Synthesis and Structures of Heterocyclic Azidogallanes $[(CH_3)ClGaN_3]_4$ and $[(CH_3)BrGaN_3]_3$ en Route to $[(CH_3)HGaN_3]_x$: An Inorganic Precursor to GaN

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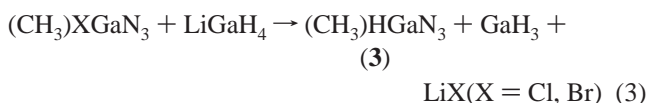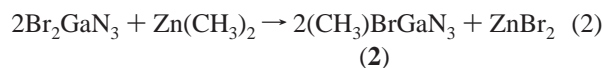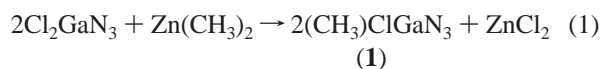
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The synthesis of $[(CH_3)ClGaN_3]_4$ (**1**) with a heterocyclic cyclooctane-like structure and $[(CH_3)BrGaN_3]_3$ (**2**) with a trimeric structure has been demonstrated. X-ray structural determinations reveal that **1** and **2** consist of Ga_4N_4 eight-membered rings and Ga_3N_3 six-membered rings, respectively, in which the Ga atoms are bridged by the α nitrogens of the azide groups. $[(CH_3)ClGaN_3]_4$ crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a = 11.017$-(4) Å, $c = 8.699(7)$ Å, and $Z = 8$. $[(CH_3)BrGaN_3]_3$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.1080$-(10) Å, $b = 9.9390(13)$ Å, $c = 10.4439(13)$ Å, $\alpha = 86.069(3)°$, $\beta = 86.771(3)°$, $\gamma = 80.829(2)°$, and $Z = 6$. The reaction of **1** and **2** with $LiGaH_4$ yields $[(CH_3)HGaN_3]_x$, which is a new low-temperature source of GaN.

Introduction

Alternative synthetic approaches to GaN heterostuctures based on single-source precursors offer the potential for significant improvement in the growth process and film quality.[1−6] Recently we reported the development of a simple and highly efficient approach for growing GaN thin films using the newly synthesized molecular source H_2GaN_3.[7] This is a volatile and a highly reactive compound and is particularly attractive as a CVD source because it eliminates extremely stable H_2 and N_2 byproducts to yield pure and stoichiometric GaN.[8] High-quality nitride heterostructures and novel nanostructures have been grown between 150 and 700 °C by UHV−CVD on sapphire, SiC, and $LiGaO_2$ at temperatures as low as 150 °C using this method.[7] Further studies have focused on synthesis of new azidogallanes with facile decomposition pathways, similar to that afforded by H_2-GaN_3, but are designed to be less reactive and thus more practical. Our investigations have led to the development of a very simple and considerably less reactive $(CH_3)HGaN_3$ compound that offers the possibility for GaN synthesis by displacement of benign and extremely stable CH_4 and H_2 byproducts. In this paper we describe the preparation of the new azidogallanes $(CH_3)ClGaN_3$ (**1**) and $(CH_3)BrGaN_3$ (**2**) and their reaction with $LiGaH_4$ to prepare $(CH_3)HGaN_3$ (**3**).

Results and Discussion

The synthesis of **1** and **2** is carried out by the reactions of Cl_2GaN_3 and Br_2GaN_3, respectively, with an appropriate amount of $ZnMe_2$. The synthetic procedure is summarized by eqs 1−3.

$$2Cl_2GaN_3 + Zn(CH_3)_2 \rightarrow 2(CH_3)ClGaN_3 + ZnCl_2 \quad (1)$$
$$(\mathbf{1})$$

$$2Br_2GaN_3 + Zn(CH_3)_2 \rightarrow 2(CH_3)BrGaN_3 + ZnBr_2 \quad (2)$$
$$(\mathbf{2})$$

$$(CH_3)XGaN_3 + LiGaH_4 \rightarrow (CH_3)HGaN_3 + GaH_3 +$$
$$(\mathbf{3})$$
$$LiX(X = Cl, Br) \quad (3)$$

