Organometallics 1992, 11, 3320–3323

Cis–Trans Isomerization and Structure of Dimeric $[Me_2Ga(\mu\text{-}NH^tBu)]_2$

Joon T. Park,*[,1a] Younsoo Kim,[1a] Jaheon Kim,[1b] Kimoon Kim,[1b] and Yunsoo Kim[1c]

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, 305-701 Korea, Department of Chemistry and Center for Biofunctional Molecules, Pohang Institute of Science and Technology, P.O. Box 125, Pohang, 790-784 Korea, and Advanced Materials Division, Korea Research Institute of Chemical Technology, Taejon, 305-606 Korea

Received March 25, 1992

The reaction of $GaMe_3$ with $^tBuNH_2$ at 110 °C affords a mixture of *trans*- (**1a**) and *cis*-$[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (**1b**) which crystallizes as pure **1a** in 75% yield. ^1H NMR study shows that the dimeric amido complex undergoes a cis–trans isomerization (**1a** → **1b**) in solution. The equilibrium has been observed to follow reversible first-order kinetics with $\Delta H° = 3.12 \pm 0.04$ kJ mol^{-1} and $\Delta S° = 4.56 \pm 0.06$ J mol^{-1} K^{-1}. The activation parameters for the conversion **1a** → **1b** are $\Delta H_1 = 120.8 \pm 7.4$ kJ mol^{-1} and $\Delta S_1 = 41.4 \pm 2.6$ J mol^{-1} K^{-1} and for the reverse reaction **1b** → **1a** are $\Delta H_{-1} = 117.8 \pm 7.9$ kJ mol^{-1} and $\Delta S_{-1} = 37.3 \pm 2.5$ J mol^{-1} K^{-1}. The isomerization is markedly accelerated in the presence of pyridine. A crossover experiment indicates that the isomer interconversion is a unimolecular process. On the basis of these data, a possible pathway for the isomerization is proposed. 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 amido groups and two terminal methyl groups bound to each gallium atom. The two N–^{t}Bu groups are trans to each other with respect to the $(Ga-N)_2$ ring. The coordination geometry of both the gallium and nitrogen atoms is distorted tetrahedral.

Introduction

Synthesis of amidogallanes, $(R_2GaNR'_2)_n$ (n = 1–3), has been of considerable current interest due to their potential as single-source precursors for the preparation of gallium nitride (GaN) thin films, employing organometallic chemical vapor deposition (OMCVD).[2] The original work of Coates et al.[3] proposed 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 subsequent thermolysis of the adducts yielded the dimeric amidogallane $(Me_2GaNR'_2)_2$ by loss of 1 equiv of methane. Nevertheless, the synthesis and structure of a monomeric (n = 1) amidogallane has not yet been reported although several examples of adducts and dimeric (n = 2) and trimeric (n = 3) amidogallanes have been structurally characterized in recent years. The examples include $^tBu_3Ga{:}NH_2Ph$,[4] $[Me(Cl)Ga(\mu\text{-}NHSiMe_3)]_2$,[5] $[Me_2Ga(\mu\text{-}NHDipp)]_2$,[6] $[Me_2Ga(\mu\text{-}NHAd)]_2$,[6] $[Me_2Ga(\mu\text{-}NHPh)]_2$,[6] $[^tBu_2Ga(\mu\text{-}NHPh)]_2$,[4] $[H_2GaN(CH_2)_2]_3$,[7] and $(H_2GaNH_2)_3$[2b] (Dipp = 2,6-$^iPr_2C_6H_3$, Ad = 1-adamantyl). In this paper, we report details of the synthesis and crystal structure of dimeric $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (**1**) together with kinetic and thermodynamic studies of the cis–trans isomerization of **1** in solution.

Experimental Section

General Comments. All experiments were performed under nitrogen either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Trimethylgallium was purchased from Strem Chemicals. *tert*-Butylamine (E. Merck) was refluxed over CaH_2 and then distilled under N_2 atmosphere. *n*-Hexane was distilled from sodium benzophenone under N_2 atmosphere.

