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Synthesis of Bis(amino)pyridines by the Stepwise Alkylation of Bis(imino)pyridines: An Unexpected and Selective Alkylation of the Aminoiminopyridine by $AlMe_3$

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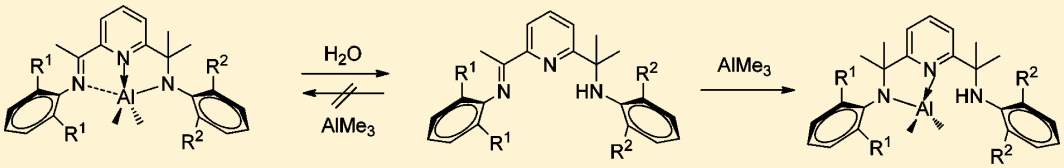
Supporting Information



a: $R^1 = CH(CH_3)_2$, $R^2 = CH(CH_3)_2$
b: $R^1 = CH(CH_3)_2$, $R^2 = CH_3$
c: $R^1 = CH_3$, $R^2 = CH_3$

ABSTRACT: Bis(imino)pyridines 2-[2,6-$(R^1)_2C_6H_3N{=}C(CH_3)$]-6-[2,6-$(R^2)_2C_6H_3N{=}C(CH_3)$](C_5H_3N) (**1a**, $R^1 = R^2 = i$-Pr; **1b**, $R^1 = i$-Pr, $R^2 = CH_3$; **1c**, $R^1 = R^2 = CH_3$) were first alkylated by $AlMe_3$ and then hydrolyzed to aminoiminopyridines 2-[2,6-$(R^1)_2C_6H_3N{=}C(CH_3)$]-6-[2,6-$(R^2)_2C_6H_3NHC(CH_3)_2$](C_5H_3N) (**3a**, $R^1 = R^2 = i$-Pr; **3b**, $R^1 = i$-Pr, $R^2 = CH_3$; **3c**, $R^1 = R^2 = CH_3$). When the aminoiminopyridines were treated with $AlMe_3$, the expected methane elimination was not found; alkylation at the imine functional group led to the aluminum complexes {2-[2,6-$(R^1)_2C_6H_3NC(CH_3)_2$]-6-[2,6-$(R^2)_2C_6H_3NHC(CH_3)_2$]-(C_5H_3N)}$AlMe_2$ (**4a**, $R^1 = R^2 = i$-Pr; **4b**, $R^1 = i$-Pr, $R^2 = CH_3$; **4c**, $R^1 = R^2 = CH_3$), which were further hydrolyzed to the bis(amino)pyridines 2-[2,6-$(R^1)_2C_6H_3NHC(CH_3)_2$]-6-[2,6-$(R^2)_2C_6H_3NHC(CH_3)_2$](C_5H_3N) (**5a**, $R^1 = R^2 = i$-Pr; **5b**, $R^1 = i$-Pr, $R^2 = CH_3$; **5c**, $R^1 = R^2 = CH_3$). The selective alkylation over elimination may come from the noninnocent property of the conjugated iminopyridine group. New magnesium, yttrium, and zirconium complexes supported by **5a** ({2,6-[2,6-(i-Pr)$_2C_6H_3NC(CH_3)_2$]$_2(C_5H_3N)$}$Mg(THF)$ (**6**), {2,6-[2,6-(i-Pr)$_2C_6H_3NC(CH_3)_2]_2(C_5H_3N)$}$Y(CH_2SiMe_3)(THF)$ (**7**), and {2,6-[2,6-(i-Pr)$_2C_6H_3NC(CH_3)_2]_2(C_5H_3N)$}$Zr(CH_2SiMe_3)_2$ (**8**)) were formed via the alkane elimination method.

Since the first independent reports by Gibson, Bennett, and Brookhart that bis(imino)pyridine-supported iron and cobalt complexes were very active for olefin polymerization,[1] tremendous research has been undertaken to understand this efficient system.[2] Studies have shown that the conjugated ligand itself is noninnocent and is involved in a series of transformations such as deprotonation reactions, alkylation, and participation in redox reactions.[3,4] One of the transformations is the monoalkylation of the bis(imino)pyridine **1a** to the aminoiminopyridine **3a** by $AlMe_3$ via the aluminum complex **2a** as the intermediate (Scheme 1).[3d,5] The aminoiminopyridine **3a** has offered a platform to numerous complexes with unique properties and applications.[6] A further straightforward modification to the ligand framework is bis(amino)pyridine, in which both of the imine groups are replaced by amine donors. Bis(amino)pyridines exert quite different electronic and steric environments and have been applied as useful supporting ligands for transition metals which mainly have applications to polymer formation.[4,7,8] While the direct reduction of bis(imino)pyridine to bis(amino)pyridine by sodium borohydride was previously reported,[9] this method cannot be applied to this ligand frame with bulky steric demands. The starting material was fully recovered when **1a** was treated in the same way. Direct alkylation of **1a** to bis(amino)pyridine **5a** also does not work.[10] A general synthesis of bis(amino)pyridines was achieved by the substitution reaction of 2,6-bis(bromomethyl)-pyridine by amines.[11]

We disclose here a convenient way to the bis(amino)pyridine **5** through selective alkylation of **3** by $AlMe_3$ followed by hydrolysis (Scheme 2). The expected formation of aluminum complex **2** from **3** via methane elimination was not found.

