Sterically Crowded Gallium Amidinate Complexes

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The sterically crowded gallium amidinate complexes {^{t}BuC(NR′)$_2$}GaX$_2$ (X = Cl, Me, Et, CH$_2$Ph; R′ = ^{i}Pr, Cy, ^{t}Bu) have been synthesized in good yield. X-ray crystallographic analyses show that the steric interactions between the ^{t}Bu and R′ groups influence the R′−N−Ga angle and the steric environment at gallium.

Introduction

Gallium compounds that incorporate amidinate ligands (RC(NR′)$_2^-$) have been studied because of their potential use as volatile precursors to nitride materials.[1] The two most common classes of Ga amidinate compounds are {RC(NR′)$_2$}GaX$_2$ species (X = Cl, alkyl; **I** in Chart 1), in which one amidinate ligand chelates the metal center, and {RC(NR′)$_2$}$_2$GaX species (X = Cl, alkyl; **II** in Chart 1), which contain two chelating amidinates.[1a,2] There are also a few examples of dinuclear ({μ-η^1:η^1-RC(NR′)$_2$}$_2$-GaMe$_2$)$_2$ complexes in which two Ga centers are linked by two bridging amidinate ligands (**III** in Chart 1). In these cases, the amidinate ligand contains at least one sterically undemanding substituent (i.e. H or Me), suggesting that steric factors influence the preference for chelating versus bridging structures. For the bulkier amidinate ligands, steric crowding between the C−R and the N−R′ groups tends to decrease the N−C−N angles, thus favoring a chelating bonding mode (**B** in Chart 2).

Chart 1

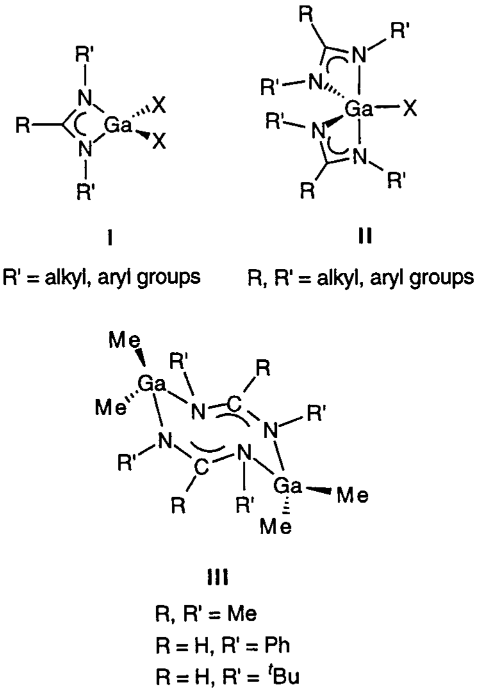
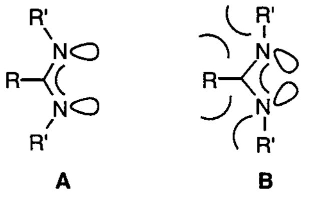


Chart 2



Our efforts in this area have been focused on the chemistry of cationic group 13 alkyl complexes of the general type {L−X}MX$^+$, which contain anionic, bidentate, four-electron-donor L−X$^-$ ligands. These species are of potential interest for applications in synthesis and catalysis.[3] We recently reported that {RC(NR′)$_2$}AlR$_2$ complexes react with the "cationic activators" [Ph$_3$C][B(C$_6$F$_5$)$_4$], B(C$_6$F$_5$)$_3$, and [NHMe$_2$Ph][B(C$_6$F$_5$)$_4$] to yield cationic amidinate Al alkyls, some of which polymerize ethylene.[3a,4] Our studies showed that the use of bulky amidinate ligands is a key requirement for generating reactive Al cations and avoiding the formation of unreactive dinuclear species. However, the low stability of the cationic Al amidinate species has complicated their

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Table 1. Summary of Crystal Data for Compounds 2b,c and 3b

