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Trans−Cis Isomerization and Structure of $[R_2Ga(\mu\text{-}NHSiEt_3)]_2$ (R = Me, Et)

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Reactions of Et_3SiNH_2 with R_3Ga in a 1:1 ratio have produced dimeric silylamidogallanes, $[R_2Ga(\mu\text{-}NHSiEt_3)]_2$ (**1**, R = Me, trans:cis = 1.5:1; **2**, R = Et, trans:cis = 1.3:1), as a mixture of trans (**a**) and cis (**b**) isomers. Purification of **1** by either recrystallization or sublimation gives only trans isomer **1a** as colorless crystals. Colorless liquid **2** has been obtained only as a mixture of the two isomers. The trans → cis isomerization of **1** has been studied by ^1H NMR spectroscopy. The equilibrium has been observed to follow reversible first-order kinetics with $\Delta H° = -0.64 \pm 0.03$ kJ mol^{-1} and $\Delta S° = -4.4 \pm 0.2$ J K^{-1} mol^{-1}. The activation parameters for the trans (**1a**) → cis (**1b**) conversion are $\Delta H_1^{\ddagger} = 72.4 \pm 1.3$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = -38.8 \pm 4.5$ J K^{-1} mol^{-1}, and those for the reverse process are $\Delta H_{-1}^{\ddagger} = 73.0 \pm 0.4$ kJ mol^{-1} and $\Delta S_{-1}^{\ddagger} = -34.4 \pm 1.7$ J K^{-1} mol^{-1}. The isomerization is markedly accelerated in the presence of Lewis bases. A crossover experiment indicates that the isomer interconversion is a unimolecular process. The thermodynamic and kinetic data have been explained based on the solvent effect and the silyl substituent effect on the nitrogen atom. The molecular structure of **1a** has been determined by a single-crystal X-ray diffraction study. The molecular geometry of **1a** consists of a centrosymmetric and dimeric unit with two bridging (triethylsilyl)amido groups and two terminal methyl groups bound to each gallium atom. The two silyl groups are trans to each other with respect to the planar $(Ga-N)_2$ ring framework. The coordination geometry of both gallium and nitrogen atoms is distorted tetrahedral.

Introduction

In recent years there has been a renewed interest in the organometallic chemistry of amidogallanes due to their potential as effective single-source precursors for gallium nitride (GaN) thin films by employing the organometallic chemical vapor deposition (OMCVD) method.[1] The original work of Coates and co-workers[2] revealed that initial reaction of Me_3Ga with various amines (NHR'_2) resulted in the formation of adducts of the formula $Me_3Ga{:}NHR'_2$, and thermolysis of the adducts yielded the dimeric amidogallane $(Me_2GaNR'_2)_2$ by loss of methane. Subsequent studies by other groups have shown numerous examples of the adducts and oligomeric amidogallanes of the formula $(R_2GaNR'_2)_n$ ($n = 1-3$). The adducts include $Me_3Ga{:}NH_2{}^tBu$[3] and $^tBu_3Ga{:}NH_2Ph$[4] possessing a donor−acceptor bonding interaction. Monomeric ($n = 1$) amidogallanes such as $^tBu_2GaN(R)SiPh_3$ (R = ^{t}Bu or 1-adamantyl), $Trip_2GaN(H)Dipp$ (Trip = 2,4,6-$^iPr_3C_6H_2$, Dipp = 2,6-$^iPr_2C_6H_3$), $Trip_2GaNPh_2$, and $Mes^*{}_2GaN(H)Ph$ (Mes* = 2,4,6-$^tBu_3C_6H_2$) have been recently prepared by introducing sterically bulky substituents at trivalent Ga and N atoms.[5] Dimers ($n = 2$)[3,4,6] or trimers ($n = 3$) are formed mainly depending on the bulkiness of the substituents at tetravalent Ga and N atoms; trimers are produced with substituents of modest size, and increasing the steric demands of the substituents results in dimer formation. The trimeric examples involve $[R_2Ga(\mu\text{-}NH_2)]_3$ (R = H,[7] Me,[8] and ^{t}Bu[9]) and $[H_2Ga(\mu\text{-}N(CH_2)_2)]_3$.[10]

We have been interested in synthesis of dimeric amidogallanes of the formula $[R_2Ga(\mu\text{-}NHR')]_2$ (R = Me, Et) as single-source precursors for GaN thin films by employing various R′ substituents on the nitrogen atom with a N−C bond (e.g., $[Me_2Ga(\mu\text{-}NH^tBu)]_2$[6e]), a N−N bond (e.g., $[Me_2Ga(\mu\text{-}NHNMe_2)]_2$[6i]), or a N−Si bond.