Compound **1** is obtained as a volatile crystalline solid in 85% yield. Elemental analysis of the product for C, H, and N was consistent with the formula $(CH_3)ClGaN_3$. An X-ray crystallographic analysis revealed that the molecules are tetrameric in the solid state and the Ga_4N_4 core of each tetramer has a conformation similar to that of cyclooctane. As shown in Figure 1, the $[(CH_3)ClGaN_3]_4$ moiety is formed by four gallium atoms bridged by the α-nitrogens of the azide groups and the nonbridged positions of the gallium atoms are occupied by alternating up and down CH_3 and Cl ligands. The bonding parameters of the azide ligand are typical of those reported for other crystalline group 13 covalent azido compounds.[3,4,9,10] The $N(1)−N(2)$ azide bond distance [1.26(2) Å] is substantially longer than the terminal $N(2)−N(3)$ bond distance [1.09(2) Å]. The Ga−N and Ga−Cl bond lengths are 1.96 (2) and 2.177(6) Å, respectively, and fall well within the range of reported values for similar compounds with azide-bridged structures.[10] The

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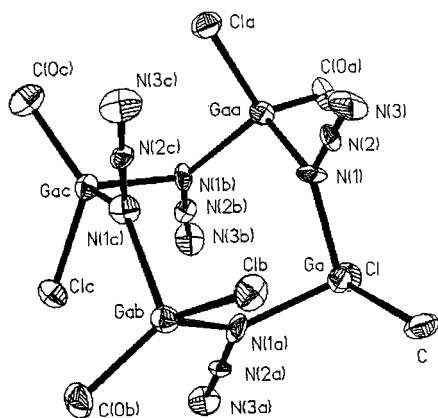
Figure 1. Molecular structure of [(CH₃)ClGaN₃]₄ (**1**). The heavy atoms are 50% probability ellipsoids.

Table 1. Structure Determination Summary for **1**

chemical formula	CH₃ClGaN₃	T (K)	173
a (Å)	11.017(4)	λ(Mo Kα), (Å)	0.710 73
b (Å)	8.699(7)	ρ_{calcd} (gcm⁻³)	2.041
V (Å³)	1055.9(3)	μ (mm⁻¹)	11.86
Z	8	R (obsd data, %)	$R = 7.25$,[a] $R_w = 9.31$
fw	162.3	R (all data, %)	$R = 7.80$,[a] $R_w = 9.81$[a]
space group	$P\bar{4}2_1c$		

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

Table 2. Structure Determination Summary for **2**

chemical formula	CH₃BrGaN₃	Z	6
a (Å)	8.1080(10)	space group	$P\bar{1}$
b (Å)	9.9390(13)	ρ_{calcd} (gcm⁻³)	2.487
c (Å)	10.4439(13)	μ (mm⁻¹)	114.15
α (deg)	86.069(3)	T (K)	173
β (deg)	86.771(3)	λ(Mo Kα (Å)	0.71073
γ (deg)	80.829(2)	R (obsd data, %)	$R = 3.5$,[a] $R_w = 3.8$[a]
V (Å³)	823.03(18)	R (all data, %)	$R = 9.9$

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

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Distances			
Ga–Cl	2.177(6)	Ga–N (1)	1.957(17)
Ga–C	1.948(22)	Ga–N (1A)	2.034(16)
N(1)–N(2)	1.264(24)	N(1)–GaA	2.034(16)
N(2)–N(3)	1.095 (25)		

Angles			
Cl–Ga–N(1)	101.1(5)	Cl–Ga–C	123.2(7)
N(1)–Ga–C	116.4(9)	Cl–Ga–N(1A)	101.6(5)
N(1)–Ga–N(1A)	98.2(9)	C–Ga–N(1A)	112.6(8)
Ga–N(1)–N(2)	120.7(12)	Ga–N(1)–GaA	124.5(9)
N(2)–N(1)-GaA	114.7(12)	N(1)–N(2)–N(3)	177.4(19)

N(1)–N(2)–N(3) bond angle is 177.4 (2)°, indicating that the azide is nearly linear (see Tables 1 and 3). A notable feature of the long-range structure is the absence of any significant intermolecular contacts, and each [(CH₃)ClGaN₃]₄ unit in the crystal appears to be independent. In contrast, the related [HClGaN₃]₄ molecule consists of highly interconnected tetrameric units to form extended chains via dative interactions between terminal Cl atoms and neighboring Ga atoms.[10] [(CH₃)-ClGaN₃]₄, and [HClGaN₃]₄ represent new examples of molecular rings with a cyclooctane-like conformation formed by bridged azides.

