

## *Trans*–*cis* isomerization and structure of dimeric [Me<sub>2</sub>M–μ–N(H)NPh<sub>2</sub>]<sub>2</sub> (M = Al, Ga)

Dongwon Cho, Jae E. Park, Byoung-Jae Bae, Kwangyeol Lee, Bongsoo Kim,  
Joon T. Park \*

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

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### Abstract

Reaction of MMe<sub>3</sub> (M = Al, Ga) with one equivalent of NH<sub>2</sub>NPh<sub>2</sub> affords a dimeric complex [Me<sub>2</sub>M–μ–N(H)NPh<sub>2</sub>]<sub>2</sub> [M = Al (**1**), M = Ga (**2**)] as a mixture of *trans* and *cis* isomers. Purification of **1** and **2** by recrystallization gives only *trans* isomers **1a** and **2a**, respectively. Variable-temperature <sup>1</sup>H-NMR studies reveal that both **1** and **2** in solution undergo *trans* → *cis* isomerization with free energy of activation (Δ*G*<sub>‡</sub>) values of 15.9 for **1** and 18.3 kcal mol<sup>-1</sup> for **2**. The solid state structures of *trans* isomers **1a** and **2a** have been determined by single-crystal X-ray diffraction studies. The molecular geometries of **1a** and **2a** consist of a centrosymmetric and dimeric unit (M–N)<sub>2</sub> with two bridging hydrazido groups and two terminal methyl groups bound to each metal atom. The two N–NPh<sub>2</sub> groups are *trans* to each other with respect to the (M–N)<sub>2</sub> core plane. The coordination geometry of both metal and nitrogen atoms are distorted tetrahedral. © 1999 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

The wide bandgap semiconductor Group 13 nitride MN (M = Al, Ga) currently receives tremendous attention due to the possibility of blue light-emitting lasers and light-emitting diodes [1]. The most successful MN (M = Al, Ga) thin films have been obtained from harsh conditions (> 900°C) using MR<sub>3</sub> and ammonia [2–5]. The high temperatures, however, can cause thermal stresses as well as nitrogen deficiency in the prepared films. Alternative nitrogen sources such as hydrazine (N<sub>2</sub>H<sub>4</sub>) [6,7], 1,1-dimethylhydrazine (NH<sub>2</sub>NMe<sub>2</sub>) [8,9], and hydrogen azide (HN<sub>3</sub>) [10–12] have been proposed to solve these problems. Single-source OMCVD (organometallic chemical vapor deposition) precursors, which can decompose at much lower temperatures, may

provide viable alternative preparation routes to the desired MN films [13–18].

We have been interested in the preparation of Group 13 MN single-source precursors, and reported the synthesis and characterization of 1,1-dimethylhydrazine derivatives [Me<sub>2</sub>M–μ–N(H)NMe<sub>2</sub>]<sub>2</sub> (**3**, M = Al; **4**, M = Ga) in previous work [19]. These dimeric hydrazido complexes exist as both *trans* and *cis* isomers in solution. We have proposed that the *trans*–*cis* isomerization of **3** and **4** is facilitated by the presence of free NMe<sub>2</sub> group in the hydrazido moiety as an internal base. To further examine the nature of the *trans*–*cis* isomerization in these hydrazido complexes, we have investigated the effect of less basic NPh<sub>2</sub> moiety in 1,1-diphenylhydrazine than the NMe<sub>2</sub> group in 1,1-dimethylhydrazine on the isomerization. Herein we report the synthesis and characterization of [Me<sub>2</sub>M–μ–N(H)NPh<sub>2</sub>]<sub>2</sub> [M = Al (**1**), Ga (**2**)] as well as the hydrazido moiety effect on the *trans* (**a**)–*cis* (**b**) isomerization of hydrazido complexes.

\* Corresponding author. Fax: +82-42-869-2810.

E-mail address: jtpark@sorak.kaist.ac.kr (J.T. Park)

## 2. Experimental

### 2.1. General comments

All experiments were performed under argon either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Dichloromethane was refluxed over  $\text{CaH}_2$  and then distilled under argon atmosphere. *n*-Hexane, toluene, and ether were distilled over sodium/benzophenone under an argon atmosphere. Trimethylaluminum and trimethylgallium were purchased from Strem Chemicals, and were used without further purification. 1,1-Diphenylhydrazine was prepared from its hydrochloride salt (97%, Aldrich) by the procedure reported previously [20].

