DOI: 10.1002/ejic.200500740

Synthesis, Structures, and Luminescent Properties of Aluminum Complexes with Chelating Anilido-Imine Ligands

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Keywords: Aluminum / N ligands / Luminescence

The syntheses of a number of four-coordinate aluminum complexes, ortho- $C_6H_4(NAr')(CH=NAr'')AlCl_2$ [Ar' = Ar'' = 2,6-iPr_2C_6H_3 (**2a**); Ar' = 2,6-iPr_2C_6H_3, Ar'' = 2,6-Me_2C_6H_3 (**2b**); Ar' = Ar'' = 2,6-Me_2C_6H_3 (**2c**); Ar' = p-MeC_6H_4, Ar'' = 2,6-iPr_2C_6H_3 (**2d**)], are described. Complexes **2a–2d** were synthesized from the reaction of $AlCl_3$ with lithium salt of the corresponding ligand at room temperature. All complexes

Introduction

Luminescent metal complexes have attracted increasing attention because of their potential application in areas of chemistry, medicine, and material science.^[1] Many luminescent complexes of main group and transition metals, such as Al^{III},^[2] Zn^{II},^[3] Pt^{II},^[4] Ir^{III},^[5] and Re^I,^[6] have been designed and synthesized in recent years. Particularly, chelated aluminum complexes have attracted much attention because of their low cost, and good luminescent and electron-transporting properties. As the well-known tris(8-hydroxyquinolinyl)aluminum (Alq₃) was found to be a good emitter, and a highly efficient electron-transporting material and host material in organic electroluminescence devices,^[7–9] a large number of its derivatives with modified 8-hydroxyquinoline ligands have been investigated.^[1b,2,10] Aluminum complexes with nitrogen-containing ligands have also been reported,^[11] while the luminescent properties of coordinative unsaturated aluminum complexes have not been extensively explored, probably because of their instability to air and moisture.^[12,13] We have recently focused our attention on the synthesis of aluminum complexes of this type. As a continuation of our studies on the luminescent alkylaluminum complexes with chelating anilido-imine ligands (Scheme 1 A),^[14d] herein we report the syntheses, characterization, and fluorescent properties of a number of aluminum dichloride complexes with anilido-imine ortholigands, $C_6H_4(NAr')(CH=NAr'')AlCl_2 [Ar' = Ar'' = 2,6-iPr_2C_6H_3]$

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molecular structures of complexes **2a**, **2b**, and **2d** were determined by X-ray crystallography. Luminescent properties of complexes **2a–2d** in both solution and the solid state were studied. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim,

were characterized by ¹H and ¹³C NMR spectroscopy and

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(2a); $Ar' = 2,6-iPr_2C_6H_3$, $Ar'' = 2,6-Me_2C_6H_3$ (2b); $Ar' = Ar'' = 2,6-Me_2C_6H_3$ (2c); $Ar' = p-MeC_6H_4$, $Ar'' = 2,6-iPr_2C_6H_3$ (2d)].



Scheme 1.

Results and Discussion

Ligand Synthesis

Free ligands, *ortho*-C₆H₄(NHAr')(CH=NAr'') [Ar' = Ar'' = 2,6-*i*Pr₂C₆H₃ (1a); Ar' = 2,6-*i*Pr₂C₆H₃, Ar'' = 2,6-Me₂C₆H₃ (1b); Ar' = Ar'' = 2,6-Me₂C₆H₃ (1c); Ar' = *p*-MeC₆H₄, Ar'' = 2,6-*i*Pr₂C₆H₃ (1d)], were synthesized by a literature procedure.^[15] Of these free ligands, compounds 1a, 1c, and 1d are known, while 1b is a new compound. The new ligand 1b was prepared by the reaction of *ortho*-C₆H₄F(CH=NC₆H₃Me₂-2,6) with LiN(H)Ar (Ar = 2,6-*i*Pr₂C₆H₃) (Scheme 2) in good yield (72% isolated yields). The reaction was carried out in THF and the crude product

