Synthesis, Structure, and Spectroscopic Characterization of Unassociated Mono-, Di-, and Triamido Derivatives of Aluminum and Gallium

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As part of a study of the possible existence of π-interactions in Al–N or Ga–N bonds, the synthesis and spectroscopic and structural characterization of several unassociated amido derivatives of aluminum and gallium are described. The compounds $\mathrm{Mes^*GaCl\{N(H)Ph\}\cdot 0.25}$ (hexane), **1**, $\mathrm{Mes^*_2GaN(H)Ph}$, **2**, $\mathrm{MesAl\{N(SiMe_3)_2\}_2}$, **3**, $\mathrm{Mes^*Ga(NHPh)_2}$, **4**, and $\mathrm{ClGa\{N(SiMe_3)_2\}_2}$, **5** (Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$, Mes* = 2,4,6-*t*-$\mathrm{Bu_3C_6H_2}$) were synthesized by simple salt elimination procedures and characterized by ^{1}H and ^{13}C NMR and X-ray crystallography. In addition, the X-ray crystal structures of the previously reported triamido compounds $\mathrm{Al\{N(\mathit{i}\text{-}Pr)_2\}_3}$, **6**, and $\mathrm{Ga\{N(SiMe_3)_2\}_3}$, **7**, are described. The Al–N and Ga–N distances in **1**–**7** fall within the narrow limits 1.790(4)–1.809(2) and 1.829(9)–1.874(4) Å, respectively, which are within the previously known range for bonds between three-coordinate nitrogen and three-coordinate aluminum or gallium. Dynamic behavior in the ^{1}H and ^{13}C NMR spectra of **2** and **3** was also observed, with a barrier near 11 kcal mol^{-1} being estimated in both molecules. The structural and dynamic NMR data suggest that any π-interactions in the M-N bonds are rather weak and are of the order of 10 kcal mol^{-1}. Crystal data at 130 K with Mo Kα (**4**, **6**, **7**, $\lambda = 0.710\,73$ Å) or Cu Kα (**1**–**3**, **5**, $\lambda = 1.541\,78$ Å) radiation: (**1**) $\mathrm{C_{25.5}H_{38.5}ClGaN}$, $a = 9.421(2)$ Å, $b = 14.413(2)$ Å, $c = 18.967(3)$ Å, $\alpha = 87.88(2)^\circ$, $\beta = 79.22(2)^\circ$, $\gamma = 80.66(2)^\circ$, triclinic, space group $P\bar{1}$, $Z = 4$, $R = 0.083$ for 3867 ($I > 3\sigma(I)$) reflections; (**2**) $\mathrm{C_{42}H_{64}GaN}$, $a = 9.945(2)$ Å, $b = 11.245(2)$ Å, $c = 17.825(2)$ Å, $\alpha = 87.28(2)^\circ$, $\beta = 85.73(2)^\circ$, $\gamma = 79.25(2)^\circ$, space group $P\bar{1}$, $Z = 2$, $R = 0.054$ for 4155 ($I > 2\sigma(I)$) reflections; (**3**) $\mathrm{C_{21}H_{47}AlN_2Si_4}$, $a = 13.403(3)$ Å, $b = 16.651(2)$ Å, $c = 26.061(5)$ Å, $\beta = 91.46(2)^\circ$, monoclinic, space group $C2/c$, $Z = 8$, $R = 0.035$ for 2992 ($I > 2\sigma(I)$) reflections; (**4**) $\mathrm{C_{30}H_{30}GaN_2}$, $a = 20.346(4)$ Å, $b = 11.696(3)$ Å, $c = 13.565(3)$ Å, $\beta = 123.17(2)^\circ$, monoclinic, space group $C2/c$, $Z = 4$, $R = 0.066$ for 1707 ($I > 3\sigma(I)$) reflections; (**5**) $\mathrm{C_{12}H_{36}ClGaN_2Si_4}$, $a = 11.657(3)$ Å, $b = 12.677(2)$ Å, $c = 15.831(3)$ Å, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $R = 0.040$ for 2577 ($I > 3\sigma(I)$) reflections; (**6**) $\mathrm{C_{18}H_{42}AlN_3}$, $a = 7.803(6)$ Å, $b = 16.590(12)$ Å, $c = 17.397(14)$ Å, $\alpha = 102.68(5)$, $\beta = 90.67(5)^\circ$, $\gamma = 96.67(5)^\circ$, triclinic, space group $P\bar{1}$, $Z = 4$, $R = 0.071$ for 4311 ($I > 2\sigma(I)$) data; (**7**) $\mathrm{C_{18}H_{54}GaN_3Si_6}$, $a = 16.008(3)$ Å, $c = 8.444(2)$ Å, trigonal, space group $P\bar{3}1c$, $Z = 2$, $R = 0.059$ for 718 ($I > 3\sigma(I)$) reflections.

Introduction

Amido or imido derivatives of aluminum and gallium are characterized by a marked tendency to oligomerize through the formation of strong metal–nitrogen bridges.[1–3] Under normal conditions, unassociated aluminum or gallium amides remain quite rare, and monomeric imido derivatives are unknown. The monomers are important because the metals are coordinatively unsaturated and the nitrogen centers possess lone pairs that are not involved in σ-bonding. These lone pairs may, in principle at least, interact with the formally empty p-orbitals on the metal to form π-bonds. The extent of these interactions, and their effect on various structural parameters are, perhaps, the major feature of inherent interest in unassociated, low-coordinate amides. For many years, the only examples of such compounds were provided by the trisilylamides $\mathrm{M\{N(SiMe_3)_2\}_3}$ (M = Al,[4,5] Ga[4], In,[4] or Tl[4]). The species $\mathrm{Al\{N(i\text{-}Pr)_2\}_3}$[6] and $\mathrm{Al(NPh_2)_3}$[7] were also reported to be monomeric in benzene solution. Full structural details have been published only for $\mathrm{Al\{N(SiMe_3)_2\}_3}$[5] and $\mathrm{Tl\{N(SiMe_3)_2\}_3}$[8] although $\mathrm{Ga\{N(SiMe_3)_2\}_3}$ and $\mathrm{In\{N(SiMe_3)_2\}_3}$ were stated to be isomorphous with $\mathrm{Fe\{N(SiMe_3)_2\}_3}$[9a] and Ga–N and In–N bond lengths of 1.857(8) and 2.057(12) Å were quoted in a review.[9b] Additional examples of structurally characterized, unassociated aluminum and gallium amides have only been published within the past year.[10,11] These studies were focused on the monoamide

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derivatives of aluminum and gallium which had the formulas t-Bu_2AlNRR' (R, R′ = t-Bu, $SiPh_3$; 1-Ad, $SiPh_3$; Mes, Mes), $Trip_2MN(H)Dipp$ (M = Al or Ga), and $Trip_2GaNPh_2$ (Mes = 2,4,6-$Me_3C_6H_2$; Dipp = 2,6-i-$Pr_2C_6H_3$; Trip = 2,4,6-i-$Pr_3C_6H_2$; 1-Ad = 1-adamantanyl). All of these compounds feature bonding between three-coordinate aluminum or gallium and nitrogen centers. The structural and spectroscopic (mainly VT ^1H NMR) data suggested that π-interactions between the metal and nitrogen centers were probably weak. In this paper, these studies have been expanded to include di- and triamides as well as some further instances of monoamides. The synthesis and characterization of these new species, especially the di- and triamides, allow the extent of π-bonding to be more accurately assessed from structural trends within this series of compounds.