Infrared spectra were obtained as KBr pellets with a Bruker Equinox-55 FTIR spectrophotometer.  $^1\text{H-NMR}$  (300 MHz) and  $^{13}\text{C-NMR}$  (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Melting points were obtained in sealed capillaries under argon (1 atm) and are uncorrected. Mass spectra were recorded on a Jeol JMS-SX-102A mass spectrometer. Microanalytical data were provided by Oneida Research Services, USA.

### 2.2. Synthesis of $[\text{Me}_2\text{Al-}\mu\text{-N(H)NPh}_2]_2$ (**1**)

A dichloromethane solution (10 ml) of 1,1-diphenylhydrazine (0.825 g, 4.48 mmol) was added dropwise to a stirred solution of trimethylaluminum (0.314 g, 4.35 mmol) in dichloromethane (10 ml) at room temperature (r.t.). The reaction mixture was heated to reflux for 5 h. The solvent and volatiles were removed in vacuo. Slow recrystallization of the residue from the dichloromethane/hexane solution at  $-20^\circ\text{C}$  gave *trans* isomer **1a** (0.630 g, 1.31 mmol, 60%) as colorless crystals: m.p.  $171^\circ\text{C}$  (dec.);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-1.01$  (s, 12H, Al–Me), 4.11 (s, 2H, N–H), 7.03 ~ 7.08, 7.24 ~ 7.30 (m, 20H, NPh<sub>2</sub>);  $^1\text{H-NMR}$  (toluene-*d*<sub>8</sub>,  $5^\circ\text{C}$ )  $\delta$   $-0.73$  (s, 12H, Al–Me), 3.95 (s, 2H, N–H), 6.74 ~ 6.79, 6.89 ~ 7.05 (m, 20H, NPh<sub>2</sub>);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-9.97$  (s, Al–Me), 121.57, 121.75, 124.26, 129.17, 151.29, 151.47 (NPh<sub>2</sub>). IR  $\nu(\text{NH})$   $3171\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{34}\text{Al}_2\text{N}_4$ : C, 69.98; H, 7.13; N, 11.66. Found: C, 69.76; H, 6.50; N, 10.89%.

*Cis* isomer **1b** (data obtained from an equilibrium mixture):  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-1.21$  (s, 6H, Al–Me),  $-0.68$  (s, 6H, Al–Me), 3.95 (s, 2H, N–H), 7.03 ~ 7.08, 7.24 ~ 7.30 (m, 20H, NPh<sub>2</sub>);  $^1\text{H-NMR}$  (toluene-*d*<sub>8</sub>,  $5^\circ\text{C}$ )  $\delta$   $-0.84$  (s, 6H, Al–Me),  $-0.51$  (s, 6H, Al–Me), 3.72 (s, 2H, N–H), 6.74 ~ 6.79, 6.89 ~ 7.05 (m, 20H, NPh<sub>2</sub>);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-12.32$  (s, Al–Me),  $-7.08$  (s, Al–Me), 121.57, 121.75, 124.26, 129.17, 151.29, 151.47 (NPh<sub>2</sub>).

### 2.3. Synthesis of $[\text{Me}_2\text{Ga-}\mu\text{-N(H)NPh}_2]_2$ (**2**)

A toluene solution (10 ml) of 1,1-diphenylhydrazine (0.529 g, 2.87 mmol) was added slowly to a stirred solution of trimethylgallium (0.326 g, 2.84 mmol) in toluene (10 ml) at r.t. The reaction mixture was heated to reflux for 5 h. The solvent and volatiles were removed in vacuo. Slow recrystallization from a dichloromethane/toluene/hexane solution at  $-20^\circ\text{C}$  gave the *trans* isomer **2a** (0.504 g, 0.89 mmol, 63%) as colorless crystals: m.p.  $185^\circ\text{C}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-0.58$  (s, 12H, Ga–Me), 3.99 (s, 2H, N–H), 6.97 ~ 7.02, 7.22 ~ 7.28 (m, 20H, NPh<sub>2</sub>);  $^1\text{H-NMR}$  (toluene-*d*<sub>8</sub>,  $25^\circ\text{C}$ )  $\delta$   $-0.39$  (s, 12H, Al–Me), 3.83 (s, 2H, N–H), 6.75 ~ 6.87, 6.95 ~ 7.00 (m, 20H, NPh<sub>2</sub>);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-7.03$  (s, Ga–Me), 121.29, 121.46, 123.60, 129.02, 129.05, 151.25, 151.42 (NPh<sub>2</sub>). MS (70 eV)  $m/z$  564 ( $\text{M}^+$ ,  $^{69}\text{Ga}$ ); IR  $\nu(\text{NH})$   $3188\text{ cm}^{-1}$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{34}\text{Ga}_2\text{N}_4$ : C, 59.41; H, 6.05; N, 9.90. Found: C, 59.29; H, 5.68; N, 9.41%.

