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H_2GaN_3 and Derivatives: A Facile Method to Gallium Nitride

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We describe the formation and properties of H_2GaN_3 (**1**), which is a very simple and stable molecular source for chemical vapor deposition (CVD) of GaN heterostructures. Compound **1** and the perdeuterated analogue D_2GaN_3 (**2**) are prepared by the $LiGaH_4$ and $LiGaD_4$ reduction of Br_2GaN_3 (**3**), respectively. Compound **3** is obtained from the thermal decomposition of the crystalline adduct $SiMe_3N_3{\cdot}GaBr_3$ (**4**) via loss of $SiMe_3Br$. A single-crystal X-ray structure of **4** reveals that the molecule is essentially a Lewis acid−base complex between $SiMe_3N_3$ and $GaBr_3$ and crystallizes in the orthorhombic space group $Pna2_1$, with $a = 14.907(5)$ Å, $b = 7.759(3)$ Å, $c = 10.789(5)$ Å, $V = 1248(1)$ Å,^{3} and $Z = 4$. The new azidobromogallane $HBrGaN_3$ (**5**) is also prepared by reaction of appropriate amounts of **3** and $LiGaH_4$. Both H_2GaN_3 (**1**) and D_2GaN_3 (**2**) are volatile species at room temperature and can be readily distilled at 40 °C (0.20 Torr) without decomposition. Normal-mode analysis and ab initio theoretical calculations suggest that the vapor phase IR spectra of **1** and **2** are consistent with a trimeric $(H_2GaN_3)_3$ and $(D_2GaN_3)_3$ molecular structure of C_{3v} symmetry. On the basis of the mass spectrum, **1** is a trimer in the vapor phase and decomposes readily at low temperatures by elimination of only H_2 and N_2 to yield pure and highly stoichiometric GaN thin films. Crucial advantages of this new and potentially practical CVD method are the significant vapor pressure of the precursor that permits rapid mass transport at 22 °C and the facile decomposition pathway that allows film growth at temperatures as low as 200 °C with considerable growth rates up to 800 Å/min.

Introduction

Synthetic methods to GaN thin film heterostructures based on single-source (particularly C−H free) precursors offer the potential of significant improvements for the film growth process and the quality of the material.[1−5] Possible advantages include lower deposition temperature, elimination of the inefficient use of ammonia, reduction of nitrogen vacancies, and complete absence of carbon impurities.

Recently we reported several related routes for GaN synthesis utilizing a new class of inorganic azide compounds that incorporate hydrogen and halide ligands[5−7] instead of organic groups. A representative example of our method is based on the disproportionation reaction at temperatures higher than 500 °C of the gaseous trimer $(Cl_2GaN_3)_3$ via elimination of $GaCl_3$ and N_2 to yield heteroepitaxial GaN on sapphire substrates. Cl_2GaN_3 is a rather involatile polymeric solid at 22 °C but sublimes readily at 70−100 °C in high vacuum and melts without decomposition at 230 °C.[6] Some disadvantages associated with the application of this compound as a practical GaN CVD precursor are the lack of any significant vapor pressure at room temperature and the inherent loss of substantial quantities of $GaCl_3$ from the trimeric molecule at high temperatures. More recently, our search for alternative precursors with higher vapor pressures and more effective decomposition pathways led to the development of the related and substantially more reactive $HClGaN_3$ compound.[5] Crystalline $HClGaN_3$ is a moderately volatile molecular system consisting of interconnected tetrameric Ga_4N_4 units that have a conformation similar to cyclooctane (Figure 1). The vapor of the compound consists of $(HClGaN_3)_3$ trimers which decompose readily at low temperatures by elimination of HCl and N_2 to grow GaN layers on sapphire and Si substrates. Solid $[HClGaN_3]_4$ decomposes

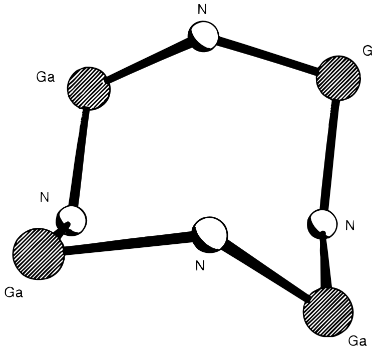

Figure 1. Representation of the Ga_4N_4 cyclic core of $(HClGaN_3)_4$.[5]

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exothermically near the melting point (70 °C) to yield nanocrystalline GaN bulk material.

Potentially more attractive is the simpler hydride analogue H_2GaN_3 (**1**) because it could eliminate benign H_2 and N_2 byproducts to yield stoichiometric GaN material very effectively at low temperatures. The intended decomposition pathway (eq 1) represents one of the simplest chemical routes to gallium nitride.[5]

$$H_2GaN_3 \rightarrow H_2 + N_2 + GaN \qquad (1)$$

Our original synthesis of **1** utilized a metathesis reaction involving the interaction of H_2GaCl and LiN_3 at 22 °C.[5] We found, however, that the preparation of uncontaminated H_2GaN_3 (**1**) by this method required high-quality H_2GaCl, a material that is difficult to synthesize and maintain as a pure compound, particularly at ambient temperatures.[8] Halide-containing impurities presumably resulting from impure starting material or from reaction byproducts were not easily separated from the H_2GaN_3 (**1**) product and eventually seemed to facilitate decomposition of the compound especially in solution. Since high purity is necessary to explore the application of the compound as a viable precursor for GaN synthesis, our efforts have been focused on the development of an alternate reaction method that would provide access to a pure product.

This paper is focused on a new and practical synthetic pathway to high-yield, high-purity H_2GaN_3 (**1**) and its derivatives and includes complete characterization, as well as determination of physical and chemical properties (including stability issues) of this unique compound. We have also used ab initio methods and normal-mode analysis to calculated the vibrational properties of the trimeric $(H_2GaN_3)_3$ C_{3v} and dimeric $(H_2GaN_3)_2$ D_{2h} forms of the compound. The vapor IR and mass spectra are consistent with the trimeric model of C_{3v} symmetry. Moreover, we have demonstrated by deposition studies that the gas-phase decomposition reaction of **1** on sapphire and Si surfaces occurs via loss of H_2 and N_2 (as illustrated in eq 1) to form GaN layers at temperatures as low as 300 °C.