RESULTS AND DISCUSSION

We found this reaction by serendipity. When we prepared the ligand **3a** according to the literature (Scheme 1),[3d,5] the bis(imino)pyridine **1a** was not completely transformed into **3a** (>90% conversion). In order to obtain a higher conversion rate, which is necessary for ease of purification of the product, the

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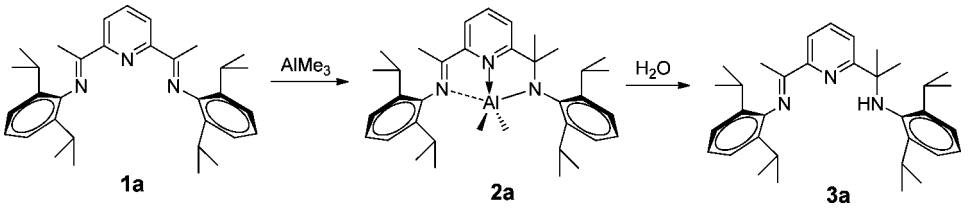
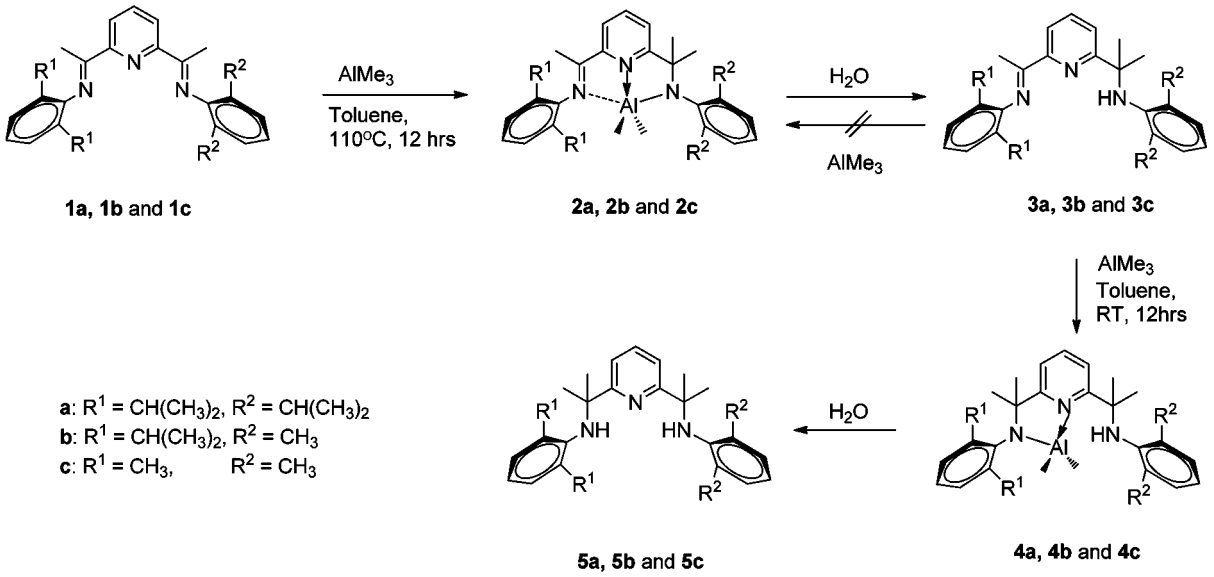
Scheme 1. Monoalkylation of Bis(imino)pyridine 1a by $AlMe_3$



Scheme 2. Alkylation of 3 by $AlMe_3$



crude mixture of **1a** and **3a** was treated with a second excess portion of $AlMe_3$. To our surprise, the main product was not **3a** but the bis(amino)pyridine **5a** after workup. This spurred us to investigate the reaction further. We tried the reaction of pure **3a** with 1 equiv of $AlMe_3$ in toluene at room temperature for 12 h. Instead of the product **2a**, formed via methane elimination like other group III and IV metal complexes depicted in the literature,[6] only the selective alkylation product **4a** was obtained in quantitative yield (Scheme 2). **4a** has been isolated as a byproduct and characterized by X-ray diffraction in the reaction of ligand **3a** with $[Ln(AlMe_4)_3]$ in the literature.[10] Although the author claims the alkylation proceeds via the [Ln−Me] moiety rather than [Al−Me], we think the high reactivity of the Al−Me bond and the noninnocent conjugated iminopyridine group may dominate the alkylation reaction selectively. **4a** was further hydrolyzed to the bis(amino)pyridine **5a** with an isolated yield of 93% after recrystallization from methanol. **4a** and **5a** have been characterized by NMR spectroscopy, elemental analysis, etc. Single crystals for X-ray structure analysis were also obtained from **5a** by the slow evaporation of its solution in methanol/ether (Figure 1).

