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Reaction of $GaMe_3$ with $H_2NCH_2CH_2NMe_2$: Synthesis and Characterization of Adducts and Imidogallane

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Reaction of $GaMe_3$ with *N,N*-dimethylethylenediamine (DMEDA) produces adducts, $Me_3Ga{:}NH_2C_2H_4NMe_2$ (1:1, **1**) and $Me_3Ga{:}NH_2C_2H_4NMe_2{:}GaMe_3$ (2:1, **2**). A fast concerted intermolecular exchange of the two inequivalent $GaMe_3$ moieties occurs in **2** at room temperature. Thermolysis of **2** at 210 °C in a sealed ampule produces a mixture of cis and trans isomers of tetrametallic imidogallane, $[Me_2Ga(\mu\text{-}\overline{NC_2H_4NMe_2Ga}Me_2)]_2$ (**3**). Slow recrystallization of **3** affords only the cis isomer as colorless crystals, but in solution the cis isomer equilibrates with the trans isomer. The cis → trans isomerization of **3** has been studied by ^1H NMR spectroscopy. The equilibrium has been observed to follow reversible first-order kinetics with $\Delta H° = -3.35 \pm 1.70$ kJ mol^{-1} and $\Delta S° = -10.4 \pm 1.7$ J mol^{-1} K^{-1}. The activation parameters for the cis → trans conversion are $\Delta H^{\ddagger}_{1} = 144.6 \pm 6.2$ kJ mol^{-1} and $\Delta S^{\ddagger}_{1} = 105.6 \pm 1.5$ J mol^{-1} K^{-1}, and those for the reverse process are $\Delta H^{\ddagger}_{-1} = 147.6 \pm 6.4$ kJ mol^{-1} and $\Delta S^{\ddagger}_{-1} = 115.4 \pm 1.5$ J mol^{-1} K^{-1}. The isomerization process has been proposed to be assisted by the NMe_2 end of DMEDA as an internal Lewis base. The molecular structures of **2** and *cis*-**3** have been determined by single-crystal X-ray diffraction studies. The geometry about the gallium atom of **2** is distorted tetrahedral with a Ga−C (av) distance of 1.98(1) Å and a Ga−N distance of 2.16(1) Å. The molecular geometry of *cis*-**3** involves one four-membered Ga_2N_2 ring and two five-membered GaN_2C_2 rings of cis conformation, and it has approximate C_2 symmetry with the C_2 axis going through the center of the Ga_2N_2 ring.

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Introduction

In recent years, there has been a renewed interest in the synthesis of hydrazido derivatives of group 13 elements (M) with a nitrogen source alternative to ammonia as single-source precursors for MN thin films using organometallic chemical vapor deposition (OMCVD) methods.[1] We have previously reported that the reaction of $AlMe_3$ with H_2NNMe_2 (1,1-dimethylhydrazine) affords the dimeric amidoalane $[Me_2Al\text{-}\mu\text{-}N(H)\text{-}NMe_2]_2$[1g] as a mixture of trans and cis isomers, which was employed as a single-source precursor for the fabrication of AlN thin films using an OMCVD method.[1h] As an extension of this work on bidentate diamine ligands containing two acidic hydrogens on the same nitrogen atom, we have investigated the reactions of $AlMe_3$ with $H_2NCH_2CH_2NMe_2$ (*N,N*-dimethylethylenediamine, DMEDA).[2] These reactions resulted in various interesting products, such as adducts, chelated monomers, tetrametallic imidoalanes, and hexameric imidoalanes.

Herein we report full details of the reactions shown in Scheme 1, together with structural characterization of a 2:1 adduct, $Me_3Ga{:}NH_2C_2H_4NMe_2{:}GaMe_3$ (**2**), and a tetrametallic imidogallane, *cis*-$[Me_2Ga(\mu\text{-}\overline{NC_2H_4NMe_2Ga}Me_2)]_2$ (*cis*-**3**). To our knowledge, *cis*-**3** represents the first report of a structure with cis conformation among dimeric $(Ga{-}N)_2$ amidogallanes in which both substituents on the gallium atom are alkyl groups, although structures of several dimeric *cis*-amidoalanes have been previously reported for those with sterically demanding substituents.[3]

Results and Discussion

Synthesis of 1−3. The reaction of $GaMe_3$ with 1 equiv of DMEDA at ambient temperature produces a

