Similarly, in **6**, θ averages 130.3° but φ is 46.5°. These values are well outside the range predicted in ref 33. Other compounds display even more dramatic deviations from that correlation. For example, in the recently synthesized dimers $[M(SAr)_2]_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$; M = Mn, Fe, or Co),[36] and θ and φ angles for the sulfurs in the M_2S_2 cores are as follows: Mn, $\theta = 93.3°$, $\varphi = 36.3°$; Fe, $\theta = 87.2°$, $\varphi = 43.2°$; Co, $\theta = 76.8°$, $\varphi = 52.4°$. These data demonstrate that θ values which differ by about 40° can have similar φ values as illustrated by compounds **6** and $[Fe(SAr)_2]_2$. On the basis of these data it is not possible to argue that an acute angle within an M_2S_2 ring necessarily implies a very pyramidal sulfur. This suggests that the sulfur centers in **5**, **6**, or **7** are not required to be either very pyramidal or nearly planar by the internal ring angle. Clearly, there is a tendency, but not a requirement, to adopt a particular sulfur geometry on the basis of the internal ring angles. In short the data allow for the possibility that some delocalization may indeed occur in the six-membered Zn_3S_3 rings.

Acknowledgment. We thank the National Science Foundation (CHE-8618739 and instrumentation Grant (CHE-8802721) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Full tables of crystallographic data, summary of data collection and refinement, positional parameters for non-hydrogen atoms, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (57 pages); listing of observed and calculated structure factors (163 pages). Ordering information is given on any current masthead page.

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Reactions of Trimethylaluminum or Trimethylgallium with Bulky Primary Amines: Structural Characterization of the Thermolysis Products

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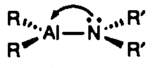
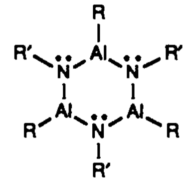
Abstract: The reaction of trimethylaluminum or trimethylgallium with bulky primary amines affords, in the first instance, dimeric aminoalkylalanes and gallanes via the elimination of 1 equiv of methane. Additional loss of methane may be accomplished by further heating of the aminometallanes to give either associated iminoalanes, orthometalated aminoalanes, or orthometalated aminogallanes. The aminometallane compounds $(Me_2MNHDipp)_2$ (Dipp = 2,6-*i*-Pr_2-C_6H_3; M = Al (**1**) or Ga (**2**)), $[Me_2MNH(1\text{-}Ad)]_2$ (1-Ad = 1-adamantyl; M = Al (**3**) or Ga (**4**)), and $(Me_2GaNHPh)_2$ (**5**) were isolated by the treatment of MMe_3 (M = Al or Ga) with 1 equiv of the primary amine in refluxing toluene. Each compound has been structurally and spectroscopically characterized by X-ray crystallography and/or ^1H, ^{13}C, and ^{27}Al NMR spectroscopy. The structures of **1**–**5** are all dimeric with bridging amide groups and distorted tetrahedral geometries at the metal. The aluminum and gallium compounds are invariably isomorphous. The bulky substituents present in **1** and **2** induce a remarkable 4-coordinate geometry at the nitrogen in which three of the substituents are coplanar with nitrogen and the fourth substituent occupies one of the axial positions of the pseudo-trigonal-bipyramidal arrangement. Further heating of the aluminum species **1** resulted in the isolation of the unique "alumazene" trimer $(MeAlNDipp)_3$ (**6**), whereas the corresponding reaction in the case of the gallium analogue **2** afforded the orthometalated species $[GaMe\{\mu\text{-}NHC_6H_3\text{-}i\text{-}Pr\text{-}6\text{-}CMeHCH_2\text{-}2\}]_2$ (**7**). Heating H_2NMes with $AlMe_3$ or $GaMe_3$ to a higher temperature resulted in the direct isolation of the cubane species $(MeAlNMes)_4\cdot 3C_7H_8$ (**8**) or the orthometalated compounds $[GaMe\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}CH_2\text{-}2\}]_2$ (**9**) and $Ga[\{NHC_6H_2Me_2\text{-}4,6,13,15\text{-}CH_2\text{-}2,11\}_2\mu\text{-}GaMe_2]$ (**10**). These products were also fully characterized by X-ray crystallography and/or ^1H, ^{13}C, and ^{27}Al NMR spectroscopy. The data reveal remarkable differences in the reactivity of aluminum and gallium. Thus, whereas the aluminum compounds eliminate a second equivalent of methane to afford the iminoalanes $(MeAlNR)_n$ (n = 3, 4), the gallium analogues prefer to eliminate methane by the activation of a C–H bond and subsequent cyclometalation. Compounds **3** and **4** exhibited remarkable stability and did not eliminate a second equivalent of methane below 300 °C. Compound **5** sublimed upon heating without further elimination of methane. The structure of **3** is currently the sole example of a trimeric iminoalane wherein both the aluminum and the nitrogen are three coordinate. It is, in effect, the aluminum analogue of borazine. The structure of **8** is one of a handful of structurally characterized tetrameric iminoalanes. The structures of **7**, **9**, and **10** are the first well-characterized cyclometalated gallium amide compounds.

In comparison to boron–nitrogen compounds the analogous species involving Al–N, Ga–N, In–N, or Tl–N bonds have received much less attention.[1] At present, for example, there are many classes of B–N compounds for which no heavier congeners involving the elements Al–Tl are structurally characterized. Simple examples include monomeric aminometallanes (R_2MNR_2', M = Al–Tl; R, R′ = alkyl or aryl), monomeric iminometallanes (RMNR′), and, until recently, aluminum analogues of borazine. These species, which may be illustrated schematically by


aminoalane


iminoalane


"alumazene"

are of interest because of the lower coordination numbers (3 and 2) of Al and N and/or the presence of adjacent nitrogen lone pairs and empty metal p-orbitals which may enable multiple bonding to occur. In fact, very few compounds that have bonding between

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three coordinate heavier main group 3 elements and nitrogen have been structurally characterized.[2-4] Amido or imido derivatives of the heavier elements are characterized by their tendency to associate with an increase in coordiantion number at both the metal and nitrogen. For example, polymeric iminoalanes $(RAlNR')_n$ (n = 4–16), which have three-dimensional cage structures, constitute a very interesting class of aluminum nitrogen compounds in which both Al and N are four coordinate.[5,6] Some gallium analogues of these compounds are also known.[7]

In this paper a study of the reaction of trimethylaluminum or trimethylgallium with bulky primary amines has been carried out with the objective of synthesizing either amino- or iminometallanes with low coordination numbers at the metal or nitrogen. Some of these studies, which resulted in the synthesis of $(MeAlNDipp)_3$,[8] have been described in a preliminary communication. In addition, a recent paper, which described the reaction between $AlMe_3$ and the very bulky primary amine $H_2N(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$, has also appeared.[9] More extensive studies from this laboratory on this theme are now reported.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques or a Vacuum Atmosphere HE-63 drybox. Solvents were freshly distilled under N_2 from Na/K and degassed three times immediately before use.

Physical Measurements. ^{1}H, ^{13}C, and ^{27}Al NMR spectra were obtained on a General Electric QE-300 spectrometer. All compounds gave satisfactory C, H, and N analyses.

Starting Materials. The compounds H_2NDipp, H_2NMes (purified by distillation from CaH_2 under reduced pressure), and $H_2N(1\text{-}Ad)$ and solutions of 1.0 M $AlMe_3$ in hexane and of 2.0 M $AlMe_3$ in toluene were purchased from commercial suppliers. $GaMe_3$ was synthesized by a literature procedure.[10]

[Me$_2$AlNHDipp]$_2$ (1). A 2.0 M solution of $AlMe_3$ (13 mL, 26 mmol) in toluene was added dropwise to a solution of H_2NDipp (4.9 mL, 26 mmol) in toluene (50 mL) at room temperature. The mixture was then refluxed for 20 h. Concentration under reduced pressure to ca. 20 mL and cooling overnight in a −20 °C freezer afforded colorless crystals of **1**: yield 4.8 g, 79%; mp 132–5 °C; ^{1}H NMR (C_6D_6) δ −0.31 (s, Al-Me), 1.25 (d, $CHMe_2$), 3.40 (sept, CH), 4.58 (s, NH), 7.1 (m, aryl-H); ^{13}C NMR (C_6D_6) δ −7.25 (Al-Me); ^{27}Al NMR (C_6D_6) δ 159.

[Me$_2$GaNHDipp]$_2$ (2). H_2NDipp (0.89 g, 0.95 mL, 5 mmol) was added to $GaMe_3$ (0.815 M in toluene, 6.13 mL, 5 mmol) in toluene (30 mL) and the mixture was refluxed overnight. The solvent was removed under reduced pressure. The cream-colored solid was redissolved in ca. 10 mL of hexane. Cooling overnight in a −20 °C freezer gave the product **2** as colorless crystals: yield 1.23 g, 89%; mp 150–2 °C; ^{1}H NMR (C_6D_6) δ 0.04 (s, Ga-Me), 1.26 (d, $CHMe_2$), 3.42 (sept, CH), 4.69 (s, NH), 7.05 (m, aryl-H); ^{13}C NMR (C_6D_6) δ −3.40 (Ga-Me).

