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Reactions of trialkylgalliums with substituted hydrazines leading to the formation of rings and cages: X-ray structures of $(^{i}Pr_2GaNHNMe_2)_2$ and $(MeGaNHN^{t}Bu)_4$☆

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Abstract

The reaction of trialkylgalliums with substituted hydrazines forms simple Lewis acid–base adducts at room temperature. Subsequent thermolysis of these adducts leads to step by step alkane loss forming first dimeric rings, then tetrameric cages. Thus the dimeric compounds $[Me_2GaNHNMe_2]_2$, $[Et_2GaNHNMe_2]_2$, $[Me_2GaNHNPh_2]_2$, $[Et_2GaNHNPh_2]_2$, $[^{i}Pr_2GaNHNMe_2]_2$, and $[Me_2GaNHNH^{t}Bu]_2$, have been synthesized. In addition, $[^{i}Pr_2GaNHNMe_2]_2$ has been characterized crystallographically. Although exclusively in the *anti* conformation in the solid state, the dimers are fluxional in solution at room temperature. The fluxionality is examined in detail by NMR spectroscopy. The tetrameric $[MeGaNHN^{t}Bu]_4$ has been isolated and crystallographically characterized. It is shown to have a cage structure consisting of two hexagonal and four pentagonal rings. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Trialkylgallium; Hydrazine; Cage

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1. Introduction

Compounds containing Ga–N bonds have a long and fascinating history [1–3]. Recent work in this area has greatly extended our knowledge of these materials, a considerable focus being directed toward using compounds of this type as precursors to GaN, a wide band-gap semiconductor [4–24].

In CVD studies using trialkylgalliums with hydrazine as a source of nitrogen, we obtained evidence for complex formation from mass spectroscopy [25]. These results prompted us to investigate the chemical nature of these interactions, which had not been addressed in the literature at the time. Cowley, Jones, and co-workers described the first examples of gallium hydrazides in 1995 and the X-ray crystal structure of a complex with a four-membered Ga_2N_2-ring, prepared by metathetical reaction between $LiNHNPh_2$ and Et_2GaCl, was reported [26]. In a recent communication, we reported preliminary results on reactions of trimethylgallium with phenylhydrazine, which lead to the isolation of rings and cages with Ga–N interactions [27]. Details of continuing studies with a range of trialkylgallliums and substituted hydrazines are described here.

2. Results and discussion

2.1. Lewis acid–base adducts

Given the well-known ability of Group 13 metals to form simple Lewis acid–base adducts with amines, it is no surprise hydrazines display the same types of behavior [28,29]. As shown in Eq. (1), a range of alkyl

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☆ Dedicated to Professor Alan H. Cowley FRS on the occasion of his 65th birthday.

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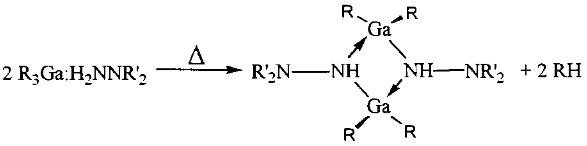
substituted hydrazines interact with $GaMe_3$, $GaEt_3$ or Ga^iPr_3 to form simple 1:1 adducts, in the form of oils or solids, that we were able to isolate and characterize by NMR and IR spectroscopy and, for the solids, by combustion analysis.

$$R_3Ga + H_2NNR'_2 \rightarrow R_3Ga{:}H_2NNR'_2 \qquad (1)$$

Our data do not distinguish between the two possible geometrical isomers, i.e. H_2N- versus R_2N-bound. Sterically, the unsubstituted nitrogen is more accessible; electronically, the alkyl-substituted nitrogen is more basic. At this point, we favor the H_2N-bound isomer based solely on the subsequent connectivity that we observed in products resulting from thermolysis of these adducts (see below). X-ray crystallography would clarify the issue but such studies are dependent on the isolation of suitable crystals which thus far has proved impossible.

2.2. Four-membered Ga_2N_2 rings

Subsequent heating of the 1:1 adducts led to the elimination of one equivalent of the respective alkane and dimerization to form the compounds shown in Eq. (2).



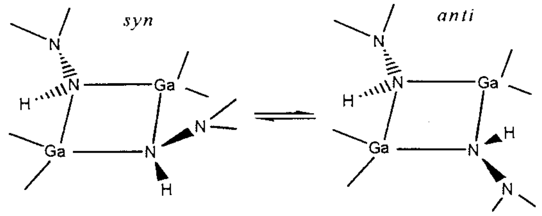
(2)

Ga_2N_2 ring structures were proposed many years ago by Coates [28] for the thermolysis product of trimethylgallium amine adducts and have since been confirmed for a number of Group 13/15 complexes [4,9,23,30–37]. Fetter and Bartocha proposed a related structure for the product resulting from the interaction of trimethylaluminum and 1,1-dimethylhydrazine [38].

