Inorg. Chem. **2002**, *41*, 2987–2994

Inorganic Chemistry

Article

Reactions of Amides with Organoaluminum Compounds: Factors Affecting the Coordination Mode of Aluminum Amidates

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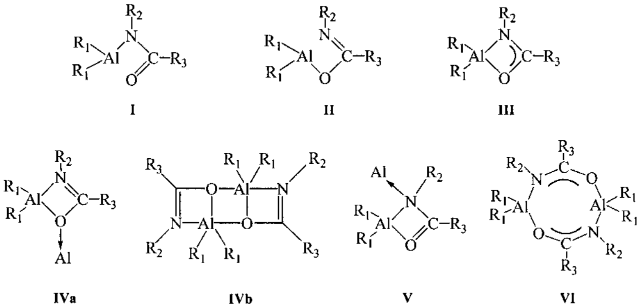
Received October 16, 2001

Factors affecting the coordination mode of an amidato group on aluminum will be presented. The reaction of *N-tert*-butylalkylacetamide (^{t}BuNHCR(=O)) with 1.1 molar equiv of Me_3Al in refluxing hexane affords a pentacoordinated, dimeric compound $\{Me_2Al[\eta^2\text{-}^tBuNC(R)(\mu_2\text{-}O)]\}_2$ (**3**, R = *p*-^{t}Bu-C_6H_4; **4**, R = 2,6-F,F-C_6H_3; **5**, R = Me; **6**, R = CF_3; **7**, R = *p*-F_3C-C_6H_4). However, in the presence of 2.2 molar equiv of Me_3Al, *N-tert*-butyl-4-*tert*-butylbenzamide (^{t}BuNHC(*p*-^{t}Bu-C_6H_4)(=O)) in refluxing hexane gives $\{Me_2Al[\eta^2\text{-}^tBuNC(p\text{-}^tBu\text{-}C_6H_4)(\mu_2\text{-}O)]AlMe_3\}$, **8**. In contrast, the reaction of R′NHCR″(=O) with 1 molar equiv of R_3Al at room temperature produces tetracoordinated, dimeric, eight-membered ring aluminum compounds $\{R_2Al[\mu,\eta^2\text{-}R'NC(R'')O]\}_2$ (**9**, R = Me, R′ = 2,6-^{i}Pr, ^{i}Pr-C_6H_3, R″ = Ph; **10**, R = Me, R′ = ^{i}Bu, R″ = Ph; **11**, R = Et, R′ = Bn, R″ = Ph; **12**, R = Me, R′ = Ph, R″ = CF_3; **13**, R = Me, R′ = Bn, R″ = CF_3). On the other hand, 4′-chlorobenzanilide ((*p*-Cl-C_6H_4)-NHCPh(=O)) reacts with R_3Al to produce trimeric, twelve-membered ring aluminum compounds $\{R_2Al[\mu,\eta^2\text{-}(p\text{-}Cl\text{-}C_6H_4)NC(Ph)O]\}_3$ (**14**, R = Me; **15**, R = Et). Furthermore, the reaction of 2′-methoxybenzanilide with 1 molar equiv of Me_3Al in hexane yields a dinuclear aluminum complex $[Me_2Al(o\text{-}OMe\text{-}Ph)NC(Ph)(O)AlMe_3]$, **16**.

Introduction

Despite amidato groups being the common ligands in transition metal coordination chemistry,[1] reports on the reactions of amides with trialkylaluminum compounds are rather scant. For an amidato group coordinated to aluminum, there are several coordination modes possible as shown in Chart 1. Among them, only a few examples have been structurally characterized. The first organoaluminum amidates, $[Me_2Al(RNC(O)R')]_2$ have been independently reported by Wade et al.[2] and Lappert et al.[3] as dinuclear complexes that possess an eight-membered ring with the mode VI based on spectroscopic studies. Furthermore, the coordination mode of $[Me_2Al(PhNC(O)Ph)]_2$ has been confirmed by Kakudo et al.[4] using X-ray crystal structure determination. However, in the presence of $O{=}NMe_3$, Me_3Al reacts with benzanilide (PhNHC(O)Ph) yielding $[Me_2Al(PhNC(O)Ph)(ONMe_3)]$, which is isolated as a monomer adopting mode II. The amidato group is coordinated to the aluminum center in $[Me_2Al(PhNC(O)Ph)(ONMe_3)]$ through the oxygen atom.[5] In addition, Barron[6] reported the mono-

Chart 1



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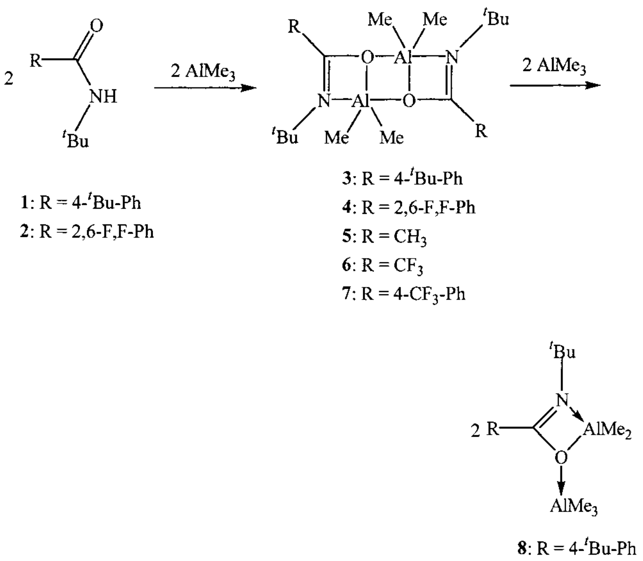
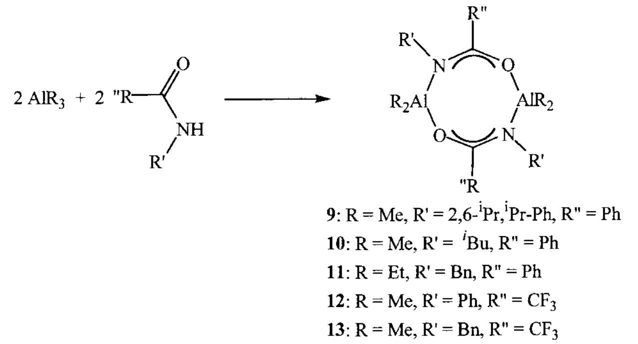
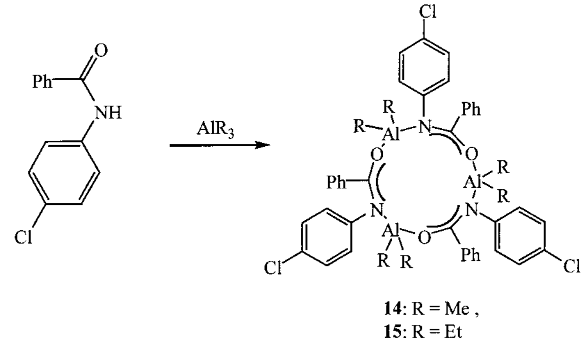
Scheme 1