The compound was further characterized by spectroscopic methods. The infrared spectra are consistent with the (CH₃)-ClGaN₃ molecular core, and the highest peak observed in the mass spectrum corresponds to the "dimeric" [(CH₃)ClGaN₃]₂ species. In contrast to the high symmetry observed in the solid-state structure, the solution ¹H NMR spectra of **1** in C₆D₆ are

surprisingly complicated. At 22 °C, the spectrum shows three closely spaced resonances that clearly represent three different Ga–CH₃ environments [δ 0.19, δ 0.083, and δ −0.135]. Heating the sample to 75 °C in the spectrometer causes the resonances to coalesce to a single broad peak (δ 0.025), and this process was found to be reversible. These results suggest the presencce of different isomers that interconvert very slowly on the NMR time scale at 22 °C. This also could be due to dimer−trimer−tetramer equilibrium.

The analogous CH₃BrGaN₃ (**2**) molecule is isolated as colorless needles in typically 65% yield and can be further purified by sublimation. The compound melts sharply at 80 °C, and it was identified by its spectroscopic properties and elemental analysis. The highest mass peak appeared at 605 amu, and the observed isotopic pattern corresponds to that calculated for {[(CH₃)BrGaN₃]₃⁺ − CH₃}. The IR spectrum revealed the presence of the azide group (ν(N₃) = 2146 cm⁻¹) and the Ga–CH₃ group (ν(C–H) = 2970−2920 cm⁻¹). The Ga–CH₃ moiety is also evident in the ¹H NMR spectrum (δ −0.079). Elemental analysis for C, H, and Br seems to be acceptable (see the Experimental Section). However, the nitrogen content is low presumably due to either loss of N₂ from the azido group or formation of refractory nitrides during analysis. The discrepancy in the nitrogen content prompted further characterization of the molecule by X-ray diffraction (Table 2). The crystallographic analysis indicated that the compound is trimeric, and revealed two kinds of significant disorder which were successfully modeled in the structure. The major component of the molecule is shown in Figure 2, and the disordered model is shown in Figure 3. The first disorder occurs about the Ga(2) site where Br(2) and C(2) essentially exchange positions in a minor fraction (18%) of the structure. The disordered bromine in the vicinity of C(2) is designated as Br(4). The occupancy of Br(4) was constrained to be 1-occ (occupancy) of the major component Br(2). As expected the 18% minority carbon in the vicinity of Br(2) was not located. At the other side of the molecule the bridging position between Ga(1) and Ga(3) shows a clear disorder between the azide N(7)−N(8)−N(9), which is the major bridging component, and the bromine Br(5). Refinement of constrained occupancy for the azide [(N(7)−N(8)−N(9)] and the bromine Br(5) converged with Br(5) at 9.2% occupancy. To allow for the existence of Br(5), adjustment of the occupancies of Br(1) and Br(3) was necessary and led to refined occupancies of 94% Br(1) and 96.5% Br(3). As expected no sign of the corresponding 6% and 3.5% N₃ was found. In conclusion this model postulates that the majority fraction of the molecules is the trimer Ga₃(μ_2-N₃)₃Br₃Me₃ (Figure 2) with a minor component of Ga₃(μ_2-N₃)₂μ_2-BrBr₂N₃Me₃ (Figure 3).