Results and Discussion

H_2GaN_3 (**1**) and D_2GaN_3 (**2**) are prepared via reduction of Br_2GaN_3 (**3**) with an excess of $LiGaH_4$ and $LiGaD_4$, respectively. The bromide is prepared from the Lewis acid−base adduct $SiMe_3N_3{\cdot}GaBr_3$ (**4**), a crystalline solid that is stable at room temperature but decomposes thermally via elimination of 1 mol of $SiMe_3Br$ at $T > 50$ °C to yield **3** as a colorless polymeric solid. Interestingly, the reaction of equimolar quantities of **3** with $LiGaH_4$ yields a new compound with composition $HBrGaN_3$ (**5**). The synthetic procedure is summarized by the eqs 2−6.

$$GaBr_3 + SiMe_3N_3 \rightarrow SiMe_3N_3{\cdot}GaBr_3 \qquad (2)$$

$$SiMe_3N_3{\cdot}GaBr_3 \rightarrow SiMe_3Br + Br_2GaN_3 \qquad (3)$$

$$Br_2GaN_3 + LiGaH_4 \rightarrow HBrGaN_3 + LiBr + GaH_3 \qquad (4)$$

$$Br_2GaN_3 + 2LiGaH_4 \rightarrow H_2GaN_3 + 2LiBr + 2GaH_3 \qquad (5)$$

$$Br_2GaN_3 + 2LiGaD_4 \rightarrow D_2GaN_3 + 2LiBr + 2GaD_3 \qquad (6)$$

$SiMe_3N_3{\cdot}GaBr_3$ (4). Formation of stable complexes between the Lewis base $SiMe_3N_3$ and Lewis acids $GaCl_3$, $SnCl_4$, and BBr_3 has been previously demonstrated.[7,9] In the case of $SiMe_3N_3{\cdot}GaCl_3$, a structural characterization showed a bridging Ga−N−Si azide linkage rather than a Ga−N−N−N−Si linkage.[7] The $SiMe_3N_3{\cdot}GaBr_3$ (**4**) compound was readily obtained by a combination of freshly sublimed $GaBr_3$ with $SiMe_3N_3$ and crystallized in toluene to give colorless needle-shaped crystals. An X-ray crystallographic analysis (Tables 1 and 2) reveals that the molecule has a geometry similar to that of $SiMe_3N_3{\cdot}GaCl_3$ and consists of monomeric units containing a Ga−N−Si linkage (Figure 2). Interestingly the Si−C bond (1.804 Å) is significantly shorter than expected for a single bond, and the Ga−N bond distance (2.022 Å) is very close to the Ga−N distances found for the $(Me_3GaN_3)_x$ polymer in which the Ga atoms are linked together by the α-nitrogens of the azide group to form an one-dimensional polymeric chain. There are two distinct N−N distances in the azide group, with the shorter one corresponding to the terminal N−N bond (1.129 Å), a feature which is common among gallium compounds with bridging azides. Spectroscopic characterizations by IR and NMR and elemental analysis are consistent with the molecular formula derived from the X-ray structure. The compound decomposes in the mass spectrometer to give $SiMe_3Br$ and Br_2GaN_3 (**3**) species.

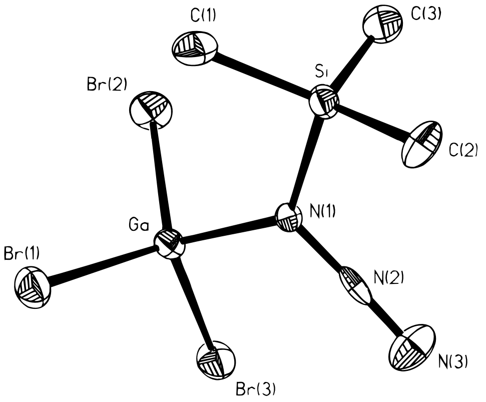

Figure 2. Molecular structure of $SiMe_3N_3{\cdot}GaBr_3$ showing the atomic labeling scheme.

Table 1. Structure Determination Summary for **4**

chem formula	$C_3H_9Br_3GaN_3Si$	fw	424.7
cryst system	orthorhombic	space group	$Pna2_1$
a (Å)	14.907(5)	T (K)	173
b (Å)	7.759(3)	λ(Mo Kα) (Å)	0.710 73
c (Å)	10.789(5)	ρ_{calc} (gcm^{-3})	2.26
V (Å^3)	1248(1)	μ (mm^{-1})	11.86
Z	4	wR^a (%)	4.05
		R^b (%)	5.06

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

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

Ga−N1	2.022(15)	N2−N3	1.129(20)
Si−N1	1.826(13)	Si−C1	1.804(19)
Ga−Br1	2.300(19)	Si−C2	1.807(19)
N1−N2	1.267(18)	Si−C3	1.810(26)
Br1−Ga−Br2	113.7(3)	Ga−N1−Si	129.8(6)
C1−Si−C2	115.0(11)	Ga−N1−N2	115.0(5)
C2−Si−C3	113.7(9)	N2−N1−S1	1152(10)
C1−Si−C3	112.6(9)	Br2−Ga−N1	103.7(6)
N1−Si−C1	106.4(8)	Br1−Ga−Br3	112.9(9)
N1−N2−N3	176.2(19)	Br1−Ga−N1	107.0(8)

Br_2GaN_3 (3). Heating **4** under vacuum at about 50 °C eliminated $SiMe_3Br$ quantitatively and resulted in the formation of **3** as a finely divided colorless solid. The IR spectrum of the

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material is identical to the product of the reaction of I_2GaN_3 with liquid Br_2.[10] Mass spectrometric analysis of **3** obtained by direct vaporization of a sample into the spectrometer at 70 °C reveals the highest mass peak at 773 amu which corresponds to $[(Br_2GaN_3)_3 - N_3]^+$. This is consistent with the vapor containing trimeric $(Br_2GaN_3)_3$ units. On the other hand, higher intensity peaks at 502 and 229 amu, corresponding to $[(Br_2GaN_3)_2 - N_3]^+$ and $[(Br_2GaN_3) - N_3]^+$, respectively, suggest that the presence of dimers and monomers is also possible, although these species could have been generated through the cleavage of the parent ion.

