Synthesis and Characterization of $HC\{C(Me)N(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)\}_2MX_2$ (M = Al, X = Cl, I; M = Ga, In, X = Me, Cl, I): Sterically Encumbered β-Diketiminate Group 13 Metal Derivatives

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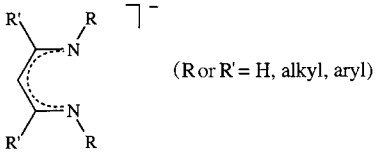
A series of group 13 metal complexes featuring the β-diketiminate ligand $[\{(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)NC(Me)\}_2CH]^-$ (i.e., $[Dipp_2nacnac]^-$, Dipp = C_6H_3-2,6-*i*-Pr_2) have been prepared and spectroscopically and structurally characterized. The chloride derivatives $Dipp_2nacnacMCl_2$ (M = Al (**3**), Ga (**5**), In (**8**)) were isolated in good yield by the reaction of 1 equiv of $Dipp_2nacnacLi{\cdot}Et_2O$ (**2**) and the respective metal halides. The iodide derivatives $Dipp_2nacnacMI_2$ (M = Al (**4**), Ga (**6**), In (**9**)), which are useful for reduction to afford M(I) species, were made by a variety of routes. Thus, **4** was obtained by treatment of the previously reported $Dipp_2nacnacAlMe_2$ with I_2, whereas the gallium analogue **6** was obtained as a product of the reaction of "GaI" with $Dipp_2nacnacLi{\cdot}Et_2O$, and **9** was obtained by direct reaction of InI_3 and the lithium salt. The methyl derivatives $Dipp_2nacnacMMe_2$ (M = Ga (**7**), In (**10**)), which are analogous to the previously reported $Dipp_2nacnacAlMe_2$, were synthesized by the reaction of $GaMe_3$ with $Dipp_2nacnacH$ (**1**) or by reaction of the indium chloride derivative **8** with 2 equiv of MeMgBr in diethyl ether. The compounds **3**−**10** exist as colorless, air- and moisture-sensitive crystalline solids. Their X-ray crystal structures feature nearly planar C_3N_2 arrays in the $Dipp_2nacnac$ ligand backbone with short C−C and C−N distances that are consistent with a delocalized structure. However, there are large dihedral angles between the C_3N_2 plane and the N_2M metal coordination plane which have been attributed mainly to steric effects. The relatively short M−N distances are consistent with the coordination numbers of the metals and the normal/dative character of the nitrogen ligands. The compounds were also characterized by ^1H and ^{13}C NMR spectroscopy. ^1H NMR data for **7** revealed equivalent methyl groups whereas the spectrum of **10** displayed two In−Me signals which indicated that ring wagging was slow on the ^1H NMR time scale.

Introduction

The monoanionic, bidentate β-diketiminate ligands shown by the formula are members of a fundamentally important class of



β-difunctional, uninegative, chelating ligands. Metal complexes of these ligands were first synthesized more than four decades ago,[1] and they have been studied extensively for their unique geometric and electronic properties.[1−6] Although the level of activity in the area subsequently waned,[7] the last 5 years have seen an impressive revival of interest. This is especially true for the more sterically encumbered derivatives (i.e., R = bulky group, especially ortho-substituted aryl groups), which have found use as either neutral[8] or monoanionic[9−20] ligands in a

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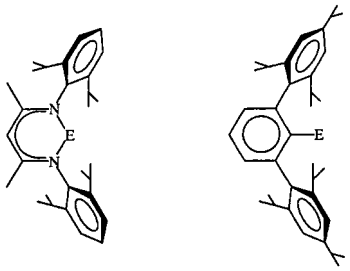
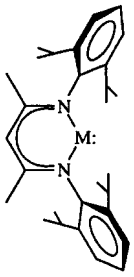
wide range of transition metal,[8−21] main group element,[22−31] and lanthanide[32] complexes. These are of interest owing to their behavior as olefin polymerization catalysts[8,11,13,23,25] or as models for active sites in metalloproteins.[19,20] In addition, the ability of these ligands to stabilize low coordination numbers, rare coordination geometries, or low oxidation states has been recognized.[19,20,30,31] The bulky [Dipp$_2$nacnac]$^-$ ligand[8,33] (i.e., [{(Dipp)N(Me)C}$_2$CH]$^-$; Dipp = C$_6$H$_3$-2,6-i-Pr$_2$) has played a leading role in these investigations. Our interest in this ligand derives in part from its steric resemblance to the terphenyl ligand 2,6-Trip$_2$H$_3$C$_6$ (Trip = C$_6$H$_2$-2,4,6-i-Pr$_3$) as shown. The latter



Dipp$_2$nacnacE 2,6-Trip$_2$H$_3$C$_6$E

has been demonstrated to be effective in the stabilization of a wide variety of new compounds.[34] Very recently, it has been shown that the use of the Dipp$_2$nacnac ligand can stabilize the unusual monomeric M(I) species Dipp$_2$nacnacM: (M = Al or