With the large number of bis(imino)pyridine ligands that have been reported, it is interesting to see if this route is more general for sterically less bulky ligands. We have prepared a series of bis(imino)pyridine compounds **1** with different substituents at the imine nitrogen atoms according to literature methods.[1d,9,12] The results show that the substituents with steric demands are necessary for the successful alkylation of the imine functional groups. While **1b,c** were smoothly transformed to the corresponding **3b,c** and **5b,c**, symmetric bis(imino)pyridine ligands with less bulky subsituents such as

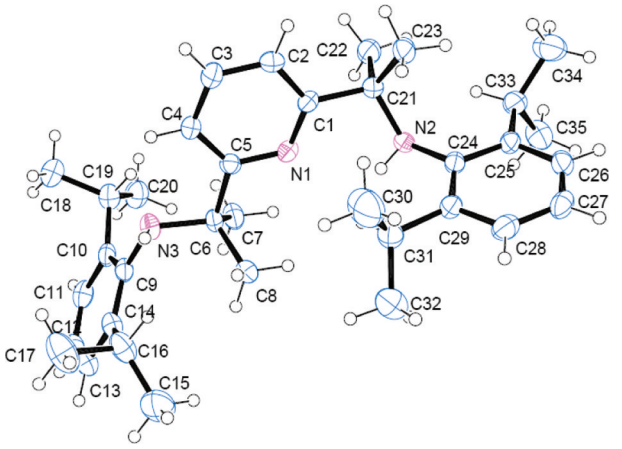


Figure 1. ORTEP drawing of the molecular structure of **5a** (anisotropic displacement parameters set at the 30% probability level). Selected bond lengths (Å) and angles (deg): C(1)−N(1) = 1.336(5), C(1)−C(21) = 1.548(5), C(21)−N(2) = 1.485(5), C(5)−N(1) = 1.355(5), C(5)−C(6) = 1.531(6), C(6)−N(3) = 1.500(5); C(1)−C(21)−N(2) = 109.6(3), C(5)−C(6)−N(3) = 107.2(3).

n-butyl and *p*-methylphenyl groups underwent a complicated reaction in the presence of trimethylaluminum, and no clean products could be obtained for the first step of alkylation. Just as expected, in the case of **1b**, the alkylation took place on the imine with the less bulky 2,6-dimethylphenyl substituent. The structures of the new compounds **3b,c** have been also confirmed by NMR spectroscopy, elemental analysis, and X-ray diffraction studies (see the Experimental Section and Supporting Information).

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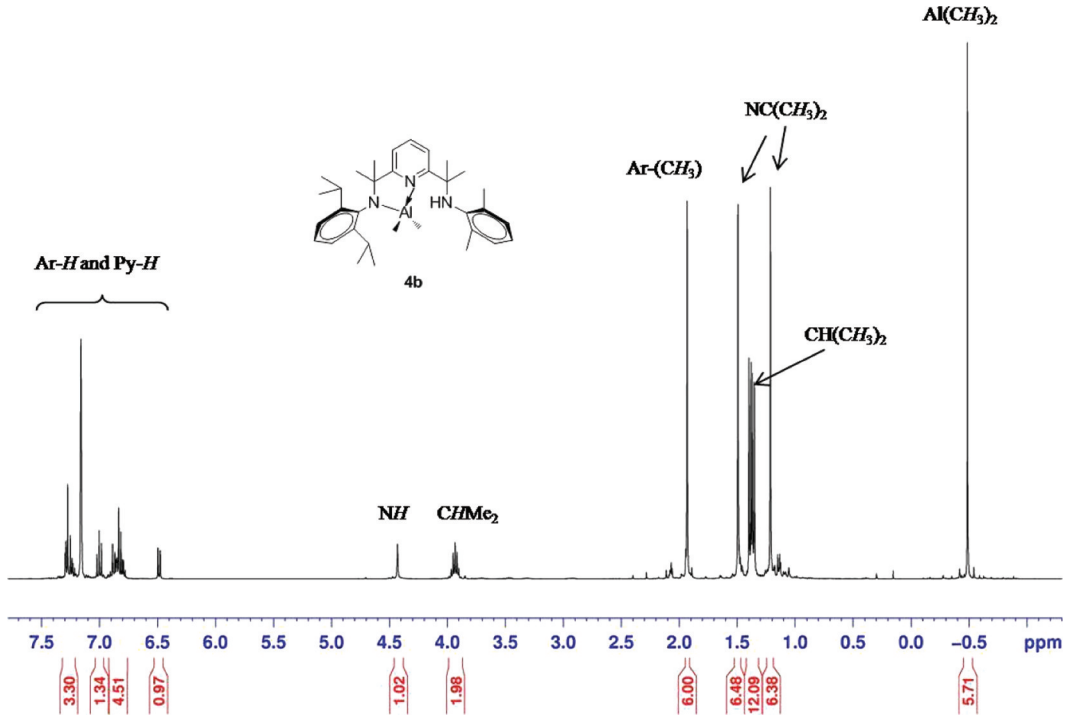
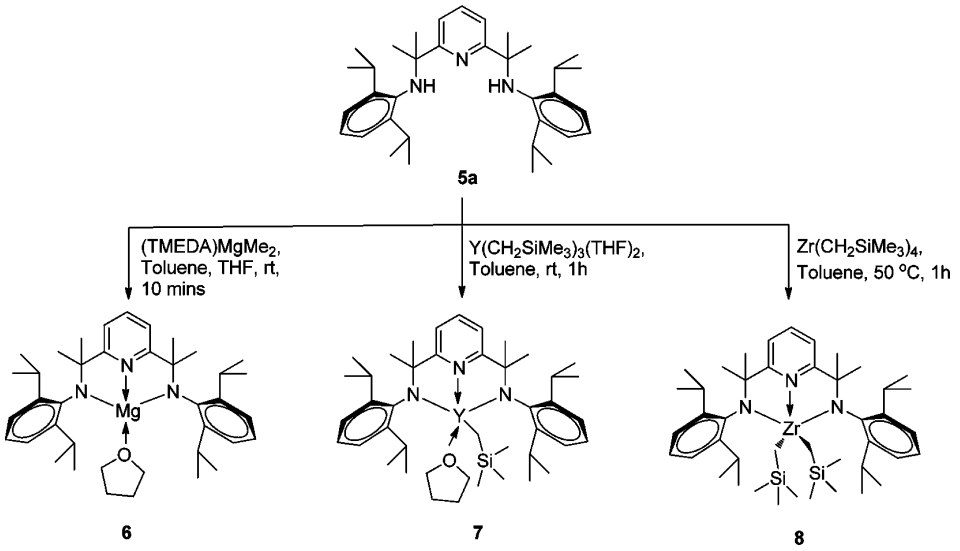


Figure 2. ^{1}H NMR spectrum of **4b** (400 MHz, d_6-benzene, 298 K).