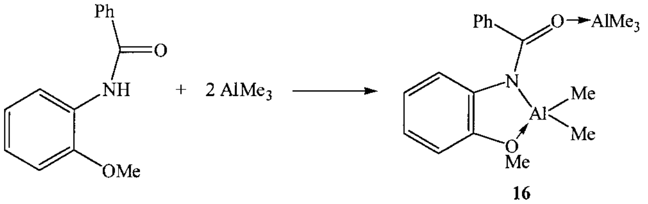
Scheme 2



Scheme 3



Scheme 4



meric nature of [$(BHT)_2Al(MeNCOPh)$] (BHT-H = 2,6-di-*tert*-butyl-4-methylphenol) having mode III according to ^{27}Al-NMR and other spectroscopic studies in 1990. Unfortunately, discussion of the factors affecting the coordination mode of amidato ligands on aluminum has never been attempted. Most recently, we found that both the monomeric compound {$Me_2Al[\eta^2\text{-}^tBuNCPh(O)]AlMe_3$} and the dimeric compound {$Me_2Al[\eta^2\text{-}^tBuNCPh(O)]$}$_2$ adopt mode IV. However, {$Me_2Al[\mu,\eta^2\text{-}ArNC(Ph)O]$}$_2$ (Ar = 4-OMe-C_6H_4) is a dimer having mode VI.[7] Therefore, to understand the role of amidato groups on the coordination mode of aluminum amidates is of great interest. Here, we report the preparation and crystal structure studies of a variety of aluminum amidates and discuss the factors affecting their coordination modes.

Results and Discussion

Syntheses. Compounds **1** and **2** were synthesized by the reaction of *tert*-butylamine with 4-*tert*-butylbenzoyl chloride and 2,6-difluorobenzoyl chloride, respectively. All other amides of [(Ar)C(O)NH(^{t}Bu)] were prepared according to the methods described in the literature,[8] and have been characterized by spectroscopic studies as well as microanalyses. Furthermore, the reaction of amides (^{t}Bu(H)NCR(=O)) with 1.1 molar equiv of Me_3Al in refluxing hexane afforded the corresponding pentacoordinated, dimeric aluminum compounds {$Me_2Al[\eta^2\text{-}^tBuNC(R)(\mu_2\text{-}O)]$}$_2$ (**3**, R = p-^{t}Bu-C_6H_4; **4**, R = 2,6-F,F-C_6H_4; **5**, R = Me; **6**, R = CF_3; **7**, R = p-F_3C-C_6H_4), as shown in Scheme 1. However, in the presence of 2.2 molar equiv of Me_3Al, *N-tert*-butyl-4-*tert*-butylbenzamide (**1**) in refluxing hexane gave a monomeric, dinuclear aluminum compound {$Me_2Al[\eta^2\text{-}^tBuNC(4\text{-}^tBu\text{-}C_6H_4)(\mu_2\text{-}O)]\text{-}AlMe_3$}, **8**. Compound **8** can also be prepared by the reaction of **3** with 1.1 molar equiv of Me_3Al in refluxing hexane.

Surprisingly, the reaction of R′NHCR″(=O) with 1 molar equiv of R_3Al at room temperature produced tetracoordinated, dimeric, eight-membered ring aluminum compounds {$R_2Al[\mu,\eta^2\text{-}R'NC(R'')O]$}$_2$ (**9**, R = Me, R′ = 2,6-^{i}Pr,^{i}Pr-C_6H_4, R″ = Ph; **10**, R = Me, R′ = ^{i}Bu, R″ = Ph; **11**, R = Et, R′ = Bn, R″ = Ph; **12**, R = Me, R′ = Ph, R″ = CF_3; **13**, R = Me, R′ = Bn, R″ = CF_3), as shown in Scheme 2. By contrast, the addition of 4′-chlorobenzanilide with R_3Al in toluene yielded a trimeric aluminum compound {$R_2Al\text{-}[\mu,\eta^2\text{-}(p\text{-}Cl\text{-}C_6H_4)NC(Ph)O]$}$_3$ (**14**, R = Me; **15**, R = Et) (Scheme 3) containing a twelve-membered ring. In addition, the reaction of 2′-methoxybenzanilide with 1 molar equiv of Me_3Al in hexane gave a dinuclear aluminum complex [$Me_2Al(o\text{-}OMe\text{-}Ph)NC(Ph)(O)AlMe_3$] (**16**), as shown in Scheme 4. All of the compounds **3**−**16** are very soluble in toluene, THF, and dichloromethane, and have been characterized by spectroscopic studies as well as elemental analyses. The yields of **3**−**16** as determined by ^{1}H-NMR spectroscopic studies were well above 80%, but because of the similar solubilities of these compounds and their byproducts, the isolated yields are only low to moderate. Their molecular

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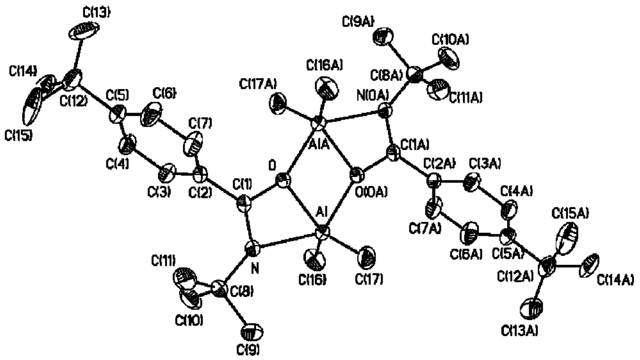

Figure 1. Molecular structure of compound **3** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. The Comparison of Selected Bond Lengths (Å) and Angles (deg) for Compounds **3**−**7**

	3	**4**	**5**	**6**	**7**
Al−N	2.175(2)	2.221(2)	2.136(2)	2.232(2)	2.177(2)
Al−O	1.904(1)	1.905(1)	1.899(2)	1.905(2)	1.900(2)
Al−O(a)	2.001(2)	2.014(1)	2.034(2)	2.036(2)	2.008(2)
C−N	1.279(2)	1.266(2)	1.256(3)	1.259(3)	1.273(3)
C−O	1.336(2)	1.333(2)	1.319(3)	1.334(3)	1.331(3)
O−C−N	110.1(1)	112.3(2)	111.0(2)	113.2(2)	110.3(2)

structures and coordination modes have been further verified by the X-ray diffraction studies.