Ga).[30,31] These results parallel the recent finding that monomeric, monovalent group 13 metal complexes can also be stabilized by terphenyl ligands as exemplified by the compounds 2,6-Trip$_2$H$_3$C$_6$M: (M = In or Tl).[35] The unusual composition and structure of the low-valent group 13 metal Dipp$_2$nacnac complexes requires that structural and spectroscopic data from other group 13 derivatives be available for comparison. Currently, such data are scant and are available only for Dipp$_2$nacnacAlMe$_2$ (and related less crowded derivatives),[22] [Dipp$_2$nacnacAlMe][B(C$_6$F$_5$)$_4$],[25] [{Dipp$_2$nacnacAlMe}$_2${B(C$_6$F$_5$)$_3$-Me}],[25] Dipp$_2$nacnacAl(SeH)$_2$,[27] and {Dipp$_2$nacnacAl(SeH)}$_2$Se.[27] Our objectives in this work were the preparation and characterization of a range of Dipp$_2$nacnacMX$_2$ (M = Al, Ga, or In, X = halogen or methyl) species and then to compare their spectroscopic and structural properties with the new monovalent metal derivatives in order to draw conclusions regarding the bonding in the latter species.

Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed three times before use. The compounds Dipp$_2$nacnacH (**1**)[8] and Dipp$_2$nacnacLi·OEt$_2$ (**2**)[27] were prepared as previously described. Aluminum(III) chloride and iodide were sublimed prior to use. High-purity GaCl$_3$ (99.999%), InCl$_3$, and InI$_3$ (99.99%) were purchased commercially and used as received. The compound "GaI" was prepared in accordance with the literature procedure.[36] ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Varian INOVA 400 MHz spectrometer and referenced to the deuterated solvent.

Dipp$_2$nacnacMCl$_2$ (M = Al (3), Ga (5), In (8)). For **3**, A toluene solution (20 mL) of Dipp$_2$nacnacLi·OEt$_2$ (**2**) (1.92 g, 4.53 mmol) was added dropwise to a chilled (ca. 0 °C) suspension of freshly sublimed AlCl$_3$ (0.63 g, 4.73 mmol) with rapid stirring. The mixture was allowed to warm to room-temperature overnight, whereupon the solvents were removed under reduced pressure. The crude product was extracted with hexane (30 mL), and filtration produced a clear pale yellow solution which, upon concentration and cooling, afforded the product **3** as colorless crystals. The compounds **5** and **8** were prepared in a similar manner. **3**: yield 1.70 g (73%); mp 211−213 °C. Anal. Calcd for C$_{29}$H$_{41}$AlCl$_2$N$_2$: C, 67.57; H, 8.00; N, 5.44. Found: C, 67.91; H, 8.11; N, 5.61. ^{1}H NMR (C$_6$D$_6$, 399.77 MHz, 25 °C): δ 1.10 (d, 12H, J = 6.8 Hz, CH(CH$_3$)$_3$, 1.42 (d, 12H, J = 6.8 Hz, CH(CH$_3$)$_3$), 1.50 (s, 6H, *C*H$_3$), 3.43 (sept, 4H, J = 6.8 Hz, C*H*(CH$_3$)$_3$), 4.91 (s, H, γ-*CH*), 7.1−7.2 (br, 6H, Ar). ^{13}C{^{1}H}NMR (C$_6$D$_6$, 100.53 MHz, 25 °C): 24.7 (CH$_3$), 24.9 (*C*H(CH$_3$)$_2$), 25.5 (CH(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 98.9 (γ-*C*), 124.9 (Ar), 138.2 (Ar), 144.8 (Ar), 172.3 (CN). **5**: colorless crystals, yield: 2.21 g (87%); mp 183−184 °C. Anal. Calcd for C$_{29}$H$_{41}$Cl$_2$GaN$_2$: C, 62.40; H, 7.39; N, 5.02. Found: C, 62.1; H, 7.12; N, 4.78. ^{1}H NMR (C$_6$D$_6$, 399.77 MHz, 25 °C): δ 1.13 (d, J = 6.8 Hz, 12H, CH(*CH*$_3$)$_2$), 1.43 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.58 (s, 6H, *CH*$_3$), 3.42 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.7 (s, 1H, C*H*), 7.10 (m, 6H, Ar*H*). ^{13}C-{^{1}H}NMR (C$_6$D$_6$, 100.53 MHz, 25 °C): δ 24.6 (*C*H$_3$), 25.2 (*C*H(CH$_3$)$_2$), 29.0 (*C*H(CH$_3$)), 98.4 (γ-C), 124.19 (Ar), 138.5 (Ar), 144.9 (Ar), 172.9 (CN). **8**: colorless crystals, yield: 2.40 g (ca. 80%); mp 140 °C, dec 216 °C. ^{1}H NMR (C$_6$D$_6$, 399.77 MHz, 25 °C): δ 1.07 (d, J = 6.8 Hz,

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12H, CH(CH_3)$_2$), 1.41 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.57 (s, 6H, CH_3), 3.15 (sept, J = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 3.84 (sept, J = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 4.79 (s, 1H, CH), 7.13 (m, 6H, ArH). ^{13}C{^{1}H}NMR (C_6D_6, 100.53 MHz, 25 °C): δ 24.5 (*C*H$_3$), 25.0 (CH(*C*H$_3$)$_2$), 25.3 (s), 28.6 (*C*H(CH$_3$)$_2$), 98.9 (γ-C), 124.64 (Ar), 138.1 (Ar), 144.8 (Ar), 172.7 (CN).

