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Aluminum Alkyl Complexes Supported by Bidentate N,N Ligands: Synthesis, Structure, and Catalytic Activity for Guanylation of Amines

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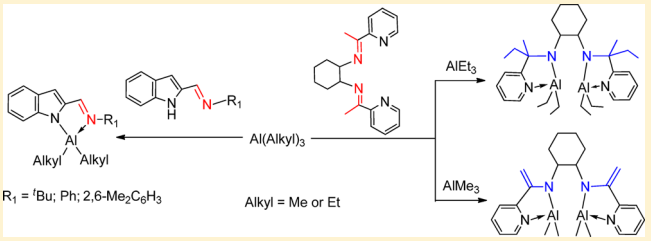
Supporting Information

ABSTRACT: The reactions of $AlMe_3$ or $AlEt_3$ with 2-pyridyl- or indolyl-substituted imines were studied, leading to the formation of different organoaluminum complexes. While the reactions of the iminopyridine Cy[N=CMe-2-(C_5H_4N)]$_2$ (**L^1**) derived from 1-(pyridin-2-yl)ethanone and *trans*-1,2-cyclohexanediamine with $AlEt_3$ gave the aluminum complex Cy[NC(Me)(Et)-2-(C_5H_4N)$AlEt_2$]$_2$ (**1**), in which the two ketimine groups of the ligand were transformed into the amido functionality through the addition of two ethyl groups, the reaction of **L^1** with $AlMe_3$ afforded the aluminum complex Cy[NC(=CH_2)-2-(C_5H_4N)$AlMe_2$]$_2$ (**2**) via a sp^3 C−H activation with elimination of two methane molecules. The reactions of indolyl-2-aldimines (2-(RN=CH)C_8H_5NH (R = ^{t}Bu (**L^{2}H**), C_6H_5 (**L^{3}H**), 2,6-$Me_2C_6H_3$ (**L^{4}H**)) with $AlMe_3$ or $AlEt_3$ afforded only the deprotonated indolyl aluminum complexes [2-(RN=CH)C_8H_5N]$AlMe_2$ (R = ^{t}Bu (**3**), C_6H_5 (**4**), 2,6-$Me_2C_6H_3$ (**5**)) and [2-(2,6-$Me_2C_6H_3$N=CH)C_8H_5N]$AlEt_2$ (**6**), respectively. The structures of complexes **2**−**6** were characterized by spectral methods and X-ray crystallographic analyses. These aluminum complexes showed a high catalytic activity in the addition of amines to carbodiimides to form guanidines. The mechanism of the catalytic process was studied by control experiments and ^{1}H NMR monitoring. Together with the isolation of the complex [2-(2,6-$Me_2C_6H_3$N=CH)C_8H_5N][CyN=C(4-MeC_6H_3N)(NHCy)]AlMe (**7**), a probable mechanism for the guanylation reaction was proposed.



INTRODUCTION

Organometallic aluminum complexes have attracted increasing attention due to their widespread applications in organic synthesis[1] and polymerization,[2] as well as their ready availability at relatively low cost. As the catalytic properties of the aluminum complexes are greatly influenced by modifying the structures of the coordinating ligands, various organic ligands have been synthesized and investigated in this field. Bidentate or multidentate ligands bearing N- or O-donor atoms, such as iminopyridine,[3] β-diketiminato,[4] guanidinato,[5] biphenol,[6] phenoxy-imine,[7] and related Schiff base derivatives,[8] are used extensively in synthesizing organoaluminum complexes. In particular, in the reactions of imine ligands with aluminum alkyls, alkylation of the ligand may occur depending on the nature of the alkyl group or ligand.[9] Moreover, reaction of an iminopyridine ligand with alkyllithium was serendipitously found to proceed via an initial alkylation of the pyridine N atom followed by elimination of methane.[10] However, the reaction of iminopyridine ligands with aluminum alkyls still remains to be revealed.

Over the past decades, metal complex catalyzed C−N bond formation for the construction of N-substituted guanidines has attracted much attention, as it was one of the most straightforward and atom-economical route to guanidines.[11] Since the pioneering work reported in 2003 by Richeson and co-workers on the catalytic guanylation reaction of primary aromatic amines with carbodiimides by using titanium imido complexes,[12] complexes of transition metals,[13] rare-earth metals,[14] and other main-group metals[15] have all been used for the catalytic guanylation of various amines with carbodiimides. Recently, aluminum alkyl reagents such as $AlEt_3$, $AlEt_2Cl$, and $AlMe_3$ have been used as efficient precatalysts for this reaction.[15a] We report herein the preparation of novel neutral organoaluminum complexes from the reactions of $AlMe_3$ or $AlEt_3$ with 1,2-*trans*-diaminocyclohexane-derived iminopyridine or indolyl-2-aldimines and their catalytic activity toward the guanylation reation of arylamines. The coordinating ligand's effect on the catalytic activity of these aluminum complexes for the guanylation and the catalytic mechanism have also been probed.