Molecular Structure Studies. The molecular structure of **3** is depicted in Figure 1, and selected bond distances and angles for **3**−**7** are compared in Table 1. Complex **3** is a dimeric form adopting mode IV, as shown in Chart 1, in which the N-*tert*-butyl-4-*tert*-butylbenzamidato group acts as a chelating ligand bridging two aluminum atoms through the oxygen atom, a result similar to that observed for $\{Me_2Al[\eta^2\text{-}{}^tBuNC(Ph)(\mu_2\text{-}O)]\}_2$ (**A**).[7] The bond lengths for C(1)−N of 1.279(2) Å and C(1)−O of 1.336(2) Å indicate a localized structure with a C═N double bond and a C−O single bond.[1c,d] The C═N double bond character can be further verified by a very long Al−N distance (2.175(2) Å) indicating a dative bonding from a neutral nitrogen atom to aluminum.[9] It is worthwhile to note that the Al−O distances within the four-membered Al_2O_2 chelate ring are asymmetric with bond lengths for Al−O and Al−O(0a) of 1.904(1) and 2.001(2) Å, respectively, and they are similar to the normal Al−O distance observed for an Al_2O_2 core in the other five-coordinate aluminum alkoxides.[10] An interesting feature of complex **3** is that it contains a 4,4,4-fused ring where Al, N, C(1), and O atoms are coplanar with the angle between planes AlNC(1)O and AlOAl(a)O(0a) being only 1.9°. The only difference between compounds **4**−**7** and **3** is the substituent group attached to the carbon atom of the amidato ligand. Crystallographic studies of compounds **4**−**7** show that the central structure unit is almost identical to that of **3**. On the basis of this observation, it seems that the geometry of aluminum amidates is determined by the ^{t}Bu group on the nitrogen atom of the amidato ligand. Therefore, the substituent group on the carbon atom of the amidato ligand has little effect on the Al−O, C−O, and N−O bond lengths.

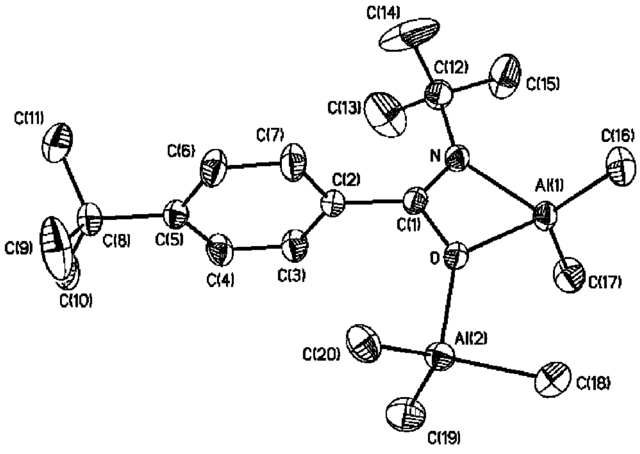

Figure 2. Molecular structure of compound **8** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound **8**

Al(1)−O	1.925(3)	Al(1)−N	1.958(4)
Al(1)−C(1)	2.372(5)	Al(1)−C(17)	1.931(6)
Al(1)−C(16)	1.935(6)	O−C(1)	1.346(5)
N−C(1)	1.274(6)	Al(2)−O	1.927(3)
Al(2)−C(19)	1.954(6)	Al(2)−C(20)	1.958(5)
Al(2)−C(18)	1.973(6)		
N−C(1)−O	109.9(4)	O−Al(1)−C(17)	109.2(2)
O−Al(1)−C(16)	115.2(2)	C(17)−Al(1)−C(16)	124.8(3)
O−Al(1)−N	67.03(15)	C(17)−Al(1)−N	112.6(2)
C(16)−Al(1)−N	113.9(2)	C(16)−Al(1)−C(1)	120.4(2)
C(17)−Al(1)−C(1)	114.8(2)	Al(1)−O−Al(2)	128.9(1)
Al(1)−O−C(1)	91.2(1)	Al(2)−O−C(1)	138.7(1)

The Al−O bond in the Al_2O_2 core of **3** can be detached by the addition of an excess of Me_3Al to give a monomeric complex **8**. The ORTEP diagram of **8** is shown in Figure 2, and selected bond lengths and angles are given in Table 2. The bond lengths for C(1)−N of 1.274(6) Å and C(1)−O of 1.346(5) Å in **8** are found to be similar to those in **3** indicating a localized structure with a C═N double bond and a C−O single bond. The geometry around the oxygen in **8** is distorted from the trigonal planar with the bond angles of Al(1)−O−C(1) at 91.2(1)°, Al(2)−O−C(1) at 138.7(1)°, and Al(1)−O−Al(2) at 128.9(1)°.

The molecular structure of **9** is illustrated in Figure 3, and selected bond lengths and bond angles of **9**−**13** are listed in Table 3. The central structures of compounds **9**−**13** are almost identical, with the differences being on the substituent attached to the carbon or nitrogen atom of the amidato ligand.

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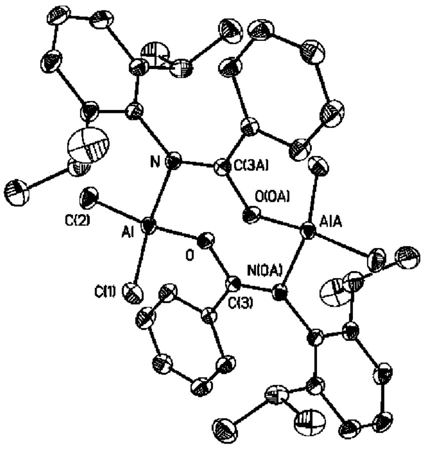


Figure 3. Molecular structure of compound **9** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. The Comparison of Selected Bond Lengths (Å) and Angles (deg) for Compounds **9**−**13**

	9	**10**	**11**	**12**	**13**
Al−N	1.973(1)	1.967(2)	1.959(1)	1.987(2)	1.985(2)
Al−O	1.811(1)	1.806(2)	1.808(1)	1.822(2)	1.831(1)
C−N	1.308(2)	1.301(3)	1.300(2)	1.292(3)	1.285(3)
C−O	1.302(2)	1.302(2)	1.299(2)	1.272(3)	1.288(2)
O−C−N	116.2(1)	118.5(2)	119.4(1)	122.4(2)	122.2(2)

Complex **9** crystallizes in a dimeric form and is composed of a centrosymmetrical eight-membered ring (mode VI). The bridging NCO group coordinates to two aluminum atoms through both nitrogen and oxygen atoms. The geometry around the aluminum atom is a distorted tetrahedron consisting of two methyl carbons, nitrogen, and oxygen atoms. It is interesting to note that the bond lengths for C(3)−N(0A) of 1.308(2) Å and C(3)−O of 1.302(2) Å indicate a delocalized structure within the OCN group which is different from the results observed for compounds **3**−**8**. The bond distances for Al−O of 1.811(1) Å, Al−N of 1.973(2) Å, Al−C(1) of 1.955(2) Å, and Al−C(2) of 1.957(2) Å in **9** are all similar to those of its analogues [$Me_2Al(\mu,\eta^2$-ArNCOPh)]$_2$.[4,7]

The molecular structure of **14** is depicted in Figure 4, and selected bond lengths and angles of compounds **14** and **15** are listed in Table 4. Compounds **14** and **15** are isostructural, the only difference being the methyl or ethyl groups attached to the aluminum atom. Complex **14** crystallizes in a trimeric form composed of a twelve-membered ring in which three aluminum atoms are connected by three bridging amidato ligands. The coordinating mode of **14** can be considered as mode VI, because the NCO group is cross-bridged between two aluminum centers and is similar to that in compounds **9**−**13**. The average bond lengths of C−N and C−O are 1.305 and 1.283 Å, respectively, and are all compatible with the values observed for compounds **9**−**13**; therefore, they can be classified as a delocalized structure within the OCN group.