	2b	**2c**	**3b**
formula	$C_{17}H_{31}Cl_2GaN_2$	$C_{13}H_{27}Cl_2GaN_2$	$C_{19}H_{37}GaN_2$
fw	404.06	351.99	363.22
cryst size (mm)	0.40 × 0.20 × 0.13	0.22 × 0.16 × 0.05	0.25 × 0.16 × 0.16
color/shape	colorless/block	colorless/irregular	colorless/block
d(calcd), Mg/m^3	1.350	1.368	1.205
cryst syst	monoclinic	trigonal	monoclinic
space group	$P2_1/n$	$P3_12_1$	$C2/c$
a, Å	9.8766(3)	9.2959(7)	26.7590(6)
b, Å	17.5856(4)	9.2959(7)	10.1472(2)
c, Å	11.4500(3)	17.132(1)	17.6303(3)
β (deg)	90.772(1)		123.205(1)
V, Å^3	1988.52(9)	1282.1(2)	4005.5(1)
Z	4	3	8
T (K)	173(2)	173(2)	173(2)
diffractometer		Siemens SMART Platform CCD	
radiation, λ (Å)		Mo Kα, 0.710 73	
2θ range (deg)	$4.24 < 2\theta < 50.00$	$5.1 < 2\theta < 50.2$	$3.6 < 2\theta < 50.1$
data Collected: *h;k;l*	±11; 0−20; 0−13	−9 to 0; 0−11; 0−20	−31 to +26; 0−12; 0−20
no. of rflns	10 018	6597	9828
no. of unique rflns	3481	907	3509
R_{int}	0.0237	0.0502	0.0330
no. of obsd rflns	$I > 2\sigma(I)$, 2810	$I > 2\sigma(I)$, 790	$I > 2\sigma(I)$, 2701
μ, mm^{-1}	1.651	1.910	1.374
transmissn range (%)	82−100	80−100	71−100
structure soln	direct methods[a]	direct methods[b]	direct methods[b]
GOF on F^2	1.027	0.989	1.046
R indices ($I > 2\sigma(I)$)	R1 = 0.0285,[c] wR2 = 0.0587[d]	R1= 0.0397,[c] wR2 = 0.0772[d]	R1= 0.0431,[c] wR2 = 0.1066[d]
R indices (all data)	R1 = 0.0425,[c] wR2 = 0.0626[d]	R1= 0.0526,[c] wR2 = 0.0822[d]	R1= 0.0633,[c] wR2 = 0.1167[d]
max resid density (e/Å^3)	0.26	0.37	0.697

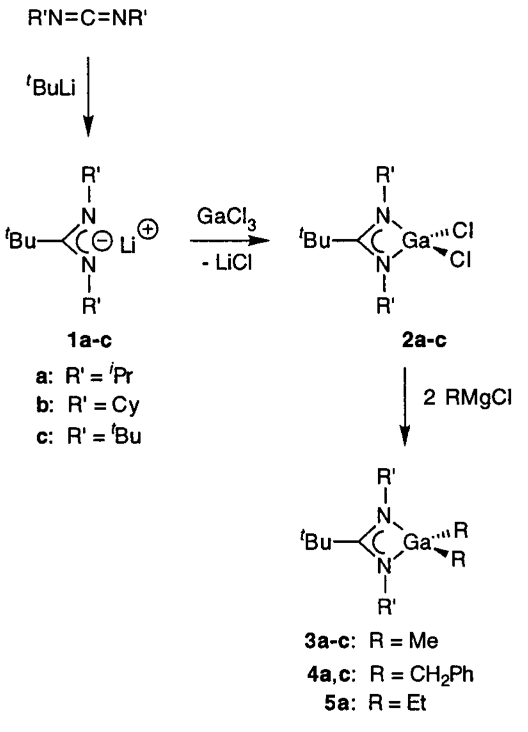
[a] SHELXTL-Plus version 5, Siemens Industrial Automation, Inc., Madison, WI. [b] MULTAN, Multan80, University of York, York, England. [c] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$.

characterization.[4] To aid in the characterization of cationic Al amidinate alkyls, we have studied analogous Ga cations which are more stable due to the lower reactivity of the Ga−C bond vs the Al−C bond.[4,5] In this note, we describe the synthesis and structures of a range of extremely bulky $\{RC(NR')_2\}GaX_2$ (X = Cl, alkyl) complexes, which are precursors to cationic species.

Results and Discussion

$\{^tBuC(NR')_2\}GaX_2$ Complexes. Gallium amidinate complexes have been synthesized previously by the reaction of gallium halides with preformed amidinate reagents.[2f] We have exploited this general route to prepare a series of amidinate gallium alkyl and halide compounds (Scheme 1). The ^{t}Bu-amidinate reagents $Li[^tBuC(NR')_2]$ (**1a**, R′ = ^{i}Pr; **1b**, R′ = Cy; **1c**, R′ = ^{t}Bu) are formed by the reaction of ^{t}BuLi with the appropriate carbodiimide (Et_2O, 0 °C). **1a**,**b** can be isolated in good yield, whereas **1c** was only generated in situ for use in subsequent reactions. The reaction of **1a**−**c** with 1 equiv of $GaCl_3$ (Et_2O, −78 °C) yields $\{^tBuC(NR')_2\}GaCl_2$ (**2a**−**c**). The reaction of **2a**−**c** with MeMgCl (Et_2O, −78 °C) yields the dimethyl complexes **3a**−**c**. Similarly, the reaction of **2a**,**b** with $PhCH_2MgCl$ yields the dibenzyl complexes **4a**,**b** and the reaction of **2a** with EtMgCl yields the diethyl complex **5a**. Compounds **4a**,**b** and **5a** are isolated as colorless liquids by extraction with pentane and removal of the volatiles, but **4a**,**b** solidify upon storage at −40 °C. In contrast, **3a**−**c** are isolated directly as white crystalline solids by recrystallization from pentane.