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was purified by crystallization from methanol. Compound **1b** was characterized by ¹H and ¹³C NMR spectroscopy along with elemental analysis. The ¹H NMR spectrum of **1b** exhibits resonance at $\delta = 8.39$ ppm for the imino CH proton, with the corresponding ¹³C NMR resonance at $\delta =$ 166.25 ppm. The NH resonance appears at characteristically low field ($\delta = 10.5$ ppm). The infrared absorption band of the imine C=N stretch occurs in the region 1617 cm⁻¹. Those data are similar to the corresponding values of **1a**, **1c**, and **1d**.^[14d]



Scheme 2. Synthetic procedure of ligands 1a-1d.

 C_s -symmetric structures in solution. All complexes are more stable than the corresponding alkylaluminum complexes in solution; they have pretty good thermal stability and can be heated in boiling toluene for several hours without obvious decomposition.



Complex Synthesis

The aluminum dichloride complexes 2a-2d were synthesized in reasonable yields (68-75%) by reaction of AlCl₃ with the lithium salt of the corresponding ligand that was generated in situ by treating the free ligand with nBuLi in hexanes at -78 °C (Scheme 3). All complexes are well soluble in toluene, dichloromethane, diethyl ether, and THF, but sparingly soluble in saturated hydrocarbon solvents. Complexes 2a-2d were all characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy, and satisfactory analytic results were obtained for all compounds. In the ¹H NMR spectra of these complexes, the resonances for the imino CH protons (δ = 7.32–7.90 ppm) shift about 1 ppm towards high field compared to the corresponding signals of the free ligands. However, the resonances ($\delta = 173.5 - 174.5$ ppm) for the imino CH carbons in the ¹³C NMR spectra shift to low field in comparison with the corresponding ones of the free ligands and the dialkylaluminum complexes.^[14d] The N-H signals of the free ligands disappear in the ¹H NMR spectra of complexes 2a-2d, which is indicative of formation of an Al-N bond in these compounds. The two methyl groups of the isopropyl units in complexes 2a, 2b, and 2d are inequivalent, as the coordination of the anilido-imine ligands to the aluminum center causes rotation about the N-aryl bond to become slow on the NMR timescale.^[16] In addition, ¹H and ¹³C NMR spectra reveal that these complexes all have

Scheme 3. Synthetic procedure of complexes 2a-2d.

Crystal Structure

The molecular structures of the complexes 2a, 2b, and 2d were determined by X-ray crystallographic analysis. Crystals of all three complexes suitable for X-ray crystal structure determination were grown from n-hexane at room temperature. The ORTEP drawings of molecular structures of 2a, 2b, and 2d are shown in Figure 1 (top), Figure 2, and Figure 3, respectively. Selected bond lengths and angles for these complexes are given in Table 1. The X-ray analysis reveals that all three complexes adopt a distorted tetrahedral geometry with the metal center chelated by the bidentate ligand through the imine and amido nitrogen atoms. The N-Al-N bite angle in **2b** [99.27 (6)°] is larger than those in **2a** [97.59 (8)°] and **2d** [97.82 (8)°], but similar to the one in the related β -diketiminato aluminum complex [Scheme 1; B_1 99.36 (4)°, B_2 99.41(12)°],^[17a,17b] which contains a similar six-membered C₃N₂Al metallacycle. In these three complexes, the six-membered chelating rings are nearly planar with the aluminum atom lying 0.5017, 0.0963, and 0.3065 Å out of the plane, respectively. The imino C=N bonds in these complexes retain their double bond character, being 1.303(2), 1.303(2), and 1.310(3) Å for 2a, 2b, and 2d, respectively. The Al-N (amido) distances [1.8327(19) Å