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. ^1H NMR or ^{13}C NMR spectra were obtained on a General Electric QE-300 spectrometer using either C_6D_6 or C_7D_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. With the exception of **5** (vide infra) all compounds gave C, H, and N analyses consistent with their formulas.

Starting Materials. H_2NPh (Aldrich) and $HN(i$-$Pr)_2$ (Aldrich) were purified by distillation from Na or CaH_2. $AlCl_3$ and $AlBr_3$ (Aldrich) were purified by sublimation. $GaCl_3$ (Strem) and $HN(SiMe_3)_2$, MesBr, n-BuLi (1.6 M in hexane), and $MgBu_2$[12] (Aldrich, 1 M in heptane) were used as received. MesLi,[13] Mes*Br,[14] Mes*Li,[15] Mes*$GaCl_2$,[16] $Mes^*{}_2GaCl$[17] (Mes* = 2,4,6-t-$Bu_3C_6H_2$), and $Ga\{N(SiMe_3)_2\}_3$[4] were synthesized by literature procedures. $Al\{N(i$-$Pr)_2\}_3$, **6**, was synthesized by the reaction of 3 equiv of $LiN(i$-$Pr)_2$ (generated from $HN(i$-$Pr)_2$ and n-BuLi) with $AlCl_3$ in benzene. The product, which was crystallized from hexane after the usual workup, had a melting point identical to that described in the literature.[6] ^1H NMR (C_7D_8): $\delta = 1.23$ (d, CH_3, $^3J_{H-H} = 6.6$ Hz), 3.38 (sept, CH). $^{13}C\{^1H\}$ NMR (C_7D_8): $\delta = 25.6$ (CH_3), 46.2 (CH).

Synthesis. Mes*GaCl{N(H)Ph}·0.25(hexane), 1. A solution of Mes*$GaCl_2$ (0.7 g, 1.81 mmol) in Et_2O (10 mL) was added to a suspension of $[(THF)MgNPh]_6$[18] (0.34 g, 1.81 mmol) in Et_2O (25 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 4 h. During this time the color of the suspended material lightened from buff to off-white. The ether was removed under reduced pressure, and the residue was extracted with hexane (25 mL). Reduction of the solvent volume to *ca.* 10 mL and cooling in a −20 °C freezer for several days afforded the product **1** as colorless crystals (yield 0.24 g, 30%). Mp: 130 °C. ^1H NMR (C_6D_6): $\delta = 7.53$ (s, 2H, m-H (Mes*)), 6.83 (t, 2H, m-H (Ph)), 6.55 (t, 1H, p-H (Ph)), 6.48 (d, 2H, o-H (Ph)), 4.21 (s, 1H, NH), 1.46 (s, 18H, o-$C(CH_3)_3$), 1.24 (s, 9H, p-$(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 31.27$ (p-$C(CH_3)_3$), 32.46 (o-$C(CH_3)_3$), 34.97 (p-$C(CH_3)_3$), 37.50 (o-$C(CH_3)_3$), 115.96, 117.89, 122.79, 129.81, 149.60, 152.43, 156.66 (Ar peaks). IR: 3383 (ν_{NH}), 246 (ν_{GaCl}) cm^{-1}. It is presumed that the presence of an amide group in the product is due to proton abstraction from ether.

Mes_2*GaN(H)Ph, 2. A solution of LiNHPh was prepared by adding n-BuLi (2.3 mL of a 1.6 M solution in hexane, 3.7 mmol) to aniline (0.35 g, 3.7 mmol) in ether (20 mL) with cooling in an ice bath. This solution was stirred for 4 h and allowed to warm to room temperature after which it was added dropwise to a solution of $Mes^*{}_2GaCl$[17] (1.35 g, 2.3 mmol) in ether (15 mL) with cooling in an ice bath. After warming to room temperature the solution was stirred for a further 18 h. The solvent was removed under reduced pressure and the residues were taken up in hexane (30 mL). The precipitate was removed by filtration, and the filtrate was concentrated to *ca.* 10 mL. Cooling overnight in a −20 °C freezer afforded the product **2** as colorless crystals (yield 0.35 g, 24%). Mp: 155–7 °C (softens at *ca.* 99 °C). ^1H NMR (C_6D_6): $\delta = 7.54$ (s, 4H, m-H (Mes*)), 6.89 (t, 2H, m-H(Ph)), 6.56 (d, 3H, o,p-H(Ph)), 4.27 (s, 1H, NH), 1.46 (s, 36H, o-$C(CH_3)$, 1.32 (s, 18 H, p-$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR C_6D_6): 31.37 (p-$C(CH_3)_3$, 33.28 (o-$C(CH_3)_3$), 34.68 (p-$C(CH_3)_3$), 38.79 (o-$C(CH_3)_3$), 116.61, 117.01, 122.76, 129.31, 157.81 (Ar peaks).

$MesAl\{N(SiMe_3)_2\}_2$, 3. A solution of $LiN(SiMe_3)_2$, generated from $HN(SiMe_3)_2$ (8.05 g, 50 mmol) in hexane (70 mL) and n-BuLi (31.25 mL of a 1.6 M solution in hexane), was added dropwise to a suspension of $AlBr_3$ (6.67 g, 25 mmol) in hexane (100 mL) with cooling in an ice bath. The mixture was allowed to warm slowly to room temperature and stirred for a further 16 h. The white precipitate was filtered off, and the filtrate was concentrated under reduced pressure to give an almost colorless pale yellow oil. This was fractionated at 0.05-mm pressure to give the crude product $BrAl\{N(SiMe_3)_2\}_2$ as a colorless oil between 95 and 99 °C (yield 5.12 g, ~50% based on Al). ^1H NMR studies of this oil in C_6D_6 solution showed that it was approximately 90% $BrAl\{N(SiMe_3)_2\}_2$ ($\delta = 0.273$, $Si(CH_3)_3$), with the other main component being the triamide $Al\{N(SiMe_3)_2\}_3$ ($\delta = 0.233$). Upon standing for 1 week in a refrigerator (ca. 5 °C) the oil deposited some crystals identified as $Al\{N(SiMe_3)_2\}_3$. To a solution of 2.07 g of oil ($BrAl\{N(SiMe_3\}_2$ content *ca.* 4.0 mmol) in hexane (50 mL) was added a slurry of LiMes in hexane (40 mL) with rapid stirring. This mixture was then stirred at room temperature for 24 h, after which it was filtered through Celite. The filtrate was concentrated to *ca.* 5–6 mL (it may be necessary to filter off further small quantities of LiBr at this stage) and cooled in a −20 °C freezer for 2 days to afford the product **3** as colorless crystals (yield 0.4 g, 0.71 mmol, 17.7%). Mp 146–152 °C (softens at 139 °C). ^1H NMR (C_6D_6): $\delta = 6.75$ (s, 2H, m-H), 2.58 (s, 6H, o-CH_3), 2.09 (s, 3H, p-CH_3), 0.26 (s, 36H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 144.4$ (s, o-C), 143.81 (s, br, *ipso*-C), 139.2 (s, p-C), 127.6 (s, m-C), 26.8 (s, o-CH_3), 21.4 (s, p-CH_3), 4.9 (s, $Si(CH_3)_3$). IR: 438, 376 cm^{-1} (tentatively assigned to $AlNSi_2$ group vibrations).[4]

