Bis(dimethylamido) Complexes of Alkyl- and Phenylgallium. Useful Precursors to the RGa^{2+} Synthon

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Alkyl- and phenylbis(dimethylamido)gallium, $[RGa(NMe_2)_2]_2$ [R = Me (**1**), Et (**2**), ^{n}Bu (**3**), ^{n}Hx (**4**), and Ph (**5**)], were synthesized by reactions of $LiNMe_2$ with $(RGaCl_2)_2$. The crystal structure of compound **1** was a disordered mixture of anti and syn isomers, with the ratio of anti/syn being 64:36, which was consistent with the ratio (57:43) found in the ^{1}H NMR spectrum. The Ga_2N_2 cores of the anti and syn structures were nonplanar. ^{1}H NMR spectra indicated the presence of both anti and syn isomers for all of the other substituents. ^{1}H NMR and mass spectra indicated that a species with the general formula of $R_3Ga_2(NMe_2)_3$ was formed when these compounds were heated at high temperatures.

Introduction

A stable intermediate, poly(imidogallane), $[HGaNH]_n$, was recently reported to form in the ammonothermal conversion of $[H_2GaNH_2]_3$ to GaN.[1,2] Interest in extending this chemistry to organogallium derivatives, $[RGaNH]_n$, required a clean source of the synthon, RGa^{2+}. The usual synthetic approach to known $[RGaNR']_n$ and related aluminum imides involves the initial reaction of R_3Ga or R_3Al with a primary amine. The diprotic nature of $R'NH_2$ provides a natural stopping point to the alkane elimination steps. Part of our interest in these materials was to synthesize a family of compounds where R′ = H. This requires the use of NH_3, and pyrolysis of R_3Ga and ammonia often leads to complex mixtures from which it can be difficult to isolate high yields of pure imido clusters. A method was needed to differentiate the reactivity of the alkyl from the two other ligands. The known alkyl and aryl dihalides, $[RGaX_2]_2$,[3−5] suffer from the acidity of $[NH_4]X$, which would form as a byproduct in ammonia and which could lead to protonolysis of the desired alkyl ligand. In addition, should the desired oligo- or polymeric organogallium imide be insoluble, separation from $[NH_4]X$ might prove difficult. Compounds having the formula $RGa(NR_2)_2$ were attractive because of the expected facile substitution of the Ga−N bonds relative to the Ga−C bond and because of the lack of acidity of the HNR_2 byproducts.

With the exception of $[ClGa(NMe_2)_2]_2$,[6] existing gallium diamide compounds are limited to monomeric compounds containing bulky ligands including 2,2,6,6-tetramethylpiperidino (TMP) derivatives, $XGa(TMP)_2$ [X = Cl, Br, Me, Ph, −OPh, and $-O(2,6\text{-}C_6H_4)$];[7] bis(trimethylsilyl)amido derivatives, $YGaN(SiMe_3)_2$ (Y = Cl[8] and Me[9]); $(2,4,6\text{-}^tBu_3C_6H_2)Ga(NHPh)_2$;[8] and $RGa[NH(2,4,6\text{-}^tBu_3C_6H_2)]_2$ (R = Me[10] and Et[11]). In this paper, we report the high-yield syntheses of a family of alkyl- and phenyldimethylamido complexes of gallium. In addition to the advantages mentioned above for using amido ligands, the byproduct of the ammonolysis of $[RGa(NMe_2)]_2$ is $HNMe_2$, which because of its low boiling point will simplify the purification of the imido product(s). In subsequent papers, we will describe the use of these precursors to prepare oligo- and polymeric imides with the RGa^{2+} synthon.

Experimental Section

General Procedures. All of the manipulations were carried out with the rigorous exclusion of oxygen and moisture using standard Schlenk and drybox techniques (Vacuum Atmospheres Company, Dri-Train model 40-1). Diethyl ether, pentane, hexanes, benzene, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. Gallium(III) chloride (Strem), trimethylgallium (Strem), triethylgallium (Strem), and *n*-hexyllithium (Aldrich) were used as received. Lithium dimethylamide was prepared as a white powder from the reaction of *n*-butyllithium (Aldrich) and anhydrous dimethylamine (Aldrich). Methylgallium dichloride ($MeGaCl_2$),[10] ethylgallium dichloride ($EtGaCl_2$),[11] *n*-butylgallium dichloride ($^nBuGaCl_2$),[4] and phenylgallium dichloride ($PhGaCl_2$)[5] were obtained from the ligand exchange reactions reported in the literature.

Infrared spectra were acquired on NaCl plates (liquids) or as KBr pellets (solids) on a Nicolet Magna-IR 560 spectrometer. Except those indicated otherwise, ^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer in C_6D_6 at ambient temperature and were referenced to the residual protons in the solvent (7.15 ppm). Chemical ionization mass spectra were acquired on a Finnigan Mat 95 spectrometer using a direct insertion probe. The samples were evaporated at a temperature range of 25−360 °C, and the ionization gas mixture was methane with 4% ammonia. Melting points were obtained in sealed, nitrogen-filled capillaries and were uncorrected. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, and Desert Analytics, Tucson, AZ.

