# Dialkylaluminum Complexes with Chelating Anilido-Imine Ligands: Synthesis, Structures, and Luminescent Properties

Xiaoming Liu,[†] Wei Gao,[†] Ying Mu,[*,†] Guanghua Li,[‡] Ling Ye,[†] Hong Xia,[†]
Yi Ren,[†] and Shouhua Feng[‡]

*Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, School of Chemistry, Jilin University, 10 Qianwei Road, Changchun 130012, People's Republic of China, and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, School of Chemistry, Jilin University, 10 Qianwei Road, Changchun 130012, People's Republic of China*

*Received November 7, 2004*

Syntheses of three new chelating anilido-imine conjugated ligands, *ortho*-$C_6H_4(NHAr')(CH{=}NAr'')$ [$Ar' = Ar'' = 2,6\text{-}Me_2C_6H_3$ (**2b**); $Ar' = p\text{-}MeC_6H_4$, $Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**2c**); $Ar' = Ar'' = p\text{-}MeC_6H_4$ (**2d**)], as well as their four-coordinate dialkyl aluminum complexes, *ortho*-$C_6H_4(NAr')(CH{=}NAr'')AlMe_2$ [$Ar' = Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**3a**); $Ar' = Ar'' = 2,6\text{-}Me_2C_6H_3$ (**3b**); $Ar' = p\text{-}MeC_6H_4$, $Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**3c**); $Ar' = Ar'' = p\text{-}MeC_6H_4$ (**3d**)], are described. Complexes **3a**−**d** were synthesized from the reaction of $AlMe_3$ with the corresponding ligand at room temperature by alkane elimination. All complexes were characterized by $^1H$ and $^{13}C$ NMR spectroscopy, and the molecular structures of complexes **3a**, **3c**, and **3d** were determined by X-ray crystallography. Luminescent properties of the ligands **2a**−**d** and the complexes **3a**−**d** in solution were studied, and it was found that emission maxima of **3a**−**d** are in the range 519−582 nm, depending on the substituents on the aryl rings of their ligands. Complexes **3a**−**d** exhibit intense photoluminescence in the solid state, and the maximum emission wavelengths at room temperature are in the range 532−552 nm.

## Introduction

Luminescent coordination compounds have been one of the most active research areas because of their potential application in light emitting diodes (LEDs).[1] Luminescent main group and transition metal complexes, such as Al(III),[2] Zn(II),[3] Pt(II),[4] and Ir(III)[5] complexes, have been designed and synthesized in recent years. Particularly, chelated aluminum complexes have attracted much attention due to their good luminescent properties. For example, tri(8-hydroxyquinolinyl)aluminum ($Alq_3$) and a large number of its derivatives with modified 8-hydroxyquinoline ligands have been investigated;[2,6,7] aluminum complexes with nitrogen-containing ligands have also been reported.[8] It has been demonstrated that the emission color of aluminum complexes can be modulated in a wide range by modifying their ligands or coordination environments around the aluminum atom.[9]

A critical issue to be considered in designing, synthesizing, and fabricating luminescent materials is the control of their emission wavelengths.[2,4a,5b,10] Emission

---

[*] To whom correspondence should be addressed. E-mail: ymu@mail.jlu.edu.cn. Fax: (+86)431-5193421.

[†] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education.

[‡] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry.

(1) (a) Wang, S. N. *Coord. Chem. Rev.* **2001**, *215*, 79. (b) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161.

(2) (a) Pohl, R.; Montes, V. A.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* **2004**, *69*, 1723. (b) Pohl, R.; Anzenbacher, P., Jr. *Org. Lett.* **2003**, *5*, 2769.

(3) (a) Chang, K. H.; Huang, C. C.; Liu, Y. H.; Hu, Y. H.; Chou, P. T.; Lin, Y. C. *J. Chem. Soc., Dalton Trans.* **2004**, 1731. (b) Kang, Y. J.; Seward, C.; Song, D. T.; Wang, S. N. *Inorg. Chem.* **2003**, *42*, 2789. (c) Jia, W. L.; Song, D. T.; Wang, S. N. *J. Org. Chem.* **2003**, *68*, 701. (d) Ho, K. Y.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1581.

(4) (a) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Che, C. M.; Zhu, N. Y.; Lee, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 4958. (b) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. K. *Inorg. Chem.* **2002**, *41*, 3055. (c) Liu, Q. D.; Jia, W. L.; Wu, G.; Wang, S. N. *Organometallics* **2003**, *22*, 3781.

(5) (a) Huang, W. S.; Lin, J. T.; Chien, C. H.; Tao, Y. T.; Sun, S. S.; Wen, Y. S. *Chem. Mater.* **2004**, *16*, 2480. (b) Laskar, I. R.; Chen, T. M. *Chem. Mater.* **2004**, *16*, 111. (c) Lamansky, S.; Djurovoch, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H. E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304.

(6) (a) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Tang, C. W.; Vanslyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3611. (c) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807. (d) Hamada, Y.; Sano, T.; Fujita, M.; Fujii, T.; Nishio, Y.; Shibata, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L514. (e) Bulovic, v.; Gu, G.; Burrows, P. E.; Forrest, S. R. *Nature* **1996**, *380*, 29.

(7) (a) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, L713. (b) Asachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799. (c) Hamada, Y.; Sano, T.; Fujita, M.; Fujii, T.; Nishio, Y.; Shibata, K. *Chem. Lett.* **1993**, 905. (d) Shen, Z.; Bulovic, V.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Science* **1999**, *283*, 1900. (e) Wu, Q.; Esteghamatian, M.; Hu, N. H.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater.* **2000**, *12*, 79. (f) Jang, H.; Do, L.-M.; Kim, Y.; Kim, J. G.; Zyung, T.; Do, Y. *Synth. Met.* **2001**, *121*, 1669.

