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Synthesis and Characterization of 8-(Dimethylamino)-1-naphthyl Derivatives of Aluminum, Gallium, and Indium

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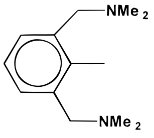
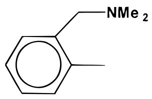
The group 13 dichlorides of formula Ar′MCl_2 [Ar′ = 8-(dimethylamino)-1-naphthyl (8-(Me_2N)$C_{10}H_6$)], M = Al (**1**), Ga (**2**), and In (**3**), have been prepared via the salt elimination reaction of 1 equiv of Ar′Li with MCl_3 in toluene solution at −78 °C. The reaction of **1** with $LiAlH_4$ in diethyl ether solution at −78 °C produced the dihydride [Ar′AlH_2]$_2$ (**4**). The X-ray crystal structures of **1**−**4** have been determined and show that **1** and **2** are monomeric while **3** and **4** are dimeric in the solid state. The reaction of **1** with RLi in toluene solution at −78 °C results in ligand redistribution and formation of Ar′$_2$AlR (R = Me (**5**), *t*-Bu (**6**)). The chloride analogue of **5** and **6**, Ar′$_2$AlCl (**7**), can be prepared directly from the reaction of 2 equiv of Ar′Li with $AlCl_3$ in toluene solution at −78 °C. The homoleptic derivative Ar′$_3$Al (**8**) was obtained when 3 equiv of Ar′Li was employed. Crystal data for **1**: monoclinic, space group $P2_1$, $a = 6.534(1)$ Å, $b = 10.801(1)$ Å, $c = 9.631(2)$ Å, $\beta = 105.57(2)°$, $V = 654.8(2)$ Å^3, $Z = 2$, $R = 0.0453$. Crystal data for **2**: monoclinic, space group $P2_1$, $a = 6.552(2)$ Å, $b = 10.833(2)$ Å, $c = 9.601(2)$ Å, $\beta = 106.05(2)°$, $V = 654.9(3)$ Å^3, $Z = 2$, $R = 0.0609$. Crystal data for **3**: monoclinic, space group $P2_1/c$, $a = 7.401(2)$ Å, $b = 15.746$ Å, $c = 10.801(4)$ Å, $\beta = 92.37(3)°$, $V = 1257.6(7)$ Å^3, $Z = 2$, $R = 0.0712$. Crystal data for **4**: monoclinic, space group $P2_1/c$, $a = 13.343(2)$ Å, $b = 11.228(2)$ Å, $c = 7.505(1)$ Å, $\beta = 100.64(1)°$, $V = 1105.0(4)$ Å^3, $Z = 4$, $R = 0.0560$.

Introduction

There is currently considerable interest in the use of intramolecularly stabilized aryl ligation in both main group[1] and transition metal chemistry.[2] For the heavier group 13 elements (Al, Ga, In), complexes with ligands of types **A** and **B** have



(A)



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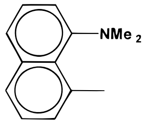

(C)

been reported.[3−7] Ligand **C** (8-(dimethylamino)-1-naphthyl or Ar′) has been employed for the coordination of group 14[8] and 15 elements;[9] however, to the best of our knowledge no complexes with group 13 elements have been reported. Group 13 derivatives with Ar′ are of interest for their potential as precursors to electronic materials.[10] In addition, we were interested in examining the effects of replacing the flexible −CH_2NMe_2 pendant side arm of **B** with a dimethylamino unit attached to the considerably more rigid naphthyl ring system of **C**.

We report here the syntheses and X-ray crystal structures of the dichloride derivatives Ar′MCl_2 (M = Al, Ga, In (**1**−**3**)) as well as the aluminum dihydride [Ar′AlH(μ-H)]$_2$ (**4**). The syntheses of the bis-ligand complexes of formula Ar′$_2$AlX (X = Me (**5**), t-Bu (**6**), Cl (**7**)) and the homoleptic derivative Ar′$_3$Al (**8**) are also described.

Results and Discussion

The dichlorides of Al, Ga, and In of formula Ar′MCl_2 (Ar′ = 8-(dimethylamino)naphthyl; M = Al, Ga, In) (**1**−**3**) were all prepared by the reaction of 1 equiv of Ar′Li with MCl_3 in toluene solution at −78 °C (Scheme 1). Each compound was isolated as a colorless crystalline solid following evaporation to dryness of the reaction mixture and subsequent recrystallization from toluene solution at −30 °C. Compounds **1**−**3** are air sensitive and decompose readily when exposed to the atmosphere. The proposed formulations are consistent with microanalytical data as well with ^{1}H and ^{13}C NMR spectroscopic data. The CI-MS of all three complexes indicated the predominance of monomers in the gas phase (**1**, *m*/*z* 269 (M^+); **2**, *m*/*z* 310 (M^+); **3**, *m*/*z* 355 (M^+)). However, X-ray diffraction studies were necessary in order to determine the degree of oligomerization, the presence or absence of intramolecular N→metal bonding, and other pertinent structural details.