Within experimental errors, the azide ligands are nearly linear [N(1)−N(2)−N(3) 179(2)°, N(4)−N(5)−N(6) 179(1)°, and N(7)−N(8)−N(9) 178(4)°] and all the angles on the bridging nitrogens are nearly 120° [e.g., Ga(1)−N(1)−Ga(2) 122.1(6)°, Ga(2)−N(1)−N(2) 118(1)°, Ga(1)−N(1)−N(2) 119(1)]. The ring angles N(1)−Ga(2)−N(7) and N(4)−Ga(3)−N(7) are nearly equal at 96.6(8)° and 95.1(6)°, respectively. The remaining ring angle N(1)−Ga(2)−N(4) is 88.7(5)°. The bond distances N(4)−N(5) and N(7)−N(8) (Table 4) are longer than the corresponding terminal distances N(5)−N(6) and N(8)−N(9) a result which is consistent with previously published structures of gallium azides.[3,4,9,10] However, the N(1)−N(2) distance [1.09(1) Å] is shorter than the terminal N(2)−N(3) bond distance [1.19(2) Å]. This deviation is likely due to the crystal disorder and the consequent lack of accuracy in the atomic positions.
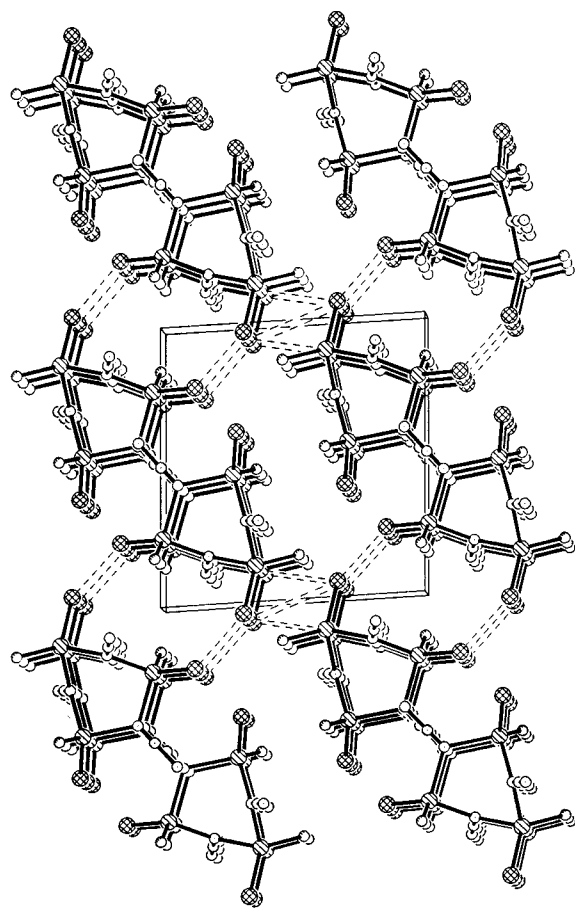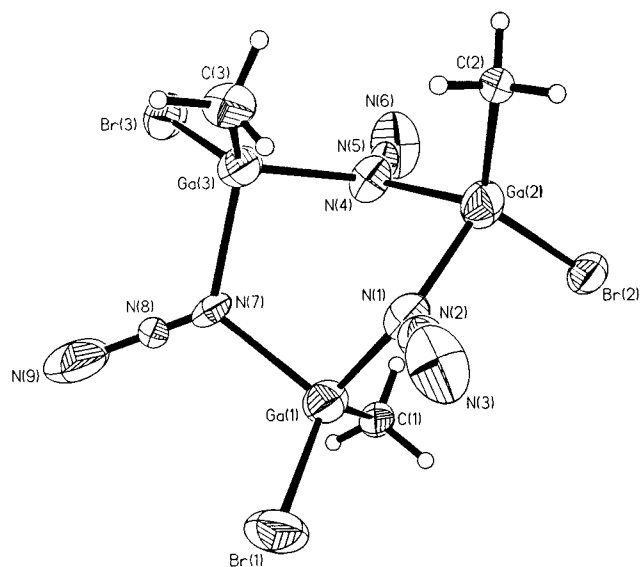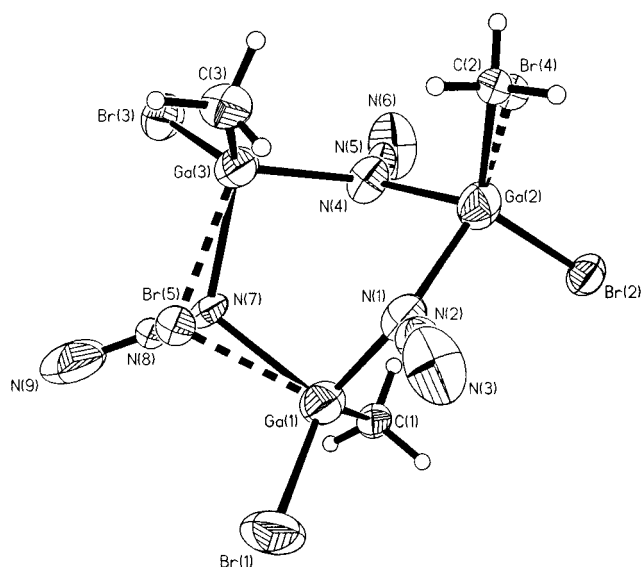
Figure 3. Disordered model of $[(CH_3)BrGaN_3]_3$. Dotted lines indicate the minor occupancies.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**

