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Synthesis and X-ray crystallographic structures of $[HGa(NMe_2)_2]_2$ and $[PhGa(NHNMe_2)_2]_2$, and room-temperature conversions of $[HGa(NMe_2)_2]_2$ to $(HGaNH)_n$ and $(HGaNMe)_n$

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Abstract

The reactivity of bis(dimethylamido) complexes of phenyl- and hydridogallium with ammonia, dimethylamine and 1,1-dimethylhydrazine is described. Synthesis of the starting gallium hydride, $[HGa(NMe_2)_2]_2$, was achieved in nearly quantitative yield from the reaction of $HGaCl_2$(quinuclidine) with $LiNMe_2$. In neat ammonia or methylamine at room temperature both dimethylamido ligands in $[HGa(NMe_2)_2]_2$ were substituted by a single equivalent of NH_3 or $MeNH_2$ to produce amorphous $(HGaNH)_n$ or $(HGaNMe)_n$, respectively. In contrast, the reaction of $[PhGa(NMe_2)_2]_2$ with neat Me_2NNH_2, at room temperature consumed two equivalents of the substituted hydrazine to form $[PhGa(NHNMe_2)_2]_2$ in a 73% yield. Single crystal X-ray crystallographic analyses of $[HGa(NMe_2)_2]_2$ and $[PhGa(NHNMe_2)_2]_2$ establish that in the solid state both compounds adopt a cyclic Ga–N–Ga–N structure with a crystallographic center of symmetry located at the center of the ring.

Keywords: Gallium; Amide; Hydrazide; Hydride; Synthesis; Structure

1. Introduction

Amido and hydrazido gallium compounds have attracted considerable attention, in part due to their potential to act as precursors to gallium nitride [1–4]. Recent publications have highlighted the value of bis(dimethylamido) complexes of hydrocarbylgallium, $[RGa(NMe_2)_2]_2$, as precursors to larger Ga–N clusters and novel solid state materials [5,6]. These complexes can be prepared in high yield, and their subsequent reactions with amines occur under mild conditions releasing gaseous dimethylamine thus facilitating product isolation (Eqs. (1)–(3)).

$$[EtGa(NMe_2)_2]_2 + EtNH_2 \xrightarrow[2h,\,-Me_2NH]{-78\text{ to }rt} [EtGaNEt]_6 \quad (56\%\text{ yield}) \qquad (1)$$

$$[PhGa(NMe_2)_2]_2 + {}^{i}BuNH_2 \xrightarrow[-Me_2NH]{rt,\,15h} [(PhGa)_4(NH^{i}Bu)_4(N^{i}Bu)_2] \quad (51\%\text{ yield}) \qquad (2)$$

$$[PhGa(NMe_2)_2]_2 + MeNH_2 \xrightarrow[2h,\,-Me_2NH]{-78\text{ to }rt} [(PhGa)_7(NHMe)_4(NMe)_5] \quad (31\%\text{ yield}) \qquad (3)$$

In essence, $[RGa(NMe_2)_2]_2$ serves as a useful synthon for the "RGa^{2+}" moiety [7]. In this paper we report the extension of this reaction to form a new bis(dimethylhydrazido) complex of phenylgallium. In addition, the synthesis of $[HGa(NMe_2)_2]_2$ is described and its reactivity demonstrates an ability to serve as a source of "HGa^{2+}".

2. Results and discussion

2.1. $[HGa(NMe_2)_2]_2$ (1)

Compound **1** was synthesized nearly quantitatively as a colorless crystalline solid from the reaction depicted in

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Eq. (4). The quinuclidine was easily removed by sublimation under vacuum. Compound **1** was characterized by spectroscopic methods, elemental analysis

$$HGaCl_2(\text{quinuclidine}) + 2LiNMe_2 \rightarrow \frac{1}{2}[HGa(NMe_2)_2]_2 + LiCl + \text{quinuclidine} \quad (4)$$