Scheme 1



The ^{1}H and ^{13}C NMR spectra of the $\{^tBuC(NR')_2\}GaX_2$ complexes (X = Cl, alkyl) complexes exhibit patterns that are consistent with C_{2v}-symmetric structures. In addition, the electron-impact (EI) mass spectra of **2a**,**b**, **3a**, and **4a,b** only contain signals corresponding to monomeric ions, which is consistent with monomeric structures.

X-ray Crystallographic Analysis of $\{^tBuC(NR')_2\}GaX_2$ Complexes. Crystal data for **2b**,**c** and **3b** are summarized in Table 1, and selected bond distances are collected in Table 2. The molecular geometries and

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(5) $\chi_{Al} = 1.6$, and $\chi_{Ga} = 1.8$.

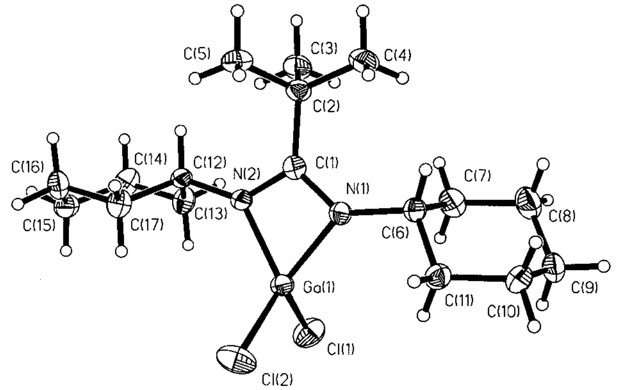

Figure 1. Molecular structure of {^{t}BuC(NCy)$_2$}GaCl$_2$ (**2b**).

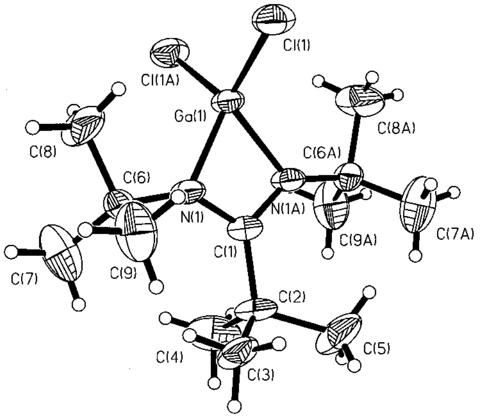

Figure 2. Molecular structure of {^{t}BuC(N^{t}Bu)$_2$}GaCl$_2$ (**2c**).

Table 2. Selected Bond Lengths (Å) for 2b,c and 3c

	{^{t}BuC(NCy$_2$}GaCl$_2$ (**2b**)		
Ga(1)−N(1)	1.945(2)	Ga(1)−N(2)	1.936(2)
Ga(1)−Cl(1)	2.1541(7)	Ga(1)−Cl(2)	2.1572(6)
N(1)−C(1)	1.349(3)	N(1)−C(6)	1.471(3)
N(2)−C(1)	1.341(1)	N(2)−C(12)	1.466(3)
C(1)−C(2)	1.541(3)		
	{^{t}BuC(N^{t}Bu)$_2$}GaCl$_2$ (**2c**)		
Ga(1)−N(1)	1.921(4)	N(1)−C(1)	1.359(7)
Ga(1)−Cl(1)	2.158(2)	N(1)−C(6)	1.483(7)
	{^{t}BuC(NCy)$_2$}GaMe$_2$ (**3b**)		
Ga(1)−N(1)	1.993(3)	Ga(1)−N(2)	1.978(3)
Ga(1)−C(18)	1.991(3)	Ga(1)−C(19)	2.027(3)
N(1)−C(1)	1.341(4)	N(1)−C(6)	1.462(4)
N(2)−C(1)	1.338(4)	N(2)−C(12)	1.457(4)
C(1)−C(2)	1.545(5)		

atom-labeling schemes are shown in Figures 1−3, and selected bond angles are given in Figure 4.

Complexes **2b**,**c** and **3b** adopt distorted-tetrahedral structures that are very similar to the structures of analogous Al compounds.[2a] For the dichloride complexes **2b**,**c** the amidinate bite angles (N−Ga−N) are rather acute (**2b**, 68.11(7)°; **3b**, 69.4(3)°) which is compensated by the opening of the N−Ga−Cl angles (117.88(2)° average). The dimethyl complex **3b** exhibits similar N−Ga−N (66.21(1)°) and N−Ga−C (114.58(3)° average) angles. The Cl−Ga−Cl angles (**2b**, 109.80(3)°; **2c**, 112.48(9)°) are close to the ideal tetrahedral angle of 109.47°, but the C−Ga−C angle in **3b** is ca. 11° larger (120.4(2)°). The smaller values for Cl−Ga−Cl angles can be rationalized in terms of simple VSEPR concepts; i.e., the Ga−Cl bonding electron pair is smaller than the Ga−CH$_3$ bonding electron pair due to the higher electronegativity of Cl vs C. Alternatively, the bond angle trend can be rationalized in terms of hybridization effects; i.e., the smaller values for the Cl−Ga−Cl angles reflect increased p character in the Ga hybrid orbitals in bonding to the electronegative Cl ligands (Bent's rule).[6,7] The Ga−N bond distances are very similar within each molecule and are slightly shorter for the dichlorides (1.934(2) Å average) than for the dimethyl species (1.985(2) Å average) due to the stronger electron-

