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Synthesis and Characterization of the Monomeric Gallium Monoamides *t*-Bu$_2$GaN(R)SiPh$_3$ (R = *t*-Bu, 1-Adamantyl), Trip$_2$MN(H)Dipp (M = Al, Ga; Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$; Dipp = 2,6-*i*-Pr$_2$C$_6$H$_3$), and Trip$_2$GaNPh$_2$

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The synthesis and characterization of the monomeric, main group 3 monoamides *t*-Bu$_2$GaN(R)(SiPh$_3$) (R = *t*-Bu (**1**); R = 1-Adamantyl (1-Ad) (**2**)), Trip$_2$MN(H)Dipp (M = Al (**3**); M = Ga (**4**)) (Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$, Dipp = 2,6-*i*-Pr$_2$C$_6$H$_3$), and Trip$_2$GaNPh$_2$ (**5**) are described. The compounds were characterized by X-ray crystallography and ^{1}H NMR and IR spectroscopy. The crystal structures show the molecules to be monomeric with trigonal planar metal and nitrogen coordination. The Ga–N bond lengths range from 1.847(12) Å in **4** to 1.924(2) Å in **2**. The Al–N bond length observed in **3** is 1.784(3) Å. The variation may be explained mostly on the basis of different steric and electronic properties of the bulky ligands. It was concluded, on the basis of VT ^{1}H NMR data, that the p–p π-bonding contribution to M–Nbond strength in the aluminum or gallium species is <10 kcal mol^{-1}. Crystal data at 130 K, with Mo Kα (λ = 0.71069 Å) radiation, are as follows: *t*-Bu$_2$GaN(t-Bu)SiPh$_3$ (**1**), a = 14.795(6) Å, b = 9.807(6) Å, c = 19.657(9) Å, β = 99.39(4)°, V = 2824(1) Å^3, space group $P2_1/c$, Z = 4, 2361 ($I > 2\sigma(I)$) data, R = 0.053; *t*-Bu$_2$GaN(1-Ad)SiPh$_3$ (**2**), a = 10.191(3) Å, b = 10.740(3) Å, c = 15.467(5) Å, α = 69.82(2)°, β = 82.79(2)°, γ = 82.75(2)°, V = 1568.4(8) Å^3, space group $P\bar{1}$, Z = 2, 5130 ($I > 3\sigma(I)$) data, R = 0.037; Trip$_2$AlN(H)Dipp (**3**), a = 11.643(5) Å, b = 18.460(6) Å, c = 37.165(14) Å, β = 95.86(3)°, V = 7947(5) Å^3, space group $C2/c$, Z = 8, 3639 ($I > 2\sigma(I)$) data, R = 0.056; Trip$_2$GaN(H)Dipp (**4**), a = 11.588(8) Å, b = 18.496(14) Å, c = 37.27(2) Å, β = 95.17°, V = 7956(9) Å^3, space group $C2/c$, Z = 8, 1837 ($I > 2\sigma(I)$) data, R = 0.084; Trip$_2$GaNPh$_2$ (**5**), a = 12.732(4) Å, b = 15.656(5) Å, c = 18.462(6) Å, V = 3680(2) Å^3, space group $Pccn$, Z = 4, 1944 ($I > 2\sigma(I)$) data, R = 0.092.

Introduction

Recent publications have described species that have multiple bonding between boron and phosphorus[1,2] or arsenic.[3,4] These compounds are analogous to well-known boron–nitrogen species that have various degrees of B–N π-bonding.[5] In contrast to these studies, π-bonding in compounds in which the boron and nitrogen atoms are replaced by aluminum or gallium and phosphorus or arsenic have received much less attention. Some preliminary work has led to the publication of the syntheses and structures of compounds such as *t*-Bu$_2$GaP(Mes*)SiPh$_3$,[6] MesP(GaTrip$_2$)$_2$,[7] and PhAs(GaTrip$_2$)$_2$[7] (Mes = 2,4,6-Me$_3$C$_6$H$_2$; Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) which can display weak Ga–P π-bonding. We were anxious to compare these compounds to their lighter homologues with Al–N or Ga–N bonds. A search of the literature, however, revealed that there were no monomeric Al–N or Ga–N species of formula R$_2$MNR$'_2$ (R and R$'$ = alkyl, aryl, or silyl group) that had been well characterized. In fact, prior to the work described here, the only well-known compounds that involved bonding between three-coordinate aluminum or gallium and nitrogen were M[N(SiMe$_3$)$_2$]$_3$ (M = Al,[8,9] Ga[8]) and (MeAlNDipp)$_3$.[10] In these species the metal interacts with two or more nitrogen centers. This has the effect of dividing any M–N π-interaction that may occur between two or more M–N bonds and reduces the effect that π-bonding would have on structural parameters such as the M–N bond length. A major objective, therefore, was the synthesis of compounds that have a single M–N bond in order to study the possible existence of p–p π-bonding in Al–N and Ga–N bonds. In a previous publication, initial results on Al–N species have been outlined.[11] In this paper emphasis is placed on Ga–N-bonded compounds, and the synthesis and spectroscopic and structural studies of several simple species that have bonds between three-coordinate gallium and nitrogen centers are reported.

