Synthesis and Structural Characterization of Some Monomeric Group 13 Amides

Joel S. Silverman, Claire J. Carmalt, Alan H. Cowley,* Robert D. Culp, Richard A. Jones,* and Brian G. McBurnett

Department of Chemistry & Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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Three monomeric, base-free tris(primary amido) compounds of the type E[N(H)Mes*]$_3$ (**1**, E = Al; **2**, E = Ga; **3**, E = In; Mes* = 2,4,6-tri-*tert*-butylphenyl) have been synthesized via the salt elimination reaction of Mes*N(H)Li with ECl$_3$. The singly base-stabilized tris(primary amido) derivatives, [E{N(H)Dipp}$_3$(py)] (**7**, E = Al; **8**, E = Ga; Dipp = 2,6-diisopropylphenyl), have been prepared via the amine elimination reaction of H$_2$NDipp with [E(NMe$_2$)$_3$]$_2$. The related indium compound, [In{N(H)Dipp}$_3$(py)$_2$] (**9**), which features two coordinated bases, was prepared by treatment of DippN(H)Li with InCl$_3$ followed by pyridine. The X-ray crystal structures of **3**, **8**, and **9** have been determined.

Introduction

One of the driving forces for the heightened interest in nitrogen-containing derivatives of the group 13 elements relates to their use as single source precursors to the technologically important group 13 nitride semiconductors, EN (E = Al, Ga, In).[1] The conventional organometallic chemical vapor deposition (OMCVD) approach to the synthesis of group 13 nitride films, such as GaN, involves the reaction of GaMe$_3$ with NH$_3$ at temperatures in excess of 900 °C.[2] In addition to creating stresses in the cooling films, the use of high deposition temperatures also results in the loss of stoichiometry due to the elimination of molecular nitrogen.[3] Carbon contamination is another problem that arises from the utilization of sources with metal−carbon bonds. Accordingly, we have turned our attention to the development of single source precursors with all-nitrogen coordination environments. This design principle was initially demonstrated with [(Me$_2$N)(N$_3$)Ga(μ-NMe$_2$)]$_2$, a precursor that was found to deposit epitaxial single crystalline films of GaN at 580 °C.[4] Subsequently, this idea was taken one step further with the synthesis and structural characterization of Ga(N$_3$)$_3$(py)$_3$.[5,6] More recently, Fischer *et al.*[7] demonstrated that the detonation of (Et$_3$N)Ga(N$_3$)$_3$ results in hexagonal nanocrystals of GaN.

The tris(amides) of the group 13 elements represent an alternative class of precursor that feature an all-nitrogen coordination sphere. Compounds of the type E(NH$_2$)$_3$ (E = Al,[8] Ga,[9] In[10]) have been synthesized but not structurally characterized. Moreover, the aluminum and gallium derivatives are reported to be thermally unstable. Furthermore, [Ga(NH-*t*-Bu)$_3$]$_2$[11] and [Al(NH-*t*-Bu)$_3$(LiNH-*t*-Bu)]$_2$,[12] the only structurally characterized examples of group 13 tris(primary amides), possess dimeric structures in the solid state. Examples of more highly substituted tris(amides), E(NR$_1$R$_2$)$_3$ (R$_1$, R$_2$ = alkyl, aryl, Me$_3$Si), are more common, particularly those of aluminum and gallium.[13] However, the only such examples for indium are In[N(SiMe$_3$)$_2$]$_3$[14] and In(TMP)$_3$ (TMP = 2,2,6,6,-tetramethylpiperidide).[15]

In this contribution, we present the synthesis and X-ray structural characterization of the first monomeric tris(primary amido) compounds of aluminum, gallium, and indium. From the standpoint of nitride precursor chemistry, monomeric derivatives are, in general, more desirable than dimers or higher oligomers because of (i) increased volatility and (ii) simpler deposition processes. Since, as pointed out above, the bulky alkyl derivative [Ga(NH-*t*-Bu)$_3$]$_2$ is dimeric, we chose to employ

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* To whom correspondence should be addressed.