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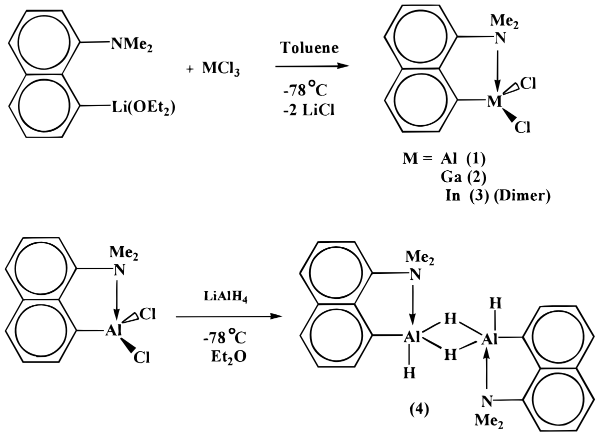
10.1021/ic990707q CCC: $19.00

Scheme 1



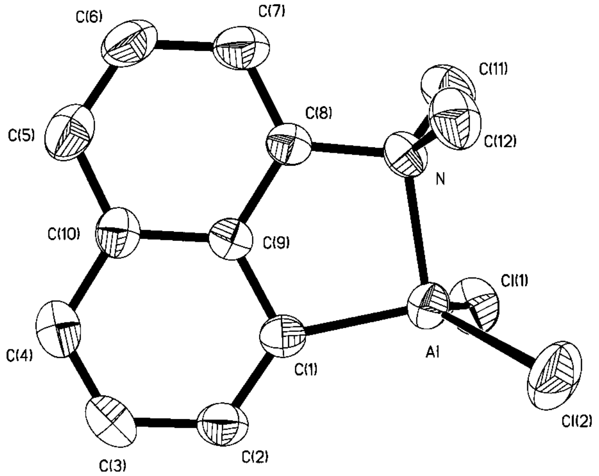


Figure 1. View of $Ar'AlCl_2$ (**1**), showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% probability level.

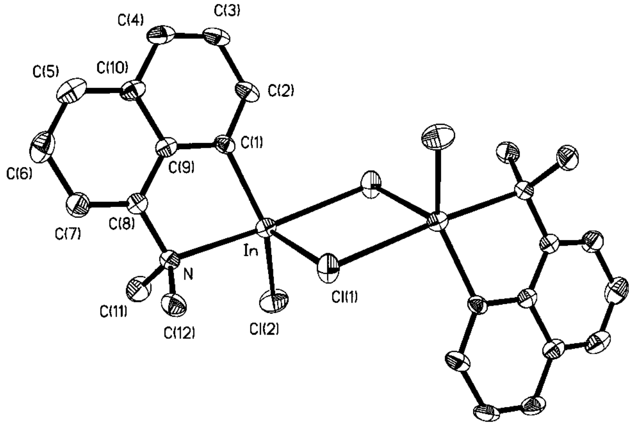


Figure 2. View of $[Ar'InCl_2]_2$ (**3**) showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% probability level.

The structures of **1** and **3** are shown in Figures1 and 2, respectively, and selected bond distances and angles are compiled in Table 1. The solid-state structures all comprise individual molecules with no unusually short intermolecular contacts. The structures of monomeric **1** and **2** are very similar while **3** is dimeric in the solid state. Compounds **1** and **2** both crystallize in the monoclinic space group $P2_1$ with two monomers per unit cell, and there are no unusually close intermolecular contacts. The analogous complexes with the "side arm" ligand **B** have been reported for both Al and Ga, and the X-ray crystal structures of $[o\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$ and $[o\text{-}(Me_2NCH_2)C_6H_4]AlBr_2$ have been described.[11] The complex $[o\text{-}(Me_2NCH_2)C_6H_4]AlCl_2$ has also been reported but to the best of our knowledge has not been structurally characterized.[12] Intramolecular coordination of the aryl dimethylamino group results in four-coordinate metal centers in both **1** and **2**. However, the geometries of the central metals exhibit considerable distortions from the ideal tetrahedral arrangement with the range of angles about Al or Ga varying from 90.0(2)° (C(1)−Al−N) to 119.9(1)° (C(1)−Al−Cl(2)) for **1** and from 88.8(3)° (C(1)−Ga−N) to 121.9(2)° (C(1)−Ga−Cl(2)) in **2**. Similar distortions were found in the solid-state structures of $[o\text{-}(Me_2NCH_2)C_6H_4]AlBr_2$ and $[o\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$.[11] The metal−nitrogen bond lengths in **1** (2.016(4) Å) and **2** (2.071(7) Å) are the same, within experimental error, as the analogous Al−N and Ga−N distances in $[o\text{-}(Me_2NCH_2)C_6H_4]AlBr_2$ (2.003(5) Å) and $[o\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$ (2.071(2) Å). The metal−carbon bond lengths in **1** (1.935(4) Å) and **2** (1.936(1) Å) are also comparable to those reported for $[o\text{-}(Me_2NCH_2)C_6H_4]AlBr_2$ (1.967(6) Å) and $[o\text{-}(Me_2NCH_2)C_6H_4GaCl_2$ (1.951(2) Å).[11]