Experimental Section.

General Procedures. All work was performed under anaerobic and anhydrous conditions by using Schlenk techniques or a Vacuum Atmospheres HE-43-2 drybox. Solvents were distilled from sodium/potassium alloy and degassed twice prior to use.

Physical Measurements. ^{1}H NMR spectra were obtained on a General Electric QE-300 spectrometer using either C$_6$D$_6$ or C$_7$D$_8$ as a solvent. IR spectra were recorded in the range 4000–200 cm^{-1} as a Nujol mull between CsI plates using a Perkin-Elmer PE 1420 spectrometer.

Starting Materials. HNPh$_2$ (Fisher), *n*-BuLi (Aldrich), *t*-BuLi (Aldrich), GaCl$_3$ (Strem), and H$_2$N(1-Ad) (Aldrich) were used as received. Si(Cl)Ph$_3$ (Petrarch) was purified by recrystallization from toluene; H$_2$NDipp and H$_2$N(*t*-Bu) were purified by distillation from CaH$_2$. Trip$_2$GaCl,[12] *t*-Bu$_2$GaCl,[13] and (Trip$_2$AlBr)$_2$[12] were synthesized by literature procedures. HN(*t*-Bu)SiPh$_3$ and HN(1-Ad)SiPh$_3$ were synthesized by the treatment of H$_2$NR (R = *t*-Bu, 1-Ad) with *n*-BuLi in ether at 0 °C and the addition of the lithium amide to Si(Cl)Ph$_3$ in diethyl ether at 0 °C. After 18 h of stirring, followed by filtration, reduction of the volume, and storage of the solution at –30 °C, colorless crystals were obtained in good yield. Characterization was made by ^{1}H NMR and C, H, and N elemental analysis.

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(1) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *30*, 449.

(2) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

(3) Petrie, M. A.; Shoner, S. C.; Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033.

(4) Petrie, M. A.; Power, P. P. *J. Am. Chem. Soc.*, in press.

(5) Niedenzu, R.; Dawson, J. W. *Boron-Nitrogen Compounds*; Springer-Verlag: Berlin, 1965.

(6) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1992**, *31*, 4038.

(7) Petrie, M. A.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1309.

(8) Bürger, H.; Achen, J.; Goetze, U.; Wannagat, U.; Wismar, H. J. *J. Organomet. Chem.* **1971**, *33*, 1.

(9) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.

(10) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(11) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135.

(12) Petrie, M. A.; Dias, H. V. R.; Power, P. P.; Ruhlandt-Senge, K.; Waggoner, K. M. *Organometallics* **1993**, *12*, 1086.

(13) Cleaver, W. M.; Barron, A. R. *Chemtronics* **1989**, *4*, 146.

0020-1669/93/1332-2557$04.00/0

Table I. Summary of Data Collection and Structure Solution and Refinement Parameters for Compounds **1–5**

	1	**2**	**3**	**4**	**5**
formula	$C_{30}H_{42}GaNSi$	$C_{36}H_{48}GaNSi$	$C_{42}H_{64}AlN$	$C_{42}H_{64}GaN$	$C_{42}H_{56}GaN$
fw	514.5	592.6	609.9	652.7	644.6
crystal description	colorless plates	colorless blocks	colorless needles	colorless plates	colorless parallelpipeds
crystal size	0.02 × 0.20 × 0.36	0.15 × 0.27 × 0.27	0.3 × 0.9 × 0.08	0.05 × 0.30 × 0.475	0.15 × 0.20 × 0.30
a, Å	14.795(6)	10.191(3)	11.643(5)	11.588(8)	12.732(4)
b, Å	9.807(6)	10.740(3)	18.460(6)	18.496(14)	15.656(5)
c, Å	19.657(9)	15.467(5)	37.165(14)	37.27(2)	18.462(6)
α, deg		69.82(2)			
β, deg	99.39(4)	82.79(2)	95.86(3)	95.17(5)	
γ, deg		82.75(2)			
V, Å^3	2824(1)	1568.4(8)	7947(5)	7956(9)	3680(2)
Z	4	2	8	8	4
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$	$Pccn$
d(calc), g/cm^3	1.210	1.255	1.020	1.090	1.163
Lin abs coeff, cm^{-1}	10.34	9.40	7.80	7.13	7.76
2θ range, deg	0–51	0–55	0–46	0–42	0–50
no. of reflns	2361 ($I > 2\sigma(I)$)	5130 ($I > 3\sigma(I)$)	3639 ($I > 2\sigma(I)$)	1837 ($I > 2\sigma(I)$)	1944 ($I > 2\sigma(I)$)
no. of variables	298	352	397	187	200
R, R_w	0.053, 0.048	0.037, 0.037	0.056, 0.060	0.084, 0.076	0.092, 0.064