$HBrGaN_3$ (5). The synthesis of **5** was accomplished by the interaction of **3** with 1 equiv of $LiGaH_4$ in C_6H_6. The product was isolated as a clear and slightly viscous liquid after filtration from the insoluble byproducts, which consist of crystalline LiBr and a gray material that presumably resulted from the decomposition of GaH_3. Elemental analysis of the product indicates the formula $HBrGaN_3$ and reveals a lack of significant carbon impurities. The infrared spectrum is very simple and includes vibrations at 2148 cm^{-1} [$\nu_{as}(N_3)$], 1995 [$\nu_{as}(Ga-H)$], and a strong band at 580 cm^{-1} corresponding to Ga−H deformations. The ^1H NMR spectrum in toluene-d_8 at 20 °C contains a broad peak at δ 5.093, upfield from that of δ 5.25 in the spectrum of $HClGaN_3$, a shift characteristic of terminal Ga−H groups. The mass spectrum obtained by direct vaporization of the compound at 20 °C displays isotopic bands for $(M_3^+ - H)$ [$M_3 = (HBrGaN_3)_3$] at 578 amu, $(M_3^+ - N_3)$, $(M_3^+ - Br)$, and $(M_2^+ - Br)$. The observed patterns are in good agreement with the calculated patterns.

The reduction of Cl_2GaN_3 by $LiGaH_4$ under conditions similar to those for the reduction of **3** was incomplete and led to a mixture of $HClGaN_3$ and the starting material (Cl_2GaN_3). Attempts to synthesize azidogallanes via reduction of X_2GaN_3 (X = Cl, Br) by a range of other inorganic and organometallic reducing agents of boron, aluminum, and silicon [i.e. $LiBH_4$, $LiB(Et)_3$, LiAlH4, $AlH(butyl)_2$, and $SiMe_3H$] were unsuccessful. In most cases ligand exchange (azide or organic) between the reducing and the reduced species was obtained.

H_2GaN_3 (1). The reaction of **3** with 2 equiv of $LiGaH_4$ followed by filtration and removal of the solvent yielded compound **1** as a clear viscous liquid that decomposes rapidly upon exposure to air. The IR (thin liquid film) and NMR spectra of the compound are essentially identical to those obtained from the product of the reaction of H_2GaCl with LiN_3 (see Experimental Section for details).[5] The low-temperature ^1H NMR spectrum obtained in toluene-d_8 at −50 °C displays a very sharp peak at δ 4.81 that is substantially different than the value obtained for $HBrGaN_3$ (**5**). Figure 3 illustrates a representative low-temperature ^1H NMR spectrum of a sample that was kept at room temperature for 5 days after preparation. The spectrum shows that the compound is reasonably pure and indicates good stability over time. The mass spectrum of **1** was obtained by direct vaporization confirms that the compound is pure and free of any halide contamination. The highest mass peak was observed at 341 amu which corresponds to the mass of $(H_2GaN_3)_3^+ - H$. Trap-to-trap distillation from room temperature into a series of traps held at 0, −15, and −196 °C resulted in a collection of the pure sample at the −15 °C trap. The distillation experiments demonstrate that the compound is quite volatile at 20 °C and also has a significant vapor pressure at room temperature. This kind of volatility is a crucial factor for its application as a practical CVD precursor. The compound was conveniently purified by reduced-pressure distillation to give a colorless liquid (bp 40 °C, 0.200 Torr). Elemental analysis of the purified product is consistent with the H_2GaN_3 formula and revealed no measurable carbon impurities.

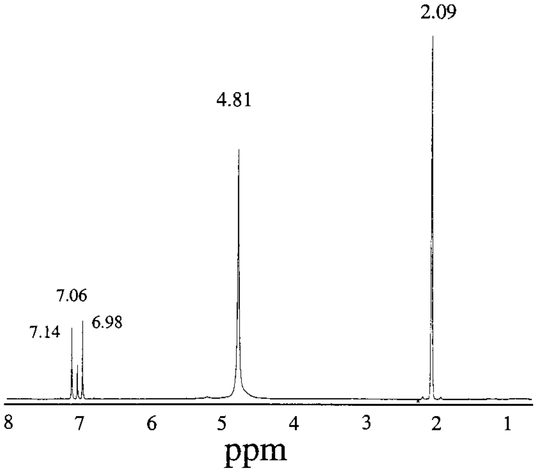

Figure 3. ^1H NMR spectrum of H_2GaN_3 at −50 °C dissolved in toluene-d_8.

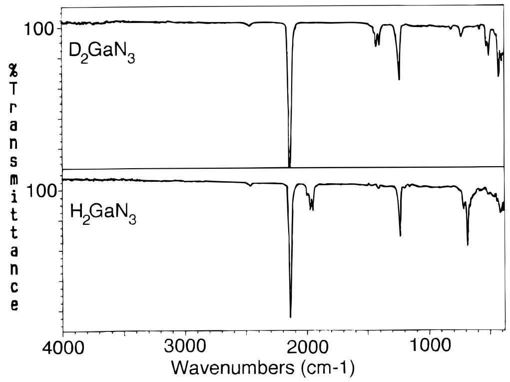

Figure 4. FTIR gas-phase spectra of D_2GaN_3 and H_2GaN_3 obtained with a 10 cm path length glass cell fitted with KBr windows.

D_2GaN_3 (2). The perdeuterated azidogallane was obtained from the reaction of an excess of $LiGaD_4$ with **3** and was readily distilled at a reduced pressure (bp 40 °C, 0.20 Torr) to give a viscous liquid which is thermally more stable than the isotopically normal analogue. The compound was characterized by its IR (liquid thin film and gas phase) and mass spectra and its identity was confirmed by elemental analysis. The mass spectrum revealed a prominent isotopic envelope for $[D_2GaN_3]_3^+ - D$ at 345 amu which was in an excellent agreement with the calculated pattern, and its fragmentation pattern was consistent with a trimeric structure. Particularly instructive is the simplicity of the gas-phase IR spectrum of **2,** which was obtained at 25 °C in a 10 cm cell fitted with KBr windows. It is compared in Figure 4 to the corresponding spectrum of **1** which was recorded at nearly identical conditions. The main point is that the absorptions near 1950−2000 and 680−725 cm^{-1} representing the stretching and bending modes of terminal Ga−H bonds, respectively, have shifted to 1400−1450 and 500−502 cm^{-1}, respectively, for the perdeuterated compound. The energy shifts induced by the deuteration are remarkably close to the calculated values and provides further evidence for the identification of the H_2GaN_3 molecule. The frequencies of the azide absorptions at 2145 and 1232 cm^{-1} corresponding to antisymmetric and symmetric stretching vibrations, respectively, remain unchanged. Furthermore, the IR spectra revealed multiple Ga−H and Ga−D bands at (1997, 1973, 1950) and (1425, 1400) cm^{-1}, respec-