Since ligand **C** possesses a rigid naphthyl backbone, it was anticipated that the metal−N−C−C−C ring formed in **1** and **2** would exhibit only minor deviations from planarity. In the complexes of the more flexible ligand **B**, there are significant distortions of of this chelate ring. Specifically, the nitrogen atom lies out of the ring by 0.47 and 0.65 Å in $[o\text{-}(Me_2\ NCH_2)C_6H_4]AlBr_2$ and $[o\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$, respectively. In the case of **1** and **2**, there is less distortion, with the nitrogen atom lying below the plane by 0.208 Å in **1** and by 0.168 Å in **2** while the metals are slightly above it (0.107 Å (**1**) and 0.09 Å (**2**)). The ring conformation for **1** is illustrated in Figure 3.

In contrast to the monomeric structures for **1** and **2**, the indium analogue, **3**, is dimeric in the solid state (Figure 2). Molecules of **3** crystallize in the monoclinic space group $P2_1/c$ with two molecules per unit cell. Each dimer is located on a crystallographic inversion center. The bridging In_2Cl_2 moiety is very distorted with two significantly different indium−chlorine distances (In−Cl(1) = 2.473(2) Å, In−Cl(1)#1 = 2.764(3) Å) The geometry about each In atom can best be described as distorted trigonal bipyramidal. The two axial ligands N and Cl(1)#1 form an angle of 173.0(2)° at In while for the equatorial ligands C(1), Cl(2), and Cl(1) the sum of the angles about In = 360.0(2)°, thus confirming their coplanarity. Note, however, that the C(1)−In−Cl(2) angle (141.5(2)°) is appreciably larger than the other two. A similar structure has been observed for the indium iodide derivative $[\{2\text{-}(Me_2NCH_2)C_6H_4\}InI_2]_2$.[13] The In−N and In−C(1) bond distances of **3** may also be compared to those of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}InI_2]_2$. Thus the In−N (2.405(7) Å) and In−C (1) (2.112(9) Å) bond distances are similar to those reported for the indium iodide (2.35(1) and 2.13(1) Å, respectively). Although barely statistically significant, the slightly longer In−N bond length in **3** may be due to the less flexible nature of the naphthyl backbone in ligand **C** as opposed to **B**.

The reaction of **1** with $LiAlH_4$ in diethyl ether solution at −78 °C afforded the dihydride derivative $[Ar'AlH(\mu\text{-}H)]_2$ (**4**) in good yield (Scheme 1). The analogous aluminum dihydride derivative of ligand **B**, i.e. $[\{o\text{-}(Me_2NCH_2)C_6H_4\}(H)Al(\mu\text{-}H)]_2$, has also been reported recently.[11] The structure of **4** is dimeric in the solid state, and an ORTEP view of the molecule is shown in Figure 4. Key bond lengths and angles are presented in Table 1. Molecules of **4** lie on a crystallographic center of inversion

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Table 1. Selected Bond Lengths (Å) and Bond Angles for Compounds **1**−**4**