***t*-Bu$_2$GaN(*t*-Bu)SiPh$_3$ (1).** HN(*t*-Bu)SiPh$_3$ (0.66 g, 2 mmol) was dissolved in hexane (20 mL), and the solution was cooled in an ice bath and treated with *n*-BuLi (2 mmol, 1.25 mL of a 1.6 M solution in hexane). The cloudy mixture was stirred at room temperature for 2 h and added dropwise to a solution of *t*-Bu$_2$GaCl (0.44 g, 2 mmol) in hexane. The solution was stirred overnight at room temperature. Filtration through a Celite-padded filter frit and reduction of the volume to 15 mL afforded **1** as colorless crystals. Yield: 0.69 g (67%). Mp: 143–145 °C. ^{1}H NMR (C_7D_8): δ 1.07 (s, Ga(*t*-Bu)$_2$), 2.10 (s, N(*t*-Bu)), 7.50 (t, m, aryl H), 7.75 (aryl *m*-, *o*-, *p*-H). IR: 3031 w, 3021 w, 1582 w, 1358 m, 1300 w, 1256 w, 1222 w, 1181 m, 1112 sh, 1098 s, 1062 w, 1038 m, 1007 m, 992 m, 842 s, 802 m, 762 m, 738 s, 698 vs, 545 m, br, 498 s cm^{-1}.

***t*-Bu$_2$GaN(1-Ad)SiPh$_3$ (2).** HN(1-Ad)(SiPh$_3$) (0.44 g, 1.07 mmol) was dissolved in *n*-hexane (40 mL), and the solution was cooled in an ice bath and treated dropwise with *n*-BuLi (0.67 mL, 1.07 mmol, 1.6 M solution in hexane). The mixture became cloudy and was stirred at room temperature for 18 h. *t*-Bu$_2$GaCl (0.24 g) was dissolved in hexane (20 mL), the solution was cooled to 0 °C, and the lithium amide was added slowly via a double-tipped needle. The white suspension was allowed to warm to room temperature and stirred for a further 18 h, after which it was filtered through a Celite-padded filter frit, yielding a colorless solution. Reduction of the volume to 10 mL afforded colorless crystals of **2** that were suitable for X-ray crystallography. Yield: 0.42 g (67%). Mp: 125–127 °C. ^{1}H NMR (C_7D_8): δ 1.18 (s, Ga(*t*-Bu)$_2$), 1.44, 1.81 (br, intensity ratio 2:1:2), 2.02 (1-Ad), 7.19 (m, *m*-H for Ph), 7.85 (*m*-, *o*-, *p*-H for Ph). IR: 3062 w, 3042 w, 1582 vw, 1563 vw, 1373 m, 1362 w, 1352 w, 1347 2, 1339 w, 1305 sh, 1298 m, 1258 m, 1135 w, 1141 w, 1108 m, 1095 s, 1005 m, 995 sh, 962 m, 938 w, 858 m, 812 sh, 808 m, 772 w, 738 m, 722 m, 709 sh, 698 s, 672 w, 642 m, 576 w, 506 s, 495 sh cm^{-1}.

Trip$_2$AlN(H)Dipp (3). A slurry of 1.05 mmol of LiN(H)Dipp in 50 mL of *n*-hexane (prepared by the reaction of 0.186 g of NH$_2$Dipp with 0.66 mL of 1.6 M *n*-BuLi solution) was added slowly to a solution of 0.54 g (0.525 mmol) of (Trip$_2$AlBr)$_2$ in 30 mL of *n*-hexane at 0 °C. The mixture was slowly warmed to room temperature, stirred overnight, and refluxed for 1 h to complete the reaction. Removal of the precipitate by filtration resulted in a colorless solution. All volatile materials were then removed in vacuum. The residue material was crystallized from a minimal amount of *n*-hexane. Yield: 0.64 g (40%). Mp: 135–139 °C. ^{1}H NMR (C_7D_8): δ 1.05 (d, *p*-CH$_3$ (Trip)), 1.19 (d, *o*-CH$_3$ (Dipp)), 1.24 (d, *o*-CH$_3$ (Trip)), 2.77 (sept, *p*-CH (Trip)), 3.08 (sept, *o*-CH (Trip)), 3.42 (sept, *o*-CH (Dipp)), 3.77 (NH (Dipp)), 6.98 (*m*-H (Trip)), 7.02 (m, *p*-H (Dipp)). IR: 3342 w (ν(N–H)), 3015 m, 1898 vw, 1842 vw, 1755 vw, 1735 vw, 1581 s, 1546 m, 1413 s, 1358 s, 1328 s, 1256 s, 1229 m, 1187 w, 1167 w, 1150 w, 1132 m, 1098 w, 1052 m, 1037 m, 933 w, 890 s, 872 s, 836 m, 793 w, 749 s, 726 m, 654 m, 632 w, 608 vw, 511 vw, 495 m, br, 414 m, 375 vw cm^{-1}.