Dipp$_2$nacnacMI$_2$ (M = Al (4), Ga (6), In (9)). The synthesis and spectroscopic characterization of **4** has been given previously in ref 27. For **6**, solid **2** (2.5 g, 5 mmol) was added to a rapidly stirred slurry of "GaI" (1.5 g, 7.6 mmol)[36] of toluene (30 mL) with cooling in a dry ice/acetone bath. The mixture was allowed to come to room-temperature overnight, and the volume was reduced to ca. 10 mL. The solution was then placed in a ca. −20 °C freezer for 48 h to give yellow crystals of Dipp$_2$nacnacGa in ca. 40% yield. The supernatant liquid was separated and pumped to dryness and washed with hexane. The remaining, almost colorless solid was recrystallized from the minimum volume of hot toluene (ca. 5 mL) with cooling in a −20 °C freezer to give **6** as colorless crystals. Yield: 0.70 g (26%), mp 246−248 °C. Anal. Calcd for $C_{29}H_{41}GaI_2N$: C, 47.00; H, 5.56; N, 3.79. Found: C, 47.61; H, 5.79; N, 3.38. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ 1.10 (d, J = 6.3 Hz, 12H, CH(CH_3)$_2$), 1.43 (d, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.50 (s, 6H, CH_3), 3.56 (sept, J = 6.6 Hz, 4H, CH(CH$_3$)$_2$), 4.92 (s, H, λ-CH), 7.11 (m, br, 6H, ArH). ^{13}C{^{1}H}NMR (C_6H_6, 100.53 MHz, 25 °C): δ 24.5 (*C*H(CH$_3$)$_2$), 24.7 (CCH$_3$), 27.0 (CH(CH$_3$)$_2$), 29.3 (*C*H-(CH$_3$)$_2$), 98.5 (γ-C), 125.0 (*m*-C), 127.3 (*p*-C), 139.3 (*o*-C), 144.8 (*C*(CH$_3$)), 170.8 (CN). For **9**, a diethyl ether solution (20 mL) of **2** (1.24 g, 2.48 mmol) was added dropwise to a stirred solution of InI$_3$ (1.23 g, 2.48 mmol) in diethyl ether (20 mL) with cooling in a dry ice/acetone bath. The cooling bath was then removed, and the solution was allowed to come to room temperature and stirred for a further 24 h. The solvent was removed under reduced pressure, and the crude product was dissolved in hexane (30 mL). Filtration through Celite followed by cooling in a ca. −20 °C freezer afforded the product **9** as very pale yellow needles. Yield: 1.69 g (87%). Mp: 168−171 °C. Anal. Calcd for $C_{29}H_{41}I_2InN_2$: C, 44.3; H, 5.24; N, 3.56. Found: C, 43.71; H, 5.01; N, 3.46. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ 1.11 (d, 12H, J = 6.8 Hz, CH(CH_3)$_2$), 1.40 (d, 12H, J = 6.8 Hz, CH(CH_3)$_2$), 1.50 (s, 6H, CH$_3$), 3.48 (sept, 4H, J = 6.8 Hz), 4.73 (s, 1H, γ-CH), 7.1−7.2 (br, 6H, Ar). ^{13}C{^{1}H}NMR (C_6D_6, 100.53 MHz, 25 °C): δ 24.3, 24.6 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 97.0 (γ-C), 124.6, 137.7, 143.7 (Ar), 171.8 (CN).

Dipp$_2$nacnacMMe$_2$ (M = Ga (7), In (10)). For **7**, a toluene (15 mL) solution of GaMe$_3$ (0.59 g, 5.17 mmol) was treated dropwise with a diethyl ether solution (30 mL) of **1** (2.58 g, 5.17 mmol) with cooling in a dry ice/acetone bath. The solution was then allowed to warm to room temperature and refluxed for 48 h. The solvents were removed under reduced pressure, and the residue was extracted with hexane (30 mL) and filtered. Concentration to ca. 10 mL and storage in ca. −20 °C freezer for 5 d afforded the product **7** as colorless crystals. Yield: 2.27 g (85%). Mp: 156−158 °C. Anal. Calcd for $C_{31}H_{47}GaN_2$: C, 71.95; H, 9.16; N, 5.42. Found: C, 72.41; H, 9.00; N, 5.01. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ −0.18 (s, 6H, Ga(CH$_3$)$_2$), 1.15 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.30 (d, J = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.58 (s, 6H, CH_3), 3.43 (sept, J = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 4.80 (s, 1H, CH), 7.12 (br, m, 6H, ArH). ^{13}C{^{1}H}NMR (C_6D_6, 100.53 MHz, 25 °C): δ 24.3 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 95.91 (γ-C), 124.2 (s), 125.7, 126.6, 142.0, 142.6, 144.03 (Ar), 172.2 (CN). For **10**, methylmagnesium bromide (3.6 mmol, 1.2 mL of 3M solution) in diethyl ether was added to a rapidly stirred diethyl ether (30 mL) solution of **8** (1.00 g, 1.66 mmol) with cooling in a dry ice/acetone bath. The bath was then removed, and the solution was allowed to come to room temperature, whereupon it was stirred for a further 12 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (30 mL) and filtered. Concentration to ca. 5 mL and storage in a ca. −20 °C freezer for 2 d afforded the product **10** as colorless crystals. Yield: 0.86 g (92%). Mp: 154−157 °C. Anal. Calcd for $C_{31}H_{47}InN_2$: C, 66.18; H, 8.42; N, 4.98. Found: C, 65.48; H, 8.01; N, 4.71. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ −0.02 (s, 3H, InCH_3), 0.34 (s, 3H, InCH_3), 1.23 (d, 12H, J = 6.9 Hz, CH(CH$_3$)$_2$), 1.32 (d, 12H, J = 6.9 Hz, CH(CH_3)$_2$), 1.66 (s, 6H, Me), 3.48 (sept, 4H, J = 6.9 Hz), 4.79 (s, 1H, γ-CH), 7.1−7.2 (br, m, 6H, ArH). ^{13}C-{^{1}H}NMR (100.53 MHz, 25 °C): δ −8.8 (In*C*H$_3$), 1.6 (InCH$_3$), 24.2 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 95.6 (γ-C), 124.2, 143.2, 143.8 (Ar), 168.3 (s, CN).