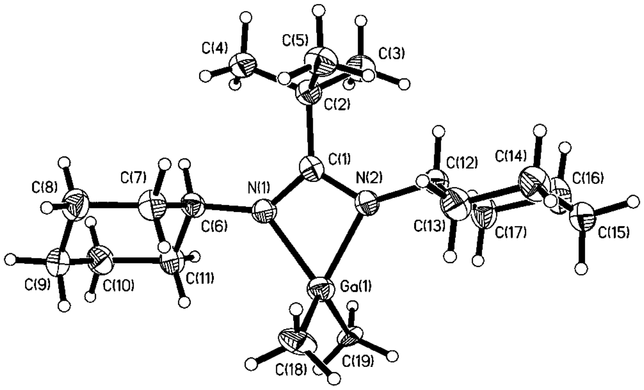

Figure 3. Molecular structure of {^{t}BuC(NCy)$_2$}GaMe$_2$ (**3b**).

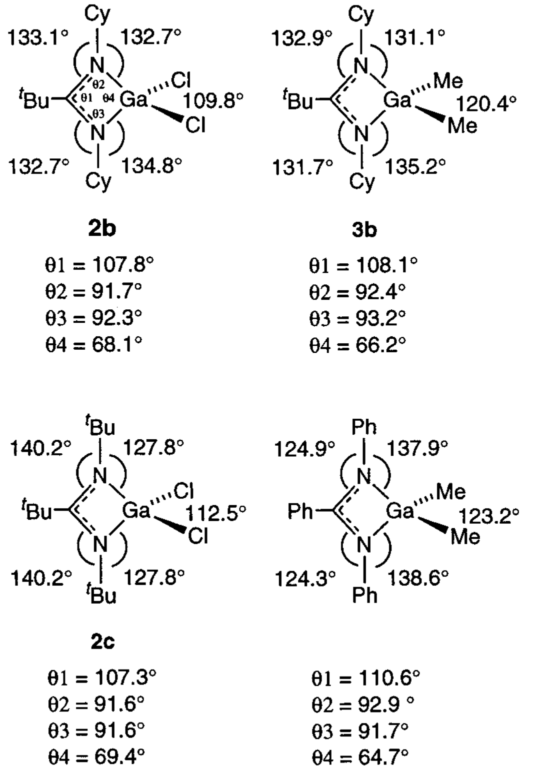

Figure 4. Schematic representation of the core structures of {RC(NR′)}GaX$_2$ compounds **2b**,**c**, **3b**, and {PhC(NPh)$_2$}GaMe$_2$. Data for the last compound are taken from ref 1a. The angles $\theta1$, $\theta2$, $\theta3$, and $\theta4$ are defined in the same manner for each compound and are indicated for **2b**.

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(6) (a) The Ga−Cl and Ga−CH$_3$ cone angles (θ)^{6b} are estimated to be 108° and 102°, respectively, on the basis of the crystallographic data for **2b**,**c** and **3b** and van der Waals radii taken from: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Therefore, the Cl−Ga−Cl angles in **2b**,**c** would be predicted to be slightly larger than the C−Ga−C angle in **3b** on the basis of steric effects. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (c) Note that the Al−Cl and Al−CH$_3$ cone angles given in ref 2a are θ/2 values.

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donor ability of Me vs Cl. The Ga−N bond distances in **3b** are shorter than those in $\{PhC(NPh)_2\}GaMe_2$ (2.039(3) Å average)[1a] due to the stronger electron-donor ability of alkyl vs Ph groups. The Ga−Cl bond distances in **2b**,**c** (2.156(1) Å average) are slightly longer than the Ga−Cl distances in Ga_2Cl_6 (terminal Ga−Cl = 2.06(2) Å),[8] while the Ga−Me distances in **3b** (1.985(2) Å average) are comparable to the Ga−Me bond distances in $GaMe_3$ (1.97(1) Å).[9]

In all of the $\{^tBuC(NR')_2\}GaX_2$ complexes, the $\{^tBuC(NR')_2\}Ga$ core forms a nearly planar metallacycle (|(N−Ga−N−C torsion angles)| < 3.6°). The amidinate carbon and nitrogen atoms exhibit distorted-trigonal-planar coordination (sum of angles ca. 360°). The two C−N distances (1.34(2) Å average) are very similar within each molecule and consistent with fully delocalized π-bonding within the amidinate unit.[10]