[Me$_2$AlNH(1-Ad)]$_2$ (3). $H_2N(1\text{-}Ad)$ (0.76 g, 5 mmol) in toluene (15 mL) was added to $AlMe_3$ (1.0 M in hexane, 5 mL, 5 mmol) in toluene (15 mL) and the mixture was refluxed overnight. Slow cooling of the mixture to room temperature gave the product **3** as colorless crystals: yield 0.66 g, 64%; mp 225–7 °C; ^{1}H NMR(C_6D_6) δ −0.29 (s, Al-Me), 1.44 (s, 1-Ad-CH_2), 1.65 (s, 1-Ad-CH_2), 1.85 (s, 1-Ad-CH) (NH were not observed, perhaps, because of the poor solubility of **3** in benzene); ^{13}C NMR (C_6D_6) δ 30.24, 36.20, 46.04 (1-Ad-C) (Al-Me were also unobserved); ^{27}Al NMR (C_6D_6) δ 169.

[Me$_2$GaNH(1-Ad)]$_2$ (4). $H_2N(1\text{-}Ad)$ (0.76 g, 5 mmol) in toluene (15 mL) was added to $GaMe_3$ (0.815 M in toluene, 6.13 mL, 5 mmol) in toluene (15 mL) and refluxed overnight. Slow cooling of the mixture to room temperature gave the product **4** as colorless crystals: yield 0.84 g, 67%; mp 204–7 °C; ^{1}H NMR (C_6D_6) δ 0.04 (s, Ga-Me), 1.47 (s, 1-Ad-CH_2), 1.57 (s, 1-Ad-CH_2), 1.89 (s, 1-Ad-CH) (NH were not observed for the same reasons as for **3**); ^{13}C NMR (C_6D_6) δ 30.38, 36.46, 46.10 (1-Ad-C) (Ga-Me were also unobserved).

[Me$_2$GaNHPh]$_2$ (5). H_2NPh (0.65 g, 0.64 mL, 7 mmol) in toluene (15 mL) was added to $GaMe_3$ (0.815 M in toluene, 7 mmol) in toluene (15 mL) and refluxed overnight. The toluene was removed under reduced pressure and the residue was dissolved in warm hexane. Slow cooling in a 4 °C refrigerator gave the product **5** as colorless crystals: yield 1.26 g, 94%; mp 145–6 °C; ^{1}H NMR (C_6D_6) δ −0.14 (s, Ga-Me), 3.27 (s, NH), 6.87 (m, aryl-H).

[MeAlNDipp]$_3$ (6). Compound **1** (4.8 g, 10.3 mmol) was heated gradually (1 h) to 170 °C in an oil bath. Frothing occurred due to evolution of methane. After ca. 10 min gas evolution ceased and the reaction mixture resolidified to give **6** in essentially quantitative yield. Crystals for X-ray structural characterization were grown from hexane: mp 272–4 °C; ^{1}H NMR (C_6D_6) δ −0.82 (s, Al-Me), 1.31 (d, $CHMe_2$), 3.73 (sept, CH), 7.15 (m, aryl-H); ^{13}C NMR (C_6D_6) δ −16.23 (Al-Me); ^{27}Al NMR (C_6D_6) δ 160.

[GaMe{μ-NHC$_6$H$_3$-*i*-Pr-6-CMeHCH$_2$-2}]$_2$ (7). Compound **2** (1.23 g, 2.23 mmol) was heated to 190 °C in an oil bath for 2.5 h during which time methane was eliminated. The glassy residue was then dissolved in ca. 10 mL of hexane. Cooling overnight in a −20 °C freezer gave the product **7** as colorless crystals: yield 0.69 g, 56.0%; mp 191–3 °C; ^{1}H NMR (C_6D_6) δ −0.25 (s, Ga-Me), 1.33 (d, $CHMe_2$), 1.65 (d, C-Me), 2.98 (m, CH), 3.43 (sept, CH), 4.47 (s, NH), 7.15 (m, aryl-H); ^{13}C NMR (C_6D_6) δ −9.30 (Ga-Me).

(MeAlNMes)$_4$·3C$_7$H$_8$ (8). H_2NMes (2.43 g, 2.52 mL, 18 mmol) was added to $AlMe_3$ (1.0 M in hexane, 18 mL, 18 mmol) in toluene (30 mL) and refluxed overnight. The toluene was removed under reduced pressure. The pale yellow residue was heated to 170 °C in an oil bath. Methane evolution was apparent from the observed frothing. After ca. 30 min, gas evolution ceased and the mixture resolidified. The solid was dissolved in ca. 15 mL of toluene. Cooling overnight in a −20 °C freezer gave the product **8** as colorless crystals: yield 3.4 g, 77%; mp 293–5 °C; ^{1}H NMR (C_6D_6) δ −0.29 (s, Al-Me), 2.08 (s, *p*-Me), 2.40 (s, *o*-Me), 6.71 (s, aryl-H); ^{13}C NMR (C_6D_6) δ −0.40 (Al-Me); ^{27}Al NMR (C_6D_6) δ 155.

[GaMe{μ-NHC$_6$H$_2$Me$_2$-4,6-CH$_2$-2}]$_2$ (9) **and** **Ga[{NHC$_6$H$_2$Me$_2$-4,6,13,15-CH$_2$-2,11}$_2$$\mu$-GaMe$_2$] (10).** H_2NMes (0.55 g, 0.57 mL, 4.07 mmol) in toluene (20 mL) was added to $GaMe_3$ (0.815 M in toluene, 5 mL, 4.07 mmol) and refluxed overnight. The volatile materials were removed under reduced pressure. The pale yellow residue was placed in a preheated 190 °C oil bath for 3 h. Methane evolution was apparent from the observed bubbling. The glassy residue was then dissolved in ca. 10 mL of hexane. Cooling overnight in a −20 °C freezer gave a mixture of the isomers **9** and **10** as colorless crystals: yield 0.57 g, 65%; mp 185–192 °C. In a similar experiment, the pale yellow residue was placed in a preheated 240 °C oil bath for 3 h. Crystallization of the glassy residue from ca. 10 mL of hexane gave predominantly isomer **9** based on ^{1}H NMR: yield 0.61 g, 69%; mp 191–4 °C; ^{1}H NMR (C_6D_6) δ −0.52 (s, Ga-Me), 1.72 (s, *p*-Me), 1.82 (s, CH_2), 2.10 (s, *o*-Me), 2.63 (s, N-H), 6.57 (s, m-H), 7.04 (s, m-H). The ^{1}H NMR spectrum of the mixture of **9** and **10** also provides evidence that at least one more, as yet unidentified, compound is generated by the thermolysis.

X-ray Crystallography. Crystals of the compounds were mounted on the diffractometer by transferring them from the Schlenk tubes under N_2 to Petri dishes and immediately covering them with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber with silicone grease, and immediately placed in the low-temperature nitrogen stream.[11]

The X-ray data for compounds **1–4** and **6–10** were collected by using a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 device for low-temperature work and graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Crystal data are as follows: **1**, $(Me_2AlNHDipp)_2$, $C_{28}H_{48}Al_2N_2$, a = 10.029 (5) Å, b = 18.605 (7) Å, c = 15.546 (7) Å, β = 90.35 (4)°, Z = 4, space group $Pbn2_1$, 1095 ($I > 2\sigma I$) data, R = 0.085; **2**, $(Me_2GaNHDipp)_2$, $C_{28}H_{48}Ga_2N_2$, a = 10.056 (2) Å, b = 15.542 (3) Å, c = 18.451 (4) Å, Z = 4, space group $Pc2_1n$, 1528 ($I > 2\sigma I$) data, R = 0.052; **3**, $[Me_2AlNH(1\text{-}Ad)]_2$, $C_{24}H_{44}Al_2N_2$, a = 6.632 (1) Å, b = 9.739 (3) Å, c = 10.264 (3) Å, α = 74.71 (2)°, β = 74.57 (2)°, γ = 72.68 (2)°, Z = 1, space group $P\bar{1}$, 1757 ($I > 2\sigma I$)

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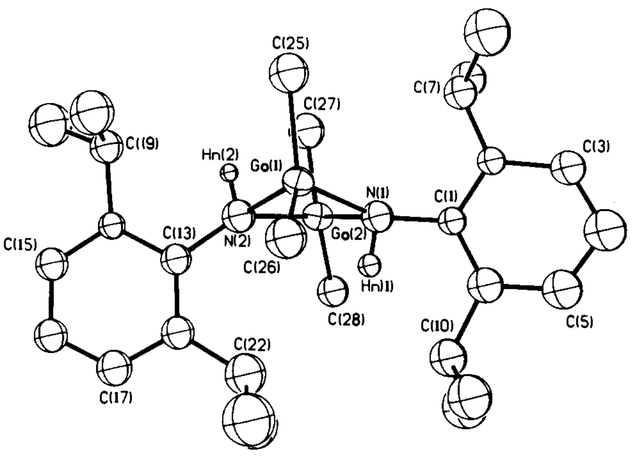

Figure 1. The structure of $[Me_2GaNHDipp]_2$ (**2**). The structure of $[Me_2AlNHDipp]_2$ (**1**) is isomorphous with **2**. Important bond distances and angles are provided in Table II.