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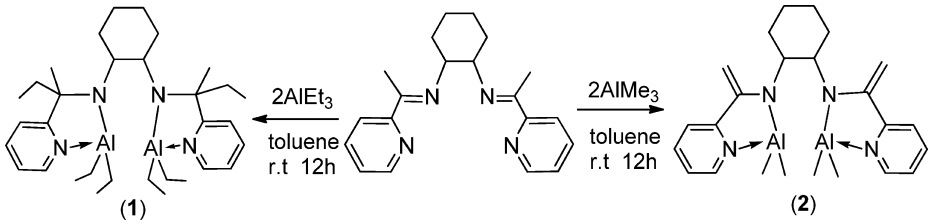
Scheme 1. Preparation of Complexes 1 and 2



RESULTS AND DISCUSSION

Synthesis and Characterization of Aluminum Alkyl Complexes. The reactions of the iminopyridine Cy[N=CMe-2-(C_5H_4N)]$_2$ ($\mathbf{L^1}$, Cy = cyclohexyl) with aluminum alkyls AlR_3 (R = Et, Me) are shown in Scheme 1. The treatment of $\mathbf{L^1}$ with 2 equiv of $AlEt_3$ in toluene afforded the aluminum complex Cy[NC(Me)(Et)-2-(C_5H_4N)$AlEt_2$]$_2$ (**1**) via nucleophilic addition of one of the ethyl groups of $AlEt_3$ to the imine, which has also been previously observed in the reactions of related neutral imine ligands with alkyaluminum reagents.[16] However, the same reaction of $\mathbf{L^1}$ with $AlMe_3$ instead of $AlEt_3$ proceeded via elimination of two methane molecules to provide the dinuclear four-coordinate dimethylaluminum complex **2** in good yield.

The structures of complexes **1** and **2** have been confirmed by single-crystal X-ray diffraction and are shown in Figures 1 and 2, and a selection of bond distances and angles is collected in Table 1. The coordination geometry around the Al center is described as a four-coordinate distorted tetrahedron, being surrounded by two alkyl groups and two nitrogen atoms. In the structure of **1** (Figure 1), the imino groups have been transformed into the amido functionality, forming the cyclohexyl-bearing dinuclear aluminum metallacycle, and the N1−C3 bond length of 1.473(4) Å is consistent with a typical C−N single bond. The C3−C4 bond length of 1.348(2) Å in **2** is an indicative of a C=C double bond, which is supported by the ^{1}H NMR spectrum, showing the resonance of the protons of C=CH_2 at δ 4.87 and 4.48 ppm. The N1−C3 bond length of 1.378(2) Å is shorter than that of a typical C−N single bond, suggesting electron delocalization between the C=C double bond and N1 lone pair electrons. The Al−N2(pyridine) bond of 1.973(1) Å is longer than that of Al−N1 at 1.861(1) Å, mainly due to the difference of the donor bond character of Al−N2 and the σ-bond character of Al−N1. The two high-field singlet resonances in ^{1}H NMR spectrum of **2** (−0.13 and −0.56 ppm) are attributed to the two methyl groups at the Al site with a rational integral ratio. The observed different reactivities of $AlEt_3$ and $AlMe_3$ toward $\mathbf{L^1}$ may be attributed to steric factors; the sterically bulkier $AlEt_3$ may prevent the Et of $AlEt_3$ from interaction with the protons of the methyl group connected to the imino carbon. Thus, the observed result of $AlEt_3$ shows a preference for nucleophilic addition.[9b] However, the activity of aluminum trialkyls cannot be ruled out. Elemental analysis results of complexes **1** and **2** are also in agreement with those of NMR and X-ray studies.

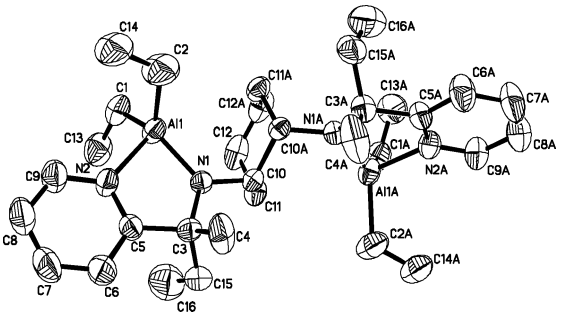


Figure 1. ORTEP representation of the X-ray structure of complex **1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

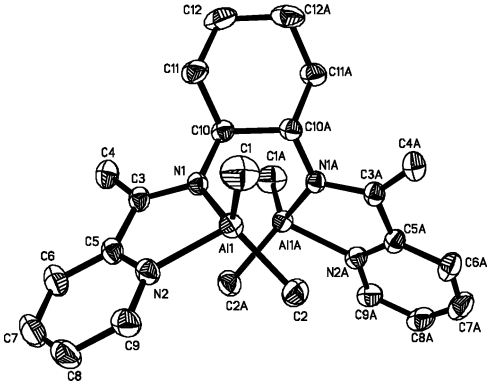


Figure 2. ORTEP representation of the X-ray structure of complex **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

The above results prompted us to examine the reactivities of other imino-functionalized hetroaromatic compounds with aluminum alkyls. Three different 2-imino-functionalized indoles 2-(RN=CH)C_8H_5NH (R = ^{t}Bu ($\mathbf{L^2H}$), C_6H_5 ($\mathbf{L^3H}$), 2,6-$Me_2C_6H_3$ ($\mathbf{L^4H}$)) were subjected to reaction with 1 equiv of AlR_3 (R = Me, Et), producing the corresponding dialkylaluminum complexes formulated as [2-(RN=CH)C_8H_5N]$AlMe_2$ (R = ^{t}Bu (**3**), C_6H_5 (**4**), 2,6-$Me_2C_6H_3$ (**5**)) and [2-(2,6-$Me_2C_6H_3N$=CH)C_8H_5N]$AlEt_2$ (**6**) in good yields (Scheme 2). Different from the formation of complexes **1** and **2**, neither sp^3 C−H activation nor alkyl addition to the imino C=N bond was observed; only the acid−base process was observed in the preparation of **3**−**6**. This observation could be attributed to different pK_a values of corresponding protons of the methyl group connected to the imine group (the pK_a value of protons of the methyl group connected to imine should be between those of propylene (pK_a = 43) and acetonitrile (pK_a = 25), and the pK_a value of indole is 16.2). X-ray analyses reveal that the N1−Al1−N2 angles ((84.9(1)° for **3**, 84.6(1)° for **4**, 84.3(1)° for **5**, and 84.1(1)° for (**6**)) largely deviated from ideal tetrahedral angles, leading to a distorted-tetrahedral geometry around the aluminum (the structure of complexes **3**−**6** are shown in Figures 3−6). The N1−Al1−N2 angles of 84.9(1)° for **3**, 84.6(1)° for **4**, 84.3(1)° for **5**, and 84.1(1)° for **6** are smaller than that the 86.6(1)° observed in [2-(2,6-^{i}Pr$_2$$C_6H_3$N=CH)-5-^{t}Bu$C_4H_2$N]AlMe(Cl).[1c] The Al−N-(imino) bond lengths of compounds **3**−**6** (1.993(2) Å for **3**,