*Cis* isomer **2b** (data obtained from an equilibrium mixture):  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-0.83$  (s, 6H, Ga–Me),  $-0.21$  (s, 6H, Ga–Me), 3.94 (s, 2H, N–H), 6.97 ~ 7.02, 7.22 ~ 7.28 (m, 20H, NPh<sub>2</sub>);  $^1\text{H-NMR}$  (toluene-*d*<sub>8</sub>,  $25^\circ\text{C}$ )  $\delta$   $-0.54$  (s, 6H, Al–Me),  $-0.14$  (s, 6H, Al–Me), 3.72 (s, 2H, N–H), 6.75 ~ 6.87, 6.95 ~ 7.00 (m, 20H, NPh<sub>2</sub>);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ )  $\delta$   $-9.73$  (s, Ga–Me),  $-3.49$  (s, Ga–Me), 121.29, 121.46, 123.60, 129.02, 129.05, 151.25, 151.42 (NPh<sub>2</sub>).

### 2.4. X-ray data collection and structure solution of **1a** and **2a**

Colorless crystals of *trans* isomers **1a** and **2a** were mounted in thin-walled glass capillaries under an argon atmosphere and then flame-sealed. The determination of unit cell parameters and collection of intensity data were made on an Enraf–Nonius CAD4 diffractometer utilizing graphite-monochromated  $\text{Mo-K}\alpha$  radiation. The accurate cell parameters of **1a** and **2a** were obtained from 24 reflections in the range  $11.56^\circ < \theta < 15.30^\circ$  and from 25 reflections in the range  $11.75^\circ < \theta < 14.19^\circ$ , respectively. Reflections were measured with the index range  $-7 < h < 7$ ,  $-11 < k < 11$ ,  $0 < l < 26$  using  $\omega$ - $2\theta$  scan mode ( $\omega$  scan angle =  $(0.8 + 0.35 \tan \theta)^\circ$  with  $2\theta_{\text{max}} = 50^\circ$  (**1a**) and  $2\theta_{\text{max}} = 46^\circ$  (**2a**)). Intensities of three standard reflections monitored every 4 h showed no significant decay over the course of data collection. Lorentz and polarization corrections were applied to the intensity data. Crystallographic data and details of data collection are summarized in Table 1. All calculations were carried out with the SHELXTL computer programs [21]. The structures were solved by direct methods and were refined by the full-matrix least-squares methods employing unit weights. All non-hydrogen atoms were refined an-

isotropically while hydrogen atoms were refined isotropically with common thermal parameters. The maximum shifts to sigma ratio were less than 0.001. The highest and deepest peaks in the last difference map were 0.199 and  $-0.197 \text{ e } \text{Å}^{-3}$  for **1a**, and 0.593 and  $-0.616 \text{ e } \text{Å}^{-3}$  for **2a**. There are two equivalent molecules in the crystallographic unit for both **1a** and **2a**.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of **1a–2b**

Reactions of  $\text{MMe}_3$  ( $\text{M} = \text{Al}, \text{Ga}$ ) with one equivalent of  $\text{NH}_2\text{NPh}_2$  produce the dimeric hydrazidoalane  $[\text{Me}_2\text{Al}-\mu\text{-N}(\text{H})\text{NPh}_2]_2$  (**1**) and hydrazidogallane  $[\text{Me}_2\text{Ga}-\mu\text{-N}(\text{H})\text{NPh}_2]_2$  (**2**) complexes as mixtures of *trans* and *cis* isomers (ca. 1:1 ratio) by methane elimination. The dimeric formulation has been indicated by observation of the molecular ion of **2** in the EI mass spectrum, but the molecular ion of **1** could not be observed. Purification of compounds **1** and **2** by recrystallization affords colorless crystals of *trans* isomers, **1a** and **2a**, respectively. X-ray crystal structure determination revealed that only *trans* isomers **1a** and **2a** exist in

