4036 *Organometallics* **2000,** *19,* 4036−4042

New Types of Base-Stabilized Alkyl Aluminum, Gallium, and Indium Complexes

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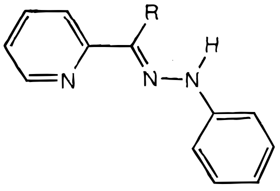
Received April 3, 2000

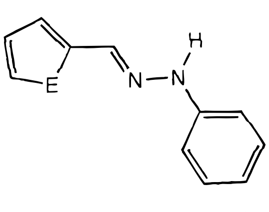
Novel dinuclear metal complexes with the general formula $[(Me_2M)\{NC_5H_4\,C(R)NNC_6H_5\}(MMe_3)]$ (M = Al, R = CH_3 (**1**); M = Ga, R = CH_3 (**2**); M = Al, R = H (**3**); M = Ga, R = H (**4**)) result when 2-pyridinecarboxaldehyde phenyl hydrazone ligands are mixed with trimethylaluminum and -gallium. The decagallium complex $(GaMe_2)_8(GaMe)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(C_{12}H_{10}N_3)_2$ (**5**) was isolated during the synthesis of **4** as a minor orange product. Three dinuclear metal compounds of the general formula $[(Me_2M)(SC_4H_3CHNNC_6H_5)]_2$ (M = Al (**6**); M = Ga (**7**); M = In (**8**)) were synthesized by the methane elimination reaction of thiophenecarboxaldehyde phenylhydrazone with trimethyl aluminum, -gallium, and -indium. The μ_4-oxo complex $[(Me_2In)_2(OC_4H_3CH\ NNC_6H_5)]_2O$ (**9**) was prepared via the reaction of furancarboxaldehyde phenylhydrazone with trimethylindium. The X-ray crystal structures of **1**, **4**, **5**, **7**, and **9** are described. The structural data revealed that **5** is a decanuclear gallium compound that contains an eight-membered Ga_4O_4 cyclic core and that **9** is a tetranuclear indium compound with a weak interaction between the pendant furan and the indium center.

Introduction

The chemistry of alkyl group 13 amido and imido compounds has recently attracted much attention due to the rich structural chemistry of this class of complexes and because of their possible applications in the preparation of ceramic materials.[1−3] Because of the efforts to investigate the assembly of the polynuclear group 13 organometallic complexes using polydentate amido and imido ligands, there has been a recent resurgence of interest in the preparation of the alkyl complexes of these elements. Polydentate amido and imido ligands not only can offer additional coordination sites but also may provide group 13 complexes with unusual structural features and chemical reactivities.[4] Recently, we prepared a series of di- and trinuclear group 13 heterocyclic carboxaldehyde thiosemicarbazone complexes[5,6] and trinuclear group 13 complexes of bis(thiosemicarbazone).[7,8] The coordination ability of the thiosemicarbazone was useful for the construction of polynuclear complexes with an uncommon coordination geometry. Motivated by an interest in the effects of ligand geometry on the coordination environments of the group 13 elements, we decided to investigate the coordination ability of 2-pyridinecarboxaldehyde phenyl hydrazone (L_1), which contains an amine N−H bond and two imine nitrogens. In addition, we were interested in conducting a systematic study of the use of possible terdentate ligands obtained by replacing the pyridine moiety with the thiophene (L_2) and furan (L_3) moieties. Our interest in preparing intramolecularly base-coordinated compounds of the group 13 elements focused on their hydrolysis. We also were interested to what extent alkyl species would coordinate additional ligands if the donor sites were constrained to lie close to or within the primary coordination sphere. As part of our continuing studies on the synthetic utility and understanding of complexes of these ligands with group 13 elements, we attempted to synthesize a variety of such complexes. We now report the synthesis and characterization of the group 13 complexes of 2-heterocyclic



L_1



E = S (L_2) , E = O (L_3)

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10.1021/om000285o CCC: $19.00
Publication on Web 08/25/2000

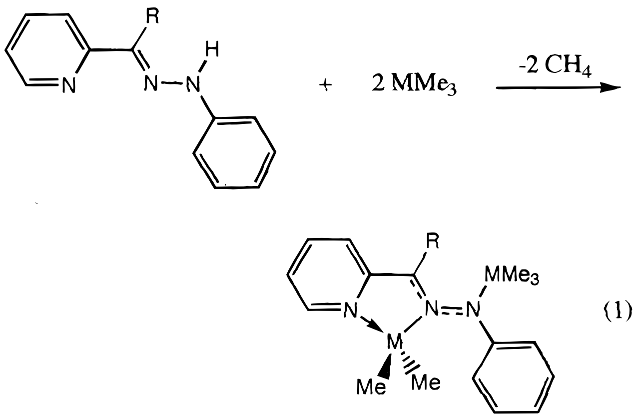
Table 1. Crystal Data of Compounds 1, 4, 5, 7, and 9

