldrick, Bruker Analytical X-Ray Division, Madison, WI, 1999). The structure was solved by direct methods and refined by full-matrix least-squares methods. The hydrogen atoms were treated using appropriate riding model (AFIX m3). A projection view of the molecule with non-hydrogen atoms represented by 50% probability ellipsoids, and showing the atom labeling is presented in Fig. 3.

Crystallographic data for $C_{24}H_{66}Ga_3N_9Si_6$ **3**: M = 858.56, triclinic, space group $P\bar{1}$, a = 12.3854(1), b = 13.5088(2), c = 15.2823(2) Å; α = 86.595(1), β = 67.665(1), γ = 87.91°, V = 2360.64(5) Å^3, T = 218(2) K, Z = 2, μ = 1.877 mm^{-1}, measureded refl. 38359, independent refl. 8268, R_{int} = 0.14, R_1 = 0.0643, wR $[I > 2\sigma(I)]$ = 0.1292.

CCDC reference number 214951.

See http://www.rsc.org/suppdata/dt/b3/b307813b/ for crystallographic data in CIF or other electronic format.

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