X-ray quality crystals of $[^iPr_2GaNHNMe_2]_2$ were obtained from a solution of hexanes cooled to −28°C. The results of an X-ray crystallographic analysis are shown in Fig. 1 and Table 1. The complex crystallizes in the triclinic space group $P\bar{1}$ with an occupancy of one. There are no short intermolecular contacts. The molecular structure is dimeric in the solid state, with the two 'monomers' related by an inversion center and a C_2 axis along the Ga–Ga* vector. The gallium and endocyclic nitrogen atoms all have a distorted tetrahedral geometry with bond angles ranging from 85 to 125° indicating a highly constrained ring. Conversely, the exocyclic nitrogens exhibit geometries close to tetrahedral as seen in free hydrazine [39]. The structure of the ring is rhombohedral with an acute N–Ga–N angle and obtuse Ga–N–Ga angle. The Ga–N bond lengths (2.026 Å) are the same within experimental error and fall well within reported values for similar Ga_2N_2 cyclic structures. The Ga–Ga* distance is 2.98 Å. The N–N bond lengths (1.455 Å) are well in line with other hydrazine complexes [40,41], and are very close to the accepted bond length in hydrazine (1.454 Å).

In contrast to the rather high symmetry observed in the solid state, ^1H-NMR spectra of these compounds are surprisingly complex. For instance, both the room temperature (r.t.) ^1H- and $^{13}C\{^1H\}$-NMR spectra of $[Me_2GaNHNMe_2]_2$ show three Ga–*Me* resonances corresponding to three different methyl environments. In addition, two distinct resonances are seen for the N–*H* protons. Variable temperature ^1H-NMR spectroscopy showed that both sets of peaks were temperature dependent and on warming each coalesce to two single resonances at 51°C, corresponding to a $\Delta G^{\ddagger}$ of 16 kcal mol^{-1} at this temperature.

These solution data suggest that in contrast to the solid state (where a single isomer—the *anti*—is observed) both *syn*- and *anti*-isomers are present and these interconvert slowly on the NMR time-scale at r.t.



In the *anti*-conformation the methyl and amine protons are equivalent due to the inversion center, leading to one resonance for each. In the *syn* conformation, the Ga–*Me* are inequivalent, giving rise to two equal intensity resonances. The N–*H* in a given isomer are equivalent, therefore a singlet is seen for each. At high temperature, fast interconversion of the two isomers results in an averaged spectrum. This process is completely reversible; however, heating to higher temperatures resulted in a further elimination reaction described below.

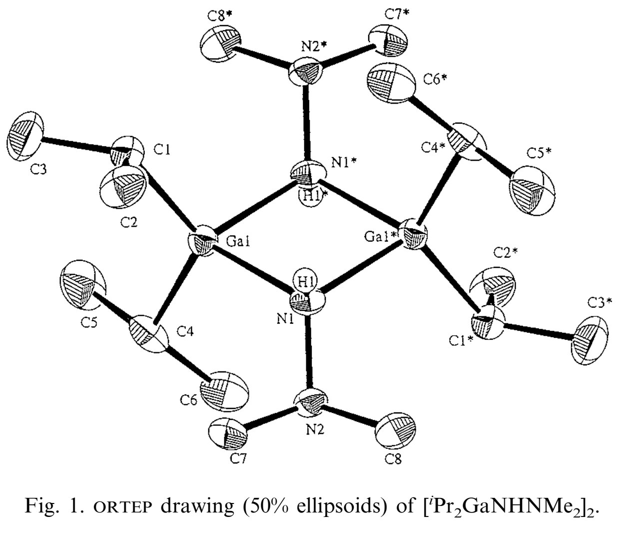


Fig. 1. ORTEP drawing (50% ellipsoids) of $[^iPr_2GaNHNMe_2]_2$.

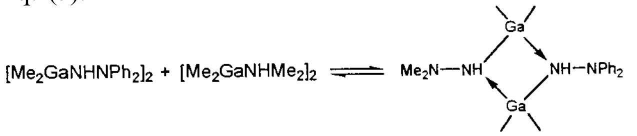
Table 1
Significant bond lengths (Å) and angles (°) for [^{i}Pr$_2$GaNHNMe$_2$]$_2$ and [MeGaNHN^{t}Bu]$_4$