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for 2a, 1.8397(14) Å for 2b, 1.826(2) Å for 2d] are much shorter than the Al-N (imine) distances [1.894(2) Å for 2a, 1.8927(15) for **2b**, 1.8937(19) Å for **2d**] because the anionic amido nitrogen can also π -donate to the aluminum, whereas the neutral imine nitrogen does not have an available lone pair for π -donation. The Al–N (imine) distances (1.893 Å average) are shorter than the values (1.953 Å average) previously reported for $ortho-C_6H_4(NAr')(CH=NAr')$ AlMe₂^[14d] because of the more electrophilic aluminum center in the dichloro aluminum compounds, but larger than the one [1.850(2) Å] in (TTP)AlCl₂.^[17b] The Cl-Al-Cl angles (109.40° average) in 2a and 2d are close to the ideal tetrahedral angle of 109.47°, and they are similar to that of the reported diketiminatolaluminum complex (Scheme 1; B).^[17] In addition, X-ray diffraction analysis reveals that intermolecular π - π interaction appears in the solid state of complex 2a (Figure 1, bottom). One phenyl ring in the ligand of 2a stacks together with the corresponding one in an adjacent molecule by the π - π interaction with a distance of 3.6 Å.^[18]



Figure 1. Top: Molecular structure of complex 2a; bottom: Crystal packing diagram between two adjacent molecules of 2a showing the existence of a π - π stacking interaction in the solid state. (Thermal ellipsoids are drawn at the 30% probability level.).



Figure 2. Molecular structure of complex 2b (thermal ellipsoids are drawn at the 30% probability level).



Figure 3. Molecular structure of complex 2d (thermal ellipsoids are drawn at the 30% probability level).

Fluorescent Properties

Table 2 summarizes the UV/Vis and fluorescent properties of compounds 1a-1d and 2a-2d determined in both solution and the solid state. In solution, the free ligands 1a-1d have a weak emission band at $\lambda_{max} = 419, 420, 423, and$ 430 nm, respectively. When these ligands were bound to an aluminum center, strong green luminescence was observed. The observed luminescence of the complexes could be attributed to a $\pi^*-\pi$ transition of their chelated anilido-imine conjugated ligands. As shown in Figure 4, in contrast to the free ligands, each of complexes 2a-2d in solution gives a broad emission band (bandwidth at half-height = 70-90 nm) with $\lambda_{\text{max}} = 512, 510, 505, \text{ and } 554 \text{ nm}$, respectively. The emission energies of these complexes are significantly red-shifted in comparison with the free ligands. The role of the aluminum atom in the luminescence of 2a-2d should be twofold, as pointed out in the literature for coordination complexes.^[19] First, the formation of covalent bonds between the Al and N atoms by the donation of lone pairs of the N atom to the Al atom changes the emission energy, owing to the lowering of the energy gap between π^* and π . Second, after coordination with the Al atom, the ligand becomes more rigid, which can reduce the loss of energy by vibrational motions and increase the emission efficiency. The emission maxima of complexes 2a-2c in solution are