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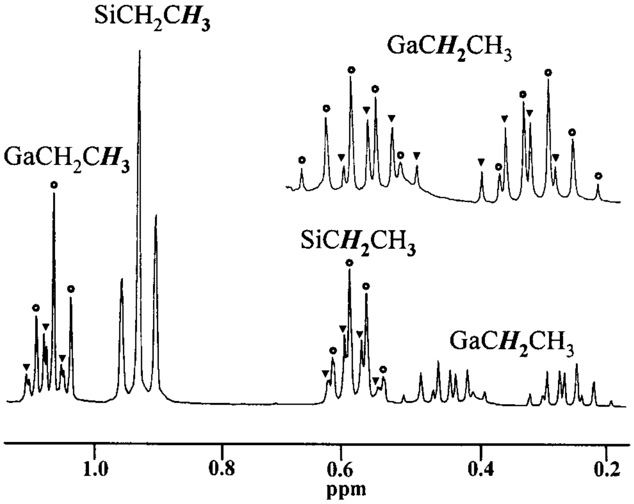

Figure 1. ^1H NMR spectra (300 MHz, $CDCl_3$) of a mixture of trans **2a** (○) and cis **2b** (▼).

These precursors are intended to be prepared and evaluated in terms of carbon contamination in GaN thin films, which is a crucial problem in film formation by single-source OMCVD method.[11] As a part of our investigation, we have examined the reactions of (triethylsilyl)amine with R_3Ga (R = Me, Et). Herein we report details of synthesis and characterization of silylamidogallanes with a N−Si bond, $[R_2Ga(\mu\text{-NH-SiEt}_3)]_2$ (R = Me (**1**), Et (**2**)), together with thermodynamic and kinetic studies of trans−cis isomerization of **1** and structural characterization of trans isomer **1a**. Compounds **1** and **2**, to our knowledge, are the first dimeric silylamidogallanes in which both substituents on the gallium atom are alkyl groups.

Results and Discussions

Synthesis and Characterization of 1 and 2. Reactions of (triethylsilyl)amine with trialkylgallium in a 1:1 ratio at 110 °C in toluene produce a mixture of trans and cis isomers of dimeric silylamidogallane complexes, $[R_2Ga(\mu\text{-NHSiEt}_3)]_2$ (**1**, R = Me, trans:cis = 1.5:1; **2**, R = Et, trans:cis = 1.3:1), by alkane elimination followed by condensation reaction. The dimeric formulations of **1** and **2** have been indicated by the observation of $[M-R]^+$ ion in the EI mass spectra. Either sublimation under vacuum or slow recrystallization of **1** affords colorless crystals of only the trans isomer **1a**, but in solution it equilibrates with the cis isomer **1b**. Colorless liquid **2** could be obtained only as a mixture of trans (**2a**) and cis (**2b**) isomers.

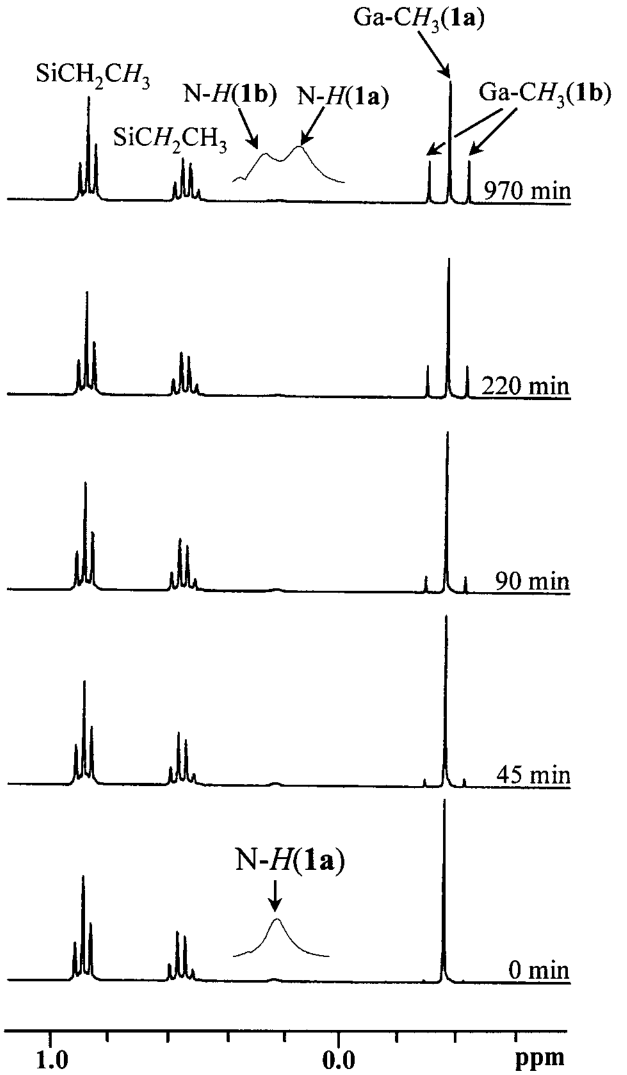

Figure 2. Time-resolved ^1H NMR spectra (300 MHz, $CDCl_3$) of **1a** and **1b** at 5 °C.