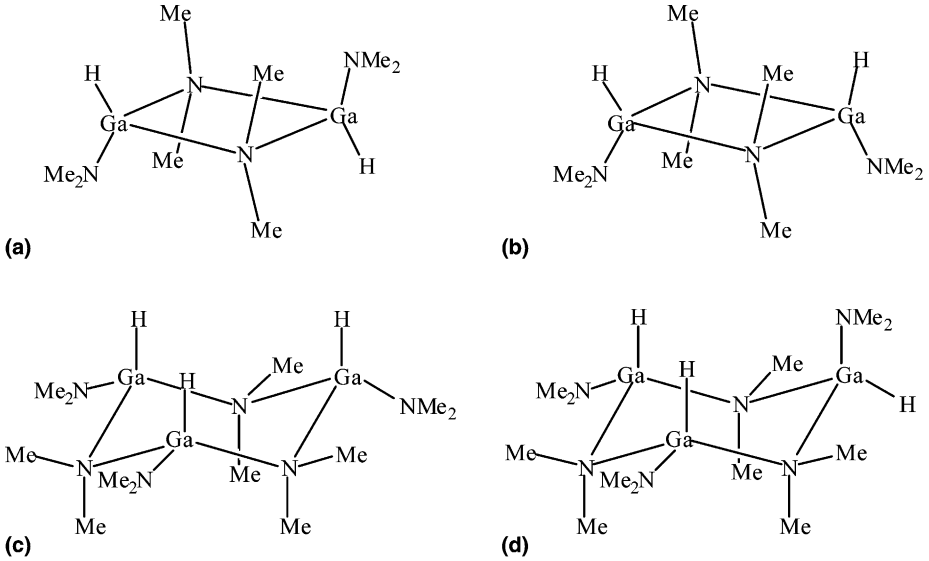
and single-crystal XRD analysis. Its IR spectrum exhibited a strong Ga–H stretching absorption at 1900 cm^{-1}. The base peak in the chemical-ionization mass spectrum was the parent ion (plus 1) and the second most intense ion was $(\mathbf{1} - NMe_2)^+$.

The ^1H NMR spectrum of **1** was surprisingly complex. Two groups of peaks at 2.31–2.47 and 2.79–2.96 ppm comprised six and five intense singlets, respectively. Several weak singlets were also observed in each group. The total integrated areas for each of the two groups were equal. Referenced to $[RGa(NMe_2)_2]_2$ (R = Me and Et) [7], the resonances at 2.31–2.47 ppm were assigned to the bridging NMe_2 ligands, and at 2.79–2.96 ppm, to the terminal NMe_2 ligands. The singlets at 2.33 and 2.93 ppm, accounting for 60% of the total NMe_2 resonances, were assigned to the *trans* structure (Scheme 1(a)) found in the solid state. We suggest that at least two additional isomers were present in the solution. The only other dimeric isomer, the *cis* dimer (Scheme 1(b)), if it existed in solution as for $[RGa(NMe_2)_2]_2$ (R = Me and Et), would only afford three singlets. Thus one or more of the other isomer(s) shown in Scheme 1 must be present, however, a specific assignment was not achieved. It is known that some amido gallium compounds including $(H_2GaNCH_2CH_2)_3$ [8], $(Me_2GaNH_2)_3$ [9], $(^tBu_2GaNH_2)_3$ [10] and $(H_2GaNH_2)_3$ [11] are trimeric. If trimeric isomers of **1** existed in solution, there would be several possible isomers producing a number of NMe_2 resonances. For example, assuming that the trimers of **1** adopted a chair structure [8,11], we identified four isomers with zero to three NMe_2 ligands on gallium in the axial positions. After ruling out those with two and three NMe_2 groups in axial positions due to steric repulsions, the remaining two isomers would still afford nine methyl resonances; three for the isomer without any axial NMe_2 groups (Scheme 1(c)) and six for the isomer with one axial and two equatorial NMe_2 ligands (Scheme 1(d)). Despite the difficulty in characterizing all of the isomers, their presence was further supported by the variable-temperature ^1H NMR data. In spectra of a toluene-d_8 solution collected at temperatures from 20 to 100 °C, some coalescence occurred at temperatures above 70 °C between peaks within each group. By 100 °C, however, three broad bridging and four terminal NMe_2 resonances remained indicating that isomerization was slow compared to the NMR time scale.