Complex 2a	-		
Al(1)–N(1)	1.894(2)	N(1)-Al(1)-Cl(2)	114.54(7)
Al(1)-N(2)	1.8327(19)	N(2) - Al(1) - Cl(1)	115.53(7)
Al(1)-Cl(2)	2.0978(10)	N(1)-Al(1)-Cl(1)	106.18(7)
Al(1)-Cl(1)	2.1190(11)	Cl(2)-Al(1)-Cl(1)	109.46(4)
N(1)-C(1)	1.303(3)	C(1)-N(1)-Al(1)	119.83(16)
N(2)-C(7)	1.370(3)	C(14)-N(1)-Al(1)	123.33(15)
N(1)-Al(1)-N(2)	97.59(8)	C(7)-N(2)-Al(1)	122.40(15)
N(2)-Al(1)-Cl(2)	113.02(7)	C(8)-N(2)-Al(1)	120.78(14)
Complex 2b			
Al(1)–N(1)	1.8927(15)	N(1)-Al(1)-Cl(1)	109.36(5)
Al(1)-N(2)	1.8397(14)	N(2) - Al(1) - Cl(2)	116.17(6)
Al(1)-Cl(1)	2.1154(8)	N(1)-Al(1)-Cl(2)	110.40(5)
Al(1)-Cl(2)	2.1182(9)	Cl(1)-Al(1)-Cl(2)	107.00(4)
N(1)-C(1)	1.303(2)	C(1)-N(1)-Al(1)	121.47(11)
N(2)-C(7)	1.372(2)	C(14)-N(1)-Al(1)	122.05(10)
N(2)-Al(1)-N(1)	99.27(6)	C(7)-N(2)-Al(1)	125.07(11)
N(2)-Al(1)-Cl(1)	114.36(6)	C(8)-N(2)-Al(1)	117.04(11)
Complex 2d			
Al(1)–N(1)	1.8937(19)	N(1)-Al(1)-Cl(2)	110.46(7)
Al(1)-N(2)	1.826(2)	N(2)-Al(1)-Cl(1)	110.55(7)
Al(1)-Cl(2)	2.1064(12)	N(1)-Al(1)-Cl(1)	113.73(7)
Al(1)-Cl(1)	2.1146(10)	Cl(2) - Al(1) - Cl(1)	109.34(5)
N(1)-C(1)	1.310(3)	C(1)-N(1)-Al(1)	120.93(15)
N(2)-C(7)	1.367(3)	C(14)-N(1)-Al(1)	123.09(13)
N(2)-Al(1)-N(1)	97.82(8)	C(7) - N(2) - Al(1)	126.00(15)
N(2)-Al(1)-Cl(2)	114.65(8)	C(8)–N(2)–Al(1)	114.41(13)

Table 1. Selected bond lengths [Å] and angles [°].

close to each other, while the emission maximum of 2d is red-shifted about 40 nm compared to other complexes. This result could be attributed to the differences in the number and size of the *ortho*-substituents on the rotatable aryl rings of their ligands, which might affect the conjugated extent of these complexes.^[14a-14d] In addition, the lower basicity and lower electron density of the anilide may also be responsible for the emission red shift in 2d.^[14e] The quantum yields of these compounds are low in solution. Complexes 2a-2d all emit bright fluorescence in the solid state when irradiated by exciting light. The emission spectra of complexes **2a–2d** in the solid state are shown in Figure 5. Complexes **2b**, **2c**, and **2d** each have a relatively narrow band (bandwidth at half-height: 60–70 nm) in the solid state with $\lambda_{\text{max}} = 497$, 498, and 544 nm, respectively. The emission



Figure 4. Emission spectra of ligands 1a-1d and complexes 2a-2d in *n*-hexane.



Figure 5. Emission spectra of complexes 2a-2d in the solid state.

Table 2.	Photo	luminescent	data for	[·] ligands	1a–1d	and cor	nplexes	2a-2	2d
				<u> </u>					

Compound	$\varepsilon [\mathrm{M}^{-1} \cdot \mathrm{cm}^{-1}]$	$\lambda_{abs} [nm]$	$\lambda_{\rm em}$ [nm]	Quantum yields $[\Phi]^{[a]}$	Conditions
1a	9011	370	419	0.036	hexane, 298 K
			431		solid, 298 K
1b	11265	371	420	0.029	hexane, 298 K
			432		solid, 298 K
1c	13214	373	423	0.023	hexane, 298 K
			432		solid, 298 K
1d	10745	382	430	0.009	hexane, 298 K
			462		solid, 298 K
2a	12645	437	512	0.093	hexane, 298 K
			540		solid, 298 K
2b	12495	436	510	0.098	hexane, 298 K
			497		solid, 298 K
2c	11932	436	505	0.085	hexane, 298 K
			498		solid, 298 K
2d	10876	447	554	0.066	hexane, 298 K
			544		solid, 298 K

[a] Determined using quinine sulfate in 0.1 M sulfuric acid as a standard.