Both ^1H NMR and ^{13}C NMR spectra of trans **1a** show a single peak for the $Ga-CH_3$ groups (see Experimental Section) and are consistent with the C_{2h}-symmetric nature of the trans isomer in solution. Those of **1b**, however, exhibit two distinct resonances due to methyl groups on the gallium atom, and thus **1b** was assumed to be a cis isomer (C_{2v} symmetry) with the *N*-silyl groups cis to the $(Ga-N)_2$ ring. The resonances due to triethylsilyl protons are coincident for **1a** and **1b**, but the N−H resonances are well resolved at δ 0.23 for **1a** and δ 0.27 for **1b** (see the top spectrum of Figure 2). The IR spectra of both pure **1a** and an equilibrium mixture of **1** are essentially identical and contain only one strong N−H stretch at 3255 cm^{-1}. One strong N−H stretch was commonly observed for a mixture of trans and cis isomers for all known amidogallanes,[4,6d,e,k] although

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three N−H stretches are expected, one (ν_s) for the trans isomer and two (ν_s and ν_{as}) for the cis isomer.

The general features of the ^{1}H NMR spectrum of **2** are quite similar to those of **1**, although the former spectrum is much more complicated due to the presence of inequivalent and diasterotopic hydrogens of ethyl groups on gallium atoms as shown in Figure 1.[12] The pseudo-triplet pattern (denoted as ○) at δ 1.06 for Ga−CH_2CH_3 groups of trans **2a** is an overlap of a dd pattern due to couplings of methyl protons to diastereotopic CH_2 hydrogens. A pair of the triplet pattern (denoted as ▼) at δ 1.071 and 1.067 is assigned to the methyl moieties of the inequivalent ethyl groups on each gallium atom of cis **2b**. Each of the two pseudo-quintet patterns (○, see the inset in Figure 1) at δ 0.43 and 0.27 results from two overlapped quartets due to a mutual coupling (H_a and H_b) of the two diastereotopic CH_2 hydrogens ($^2J_{HH}$ = 45 Hz) and further couplings of H_a and H_b to methyl protons for the Ga−CH_2CH_3 moieties of **2a**. The two quartet patterns (▼, see the inset in Figure 1) at δ 0.46 and 0.24 are assigned to the CH_2 hydrogens of the inequivalent ethyl groups on each gallium atom of **2b**. For triethylsilyl groups, the resonances of methylene protons are well resolved in the region of δ 0.63−0.54 as multiplets for **2a** (○) and **2b** (▼), while those of methyl protons are overlapped at δ 0.92 as a pseudo-triplet. McGarvey et al.[13] calculated an exact solution of the spin Hamiltonian for the ethyl group of CH_3CH_2X type compounds and explained the complex patterns of the ethyl proton resonances for cases where the separation of the methylene and methyl resonances is small. Their results account for the multiplet patterns of the methylene hydrogens for triethylsilyl groups of both **2a** and **2b**, which are similar to those observed in $(C_2H_5)_2S$.[13] The NH resonances of **2a** and **2b** were not observed and may be obscured under other resonances, but the existence of N−H protons is clearly provided by one strong N−H peak at 3259 cm^{-1} in the IR spectrum of **2**. The ^{1}H NMR peak assignments and coupling patterns of **2** have been confirmed by both the decoupling experiment and the 2D ^{1}H−^{1}H correlated NMR spectrum.

Trans−Cis Isomerization of 1. The trans (**1a**) → cis (**1b**) isomerization reaction of **1** has been investigated by ^{1}H NMR spectroscopy. Typical time-resolved ^{1}H NMR spectra of **1** in $CDCl_3$ at 5 °C are shown in Figure 2. As the intensities of the resonances of **1a** decrease, those corresponding to **1b** increase in intensity. Relative concentrations of the two isomers were measured by integration of the peaks of Ga−CH_3 at δ −0.34 for **1a** and at δ −0.26 and −0.41 for **2b**. Analyses according to reversible first-order kinetics give excellent fits of experimental data at various temperatures as shown in Figure 3. The kinetic and thermodynamic data are listed in Table 1. The equilibrium constants, K_{eq} = [**1b**]/[**1a**], measured for the isomerization range from 0.695 ± 0.003 at 0 °C to 0.676 ± 0.004 at 30 °C, indicate that trans **1a** is favored in this equilibrium. The plot of $\ln K_{eq}$ vs $1/T$ (correlation coefficient, 0.9924) yields $\Delta H° = -0.64 \pm 0.03$ kJ mol^{-1} and $\Delta S° = -4.4 \pm 0.2$ J K^{-1} mol^{-1} for the process, **1a** → **1b**. Activation parameters derived from the Eyring plots of $\ln(k/T)$ vs $1/T$ and $\ln(k_{-1}/T)$ vs $1/T$ (correlation coefficients 0.9808 and 0.9813, respectively) are $\Delta H_1^‡ = 72.4 \pm 1.3$ kJ mol^{-1} and $\Delta S_1^‡ = -38.8 \pm 4.5$ J K^{-1} mol^{-1} for the forward isomerization **1a** → **1b** and $\Delta H_{-1}^‡ = 73.0 \pm 0.4$ kJ mol^{-1} and $\Delta S_{-1}^‡ = -34.4 \pm 1.7$ J K^{-1} mol^{-1} for the reverse isomerzation **1b** → **1a**. The net enthalpy and entropy changes for **1a** to **1b** from the thermodynamic data are in good agreement with those obtained from the kinetic data, $\Delta H_1^‡ - \Delta H_{-1}^‡ = \Delta H°$ and $\Delta S_1^‡ - \Delta S_{-1}^‡ = \Delta S°$, within experimental error.