(^{i}Pr$_2$GaNHNMe$_2$)$_2$					
Ga(1)–N(1)	2.031(2)	N(1)–Ga(1)–N(1)*	85.7(1)	Ga(1)–N(1)–N(2)	119.3(2)
Ga(1)–N(1)*	2.026(2)	Ga(1)–N(1)–Ga(1)*	94.53(1)	Ga(1)*–N(1)–N(2)	118.2(2)
Ga(1)–C(1)	1.991(3)	N(1)–Ga(1)–C(1)	108.6(1)	N(1)–N(2)–C(7)	109.5(2)
Ga(1)–C(4)	1.998(3)	N(1)*–Ga(1)–C(1)	112.7(1)	N(1)–N(2)–C(8)	109.1(2)
N(1)–N(2)	1.455(3)	N(1)–Ga(1)–C(4)	111.6(1)	C(7)–N(2)–C(8)	108.9(3)
N(2)–C(7)	1.460(4)	N(1)*–Ga(1)–C(4)	106.3(1)		
N(2)–C(8)	1.464(4)	C(1)–Ga(1)–C(4)	125.1(1)		
(MeGaNHN^{t}Bu)$_4$					
Ga(1)–N(1)	2.003(5)	N(1)–Ga(1)–N(3)	94.2(2)	Ga(1)–N(1)–Ga(2)	108.2(2)
Ga(1)–N(3)	1.872(4)	N(1)–Ga(1)–N(5)	92.3(2)	Ga(1)–N(1)–N(2)	113.1(3)
Ga(1)–N(5)	1.990(5)	N(1)–Ga(1)–C(1)	118.0(2)	Ga(2)–N(1)–N(2)	111.6(3)
Ga(1)–C(1)	1.955(6)	N(3)–Ga(1)–N(5)	107.6(2)	Ga(3)–N(2)–N(1)	107.7(3)
Ga(2)–N(1)	1.990(5)	N(3)–Ga(1)–C(1)	124.3(2)	Ga(3)–N(2)–C(5)	135.1(4)
Ga(2)–N(4)	1.997(5)	N(5)–Ga(1)–C(1)	114.4(2)	N(1)–N(2)–C(5)	115.9(4)
Ga(2)–N(8)	1.888(4)	N(1)–Ga(2)–N(4)	93.1(2)	Ga(1)–N(3)–N(4)	108.4(3)
Ga(2)–C(2)	1.966(6)	N(1)–Ga(2)–N(8)	109.1(2)	Ga(1)–N(3)–C(9)	136.2(4)
Ga(3)–N(2)	1.871(5)	N(1)–Ga(2)–C(2)	112.5(2)	N(4)–N(3)–C(9)	114.1(4)
Ga(3)–N(5)	2.011(5)	N(4)–Ga(2)–C(2)	116.5(2)	Ga(2)–N(4)–Ga(4)	108.3(2)
Ga(3)–N(7)	1.988(4)	N(8)–Ga(2)–C(2)	126.2(2)	Ga(2)–N(4)–N(3)	107.8(3)
Ga(3)–C(3)	1.956(6)	N(2)–Ga(3)–N(5)	96.9(2)	Ga(4)–N(4)–N(3)	115.9(3)
Ga(4)–N(4)	1.994(5)	N(1)–Ga(3)–N(7)	104.2(2)	Ga(1)–N(5)–Ga(3)	108.7(2)
Ga(4)–N(6)	1.886(4)	N(2)–Ga(3)–C(3)	127.3(2)	Ga(1)–N(5)–N(6)	116.9(3)
Ga(4)–N(7)	1.999(5)	N(5)–Ga(3)–N(7)	93.1(2)	Ga(3)–N(5)–N(6)	107.3(3)
Ga(4)–C(4)	1.946(6)	N(5)–Ga(3)–C(3)	114.2(2)	Ga(4)–N(6)–N(5)	107.3(3)
N(1)–N(2)	1.487(6)	N(7)–Ga(3)–C(3)	114.7(2)	Ga(4)–N(6)–C(13)	134.3(4)
N(2)–C(5)	1.442(7)	N(4)–Ga(4)–N(6)	108.2(2)	N(5)–N(6)–C(13)	114.1(4)
N(3)–N(4)	1.488(6)	N(4)–Ga(4)–N(7)	92.7(2)	Ga(3)–N(7)–Ga(4)	108.0(2)
N(3)–C(9)	1.463(6)	N(4)–Ga(4)–C(4)	115.5(2)	Ga(3)–N(7)–N(8)	119.0(3)
N(5)–N(6)	1.489(6)	N(6)–Ga(4)–N(7)	94.7(2)	Ga(4)–N(7)–N(8)	106.8(3)
N(6)–C(13)	1.447(7)	N(6)–Ga(4)–C(4)	124.4(2)	Ga(2)–N(8)–N(7)	106.4(3)
N(7)–N(8)	1.498(6)	N(7)–Ga(4)–C(4)	115.6(2)	Ga(2)–N(8)–C(17)	132.4(4)
N(8)–C(17)	1.454(7)			N(7)–N(8)–C(17)	114.1(4)

Qualitatively similar NMR behavior is seen in all cases we have examined, with the exception that the ratios of *syn* to *anti* isomers show a marked dependence on the nature of the substituents on both Ga and N. For example, in the case of [Me$_2$GaNHNMe$_2$]$_2$ described above (one of the least hindered complexes), a 1:1 non-temperature dependent ratio of *syn*:*anti* is observed. As the size of the substituents increases, the *anti* isomer predominates: thus, the ratio in [Et$_2$GaNHNMe$_2$]$_2$ is 1.1:1, while that in [Me$_2$GaNHNH^{t}Bu]$_2$ was 1.6:1. The strongest preference for the *anti* isomer, however, was found for the compound [^{i}Pr$_2$GaNHNMe$_2$]$_2$ where a ratio of 2.25:1 was determined.

It is noteworthy that a related aluminum hydrazide complex reported by Fetter and Bartocha does not display the same fluxionality [38]. Nonetheless, fluxional behavior is well documented in related Group 13/15 ring systems [20,33], and Wells [42] has reported extensive dynamic NMR data on *cis*/*trans* isomerization in {[(Me$_3$SiCH$_2$)$_2$As]$_2$GaBr}$_2$. The lack of fluxionality in aluminum can be ascribed to the fact that Al is both a smaller and a stronger Lewis acid than Ga, rendering it less likely to participate in ring-opening reactions that could lead to exchange.