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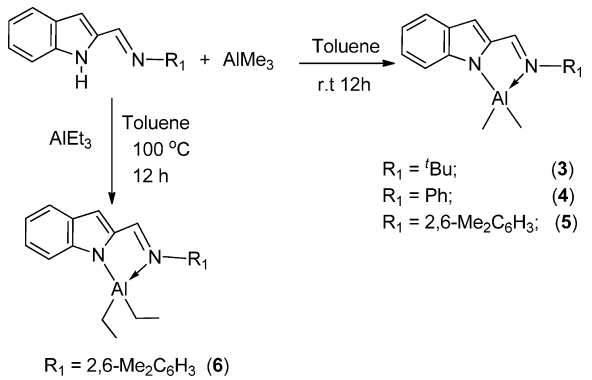
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of Complexes 1−6

	1	2	3	4	5	6
Al(1)−N(1)	1.832(3)	1.861(1)	1.882(2)	1.901(2)	1.902(2)	1.910(2)
Al(1)−N(2)	1.974(4)	1.973(1)	1.993(2)	2.011(3)	1.989(2)	1.997(2)
Al(1)−C(1)	1.964(5)	1.959(2)	1.943(3)	1.944(4)	1.952(2)	1.959(2)
Al(1)−C(2)	2.010(5)	1.959(2)	1.942(3)	1.960(4)	1.952(2)	1.959(2)
C(3)−N(1)	1.473(4)	1.378(2)				
C(4)−C(3)	1.611(2)	1.348(2)				
N(1)−Al(1)−C(1)	124.6(2)	115.7(1)	113.7(1)	112.8(2)	114.3(1)	111.2(1)
N(1)−Al(1)−C(2)	119.9(2)	122.2(1)	111.0(1)	114.6(1)	111.4(1)	114.1(1)
C(1)−Al(1)−C(2)	109.8(2)	114.7(1)	119.3(1)	119.8(2)	118.8(1)	119.9(1)
N(1)−Al(1)−N(2)	85.2(2)	83.9(1)	84.9(1)	84.6(1)	84.3(1)	84.1(1)
C(1)−Al(1)−N(2)	104.3(2)	109.2(1)	112.3(1)	111.6(2)	110.0(1)	114.6(1)
C(2)−Al(1)−N(2)	105.6(2)	104.4(1)	110.5(1)	107.7(1)	113.0(1)	107.5(1)

Scheme 2. Preparation of Complexes 3−6



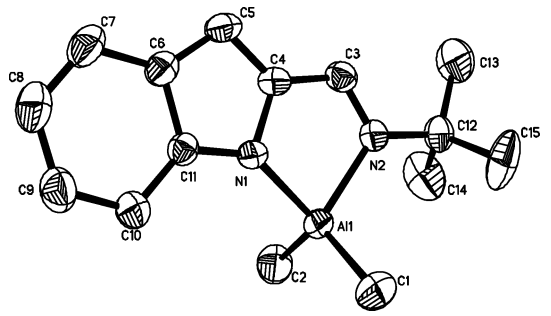


Figure 3. ORTEP representation of the X-ray structure of complex **3**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

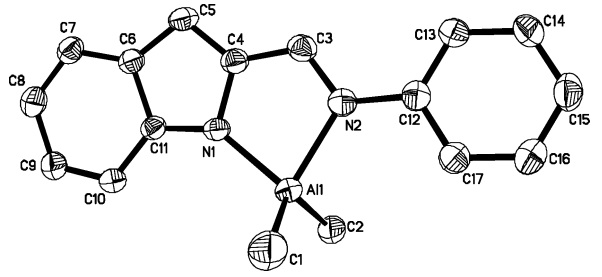


Figure 4. ORTEP representation of the X-ray structure of complex **4**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

2.011(3) Å for **4**, 1.989(2) Å for **5**, 1.997(2) Å for **6**) are similar, which are slightly longer than those found in salicylaldiminato aluminum complexes (range 1.94−1.98 Å)[17]

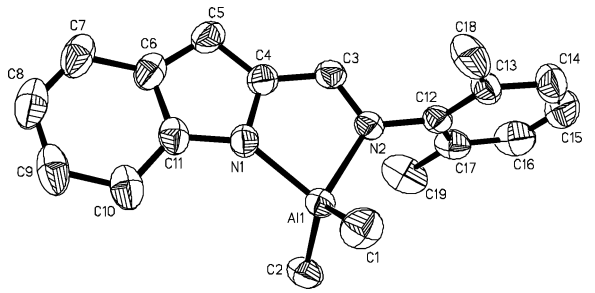


Figure 5. ORTEP representation of the X-ray structure of complex **5**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