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Synthesis of $[MeGa(NMe_2)_2]_2$ (1). To a stirred suspension of $LiNMe_2$ (88.2 mmol, 4.50 g) in Et_2O (50 mL) at −78 °C was added a solution of $MeGaCl_2$ (44.1 mmol, 6.87 g) in Et_2O (50 mL). The suspension was stirred at −78 °C for 30 min and then allowed to warm slowly to 25 °C. The mixture was stirred overnight, and volatiles were removed under vacuum. Pentane (50 mL) was added and filtered, resulting in a white precipitate (LiCl) and a colorless solution. After the filtrate was concentrated to approximately 10 mL and cooled to −78 °C, colorless needles formed and were isolated (4.73 g, yield 62%). Several of these crystals were suitable for single-crystal X-ray diffraction studies. Mp: 42−51 °C. ^{1}H NMR for the anti isomer: δ −0.20 (s, 6H, GaMe), 2.27 (s, 12H, μ-NMe_2), 2.88 (s, 12H, terminal NMe_2). ^{1}H NMR for the syn isomer: δ −0.29 (s, 6H, GaMe), 2.06 (s, 6H, μ-NMe_2), 2.50 (s, 6H, μ-NMe_2), 2.91 (s, 12H, terminal NMe_2). The molar ratio of the anti/syn isomer was 1.3:1. IR (KBr): 2993 w, 2962 m, 2887 m, 2916 m, 2801 m, 2760 s, 1460 s, 1256 s, 1175 s, 1126 m, 970 s, 900 s, 719 m. CI MS {assignment, % relative intensity}: 347 {(dimer + H)$^+$, 20.5}, 331 {(dimer − Me)$^+$, 2.2}, 318 {$[Me_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 4.5}, 302 {(dimer − NMe_2)$^+$, 100}, 288 {$[MeGa_2(NMe_2)_2(HNMe_2)]^+$, 2.9}, 274 {$[Me_2Ga_2(NMe_2)_2(NH_2)]^+$, 5.7}, 259 {$[Me_2Ga_2(NMe_2)(HNMe_2)]^+$, 1.0}, 173 {(monomer + H)$^+$, 0.4}, 145 {$[MeGa(NMe_2)(NH_3)]^+$, 0.4}, 114 {$[Ga(HNMe_2)]^+$, 0.3}, 69 {Ga^+, 0.3}. Anal. Calcd for $C_{10}H_{30}Ga_2N_4$: C, 34.73; H, 8.74; N, 16.20. Found: C, 32.53; H, 8.46; N, 14.69.

Synthesis of $[EtGa(NMe_2)_2]_2$ (2). Following the previous procedure using $LiNMe_2$ (88.2 mmol, 4.50 g), $EtGaCl_2$ (44.1 mmol, 7.48 g), and Et_2O (100 mL), compound **2** was isolated as a colorless crystalline solid (6.92 g, yield 84%) from a pentane solution (12 mL) at −78 °C. Mp: 39−44 °C. ^{1}H NMR for the anti isomer: δ 0.59 (q, 4H, $GaCH_2CH_3$), 1.30 (t, 6H, $GaCH_2CH_3$), 2.33 (s, 12H, μ-NMe_2), 2.91 (s, 12H, terminal NMe_2). ^{1}H NMR for the syn isomer: δ 0.50 (q, 4H, $GaCH_2CH_3$), 1.27 (t, 6H, $GaCH_2CH_3$), 2.15 (s, 6H, μ-NMe_2), 2.50 (s, 6H, μ-NMe_2), 2.93 (s, 12H, terminal NMe_2). The molar ratio of the anti/syn isomer was 1:1. IR (KBr): 2997 w, 2950 m, 2906 m, 2867 m, 2809 m, 2763 m, 1457 s, 1257 s, 1173 s, 1124 m, 1039 m, 971 s, 898 s. CI MS {assignment, % relative intensity}: 375 {(dimer + H)$^+$, 5.5}, 360 {$[Et_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 1.1}, 346 {(dimer − Et)$^+$, 1.3}, 330 {(dimer − NMe_2)$^+$, 100}, 317 {$[EtGa_2(NMe_2)_3(NH_2)]^+$, 1.4}, 302 {$[EtGa_2(NMe)_2(HNMe_2)]^+$, 4.2}, 287 {$[Et_3Ga_2(NMe_2)(NH_2)]^+$, 4.6}, 204 {(monomer + NH_4)$^+$, 0.6}, 187 {(monomer + H)$^+$, 1.6}, 159 {$[EtGa(NMe_2)(NH_3)]^+$, 1.5}, 144 {$[Et_2Ga(NH_3)]^+$, 1.4}, 114 {$[Ga(HNMe_2)]^+$, 2.8}, 69 {Ga^+, 4.0}. Anal. Calcd for $C_{12}H_{34}Ga_2N_4$: C, 38.55; H, 9.17; N, 14.99. Found: C, 35.88; H, 8.59; N, 13.06.