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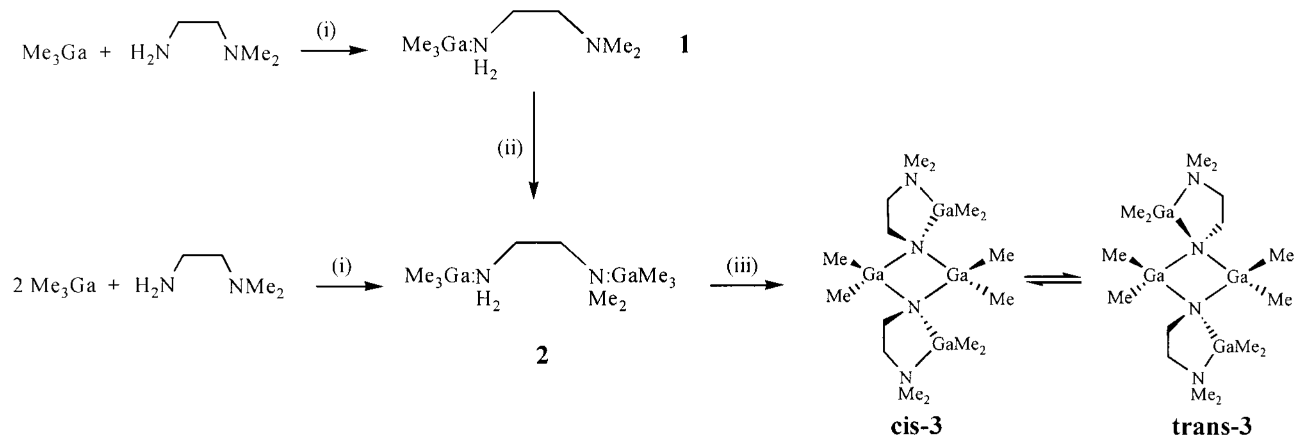
Scheme 1



Reagents and conditions : (i) CH_2Cl_2, room temp., 3 h; (ii) 1equiv of Me_3Ga, CH_2Cl_2, room temp., 2 h; (iii) sealed ampoule, 210 °C, 2 h.

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1:1 adduct, $Me_3Ga{:}NH_2C_2H_4NMe_2$ (**1**), as a yellowish oil. The NH_2 proton resonance of **1** (δ 1.52) is shifted to lower field by ca. 0.7 ppm compared with that of free DMEDA ligand (δ 0.81), which would be expected if the less sterically hindered NH_2 end of DMEDA is bound to the Ga atom. Attempted purification of the crude yellowish oil by vaccum distillation unexpectedly afforded a 2:1 adduct, $Me_3Ga{:}NH_2C_2H_4NMe_2{:}GaMe_3$ (**2**), as a colorless solid. This observation can be accounted for by the following disproportionation reaction as shown in eq 1. Beachley and co-workers[4] have previously shown a similar result where the reaction of $Ga(CH_2SiMe_3)_3$ with a large excess of $Me_2NC_2H_4NMe_2$ (TMEDA) afforded a 2:1 adduct, $[(Me_3SiH_2C)_3Ga]_2\cdot$TMEDA, after purification by sublimation. Storr et al.[5] also reported that the reactions of Me_3Ga with a series of diamines yielded respectively 1:1 and 2:1 adducts. They suggested that the steric factors and hydrogen bonding in adducts may play important roles in the relative stability of the 1:1 and 2:1 complexes. Compound **2** can be alternatively prepared either by successive additions of 1 equiv of $GaMe_3$ (67% overall yield) or by an addition of 2 equiv of $GaMe_3$ (80% yield) to DMEDA, as shown in Scheme 1.

$$2\,Me_3Ga{:}NH_2C_2H_4NMe_2 \rightleftarrows Me_3Ga{:}NH_2C_2H_4NMe_2{:}GaMe_3 + NH_2C_2H_4NMe_2 \quad (1)$$

The proton signals for NH_2 (δ 2.14) and NMe_2 (δ 2.32) groups of **2** are observed at lower fields than those (δ 0.82 and 2.02) of free DMEDA, which is indicative of both ends of DMEDA being coordinated by $GaMe_3$. The methyl protons on the two gallium atoms appear as a single resonance at δ −0.31 (toluene-d_8, 298 K), which is resolved into two distinct resonances at the lower temperature (δ −0.19 and −0.21, 213 K) because of the two inequivalent $GaMe_3$ moieties. To address the detailed fluxional processes in **2**, variable-temperature (VT) ^{13}C NMR spectra (100 MHz, toluene-d_8) have been obtained at various concentrations (14.9, 22.3, and 44.6 mM). Typical VT ^{13}C NMR spectra of **2** at a concentration of 14.9 mM are shown in Figure 1. The carbon resonances due to the methyl groups on the gallium atoms appear as two distinct peaks (δ −5.54 and −6.19) in a 1:1 ratio at 203 K. As the temperature increases, the two resonances coalesce at 248 K and become sharp at room temperature, while the other resonances remain unaffected. The coalescence temperature (T_c) decreases with increasing concentrations of **2**: T_c = 248 K at 14.9 mM, 243 K at 22.3 mM, and 218 K at 44.6 mM. This observation could be interpreted as the presence of a fast concerted intermolecular exchange of the two inequivalent $GaMe_3$ moieties at the ends of the DMEDA molecule, as depicted in Figure 1.

In previous work pyrolysis reactions (110 °C) of the aluminum analogues of **1** and **2** afforded respective chelated monomers, $Me_2\overline{AlN(H)C_2H_4N}Me_2$ and $Me_3Al\overline{N(H)C_2H_4NMe_2Al}Me_2$, by methane elimination.[2] Analogous thermal reactions of **1** and **2**, however, were very sluggish and did not produce any isolable products. This observation can be ascribed to the reluctant methane elimination in **1** and **2** compared with their aluminum analogues due to the lower acidity of $GaMe_3$ than that of $AlMe_3$.[6] Thermolysis of **2** at 210 °C in a sealed ampule, however, produces a mixture of cis and trans isomer of tetrametallic imidogallane, $[Me_2Ga(\mu\text{-}\overline{NC_2H_4NMe_2Ga}Me_2)]_2$ (**3**, cis:trans = 10:1) in 70% yield. The dimeric formulation of **3** has been indicated by the observation of the ($M^+ - CH_3$) ion in the EI mass spectrum. Slow recrystallization of the isomeric mixture affords crystals of only the cis isomer, but in solution *cis*-**3** equilibrates with *trans*-**3**. The cis isomer involves the two five-membered GaN_2C_2 rings in a cis conformation with respect to the four-membered Ga_2N_2 ring, as shown in Scheme 1 (vide infra).