Although we have not probed the mechanism of the isomerization process in detail, we note that mixing equimolar amounts of [Me$_2$GaNHNMe$_2$]$_2$ and [Me$_2$GaNHNPh$_2$]$_2$ in benzene-*d*$_6$ at r.t. gives rise to a new set of peaks in the ^{1}H-NMR spectrum (see Fig. 2), which can be attributed to the mixed species shown in Eq. (3).



(3)

These data may be interpreted as evidence for a facile ring-opening mechanism in solution. Associative pathways (i.e. dimer + dimer interactions) cannot be excluded without further kinetic studies, but we feel they are unlikely due to the four-coordinate nature of both the Ga and N in the four-membered rings. Attempts to isolate the pure mixed dimer are complicated by the equilibrium present in solution.

2.3. Cage structures

In the case of dimers prepared using monosubstituted hydrazines, a further alkane elimination reaction is facile and, in two cases, we have been able to isolate and characterize the resulting products. Thus, further thermolysis of $[Me_2GaNHNH^tBu]_2$ led to a new complex which displayed a simple, non-temperature dependent ^{1}H-NMR spectrum. Monitoring the reaction mixture by ^{1}H-NMR spectroscopy and elemental analysis of the crystalline product obtained subsequently was in accord the stoichiometry shown in Eq. (4).

$$[Me_2GaNHNH^tBu]_2 \xrightarrow{\Delta} 1/2[Me_2GaNHN^tBu]_4 \qquad (4)$$

The molecularity of the product was determined in the solid-state by crystallography; an ORTEP view of the molecular structure is shown in Fig. 3, significant bond lengths and angles are shown in Table 1. The complex crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the asymmetric unit. The core structure is very similar to that seen in the aryl derivative $[MeGaNHNPh]_4$ we described earlier [27], and both are related to a boron analog reported some time ago [43]. The structure can be visualized as two hexagonal rings, in the boat conformation, bound together by four dative bonds. Although the molecule is highly symmetrical in solution, there is no crystallographically imposed symmetry in this structure; this contrasts with the phenyl analog where the cage sits on the intersection of three mutually perpendicular mirror planes [27].

The bond angles around gallium fall into two groups, making for a geometry best described as distorted tetrahedral: those for the N–Ga–N are on the order of 92–97°, while the N–Ga–C angles are more obtuse (114–126°). The pseudo-tetrahedral coordination about the four-coordinate nitrogens is quite regular in comparison. Angles at N2, N3, N6, and N8 (i.e. the three-coordinate nitrogens) show substantial distortions from trigonal planar, with values over a broad range from 106 to 136°. Similar trends are apparent in the phenyl derivative although the overall geometry appears less distorted, presumably due to the lower steric demands in the latter. As expected, bond lengths between gallium and four-coordinate nitrogens (ca. 2.0 Å) are all noticeably longer than those in the three-coordinate nitrogens (ca. 1.88 Å). The N–N bond lengths are equivalent within experimental error (average 1.49 Å) and are slightly longer than predicted for a N–N single bond (1.454 Å). Nonetheless, these data are in accord with values reported for related hydrazine cage structures and other complexes with bridging hydrazines [40].