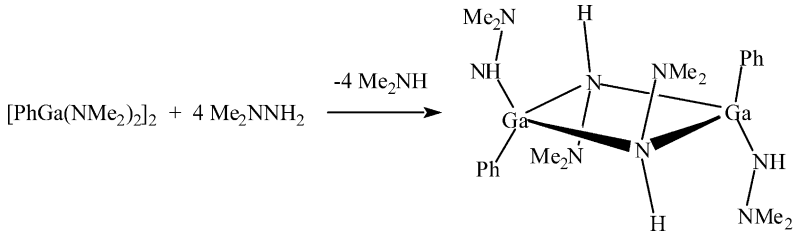
2.2. $[PhGa(NHNMe_2)_2]_2$ (**2**)

Compound **2** was isolated as colorless crystals in a 73% yield from the reaction shown in Scheme 2. In its IR spectrum, the NH moieties were detected as a weak, broad absorption at 3256 cm^{-1}. The *trans* dimeric structure with intramolecular hydrogen bonds was characterized by single-crystal XRD analysis.

The ^1H NMR spectrum of **2** was consistent with the solid-state structure. Two NH singlets were found at 3.64 and 4.05 ppm with the downfield resonance assigned as the hydrogen-bonded NH. The two chemically inequivalent methyls were assigned to the two singlets at 2.51 and 2.62 ppm. The resonance for the NMe_2 groups on the bridging nitrogen atoms was located at 2.19 ppm with its intensity being twice of each of the above two. There were also three weak NMe_2 peaks at 2.07, 2.25 and 2.28 ppm accounting for ca. 10% of the total NMe_2



Scheme 1. Possible Isomers of $[HGa(NMe_2)_2]_2$ (**1**).



Scheme 2. Synthesis of $[PhGa(NHNMe_2)_2]_2$ (**2**).

peak intensity. These resonances were attributed to an isomer of **2** with one or more *cis* ligand orientations on gallium or bridging nitrogen atoms. It was reported that both *trans* and *cis* isomers were present in solutions for known gallium hydrazide derivatives including $(Me_2GaNHNMe_2)_2$ [12] and $(Me_2GaNHNPh_2)_2$ [13].

Perhaps due to the lack of volatility below its decomposition temperature at 115 °C, the chemical-ionization mass spectrum of **2** exhibited only a few low-mass peaks (less than 117 amu). The only significant component was $Me_2NNH_3^+$ and no gallium-containing fragments were found, suggesting that the decomposition led to an involatile residue. This same thermal sensitivity may have contributed to the inaccurate C, H and N analyses.

The reaction of $[PhGa(NMe_2)_2]_2$ with dimethylhydrazine was carried out to examine the possibility of forming a gallium-nitrogen cluster in a similar route to the transamination followed by amine elimination proposed for the reactions of $[RGa(NMe_2)_2]_2$ with primary amines (Eqs. (1)–(3)). The result showed that neither full nor partial dimethylhydrazine elimination occurred from **2** at room temperature to produce $[PhGa(NNMe_2)]_n$ or $[(PhGa)_x(NHNMe_2)_y(NNMe_2)_z]$, respectively. The reduced acidity of the dimethylhydrazido ligand in **2** may retard the elimination reaction and contribute to our ability to isolate this compound. Reacting $[PhGa(NMe_2)_2]_2$ in refluxing H_2NNMe_2 at 80 °C for 20 h did promote further reactions, but the products were an uncharacterized mixture of a white precipitate and a waxy, polymeric-like solid soluble in H_2NNMe_2.

2.3. Structural analyses of $[HGa(NMe_2)_2]_2$ and $[PhGa(NHNMe_2)_2]_2$

The structures of **1** and **2** are plotted in Figs. 1 and 2, and the selected bond lengths and angles are listed in Tables 2 and 3, respectively. Both compounds crystallized in space group $P\bar{1}$ with one-half of a molecule residing in each asymmetric unit. Each molecule possessed a crystallographically imposed inversion center at the center of a planar Ga_2N_2 ring. The geometries of the rings in **1** and **2** were typical for dimeric amido and hydrizido gallium compounds [2,3]. In **1**, the terminal Ga(1)–N(2) bond length was 1.8454(16) Å and the bridging Ga(1)–N(1) and Ga(1A)–N(1) bond lengths

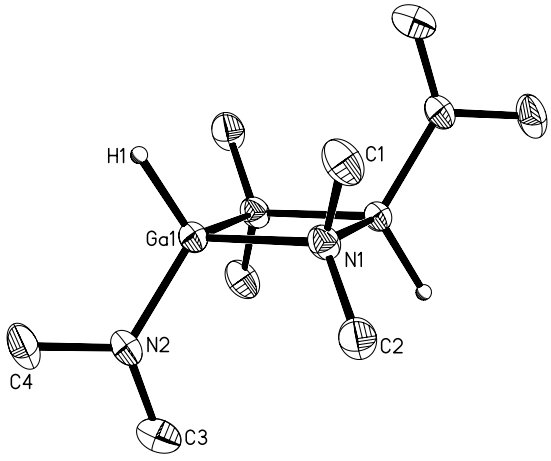


Fig. 1. Molecular structure of **1**. Atoms are shown at the 50% thermal ellipsoid level, and the methyl hydrogen atoms are omitted for clarity.