Synthesis of $[^nBuGa(NMe_2)_2]_2$ (3). To a suspension of $LiNMe_2$ (40.5 mmol, 2.06 g) in 40 mL of Et_2O at −78 °C was added a solution of $^nBuGaCl_2$ (20.2 mmol, 4.00 g). The resulting suspension was allowed to slowly warm to 25 °C, stirred for 20 h, and then filtered, resulting in a white precipitate (LiCl) and a colorless solution. The filter cake was washed with Et_2O (10 mL), and the volatiles were then removed from the combined filtrates, resulting in the isolation of **3** as a nearly colorless oil (3.83 g, yield 88%). ^{1}H NMR for the anti isomer: δ 0.63 (t, 4H, $GaCH_2CH_2CH_2CH_3$), 1.02 (t, 6H, $GaCH_2CH_2CH_2CH_3$), 1.44 and 1.60 (m, 4H and 4H, respectively, $GaCH_2CH_2CH_2CH_3$), 2.36 (s, 12H, μ-NMe_2), 2.90 (s, 12H, NMe_2). ^{1}H NMR for the syn isomer: δ 0.55 (t, 4H, $GaCH_2CH_2CH_2CH_3$), 1.02 (t, 6H, $GaCH_2CH_2CH_2CH_3$), 1.44 and 1.60 (m, 4H and 4H, respectively, $GaCH_2CH_2CH_2CH_3$), 2.19 (s, 6H, μ-NMe_2), 2.51 (s, 6H, μ-NMe_2), 2.92 (s, 12H, terminal NMe_2). The triplet at 1.02 ppm and the multiplets at 1.44 and 1.60 ppm were overlapping resonances from both isomers. The molar ratio of the anti/syn isomer was 1:1. IR (neat, NaCl): 2955 s, 2919 s, 2882 m, 2800 m, 2762 s, 1458 s, 1256 m, 1226 m, 1173 s, 1131 s, 1067 w, 1042 m, 970 s, 899 s. CI MS {assignment, % relative intensity, data collected approximately 1 min after the sample injection}: 444 {$[^nBu_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 0.6}, 431 {(dimer + H)$^+$, 8.7}, 386 {(dimer − NMe_2)$^+$, 100}, 373 {(dimer − ^{n}Bu)}$^+$, 14.6}, 358 {$[^nBu_2Ga_2(NMe_2)_2(NH_2)]^+$, 2.7}, 343 {$[^nBu_2Ga_2(NMe_2)(HNMe_2)]^+$, 6.7}, 330 {$[^nBuGa_2(NMe_2)_2(HNMe_2)]^+$, 3.3}, 317 {$[^nBuGa_2(NMe_2)_2(NH_2)_2]^+$, 1.1}, 215 {(monomer + H)$^+$, 3.0}, 187 {$[^nBuGa(NMe_2)(NH_3)]^+$, 2.3}, 114 {$[Ga(HNMe_2)]^+$, 6.2}, 69 {Ga^+, 7.1}. MS (data collected approximately 2 min after the sample injection): 444 {$[^nBu_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 75.9}, 431 {(dimer + H)$^+$, 23.2}, 416 {$[^nBu_3Ga_2(NMe_2)_2(NH_3)]^+$, 25.2}, 399 {$[^nBu_3Ga_2(NMe_2)_2]^+$, 20.2}, 386 {(dimer − NMe_2)$^+$, 100}, 373 {(dimer − ^{n}Bu)}$^+$, 27.0}, 358 {$[^nBu_2Ga_2(NMe_2)_2(NH_2)]^+$, 6.6}, 345 {$[^nBuGa_2(NMe)_3(NH_2)]^+$, 3.2}, 330 {$[^nBuGa_2(NMe_2)_2(HNMe_2)]^+$, 7.1}, 317 {$[^nBuGa_2(NMe)_2(NH_2)_2]^+$, 4.3}, 302 {$[^nBuGa_2(NMe_2)_2(NH_3)]^+$, 2.8}, 245 {$[^nBu_2Ga(HNMe_2)(NH_3)]^+$, 3.2}, 228 {$[^nBu_2Ga(HNMe_2)]^+$, 10.6}, 215 {(monomer + H)$^+$, 8.2}, 187 {$[^nBuGa(NMe_2)(NH_3)]^+$, 5.6}, 114 {$[Ga(HNMe_2)]^+$, 9.8}, 69 {Ga^+, 6.3}.