Distances			
Br(1)−Ga(1)	2.297(2)	Br(3)−Ga(3)	2.299(2)
Ga(1)−N(1)	2.02(1)	Ga(2)−N(4)	1.99(1)
Ga(1)−N(7)	2.09(2)	Ga(3)−N(7)	2.08(2)
Ga(2)−N(1)	2.04(1)	Ga(3)−N(4)	1.99(1)
Br(2)−Ga(2)	2.274(3)	Ga(1)−C(1)	1.931(12)
C(1)−H(1)	0.95	Ga(2)−C(2)	2.21(2)
C(2)−H(4)	0.95	Ga(3)−C(3)	1.939(11)
N(1)−N(2)	1.09(1)	N(2)−N(3)	1.19(1)
N(4)−N(5)	1.22(1)	N(5)−N(6)	1.18(1)
N(7)−N(8)	0.90(4)	N(8)−N(9)	1.22(2)
Angles			
N(1)−Ga(2)−N(4)	88.7(5)	Ga(3)−N(7)−N(8)	122(2)
N(7)−Ga(3−C(3)	113.5(8)	Ga(1)−N(7)−N(8)	121(2)
N(1)−Ga(2)−C(2)	104.7(7)	N(4)−Ga(2)−C(2)	108.9(7)
N(1)−Ga(1)−N(7)	96.6(8)	Ga(1)−N(1)−Ga(2)	122.1(6)
N(1)−Ga(1)−C(1)	114.6(5)	N(4)−Ga(3)−C(3)	111.8(5)
N(4)−Ga(3)−N(7)	95.1(60)	N(1)−N(2)−N(3)	179(2)
Ga(1)−N(1)−N(2)	119(1)	N(7)−N(8)−N(9)	178(4)
Ga(2)−N(1)−N(2)	118(1)	Ga(2)−N(4)−N(5)	118.8(9)
Ga(2)−N(4)−Ga(3)	122.3(5)	Ga(3)−N(4)−N(5)	118.4(9)
Ga(2)−Br(4)−C(2)	117(6)	Br(2)−Ga(2)−N(1)	105.4(3)
N(7)−Ga(1)−C(1)	109.2(8)	N(4)−N(5)−N(6)	179(1)
Br(2)−Ga(2)−Br(4)	124.1(3)	Br(2)−Ga(2)−N(4)	109.0(3)
GA(1)−N(7)−Ga(3)	117(1)	Br(1)−Ga(1)−N(7)	107.2(5)
R(3)−Ga(3)−N(4)	104.8(3)	Br(1)−Ga(1)−N(1)	102.7(3)

respectively. The mass spectrum displays the calculated isotopic patterns for the trimeric ion $\{[(CH_3)HGaN_3)]_3^+ - H\}$ as the highest mass peak at 382 amu, as well as those for the dimeric $\{[(CH_3)HGaN_3)]_2^+ - H\}$ and the monomeric $\{[(CH_3)HGaN_3)]^+ - H\}$ ions at 255 and 126 amu, respectively. The ^1H NMR spectrum at 22 °C shows two Ga−Me resonances corresponding to two different Me environments (δ −0.165 and δ −0.215). In addition two distinct and closely spaced resonances are observed for the Ga−H protons (δ 5.13 and δ 5.00). Upon heating to 90 °C, each set reversibly coalesces into a single resonance at δ −0.112 and δ 5.18, respectively, suggesting the presence of different isomers. This also could be due to monomer−dimer−trimer equilibrium.