Trip$_2$GaN(H)Dipp (4). H$_2$NDipp (0.35 g, 2 mmol) was dissolved in 20 mL of hexane, and the solution was added dropwise via syringe. The solution was stirred for 2 h and added dropwise to a solution of Trip$_2$GaCl (1.02 g, 2 mmol) in hexane (30 mL). The mixture was stirred at room temperature for 18 h and filtered. The solvent was removed under reduced pressure, to afford a pale yellow oil. The oily residue was heated to 70 °C in vacuum for 3 h, during which time it solidified. The solid was extracted with pentane, and the solution was filtered. A reduction of the volume to ca. 3 mL afforded colorless crystals. Yield: 0.75 g (61%). Mp: 134–137 °C. ^{1}H NMR (C_7D_8): δ 1.07 (d, *p*-CH$_3$ (Trip)), 1.18 (d, *o*-CH$_3$ (Dipp)), 1.24 (d, *o*-CH$_3$ (Trip)), 2.46 (NH (Dipp)), 2.77 (sept, *p*-CH (Trip)), 3.01 (sept, *o*-CH (Trip)), 3.33 (sept, *o*-CH (Dipp)), 6.94 (*m*-H (Trip)), 7.00 (m, *p*-H (Dipp)). IR: 3375 w (N–H), 2718 w, 1618 w, 1591 m, 1552 m, 1416 m, 1358 m, 1323 m, 1368 sh, 1256 m, 1229 sh, 1196 sh, 1198 w, 1165 w, 1150 vs, 1131 s, 1092 m, 1052 w, 942 sh, 932 m, 918 sh, 882 sh, 872 s, 855 m, 844 w, 802 sh, 792 m, 749 s, 718 w, 698 w, 642, 390 s cm^{-1}.

Trip$_2$GaNPh$_2$ (5). A solution of Trip$_2$GaCl (2.04 g, 4 mmol) in Et$_2$O (40 mL) was added dropwise to a solution of LiNPh$_2$ (5 mmol) generated in Et$_2$O (20 mL) from 3.0 mL of a 1.6 M solution of *n*-BuLi in hexane and 0.845 g of HNPh$_2$) with rapid stirring at room temperature. A white precipitate appeared after several minutes, and stirring was continued for a further 20 h. The solution was then filtered through Celite and the filtrate was concentrated under reduced pressure to a volume of ca. 10 mL. Storage of this solution at −20 °C for 24 h afforded the product **5** as colorless blocks. Yield: 1.61 g (62%). Mp: 140 °C. ^{1}H NMR (C_7D_8): δ 1.12 (d, *p*-CH$_3$ (Trip)), 1.16 (d, *o*-CH$_3$ (Trip)), 2.68 (sept, *p*-CH (Trip)), 2.96 (sept, *o*-CH (Trip)), 6.98 (d, *m*-H (Trip)), 6.59 (t, *p*-H (Ph)), 6.90 (t, *m*-H (Ph)), 7.13 (d, *o*-H (Ph)). IR: 3025 m, 1728 w, 1592 s, 1550 m, 1500 m, 1490 m, 1413 m, 1283 vw, 1258 s, 1070 s, 1050 m, 1018 s, 932 m, 915 m, 887 vw, 872 s, 833 w, 796 s, 753 m, 689 m, 642 w, 610 w, 560 vw, 505 w, 455 w, 388 s cm^{-1}.

X-ray Crystallographic Studies

The crystals were removed from the Schlenk tube under a stream of N$_2$ and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 14.

Compounds **1**, **2**, and **4** were collected at 130 K with the use of a Siemens R3 m/V diffractometer (Mo Kα radiation λ = 0.710 69 Å) equipped with a graphite monochromator and a locally modified Enraf-Nonius Universal Low-Temperature device for low-temperature work. The intensity data sets for compounds **3** and **5** were collected at 130 K on a Syntex P2$_1$ diffractometer, equipped with a locally modified LT-1 device and using graphite-monochromated Mo Kα radiation. Crystallographic programs used for the structure solutions and refinements were those of SHELXTL-Plus[15] installed on a Micro Vax work station 3200. Scattering factors were from common sources.[16] An absorption correction was applied using the method described in ref 17. Some details of data

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(14) This method is described by: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(15) Sheldrick, G. M. SHELXTL-Plus program package for the solution and refinement of X-ray crystallographic data. University of Göttingen, 1990.

(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

(17) The absorption correction was made using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences (Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987).