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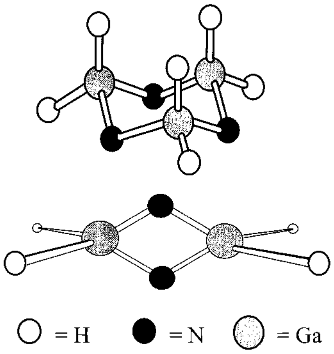

Figure 5. Representations of trimer $(H_2GaN_3)_3$ with C_{3v} symmetry (top) and the dimer $(H_2GaN_3)_2$ with D_{2h} symmetry (bottom). The structures incorporate bridging azides ligands; however, the terminal N−N moiety of the azide is omitted for clarity reasons.

tively. Interestingly a similar splitting pattern was observed for ν(Ga−H) in the IR spectra of Ga_2H_6 vapor and was attributed to unresolved P and R branches in this highly symmetric compound.[12,13] In our case the presence of cyclic $[(D_2)H_2GaN_3]_2$ dimers and $[(D_2)H_2GaN_3]_3$ trimers in the gas-phase samples cannot be ruled out and a mixture of these could give rise to the IR bands in the Ga−H and Ga−D stretching regions of the spectrum. Clearly high-resolution spectra are needed to derive precise structural information for this very simple molecular system.

Normal-Mode Analysis and ab Initio Calculations of $[H_2GaN_3]_2$, D_{2h} and $[H_2GaN_3]_3$, C_{3v}. The observation of multiple bands in the Ga−H stretching region of the IR spectra prompted a qualitative normal-mode analysis for the possible dimeric $[H_2GaN_3]_2$ and the trimeric $[H_2GaN_3]_3$ forms of compound **1**. (In this section we only refer to compound **1**. Note, however, that the same theoretical treatment applies to compound **2**.) We also performed ab initio computations of related but simpler model compounds, which aid in the actual assignment of the observed spectra.

The dimer $[H_2GaN_3]_2$ has a D_{2h} structure in which the terminal GaH_2 groups are in one plane and the two bridging azides groups are perpendicular to this plane, as illustrated in Figure 5. The normal-mode analysis may be restricted to the Ga−H bond stretching and the H−Ga−H bond bending to facilitate assignment of the observed peaks attributable to the corresponding stretching and bending modes. Group theoretical analysis of the Ga−H terminals bonds reveals that they correlate into $A_g + B_{3g} + B_{1u} + B_{2u}$ irreducible representations in the D_{2h} group. On the other hand, the H−Ga−H bond angles correlate into $A_g + B_{2u}$ modes. Among the four stretching modes, which correspond to the Ga−H stretches for the dimer, only the B_{1u} and B_{2u} modes are IR active on the basis of dipole selection rules. Thus only two IR stretching bands should be observed for the dimer.

The trimeric $[H_2GaN_3]_3$ considered has an equilibrium chair conformation and a C_{3v} symmetry. The normal-mode analysis was again restricted to the Ga−H stretching and H−Ga−H bending modes. The six Ga−H bonds of the trimer correlate in the C_{3v} group into two A_1 + two E normal stretching modes all of which are IR and Raman active in the C_{3v} symmetry. The H−Ga−H bond angles correlate into $A_1 + E$ bending normal modes which are IR active.

To gain quantitative insight into the vibrational frequencies of the various modes we carried out ab initio computations using Møller−Plesset second- and fourth-order perturbation (MP2 and MP4) computations. We employed relativistic effective core potentials (RECPs) for the Ga atom that retained the outer $4s^24p^1$ shells in the valence space replacing the remaining electrons with RECPs. These RECPs were used in conjunction with valence Gaussian (3s3p1d) basis sets for Ga and [5s1p/3s1p] basis sets for the hydrogens described earlier.[14] Thus the Ga basis set is very flexible with a set of 3d polarization functions. There have been several theoretical studies on the electronic structure of Ga-containing species, the most recent by Schaefer and co-workers[15] which describes the possibility of a Ga−Ga triple bond in organometallic complexes. All computations were carried out using the Gaussian 94 package of codes. [16]

We choose GaH_3 and GaH_2 molecules as tractable models to compute the normal-mode frequencies of these species. At the MP2 level of theory the GaH_3 planar molecule (D_{3h}) with ${}^1A_1'$ ground state has A_1' and E' stretching modes with the frequencies of 2011.6 and 1988.8 cm^{-1}, respectively. The IR intensities of the E' and A_1' modes are 238.3 and 0.0, respectively in the D_{3h} symmetry. The MP4 level of theory yields slightly lower (5%) frequencies. The bending frequencies are 770 and 815 cm^{-1}, respectively for the A_2'' and E' modes. The IR intensities are 241 and 181, respectively. The MP4 and MP2 bending frequencies are very close (within 2−7 cm^{-1}). The GaH_2 triatomic has a C_{2v} structure with a ${}^2A_1$ ground state. Since the trivalency of Ga is not fully satisfied in this radical, it has lower vibrational frequencies. At the MP2 level of theory the A_1 (symmetric) and B_2 (asymmetric) Ga−H stretches have vibrational frequencies of 1811 and 1848 cm^{-1}, respectively, while the A_1 bending mode has a frequency of 805.1 cm^{-1}. The computed IR intensities are 343 and 66 for the B_2 and A_1 stretching modes, while it is 160 for the bending mode.