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maxima of these complexes in the solid state are blue shifted compared to their corresponding emission maxima in solution, which probably resulted from the reduced conjugated extent of the three complexes, as the free rotation of the aryl rings in these complexes is blocked in the solid state. The emission maximum of complex **2a** ($\lambda_{max} =$ 540 nm) in the solid state is red shifted compared to its corresponding emission maximum in solution, which is normal considering that red shifting of the emission maximum can be observed for most fluorescent compounds in the solid state, probably because of π - π stacking of aromatic rings in the molecules (see Figure 1, bottom). This result also implies that the rotation of 2,6-*i*Pr₂Ph groups about the Naryl bond in complex **2a** is slow in solution, which is consistent with the ¹H NMR experimental result.

Conclusion

Our research results indicate that the chelating bidentate anilido-imine conjugated ligands are well suited for synthesizing the four-coordinate aluminum complexes by a salt metathesis reaction of AlCl₃ with the lithium salt of corresponding ligands at room temperature. ¹H and ¹³C NMR spectra reveal that these aluminum complexes have C_s -symmetric structures in solution and X-ray diffraction analysis indicates that the six-membered chelating ring in these complexes is nearly planar with the aluminum lying slightly out of the plane. These complexes produce bright fluorescence in both solution and the solid state, and the emission color in solution can be tuned by the *ortho* substituents on the rotatable aryl rings of the ligands. The four-coordinate aluminum complexes are a new class of luminescent material with potential applications in optoelectronic devices.

Experimental Section

All reactions were performed using standard Schlenk techniques in high-purity nitrogen or glovebox techniques. Toluene, *n*-hexane, THF, and diethyl ether were dried by refluxing over sodium and benzophenone and distilled under nitrogen prior to use. C_6D_6 was dried with activated 4 Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. CDCl₃ was dried with CaH₂ for 48 h and vacuum-transferred to an air-free flask. AlCl₃ and *n*BuLi were purchased from Aldrich and used as received. NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. The elemental analysis was performed with a Perkin–Elmer 2400 analyzer. UV/Vis absorption spectra were recorded with a UV-3100 spectrophotometer. Fluorescence measurements were carried out on an RF-5301PC.

ortho-C₆H₄[NH(C₆H₃iPr₂-2,6)](CH=NC₆H₃Me₂-2,6) (1b): A solution of *n*BuLi (30.32 mL, 48.5 mmol) in hexanes was added to a solution of 2,6-diisopropylaniline (8.1 mL, 48.5 mmol) in THF (30 mL) at -78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The resulting solution of LiNHAr was transferred into a solution of *ortho*-C₆H₄F(CH=NC₆H₃Me₂-2,6) (11.0 g, 48.5 mmol) in THF (40 mL) at 25 °C. After stirring

for 2 h, the reaction was quenched with H₂O (25 mL), extracted with *n*-hexane, and the organic phase was evaporated to dryness in vacuo to give the crude product as a yellow solid. Pure product (13.4 g, 72%) was obtained as yellowish-green crystals by recrystallization from ethanol at -20 °C. C₂₇H₃₂N₂ (384.56): calcd. C 84.33, H 8.39, N 7.28; found C 84.28, H 8.48, N 7.24. ¹H NMR (300 MHz, CDCl₃, 293 K): $\delta = 1.15$, 1.17 [d, J = 6.6 Hz, 2×6 H, CH(CH₃)₂], 2.21 (s, 6 H, CH₃), 3.22 [sept, J = 6.6 Hz, 2 H, CH(CH₃)₂], 6.30 (d, J = 8.1 Hz, 1 H, Ph-*H*), 6.71 (t, J = 6.6 Hz, 1 H, Ph-*H*), 6.98 (t, J = 7.2 Hz, 1 H, Ph-*H*), 7.09–7.38 (m, 7 H, Ph-*H*), 8.39 (s, 1 H, CH=NAr), 10.53 (s, 1 H, N*H*) ppm. ¹³C{¹H} NMR (300 MHz, CDCl₃, 293 K): $\delta = 18.7$ (CH₃), 23.2 [CH(CH₃)₂], 25.0 [CH(CH₃)₂], 28.8 [CH(CH₃)₂], 112.2, 115.3, 116.5, 124.0, 127.7, 127.9, 128.3, 132.5, 134.7, 134.8, 147.7, 150.2, 151.1 (Ph), 166.2 (CH=NAr) ppm.