The ORTEP diagram of **16** is shown in Figure 5, and selected bond lengths and angles are listed in Table 5. Complex **16** is a monomeric, dinuclear aluminum complex. The central unit consists of a four-membered ring in which the 2′-methoxybenzanilide ligand is coordinated to a Me_2Al center using the oxygen atom of the methoxy group and the nitrogen atom of the amidato group. However, the carbonyl oxygen atom of the amidato ligand is coordinated to another Me_3Al group. The bond distances for C(3)−O(1) and C(3)−N of 1.261(2) and 1.320(2) Å, respectively, are all consistent with a localized structure with a C═N double bond and a C−O single bond as depicted for mode I in Chart 1. This is the first time that an aluminum amidate with this kind of unusual coordination mode has been observed.

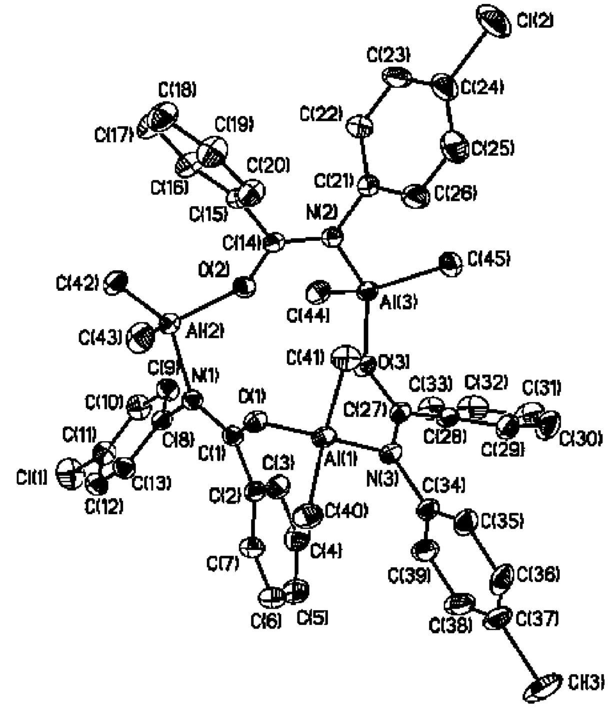


Figure 4. Molecular structure of compound **14** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

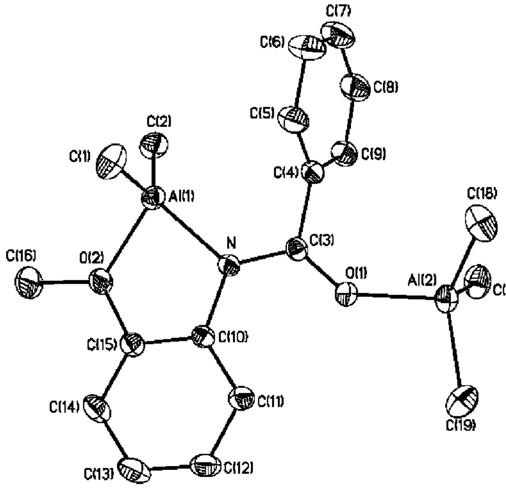


Figure 5. Molecular structure of compound **16** as 20% ellipsoids. Hydrogen atoms are omitted for clarity.

On the basis of the crystal structure studies of compounds **3**−**16** and [$Me_2Al(\mu,\eta^2$-PhNC(Ph)O)]$_2$ (**A**),[7] we conclude that the coordination mode of the amidato ligand on aluminum depends strongly on the Lewis basicity of the amidato ligands

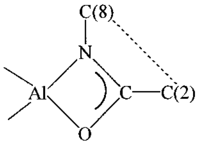
Table 4. The Comparison of Selected Bond Lengths (Å) for Compounds **14** and **15**

	14	15
Al(1)−N(3)	1.963(2)	1.969(3)
Al(2)−N(1)	1.962(2)	1.954(3)
Al(3)−N(2)	1.974(2)	1.953(2)
Al(1)−O(1)	1.813(2)	1.825(2)
Al(2)−O(2)	1.819(2)	1.805(2)
Al(3)−O(3)	1.829(2)	1.815(2)
O(1)−C(1)	1.277(3)	1.297(3)
O(2)−C(14)	1.288(3)	1.281(3)
O(3)−C(27)	1.284(3)	1.284(3)
N(1)−C(1)	1.307(3)	1.308(4)
N(2)−C(14)	1.289(3)	1.318(3)
N(3)−C(27)	1.318(3)	1.306(4)

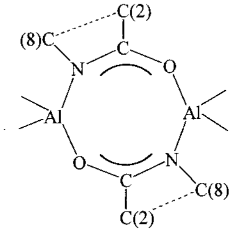
Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound **16**

Al(1)−N	1.924(2)	Al(1)−O(2)	1.934(2)
Al(1)−C(1)	1.932(3)	Al(1)−C(2)	1.937(2)
Al(2)−O(1)	1.880(2)	Al(2)−C(19)	1.965(3)
Al(2)−C(17)	1.962(3)	Al(2)−C(18)	1.972(3)
O(1)−C(3)	1.261(2)	O(2)−C(15)	1.406(2)
O(2)−C(16)	1.444(3)	N−C(3)	1.320(2)
N−C(10)	1.430(2)		
N−Al(1)−O(2)	82.4(1)	N−Al(1)−C(1)	111.9(1)
O(2)−Al(1)−C(1)	104.0(1)	N−Al(1)−C(2)	118.4(1)
O(2)−Al(1)−C(2)	106.7(1)	C(1)−Al(1)−C(2)	123.4(1)
O(1)−Al(2)−C(19)	101.9(1)	O(1)−Al(2)−C(17)	104.23(1)
C(19)−Al(2)−C(17)	113.1(1)	O(1)−Al(2)−C(18)	108.5(1)
C(19)−Al(2)−C(18)	113.7(1)	C(17)−Al(2)−C(18)	114.1(1)
C(3)−N−C(10)	123.2(2)		