The ^1H NMR spectrum (Figure 2) of *cis*-**3** exhibits two distinct resonances (δ −0.14 and −0.32 labeled as **e**) due to inequivalent methyl groups on each gallium atom of the Ga_2N_2 ring, whereas that of *trans*-**3** shows a single peak (δ −0.25, **e′**) for the four equivalent Ga−CH_3 groups of the Ga_2N_2 ring. The methyl groups on the Ga atom of the five-membered GaN_2C_2 ring appear as

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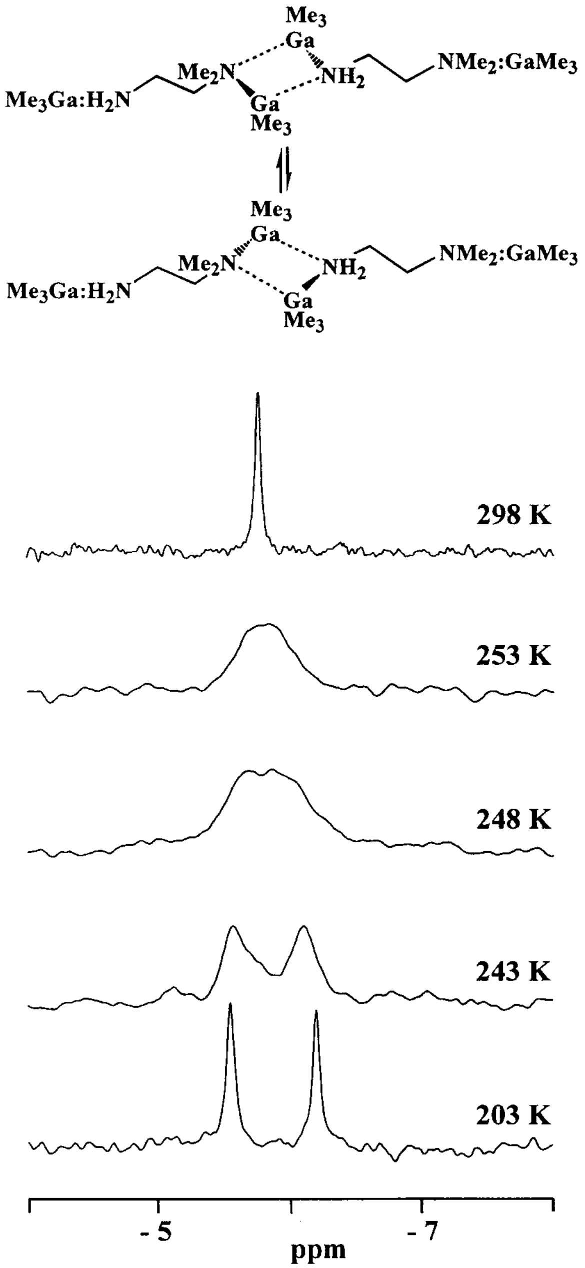

Figure 1. Proposed fluxional process and VT ^{13}C NMR spectra (100 MHz, toluene-d_8) of **2**.

single peaks at δ −0.34 (**d**) for *cis*-**3** and −0.30 (**d′**) for *trans*-**3**, since all four methyl groups of each isomer are equivalent. This observation and the rest of the proton resonances patterns are consistent with the symmetry properties of *cis*-**3** (C_{2v}) and *trans*-**3** (C_{2h}) isomers in solution. Compound **3** is likely to be formed from **2** by 2 equiv of methane elimination upon thermolysis to afford $Me_2Ga\overline{{=}NC_2H_4NMe_2Ga}Me_2$ as an intermediate followed by dimerization of this species. Beachley and coworkers[7] previously proposed that the cis isomer is a preferred kinetic product due to the orthogonal approach of the Ga=N π-bonds of two intermediates in the least hindered orientation followed by a cycloaddition reaction.