Scheme 3. Synthesis of the Bis(amido)pyridinato Ligand 5a Supported Complexes of Magnesium, Yttrium, and Zirconium



It is worthy of note that, when **3b** was reacted with trimethylaluminum, only the selective alkylation of the more bulky imine group over the methane elimination at the other side of amine was found, and the aluminum complex **4b** was confirmed as the sole product (Figure 2). The noninnocent conjugated iminopyridine group may again be the reason. **3c** can be alkylated to **4c** in the same way. Upon hydrolysis, **4b,c** released the free ligands **5b,c**. Although the second step of alkylation proceeds smoothly at room temperature, it is beneficial to do the reaction with an excess of trimethylaluminum (1.2 equiv) at higher temperature (50 °C). The complete conversion of **3** makes it easier for the separation of product **5**, which can be recrystallized from methanol.

To test the feasibility of using bis(amino)pyridines **5** as facile ligands for transition metals, we have successfully synthesized magnesium, yttrium, and zirconium complexes supported by **5a** (Scheme 3). The bis(amino)pyridine **5a** reacted smoothly with metal alkyls by alkane elimination and gave the desired complexes cleanly with or without donor solvent (THF) coordinated for electronic and steric requirements. In solution, complexes **6**−**8** exhibit ^{1}H NMR spectra typical for rigid coordination. There is a high rotational barrier for the phenyl rings, making the two methyl groups of each isopropyl group diastereotopic at room temperature (Experimental Section). In the solid-state structure of **6** (Figure 3), the four-coordinate magnesium metal center adopts a planar geometry and a symmetry plane along O(1)−Mg(1)−N(1) (180°) bisects the whole molecule. The doubly alkylated ligand **5a** exhibits a spatially congested environment around the metal center. Only one molecule of THF is coordinated to the magnesium atom,

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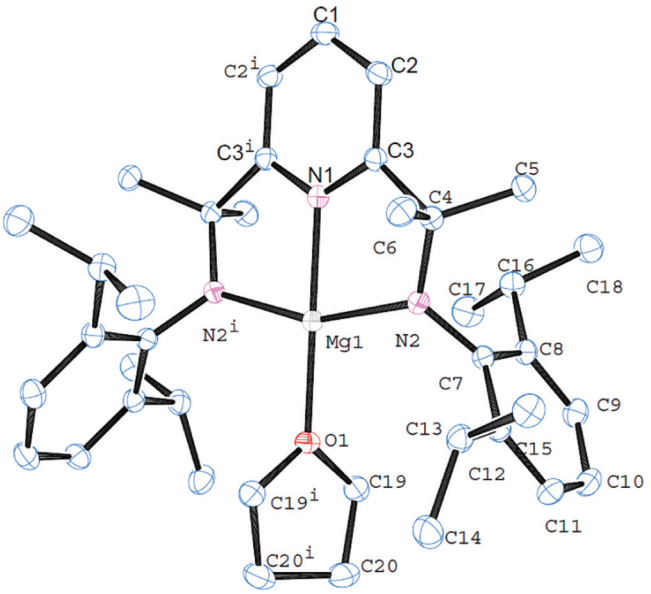

Figure 3. ORTEP drawing of the molecular structure of **6** (anisotropic displacement parameters set at 30% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) = 2.0616(18), Mg(1)−O(1) = 2.0271(16), Mg(1)−N(2) = 2.0169(12), C(3)−N(1) = 1.3407(15), C(3)−C(4) = 1.5453(18), C(4)−N(2) = 1.4730(17), C(7)−N(2) = 1.4143(16); O(1)−Mg(1)−N(1) = 180.0, N(1)−C(3)−C(4) = 114.38(12), N(2)−C(4)−C(3) = 108.02(10), C(4)−N(2)−Mg(1) = 116.40(8), N(2)−Mg(1)−N(1) = 78.65(4), C(7)−N(2)−Mg(1) = 118.87(9).

while two molecules of THF and/or a five-coordinate geometry prevail in other cases.[3b,13] This is also true for the yttrium complex **7**, in which the ligand frame's spatial congestion prevents the coordination of a second molecule of THF to the metal center. On the other hand, two coordinated THF molecules were found in a similar yttrium compound supported by a less bulky ligand.[7f] For the zirconium complex **8**, although its ^{1}H NMR spectrum shows a C_{2v} symmetry like that of **6** at room temperature, there must be a fast fluxion between the two (trimethylsilyl)methyl groups as all six methyl groups show only one signal at −0.05 ppm. This can be easily seen from the X-ray structure of **8** in its solid state (Figure 4). The geometry around the zirconium center is best described as distorted square pyramidal. C23 forms an equatorial plane with N4, N5, and N5^i, while C14 occupies the apical position. This makes an evident contrast to the reported example with a similar but less bulky ligand, for which a perfect C_{2v} symmetry is adopted.[11] The bulk of the isopropyl substituents in compound **8** prevents the adjacent residence of trimethylsilyl groups and makes them point outward. This is also found in another literature report.[7g]

Since this bis(amino)pyridine ligand frame induces a different electronic and steric effect on the metal center, new properties and catalytic behaviors would be expected from the complexes supported by the dianionic bis(amido)pyridinato ligands. Work to explore the applications of this kind of reaction in metal catalysis is still under way in our laboratory.