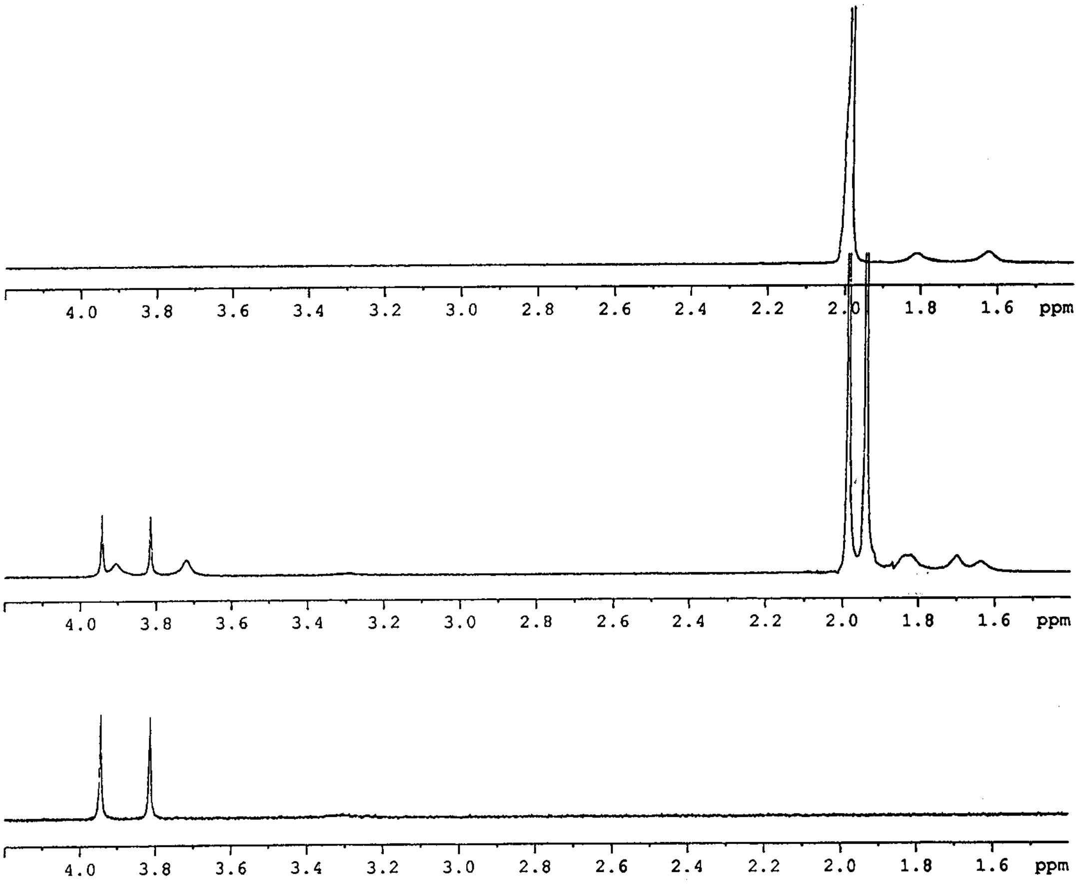


Fig. 2. NMR mixing experiment. Bottom to top: $[Me_2GaNHNPh_2]_2$, equimolar mixture of each, $[Me_2GaNHNMe_2]_2$.

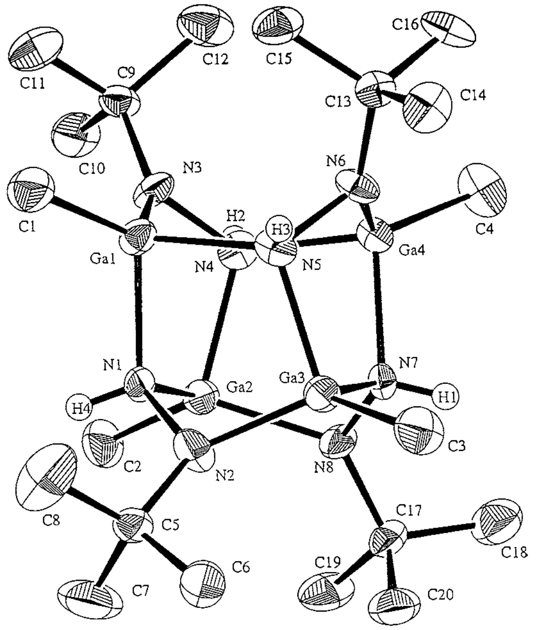


Fig. 3. ORTEP drawing (50% ellipsoids) of [MeGaNHN^{t}Bu]$_4$.

These compounds are being evaluated as single-source precursors to gallium nitride. Preliminary studies have already been described [26] and full details will be the topic of a subsequent publication.

3. Experimental

3.1. General considerations

All manipulations were performed using standard Schlenk techniques or in a dry box under a nitrogen atmosphere. Anhydrous solvents were purchased from Aldrich and further dried by passing through a column of activated alumina and degassed before use. Deuterated solvents were dried over sodium or CaH and vacuum transferred prior to use. Reagents were from Aldrich unless stated otherwise. NMR spectra were referenced to residual protium in the solvent. IR spectra were taken as mineral oil mulls between KBr plates; oils were taken neat between KBr plates. C, H and N analyses were carried out in our departmental analytical facilities. X-ray data were collected and the structures solved at our in-house X-ray facility, CHEXRAY. Electronic grade $GaEt_3$ (Strem) was used as received. MOCVD grade $GaMe_3$ and Ga^iPr_3 were donated by Epichem and used as received. H_2NNPh_2 was generated from the HCl salt by reaction with NaOH in methanol and crystallized from ether. H_2NNMe_2 was dried over sodium metal and distilled. *t*-Butylhydrazine was generated from the HCl salt by reaction with *n*-butyllithium in toluene. The mixture was distilled and the concentration in toluene determined by titration.

3.2. Preparation of $Me_3GaNH_2NMe_2$

A sample of H_2NNMe_2 (2.0 ml, 20 mmol) was added to Me_3Ga (2.0 ml, 20 mmol) by syringe and the resulting solution was stirred overnight. The solvent was removed under reduced pressure to afford a dry colorless solid that was recrystallized from hexanes. Yield 3.11 g (89%). M.p.: 63–65°C. Anal. Calc. for $C_5H_{17}GaN_2$: C, 34.33; H, 9.80; N, 16.01. Found C, 34.70; H, 10.03; N, 16.06. IR (ν, cm^{-1}): 3437 (m), 1594 (s), 1193 (s), 1092 (w), 1042 (m), 999 (m), 922 (m), 810 (s). ^{1}H-NMR (400 MHz, C_6D_6): δ -0.22 (s, 9H, GaMe_3), 1.85 (s, 6H, NMe_2), 2.47 (s, 2H, NH_2). ^{13}C{^{1}H}-NMR (75.4 MHz, C_6D_6): δ -6.6 (m, Ga*Me*), 49.8 (s, N*Me*). The product is air sensitive; it sublimes at 100 mTorr and 23°C.