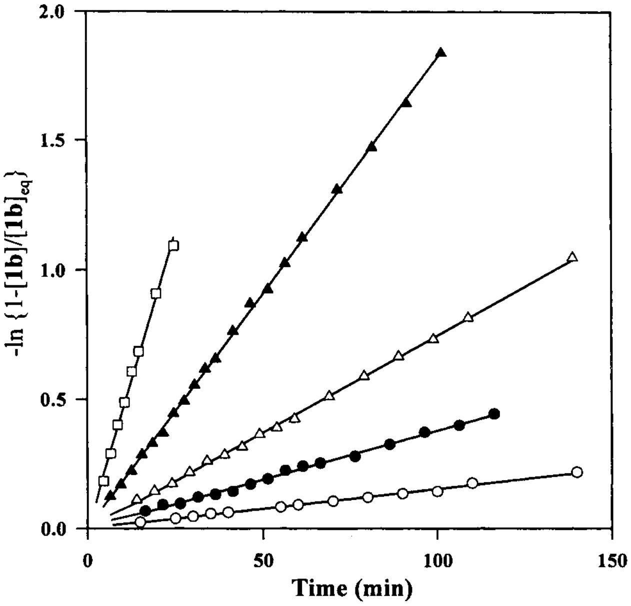
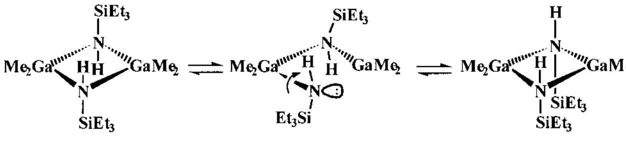


Figure 3. Kinetics plots for the isomerization of **1a** to **1b** in $CDCl_3$ at 0 (○), 5 (●), 10 (△), 20 (▲), and 30 (□) °C.

Table 1. Kinetic and Thermodynamic Data of 1 in $CDCl_3$

T, °C	K_{eq} = [**1b**]/[**1a**]	10^{-3} k_{obs}, min^{-1}	10^{-3} k_1, min^{-1}	10^{-3} k_{-1}, min^{-1}
0	0.695 ± 0.003	1.52 ± 0.05	0.62 ± 0.05	0.90 ± 0.01
5	0.692 ± 0.004	3.78 ± 0.13	1.55 ± 0.04	2.23 ± 0.12
10	0.689 ± 0.005	7.52 ± 0.08	3.07 ± 0.04	4.45 ± 0.05
20	0.682 ± 0.005	18.2 ± 0.2	7.36 ± 0.01	10.8 ± 0.1
30	0.676 ± 0.004	46.6 ± 3.1	18.4 ± 0.1	27.2 ± 3.0

Scheme 1



trans **1a** **I** cis **1b**

We previously reported thermodynamic and kinetic studies of trans−cis isomerization of $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (**3**)[6e] and $[Me_2M(\mu\text{-}NHNMe_2)]_2$ (**4**, M = Ga; **5**, M = Al),[6i] in which the isomerization pathway is proposed to be an initial breaking of the Ga−N bond to form species **I**, followed by the rotation about the nonbridged Ga−N bond and rebridging as shown in Scheme 1. The rate of isomerization, therefore, has been accelerated by the presence of Lewis bases due to the facile cleavage of the M−N (M = Al or Ga) bond by an attack of Lewis bases on the M atom, as was well documented in $[Me_2Al(\mu\text{-}$