The above symmetry and quantitative analysis reveals that there are two possibilities for the assignment of the three bands in the 1950−2000 cm^{-1} region of the observed spectrum. As discussed earlier, the Ga−H stretching modes for the trimer **1** yield two A_1 and two E normal modes all of which are expected to be IR active. On the basis of the computed vibrational frequencies for GaH_3 stretching modes, we determined that the E mode has a slightly lower frequency (1988.8 cm^{-1}) than the A_1 (2011.6 cm^{-1}). However, for the trimer **1** since there are three GaH_2 groups, the two E stretching modes would interact since their symmetries are the same and their frequencies are expected to be very close. Furthermore, on the basis of our computed results, the E peaks would have substantially larger IR intensities compared to A_1. Thus the two peaks with higher intensities for the protonated compound **1** at 1950 and 1973 cm^{-1} are tentatively assigned to the two Ga−H stretching modes of E symmetry of the trimer **1**. The other lower intensity peak at 1997 cm^{-1} is due to the A_1 stretching mode in which all three Ga−H bonds pointing up (likewise the three bonds down)

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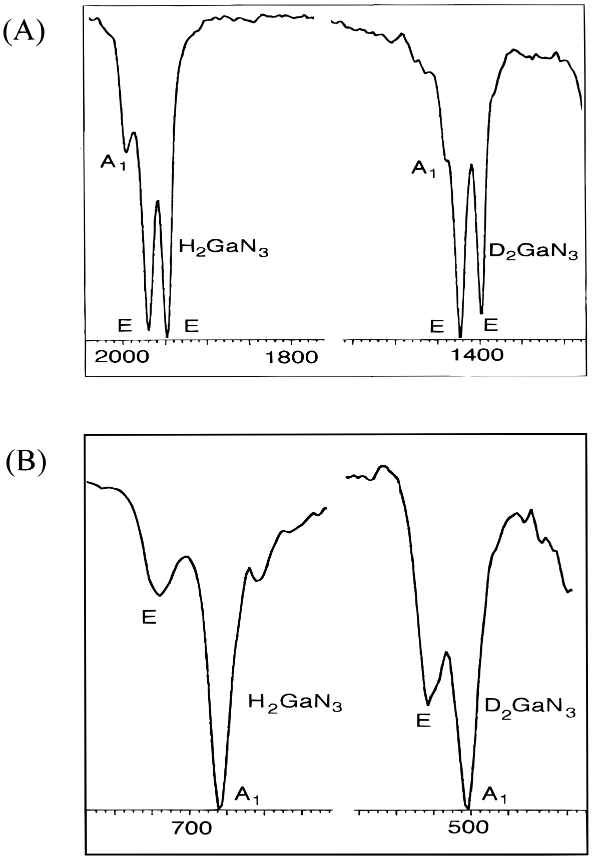

Figure 6. Enlarged view of IR regions. Upper traces: peaks corresponding to the [Ga−H, (D)] stretching modes. Lower traces: the corresponding [H−Ga−H, (D)] bending modes. On the basis of normal-mode analysis and ab initio calculations, these modes are attributable to the trimeric cyclohexane-like structure of C_{3v} symmetry.

move in the same direction in a coherent manner as in a breathing mode. Note that, for the planar D_{3h} GaH_3 structure, this mode has zero IR intensity and is not IR active but for the nonplanar C_{3v} structure this mode would appear but with reduced intensity compared to the E mode. This analysis is fully consistent with the observed frequency and relative intensity of the band at 1997 cm^{-1} (Figure 6).

The $(H_2GaN_3)_2$ dimer has only two IR-active Ga−H stretching modes with B_{1u} and B_{2u} symmetry. The vapor IR spectrum of the structurally analogous gallane (Ga_2H_6) indeed reveals only two peaks in the higher-frequency stretching region near 1980 cm^{-1}. In contrast the IR spectrum of our sample displays at least three prominent peaks in the high-frequency region and another weak peak may also be present near 2000 cm^{-1}. These peaks cannot only be due to a pure dimer although the possibility of a dimer−trimer mixture cannot be entirely eliminated. However, on the basis of our analysis, we are inclined to argue that the spectrum is most likely due to the trimeric $[H_2GaN_3]_3$ which is expected to display two strong closely spaced E modes and in addition two weaker A_1 modes. We certainly observe the E modes and at least one of the A modes in our spectrum.

The low-frequency modes in the 665−725 cm^{-1} region can be assigned to the H−Ga−H bending modes. The computed vibrational frequencies of the A_1' and E' bending modes of GaH_3 favor this assignment. There are three such H−Ga−H bonds for the trimer **1**, and they correspond to A_1 and E modes. The two bands at 720 and 685 cm^{-1} are assigned to the E and A_1 bending modes, respectively. The other very weak band at 663 cm^{-1} may be due to a ring-shearing mode or a Ga−N type mode. The vibrational data and corresponding assignments are summarized in Table 3.

Table 3. Gas IR Spectra of H_2GaN_3 and D_2GaN_3 (350−4000 cm^{-1}) at 25 °C

H_2GaN_3		D_2GaN_3		
ν/cm^{-1}	intensity	ν/cm^{-1}	intensity	assignment*
2462	vw	2462	vw	2 × 1231
2144	vs	2140	vs	asym $\nu(N_3)$
1995	w	1445	w	ν(Ga−H) A_1
1973	m	1426	m	ν(Ga−H) E
1950	m	1399	m	ν(Ga−H) E
1231	s	1234	m	sym $\nu(N_3)$
		730	vw	$\delta(N_3)$
724	m	530	m	(H−Ga−H) E bending
685	s	502	s	(H−Ga−H) A_1 bending

[a] The peak assignment for the Ga−H modes is based on the trimeric $(H_2GaN_3)_3$ ring structure with C_{3v} symmetry.

The Raman spectra of the observed species and more detailed computational analysis of the actual trimer **1** are under consideration and would be the subject of a future investigation. If the dimer were to be present in the sample, the Raman spectrum should show two new stretches corresponding to A_g and B_{3g} Raman active modes, while the IR active B_{1u} and B_{2u} modes should disappear. On the other hand, all modes are Raman active for the trimer.

Reactions of H_2GaN_3 with C_5H_5N and NMe_3 (TMA). Neat H_2GaN_3 (**1**) (in the absence of solvents) is a highly reactive substance. Although the compound is stable at room temperature, abrupt scraping of the sample can initiate a vigorous decomposition via loss of N_2 and H_2 to yield pure GaN. It is, therefore, of immediate interest to increase its stability by coordination of the unsaturated monomeric units of the compound with Lewis bases to form potentially less reactive adducts that could lead to a new class of GaN precursors. Our preliminary survey of reactions between H_2GaN_3 with selected Lewis bases such as C_5H_5N and NMe_3 (TMA) are described below.