Infrared spectra were obtained as KBr pellets with a Bomen MB-100 FT-IR spectrophotometer. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. 2D COSY NMR spectra were recorded on a Bruker AMX-500 spectrometer. The melting point was obtained in a sealed capillary under nitrogen (1 atm) and is uncorrected. Mass spectra were recorded by the staff of the Analytical Laboratory at the Korea Advanced Institute of Science and Technology using a Hewlett-Packard 5985B mass spectrometer. All m/z values are referenced to ^{69}Ga. Microanalytical data were provided by the Analytical Laboratory of the Korea Research Institute of Chemical Technology.

Synthesis of 1. The compounds $GaMe_3$ (1.06 g, 9.23 mmol) and $^tBuNH_2$ (0.675 g, 9.23 mmol) were mixed at 0 °C and the reaction mixture was warmed to room temperature. A white solid formed and then was heated to 110 °C. The resulting colorless liquid was heated at 110 °C for 7 h. Gas evolution (presumably methane) was apparent from the observed frothing. The volatile material was removed under reduced pressure and the white residue was dissolved in *n*-hexane. Slow recrystallization of the solution at −20 °C gave trans isomer **1a** (1.20 g, 3.47 mmol, 75%) as colorless crystals: mp 80 °C; ^1H NMR ($CDCl_3$, 20 °C) δ −0.33 (s, Ga–Me), 0.89 (br, NH), 1.10 (s, ^{t}Bu); ^1H NMR (toluene-d_8, 20 °C) δ −0.15 (s, Ga–Me), 0.72 (br, NH), 0.93 (s, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 20 °C) δ −2.59 (Ga–Me), 32.4 (CMe_3), 52.1 (N–C); MS (70 eV) m/z 327 ($M^+ - CH_3$); IR ν(NH) 3247 cm^{-1}. Anal. Calcd for $C_{12}H_{32}N_2Ga_2$: C, 41.92; H, 9.38; N, 8.15. Found: C, 41.57; H, 9.10; N, 7.91.

cis isomer **1b** (data obtained from an equilibrium mixture): ^1H NMR ($CDCl_3$, 20 °C) δ −0.50 (s, Ga–Me), −0.15 (s, Ga–Me), 0.82 (br, NH), 1.12 (s, ^{t}Bu); ^1H NMR (toluene-d_8, 20 °C) δ −0.30 (s, Ga–Me), 0.0081 (s, Ga–Me), 0.65 (br, NH), 0.95 (s, ^{t}Bu); ^{13}C NMR ($CDCl_3$, 20 °C) δ −3.04 (Ga–Me), −2.59 (Ga–Me), 32.5 (CMe_3), 52.4 (N–C).

^1H NMR Study of Isomerization of 1a to 1b. Crystals of compound **1a** (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 nitrogen. The tubes were sealed and then heated in an NMR probe at 60, 70, 80, and 88 °C, respectively, while the resonances due to the methyl groups on the gallium atoms, at δ −0.15 for **1a** and at δ 0.0081 and −0.30 for **1b**, were monitored periodically by ^1H NMR. The isomerization reactions followed reversible first-order kinetics and showed excellent fits of data to a common plot of $-\ln\{1 - [\mathbf{1b}]/[\mathbf{1b}]_{eq}\}$ vs time. Equilibrium constants at 60, 70, 80, 88, 96, and 100 °C were measured similarly by ^1H NMR after heating six NMR tubes in

---

[1] (a) KAIST. (b) POSTECH. (c) KRICT.

[2] (a) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208. (b) Hwang, J.-W.; Hanson, S. A.; Britton, D.; Evans, J. F.; Jensen, D. F.; Gladfelter, W. L. *Chem. Mater.* **1990**, *2*, 342.

[3] (a) Coates, G. E. *J. Chem. Soc.* **1951**, 2003. (b) Beachley, O. T.; Coats, G. E.; Kohnstam, G. *Ibid.* **1965**, 3248.

[4] Atwood, D. A.; Jones, R. A.; Cowley, A. H.; Bott, S. G.; Atwood, J. L. *Polyhedron* **1991**, *10*, 1897.

[5] Nutt, W. R.; Stimson, R. E.; Leopold, M. F.; Rubin, B. H. *Inorg. Chem.* **1982**, *21*, 1909.

[6] Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

[7] Harrison, W.; Storr, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1972**, 1554.