X-ray Crystallographic Studies. Crystals of **3** and **5**−**10** 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 quickly placed in the low-temperature nitrogen stream.[37] The data were recorded near 90 K using a Bruker SMART 1000 (Mo Kα radiation and a CCD area detector). The SHELXTL version 5.03 program package was used for the structure solutions and refinements.[38] Absorption corrections were applied using the SADABS program.[39] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. The structure of **8** included 50% Br occupancy (as a result of Br contamination by an in situ preparation of LinacnacDipp$_2$ using halide-rich LiMe) at one of the Cl positions and refined satisfactorily. For **4,** data were obtained on a crystal mounted in a capillary tube at room temperature. Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

Results and Discussion

Synthesis. A number of Al(III) nacnac derivatives have been previously synthesized and structurally characterized. These include the cation [Dipp$_2$nacnacAlMe]$^+$,[25] the chloride (*p*-tolyl)$_2$nacnacAlCl$_2$,[22] and the dimethyl derivative Dipp$_2$-nacnacAlMe$_2$.[22,25] The latter species was prepared independently by two different groups[22,25] via the reaction of AlMe$_3$ with Dipp$_2$nacnacH. The chloride (*p*-tolyl)$_2$nacnacAlCl$_2$[21] was synthesized by the reaction of AlCl$_3$ with (*p*-tolyl)$_2$nacnacLi, and it was also shown that either one or both chlorides in this compound could be replaced by methyl groups.[22] In a similar manner, the aluminum, gallium, and indium chloride derivatives **3**, **5**, and **8** were prepared in 73−87% yield by the straightforward reaction of Dipp$_2$nacnacLi·OEt$_2$[27] with the respective trihalides in accordance with eq 1.

$$\underset{\mathbf{2}}{\text{Dipp}_2\text{nacnacLi}\cdot\text{Et}_2\text{O}} + \text{MCl}_3 \xrightarrow{\text{Et}_2\text{O}} \underset{\text{M = Al (}\mathbf{3}\text{), Ga (}\mathbf{5}\text{), In (}\mathbf{8}\text{)}}{\text{Dipp}_2\text{nacnacMCl}_2} + \text{LiCl} \quad (1)$$

Although chloride compounds are generally the most accessible, least expensive halide derivatives to prepare, the corresponding iodide species possess advantages as precursors. An example is the synthesis of the M(I) species Dipp$_2$nacnacAl: where the reaction of potassium with Dipp$_2$nacnacAlI$_2$ affords Dipp$_2$nacnacAl in accordance with eq 2.[30,31] In contrast, the corresponding reaction using the Dipp$_2$nacnacAlCl$_2$ was unsuccessful.

$$\underset{\mathbf{4}}{\text{Dipp}_2\text{nacnacAlI}_2} + 2\text{K} \rightarrow \text{Dipp}_2\text{nacnacAl} + 2\text{KI} \quad (2)$$

The compound Dipp$_2$nacnacAlI$_2$[4,31] was synthesized, eq 3, by the direct reaction of I_2 with the methyl derivative Dipp$_2$-nacnacAlMe$_2$.[22] This approach avoids product separation problems encountered in the more direct route involving the reaction of **2** with AlI$_3$. The reaction of "GaI"[36] with the lithium derivative **2** produces Dipp$_2$nacnacGaI$_2$ **(6)** in addition to Dipp$_2$-

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(38) *SHELXL*, version 5.1; Bruker AXS: Madison, WI.
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Table 1. Data Collection Parameters for Compounds **3**−**10**[a]

	3	**4**	**5**	**6**
formula	$C_{29}H_{41}AlCl_2N_2$	$C_{29}H_{41}AlI_2N_2$	$C_{29}H_{41}Cl_2GaN_2$	$C_{29}H_{41}GaI_2N_2$
fw	515.2	698.42	558.26	741.11
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	17.9413(7)	18.927(10)	17.071(1)	18.8237(7)
b (Å)	9.9216(4)	8.690(5)	13.095(1)	8.6190(3)
c (Å)	17.1167(7)	20.137(15)	13.736(1)	20.0720(7)
α (deg)				
β (deg)	108.842(1)	113.45(4)	108.432(2)	113.388(1)
γ (deg)				
V (Å^3)	2883.6(2)	3038(3)	2912.9(4)	2989.0(2)
Z	4	4	4	4
μ(Mo Kα) (mm^{-1})	0.275	2.118	1.147	3.759
T/K	90	300	90	90
R1	0.0326	0.0248	0.040	0.0185
wR2	0.0896	0.0608	0.1025	0.0528