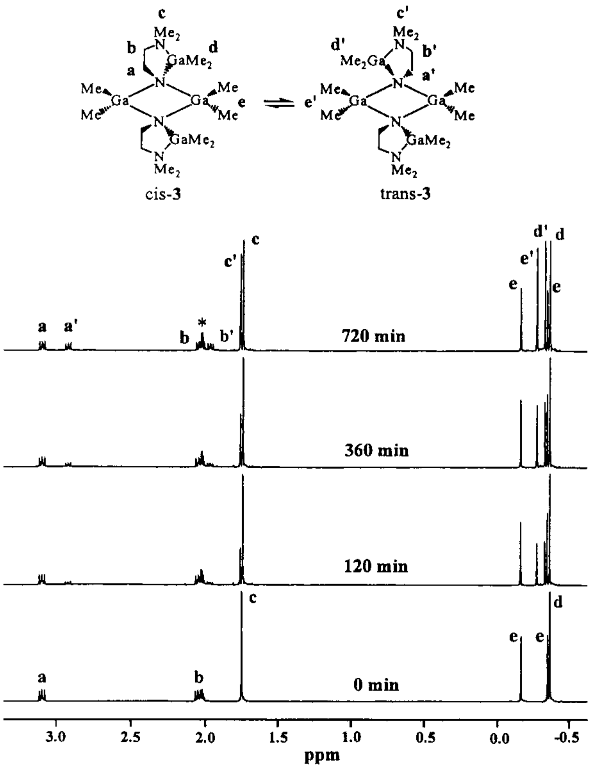

Figure 2. Time-resolved ^1H NMR spectra (300 MHz, toluene-d_8) for the cis−trans isomerization of **3** at 80 °C.

Cis−Trans Isomerization of 3. The cis → trans isomerization of **3** was studied by ^1H NMR spectroscopy. Typical time-resolved ^1H NMR spectra of **3** in toluene-d_8 at 80 °C are shown in Figure 2. As the intensities of the resonances of *cis*-**3** decrease, those corresponding to *trans*-**3** increase in intensity. Relative concentrations of the two isomers were measured by integration of the peaks due to $Ga-CH_3$ at δ −0.14 (**e**, half of the total concentration) for *cis*-**3** and at δ −0.25 (**e′**) for *trans*-**3**. 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} = [*trans*-**3**]/[*cis*-**3**], measured for the isomerization range from 0.84 to 0.91, indicating that the cis isomer is favored in this equilibrium. The plot of ln K_{eq} vs $1/T$ (correlation coefficient, 0.9875) yields $\Delta H° = -3.35 \pm 1.70$ kJ mol^{-1} and $\Delta S° = -10.4 \pm 1.7$ J mol^{-1} K^{-1} for the process. The trans isomer is thermodynamically more stable, but the negative entropy change favors the cis isomer. Activation parameters derived from the Eyring plots of $\ln(k/T)$ vs $1/T$ and $\ln(k_{-1}/T)$ vs $1/T$ (correlation coefficients, 0.9937 and 0.9937, respectively) are listed in Table 2. The net enthalpy and entropy changes for *cis*-**3** to *trans*-**3** from the thermodynamic data are in good agreement with those obtained from the kinetic data; $\Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_{-1} = \Delta H°$ and $\Delta S^{\ddagger}_1 - \Delta S^{\ddagger}_{-1} = \Delta S°$, within experimental error.

All of the known amidogallane dimers of the formula $[R_2Ga(\mu\text{-}NHR')]_2$ crystallize as the trans isomer and undergo cis−trans isomerization in solution. We previously reported kinetic studies of the cis−trans isomerization of dimeric amidogallanes $[Me_2Ga\text{-}\mu\text{-}N(H)^tBu]_2$ (**6**),[8] $[Me_2Ga\text{-}\mu\text{-}N(H)NMe_2]_2$ (**7**),[1g] and $[Me_2Ga\text{-}\mu\text{-}N(H)\text{-}$

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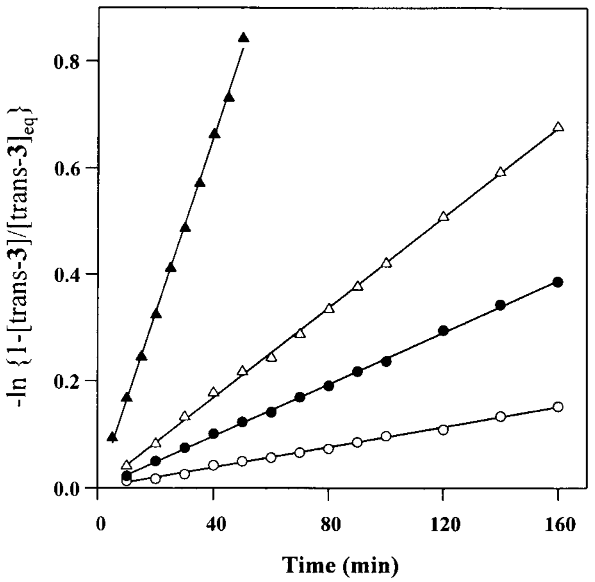

Figure 3. Kinetics plots for the cis−trans isomerization of **2** in toluene-d_8 at 75 (○), 80 (●), 85 (△), and 95 (▲) °C.

Table 1. Equilibrium and Kinetic Data in Toluene-d_8

T, °C	K_{eq}	10^3k_{obs}, min^{-1}	10^3k_1, min^{-1}	10^3k_{-1}, min^{-1}
75	0.91 ± 0.10	0.94 ± 0.02	0.45 ± 0.01	0.49 ± 0.01
80	0.89 ± 0.12	1.42 ± 0.03	1.14 ± 0.01	1.28 ± 0.02
85	0.88 ± 0.14	4.21 ± 0.21	1.97 ± 0.09	2.24 ± 0.12
95	0.86 ± 0.16	16.5 ± 0.24	7.61 ± 0.11	8.87 ± 0.13
100	0.84 ± 0.15			

$SiEt_3]_2$ (**8**),[9] in which the isomerization pathway is proposed to be an initial breaking of the Ga−N bond, followed by rotation about the nonbridged Ga−N bond and rebridging. The rate of isomerization, therefore, has been markedly accelerated by Lewis bases due to the facile cleavage of the Ga−N bond by an attack of Lewis bases on the Ga atom, as was well documented in various amidogallanes and $[Me_2Ga(\mu\text{-}NMePh)]_2$,[7b] **6**, and **8**.