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Table 2. Comparison of Kinetic and Thermodynamic Data of 1, 3, and Other Dimeric Amidogallanes

compound	ΔH °, kJ mol^{-1}	ΔS °, J K^{-1} mol^{-1}	$\Delta H_1^\ddagger$, $\Delta H_{-1}^\ddagger$, kJ mol^{-1}	$\Delta S_1^\ddagger$, $\Delta S_{-1}^\ddagger$, J K^{-1} mol^{-1}	solvent	ref
$[Me_2Ga(\mu\text{-}NHSiEt_3)]_2$ (**1**)	−0.64 ± 0.03	−4.4 ± 0.2	72.4 ± 1.3	−38.8 ± 4.5	$CDCl_3$	this work
			73.0 ± 0.4	−34.4 ± 1.7		
$[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (**3**)	3.12 ± 0.04	4.56 ± 0.06	120.8 ± 7.4	41.4 ± 2.6	toluene-d_8	6e
			117.8 ± 7.9	37.3 ± 2.5		
$[Me_2Ga(\mu\text{-}NMePh)]_2$	4.16	21.8			CD_2Cl_2	18
$[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$	2.4 ± 0.2	7.1 ± 0.6			toluene-d_8	24
$[Cl_2Ga(\mu\text{-}NMeSiMe_3)]_2$	2.4 ± 0.2	0.08 ± 0.69			toluene-d_8	24
$[Br_2Ga(\mu\text{-}NHSiMe_3)]_2$	3.7 ± 0.3	11.2 ± 0.9			toluene-d_8	25

NMePh)]$_2$,[14] $[R_2Al(\mu\text{-}NHSiR'_3)]_2$ (R = Me, R′ = Me, Et, Ph; R = Cl, R′ = Me),[15] and **3**.[6e] The proposed mechanism is further supported by the previous observation that the rate of isomerization depends on both accessibility of the metal center of dimers and steric hindrance of the base nitrogen atom.[15] The isomerization of **1** was also markedly accelerated in the presence of Lewis bases such as pyridine and γ-picoline, but the rate of isomerization was too fast to be measured in the presence of Lewis bases even at −20 °C by ^{1}H NMR spectroscopy. Similarly the isomerization process has been facilitated in dimers such as $[Me_2Al(\mu\text{-}NHCH_2\text{-}4\text{-}Py)]_2$,[16] **4**,[6i] and **5**[6i] by the uncoordinated internal amine groups which could attack the metal center and thus result in scission of the M−N bond via an intermolecular process. The rate of isomerization of **4** and **5** was found to remain unaffected in the presence of 1 equiv of pyridine.[17] No evidence for the formation of $Me_2Ga(\mu\text{-}NHSiEt_3)_2GaEt_2$ was found from the crossover reaction of $[Me_2Ga(\mu\text{-}NHSiEt_3)]_2$ and $[Et_2Ga(\mu\text{-}NHSiEt_3)]_2$, implying that the pathway for the isomerization is a unimolecular process. This apparently excludes another possible isomerization pathway of scission of the two Ga−N bonds forming monomers and subsequent recombination. The kinetic and thermodynamic data of **1** and **3** with thermodynamic data of other known dimeric amidogallanes are listed in Table 2. Thermodynamic data (ΔH° and ΔS°) of **1** for trans → cis isomerization are unusually negative in contrast to those of **3** and other amidogallanes, indicating that cis **1b** is thermodynamically more stable than trans **1a**, but entropy decreases during isomerization favoring trans **1a**. These results may be explained by the solvent effect that polar cis isomer **1b** is readily solvated and stabilized by the polar chloroform solvent molecules relative to trans **1a**. The negative values of $\Delta S_1^\ddagger$ and $\Delta S_{-1}^\ddagger$ for **1** suggest that the transition state is somewhat more ordered than **1a** and **1b**, which can also be justified by the solvent participation. The large negative entropies of activation for the intramolecular trans−cis isomerization were previously reported in cases of $[Me_2Al(\mu\text{-}NH^tBu)]_2$[19] and other types of complexes such as $(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_3(\mu\text{-}SiHTol)$[20] (Tol = $p\text{-}C_6H_4Me$) and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$;[21] this observation was accounted for by either the existence of a sterically conjested intermediate or the participation of the solvent. The activation enthalpies of $\Delta H_1^\ddagger$ and $\Delta H_{-1}^\ddagger$ for **1** are much smaller than those of **3**. The activation enthalpies may reflect the bond strength of the dissociating Ga−N bonds.[6e] The silicon-substituted amines are known to be weaker bases than carbon-substituted amines, which is attributed to delocalization of lone pair electrons of the nitrogen atom to the empty d orbitals of the silicon with $N(p_\pi){\rightarrow}Si(d_\pi)$ overlap.[22] Weaker basicity of H_2NSiEt_3 may result in weaker Ga−N bond strength, which explains the smaller values of activation enthalpies of **1** compared to those of **3** derived from the stronger base H_2N^tBu. Another possibility is that the transition state species (see **I** in Scheme 1) of **1** with a Ga−N bond dissociated may be stabilized by the $p_\pi{-}d_\pi$ overlap between N and Si atoms in contrast to that of **3**.