3.3. Preparation of $^iPr_3GaNH_2NMe_2$

The complex was synthesized in a similar manner. A sample of $^iPr_3Ga$ (0.5 ml, 5.2 mmol) and H_2NNMe_2 (0.55 ml, 5.5 mmol) reacted in diethylether to give a colorless oil, which was carried on to the dimer without further purification (see below). IR (ν, cm^{-1}): 3115 (w), 2768 (s), 1408 (m), 1219 (w), 1195 (w), 1014 (s), 988 (m), 863 (s), 825 (s). ^{1}H-NMR (400 MHz, C_6D_6): δ 0.941 (m, 3H, Ga$^i\mathit{Pr}_3$, $J = 7$ Hz), 1.45 (d, 18H, Ga$^i\mathit{Pr}_3$, $J = 7$ Hz), 1.84 (s, 6H, NMe_2), 2.67 (s, 2H, N*H*). ^{13}C{^{1}H}-NMR (75.4 MHz, C_6D_6): δ 13.9 (s, Pr), 22.7 (s, Pr), 50.5 (s, Me).

3.4. Preparation of $Me_3GaNH_2NH^tBu$

The complex was synthesized in a similar manner. A sample of Me_3Ga (1.0 ml, 10 mmol) and H_2NNH^tBu (36 ml of a 0.28 M solution in toluene, 10 mmol) were reacted in toluene. The product was crystallized from pentane to yield 1.763 g (86%). M.p.: 65–66°C. Anal. Calc. for $C_7H_{21}GaN_2$: C, 41.42; H, 10.43; N, 13.80. Found C, 41.57; H, 10.24; N, 13.47. IR (ν, cm^{-1}): 3315 (s), 3298 (s), 3223 (m), 3165 (m), 1604 (m), 1276 (w), 1229 (m), 1191, (m), 1158 (s), 1084 (w), 1043 (m), 937 (w), 793 (m), 548 (s), 445 (w). ^{1}H-NMR (500 MHz, C_6D_6): δ -0.85 (s, 12H, Ga*Me*), 0.49 (s, 9H, N*Bu*), 2.55 (s, 1H, BuN*H*), 2.89 (s, 2H, NH_2). ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6): δ -5.92 (s, Ga*Me*), 0.8 (s, N*Bu*), 53.2 (s, N*Bu*).

3.5. Preparation of $Et_3GaNH_2NMe_2$

The complex was synthesized in a similar manner to the example above. A sample of Et_3Ga (2.0 ml, 13 mmol) and H_2NNMe_2 (1.1 ml, 14 mmol) reacted in toluene to give a colorless oil. This was not further purified, but was converted subsequently to the dimer (see below). IR (ν, cm^{-1}): 33346 (m), 3304 (w), 3246 (w), 2807 (s), 2721 (w), 1594 (s), 1467 (s), 1418 (m), 1372 (w), 1095 (w), 1045(m), 997 (s), 931 (m), 808 (s), 647 (m), 527 (s). ^{1}H-NMR (500 MHz, C_6D_6): δ 0.462 (q, 6H, $\mathrm{Ga}\mathit{Et}_3$), 1.409 (t, 9H, $\mathrm{Ga}\mathit{Me}_3$), 1.809 (s, 6H, $\mathrm{N}\mathit{Me}_2$), 2.57 (s, 2H, $\mathrm{N}\mathit{H}_2$). ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6): δ 2.6 (s, Ga*Et*), 11.4 (s, Ga*Me*), 50.2 (s, N*Me*).

3.6. Preparation of $[Me_2GaNHNMe_2]_2$

A sample of $Me_3GaNH_2NMe_2$ (2.0 g, 11 mmol) was placed in a round bottom flask with 50 ml of toluene. The mixture was heated to reflux for 4 h to yield a yellow solution. The solvent was removed under reduced pressure leaving a yellow solid; crystallization from hexanes at −28°C yielded 1.82 g (80%) of colorless crystals. M.p.: 80–83°C. Anal. Calc. for $C_8H_{26}Ga_2N_4$: C, 30.24; H, 8.25; N, 17.63. Found C, 30.60; H, 8.47; N, 17.29. IR (ν, cm^{-1}): 3133 (m), 2764 (s), 1214 (m), 1196 (s), 1153 (w), 1091 (w), 1012 (s), 892 (s), 828 (s), 582 (s), 553 (w), 534 (s). ^{1}H-NMR (500 MHz, C_6D_6): δ −0.25 (s, 3H, Ga*Me*), −0.03 (s, 6H, Ga*Me*), 0.19 (s, 3H, Ga*Me*), 1.62 (s, 1H, N*H*), 1.81 (s, 1H, N*H*), 1.98 (s, 6H, $\mathrm{N}\mathit{Me}_2$). ^{13}C{^{1}H}-NMR (125.7 MHz, C_6D_6): δ −10.28, −6.87, −4.74 (m, Ga*Me*), 51.56 (s, N*Me*).