0276-7333/92/2311-3320$03.00/0

Table I. Crystallographic Data for $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (1a)

formula	$Ga_2N_2C_{12}H_{32}$
fw	343.85
space group	$P2_1/n$ (No. 14)
a, Å	6.800 (1)
b, Å	12.206 (1)
c, Å	10.890 (2)
β, deg	95.95 (1)
vol, Å^3	899.0 (2)
Z	2
temp, °C	23
dens (calculated), g/cm^3	1.270
cryst size, mm	0.50 × 0.50 × 0.25
radiation [a(Kα_1), Å]	graphite-monochromated Mo K α [0.709 26]
linear abs coeff, cm^{-1}	29.72
DIFABS abs corr range	0.747–1.280
scan mode	ω–2θ
scan speed, deg/min	2.06
2θ limits, deg	$2.0 \leq \theta \leq 27.5$
bkgd counts	$^1/_4$ of scan range on each side of reflection
scan width, deg	0.8 + 0.347 tan θ in ω
no. of unique data	2164
no. of unique data with $I > 3\sigma(I)$	1333
no. of variables	77
$R(F)$	0.0415
$R_w(F)$	0.0441
GOF	0.525

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 Data Collection and Structure Solution of 1a. A colorless crystal was sealed in a Lindemann glass capillary under nitrogen and mounted on an Enraf-Nonius CAD4 diffractometer. Cell parameters were determined by least-squares refinement of 25 centered reflections in the range 10.8° ≤ θ ≤ 15.4°. Intensities of four standard reflections monitored every 2 h showed no significant decay over the course of data collection. Crystallographic data and additional details of data collection are summarized in Table I. All the calculations were carried out with the Enraf-Nonius MolEN package[8] on a MicroVAX 2000. Lorentz and polarization corrections were applied to the intensity data. An empirical absorption correction (DIFABS)[9] was also applied at the late stage of refinement. The structure was solved by Patterson and difference Fourier methods and refined by the full-matrix least-squares methods. All nonhydrogen atoms were refined anisotropically. The amide hydrogen atom was located from the difference electron density map and refined with an isotropic thermal parameter. All other hydrogen atoms were placed in idealized positions (C-H = 0.95 Å) and, during the refinement, were allowed to ride on the attached carbon atoms, with isotropic temperature factors of 1.2 (or 1.4 for the hydrogens of methyl groups attached to Ga) times those of attached carbons. Weight scheme used: $w = \sigma(F_o)^{-2}$, $\sigma(F_o) = 0.5F^{-1}\sigma(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$, $p = 0.04$. Final cycle of the refinement converged to the R factors listed in Table I. The largest shift/esd was 0.01, and the maximum and minimum heights in the final difference map were 0.42 and −0.46 e Å^{-3}, respectively. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table II.

Results and Discussion

Synthesis and Isomerization of 1. Reaction of $GaMe_3$ with 1 equiv of $^tBuNH_2$ at 110 °C affords the dimeric amidogallane complex $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (1) in high yield (75%). The initial reaction at room temperature presumably results in the formation of the colorless adduct $Me_3Ga{:}NH_2{}^tBu$. Thermal elimination of methane from the adduct in refluxing toluene leads to the formation of a mixture of trans (**1a**) and cis (**1b**) isomers in a ratio of 3:2. However, slow recrystallization of the mixture affords crystals of only the trans isomer. X-ray crystal structure determination of 1 reveals the trans isomer (vide infra), but in solution it equilibrates with the cis isomer. Attempted separation of pure **1b** from **1a** by sublimation has not been successful. Both ^1H and ^{13}C NMR spectra of **1a** show a respective single peak for the Ga–CH_3 groups (see Experimental Section) and are consistent with the molecular structure observed in the solid state, whereas, those of **1b** exhibit two distinct resonances due to methyl groups on the gallium atom and therefore **1b** was assumed to be a cis isomer with the N-alkyl groups cis to the $(Ga-N)_2$ ring. One of the Ga–CH_3 resonances, of **1b**, overlapped with that of **1a** at δ −2.59 in the ^{13}C NMR spectrum, was unambiguously assigned from the 2D ^1H–^{13}C correlated NMR spectrum (COSY) of 1, as is shown in Figure 1. The ^1H resonances of **1b** at δ −0.15 and −0.50 are correlated with the ^{13}C resonances at δ −3.04 and −2.59, respectively. The IR spectra of both pure **1a** and an equilibrium mixture are identical and contain only one strong peak at 3247 cm^{-1} assigned to ν(NH) stretches of **1a**.