Table II. Selected Coordinates and Isotropic Thermal Parameters for Compounds **1–5**

atom	*x*	*y*	*z*
t-Bu$_2$GaN(*t*-Bu)SiPh$_3$ (**1**)			
Ga	3003(1)	2852(1)	2656(1)
N	3175(3)	3204(6)	3587(3)
Si	2289(1)	4136(2)	3795(1)
C(1)	1558(4)	4598(7)	2947(3)
C(7)	2643(5)	5768(8)	4271(4)
C(13)	1467(5)	3237(8)	4279(3)
C(19)	2476(5)	688(8)	2416(4)
C(23)	3516(5)	3700(9)	1951(4)
C(27)	4050(5)	2892(7)	4051(3)
t-Bu$_2$GaN(1-Ad)SiPh$_3$ (**2**)			
Ga(1)	897(1)	1304(1)	1954(1)
N(1)	1125(2)	–550(2)	2688(1)
Si(1)	2729(1)	–1212(1)	2824(1)
C(1)	45(3)	2696(3)	2511(2)
C(5)	1229(3)	1838(3)	562(2)
C(9)	3373(3)	–2469(3)	2227(2)
C(15)	3219(2)	–1951(3)	4060(2)
C(21)	3750(3)	259(3)	2229(2)
C(27)	–74(2)	–1297(2)	3072(2)
Trip$_2$AlN(H)Dipp (**3**)			
Al	1487(1)	764(1)	1425(1)
N	2618(3)	739(2)	1135(1)
H	3353	563	1248
C(1)	2716(3)	774(2)	755(1)
C(13)	–132(3)	899(2)	1235(1)
C(28)	2119(3)	642(2)	1930(1)
Trip$_2$GaN(H)Dipp (**4**)			
Ga	1505(2)	776(1)	1432(1)
N	2696(10)	779(8)	1135(3)
H	3403	783	1257
C(1)	2741(12)	796(10)	763(4)
C(13)	–123(12)	931(8)	1218(4)
C(28)	2140(13)	629(8)	1939(4)
Trip$_2$GaNPh$_2$ (**5**)			
Ga	2500	7500	2595(1)
N	2500	7500	3612(4)
C(1)	1669(5)	7883(4)	4013(4)
C(7)	1272(6)	8022(5)	2123(4)

collection and refinement are given in Table I; coordinates for selected atoms are given in Table II. Important bond distances and angles are provided in Table III. Further details are provided in the supplementary material.

The crystal structures of **1**, **4**, and **5** were solved by direct methods; the structure of **2** was solved by Patterson synthesis, and **3** could be solved by the use of the coordinates of **4** with which it is isomorphous. All crystal structures were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically, with the exception of **4**, in which only gallium and nitrogen were refined this way. Hydrogen atoms, except for the NH positions in **3** and **4**, were included in the refinement at calculated positions using a riding model with C–H = 0.96 Å and U_H = 1.2U for **1**, fixed U_H = 0.04 Å for **2** and **5**, U_H = 0.05 Å for **3**, and U_H = 0.03 Å for **4**. The N-bound hydrogen positions in **3** and **4** were taken from a difference map and were fixed during refinement with N–H = 0.90 Å and U_H = 0.05 Å for **3** and N–H = 0.97 Å and U_H = 0.03 Å for **4**.

Results and Discussion

Compounds **1–5** were all prepared by conventional routes that involved the reaction of the lithium salt of an amine with hindered dialkyl- or diarylaluminum or -gallium halides. The use of bulky groups to prevent oligomerization is essential to achieve a monomeric formula for each compound. The use of either Trip$_2$GaCl,[12] (Trip$_2$AlBr)$_2$,[12] or *t*-Bu$_2$GaCl[13] in combination with hindered amido groups has provided sufficient steric hindrance to achieve this aim. In the case of **3** and **4**, monomeric structures were obtained with the primary amide ligand [NHDipp]$^-$.

Structural Descriptions. *t*-Bu$_2$GaN(*t*-Bu)SiPh$_3$ (1). The structure **1** is presented in Figure 1, and it consists of neutral discrete molecules with no crystallographically imposed symmetry. The gallium and nitrogen centers have essentially planar coordination. Only minor distortions from idealized 120° angles are observed at gallium, whereas deviations as high as ca. 6° were observed at nitrogen. The gallium and nitrogen planes are twisted by 88.7° relative to each other, and the Ga–N bond length is 1.906(5) Å. The average Ga–C distance is 2.024(8) Å. The N–Si and N–C(27) bond lengths are 1.702(6) and 1.489(8) Å, respectively.

***t*-Bu$_2$GaN(1-Ad)SiPh$_3$ (2).** The structure of **2** is shown in Figure 2. Important bond lengths and angles are given in Table III. The compound consists of neutral, monomeric, well-separated molecules with no crystallographically imposed symmetry. Both the gallium and the nitrogen atoms have trigonal planar environments. The angles at gallium are close (within 1.6°) to 120°. Nitrogen is coordinated in a more distorted fashion by a 1-adamantyl and a triphenylsilyl group, resulting in angles of 115.6(1), 119.0(1), and 125.4(1)°, with the widest angle between the two organic ligands. The Ga–N bond length is 1.924(2) Å, the average Ga–C distance being 2.025(6) Å. The twist angle between the planes at gallium and nitrogen is 87.7°.