Chart 2



Compounds **3-7**



Compounds **9-13**

and the steric hindrance of the substituent on the nitrogen atom of the amide. However, the substituent on the aryl ring attached on the carbon atom has no or little affect on the coordination mode of aluminum amidates. For example, compound **3** is different from **A** by replacing an H with an Me group on the 4-position of the phenyl ring attached on carbon; however, both compounds possess dimeric, four-membered rings. It is interesting to note that compound **10** is different from compounds **3** and **A** only by the exchange of a ^{t}Bu group (e.g., **3** and **A**) for a ^{i}Bu group (e.g., **10**) on the nitrogen atom of the amidato ligand in which the aluminum amidate with the more sterically hindered ^{t}Bu group adopts a four-membered ring, but the aluminum amidate with the less sterically hindered ^{i}Bu group has an eight-membered ring. It is worthwhile noting that the average distance between the C(2) and C(8) atoms ranges from 3.173 to 3.313 Å for the four-membered ring complexes **3**−**7** but ranges from 2.894 to 3.036 Å for the eight-membered ring compounds **9**−**13** as shown in Chart 2, indicating that aluminum amidates with eight-membered rings are more sterically crowded than those with four-membered rings. In addition, both 2,6-diisopropylbenzamide and *N*-*tert*-butylbenzamide are sterically hindered ligands; however, 2,6-diisopropylbenzamide is a much stronger Lewis acid than *N*-*tert*-butylbenzamide. As a result, aluminum amidate **3** adopts mode IV, but aluminum amidate **9** has mode VI. Therefore, on the basis of these studies, we conclude that the more acidic and less sterically hindered amides, such as benzanilide, tend to form either eight-membered ring (compounds **9**−**13**) or twelve-membered ring aluminum complexes (compounds **14** and **15**). In contrast, the less acidic and more sterically hindered amides, such as *N*-*tert*-butylbenzamide, prefer to adopt a four-membered ring (compounds **3**−**7**).

In conclusion, we have prepared 14 novel aluminum amidates, and their coordination modes have been discussed. The more acidic and less sterically hindered amidato ligands tend to form an eight-membered ring when they coordinate to aluminum. However, the more sterically hindered and less acidic amidato ligands tend to form a four-membered ring.

Experimental Section

General. All experiments were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (toluene, hexane) or phosphorus pentoxide (CH_2Cl_2), and were freshly distilled prior to use. Deuterated solvents were dried over molecular sieves. Me_3Al (2.0 M in toluene), Et_3Al (1.9 M in toluene), *tert*-butylamine, 4-*tert*-butylbenzoyl chloride, and 2,6-difluorobenzoyl chloride were purchased and used without further treatment. (*p*-^{t}Bu-Ph)C(O)N(^{t}Bu)H, (2,6-F,F-C_6H_3)C(O)N(^{t}Bu)H, (*p*-F_3C-Ph)C(O)N(^{t}Bu)H, PhC(O)N(^{t}Bu)H, PhC(O)N(Bn)H, MeC(O)N(^{t}Bu)H, F_3CC(O)N(^{t}Bu)H, F_3CC(O)N(Ph)H, F_3CC(O)N(Bn)H, PhC(O)N(Ph-^{i}Pr,^{i}Pr-2,6)H, PhC(O)N(Ph-OMe-*o*)H, and PhC(O)N(Ph-Cl-*p*)H were prepared according to the literature method.[8] Melting points were determined with a Buchi 535 digital melting point apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini-200 (200 MHz), Varian VXR-300 (300 MHz), or Varian Mercury-400 (400 MHz) spectrometer with chemical shifts given in parts per million from the internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer.

[(*p*-^{t}Bu-C_6H_4)C(O)N(^{t}Bu)H] (1). To a rapidly stirred solution of *tert*-butylamine (5.25 mL, 50 mmol) in 5% NaOH aqueous solution (100 mL) was added 4-*tert*-butylbenzoyl chloride (9.8 mL, 50 mmol) at 0 °C. The reaction mixture was warmed to room temperature, and it was stirred for 1 h, during which white solids formed gradually. After filtration, the white solids were taken up in hot toluene (30 mL). Colorless crystals were obtained at room temperature after 1 h. Yield: 4.36 g (37%). Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.47; H, 10.26; N, 6.15. ^{1}H -NMR ($CDCl_3$, δ): 7.67−7.42 (m, 4H, Ph), 5.93 (br, 1H, N*H*), 1.47 (s, 9H, N^t*Bu*), 1.33 (s, 9H, Ph^t*Bu*). ^{13}C-NMR ($CDCl_3$, δ): 166.79 (*C*=O), 154.39, 133.00, 126.47, 125.28 (Ph), 51.38 (*C*-N), 34.76 (*C*Ph), 31.10 (PhC*Me*$_3$), 28.83 (NC*Me*$_3$). IR (KBr, 1500−1700 cm^{-1}): 1633.4 (s), 1542.0 (s), 1506.0 (s). Mass spectrum (EI, *m*/*e*): 233 (M$^+$, 22.2%). Mp: 140−141 °C.

[(2,6-F,F-Ph)C(O)N(^{t}Bu)H] (2). This compound was prepared according to the same procedures described for **1** using 2,6-difluorobenzoyl chloride (6.29 mL, 50 mmol). Yield: 3.3 g (31%). Anal. Calcd for $C_{20}H_{37}N_2O_2F_2$: C, 61.96; H, 6.15; N, 6.57. Found: C, 61.18; H, 6.06; N, 6.00. ^{1}H-NMR ($CDCl_3$, δ): 7.34−

6.89 (m, 3H, Ph), 5.72 (br, 1H, N*H*), 1.47 (s, 9H, ^{t}*Bu*). ^{13}C-NMR (CDCl$_3$, δ): 159.49 (*C*=O), 160.96 (d, $J_{C-F} = 5.5$ Hz), 158.47 (d, $J_{C-F} = 5.5$ Hz), 130.96 (t, $J_{C-F} = 7.5$ Hz), 115.58 (t, $J_{C-F} = 15.8$ Hz), 111.73 (d, $J_{C-F} = 19.8$ Hz), 111.73 (d, $J_{C-F} = 10.2$ Hz) (Ph), 52.42 (*C*-N), 28.67 (C*Me*$_3$). IR (KBr, 1500−1700 cm^{-1}): 1645.1 (s), 1590.7 (s), 1549.6 (s). Mass spectrum (EI, *m*/*e*): 213 (M$^+$, 52.9%). Mp: 116−117 °C.

{Me$_2$Al[η^2-^{t}BuNC(Ph-^{t}Bu-*p*)(μ_2-O)]}$_2$ (3). To a rapidly stirred solution of **1** (0.93 g, 4.0 mmol) in hexane (10 mL) was added Me$_3$Al (2.2 mL, 4.4 mmol). The reaction mixture was refluxed for 24 h, and the volatile materials were removed under vacuum giving white solids. The residue was extracted with toluene (30 mL), and the solution was allowed to concentrate to ca. 15 mL. Colorless crystals were obtained at −20 °C after 16 h. Yield: 0.95 g (82%). Anal. Calcd for $C_{34}H_{56}Al_2N_2O_2$: C, 70.56; H, 9.75; N, 4.84. Found: C, 69.99; H, 9.51; N, 5.32. ^{1}H-NMR (CDCl$_3$, δ): 7.43−7.29 (m, 4H, Ph), 1.34 (s, 9H, ^{t}*Bu*Ph), 1.10 (s, 9H, ^{t}*Bu*N), −0.88 (s, 6H, Al*Me*$_2$). ^{13}C-NMR (CDCl$_3$, δ): 168.77 (C=N), 153.20, 130.83, 127.12, 125.01 (Ph), 52.85 (C-N), 34.84 (*C*-Ph), 31.23 (C*Me*$_3$), −8.46 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1637.0 (s), 1608.9 (s), 1542.2 (s), 1504.9 (s). Mp: 118−120 °C.