Table II. Positional and Equivalent Isotropic Thermal Parameters with Esd's for $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (1a)

Atom	x	y	z	B_{eq},[a] Å^2
Ga	0.09058 (9)	0.11114 (5)	0.00786 (5)	3.41 (1)
N	−0.0707 (6)	0.0161 (4)	0.1120 (4)	3.11 (8)
C1	0.3736 (9)	0.1297 (6)	0.0671 (6)	5.6 (2)
C2	−0.066 (1)	0.2423 (6)	−0.0407 (7)	6.2 (2)
C3	−0.0400 (8)	0.0065 (5)	0.2494 (5)	4.1 (1)
C4	−0.063 (1)	0.1185 (7)	0.3048 (6)	6.9 (2)
C5	0.165 (1)	−0.0372 (7)	0.2887 (6)	7.0 (2)
C6	−0.193 (1)	−0.0709 (7)	0.2921 (6)	6.6 (2)

[a] The isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

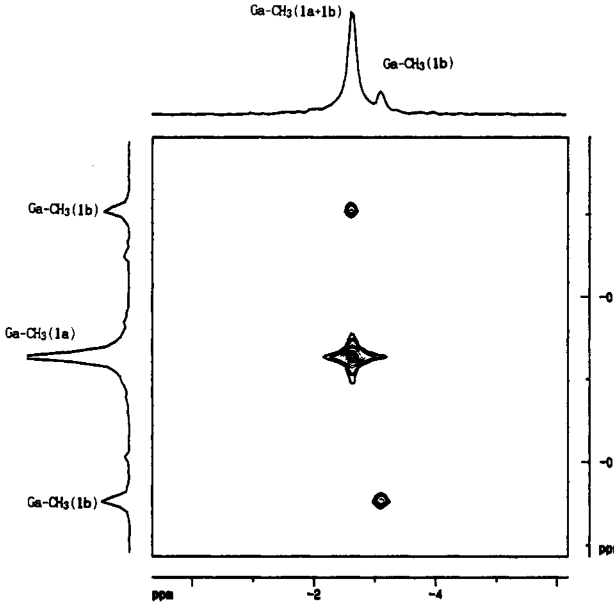

Figure 1. Partial 2D ^1H–^{13}C correlated NMR spectrum (500 MHz, $CDCl_3$) of 1. The ^{13}C NMR spectrum is projected horizontally, and the ^1H NMR spectrum vertically.

The trans → cis isomerization reaction was studied by ^1H NMR spectroscopy. Typical time-resolved ^1H NMR spectra of **1a** in toluene-d_8 at 80 °C are shown in Figure

---

[8] MolEN, An Interative Structure Solution Procedure. Enraf-Nonius, Delft, The Netherlands, 1990.

[9] Walker, N.; Stuart, D. *Acta Crystallogr.* 1983, *A39*, 158.

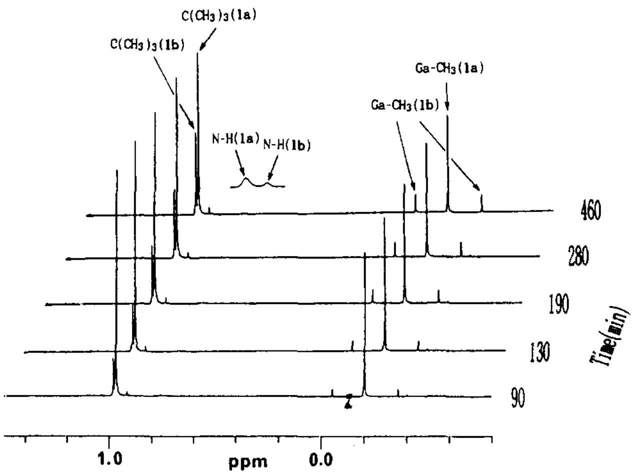

Figure 2. Time-resolved ^{1}H NMR spectra (300 MHz, toluene-d_8) of **1a** and **1b** at 80 °C.