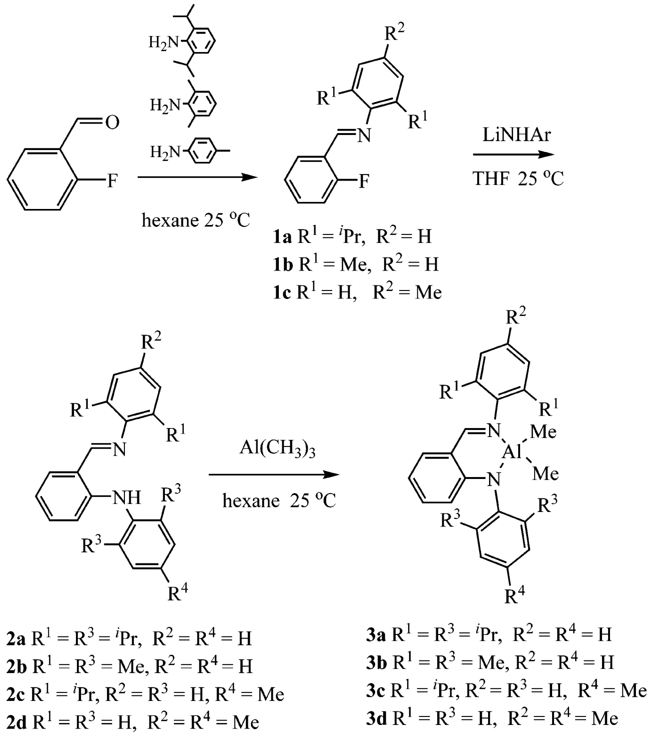
(8) (a) Ashenhurst, J.; Brancaleon, L.; Hassan, A.; Liu, W.; Schmider, H.; Wang, S.; Wu, G. *Organometallics* **1998**, *17*, 3186. (b) Ashenhurst, J.; Brancaleon, L.; Gao, S.; Liu, W.; Schmider, H.; Wang, S.; Wu, G.; Wu, Q. G. *Organometallics* **1998**, *17*, 5334. (c) Gao, S.; Wu, Q.; Wu, G.; Wang, S. *Organometallics* **1998**, *17*, 4666. (d) Ashenhurst, J.; Wang, S.; Wu, G. *J. Am. Chem. Soc.* **2000**, *122*, 3528. (e) Ashenhurst, J.; Wu, G.; Wang, S. *J. Am. Chem. Soc.* **2000**, *122*, 2541. (f) Liu, S. F.; Seward, C.; Aziz, H.; Hu, N. X.; Popovic, Z.; Wang, S. *Organometallics* **2000**, *19*, 5709.

(9) Thompson, M. E.; Forrest, S. R.; Burrows, P. E.; You, Y. J.; Shoustikov, A. U.S. Patent No.5,861,219, 1999.

10.1021/om049143a CCC: $30.25

properties of coordination compounds are in general controlled by a number of factors, including electronic properties of ligands and metal ions, coordination bond lengths and angles that affect the energy mixing, and splitting of electronic states involved in the emission. One of the convenient ways to tune the emission color of a series of complexes is to modify the ligands.[11] It has been reported that $\beta$-diketiminato (nacnac) aluminum complexes with different substituted aryl groups in the nacnac ligand can be easily synthesized.[12] However, there are few reports on the luminescent properties of similar aluminum complexes. We have synthesized a number of new aluminum complexes with similar chelating anilido-imine conjugated ligands and found that they are efficient fluorescent materials and their emission color can be modulated in the range 519–582 nm by ligand modification. We report here the syntheses, characterizations, and fluorescent properties of three new ligands, *ortho*-$C_6H_4(NHAr')(CH{=}NAr'')$ [$Ar' = Ar'' = 2,6\text{-}Me_2C_6H_3$ (**2b**); $Ar' = p\text{-}MeC_6H_4$, $Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**2c**); $Ar' = Ar'' = p\text{-}MeC_6H_4$ (**2d**)], and their four-coordinate alkyl aluminum complexes, *ortho*-$C_6H_4(NAr')(CH{=}NAr'')AlMe_2$ [$Ar' = Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**3a**); $Ar' = Ar'' = 2,6\text{-}Me_2C_6H_3$ (**3b**); $Ar' = p\text{-}MeC_6H_4$, $Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**3c**); $Ar' = Ar'' = p\text{-}MeC_6H_4$ (**3d**)].

**Scheme 1. Synthetic Procedure of Ligands 2a–d and Synthetic Procedure of Complexes 3a–d**



## Results and Discussion

**Ligand Synthesis.** Pre-ligand compounds *ortho*-$C_6H_4F(CH{=}NAr)$ [$Ar = 2,6\text{-}{}^iPr_2C_6H_3$ (**1a**); $Ar = 2,6\text{-}Me_2C_6H_3$ (**1b**); $Ar = p\text{-}MeC_6H_4$ (**1c**)] were prepared according to a literature procedure[13] in high yields by condensation reaction of *ortho*-fluorobenzaldehyde with 1 equiv of relevant amine in hexane (Scheme 1). Compound **1a** is a known compound, while **1b** and **1c** are new compounds. **1b** was obtained as a greenish oil, but **1c** was isolated as a white solid. Compounds **1a–c** were characterized by $^1H$ NMR spectroscopy and elemental analyses. The $^1H$ NMR spectra of these pre-ligands exhibit resonances in the region $\delta$ 8.57–8.81 for the CH imine protons. The ligand *ortho*-$C_6H_4(NHAr')(CH{=}NAr'')$ [$Ar' = Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$ (**2a**)] is a known compound that was synthesized by the literature method.[13] The new ligands **2b–d** were synthesized by the same procedure in good yields (>70% isolated yields) via a nucleophilic aromatic displacement of fluoride in **1a–c** by corresponding LiN(H)Ar (Scheme 1). The reactions of **1a–c** with 1 equiv of LiN(H)Ar were carried out in THF, and the crude products were purified from methanol. These compounds (**1a–c**, **2a–d**) are very soluble in most organic solvents. Compounds **2b–d** were characterized by $^1H$ and $^{13}C$ NMR spectroscopy along with elemental analyses. The $^1H$ NMR spectra of these compounds exhibit resonances in the region $\delta$ 8.32–8.68 for the CH imine protons, with the corresponding $^{13}C$ NMR resonances occurring in the range $\delta$ 162.3–166.3. The NH resonances appear at characteristically low field ($\delta$ 10.5–11.2). The infrared absorption bands of the imine C=N stretch occur in the region 1615–1634 cm$^{-1}$.