A pyridine complex is readily prepared as a mobile liquid by direct interaction of the compound with an excess of dry C_5H_5N, and it is identified by its spectroscopic properties. The ^{1}H NMR spectrum of the adduct at 22 °C reveals a broad resonance at δ 5.37 which is shifted significantly from that of the pure compound (δ 4.81). The spectrum at −50 °C displays a considerably sharper singlet at δ 5.46 which is only shifted slightly with respect to the 22 °C peak. The resonances corresponding to the pyridine protons are also present in the spectrum and are significantly shifted with respect to free pyridine (see Experimental Section). For example the resonance of the ortho hydrogens for the coordinated pyridine group has shifted upfield by 0.7 ppm with respect to that of free pyridine dissolved in toluene-d_8. Integration of the signals consistently suggests a composition of $H_2GaN_3{\cdot}C_5H_5N$. The IR spectrum confirms the presence of coordinated pyridine and shows that the frequencies of the asymmetric stretches for the azide (2086 cm^{-1}) and Ga−H (1916 cm^{-1}) have shifted to lower frequencies with respect to those of **1**, which are observed at 2129 and 1971 cm^{-1}, respectively. The $H_2GaN_3{\cdot}C_5H_5N$ compound is considerably more stable than pure H_2GaN_3.

H_2GaN_3 (**1**) also reacts readily with an excess of trimethylamine to yield a volatile colorless liquid which is isolated by trap-to-trap distillation. This product was identified by its spectroscopic properties to be the molecular adduct $H_2GaN_3{\cdot}NMe_3$. The ^{1}H NMR spectrum shows two singlets, one sharp at δ 1.60 and the other broad at δ 4.95, corresponding to the

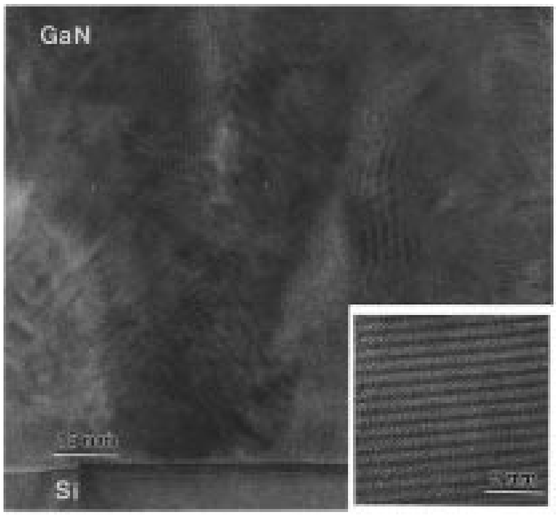

Figure 7. Cross-sectional electron micrograph showing columnar growth of a GaN layer formed by the thermal decomposition of H_2GaN_3 (**1**) at 500 °C on Si(100). The inset shows a highly enlarged view of the layer. The lattice fringes are perpendicular to the direction of the crystalline GaN columns.

protons of the NMe_3 and GaH_2 components of the adduct, respectively. The compound is volatile in the mass spectrometer, and the highest mass peak at 171 amu is attributable to the monomer $H_2GaN_3{\cdot}NMe_3$. The calculated isotopic pattern is in agreement with the experiment and supports the formation of the adduct. The IR spectra indicate a Lewis acid−base compound between H_2GaN_3 and NMe_3 (see Experimental Section) and the data are consistent with the well-established IR properties of the related $Me_3N{\cdot}GaH_3$.[12] The frequencies of the asymmetric stretches for the azide (2100 cm^{-1}) and Ga−H (1908 cm^{-1}) have shifted to lower frequencies with respect to those of **1** ($\nu(N_3)$ 2129 cm^{-1}, ν(Ga−H) 1971 cm^{-1}).

Deposition of GaN from H_2GaN_3 (1). To evaluate the feasibility of the pure compound as a viable precursor to GaN, a series of growth experiments were performed in a new ultrahigh vacuum (UHV) CVD system. The molecule was held in a glass reservoir at room temperature directly attached to the reactor, and the vapor of the compound was simply allowed to flow into the vacuum system which was typically maintained at a base pressure of 10^{-10} Torr by a corrosion resistant turpopump. A rise in pressure from 10^{-10} to approximately 2×10^{-6} Torr was immediately established from the room-temperature vapor pressure of the compound. With direct vaporization of the precursor at 22 °C and at substrate temperatures between 200 and 800 °C, a range of GaN samples were grown at remarkably high growth rates of 600−800 Å/min. Films of thicknesses ranging from 15 000 to 7000 Å were readily grown within 10−15 min of deposition time. A residual gas analyzer attached downstream from the reaction zone provided information about the volatile byproducts. The mass spectra of the residual gases were clean and simple. The only mass peaks observed are at 2, 14, and 28 amu and are due to H_2 and N_2 as indicated in the proposed decomposition reaction depicted by eq 1. Mass peaks associated with the precursor were not detected even at highest sensitivities.

Cross-sectional high-resolution electron microscopy of samples deposited on Si revealed columnar growth of the wurtzite phase, illustrated in Figure 7, for a layer grown at 500 °C. Microscopic examinations of the 200 and 300 °C samples revealed that the films were smooth and highly coherent. High-resolution images revealed that the samples consisted of nanocrystallites evenly distributed throughout the layer. The only feature displayed in the transmission IR spectrum of the same sample was a band at 560 cm^{-1} which is consistent with GaN. Vibrational modes characteristic of Ga−H and N_3 moieties were absent from the spectrum confirming that complete decomposition of the precursor has occurred at 200 °C. The composition of the films was routinely checked by Rutherford backscattering spectroscopy (RBS) including nitrogen, carbon, and oxygen resonance reactions to determine the Ga−N stoichiometry and levels of impurities (Figure 8). The analyses yielded stoichiometric nitride material free of oxygen and carbon contaminations. Auger electron spectroscopy depth profiles confirmed that the material is indeed pure. These results demonstrate that growth of pure but nanocrystalline GaN is possible at 200 °C and 10^{-6} Torr via the thermodynamically driven decomposition of H_2GaN_3. Crystalline GaN material is readily obtained at higher growth temperatures.