3.7. Preparation of $[Et_2GaNHNMe_2]_2$

The complex was synthesized in a similar manner to the above. Yield 82% of colorless crystals. M.p.: 47–48°C. Anal. Calc. for $C_{12}H_{34}Ga_2N_4$: C, 38.55; H, 9.17; N, 14.99. Found C, 38.23; H, 9.35; N, 14.61. IR (ν, cm^{-1}): 3346 (m), 3305 (w), 3245 (w), 1595 (s), 1467 (s), 1419 (m), 1371 (m), 1331 (w), 997 (s), 808 (s), 647 (s). ^{1}H-NMR (400 MHz, C_6D_6): δ 0.38 (s, 1.5H, Ga*Me*), 0.67 (s, 3.6H, Ga*Me*), 0.98 (s, 1.5H, Ga*Me*), 1.34 (m, 6H, Ga*Et*), 1.97 (s, 0.9H, N*H*), 2.04 (s, 12H, $\mathrm{N}\mathit{Me}_2$), 2.25 (s, 1.1H, N*H*). ^{13}C{^{1}H}-NMR (75.4 MHz, C_6D_6): δ 3.2 (m, Ga*Me*), 10.6 (s, Ga*Et*), 52.5 (s, N*Me*).

3.8. Preparation of $[{}^{i}Pr_2GaNHNMe_2]_2$

The complex was synthesized similarly. Yield 56% of colorless crystals. M.p.: 155°C. Anal. Calc. for $C_{16}H_{42}Ga_2N_4$: C, 44.69; H, 9.85; N, 13.03. Found C, 44.63; H, 9.97; N, 12.78. IR (ν, cm^{-1}): 3139 (m), 3118 (w), 2765 (s), 1304 (w), 1212 (m), 1149 (m), 1088 (w), 1064 (w), 1011 (m), 986 (m), 973 (m), 872 (s), 824 (m). ^{1}H-NMR (400 MHz, C_6D_6, −10°C): δ 0.721 (m, 0.39, $\mathrm{Ga}^{i}\mathit{Pr}^{i}_{3}$, $J = 7$ Hz), 1.099 (m, 2.71H, $\mathrm{Ga}^{i}\mathit{Pr}_{3}$, $J = 7$ Hz), 1.261 (d, 3H, $\mathrm{Ga}^{i}\mathit{Pr}^{i}_{3}$), 1.372 (d, 9H, $\mathrm{Ga}^{i}\mathit{Pr}^{i}_{3}$, $J = 7$ Hz), 1.425 (d, 9H, $\mathrm{Ga}^{i}\mathit{Pr}^{i}_{3}$, $J = 7$ Hz), 1.595 (d, 3H, $\mathrm{Ga}^{i}\mathit{Pr}^{i}_{3}$, $J = 7$ Hz), 2.096 (s, 12H, $\mathrm{N}\mathit{Me}_2$), 2.25 (s, 0.6H, N*H*), 2.546 (s, 1.3H, N*H*). ^{13}C{^{1}H}-NMR (75.4 MHz, C_6D_6): δ 13.8 (s, $\mathrm{Ga}\mathit{Pr}^{i}$) 22 (s, $\mathrm{Ga}\mathit{Pr}^{i}$), 53 (s, N*Me*).

3.9. Preparation of $[Me_2GaNHNH{}^{t}Bu]_2$

The complex was synthesized similarly. Yield 85% of colorless crystals. M.p.: 50–52°C. IR (ν, cm^{-1}): 3314 (w), 3360 (w), 3223 (m), 1250 (w), 1228 (m), 1201 (s), 1058 (m), 1013 (w), 945 (m), 917 (w), 864 (m), 809 (s), 680 (m), 577 (s), 534 (m), 480 (s), 463 (m). ^{1}H-NMR (400 MHz, d-Tol, −30°C): δ 0.00 (s, 2.3H, Ga*Me*), 0.12 (s, 7.3H, Ga*Me*), 0.21 (s, 2.3H, Ga*Me*), 0.81 (s, 18H, N*Bu*), 2.43 (s, 2H, $\mathrm{N}\mathit{H}_2$), 2.58 (s, 0.78H, BuN*H*), 2.71 (s, 1.21H, BuN*H*). ^{13}C{^{1}H}-NMR (125.75 MHz, C_6D_6): δ −8.3 (m, Ga*Me*), 26.9 (s, N*Bu*), 53.5 (s, N*Bu*).

3.10. Preparation of $[Me_2GaNHNPh_2]_2$

The complex was synthesized similarly to that above, except that the reaction was carried out at r.t. Yield 72%. M.p.: 193–194°C (d). Anal. Calc. for $C_{28}H_{34}Ga_2N_4$: C, 59.41; H, 6.05; N, 9.90. Found C, 59.71; H, 6.18; N, 9.63. IR (ν, cm^{-1}): 3187 (w), 1587 (m), 1490 (s), 1308 (w), 1253 (m), 1017 (w), 865 (w), 776 (m), 753 (s), 700 (s), 633 (w), 584 (m), 541 (w), 511 (m), 483 (w). ^{1}H-NMR (500 MHz, C_6D_6): δ −0.37 (s, 3H, Ga*Me*), −0.27 (s, 6H, Ga*Me*), −0.05 (s, 3H, Ga*Me*), 3.82 (s, 0.9H, N*H*), 3.95 (s, 1.1H, N*H*), 6.95 (m, 20H, $\mathrm{N}\mathit{Ph}_2$). ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6): δ −14.8 (m, Ga*Me*) 121.4, 121.6, 123.6, 128.9, 152 (s, N*Ph*).