data, $R = 0.043$; **4**, $C_{24}H_{44}Ga_2N_2$, $a = 6.668$ (1) Å, $b = 9.777$ (5) Å, $c = 10.292$ (2) Å, $\alpha = 74.35$ (3)°, $\beta = 74.36$ (2)°, $\gamma = 72.42$ (3)°, $Z = 1$, space group $P\bar{1}$, 1937 ($I > 2\sigma I$) data, $R = 0.043$; **5**, $(Me_2GaNHPh)_2$, $C_{16}H_{24}Ga_2N_2$, $a = 10.026$ (5) Å, $b = 7.251$ (3) Å, $c = 12.799$ (6) Å, $\beta = 112.01$ (4)°, $Z = 2$, space group $P2_1/c$, 1077 ($I > 2\sigma I$) data, $R = 0.055$; **7**, [GaMe{μ-NHC_6H_3-*i*-Pr-6-$MeHCH_2$-2}], $C_{26}H_{40}Ga_2N_2$, $a = 9.536$ (2) Å, $b = 9.658$ (4) Å, $c = 14.289$ (5) Å, $\alpha = 79.80$ (3)°, $\beta = 85.16$ (3)°, $\gamma = 83.44$ (3)°, $Z = 2$, space group $P\bar{1}$, 2890 ($I > 2\sigma I$) data, $R = 0.043$; **8**, $(MeAlNMes)_4 \cdot 3C_7H_8$, $C_{61}H_8Al_4N_4$, $a = 13.082$ (3) Å, $b = 19.027$ (3) Å, $c = 22.941$ (9) Å, $\beta = 101.04$ (3), $Z = 4$, space group $P2_1/c$, 5848 ($I > 2\sigma I$) data, $R = 0.055$; **9**, [GaMe{μ-$NHC_6H_2Me_2$-4,6-CH_2-2}]$_2$ $C_{20}H_{28}Ga_2N_2$, $a = 7.670$ (3) Å, $b = 15.285$ (4) Å, $c = 16.978$ (4) Å, $Z = 4$, space group *Pbca*, 971 ($I > 2\sigma I$) data, $R = 0.034$; **10**, Ga[{$NHC_6H_2Me_2$-4,6,13,15-CH_2-2,11}$_2$-μ-$GaMe_2$], $C_{20}H_{28}Ga_2N_2$, $a = 11.985$ (4) Å, $b = 13.502$ (4) Å, $c = 13.420$ (5) Å, $\beta = 113.76$ (2)°, $Z = 4$, space group $P2_1/c$, 1650 ($I > 2\sigma I$) data, $R = 0.063$.

Calculations were carried out on a Data General Eclipse computer with SHELXTL, Version 5. A Siemens R3 m/V diffractometer equipped with a locally modified Enraf-Nonius LT apparatus and Cu Kα radiation ($\lambda = 1.54178$ Å) was employed for data collection of structure **5**. Calculations for structure **5** were carried out on a Micro VAX 3200 with SHELXTL PLUS. Hydrogen atoms attached to nitrogen in compound **1** were not located due to disorder. Hydrogen atoms attached to nitrogen in structures **2**–**5** and **9** were located in corresponding difference maps and were allowed to refine with free positional parameters. In the case of compounds **7** and **10**, the amide hydrogens were located in the corresponding difference map and refined with use of a riding model with N–H of 0.980 Å. All other hydrogen atoms in the structures **1**–**10** were included at calculated positions with use of a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U_{iso}(C)$ or 1.2 $U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter. All non-hydrogen atoms were refined anisotropically except in the case of structures **2** and **10** where only the metals were made anisotropic and structures **1** and **4** where only the metals and nitrogen were made anisotropic. An ω scan method was used as described in ref 11. Scattering factors were from common sources.[12] An absorption correction was applied by using the method described in ref 13. Important bond distances and angles are listed in Table I. Crystallographic data for **6** as well as some structural data have been published in a preliminary communication.[8]

Description of Structures 1–10. **$[Me_2AlNHDipp]_2$ (1) and $[Me_2GaNHDipp]_2$ (2).** Compounds **1** and **2** are isomorphous and are represented by the illustration of **2** in Figure 1. Each compound has a noncentrosymmetric, dimeric structure and the metals are bridged by –NHDipp groups. The amide hydrogens were not located in compound **1** due, apparently, to disorder. In each compound, the metals have distorted tetrahedral environments with angles ranging form 82.6 (4)° to 122.2 (6)° in **1** and from 81.5 (4)° to 121.5 (6)° in **2**. In both compounds the N(1) and N(2) centers possess slightly different geometries. One of the bridging nitrogens, N(1), is approximately coplanar with the metal–C(1)–metal plane. The sum of the angles at N(1) is equal to 359.0° for **1** and 357.8° for **2** and the distances of the N(1) centers from the $M_2C(1)$ plane are 0.098 and 0.143 Å, respectively. In contrast, the N(2) centers have somewhat more pyramidal $NC(ipso)M_2$ arrangements and the sum of the angles is 352.2° in the case of **1** and 352.7° for **2**. The distances of the N(2) atoms from the metal–C(13)–metal plane are 0.2736 and 0.2675 Å, respectively. The Al⋯Al separation in **1** is 2.894 Å and the Ga⋯Ga separation in **2** is 2.998 Å. The internal angles in both the M_2N_2 cores are very similar with an average of 83.3 (4)° at aluminum and 94.3 (4)° at nitrogen in **1** and 82.6 (4)° at gallium and 94.2 (4)° at nitrogen in **2**. The average metal–N bond length is 1.975 Å in **1** and 2.046 Å in **2**. The M_2N_2 cores are not planar but have a fold angle of 22.7° for **1** and 25.8° for **2** between the MN_2 planes. The angle between the C(1)-aromatic ring plane and the M⋯M vector is 89.3° in **1** and 88.6° in **2** whereas the corresponding angles for the C(13)-aromatic ring plane are 80.5° in **1** and 82.7° in **2**.

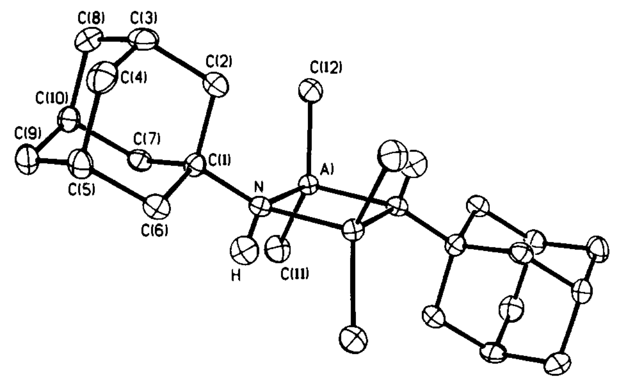

Figure 2. The structure of $[Me_2AlNH(1\text{-}Ad)]_2$ (**3**). The structure of $[Me_2GaNH(1\text{-}Ad)]_2$ (**4**) is isomorphous with **3**.

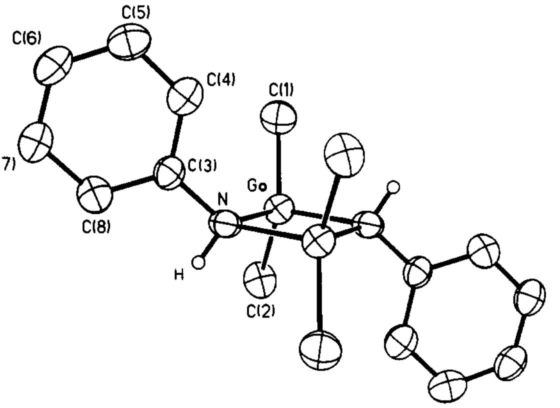

Figure 3. The structure of $[Me_2GaNHPh]_2$ (**5**).

$[Me_2AlNH(1\text{-}Ad)]_2$ (3) and $[Me_2GaNH(1\text{-}Ad)]_2$ (4). Compounds **3** and **4** (illustrated by **3** in Figure 2) are isomorphous and they have very similar, centrosymmetric, dimeric structures. The monomeric units $MMe_2NH(1\text{-}Ad)$ (M = Al or Ga) are related through an inversion center. The metals in both compounds are bridged by –NH(1-Ad) groups. The coordination of the metals is distorted tetrahedral with the angles at the metal varying from 86.5 (1) to 117.7 (1)° in compound **3** and 85.3 (1) to 118.5 (2)° in compound **4**. The average metal–N bond length is 1.963 (2) Å in **8** and 2.024 (3) Å in **9**. The M_2N_2 cores are planar for both compounds as crystallographically required. The internal angles in the M_2N_2 cores are very similar with values of 86.5 (1)° at gallium and 93.5 (1)° at nitrogen in **3** and 85.3 (1)° at gallium and 94.7 (1)° at nitrogen in **4**. The Al⋯Al separation in **3** is 2.859 Å whereas the Ga⋯Ga separation in **4** is 2.977 Å.

$[Me_2GaNHPh]_2$ (5). Compound **5** has many structural similarities to **4**. The molecule possesses a centrosymmetric, dimeric structure with gallium atoms bridged by –NHPh groups. The coordination of the gallium is distorted tetrahedral with the angles at gallium varying from 86.4 (1) to 121.9 (2)°. The average Ga–N bond distance is 2.038 (3) Å. The internal angles in the planar Ga_2N_2 core are 86.4 (1)° at gallium and 93.6 (1)° at nitrogen. The Ga⋯Ga separation is 2.972 Å. The angle between the aromatic ring and the planar Ga_2N_2 core is 89.8°.