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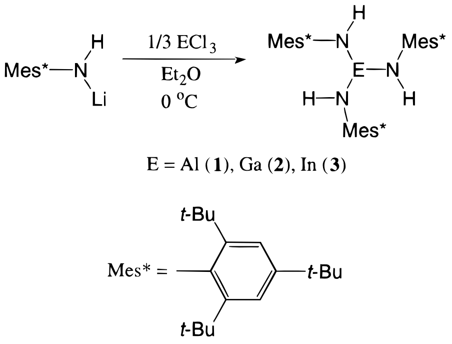
10.1021/ic980619q CCC: $18.00

Scheme 1



the bulky aryl ligands 2,4,6-tri-*tert*-butylphenyl (Mes*) and 2,6-diisopropylphenyl (Dipp) in the present work.

Results and Discussion

Three tris(primary amido) group 13 compounds of the general formula, $E[N(H)Mes^*]_3$ (**1**, E = Al; **2**, E = Ga; **3**, E = In; Mes* = 2,4,6-tri-*tert*-butylphenyl), were isolated in ca. 60−90% yields from the metathetical reactions of Mes*N(H)Li (generated in situ) with the appropriate element(III) chloride in Et_2O solution as shown in Scheme 1. Compounds **1** and **2** are white crystalline solids and **3** is a yellow crystalline solid, all of which melt without decomposition. The ^1H and ^{13}C NMR spectra for **1**−**3** were consistent with the anticipated formulas as evidenced e.g. by the observation that the integrated intensities of the amido and Mes* meta aromatic protons were 1:2 for each compound. Furthermore, the CI (CH_4) mass spectrum of each new compound exhibited a peak corresponding to the molecular ion, along with the anticipated fragmentation peaks. Analytical data were also obtained for compounds **1**−**3**. However, although the nitrogen and hydrogen analyses were satisfactory, the carbon analyses were consistently low by 3−7%. We presume that this observation is due to metal carbide formation.

Unfortunately, X-ray-quality crystals of **1** and **2** could not be isolated; however, suitable crystals were obtained for **3**. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The solid-state structure of **3** consists of individual $In(NHMes^*)_3$ molecules, one of which is illustrated in Figure 1. There are no unusually short intermolecular contacts between the monomeric units. The geometry at the indium center is trigonal planar with an average N−In−N bond angle of 120(1)°. Since **3** represents the first example of a tris(primary amide) of indium, a direct comparison of the metrical parameters with a similar known compound is not possible. However, the related compound, $[Me_2InNHAr]_2$ (Ar = 2-biphenyl) (**4**),[16] has been structurally characterized. The average In−N bond length of 2.068(7) Å for **3** is shorter than that observed for **4** [2.243(8) Å] which is anticipated because in **4** the primary amido group adopts a bridging position. Further comparisons can be made with the two known monomeric indium trisamides, $In[N(SiMe_3)_2]_3$ (**5**)[14] and In[TMP]₃ (**6**).[15] As expected, the average In−N bond lengths of **5** (2.049(1) Å) and **6** (2.08(1) Å) are very similar to those of **3** since each compound possesses a trigonal planar geometry.

Aluminum and gallium tris(primary amides) of the general formula $[E\{N(H)Dipp\}_3(py)]$ (**7**, E = Al; **8**, E = Ga) were isolated in ca. 60−70% yields from the condensation reaction of 6 equiv of H_2NDipp with $[E(NMe_2)_3]_2$, followed by treatment with pyridine, as summarized in Scheme 2. The latter step was necessary in order to isolate crystalline products. Presumably, pyridine ligation is required to compensate for the fact that the steric bulk of the Dipp ligand is less than that of the Mes* ligand. Consistent with this view, the analogous indium amide, $[In\{N(H)Dipp\}_3(py)_2]$ (**9**), required the coordination of two pyridine ligands. Compound **9** was isolated in 67% yield from the metathetical reaction of Li(H)NDipp (generated in situ) with $InCl_3$ in Et_2O solution at 0 °C, followed by the addition of pyridine, as shown in Scheme 3. Compounds **7** and **8** are yellow crystalline solids that melt without decomposition, while **9** decomposes initially at 98 °C (which is consistent with the loss of pyridine), then melts cleanly at 144−145 °C. The ^1H and ^{13}C NMR spectra for **7**−**9** were consistent with the anticipated