	1	**4**	**5**	**7**	**9**
empirical formula	$C_{18}H_{27}N_3Al_2$	$C_{17}H_{25}N_3Ga_2$	$C_{40}H_{68}N_6O_6Ga_{10}$	$C_{26}H_{30}N_4S_2Ga_2$	$C_{30}H_{42}N_4O_3In_4$
molecular wt	339.39	410.82	1426.25	600.08	965.96
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pnma*	*P*21/*n*	*P*21/*n*	*P*21/*n*
a, Å	7.9844(4)	19.9100(8)	13.5489(14)	15.996	15.670
b, Å	8.5123(6)	9.6473(15)	12.5542(13)	17.768	11.927
c, Å	15.995(2)	10.461(4)	16.545(2)	9.879	20.017
α, deg	86.262(9)				
β, deg	76.753(6)	92.169(9)	100.07	103.66	
γ, deg	81(47)				
V, Å	1043.97(16)	2009.4(7)	2811.3(5)	2764.5	3635.4
Z	2	8	4	4	4
d_{calc}, g cm^{-3}	1.080	1.358	1.685	1.442	1.765
F(000)	364	840	1416	1224	1880
abs coeff, mm^{-1}	0.142	2.681	4.753	2.121	2.538
λ, Å^3	0.71070	0.71070	0.71070	0.71070	0.71070
cryst dimens, mm	0.3 × 0.3 × 0.35	0.4 × 0.4 × 0.5	0.6 × 0.5 × 0.5	0.3 × 0.4 × 0.4	0.5 × 0.5 × 0.4
θ_{max}, deg	25.97	25.97	25.97	25.21	25.97
no. of reflns measd	4273	1947	5298	5186	7381
no. of obsd reflns	4040	1947	5102	4858	7136
no. vars	223	146	297	323	392
R	0.0513	0.0452	0.0398	0.0535	0.0436
R_w	0.1425	0.0816	0.0954	0.1200	0.1131
goodness of fit	0.997	0.944	0.510	0.858	0.446

carboxaldehyde phenylhydrazone and the single-crystal X-ray structures of five of them.

Results and Discussion

The reaction of 2-pyridinecarboxaldehyde phenylhydrazone with trimethyl aluminum or -gallium in toluene at room temperature affords the corresponding dinuclear aluminum and gallium complexes, in which one hydrogen atom has been lost from the aza hydrogen atom via the methane elimination reaction (eq 1). The resulting red products **1**−**4** were isolated as air-sensitive, crystalline solids in high yield. Compounds **1**−**4** are soluble in toluene, THF, and dichloromethane and were characterized by ^{1}H, ^{13}C, and ^{27}Al NMR, mass spectroscopy, and elemental analysis. The structures of **1** and **4** were determined by single-crystal X-ray diffraction. The initial indication of the dinuclear formulation for **1** stemmed from the observation of a parent ion in the mass spectrum at *m*/*z* 339, followed by a series of fragmentations attributable to the loss of Me groups. The ^{1}H NMR spectrum of **1** contains two resonances at 0.56 and 0.01 ppm assigned to two kinds of methyl groups in the aluminum moieties in a 9:6 ratio. The ^{13}C NMR spectrum shows two signals (9.25 and −0.03 ppm) due to the Al(1)−CH_3 and Al(2)−CH_3 groups, respectively. The carbon (C(6)) attached to the imine group appears at 148.89 ppm in the ^{13}C NMR spectrum. The ^{27}Al NMR spectrum of **1** at room temperature shows two broad resonances at 152 and 138 ppm. The resonance at 138 ppm is assigned to the four-coordinate Al(1) in an N_2AlC_2 coordination environment, which is characteristic of a four-coordinate Al atom when compared to the shift in complexes of type $[R_2AlR'_2]_2$ (R = Me, Et; R′ = NEt_2, OMe, OEt).[9] The 152 ppm resonance is assigned to the four-coordinate Al(2). The structures of **2**−**4**, as deduced from the ^{1}H and ^{13}C NMR data and elemental analyses, are similar to that of **1**. Although all the spectra are consistent with the proposed formulation, the bonding mode of C(6)−N(2)−N(3) in **1** still was unclear because it could involve tautomerism, i.e., a 1,2-proton shift. Accordingly, the dinuclear nature and the bonding mode of the aluminum and gallium centers for both **1** and **4** have been confirmed through single-crystal X-ray diffraction analyses.



R = CH_3, M = Al (**1**) ; R = CH_3, M =Ga (**2**)

R = H, M = Al (**3**) ; R = H, M = Ga (**4**)

Description of the Molecular Structure of 1. Compound **1** crystallizes in the space group $P\bar{1}$ with two molecules per unit cell. A summary of the data collection and crystallographic parameters is given in Table 1. An ORTEP diagram of the solid-state structure with selected bond lengths and angles is shown in Figure 1. No symmetric element can be present in this structure. Compound **1** contains two types of methylaluminum fragments. Two aluminum atoms, Al(1) and Al(2), have the usual four-coordinate tetrahedral organoaluminum coordination. The Al(1) atom is coordinated by two chelated nitrogen atoms. The dinuclear aluminum compound in **1**, formed by removing one hydrogen atom from the amine N−H, may be attributed to the strong

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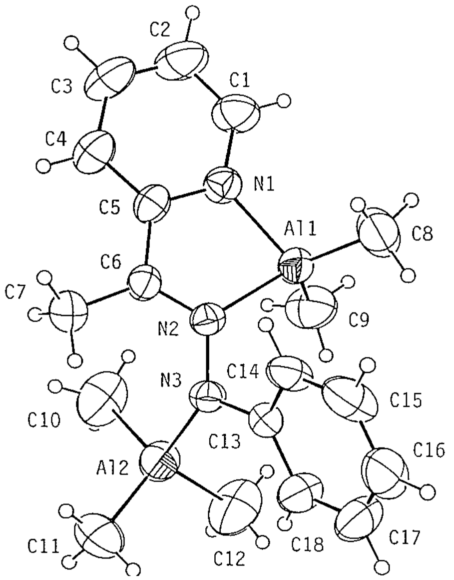
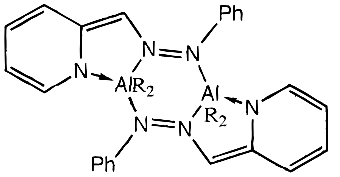