Mes*Ga{N(H)Ph}₂, 4. A solution of LiN(H)Ph was synthesized by the dropwise treatment of aniline (0.28 g, 3 mmol), dissolved in ether (20 mL), with n-BuLi (1.9 mL of a 1.6 M solution in hexane). This solution was then stirred for 4 h and added dropwise to a solution of Mes*$GaCl_2$ (0.58 g, 1.5 mmol) in ether (20 mL) with cooling in a dry ice–acetone bath. The solution was allowed to warm to room temperature and stirred for a further 15 h. The solvent was removed under reduced pressure, and the residue was taken up in hexane (30 mL). The white precipitate was removed by filtration, and the filtrate was concentrated to a volume of *ca.* 10 mL. Cooling in a −20 °C freezer afforded the product **4** as colorless crystals (yield 0.24 g, 32%). Mp: 142–143 °C dec. ^1H NMR (C_6D_6): $\delta = 7.61$ (s, 2H, m-H(Mes*)), 6.94 (t, 4H, m-H(Ph)), 6.62 (d, 6H, o,p-H(Ph)), 3.57 (s, 2H, NH), 1.49 (s, 18 H, o-$C(CH_3)_3$), 1.26 (s, 9H, p-$C(CH_3)_3$). IR: 3392 (ν_{NH}) cm^{-1}.

$ClGa\{N(SiMe_3)_2\}_2$, 5. Compound **5** was synthesized in a manner that was very similar to that employed for $BrAl\{N(SiMe_3)_2\}_2$ in the preparation of **2**. Compound **5** was isolated as a colorless oil which contained about 8% of $Ga\{N(SiMe_3)_2\}_3$ impurity. Standing in a refrigerator for several days caused this

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Table 1. Selected Crystallographic and Data Collection Parameters for Compounds 1–7[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{25.5}H_{38.5}ClGaN$	$C_{42}H_{64}GaN$	$C_{21}H_{47}AlN_2Si_4$	$C_{30}H_{30}GaN_2$	$C_{12}H_{36}ClGaN_2Si_4$	$C_{18}H_{42}AlN_3$	$C_{18}H_{54}GaN_3Si_6$
fw	464.2	652.7	466.9	488.3	470.4	327.5	550.9
color & habit	colorless needles	colorless plates	colorless plates	colorless plates	colorless plates	colorless needles	colorless needles
cryst syst	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic	trigonal
a, Å	9.421(2)	9.945(2)	13.403(3)	20.346(4)	11.657(3)	7.803(6)	16.008(3)
b, Å	14.413(2)	11.245(2)	16.651(2)	11.696(6)	12.677(2)	16.590(12)	
c, Å	18.967(3)	17.825(2)	26.061(5)	13.565(3)	15.831(3)	17.397(4)	8.444(2)
α, deg	87.88(2)	87.28(2)				102.68(5)	
β, deg	79.22(2)	85.73(2)	91.46(2)	123.17(2)		90.67(5)	
γ, deg	80.66(2)	79.25(2)				96.67(5)	
V, Å^3	2496.4(8)	1951.8(4)	5814(1)	2702(1)	2339.3(8)	2181(3)	1873.9(7)
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$	$P2_12_12_1$	$P\bar{1}$	$P\bar{3}1c$
Z	4	2	8	4	4	4	2
cryst dims, mm	0.08 × 0.13 × 0.32	0.05 × 0.20 × 0.30	0.08 × 0.16 × 0.24	0.32 × 0.34 × 0.14	0.56 × 0.58 × 0.50	0.60 × 0.20 × 0.02	0.16 × 0.10 × 0.08
D_{calc}, g cm^{-3}	1.235	1.111	1.067	1.200	1.336	0.998	0.976
μ, mm^{-1}	2.55	1.146	2.252	1.037	5.526	0.092	0.928
T, K	130	223	130	130	133	130	120
range of transm coeffs	0.73–0.85	0.85–0.95	0.71–0.86	0.74–0.88	0.04–0.12	0.98–1.00	0.90–0.94
diffractometer	Syntex $P2_1$	Syntex $P2_1$	Siemens P4/RA	Siemens R3m/V	Siemens P4/RA	Siemens R3m/V	Siemens P4/RA
scan method	2θ	2θ	2θ	ω	2θ	ω	2θ
scan speed, deg min^{-1}	14.65	14.65	60	8.08	29.3	60	20
2θ range, deg	0–115	0–115	0–108.5	0–55	0–108.5	0–50	0–55
no. of data collct	6748	5320	3729	5404	2484	7697	3258
no of obsd reflects	3867 ($I > 3\sigma(I)$)	4155 ($I > 2\sigma(I)$)	2992 ($I > 2\sigma(I)$)	1707 ($I > 3\sigma(I)$)	2577 ($I > 3\sigma(I)$)	4311 ($I > 2\sigma(I)$)	7181 ($I > 3\sigma(I)$)
no. of variables	249	403	289	150	181	397	44
R, R_w	0.083, 0.078	0.054, 0.054	0.035, 0.039	0.066, 0.041	0.040, 0.047	0.071, 0.071	0.059, 0.064

[a] Data were collected with Mo Kα (λ = 0.710 73 Å) radiation for **4**, **6**, and **7**. For **1–3** and **5** Cu Kα (λ = 1.541 78 Å) radiation was used.

oil to solidify in a crystalline mass which had a melting point of *ca.* 20 °C. ^{1}H NMR (C_6D_6): δ = 0.27. ^{13}C{^{1}H} (C_6D_6): δ = 4.91.

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 19.

Data sets were collected at 130 K with use of a Syntex $P2_1$ (**1** and **2**), Siemens R3m/V (**4**, **5**, and **6**), or a P4/RA (**3** and **7**) diffractometer equipped with low-temperature attachments. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system.[20] Neutral atom scattering factors and the correction for anomalous dispersion were from ref 21. The structures were solved by direct methods. An absorption correction was applied by using the method described in ref 22. Details of the data collection and refinement and important atom coordinates are provided in Tables 1 and 2, respectively. Further information is given in the supplementary material.

Results

Structural Descriptions. Selected structural parameters for **1–7** are summarized in Table 3.

Mes*GaCl{N(H)Ph}·0.25 (hexane) (1). The structure of **1** is illustrated in Figure 1. Two crystallographically independent, but chemically identical, molecules are included in the unit cell. There are no close interactions between individual molecules. The galliums are surrounded, in a trigonal planar fashion, by Mes*, Cl, and NHPh ligands. The Cl–Ga–C angle in each molecule is near 120° whereas the Cl–Ga–N and N–Ga–C angles are approximately 105 and 135°, respectively. The plane of the Mes* ring is almost perpendicular (76.1 and 87.9°) to the coordination plane at gallium, and in one of the two molecules the ortho *t*-Bu groups are located such that there are extremely short interactions between the C–H hydrogens (Ga(1)···H(23c) = 2.02, Ga(1)···H(16c) = 2.05 Å) and the gallium centers. The Ga–N, Ga–C, and Ga–Cl bond lengths average 1.832(10), 1.925(10), and 2.194(4) Å, respectively. The torsion angles between the perpendiculars to the coordination planes at the galliums and nitrogens are 3 and 1.8°.