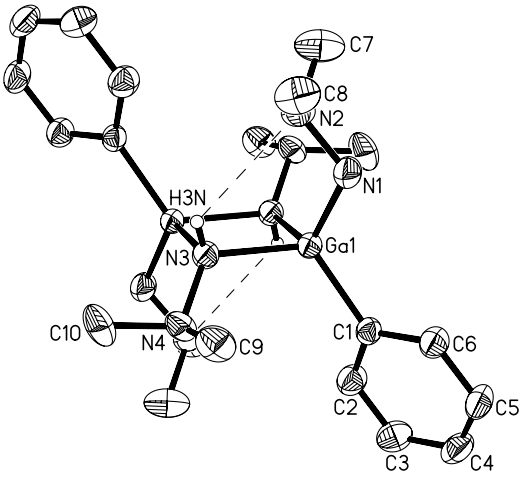


Fig. 2. Molecular structure of **2**. Atoms are shown at the 50% thermal ellipsoid level, and all hydrogen atoms are omitted except H3N. The dashed line indicates the H-bond between H3N and N2.

were 2.0099(15) and 2.0230(15) Å, respectively. The internal angle on Ga was 87.03(6)°. Within the group of bis(dimethylamido) gallium compounds, $[ClGa(NMe_2)_2]_2$ [14] has a *trans* solid-state structure while both *trans* and *cis* structures for $[MeGa(NMe_2)_2]_2$ [7] were found in the solid state. For **2**, the internal angle on Ga (85.39(8)°) was very close to that found in $(Et_2GaNHNPh_2)_2$ (85.8(3)°) [15]. The terminal Ga(1)–N(1) bond

Table 1
Crystallographic data of $[HGa(NMe_2)_2]_2$ (**1**) and $[PhGa(NHNMe_2)_2]_2$ (**2**)

Chemical formula	$C_8H_{26}Ga_2N_4$ (**1**)	$C_{20}H_{38}Ga_2N_8$ (**2**)
Formula weight	317.77	530.02
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.2653(5)	8.5628(5)
b (Å)	7.0101(6)	8.8245(5)
c (Å)	8.6612(7)	10.1905(6)
α (°)	81.805(2)	109.2530(10)
β (°)	90.146(2)	104.1150(10)
γ (°)	76.7690(10)	106.5850(10)
V (Å^3)	354.02(5)	646.27(6)
Z	1	1
T (°C)	−100	−100
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.491	1.362
μ (cm^{-1})	37.81	21.06
$R_1[I > 2\sigma(I)]$, wR_2 (all data)[a]	0.0201, 0.0483	0.0308, 0.0760

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)^2] / \sum[w\left(F_o^2\right)^2]\right\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, $P = (F_o^2 + 2F_c^2)/3$ and a, b are constants.

length was 1.845(2) Å, identical to that in **1**. Consistent with the intramolecular hydrogen bonding (N(3)–H(3N)···N(2)), the Ga(1)–N(3) [1.9935(18) Å] bond was shorter than Ga(1A)–N(3) [2.0224(18) Å] and the Ga(1)–N(3)–H(3N) bond angle (106(2)°) was smaller than Ga(1A)–N(3)–H(3N) (111.5(19)°).

2.4. Conversions of 1 to $(HGaNH)_n$ (3) and $(HGaNMe)_n$ (4)

Compound **1** reacted in neat NH_3 and $MeNH_2$ at temperatures up to room temperature affording white solids **3** and **4**, respectively (Eq. (5)). Based on earlier studies of the reactions of $[RGa(NMe_2)_2]_2$ with primary amines [5,6], the reactions of **2** are proposed to proceed through intermediates $HGa(NH_2)_2$ or $HGa(NHMe)_2$ (or their ammonia or methyl amine adducts) followed by NH_3 or $MeNH_2$ elimination (Eqs. (6) and (7)).