Nevertheless, the isomerization rate of **3** is not affected in the presence of ca. 1 equiv of pyridine or 4-methylpyridine. This observation may be attributed to the role of the NMe_2 end of DMEDA as an internal Lewis base in facilitating the Ga−N bond scission of the four-membered ring of neighboring molecules. Similar results have been precedented for **7**[1g] and the aluminum analogues of both **3**[2] and **7**,[1g] which have free NMe_2 ends in solution within the molecular framework. This internal Lewis base assisted isomerization process in tetrametallic **3** would involve scission of Ga−N bonds in both four- and five-membered rings, which explains the relatively large values of enthalpy of activation and large positive values of entropy of activation of **3** compared with those of dimeric **6**,[8] as shown in Table 2.

Crystal Structure of 2. The overall molecular geometry of **2** with the atomic labeling scheme is shown in Figure 4. Selected bond distances and angles are listed in Table 3.

The gallium and nitrogen atoms are in rather distorted tetrahedral environments. The average gallium−alkyl distance is 1.98(1) Å. The two gallium−nitrogen bond lengths are essentially the same (Ga(1)−N(1) = 2.16(1), and Ga(2)−N(2) = 2.16(1) Å), which are comparable with those observed in adducts such as $Me_3Ga{:}NH_2{}^tBu$ (2.12(1) Å),[10] $Me_3Ga{:}NMe_3$ (2.20(3) Å),[11] and $[(Me_3SiH_2C)_3Ga]_2{\cdot}TMEDA$ (2.241(9) Å).[4] All other parameters of the molecule seem normal.

Crystal Structure of *cis*-3. The overall molecular geometry of *cis*-**3** with the atomic labeling scheme is shown in Figure 5. Selected bond distances and angles are listed in Table 4.

The tetrametallic molecule **3** has one four-membered Ga_2N_2 ring and two five-membered GaN_2C_2 rings of cis conformation and possesses approximate C_2 symmetry with the C_2 axis going through the center of the Ga_2N_2 ring. Significant distortion from an ideal tetrahedral geometry is observed for all the atoms in the four-membered Ga_2N_2 ring with the ring angles of 89.0(6)° (av) at gallium and 88.0(4)° (av) at nitrogen. The four-membered ring is puckered with an Ga_2N plane fold angle of 26.4(3)°, presumably to relieve the steric congestion among methyl groups on the gallium atoms of the four- and five-membered rings. A homoleptic gallium amide, $[({}^tBu(H)N)_2Ga(\mu\text{-}N(H){}^tBu)]_2$, is the only structurally characterized example of the amidogallane with cis conformation, which adopts a puckered Ga_2N_2 ring by the minimization of steric repulsion of the ^{t}Bu groups.[12] The average bond distance of the Ga_2N_2 ring is 2.014(7) Å, which is close to that observed in other dimers.[1f,g,i,8,9,13] The imido nitrogen N(1) bridges three gallium atoms (Ga(1), Ga(1′), and Ga(2)) with a short N(1)−Ga(2) bond distance of 1.91(1) Å. The coordination environment of the gallium atom of the five-membered ring is also distorted tetrahedral. The Ga(2)−N(2) distance (2.152(6) Å) is the longest among Ga−N bonds in *cis*-**3**, as expected for a dative bond. 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. The following chemicals were obtained from commercial sources and were used as received: trimethylgallium (Strem); trimethylaluminum (Aldrich), *N,N*-dimethylethlylenediamine (Aldrich). Dichloromethane was refluxed over CaH_2 and then distilled under an argon atmosphere. *n*-Hexane and toluene were distilled over sodium/benzophenone under an argon atmosphere.

Infrared spectra were obtained as KBr pellets on a Bomem MB-100 FT-IR spectrophotometer. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer. Variable-temperature ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVANCE-400 spectrometer. Melting points were obtained in sealed capillaries under argon

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Table 2. Comparison of Kinetic and Thermodynamic Data (cis → trans) of Amidogallanes

compound	$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J K^{-1} mol^{-1}	$\Delta H^{\ddagger}_{1}$, $\Delta H^{\ddagger}_{-1}$, kJ mol^{-1}	$\Delta S^{\ddagger}_{1}$, $\Delta S^{\ddagger}_{-1}$, J K^{-1} mol^{-1}	solvent	ref
$[Me_2Ga(\mu\text{-}\overline{NC_2H_4NMe_2Ga}Me_2)]_2$ (**3**)	−3.35 ± 1.70	−10.4 ± 1.7	144.6 ± 6.2 147.6 ± 6.4	105.6 ± 1.5 115.4 ± 1.5	toluene-d_8	this work
$[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (**6**)	−3.12 ± 0.04	−4.56 ± 0.06	117.8 ± 7.9 120.8 ± 7.4	37.3 ± 2.5 41.4 ± 2.6	toluene-d_8	8

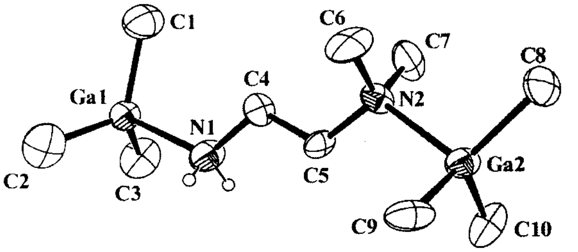

Figure 4. Molecular geometry and atomic labeling scheme for **2** with 30% probability thermal ellipsoids. Hydrogen atoms except for NH were omitted for clarity.