One important aspect of our work on cationic aluminum and gallium amidinate complexes is control of steric crowding at the metal center.[2a,4] Comparison of key bond angles within the $\{^tBuC(NR')_2\}Ga$ core as a function of the C−^{t}*Bu* and N−*R'* substituents provides insight into this issue (Figure 4). The ^{t}Bu−N−Ga angle in **2c** (127.8(4)° average) is 6° smaller than the Cy−N−Ga angles in **2b** (133.7(7)° average) and **3b** (133.1(4)° average). For comparison, the Ph−N−Ga angles in $\{PhC(NPh)_2\}GaMe_2$ (138.3(5)° average, Figure 4)[1a] are significantly larger than the R'−N−Ga angles in **2b**,**c** and **3b**. Thus, changing the N−*R'* group from Cy to ^{t}Bu decreases the R'−N−Ga angle, which projects the N−*R'* substituents more toward the metal center. As described in detail elsewhere, this effect strongly influences the structure of the cationic species formed upon Me^- abstraction from $\{RC(NR')_2\}GaMe_2$.[4]

Experimental Section

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Hexanes and diethyl ether were distilled from Na/benzophenone and stored under N_2 prior to use. $Li[^tBuC(N^iPr)_2]$ and $Li[^tBuC(NCy)_2]$ were prepared according to a literature procedure.[2a] All other chemicals were purchased from Aldrich and used as received.

^1H and ^{13}C NMR spectra were obtained on a Bruker AMX-360 spectrometer, in Teflon-valved or flame-sealed tubes, at ambient probe temperature (25 °C). ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constants are reported in Hz. Mass spectra were obtained using the direct insertion probe (DIP) method, on a VG Analytical Trio I instrument operating at 70 eV. Elemental analyses were performed by Desert Analytics Laboratory.

$\{^tBuC(N^iPr)_2\}GaCl_2$ (2a). A colorless solution of $GaCl_3$ (0.840 g, 4.75 mmol) in Et_2O (10 mL) was cooled to −78 °C and added dropwise to a slurry of $Li[^tBuC(N^iPr)_2]$ (0.904 g, 4.75 mmol) in Et_2O (40 mL), also at −78 °C. The mixture was warmed to room temperature and was stirred for 12 h, affording a slurry of a white solid in a pale yellow solution. The mixture was filtered, and the filtrate was concentrated to 30 mL and cooled at −78 °C for 18 h to yield pure $\{^tBuC(N^iPr)_2\}GaCl_2$ as colorless crystals that were collected by filtration (0.970 g, 64%). ^1H NMR (C_6D_6): δ 3.82 (septet, ^3J = 6.5, 2H, C*H*Me$_2$), 1.14 (d, ^3J = 6.2, 12H, CH*Me$_2$*), 0.96 (s, 9H, C*Me$_3$*). ^{13}C NMR (C_6D_6): δ 179.6 (N*C*N), 47.5 (*C*HMe$_2$), 38.5 (Me$_3$*C*), 28.6 (*Me$_3$*C), 25.7(CH*Me$_2$*). Anal. Calcd for $C_{11}H_{23}Cl_2GaN_2$: C, 40.78; H, 7.17; N, 8.65. Found: C, 40.45; H, 6.92; N, 8.57. EI-MS (*m/z*): 324 (M^+, 5), 309 ($M^+ - CH_3$, 36), 287 ($M^+ - Cl$, 1), 184 (8), 126 (75), 84 (100), 69 (5), 57 (26).

$\{^tBuC(NCy)_2\}GaCl_2$ (2b). The procedure described for **2a** was followed using $GaCl_3$ (0.840 g, 4.75 mmol) and $Li[^tBuC(NCy)_2]$ (1.28 g, 4.75 mmol). Crystallization from Et_2O at −78 °C for 18 h yielded pure $\{^tBuC(NCy)_2\}GaCl_2$ as colorless crystals that were collected by filtration (1.21 g, 63%). ^1H NMR (C_6D_6): δ 3.58 (br m, 2H, *Cy*), 1.96 (br d, 4H, *Cy*), 1.64−1.42 (br m, 10H, *Cy*), 1.07 (s, 9H, C*Me$_3$*), 1.3−0.9 (br m, 6H, *Cy*). ^{13}C NMR (C_6D_6): δ 179.8 (s, N*C*N), 55.7 (d, $^1J_{CH}$ = 138, Cy-*C$_1$*), 38.6 (s, *C*Me$_3$), 36.9 (t, $^1J_{CH}$ = 128, *Cy*), 28.7 (q, $^1J_{CH}$ = 127, C*Me$_3$*), 25.4 (t, $^1J_{CH}$ = 127, *Cy*), 25.2 (t, $^1J_{CH}$ = 126, *Cy*). Anal. Calcd for $C_{17}H_{31}Cl_2GaN_2$: C, 50.52; H, 7.75; N, 6.93. Found: C, 50.41; H, 7.85; N, 6.93. EI-MS (*m/z*): 404 (M^+, 79), 361 ($M^+ - Cl$, 84), 264 (45), 221 (27), 207 (14), 193 (8), 182 (61), 166 (100).