Trip$_2$MN(H)Dipp (M = Al (3), Ga (4)). Compounds **3** and **4** are isomorphous, and display no crystallographically imposed symmetry. The structure of **4** is depicted in Figure 3. Important bond lengths and angles are shown in Table III. The environments at aluminum and gallium are distorted trigonal planar, with the widest angle between the two large Trip groups. The N–M–C angles show a considerable difference (ca. 10°) owing to the divergence in size between the nitrogen substituents. The amide hydrogen atoms were located in the corresponding difference map and included at fixed positions. The angles at nitrogen show similar distortion between 106.6(2) and 137.1(2)° in **3** and between 112.9(15) and 134.0(9)° in **4**. The Al–N bond length is 1.784(3) Å, and the corresponding Ga–N bond distance is 1.847(12) Å. The twist angles between the planes at nitrogen and aluminum or gallium are 5.5 and 8.3°, respectively. The shortest metal–hydrogen approaches are 2.434 Å (Al–H(34a)) and 2.441 Å (Ga–H(34a)). The average Al–C distance is 1.960(7) Å, and the corresponding Ga–C distance is 1.992(15) Å. The angle between the aluminum plane and the C(13) and C(28) Trip rings are 56.5 and 75.8°. The corresponding angles for the gallium compound are 56.3 and 70.8°.

Trip$_2$GaNPh$_2$ (5). The molecular structure of **5** consists of neutral discrete molecules with a crystallographically imposed mirror plane along the Ga–N bond. A view of the molecule is shown in Figure 4. Important bond lengths and angles are given in Table III. The compound displays an essentially planar, three-coordinate gallium center, with angles ranging from 116.3(2) to 127.4(4)° and the widest angle seen between the two Trip groups. The Ga–N distance is 1.878(7) Å, and the shortest Ga–H distances are 2.529 Å (Ga–H(19a,b)). The Ga–C distance is 1.968(7) Å. The angle between the gallium plane and the Trip ring is 64.1°.

Compounds **1**, **2**, **4**, and **5** are the first structurally characterized examples of monomeric gallium monoamides. The aluminum species **3** is included in this paper since it allows a direct comparison with its gallium analogue **4**. In a similar manner, the structure of **2** also enables a comparison to be made with its previously described aluminum analogue **6**.[11]

The most important structural features of **1–5** relate to the M–N bond distance, the twist angle between the planes at the metal and nitrogen centers, and the rotation barrier (if any) around the M–N bond. The Ga–N distances range from 1.847(12) to 1.924(2) Å whereas the Al–N bond length in **3** is 1.784(3) Å. These experimental bond lengths may be compared with the sum of the radii of aluminum or gallium and nitrogen when modified for an ionic resonance contribution. Taking the atomic radii of aluminum and gallium to be 1.3 and 1.25 Å and that of sp^2-

Table III. Selected Bond Distances (Å) and Angles (deg) for **1–6**

	1	**6**^{b}	**2**	**3**^{b}	**4**	**5**
M–N	1.906(5)	1.853(2), 1.845(2)	1.924(2)	1.784(3)	1.847(12)	1.878(7)
M–C	2.039(8)	2.022(3), 2.009(3)	2.027(3)	1.960(4)	2.001(14)	1.968(7)
	2.010(8)	2.000(2), 2.008(3)	2.022(3)	1.959(3)	1.983(15)	
N–C	1.489(8)	1.500(3), 1.494(2)	1.492(3)	1.431(4)	1.393(18)	1.423(8)
N–Si	1.702(6)	1.716(1), 1.712(2)	1.706(2)			
N–H				0.97	0.90	
R–N–R′ ^{a}	126.1(4)	117.0(1), 125.6(1)	125.4(1)	106.6(2)	112.9(15)	117.3(7)
M–N–R	119.3(4)	121.3(1), 117.1(1)	119.0(1)	137.1(2))	134.0(9)	121.3(4)
M–N–R′	114.6(3)	121.9(1), 117.1(1)	115.6(1)	115.0(1)	113.1(11)	
C–M–C′	120.7(3)	119.5(1), 117.6(1)	118.6(1)	127.8(2)	130.9(6)	127.4(4)
angles between planes at M and N	88.75	87.7, 84.9	71.85	5.5	8.35	0

^{a} R, R′: *t*-Bu, $SiPh_3$ (**1**); Ad, $SiPh_3$ (**2**); Dipp, H (**3**); Dipp, H (**4**); Ph, Ph (**5**). ^{b} M = Al; ref 11.

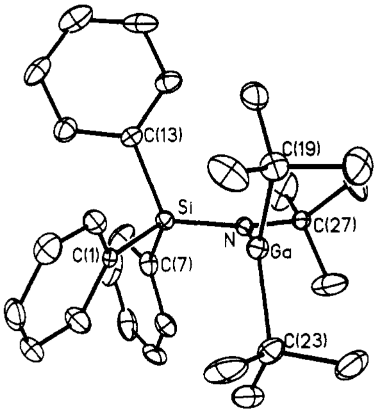

Figure 1. Computer-generated plot of **1** (thermal ellipsoids show 30% occupancy). Hydrogen atoms are omitted for clarity.