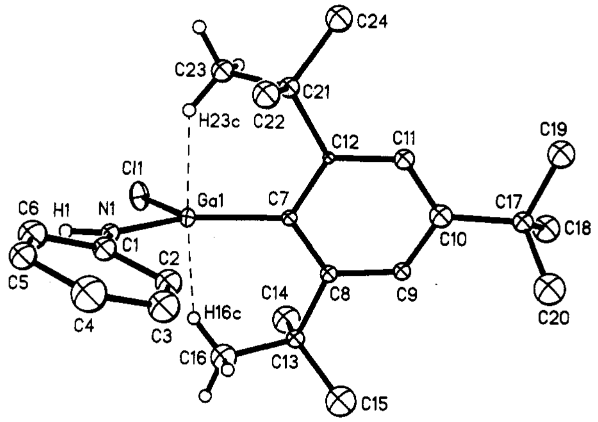

Figure 1. Thermal ellipsoidal plot of one of the molecules in the asymmetric unit of the structure of Mes*GaCl{N(H)Ph} (**1**). For clarity, only the hydrogens on nitrogen and a methyl substituent on the ortho *tert*-butyl groups are shown. Important bond distances and angles are given in Table 3.

Mes*$_2$GaN(H)Ph (2). The structure of this molecule is illustrated in Figure 2. The gallium is coordinated in an almost trigonal planar fashion (Σ°Ga 358.0(2)°) by two Mes* and an NHPh group. The C–Ga–C angle 135.3(2)° is over 20° wider than either of the N–Ga–C angles. The coordination at nitrogen is also planar, with a Ga–N–C angle of 133.4(3)° being observed. The Ga–N and Ga–C distances are 1.874(4), 1.980(5), and 2.000(4) Å. There is a torsion angle of 3.8° between the perpendiculars to the coordination planes at the gallium and nitrogen centers. An unusual feature of the structure is the distortion from normal geometry in the Ga–C(25) Mes* ring moiety. For

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

Table 2. Atom Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Selected Atoms in 1–7

	x	*y*	*z*	*U*(eq)^a
		Compound 1		
Ga(1)	2435(2)	102(1)	1226(1)	13(1)
Cl(1)	4333(4)	−988(2)	885(2)	22(1)
N(1)	2615(11)	1032(6)	548(5)	11(2)
C(1)	1780(14)	1917(9)	489(7)	17(3)
C(7)	1046(13)	−75(8)	2085(6)	8(3)
Ga(2)	−2841(2)	3320(1)	3444(1)	14(1)
Cl(2)	−1516(4)	2923(2)	4276(2)	22(1)
N(2)	−2600(1)	2283(7)	2875(5)	14(2)
C(31)	−3966(14)	4555(8)	3415(6)	14(3)
C(34)	−5629(14)	6394(9)	3387(7)	16(3)
		Compound 2		
Ga	126(1)	3349(1)	2132(1)	24(1)
N	1209(4)	2361(3)	1415(2)	32(1)
C(7)	981(4)	4735(4)	2372(2)	24(1)
C(10)	2273(5)	6732(4)	2638(3)	31(2)
C(25)	−1339(4)	2525(4)	2627(2)	24(1)
C(28)	−1928(5)	540(4)	3581(2)	30(2)
		Compound 3		
Al	2907(1)	9289(1)	1221(1)	18(1)
N(1)	2250(2)	10167(1)	988(1)	19(1)
N(2)	2263(2)	8381(1)	1402(1)	20(1)
C(13)	4374(2)	9338(2)	1279(1)	19(1)
Si(1)	1289(1)	10589(1)	1334(1)	24(1)
Si(2)	2702(1)	10644(1)	443(1)	24(1)
Si(3)	1315(1)	7982(1)	1011(1)	22(1)
Si(4)	2650(1)	7883(1)	1963(1)	24(1)
		Compound 4		
Ga(1)	0	2828(1)	2500	71(1)
N(1)	542(4)	3781(3)	2111(6)	111(6)
C(1)	0	1164(5)	2500	48(7)
C(7)	1017(3)	664(5)	5670(5)	65(4)
		Compound 5		
Ga(1)	8457(1)	589(1)	8805(1)	14(1)
Cl(1)	8420(2)	2163(1)	9275(1)	41(1)
N(1)	7047(4)	−55(4)	8701(3)	17(1)
N(2)	9878(4)	52(3)	8554(3)	13(1)
Si(1)	6866(1)	−1271(1)	9195(1)	19(1)
Si(2)	5936(1)	677(1)	8260(1)	21(1)
Si(3)	11020(1)	377(1)	9224(1)	20(1)
Si(4)	10064(1)	−675(1)	7628(1)	18(1)
		Compound 6		
Al(1)	2011(2)	2379(1)	9233(1)	23(1)
N(1)	2714(4)	2971(2)	10196(2)	26(1)
N(2)	1534(4)	2974(2)	8534(2)	26(1)
N(3)	1797(4)	1259(2)	8988(2)	27(1)
C(1)	1913(6)	3723(3)	10544(3)	33(2)
C(4)	3993(6)	2746(3)	10723(3)	34(2)
C(7)	2629(6)	3768(3)	8543(3)	31(2)
C(10)	135(6)	2763(3)	7919(3)	33(2)
C(13)	417(6)	754(3)	7346(3)	52(2)
C(16)	3002(6)	784(3)	8487(3)	30(2)
Al(2)	3299(2)	7600(1)	5761(11)	24(1)
N(4)	2515(4)	7004(2)	6455(2)	27(1)
N(5)	3740(4)	7001(2)	4809(2)	26(1)
N(6)	3621(5)	8721(2)	6002(2)	29(1)
		Compound 7		
Ga	3333	6667	2500	13(1)
N	2659(3)	7341(3)	2500	17(3)
Si	1722(1)	7029(1)	1158(2)	20(1)
C(1)	1762(6)	6241(6)	−410(8)	30(3)
C(2)	506(5)	6391(6)	2106(9)	29(3)
C(3)	1816(7)	8106(6)	136(9)	36(4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

example, there is an angle of 34.1° between the Ga–C(25) and C(25)···C(28) vectors. In addition, two hydrogens are found at distances of 2.32 Å (H(24A)) and 2.34 Å (H(15c)), affording an H(15c)···Ga···H(24b) angle of 171°. The angles between perpendiculars to the GaC_2N plane and the C(1), C(7), and C(25) aromatic rings are 13.2, 85.2, and 42.7°.