ortho- $C_6H_4N(C_6H_3iPr_2-2,6)(CH=NC_6H_3iPr_2-2,6)AlCl_2$ (2a): A solution of nBuLi in hexanes (0.28 mL, 0.45 mmol) was added dropwise to a stirred toluene solution of ortho-C₆H₄NH(C₆H₃iPr₂-2,6)(CH=NC₆H₃*i*Pr₂-2,6) (0.20 g, 0.45 mmol) at -78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl₃ (0.06 g, 0.45 mmol) at -78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at -20 °C overnight to let the product crystallize. The product was obtained as yellow-green crystals (0.18 g, 75%). C₃₁H₃₉Al₂Cl₂N (537.54): calcd. C 69.27, H 7.31, N 5.21; found C 69.20, H 7.40, N 5.25. ¹H NMR (300 MHz, C_6D_6 , 293 K): $\delta = 0.93$, 1.00 [d, J = 6.9 Hz, 2×6 H, CH(CH₃)₂], 1.38, 1.46 [d, J = 6.9 Hz, 2×6 H, CH(CH₃)₂], 3.53 [sept, J = 6.9 Hz, 2×2 H, $CH(CH_3)_2$], 6.25 (t, J = 6.1 Hz, 1 H, Ph-*H*), 6.41 (d, J = 8.8 Hz, 1 H, Ph-*H*), 6.70 (t, J = 6.6 Hz, 2 H, Ph-*H*), 7.07–7.12 (m, 6 H, Ph-*H*), 7.92 (s, 1 H, *H*C=N) ppm. ${}^{13}C{}^{1}H$ NMR (300 MHz, C_6D_6 , 293 K): $\delta = 22.9$, 24.7, 25.4, 25.7 $[4 \times CH(CH_3)_2]$, 28.7, 29.0 $[2 \times CH(CH_3)_2]$, 115.1, 117.1, 119.3, 124.7, 125.2, 129.0, 136.9, 137.2, 137.6, 141.1, 143.5, 146.7, 158.0 (Ph), 173.5 (CH=NAr) ppm.

ortho- $C_6H_4N(C_6H_3iPr_2-2,6)(CH=NC_6H_3Me_2-2,6)AlCl_2$ (2b): A solution of nBuLi in hexanes (0.33 mL, 0.52 mmol) was added dropwise to a stirred toluene solution of ortho-C₆H₄NH(C₆H₃iPr₂-2,6)(CH=NC₆H₃Me₂-2,6) (0.20 g, 0.52 mmol) at -78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl₃ (0.07 g, 0.52 mmol) at -78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at -20 °C overnight to let the product crystallize. The product was obtained as yellow-green crystals (0.18 g, 70%). C₂₇H₃₁AlCl₂N₂ (481.44): calcd. C 67.36, H 6.49, N 5.82; found C 67.30, H 6.44, N 5.91. ¹H NMR (300 MHz, C_6D_6 , 293 K): $\delta = 0.99$ [d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.42 [d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 2.67 (s, 6 H, CH_3), 3.48 [sept, J = 6.6 Hz, 2 H, $CH(CH_3)_2$], 6.27 (t, J = 6.0 Hz, 1 H, Ph-H), 6.38 (d, J = 8.7 Hz, 1 H, Ph-H), 6.60 (d, J = 8.1 Hz, 1 H, Ph-H), 6.72 (t, J = 6.6 Hz,1 H, Ph-H), 6.81–7.19 (m, 6 H, Ph-H), 7.35 (s, 1 H, CH=NAr) ppm. ¹³C{¹H} NMR (300 MHz, C₆D₆, 293 K): $\delta = 18.8 (CH_3)$, 24.6 [CH(CH_3)₂], 25.5 [CH(CH_3)₂], 28.6 [CH(CH₃)₂], 115.3, 116.7, 119.3, 125.2, 129.3, 132.7, 137.2, 137.3, 143.9, 146.7 (Ph), 173.8 (CH=NAr) ppm.