$[(CH_3)HGaN_3]_x$ (**3**) is thermally and mechanically stable, and it is considerably easier to handle than H_2GaN_3 (this is a highly reactive species, and abrupt scraping or sudden heating can initiate a vigorous exothermic decomposition). In addition, compound **3** appears to have the necessary reactivity and

Figure 2. (a, top) Molecular structure of $[(CH_3)BrGaN_3]_3$ (**2**). The heavy atoms are 50% probability ellipsoids, and the hydrogen atoms are of arbitrary size. This figure displays the major occupancy settings of the molecule. (b, bottom) Packing arrangement of compound **2** displaying the independent $[(CH_3)BrGaN_3]_3$ units (typical Br−Br and Br−Ga intermolecular contacts are 3.805 and 3.673 Å, respectively).

Compound **3** (eq 3) is obtained as a mobile liquid in 88% yield, and it distilled readily at 55 °C, 0.100 Torr. Elemental analysis of the product suggested the $(CH_3)HGaN_3$ formula. The IR spectrum shows two distinct and very intense bands at 2120 and 1949 cm^{-1} assigned to $\nu_{as}(N_3)$ and ν_{as} (Ga−H),[8,10] respectively. Weak bands corresponding to ν_{as} (C−H) and ν_{as}-(C−H) of the CH_3 ligand are observed at 2970 and 2910 cm^{-1}

volatility to serve as a new and potentially practical precursor to GaN. A brief survey of preliminary experiments indicates that **3** forms thin films via loss of CH_4 and N_2 at temperatures as low as 250 °C. The precursor vaporizes readily at 22 °C and is transported at a steady rate onto the growth surface at 10^{-4} Torr. Rutherford backscattering analyses of the films grown between 250 and 600 °C revealed stoichiometric GaN. Transmission IR of films on Si displayed a band at 560 cm^{-1}, which is consistent with the lattice mode of GaN. Cross-sectional high-resolution electron microscopy of samples grown at 250 °C revealed an array of interconnected nanocrystals, typically 20–30 Å in size, that are evenly distributed throughout the layer. The synthesis of such morphologies via this method might provide a simple chemical route to quantum dot GaN structures with a blue-shifted high-energy emission.[4] Growth experiments aimed to evaluate the feasibility of **3** as a viable precursor to monocrystalline GaN epitaxial layers are in progress.

Summary

The new inorganic azides $[(CH_3)ClGaN_3]_4$ (**1**) and $[(CH_3)BrGaN_3]_3$ (**2**) are prepared as colorless, molecular solids by reaction of the corresponding halides with $SiMe_3N_3$. The X-ray structure of **1** consists of tetrameric units in which the Ga atoms are connected by the α-nitrogens of the azide groups to form a Ga_4N_4 heterocycle similar to that in the related $[HClGaN_3]_4$ compound. Surprisingly, the X-ray diffraction analysis of **2** reveals a sterically less favorable three-membered ring structure formed by bridged azides incorporating a Ga_3N_3 core. The new and stable azidogallane $[(CH_3)HGaN_3]_x$ (**3**) is prepared by reaction of **1** and **2** with $LiGaH_4$. Compound **3** appears to have the necessary volatility and reactivity to make it useful as a GaN precursor. GaN thin films were grown at temperatures as low as 250 °C from the room temperature vapor pressure of the precursor by loss of extremely stable species such as CH_4 and N_2.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen using standard Schlenk and drybox techniques. Dry, air-free solvents were distilled from sodium–benzophenone ketyl prior to use. ^1H NMR (300 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded on a Varian Gemini 300 and a Varian Unity 500 spectrometer, respectively. FTIR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Electron impact mass spectra were performed on a Finnigan-MAT Model 312 mass spectrometer (IE = 70 eV) at the Arizona State University departmental mass spectrometry facility. $GaBr_3$ was prepared by the reaction of dry Br_2 and gallium metal, and it was purified by sublimation. $GaCl_3$ (Aldrich) and $Zn(CH_3)_2$, 2 M solution in toluene (Aldrich), were used as received. $SiMe_3N_3$ (Aldrich 95%) was purified by distillation (50 °C, 175 mmHg), and its purity was checked by NMR and gas-phase IR. $LiGaH_4$,[11] Cl_2GaN_3,[12] and Br_2GaN_3[8] were freshly prepared using literature methods.