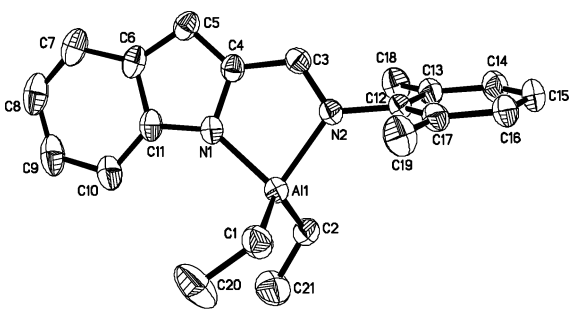


Figure 6. ORTEP representation of the X-ray structure of complex **6**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

and the monopyrrolylaldiminato aluminum complex [2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)-5-^{t}BuC$_4$H$_2$N]AlMe(Cl) (1.944 Å),[1c] which is similar to the average Al−N(imino) bond length of 1.993 Å found in the complex [2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)-C$_4$H$_3$N]$_2$AlCl.[8b] The Al−N(indole) bond lengths of complexes **3**−**6** (1.882(2) Å for **3**, 1.901(2) Å for **4**, 1.902(2) Å for **5**, 1.910(2) Å for **6**) are slightly shorter than the Al−N(pyrrole) bond length (1.96 Å) found in the complex [2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]$_2$AlCl and are similar to the Al−N(pyrrole) bond length in the complex [2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)-5-^{t}BuC$_4$H$_2$N]AlMe(Cl) (1.905 Å), indicating different electronic and steric effects of the corresponding ligands. The ^{1}H NMR spectra of these indolylaldiminato Al complexes show the proton resonances of the two methyl groups at δ −0.21 ppm for **3**, −0.48 ppm for **4**, and −0.18 ppm for **5**, respectively. The proton resonances of the imino group appear at δ 7.23 ppm for **3**, 7.11 ppm for **4**, and 7.05 ppm for **5**, which are consistent with the X-ray data.

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The ^{13}C NMR spectra show the methyl carbon resonance at −9.5 ppm for **3**, −9.9 ppm for **4**, and −9.3 ppm for **5**. The proton resonances of the methlene groups of $L^4Al(CH_2CH_3)_2$ in complex **6** appear at 0.40−0.28 ppm, and the corresponding methyl protons appear at 1.30−1.33 ppm.

Catalytic Activities of the Complexes on Guanylation of Aromatic Amines. With the above dinuclear and mononuclear aluminum complexes in hand, their catalytic activities for the guanylation reaction were studied.

Complex **2** was employed as the precatalyst for screening the optimal conditions for the model reaction between aniline and *N,N′*-dicyclohexylcarbodiimide, and the results are given in Table 2. It was found that the catalytic guanylation reaction of aniline could be completed in toluene at room temperature within 1 h, producing the product in 97% yield in the presence of 0.5 mol % of catalyst (entry 3). Increasing the catalyst loading did not improve the yield of the reaction, while decreasing the catalyst loading to 0.1 mol % led to a significantly decreased yield of 78% (entry 4). Performing the reaction in other solvents such as THF and hexane gave comparable results, and up to 96% yield could still be obtained when the reaction was carried out under solvent-free conditions (entries 5−7). It should be noted that no product formation was observed in the absence of the catalyst even when the reaction mixture was heated at 110 °C for 24 h. Then the catalytic activities of complexes **1** and **3**−**6** were examined. In general, the catalytic activities of dinuclear aluminum complexes **1** and **2** were higher than those of mononuclear complexes **3**−**6** (entries 9−14) under the same reaction conditions, probably due to dinuclear aluminum complexes with two active sites. Therefore, complex **2** was selected as the precatalyst for subsequent reaction scope studies.

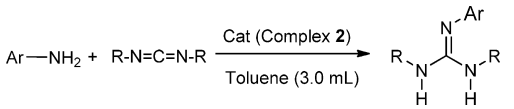
Table 2. Reaction of Aniline with *N,N′*-Dicyclohexylcarbodiimide Catalyzed by Different Aluminum Complexes under Various Conditions[a]

entry	cat.	loading (mol %)	solvent	temp (°C)	time (h)	yield[b] (%)
1	**2**	2	toluene	room temp	0.5	98
2	**2**	1	toluene	room temp	0.5	97
3	**2**	0.5	toluene	room temp	1	97
4	**2**	0.1	toluene	room temp	6	78
5	**2**	0.5	THF	room temp	1	98
6	**2**	0.5	solvent-free	room temp	1	96
7	**2**	0.5	hexane	room temp	1	96
8	none		solvent-free	110	24	0
9	**1**	0.5	toluene	room temp	1	95
10	**3**	0.5	toluene	room temp	1	71
11	**3**	1	toluene	60	3	91
12	**4**	1	toluene	60	3	90
13	**5**	1	toluene	60	3	92
14	**6**	1	toluene	60	3	91

[a]The reaction was performed by treating 1 equiv of aniline with 1 equiv of *N,N′*-dicyclohexylcarbodiimide in 3.0 mL of solvent. [b]Isolated yield.