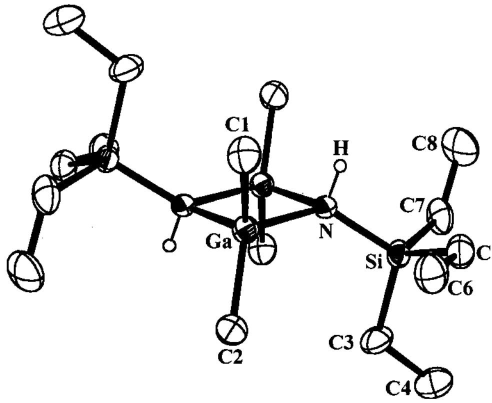

Figure 4. Molecular geometry and atomic labeling scheme for **1a**. Hydrogen atoms except for NH were omitted for clarity.

Crystal Structure of 1a. The overall molecular geometry of **1a** with the atomic labeling scheme is shown in Figure 4. Selected bond distances and angles are listed in Table 3. The molecule has a dimeric and crystallographically centrosymmetric structure with a pair of dimethylgallium units bridged by $NHSiEt_3$ groups. The coordination of the gallium atoms is in a distorted tetrahedral environment with the interligand angles ranging from N−Ga−N′ = 88.2(2)° to C(1)−Ga−C(2) = 121.6(3)°. The Ga−C(methyl) bond lengths, Ga−C(1) = 1.967(5) Å and Ga−C(2) = 1.985(5) Å suggest a covalent radius of 1.20 Å for gallium(III) in this type of environment. The $(Ga{-}N)_2$ core structure is planar; the

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Table 3. Bond Lengths [Å] and Angles [deg] with esd's for $[Me_2Ga(\mu\text{-}NHSiEt_3)]_2$ (1a)[a]

	Bond Lengths		
Ga−N	2.025(4)	Ga′−N	2.033(4)
Ga−C(1)	1.967(5)	Ga−C(2)	1.958(5)
Si−N	1.761(4)	Si−C(3)	1.859(6)
Si−C(5)	1.873(6)	Si−C(7)	1.872(6)
C(3)−C(4)	1.504(8)	C(5)−C(6)	1.510(8)
C(7)−C(8)	1.520(8)	N−H	0.910
Ga···Ga′	2.915(2)	N···N′	2.823(8)
Ga···H	2.410		
	Bond Angles		
N−Ga−N′	88.2(2)	C(1)−Ga−C(2)	121.6(3)
N−Ga−C(1)	106.7(2)	N′−Ga−C(1)	112.6(2)
N−Ga−C(2)	115.7(2)	N′−Ga−C(2)	107.2(2)
N−Si−C(3)	109.8(2)	N−Si−C(5)	109.8(2)
N−Si−C(7)	109.3(3)	C(3)−Si−C(5)	110.0(3)
C(3)−Si−C(7)	109.7(3)	C(5)−Si−C(7)	108.2(3)
Ga−N−Ga′	91.9(2)	Ga−N−Si	127.5(2)
Ga′−N−Si	122.8(2)	Si−C(3)−C(4)	115.9(5)
Si−C(5)−C(6)	116.3(4)	Si−C(7)−C(8)	116.4(4)
Si−N−H	103.9	Ga−N−H	103.9
Ga′···Ga−C(1)	117.9(2)	Ga′···Ga−C(2)	120.4(2)
N′···N−H	110.2		

[a] Atoms related by the *i* symmetry operations are labeled with a prime.

bond distances are Ga−N = Ga′−N′ = 2.025(4) and Ga−N′ = Ga′−N = 2.033(4) Å, which are slightly longer than those (av 1.992 Å) observed in other dimeric silylamidogallanes.[23−25] The internal angles in the planar $(Ga-N)_2$ core are 88.2(2)° at gallium and 91.2(2)° at nitrogen. The slightly obtuse Ga−N−Ga′ angle of 91.2(2)° and long Ga···Ga′ separation of 2.915(2) Å indicate that there is no gallium−gallium bonding interaction.