**Complex Synthesis.** Treatment of **2a–d** with 1 equiv of trimethylaluminum in hexane at room temperature caused the evolution of methane and afforded the corresponding dimethyl aluminum complexes **3a–d** in good yields (>80%) as yellow or orange crystalline solids (Scheme 1). The reaction can also be carried out in toluene, but the products were obtained in lower yields. Complexes **3a–d** were all characterized by elemental analyses and $^1H$ and $^{13}C$ NMR spectroscopy, and satisfactory analytic results were obtained on all compounds. In the $^1H$ NMR spectra of these complexes, the resonances for the CH imine protons ($\delta$ 7.32–7.85) shift about 1 ppm toward high field compared to the corresponding signals of free ligands, while the resonances ($\delta$ 167.9–171.9) for the CH imine carbons in $^{13}C$ NMR spectra shift to low field in comparison with the corresponding ones of free ligands. The disappearance of the N-H signal of the ligands and the appearance of resonances for $AlMe_2$ protons in high-field region ($\delta$ −0.24 to −0.52) in the $^1H$ NMR spectra of **3a–d** demonstrate the formation of the aluminum complexes. $^1H$ and $^{13}C$ NMR spectra reveal that these complexes all have $C_s$-symmetric structures in solution. For compounds **3a** and **3c**, coordination of the anilido-imine

---

(10) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(11) (a) Leung, L. M.; Lo, W. Y.; So, S. K.; Lee, K. M.; Choi, W. K. *J. Am. Chem. Soc.* **2000**, *122*, 5640. (b) Liu, Q.; Mudadu, M. S.; Schmider, H.; Thummel, R.; Tao, Y.; Wang, S. *Organometallics* **2002**, *21*, 4743. (c) Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. *Appl. Phys. Lett.* **1996**, *79*, 7991. (d) Matsumura, M.; Akai, T. *Jpn. J. Appl. Phys.* **1996**, *35*, 5357. (e) Van Slyke, S. A. U.S. Patent No. 5,151,629, 1992. (f) Bryan, P. S.; Lovecchio, F. V.; Van Slyke, S. A. U.S. Patent No. 5,141,671, 1992. (g) Shi, J.; Tang, C. W.; Chen, C. H. 55th Annual Device Research Conference Digest 154, 1997.

(12) (a) Peng, Y.; Fan, H.; Zhu, H.; Roesky, H. W.; Magull, Jorg.; Hughes, C. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 3443. (b) Jancik, V.; Cabrera, M. M. M.; Roesky, H. W.; Herbst-Irmer, R.; Neculai, D.; Neculai, A. M.; Noltemeyer, M.; Schmid, H. G. *Eur. J. Inorg. Chem.* **2004**, 3508. (c) Jancik, V.; Peng, Y.; Roesky, H. W.; Li, J.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2003**, *125*, 1452. (d) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794. (e) Chakrabory, D.; Rodriguez, A.; Chen, E. Y.-X. *Macromolecules* **2003**, *36*, 5470.

(13) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577.

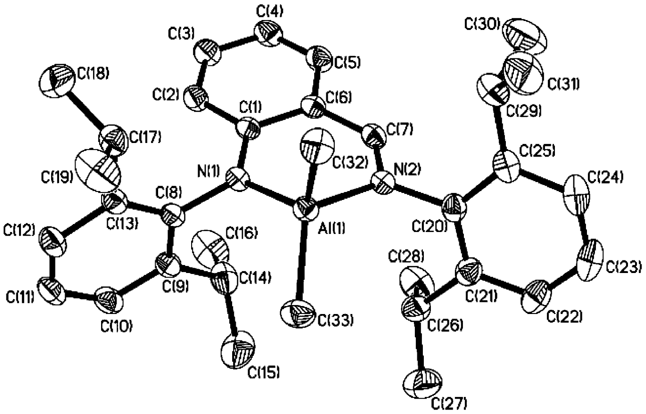


**Figure 1.** Structure of complex **3a** (thermal ellipsoids are drawn at the 30% probability level).

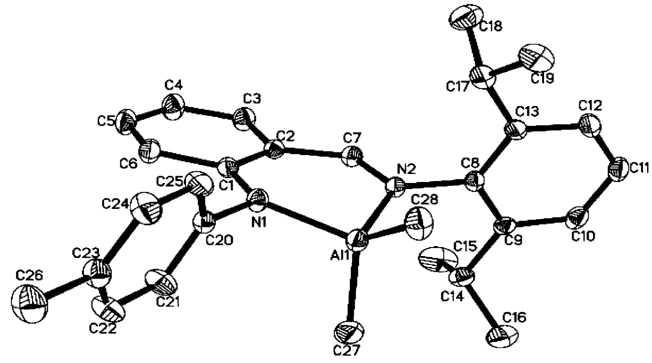


**Figure 2.** Structure of complex **3c** (thermal ellipsoids are drawn at the 30% probability level).

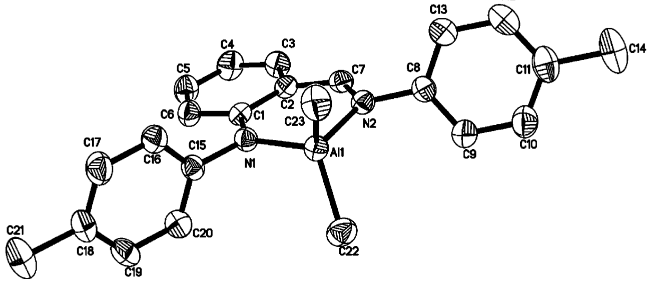


**Figure 3.** Structure of complex **3d** (thermal ellipsoids are drawn at the 30% probability level).

ligands to the aluminum center causes rotation about the N−aryl bond to become slow on the NMR time scale and renders the individual methyl groups of an isopropyl unit inequivalent in the $^1$H NMR spectrum. All complexes have good solubility in most organic solvents, including saturated hydrocarbons such as *n*-pentane or *n*-hexane. They are air and moisture sensitive in both the solid state and solution, while they have pretty good thermal stability in solution and can be heated in boiling toluene for several hours without obvious decomposition.