Table 1  
Crystallographic data for **1a** and **2a**

	<b>1a</b>	<b>2a</b>
Formula	$\text{Al}_2\text{N}_4\text{C}_{28}\text{H}_{34}$	$\text{Ga}_2\text{N}_4\text{C}_{28}\text{H}_{34}$
Formula weight	480.55	566.03
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	6.495(3)	6.593(3)
<i>b</i> (Å)	9.977(2)	9.906(1)
<i>c</i> (Å)	22.490(3)	22.636(3)
$\alpha$ (°)	92.22(1)	82.45(1)
$\beta$ (°)	98.17(2)	81.68(2)
$\gamma$ (°)	108.91(2)	70.71(2)
<i>V</i> (Å <sup>3</sup> )	1359.2(8)	1370.1(7)
<i>Z</i>	2	2
<i>T</i> (K)	291	291
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.174	1.372
Crystal size (mm)	0.693 × 0.66	0.528 × 0.462
	× 0.363	× 0.132
Radiation	Mo-K $\alpha$	Mo-K $\alpha$
$\lambda$ (Å)	0.71069	0.71069
$\mu$ (mm <sup>-1</sup> )	0.129	1.941
No. of unique reflections	3880	3917
No. of observed reflections ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3768	3804
<i>R</i> <sup>a</sup>	0.0446	0.0590
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0993	0.1184
Goodness-of-fit <sup>c</sup>	1.076	1.062

<sup>a</sup>  $R = (\sum |F_o| - |F_c|) / \sum |F_o|$ .

<sup>b</sup>  $R_w = \{[\sum w(|F_o| - |F_c|)^2] / \sum w |F_o|^2\}^{1/2}$ .

<sup>c</sup> Goodness-of-fit =  $\{[\sum w(|F_o| - |F_c|)^2] / (N_{\text{observns}} - N_{\text{params}})\}^{1/2}$ .

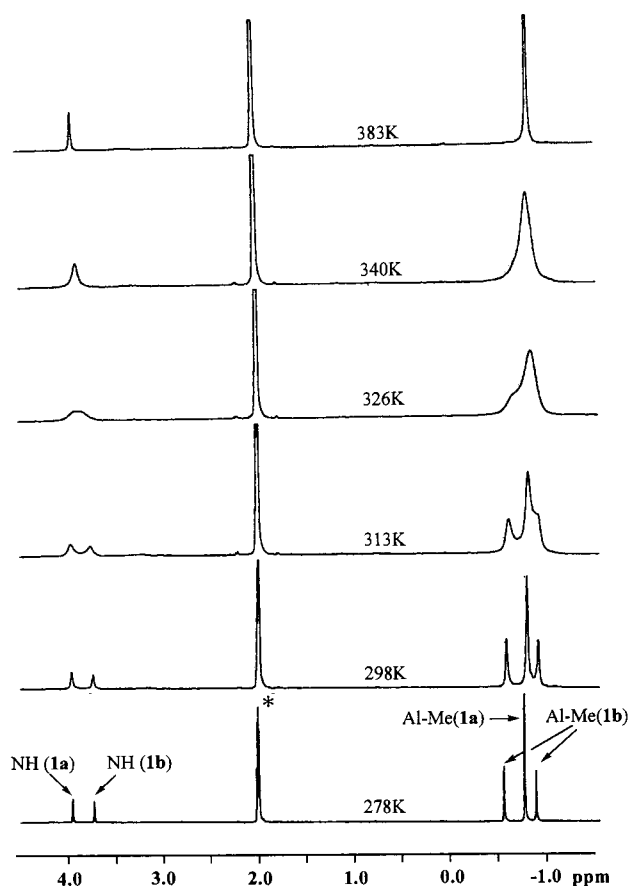
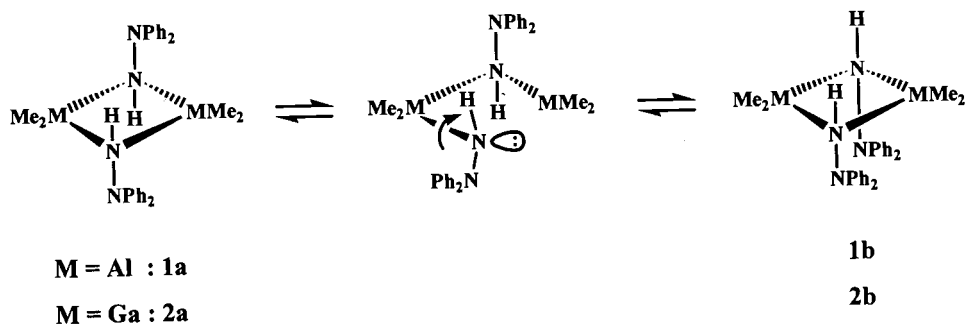