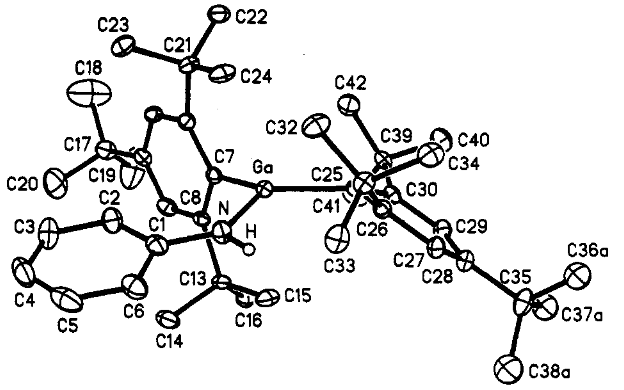

Figure 2. Thermal ellipsoidal plot of the structure of Mes_2*GaN(H)Ph (**2**). For clarity, only the hydrogen on the nitrogen is shown. Important bond distances and angles are given in Table 3.

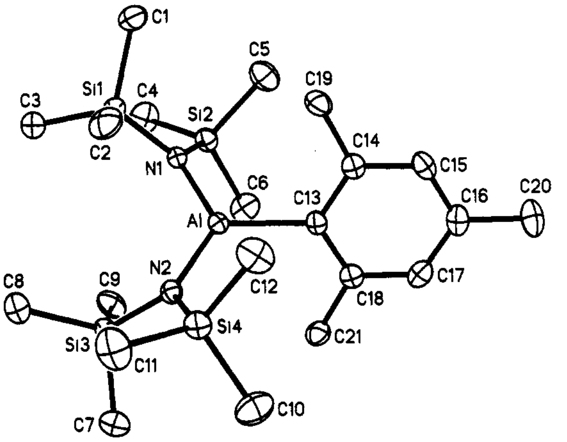

Figure 3. Thermal ellipsoidal plot of the structure of MesAl{$N(SiMe_3)_2$}$_2$ (**3**). For clarity, no hydrogens are shown. Important bond distances and angles are given in Table 3.

MesAl{$N(SiMe_3)_2$}$_2$ (3). The structure of **3** (Figure 3) consists of discrete monomeric molecules. The aluminum coordination is trigonal planar with fairly regular interligand angles (all within *ca.* 2° of 120°). The Al–N distances are 1.804(2) and 1.809(2) Å, and the Al–C bond length is 1.970(3) Å. There are torsion angles of 49.6 or 44.5° between the perpendiculars to the coordination planes at N(1) or N(2) and aluminum. The corresponding angle for the Mes plane is 56.2°. The Si–N bond lengths are in the narrow range 1.738(2)–1.749(2) Å and the Si–N–Si angles are both 120.4(1)°.

Mes*Ga{N(H)Ph}$_2$ (4). Molecules of **4** (Figure 4) have a crystallographically imposed 2-fold axis of rotation along the Ga–C bond (1.947(6) Å). The gallium therefore has planar coordination. The Ga–N distance is 1.837(8) Å and the N–Ga–N angle is 105.3(4)°. The torsion angle between the perpendiculars to the plane of the Mes* ring and the plane at gallium is 89.1°. The corresponding angle for the gallium and nitrogen planes is 7.3°. There are also close approaches between hydrogens from the ortho *t*-Bu groups and the metal. The Ga···H(6b) and the Ga···H(6a) distances are 2.37 and 2.38 Å.

ClGa{$N(SiMe_3)_2$}$_2$ (5). The structure of **5** (Figure 5) consists of discrete molecules with no imposed symmetry. The gallium and nitrogen centers have trigonal planar coordination. The wide angle (128.5(2)°) is observed between the two amide ligands. The Ga–N distances are 1.842(4) and 1.834(4) Å, and the Ga–Cl bond length is 2.130(2) Å. The torsion angles between the perpendiculars

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 1–7

	Mes*GaCl{N(H)Ph} (1)	Mes*$_2$GaN(H)Ph (2)	MesAl{N(SiMe$_3$)$_2$}$_2$ (3)	Mes*Ga{N(H)Ph}$_2$ (4)	ClGa{N(SiMe$_3$)$_2$}$_2$ (5)	Al{N(*i*-Pr)$_2$}$_3$ (6)	Ga{N(SiMe$_3$)$_2$}$_3$ (7)
M–N	1.829(9) 1.835(10)	1.874(4)	1.804(2) 1.809(2)	1.837(8)	1.844(4) 1.834(4)	two at 1.793(4) (av)[c] one at 1.801(4) (av)[c]	1.868(1)
M–N torsion angle	3.0 1.8	6.7	49.7 44.5	7.3	49.8 40.5	two at 37.4 (av)[c] one at 74.5 (av)[c]	48.6
M–C	1.926(11) 1.923(12)	1.986(5) 2.000(4)	1.970(3)	1.946(6)			
M–Cl	2.194(3) 2.194(3)				2.130(2)		
R–N–R′[a]	114(1) 116(1)	113(1)	120.9(1) 120.4(1)		124.2(3) 122.6(3)	114.7(3) (av)[c]	120.2(2)
M–N–R	131.8(7)	133.4(2)	117.7(1)		117.6(2)	two at 119.2(4) and 126.2(4)[d] corresp to 37.4 torsion angle	
M–N–R′	127.8(8) 114(1)	113(1)	121.0(1) 118.7(2)	130.2(4)	124.2(2) 117.9(2)	one at 122.0(2) and 123.2(5)[d] corresp to 74.5 torsion angle	119.9(2)
R″–M–R‴ [b]	116(1) 120.1(3) 121.3(4)	135.3(2)	120.8(2) 122.2(1)	130.2(4) 127.4(2)	119.3(2) 115.3(2)	two at 122.3 (av) opposite N(*i*-Pr)$_2$ gps with 37.4 torsion angle	120
N–M–R″	135.0(4) 132.3(5)	111.9(2)	118.1(1)	105.3(4)	128.5(2)		
N–M–R″	104.9(3) 106.4(3)	110.8(2)	119.7(1)	127.4(2)	116.2(2)	one at 115.4 (av) opposite N(*i*-Pr)$_2$ gp with 74.5 torsion angle	

[a] R, R′ = H, Ph (**1**, **2**, and **4**), SiMe$_3$, SiMe$_3$ (**3**, **5**, and **7**), *i*-Pr, *i*-Pr, (**6**). [b] R″, R‴ = Cl, Mes* (**1**), Mes*, Mes* (**2**), Mes, N(SiMe$_3$)$_2$ (**3**), Mes*, N(H)Ph (**4**), Cl, N(SiMe$_3$)$_2$ (**5**), N(*i*-Pr$_2$)$_2$, N(*i*-Pr$_2$)$_2$, (**6**), N(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$, (**7**). [c] Average value for the two molecules in the asymmetric unit. [d] Averaged for each molecule.