**Crystal Structures.** Crystals of **3a**, **3c**, and **3d** suitable for X-ray crystal structure determination are grown from *n*-hexane at room temperature or 0 °C. The ORTEP drawings of the molecular structures of **3a**, **3c**, and **3d** are shown in Figure 1, Figure 2 and Figure 3, respectively. Selected bond lengths and angles for **3a**, **3c**, and **3d** are given in Table 1. X-ray analysis reveals that **3a**, **3c**, and **3d** adopt a distorted tetrahedral geometry with the metal center chelated by the bidentate ligand via the imine and amido nitrogen atoms. In these three complexes, the six-membered chelating ring is nearly planar, with the aluminum atom lying 0.556, 0.289, and 0.059 Å out of the plane, respectively. The dihedral angles between the six-membered chelating ring and aromatic ring attached to the amido nitrogen atom are 69.2°, 85.9°, and 85.1°, and the dihedral angles between the six-membered chelating ring and aromatic ring attached to the imine nitrogen atom are 88.1°, 88.1°, and 61.7°, respectively. The imino C=N bonds in these complexes retain their double-bond character, being 1.298(2), 1.309(4), and 1.305(3) Å for **3a**, **3c**, and **3d**, respectively. The Al−N (amido) distances (1.889(1) Å for **3a**, 1.890(3) Å for **3c**, and 1.874(2) Å for **3d**) are much shorter than the Al−N (imine) distances (1.963(1) Å for **3a,** 1.955(3) Å for **3c**, and 1.942(2) Å for **3d**) because the anionic amido nitrogen can also $\pi$-donate to the aluminum, whereas the neutral imine nitrogen does not have an available lone pair for $\pi$-donation. The Al−N (imine) distances are shorter than the value (1.972(3) Å) previously reported for $\{3,5\text{-}^t\mathrm{Bu}_2\text{-}2\text{-}(\mathrm{O})\mathrm{C}_6\mathrm{H}_2\text{-}\mathrm{CH{=}NC}_6\mathrm{H}_3{}^i\mathrm{Pr}_2\text{-}2,6\}\mathrm{AlMe}_2$,[14] but larger than those values (1.922(2) and 1.935(2) Å) in Dipp$_2$nacnacAlMe$_2$.[15] The N−Al−N angles (93.8° for **3a**, 93.9° for **3c**, and 94.5° for **3d**) in these complexes are similar to that (94.72°) of a diketiminatolaluminum complex $\{\mathrm{CH[CMeN(}p\text{-}\mathrm{MeC_6H_4)]_2AlMe_2}\}$,[15] while they are larger than those in the four-membered chelating ring (69°) of $\{^t\mathrm{BuC(NCy)_2}\}$-$\mathrm{AlMe_2}$[16] and the five-membered chelating ring (84°) of $\{(^i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{AlR_2}$.[17]

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a, 3c, and 3d**

| | | | |
|---|---|---|---|
| Complex **3a** | | | |
| Al(1)−N(1) | 1.889(1) | N(1)−Al(1)−C(33) | 111.59(7) |
| Al(1)−N(2) | 1.963(1) | C(33)−Al(1)−N(2) | 114.97(7) |
| Al(1)−C(33) | 1.960(2) | N(1)−Al(1)−C(32) | 115.66(7) |
| Al(1)−C(32) | 1.968(2) | C(33)−Al(1)−C(32) | 113.83(8) |
| N(1)−C(1) | 1.370(2) | N(2)−Al(1)−C(32) | 105.32(7) |
| N(2)−C(7) | 1.298(2) | C(7)−N(2)−Al(1) | 121.07(10) |
| N(1)−Al(1)−N(2) | 93.79(5) | C(20)−N(2)−Al(1) | 121.99(9) |
| Complex **3c** | | | |
| Al(1)−N(1) | 1.890(3) | N(2)−Al(1)−C(28) | 110.7(2) |
| Al(1)−N(2) | 1.955(3) | N(1)−Al(1)−C(27) | 110.0(2) |
| Al(1)−C (28) | 1.956(5) | N(2)−Al(1)−C(27) | 112.1(2) |
| Al(1)−C (27) | 1.956(5) | C(28)−Al(1)−C(27) | 115.3(2) |
| N(1)−C(1) | 1.357(4) | C(1)−N(1)−Al(1) | 127.7(2) |
| N(2)−C(7) | 1.309(4) | C(20)−N(1)−Al(1) | 111.8(2) |
| N(1)−Al(1)−N(2) | 93.9(1) | C(7)−N(2)−Al(1) | 122.7(2) |
| N(1)−Al(1)−C(28) | 113.0(2) | C(8)−N(2)−Al(1) | 122.3(2) |
| Complex **3d** | | | |
| Al(1)−N(1) | 1.874(2) | C(22)−Al(1)−N(2) | 111.5(9) |
| Al(1)−C(22) | 1.932(2) | N(1)−Al(1)−C(23) | 113.8(1) |
| Al(1)−N(2) | 1.942(2) | C(22)−Al(1)−C(23) | 116.7(1) |
| Al(1)−C(23) | 1.943(3) | N(2)−Al(1)−C(23) | 107.3(1) |
| N(1)−C(1) | 1.360(3) | C(1)−N(1)−Al(1) | 129.0(1) |
| N(2)−C(7) | 1.305(3) | C(15)−N(1)−Al(1) | 114.7(1) |
| N(1)−Al(1)−C(22) | 110.9(1) | C(7)−N(2)−Al(1) | 123.4(2) |
| N(1)−Al(1)−N(2) | 94.49(8) | C(8)−N(2)−Al(1) | 120.7(1) |

**UV−Vis and Fluorescent Properties.** Table 3 summarizes the UV−vis and fluorescent properties of

---

[14] Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1472.

[15] Qian, B.; Ward, M. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070.

[16] Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183.

[17] Dias, H. V.; Jin, R. W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100.