Synthesis of $[^nHxGa(NMe_2)_2]_2$ (4). To a suspension of $GaCl_3$ (17.5 mmol, 3.08 g) in hexanes (30 mL) at −78 °C was slowly added a solution of ^{n}HxLi (17.5 mmol, 7.00 mL of a 2.5 M solution in hexanes). The suspension was stirred at −78 °C for 15 min, then warmed to 0 °C, and stirred for 1 h. The mixture was warmed to 25 °C and allowed to stir overnight. The suspension was then added to a suspension of $LiNMe_2$ (35.0 mmol, 1.79 g) in hexanes (40 mL) at 0 °C. The resulting suspension was allowed to slowly warm to 25 °C, stirred overnight, and then filtered, resulting in a white precipitate (LiCl) and a colorless solution. The filter cake was washed with hexanes (20 mL), and the volatiles were removed from the combined filtrates, resulting in the isolation of **4** as a nearly colorless oil (3.61 g, yield 85%). ^{1}H NMR for the anti isomer: δ 0.65 (m, 4H, $GaCH_2(CH_2)_4CH_3$), 0.96 (m, 6H, $GaCH_2(CH_2)_4CH_3$), 1.40 and 1.64 (both m, 12H and 4H, respectively, $GaCH_2(CH_2)_4CH_3$), 2.38 (s, 12H, μ-NMe_2), 2.91 (s, 12H, terminal NMe_2). ^{1}H NMR for the syn isomer: δ 0.57 (m, 4H, $GaCH_2(CH_2)_4CH_3$), 0.95 (t, 6H, $GaCH_2(CH_2)_4CH_3$), 1.40 and 1.64 (both m, 12H and 4H, respectively, $GaCH_2(CH_2)_4CH_3$), 2.22 (s, 6H, μ-NMe_2), 2.53 (s, 6H, μ-NMe_2), 2.94 (s, 12H, terminal NMe_2). The multiplets at 1.40 and 1.64 ppm were overlapping resonances from both isomers. The molar ratio of the anti/syn isomer was 1:1. CI MS {assignment, % relative intensity, data collected 2 min after the sample injection}: 528 {$[^nHx_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 12.0}, 500 {$[^nHx_3Ga_2(NMe_2)_2(NH_3)]^+$, 2.3}, 487 {(dimer + H)$^+$, 15.5}, 483 {$[^nHx_3Ga_2(NMe_2)_2]^+$, 4.5}, 442 {(dimer − NMe_2)$^+$, 100}, 414 {$[^nHx_2Ga_2(NMe_2)_2(NH_2)]^+$, 4.3}, 399 {$[^nHx_2Ga_2(NMe_2)(HNMe_2)]^+$, 3.6}, 358 {$[^nHxGa_2(NMe_2)_2(HNMe_2)]^+$, 2.9}, 330 {$[^nHxGa_2(NMe_2)_2(NH_3)]^+$, 1.1}, 313 {$[^nHxGa_2(NMe_2)_2]^+$, 1.8}, 243 {(monomer + H)$^+$, 2.7}, 215 {$[^nHxGa(NMe_2)(NH_3)]^+$, 1.4}, 114 {$[Ga(HNMe_2)]^+$, 4.0}, 69 {Ga^+, 4.0}. MS (data collected 2.7 min after the sample injection): 887 {species containing Ga_4, 8.8}, 528 {$[^nHx_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 35.7}, 524 {$[^nHx_4Ga_2(HNMe_2)]^+$, 2.8}, 516 {$[^nHx_3Ga_2(NMe_2)_2(NH_2)(NH_3)]^+$, 4.5}, 500 {$[^nHx_3Ga_2(NMe_2)_2(NH_3)]^+$, 5.8}, 487 {(dimer + H)$^+$, 15.6}, 483 {$[^nHx_3Ga_2(NMe_2)_2]^+$, 12.5}, 442 {(dimer − NMe_2)$^+$, 100}, 429 {$[^nHx_3Ga_2(NH_3)_2]^+$, 2.7}, 414 {$[^nHx_2Ga_2(NMe_2)_2(NH_2)]^+$, 5.1}, 399 {$[^nHx_2Ga_2(NMe_2)(HNMe_2)]^+$, 7.9}, 373 {$[^nHxGa_2(NMe_2)_3(NH_2)]^+$, 3.1}, 358 {$[^nHxGa_2(NMe_2)_2(HNMe_2)]^+$, 5.8}, 345 {$[^nHxGa_2(NMe_2)_2(NH_2)_2]^+$, 1.5}, 330 {$[^nHxGa_2(NMe_2)_2(NH_3)]^+$, 1.9}, 313 {$[^nHxGa_2(NMe_2)_2]^+$, 2.7}, 284 {$[^nHx_2Ga(HNMe_2)]^+$, 3.3}, 260 {$[^nHxGa(NMe_2)(HNMe_2)(NH_3)]^+$, 3.5}, 243 {(monomer + H)$^+$, 9.4}, 215 {$[^nHxGa(NMe_2)(NH_3)]^+$, 4.7}, 114 {$[Ga(HNMe_2)]^+$, 12.4}, 69 {Ga^+, 8.4}.