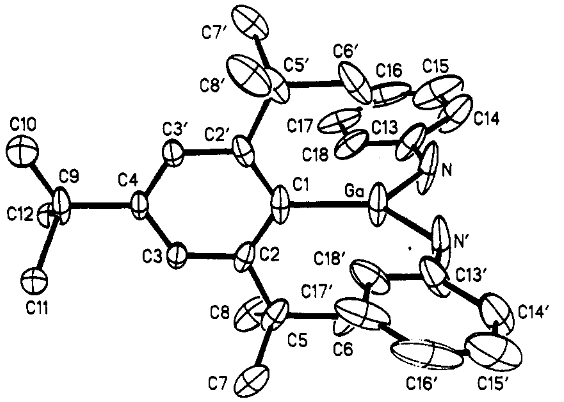

Figure 4. Thermal ellipsoidal plot of the structure of Mes*Ga(NHPh)$_2$ (**4**). For clarity, no hydrogens are shown. Important bond distances and angles are given in Table 3.

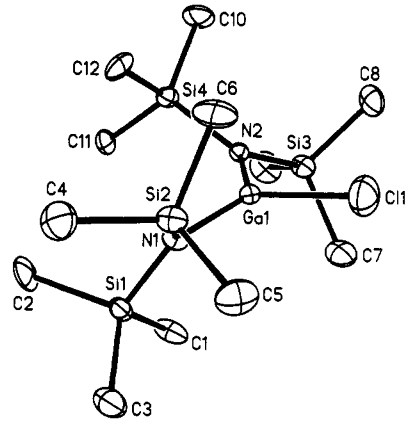

Figure 5. Thermal ellipsoidal plot of the structure of ClGa{N(SiMe$_3$)$_2$}$_2$ (**5**). For clarity, no hydrogens are shown. Important bond distances and angles are given in Table 3.

to the Ga coordination plane and the two nitrogen planes are 49.8 and 40.5°. The N–Si distances are in the range 1.740(5)–1.751(5) Å. The Si–N(1)–Si and Si–N(2)–Si angles are 124.2(3) and 122.6(3)°, respectively.

Al{N(*i*-Pr)$_2$}$_3$ (6). Compound **6** (Figure 6) crystallizes with two well-separated monomeric molecules in the asymmetric unit. The structures of the two monomers are almost identical. The aluminums and nitrogens have trigonal planar coordination. The torsion angles between the planes at the nitrogens and the AlN$_3$ plane adopt a pattern where two angles are in the range 36.5–39.1° whereas the remaining angle in each molecule is 72 (N(3)) or 77° (N(6)). The Al–N distances are in the range 1.790(4)–1.801(4) Å (the longest distances being associated with the largest torsion angles) with an average value of 1.795(5) Å. The angles at the aluminum show deviations from the idealized trigonal value with the smallest angles, N(1)–Al(1)–N(2) = 115.4(2)° and N(4)–Al–N(5) = 115.3(2)°, being associated with the nitrogen centers that subtend the smaller torsion angles mentioned above.

Ga{N(SiMe$_3$)$_2$}$_3$ (7). Compound **7** crystallizes as discrete monomers. There are crystallographically imposed 3-fold and 2-fold axes of rotation perpendicular to the GaN$_3$ plane and along the Ga–N bond. The molecular sturcture is thus defined by a gallium, nitrogen, silicon, and three carbon atoms. The Ga–N and Si–N distances are 1.868(1) and 1.743(1) Å. The Si–N–Si angle is 120.2(2)°. There is a torsion angle of 48.6° between the perpendiculars to the gallium and nitrogen coordination planes.

Discussion

Recent publications have described the synthesis and structural and spectroscopic characterization of several unassociated monoamides of aluminum,[10] gallium,[11] and

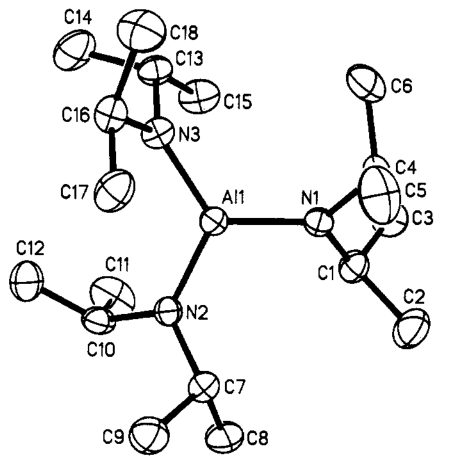

Figure 6. Thermal ellipsoidal plot of one of the molecules in the asymmetric unit of the structure of Al{N(i-Pr)$_2$}$_3$ (**6**). For clarity, no hydrogens are shown. Important bond distances and angles are given in Table 3.

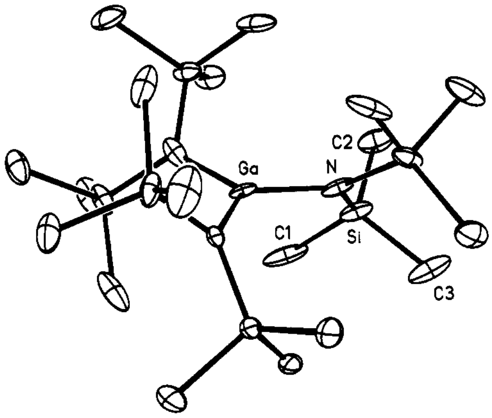

Figure 7. Thermal ellipsoidal plot of the structure of Ga{N(SiMe$_3$)$_2$}$_3$ (**7**). For clarity, no hydrogens are shown. Important bond distances and angles are given in Table 3.

indium that feature three-coordinate planar metal and nitrogen centers.[23] Prior to those reports, the only structures of unassociated amide derivatives of a heavier main group 3 element to have been reported in full were of the compounds M{N(SiMe$_3$)$_2$}$_3$ (M = Al[5] and Tl[8]). The aluminum species featured a bond length of 1.78(2) Å, which is far shorter than the sum (2.00 Å) of the covalent radii of aluminum (1.3 Å)[24,25] and nitrogen (0.7 Å).[26]

Table 4. Aluminum-Nitrogen Bond Lengths (Å) and Torsion Angles (deg) between the Aluminum and Nitrogen Coordination Planes in Unassociated Three-Coordinate Aluminum Amides

compd	Al–N	torsion angle	ref
	Monoamides		
Trip$_2$AlN(H)Dipp	1.784(3)	5.5	11
t-Bu$_2$AlNMes$_2$	1.823(4)	49.5	10
t-Bu$_2$AlN(Dipp)SiPh$_3$	1.834(3)	16.1	10
t-Bu$_2$AlN(1-Ad)SiPh$_3$	1.849(4) (av)	86.3	10
t-Bu$_2$AlN(SiPh$_3$)$_2$	1.879(4) (av)	64.3 (av)	10
	Diamides		
MesAl{N(SiMe$_3$)$_2$}$_2$, **3**	1.807(3) (av)	47.1 (av)	this work
{MeAlNDipp}$_3$	1.782(4)	0	31
	Triamides		
Al{N(SiMe$_3$)$_2$}$_3$	1.78(2)	50	5
Al{N(i-Pr)$_2$}$_3$, **6**	1.791(4) (av)	36.6 (av)	this work
	1.794(4) (av)	38.3 (av)	
	1.801(4) (av)	75.5 (av)	