Figure 1. X-ray crystal structure of **1** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): Al(1)−(1) 2.00(2). Al(1)−N(2) 1.97(5), Al(2)−N(3) 1.97(15), C(6)−N(2) 1.30(4), N(2)−N(3) 1.40(4), N(3)−C(13) 1.42(2), Al(1)−C(8) 1.93(8), Al(1)−N(9) 1.90(6), N(1)−Al(1)−N(2) 81.09(10), C(6)−N(2)−N(3) 120.04(4), N(2)−N(3)−C(13) 111.04(1).

tendency to form a stable four-coordinate configuration. The pyridyl Al(1)−N(1) distance (2.00(2) Å) is slightly longer than the amido Al(1)−N(2) distance (1.97(5) Å), a feature consistent with the literature.[10] The Al(2)−N(3) bond distance (1.97(15) Å) is within the range observed for amine adducts of $AlMe_3$ (1.88−2.09 Å).[11]

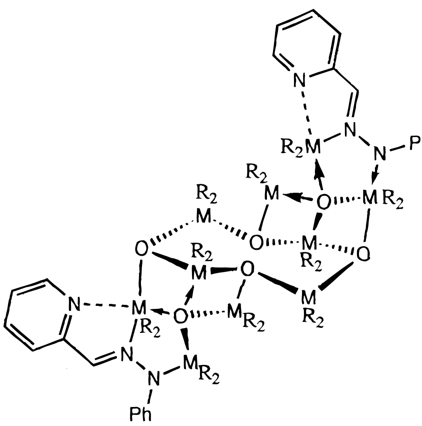
Initially we expected the product to be an N,N-bridged dimeric aluminum complex **A**. Shearer and co-workers[12] reported that the reaction of the pyridine-2-carbaldehyde oxime, $2\text{-}C_5H_4NCH{=}NOH$, with the trimethyls MMe_3 (M = Al, Ga, In), formed the dinuclear complex $[MMe_2\ (ON{=}CHC_5H_4N)]$ similar to type A. The imine C(6)−N(2) bond length (1.30(4) Å)[13] and N(2)−N(3) bond lengths (1.40(4) Å)[14] within the hydrazone core are intermediate between those of single and double bonds; consistent with the delocalization of the C⋯N⋯N π-bond. The change in bond distances for the hydrazone group [C(6)N(2)N(3)] indicates that metalation shifts the N(3)−N(2) toward its amine N(2)−H form, and bond multiplicity shifts from C(6)−N(2) toward N(2)−N(3) probably due to the displacement of the π-charge. Compound **4** has a structure similar to that of **1**. The structures of **1** and **4** show no unusual behavior. They contain two types of metal MMe_2 group chelated by the ligand and an MMe_3 group coordinated to a nitrogen atom in the ligand.



R = Me

A

Synthesis and Characterization of $(GaMe_2)_8(GaMe)_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(C_{12}H_{10}N_3)_2$ (5). Compound **5** was initially isolated in the synthesis of **4** as a minor yellow product. Thus, the addition of 5 equiv of $GaMe_3$ to a toluene solution of 2-pyridinecarboxaldehyde phenylhydrazone at 25 °C resulted in formation of a mixture of products from which compounds **4** and **5** could be separated by fractional crystallizations as the major and minor isolated products, respectively, in 19:1 ratio in ca. 88% yield. Complex **5** is a yellow crystalline solid at room temperature, soluble in benzene, toluene, and THF.



R = Me, M = Ga

5

The decanuclear gallium compounds were fully characterized by NMR spectroscopy, single-crystal X-ray diffraction, and elemental analyses. Five singlets (0.30, 0.16, 0.03, −0.11, −0.44 ppm) in the ^1H NMR spectrum and five singlets (0.46, −2.75, −3.24, −4.58, −4.93 ppm) in the ^{13}C NMR spectrum of **5** assigned to the methyl group on the gallium atoms demonstrate that the five methyl groups are not chemically equivalent. As the structure of the product cannot be deduced on the basis of the spectroscopic data, a single-crystal X-ray diffraction study was undertaken. The molecular structure is shown in Figure 2. An alternative view of the basic skeleton of the complex is shown in Figure 3. Crystallographic data are given in Table 1, with selected bond lengths and angles in Table 2. To our surprise, the X-ray study of **5** showed it to be the decanuclear gallium complex. The molecular structure of **5** has an inversion center. The structure consists of an eight-membered Ga_4O_4 cyclic core. The first such ring compound was reported by Hoard et al.,[15] and similar ring structures

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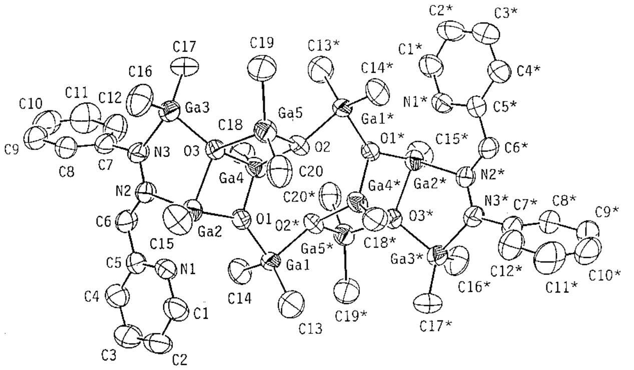


Figure 2. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 50% probability level.