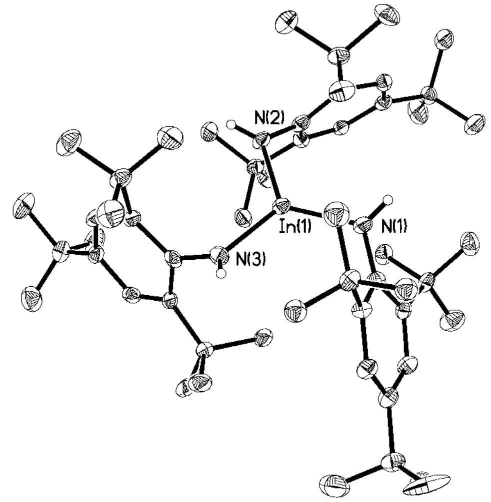
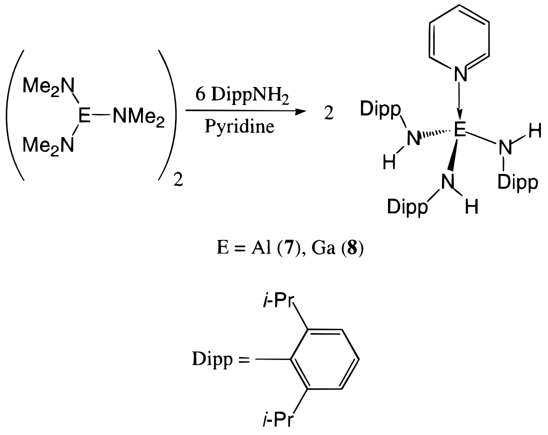
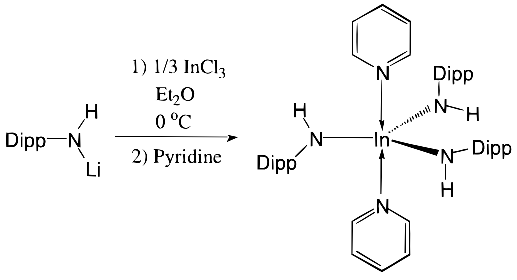


Figure 1. ORTEP drawing of $In(NHMes^*)_3$ (**3**) showing the atom-labeling scheme. Thermal ellipsoids are shown at 30% probability level. Selected hydrogen atoms have been omitted for clarity.

Scheme 2



Scheme 3



(**9**)

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **3**, **8**, and **9**

compound **3**		compound **8**		compound **9**	
In(1)−N(1)	2.061(7)	Ga(1)−N(1)	1.876(6)	In(1)−N(1)	2.110(5)
In(1)−N(2)	2.067(7)	Ga(1)−N(2)	1.878(6)	In(1)−N(2)	2.116(4)
In(1)−N(3)	2.075(6)	Ga(1)−N(3)	1.877(6)	In(1)−N(3)	2.121(4)
		Ga(1)−N(4)	2.051(7)	In(1)−N(4)	2.460(4)
		Ga(2)−N(101)	1.858(6)	In(1)−N(5)	2.421(4)
		Ga(2)−N(102)	1.863(6)		
		Ga(2)−N(103)	1.867(6)		
		Ga(2)−N(104)	2.069(7)		
		Ga(3)−N(201)	1.874(6)		
		Ga(3)−N(202)	1.864(5)		
		Ga(3)−N(203)	1.879(6)		
		Ga(3)−N(204)	2.045(7)		
N(1)−In(1)−N(2)	121.1(3)	N(1)−Ga(1)−N(3)	116.3(3)	N(1)−In(1)−N(2)	109.4(2)
N(1)−In(1)−N(3)	119.1(3)	N(1)−Ga(1)−N(2)	111.0(3)	N(1)−In(1)−N(3)	118.7(2)
N(2)−In(1)−N(3)	119.8(3)	N(3)−Ga(1)−N(2)	119.4(3)	N(2)−In(1)−N(3)	131.9(2)
		N(1)−Ga(1)−N(4)	106.6(3)	N(1)−In(1)−N(5)	94.1(2)
		N(3)−Ga(1)−N(4)	98.0(3)	N(2)−In(1)−N(5)	87.3(1)
		N(2)−Ga(1)−N(4)	102.6(3)	N(3)−In(1)−N(5)	88.1(2)
		N(101)−Ga(2)−N(102)	111.6(3)	N(1)−In(1)−N(4)	96.9(2)
		N(101)−Ga(2)−N(103)	114.2(3)	N(2)−In(1)−N(4)	91.7(1)
		N(102)−Ga(2)−N(103)	118.4(3)	N(3)−In(1)−N(4)	84.2(2)
		N(101)−Ga(2)−N(104)	108.1(3)	N(5)−In(1)−N(4)	168.7(2)
		N(102)−Ga(2)−N(104)	104.4(3)		
		N(103)−Ga(2)−N(104)	98.1(3)		
		N(202)−Ga(3)−N(201)	112.4(3)		
		N(202)−Ga(3)−N(203)	123.0(3)		
		N(201)−Ga(3)−N(203)	111.4(3)		
		N(202)−Ga(3)−N(204)	98.7(3)		
		N(201)−Ga(3)−N(204)	109.5(3)		
		N(203)−Ga(3)−N(204)	99.2(3)		