compd **1**		compd **2**		compd **3**		compd **4**	
Al−C(1)	1.935(4)	Ga−C(1)	1.936(6)	In−C(1)	2.112(9)	Al−C(1)	1.967(3)
Al−N	2.016(4)	Ga−N	2.071(7)	In−N	2.405(7)	Al−N	2.118(3)
Al−Cl(2)	2.105(2)	Ga−Cl(2)	2.151(2)	In−Cl(2)	2.351(3)	Al−Al#1	2.758(2)
Al−Cl(1)	2.118(2)	Ga−Cl(1)	2.163(2)	In−Cl(1)	2.473(2)	N−C(8)	1.464(3)
N−C(8)	1.486(5)	N−C(8)	1.473(8)	N−C(8)	1.460(11)	N−C(12)	1.484(4)
N−C(12)	1.494(6)	N−C(12)	1.517(10)	N−C(12)	1.481(12)	N−C(11)	1.495(4)
N−C(11)	1.497(5)	N−C(11)	1.494(8)	N−C(11)	1.478(12)		
				In−Cl(1)#1	2.764(3)		
				Cl(1)−In#1	2.764(3)		
C(1)−Al −N	90.0(2)	C(1)−Ga −N	88.8(3)	C(1)−In −N	79.5(3)	C(1)−Al −N	84.4(2)
C(1)−Al−Cl(2)	119.9(2)	C(1)−Ga−Cl(2)	121.9(2)	C(1)−In−Cl(2)	141.5(2)	C(1)−Al−Al#1	106.4(1)
N−Al−Cl(2)	110.0(2)	N−Ga−Cl(2)	109.1(2)	N−In−Cl(2)	96.1(2)	N−Al−Al#1	135.8(2)
C(1)−Al−Cl(1)	118.9(2)	C(1)−Ga−Cl(1)	121.4(2)	C(1)−In−Cl(1)	116.9(2)	C(8)−N−C(12)	113.4(2)
N−Al−Cl(1)	107.1(2)	N−Ga−Cl(1)	105.6(2)	N−In−Cl(1)	94.6(2)	C(8)−N−C(11)	107.5(2)
Cl(2)−Al−Cl(1)	108.3(1)	Cl(2)−Ga−Cl(1)	106.6(2)	Cl(2)−In−Cl(1)	101.6(2)	C(12)−N−C(11)	108.6(2)
C(8)−N−C(12)	108.1(3)	C(8)−N−C(12)	108.7(6)	C(8)−N−C(12)	111.5(7)	C(8)−N−Al	106.2(2)
C(8)−N−C(11)	111.7(3)	C(8)−N−C(11)	111.3(6)	C(8)−N−C(11)	110.1(7)	C(12)−N−Al	112.6(2)
C(12)−N−C(11)	109.0(4)	C(12)−N−C(11)	108.5(8)	C(12)−N−C(11)	109.0(8)	C(11)−N−Al	108.4(2)
C(8)−N−Al	104.5(2)	C(8)−N−Ga	104.4(4)	C(8)−N−In	105.5(5)		
C(12)−N−Al	110.7(3)	C(12)−N−Ga	110.8(5)	C(12)−N−In	112.0(6)		
C(11)−N−Al	112.6(3)	C(11)−N−Ga	112.9(6)	C(11)−N−In	108.8(6)		
				C(1)−In−Cl(1)#1	96.2(2)		
				Cl(2)−In−Cl(1)#1	90.6(2)		
				N−In−Cl(1)#1	173.0(2)		
				Cl(1)−In −Cl(1)#1	82.3(1)		
				In−Cl(1)−In#1	97.7(2)		

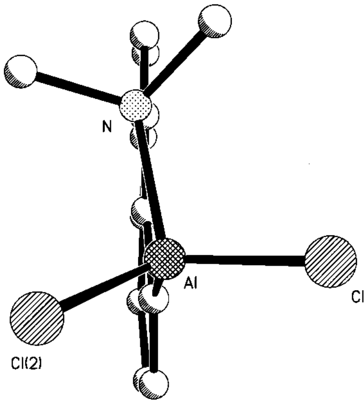


Figure 3. Illustration of the central metal−N−C−C−C ring conformation for **1**. Thermal ellipsoids are shown at the 30% probability level.

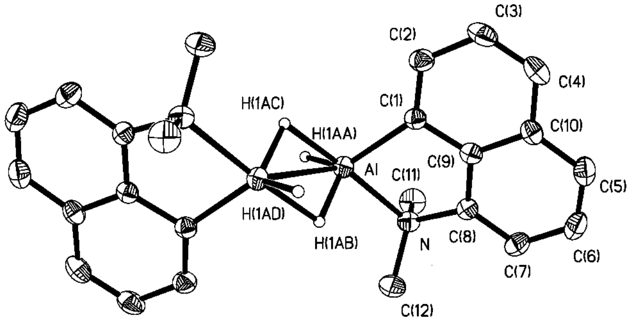
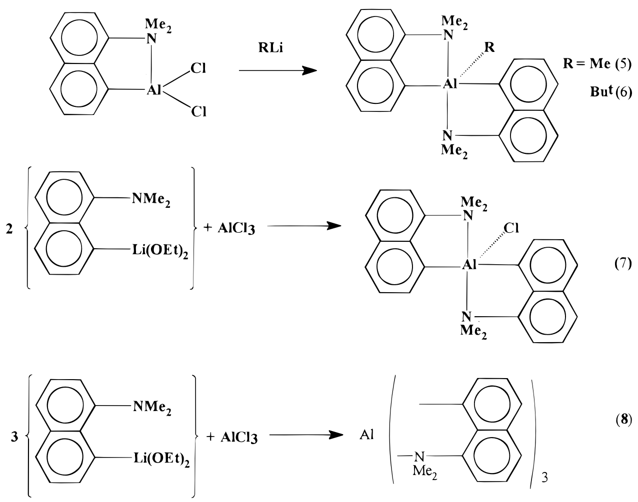


Figure 4. View of $[Ar'AlH(\mu\text{-}H)]_2$ (**4**), showing the atom-labeling scheme. Thermal ellipsoids are shown at the 30% probability level.