**Table 2. Crystal Data and Structural Refinements Details for 3a, 3c, and 3d**

| | 3a | 3c | 3d |
|---|---|---|---|
| formula | $C_{33}H_{45}AlN_2$ | $C_{28}H_{35}AlN_2$ | $C_{23}H_{25}AlN_2$ |
| fw | 496.69 | 426.56 | 356.43 |
| cryst syst | monoclinic | triclinic | monoclinic |
| space group | $P2(1)/c$ | $P\bar{1}$ | $P2(1)/c$ |
| $a$ (Å) | 17.671(4) | 9.826(3) | 11.960(2) |
| $b$ (Å) | 10.496(2) | 10.000(3) | 8.9673(18) |
| $c$ (Å) | 17.695(4) | 14.755(5) | 19.415(4) |
| α (deg) | 90 | 106.875(4) | 90 |
| $\beta$ (deg) | 108.54(3) | 103.857(4) | 96.72(3) |
| $\gamma$ (deg) | 90 | 100.180(5) | 90 |
| volume (Å$^3$) | 3111.5(11) | 1298.9(7) | 2068.0(7) |
| $Z$ | 4 | 2 | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.060 | 1.091 | 1.145 |
| $F$(000) | 1080 | 460 | 760 |
| $\theta$ range for data collection | 3.04° to 27.48° | 2.20° to 25.00° | 1.71° to 27.36° |
| limiting indices | $-22 \leq h \leq 22$<br>$-13 \leq k \leq 13$<br>$-22 \leq l \leq 22$ | $-5 \leq h \leq 11$<br>$-8 \leq k \leq 11$<br>$-17 \leq l \leq 14$ | $0 \leq h \leq 15$<br>$0 \leq k \leq 11$<br>$-25 \leq l \leq 24$ |
| no. of data/restraints/params | 7092/0/325 | 3822/0/280 | 4517/0/247 |
| goodness-of-fit on $F^2$ | 1.051 | 1.019 | 0.860 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1{}^a = 0.0477$<br>$wR_2{}^b = 0.1399$ | $R_1{}^a = 0.0610$<br>$wR_2{}^b = 0.1597$ | $R_1{}^a = 0.0523$<br>$wR_2{}^b = 0.1172$ |
| $R$ indices (all data) | $R_1{}^a = 0.0654$<br>$wR_2{}^b = 0.1510$ | $R_1{}^a = 0.1027$<br>$wR_2{}^b = 0.1886$ | $R_1{}^a = 0.1186$<br>$wR_2{}^b = 0.1328$ |
| largest diff peak/hole (e·Å$^{-3}$) | 0.238, −0.222 | 0.238, −0.323 | 0.184, −0.172 |

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

**Table 3. Optical Properties of Compounds 2a–d and 3a–d in *n*-Hexane**

| compound | abs $\lambda$ (nm) | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $E_m$ $\lambda$ (nm) |
|---|---|---|---|
| **2a** | 370 | 9011 | 419 |
| **2b** | 373 | 13 214 | 423 |
| **2c** | 382 | 10 745 | 430 |
| **2d** | 395 | 13 300 | 450 |
| **3a** | 454 | 8056 | 519 |
| **3b** | 455 | 8287 | 519 |
| **3c** | 463 | 8156 | 547 |
| **3d** | 475 | 8085 | 582 |

compounds **2a–d** and **3a–d** determined in hexane. By examining the data in Table 3, it can be seen that the UV–vis absorption and fluorescent emission peaks for these compounds are red shifted with the decrease in the size of the substituents at the *ortho*-positions of the two rotatable aryl rings, which might be because larger *ortho*-substituents on the aryl rings would lower the chance for the rotatable aryl rings to have coplanar conformations with the chelating ring, thus reducing the conjugated extent of the compounds.

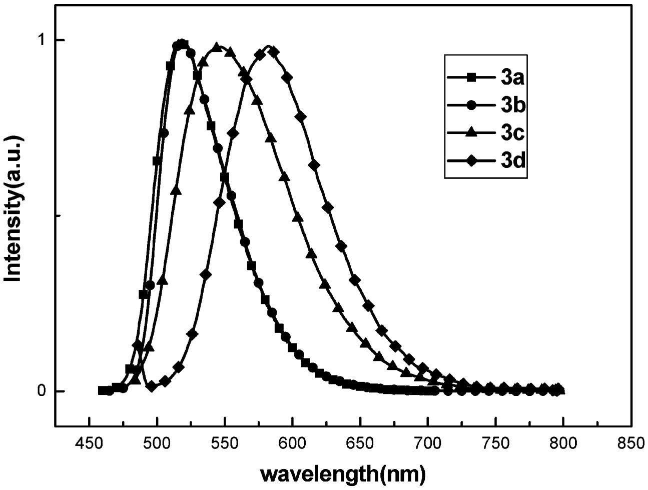


**Figure 4.** Emission spectra of complexes **3a–d** in *n*-hexane.

The free ligands **2a–d** all display weak blue fluorescence with emission maxima of 419, 423, 430, and 450 nm, respectively. In comparison, complexes **3a–d** produce bright fluorescence from green to orange-red in solution with emission maxima of 519, 519, 547, and 582 nm, respectively, as seen in Figure 4. It is remarkable that the emission maxima of complexes **3a–d** span 63 nm between 519 and 582 nm just because of the differences in the number and size of the *ortho*-substituents on the rotatable aryl rings of their ligands that might affect the conjugated extent of these complexes as mentioned above. These results provide a new way to modulate the emission color of organic, organometallic, or coordination compounds with rotatable aryl groups. It can be clearly seen that the absorption and emission frequencies of the complexes **3a–d** change with the same trend as those of the free ligands **2a–d** do. However, complexes **3a** and **3b** in solid state emit bright fluorescence with emission maxima of 532 and 533 nm (Figure 5), which are red shifted in comparison with their emission maxima in solution, while the emission maxima of complexes **3c** and **3d** (545 and 552 nm, respectively) in solid state are blue shifted compared to their corresponding emission maxima in solution. The red shift of the emission wavelength from solution to solid state is likely caused by $\pi$–$\pi$ stacking of aromatic rings in the molecules in solid state, while the blue shift of the emission wavelength for **3c** and **3d** from solution to solid state probably results from the reduced conjugated extent of the two complexes since the free rotation of the aryl rings in these complexes is blocked in the solid state. According to published literatures, the emissions of these complexes could be attributed to a $\pi^*$–$\pi$ transition of their ligands.[18] The role of the aluminum atom in the luminescence of **3a–d** might be 2-fold. First, the formation of covalent bonds

---

[18] (a) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1986**, *25*, 3858. (b) Yang, W.; Schmider, H.; Wu, Q.; Zhang, Y.; Wang, S. *Inorg. Chem.* **2000**, *39*, 2397.