formulas, as shown by the detection of coordinated pyridine and from the observation that the integrated intensities of the amido and C−H proton resonances of the isopropyl group are 1:2 in each case. Additional structural information was gleaned from mass spectral data. The CI (CH_4) mass spectra of **7** and **8** exhibited a peak corresponding to the molecular ion and a peak corresponding to the loss of pyridine. Fragmentation was much more extensive in the case of **9**; the highest mass peak in the CI (CH_4) mass spectrum occurred at 932 amu and corresponds to [In(N(H)Dipp)$_2$]$_2$ (HRMS: calcd mass for $C_{48}H_{70}In_2N_4$, 932.368; found, 932.369). As was the case for compounds **1**−**3**, the nitrogen and hydrogen analyses for **7**−**9** were satisfactory, but the carbon analyses were consistently 2−4% low, presumably due to metal carbide formation.

X-ray-quality crystals of **8** were obtained from pyridine solution at 25 °C. Compound **8** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 6$ and with three independent [Ga{N(H)-Dipp}$_3$(py)] molecules per asymmetric unit. The molecular structure of **8** (Figure 2) comprises monomeric units with no unusually short intermolecular contacts. The geometry of the gallium center is best described as distorted tetrahedral; selected bond lengths and angles are shown in Table 1. The average $\mathrm{Ga{-}N_{py}}$ bond distance of 2.06(1) Å is somewhat shorter than that found in Ga(N$_3$)$_3$(py)$_3$ (2.13(2) Å).[5] The average $\mathrm{Ga{-}N_{Dipp}}$ bond distance of 1.871(8) Å is similar to the bond length of 1.85(1) Å found in the complex [Trip$_2$GaN(H)Dipp] (Trip = 2,4,6-triisopropylphenyl).[13b] As stated previously, the only example in the literature of a structurally characterized gallium tris(primary amide) is the dimeric compound, [Ga(NH-*t*-Bu)$_3$]$_2$,[11] which has an average terminal Ga−N bond length of 1.86(6) Å.

X-ray-quality crystals of **9** were obtained from Et$_2$O solution at −20 °C, and the solid state consists of individual [In{N(H)-Dipp)$_3$}(py)$_2$] molecules (Figure 3). Compound **9** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, and there are no unusually short intermolecular contacts. The geometry around the indium center is best described as that of a distorted trigonal bipyramidal in which the pyridine and the Dipp ligands occupy axial and equatorial positions, respectively. Selected bond lengths and angles for **9** are shown in Table 1. The average $\mathrm{In{-}N_{py}}$ bond distance (2.440(4) Å) is the same, within experimental error, as that reported for InCl$_3$(py)$_3$ (2.37(2) Å),[17] and the average $\mathrm{In{-}N_{Dipp}}$ bond distance (2.116(4) Å) is longer than that found in compound **3**. These trends can be attributed to steric effects.

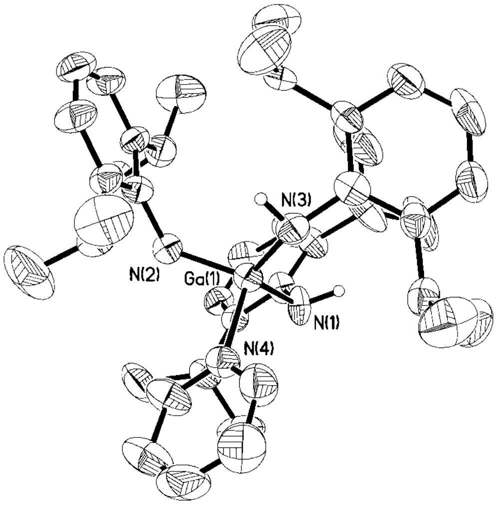

Figure 2. ORTEP drawing of [Ga{N(H)Dipp}$_3$(py)] (**8**) showing the atom-labeling scheme. Thermal ellipsoids are shown at 30% probability level. Selected hydrogen atoms have been omitted for clarity.