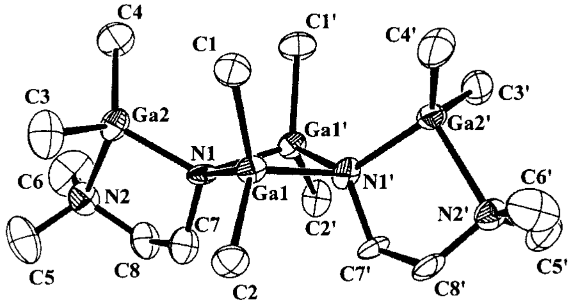

Figure 5. Molecular geometry and atomic labeling scheme for **3** with 30% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity.

Table 3. Bond Lengths [Å] and Angles [deg] with Esd's for 2

Bond Lengths			
Ga(1)−N(1)	2.16(1)	Ga(1)−C(1)	1.97(2)
Ga(1)−C(2)	1.97(2)	Ga(1)−C(3)	1.98(1)
Ga(2)−N(2)	2.16(1)	Ga(2)−C(8)	2.00(1)
Ga(2)−C(9)	1.99(1)	Ga(2)−C(10)	1.99(1)
N(1)−C(4)	1.44(1)	N(2)−C(5)	1.46(1)
N(2)−C(6)	1.52(2)	N(2)−C(7)	1.46(2)
C(4)−C(5)	1.50(2)		
Bond Angles			
C(1)−Ga(1)−C(2)	116.8(7)	C(8)−Ga(2)−C(9)	115.0(6)
C(2)−Ga(1)−C(3)	117.8(7)	C(9)−Ga(2)−C(10)	115.3(6)
C(1)−Ga(1)−C(3)	113.7(7)	C(8)−Ga(2)−C(10)	115.8(6)
N(1)−Ga(1)−C(1)	103.7(5)	N(2)−Ga(2)−C(8)	102.2(5)
N(1)−Ga(1)−C(2)	99.4(6)	N(2)−Ga(2)−C(9)	103.1(5)
N(1)−Ga(1)−C(3)	101.6(6)	N(2)−Ga(2)−C(10)	102.6(5)
Ga(1)−N(1)−C(4)	119.1(9)	Ga(2)−N(2)−C(5)	109.8(7)
C(6)−N(2)−C(7)	110(1)		

(1 atm) and were uncorrected. Mass spectra were obtained by the staff of the Korea Basic Science Center using a JEOL JMS-SX-102A mass spectrometer. All *m*/*z* values are referenced to ^{69}Ga. Elemental analyses were performed either by Oneida Research Services or by the analytical laboratory of the Agency for Defense Development, Korea.

Preparation of $Me_3Ga{:}NH_2C_2H_4NMe_2$ (1). To a dichloromethane solution (10 mL) of $GaMe_3$ (0.560 g, 4.87 mmol) at 0 °C was added a dichloromethane solution (10 mL) of DMEDA (0.440 g, 4.99 mmol). The resulting reaction mixture was stirred at room temperature for 3 h. Evaporation of the solvent in vacuo afforded **1** as a yellowish oil: ^{1}H NMR (C_6D_6, 298 K) δ −0.17 (9H, s, $Ga(CH_3)_3$), 1.52 (2H, br, N*H*), 1.62 (2H, t, $CH_2N(CH_3)_2$), 1.73 (6H, s, NCH_3), 1.97 (2H, tt, NH_2CH_2); ^{13}C NMR (C_6D_6, 298 K) δ −6.50 ($GaCH_3$), 38.27 ($CH_2N(CH_3)_2$), 44.99 (NCH_3), 59.22 (NH_2CH_2); IR ν(NH) 3251, 3344 cm^{-1}.

Table 4. Bond Lengths [Å] and Angles [deg] with Esd's for 3[a]