Table III. Kinetic and Thermodynamic Data in Toluene-d_8

t, °C	K_{eq}	10^3k_{obs}, min^{-1}	10^3k_1, min^{-1}	10^3k_{-1}, min^{-1}
60	0.563 ± 0.014	0.319 ± 0.016	0.115 ± 0.006	0.204 ± 0.010
70	0.581 ± 0.010	1.11 ± 0.03	0.408 ± 0.011	0.702 ± 0.019
80	0.598 ± 0.013	4.07 ± 0.26	1.52 ± 0.10	2.55 ± 0.16
88	0.613 ± 0.016	9.33 ± 0.30	3.55 ± 0.11	5.78 ± 0.19
96[a]	0.628 ± 0.015			
100[a]	0.633 ± 0.016			

[a] Rate data could not be obtained due to instability of the NMR instrument above 90 °C for a long period.

2. As the intensities of the resonances of **1a** decrease, the resonances corresponding to $C(CH_3)_3$ and $Ga-CH_3$ of **1b** increase in intensity. Relative concentrations of the two isomers were measured by integration of the peaks due to $Ga-CH_3$ at δ -0.15 for **1a** and at δ 0.0081 and -0.30 for **1b**. Analyses according to reversible first-order kinetics give excellent fits of experimental data, as is shown in Figure 3. The kinetic and thermodynamic data are listed in Table III. The equilibrium constants, K_{eq}, measured for the isomerization range from 0.563 ± 0.014 at 60 °C to 0.633 ± 0.016 at 100 °C, indicating **1a** is favored in this equilibrium. The plot of ln K_{eq} vs $1/T$ (correlation coefficient, 0.9994) yields $\Delta H° = 3.12 \pm 0.04$ kJ mol^{-1} and $\Delta S° = 4.56 \pm 0.06$ J mol^{-1} K^{-1} for the process, **1a** → **1b**. The trans isomer is thermodynamically more stable, but the positive entropy change favors the cis isomer. The $T\Delta S$ term is apparently responsible for the conversion of **1a** to **1b**. This may be due to the descent in symmetry from **1a** to **1b**. Activation parameters derived from the Eyring plots of ln (k/T) vs $1/T$ and ln (k_{-1}/T) vs $1/T$ (correlation coefficient, 0.9996 and 0.9995, respectively) are $\Delta H_1 = 120.8 \pm 7.4$ kJ mol^{-1} and $\Delta S_1 = 41.4 \pm 2.6$ J mol^{-1} K^{-1} for the forward isomerization **1a** → **1b** and $\Delta H_{-1} = 117.8 \pm 7.9$ kJ mol^{-1} and $\Delta S_{-1} = 37.3 \pm 2.5$ J mol^{-1} K^{-1} for the reverse isomerization **1b** → **1a**. The net enthalpy and entropy changes for **1a** → **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. The relatively large positive values of ΔS_1 and ΔS_{-1} reflect that the symmetry in the transition state is considerably reduced from that in **1a** and **1b**.

Kinetic studies of cis-trans isomerization of dimeric amidogallanes is unprecedented. Lack of the kinetic studies appears to be due to the difficulties in obtaining pure cis or trans isomer and/or kinetic instability of amidogallanes. Thermolysis of trans, dimeric amidogallanes was reported to afford either oligomeric complexes via alkane elimination[10] or cyclometalated products via C-H bond activation.[6] The only reported cis-trans isomerization study of a dimeric amidogallane complex is that of the species $[Me_2Ga(\mu-NMePh)]_2$: thermodynamic parameters for the isomerization ($\Delta H° = 4.16$ kJ mol^{-1}, $\Delta S° = 21.8$ eu) were calculated from equilibrium constants at various temperatures [K_{eq} (34 °C) = [cis]/[trans] = 2.53].[11]

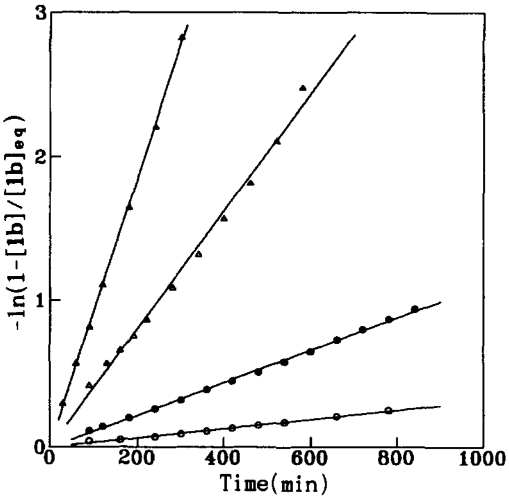

Figure 3. Kinetics plots of the isomerization of **1a** to **1b** in toluene-d_8 at 60 (○), 70 (●), 80 (tuo), and 88 (tus) °C.