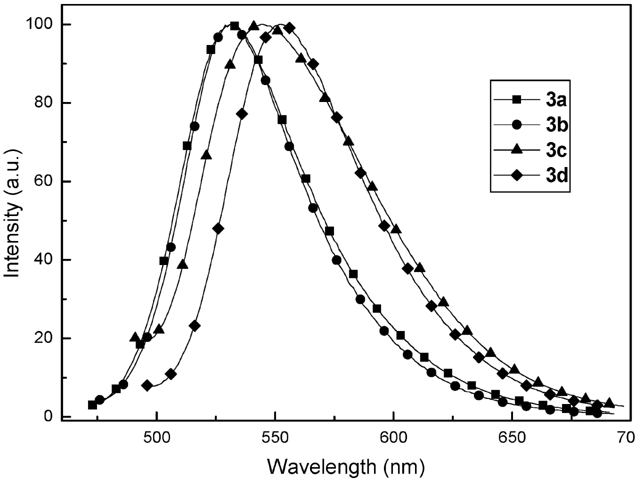


**Figure 5.** Emission spectra of complexes **3a**–**d** in the solid state.

between the Al and N atoms via the donation of lone pairs of the N atom to the Al atom changes the emission energy, perhaps owing to the lowering of the energy gap between $\pi^*$ and $\pi$. Second, after coordination with the Al atom, the rigidity of the ligands becomes stronger in comparison with free ligands, which can reduce the loss of energy via vibrational motions and increase the emission efficiency, a phenomenon well known to coordination complexes containing luminescence ligand.[19]

## Summary

Our research results indicate that the new chelating bidentate anilido-imine conjugated ligands are well suited for synthesizing the four-coordinate alkyl aluminum complexes by alkane elimination reaction of $AlMe_3$ with corresponding ligands at room temperature. $^1H$ and $^{13}C$ 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 new 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.

## Experimental Section

All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glovebox techniques. Toluene, 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 over activated 4 Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. $CDCl_3$ was dried over $CaH_2$ for 48 h and vacuum-transferred to an air-free flask. $AlMe_3$ and $^n$BuLi were purchased from Aldrich and used as received. The *ortho*-$C_6H_4F(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)$ and *ortho*-$C_6H_4(NHAr')(CH{=}NAr')$ ($Ar' = Ar'' = 2,6\text{-}{}^iPr_2C_6H_3$) were synthesized according to literature procedures.[13] NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. The elemental analysis was performed on a Perkin-Elmer 2400 analyzer. UV–vis absorption spectra were recorded on an UV-3100 spectrophotometer. Fluorescence measurements were carried out on a RF-5301PC.

***ortho*-$C_6H_4F(CH{=}NC_6H_3Me_2\text{-}2,6)$ (1b).** A mixture of *ortho*-fluorobenzaldehyde (5.0 mL, 47.1 mmol), 2,6-dimethylaniline (5.8 mL, 47.1 mmol), and $MgSO_4$ (1.0 g) in *n*-hexane (30 mL) was stirred for 2 h. The mixture was filtered and evaporated to dryness in vacuo to give the product as a yellowish oil (6.4 g, 60%). Anal. Calcd for $C_{15}H_{14}NF$ (227.28): C 79.27, H 6.21, N 6.16. Found: C 79.16, H 6.30, N 6.24. $^1H$ NMR ($CDCl_3$): $\delta$ 2.19 (s, 6H, $CH_3$), 6.97–7.32 (m, 5H, Ph-$H$), 7.51 (t, 1H, Ph-$H$), 8.30 (t, 1H, Ph-$H$), 8.58 (s, 1H, $CH{=}NAr$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 18.5 ($Me$), 116.2 (d, $^2J_{CF} = 21$ Hz, Ph), 124.1 (d, $^3J_{CF} = 4$ Hz), 124.2 (Ph), 124.8 (Ph), 127.3 (Ph), 127.9 (Ph), 128.3 (Ph), 133.3 (d, $^3J_{CF} = 9$ Hz, Ph), 151.5 (quaternary aromatic), 156.5 (d, $^3J_{CF} = 5$ Hz, $C$H=NAr), 163.1 (d, $^1J_{CF} = 256$ Hz, $C$F) ppm.

***ortho*-$C_6H_4F(CH{=}NC_6H_4Me\text{-}p)$ (1c).** A mixture of *ortho*-fluorobenzaldehyde (5.0 mL, 47.1 mmol), *p*-toluidine (5.0 g, 47.1 mmol), and $MgSO_4$ (1.0 g) in *n*-hexane (30 mL) was stirred for 2 h. The mixture was filtered, and the filtrate was concentrated to about 10 mL and kept at −20 °C overnight. Pure product was obtained as yellow crystals (8.2 g, 82%). Anal. Calcd for $C_{14}H_{12}NF$ (213.25): C 78.85, H 5.67, N 6.57. Found: C 78.80, H 5.70, N 6.54. $^1H$ NMR ($CDCl_3$): $\delta$ 2.39 (s, 3H, $CH_3$), 7.50 (t, 1H, Ph-$H$), 8.21 (t, 1H, Ph-$H$), 7.10–7.31 (m, 6H, Ph-$H$), 8.81 (s, 1H, $CH{=}NAr$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 21.2 ($Me$), 116.1 (d, $^2J_{CF} = 21$ Hz, Ph), 121.2 (Ph), 124.3 (d, $^2J_{CF} = 9$ Hz, quaternary aromatic), 124.7 (d, $^3J_{CF} = 5$ Hz, Ph), 128.1 (Ph), 130.0 (Ph), 133.0 (d, $^3J_{CF} = 9$ Hz, Ph), 136.5, 149.6 (2 quaternary aromatic), 152.8 (d, $^3J_{CF} = 5$ Hz, $C$H=NAr), 163.0 (d, $^1J_{CF} = 256$ Hz, $C$F) ppm.