$[MeAlNDipp]_3$ (6). A description of this compound has been reported in a preliminary note.[8] The structure of **6** (Figure 4) consists of a planar six-membered ring comprised of alternating Al and N atoms. The Al–N bonds are essentially equal and have a length of 1.782 (4) Å. The

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(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(13) XABS: the method obtains an empirical absorption tensor for an expression relating F_o and F_c: Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

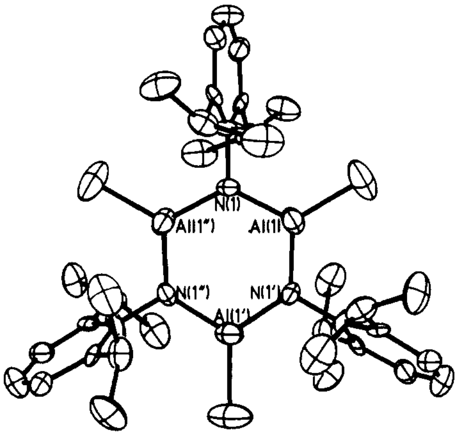

Figure 4. The structure of $[\mathrm{MeAlNDipp}]_3$ (6).

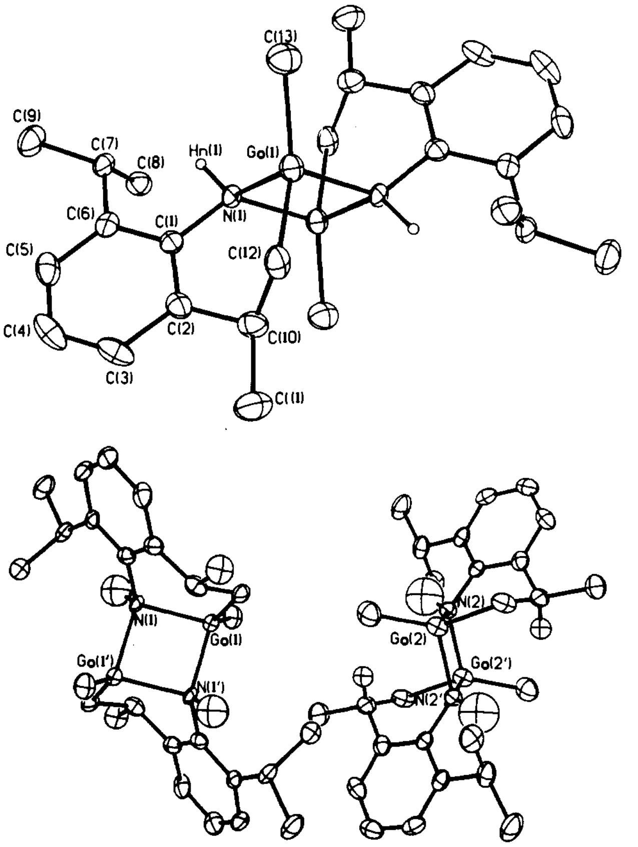

Figure 5. (a) The structure of $[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_3}\text{-}i\text{-}\mathrm{Pr}\text{-}6\text{-}\mathrm{CMeHCH_2}\text{-}2}\}]_2$ (7). (b) The depiction of the asymmetric unit of compound 7.

internal ring angles at Al and N are 115.3 (5) and 124.7 (5)°, respectively. The carbon atoms bonded to Al or N are coplanar with the $\mathrm{Al_3N_3}$ ring. The angle between the $\mathrm{Al_3N_3}$ and C(1) rings is 75.3°.

$[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_3}\text{-}i\text{-}\mathrm{Pr}\text{-}6\text{-}\mathrm{CMeHCH_2}\text{-}2}\}]_2$ (7). The structure of 7, which is illustrated in Figure 5a, consists of a centrosymmetric, dimeric molecule of $[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_3}\text{-}i\text{-}\mathrm{Pr}\text{-}6\text{-}\mathrm{CMeHCH_2}\text{-}2}\}]_2$. It is derived from, and is closely related to, the structure of 2. In this case, each gallium is coordinated to one methyl group and one of the o-i-Pr groups rather than to two methyl groups. The monomeric units are related through an inversion center. The asymmetric unit contains two crystallographically independent (but chemically identical) molecules as illustrated in Figure 5b. The $\mathrm{Ga_2N_2}$ cores are planar as crystallographically required. In each molecule the internal angles are 86.4 (2)° at gallium and 93.7 (2)° at nitrogen. The gallium atoms possess a distorted tetrahedral coordination with irregular angles varying from 86.2 (2)° to 131.0 (2)°. The average Ga–N distance is 2.025 (4) Å and the average Ga···Ga separation within each molecule is 2.97 Å. The Ga–C distances to the ortho carbons are marginally (0.02–0.04 Å) longer than the Ga–C methyl bonds. Four of the six atoms that comprise the ring formed by the ortho-metalation are almost coplanar. The C(12) of the methylene group and the gallium atom lie 1.267 and 1.274 Å from the N–C(1)–C(2)–C(10) plane so that there is, in effect, a dihedral angle of 39.8° between the N–Ga–C(12) and the N–C(1)–C(2)–C(12) planes. The angle between the coplanar portion of the six-membered ring and the aryl ring is only 2° whereas the angle to the planar $\mathrm{Ga_2N_2}$ core is ca. 76°.

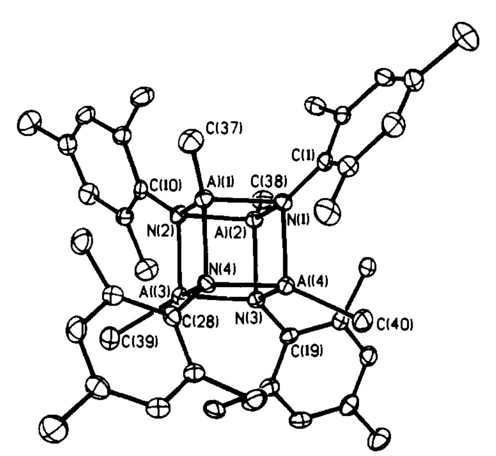

Figure 6. The structure of $(\mathrm{MeAlNMes})_4{\cdot}3\mathrm{C_7H_8}$ (8). The three toluene molecules have been omitted for clarity.

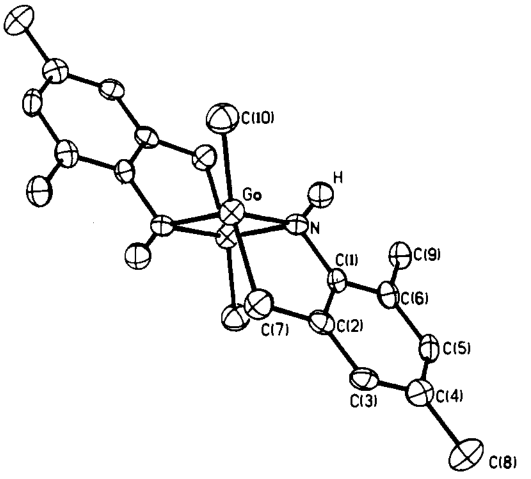

Figure 7. The structure of $[\overline{\mathrm{GaMe}\{\mu\text{-}\mathrm{NHC_6H_2Me_2}\text{-}4,6\text{-}\mathrm{CH_2}\text{-}2}\}]_2$ (9).

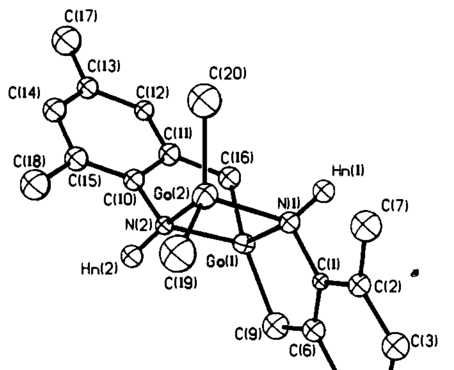

Figure 8. The structure of $\overline{\mathrm{Ga}[\{\mathrm{NHC_6H_2Me_2}\text{-}4,6,13,15\text{-}\mathrm{CH_2}\text{-}2,11}\}_2\text{-}\mu\text{-}\mathrm{GaMe_2}]$ (10).