Next, the guanylation of a variety of aromatic amines by carbodiimides was examined with complex **2** in toluene, and the results are summarized in Table 3. Generally, a wide range of substituted aromatic amines are suitable for the catalytic reaction. In the case of $^iPrN{=}C{=}N^iPr$, probably due to steric reasons, the catalytic reactions required 1 mol % of the precatalyst to give satisfactory yields of the desired products. Anilines with strongly electron donating substituents such as CH_3O-, CH_3-, and $^tBu-$ are favored for the reaction to provide excellent yields (>96%) within 1 h at room temperature (Table 3, entries 3−8), while those with strongly electron withdrawing substituents required longer reaction times at elevated reaction temperatures (Table 3, entries 21−

Table 3. Results of Reactions of Different Anilines with Carbodiimides Catalyzed by Complex 2[a]



Entry	cat. loading (mol %)	R	Ar	temp (°C)	time (h)	yield (%)[b]
1	0.5	Cy	C_6H_5	room temp	1	97
2	1	^{i}Pr		room temp	1	96
3	0.5	Cy	4-MeC_6H_4	room temp	1	97
4	1	^{i}Pr		room temp	1	96
5	0.5	Cy	4-^{t}BuC_6H_4	room temp	1	99
6	1	^{i}Pr		room temp	1	98
7	0.5	Cy	4-$OMeC_6H_4$	room temp	1	98
8	1	^{i}Pr		room temp	1	97
9	0.5	Cy	4-ClC_6H_4	room temp	1	97
10	1	^{i}Pr		room temp	1	96
11	0.5	Cy	4-BrC_6H_4	room temp	1	98
12	1	^{i}Pr		room temp	1	97
13	0.5	Cy	1-naphthyl	room temp	1	99
14	1	^{i}Pr		room temp	1	96
15	1	Cy	2-MeC_6H_4	60	3	95
16	1	^{i}Pr		60	3	94
17	2	Cy	2,6-$Me_2C_6H_3$	100	12	79
18	2	^{i}Pr		100	12	75
19	1	Cy	2-C_5H_4N	60	3	90
20	1	^{i}Pr		60	3	87
21	1	Cy	4-$NO_2C_6H_4$	60	3	92
22	1	^{i}Pr		60	3	91
23	1	Cy	2-$NO_2C_6H_4$	60	3	90
24	1	^{i}Pr		60	3	88

[a]The reaction was performed by treating 1 equiv of anilines with 1 equiv of *N,N′*-dialkylcarbodiimide. [b]Isolated yield.

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24). As observed in previous relevant studies,[15a] anilines with substituents at the ortho positions required a higher reaction temperature and longer reaction time to give high yields, which might be ascribed to steric reasons (Table 3, entries 15−18).

Catalytic Mechanism. In recent reports, mixed Al alkyl/halide and guanidinate-supported Al complexes were successful precatalysts for the guanylation of anilines with carbodiimides.The catalytic cycle has been proposed to proceed via amine exchange with the supporting ligand to form a catalytically active three-coordinate Al species, which could subsequently add to carbodiimides to form Al guanidinate species.[5a,15a]

To provide evidence for the catalytic reaction mechanism of the above aluminum complexes, the 1:1:1 reaction of complex **5**, 4-$MeC_6H_4NH_2$, and CyN═C═NCy was carried out in toluene at 80 °C to give the aluminum guanidinate complex **7** (Figure 7). This result could be explained by the interaction of

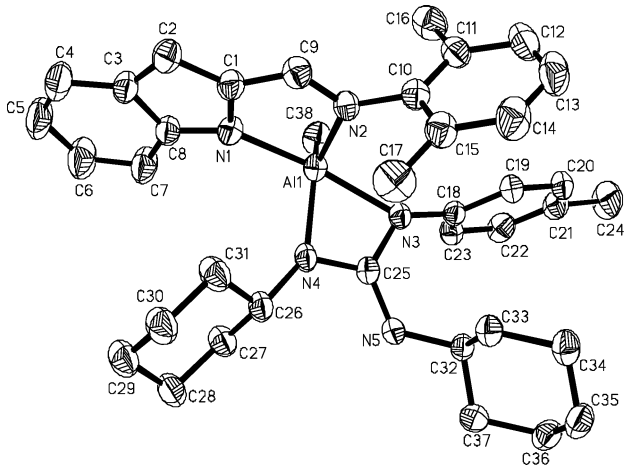


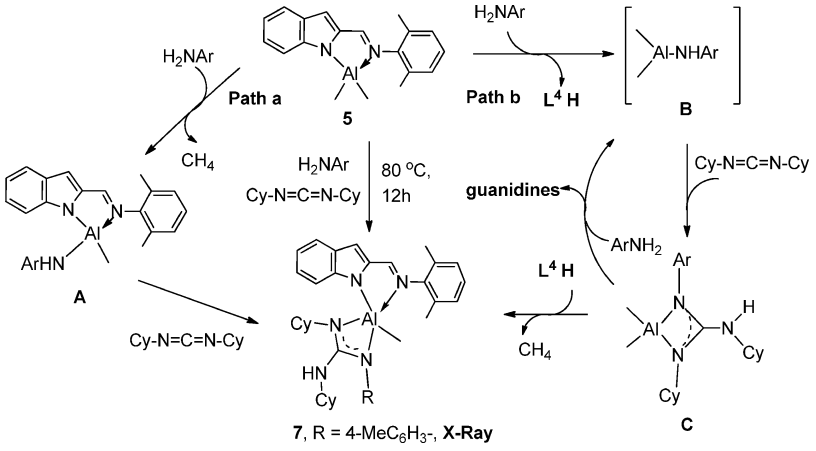
Figure 7. ORTEP representation of the X-ray structure of complex **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−N(1), 1.968(2); Al(1)−N(2), 2.037(2); Al(1)−N(3), 2.027(2); Al(1)−N(4), 1.921(2); Al(1)−C(38), 1.969(3); N(1)−Al(1)−N(2), 80.4(1); N(4)−Al(1)−N(3), 67.4(1).