The two most obvious pathways of the isomer interconversion are (1) initial breaking of a Ga-N bond, followed by rotation about the nonbridged Ga-N bond and rebridging, or (2) complete dissociation of the dimer and reassociation of the monomers. The isomerization of **1a** to **1b** is markedly accelerated in the presence of pyridine (ca. 8 times with 1.3 equiv of pyridine at 70 °C). Similar acceleration and formation of an adduct between an amidoaluminane and a Lewis base have been observed previously in the case of $[Me_2Al(\mu-NMePh)]_2$ and 4-methylpyridine.[12] However, formation of an intermediate in the present case was not observed, when monitored by ^{1}H NMR spectroscopy. Coordination of the pyridine to the gallium atom of **1a** may result in facile scission of a Ga-N bond and thus lower the barrier of the isomerization to **1b**. The crossover reaction of $[Me_2Ga(\mu-NH^tBu)]_2$ and $[Me_2Al(\mu-NH^tBu)]_2$[13] was carried out in toluene-d_8. No indication of formation of $Me_2Ga(\mu-NH^tBu)_2AlMe_2$ was observed in the NMR spectrum when the reaction mixture was heated for a prolonged period (15 h) at 70 °C. This result indicates that the isomerization is a unimolecular process, which is further supported by the crossover reaction of the analogous amidoaluminane complex.[14] In conclusion, the former pathway is consistent with the observed results for the cis-trans isomerization of **1**. Therefore, ΔH_1 and ΔH_{-1} obtained for **1** may reflect the bond strength of the dissociating Ga-N bonds in **1a** and **1b**, respectively. For comparison, we note that the Ga-N bond dissociation enthalpy of 88 kJ mol^{-1} is found for the adduct Me_3GaNMe_3[15] and the activation energy of 96 kJ

---

[10] Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206.

[11] Beachley, O. T., Jr.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* **1981**, *20*, 2423.

[12] Wakatsuki, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1475.

[13] The compound $[Me_2Al(\mu-NH^tBu)]_2$ has been reported to exist only as the trans isomer in solution up to 190 °C: Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1985**, 1929. However, we observed that this compound undergoes cis-trans isomerization even at room temperature.

[14] No evidence for the formation of $Me_2Al(\mu-NH^tBu)_2AlEt_2$ was observed from the crossover reaction of $[Me_2Al(\mu-NH^tBu)]_2$ and $[Et_2Al(\mu-NH^tBu)]_2$. J. T. Park et al., to be submitted for publication.

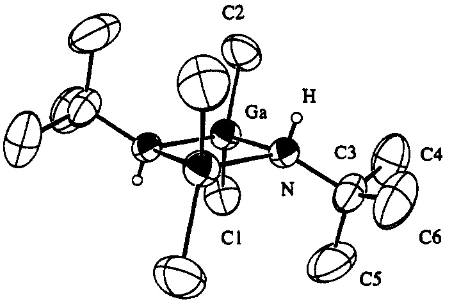

Figure 4. Molecular geometry and atomic labeling for **1a**. Hydrogen atoms except for NH were omitted for clarity.