Scheme 2



with two complete molecules occupying the unit cell. The bridging and terminal hydrides (H(1AB) and H(1AA)) were both located and refined isotropically while the remaining hydrogens were placed in idealized positions. As in the case of **3**, the geometry about each Al atom is best described as distorted trigonal bipyramidal. For the Al atom, the axial ligands comprise one of the bridging hydrides (H(1AC) and N (H(1AC)−Al−N = 168.9(2)°), which may be compared to an analogous angle of 170.4(2)° in $[\{o\text{-}(Me_2NCH_2)C_6H_4\}HAl(\mu\text{-}H)]_2$.[11] The sum of the angles subtended by the three equatorial ligands about Al (H(1AA), C(1), and H(1AB)) is 359.7°. The symmetry-related bridging hydrides H(1AC) and H(1AB) have one long (1.91(2) Å) and one short (1.61(2) Å) Al−H bond which are similar in length to those found in $[\{o\text{-}(Me_2NCH_2)C_6H_4\}HAl(\mu\text{-}H)]_2$ (1.688 and 1.928(3) Å).[11] The Al−C(1) and Al−N bond lengths (1.967(3) and 2.118(3) Å) are similar to those found in the monomeric dichloride derivative, **1** (1.935(4) and 2.016(4) Å).

The reaction of **1** with **2** equiv of RLi (R = Me, *t*-Bu) in toluene solution at −78 °C resulted in a redistribution reaction and the formation of the bis(aryl) complexes Ar'_2AlR (R = Me, **5**, and *t*-Bu, **6**) in good yields (Scheme 2). The chloride analogues of **5** and **6**, Ar'_2AlCl (**7**), may also be prepared by the direct reaction of 2 equiv of Ar′Li with $AlCl_3$ in toluene solution at −78 °C. Both compounds are colorless crystalline solids which are moderately air sensitive. So far, it has not been possible to obtain crystals of sufficient quality for single-crystal

X-ray diffraction studies. However, it is reasonable to assume that the molecular structures of **5**−**7** have distorted trigonal-bipyramidal geometries—i.e., similar to those found in the 2-[(dimethylamino)methyl]phenyl complexes $[o\text{-}(Me_2NCH_2)\text{-}C_6H_4]_2MX$[12] (M = Al, X = Me;[12] M = In, X = Cl;[5] M = Ga, X = Cl[6]).

The use of 3 equiv of Ar′Li per $AlCl_3$ unit resulted in the formation of the homoleptic compound Ar'_3Al (**8**) (Scheme 2). Unfortunately, it has not been possible to obtain crystals of **8** suitable for a single-crystal X-ray diffraction study. Moreover, the NMR data for **8** were not structurally diagnostic. We note, however, that the analogus complex $[o\text{-}(Me_2NCH_2)C_6H_4]_3Ga$ has an interesting five coordinate structure.[6]

Experimental Section

General Procedures. All experiments were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques. All solvents were dried over sodium and distilled from either sodium or sodium benzophenone ketyl under nitrogen prior to use. The reagent $C_{10}H_6NMe_2LiOEt_2$ was prepared according to literature methods.[15] All other reagents were purchased from Aldrich Chemicals and used without further purification. Physical measurements were made as follows: CI mass spectra were run on a Finnigan MAT TSQ-70 instrument with CH_4 at 2 Torr. NMR spectra were measured on a GE QE-300 spectrometer (^1H, 300.17 MHz; ^{13}C, 75.48 MHz). ^1H and ^{13}C NMR spectra were recorded at 298 K, and the chemical shifts were referenced to the deuterated solvent. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Synthesis of $(Me_2N)C_{10}H_6AlCl_2$ (1). A solution of $(Me_2N)C_{10}H_6\text{-}Li\cdot Et_2O$ (1.85 g, 7.36 mmol) in toluene (75 mL) was added via cannula to a stirred slurry of $AlCl_3$ (0.95 g., 7.12 mmol) in toluene (25 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight (12 h). The reaction mixture was then filtered to remove lithium chloride, and the solvent was removed under vacuum. The resulting residue was then redissolved in toluene (30 mL), and the volume of the solution was reduced under vacuum (10 mL). Cooling (−30 °C) afforded colorless crystals of **1**. Yield: 1.14 g, 60% (mp 162−166 °C). CIMS (CH_4): m/z 269 (M^+), 172 (ligand + 2H). ^1H NMR (C_6D_6/CD_3COCD_3): δ 2.72 (s, 6H, NMe_2), 7.25 (m, 3H, ring), 7.34 (d, ^3J = 6 Hz, 1H, ring), 7.47 (d, ^3J = 9 Hz, 1H, ring), 7.65 (dd,^3J = 6 Hz, ^4J = 2.5, 1H, ring). $^{13}C\{^1H\}$ NMR (C_6D_6/CD_3COCD_3): δ 45.72 (s, CH_3), 125.79 (s, CH), 126.70 (s, CH), 128.95 (s,CH), 135.10 (s, CH).