aniline with the methyl ligand of the complex to produce intermediate **A**, which then interacted with carbodiimide via an insertion reaction to give the final product (Scheme 3, path **a**). However, when the 1:1 reaction of complex **5** with 4-$MeC_6H_4NH_2$ in C_6D_6 at 80 °C was probed by ^{1}H NMR techniques, it showed no change in Al−CH_3 signals after 12 h, indicating inactivity of the methyl group of the complex to the aniline. For the addition of CyN═C═NCy to the mixture at room temperature, the resonances of the guanidine product 4-MeC_6H_4N═$C(NHCy)_2$ and the free ligand $\mathbf{L^4H}$ were observed after 1 h in the ^{1}H NMR spectra, and more strong resonances of the free ligand $\mathbf{L^4H}$ were observed after 16 h at room temperature. Surprisingly, the resonances of the corresponding free ligand $\mathbf{L^4H}$ gradually disappeared in the ^{1}H NMR spectra when the reaction was prolonged to 22 h, and the resonances of complex **7** were observed as the disappearance of the free ligand $\mathbf{L^4H}$. This observation suggested that the methyl moieties on the metal center are not involved in the initiation step of the catalytic reaction; the interaction of aniline with complex **5** produced the amido intermediate **B** with release of the free ligand $\mathbf{L^4H}$ probably due to the small Al ion, and insertion of the carbodiimide into the Al−N (amido intermediate **B**) bond gave the guanidinate intermediate **C**. The released free ligand then interacted with one of methyl groups, resulting in the final complex **7**. In the catalytic cycle, interaction of the intermediate **C** with aniline produced the guanidine products (Scheme 3, path **b**; ^{1}H NMR probing spectra are provided in the Supporting Information).

CONCLUSIONS

In summary, reactions of different heteroaromatic imines with trialkylalanes showed different reactivities, with the isolation of different types of aluminum alkyl complexes. A study of the catalytic activities of aluminum complexes toward the guanylation of aryl amines showed that the dinuclear aluminum complexes **1** and **2** exhibited catalytic activities higher than those of mononuclear aluminum complexes **3**−**6**. The ^{1}H NMR probing experiments gave evidence that the methyl groups of the complexes are inactive toward the aniline, and the results supported the dissociation of the supporting ligand in the initiation step, which is different from the catalytic mechanism of aluminum trialkyl catalyzed guanylation reactions. The results suggested that different aluminum complex catalyzed guanylation reactions would involve different catalytic mechanisms. Further works in this field are now in progress.

Scheme 3. Proposed Mechanism and the Formation of the Aluminum Guanidinate Complex 7



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EXPERIMENTAL SECTION

General Methods. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and under an oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Iminopyridine[18] and indolyl-2-aldimine[19] ligands were prepared according to literature procedures. All amines were predried, sublimed, recrystallized, or distilled before use, and *N,N*-dicyclohexylcarbodiimide and *N,N*-diisopropylcarbodiimide were purified before use. $AlMe_3$ and $AlEt_3$ were purchased from Acros and used as received. Elemental analyses were performed on a PerkinElmer 2400 CHN analyzer. Melting points were determined in sealed capillaries without correction. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR or AV-500 NMR spectrometer (300 or 500 MHz in C_6D_6 for aluminum complexes). Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by use of J. Young valve NMR tubes. Chemical shifts (δ) were reported in ppm. J values were reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer (KBr pellet). Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector.

Preparation of Cy[NC(Me)(Et)-2-(C_5H_4N)$AlEt_2$]$_2$ (1). A solution of $AlEt_3$ (1.0 mL, 2.0 M in toluene, 2.0 mmol) was added slowly to a solution of $\mathbf{L^1}$ (0.320g, 1.0 mmol) in 20 mL of toluene. The resulting solution was stirred at room temperature for 12 h. The solvent was removed under vacuum, and the residue was diluted with toluene and filtered. The toluene solution was cooled to −35 °C. Pale yellow crystals that were suitable for X-ray diffraction were obtained from the solution after several days. (0.466 g, 85%). Mp: 178−180 °C under Ar. ^1H NMR (500 MHz, C_6D_6): δ 7.89 (t, J = 5.0 Hz, J = 5.5 Hz, 2H), 6.83 (t, J = 5.0 Hz, J = 7.0 Hz, 2H), 6.70 (d, J = 3.5 Hz, 2H), 6.33 (d, J = 5.0 Hz, 2H), 3.37 (d, J = 9.0 Hz, 2H), 2.58−2.29 (m, 4H), 2.18−1.97 (m, 4H), 1.95−1.93 (m, 2H), 1.59 (s, 6H), 1.52 (s, 6H), 1.51−1.42 (m, 6H), 1.35−1.31 (m, 2H), 0.69 (t, J = 7.0 Hz, J = 7.5 Hz, 6H), 0.62−0.57 (m, 8H). ^{13}C NMR (75 MHz, C_6D_6): δ 171.3, 171.2, 171.0, 143.0, 142.9, 139.1, 122.2, 122.1, 122.0, 121.7, 67.5, 67.4, 57.0, 56.7, 56.6, 56.3, 33.2, 32.8, 32.6, 32.0, 31.9, 31.7, 31.6, 31.0, 22.4, 21.9, 21.7, 21.4, 11.4, 11.2, 11.0, 10.6, 9.6, 9.5, 9.0, 4.8, 1.4. IR (KBr pellet, cm^{-1}): ν 3049 (s), 2966 (m), 2929 (w), 2854 (m), 1587 (s), 1570 (s), 1460 (m), 1429 (m), 1375 (s), 1300 (s), 1153 (s), 777 (m), 748 (m), 684 (m). Anal. Calcd for $C_{32}H_{54}Al_2N_4$: C, 70.04; H, 9.92; N, 10.21. Found: C, 69.92; H, 9.72; N, 10.53.