In summary, the first examples of structurally characterized tris(primary amides) of aluminum, gallium, and indium have

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Table 2. Crystal Data, Details of Intensity, Measurement, and Structure Refinement for Compounds **3**, **8**, and **9**

	3	**8**	**9**
formula	$C_{54}H_{90}InN_3$	$C_{41}H_{59}GaN_4$	$C_{46}H_{64}InN_5$
fw	896.11	677.64	801.84
temperature (°C)	−100	25	25
λ	0.71073	0.71073	0.71073
Cryst syst	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	14.463(2)	11.569(2)	10.966(1)
b (Å)	11.974(1)	22.130(6)	12.787(2)
c (Å)	31.179(3)	24.920(5)	16.861(1)
α (deg)	90	100.60(2)	87.558(7)
β (deg)	101.564(8)	102.80(2)	85.739(7)
χ (deg)	90	90.25(2)	72.380(8)
volume (Å^3)	5290(1)	6108(3)	2246.7(4)
Z	4	6	2
d (calc) (g/cm^3)	1.125	1.105	1.185
abs. coeff (cm^{-1})	4.81	7.06	5.61
crystal size (mm)	0.52 × 0.36 × 0.15	0.69 × 0.47 × 0.41	0.56 × 0.32 × 0.32
Theta range (deg)	1.33 to 25.00	2.26 to 22.48	2.04 to 27.50
total no. of rflns	11315	18841	6305
no. of obsd rflns	9170	15924	6134
no. of ref params	556	1255	487
GOF on F^2	1.571	0.992	1.069
wR2/R1^a [$I > 2\sigma(I)$]	0.2172/0.0784	0.1266/0.0621	0.1038/0.0527

[a] $R = \sum||F_o| - |F_N|/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $1/[\sigma^2(F_o^2) + (aP)^2 = bP]$, where $P = [\mathrm{Max}(0, F_o^2)/3 + 2F_c^2/3]$.

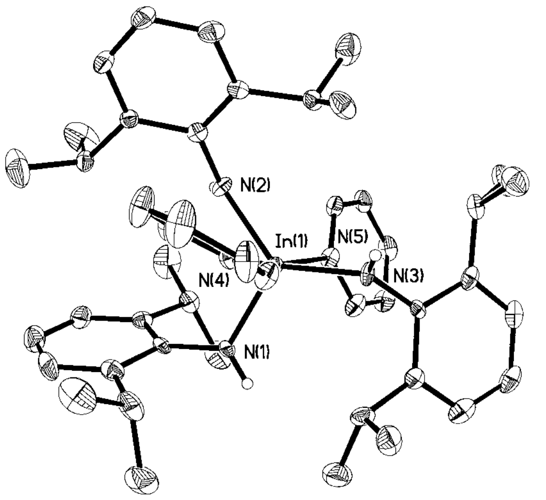

Figure 3. ORTEP drawing of $[In\{N(H)Dipp\}_3(py)_2]$ (**9**) showing the atom-labeling scheme. Thermal ellipsoids are shown at 30% probability level. Selected hydrogen atoms have been omitted for clarity.

been presented. A future publication will be devoted to the thermolysis and deposition chemistry of these compounds.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or an Innovative Technology System One-M drybox. Unless stated otherwise, all solvents were dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. The reagents $[Al(NMe_2)_3]_2$ and $[Ga(NMe_2)_3]_2$ were prepared according to the respective literature methods.[18] All other reagents were obtained from commercial sources and used without further purification, except for 2,6-DippNH$_2$ which was distilled over NaOH at 19 °C/0.1 Torr prior to use. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

Physical Measurements. Mass spectra (CIMS) were run on a Finnigan MAT 4023 instrument, and NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.19 MHz; ^{13}C, 75.48 MHz). NMR spectra are referenced to C_6D_6 or CD_2Cl_2, both of which were dried over sodium−potassium alloy and distilled prior to use; ^{1}H and ^{13}C chemical shifts are reported relative to $Si(CH_3)_4$ (0.00 ppm). Melting points were obtained in sealed glass capillaries under argon and are uncorrected.