Synthesis of $[PhGa(NMe_2)_2]_2$ (5). The procedure was as that for **1** using $LiNMe_2$ (37.2 mmol, 1.90 g), $PhGaCl_2$ (18.6 mmol, 4.05 g), and Et_2O (70 mL). Compound **5** was isolated as a colorless crystalline solid (3.56 g, yield 81%) from a pentane solution (15 mL) at −20 °C. Mp: 82.0−86.0 °C. ^{1}H NMR for the anti isomer: δ 2.55 (s, 12H, μ-NMe_2), 2.79 (s, 12H, terminal NMe_2), 7.27, 7.52, and 7.65 (all m, aromatic). ^{1}H NMR for the syn isomer: δ 2.38 (s, 6H, one Me of μ-NMe_2), 2.62 (s, 6H, one Me of μ-NMe_2), 2.98 (s, 12H, terminal NMe_2), 7.27, 7.52, and 7.65 (all m, aromatic). The resonances of the aromatic hydrogen atoms of the two isomers were not distinguished. The molar ratio of the anti/syn isomer was 1:1. CI MS {assignment, % relative intensity}: 504 {$[Ph_3Ga_2(NMe_2)_2(HNMe_2)]^+$, 88.4}, 476 {$[Ph_3Ga_2(NMe_2)_2(NH_3)]^+$, 15.1}, 471 {(dimer + H)$^+$, 23.7}, 459 {$[Ph_3Ga_2(NMe_2)_2]^+$, 13.4}, 438 {$[PhGa_2(NMe_2)_4(HNMe_2)]^+$, 4.2}, 426 {(dimer − NMe_2)$^+$, 100}, 398 {$[Ph_2Ga_2(NMe_2)_2(NH_2)]^+$, 9.2}, 393 {(dimer − Ph)$^+$, 8.9}, 383 {$[Ph_2Ga_2(NMe_2)(HNMe_2)]^+$, 4.2}, 365 {$[PhGa_2(NMe_2)_3(NH_2)]^+$, 5.2}, 337 {$[PhGa_2(NMe_2)_2(NH_2)_2]^+$, 3.2}, 309 {$[PhGa_2(NMe_2)(NH_2)_3]^+$, 3.1}, 285 {$[Ph_2Ga(HNMe_2)(NH_3)]^+$, 1.5}, 268 {$[Ph_2Ga(HNMe_2)]^+$, 1.8}, 252 {(monomer + NH_4)$^+$, 1.6}, 240 {$[Ph_2Ga(NH_3)]^+$, 1.2}, 235 {(monomer + H)$^+$, 2.0}, 223 {Ph_2Ga^+, 1.6}, 207 {$[PhGa(NMe_2)(NH_3)]^+$, 2.1}, 114 {$[Ga(HNMe_2)]^+$, 3.3}, 69 {Ga^+, 8.4}. Anal. Calcd for $C_{20}H_{34}Ga_2N_4$: C, 51.11; H, 7.29; N, 11.92. Found: C, 50.53; H, 7.16; N, 10.94.

Table 1. Crystallographic Data of Compound **1**

chemical formula	$C_{10}H_{30}Ga_2N_4$ (**1**)
formula weight	345.82
space group	$P2_1/n$
a, Å	8.6050(9)
b, Å	15.439(2)
c, Å	12.410(1)
β, deg	90.146(2)
V, Å^3	1648.7(3)
Z	4
T, °C	−100
λ, Å	0.710 73
ρ_{calcd}, g cm^{-3}	1.393
μ, cm^{-1}	32.54
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0386, 0.0868

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

Single-Crystal X-ray Diffraction of Compound 1. A suitable crystal was attached to a glass fiber under a nitrogen atmosphere and mounted on a Siemens SMART platform with data collected at 173 K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These sets of frames were orientated such that the orthogonal wedges of reciprocal space were surveyed. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω. The final cell constants were calculated from a set of 2918 strong reflections from the actual data collection.

The space group $P2_1/n$ was determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution was applied to the structure that provided the most non-hydrogen atoms from the E maps. Several full-matrix, least-squares/difference Fourier cycles were performed, which located the remainder of the non-hydrogen atoms. All of the hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. All of the calculations were performed on SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs. The experimental conditions and unit cell information are summarized in Table 1. In the structure of **1**, one of the gallium centers was found to be disordered over two sites. Several restraints were used in the modeling of this disorder: the anisotropic displacement parameters of [C(8) and C(10′)] and [C(8′) and C(10)] were set to be equivalent because of the near overlap of these atoms, and the U_{ij} displacement parameters of the disordered atoms were restrained to be similar.