Synthesis of $(Me_2N)C_{10}H_6GaCl_2$ (2). A solution of $(Me_2N)C_{10}H_6\text{-}Li\cdot Et_2O$ (1.52 g, 6.05 mmol) in toluene (75 mL) was added via cannula to a stirred solution of $GaCl_3$ (1.00 g., 5.68 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. (12 h) The reaction mixture was then filtered to remove lithium chloride, and the solvent was removed under vacuum. The resulting residue was then redissolved in toluene (50 mL) and the volume reduced under vacuum (10 mL). Cooling (−30 °C) afforded colorless crystals of **2**. Yield: 1.28 g, 73% (mp 139−141 °C). Anal. Calcd for $(Me_2N)C_{10}H_6GaCl_2$: C, 46.37; H, 3.89; N, 4.51. Found: C, 46.32; H, 3.93; N, 4.50. CIMS (CH_4): m/z 310 (M^+), 276 (M^+ − Cl). ^1H NMR (C_6D_6/CD_3COCD_3): δ 2.29 (s, 6H, NMe_2), 6.51 (dd,^3J = 6 Hz, ^4J = 1.5 Hz, 1H, ring), 6.97 (t, ^3J = 7.5 Hz, 1H, ring), 7.20 (dd, ^3J = 9 Hz, ^4J = 6 Hz, 1H, ring), 7.37 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 1H, ring), 7.47 (dd, ^3J = 9 Hz, ^4J = 1.5 Hz, 1H, ring), 7.58 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 1H, ring). $^{13}C\{^1H\}$ NMR (C_6D_6/CD_3COCD_3): δ 49.81 (s, CH_3), 116.23 (s, CH), 125.36 (s, CH), 133.38 (s, CH), 134.12 (s, CH), 147.82 (s, CH).

Synthesis of $[(Me_2N)C_{10}H_6InCl_2]_2$ (3). A solution of $(Me_2N)C_{10}H_6\text{-}Li\cdot Et_2O$ (2.07 g, 8.24 mmol) in toluene (75 mL) was added via cannula to a stirred slurry of $InCl_3$ (1.75 g, 7.91 mmol) in THF (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight (12 h). The reaction mixture was then filtered to remove lithium chloride, and the solvent was removed under vacuum. The resulting residue was then redissolved in THF (30 mL) and the volume reduced under vacuum (10 mL). Cooling (−30 °C) afforded colorless crystals of **3**. Yield: 1.51 g, 54% (mp 190−200 °C (dec)). Anal. Calcd for $[(Me_2N)C_{10}H_6InCl_2]_2$: C, 40.49; H, 3.40; N, 3.93. Found: C, 38.85; H, 3.84; N, 3.40. CIMS (CH_4): m/z 355 (M^+, monomer), 320 (M^+ − Cl, monomer), 172 (ligand + 2H). ^1H NMR (C_6D_6): δ 2.91 (s, 6H, NMe_2), 7.57 (dd, ^3J = 15 Hz, ^4J = 6 Hz, 1H, ring), 7.73 (d, ^3J = 6 Hz, 2H, ring), 7.84 (d, ^3J = 9 Hz, 1H, ring), 7.95 (t, ^3J = 6 Hz, 2H, ring). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 49.53 (s, CH_3), 118.46 (s, CH), 126.49 (s, CH), 127.66 (s,CH), 127.98 (s, CH), 129.59 (s, CH), 134.82 (s, C), 136.54 (s, CH), 149.95 (s, C).

Synthesis of $[(Me_2N)C_{10}H_6AlH_2]_2$ (4). A solution of **2** (0.60 g, 2.23 mmol) in toluene (100 mL) was added via cannula to a stirred solution of $LiAlH_4$ (0.17 g, 4.48 mmol) in diethyl ether (50 mL) at −78 °C over a 1-h period. The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting white powder was redissolved in diethyl ether (50 mL), and the volume was reduced under vacuum (5 mL). Cooling (−30 °C) afforded colorless crystals of **4**. Yield: 0.29 g, 64%. CIMS (CH_4): m/z 397 (M^+, dimer), 198 (M^+, monomer). ^1H NMR (C_6D_6): δ 2.43 (s, 6H, NMe_2), 4.81 (bs, 2H, hydride), 6.77 (d, ^3J = 9 Hz, 1H, ring), 7.25 (m, 1H, ring), 7.45 (dd, ^3J = 9 Hz, ^4J = 6 Hz, 1H, ring), 7.57 (t, ^3J = 6 Hz, 1H, ring), 7.66 (d, ^3J = 6 Hz, 1H, ring), 8.15 (d, ^3J = 6 Hz, 1H, ring).$^{13}C\{^1H\}$ NMR (C_6D_6): δ 45.09 (s, CH_3), 114.48 (s, CH), 115.20 (s, C), 123.39 (s, C), 124.79 (s, CH), 126.05 (s, CH), 126.43 (s, CH), 128.92 (s, CH), 129.83 (s, CH), 136.21 (s, C).