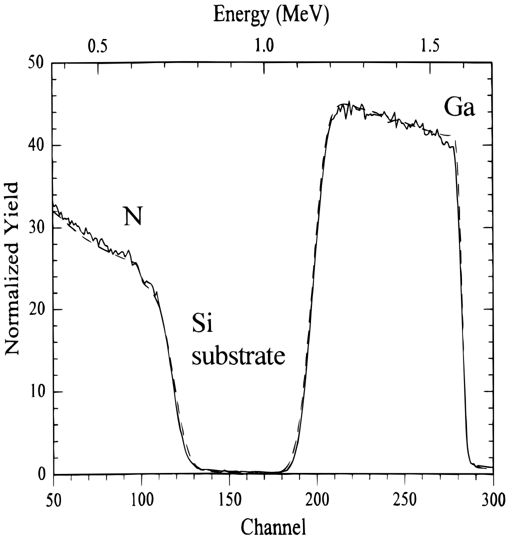

Figure 8. RBS spectrum of GaN grown at 300 °C on Si(100). Simulation of composition and thickness using the program RUMP[17] (dotted line) indicates a 7000 Å layer of stoichiometric nitride material.

Conclusion

The decomposition of H_2GaN_3 (**1**) clearly follows the expected pathway and occurs at very low temperatures (200 °C) via loss of the extremely stable H_2 and N_2 byproducts, leading to highly stoichiometric GaN. A crucial advantage of this method is the significant room-temperature vapor pressure of the precursor that permits mass transport onto the growth surface and allows film growth at a substantial rate up to 800 Å/min. High growth rates are important for possible commercial applications. Although H_2GaN_3 (**1**) is a unique and highly versatile CVD source, the high reactivity of the molecule, which is a significant advantage with respect to formation of GaN, requires careful manipulation of the neat product. The compound remains stable under vacuum or under inert gas at ambient temperature; however, abrupt scraping can initiate a vigorous exothermic decomposition. Current efforts are aimed at the synthesis of new adducts that are designed to retain the simple decomposition pathway afforded by H_2GaN_3 but are less reactive and possibly stable in air. The pyridine and trimethylamine complexes are readily formed, and the latter appears to have some volatility at room temperature. The calculated and experimental vibrational properties as well as the mass spectra

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(17) Doolittle, L. R. *Nucl. Instrum. Methods* **1985**, B9, 344.

of H_2GaN_3 (**1**) and D_2GaN_3 (**1**) suggest a heterocyclic cyclohexane-like gas-phase structure of C_{3v} symmetry for both **1** and **2**.

Br_2GaN_3 (**3**) is a nonvolatile polymeric solid that does not sublime readily even at high temperatures ($T > 150$ °C), and it is a rather ineffective CVD precursor to GaN. $SiMe_3N_3{\cdot}GaBr_3$ (**4**) sublimes slowly between 30 and 50 °C, but it decomposes to form Me_3SiBr and Br_2GaN_3 above 50 °C and its role as a GaN precursor was not explored. This compound is, however, important for the synthesis of pure Br_2GaN_3, which provides the best route for synthesis of H_2GaN_3. Reduction of the analogous Cl_2GaN_3 by $LiGaH_4$ has resulted in formation of azidogallanes contaminated with Cl impurities.

Experimental Section

General Considerations. Reactions were performed under pre-purified 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 either as a Nujol mull between KBr plates or in a 10 cm gas cell with KBr windows. 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, source $T = 225$ °C) in the ASU departmental mass spectrometry facility. $GaBr_3$ was prepared by the reaction of dry Br_2 and gallium metal, and it was purified by sublimation. Azidotrimethylsilane (Aldrich 95%) was purified by distillation (50 °C/175 mm), and its purity was checked by NMR and gas-phase IR. $LiGaH_4$ was freshly prepared using literature methods.[11]

Synthesis of $SiMe_3N_3{\cdot}GaBr_3$ (4). To a suspension of $GaBr_3$ (5.0 g, 16.12 mmol) in hexane was added $SiMe_3N_3$ (2.15 mL, 16.20 mmol) by syringe at room temperature. The mixture was stirred until all the material dissolved and a clear solution was obtained. Concentration and cooling of the solution yielded 6.65 g (95%) of **4** as colorless needles; mp 38 °C. ^1H NMR: δ 0.64 (singlet, $CDCl_3$). IR (Nujol): 3343 (w), 2404 (m), 2173 (vs), 1421 (w), 1263 (s), 1208 (s), 1100 (w), 860 (vs), 789, 768, 755 (s), 638(w), 556 (w), 480 (m), 347 (m). Anal. Calcd: Ga, 16.47; Br, 56.47. Found: Ga, 16.17; Br, 54.98.

X-ray Structure of 4. A suitable specimen was loaded into a 0.3 mm X-ray capillary and sealed under nitrogen. The capillary was mounted vertically in a Siemens P4 Autodiffractometer equipped with a LT-2a low-temperature device pre-set at −100 °C. Centering of 25 randomly selected reflections between 15 and 30° in 2θ revealed a primitive orthorhombic cell. Data collection gave 1701 reflections that merged to 1159 unique reflections. The data were corrected for absorption by use of ψ scan data collected at 10° intervals for four reflections with χ values near 90°. Solution by direct methods showed the asymmetric unit to be independent $SiMe_3N_3{-}GaBr_3$ molecules. The closest intermolecular distance is 3.82 Å between Br(1) and N(3). The Br(3) atom is 3.14 from the position of the H(1a) atom [riding on C(1)].

Synthesis of Br_2GaN_3 (3). A sample of $SiMe_3N_3{\cdot}GaBr_3$ (**4**) (2.4 g, 5.66 mmol) was heated at 50−70 °C under vacuum for 4 h to yield **2** (1.5 g, 5.52 mmol, 97%) as a colorless solid and a volatile liquid that was collected at −196 °C and was identified as $SiMe_3Br$ (0.86 g, 5.623 mmol) by gas-phase IR. Compound **2**: mp 250 °C. EIMS *m*/*e* shows isotopic envelopes centered at 773 $(M^+)_3 - N_3$, 734 $(M^+)_3 - Br$, 501 $(M^+)_2 - N_3$, 229 $(M^+) - N_3$; IR (Nujol) 3343 (w, $\nu_{as}(N_3) + \nu_s(N_3)$), 2394 (m, $2\nu_s(N_3)$), 2170, (vs, $\nu_{as}(N_3)$), 1197 (s, $\nu_s(N_3)$), 1096 (w, comb. band), 734 (s, $\delta(N_3)$), 548 (m, $\gamma(N_3)$), 452 (s, $\nu_{as}(Ga{-}N)$), 343 (s, δ(NGaN)).