Results and Discussion

Synthesis and Characterization of RGa(NMe$_2$)$_2$. A series of alkyl- and phenylbis(dimethylamido)gallium having the formula of $[RGa(NMe_2)_2]_2$ [R = Me (**1**), Et (**2**), ^{n}Bu (**3**), ^{n}Hx (**4**), and Ph(**5**)] were synthesized via the reactions of $[RGaCl_2]_2$ and $LiNMe_2$ as depicted in eqs 1−2.

$$R_3Ga + [GaCl_3]_2 \xrightarrow{\Delta} 1.5[RGaCl_2]_2 \xrightarrow[-6LiCl]{\overset{6LiNMe_2}{Et_2O}} 1.5[RGa(NMe_2)_2]_2 \quad (1)$$

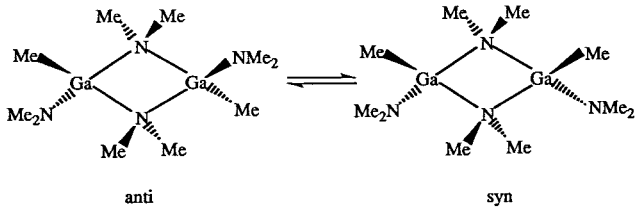
R = Me (**1**), Et (**2**), ^{n}Bu (**3**), and Ph (**5**)

$$2RLi + [GaCl_3]_2 \xrightarrow[-2LiCl]{hexanes} [RGaCl_2]_2 \xrightarrow[-4LiCl]{\overset{4LiNMe_2}{hexanes}} [RGa(NMe_2)_2]_2 \quad (2)$$

R = ^{n}Hx (**4**)

Compounds **1**, **2**, and **5** were isolated as colorless, crystalline solids, while **3** and **4** were isolated as nearly colorless liquids.

Scheme 1



In the elemental analysis for compounds **1**, **2**, and **5**, the measured carbon and nitrogen percentages were lower than the calculated values by 0.58−2.7 and 0.98−1.9%, respectively. This was attributed to the formation of involatile materials containing carbon, nitrogen, and gallium during the analytical process. The attempts to purify compounds **3** and **4** by low-pressure distillation resulted in decomposition.

The ^{1}H NMR spectrum of compound **1** possessed two Ga−Me environments and five Ga−NMe$_2$ environments, consistent with the presence of two isomers. The presence of five NMe$_2$ resonances suggested an anti/syn rather than a dimer/trimer isomerization (Scheme 1). The single resonance at 2.27 ppm was assigned to the bridging NMe$_2$ groups of the anti isomer, while the peaks at 2.06 and 2.50 ppm were assigned to the inequivalent methyls of bridging NMe$_2$ groups in the syn isomer. On the basis of the relative intensity of the bridging NMe$_2$ groups, the peaks at 2.88 and 2.91 ppm were assigned to the terminal NMe$_2$ groups of the anti and syn isomers, respectively. The resonances of the Ga−Me groups of the anti and syn isomers were at −0.20 and −0.29 ppm, respectively. Integration of the NMR data indicated that the isomers were present in a 57:43 anti/syn ratio. ^{1}H NMR spectra of compounds **2**−**5** also indicated the presence of equal amounts of anti and syn dimers in solution. This result made it impossible to differentiate some of resonances of the anti isomer from those of the syn isomer from these spectra alone, but the assignment of these spectra was achieved by a comparison to the spectrum of compound **1**. The ^{1}H NMR spectrum of compound **3** indicated that only trace impurities were present; however, in the spectrum of compound **4**, there were four unassigned singlets at 2.27, 2.42, 2.58, and 2.96 ppm that were within the NMe$_2$ resonance region. The sum of integrations of these peaks was ∼20% of the sum of the integrations of all of the peaks belonging to the NMe$_2$ groups. No resonance belonging to the impurities was found in the gallium alkyl region of the spectrum. In the ^{1}H NMR spectrum of compound **5**, there were several unassigned singlets in the NMe$_2$ region with three major peaks at 2.86, 2.60, and 2.50 ppm. The total integration of these peaks was ∼8% of the sum of the integrations of all of the NMe$_2$ groups. These peaks existed in the spectra of all of the samples that were prepared in repeated reactions and purified either by recrystallization or by sublimation. Variable-temperature NMR experiments, carried out in a benzene-d_6 solution at a temperature range of 20−70 °C, showed that the relative integrations of these resonances to the sum of integrations of the resonances of the anti and syn isomers were unchanged. In the spectra for several samples isolated by heating compound **5** in a Et$_2$O or toluene solution for several days at temperatures ranging from 40 to 100 °C, the relative integrations of these resonances increased, but the integration ratio of the peaks at 2.86, 2.60, and 2.50 ppm was constantly 1:1:1. These results suggest that these peaks should be attributed to impurities rather than to other isomeric forms of compound **5**. Specifically, the resonances at 2.86, 2.60, and 2.50 ppm were attributed to $Ph_3Ga_2(NMe_2)_3$, a suggestion supported by the mass spectral data in the following discussion.