Synthesis of $[(Me_2N)C_{10}H_6]_2AlCH_3$ (5). A solution of MeLi (8.1 mL of 0.516 M solution in Et_2O) was added to a stirred solution of **1** (0.56 g., 2.1 mmol) in toluene (150 mL) at −78 °C over a 30 min period. The solution was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting residue was then redissolved in diethyl ether (50 mL), and the volume was reduced under vacuum (5 mL). Cooling (−30 °C) afforded a 65% yield (0.52 g) of colorless crystals of **5** (mp 230−240 °C (dec)). Anal. Calcd for $((Me_2N)C_{10}H_6)_2\text{-}AlCH_3$: C, 78.60; H, 7.14; N, 7.33. Found: C, 78.05; H, 7.09; N, 7.30. CIMS (CH_4): m/z 383 (M^+), 367 ($M^+ - CH_4$), 212 ($M^+ - (Me_2N)\text{-}C_{10}H_6$), 172 ($(Me_2N)C_{10}H_6$). ^1H NMR (C_6D_6): δ −0.53 (s, 3 H, CH_3), 2.51 (s, 12H, NMe_2), 6.90 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 2H, ring), 7.25 (t, ^3J = 7.5 Hz, 2H, ring), 7.41 (dd, ^3J = 9 Hz, ^4J = 6 Hz, 2H, ring), 7.58 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 2H, ring), 7.67 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 2H, ring), 7.90 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 2H, ring). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6): δ 44.25 (s, NCH_3), 114.72 (s, CH), 123.48 (s, CH), 124.46 (s, C), 124.99 (s, CH), 125.61 (s, CH), 126.51 (s,CH), 129.02 (s, CH), 129.70 (s, C), 135.65 (s, C), 151.71 (s, C).

Synthesis of $[(Me_2N)C_{10}H_6]_2Al(t\text{-}Bu)$ (6). A solution of t-BuLi (3.4 mL of 1.7 M solution in pentane) was added to a stirred solution of **1** (0.75 g, 2.80 mmol) in toluene (150 mL) at −78 °C over a 30 min period. The reaction mixture was allowed to warm to room temperature and was stirred overnight (16 h). The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting white powder was redissolved in toluene (50 mL), and the volume was reduced under vacuum (5 mL). Cooling (−30 °C) afforded a 62% yield (0.74 g) of **6**. Anal. Calcd for $((Me_2N)C_{10}H_6)_2Al(t\text{-}Bu)$: C, 79.31; H, 7.86; N, 6.60. Found: C, 78.88; H, 7.67; N, 6.58. CIMS (CH_4): m/z 425 (M^+), 367 (M^+ − t-Bu), 254 ($M^+ - (Me_2N)C_{10}H_6$), 172 ($(Me_2N)C_{10}H_6$). ^1H NMR (C_6D_6): δ 1.12 (s, 9 H, t-Bu), 2.37 (s, 12 H, NMe_2), 6.81 (d, ^3J = 9 Hz, 2H, ring), 7.21 (d, ^3J = 6 Hz, 2H, ring), 7.58 (m, 4H, ring), 7.77 (d, ^3J = 9 Hz, 2H, ring), 8.33 (d, ^3J = 6 Hz, 2H, ring).

Synthesis of $[(Me_2N)C_{10}H_6]_2AlCl$ (7). A solution of $(Me_2N)C_{10}H_6\text{-}Li\cdot Et_2O$ (2.30 g, 9.15 mmol) in toluene (75 mL) was added via cannula to a stirred slurry of $AlCl_3$ (0.59 g., 4.43 mmol) in toluene (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight for 12 h. The mixture was then

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Table 2. Crystal Data and Details of Intensity Measurements and Structure Refinements for **1**−**4**

cryst data	**1**	**2**	**3**	**4**
formula	$C_{12}H_{12}AlCl_2N$	$C_{12}H_{12}Cl_2GaN$	$C_{24}H_{24}Cl_4In_2N_2$	$C_{24}H_{28}Al_2N_2$
fw	268.11	310.85	355.95	398.44
cryst dimens	0.29 × 0.30 × 0.34	0.10 × 0.54 × 0.76	0.35 × 0.44 × 0.76	0.44 × 0.22 × 0.19
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1/c$	$P2_1/c$
a (Å)	6.534(1)	6.552(2)	7.401(2)	13.343(2)
b (Å)	10.801(1)	10.833(2)	15.746(5)	11.228(2)
c (Å)	9.631(2)	9.601(2)	10.801(4)	7.505(1)
β (deg)	105.57(2)	106.05(2)	92.37(3)	100.64(1)
V (Å^3)	654.8(2)	654.9(3)	1257.6(7)	1105.0(4)
Z	2	2	2	2
μ (cm^{-1})	5.35	24.80	22.74	1.43
d(calce) (g cm^{-3})	1.360	1.576	1.880	1.197
F(000)	276	312	696	424
θ range (deg)	2.20−27.47	2.90−27.44	3.20−27.46	2.39−24.97
scan type	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
reflcns collcd	2177	2164	3774	2670
indepdt reflcns	1739	1730	2874	1938
R(int)	0.1231	0.1338	0.0436	
GOF on F^2	1.069	1.106	1.064	1.034
R1^a [$I > 2\sigma(I)$]	0.0453	0.0609	0.0712	0.0560
wR2^b	0.1011	0.1362	0.1377	0.1006
largest diff peak and hole (e A^{-3})	0.290 and −0.198	0.980 and −0.912^c	2.150 and −0.833^d	0.247 and −0.170