Table IV. Bond Lengths (Å) and Angles (deg) with Esd's for $[Me_2Ga(\mu\text{-}NH^tBu)]_2$ (1a)

	Bond Lengths		
Ga–N	2.022 (4)	Ga···Ga′	2.9755 (9)
Ga′–N	2.024 (4)	Ga···H	2.28 (4)
Ga–C1	1.979 (6)	Ga′···H	2.29 (4)
Ga–C2	1.964 (7)	N···N′	2.741 (6)
C3–C4	1.507 (10)	N–C3	1.495 (6)
C3–C5	1.515 (9)	N–H	0.73 (4)
C3–C6	1.512 (10)		
	Bond Angles		
N–Ga–N′	85.3 (2)	N–C3–C4	108.7 (5)
N–Ga–C1	116.6 (2)	N–C3–C5	109.9 (5)
N–Ga–C2	107.9 (3)	N–C3–C6	109.1 (4)
C1–Ga–C2	118.5 (3)	C4–C3–C5	109.6 (6)
Ga–N–Ga′	94.7 (2)	C4–C3–C6	109.9 (6)
Ga–N–C3	125.4 (3)	C5–C3–C6	109.6 (6)
Ga′–N–C3	125.4 (4)	Ga–N–H	102 (3)
		Ga′–N–H	102 (3)
		C3–N–H	104 (3)

mol^{-1} is reported for the exchange process of Me_3N between molecules of Me_3Ga.[16]

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 IV. The molecule has a centrosymmetric and dimeric structure with gallium atoms bridged by $-NH^tBu$. The coordination of the gallium atoms is in a distorted-tetrahedral environment with interligand angles ranging from N–Ga–N′ = 85.3 (2)° to C1–Ga–C2 = 118.5 (3)°. The gallium–methyl bond lengths, Ga–C1 = 1.979 (6) Å and Ga–C2 = 1.964 (7) Å suggest a covalent radius of 1.20 Å for gallium(III) in this type of environment.[17] The $(Ga-N)_2$ core structure is planar; the bond distances are Ga–N = Ga′–N′ = 2.022 (4) and Ga–N′ = Ga′–N = 2.024 (4) Å, which are close to those observed in other dimers.[4-6] The internal angles in the planar $(Ga-N)_2$ core are 85.3 (2)° at gallium and 94.7 (2)° at nitrogen. The obtuse Ga–N–Ga′ angle of 94.7 (2)° and long Ga···Ga′ distance of 2.9755 (9) Å indicate that there is no gallium–gallium bonding.

As shown in Figure 4, the bridging NH^tBu groups take up a mutually trans arrangement which has been observed for all other known amidogallanes.[4-6] The N–H bond distance of 0.73 (4) Å in **1a** is unusually short, yet the origin of the short N–H bond distance is not well understood at the moment. The following N–H distances have been previously observed in other dimeric amidogallanes: 0.84 (5) Å in $[Me_2Ga(\mu\text{-}NHAd)]_2$,[6] 0.87 (7) Å in $[Me_2Ga(\mu\text{-}NHPh)]_2$,[6] 0.95 (4) Å in $[Me_2Ga(\mu\text{-}NHDipp)]_2$,[6] and 1.105 Å in $[^tBu_2Ga(\mu\text{-}NHPh)]_2$.[4] The amide hydrogen is almost symmetrically located 2.29 (4) Å from both gallium atoms. The C3–N–H bond angle is an expected value of 104 (3)°. However, the C–N–H angle in $[^tBu_2Ga(\mu\text{-}NHPh)]_2$ was reported to be unusually acute, 74.5°, which was explained by considering that the amide proton is attracted to the electron density of the $(Ga-N)_2$ ring.[4] All other features of the molecular geometry are within the expected range. The Ga–C bond lengths are 1.969 (7) and 1.979 (6) Å, and carbon–carbon distances range from 1.507 (10) to 1.515 (9) Å.

Acknowledgment. We are grateful to the Korea Advanced Institute of Science and Technology (KAIST) for partial financial support of this research. Additional support to Yunsoo Kim was provided by the Ministry of Science and Technology of Korea. K.K. thanks POSTECH for support of the X-ray analysis. Professor S. Kim of KAIST is thanked for valuable discussions, and Mr. H.-S. Shin is acknowledged for help with NMR measurements.

Supplementary Material Available: A table of anisotropic thermal parameters for **1a** (1 page). Ordering information is given on any current masthead page.

OM920170N

---

(15) Coates, G. E.; Huck, N. D. *J. Chem. Soc.* **1952**, 4501.

(16) DeRoos, J. B.; Oliver, J. P. *Inorg. Chem.* **1965**, *4*, 1741.

(17) The average value of Ga–C lengths [1.972 (7) Å] − the covalent radius of carbon (0.77 Å) = 1.20 Å.