Synthesis of CH_3ClGaN_3. A suspension of Cl_2GaN_3 (2.37 g, 13.02 mmol) in hexane (100 mL) was treated with a hexane solution (40 mL) of 2 M Zn (CH$_3$)$_2$ (3.5 mL, 7.0 mmol). The $Zn(CH_3)_2$ reagent was added slowly over a period of 1 h at −40 °C, and the mixture was allowed to stir for an additional 12 h at 22 °C. The mixture is filtered, and the clear filtrate was cooled at −5 °C to yield a crystalline solid (mp 80 °C) which was collected in several crops by concentrating and cooling the hexane solution (yield 1.81 g, 86%). Anal. Calcd for CH_3ClGaN_3: C, 7.40; H, 1.86; N, 25.90. Found: C, 7.27; H, 1.74; N, 25.55. ^1H NMR (C$_6$D$_6$): δ 0.19, 0.083, and −0.135 at 22 °C and δ 0.025 (br)

at 70 °C. IR: 3348 (w, $\nu_{as}(N_3) + \nu_{sym}(N_3)$), 2970−2925 (w, $\nu_{as}(CH_3)$ and $\nu_{sym}(CH_3)$), 2430 (w, 2 × $\nu_{sym}(N_3)$), 2145 (vs, $\nu_{as}(N_3)$), 1220 (m, $\nu_{sym}(N_3)$), 756 (s), 725 (s), 606 (m), 564 (w), 435 (m). EIMS (*m/e*): 309 [(CH$_3$ClGaN$_3$)$_2^+$ − CH$_3$], 282 [(CH$_3$ClGaN$_3$)$_2^+$ − N$_3$], 126 [(CH$_3$ClGaN$_3$)$^+$ − Cl], 120 [(CH$_3$ClGaN$_3$)$^+$ − N$_3$].

Synthesis of $(CH_3)BrGaN_3$. A suspension of Br_2GaN_3 (1.54 g, 5.66 mmol) in 200 mL of hexane was treated with a hexane solution (30 mL) of 2.0 M $Zn(CH_3)_2$ (1.5 mL, 3 mmol) at −40 °C. The reaction mixture was stirred at room temperature for about 14 h and then filtered. The clear filtrate was cooled at 5 °C to yield a crystalline solid (mp 80 °C) which was collected in several crops by concentrating and cooling the hexane solution (yield 0.725 g, 62%). Anal. Calcd for CH$_3$-BrGaN$_3$: C, 5.79; H, 1.44; N, 20.29. Br, 38.64. Found: C, 5.73; H, 1.35; N, 17.72; Br, 37.54. ^1H NMR (C$_6$D$_6$, 25 °C): δ −0.079. FT-IR (Nujol mull, cm^{-1}): 3350 (w), 2464 (w), 2146 (vs), 1232 (s), 1138 (vw), 745 (s), 722 (sh), 596 (m), 569 (m), 422 (s). EIMS: 605 (M$^+$)$_3$ −CH$_3$, 578 (M$^+$)$_3$ − N$_3$, 539 (M$^+$)$_3$− Br, 400 (M$^+$)$_3$− CH$_3$, 371 (M$^+$)$_2$− N$_3$, 332 (M$^+$)$_2$− Br.