$[\mathrm{MeAlNMes}]_4{\cdot}3\mathrm{C_7H_8}$ (8). The structure of 8 is presented in Figure 6. The asymmetric unit includes 3 molecules of toluene which have been omitted from the illustration for clarity. The compound is a tetramer that is comprised of MeAlNMes units and possesses an almost perfectly cubic $\mathrm{Al_4N_4}$ core. Each face of the cube displays only minor (ca. 1°) distortions from a perfectly square configuration. The average Al–N distance is 1.948 (7) Å. The average Al···Al or N···N separation is 2.754 Å. For each aluminum, two of the three C–Al–N angles have an average value

Table I. Some Important Bond Distances (Å) and Angles (deg) for **1–10**

				1			
Al(1)–N(1)	1.981 (12)	Al(1)···Al(2)	2.894	N(1)–Al(1)–N(2)	82.6 (4)	C(27)–Al(1)–C(28)	115.7 (7)
Al(1)–N(2)	1.992 (11)	N(1)–C(1)	1.445 (15)	N(1)–Al(1)–C(27)	113.6 (6)	Al(1)–N(1)–Al(2)	94.7 (5)
Al(1)–C(27)	1.951 (14)	N(1)···N(2)	2.623	N(1)–Al(1)–C(28)	115.9 (6)	Al(1)–N(1)–C(1)	131.4 (8)
Al(1)–C(28)	1.969 (16)			N(2)–Al(1)–C(27)	107.5 (6)	Al(2)–N(1)–C(1)	132.9 (9)
				N(2)–Al(1)–C(28)	117.0 (6)		
				2			
Ga(1)–N(1)	2.024 (11)	N(1)–H(N1)	0.95 (4)	N(1)–Ga(1)–N(2)	83.6 (4)	Ga(1)–N(1)–Ga(2)	94.2 (4)
Ga(1)–N(2)	2.026 (11)	N(1)–C(1)	1.427 (15)	N(1)–Ga(1)–C(25)	113.5 (6)	Ga(1)–N(1)–H(N1)	97 (5)
Ga(1)–C(25)	1.990 (12)	N(2)–H(N2)	0.96 (5)	N(1)–Ga(1)–C(26)	113.7 (5)	Ga(1)–N(1)–C(1)	134.2 (8)
Ga(1)–C(26)	1.981 (15)	N(1)···N(2)	2.699	N(2)–Ga(1)–C(25)	106.1 (5)	Ga(2)–N(1)–H(N1)	91 (4)
Ga(1)···Ga(2)	2.998			N(2)–Ga(1)–C(26)	114.4 (5)	Ga(2)–N(1)–C(1)	129.4 (8)
				C(25)–Ga(1)–C(26)	119.7 (7)	H(N1)–N(1)–C(1)	96 (4)
				3			
Al–N	1.968 (2)	N–H	0.87 (3)	N–Al–C(11)	107.6 (1)	Al–N–H	102 (2)
Al–C(11)	1.957 (3)	N–C(1)	1.497 (3)	N–Al–C(12)	117.7 (1)	Al–N–C(1)	124.8 (1)
Al–C(12)	1.959 (3)	Al···Al′	2.859	N–Al–N′	86.5 (1)	Al–N–Al′	93.5 (1)
Al–N′	1.958 (2)	N···N′	2.691	C(11)–Al–C(12)	116.2 (1)	H–N–C(1)	105 (2)
				C(11)–Al–N′	116.4 (1)	H–N–Al′	100 (1)
				C(12)–Al–N′	109.0 (1)	C(1)–N–Al′	127.0 (2)
				4			
Ga–N	2.031 (3)	N–H	0.84 (5)	N–Ga–C(11)	117.4 (2)	Ga–N–H	108 (3)
Ga–C(11)	1.968 (5)	N–C(1)	1.503 (5)	N–Ga–C(12)	106.6 (1)	Ga–N–C(1)	123.7 (2)
Ga–C(12)	1.969 (5)	Ga···Ga′	2.977	N–Ga–N′	85.3 (1)	Ga–N–Ga′	94.7 (1)
Ga–N′	2.018 (3)	N···N′	2.744	C(11)–Ga–C(12)	118.5 (2)	H–N–C(1)	101 (3)
				C(11)–Ga–N′	108.1 (1)	H–N–Ga′	101 (3)
				C(12)–Ga–N′	116.5 (2)	C(1)–N–Ga′	125.8 (3)
				5			
Ga–N	2.039 (3)	N–H	0.87 (7)	N–Ga–C(1)	113.1 (2)	Ga–N–H	118 (3)
Ga–C(1)	1.954 (6)	N–C(3)	1.427 (6)	N–Ga–C(2)	109.3 (2)	Ga–N–C(3)	120.8 (3)
Ga–C(2)	1.936 (6)	Ga···Ga′	2.972	N–Ga–N′	86.4 (1)	Ga–N–Ga′	93.6 (1)
Ga–N′	2.036 (4)	N···N′	2.789	C(1)–Ga–C(2)	121.9 (2)	H–N–C(3)	96 (3)
				C(1)–Ga–N′	107.9 (2)	H–N–Ga′	107 (4)
				C(2)–Ga–N′	112.6 (2)	C(3)–N–Ga′	121.6 (3)
				6			
Al(1)–N(1)	1.782 (4)	Al(1)–C(13)	1.978 (15)	N(1)–Al(1)–N(1)′	115.3 (5)	Al(1)–N(1)–Al(1)′	124.7 (5)
N(1)–C(1)	1.442 (14)						
				7[a]			
Ga(1)–N(1)	2.023 (4)	N(1)–C(1)	1.447 (6)	N(1)–Ga(1)–C(12)	98.7 (2)	Ga(1)–N(1)–HN(1)	123.4 (1)
Ga(1)–C(12)	1.980 (5)	C(1)–C(2)	1.417 (8)	N(1)–Ga(1)–C(13)	113.8 (2)	Ga(1)–N(1)–C(1)	115.5 (3)
Ga(1)–C(13)	1.964 (6)	C(2)–C(10)	1.534 (8)	N(1)–Ga(1)–N(1)′	86.2 (2)	Ga(1)–N(1)–Ga(1)′	93.8 (2)
Ga(1)–N(1)′	2.045 (4)	C(10)–C(11)	1.534 (8)	C(12)–Ga(1)–C(13)	131.0 (2)	HN(1)–N(1)–C(1)	89.1 (3)
N(1)–H(N1)	0.980	C(10)–C(12)	1.537 (7)	C(12)–Ga(1)–N(1)′	102.1 (2)	HN(1)–N(1)–Ga(1)′	112.4 (1)
				C(13)–Ga(1)–N(1)′	115.0 (2)	C(1)–N(1)–Ga(1)′	125.7 (3)
				8[b]			
Al–N	1.948 (7)	Al···Al	2.753	Al–N–Al	89.9 (6)	N(4)–Al(1)–C(37)	119.2 (1)
Al–C	1.949 (3)	N···N	2.755	N–Al–N	90.1 (6)	Al(1)–N(1)–C(1)	116.8 (2)
N–C	1.451 (3)			N(1)–Al(1)–C(37)	114.2 (1)	Al(4)–N(1)–C(1)	121.4 (2)
				N(2)–Al(1)–C(37)	140.7 (1)	Al(2)–N(1)–C(1)	136.6 (2)
				9			
Ga–N	2.029 (4)	N–C(1)	1.446 (6)	N–Ga–C(7)	89.5 (2)	Ga–N–Ga′	92.3 (2)
Ga–C(7)	1.970 (5)	C(1)–C(2)	1.399 (7)	N–Ga–C(10)	117.2 (2)	H–N–C(1)	108 (3)
Ga–C(10)	1.962 (5)	C(2)–C(7)	1.516 (7)	N–Ga–N′	87.7 (2)	H–N–Ga′	115 (3)
Ga–N′	2.016 (4)	Ga···Ga′	2.918	C(7)–Ga–C(10)	134.0 (2)	C(1)–N–Ga′	117.8 (3)
N–H	0.82 (4)	N···N′	2.801	C(7)–Ga–N′	108.4 (2)	N–C(1)–C(2)	118.2 (4)
				C(10)–Ga–N′	109.3 (2)	C(1)–C(2)–C(7)	118.9 (4)
				Ga–N–H	117 (3)	C(2)–C(7)–Ga	105.4 (3)
				Ga–N–C(1)	106.4 (3)		
				10			
Ga(1)–N(1)	2.032 (10)	N(1)–HN1	0.98	N(2)–Ga(1)–N(1)	88.3 (4)	N(2)–Ga(2)–N(1)	87.5 (4)
Ga(1)–N(2)	1.995 (9)	N(2)–C(10)	1.447 (17)	C(9)–Ga(1)–N(1)	90.5 (6)	C(19)–Ga(2)–N(1)	113.4 (6)
Ga(1)–C(9)	1.967 (18)	N(2)–HN2	0.980	C(9)–Ga(1)–N(2)	118.9 (6)	C(19)–Ga(2)–N(2)	110.8 (7)
Ga(1)–C(16)	1.949 (16)	C(1)–C(6)	1.355 (22)	C(16)–Ga(1)–N(1)	114.4 (6)	C(20)–Ga(2)–N(1)	105.6 (7)
Ga(2)–N(1)	2.034 (10)	C(6)–C(9)	1.510 (19)	C(16)–Ga(1)–N(2)	88.5 (5)	C(20)–Ga(2)–N(2)	107.6 (6)
Ga(2)–N(2)	2.024 (10)	C(10)–C(11)	1.396 (22)	C(16)–Ga(1)–C(9)	144.2 (6)	C(20)–Ga(2)–C(19)	125.3 (9)
Ga(2)–C(19)	1.958 (22)	C(11)–C(16)	1.514 (18)	Ga(2)–N(1)–Ga(1)	91.3 (4)	Ga(2)–N(2)–Ga(1)	92.7 (4)
Ga(2)–C(20)	1.955 (25)	Ga(1)···Ga(2)	2.908	HN1–N(1)–Ga(1)	125.0 (4)	HN2–N(2)–Ga(1)	122.2 (4)
N(1)–C(1)	1.461 (17)	N(1)–N(2)	2.805	HN1–N(1)–Ga(2)	115.3 (4)	HN2–N(2)–Ga(2)	115.9 (3)
				C(1)–N(1)–Ga(1)	106.2 (9)	C(10)–N(2)–Ga(1)	109.8 (8)
				C(1)–N(1)–Ga(2)	117.2 (8)	C(10)–N(2)–Ga(2)	116.8 (9)
				C(1)–N(1)–HN1	102.5 (7)	C(10)–N(2)–HN2	100.5 (8)
				N(1)–C(1)–C(6)	116.7 (10)	C(11)–C(10)–N(2)	114.6 (10)
				C(1)–C(6)–C(9)	123.3 (14)	C(16)–C(11)–C(10)	119.6 (13)
				C(6)–C(9)–Ga(1)	103.2 (12)	C(11)–C(16)–Ga(1)	106.5 (11)

[a] Values are reported for molecule 1 only. [b] Averaged bond distances and angles. The angles for the Al(1) and N(1) centers are provided to illustrate the distortion in the geometry.