***ortho*-$C_6H_4\{NH(C_6H_3Me_2\text{-}2,6)\}(CH{=}NC_6H_3Me_2\text{-}2,6)$ (2b).** A solution of $^n$BuLi (30.32 mL, 48.5 mmol) in hexanes was added to a solution of 2,6-dimethylaniline (6.0 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 ($Ar = C_6H_3Me_2\text{-}2,6$) was transferred into a solution of *ortho*-$C_6H_4F(CH{=}NC_6H_3Me_2\text{-}2,6)$ (11.0 g, 48.5 mmol) in THF (40 mL) at 25 °C. After stirring for 2 h, the reaction was quenched with $H_2O$ (25 mL) and 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 (11.5 g, 72%) was obtained as yellowish-green crystals by recrystallization from ethanol at −20 °C. Anal. Calcd for $C_{23}H_{24}N_2$ (328.45): C 84.11, H 7.37, N 8.52. Found: C 84.18, H 7.25, N 8.57. $^1H$ NMR ($CDCl_3$): $\delta$ 2.22 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 6.32 (d, 1H, Ph-$H$), 6.76 (t, 1H, Ph-$H$), 7.01 (t, 1H, Ph-$H$), 7.12–7.24 (m, 6H, Ph-$H$), 7.37 (d, 1H, Ph-$H$), 8.42 (s, 1H, $CH{=}NAr$), 10.60 (s, 1H, N$H$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 18.6 ($C$H$_3$), 18.8 ($C$H$_3$), 112.0, 115.6, 117.0, 124.1, 126.6, 127.9, 128.4, 128.6, 132.5, 134.8, 137.0, 137.7, 148.7, 151.0, 166.2 ($C$H=NAr) ppm.

***ortho*-$C_6H_4\{NH(C_6H_4Me\text{-}p)\}(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)$ (2c).** A solution of $^n$BuLi (29.2 mL, 46.7 mmol) in hexanes was added to a solution of *p*-toluidine (5.0 g, 46.7 mmol) in THF (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solution of LiNHAr ($Ar = C_6H_4Me\text{-}p$) was transferred into a solution of *ortho*-$C_6H_4F(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)$ (13.2 g, 46.7 mmol) in THF (40 mL) at 25 °C. After stirring for 2 h, the reaction was quenched with $H_2O$ (20 mL) and 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 (11.9 g, 69%) was obtained as yellow crystals by recrystallization from ethanol at −20 °C. Anal. Calcd for $C_{26}H_{30}N_2$ (370.53): C 84.28, H 8.16, N 7.56. Found: C 84.19, H 8.21, N 7.60. $^1H$ NMR ($CDCl_3$): $\delta$ 1.19 (d, 6H, $CH(CH_3)_2$), 1.21 (d, 6H, $CH(CH_3)_2$), 2.36 (s, 3H, $CH_3$), 3.07 (sept, 2H, $CH(CH_3)_2$), 6.81 (t, 1H, Ph-$H$), 7.14–7.38 (m, 10H, Ph-$H$), 8.32 (s, 1H, $CH{=}NAr$), 11.16 (s,

---

[19] (a) *Fluorescence and Phosphorescence*; Rendell, D., Eds.; Wiley: New York, 1987. (b) *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, 1987. (c) *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975.

1H, N*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.1 ($CH_3$), 23.8 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 112.7, 116.8, 117.8, 123.0, 123.3, 124.7, 130.1, 132.3, 133.3, 135.2, 138.4, 147.2, 148.8, 165.7 ($CH{=}NAr$) ppm.

***ortho*-$C_6H_4\{NH(C_6H_4Me\text{-}p)\}(CH{=}NC_6H_4Me\text{-}p)$ (2d).** A solution of $^nBuLi$ (29.2 mL, 46.7 mmol) in hexanes was added to a solution of *p*-toluidine (5.0 g, 46.7 mmol) in THF (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solution of LiNHAr (Ar = $C_6H_4Me\text{-}p$) was transferred into a solution of *ortho*-$C_6H_4F(CH{=}NC_6H_4Me\text{-}p)$ (9.9 g, 46.7 mmol) in THF (40 mL) at 25 °C. After stirring for 2 h, the reaction was quenched with $H_2O$ (20 mL) and extracted with *n*-hexane, and the organic phase was evaporated to dryness in vacuo to give the crude product. Pure product was obtained by recrystallization from ethanol at −20 °C as orange crystals (9.8 g, 70%). Anal. Calcd for $C_{21}H_{20}N_2$ (300.40): C 83.96, H 6.71, N 9.33. Found: C 83.86, H 6.78, N 9.36. $^1H$ NMR ($CDCl_3$): δ 2.43 (s, 3H, $CH_3$), 2.45 (s, 3H, $CH_3$), 6.85 (t, 1H, Ph-*H*), 7.21−7.37 (m, 10H, Ph-*H*), 7.47 (d, 1H, Ph-*H*), 8.67 (s, 1H, C*H*=NAr), 11.24 (s, 1H, N*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.1 ($CH_3$), 21.2 ($CH_3$), 112.9, 116.9, 118.4, 121.1, 123.0, 130.0, 130.1, 132.0, 133.2, 135.1, 135.9, 138.6, 147.0, 148.9, 162.3 ($CH{=}NAr$) ppm.

***ortho*-$C_6H_4N(C_6H_3{}^iPr_2\text{-}2,6)(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)Al(CH_3)_2$ (3a).** A solution of *ortho*-$C_6H_4\{NH(C_6H_3{}^iPr_2\text{-}2,6)\}(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)$ (0.20 g, 0.46 mmol) in 10 mL of *n*-hexane was slowly added to a solution of $AlMe_3$ (0.46 mmol) in 15 mL of *n*-hexane at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and at room temperature for additional 2 h, then was concentrated to about 10 mL and kept at −20 °C overnight to let the product crystallize. The product was obtained as orange-green crystals (0.20 g, 88%). Anal. Calcd for $C_{33}H_{45}N_2Al$ (496.70): C 79.80, H 9.13, N 5.64. Found: C 79.71, H 9.08, N 5.78. $^1H$ NMR ($C_6D_6$, 293 K): δ −0.52 (s, 6H, $Al(CH_3)_2$), 1.02, 1.11 (d, 2 × 6H, $CH(CH_3)_2$), 1.31, 1.37 (d, 2 × 6H, $CH(CH_3)_2$), 3.41, 3.53 (sept, 2 × 2H, $CH(CH_3)_2$), 6.25 (t, 1H, Ph-*H*), 6.33 (d, 1H, Ph-*H*), 6.78 (m, 2H, Ph-*H*), 7.09−7.24 (m, 6H, Ph-*H*), 7.86 (s, 1*H*, HC=N) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 293 K): δ −9.0 ($Al(CH_3)_2$), 22.7, 24.7, 25.6, 25.8 (4 × $CH(CH_3)_2$), 28.4, 28.5 (2 × $CH(CH_3)_2$), 115.1, 115.7, 119.4, 124.4, 124.8, 126.9, 128.1, 135.9, 136.9, 140.8, 142.9, 143.3, 146.6, 158.2, 171.5 ($CH{=}NAr$) ppm.