Fig. 1. VT <sup>1</sup>H-NMR spectra (300 MHz, toluene-*d*<sub>8</sub>, solvent peaks (\*) of **1**.

the solid state (vide infra), but in solution *trans* isomers **1a** and **2a** equilibrate with respective *cis* isomers **1b** and **2b**. IR spectra (KBr pellets) of **1a** and **2a** contain one strong  $\nu(\text{NH})$  stretch as expected for the *trans* isomer at 3171 and 3188  $\text{cm}^{-1}$ , respectively. Two possible  $\nu(\text{NH})$  stretches for the corresponding *cis* isomer, however, could not be observed in the IR spectra of each equilibrium mixture of **1** and **2**. Similar features of IR spectra were observed with compounds  $[\text{Me}_2\text{Al}-\mu\text{-N}(\text{H})\text{NMe}_2]_2$  (**3**) and  $[\text{Me}_2\text{Ga}-\mu\text{-N}(\text{H})\text{NMe}_2]_2$  (**4**), and the  $\nu(\text{NH})$  stretches for the *trans* isomers (**1a** and **2a**) compare with those for **3a** (3131  $\text{cm}^{-1}$ ) and **4a** (3136  $\text{cm}^{-1}$ ) [19].

Variable-temperature (VT) <sup>1</sup>H-NMR spectra (278 ~ 383 K) of a *trans-cis* mixture of **1** in toluene-*d*<sub>8</sub> are shown in Fig. 1. The limiting low temperature spectrum at 278 K shows a single peak at  $\delta -0.73$  for the Al-Me groups of *trans-1a* and two distinct resonances at  $\delta -0.84$  and  $-0.51$  due to the inequivalent Al-Me groups of *cis-1b*. As the temperature increases, both N-H ( $\delta$  3.95 for **1a** and 3.72 for **1b**) and Al-Me signals become broad and the two N-H peaks coalesce to a single peak at 326 K. Free energy of activation ( $\Delta G_{\ddagger}$ ,  $T_c = 326 \text{ K}$ ) value of 15.9 kcal mol<sup>-1</sup> for the *trans* → *cis*



Scheme 1.

isomerization of **1** was derived from the coalescence temperature and peak separation of the N–H resonances using the Eyring equation [22]. General features of VT  $^1\text{H-NMR}$  spectra of **2** in toluene- $d_8$  are essentially identical with those of **1**, and a similar line shape analysis gives  $\Delta G_c^\ddagger = 18.3 \text{ kcal mol}^{-1}$  ( $T_c = 363 \text{ K}$ ) for the isomerization process of **2**. Both VT  $^1\text{H-NMR}$  spectra of **1** and **2** show reversible temperature behaviors.

We have previously reported kinetic studies of the *trans*–*cis* isomerization for various dimeric amidalanes and amidogallanes such as **3**, **4**,  $[\text{Me}_2\text{M}-\mu\text{-N}(\text{H})\text{Bu}]_2$  ( $\text{M} = \text{Al}$  (**5**) [23],  $\text{Ga}$  (**6**) [24]), and  $[\text{Me}_2\text{Al}(\mu\text{-NC}_2\text{H}_4\text{NMe}_2\text{AlMe}_2)]_2$  (**7**) [25], in which the isomerization pathway is proposed to be an initial breaking of the M–N bond, followed by rotation about the nonbridged M–N bond and rebridging as shown in Scheme 1.