	7	**8**	**9**	**10**
formula	$C_{31}H_{47}GaN_2$	$C_{29}H_{41}Br_{0.50}Cl_{1.50}InN_2$	$C_{29}H_{41}I_2InN_2$	$C_{31}H_{47}InN_2$
fw	517.43	625.59	786.26	562.53
cryst system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	12.6644(5)	17.942(2)	18.7802(8)	10.3346(4)
b (Å)	19.3511(8)	10.1655(9)	8.6647(4)	12.5671(5)
c (Å)	13.3291(5)	17.4672(15)	20.3412(8)	12.9080(5)
α (deg)				69.829(1)
β (deg)	107.02(1)	108.984(2)	113.0306(1)	76.852(1)
γ (deg)				74.993(1)
V (Å^3)	2910.5(2)	3012.6(4)	3046.1(2)	1502.2(1)
Z	4	4	4	2
μ(Mo Kα) (mm^{-1})	0.965	1.599	2.822	0.806
T/K	90	90	90	90
R1	0.0431	0.0323	0.0211	0.0215
wR2	0.0696	0.0810	0.0434	0.0562

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)]]^{1/2}$.

nacnacGa:. The diiodide **6** also undergoes reduction with potassium to give Dipp$_2$nacnacGa:.[30] Dipp$_2$nacnacInI$_2$ (**9**) was synthesized by the direct reaction of Dipp$_2$nacnacLi·OEt$_2$ with InI$_3$. Thus, the three iodides **4**, **6**, and **9** were each synthesized by a different method. The gallium methyl compound **7** was synthesized in a manner very similar to that of its aluminum analogue. However, the indium methyl species **10** was made by the reaction of 2 equiv of the Grignard MeMgBr with the chloride **8** in diethyl ether solution.

$$\underset{\mathbf{4}}{\text{Dipp}_2\text{nacnacAlMe}_2} + 2I_2 \rightarrow \text{Dipp}_2\text{nacnacAlI}_2 + 2\text{MeI} \quad (3)$$

All compounds afforded simple ^{1}H and ^{13}C NMR spectra. There are only minor differences in the observed chemical shifts for the Dipp$_2$nacnac ligand in compounds **3**−**10**. However, the ^{1}H NMR shifts of the *β*-Me and *γ*-H hydrogens of the lower valent Dipp$_2$nacnacM: derivatives (M = Al or Ga) are ca. 0.05 and 0.2 ppm further downfield. The ^{1}H NMR metal methyl resonances of compounds **7** and **10** were found at upfield shifts. The gallium methyl signal was observed as a single peak like its aluminum counterpart,[21,22] despite the puckering of the ring which renders distinct environments to the two metal methyl groups in the solid state. The solid state structures are likely to be maintained in solution, so that methyl site exchange must be rapid on the NMR time scale. For **10**, however, two distinct methyl signals are observed suggesting that the exchange is quite slow. It is possible that the rate of exchange observed for **10** is connected to the puckering of the ring which is the largest of any compound in the series **3**−**10** (vide infra).

Structural Data. The structures of compounds **3**−**10** are represented by the thermal ellipsoid plots in Figures 1−3.

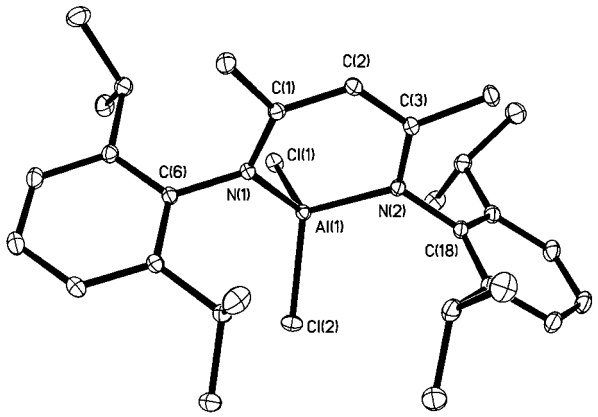

Figure 1. Thermal ellipsoid plot (30%) of **3**. H atoms are not shown for clarity. Structural data are given in Table 2.

Selected bond distances and angles are listed in Table 2. The structures have several features in common: (a) The C_3N_2 ring fragment is planar or close to planar in each molecule. (b) The metals lie significantly out of the C_3N_2 planes such that there are considerable dihedral angles between the C_3N_2 and MN_2 arrays. (c) The ring C−C and C−N distances lie within the narrow ranges 1.387(6)−1.418(3) and 1.320(2)−1.353(2) Å, which are indicative of considerable multiple character in these bonds. (d) Within the C_3N_2M (M = Al, Ga or In) rings the N−M−N angle is invariably the narrowest (usually ≤100°) whereas the other angles are all ≥117° with widest angle (130-(±3)°) observed at the C(2) carbon position.