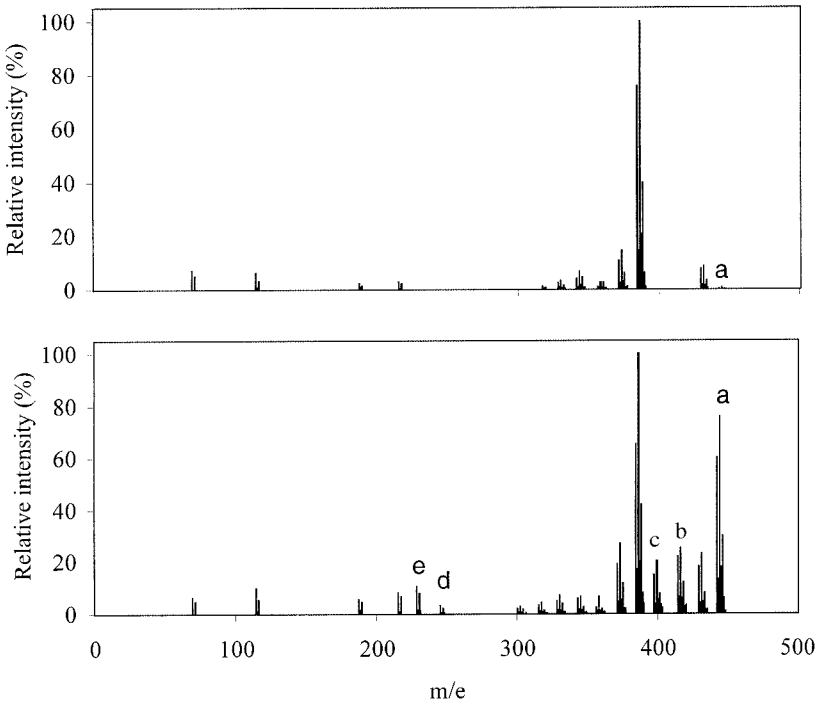


Figure 1. Comparison of the mass spectra of compound **3**. Top and bottom spectra were recorded 1 and 2 min after the sample injection, respectively. Only species related to the thermal decomposition product, $^{n}Bu_3Ga_2(NMe_2)_3$, are labeled: (a) $[^{n}Bu_3Ga_2(NMe_2)_2(HNMe_2)]^+$; (b) $[^{n}Bu_3Ga_2(NMe_2)_2(NH_3)]^+$; (c) $\{[^{n}Bu_3Ga_2(NMe_2)_2]^+$; (d) $[^{n}Bu_2Ga(HNMe_2)(NH_3)]^+$; (e) $[^{n}Bu_2Ga(HNMe_2)]^+$.

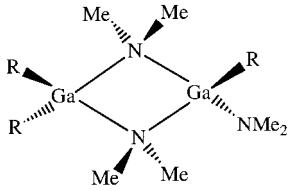


Figure 2. Proposed structure of $R_3Ga_2(NMe_2)_3$.

The chemical-ionization mass spectra of all of the compounds were collected in an atmosphere of methane with 4% ammonia. For compounds **3** and **4**, the ion abundance changed significantly as a function of time. Two spectra for **3** and **4** were given in the Experimental Section, with the first spectrum corresponding to the first maxima in the ion abundance versus time curve. The second set of data corresponded to the largest peak in ion current. Specifically, the two spectra of **3** were collected at 1 and 2 min after the sample injection, and the corresponding temperatures of the insertion probe were approximately 40 and 200 °C, respectively. The two spectra of **4** were collected at 2 and 2.7 min, where the temperatures were approximately 200 and 300 °C, respectively. A comparison of the two mass spectra of compound **3** is shown in Figure 1.

All of the mass spectra of the five compounds exhibited base peaks of $[\text{dimer} - NMe_2]^+$. The intensities of peaks attributed to the parent ions $[\text{dimer} + H]^+$ were found in the range from 5.5 to 24% of the base peaks. All of the spectra also exhibited peaks that could be assigned to a second compound having the general formula of $R_3Ga_2(NMe_2)_3$ (+1). The intensities of ions from $R_3Ga_2(NMe_2)_3$ relative to the corresponding base peaks were 4.5% for R = Me, 1.1% for Et, 0.6% and 76% in the two spectra for ^{n}Bu, 12% and 36% in the two spectra for ^{n}Hx, and 88% for Ph. Because elevated temperatures were employed for the evaporation of the samples in the MS experiments, it was possible that $R_3Ga_2(NMe_2)_3$ resulted from the thermal decomposition of compounds **1**−**5**. Figure 1 further illustrates that the relative amount of $R_3Ga_2(NMe_2)_3$ increased when the samples