In summary, bulky bis(imino)pyridines can be alkylated in a stepwise fashion selectively by $AlMe_3$. The clean and easily handled reaction should open the door to a series of bis(amino)pyridine derivatives with different electronic and steric requirements, due to the ease of modification of the bis(imino)pyridine framework. The selectivity of alkylation

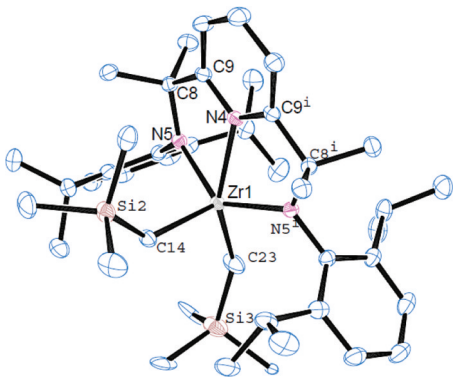

Figure 4. ORTEP drawing of the molecular structure of **8** (anisotropic displacement parameters set at 30% probability, hydrogen atoms and the toluene molecule omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr(1)−N(4) = 2.288(3), Zr(1)−N(5) = 2.133(2), N(5)−C(8) = 1.502(4), C(8)−C(9) = 1.517(4), N(4)−C(9) = 1.362(3), Zr(1)−C(14) = 2.245(4), Zr(1)−C(23) = 2.230(5); N(5)−Zr(1)−N(4) = 70.48(7), C(14)−Zr(1)−N(4) = 102.7(1), C(23)−Zr(1)−N(4) = 151.1(1), C(23)−Zr(1)−C(14) = 106.2(2), Zr(1)−C(23)−Si(3) = 145.1(2), Zr(1)−C(14)−Si(2) = 133.5(2), N(5)^i−Zr(1)−N(5) = 136.11(9).

over elimination reactions may come from the noninnocence of the conjugated iminopyridine group.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were dried and purified with MBRAUN solvent purification system. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in δ, referenced to ^{1}H (of residual protons) and ^{13}C signals of deuterated solvents as internal standards. Elemental analysis was performed on aThermo Flash 2000 CHNS analyzer. **1a**,[1d] **1b**,[12a] **1c**,[1d] **2a**,[3d,5] **2c**,[14] **3a**,[5] (TMEDA)-$MgMe_2$,[15] $Y(CH_2SiMe_3)_3(THF)_2$,[16] and $Zr(CH_2SiMe_3)_4$[17] were prepared according to literature methods.

X-ray Crystal Structure Analyses. Data sets were collected with a Rigaku Saturn 70 CCD diffractometer at 110 K with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å). The data was corrected for Lorentz and polarization effects and absorption (REQAB). The structure was solved by direct methods (SHELXS-97) and refined on F^2 against all reflections (SHELXL-97).[18] Crystal data for **5a**: $C_{35}H_5N_3$, M_r = 513.79, orthorhombic, space group *Pccn*, a = 15.873(3) Å, b = 32.135(6) Å, c = 12.193(2) Å, α = 90°, β = 90°, γ = 90°, V = 6219(2) Å^3, Z = 8, ρ(calcd) = 1.097 g/cm^{-3}, R1 ($I > 2\sigma(I)$) = 0.1219, wR2 (all data) = 0.2615, GOF = 1.234. Crystal data for **6**: $C_{39}H_{57}MgN_3O$, M_r = 608.19, monoclinic, space group *C*2/*c*, a = 9.4750(19) Å, b = 16.603(3) Å, c = 22.150(4) Å, α = 90°, β = 95.26(3)°, γ = 90°, V = 3469.8(12) Å^3, Z = 4, ρ(calcd) = 1.164 g/cm^{-3}, R1 ($I > 2\sigma(I)$) = 0.0593, wR2 (all data) = 0.1704, GOF = 1.211. Crystal data for **8**: $C_{50}H_{79}N_3Si_2Zr$, M_r = 869.59, orthorhombic, space group *Pnma*, a = 24.951(10) Å, b = 13.912(5) Å, c = 14.168(6) Å, α = 90°, β = 90°, γ = 90°, V = 4917.7(33) Å^3, Z = 4, ρ(calcd) = 1.174 g/cm^{-3}, R1 ($I > 3\sigma(I)$) = 0.082, wR2 ($I > 3\sigma(I)$) = 0.080, GOF = 3.807.