$\{^tBuC(N^tBu)_2\}GaCl_2$ (2c). A colorless solution of $^tBuN{=}N{=}C^tBu$ (2.00 g, 13.0 mmol) in Et_2O (35 mL) was cooled to 0 °C, and ^tBuLi (7.62 mL of 1.7 M solution in pentane, 13.0 mmol) was added dropwise by syringe. The mixture was warmed to room temperature and was stirred for 1 h, resulting in a white slurry. The mixture was cooled to −78 °C, and a colorless solution of $GaCl_3$ (2.29 g, 13.0 mmol) in Et_2O (10 mL), which was also cooled to −78 °C, was added dropwise. The resulting mixture was warmed to room temperature and was stirred for 12 h, affording a slurry of a white solid in a pale yellow solution. The mixture was filtered. The filtrate was concentrated to 25 mL and cooled to −78 °C for 18 h to yield pure $\{^tBuC(N^tBu)_2\}GaCl_2$ as colorless crystals that were collected by filtration (0.710 g, 17%). ^1H NMR (C_6D_6): δ 1.41 (s, 18H, NC*Me$_3$*), 1.13 (s, 9H, CC*Me$_3$*). ^{13}C NMR (C_6D_6): δ 183.7 (N*C*N), 56.0 (N*C*Me$_3$), 37.3 (C*C*Me$_3$), 34.0 (NC*Me$_3$*), 31.2 (CC*Me$_3$*). Anal. Calcd for $C_{13}H_{27}Cl_2GaN_2$: C, 44.36; H, 7.75; N, 7.96. Found: C, 44.43; H, 7.82; N, 7.70.

$\{^tBuC(N^iPr)_2\}GaMe_2$ (3a). $\{^tBuC(N^iPr)_2\}GaCl_2$ (**2a**) was generated in situ in Et_2O (50 mL) as described above. The resulting mixture was cooled to −78 °C, and 2 equiv of CH_3MgCl (6.34 mL of a 3.0 M solution in THF, 19.1 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was concentrated to 15 mL and cooled to −78 °C for 18 h to yield pure $\{^tBuC(N^iPr)_2\}GaMe_2$ as colorless crystals which were collected by filtration (1.36 g, 51%). ^1H NMR (C_6D_6): δ 4.10 (septet, ^3J = 6.1, 2H, C*H*Me$_2$), 1.21 (s, 9H, C*Me$_3$*), 1.12 (d, ^3J = 6.1, 12H, CH*Me$_2$*), 0.24 (s, 6H, Ga*Me$_2$*). ^{13}C NMR (C_6D_6): δ 173.9 (s, N*C*N), 46.3 (d, $^1J_{CH}$ = 139, *C*HMe$_2$), 39.3 (s, *C*Me$_3$), 29.6 (q, $^1J_{CH}$ = 127, CH*Me$_2$*), 26.2 (q, $^1J_{CH}$ = 125, C*Me$_3$*), −4.7 (q, $^1J_{CH}$ = 123, Ga*Me$_2$*). Anal. Calcd for $C_{13}H_{29}GaN_2$: C, 55.14; H, 10.34; N, 9.89. Found: C, 55.18; H, 10.44; N, 9.90. EI-MS (*m/z*): 282 ($M^+ - H$, 1), 267 ($M^+ - CH_3$, 45), 126 (38), 99 (3), 84 (100), 69 (5), 57 (46).

$\{^tBuC(NCy)_2\}GaMe_2$ (3b). $\{^tBuC(NCy)_2\}GaCl_2$ (**2b**) was generated in situ in Et_2O (50 mL) as described above. The mixture was cooled to −78 °C, and 2 equiv of CH_3MgCl (6.34 mL of a 3.0 M solution in THF, 19.1 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was concentrated to 15 mL and cooled to −78 °C for 18 h to yield pure $\{^tBuC(NCy)_2\}GaMe_2$ as large colorless crystals which were collected by filtration (1.81 g, 53%). ^1H NMR (C_6D_6): δ 3.72 (br m, 2H, *Cy*), 2.00−1.95 (br m, 4H, *Cy*), 1.74−1.70 (br m, 4H, *Cy*), 1.61−1.57 (br m, 2H, *Cy*), 1.30−1.00 (br m, 10H, *Cy*), 1.29 (s, 9H,

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[10] The C−N distance of 1.34 Å is intermediate between the normal $C{=}N_{imine}$ double-bond distance (1.29 Å) and the normal $C(sp^2)-N$ single-bond distance (1.47 Å).