Synthesis of $(CH_3)HGaN_3$. To a solution of $(CH_3)ClGaN_3$ (0.5 g, 3.1 mmol) in benzene (40 mL) was added $LiGaH_4$ (0.375 g, 4.65 mmol) at 0 °C by a solid addition funnel. The mixture was stirred at 20 °C for 3 h, during which time the suspension became gray. The mixture was then filtered, and the benzene was removed in a vacuum to yield (CH$_3$)-HGaN$_3$ as a clear mobile liquid. The product was purified by short-path distillation between 53 and 55 °C and at 0.100 Torr (yield 0.35 g, 88%). Anal. Calcd for CH$_4$GaN$_3$: C, 9.3; H, 3.1; N, 32.8. Found: C, 7.5; H, 2.7; N, 31.6 (the analyses were consistently low for C and H, indicating possible loss of CH$_4$ from the product). ^1H NMR (C$_6$D$_6$): δ 5.13, 4.99, −0.165, and −0.215 at 22 °C and δ 5.18 and −0.112 at 90 °C. IR: 3343 (w, $\nu_{as}(N_3) + \nu_{sym}(N_3)$), 2970−2910 (w, $\nu_{as}(CH_3)$ and $\nu_{sym}(CH_3)$), 2470 (w, 2 × $\nu_{sym}(N_3)$), 2120 (vs, $\nu_{as}(N_3)$), 1949 (s, ν_{as^-}(Ga−H)), 1241 (m, $\nu_{sym}(N_3)$), 756 (s), 750 (m) 703 (s, $\rho(CH_3)$), 671 (s), 605 (m, ν_{as}(Ga−C)), 580 (m, δ N$_3$), 564 (w), 486 (w), 405 (m, ν(Ga−N)), 351 (m). EIMS (*m/e*): 382 [M$_3^+$ − H], {M = (CH$_3$)-HGaN$_3$)} 368 [M$^+$ − CH$_3$], 354 [M$_3^+$ − 2(CH$_3$)], 340 [M$_3^+$ − HN$_3$], 327 [M$_3^+$ − H$_3$ − N$_3$], 313 [M$_3^+$ − N$_3$ − N$_2$], 255 [(M$^+$)$_2$ − H], 241-[(M$^+$)$_2$ − CH$_3$], 214 [(M$^+$)$_2$ − N$_3$], 198 [(M$^+$)$_2$ − N$_3$ − CH$_3$], 184 [H$_2$Ga$_2$N$_3$], 126 [M$^+$ − H], 112 [M$^+$ − CH$_3$].

X-ray Structure of 1 and 2. A colorless plate of the compound was positioned lengthwise inside a 0.3 mm capillary and sealed under nitrogen. The sample was mounted vertically on a P4 autodiffractometer equipped with a LT-2a low-temperature device preset at −100 °C. Centering of 25 randomly selected reflections between 15 and 30 °C revealed a primitive tetragonal cell. Data collection of one-quarter of the hemisphere out to 45 °C gave 417 independent reflections with intensity greater than 4σ. Solution by direct methods and subsequent cycles of least-squares refinement showed the asymmetric unit to be the $(CH_3)ClGaN_3$ moiety. The independent molecules are tetramers of the $(CH_3)ClGaN_3$ unit.

A fragment of a colorless blocky crystal of compound **1** having approximate dimensions of 0.05 × 0.10 × 0.12 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART CCD area detector. Cell constants and an orientation matrix obtained from a least-squares refinement using the measured positions of 963 reflections in the range $3.00° < 2\theta < 45.00°$ corresponded to a primitive triclinic cell. The data were collected at −120 °C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10.0 s/frame. Data were integrated by the program SAINT to a maximum 2θ value of 49.3°. The structure was solved by direct methods. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Details of the occupancy refinement are given in the Results and Discussion. In addition the thermal parameters of C(2) and of Br(4) were constrained to be the same. This was necessary to allow the refinement to converge to reasonable values. The final cycle of full-matrix least-squares refinement was based on 1129 observed reflections ($I > 3.00\sigma(I)$) and 162 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.35$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2} = 0.38$. Additional experimental conditions and unit cell information are summarized in Table 2.

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Supporting Information Available: Full tables of bond lengths and angles, atomic coordinates, and displacement parameters for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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