3.11. Preparation of $[Et_2GaNHNPh_2]_2$

The complex was synthesized in a similar manner to the phenyl species above. Yield 66%. M.p.: 130–133°C. Anal. Calc. for $C_{32}H_{42}Ga_2N_4$: C, 61.78; H, 6.80; N, 9.01. Found C, 61.49; H, 7.00; N, 8.99. IR (ν, cm^{-1}): 3200 (w), 1585 (m), 1490 (s), 1421 (w), 1310 (w), 1257 (m), 1218 (m), 1086 (w), 1075 (w), 1017 (w), 1004 (m), 847 (m), 779 (s), 752 (s), 703 (s), 663 (s) 560 (m), 511 (m). ^{1}H-NMR (500 MHz, C_6D_6): δ 0.47 (m, 8H, Ga*Et*), 0.93 (t, 2.4H, Ga*Me*, $J = 8$ Hz), 1.17 (t, 7H, Ga*Me*, $J = 8$ Hz), 1.31 (t, 2.6H, Ga*Me*, $J = 8$ Hz), 4.25 (s, 0.8H, N*H*), 4.46 (s, 1.2H, N*H*), 6.83 (m, 4H, N*Ph*), 7.06 (m, 16H, $\mathrm{N}\mathit{Ph}_2$). ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6): δ 3.9 (m, Ga*Me*), 10.43 (m, Ga*Et*), 121.4, 121.7, 123.8, 128.9, 152, s (N*Ph*).

3.12. Preparation of $[MeGaNHN{}^{t}Bu]_4$

A sample of $[Me_2GaNHNH{}^{t}Bu]_2$ (496 mg, 1.32 mmol) was heated to reflux for 36 h in toluene to yield a yellow solution. Volatiles were removed under reduced pressure and the resulting dry solid was recrystallized from pentane. Yield 310 mg (70%) of colorless crystals. M.p.: 188–189°C. Anal. Calc. for $C_{20}H_{52}Ga_4N_8$: C, 35.14; H, 7.67; N, 16.39. Found C, 34.81; H, 7.36; N, 15.99. IR (ν, cm^{-1}): 3286 (w), 1356

Table 2
Crystal data and collection details

Compound	$[^i\text{Pr}_2\text{GaNHNMe}_2]_2$	$[\text{MeGaNHN}^t\text{Bu}]_4$
Formula	$C_{16}H_{42}Ga_2N_4$	$C_{20}H_{52}Ga_4N_8$
Formula weight	429.97	683.57
Crystal size (mm)	0.25 × 0.21 × 0.15	0.11 × 0.22 × 0.20
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$; 2	$P2_1/c$; 14
T (°C)	−160	−98
a (Å)	8.5020(7)	12.107(1)
b (Å)	8.5703(7)	15.631(2)
c (Å)	9.4062(8)	16.766(2)
α (°)	112.216(2)	90
β (°)	113.729(1)	105.907(6)
γ (°)	98.830(2)	90
V (Å^3)	550.34(8)	3051.3(5)
Z	1.0	4.0
Reflections/unique	2296/1527	14535/5597
Variables	104	301
R	0.027	0.033
R_w	0.036	0.035
GOF	1.63	1.07
Refinement	F	F

(m), 1306 (w), 1209 (s), 1033 (w), 1002 (w), 943 (m), 916 (w), 834 (m), 610 (m), 566 (s), 500 (m), 477 (m). NMR (500 MHz, C_6D_6): δ −0.02 (s, 12H, Ga*Me*), 1.14 (s, 36H, N*Bu*), 2.09 (s, 4H, N*H*). $^{13}C\{^1H\}$-NMR (125.75 MHz, C_6D_6): δ −7.8 (s, Ga*Me*), 29.93 (s, N*Bu*), 55.41 (s, N*Bu*).

3.13. X-ray crystal structure determinations

Intensity data of $[^i\text{Pr}_2\text{GaNHNMe}_2]_2$ and $[\text{MeGaNHN}^t\text{Bu}]_4$ were collected on a Siemens SMART diffractometer/CCD area detector at low temperature (see Table 2) using Mo–K$_\alpha$ graphite collimated radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo–K}_\alpha) = 36.3\ \text{cm}^{-1}$. Absorption corrections were applied and the structures were solved using direct methods and refined by full least squares procedures using the Texsan package.

For $[\text{MeGaNHN}^t\text{Bu}]_4$, all non-hydrogen atoms were refined anisotropically. In the case of $[^i\text{Pr}_2\text{GaNHNMe}_2]_2$, all hydrogens were located in the difference map; those on the ring were not refined, the remainder were refined anisotropically. Crystal data and details on data collection are shown in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 114039 for $[\text{MeGaNHN}^t\text{Bu}]_4$ and 114038 for $[^i\text{Pr}_2\text{GaNHNMe}_2]_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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