CMe_3), 0.26 (s, 6H, GaMe_2). ^{13}C NMR (C_6D_6): δ 174.1 (s, N*C*N), 55.0 (d, $^1J_{CH}$ = 128, Cy-C_1), 39.4 (s, *C*Me$_3$), 37.5 (t, $^1J_{CH}$ = 127, *Cy*), 29.7 (q, $^1J_{CH}$ = 122, CMe_3), 26.0 (t, $^1J_{CH}$ = 125, *Cy*), 25.9 (t, $^1J_{CH}$ = 125, *Cy*), −4.6 (q, $^1J_{CH}$ = 120, GaMe_2). Anal. Calcd for $C_{19}H_{37}GaN_2$: C, 62.81; H, 10.27, N, 7.71. Found: C, 62.12; H, 10.28; N, 7.60.

$\{{}^t$BuC(N^{t}Bu)$_2\}$GaMe$_2$ (3c). $\{{}^t$BuC(N^{t}Bu)$_2\}$GaCl$_2$ (**2c**) was generated in situ in Et$_2$O (35 mL) as described above. The resulting mixture was cooled to −78 °C, and 2 equiv of CH$_3$MgCl (12.6 mL of 3.0 M solution in THF, 37.6 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a colorless solid. The solid was sublimed under reduced pressure (<0.001 mmHg) at 70 °C for 3 h, affording pure $\{{}^t$BuC(N^{t}Bu)$_2\}$GaMe$_2$ as colorless crystals (2.75 g, 45%). ^{1}H NMR (C_6D_6): δ 1.42 (s, 18H, NCMe_3), 1.35 (s, 9H, CCMe_3), 0.23 (s, 6H, GaMe_2). ^{13}C NMR (C_6D_6): δ 177.0 (s, N*C*N), 53.7 (s, N*C*Me$_3$), 37.3 (s, C*C*Me$_3$), 34.3 (q, $^1J_{CH}$ = 125, CMe_3), 31.9 (q, $^1J_{CH}$ = 124, CMe_3), −3.6 (q, $^1J_{CH}$ = 120, GaMe_2). Anal. Calcd for $C_{15}H_{33}GaN_2$: C, 57.88; H, 10.71, N, 9.00. Found: C, 58.08; H, 10.43; N, 8.94.

$\{{}^t$BuC(N^{i}Pr)$_2\}$Ga(CH$_2$Ph)$_2$ (4a). $\{{}^t$BuC(N^{i}Pr)$_2\}$GaCl$_2$ (**2a**) was generated in situ in Et$_2$O (50 mL) as described above. The resulting mixture was cooled to −78 °C, and 2 equiv of PhCH$_2$MgCl (9.51 mL of a 1.0 M solution in Et$_2$O, 9.51 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a pale yellow oil that was extracted with hexanes (70 mL). The extract was dried under vacuum for 12 h, yielding pure $\{{}^t$BuC(N^{i}Pr)$_2\}$Ga(CH$_2$Ph)$_2$ as a colorless oil (1.36 g, 51%) which solidified upon storage in a freezer at −20 °C. ^{1}H NMR (C_6D_6): δ 7.30−7.24 (m, 8H, *o*- and *m*-Ph), 7.1−7.0 (m, 2H, *p*-Ph), 3.90 (septet, ^3J = 5.8, 2H, C*H*Me$_2$), 2.35 (s, 4H, CH_2Ph), 1.14 (s, 9H, CMe_3), 0.88 (d, ^3J = 6.1, 12H, CHMe_2). ^{13}C NMR (C_6D_6): δ 175.9 (s, N*C*N), 145.4 (s, *ipso*-Ph), 128.4 (d, $^1J_{CH}$ = 160, *o*- or *m*-Ph), 127.9 (d, $^1J_{CH}$ = 155, *o*- or *m*-Ph), 122.6 (d, $^1J_{CH}$ = 165, *p*-Ph), 45.9 (d, $^1J_{CH}$ = 136, C*H*Me$_2$), 39.2 (s, *C*Me$_3$), 29.5 (q, $^1J_{CH}$ = 127, CHMe_2), 26.2 (q, $^1J_{CH}$ = 129, CMe_3), 23.6 (t, $^1J_{CH}$ = 123, *C*H$_2$Ph). Anal. Calcd for $C_{25}H_{37}GaN_2$: C, 68.97; H, 8.58; N, 6.44. Found: C, 69.00; H, 8.68; N, 6.44. EI-MS (*m*/*z*): 434 (M$^+$, 2), 343 (M$^+$ − C_7H_7, 48), 251 (39), 183 (11), 160 (18), 126 (62), 84 (100), 69 (85), 57 (64), 43 (23).