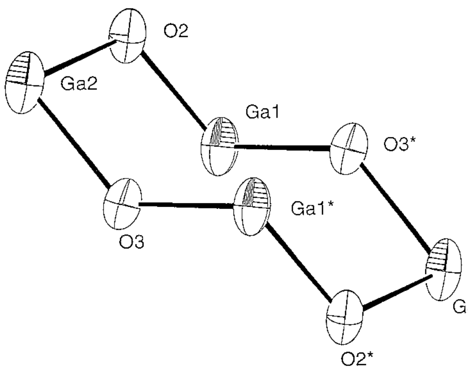
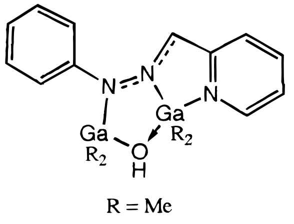


Figure 3. Illustration of the central Ga_4O_4 cyclic core for **5**.

with sulfur have been described for several metal sulfur derivatives.[16] The eight-membered ring in **5** adopts a chairlike conformation (Figure 3). Similar chairlike conformations have been observed for the gallium diphenyl phosphinate compounds $[R_2Ga(\mu\text{-}O_2PPh_2)]_2$.[17] The interesting feature of the molecular structure of **5** is the presence of two unusual five-coordinate gallium centers,[18] Ga(2) and Ga(2)*, and eight four-coordinate gallium environments. The environment about the five-coordinate Ga(2) and Ga(2)* may be described as a distorted trigonal bipyramid in which N(1) and O(3) occupy the axial positions, i.e., N(1)−Ga(2)−O(3) 157.14(3)°. The eight gallium atoms have an approximate tetrahedral configuration. The Ga−O distances are of two types, those (1.850(6)−1.903 (5) Å) for the μ_3-oxide bridges and those (1.928(6)−2.094(6) Å) for the μ_4-oxo bridges. The μ_3-oxo ligand bridges three aluminum centers with an approximate pyramidal geometry. A similar bonding mode of the μ_3-oxo ligand has been reported in the di-2-pyridylamido complex $[Al_4(CH_3)_6(\mu_3\text{-}O)_2(dpa)_2]$,[4b] the cube complex $Ga_8(pz)_{12}O_4Cl_4{\cdot}2thf$,[19] and the galloxane complex $[Ga_{12}{}^tBu_{12}(\mu_3\text{-}O)_8(\mu\text{-}O)_2(\mu\text{-}OH)_4]$.[20] The oxygen atoms O(3) and O(3)* have a tetrahedral geometry and bridge four gallium atoms with nearly equal Ga−O(3) bond lengths. The Ga−O bond lengths are in the normal range of the known Ga−O bond lengths.[21] The lengths and angles within the ligand unit are indicative of delocalization through the C(6)−N(2)−N(3) bonds.

The formation of compound **5** raises the following question. What is the source of the oxygen atoms? A possible solution is that traces of water in the solvent entered the system, resulting in oxygen incorporation. To generate the complex **5**, in an independent experiment, we carried out the controlled hydrolysis of a mixture of 2-pyridinecarboxaldehyde phenylhydrazone, $GaMe_3$, and H_2O in 1:5:3 ratio in toluene at −20 °C. The ^1H and ^{13}C NMR analyses of the yellow powder that was produced were identical to those of **5**.

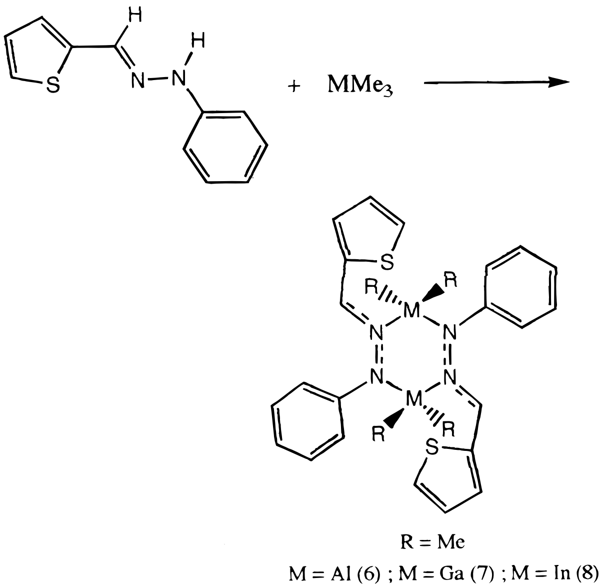
A reasonable mechanism for the formation of **5** involves the initial hydrolysis of $GaMe_3$ coordinated to the nitrogen atom of **4**, leading to intermediate **B**, followed by the attack of $GaMe_3$ and H_2O.



B

Synthesis and Characterization of $[(Me_2M)(SC_4H_3\ CHNNC_6H_5)]_2$ (M = Al, Ga, In).

The orange crystalline compounds **6**−**8** were prepared via the methane elimination reaction of 2-thiophenecarboxaldehyde phenylhydrazone with trimethylaluminum, trimethylgallium, and trimethylindium in toluene, as shown in eq 2. Compounds **6**−**8** are soluble in toluene and THF and were characterized by ^1H and ^{13}C NMR and mass spectroscopy and elemental analysis. Although no parent ion was observed in the mass spectrum of **6** at *m/e* 517, the presence of fragmentation ($M^+{-}CH_3$ = 502 amu) confirmed the dimeric nature of **6**. To determine the extent to which a sulfur atom in a pendent arm is coordinated to the group 13 element



(2)

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Table 2. Selected Bond Distances [Å] and Angles [deg] for 5 and 9