Synthesis of Al[N(H)Mes*]$_3$ (1). *n*-Butyllithium (4.0 mL, 1.6 M solution in hexane) was added dropwise to a stirred solution of Mes*NH$_2$ (1.67 g, 6.39 mmol) in diethyl ether (35 mL) at −78 °C. The stirred solution was allowed to warm to 25 °C over a 3 h period. The resulting Mes*N(H)Li solution was added dropwise over a 1 h period to a stirred solution of $AlCl_3$ (0.29 g, 2.2 mmol) in diethyl ether (30 mL) at 0 °C. The reaction mixture was stirred for 16 h and then filtered over Celite. The volume of the resulting red-brown solution was reduced by half and stored at −20 °C. After 24 h, a white powder was obtained (1.0 g, 57%). Mp: 175−177 °C. HRMS: calcd for $C_{54}H_{90}AlN_3$, 808.703; found, 808.701. ^{1}H NMR (300.15 MHz, C_6D_6): δ 1.36 (s, 27 H, *p*-(C*H*$_3$)$_3$C), 1.42 (s, 54 H, *o*-(C*H*$_3$)$_3$C), 3.13 (s, 3 H, NH), 7.35 (s, 6 H, C_6H_2). ^{13}C NMR (300.15 MHz, C_6D_6): δ 32.36 (s, *o*-(CH$_3$)$_3$*C*), 33.48 (s, *o*-(*C*H$_3$)$_3$C), 34.94 (s, *p*-(CH$_3$)$_3$*C*), 36.90 (s, *p*-(*C*H$_3$)$_3$C), 142.34 (s, *p*-C_6H_2), 142.65 (s, *m*-C_6H_2), 143.61 (s, *o*-C_6H_2). Anal. Calcd for $C_{54}H_{90}AlN_3$: C, 80.30; H, 11.15; N, 5.20. Found: C, 72.97; H, 10.77; N, 4.66.

Synthesis of Ga[N(H)Mes*]$_3$ (2). *n*-Butyllithium (2.5 mL, 1.6 M solution in hexane) was added dropwise to a stirred solution of Mes*NH$_2$ (1.01 g, 3.82 mmol) in diethyl ether (40 mL) at −78 °C. The stirred solution was allowed to warm to 25 °C over a 3 h period. The resulting Mes*N(H)Li solution was added dropwise over a 1 h period to a stirred solution of $GaCl_3$ (0.22 g, 1.3 mmol) in diethyl ether (30 mL) at 0 °C. The reaction mixture was stirred for 2.5 days, then filtered over Celite and stored at −20 °C. After 24 h, a white powder was obtained (0.79 g, 73%). Mp: 238−241 °C. HRMS: calcd for $C_{54}H_{90}GaN_3$, 849.639; found, 849.641. ^{1}H NMR (300.15 MHz, C_6D_6): δ 1.39 (s, 54 H, *o*-(C*H*$_3$)$_3$C), 1.41 (s, 27 H *p*-(C*H*$_3$)$_3$C), 3.83 (s, 3 H, NH), 7.34 (s, 6 H, C_6H_2). ^{13}C NMR (300.15 MHz, C_6D_6): δ 30.78 (s, *o*-(*C*H$_3$)$_3$C), 33.31 (s, *p*-(*C*H$_3$)$_3$C), 34.97 (s, *o*-(CH$_3$)$_3$*C*), 36.94 (s, *p*-(CH$_3$)$_3$*C*), 134.14 (s, *p*-C_6H_2), 139.66 (s, *m*-C_6H_2), 144.86 (s, *o*-C_6H_2). Anal. Calcd for $C_{54}H_{90}GaN_3$: C, 76.26; H, 10.59; N, 4.94. Found: C, 73.36; H, 10.66; N, 4.74.

Synthesis of In[N(H)Mes*]$_3$ (3). *n*-Butyllithium (4.6 mL, 1.6 M solution in hexane) was added dropwise to a stirred solution of Mes*NH$_2$ (1.93 g, 7.38 mmol) in diethyl ether (30 mL) at −78 °C. The stirred solution was allowed to warm to 25 °C over a 3 h period. The resulting Mes*N(H)Li solution was added dropwise over a 1 h period to a stirred solution of $InCl_3$ (0.54 g, 2.4 mmol) in diethyl ether (50 mL) at 0 °C. The reaction mixture was stirred for 16 h, then filtered

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(18) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron*, **1990**, *9*, 257.