Preparation of Cy[NC(=CH_2)-2-(C_5H_4N)$AlMe_2$]$_2$ (2). Complex **2** was prepared following a procedure similar to that described for **1** from $\mathbf{L^1}$ (0.320 g, 1.0 mmol) and $AlMe_3$ (2.0 mL, 1.0 M in toluene, 2.0 mmol). The reaction yielded yellow crystals of **2** (0.385 g, 89%). Mp: 181−182 °C under Ar. ^1H NMR (500 MHz, C_6D_6): δ 7.49 (d, J = 5.0 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.68 (t, J = 7.5 Hz, J = 8.0 Hz, 2H), 6.17 (t, J = 6.0 Hz, J = 6.0 Hz, 2H), 4.87 (s, 2H), 4.48 (s, 2H), 3.93 (m, 2H), 3.03 (m, 2H), 1.77 (m, 2H), 1.46 (m, 4H), −0.13 (s, 6H), −0.56 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 158.1, 148.9, 142.7, 138.7, 128.4, 122.4, 120.4, 81.5, 60.9, 30.9, 26.3, −7.3, −7.8. IR (KBr pellet, cm^{-1}): ν 2922 (m), 1627 (s), 1614 (s), 1589 (m), 1560 (m), 1465 (m), 1425 (w), 1344 (m), 1290 (m), 1190 (m), 1118 (m), 1089 (m), 1033 (m), 948 (m), 796 (m), 738 (m), 684 (m). Anal. Calcd for $C_{24}H_{34}Al_2N_4$: C, 66.65; H, 7.92; N, 12.95. Found: C, 66.90; H, 7.88; N, 12.59.

Preparation of [2-(^{t}Bu-N=CH)C_8H_5N]$AlMe_2$ (3). This complex was prepared following a procedure similar to that described for **1** from $\mathbf{L^2H}$ (0.200 g, 1.0 mmol) and $AlMe_3$ (0.5 mL, 2.0 M, 1.0 mmol). Light yellow crystals were obtained after recrystallization from hexane at 0 °C for several days (0.231 g, 90% yield). Mp: 158−160 °C under Ar. ^1H NMR (500 MHz, C_6D_6): δ 7.82 (d, J = 7.5 Hz, 1H), 7.63 (s, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.26 (t, 1H), 7.14 (t, 1H), 6.94 (s, 1H), 0.90 (s, 12H), −0.21 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ 157.7, 144.8, 138.5, 131.0, 125.1, 121.9, 119.2, 114.6, 110.2, 56.2, 28.7, −9.5. IR (KBr pellet, cm^{-1}): ν 2970 (m), 1664 (w), 1635 (s), 1616 (m), 1577 (w), 1427 (w), 1346 (m), 1296 (m), 1207 (w), 1128 (m), 1045 (w), 931 (w), 796 (m), 756 (w), 678 (m). Anal. Calcd for $C_{15}H_{21}N_2Al$: C, 70.29; H, 8.26; N, 10.93. Found: C, 70.07; H, 8.21; N, 11.04.

Preparation of [2-(C_6H_5-N=CH)C_8H_5N]$AlMe_2$ (4). This complex was prepared following a procedure similar to that described for **1** from $\mathbf{L^3H}$ (0.220g, 1.0 mmol) and $AlMe_3$ (0.5 mL, 2.0 M, 1.0 mmol). Yellow crystals were obtained after recrystallization from hexane at 0 °C for several days (0.243 g, 88% yield). Mp: 185−188 °C under Ar. ^1H NMR (300 MHz, C_6D_6): δ 7.41 (d, J = 8.1 Hz, 1H), 7.20 (s, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.90−6.85 (m, 1H), 6.78−6.70 (m, 1H), 6.60 (s, 1H), 6.63−6.56 (m, 5H), −0.48 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 146.7, 143.5, 140.0, 132.2, 129.7, 127.5, 127.2, 123.2, 120.8, 120.6, 115.7, 114.2, −9.9. IR (KBr pellet, cm^{-1}): ν 2945 (w), 1604 (m), 1570 (s), 1531 (w), 1489 (w), 1344 (m), 1301 (m), 1120 (m), 1029 (m), 943 (m), 792 (w), 759 (m), 690 (m), 648 (m). Anal. Calcd for $C_{17}H_{17}N_2Al$: C, 73.93; H, 6.20; N, 10.14. Found: C, 73.68; H, 6.17; N, 10.02.

Preparation of [2-(2,6-$Me_2C_6H_3$-N=CH)C_8H_5N]$AlMe_2$ (5). This complex was prepared following a procedure similar to that described for **1** from $\mathbf{L^4H}$ (0.248g, 1.0 mmol) and $AlMe_3$ (0.5 mL, 2.0 M, 1.0 mmol). Yellow crystals were obtained after recrystallization from hexane at 0 °C for several days (0.277 g, 91% yield). Mp: 160−162 °C under Ar. ^1H NMR (300 MHz, C_6D_6): δ 7.85 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.05 (s, 1H), 7.0−6.94 (m, 3H), 6.92 (s, 1H), 2.05 (s, 6H), −0.18 (s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ 165.3, 146.5, 143.4, 139.4, 132.0, 131.4, 128.7, 127.0, 127.0, 123.3, 120.5, 115.8, 113.7, 18.1, −9.3. IR (KBr pellet, cm^{-1}): ν 2922 (w), 1627 (s), 1414 (s), 1589 (m), 1566 (m), 1465 (m), 1425 (w), 1344 (m), 1290 (m), 1193 (m), 1118 (m), 1089 (m), 796 (m), 761 (m), 684 (m), 657 (m). Anal. Calcd for $C_{19}H_{21}N_2Al$: C, 74.98; H, 6.95; N, 9.20. Found: C, 74.87; H, 7.00; N, 9.18.