		5			
N(2)−N(3)	1.336(9)	N(3)−Ga(3)	1.983(7)	Ga(3)−O(3)	1.928(6)
O(3)−Ga(4)	2.024(6)	Ga(4)−O(1)	1.858(6)	Ga(4)−O(2)	1.852(5)
Ga(5)−O(3)	1.996(6)	Ga(5)−O(2)	1.940(6)	N(2)−C(6)	1.300(10)
Ga(2)−N(1)	2.180(7)				
O(2*)−Ga(1)−O(1)	90.7(2)	O(1)−Ga(4)−O(2)	109.9(3)	O(1)−Ga(2)−N(2)	109.6(3)
Ga(2)−N(2)−N(3)	119.1(5)	N(3)−Ga(3)−O(3)	91.5(3)	O(2)−Ga(5)−O(3))	85.6(2)
O(2)−Ga(4)−O(3)	87.1(2)	Ga(2)−O(1)−Ga(4)	103.6(3)	Ga(2)−O(3)−Ga(4)	90.1(2)
Ga(4)−O(3)−Ga(5)	89.9(2)				
		9			
In(1)−O(1)	2.182(7)	In(1)−N(1)	2.318(8)	N(1)−C(5)	1.300(13)
N(1)−N(2)	1.349(11)	N(2)−In(2)	2.154(8)	In(2)−O(1)	2.229(6)
O(1)−In(1′)	2.186(6)	In(1′)−N(1′)	2.300(8)	N(1′)−N(2′)	1.379(1)
In(2′)−O(1)	2.189(6)	N(1′)−C(5′)	1.286(12)		
O(1)−In(1)−N(1)	92.9(3)	In(1)−N(1)−N(2)	111.0(6)	N(1)−N(2)−In(2)	117.4(6)
N(2)−In(2)−O(1)	88.4(3)	In(1)−O(1)−In(2)	103.4(3)	In(1′)−O(1)−In(2′)	105.0(3)
O(1)−In(2′)−N(2′)	91.0(3)	In(2′)−N(2′)−N(1′)	116.1(6)	N(2′)−N(1′)-In(1′)	114.4(6)

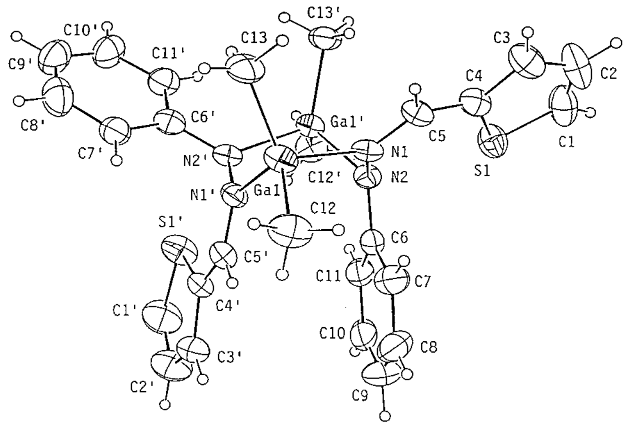

Figure 4. X-ray crystal structure of **1** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): N(1)−N(2) 1.422(9). N(1)−C(5) 1.296(11), Ga(1′)−N(2) 1.985(7), Ga(1)−N(1) 2.040(8), Ga(1)−N(1′) 2.023(7), N(1′)−N(2′) 1.422(9), Ga(1′)−N(2′) 1.991(7), N(1)−Ga(1)−N(1′) 89.5(3), N(2)−Ga(1′)−N(2′) 94.7(3).

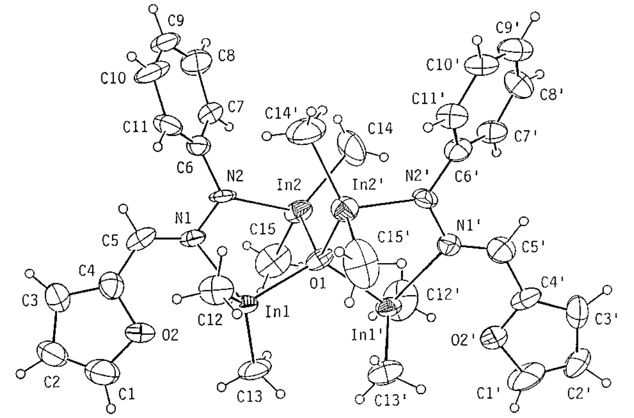

Figure 5. ORTEP drawing of **9**. Thermal ellipsoids are drawn at the 30% probability level.

centers, the ^{1}H NMR spectra of **6** were measured in CD_2Cl_2 at temperatures ranging from room temperature to −60 °C. In the ^{1}H NMR spectrum of the aluminum dimer **6** at room temperature two signals at 0.19 and −0.08 ppm in the methyl region were observed; these signals persisted down to −60 °C, and the chemical shift values did not vary significantly. The equivalence of the values suggests that the aluminum dimer **6** adopts the same configuration in solution and in the solid. Confirmation of the dinuclear structure of **6** was provided by X-ray crystallography.

The molecular sturcture of **7** is shown in Figure 5. The solid-state structure of **7** comprises an individual molecule, and there are no unusually short intermolecular contacts between the monomeric units. The molecule consists of a six-membered Ga_2N_4 cyclic core. The coordination sphere of Ga(1) consists of a distorted tetrahedral configuration. The six-membered skeleton is very similar to that found in the related In(−N−N−)$_2$In core of the dimeric molecule.[22] The six-membereddigalla cycle Ga(1)−N(1)−N(2)−Ga(1)′−N(2)′−N(1)′ has a tilted butterfly shape around its Ga(1)−Ga(1)′ hinge. The imine Ga(1)−N(1) distance (2.040 (8) Å) is slightly longer than the amido Ga(1)−N(1)′ distance (2.023 (7) Å), a feature consistent with that reported in the literature.[6]

The next question arises as to which effect is the most influential one in affording the different configuration in the reaction of 2-pyridinecarboxaldehyde and thiophenecarboxaldehyde phenylhydrazone with trimethylgallium. Nitrogen is a stronger Lewis base toward gallium than sulfur. Thus, the Ga−N bonding interaction would be more extensive than the Ga−S interaction. Consequently, the easy formation of the five-membered chelate compound with an N,N-coordination mode may lead to the stable dimeric structure of **2**. On the other hand, the reaction of 2-thiophenecarboxaldehyde phenylhydrazone with trimethylgallium afforded the cyclic, four-coordinated compound by an intermolecular coordination of nitrogen because the Ga···S contact between the pendent thiophene appears to be absent. Therefore, any association between the pendent donor atom and gallium may be the most important factor in determining the geometric configuration.