2-[2,6-(*i*-Pr)$_2$C$_6$H$_3$N═C(CH$_3$)]-6-[2,6-(CH$_3$)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-(C$_5$H$_3$N) (3b). $AlMe_3$ (1.4 mL, 2.0 M in toluene, 2.8 mmol) was added slowly to a solution of **1b** (1.13 g, 2.65 mmol) in 20 mL of toluene. The resultant dark brown solution was stirred at 110 °C for 12 h. After it was cooled to room temperature, the dark red solution was treated with water (0.4 mL) slowly under argon until a yellow solution was obtained. The toluene solution was filtered and evaporated under reduced pressure. The residue was purified by recrystallization from methanol to give the product as a yellow powder. Yield: 0.92 g, 2.07 mmol, 78%. Anal. Calcd for $C_{30}H_{39}N_3$: C, 81.59; H, 8.90; N, 9.51. Found: C, 80.88; H, 8.62; N, 9.16. MS: m/z (%) 442.3

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[M^+ + H]. ^{1}H NMR (400 MHz, *d*-chloroform, 298 K): δ 8.21 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, Py-*H*), 7.80 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Py-*H*), 7.69 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, Py-*H*), 7.18−6.86 (m, 6H, Ar-*H*), 4.39 (s, 1H, N*H*), 2.77 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 2.21 (s, 3H, N═C(C*H*$_3$)), 2.14 (s, 6H, Ar-(C*H*$_3$)), 1.56 (s, 6H, NC(C*H*$_3$)$_2$), 1.17, 1.15 (each d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, *d*-chloroform, 298 K): δ 167.4, 166.9, 154.7, 146.6, 144.1, 136.9, 135.8, 134.7, 128.4, 123.5, 123.2, 123.0, 120.7, 118.7, 60.0, 29.3, 28.2, 23.2, 22.9, 20.3, 17.4. Crystals suitable for X-ray structure analysis were also obtained for **3b** by the slow evaporation of its solution in methanol/dichloromethane at room temperature.

2-[2,6-(CH$_3$)$_2$C$_6$H$_3$N═C(CH$_3$)]-6-[2,6-(CH$_3$)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-(C$_5$H$_3$N) (3c). **3c** was obtained similarly from **1c** (1.64 g, 4.44 mmol) and AlMe$_3$ (2.3 mL, 2.0 M in toluene, 4.6 mmol). Yield: 1.12 g, 2.91 mmol, 65%. Anal. Calcd for $C_{26}H_{31}N_3$: C, 81.00; H, 8.10; N, 10.90. Found: C, 80.53; H, 8.19; N, 10.48. MS: *m*/*z* (%) 386.3 [M^+ + H]. ^{1}H NMR (400 MHz, *d*-chloroform, 298 K): δ 8.23 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, Py-*H*), 7.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Py-*H*), 7.72 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, Py-*H*), 7.08−6.86 (m, 6H, Ar-*H*), 4.33 (s, 1H, N*H*), 2.19 (s, 3H, N═C(C*H*$_3$)), 2.13, 2.05 (each s, each 6H, Ar-(C*H*$_3$)), 1.55 (s, 6H, NC(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, *d*-chloroform, 298 K): δ 167.6, 167.0, 154.6, 148.8, 144.1, 136.8, 134.6, 128.4, 127.9, 125.5, 123.2, 122.9, 120.8, 118.7, 60.0, 29.4, 20.3, 18.0, 16.6. Crystals suitable for X-ray structure analysis were also obtained for **3c** by the slow evaporation of its solution in methanol/ether at −30 °C.

{2-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NC(CH$_3$)$_2$]-6-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-(C$_5$H$_3$N)}AlMe$_2$ (4a). AlMe$_3$ (2.5 mL, 2.0 M in toluene, 5.0 mmol) was added slowly to a solution of **3a** (2.5 g, 5.02 mmol) in 20 mL of toluene cooled with a water bath. The resultant dark brown solution was stirred at room temperature overnight. A small portion of the solution was taken out, and toluene was removed. The brown solid obtained was analyzed by NMR spectroscopy and elemental analysis. NMR studies showed the quantitative formation of **4a**, and the elemental analysis results were in agreement with the expected composition. Anal. Calcd for $C_{37}H_{56}AlN_3$: C, 77.99; H, 9.91; N, 7.37. Found: C, 78.18; H, 10.32; N, 7.10. ^{1}H NMR (400 MHz, d_6-benzene, 298 K): δ 7.26 (m, 3H, Ar-*H*), 7.01 (m, 3H, Ar-*H*), 6.88 (t, $^3J_{HH}$ = 7.8 Hz,1H, Py-*H*), 6.87 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Py-*H*), 6.64 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Py-*H*), 4.55 (s, 1H, N*H*), 3.82 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*Me$_2$), 2.76 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 1.50 (s, 6H, NC(C*H*$_3$)$_2$), 1.37 (s, 6H, NC(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.10 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), −0.23 (s, 6H, Al(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, d_6-benzene, 298 K): δ 175.6, 165.9, 150.7, 145.4, 144.0, 140.0, 139.4, 125.0, 124.3, 124.2, 123.7, 119,3, 117.2, 62.4, 58.4, 31.3, 30.3, 28.5, 28.1, 26.9, 25.0, 24.5, −2.5.