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = (\sum[w(F_o^2 - F_c^2)^2/\sum[wF_o^4])^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0470P)^2 + (0.0000P)]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$. ^{c} Found near Ga. ^{d} Found near In.

filtered, and the solvent was removed under vacuum. The resulting residue was then redissolved in toluene (35 mL) and filtered, and the volume was reduced under vacuum (10 mL). Cooling (−30 °C) afforded pale yellow crystals of **7**. Yield: 1.35 g, 76%. Anal. Calcd for $((Me_2N)C_{10}H_6)_2AlCl$: C, 71.68; H, 6.02; N, 6.96. Found: C, 71.23; H, 6.20; N, 7.00. CIMS (CH_4): *m/z* 403 (M^+), 367 ($M^+ - Cl$), 172 ($(Me_2N)C_{10}H_6$). ^{1}H NMR (C_6D_6): δ 2.05 (s, 3H, NMe_2), 7.30 (m, 2H, ring), 7.54 (d, ^3J = 9 Hz, 1H, ring), 7.65 (m, 1H, ring), 7.86 (d, ^3J = 6 Hz, 1H, ring), 8.19 (d, ^3J = 6 Hz, 1H, ring). ^{13}C{^{1}H} NMR (C_6D_6): δ 43.37 (s, *C*H$_3$), 114.48 (s, *C*H), 123.41 (s, *C*H), 124.78 (s, *C*), 125.41 (s, *C*H), 126.05 (s, *C*H), 126. 41 (s, *C*H), 128.79 (s, *C*H), 129.72 (s, *C*), 135.73 (s, *C*).

Synthesis of [(Me$_2$N)C$_{10}$H$_6$]$_3$Al (8). A solution of $(Me_2N)C_{10}H_6Li\cdot Et_2O$ (3.02 g, 12.02 mmol) in toluene (75 mL) was added via cannula to a stirred slurry of $AlCl_3$ (0.53 g., 3.97 mmol) in toluene (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight for 14 h. The reaction mixture was then filtered, and the solvent was removed under vacuum. The resulting residue was then redissolved in toluene (40 mL) and filtered, and the volume was reduced under vacuum (5 mL). Cooling (−30 °C) afforded a 57% yield (1.21 g) of pale white crystals of **8**. Anal. Calcd for $((Me_2N)C_{10}H_6)_2AlCl$: C, 80.41; H, 6.75; N, 7.81. Found: C, 79.93; H, 6.87; N, 7.80. CIMS (CH_4): *m/z* 538 (M^+), 566 ($M^+ + 2CH_2$), 172 ($(Me_2N)C_{10}H_6$). ^{1}H NMR (C_6D_6): δ 2.04 (s, 3H, NMe_2), 6.86 (dd, ^3J = 6 Hz, ^4J = 1.5 Hz, 1H, ring), 7.22 (t, ^3J = 6 Hz, 1H, ring), 7.36 (dd, ^3J = 9 Hz, ^4J = 6 Hz, 1H, ring), 7.55 (dd, ^3J = 9 Hz, ^4J = 1.5 Hz, 1H, ring), 7.65 (dd, ^3J = 9 Hz, ^4J = 1.5 Hz, 1H, ring), 8.20 (d, ^3J = 6 Hz, 1H, ring).^{13}C{^{1}H} NMR (C_6D_6): δ 45.19 (s, *C*H$_3$), 113.89 (s, *C*H), 122.84 (s, *C*H), 124.14 (s, *C*), 125.09 (s, *C*H), 125.66 (s, *C*H), 125.74 (s, *C*H), 128.30 (s, *C*H), 128.83 (s, *C*), 134.81 (s, *C*), 150.88 (s, *C*).

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **1**−**4** are given in Table 2. Crystals of **1** and **2** were grown from toluene solutions at −30 °C. Crystals of **3** were grown from a THF solution at −30 °C. Crystals of **4** were grown from a diethyl ether solution at −30 °C. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 25 °C using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the Siemens SHELXTL PLUS 5.0 (PC) software package.[14] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. In the cases of **1**−**3** all hydrogen atoms were placed in idealized positions and refined using the riding model with general isotropic temperature factors. In the case of **4**, all hydrogen atoms except for H(1AA) and H(1AB) were refined as described above. Hydrogen atoms H(1AA) and H(1AB) were located by difference Fourier maps and refined isotropically. The final values of the atomic positional parameters for **1**−**4** are available as Supporting Information.

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Supporting Information Available: Details of the X-ray structure determinations, in CIF format, of the structures of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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