Table 5. Gallium-Nitrogen Bond Lengths (Å) and Torsion Angles (deg) between the Gallium and Nitrogen Coordination Planes in Unassociated Gallium Amides

compd	Ga–N	torsion angle	ref
	Monoamides		
Mes*Ga(Cl)NHPh, **1**	1.832(10) (av)	2.4 (av)	this work
Trip$_2$GaN(H)Dipp	1.847(12) (av)	9.0	11
Mes*$_2$GaN(H)Ph, **2**	1.874(4)	6.7	this work
Trip$_2$GaNPh$_2$	1.878(7)	0	11
t-Bu$_2$GaN(t-Bu)SiPh$_3$	1.906(5)	88.7	11
t-Bu$_2$GaN(1-Ad)SiPh$_3$	1.924(2)	72.5	11
	Diamides		
ClGa{N(SiMe$_3$)$_2$}$_2$, **5**	1.844(4)	49.5	this work
	1.834(4)	40.5	
Mes*Ga{N(H)Ph}$_2$, **4**	1.837(8)	7.3	this work
	Triamides		
Ga{N(SiMe$_3$)$_2$}$_3$, **7**	1.868(1)	48.6	this work

The difference between the predicted and experimental bond lengths can be accounted for mostly in terms of an ionic resonance contribution[27] to the bond strength. For instance, the predicted Al–N bond lengths, modified for ionic effects, are in the range 1.79–1.85 Å,[28] depending on which empirical approximation is used to estimate the ionic factor.[29,30] Similarly, the Ga–N bond length predicted from the sum of the covalent radii is 1.95 Å, assuming a gallium radius of 1.25 Å.[11] When corrected for ionic effects,[29,30] 1.95 Å becomes shortened to 1.80–1.84 Å.

Inspection of the data in Tables 4 and 5 shows that, for both the gallium and aluminum monoamides, M–N bond distances outside the predicted ranges are found only in the case of the bulkiest amide substituents, *e.g.* –N(SiPh$_3$)$_2$ for aluminum and –N(R)SiPh$_3$ (R = t-Bu or 1-Ad (1-adamantanyl)) for gallium. In other words, significant deviation from the predicted M–N distances is only found in the most severely crowded molecules where, presumably, steric effects induce some elongation of the M–N bond.

Another significant feature of the data for the monoamides in Tables 4 and 5 is that there appears to be no strong correlation between the bond length and torsion angle. For example, the first four gallium monoamides in Table 5 display Ga–N distances in the range 1.832(10) (average) –1.878(7) Å even though the torsion angles are in the narrow range 0–9°. Similarly, of the first four aluminum monoamides in Table 4, there is a seemingly random variation of Al–N bond length with torsion angle. It is true, however, that the longest Al–N and Ga–N bond lengths for monoamides are generally associated with the

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[23] Petrie, M. A.; Ruhlandt-Senge, K.; Hope, H.; Power, P. P. *Bull. Soc. Chim. Fr.* **1993**, *130*, 851.

[24] A value of 1.3 Å for the covalent radius of aluminum was used. This value is widely accepted[25] and is in reasonable agreement with recently reported structures featuring Al–Al bonds involving three-coordinate metals. For example, Al–Al bond lengths of 2.660(1) and 2.647(3) Å have been reported: Uhl, W. *Z. Naturforsch.* **1988**, *43B*, 1113. Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. These Al–Al distances may be slightly elongated owing to the large size of the substituents.

[25] Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 258.

[26] A slightly smaller value (0.7 Å) for the radius of sp^2-hybridized nitrogen, which takes into account its planar coordination is used. For more information see the following reference: Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528.

[27] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 196.

[28] An Al–N bond length of 1.822 Å was predicted for a three-coordinate aluminum bond to a three-coordinate nitrogen. See: Haaland, A. Reference 3, Chapter 1.

[29] Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

[30] Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *129*, 1.

highest torsion angles. These high torsion angles and longer M–N distances are, as already noted, observed only with the bulkiest amide substituents. In effect, the bulkier groups induce large torsion angles and longer M–N distances in order to reduce steric interference. The data for these monoamides therefore suggest that possible M–N, p–p π-overlap, which requires low M–N torsion angles, is not of greater importance than steric effects in determining M–N bond length.

This conclusion appears to be supported by the data for the di- and triamides. For example, the structures of the diamidogallium derivatives 4 and 5 (Table 5) have very similar Ga–N distances, although the torsion angles are quite different. Moreover, these Ga–N bond lengths are not greatly different from those observed for the less hindered monoamides and the triamide $Ga\{N(SiMe_3)_2\}_3$, 7. In the case of the aluminum diamide 3, and the related species $\{MeAlNDipp\}_3$[31] (Dipp = 2,6-*i*-$Pr_2C_6H_3$) (Table 4), the Al–N distances are near the lower end of the Al–N scale for the monoamides and almost identical to the Al–N lengths observed for the triamides $Al\{N(i\text{-}Pr)_2\}_3$, 6, and $Al\{N(SiMe_3)_2\}_3$.[5] These observations also point to a minor role for Al–N, p–p π-bonding. This is because π-bonding in the di- and triamides is delocalized over two or three bonds; therefore, if π-bonding was important, longer M–N distances should be observed in the di- and triamides because of weaker π-bonds. In fact, the opposite trend is observed in the case of aluminum amides. It is notable that a similar pattern is discernible in the related aluminum aryloxide derivatives *t*-$Bu_2AlO(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$[32a] (Al–O = 1.710(2) Å), $MeAl\{O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)\}_2$[32b] (Al–O = 1.686(2) Å), and $Al\{O\text{-}(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)\}_3$ (Al–O = 1.648(7) Å).[32c]

For gallium amides the Ga–N bond lengths for the di- and triamides appear in the middle of the range of monoamide Ga–N distances. Thus, the pattern of bond lengths observed in these metal amides (especially the aluminum amides) is more consistent with the progressive contraction of the bonding radius of the metal with an increasing number of electronegative substituents.[28] The pattern is less pronounced in the case of the gallium amides, perhaps, because of the lower ionic character of these compounds owing to the higher electronegativity of gallium. The trend in the heavier main group 3 amides in Tables 4 and 5 may be contrasted with the corresponding boron derivatives which are known to involve significant B–N, p–p π-bonding.[1,33] In these compounds, the diamides usually have longer B–N bonds than the monoamides. With triamides the boron may interact with just two amides in a π-fashion and σ-bond to the remaining amide, giving a significant difference in the B–N bond lengths[34] depending on the presence or absence of a B–N π-interaction.

The compounds 2, 3, 5, and 6 were also investigated by VT NMR. In the case of 2 a VT $^{13}C\{^1H\}$ NMR study in C_7D_8 displayed a coalescence temperature of –55 °C for the *o*-C(CH$_3$) signals which afforded an energy of activation for the dynamic process[35] of 10.2 kcal mol^{-1} for a peak separation of 113 Hz. The *p*-$C(CH_3)_3$ signal had a coalescence temperature of –60 °C for a peak separation of 83 Hz, which yielded a barrier of 10.1 kcal mol^{-1}. A similar study of the VT behavior of the ^{1}H NMR showed a similar pattern with a coalescence of the *o*-$C(CH_3)_3$ signals observed at –70 °C with a maximum separation of 31 Hz between the signals. These data gave a barrier of 10.0 kcal mol^{-1}. This dynamic behavior is similar to that observed previously for $Trip_2GaN(H)Dipp$ where a barrier of 9.7 kcal mol^{-1} was calculated (a barrier of 9.4 kcal mol^{-1} was measured for the corresponding Al–N compound). Significantly, perhaps, splitting of the para group signals of the gallium substituents was observed for both this compound and 2. This suggests that the dynamic process may not be ring flipping but rather a restricted rotation around the Ga–N bonds. The similar values obtained for the Ga–N rotational barriers are consistent with the very similar Ga–N distances observed (*cf.* data in Table 5). A VT ^{1}H NMR study of the Mes^*_2GaCl precursor to 2 showed no dynamic behavior in the same temperature range, which also suggests that the dynamic process observed in 2 is indeed a restricted rotation around the Ga–N bond.