$$[HGa(NMe_2)_2]_2 + 2H_2NR \rightarrow 2/n(HGaNR)_n + 4HNMe_2 \quad R = H\ (\mathbf{3})\ \text{and}\ Me\ (\mathbf{4}) \tag{5}$$

$$[HGa(NMe_2)_2]_2 + 6H_2NR \rightarrow 2HGa(NHR)_2(H_2NR) + 4HNMe_2 \tag{6}$$

$$nHGa(NHR)_2(H_2NR) \rightarrow (HGaNR)_n + 2nH_2NR \tag{7}$$

Both **3** and **4** were insoluble in common organic solvents. No NH absorptions were detected in the IR spectrum of **4**, and the IR spectrum of **3** was identical to that reported for $(HGaNH)_n$ prepared from the reaction of cyclotrigallazane $(H_2GaNH_2)_3$ with supercritical ammonia at 150 °C [16]. For **4**, the ν_{GaH} absorption was found at 1874 cm^{-1}, almost the same

Table 2
Selected bond lengths (Å) and angles (°) for $[HGa(NMe_2)_2]_2$ (**1**)

Ga(1)–N(1)	2.0099(15)	Ga(1)–N(2)	1.8454(16)
Ga(1A)–N(1)	2.0230(15)	Ga(1)–H(1)	1.45(2)
N(1)–Ga(1)–N(2)	114.75(7)	N(1)–Ga(1)–N(1A)	87.03(6)
N(1A)–Ga(1)–N(2)	116.05(7)	N(1)–Ga(1)–H(1)	111.7(9)
N(2)–Ga(1)–H(1)	113.6(9)	N(1A)–Ga(1)–H(1)	111.0(9)
C(1)–N(1)–C(2)	108.84(16)	C(1)–N(1)–Ga(1)	111.69(12)
C(1)–N(1)–Ga(1A)	113.74(11)	C(2)–N(1)–Ga(1)	116.71(12)
C(2)–N(1)–Ga(1A)	112.33(13)	Ga(1)–N(1)–Ga(1A)	92.97(6)
C(3)–N(2)–C(4)	111.62(17)	C(3)–N(2)–Ga(1)	127.09(13)
C(4)–N(2)–Ga(1)	119.47(14)	Angle sum on N(2)	358.2(4)

Table 3
Selected bond lengths (Å) and angles (°) for $[PhGa(NHNMe_2)_2]_2$ (**2**)

Ga(1)–N(1)	1.845(2)	N(3)–N(4)	1.449(3)
Ga(1)–N(3)	1.9935(18)	N(3)–H(3N)	0.88(3)
Ga(1)–C(1)	1.961(2)	H(3N)···N(2)	2.67(3)
Ga(1A)–N(3)	2.0244(18)	N(2)···N(3)	3.186(3)
N(1)–N(2)	1.425(3)		
C(1)–Ga(1)–N(1)	116.40(9)	N(1)–Ga(1)–N(3)	103.76(9)
C(1)–Ga(1)–N(3)	120.01(8)	N(1)–Ga(1)–N(3A)	115.94(9)
C(1)–Ga(1)–N(1A)	111.60(9)	N(3)–Ga(1)–N(3A)	85.39(8)
Ga(1)–N(3)–Ga(1A)	94.61(8)	N(4)–N(3)–H(3N)	106.6(19)
Ga(1)–N(3)–N(4)	117.18(14)	Ga(1)–N(1)–N(2)	117.18(15)
Ga(1A)–N(3)–N(4)	120.03(14)	Ga(3)–N(1)–H(1N)	131(2)
Ga(1)–N(3)–H(3N)	106(2)	N(2)–N(1)–H(1N)	109(2)
Ga(1A)–N(3)–H(3N)	111.5(19)	N(3)–H(3N)···N(2)	118(2)

wave number as for **3** (1876 cm^{-1}). Good agreement for carbon and hydrogen percentages was obtained in the elemental analysis of **4**, but the nitrogen percentage was 1.2% lower than the calculated value possibly due to the formation of involatile GaN in the analytical process.

In earlier reports of the synthesis of $(HGaNH)_n$ in supercritical ammonia at 150 °C the product gave rise to distinct powder X-ray reflections that were assigned to the hexagonal crystal system [16]. Powder XRD pattern of **3** established that is was essentially amorphous. A weak, broad reflection at 14° for **3** corresponded to the most intense reflection observed in the more highly crystalline samples prepared in the ammonothermal reaction. The powder XRD pattern of **4** exhibited two weak, broad reflections at 22° and 34° that also indicated limited crystallinity. Higher reaction temperatures are needed to facilitate the formation of crystals in these oligo- or polymeric structures.