Synthesis and Characterization of [$(Me_2In)_2(OC_4H_3CHNNC_6H_5)]_2(\mu_4\text{-}O)$ (9). The 2-furancarboxaldehyde phenylhydrazone complex of trimethylindium was synthesized using the same procedure as described for **1**. Since there were no sources of oxygen available in the original synthesis of **9**, we postulated that the

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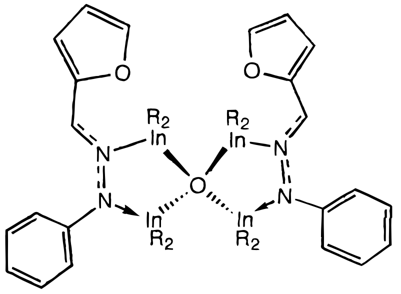
oxygen atom was produced by the reaction of the methyl group of indium with a trace of H_2O present in the reaction medium. In fact, when the reaction was carried out in the presence of 0.5 equiv of H_2O in toluene at −20 °C, it was converted into **9** in 30% yield after 12 h.



R = Me

9

Complex **9** is an orange crystalline solid that is soluble in benzene, toluene, and THF. Satisfactory elemental data were obtained for the complex. The ^1H and ^{13}C NMR spectra of **9** at 25 °C show two resonances for the methyl groups, indicating that compound **9** is fluxional in solution at that temperature. At lower temperature, −35 °C, the ^1H NMR spectrum in CD_2Cl_2 revealed two resonances at 0.08 ppm (broad, two overlapping signals) and −0.12 ppm (broad, two overlapping signals), demonstrating the presence of the methyl groups in different environments. Since these data were insufficient to unambiguously determine the structure of the molecule, an X-ray study was carried out. The molecular structure of **9** is shown in Figure 5. Compound **9** crystallizes in the space group $P2_1/n$ with four molecules per unit cell. Compound **9** contains four indium atoms. The ligand binds to two indium centers through the imido and amido sites. The oxo ligand, produced by the reaction of one H_2O with two methyl groups of the indium complexes, bridges four indium centers with an approximate tetrahedral geometry. A similar bonding mode for the μ_4-oxo ligand has been reported in the complex $[InMe(OH)(O_2PPh_2)]_4{\cdot}py_4$.[23] The In−O bond lengths (2.182(7)−2.229(6) Å) are in the normal range of the known In−O bond lengths.[24] In the previous crystal structure of **7**, any association in the solid via Ga···S interactions is likely to be weak. Oxygen is a stronger Lewis base toward indium than sulfur. Thus, the Ga−O bond interaction would be more extensive. The In(1)···O(2) contact (2.239 Å) appears to be strong, having a bond length greater than that normally seen for In−O dative bonds. The In···O vector lies approximately trans to the In(1)−O(1) bond, with an O···In−O angle of 159.2(3)°. If this subsidiary In···O interaction is included, the overall geometry at indium is that of a distorted trigonal bipyramid. Such interactions have been observed in group 13 compounds.[25] The amido In(2)−N(2) bond distance (2.154 (8) Å) is slightly shorter than the imine In(1)−N(1) bond distance (2.318 (8) Å), indicating that the negatively charged amido nitrogen atom is a stronger donor to the indium center than the neutral imine nitrogen atom. The In−N bond distance compared well with those in diphenyltriazene complex $[InMe_2(dpt)(3,5\text{-}Me_2py)]$ (2.153(6)−2.430(4) Å)[26] and indium benzylaminopyridine complex $[In\{2\text{-}[N\text{-}(CH_2C_6H_5)\ NC_5H_4\}_2\ Me$ (2.146(2)−2.349(2) Å].[27]

Summary

The nine new compounds described here expand upon the few examples of well-characterized aluminum, gallium, and indium compounds of heterocyclic carboxaldehyde phenylhydrazones. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The multidentate heterocyclic carboxaldehyde phenylhydrazones are valuable for the synthesis of new polynuclear alkylaluminum, -gallium, and -indium compounds with different coordination environments. The different bonding modes may be attributable to the difference in the M−N, M−O, and M−S contacts between the pendent moieties and the metal. When the pendent nitrogen was strongly coordinated to the aluminum and gallium, the dimeric compounds such as **1**−**4** were formed. However, when there is substantially no interaction between the pendent thiophene and the group 13 compounds, the tetrahedral configuration of the MN_2C_2 type by an intermolecular coordination is more favored. On the other hand, when the subsidiary M−O interaction is included and the large metal such as indium is involved, the most stable configuration at the indium is that of a distorted trigonal bipyramid. These ligands also display complicated bonding modes which require further investigation in order to be understood.