As shown in Figure 4, the bridging $NHSiEt_3$ groups take up a mutually trans arrangement, which has been observed for all known dimeric silylamidogallanes such as $[MeClGa(\mu\text{-}NHSiMe_3)]_2$,[23] $[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$,[24] $[Cl_2Ga(\mu\text{-}NMeSiMe_3)]_2$,[24] and $[Br_2Ga(\mu\text{-}NHSiMe_3)]_2$.[25] The N−H bond distance of 0.910 Å is longer than that of 0.838(47) Å in $[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$, the only N−H distance reported for dimeric silylamidogallanes. The amide hydrogen is symmetrically located 2.410 Å from both gallium atoms with the N′···N−H angle of 110.2°. This short Ga···H distance was previously interpreted by considering that the amide proton is attracted to the electron density of the $(Ga-N)_2$ ring.[4] The Si−N bond distance of 1.761(4) Å is rather short relative to known dimers: 1.744(8) Å in $[MeClGa(\mu\text{-}NHSiMe_3)]_2$, 1.805(4) Å in $[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$, 1.816(7) Å in $[Cl_2Ga(\mu\text{-}NMeSiMe_3)]_2$, and 1.801(18) Å in $[Br_2Ga(\mu\text{-}NHSiMe_3)]_2$. The sum of the Ga−N−Ga′, Ga−N−Si, and Ga′−N−Si angles is 342.3(3)° less than that required for planarity. This value is, however, greater than the corresponding sum of 337.6(3)° for $[Cl_2Ga(\mu\text{-}NHSiMe_3)]_2$ and 337.9(13)° for $[Br_2Ga(\mu\text{-}NHSiMe_3)]_2$. Both the short Si−N bond distance and almost planar geometry of Ga_2Si moieties around the nitrogen atom of **1a** reveal an increased sp^2 character of the nitrogen atom and evidence for $p_\pi-d_\pi$ bonding character between N and Si atoms. There are no abnormally close contacts between discrete molecules of **1a**. All other features of the molecular geometry are within the expected range.

Experimental Section

General Comments. All experiments were performed under an atmosphere of argon either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. All solvents were dried under argon according to standard methods, distilled, and stored over 4 Å molecular sieves. The following chemicals were obtained from commercial sources and were used as received: Et_3SiCl (Aldrich); Me_3Ga, Et_3Ga (Strem); NH_3 (Union Carbide, anhydrous grade). (Triethylsilyl)amine was prepared by the procedure reported previously.[15]

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer and referenced against residual protons or carbons of the deuterated solvents. Infrared spectra were recorded on a Bruker EQUINOX-55 FT-IR spectrophotometer. The melting point was obtained on an Electrothermal melting point apparatus in a sealed capillary under argon (1 atm) and is uncorrected. Mass spectral data were collected by the staff of the Korea Basic Science Center using a JEOL JMS-SX 102A spectrometer, and all *m*/*z* values are referenced to ^{69}Ga. Elemental analyses were performed by Oneida Research Services.

Synthesis of $[Me_2Ga(\mu\text{-}NHSiEt_3)]_2$ (1). (Triethylsilyl)amine (0.411 g, 3.13 mmol) was added to a stirred toluene (15 mL) solution of trimethylgallium (0.358 g, 3.12 mmol) at room temperature. The resulting colorless solution was refluxed for 6 h. Gas evolution (presumably methane) was apparent from the observed frothing. The solvents and volatiles were removed under reduced pressure. Purification by either sublimation under vacuum (10^{-3} mmHg, 70 °C) or recrystallization in toluene at −5 °C gave the pure trans isomer (**1a**, 0.567 g, 1.21 mmol, 78%) as colorless crystals. Trans isomer **1a**: mp 47−48 °C; ^1H NMR ($CDCl_3$, 298 K) δ 0.89 (18H, t, CH_2CH_3), 0.57 (12H, q, CH_2CH_3), 0.23 (2H, br, N*H*), −0.34 (12H, s, $GaCH_3$); ^{13}C NMR ($CDCl_3$, 298 K) δ 7.24 (s, CH_2CH_3), 6.41 (s, CH_2CH_3), −3.05 (s, $GaCH_3$). IR (KBr, cm^{-1}) ν(N−H) 3255; MS (70 eV) *m*/*z* 443 $[M - CH_3]^+$. Anal. Calcd for $C_{16}H_{44}Ga_2N_2Si_2$: C, 41.91; H, 9.68; N, 6.11. Found: C, 41.58; H, 9.35; N, 5.98. Cis isomer **1b** (data obtained from an equilibrium mixture): ^1H NMR ($CDCl_3$, 298 K) δ 0.89 (18H, t, CH_2CH_3), 0.57 (12H, q, CH_2CH_3), 0.27 (2H, br, N*H*), −0.26, −0.41 (6H each, s, $GaCH_3$); ^{13}C NMR ($CDCl_3$, 298 K) δ 7.24 (s, CH_2CH_3), 6.41 (s, CH_2CH_3), −2.39, −3.79 (s, $GaCH_3$).