over Celite. The volume of the resulting yellow solution was reduced by half and stored at −20 °C. After a few days, yellow crystals of X-ray quality were obtained (2.0 g, 89%). Mp: 155−157 °C. HRMS: calcd for $C_{54}H_{90}InN_3$, 895.617; found, 895.617. ^{1}H NMR (300.15 MHz, C_6D_6): δ 1.38 (s, 27 H, *p*-$(CH_3)_3C$), 1.43 (s, 54 H, *o*-$(CH_3)_3C$), 3.98 (s, 3 H, NH), 7.32 (s, 6 H, C_6H_2). ^{13}C NMR (300.15 MHz, C_6D_6): δ 30.41 (s, *o*-$(CH_3)_3C$), 32.16 (s, *o*-$(CH_3)_3C$), 34.60 (s, *p*-$(CH_3)_3C$), 36.29 (s, *p*-$(CH_3)_3C$), 139.99 (s, *p*-C_6H_2), 141.21 (s, *m*-C_6H_2), 149.29 (s, *o*-C_6H_2). Anal. Calcd for $C_{54}H_{90}InN_3$: C, 72.40; H, 10.06; N, 4.69. Found: C, 68.78; H, 9.86; N, 4.45.

Synthesis of [Al{N(H)Dipp}$_3$(py)] (7). 2,6-Diisopropylaniline (1.6 mL, 1.5 g, 8.8 mmol) was added dropwise over a 5 min period to a stirred solution of $[Al(NMe_2)_3]_2$ (0.46 g, 2.9 mmol) in hexane (30 mL) at 25 °C. Pyridine (ca. 5 mL) was added, yielding a bright yellow solution that was stirred for 14 h. The solvent was removed in vacuo resulting in a yellow oil. The oil was redissolved in pyridine (15 mL) and stored at −20 °C. After a few days, yellow crystals of **7** were obtained but were not of X-ray quality (1.4 g, 78%). Mp: 156−160 °C. HRMS: calcd mass for $C_{41}H_{59}AlN_4$, 635.463; found, 635.464. ^{1}H NMR (300.15 MHz, CD_2Cl_2): δ 1.00 (d, 36 H, $(CH_3)_2CH$, $J = 6.0$ Hz), 2.89 (s, 3 H, NH), 3.03 (m, 6 H, $(CH_3)_2CH$, $J = 6.0$ Hz), 6.69 (t, 3 H, *p*-C_6H_3, $J = 7.5$ Hz), 6.92 (d, 6 H, *m*-C_6H_3, $J = 7.5$ Hz), 7.65 (m, C_5H_5N), 8.11 (m, C_5H_5N), 8.90 (m, C_5H_5N). ^{13}C NMR (300.15 MHz, C_6D_6): δ 23.71(s, $(CH_3)_2CH$), 28.93 (s, $(CH_3)_2CH$), 123.14 (s, *m*-C_6H_3), 123.30 (s, C_5H_5N), 132.93 (s, *m*-C_6H_3), 138.22 (s, *p*-C_6H_3 and C_5H_5N), 146.43 (s, C_5H_5N). Anal. Calcd for $C_{41}H_{59}AlN_4$: C, 77.60; H, 9.31; N, 8.83. Found: C, 73.27; H, 9.30; N, 8.24.

Synthesis of [Ga{N(H)Dipp}$_3$(py)] (8). 2,6-Diisopropylaniline (2.5 mL, 2.4 g, 13 mmol) was added dropwise over a 5 min period to a stirred solution of $[Ga(NMe_2)_3]_2$ (0.51 g, 2.5 mmol) in pyridine (30 mL) at 25 °C and stirred for a further 14 h. The solvent was removed in vacuo, resulting in a brown oil which was stored at 25 °C. After 24 h, yellow crystals of X-ray quality were obtained (1.1 g, 62%). Mp: 108−110 °C. HRMS: calcd for $C_{41}H_{59}GaN_4$, 677.639; found, 677.641. ^{1}H NMR (300.15 MHz, CD_2Cl_2): δ 0.96 (d, 36 H, $(CH_3)_2CH$, $J = 6.6$ Hz), 2.68−2.74 (m, 6 H, $(CH_3)_2CH$, $J = 6.7$ Hz), 2.92 (s, 3 H, NH), 6.70 (t, 3 H, *p*-C_6H_3, $J = 7.8$ Hz), 6.91 (d, 6 H, *m*-C_6H_3, $J = 7.5$ Hz), 7.64 (m, C_5H_5N), 8.12 (m, C_5H_5N), 9.01 (m, C_5H_5N). ^{13}C NMR (300.15 MHz, CD_2Cl_2): δ 23.97 (s, $(CH_3)_2CH$), 28.33 (s, $(CH_3)_2CH$), 119.01 (s, *m*-C_6H_3), 122.95 (s, C_5H_5N), 138.53 (s, *p*-C_6H_3 and C_5H_5N), 146.69 (s, C_5H_5N). Anal. Calcd for $C_{41}H_{59}GaN_4$: C, 72.67; H, 8.78; N, 8.27. Found: C, 72.44; H, 8.85; N, 7.87.