ortho-C₆H₄N(C₆H₃Me₂-2,6)(CH=NC₆H₃Me₂-2,6)AlCl₂ (2c): A solution of *n*BuLi in hexanes (0.38 mL, 0.61 mmol) was added dropwise to a stirred toluene solution of ortho-C₆H₄NH(C₆H₃Me₂-2,6)(CH=NC₆H₃Me₂-2,6) (0.20 g, 0.61 mmol) at -78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl₃ (0.08 g, 0.61 mmol) at -78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with *n*-hexane (30 mL). Insoluble materials were removed by filtration through Celite. The vellow filtrate was concentrated to about 20 mL and kept at -20 °C overnight to let the product crystallize. The product was obtained as yellow crystals (0.18 g, 68%). C23H23AlCl2N2 (425.33): calcd. C 64.95, H 5.45, N 6.59; found C 64.82, H 5.56, N 6.64. ¹H NMR (300 MHz, C₆D₆, 293 K): δ = 2.27 (s, 6 H, CH₃), 2.37 (s, 6 H, CH_3), 6.33 (t, J = 6.3 Hz, 1 H, Ph-H), 6.68 (d, J = 8.5 Hz, 1 H, Ph-H), 6.76-7.04 (m, 8 H, Ph-H), 7.35 (s, 1 H, CH=NAr) ppm. ¹³C{¹H} NMR (300 MHz, C₆D₆, 293 K): δ = 18.9 (CH₃), 115.3, 116.5, 116.7, 127.2, 128.1, 129.2, 129.6, 132.9, 136.4, 137.5, 138.3, 139.8, 143.5, 156.5, 174.3 (CH=NAr) ppm.

ortho-C₆H₄N(C₆H₄Me-*p*)(CH=NC₆H₃*i*Pr₂-2,6)AlCl₂ (2d): A solution of *n*BuLi in hexanes (0.34 mL, 0.54 mmol) was added dropwise to a stirred toluene solution of ortho-C₆H₄NH(C₆H₄Me-*p*)-(CH=NC₆H₃*i*Pr₂-2,6) (0.20 g, 0.54 mmol) at -78 °C. After the addition, the reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was added dropwise to a toluene suspension solution of AlCl₃ (0.08 g, 0.54 mmol) at -78 °C with stirring. The mixture was warmed to room temperature and stirred for 12 h, and the solution was evaporated to dryness in vacuo. The solid residue was extracted with hexane (30 mL). Insol-

uble materials were removed by filtration through Celite. The yellow filtrate was concentrated to about 20 mL and kept at $-20 \,^{\circ}$ C overnight to let the product crystallize. The product was obtained as yellow crystals (0.16 g, 71%). C₂₆H₂₉AlCl₂N₂ (467.41): calcd. C 66.81, H 6.25, N 5.99; found: C 66.92, H 6.11, N 5.90. ¹H NMR (300 MHz, C₆D₆, 293 K): $\delta = 0.89$ [d, J = 6.6 Hz, 6 H, CH(CH₃)₂], 1.38 [d, J = 6.6 Hz, 6 H, CH(CH₃)₂], 6.31 (t, J = 6.9 Hz, 1 H, Ph-H), 6.62 (d, J = 8.8 Hz, 1 H, Ph-H), 6.72 (d, J = 8.1 Hz, 1 H, Ph-H), 6.81 (t, J = 6.6 Hz, 1 H, Ph-H), 6.94 (d, J = 8.4 Hz, 2 H, Ph-H), 7.07–7.13 (m, 2 H, Ph-H), 7.33 (d, J = 6.5 Hz, 2 H, Ph-H), 7.94 (s, 1 H, CH=NAr) ppm. ¹³C{¹H} NMR (300 MHz, C₆D₆, 293 K): $\delta = 20.8$ (CH₃), 22.8 [CH(CH₃)₂], 26.0 [CH(CH₃)₂], 28.9 [CH(CH₃)₂], 114.7, 116.7, 117.6, 124.7, 128.5, 129.2, 131.0, 136.4, 137.0, 138.1, 140.1, 140.7, 143.8, 158.0 (Ph), 173.6 (CH=NAr) ppm.