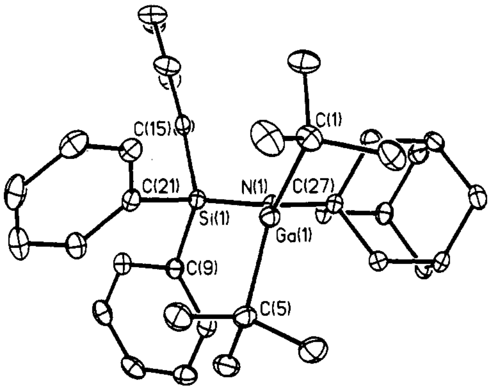

Figure 2. Computer-generated plot of **2** (thermal ellipsoids show 30% occupancy). Hydrogen atoms are omitted for clarity.

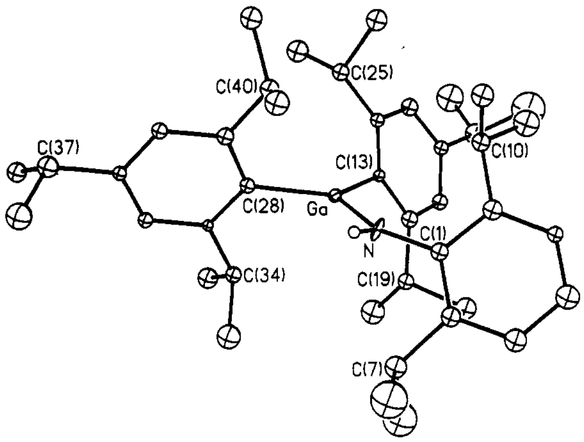

Figure 3. Computer-generated plot of **4** (thermal ellipsoids show 30% occupancy). Hydrogen atoms are omitted for clarity.

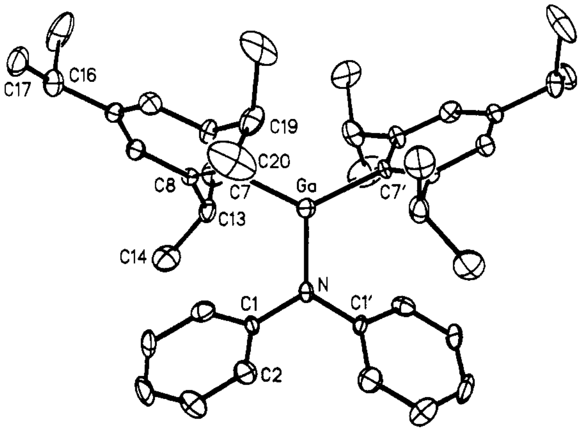

Figure 4. Computer-generated plot of **5** (thermal ellipsoids show 30% occupancy). Hydrogen atoms are omitted for clarity.

Table IV. Comparison of Ga–N Bond Lengths (Å) and Twist Angles (deg) between the Gallium and Nitrogen Planes

compd	Ga–N	twist	compd	Ga–N	twist
1	1.906(5)	88.7	**4**	1.847(12)	9.0
2	1.924(2)	72.5	**5**	1.878(7)	0

hybridized nitrogen to be 0.7 Å, values of 2.0 and 1.95 Å are obtained for the Al–N and Ga–N bond lengths by simple addition.[18] If these values are adjusted for ionic contributions, by the formula described in ref 19, they become 1.85 Å (Al–N) and 1.84 Å (Ga–N). Values of 1.79 Å (Al–N) and 1.80 Å (Ga–N) were calculated by the formula described in ref 20. By these criteria, at least, similar lengths are expected for Al–N and Ga–N bonds. This prediction could be rationalized by assuming that the greater ionic character of the Al–N bond (owing to the higher EN of Al vs. Ga) results in a bond length that is approximately equal to that of Ga–N in spite of the smaller size of gallium. Experimentally, however, a comparison of the Al–N and Ga–N bond distances in the identically substituted compounds in **3** and **4** or **6** and **2** show that the Ga–N distances are about 0.06–0.07 Å longer in both pairs. Moreover, this difference appears to be independent of the twist angle between the metal and nitrogen planes. It is also notable that the shorter M–N distances (in **3** and **4**) are associated with the smaller twist angle between the planes at the metal and the nitrogen (ca. 7° in the case of **3** and **4** and ca. 85–88° for **6** and **2**). This correspondence favors the existence of a π-bond between the metal and nitrogen p-orbitals.

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(18) Pauling L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(19) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37. In this paper the empirical formula $r_{A-B} = r_A + r_B - 0.09(EN_A - EN_B)$ is used to calculate bond lengths. We used the values 1.3 and 1.25 Å for the radii of Al and Ga and a value of 0.7 Å for the radius of three-coordinate, sp^2-hybridized nitrogen. The Allred–Rochow electronegativity scale was employed.

(20) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *129*, 21. In this paper the modified formula $r_{A-B} = r_A + r_B - 0.085(EN_A - EN_B)^{1.4}$ is used to calculate bond lengths. However, the authors specify radii of 1.22 Å for Al, 1.19 Å for Ga, and 0.73 Å for nitrogen and employ the Allred–Rochow electronegativity scale.