3. Experimental

3.1. Materials and general procedures

Gallium chloride was purchased from Strem and used as received. Other chemicals were obtained from Aldrich. Anhydrous ammonia, methylamine and dimethylamine were used as received. Diethyl ether and pentane were predried over calcium hydride and freshly distilled over sodium/benzophenone under nitrogen. Dimethylhydrazine, benzene-d_6 and toluene-d_8 were distilled over CaH_2 under nitrogen. The quinuclidine dichlorogallane adduct, $HGaCl_2$(quinuclidine) [17] and bis(dimethylamido) phenylgallium, $[PhGa(NMe_2)_2]_2$ [7] were prepared as previously reported. $LiNMe_2$ was prepared as a white powder from the reaction of $HNMe_2$ with 1 equivalent of *n*-butyllithium in hexanes. All experiments were conducted under an oxygen-free, dry-nitrogen atmosphere using standard Schlenk and glovebox techniques.

Proton NMR spectra were obtained in benzene-d_6 solutions at room temperature and in toluene-d_8 solutions at higher temperatures on a Varian INOVA 300 or a UNITY plus 500 spectrometer. The residual proton (7.15 ppm) in benzene-d_6 or the sharp singlet from silicon grease (0.29 ppm) for toluene-d_8 solutions was used as the internal standard. The IR spectra of KBr pellets were recorded on a Nicolet MAGNA-IR 560 spectrometer. Chemical-ionization mass spectra were acquired on a Finnigan Mat 95 spectrometer using a direct insertion probe. The samples were evaporated at a temperature range of 25–340 °C and the ionization gas mixture was methane with 4% ammonia. Melting points were measured in sealed glass capillaries and were uncorrected. The elemental analyses were performed by Desert Analytics, Tucson, AZ. Powder X-ray diffraction experiments were conducted on a Siemens 5005 diffractometer using monochromatic (graphite) Cu Kα radiation with a 45 kV source voltage and a 40 mA current. The XRD patterns were collected over 2–50° in 2θ with a step of 0.05° and a dwell time of 2 s. In the experiments, samples previously protected under nitrogen were quickly placed onto sample holders in air and mounted on the diffractomer. During data collection no degradation was observed.

3.2. Synthesis of $[HGa(NMe_2)_2]_2$ (**1**)

To a stirred slurry of $LiNMe_2$ (4.16 g, 81.5 mmol) in 20 ml of Et_2O at −78 °C was added dropwise a solution of $HGaCl_2$(quin) (10.30 g, 40.7 mmol) in 250 ml of Et_2O. The mixture was allowed to warm to room temperature and stirred for 17 h. Volatiles were removed under vacuum affording a white solid. Pentane (100 ml) was added and the resulting slurry was filtered to separate a white solid (LiCl) and a colorless filtrate. After the filtrate was concentrated to ca. 20 ml and stored at −20 °C overnight, colorless plates were collected (6.28 g, 97% yield). Mp: 67.5–69.0 °C. ^1H NMR (C_6D_6, 20 °C): δ 2.33 (12H, s, bridging NMe_2), 2.93 (12H, s, terminal NMe_2), 4.79 (2H, br s, GaH). There were additional singlets at δ 2.31, 2.35, 2.40, 2.41, 2.47, 2.79, 2.85, 2.89, 2.91 and 2.96, attributable to isomers of **1** (see Section 2). IR (cm^{-1}): ν_{GaH}, 1900. CI MS {assignment, % relative intensity}: 319 $\{(M+H)^+, 100\}$, 291 $\{(M-NMe_2+NH_3)^+, 16\}$, 274 $\{(M-NMe_2)^+, 61\}$, 231 $\{(0.5M+GaH_2)^+, 5.5\}$, 176 $\{[0.5M+NH_4)]^+, 2.4\}$, 159 $\{(0.5M+H)^+, 3.0\}$, 69 $\{Ga^+, 26\}$. Anal. Calc. for $C_8H_{26}Ga_2N_4$: C, 30.24; H, 8.25; N, 17.63. Found: C, 29.96; H, 8.34; N, 17.04.