Synthesis of $HBrGaN_3$ (5). To a suspension of Br_2GaN_3 (**3**) (1.0 g, 3.67 mmol) in benzene, $LiGaH_4$ (0.297 g, 3.67 mmol) was added by a solid addition funnel at 5 °C. The mixture was stirred for 4 h at room temperature during which time a gray precipitate formed. The mixture was filtered, and the solvent was removed in a vacuum to yield a viscous colorless oil (0.56, 2.93 mmol, 80% yield). IR: 3337 (w), 2415 (w), 2148 (vs), 1996 (m), 1206 (s), 1106 (sh), 758(m), 674 (vw), 580 (vs), 410 (vs), 326 (s). ^1H NMR (toluene-d_8): δ 5.093 at 20 °C and δ 4.98 at −50 °C. Anal. Calcd: C, 0.0; H, 0.52; N, 21.76; Br, 41.45. Found: C, 0.4; H, 0.87; Br, 40.61; N, 18.5 (the instability of the compound toward GaN formation (a refractory) at almost 70 ºC prevents determination of exact N analysis). EIMS (*m*/*e*): isotopic envelopes centered at 578 $(M^+)_3$, 535 $(M^+)_3 - N_3$, 498 $(M^+)_3 - Br$, 457 $(M^+)_3 - N_3 - Br$, 418 $(M^+)_3 - Br_2$, 344 $(M^+)_2 - N_3$. The precipitatewas identified as LiBr by powder X-ray diffraction.

Synthesis of H_2GaN_3 (1). To a suspension of $LiGaH_4$ (0.750 g, 9.25 mmol) in benzene, **3** (1.0 g, 3.67 mmol) was added at 5 °C by a solid addition funnel. The mixture was stirred at 20 °C for 3−4 h during which time the suspension became light gray. The mixture was then filtered and the solvent was removed in a vacuum to yield H_2GaN_3 (**1**) as a clear viscous liquid. Bp: 40 °C, 0.20 Torr. IR: 3344 (w), 2465 (w), 2130 (vs), 1970 (s), 1240 (s), 661 (s), 578 (vw), 466 (m), 343 (m). (IR gas phase: see Table 3.) ^1H NMR (toluene-d_8): δ 4.86 at 22 °C and δ 4.81 at −50 °C. Anal. Calcd: C, 0.0; H, 1.75; N, 36.84. Found: C, 0.34; H, 1.59; N, 35.67. EIMS (*m*/*e*): isotopic envelopes centered at 340 $(M^+)_3 - H_2$, 299 $(M^+)_3 - H_2 - N_3$, 227 $(M^+)_2 - H$, 186 $(M^+)_2 - N_3 - 114$ (M^+). **CAUTION:** Neat H_2GaN_3 can be unstable in contact with sharp objects. It should be handled with care.

Synthesis of D_2GaN_3 (2). To a suspension of **3** (1.0 g, 3.67 mmol) in 25 mL of C_6H_6 was added (0.77 g, 9.2 mmol) of $LiGaD_4$ by solid addition funnel at 5 °C. The mixture was stirred at room temperature for 5 h during which time the suspension became gray. The mixture was then filtered, and the solvent in the filtrate was removed in a vacuum to yield the product as a clear liquid (0.350 g, 83%). Bp: 40 °C, 0.20 Torr. IR (thin film): 3340 (w), 2470 (w), 2120 (vs), 1426 (s),1400 (s), 1235 (s), 728 (s), 680 (w), 504 (m), 390 (m). (IR gas phase: see Table 3.) EIMS (*m*/*e*): isotopic envelopes centered at 345 $(M^+)_3 - D$, 305 $(M^+)_3 - N_3$, 230 $(M^+)_2$ 190 $(M^+)_2 - N_3$.

Reactions of H_2GaN_3 with C_5H_5N and NMe_3 (TMA). H_2GaN_3 (**1**) (0.50 g, 4.40 mmol) was combined with an excess of dry C_5H_5N at 0 °C. The reaction mixture was stirred at room temperature for 2 h under nitrogen, and then the unreacted C_5H_5N was removed under vacuum to yield **6** as a mobile liquid. IR (thin film): 3118−300 (w), 2093 (vs), 1917 (s), 1614 (s), 1454 (s), 1349−1296 (m), 1072−1020 (m), 763−643 (s), 495 (m), 411 (m). ^1H NMR (toluene-d_8, 22 °C): δ 5.38 for Ga−H; resonances corresponding to the coordinated C_5H_5N, 8.50 (d, 2H), 6.77 (t, 1H), 6.38 (m, 2H). The complex is more stable than the uncoordinated H_2GaN_3; however, attempts to distill the product at low pressures and $T > 40$ °C resulted in the disproportionation of the adduct.

Dry trimethylamine (0.37 g, 6.2 mmol) was combined at −196 °C with H_2GaN_3 (0.600 g, 5.25 mmol). The reaction mixture was stirred at room temperature for 2 h under nitrogen and then evacuated to eventually obtain a mobile liquid which was purified by trap-to-trap distillation from 22 to −20 °C. IR (thin film): 2983−2850 (m), 2101 (vs), 1908 (s), 1475 (s), 1346 (m), 1293 (m), 1111 (m), 1004 (s), 731 (s), 683 (s), 496 (m), 412 (m). EIMS (*m*/*e*): 171 $(M^+ - H)$, 130 $(M^+ - N_3)$. ^1H NMR (toluene-d_8): δ 1.60 and 4.95 at 22 °C.

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Supporting Information Available: Tables of X-ray crystallographic datta and an ORTEP diagram for the structure determination of $SiMe_3N_3{\cdot}GaBr_3$ (**4**) (5 pages). Ordering information is given on any current masthead page.

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