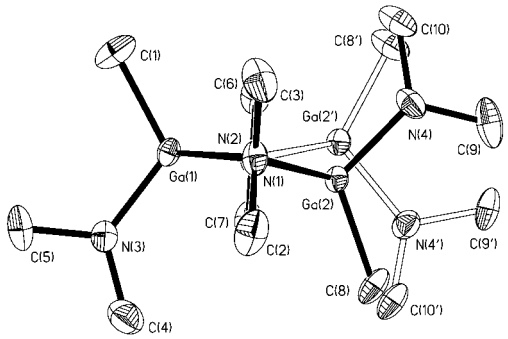


Figure 3. Molecular structure and atom labeling scheme for $[MeGa(NMe_2)_2]_2$ **1**, showing the disorder at Ga(2). The hollow bonds link the minor disordered portion of the structure. Atoms are shown at the 30% probability level. All of the hydrogen atoms are omitted for clarity.

were heated for a longer time and at higher temperatures. Shown in Figure 2 is the proposed structure of $R_3Ga_2(NMe_2)_3$ that was supported by the NMR data. The three expected ^{1}H resonances for the NMe_2 groups of this proposed structure were singlets with equal intensities observed at 2.86, 2.60, and 2.50 ppm for **5**. A ligand redistribution coupled with scrambling of $RGa(NMe_2)_2$ and $R_2Ga(NMe_2)$ units (eqs 3−5) could be responsible for the formation of $R_3Ga_2(NMe_2)_3$.

$$[RGa(NMe_2)_2]_2 \rightleftharpoons 2RGa(NMe_2)_2 \quad (3)$$

$$2RGa(NMe_2)_2 \rightleftharpoons R_2Ga(NMe_2) + Ga(NMe_2)_3 \quad (4)$$

$$RGa(NMe_2)_2 + R_2Ga(NMe_2) \rightleftharpoons R_3Ga_2(NMe_2)_3 \quad (5)$$

This sequence should also produce the known amide $Ga(NMe_2)_3$[12] which was not observed. It might be that $Ga(NMe_2)_3$

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $C_{10}H_{30}Ga_2N_4$ (**1**)

Ga(1)−N(1)	2.020(3)	Ga(1)−N(2)	2.016(3)
Ga(1)−N(3)	1.837(3)	Ga(1)−C(1)	1.972(4)
Ga(2)−N(1)	2.034(3)	Ga(2)−N(2)	2.028(3)
Ga(2)−N(4)	1.837(6)	Ga(2)−C(8)	1.98(2)
Ga(2′)−N(1)	2.035(4)	Ga(2′)−N(2)	2.052(4)
Ga(2′)−N(4′)	1.858(10)	Ga(2′)−C(8′)	1.93(3)
N(3)−Ga(1)−C(1)	114.9(2)	N(1)−Ga(1)−N(2)	86.56(12)
Ga(1)−N(1)−Ga(2)	93.22(12)	Ga(1)−N(2)−Ga(2)	93.53(12)
Ga(1)−N(1)−Ga(2′)	93.18(13)	Ga(1)−N(2)−Ga(2′)	92.79(13)
N(4)−Ga(2)−C(8)	116.7(6)	N(4′)−Ga(2′)−C(8′)	113(2)
N(1)−Ga(2)−N(2)	85.86(13)	N(1)−Ga(2′)−N(2)	85.2(2)

formed dinuclear complexes with several of the other gallium monomers, thus reducing the intensity of its spectroscopic signature.

Structure of $[MeGa(NMe_2)_2]_2$ (1). The molecular structure of **1** is shown in Figure 3, and relevant bond lengths and angles are listed in Table 2. The presence of both the anti and syn isomers was observed in the form of disorder in one of the Ga sites [Ga(2)]. The major site (64% occupation) was oriented such that N(3) and N(4) were anti with respect to one another, while in the minor site (36% occupation), N(3) and N(4′) were syn. This anti/syn ratio of 64:36, found at 173 K in the solid state, was consistent with that found in a benzene solution at 298 K (57:43). The Ga−C bond lengths were 1.972(4) Å [Ga(1)−C(1)], 1.98(2) Å [Ga(2)−C(8)], and 1.93(3) Å [Ga(2′)−C(8′)], while the bridging and terminal Ga−N bond lengths were 2.020(3) Å [Ga(1)−N(1)] and 1.837(3) Å [Ga(1)−N(3)], respectively. The Ga_2N_2 cores of the anti and syn isomers in this disordered structure exhibited torsion angles of 6.9(2)° for the anti geometry [N(2)−Ga(1)−N(1)−Ga(2)] and −11.5(2)° for the syn configuration [N(2)−Ga(1)−N(1)−Ga(2′)]. A nonplanar "butterfly" geometry was previously found in the structure of $\{[^tBu(H)N]_2Ga[\mu\text{-}N(H)^tBu]\}_2$,[13] which adopted a syn geometry with respect to the substituents on nitrogen. Except for the nonplanar core, other features of the structure of compound **1** were consistent with those found in the structures of $[ClGa(NMe_2)_2]_2$[6] and related alkylgallium amides.[14]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of compounds **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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