Experimental Section

All experiments were performed in a dry nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene and hexane were distilled from sodium benzophenone ketyl. All the ^1H, ^{13}C, and ^{27}Al NMR spectra were recorded on a Varian Gemini 200 spectrometer. Chemical shifts were referenced relative to either TMS (^1H) or benzene-d_6 (^1H, δ 7.155; $^{13}C\{^1H\}$, δ 128.00), while ^{27}Al NMR spectra were referenced relative to $Al(H_2O)_6^{3+}$. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Mass spectra were recorded on a high-resolution VG70-VSEG instrument, and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. $AlMe_3$, $GaMe_3$, and $InMe_3$ were purchased from Strem Chemicals. Pyridinecarboxaldehyde, thiophenecarboxaldehyde, furancarboxaldehyde, and phenylhydrazine were purchased from Aldrich Chemical. The heterocyclic carboxaldehyde phenylhydrazones were prepared from the condensation reaction of heterocyclic-2-carboxaldehyde and phenylhydrazine according to published procedures or slight adaptations thereof.[28]

General Synthesis of $(Me_2M)[NC_5H_4C(R)NNC_6H_5]$-$(MMe_3)$. In a typical synthesis, a solution of 2-acetylpyridine phenylhydrazone (0.21 g, 1 mmol) in toluene (10 mL) was treated with $AlMe_3$ (0.48 mL, 5 mmol) in toluene (10 mL) at room temperature. The color of the mixture immediately changed from yellow to blackish red. The solution was stirred

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for 12 h at that temperature and then decanted. The solution was layered with hexane (5 mL) and stored at −15 °C for 2 days, whereupon red crystals formed in 80−86% yield.

$(Me_2Al)[NC_5H_4C(CH_3)NNC_6H_5](AlMe_3)$ (1). Mp: 101−104 °C. ^{1}H NMR (C_6D_6): δ 8.22−6.61 (m, 9H, *Py* and *Ph*), 2.03 (s, 3H, CCH_3), 0.56 (s, 9H, AlCH_3), 0.01 (s, 6H, AlCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 148.89(*C*(CH_3)N), 136.37, 129.50, 129.18, 128.53, 127.44, 127.40, 126.55, 123.18, 122.19, 121.37, 113.78 (*Py* and *Ph*), 25.48 (CCH_3), 9.25 (AlCH_3), −0.03(AlCH_3). ^{27}Al NMR: δ 152, 138. MS(EI): *m/z* 339 (M^+). Anal. Calcd for $C_{18}H_{27}N_3Al_2$: C, 63.70; H, 8.02. Found: C, 63.33; H, 7.84.

$(Me_2Ga)[NC_5H_4C(CH_3)NNC_6H_5](GaMe_3)$ (2). Yield: 83%. Mp: 108−112 °C. ^{1}H NMR (C_6D_6): δ 8.08−6.64 (m, 9H, *Py* and *Ph*), 2.02 (s, 3H, CCH_3), 0.30 (s, 9H, GaCH_3), 0.15 (s, 6H, GaCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 144.63 (*C*(CH_3)N), 141.33, 138.56, 0.131.64, 0.129.11, 125.60, 124.17, 123.71, 118.21, 116.83, 115.90, 109.81 (*Py* and *Ph*), 27.93 (CCH_3), 5.26 (GaCH_3), 0.14 (GaCH_3). MS(EI): *m/z* 429 (M^+). Anal. Calcd for $C_{18}H_{27}N_3Ga_2$: C, 50.88; H, 6.41. Found: C, 50.41; H, 6.28.

$(Me_2Al)[NC_5H_4CHNNC_6H_5](AlMe_3)$ (3). Yield: 82%. Mp: 101−102 °C. ^{1}H NMR (C_6D_6): δ 8.18−6.58 (m, 9H, *Py* and *Ph*), 3.58 (s, 1H, C*H*), −0.09 (s, 9H, AlCH_3), −0.79 (s, 6H, AlCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 149.22 (H*C*=N), 143.56, 141.42, 130.45, 129.37, 128.48, 128.28, 127.52, 126.90, 125.26, 120.79, 120.42 (*Py* and *Ph*), 3.11 (AlCH_3), −8.76 (AlCH_3). ^{27}Al NMR: δ 150, 136. MS(EI): *m/z* 325 (M^+). Anal. Calcd for $C_{17}H_{25}N_3Al_2$: C, 62.76; H, 7.75. Found: C, 63.04; H, 7.96.

$(Me_2Ga)[NC_5H_4CHNNC_6H_5](GaMe_3)$ (4). Yield: 86%. Mp: 105−108 °C. ^{1}H NMR (C_6D_6): δ 8.08−6.62 (m, 9H, *Py* and *Ph*), 3.49 (s, 1H, C*H*), 0.23 (s, 9H, GaCH_3), −0.39 (s, 6H GaCH_3), ^{13}C{^{1}H} NMR (C_6D_6): δ 148.22 (H*C*=N), 143.29, 139.96, 129.40, 128.99, 128.47, 128.27, 127.50, 126.54, 126.27, 122.50, 120.43 (*Py* and *Ph*), 1.37 (GaCH_3), −4.29 (GaCH_3). MS (EI): *m/z* 411 (M^+). Anal. Calcd for $C_{17}H_{25}N_3Ga_2$: C, 49.70; H, 6.13. Found: C, 50.14; H, 6.32.

$[(Me_2Ga)_3(NC_5H_4CHNNC_6H_5)(GaMe_2)_2]_2(\mu_3\text{-}O)_4(\mu_4\text{-}O)_2$ (5). A solution of 2-pyridinecarboxaldeyhde phenylhydrazone (0.25 g, 0.61 mmol) in toluene (10 mL) was treated with $GaMe_3$ (0.18 mL, 1.82 mmol) in toluene (5 mL) at room temperature. The solution was cooled to −30 °C, whereupon degassed H_2O (0.032 mL, 1.82 mmol) was slowly added. The reaction mixture was stirred for 1 h at −30 °C and then warmed to room temperature. The solution was layered with hexane (5 mL) and stored at −15 °C for 2 days, whereupon a yellow powder formed in 42% yield. Mp: 148−152 °C. ^{1}H NMR (C_6D_6): δ 7.92−6.58 (m, 18H, *Py* and *Ph*), 3.08 (s, 2H, C*H*), 0.30 (s, 12H, GaCH_3), 0.16 (s, 12H GaCH_3), 0.03 (s, 6H GaCH_3), −0.11 (s, 12H GaCH_3), −0.44 (s, 6H GaCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 147.72 (H*C*=N), 140.64, 137.83, 129.58, 128.50, 128.30, 127.53, 126.30, 125.63, 122.76, 121.05, 113.73 (*Py* and *Ph*), 0.46 (GaCH_3), −2.75 (GaCH_3). −3.24 (GaCH_3), −4.58(GaCH_3), −4.93(GaCH_3). Anal. Calcd for $C_{40}H_{68}N_6O_6Ga_{10}$: C, 33.69; H, 4.81. Found: C, 33.32; H, 4.58.