X-ray Structure Determinations of 2a, 2b, and 2d: Single crystals of **2a, 2b**, and **2d** suitable for X-ray structural analysis were obtained from *n*-hexane. Diffraction data were collected at 293 K with a Rigaku R-AXIS RAPID IP diffractometer equipped with graphitemonochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) for **2a, 2b**, and **2d**. Details of the crystal data, data collections, and structure refinements are summarized in Table 3. The structures were solved by direct methods^[20] and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL^[21] crystallographic software packages.

CCDC-279167 (for **2a**), -279168 (for **2b**), and -279169 (for **2d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structural refinement details for 2a, 2b, and 2d.

	2a	2b	2d
Empirical formula	C ₃₁ H ₃₉ AlCl ₂ N ₂	C ₂₇ H ₃₁ AlCl ₂ N ₂	C ₂₆ H ₂₉ AlCl ₂ N ₂
Formula mass	537.5	481.42	467.39
Temp. [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2(1)/c	P2(1)/n	$P\overline{1}$
a [Å]	17.474(4)	8.9391(18)	9.5066(19)
b [Å]	10.448(2)	26.151(5)	9.866(2)
c [Å]	17.528(4)	11.242(2)	14.837(3)
	90	90	107.24(3)
β[°]	108.65(3)	96.02(3)	103.70(3)
γ [°]	90	90	99.30(3)
$V[Å^3]$	3032.1(11)	2613.6(9)	1250.3(4)
Z	4	4	2
$D_{\text{calcd}} [\text{Mg} \cdot \text{m}^{-3}]$	1.177	1.223	1.241
F(000)	1144	1016	492
Crystal size [mm]	$0.40 \times 0.28 \times 0.24$	$0.51 \times 0.32 \times 0.21$	$0.41 \times 0.28 \times 0.21$
θ Range for data collection (°)	1.23-27.50	3.07-27.44	1.51-27.48
Limiting indices	$-18 \le h \le 22$	$-11 \le h \le 11$	$0 \le h \le 12$
	$-13 \le k \le 13$	$-31 \le k \le 33$	$-12 \le k \le 12$
	$-17 \le l \le 22$	$-14 \leq l \leq 14$	$-19 \le l \le 18$
Data/restraints/parameters	6955/0/333	5941/0/413	5697/0/396
Goodness-of-fit on F^2	0.865	1.020	0.850
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1^{[a]} = 0.0480$	$R_1^{[a]} = 0.0404$	$R_1^{[a]} = 0.0424$
	$wR_2^{[b]} = 0.1098$	$wR_2^{[b]} = 0.1032$	$R_2^{[b]} = 0.1062$
R indices (all data)	$R_1^{[a]} = 0.1159$	$R_1^{[a]} = 0.0642$	$\bar{R_1^{[a]}} = 0.0776$
× /	$wR_2^{[b]} = 0.1258$	$wR_2^{[b]} = 0.1157$	$w R_2^{[b]} = 0.1207$
Largest diff. peak/hole [e·Å-3]	$0.3\overline{4}4, -0.246$	0.251, -0.285	0.850, -0.301

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. [b] $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}$.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20374023) and the Ministry of Science and Technology of China (No. 2002CB6134003).

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Received: August 21, 2005 Published Online: February 2, 2006