{Me$_2$Al[η^2-^{t}BuNC(Ph-F,F-2,6)(μ_2-O)]}$_2$ (4). This compound was prepared according to the same procedures described for **3** using **2** (0.85 g, 4.0 mmol). Colorless crystals were obtained in toluene at room temperature after 12 h. Yield: 0.72 g (67%). Anal. Calcd for $C_{26}H_{36}Al_2N_2O_2F_4$: C, 57.99; H, 6.74; N, 5.20. Found: C, 58.33; H, 6.68; N, 5.72. ^{1}H-NMR (CDCl$_3$, δ): 7.45−7.39, 7.01−6.95 (m, 3H, Ph), 1.11 (s, 9H, ^{t}*Bu*N), −0.87 (s, 6H, AlMe$_2$). ^{13}C-NMR (CDCl$_3$, δ): 167.38 (C=N), 160.33 (d, $J_{C-F} = 7.4$ Hz), 156.99 (d, $J_{C-F} = 7.4$ Hz), 132.02 (t, $J_{C-F} = 10.1$ Hz), 113.57 (t, $J_{C-F} = 22.8$ Hz), 111.63 (d, $J_{C-F} = 23.7$ Hz), 111.63 (d, $J_{C-F} = 18.3$ Hz, Ph), 53.36 (*C*-N), 29.96 (C*Me*$_3$), −9.37 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1647.4 (s), 1623.9 (s), 1589.9 (s), 1550.5 (s). Mp: 168−170 °C.

{Me$_2$Al[η^2-^{t}BuNC(Me)(μ_2-O)]}$_2$ (5). To a rapidly stirred solution of *N*-*tert*-butylacetamide (0.46 g, 4.0 mmol) in CH$_2$Cl$_2$ (10 mL) was added Me$_3$Al (2.2 mL, 4.4 mmol). The reaction mixture was stirred for 24 h, and the volatile materials were removed under a vacuum giving white solids. The residue was extracted with toluene (30 mL), and the solution was allowed to concentrate to ca. 15 mL. Colorless crystals were obtained at 5 °C after 72 h. Yield: 0.41 g (60%). Anal. Calcd for $C_{16}H_{36}Al_2N_2O_2$: C, 56.12; H, 10.60; N, 8.18. Found: C, 56.22; H, 10.81; N, 7.89. ^{1}H-NMR (CDCl$_3$, δ): 2.15 (s, 3H, CH$_3$), 1.27 (s, 9H, ^{t}*Bu*), −0.79 (s, 6H, Al*Me*$_2$). ^{13}C-NMR (CDCl$_3$, δ): 168.09 (C=N), 51.40 (C-N), 30.03 (C*Me*$_3$), 18.40 (*Me*), −8.55 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1639.4 (s), 1559.5 (m). Mp: 83−85 °C.

{Me$_2$Al[η^2-^{t}BuNC(CF$_3$)(μ_2-O)]}$_2$ (6). This compound was prepared according to the same procedures described for **3** using *N*-*tert*-butyltrifluoroacetamide (1.00 g, 6.0 mmol). Colorless crystals were obtained at −20 °C after 24 h. Yield: 0.75 g (55.6%). Anal. Calcd for $C_8H_{15}AlF_3NO$: C, 42.67; H, 6.71; N, 6.22. Found: C, 42.75; H, 6.33; N, 6.16. ^{1}H-NMR (CDCl$_3$, δ): 1.35 (s, 9H, ^{t}Bu), −0.71 (s, 6H, Me). ^{13}C-NMR (CDCl$_3$, δ): 149.8 (q, $J_{C-F} = 43.5$ Hz), 115.21 (q, $J_{C-F} = 282.7$ Hz), 54.76 (N-*C*), 30.40 (q, $J_{C-F} = 2.3$ Hz), −9.78 (Al-*C*H$_3$). IR (KBr, 1500−1700 cm^{-1}): 1689.4 (s), 1664.5 (s), 1553.1 (m), 1535.2 (m). Mp: 82−84 °C.

{Me$_2$Al[η^2-^{t}BuNC(Ph-CF$_3$-*p*)(μ_2-O)]}$_2$ (7). This compound was prepared according to the same procedures described for **3** using *N*-*tert*-butyl-4-trifluoromethylbenzamide (0.49 g, 2.0 mmol) and Me$_3$Al (1.1 mL, 2.2 mmol). Colorless crystals were obtained in toluene at 5 °C after the compound sat overnight. Yield: 0.43 g (71%). Anal. Calcd for $C_{28}H_{38}Al_2N_2O_2F_6$: C, 55.81; H, 6.36; N, 4.65. Found: C, 55.70; H, 6.95; N, 4.55. ^{1}H-NMR (CDCl$_3$, δ): 7.72−7.51 (m, 4H, Ph), 1.09 (s, 9H, ^{t}*Bu*N), −0.91 (s, 6H, AlMe$_2$). ^{13}C-NMR (CDCl$_3$, δ): 175.41 (C=N), 138.76, 131.62 (q, $J_{C-F} = 32.8$ Hz), 127.34, 125.29 (q, $J_{C-F} = 3.7$ Hz, Ph), 123.65 (q, $J_{C-F} = 278.6$ Hz, *C*F$_3$), 52.05 (C-N), 31.25 (C*Me*$_3$), −8.30 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1642.1 (s), 1549.9 (s), 1508.8 (w). Mp: 110−112 °C.

{Me$_2$Al[η^2-^{t}BuNC(*p*-^{t}Bu-Ph)(μ_2-O)]AlMe$_3$} (8). This compound was prepared according to the same procedures described for **3** using 2.2 molar equiv of Me$_3$Al. Colorless crystals were obtained at 5 °C after 24 h. Yield: 0.85 g (64%). Anal. Calcd for $C_{20}H_{37}AlNO$: C, 66.45; H, 10.32; N, 3.87. Found: C, 66.26; H, 9.43; N, 3.36. ^{1}H-NMR (CDCl$_3$, δ): 7.50−7.29 (m, 4H, Ph), 1.35 (s, 9H, ^{t}*Bu*Ph), 1.19 (s, 9H, ^{t}*Bu*N), −0.45 (s, 9H, Al*Me*$_3$), −1.19 (s, 6H, Al*Me*$_2$). ^{13}C-NMR (CDCl$_3$, δ): 173.54 (C=N), 155.23, 127.29, 126.54, 125.22 (Ph), 54.35 (C-N), 35.04 (*C*-Ph), 31.09 ((*C*H$_3$)$_3$CN), 30.75 ((*C*H$_3$)$_3$CPh), −8.13 (Al*Me*$_3$), −10.39 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1620.3 (br, s), 1558.1 (m), 1503.5 (m). Mp: 105−106 °C.