2,6-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N) (5a). A 1.1 mL portion of water was added dropwise to the above toluene solution cooled with an ice bath. Effervescence was found immediately, and a white precipitate started to form. The dark reaction mixture gradually lightened and was stirred until all of the aluminum complex **4** was completely hydrolyzed to an orange solution. The resultant solution was filtered, and the residue was washed with toluene. The combined toluene solution was evaporated under vacuum to yield the crude product, which was recrystallized from methanol to give yellow crystals. Yield: 2.41 g, 4.7 mmol, 93%. Anal. Calcd for $C_{35}H_{51}N_3$: C, 81.82; H, 10.00; N, 8.18. Found: C, 81.99; H, 10.19; N, 7.92. MS: *m*/*z* (%) 513.7 [M^+ − H]. ^{1}H NMR (400 MHz, *d*-chloroform, 298 K): δ 7.65 (t, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 7.39 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz, 2H, Py-*H*), 7.08 (m, 6H, Ar-*H*), 4.26 (s, 2H, N*H*), 3.31 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 1.49 (s, 12H, NC(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, *d*-chloroform, 298 K): δ 167.0, 146.8, 140.3, 136.8, 124.5, 123.0, 116.7, 59.4, 29.0, 28.2, 24.1. Crystals suitable for X-ray structure analysis were also obtained for **5a** by the slow evaporation of its solution in methanol/ether −30 °C.

{2-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NC(CH$_3$)$_2$]-6-[2,6-(CH$_3$)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-(C$_5$H$_3$N)}AlMe$_2$ (4b). AlMe$_3$ (0.42 mL, 2.0 M in toluene, 0.84 mmol) was added slowly to a solution of **3b** (315 mg, 0.71 mmol) in 20 mL of toluene cooled with a water bath. The resultant dark brown solution was stirred at room temperature for 4 h. A small portion of the solution was taken out, and toluene was removed. The red solid obtained was analyzed by NMR spectroscopy. NMR studies showed the quantitative formation of **4b**. ^{1}H NMR (400 MHz, d_6-benzene, 298 K): δ 7.23 (m, 3H, Ar-*H* or/and Py-*H*), 7.00 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-*H* or/and Py-*H*), 6.84 (m, 4H, Py-*H* or/and Py-*H*), 6.48 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Py-*H*), 4.43 (s, 1H, N*H*), 3.93 (sept, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*Me$_2$), 1.93 (s, 6H, Ar-(C*H*$_3$)), 1.50 (s, 6H, NC(C*H*$_3$)$_2$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.22 (s, 6H, NC(C*H*$_3$)$_2$), −0.49 (s, 6H, Al(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, d_6-benzene, 298 K): δ 173.2, 164.2, 150.7, 146.4, 143.3, 139.7, 131.3, 129.5, 124.1, 124.0, 123.8, 119.1, 116.7, 61.7, 58.4, 31.1, 30.8, 28.1, 27.0, 24.8, 20.5, −2.3.

2-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-6-[2,6-(CH$_3$)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]-(C$_5$H$_3$N) (5b). The above toluene solution was heated at 50 °C overnight. A 0.2 mL portion of water was added dropwise to hydrolyze the aluminum complex **4b** until a yellow solution was obtained. The resulting solution was filtered, and the residue was washed with toluene. The combined toluene solution was evaporated under vacuum to yield the crude product, which was recrystallized from methanol to give yellow crystals. Yield: 247 mg, 0.54 mmol, 76%. Anal. Calcd for $C_{31}H_{43}N_3$: C, 81.35; H, 9.47; N, 9.18. Found: C, 81.27; H, 9.39; N, 9.18. MS: *m*/*z* (%) 458.4 [M^+ + H]. ^{1}H NMR (400 MHz, *d*-chloroform, 298 K): 7.65 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py-*H*), 7.51 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py-*H*), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py-*H*), 7.07 (peudo s, 3H, Ar-*H*), 6.98 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-*H*), 6.87 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-*H*), 4.24 (s, 1H, N*H*), 4.18 (s, 1H, N*H*), 3.28 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*Me$_2$), 2.09 (s, 6H, Ar-(C*H*$_3$)), 1.55, 1.47 (each s, each 6H, NC(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, *d*-chloroform, 298 K): δ 167.1, 166.5, 146.7, 144.3, 140.4, 136.7, 134.5, 128.4, 124.4, 123.0, 122.9, 117.2, 116.7, 59.8, 59.4, 29.4, 29.1, 28.2, 24.1, 20.2.

2,6-[2,6-(CH$_3$)$_2$C$_6$H$_3$NHC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N) (5c). **5c** was obtained similarly from **3c** (870 mg, 2.26 mmol) and AlMe$_3$ (1.3 mL, 2.0 M in toluene, 2.6 mmol) as yellow crystals. Yield: 753 mg, 1.88 mmol, 83%. Anal. Calcd for $C_{27}H_{35}N_3$: C, 80.75; H, 8.78; N, 10.46. Found: C, 80.30; H, 8.74; N, 10.22. MS: *m*/*z* (%) 402.3 [M^+ + H]. ^{1}H NMR (400 MHz, *d*-chloroform, 298 K): δ 7.65 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py-*H*), 7.48 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Py-*H*), 6.97 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar-*H*), 6.86 (t, 6H, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-*H*), 4.17 (s, 2H, N*H*), 2.09 (s, 12H, Ar-(C*H*$_3$)), 1.52 (s, 12H, NC(C*H*$_3$)$_2$). ^{13}C{^{1}H}NMR (100 MHz, *d*-chloroform, 298 K): δ 166.7, 144.4, 136.7, 134.5, 128.4, 123.0, 117.1, 59.8, 29.4, 20.3.