One of the most noticeable aspects of the structures is the presence of a dihedral angle between the N(1)C(1)C(2)C(3)N-

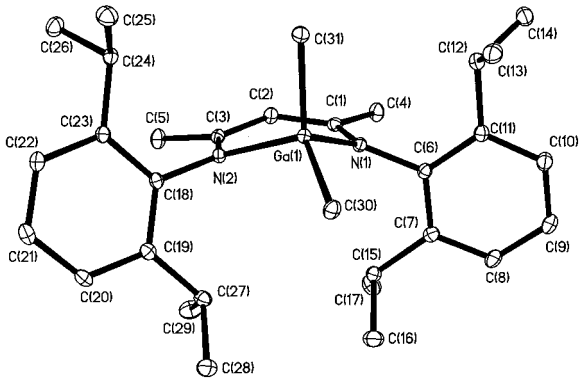

Figure 2. Thermal ellipsoid plot (30%) of **7**. H atoms are not shown for clarity. Structural data are given in Table 2.

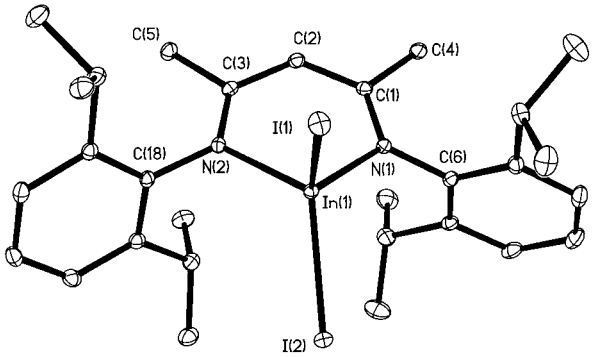

Figure 3. Thermal ellipsoid plot (30%) of **9**. H atoms are not shown for clarity. Structural data are given in Table 2.

(2) and N(1)MN(2) (M = Al, Ga or In) arrays. This is also found in many other derivatives of these ligands from different groups of the periodic table.[10−18,22−29] The folding of the rings in **3**−**10** can be expressed by either the angle between the planes or the distance of the metal from the averaged extended plane formed by the N(1)C(1)C(2)C(3)N(2) array. These data are listed in Table 3. It can be seen that the deviation from planarity of the chloride and iodide derivatives is similar, whereas the values for the methyl derivatives are considerably greater. There is also some correlation between the NMN angles and the degree of ring folding; the narrower the N−M−N angle is, the greater the folding. However, the monomeric aluminum and gallium species $Dipp_2$nacnacM: (M = Al or Ga),[30,31] which have planar C_3N_2M arrays, have narrower angles of 89.36(8) and 87.53(5)°. It seems probable that more highly charged and polarizing metal cations such as Al^{3+}, Ga^{3+}, or In^{3+} result in shorter M−N bonds and greater steric interactions involving the Dipp and metal substituents which results in folding of the ring for steric reasons. The planar geometries observed for $Dipp_2$nacnacM: (M = Al or Ga) molecules are consistent with this argument since the M−N bonds in these molecules are long and the metals are unsubstituted by other groups so that steric crowding is much lower. A ring geometry, which is much closer to planarity, is also observed for $[Dipp_2nacnacAlMe][B(C_6F_5)_4]$[25] which, although it has shorter Al−N distances, features a less crowding, essentially three coordinate environment at aluminum.

The aluminum chloride and iodide derivatives **3** and **4** bear a very close structural resemblance. Inspection of the data in Table 2 shows that the Al−N bonds in **3** and **4** have an average distance of 1.88(1) Å and nearly equal N(1)−Al(1)−N(2) angles of 99.36(4) and 99.8(1)°. The angles between the halogens are also very close, having the values 108.02(2) and 108.40(5)°. The Al−N bond lengths are similar to those observed for terminal Al−N bonds in aluminum amides having four coordinate aluminum,[40] although they are shorter than those values (1.922(2) and 1.935(2) Å) recently reported for $Dipp_2$-

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**−**10**

3		**4**	
Al(1)−N(1)	1.8843(9)	Al(1)−N(1)	1.872(2)
Al(1)−N(2)	1.8663(9)	Al(1)−N(2)	1.893(3)
Al(1)−Cl(1)	2.1344(4)	Al(1)−I(1)	2.501(1)
Al(1)−Cl(2)	2.1185(4)	Al(1)−I(2)	2.541(1)
N(1)−C(1)	1.341(1)	N(1)−C(1)	1.338(3)
N(2)−C(3)	1.348(1)	N(2)−C(2)	1.340(3)
C(1)−C(2)	1.405(1)	C(1)−C(2)	1.391(4)
C(2)−C(3)	1.396(1)	C(2)−C(3)	1.394(4)
N(1)−Al(1)−N(2)	99.36(4)	N(1)−Al(1)−N(2)	99.9(1)
Cl(1)−Al(1)−Cl(2)	108.02(2)	I(1)−Al(1)−I(2)	108.40(5)
Al(1)−N(1)−Cl(1)	119.33(7)	Al(1)−N(1)−I(1)	118.2(2)
Al(1)−N(2)−C(3)	119.73(7)	Al(1)−N(2)−C(3)	117.7(2)
N(1)−C(1)−C(2)	120.76(9)	N(1)−C(1)−C(2)	123.1(2)
C(1)−C(2)−C(3)	127.7(1)	C(1)−C(2)−C(3)	128.1(2)
C(2)−C(3)−N(2)	122.78(9)	C(2)−C(3)−N(2)	123.8(2)