{Me$_2$Al[μ,η^2-(2,6-^{i}Pr,^{i}Pr-Ph)NCOPh]}$_2$ (9). To a rapidly stirred solution of *N*-(2,6-diisopropylphenyl)benzamide (0.56 g, 2 mmol) in toluene (10 mL) was added Me$_3$Al (1.2 mL, 2.4 mmol). The reaction mixture was stirred at 25 °C for 16 h, and the volatile materials were removed under vacuum giving white solids. The residue was extracted by toluene (20 mL), and the solution was allowed to concentrate to ca. 10 mL. Colorless crystals were obtained at −20 °C after the solution sat overnight. Yield: 0.35 g (52%). Anal. Calcd for $C_{42}H_{56}Al_2N_2O_2$: C, 74.75; H, 8.36; N, 4.15. Found: C, 74.38; H, 8.66; N, 4.29. ^{1}H-NMR (CDCl$_3$, δ): 7.41−7.15 (m, 8H, Ph), 3.23 (m, 2H, $J_{H-H} = 6.8$ Hz, Me$_2$C*H*), 1.25, 0.84 (d, 6H, $J_{H-H} = 6.8$ Hz, CH$_3$), −0.89 (s, 6H, AlMe$_2$). ^{13}C-NMR (CDCl$_3$, δ): 173.80 (*C*-Ph), 143.00, 137.85, 132.80, 131.92, 130.67, 127.83, 127.46, 124.48 (Ph), 28.23 (*C*Me$_2$), 24.47, 24.05 (C*Me*$_2$), −10.00 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1643.4 (s), 1586.2 (s), 1530.9 (s). Mp: 160−162 °C dec.

{Me$_2$Al[μ,η^2-^{i}BuNC(O)Ph]}$_2$ (10). This compound was prepared according to the same procedures described for **4** using *N*-isobutylbenzamide (0.71 g, 4.0 mmol). Colorless crystals were obtained in toluene at 5 °C after 12 h. Yield: 0.4 g (43%). Anal. Calcd for $C_{26}H_{40}Al_2N_2O_2$: C, 66.93; H, 8.64; N, 6.00%. Found: C, 66.58; H, 9.12; N, 6.64%. ^{1}H-NMR (CDCl$_3$, δ): 7.48−7.39 (m, 5H, Ph), 3.18 (d, 2H, $J_{H-H} = 3.8$ Hz, CH$_2$), 1.73 (m, 1H, $J_{H-H} = 3.4$ Hz, Me$_2$C*H*), 0.68 (d, 6H, $J_{H-H} = 3.4$ Hz, C*Me*$_2$), −1.00 (s, 6H, Al*Me*$_2$). ^{13}C-NMR (CDCl$_3$, δ): 176.33 (*C*-Ph), 134.84, 130.33, 128.33, 126.80 (Ph), 56.13 (*C*-N), 29.53 (*C*Me$_2$), 19.82 (C*Me*$_2$), −10.39 (Al*Me*$_2$). IR (KBr, 1500−1700 cm^{-1}): 1636.9 (s), 1608.1 (s), 1589.2 (s). Mp: 120−122 °C.

{Et$_2$Al[μ,η^2-BnNC(O)Ph]}$_2$ (11). To a rapidly stirred solution of *N*-benzylbenzamide (0.63 g, 3.0 mmol) in toluene (30 mL) was added Et$_3$Al (1.6 mL, 3.0 mmol). The reaction mixture was stirred at room temperature for 6 h and was then concentrated to ca. 10 mL. Colorless crystals were obtained at −20 °C after 48 h. Yield: 0.52 g (59%). Anal. Calcd for $C_{11}H_{13}AlF_3NO$: C, 73.20; H, 7.51; N, 4.74. Found: C, 73.67; H, 8.05; N, 4.62. ^{1}H-NMR (CDCl$_3$, δ): 7.43−7.11 (m, 5H, Ph), 4.53 (s, 2H, Ph-CH$_2$), 0.75 (t, 3H, $J_{H-H} = 8.4$ Hz, Me), −0.34 (q, 2H, $J_{H-H} = 8.2$ Hz, Al-CH$_2$). ^{13}C-NMR (CDCl$_3$, δ): 178.06 (*C*-O), 138.45, 134.23, 130.49, 128.39, 128.35, 127.25, 127.09, 126.94 (Ph), 51.43 (Ph-*C*-N), 8.09 (*C*H$_3$), −0.53 (Al-*C*H$_2$). IR (KBr, 1500−1700 cm^{-1}): 1574.4 (s). Mp: 106−112 °C.

{Me$_2$Al[μ,η^2-PhNC(O)CF$_3$]}$_2$ (12). This compound was prepared according to the same procedures described for **11** using 2,2,2-trifluoro-*N*-phenylacetamide (1.07 g, 6.0 mmol) and Me$_3$Al (3.0

Table 6. Crystallographic Data for Compounds **3, 8, 9, 14**, and **16**

	3	**8**	**9**	**14**	**16**
chemical formula	$C_{34}H_{38}Al_2N_2O_2$	$C_{20}H_{37}Al_2NO$	$C_{42}H_{56}Al_2N_2O_2$	$C_{45}H_{45}Al_3Cl_3N_3O_3\cdot 0.5C_7H_8\cdot 0.5H_2O$	$C_{19}H_{27}Al_2NO_2$
M	560.62	361.47	674.84	809.17	355.38
space group	$P2(1)/c$	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$	$P2(1)/n$
a(Å)	9.1699(7)	12.275(2)	9.0983(8)	12.8843(10)	10.1704(9)
b(Å)	12.8530(10)	10.645(2)	14.8510(13)	13.5017(10)	20.4082(18)
c(Å)	16.5372(13)	18.810(4)	14.8892(13)	16.5742(13)	10.2328(9)
α(deg)	−	−	−	88.337(2)	−
β(deg)	93.523(2)	93.975(4)	96.071(2)	75.421(1)	97.741(2)
ρ(Deg)	−	−	−	70.823(2)	−
V(Å)^3	1945.4(3)	2452.1(8)	2000.5(3)	2631.0(3)	2104.6(3)
Z	2	4	2	2	4
μ (Mo Kα)(mm^{-1})	0.100	0.124	0.108	0.263	0.148
N_{ref}(obs), ($F > 4\sigma(F)$)	3827	4823	3899	10214	4142
no. parameters	208	217	217	553	217
R1[a]	0.0487	0.1076	0.0424	0.0595	0.0431
wR2[b]	0.1458	0.3197	0.1429	0.1832	0.1355
GoF[c]	1.073	1.956	1.159	1.001	1.029
min, max residual density(e Å^{-3})	−0.175, 0.171	−0.278, 0.615	−0.248, 0.229	−0.352, 0.868	−0.218, 0.280

[a] $R1 = |\Sigma(|F_o| - |F_c|)/|\Sigma|F_o||$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 0.10$. [c] $GoF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

mL, 6.0 mmol). Yield: 0.77 g (52%). Anal. Calcd for $C_{10}H_{11}AlF_3NO$: C, 48.99; H, 4.52; N, 5.71. Found: C, 48.44; H, 4.90; N, 5.32. ^{1}H-NMR ($CDCl_3$, δ): 7.44−7.09 (m, 5H, Ph), −0.85 (s, 6H, Me). ^{13}C-NMR ($CDCl_3$, δ): 159.73 (q, J_{C-F} = 36 Hz), 137.73, 129.13, 127.87, 125.06 (Ph), 116.11 (q, J_{C-F} = 288 Hz), −11.97 (Al-CH_3). IR (KBr, 1500−1700 cm^{-1}): 1634.0 (s), 1593.6 (s), 1551.1 (m). Mp: 105−107 °C.