The rate of isomerization, therefore, has been markedly accelerated by Lewis bases due to the facile cleavage of the M–N bond by an attack of Lewis bases on the M atom, as was well documented in  $[\text{Me}_2\text{M}-\mu\text{-N}(\text{Me})\text{Ph}]_2$  ( $\text{M} = \text{Al}$ ,  $\text{Ga}$ ) [**26**], **5** and **6**. The isomerization of **3**, **4** and **7**, however, was not affected by external bases (ca. one equivalent of pyridine or 4-methylpyridine). This observation was proposed to be attributed to the role of  $\text{NMe}_2$  end of the hydrazido (**3** and **4**) and the dimethylethylenediamine (**7**) moieties as internal Lewis bases in facilitating the M–N bond scission via an intermolecular process during isomerization process. The isomerizations of **1** and **2** are assumed to follow similar isomerization pathways to those of **3**, **4** and **7**. The  $\Delta G_c^\ddagger$  values obtained for **1** ( $15.9 \text{ kcal mol}^{-1}$ ) and **2** ( $18.3 \text{ kcal mol}^{-1}$ ) are larger than those for **3** ( $9.3 \text{ kcal mol}^{-1}$ ) and **4** ( $15.6 \text{ kcal mol}^{-1}$ ) [19], clearly reflecting the weaker basic nature of the  $\text{NPh}_2$  moiety in **1** and **2** compared to the  $\text{NMe}_2$  moiety in **3** and **4** as an internal base (cf.  $K_b = 6 \times 10^{-14}$  for  $\text{Ph}_2\text{NH}$  [27] and  $K_b = 5.4 \times 10^{-4}$  for  $\text{Me}_2\text{NH}$  [28]). Consistent with Lewis acidities of Group 13 elements ( $\text{Me}_3\text{Al} > \text{Me}_3\text{Ga}$ ) [29], the aluminum analogs **1** and **3** undergo a faster isomerization than the gallium analogs **2** and **4**. The

observations with hydrazido complexes **1** and **2** further support the isomerization mechanism shown in Scheme 1.

### 3.2. Crystal structures of **1a** and **2a**

The overall molecular geometry of *trans* isomer **1a** with the atomic labeling scheme is shown in Fig. 2. Selected bond distances and angles of two equivalent molecules of **1a** are listed in Table 2. The molecule has a centrosymmetric and dimeric structure with aluminum atoms bridged by  $\text{N}(\text{H})\text{NPh}_2$ . The aluminum atoms are in distorted tetrahedral environments with interligand angles ranging from  $\text{N}(1)\text{--Al}(1)\text{--N}(1') = 87.4(1)$  to  $\text{C}(1)\text{--Al}(1)\text{--C}(2) = 123.6(2)^\circ$ . The  $(\text{Al}\text{--N})_2$  core structure is planar; the bond distances are  $\text{Al}(1)\text{--N}(1) = \text{Al}(1')\text{--N}(1') = 1.976(3)$  and  $\text{Al}(1)\text{--N}(1') = \text{Al}(1')\text{--N}(1) = 1.989(3) \text{ \AA}$ . The internal angle at nitrogen ( $92.6(1)^\circ$ ) is larger than that at aluminum ( $87.4(1)^\circ$ ), which is a general structural feature of the  $(\text{M}\text{--N})_2$  cores of virtually all Group 13/15 dimers. The sum ( $344.8^\circ$ ) of the angles  $\text{C}(3)\text{--N}(2)\text{--N}(1)$ ,  $\text{C}(9)\text{--N}(2)\text{--N}(1)$ , and  $\text{C}(3)\text{--N}(2)\text{--C}(9)$  is larger than that ( $326.5^\circ$ ) in the analogous compound *trans*- $[\text{Me}_2\text{Al}-\mu\text{-N}(\text{H})\text{NMe}_2]_2$  (**3a**) [19]. This structural feature indicates that the electron density of the lone pairs of  $\text{N}(2)$  and

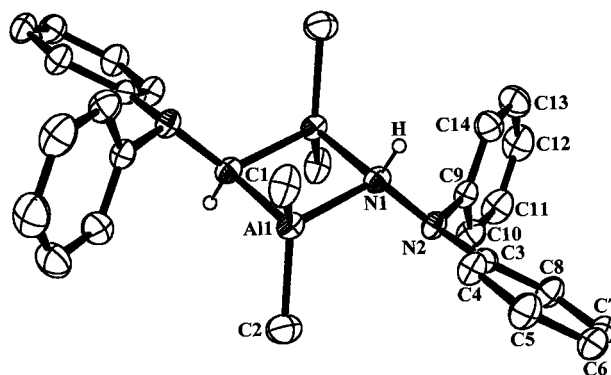


Fig. 2. Molecular geometry and atomic labeling for **1a**. Hydrogen atoms except for NH were omitted for clarity.