It is possible, however, that the difference in size between the substituents in the pairs 6, 2 and 3, 4 could account for a significant portion of the difference. Support for this view comes from previous results obtained in a study of aluminum compounds[11] where there is little correlation between the Al–N bond length and the twist angle between the Al and N planes. In addition, a comparison of the structures of **4** and **5** shows that the Ga–N bond length is 1.847(12) Å and the twist angle between the planes at gallium and nitrogen is 8.35°. In **5**, however, the Ga–N distance, 1.878(7) Å, is longer whereas the angle between the planes is only ca. 1.0°. Furthermore, if the structures of **1** and **2** are compared, the gallium and nitrogen planes are almost orthogonal in **1**, where there is a Ga–N distance of 1.906(5) Å, whereas the Ga–N distance in **2**, where the twist angle is 71.85°, is 1.924(2) Å.

Although compounds **1–6** are monomeric owing to the prevention of association by the size of the substituent groups, there is little evidence of severe structural distortion or strain that might result from steric effects. For example, the C–Ga–C angles in **4** (130.9(6)°) and **5** (127.4(4)°) are a little narrower than those observed in $Trip_2GaCl$ (133.8(7)°).[12] In addition, the Ga–C distances in **5** (1.968(7) Å) are marginally longer than those observed in $Trip_2GaCl$ (1.954(16) Å). In essence, it appears that **4** and **5** are more crowded molecules (but not severely so) than $Trip_2GaCl$. This allows alignment of coordination planes at the metals and nitrogen in both **4** and **5** and in the related aluminum species **3**. It is also notable that the Ga–N distances observed in **4** (1.847(12) Å) and **5** (1.878(7) Å) are very close to the value predicted by the sum of the atomic radii with allowance for a resonance contribution.[19] These two compounds offer the best opportunity for Ga–N π-bonding, but their experimental Ga–N bond lengths do not require the presence of a significant π-interaction to account for their length. It should also be noted that the Al–N distance in **3** is similar to those observed in $Al[N(SiMe_3)_2]_3$ (Al–N = 1.78(2) Å),[9] $Al[N(i\text{-}Pr)_2]_3$ (Al–N = 1.795(5) Å),[21] $[MeAlNDipp]_3$ (Al–N = 1.782(4) Å),[10] and $MesAl[N(SiMe_3)_2]_2$ (Al–N = 1.807(3) Å),[21] which have twist angles between the planes at aluminum and nitrogen of 50, 48.1, 0, and 47.1°, respectively. Since there is no obvious correlation between the length of the Al–N bond and the angle between the aluminum and nitrogen p-orbitals, the current structural data do not support the presence of a strong p–p π-bond.

Variable-Temperature ^{1}H NMR Studies. The temperature dependence of the ^{1}H NMR spectra of **1–5** was also investigated. For **1** and **2**, no dynamic behavior was observed in the temperature range −90 to +25 °C. The spectrum of **3** shows well-resolved peaks at 25 °C; however, the peaks of the $Trip_2Al$ group broaden upon cooling to −40 °C. Further cooling to −85 °C results in the splitting of the ortho *i*-Pr groups, which become inequivalent. Insertion of this temperature (T_c = −85 °C) together with the maximum peak separation of 20.2 Hz into an approximate formula[22] affords a barrier (ΔG^*) of about 9.4 kcal mol^{-1} for the dynamic process. This phenomenon could not be monitored for the meta and para groups owing to overlap of the peaks. In the case of **4**, the gallium analogue, a peak broadening was observed at −40 °C; the coalescence temperature of the $-CH_3$ signals of the para *i*-Pr groups at −70 °C together with a maximum peak separation of 60.5 Hz leads to a barrier to rotation of $\Delta G^* = 9.7$ kcal mol^{-1}. The $-CH_3$ signals of the ortho *i*-Pr groups begin to show similar behavior at −70 °C, and a barrier of $\Delta G^* = 9.6$ kcal mol^{-1} is calculated in this case. The *m*-H peaks cannot be monitored due to peak overlap with the solvent. In the case of **5**, dynamic behavior was also observed for the Trip signals upon cooling the sample. The spectral parameters and the temperature reveal that the barrier to the process is ca. 9.5 kcal mol^{-1}. Since the two substituents on the nitrogen are identical, the dynamic process may be assigned to flipping of the Trip groups rather than a restriction in rotation around the Ga–N bond. The similarity of this barrier to those observed in **3** and **4** suggests that a similar process may be occurring.

Conclusion

On the basis of these data, it is possible to conclude that the rotation barrier around the Al–N or Ga–N bonds is no greater than ca. 10 kcal mol^{-1} in the compounds studied here. This value is consistent with the conclusions based on the structural and spectroscopic results obtained for a range of Al–N species.[11] The lengths of the Ga–N and Al–N bonds appear to be dependent on (i) ionic contributions to bond strength, which are affected by factors such as the $M:NR_2$ ratio and the types of substituent, and (ii) the degree of steric crowding in the molecules.

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Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (41 pages). Ordering information is given on any current masthead page.

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[21] Olmstead, M. M.; Power, P. P. Unpublished results.

[22] Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.