Synthesis of [In{N(H)Dipp}$_3$(py)$_2$] (9). *n*-Butyllithium (11 mL, 1.6 M solution in hexane) was added dropwise to a stirred solution of $DippNH_2$ (3.3 mL, 3.1 g, 18 mmol) in pentane (25 mL) at −78 °C, and the stirred reaction mixture was allowed to warm to 25 °C overnight. The pentane was removed, and the resulting white solid was dissolved in diethyl ether (30 mL) and added dropwise over a 1 h period to a stirred solution of $InCl_3$ (1.31 g, 5.88 mmol) in diethyl ether (50 mL) at 0 °C. Pyridine (ca. 5 mL) was added, and the reaction mixture was stirred for an additional 16 h, following which it was filtered over Celite. The volume of the resulting yellow solution was reduced by half. After 2 days storage at −20 °C, yellow crystals of X-ray quality were obtained (2.8 g, 67%). Mp: 96 °C (dec), 145−146 °C. ^{1}H NMR (300.15 MHz, CD_2Cl_2): δ 1.00 (d, 36 H, $(CH_3)_2CH$, $J = 6.6$ Hz), 2.72 (m, 6 H, $(CH_3)_2CH$, $J = 6.6$ Hz), 3.12 (s, 3 H, NH), 6.68 (t, 3 H, *p*-C_6H_3, $J = 7.6$ Hz), 6.92 (d, 6 H, *m*-C_6H_3, $J = 7.6$ Hz), 7.42 (m, C_5H_5N), 7.84 (m, C_5H_5N), 8.68 (m, C_5H_5N). ^{13}C NMR (300.15 MHz, CD_2Cl_2): 23.40 (s, $(CH_3)_2CH$), 28.93 (s, $(CH_3)_2CH$), 123.08 (s, *m*-C_6H_3), 125.26 (s, C_5H_5N), 137.37 (s, *p*-C_6H_3 and C_5H_5N), δ 149.59 (s, C_5H_5N). Anal. Calcd for $C_{46}H_{64}InN_5$: C, 68.91; H, 7.99; N, 8.74. Found: C, 66.20; H, 8.47; N, 7.97.

X-ray Crystallography. Crystallographic data and details of the data collection procedures and structure refinement for **3**, **8**, and **9** are presented in Table 2. Crystals of **3** and **9** were grown from Et_2O solution at −20 °C, while those of **8** were grown from pyridine solution at −25 °C. Crystals of **3** were mounted on glass fibers, whereas crystals of **8** and **9** were mounted in thin-walled glass capillaries and sealed under argon. The data set for compound **3** was collected on a Siemens P4 diffractometer at −100 °C, and those for **8** and **9** were collected on an Enraf Nonius CAD4 diffractometer at 25 °C. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used in each case. Accurate unit cell parameters were determined by recentering 25 optimal high-angle reflections. Three standard reflections were measured every 1800 s during data collection, and no decreases in intensities were observed. Corrections were applied for Lorentz−polarization and absorption effects. The structures were solved for the heavy atoms by direct methods. Subsequent difference syntheses gave all other non-hydrogen atomic positions and these were refined by full-matrix least-squares on F^2 using the Siemens SHELXL PLUS 5.0 (PC) software package.[19] All non-hydrogen atoms were allowed anisotropic thermal motion. The hydrogen atoms were included at calculated positions (C−H, 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter.

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Note Added in Proof. While the present work was in press, a paper appeared describing the synthesis and structure of $In(NPh_2)_3(py)$: Kim, J.; Bott, S. G.; Hoffman, D. M. *Inorg. Chem.* **1998**, *37*, 3835.

Supporting Information Available: Listings of structure refinement details, bond distances, bond angles, atomic coordinates, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] Sheldrick, G. M. *SHELXTL PC,* Version 5.0; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.