$\{Me_2Al[\mu,\eta^2$-BnNC(O)CF$_3]\}_2$ (13). This compound was prepared according to the same procedures described for **11** using 2,2,2-trifluoro-*N*-benzylacetamide (1.13 g, 6.0 mmol) and Me_3Al (3.0 mL, 6.0 mmol). Yield: 1.27 g (81%). Anal. Calcd for $C_{11}H_{13}AlF_3NO$: C, 50.91; H, 5.06; N, 5.40. Found: C, 50.97; H, 5.24; N, 5.48. ^{1}H-NMR ($CDCl_3$, δ): 7.37−7.14 (m, 5H, Ph), 4.74 (s, 2H, N-CH_2), −0.90 (s, 6H, Me). ^{13}C-NMR ($CDCl_3$, δ): 161.87 (q, J_{C-F} = 35.8 Hz), 135.25, 128.71, 127.97, 127.03 (Ph), 127.99 (q, J_{C-F} = 287.7 Hz), 48.58 (q, J_{C-F} = 3.0 Hz), −11.18 (Al-CH_3). IR (KBr, 1500−1700 cm^{-1}): 1652.3 (s), 1612.1 (s). Mp: 104−106 °C.

$\{[\mu,\eta^2$-(p-Cl-Ph)NC(O)(Ph)AlMe$_2]\}_3$ (14). To a rapidly stirred solution of *N*-(4′-chlorophenyl)benzamide (0.92 g, 4.0 mmol) in toluene (20 mL) was added Me_3Al (2.2 mL, 4.4 mmol). The reaction mixture was stirred at 25 °C for 24 h, and the volatile materials were removed under a vacuum giving white solids. The residue was extracted by toluene (25 mL), and the solution was allowed to concentrate to ca. 15 mL. Colorless crystals were obtained at room temperature after 24 h. Yield: 0.78 g (23%). Anal. Calcd for $C_{45}H_{45}Al_3N_3O_3Cl_3$: C, 62.62; H, 5.25; N, 4.87. Found: C, 62.81; H, 5.64; N, 5.67. ^{1}H-NMR ($CDCl_3$, δ): 7.38−6.48 (m, 9H, Ph), −0.91 (s, 6H, $AlMe_2$). ^{13}C-NMR ($CDCl_3$, δ): 175.21 (C=N), 141.39, 133.68, 131.07, 130.10, 129.35, 129.13, 128.08, 127.89 (Ph), −8.73 (AlMe_2). IR (KBr, 1500−1700 cm^{-1}): 1653.0 (s), 1552.4 (s). Mp: 118−120 °C dec.

$\{[\mu,\eta^2$-(p-Cl-Ph)NC(O)(Ph)AlEt$_2]\}_3$ (15). This compound was prepared by following the same procedures described for **14** using Et_3Al (2.2 mL, 4.2 mmol). Colorless crystals were obtained in hexane at room temperature after 24 h. Yield: 0.93 g (25%). Anal. Calcd for $C_{51}H_{57}Al_3N_3O_3Cl_3$: C, 64.66; H, 6.06; N, 4.44. Found: C, 64.06; H, 7.71; N, 5.02. ^{1}H-NMR ($CDCl_3$, δ): 7.50−6.47 (m, 9H, Ph), 0.82 (t, 3H, J_{H-H} = 8.2 Hz, Al($CH_2$$CH_3$)$_2$), −0.89 (q, 2H, J_{H-H} = 8.2 Hz, Al($CH_2$$CH_3$)$_2$). ^{13}C-NMR ($CDCl_3$, δ): 175.84 (C=N), 141.45, 133.81, 131.87, 130.90, 129.13, 129.05, 128.06, 127.80 (Ph), 9.00 (Al(CH_2CH_3)$_2$), −0.47 (Al(CH_2CH_3)$_2$). IR (KBr, 1500−1700 cm^{-1}): 1654.7 (m), 1588.2 (s), 1531.9 (s). Mp: 81−83 °C.

[Me_2Al(p-MeO-Ph)NC(O)(Ph)AlMe$_3$] (16). To a rapidly stirred solution of 2′-methoxybenzanilide (0.91 g, 4.0 mmol) in hexane (20 mL) was added $AlMe_3$ (2.2 mL, 4.2 mmol). The reaction mixture was stirred at 0 °C for 4 h and was then dried under a vacuum to give white solids. The residue was extracted into a hot hexane solution (50 mL) which was then concentrated to ca. 15 mL. Colorless crystals were obtained at room temperature after 24 h. Yield: 0.61 g (43%). Anal. Calcd for $C_{19}H_{27}Al_2NO_2$: C, 64.21; H, 7.66; N, 3.94. Found: C, 63.87; H, 7.62; N, 3.63. ^{1}H-NMR ($CDCl_3$, δ): 8.45−6.80 (m, 7H, Ph), 4.19 (s, 3H, OCH_3), −0.96 (s, 6H, AlMe_2), −1.02 (s, 9H, AlMe_3). ^{13}C-NMR ($CDCl_3$, δ): 174.91 (C=N), 146.89, 136.60, 132.47, 130.99, 129.40, 127.36, 125.80, 124.41, 110.12 (Ph), 57.87 (OMe), −7.62 (AlMe_2), −11.06 (AlMe_3). IR (KBr, 1500−1700 cm^{-1}): 1586 (m), 1553 (s). Mp: 119−121 °C.

X-ray Crystallographic Studies. Suitable crystals from compounds **3**−**16** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[11] The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[12] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Crystallographic data of **3**, **8**, **9**, **14**, and **16** are listed in Table 6. In compound **3,** the *tert*-butyl group on the nitrogen atom is disordered. There are two positions for each carbon atom attached on the carbon attached to the nitrogen atoms, and the final value for the site occupancy of the two *tert*-butyl groups is 50/50. In compounds **6**, **7**, and **12** the trifluoromethyl groups are

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(11) Sheldrick, G. M. *SADABS: Siemens Area Detector Absorption Correction Softwares*; University of Göttingen: Göttingen, Germany, 1998.

(12) Sheldrick, G. M. *SHELXTL-Plus, NT Crystallographic System*, release 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1998.

disordered. There are two positions for each fluorine atom attached on the carbon, and the final value for the site occupancy of these two trifluoromethyl groups is 50/50. A half-molecule of toluene and a half-molecule of H_2O per asymmetric unit are observed in compound **14**. In compound **15**, two positions with the site occupancy of 50/50 are found for the end carbon atoms of these two ethyl groups. A half-molecule of hexane per asymmetric unit is also observed.

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully acknowledged.

Supporting Information Available: Further details of the crystal structure determination of compounds **3**−**16**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011072+