$[(Me_2Al)(SC_4H_3CHNNC_6H_5)]_2$ (6). Compound **6** was prepared using the same procedure as described for **1** from thiophenecarboxaldehyde phenlyhydrazone (0.20 g, 1 mmol) and trimethylaluminum (0.48 mL, 5 mmol) in 63% yield. Mp: 132−136 °C. ^{1}H NMR (C_6D_6): δ 7.94−6.55 (m, 16H, *Th* and *Ph*), 3.14 (s, 2H, C*H*), 0.16 (s, 6H, AlCH_3), −0.13 (s, 6H AlCH_3), ^{13}C{^{1}H} NMR (C_6D_6): δ 144.89 (H*C*=N), 141.24, 132.16, 129.51, 128.32, 127.68, 127.12, 126.07, 125.88, 120.38, 113.10 (*Th* and *Ph*), −1.34 (AlCH_3), −2.64 (AlCH_3). ^{27}Al NMR: δ 146. MS (EI): *m/z* 502 ($M^+ - CH_3$). Anal. Calcd for $C_{26}H_{30}N_4S_2Al_2$: C, 60.45; H, 5.85. Found: C, 60.86; H, 5.98.

$[(Me_2Ga)(SC_4H_3CHNNC_6H_5)]_2$ (7). Yield: 54%. Mp: 138−140 °C. ^{1}H NMR (C_6D_6): δ 7.95−6.25 (m, 16H, *Th* and *Ph*), 3.20 (s, 2H, C*H*), 0.29 (s, 6H, GaCH_3), 0.05 (s, 6H GaCH_3), ^{13}C{^{1}H} NMR (C_6D_6): δ 145.27 (H*C*=N), 141.23, 132.22, 129.51, 128.33, 127.16, 126.13, 121.26, 120.35, 114.08, 113.10 (*Th* and *Ph*), −0.14 (GaCH_3), −1.68 (GaCH_3). MS (EI): *m/z* 602 (M^+). Anal. Calcd for $C_{26}H_{30}N_4S_2Ga_2$: C, 51.86; H, 5.02. Found: C, 51.42; H, 4.94.

$[(Me_2In)(SC_4H_3CHNNC_6H_5)]_2$ (8). Yield: 34%. Mp: 152−154 °C. ^{1}H NMR (C_6D_6): δ 7.82−6.62 (m, 16H, *Th* and *Ph*), 3.06 (s, 2H, C*H*), 0.16 (s, 6H, InCH_3), −0.98 (s, 6H InCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 145.92 (H*C*=N), 140.94. 137.24. 130.27. 128.23. 124.03. 122.13. 121.89. 116.39. 110.11. 109.13 (*Th* and *Ph*), −0.64 (InCH_3), −2.82 (InCH_3). MS (EI): *m/z* 692 (M^+). Anal. Calcd for $C_{26}H_{30}N_4S_2In_2$: C, 45.10; H, 4.37. Found: C, 44.76; H, 4.18.

$[(Me_2In)(OC_4H_3CHNNC_6H_5)]_2O$ (9). Compound **9** was prepared using the same procedure as described for **1** from 2-furaldehyde phenylhydrazone (0.09 g, 0.5 mmol) and trimethylindium (0.24 g, 1.5 mmol) in 30% yield. Mp: 154−156 °C. ^{1}H NMR (C_6D_6): δ 7.62−6.48 (m, 16H, *Fu* and *Ph*), 3.12 (s, 2H, C*H*), −0.06 (s, 12H, InCH_3), −0.09 (s, 12H InCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 142.76 (H*C*=N), 129.63, 129.54, 128.55, 128.35, 127.78, 127.58, 120.41, 113.15, 111.87, 108.34 (*Fu* and *Ph*), 3.44 (InCH_3), −1.28 (InCH_3). MS (EI): *m/z* 966 (M^+). Anal. Calcd for $C_{30}H_{42}N_4O_3In_4$: C, 37.30; H, 4.38. Found: C, 37.68; H, 4.52.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **1**, **4**, **5**, **7**, and **9** are given in Table 1. Crystals of **1**, **4**, **5**, **7**, and **9** suitable for X-ray diffraction were obtained from toluene/hexane. For the room-temperature X-ray examination and data collection, each crystal was coated with a light film of epoxy resin and mounted on a glass fiber. Intensity data for **1**, **4**, **5**, **7**, and **9** were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonious CAD-4 diffractometer. Each structure was solved by the application of direct methods using the SHELXS-96 program[29a] and least-squares refinement using SHELXL-97.[29b] All non-hydrogen atoms in compounds **1**, **4**, **5**, **7**, and **9** were anisotropically refined. All other hydrogen atoms were located from the difference Fourier and then refined.

Acknowledgment. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998 (1998-001-D00410).

Supporting Information Available: Tables listing crystallographic information, atomic coordinates and B_{eq} values, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles for **1**, **4**, **5**, **7**, and **9**.

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