A VT ^{1}H and $^{13}C\{H\}$ NMR study of 3 in C_7D_8 displayed coalescence of the Me_3Si signals at *ca.* –30 °C which, with a maximum peak separation of about 87 Hz, afforded a consistent value of 11.5 kcal mol^{-1} for the dynamic process. It is notable that this value is higher than that observed in 2 and inconsistent with the value of 9.4 kcal mol^{-1} measured for $Trip_2AlN(H)Dipp$ which has a shorter Al–N distance of 1.784(3) Å[11] (*cf.* 1.807(3) Å in 3). In addition, the average torsion angle observed in 3 is 47.1°, which is incompatible with the existence of a strong Al–N π-interaction. Moreover, the aluminum center in 3 interacts with two nitrogen centers, which suggests that the π-interaction, if it exists in 3, should be weaker than that in 2. It may be concluded therefore that the dynamic process in 3 does not originate in Al–N π-bonding. Instead, the observation of different Me_3Si signals at low temperature is more consistent with the flipping of the nitrogen coordination planes that is slow on the NMR time scale at low temperatures. The different magnetic environments observed for the Me_3Si signals are a consequence of the introduction of the bulky mesityl substituent at aluminum and the tilting of the $-NSi_2$ planes with respect to the coordination plane at aluminum. It is significant that no dynamic behavior was observed in the ^{1}H NMR spectrum of 5 and 6 in the same temperature range.

In addition to the implications that the structural and dynamic NMR studies outlined above have for the existence of Al–N or Ga–N π-bonding, compounds 1–7 possess several other features of interest that are worthy of mention. For example, the structures of 1, 2, and 4 all possess a Mes* substituent on gallium whose ring plane is almost perpendicular to the coordination plane at the metal. One consequence of this is that the ortho *tert*-butyl groups of the Mes* substituent are brought into proximity with the metal such that the distances between hydrogens and the metal are relatively short. In 1 two hydrogens are found at distances of 2.02 Å (H(23c)) and 2.05 Å (H(16c)). These values probably signify a weak interaction (≤1–2 kcal mol^{-1}) with the metal. In the structure of 2 it is possible that, in order for interactions

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Table 6. Bond Distances (Å) and Angles (deg) for the Compounds $M\{N(SiMe_3)_2\}_3$ (M = Al, Ga, In, or Tl)

compd	M–N	torsion angle	N–Si	Si–N–Si	ref
$Al\{N(SiMe_3)_2\}_3$	1.78(2)	50	1.75(1)	118(1)	5
$Ga\{N(SiMe_3)_2\}_3$, 7	1.868(1)	48.6	1.743(3)	120.2(2)	this work
$In\{N(SiMe_3)_2\}_3$	2.049(1)	48.6	1.739(1)	122.7(1)	23
$Tl\{N(SiMe_3)_2\}_3$	2.089(18)	49.1	1.738(19)	122.5	8

of gallium with hydrogens from an *o-t*-Bu group from one Mes* ring to occur, the other Mes* ring becomes quite distorted to minimize steric interference between the two Mes* groups. Thus, the angle between the C(25)–C(28) vector and the Ga–C(25) bond is 34.1°. A similar distortion has been observed in the structure of Mes^*_2GaCl.[17]

In the structure of 6, longer Al···H distances of 2.64–2.71 Å were observed. This compound is the only structurally characterized example of a monomeric tris(dialkylamido)aluminum species. The Al–N bond lengths are within a standard deviation of that observed in $Al\{N(SiMe_3)_2\}_3$. The two molecules in the asymmetric unit of 6 have almost identical structures, as already noted. Two of the $-N(i\text{-}Pr)_2$ groups in each molecule of the asymmetric unit have lower torsion angles and shorter Al···H distances than the remaining group. There is a correlation between the Al–N bond length and the torsion angle between the aluminum and nitrogen coordination planes, the longer distance being associated with the higher angle. Although the differences in Al–N bond lengths are rather small, they are supportive of the existence of a small π-component in the Al–N bond. The structure 6 is similar to that observed for $Cr\{N(i\text{-}Pr)_2\}_3$[36] although the crystals are not isomorphous. Different torsion angles between the coordination planes at chromium and the nitrogens are observed for this compound, and these may be responsible for slightly different packing arrangements.

The Ga–N distance of 1.868(9) Å observed in $Ga\{N(SiMe_3)_2\}_3$, 7 is almost within a standard deviation of the value (1.857(8) Å) mentioned in a review.[9b] Full details of the structure of $Ga\{N(SiMe_3)_2\}_3$ were not given, however, and among trisilylamido derivatives of the heavier main group 3 elements, only the structures of $Al\{N(SiMe_3)_2\}_3$[5] and $Tl\{N(SiMe_3)_2\}_3$[8] have been completely described. This group has recently determined the structure of $In\{N(SiMe_3)_2\}_3$,[23] and the series is now completed by the structure of 7 given here. For comparison purposes, some details of all the structures of heavier main group 3 trisilylamides are provided in Table 6. With the exception of the change in the M–N distance with increasing atomic number, the other geometrical details are virtually constant throughout the four structures. Most notably, the torsion angles are in the range 48.6–50°, suggesting that any π-interaction in the M–N bonds is very small.

The results in this paper demonstrate that there can be a small but significant π-component in the Al–N and Ga–N bonds of aluminum or gallium amides. The magnitude of these interactions has a maximum value near 10 kcal mol^{-1} in the compounds studied thus far. The shortening observed in the Al–N and Ga–N bonds is due mainly to an ionic resonance component with a minor contribution from an Al–N or Ga–N π-interaction. These experimental findings are in good agreement with recent theoretical data.[37]

Note Added in Proof. During the review process of this paper, two further examples of unassociated gallium amides, $Er_2GaN(t\text{-}Bu)$[38a] and $(Me_3Si)_3SiGa(2,2,6,6\text{-}tetramethylpiperidino)_2$,[38b] were published. The Ga–N distances (Å) and torsion angles (deg) between the planes at Ga and N are 1.937(3) and 69.7, and 1.911(3) (av) and 71.3 (av), respectively. These structural parameters can be rationalized on the same basis as those of 1–7.

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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 (56 pages). Ordering information is given on any current masthead page.

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[37] Professor T. P. Hamilton and co-workers at the University of Alabama have calculated (MP 6-31 G**) the π-bond energies of H_2MEH_2 (M = B, Al, or Ga; E = N, P, or As) and have concluded that the Al–N and Ga–N π-bond interactions are near 10 kcal mol^{-1}.

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