Scheme I. Summary of the Reactions of $AlMe_3$ or $GaMe_3$ with Bulky Primary Amines

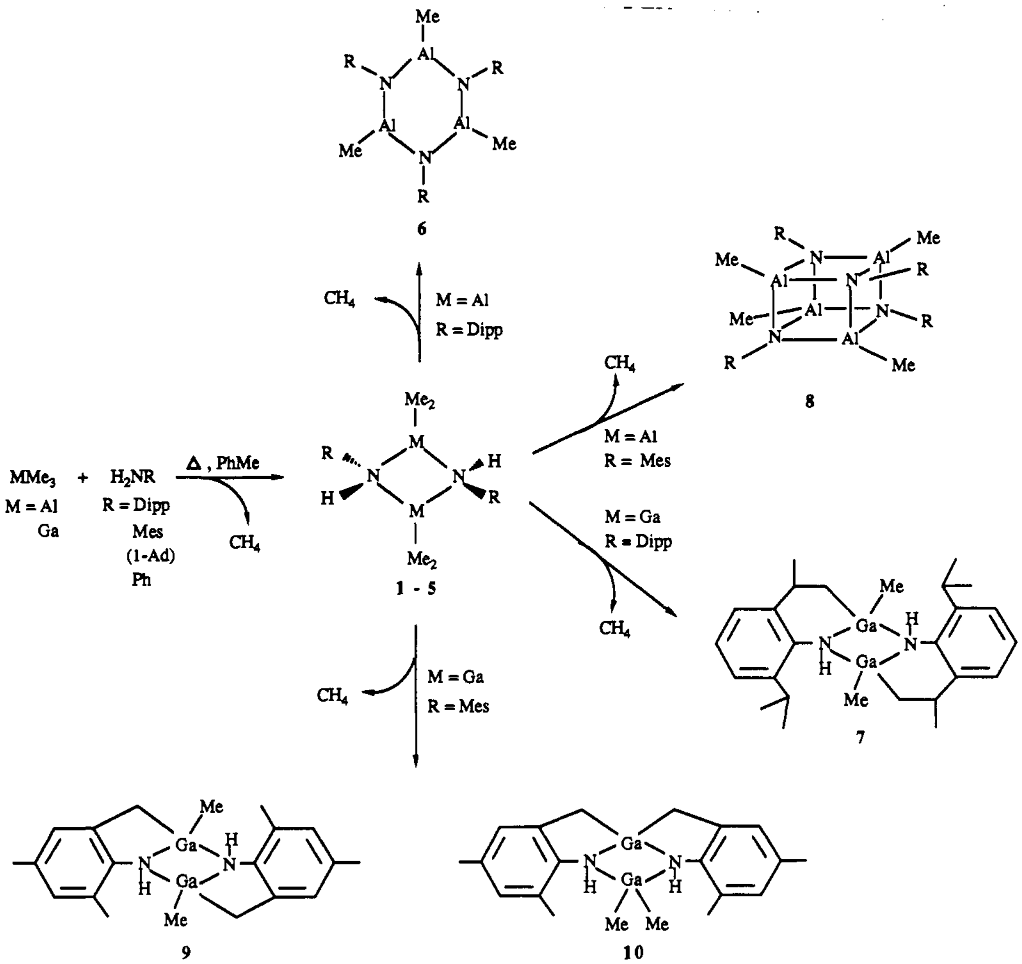

Table II.[a,b] Energy of Reaction Results for Homodesmotic[c] Reactions of C_6H_6, $B_3N_3H_6$, $Al_3N_3H_6$, and $B_3P_3H_6$

	ΔE_{rxn}, kcal		
reaction	RHF 3-21G*	RHF 3-21G*	MP4SDQ 6-31G*
$C_6H_6 + 3C_2H_4 \rightarrow 3C_4H_6$	27.7	24.7	22.1
$B_3N_3H_6 + 3H_2BNH_2 \rightarrow 3B_2N_2H_6$	7.7	8.4	11.1
$Al_3N_3H_6 + 3H_2AlNH_2 \rightarrow 3Al_2N_2H_6$	1.8	0.8	1.9
$B_3P_3H_6 + 3H_2BPH_2 \rightarrow 3B_2P_2H_6$	8.1	7.4	12.7

[a] Reference 37. [b] Transoid optimized geometries were used for all butadiene analogues and chair conformers for all cyclohexane analogues. [c] The term homodesmotic has been used to indicate that the number, hybridization, and bonding of the atoms on each side of the equation are the same. The energy difference is taken to be the result of the delocalization. For futher discussion see refs 37 and 38.

of 116.3 (1)° whereas the third C–Al–N angle has a larger average value of 141.0 (1)°. Similarly, for the three C–N–Al angles, the average values are 115.9 (2), 122.7 (2), and 136.1 (2)°.

$[GaMe\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}CH_2\text{-}2\}]_2$ (9) and $Ga[\{NHC_6H_2Me_2\text{-}4\text{-}6,13,15\text{-}CH\text{-}2,11\}_2\mu\text{-}GaMe_2]$ (10). The isomers **9** and **10** are similar to **7** since they are derived from metalation of the ortho substituent of the aromatic group. In addition, both are derived from similar precursors (which were not isolated) in which the –NHDipp group is replaced by an –NHMes group. Compound **9** (Figure 7) consists of a dimeric $[GaMe\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}CH_2\text{-}2\}]_2$ unit where each gallium is coordinated to one methyl and one $-CH_2Ar$ group rather than to two methyls as in the precursor. Compound **10** (Figure 8) consists of a $Ga[NHC_6H_2Me_2\text{-}4,6,13,15\text{-}CH_2\text{-}2,11]_2$ unit where one gallium is bonded to two $-CH_2Ar$ groups and the other gallium remains bonded to two methyls. In other words, each gallium is involved in bonding to one o-CH_2 group in compound **9**, but only one gallium participates in such bonding in compound **10**. The Ga_2N_2 core in **9** is perfectly planar with internal angles of 87.7 (2)° at gallium and 92.3 (4)° at nitrogen. The Ga_2N_2 core in **10** displays only minor deviations from prefect planarity and has average internal angles of 87.9 (4)° at gallium and 92.0 (4)° at nitrogen. The gallium atoms in compound **9** possess a distorted tetrahedral coordination with irregular angles that vary from 87.7 (2) to 134.0 (2)°. The gallium centers in the compound also have distorted tetrahedral coordination. However, the external core angles at Ga(1) and Ga(2) are quite different as is expected from the asymmetry of the molecule. For example, the more restricted methylene–Ga(1)–N angles have an average value of 89.5 (5)° whereas the methyl–Ga(2)–N angles have an average value of 110.5 (6)°. Similarly, the C(16)–Ga(1)–C(9) angle is 144.2 (6)° whereas the C(19)–Ga(2)–C(20) angle is 125.3°. The angle between the ring formed by the ortho-metalation and the aryl ring is 6.9° for **9** and only 1.2° for **10**. The corresponding angle to the planar Ga_2N_2 core is 113.0° for **9** and an average of 117.1° for **10**. In both compounds the average Ga···Ga separation is 2.91 Å.

Discussion

Formation of the Aminoalkylalanes and Aminoalkylgallanes, 1–5. The reactions of trimethylaluminum or trimethylgallium with bulky primary amines are summarized in Scheme I. The elimination reactions are more facile for aluminum than gallium.[14] This observation may be rationalized in part by consideration of the charge distribution within the precursor adducts Me_3M: NH_2R'.[15,16] The greater the electropositive character of the metal (Al > Ga) the stronger the M←N dative bond. The increased M←N bond strength enhances the acidity of the NH bond and also the carbanionic character of the methyl groups.[17] Thus, in general, aluminum adducts have been observed to eliminate alkane at temperatures where the gallium analogues were unaffected.