5		**6**	
Ga(1)−N(1)	1.926(3)	Ga(1)−N(1)	1.924(1)
Ga(1)−N(2)	1.906(3)	Ga(1)−N(2)	1.948(1)
Ga(1)−Cl(1)	2.228(1)	Ga(1)−I(1)	2.5528(2)
Ga(1)−Cl(2)	2.218(1)	Ga(1)−I(2)	2.5082(2)
N(1)−C(1)	1.337(5)	N(1)−C(1)	1.340(2)
N(2)−C(3)	1.353(2)	N(2)−C(3)	1.337(2)
C(1)−C(2)	1.403(6)	C(1)−C(2)	1.400(2)
C(2)−C(3)	1.387(6)	C(2)−C(3)	1.401(2)
N(1)−Ga(1)−N(2)	100.2(1)	N(1)−Ga(1)−N(2)	99.25(5)
Cl(1)−Ga(1)−Cl(2)	110.20(4)	I(1)−Ga(1)−I(2)	109.413(7)
Ga(1)−N(1)−C(1)	118.3(3)	Ga(1)−N(1)−C(1)	118.0(1)
Ga(1)−N(2)−C(3)	117.6(3)	Ga(1)−N(2)−C(3)	117.4(1)
N(1)−C(1)−C(2)	123.4(4)	N(1)−C(1)−C(2)	123.6(1)
C(1)−C(2)−C(3)	129.6(4)	C(1)−C(2)−C(3)	129.1(1)
C(2)−C(3)−N(2)	123.7(4)	C(2)−C(3)−N(2)	124.2(1)

7		**8**	
Ga(1)−N(1)	1.979(2)	In(1)−N(1)	2.123(3)
Ga(1)−N(2)	2.001(2)	In(1)−N(2)	2.111(3)
Ga(1)−C(30)	1.970(2)	In(1)−Cl(1)	2.3872(9)
Ga(1)−C(31)	1.979(2)	In(1)−Cl(2)	2.404(3)
N(1)−C(1)	1.333(3)	In(1)−Br(1)	2.546(1)
N(2)−C(3)	1.325(2)	N(1)−C(1)	1.335(4)
C(1)−C(2)	1.400(3)	N(2)−C(3)	1.332(4)
C(2)−C(3)	1.415(3)	C(1)−C(2)	1.406(5)
		C(2)−C(3)	1.400(5)
N(1)−Ga(1)−N(2)	93.92(7)	N(1)−In(1)−N(2)	92.5(1)
C(30)−Ga(1)−C(31)	122.44(9)	Cl(1)−In(1)−Cl(2)	108.99(8)
Ga(1)−N(1)−C(1)	118.5(1)	In(1)−N(1)−C(1)	120.0(2)
Ga(1)−N(2)−C(3)	118.5(1)	In(1)−N(2)−C(3)	120.5(2)
N(1)−C(1)−C(2)	123.3(2)	N(1)−C(1)−C(2)	124.8(3)
C(1)−C(2)−C(3)	127.7(2)	C(1)−C(2)−C(3)	131.2(3)
C(2)−C(3)−N(2)	123.8(2)	C(2)−C(3)−N(2)	124.7(3)

9		**10**	
In(1)−N(1)	2.121(2)	In(1)−N(1)	2.190(1)
In(1)−N(2)	2.147(1)	In(1)−N(2)	2.204(1)
In(1)−I(1)	2.7008(2)	In(1)−C(30)	2.148(1)
In(1)−I(2)	2.6050(2)	In(1)−C(31)	2.168(1)
N(1)−C(1)	1.338(2)	N(1)−C(1)	1.332(2)
N(2)−C(3)	1.333(2)	N(2)−C(3)	1.320(2)
C(1)−C(2)	1.401(2)	C(1)−C(2)	1.403(2)
C(2)−C(3)	1.405(2)	C(2)−C(3)	1.418(2)
N(1)−In(1)−N(2)	92.42(5)	N(1)−In(1)−N(2)	86.76(4)
I(1)−In(1)−I(2)	111.748(6)	C(30)−In(1)−C(31)	130.94(6)
In(1)−N(1)−C(1)	118.9(1)	In(1)−N(1)−C(1)	119.35(7)
In(1)−N(2)−C(3)	118.9(1)	In(1)−N(2)−C(3)	120.08(8)
N(1)−C(1)−C(2)	125.0(2)	N(1)−C(1)−C(2)	124.5(1)
C(1)−C(2)−C(3)	131.3(2)	C(1)−C(2)−C(3)	129.6(1)
C(2)−C(3)−N(2)	125.1(2)	C(2)−C(3)−N(2)	124.3(1)

Table 3. Folding Parameters for the C_3N_2 and MN_2 Arrays of Compounds **3**−**10**

compd	metal dist from the C_3N_2 plane (Å)	dihedral angle between the C_3N_2 and MN_2 arrays (deg)
Dipp$_2$nacnacAlCl$_2$ (**3**)	0.525	155.0
Dipp$_2$nacnacAlI$_2$ (**4**)	0.571	152.5
Dipp$_2$nacnacAlMe$_2$[a]	0.72	
Dipp$_2$nacnacGaCl$_2$ (**5**)	0.507	156.2
Dipp$_2$nacnacGaI$_2$ (**6**)	0.568	153.7
Dipp$_2$nacnacGaMe$_2$ (**7**)	0.76	146.8
Dipp$_2$nacnacInBr$_{0.5}$Cl$_{1.5}$ (**8**)	0.551	158.3
Dipp$_2$nacnacInI$_2$ (**9**)	0.643	154.7
Dipp$_2$nacnacInMe$_2$ (**10**)	0.892	146.7