$\{{}^t$BuC(NCy)$_2\}$Ga(CH$_2$Ph)$_2$ (4b). A colorless solution of $\{{}^t$BuC(NCy)$_2\}$GaCl$_2$ (1.03 g, 2.55 mmol) in Et$_2$O (40 mL) was cooled to −78 °C, and 2 equiv of PhCH$_2$MgCl (5.10 mL of a 1.0 M solution in Et$_2$O, 5.10 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a pale yellow oil that was extracted with hexanes (70 mL). The extract was dried under vacuum for 12 h, yielding pure $\{{}^t$BuC(NCy)$_2\}$Ga(CH$_2$Ph)$_2$ as a colorless oil (1.31 g, 70%). ^{1}H NMR (C_6D_6): δ 7.33−7.26 (m, 8H, *o*- and *m*-Ph), 7.10−7.05 (m, 2H, *p*-Ph), 3.54 (m, 2H, *Cy*), 2.40 (s, 4H, CH_2Ph), 1.73−1.56 (m, 10H, *Cy*), 1.21 (s, 9H,CMe_3), 1.17−0.80 (m, 10H, *Cy*). ^{13}C NMR (C_6D_6): δ 175.9 (s, N*C*N), 145.6 (s, *ipso*-Ph), 128.4 (d, $^1J_{CH}$ = 158, *o*- or *m*-Ph), 128.0 (d, $^1J_{CH}$ = 156, *o*- or *m*-Ph), 122.7 (d, $^1J_{CH}$ = 155, *p*-Ph), 54.6 (d, $^1J_{CH}$ = 132, *Cy*), 39.2 (s, *C*Me$_3$), 37.2 (t, $^1J_{CH}$ = 127, *Cy*), 29.6 (q, $^1J_{CH}$ = 131, CMe_3), 25.8 (t, $^1J_{CH}$ = 125, *Cy*), 25.7 (t, $^1J_{CH}$ = 125, *Cy*), 23.8 (t, $^1J_{CH}$ = 124, *C*H$_2$Ph). Anal. Calcd for $C_{31}H_{45}GaN_2$: C, 72.22; H, 8.82; N, 5.43. Found: C, 71.87; H, 8.54; N, 5.31. EI-MS (*m*/*z*): 423 (M$^+$ − C_7H_7, 76), 263 (5), 166 (66), 91 (57), 84 (100), 69 (20), 57 (51), 41 (20).

$\{{}^t$BuC(N^{i}Pr)$_2\}$GaEt$_2$ (5a). $\{{}^t$BuC(N^{i}Pr)$_2\}$GaCl$_2$ (**2a**) was generated in situ in Et$_2$O (50 mL) as described above. The mixture was cooled to −78 °C, and 2 equiv of EtMgCl (9.51 mL of a 2.0 M solution in Et$_2$O, 19.1 mmol) was added dropwise by syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under reduced pressure, affording a pale yellow solid that was extracted with hexanes (70 mL). The extract was dried under vacuum for 12 h, yielding pure $\{{}^t$BuC(N^{i}Pr)$_2\}$GaEt$_2$ as a colorless oil (1.72 g, 58%). ^{1}H NMR (C_6D_6): δ 4.06 (septet, ^3J = 6.1, 2H, C*H*Me$_2$), 1.55 (t, ^3J = 7.9, 6H, GaCH$_2$CH_3), 1.23 (s, CMe_3, 9H), 1.12 (d, ^3J = 6.5, CHMe_2, 12H), 0.85 (q, ^3J = 7.9, 4H, GaCH_2CH$_3$). ^{13}C NMR (C_6D_6): δ 174.2 (s, N*C*N), 45.9 (d, $^1J_{CH}$ = 134, *C*HMe$_2$), 39.4 (s, *C*Me$_3$), 29.7 (q, $^1J_{CH}$ = 127, CHMe_2), 26.3 (q, $^1J_{CH}$ = 125, CMe_3), 10.7 (q, $^1J_{CH}$ = 124, GaCH$_2$*C*H$_3$), 5.0 (t, $^1J_{CH}$ = 123, Ga*C*H$_2$). Anal. Calcd for $C_{15}H_{33}GaN_2$: C, 57.88; H, 10.71; N, 9.00. Found: C, 57.82; H, 10.42; N, 8.70.

X-ray Crystallography. **2b and 3b.** Crystals of **2b** were grown by crystallization from Et$_2$O at −78 °C for **2b**. Crystals of **3b** were grown from hexane at −78 °C. In both **2b** and **3b**, all non-H atoms were refined anisotropically, and all H atoms were placed in ideal positions and refined as riding atoms with group isotropic displacement factors.

2c. Crystals of **2c** were grown by crystallization from Et$_2$O at −78 °C. The ^{t}Bu methyl C atoms attached to C(1) were found to be disordered. C(1), C(2), and the Ga atom are on a 2-fold axis, and the disordered ^{t}Bu group is found in two orientations, each half-occupied. The structure was also found to be twinned, and the twins are related as enantiomers with approximately equal occupation (50%).

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Supporting Information Available: Tables of atomic coordinates, isotropic displacement parameters, anisotropic displacement parameters, bond distances and bond angles, and hydrogen atom coordinates for **2b**,**c** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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