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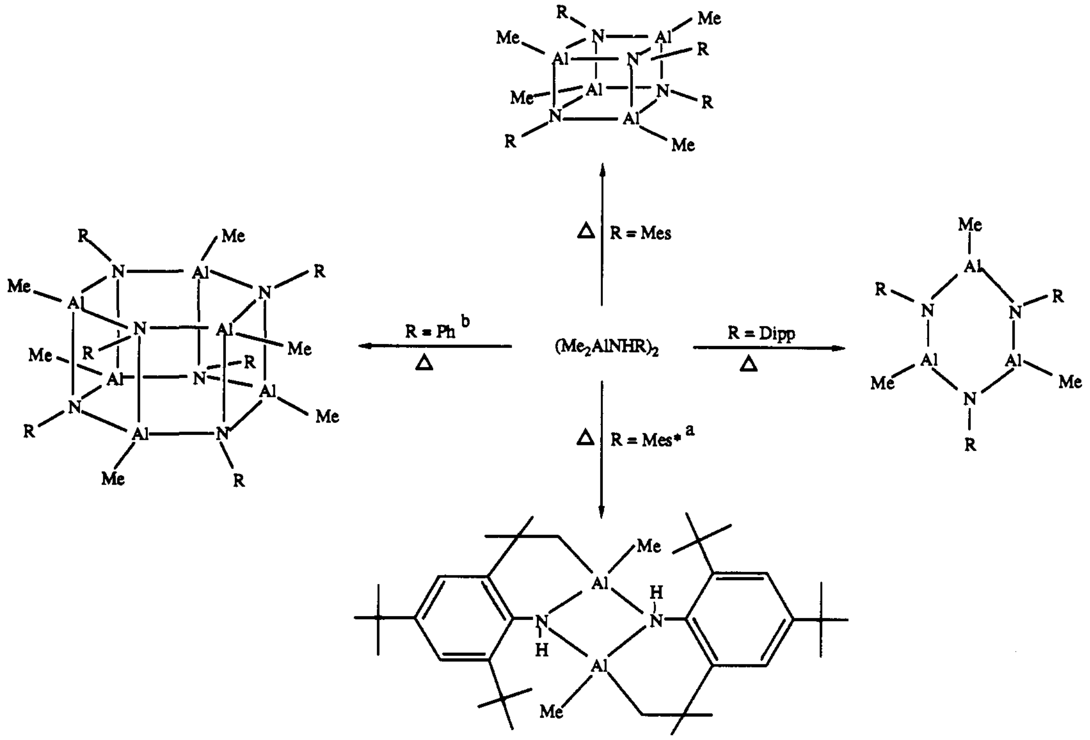
(14) Beachley, O. T.; Coates, G. E.; Kohnstam, G. *J. Chem. Soc.* **1965**, 3241, 3248.

(15) Storr, A. *J. Chem. Soc. A* **1968**, 2605.

(16) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101.

(17) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1, Chapter III.

Scheme II. Illustration of the Influence of the Size of the Nitrogen Substituent R on the Degree of Aggregation of Iminoalanes



[a] Reference 9. [b] Reference 30.

In addition, an extension of the study to include phosphorus and arsenic adducts has shown that the ease of formation of the alane follows the order N < P < As whereas the reverse order is observed for formation of the gallanes.[14,18]

The initial reaction presumably results in the formation of an adduct of the type $Me_3M{:}NH_2R'$ although none of these were isolated. The subsequent loss of 1 equiv of methane affords the associated aminoalane $(R_2MNHR')_n$. The degree of association of the amide is governed mainly by steric factors, and in the case of **1**–**5**, n is always 2. Although the structures of no monomers ($n = 1$) have yet been described, compounds where $n = 2$ or 3 are already known even though few enough have been structurally characterized. Examples are $(Cl_2AlNMe_2)_2$,[19] $(Me_2AlNMe_2)_2$,[20] $(Me_2AlNPh_2)_2$,[21] and $(H_2GaNMe_2)_2$[22] which have Al–N distances of 1.95–1.96 Å and a Ga–N distance of 2.027 (4) Å. In **1**–**5** where the substituents are the same, the aluminum and gallium dimers are isomorphous. This is not surprising because of somewhat similar covalent radii of the two metals. With the exception of the M–N and M–C bond lengths, the metric features of species **1** and **2** and **3** and **4** are almost identical. The Al–N and Ga–N bond lengths are similar to those previously observed in other dimers and trimers.[19-23] The Al–N bond lengths of 1.968–1.991 Å in **1** and **3**, however, are generally longer than those previously observed. The origin of their lengthening may be steric, owing to the slightly smaller size of Al. In the Ga compounds **2**, **4**, and **5** the Ga–N bonds remain remarkably constant and close to those observed in relatively unhindered compounds such as $(H_2GaNMe_2)_2$. Compounds **3**, **4**, and **5** have centrosymmetric structures with monomeric units related through an inversion center. In contrast, **1** and **2** are noncentrosymmetric with no imposed symmetry. This may be an effect of the pendant isopropyl groups on the aryl rings of **1** and **2** which may destroy the symmetry by rotation around a C–C bond. The hybridization at nitrogen appears to display increased sp^2 character with increasing size of the R groups attached to nitrogen. For example, when R = phenyl (**5**), the sum of the Ga–N–Ga′, Ga–N–C, and Ga′–N–C angles is 336.8°, or 23° less than that required for planarity. When R = 1-adamantyl, the corresponding sum is 345.3° for **3** and 344.2° for **4**. However, when R = 2,6-diisopropylphenyl, the sum of the angles is 359.0° at N(1) and 352.2° at N(2) in **1** and 357.8° at N(1) and 352.7° at N(2) in **2**. Thus, these N centers possess a remarkable geometry which is based upon a trigonal bipyramid that has one of the axial positions occupied by the amine hydrogen and the other axial position unoccupied.

Thermolysis of the Aminoalkylalanes. Since the aminoalanes and aminogallanes in this study possess adjacent N–H and M–Me units, a further elimination of methane is possible when the temperature is raised. Indeed, this reaction sequence has been known for a long time[24] but structural characterizations of the thermolysis products were not reported until relatively recently. For example, the thermolysis of $H_3N{:}AlMe_3$ and $MeH_2N{:}AlMe_3$ to yield $(HNAlMe)_x$ and $(MeNAlMe)_x$ respectively was observed approximately 50 years ago,[24] but the thermolysis products were described as glassy, nonvolatile materials. Similar reports of polymeric or amorphous materials, insoluble in organic solvents, continued to appear in the literature 30 years later.[25,26] The first structurally characterized iminoalane concerned the species $(PhAlNPh)_4$, which was first reported in 1962[27] with more extensive details appearing in 1972.[28] Since then structurally characterized iminoalanes involving tetramers (2),[29] hexamers

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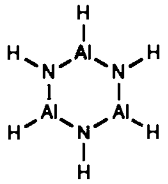
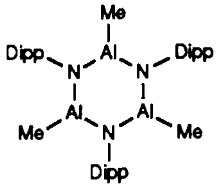
(4),[30–33] a heptamer,[34] and an octamer[32] have been reported. All these compounds feature three-dimensional cage frameworks that possess extremely interesting structures. An iminogallane structure, which is based on a hexameric framework, has also been published.[35] The thermolysis of the bulkier precursors $(Me_2MNHR)_2$ (M = Al, Ga; R = Dipp, Mes) (discussed below) afforded results which are in sharp contrast to those previously obtained. In addition, the thermolysis of $[Me_2MNH(1\text{-}Ad)]_2$, **3** and **4**, did not result in the elimination of a second equivalent of methane when heated to 300 °C. Similarly, $(Me_2GaNHPh)_2$ (**5**) sublimed upon heating without further elimination of methane. In the case of compounds **3** and **4**, the lower reactivity may be due to the decreased acidity of aliphatic amine N–H in comparison to aromatic amines.

The thermolysis of the alanes, $(Me_2AlNHR)_2$, results in a variety of interesting structures in which the degree of aggregation depends greatly on the R group attached to nitrogen (see Scheme II). In the case of R = phenyl, the hexameric thermolysis product $(MeAlNPh)_6$[30] has been characterized previously. By using progressively more hindering R groups, the compounds $(MeAlNMes)_4$ (**8**) and $(MeAlNDipp)_3$ (**6**) have been prepared and characterized.[8] The reaction between Me_3Al and the even bulkier amine Mes^*NH_2 (Mes* = 2,4,6-tri-*tert*-butylphenyl) followed by thermolysis has recently been found to yield the unexpected cyclometalation product rather than the iminoalane as depicted in Scheme II.[9] The role of steric factors, valency, angle strain, entropy, and the nature of the reaction intermediates in determining the degree of association of various Al compounds has already been discussed elsewhere.[14] The results in Scheme II can be rationalized by extrapolation of these considerations to include the bulkier iminoalanes. Clearly, increasing the size of the substituent results in lower association numbers. The observation of an ortho-metalation pathway in preference to methane elimination involving an N–H hydrogen is less easily explained. As already pointed out, the elimination of methane via CH activation rather than the capture of the NH is remarkable.[9] For Al this only occurs in the extreme case where the ortho substituent is the very bulky *tert*-butyl group. It is probable that the precursor *trans*-$[AlMe_2(\mu\text{-}NHMes^*)]_2$[9] undergoes ortho-metalation because of a favorable orientation of the *t*-Bu group. An intermolecular association pathway for elimination is probably completely blocked because of steric requirements. An intramolecular condensation via CH activation is thus likely to be favored when the association and the consequent intermolecular pathway is blocked by steric effects. Intramolecular CH_4 elimination via NH capture with subsequent multiple bond formation to yield a formally antiaromatic Al_2N_2 system is also less favored for both kinetic and, perhaps, thermodynamic reasons.