Preparation of [2-(2,6-$Me_2C_6H_3$-N=CH)C_8H_5N]$AlEt_2$ (6). A solution of $AlEt_3$ (1.0 mL, 1.0 M in toluene, 1.0 mmol) was added slowly to a solution of $\mathbf{L^4H}$ (0.248 g, 1.0 mmol) in 20 mL of toluene. The resulting solution was then heated to 100 °C for 12 h. The solvent was removed under vacuum, and the residue was diluted with hexane and filtered. Yellow crystals that were suitable for X-ray diffraction were obtained from the solution after several days at −35 °C (0.259 g, 78% yield). Mp: 168−170 °C under Ar. ^1H NMR (500 MHz, C_6D_6): δ 7.75 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.95 (s, 1H), 6.92−6.87 (m, 1H), 6.83 (t, J = 6.4 Hz, 3H), 1.96 (s, 6H), 1.31 (t, J = 8.2 Hz, 6H), 0.40−0.28 (m, 4H). ^{13}C NMR (125 MHz, C_6D_6): δ 165.4, 147.1, 143.9, 139.8, 128.9, 128.4, 127.4, 127.3, 120.8, 116.3, 114.1, 18.3, 9.2, 0.4. IR (KBr pellet, cm^{-1}): ν 2941 (w), 1627 (s), 1614 (s), 1589 (m), 1465 (m), 1425 (m), 1338 (m), 1294 (m), 1193 (m), 1126 (m), 1089 (m), 800 (m), 750 (m), 736 (m). Anal. Calcd for $C_{21}H_{25}N_2Al$: C, 75.88; H, 7.58; N, 8.43. Found: C, 75.67; H, 7.59; N, 8.45.

Preparation of [2-(2,6-$Me_2C_6H_3$-N=CH)C_8H_5N][CyN=C(4-MeC_6H_3N)(NHCy)]AlMe (7). A Schlenk flask was charged with complex **5** (0.304 g, 1.0 mmol), *p*-toluidine (0.107 g, 1.0 mmol), *N,N′*-dicyclohexylcarbodiimide (0.206 g, 1.0 mmol), and toluene (30 mL). The reaction mixture was stirred overnight at 80 °C. The solvent was evaporated to yield the crude product, which was recrystallized from toluene and hexane to give yellow crystals at 0 °C after several days (0.493 g, 82%). Mp: 171 °C under Ar. ^1H NMR (500 MHz, C_6D_6): δ 7.95 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.36 (t, 1H), 7.15−7.07 (m, 2H), 7.03−6.89 (m, 4H), 6.85 (d, J = 7.5 Hz, 2H), 6.35 (s, 2H), 3.93 (d, J = 8.5 Hz, 1H), 2.89 (m, 2H), 2.19 (s, 3H), 2.04 (s, 6H), 1.76−1.59 (m, 4H), 1.54−1.26 (m, 6H), 1.17−1.02 (m, 4H), 0.79−0.66 (m, 6H), −0.01 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6): δ 166.0, 162.3, 147.8, 144.9, 139.3, 132.7, 130.8, 129.2, 128.4, 126.4, 125.6, 124.7, 123.3, 119.8, 117.7, 111.6, 54.4, 51.2, 35.3, 34.4, 34.0, 33.6, 33.2, 26.5, 25.8, 25.6, 24.9, 24.7, 20.9, 18.9, −6.8. IR (KBr pellet, cm^{-1}): ν 2927 (w), 2852 (m), 1629 (s), 1616 (s), 1504 (m), 1448 (w), 1344 (m), 1193 (m), 1126 (m), 1089 (m), 804 (m), 752 (m), 736 (m). Anal. Calcd for $C_{38}H_{48}Al\,N_5$: C, 75.84; H, 8.04; N, 11.64. Found: C, 76.06; H, 7.98; N, 11.81.

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X-ray Crystallographic Analyses of Aluminum Complexes. Suitable crystals of complexes **1**−**7** were each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART APEXII CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K, with φ and ω scan techniques. An empirical absorption correction was applied using the SADABS program.[20] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.[21] The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities were of no chemical significance. Selected bond lengths and angles are compiled in Table 1, and crystal data and details of the data collection and structure refinements are given in the Supporting Information.

General Procedure for the Direct Synthesis of Guanidines from the Reaction of Aromatic Amines with Carbodiimides Catalyzed by Complex 2. A 25.0 mL Schlenk tube was charged with the dinuclear dimethylaluminum complex **2** (0.005 or 0.01 equiv), aromatic amine (1.0 equiv), and toluene (3.0 mL) under dried argon. To the mixture was added carbodiimide (1.0 equiv). The resulting mixture was stirred at room temperature or was heated to 60 or 100 °C, as shown in Table 3. After the reaction was completed, the reaction mixture was hydrolyzed by water (3.0 mL), extracted with dichloromethane (3 × 10.0 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the final products were further purified by washing with diethyl ether or hexane.

^{1}H NMR Monitoring of the Catalytic Reaction. In a glovebox, a J. Young valve NMR tube was charged with complex **5** (9.1 mg, 0.03 mmol), C_6D_6 (0.5 mL), and aniline (3.2 mg, 0.03 mmol), and the reaction was run at 80 °C for 12 h in an oil bath, at which time no change in Al−CH_3 signals was monitored by ^{1}H NMR spectroscopy. Then the reaction mixture was cooled to room temperature, followed by the addition of *N*,*N*′-dicyclohexylcarbodiimide (6.2 mg, 0.03 mmol). The reaction process was monitored by ^{1}H NMR spectroscopy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving characterization data and spectral data and X-ray crystallographic data and structure refinement details for complexes **1**−**7**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00101.

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Notes

The authors declare no competing financial interest.

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