Bond Lengths			
Ga(1)−N(1)	2.03(1)	Ga(1)−N(1′)	2.02(1)
Ga(1)−C(1)	1.99(1)	Ga(1)−C(2)	1.99(1)
Ga(2)−N(1)	1.91(1)	Ga(2)−N(2)	2.15(1)
Ga(2)−C(3)	1.93(1)	Ga(2)−C(4)	1.93(1)
Ga(1′)−N(1)	2.00(1)	Ga(1′)−N(1′)	2.01(1)
Ga(1′)−C(1′)	1.97(1)	Ga(1′)−C(2′)	2.01(1)
Ga(2′)−N(1′)	1.93(1)	Ga(2′)−N(2′)	2.12(1)
Ga(2′)−C(3′)	1.96(1)	Ga(2′)−C(4′)	1.96(1)
N(1)−C(7)	1.51(1)	N(1′)−C(7′)	1.49(2)
Ga(1)···Ga(1′)	2.797(2)		
Bond Angles			
N(1)−Ga(1)−N(1′)	88.4(4)	C(1)−Ga(1)−C(2)	117.4(6)
N(1)−Ga(2)−N(2)	88.7(4)	C(3)−Ga(2)−C(4)	117.1(7)
N(1′)−Ga(1′)−N(1)	89.5(4)	C(1′)−Ga(1′)−C(2′)	116.8(5)
N(1′)−Ga(2′)−N(2′)	88.6(4)	C(3′)−Ga(2′)−C(4′)	118.3(7)
Ga(1)−N(1)−Ga(1′)	87.9(3)	Ga(2)−N(1)−C(7)	104.9(7)
Ga(1′)−N(1′)−Ga(1)	88.0(3)	Ga(1)−N(1′)−C(7′)	111.4(7)
Ga(2)−N(2)−C(8)	101.4(7)	Ga(2′)−N(2′)−C(5′)	113.4(9)
Ga(2)−N(2)−C(5)	112.1(8)	C(5)−N(2)−C(6)	109(1)
Ga(2′)−N(2′)−C(8′)	102.7(7)	C(5′)−N(2′)−C(6′)	108(1)

[a] Atoms related by the pseudo-C_2 symmetry operations are labeled with a prime.

Preparation of $Me_3Ga{:}NH_2C_2H_4(Me)_2N{:}GaMe_3$ (2). (a) To a dichloromethane solution (10 mL) of $GaMe_3$ (0.980 g, 8.53 mmol) at 0 °C was added a dichloromethane solution (10 mL) of DMEDA (0.370 g, 4.20 mmol). The resulting colorless mixture was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure. Upon sublimation (10^{-3} mmHg, 35 °C), compound **2** (1.068 g, 3.36 mmol, 80%) was obtained as a colorless solid. mp 57−59 °C; ^{1}H NMR ($CDCl_3$, 298 K) δ −0.58 (18H, s, $Ga(CH_3)_3$), 2.14 (2H, br, N*H*), 2.32 (6H, s, NCH_3), 2.60 (2H, AA′BB′ pattern, $CH_2N(CH_3)_2$), 2.89 (2H, t of AA′BB′ pattern, NH_2CH_2); ^{13}C NMR ($CDCl_3$, 298 K) δ −6.19 ($GaCH_3$), 36.47 ($CH_2N(CH_3)_2$), 45.11 (NCH_3), 59.66 (NH_2CH_2); IR ν(NH) 3298, 3318 cm^{-1}. Anal. Calcd for $C_{10}H_{30}Ga_2N_2$: C, 37.79; H, 9.51; N, 8.82. Found: C, 37.47; H, 9.12; N, 8.50.

(b) Vaccum distillation (10^{-3} mmHg, 40 °C) of **1** (0.982 g, 4.81 mmol) afforded **2** (0.445 g, 1.40 mmol, 58%).

(c) Trimethylgallium (0.492 g, 4.24 mmol) was added to a dichloromethane solution (10 mL) of **1** (0.861 g, 4.22 mmol) at 0 °C. The resulting colorless mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure. Sublimation (10^{-3} mmHg, 35 °C) of the residue produced **2** (0.900 g, 2.83 mmol, 67%).

Preparation of $[Me_2Ga(\mu\text{-}\overline{NC_2H_4N(Me)_2Ga}Me_2)]_2$ (3). Compound **1** (1.068 g, 3.36 mmol) was heated at 210 °C for 2 h in a sealed ampule. The crude product was purified by recrystallization in dichloromethane at −20 °C to produce **3** (0.672 g, 1.18 mmol, 70%, cis:trans = 10:1) as a colorless solid. *cis*-**3**: mp 147−150 °C; ^{1}H NMR (C_6D_6, 298 K) δ −0.14 (12H, s, $GaCH_3$), −0.07 (6H, s, $GaCH_3$), 0.18 (6H, s, $GaCH_3$), 1.59 (12H, s, $N(CH_3)_2$), 1.98 (4H, t, $CH_2N(CH_3)_2$), 3.17 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −9.52 ($GaCH_3$), −5.11 ($GaCH_3$), −2.43 ($GaCH_3$), 46.75 ($N(CH_3)_2$), 48.32 ($CH_2N(CH_3)_2$), 65.56

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Table 5. Crystal Data and Structure Refinement for 2 and *cis*-3

	2	*cis*-**3**
formula	$C_{10}H_{30}Ga_2N_2$	$C_{16}H_{44}Ga_2N_2$
fw	317.80	571.43
temp (K)	293(2)	293(2)
λ(Mo Kα)	0.71073	0.71069
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	16.662(4)	18.248(2)
b (Å)	7.594(3)	7.675(2)
c (Å)	13.222(3)	18.432(3)
β (deg)	95.0(1)	92.6(1)
V (Å^3)	1666.7(9)	2583.9(8)
Z	4	4
D_{calcd} (Mg m^{-3})	1.267	1.469
abs coeff (mm^{-1})	3.209	4.132
F(000)	664	1168
cryst dimens (mm)	0.41 × 0.37 × 0.14	0.53 × 0.46 × 0.26
θ range (deg)	1.23 to 20.00	2.21 to 20.50
hkl ranges	$-15 \le h \le 16$, $-6 \le k \le -6$, $-120 \le l \le 2$	$-18 \le h \le 18$, $0 \le k \le 7$, $0 \le l \le 18$
no. of rflns measd	2314	2700
no. of ind rflns	1389 [$R_{\text{int}} = 0.0784$]	2589 [$R_{\text{int}} = 0.0269$]
no. of data/restraints/param	1389/0/135	2589/6/218
goodness-of-fit on F^2	1.145	1.072
final R indices[a] [$I > 2\sigma(I)$]	$R = 0.0667$ $R_w = 0.1926$	$R = 0.0691$ $R_w = 0.1659$
R indices (all data)	$R = 0.0761$ $R_w = 0.2108$	$R = 0.0948$ $R_w = 0.1909$
D(r) and hole, e Å^{-3}	0.690 and −0.547	1.251 and −1.638