Table 2

Bond lengths (Å) and angles (°) with estimated S.D. values for two equivalent molecules of [Me<sub>2</sub>Al-μ-N(H)NPh<sub>2</sub>]<sub>2</sub> (**1a**)<sup>a</sup>

<i>Bond lengths</i>			
Al(1)–N(1)	1.976(3), 1.976(3)	N(1)–N(2)	1.454(3), 1.456(3)
Al(1)–N(1')	1.989(3), 1.985(2)	N(2)–C(3)	1.423(4), 1.421(4)
Al(1)–C(1)	1.956(3), 1.955(3)	N(2)–C(9)	1.442(4), 1.441(4)
Al(1)–C(2)	1.936(3), 1.941(4)	Al(1)⋯Al(1')	2.867(2), 2.866(2)
<i>Bond angles</i>			
N(1)–Al(1)–N(1')	87.4(1), 87.3(1)	Al(1)–N(1)–Al(1')	92.6(1), 92.7(1)
N(1)–Al(1)–C(1)	107.7(1), 107.6(1)	Al(1)–N(1)–N(2)	119.9(2), 120.1(2)
N(1)–Al(1)–C(2)	110.6(2), 110.2(2)	Al(2)–N(1)–N(2)	118.8(2), 118.7(2)
N(1')–Al(1)–C(1)	113.8(1), 113.8(1)	N(1)–N(2)–C(3)	116.4(2), 116.0(2)
N(1')–Al(1)–C(2)	107.8(1), 108.1(1)	N(1)–N(2)–C(9)	113.2(2), 113.3(2)
C(1)–Al(1)–C(2)	123.6(2), 124.0(2)	C(3)–N(2)–C(9)	115.2(2), 115.6(2)

<sup>a</sup> Atoms related by the *i*-symmetry operations are labeled with a prime.

Table 3

Bond lengths (Å) and angles (°) with estimated S.D. values for two equivalent molecules of [Me<sub>2</sub>Ga-μ-N(H)NPh<sub>2</sub>]<sub>2</sub> (**2a**)<sup>a</sup>

<i>Bond lengths</i>			
Ga(1)–N(1)	2.040(7), 2.037(6)	N(1)–N(2)	1.436(8), 1.437(8)
Ga(1)–N(1')	2.048(6), 2.047(6)	N(2)–C(3)	1.445(10), 1.432(10)
Ga(1)–C(1)	1.945(9), 1.948(9)	N(2)–C(9)	1.424(10), 1.431(10)
Ga(1)–C(2)	1.971(9), 1.965(8)	Ga(1)⋯Ga(1')	2.965(2), 2.969(2)
<i>Bond angles</i>			
N(1)–Ga(1)–N(1')	87.0(3), 86.7(2)	Ga(1)–N(1)–Ga(1')	93.0(3), 93.3(3)
N(1)–Ga(1)–C(1)	108.9(4), 109.1(4)	Ga(1)–N(1)–N(2)	119.4(5), 120.1(5)
N(1)–Ga(1)–C(2)	106.7(3), 107.5(3)	Ga(2)–N(1)–N(2)	118.8(4), 119.1(4)
N(1')–Ga(1)–C(1)	106.5(4), 106.9(3)	N(1)–N(2)–C(3)	114.3(6), 114.0(6)
N(1')–Ga(1)–C(2)	112.8(3), 112.1(3)	N(1)–N(2)–C(9)	117.3(6), 115.7(6)
C(1)–Ga(1)–C(2)	127.5(5), 127.1(4)	C(9)–N(2)–C(3)	114.0(6), 116.5(6)

<sup>a</sup> Atoms related by the *i*-symmetry operations are labeled with a prime.

N(2') atoms is delocalized onto the electron withdrawing phenyl rings in **1a** and explains the weaker basicity of **1a** compared to that of **3a**. The overall structural

features of the gallium analog **2a** are similar to those of **1a**. Selected bond distances and angles of two equivalent molecules of **2a** are listed in Table 3.

#### 4. Supplementary material

Crystallographic data (including a full listing of positional and thermal parameters, complete lists of bond distances and angles, and structure factor tables) for the structures of **1a** and **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 119395 and CCDC 119396, respectively. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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