The structure of the so far unique compound **6**, (MeAlNHDipp)$_3$, has been reported in a preliminary note.[8] The structure consists of a central planar six-membered ring of alternating aluminum and nitrogen atoms. The Al–N bond length is 1.782 (4) Å which is considerably shorter than the 1.89–1.96-Å range observed in higher polyiminoalanes.[29–32] It is difficult to assess accurately the degree of shortening of the Al–N bond in **6**. This is due to the lack of extensive structural information concerning Al–N bonds between three-coordinate aluminum and nitrogen. Compound $Al[N(SiMe_3)_2]_3$ appears to be the only other structurally characterized compound featuring Al and N in this coordination number.[4] This species has a trigonal-planar AlN_3 core with Al–N bond lengths of 1.78 Å which is almost exactly the same value as those found for $(MeAlNHDipp)_3$. The difficulty in estimating the bond order in "alumazene" is partially remedied by calculations on the hypothetical molecule $Al_3N_3H_6$. The resulting structural parameters were derived from calculations at the SCF level with the basis set 6-31G*.[37] Where applicable,


calculated[37]

Al–N = 1.7910 Å
N–H = 1.0026 Å
Al–H = 1.5838 Å
N–Al–N = 114.7°
Al–N–Al = 125.1°


measured[8]

Al–N = 1.782 (4) Å
N–R' = 1.442 (14) Å
Al–R = 1.978 (15) Å
N–Al–N = 115.3 (5)°
Al–N–Al = 124.7 (5)°

the calculated parameters are in good agreement with the experimental values for **6** which were obtained by X-ray crystallography.[8] A further important objective of these calculations was the estimation of the aromatic character and the extent of delocalization in the Al–N ring system. This objective may be approached by ab initio calculations of the homodesmotic[38] reaction sequence involving the hypothetical Al–N analogues of benzene, ethylene, and butadiene. The overall reaction may be represented by the equation

$$Al_3N_3H_6 + 3H_2AlNH_2 \rightarrow 3H_2AlN(H)Al(H)NH_2$$

Since the number and types of bonds remain the same on both sides of the equation the difference in energy is then taken to represent the stabilization energy imparted to the ring by the delocalization process. For comparison, calculated values for benzene, borazine, $Al_3N_3H_6$, and the hypothetical molecule $B_3P_3H_6$ are presented in Table II. In the case of benzene, there is good agreement between the calculated value of 22.1 kcal mol^{-1} and the experimentally observed value of 22.9 kcal mol^{-1} with use of combustion data.[39] The lack of similar hydrogen substituted compounds or their ethylene or 1,3-butadiene analogues for the B–N, Al–N, or B–P does not allow a similar experimental comparison for borazine or the Al_3N_3 or B_3P_3 rings. However, the good agreement between experiment and theory obtained for benzene gives grounds for confidence in the case of the other hypothetical molecules. As expected, the calculations indicate the largest energy of stabilization for benzene. The delocalization in $B_3P_3H_6$ results in a stabilization energy which is over half the magnitude for benzene and slightly greater than the value for borazine. The value calculated for alumazene, however, indicates the presence of little or no delocalization and consequently little aromatic character in the molecule. The synthesis, characterization, and properties of quasiaromatic ring systems involving heavier main group elements have been recently reviewed.[40]

Cubane compound **8**, $(MeAlNMes)_4 \cdot 3C_7H_8$, is one of a handful of structurally characterized iminoalanes of this type. It possesses many similarities to the previously reported compounds $(PhAlNPh)_4$,[28] $[HAlN(i\text{-}Pr)]_4$,[29] and $[MeAlN(i\text{-}Pr)]_4$.[29] All of these possess a regular cubic Al_4N_4 core structure. The faces show very little deviation from planarity. The average Al–N bond length of 1.948 (7) Å for **8** is slightly longer than the 1.913 (2), 1.934 (1), and 1.90 (1) Å distances reported for the other compounds. This is probably a consequence of the increased steric requirements of the mesityl group on nitrogen. A trend, wherein the Al–N–Al

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bond angle of $[\text{HAlN}(i\text{-Pr})]_4$[29] and $[\text{MeAlN}(i\text{-Pr})]_4$[29] tends to be slightly smaller than the N–Al–N bond angle, has been noted previously. This trend was followed by other cage compounds that were studied.[31,41] However, in $(\text{PhAlNPh})_4$,[28] the Al–N–Al and N–Al–N angles were equal as required by the symmetry of the molecule. This trend could not be confirmed with $(\text{MeAlNMes})_4$ since the differences are within the standard deviation of the angular values at Al and N. On the other hand, it is notable that in compound **5**, two of the three C–Al–N angles have an average value of 116.3 (1)° whereas the third C–Al–N angle has a larger average value of 141.0 (1)°. Similarly, the three C–N–Al angles have the average values 115.9 (2), 122.7 (2), and 136.1 (2)°. A more detailed comparison with $(\text{PhAlNPh})_4$,[28] $[\text{HAlN}(i\text{-Pr})]_4$,[29] and $[\text{MeAlN}(i\text{-Pr})]_4$[29] was not possible since only the mean distances were reported in the two former molecules and imposed symmetry excluded the latter.

Thermolysis of Gallanes. The close structural similarity between the aluminum and gallium precursors **1–5** might have led to the prediction that further heating would have led to similar products in the case of gallium compounds. The aminogallanes have, however, demonstrated a much greater preference for methane elimination via C–H activation over elimination via capture of N–H hydrogen (Scheme I). For example, although the reaction between AlMe_3 and H_2NDipp gave the trimeric $(\text{MeAlNDipp})_3$ (**6**) compound, the parallel reaction with GaMe_3 gave compound **7**, in which the *o*-isopropyl methyl group on the aryl ring becomes bonded to gallium. Similarly, whereas the reaction between AlMe_3 and H_2NMes gave the cubic species $(\text{MeAlNMes})_4$ (**8**), the parallel reaction with GaMe_3 gave isomers **9** and **10** demonstrating a preference for activation of the *o*-methyl C–H bond on mesityl. Cyclometalations in aluminum and gallium chemistry via C–H activation have, of course, been reported[42–44] previously, but, with the exception of the work in ref 9, no work has appeared on amides. The structures of **7**, **9**, and **10** are, apparently, the first reported structures of this type for gallium.

On the basis of the results of these parallel reactions, it is unlikely that the amino gallanes undergo intramolecular cyclometalation for steric reasons. On the contrary, since gallium is slightly larger than aluminum, an intermolecular condensation reaction is more likely in the case of gallium since it is less hindered. Subtle differences in the reactivity and structure of similar aluminum and gallium compounds have been reported previously. For example, it has been reported that five-coordination is apparently a less stable geometry in gallium compounds than it is in the corresponding aluminum species.[45,46] In addition, the imino derivative $(\overline{\text{CH}_2\text{CH}_2\text{N}}\text{MEt}_2)_n$ (M = Al, Ga) exists as a trimer ($n = 3$) when M = Al, whereas it is a dimer ($n = 2$) when M = Ga.[47] In another example, a study of the reaction of aluminum and gallium alkyls with terminal acetylenes revealed some surprising differences. Aluminum alkyls add to the triple bond of acetylenes resulting in a substituted alkene.[48] In contrast, gallium alkyls provoke the pseudo-acidic character of the terminal acetylene leading to nucleophilic attack of the alkyl on hydrogen and subsequent elimination of alkane.[48] The carbon–carbon triple bond remains intact. Clearly, there is adequate precedent for significantly different behavior in Al and Ga compounds. An alternative explanation of the difference in reactivity between Al and Ga compounds relates to the more electropositive nature of Al in comparison to Ga. The more electropositive metal (Al) favors intermolecular association and the concomitant N–H capture, whereas the less strongly electropositive (less Lewis acidic) Ga centers are less inclined to associate further. The lower Lewis acidity of Ga has been well-established in other derivatives.[14,18,48] A well-known manifestation of this phenomenon is the monomeric nature of GaMe_3 versus the dimeric nature of Al_2Me_6.

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Supplementary Material Available: Full tables of atom coordinates, crystallographic data, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (47 pages); listing of structure factors (97 pages). Ordering information is given on any current masthead page.

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Relative Aromaticity in Heteropolar Inorganic Analogues of Benzene

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Abstract: Ab initio electronic structure calculations have been carried out on a series of heteropolar inorganic analogues of hydrocarbons in order to evaluate reaction energies for an isodesmic reduction by ethane and homodesmotic reactions as indicators of the relative aromaticities of the recently synthesized $\text{X}_3\text{Y}_3\text{R}_6$ rings where XY is BP and AlN. Calculations where XY is CC and BN are also reported to establish the scale. Optimized geometries and energies through RHF/6-31G* are reported for both reactions, and energies at the SCF optimized geometries including fourth-order Moller–Plesset perturbation corrections are reported for the homodesmotic reaction. The homodesmotic reactions are taken to be the most useful index and give the results with MP4(SDQ) of CC (22.1 kcal/mol) ≫ BP (12.7 kcal/mol) ~ BN (11.1 kcal/mol) > AlN (1.9 kcal/mol).

Introduction

The recent synthesis of inorganic planar six-membered-ring molecules involving the heavier main group elements[1–3] draws attention to the issue of aromaticity and the utility of its possible extension to help in understanding the chemistry of these new

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