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

(NCH_2); MS (EI, 70 eV) m/z 553 $[M - CH_3]^+$, 269 $[M/2 - CH_3]^+$. Anal. Calcd for $C_{16}H_{44}Ga_4N_4$: C, 33.63; H, 7.76; N, 9.81. Found: C, 33.52; H, 7.34; N, 9.45.

trans-**3** (data obtained from an equilibrium mixture): ^{1}H NMR (C_6D_6, 298 K) δ −0.10 (12H, s, GaCH_3), 0.03 (12H, s, GaCH_3), 1.61 (12H, s, N$(CH_3)_2$), 1.89 (4H, t, $CH_2N(CH_3)_2$), 2.99 (4H, t, NCH_2); ^{13}C NMR (C_6D_6, 298 K) δ −9.51 (GaCH_3), 46.89 ($CH_2N(CH_3)_2$), 47.22 (N$(CH_3)_2$), 65.80 (NCH_2).

^{1}H NMR Study of Isomerization of *cis*-3 to *trans*-3. Crystals of *cis*-**3** (ca. 5 mg) were transferred to four 5 mm NMR tubes, and toluene-d_8 (0.6 mL) was added to each NMR tube under an atmosphere of argon. The tubes were sealed and then heated in an NMR probe at 75, 80, 85, and 95 °C, respectively, while the resonances due to the methyl groups on the gallium atoms, at δ −0.14 for *cis*-**3** and −0.25 for *trans*-**3**, were monitored periodically by ^{1}H NMR. The isomerization reaction followed reversible first-order kinetics and showed excellent fits of data to a common plot of $-\ln\{1 - [trans\text{-}\mathbf{3}]/[trans\text{-}\mathbf{3}]_{eq}\}$ vs time. Equilibrium constants at 75, 80, 85, and 95 °C were measured similarly by ^{1}H NMR after heating four NMR tubes in heated oil baths at controlled (±0.5 °C) temperatures, respectively. After equilibrium was reached, each NMR tube was quickly removed from the oil bath and placed into an ice bath to quench isomerization.

X-ray Structure Determination for 2. Crystals suitable for an X-ray diffraction study were obtained by slow recrystallization from a hexane solution of **2** at −20 °C. A colorless crystal was mounted on a capillary, transferred to a Siemens SMART diffractometer/CCD area detector employing a 3 kW sealed tube X-ray source operating at 2 kW, and centered in the beam. Data were collected at room temperature for 8 h. Preliminary orientation matrix and cell constants were determined with a set of 15 data frames with 10 s collection per frame, followed by spot integration and least-squares refinement. A hemisphere of data was collected using 0.3° ω scans at 10 s per frame. The raw data were integrated (XY spot spread = 1.60, Z spot spread = 0.6), and the unit cell parameters were refined using SAINT.[14] Data analysis and absorption correction were performed by using Siemens XPREP.[15] The unit cell parameters indicated a primitive monoclinic cell, and systematic absences indicated space group $P2_1/c$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Details of the relevant crystallographic data are given in Table 5.

All calculations were performed using the SHELXTL system of computer programs.[16] Scattering factors for all atoms were included in the software package. The positions of Ga 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.

X-ray Structure Determination for *cis*-3. Crystals suitable for an X-ray study were obtained by slow recrystallization from a mixed solvent of toluene and hexane at −20 °C. The colorless cubic crystal was mounted in a thin-walled glass capillary under an argon atmosphere and then flame-sealed. The determination of the unit cell parameters, the orientation matrix, and the collection of intensity data were made on an Enraf-Nonius CAD-4 diffractometer, employing graphite-monochromated Mo Kα radiation. The unit cell parameters and occurrences of equivalent reflections and systematic absences in the diffraction data were consistent with the $P2_1/c$ space group. Lorentz and polarization corrections were applied to the intensity data, while no absorption correction was applied. Crystallographic details are presented in Table 5.

All calculations were performed using the SHELXTL system of computer programs.[16] The structure was solved using direct methods, completed by difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions. 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 displacement parameters for **2** and *cis*-**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] *SAINT*, SAX Area-Detector Integration Program, version 4.050; Siemens Analytical Instrumentation, Inc.: Madison WI, 1995.

[15] *XPREP*, part of the SHELXTL, Crystal Structure Determination Package, version 5.04; Siemens Analytical Instrumentation, Inc.: Madison WI, 1994.

[16] (a) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXL-93. *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.