[a] Reference 22.

nacnacAlMe$_2$.[22] The difference is probably due to the increased positive charge on the metals in **3** and **4** (and a stronger ionic Al−N bonding component) as a result of their bonding to halides. This argument is supported by the fact that even shorter Al−N bonds (average 1.826(1) Å) were observed in the complex [Dipp$_2$nacnacAlMe][B(C$_6$F$_5$)$_4$].[25] Nonetheless, the Al−N distances are marginally longer than the 1.850(2) Å bond length in [HC{C(Me)N(C$_6$H$_4$-4-Me)}$_2$]AlCl$_2$,[21] possibly as a result of the greater steric hindrance in **3** and **4**. The aluminum chlorine distances in **3** (average 2.126(1) Å) are slightly longer than Al−Cl distances (2.106(4) Å) in {Cl$_2$Al(μ-NMe$_2$)}$_2$.[41] The Al−I bonds (average 2.52(2) Å) in **4** are essentially the same as the average Al−I bond of 2.49(1) Å in {I$_2$Al(μ-NMe$_2$)}$_2$ although it is considerably shorter than the 2.704(1) Å measured for (pyridine)(I)Al(2,2,6,6-tetramethylpiperidino)$_2$.[42] In the latter species the very crowded four-coordinate aluminum environment may cause lengthening of the Al−N bond. The steric argument is supported by the observation of a much shorter Al−I bond (ca. 2.57 Å) in the less crowded (pyridine)(I)$_2$Al(2,2,6,6-tetramethylpiperidino) molecule.[42]

The Ga−N bond lengths for the gallium compounds **5**−**7** follow a pattern similar to that for the aluminum species **3** and **4** and their methyl analogue Dipp$_2$nacnacAlMe$_2$, presumably for similar reasons. For the pair of compounds **5** and **6**, the average Ga−N distances 1.916(10) and 1.936(12) Å are essentially equal. These distances are significantly shorter than the average of 1.990(11) Å observed for the methyl derivative **7**. The compounds most closely related to **5**−**7** are the amidinate species {PhC(NPh)$_2$}GaMe$_2$,[43] {*t*-BuC(NCy)$_2$}GaCl$_2$,[44] and {*t*-BuC(NCy)$_2$}GaMe$_2$[44] and the *N*-methyl-2-(methyamino)troponiminate [(Me)$_2$ATI]$^-$ derivative {(Me)$_2$ATI}$_2$GaI.[45] In the amidinate gallium chloride and methyl derivatives the Ga−N bonds average 1.941(5) and 1.986(5) Å. The difference between these values is similar to that between the Ga−N distances in **5** and **7**. The (Me)$_2$ATI and related ligands[46] also resemble nacnac ligands in that they are uninegative bidentate dimine donors. In {(Me)$_2$ATI}$_2$GaI the Ga−N bond lengths average 1.968(14) Å, which is not significantly different from the 1.936(12) Å average Ga−N distance in the iodide **6**. However, the Ga−I distance in {(Me)$_2$ATI}$_2$GaI is 2.7178(5) Å, which is ca. 0.2 Å longer than that in **6**. Clearly, the different coordination numbers and steric environment have very large effects on the Ga−I distance in these compounds, and this is also consistent with the data for the aluminum compounds.[47] The Ga−C distances in **7**, average 1.975(5) Å are well within the range ca. 1.94−2.03 Å for Ga−C bonds.[47]

The indium halide compounds **8** and **9** have similar In−N bond lengths in the narrow range 2.111(3)−2.147(1) Å, whereas those of the methyl derivative have a somewhat longer average In−N distance of ca. 2.197(7) Å. This is, of course, similar to the pattern observed for both the aluminum and gallium series. The In−N bond lengths in **8**−**10** are very similar to the average of 2.145(3) Å (In−N(eq) and 2.171(4) Å (In−N(ax)) observed in the species {(Me)$_2$ATI}$_2$InCl[42] despite the higher indium coordination number. The In−Cl distance in {(Me)$_2$ATI}$_2$InCl, 2.4174(9) Å, is also very similar to the value, 2.3872(9) Å, observed for **8**. The similarity in these metal chloride bonds is in sharp contrast to the large differences between the Ga−I distances in the corresponding pair of gallium iodide derivatives **6** and {(Me)$_2$ATI}$_2$GaI. Structural data for the five coordinate In−I species phthalocyaninatoindium(III) iodide[48] and the tris-(3,5-di-*tert*-butylpyrazolyborato)diiodoindium(III)[49] also show that their In−I distances of 2.672(1)[45] and 2.743(20) Å[46] are similar to the 2.6050(2) and 2.7008(2) Å observed in **9**. Perhaps, the larger size of indium in comparison to gallium renders steric effects less important in the heavier element compounds. The In−C distances, ca. 2.16 Å, lie within the range for indium terminally bound to carbon.[47]

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Supporting Information Available: Eight X-ray files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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