Synthesis of $[Et_2Ga(\mu\text{-}NHSiEt_3)]_2$ (2). A toluene solution (15 mL) of (triethylsilyl)amine (0.498 g, 3.03 mmol) and triethylgallium (0.474 g, 3.02 mmol) was heated at reflux for 8 h. Gas evolution (presumably ethane) was apparent from the observed frothing. The volatiles were removed in vacuo. Purification by vacuum distillation (10^{-3} mmHg, 140 °C) afforded a colorless liquid (**2**, 0.462 g, 0.895 mmol, 60%) as a mixture of (1.3:1) trans (**2a**) and cis (**2b**) isomers. The following spectroscopic data for **2a** and **2b** were obtained from an equilibrium mixture. Trans isomer **2a**: ^1H NMR ($CDCl_3$, 298 K) δ 1.06 (12H, dd (pseudo t), $GaCH_2CH_3$), 0.92 (18H, t, $SiCH_2CH_3$), 0.58 (12H, q, $SiCH_2CH_3$), 0.47, 0.24 (4H each, dq (pseudo qn), $^2J_{HH}$ = 45 Hz, $GaCH_2CH_3$). Cis isomer **2b**: ^1H NMR ($CDCl_3$, 298 K) δ 1.071, 1.067 (6H each, t, $GaCH_2CH_3$), 0.92 (18H, t, $SiCH_2CH_3$), 0.59 (12H, q, $SiCH_2CH_3$), 0.42, 0.27 (4H each, q, $GaCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 298 K) δ 10.2 (s, $GaCH_2CH_3$), 7.40 (s, $SiCH_2CH_3$), 6.67 (s, $SiCH_2CH_3$), 6.16 (s, $GaCH_2CH_3$); IR ($CDCl_3$, cm^{-1}) ν(N−H) 3259; MS (40 eV) *m*/*z* 487 $[M - C_2H_5]^+$. Anal. Calcd for $C_{20}H_{52}Ga_2N_2Si_2$: C, 45.61; H, 10.19; N, 5.25. Found: C, 45.51; H, 10.02; N, 4.95.

^1H NMR Study of Isomerization of Trans 1a to Cis 1b. Crystals of compound **1a** (ca. 3 mg) were transferred to five 5-mm NMR tubes. Chloroform-d_1 (0.6 mL) was added to each NMR tube under an atmosphere of argon, and then the tubes were quickly placed into a dry ice bath to prevent isomeriza-

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Table 4. Crystal Data and Structure Refinement for $[Me_2Ga(\mu\text{-}NHSiEt_3)]_2$ (1a)

formula	$C_{16}H_{44}Ga_2N_2Si_2$
fw	460.16
temp (K)	293(2)
λ (Mo Kα)	0.71069
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	7.0241(9)
b (Å)	8.599(3)
c (Å)	11.079(2)
α (deg)	105.18(2)
β (deg)	99.22(1)
γ (deg)	101.76(2)
V (Å^3)	615.8(3)
Z	1
D_{calcd} (g cm^{-3})	1.241
abs coeff (mm^{-1})	2.232
$F(000)$	244
cryst dimens (mm)	0.264 × 0.165 × 0.132
θ range (deg)	2.54−23.00
hkl ranges	$-7 \leq h \leq 7, -9 \leq k \leq 9, 0 \leq l \leq 12$
intensity variation (%)	0.76
no. of rflns measd	1829
no. of indepdt rflns	1722 [$R_{int} = 0.0210$]
no. of data/restraints/params	1722/0/100
goodness-of-fit on F^2	1.065
final R indices[a] [$I > 2\sigma(I)$]	$R = 0.0418$, $R_w = 0.0885$
R indices[a] (all data)	$R = 0.0617$, $R_w = 0.0993$
$D(r)$ and hole, e Å^{-3}	0.427 and −0.406

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

tion. The tubes were transferred to an NMR probe maintained at 0, 5, 10, 20, and 30 °C, respectively, while the resonances due to the methyl groups on the gallium atoms, at δ −0.34 for **1a** and at δ −0.26 and −0.41 for **1b**, were monitored periodically by ^{1}H NMR. The isomerization reactions followed reversible first-order kinetics approaching equilibrium and showed excellent fits of data to a common plot of $-\ln\{1 - [\mathbf{1b}]/[\mathbf{1b}]_{eq}\}$ vs time. The equilibrium constants at each temperature were obtained when no further change in each spectrum was observed.

X-ray Data Collection and Structure Determination of 1a. A crystal suitable for X-ray study was obtained by slow cooling of a neat liquid at 60 °C to room temperature under vacuum. A colorless cubic crystal was mounted in a thin-walled glass capillary under an argon atmosphere, and the capillary was temporarily sealed with silicon grease and then flame-sealed. The determination of unit cell parameters and the orientation matrix and the collection of intensity data were made on an Enraf-Nonius CAD-4 diffractometer utilizing graphite-monochromated Mo Kα radiation. The unit cell parameters, occurrences of equivalent reflections, and systematic absences in the diffraction data, were consistent with the $P\bar{1}$ space group. Lorentz and polarization corrections were applied to the intensity data while no absorption correction was applied. Relevant crystallographic details are presented in Table 4. All calculations were performed using the SHELXTL programs.[26] Scattering factors for all atoms were included in the software package. The positions of the Ga and Si atoms were obtained from a Patterson map, and those of the C and N atoms were taken from difference Fourier maps. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and allowed to ride on the appropriate carbon or nitrogen atoms. In the final cycle of refinement the mean shift/esd was less than 0.001.

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Supporting Information Available: Tables of anisotropic thermal parameters and complete atomic coordinates and equivalent isotropic thermal parameters for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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