3.3. Synthesis of $[PhGa(NHNMe_2)_2]_2$ (**2**)

Excess H_2NNMe_2 (2.0 ml, 26 mmol) was added into a flask containing $[PhGa(NMe_2)_2]_2$ (1.00 g, 4.26 mmol) at room temperature. Gas evolution was immediately observed resulting in a colorless solution. The solution was stirred for 2 h and volatiles were removed under vacuum to give a white solid. Ether (15 ml) was added to dissolve the solid and the solution was stored at −20 °C overnight affording colorless blocks (0.82 g, 73% yield). Mp: 115–123 °C, decomp. ^1H NMR: δ 2.19 (12H, s, NMe_2 of the bridging $NHNMe_2$), 2.51 and 2.62 (each 6H, s, NMe_2 of the terminal $NHNMe_2$), 3.64 and 4.05 (each 2H, s, NH), 7.30, 7.37, 8.01 and 8.17 (total 10H, m, Ph). Three additional NMe_2 singlets at 2.07, 2.25 and 2.28 ppm accounting for ca. 10% of the total NMe_2 peak integration were attributed to an isomer of **2**. IR (cm^{-1}): 3256. The CI MS and elemental analysis were unsatisfactory. CI MS {assignment, % relative intensity}: 61 $\{Me_2NNH_3^+, 100\}$. Other four masses, 87 (9% relative to

mass 61 amu), 92 (3.5%) and 117 (2%) amu, were not assigned.

3.4. Synthesis of $(HGaNH)_n$ (3)

Anhydrous ammonia (ca. 4 ml) was condensed into a flask containing $[HGa(NMe_2)_2]_2$ (0.500 g, 1.57 mmol) at −196 °C. The mixture was placed in a 2-propanol/dry-ice bath (−78 °C) and allowed to warm naturally to room temperature. A white solid precipitated at low temperatures and accumulated as liquid NH_3 evaporated. The solid was pumped for 0.5 h to remove residual NH_3 and collected (0.25 g, 94% yield). The IR spectrum of **3** was identical to that of the authentic $(HGaNH)_n$ prepared from the reaction of $(H_2GaNH_2)_3$ with NH_3 at 150 °C [16]. IR (cm^{-1}): 3279 m (ν_{NH}), 1876 s (ν_{GaH}), 1510 w, 957 s, 901 s.

3.5. Synthesis of $(HGaNMe)_n$ (4)

$MeNH_2$ (ca. 5 ml) was condensed into a flask containing **1** (0.500 g, 1.57 mmol) at −78 °C. The mixture was allowed to warm to room temperature and a white solid precipitated. After all the amines evaporated and the residue was pumped for 0.5 h, **4** (0.29 g, 92% yield) was collected as a white powder. It was insoluble in common organic solvents. IR (cm^{-1}): 2951 m, 2921 m, 2882 m, 2808 m, 1874 s (ν_{Ga-H}), 1479 w, 1455 w, 1426 w, 1131 w, 1053 w, 971 s, 686 w. Anal. Calc. for $(CH_4GaN)_n$: C, 12.04; H, 4.04; N, 14.04. Found: C, 11.92; H, 4.30; N, 12.86.

3.6. Single-crystal X-ray data collection, structure solution and refinement

Crystals of compounds **1** and **2** were mounted on glass fibers under nitrogen. The data collections were conducted on a Siemens SMART system. For each crystal, an initial set of cell constants was calculated from reflections harvested from three sets of 30 frames. These sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. The data collection technique was a hemisphere collection. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.77 Å for **1** and 0.84 Å for **2**. Three major swaths of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of −28° in 2θ. The final cell constants were calculated from a set of 876 strong diffractions for **1** and 4237 for **2**.

For both structures, the space group $P\bar{1}$ was determined based on lack of systematic absences and on the intensity statistics. Successful direct-methods solutions were applied to both structures that provided most of the non-hydrogen atoms from the *E*-maps. Several full-matrix, least-squares/difference Fourier cycles were performed to locate the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **1**, the hydrogen atom H(1) on gallium was found from the Fourier map and all of the other hydrogen atoms were placed in ideal positions. For **2**, all of the hydrogen atoms were located from the Fourier map and were refined isotropically. The experimental conditions and unit cell information are summarized in Table 1. The calculations were performed using the SHELXTL V5.0 suite of programs. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 222002 for **1** and No. 222003 for **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, Fax. (int. code) +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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