{2,6-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N)}Mg(THF) (6). (TMEDA)MgMe$_2$ (34 mg, 0.20 mmol) in 1 mL of toluene was added to a solution of **5a** (103 mg, 0.20 mmol) in 2 mL of toluene and 0.1 mL of THF at room temperature. The yellow solution turned darker brown immediately and was stirred for another 10 min. The solvent was evaporated, and the residue was dissolved in 0.2 mL of toluene and 0.8 mL of pentane and stored at −20 °C overnight. The product precipitated as crystalline yellow crystals. Yield: 79 mg, 0.13 mmol, 65%. Anal. Calcd for $C_{39}H_{57}MgN_3O$: C, 77.02; H, 9.45; N, 6.91. Found: C, 76.86; H, 9.43; N, 6.93. ^{1}H NMR (400 MHz, d_6-benzene, 298 K): δ 7.23 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Py-*H*), 7.18 (m, 4H, Ar-*H*), 7.09 (m, 2H, Ar-*H*), 6.94 (d, 2H, $^3J_{HH}$ = 7.0 Hz, Py-*H*), 3.98 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*Me$_2$), 2.88 (pseudo s, 4H, THF-*α*-*H*), 1.61 (s, 12H, NC(C*H*$_3$)$_2$), 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.96 (m, 4H, THF-*β*-*H*). ^{13}C{^{1}H} NMR (100 MHz, d_6-benzene, 298 K): δ 171.9, 155.3, 149.6, 138.5, 123.3, 121.8, 115.8, 70.4, 62.3, 33.1, 27.7, 25.8, 25.1, 25.0. Single crystals for X-ray structure analysis were obtained by the diffusion of pentane vapor into a toluene solution of **6** at −20 °C.

{2,6-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N)}Y(CH$_2$SiMe$_3$)(THF) (7). Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (315 mg, 0.64 mmol) in 2 mL of toluene was added to a solution of **5a** (327 mg, 0.64 mmol) in 5 mL of toluene at room temperature. The yellow solution was stirred for 1 h. The solvent was evaporated, and the residue was treated with 5 mL of pentane and filtered. The filtrate was stored at −20 °C for 2 days. The

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product precipitated as a pale yellow solid containing cocrystallized pentane, which was isolated by filtration and dried under vacuum. The solid product changed to a powder under vacuum, while the cocrystallized pentane was lost. Yield: 374 mg, 0.49 mmol, 77%. Anal. Calcd for $C_{43}H_{68}N_3OiY$: C, 67.95; H, 9.02; N, 5.53. Found: C, 67.53; H, 9.03; N, 5.36. ^{1}H NMR (400 MHz, d_6-benzene, 298 K): δ 7.25 (m, 2H, Ar-*H*), 7.16 (m, 1H, Py-*H*), 7.08 (m, 4H, Ar-*H*), 6.83 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Py-*H*), 4.64 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 3.20 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 2.88 (m, 4H, THF-α-*H*), 1.94 (s, 6H, NC(C*H*$_3$)$_2$), 1.50 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (s, 6H, NC(C*H*$_3$)$_2$), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.81 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 0.80 (m, 4H, THF-β-*H*), 0.39 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), −0.35 (d, $^2J_{YH}$ = 3.6 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (100 MHz, d_6-benzene, 298 K): δ 175.1, 149.7, 149.2, 148.9, 138.7, 124.4, 123.4, 123.3, 115.6, 70.4, 66.9, 40.7, 29.7 (d, $^1J_{YC}$ = 47 Hz, *C*H$_2$Si(CH$_3$)$_3$), 28.2, 28.1, 27.4, 27.2, 27.1, 26.5, 24.9, 23.9, 4.6 (CH$_2$Si(*C*H$_3$)$_3$).

{2,6-[2,6-(*i*-Pr)$_2$C$_6$H$_3$NC(CH$_3$)$_2$]$_2$(C$_5$H$_3$N)}Zr(CH$_2$SiMe$_3$)$_2$ (8). Zr(CH$_2$SiMe$_3$)$_4$ (377 mg, 0.86 mmol) in 2 mL of toluene was added to a solution of **5a** (440 mg, 0.86 mmol) in 4 mL of toluene at room temperature. The reaction mixture was stirred at 50 °C for 1 h. The solvent was evaporated, and the residue was washed with 5 mL of pentane and dried under vacuum to give a white solid. Yield: 575 mg, 0.74 mmol, 86%. Anal. Calcd for $C_{43}H_{71}N_3Si_2Zr$: C, 66.43; H, 9.21; N, 5.40. Found: C, 66.21; H, 9.16; N, 4.83. ^{1}H NMR (400 MHz, d_6-benzene, 298 K): δ 7.22 (m, 6H, Ar-*H*), 7.05 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py-*H*), 6.60 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Py-*H*), 3.68 (sept, $^3J_{HH}$ = 6.4 Hz, 4H, C*H*Me$_2$), 1.45 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 1.38 (s, 12H, NC(C*H*$_3$)$_2$), 1.26 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$), 0.76 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), −0.05 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (100 MHz, d_6-benzene, 298 K): δ 173.1, 147.7, 146.8, 139.9, 125.8, 124.9, 116.5, 70.9, 63.3, 33.6 (CH$_2$Si(CH$_3$)$_3$), 28.4, 27.4, 25.5, 2.8 (CH$_2$Si(*C*H$_3$)$_3$). Single crystals suitable for X-ray structure analysis were obtained by the diffusion of pentane vapor into a toluene solution of **8** at −20 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for **3b,c**, **5a**, **6**, and **8** and figures giving ORTEP drawings for **3b,c** and NMR spectra for all of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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