***ortho*-$C_6H_4N(C_6H_3Me_2\text{-}2,6)(CH{=}NC_6H_3Me_2\text{-}2,6)Al(CH_3)_2$ (3b).** A solution of *ortho*-$C_6H_4\{NH(C_6H_3Me_2\text{-}2,6)\}(CH{=}NC_6H_3Me_2\text{-}2,6)$ (0.20 g, 0.61 mmol) in 10 mL of *n*-hexane was slowly added to a solution of $AlMe_3$ (0.61 mmol) in 15 mL of *n*-hexane at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and at room temperature for additional 2 h, then was concentrated to about 10 mL and kept at −20 °C overnight to let the product crystallize. The product was obtained as orange-green crystals (0.21 g, 90%). Anal. Calcd for $C_{25}H_{29}N_2Al$ (384.49): C 78.09, H 7.60, N 7.29. Found: C 78.21, H 7.51, N 7.37. $^1H$ NMR ($C_6D_6$, 293 K): δ −0.50 (s, 6H, $Al(CH_3)_2$), 2.15 (s, 6H, Ph-$CH_3$), 2.29 (s, 6H, Ph-$CH_3$), 6.31 (t, 1H, Ph-*H*), 6.73 (d, 1H, Ph-*H*), 6.80−7.16 (m, 8H, Ph-*H*), 7.32 (s, 1H, *H*C=N) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 293 K): δ −7.6 ($Al(CH_3)_2$), 18.6 ($CH_3$), 18.7 ($CH_3$), 114.6, 115.7, 116.5, 126.0, 127.2, 129.1, 129.4, 132.3, 136.1, 137.1, 137.4, 142.9, 145.6, 156.7, 171.9 ($CH{=}NAr$) ppm.

***ortho*-$C_6H_4N(C_6H_4Me\text{-}p)(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)Al(CH_3)_2$ (3c).** A solution of *ortho*-$C_6H_4\{NH(C_6H_4Me\text{-}p)\}(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)$ (0.20 g, 0.54 mmol) in 10 mL of *n*-hexane was slowly added to a solution of $AlMe_3$ (0.54 mmol) in 15 mL of hexanes at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and at room temperature for additional 2 h, then was concentrated to about 10 mL and kept at −20 °C overnight to let the product crystallize. The product was obtained as orange crystals (0.21 g, 91%). Anal. Calcd for $C_{28}H_{35}N_2Al$ (426.56): C 78.84, H 8.27, N 6.57. Found: C 78.73, H 8.11, N 6.69. $^1H$ NMR ($C_6D_6$, 293 K): δ −0.38 (s, 6H, $Al(CH_3)$), 0.92 (d, 6H, $CH(CH_3)_2$), 1.27 (d, 6H, $CH(CH_3)_2$), 2.10 (s, 3H, Ph-$CH_3$), 3.34 (sept, 2H, $CH(CH_3)_2$), 6.28 (t, 1H, Ph-*H*), 6.67 (d, 1H, Ph-*H*), 6.78 (d, 1H, Ph-*H*), 6.87 (t, 1H, Ph-*H*), 6.99−7.20 (m, 7H, Ph-*H*), 7.84 (s, 1H, *H*C=N) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 293 K): δ −8.0 ($Al(CH_3)_2$), 20.9 ($CH_3$), 22.7 ($CH(CH_3)_2$), 26.0 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 114.7, 115.5, 117.7, 124.4, 130.9, 134.8, 136.8, 136.9, 143.1, 143.2, 143.7, 157.9, 171.5 ($CH{=}NAr$) ppm.

***ortho*-$C_6H_4N(C_6H_4Me\text{-}p)(CH{=}NC_6H_4Me\text{-}p)Al(CH_3)_2$ (3d).** A solution of *ortho*-$C_6H_4\{NH(C_6H_4Me\text{-}p)\}(CH{=}NC_6H_4Me\text{-}p)$ (0.20 g, 0.67 mmol) in 10 mL of *n*-hexane was slowly added to a solution of $AlMe_3$ (0.67 mmol) in 15 mL of *n*-hexane at 0 °C with stirring. The mixture was stirred at 0 °C for 30 min and at room temperature for additional 2 h, then was concentrated to about 10 mL and kept at −20 °C overnight to let the product crystallize. The product was obtained as orange crystals (0.20 g, 85%). Anal. Calcd for $C_{23}H_{25}N_2Al$ (356.44): C 77.50, H 7.07, N 7.86. Found: C 77.62, H 7.16, N 7.74. $^1H$ NMR ($C_6D_6$, 293 K): δ −0.25 (s, 6H, $Al(CH_3)_2$), 2.02 (s, 3H, Ph-$CH_3$), 2.11 (s, 3H, Ph-$CH_3$), 6.31 (t, 1H, Ph-*H*), 6.65 (d, 1H, Ph-*H*), 6.68 (d, 1H, Ph-*H*), 6.83−7.20 (m, 9H, Ph-*H*), 7.65 (s, 1H, C*H*=N) ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 293 K): δ −7.7 ($Al(CH_3)_2$), 20.8 ($CH_3$), 20.9 ($CH_3$), 114.5, 116.3, 117.4, 122.7, 130.3, 130.9, 134.9, 136.6, 137.1, 137.4, 143.8, 145.6, 157.7, 168.0 ($CH{=}NAr$) ppm.

**X-ray Structure Determinations of 3a, 3c, and 3d.** Single crystals of **3a**, **3c**, and **3d** suitable for X-ray structural analysis were obtained from *n*-hexane. Diffraction data were collected at 293 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for **3c** and on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for **3a** and **3d**. Details of the crystal data, data collections, and structure refinements are summarized in Table 2. 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 position. All calculations were performed using the SHELXTL[21] crystallographic software packages.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China (No. 20374023 and 29734143) and Ministry of Science and Technology of China (No. 2002CB6134003).

**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra for **1b**, **1c**, **2b**−**d**, and **3a**−**d**. X-ray crystallographic files (CIF) for **3a**, **3c**, and **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049143A

---

[20] *SHELXTL*; PC Siemens Analytical X-ray Instruments: Madison, WI, 1993.

[21] Sheldrick, G. M. *SHELXTL Structure Determination Programs*, Version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.