Synthesis and Characterization of Organoaluminum Complexes Containing Bi- or Tridentate-Substituted Pyrrole Ligands

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Received November 8, 2000

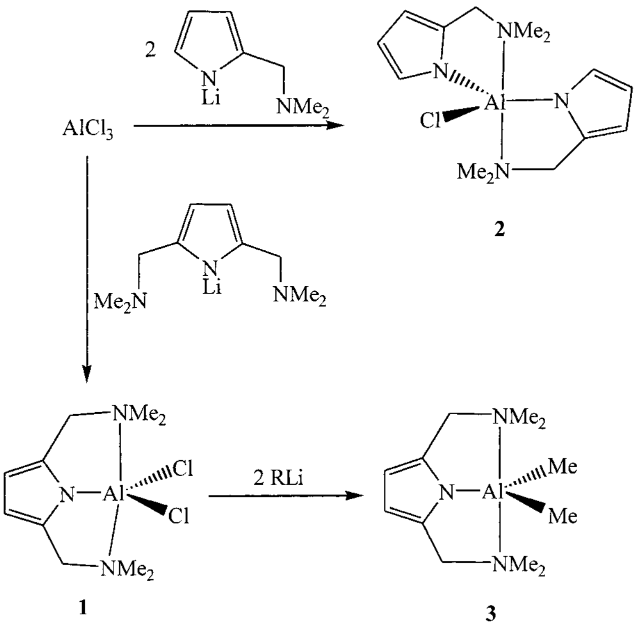
*Summary: Reactions of $AlCl_3$ with 1 equiv of Li{$C_4H_2N(CH_2NMe_2)_2$-2,5} or 2 equiv of Li{$C_4H_3N(CH_2NMe_2)$-2} in diethyl ether at −78 °C afforded $AlCl_2${$C_4H_2N(CH_2NMe_2)_2$-2,5} (**1**) and AlCl{$C_4H_3N(CH_2NMe_2)$-2} (**2**), respectively. Alkylation of **1** with MeLi in diethyl ether generates the aluminum dimethyl complex **3**. Compound **2** is thermally unstable and was converted to uncharacterized product in $CHCl_3$ within 2 days at 80 °C. Compounds **1**, **2**, and **3** were characterized by NMR spectroscopy and X-ray structure determination.*

Introduction

Lewis acidic aluminum halide or alkyl compounds, AlX_3 or AlR_3, have been observed to form simple adducts with Lewis bases, such as amines[1] and ethers,[2] which normally adopt a monomeric, four-coordinate tetrahedral geometry. Similarly, the use of bi- and tridentate ligands, such as arylamines,[3] bifunctional, multidentate phenolates,[4] multidentate amides,[5] and amidophosphines,[6] in the preparation of high-coordinate group 13 metal complexes has seen widespread popularity.

Our investigations have noted that monoanionic, bi- and tridentate pyrrole ligands containing dimethylamino part(s) type ligands, {$C_4H_3N(CH_2NMe_2)$-2}$^-$ and {$C_4H_2N(CH_2NMe_2)_2$-2,5}$^-$, were first synthesized in 1947.[7a] However, very few examples of organometallic complexes containing these bi- or tridentate ligands have been reported. In fact, thus far, only one compound, involving the monoanionic, bidentate ligand bound to a chromium atom, has been identified using X-ray diffraction.[7]

Scheme 1



In continuing our efforts in the chemistry of substituted pyrrolate compounds of early transition metals, we have focused our attention on group 13. Herein, we report the chemistry of aluminum chloride with bi- and tridentate-substituted pyrrolate ligands.

Results and Discussion

The reactions of $AlCl_3$ with {$C_4H_3N(CH_2NMe_2)$-2}$^-$ and {$C_4H_2N(CH_2NMe_2)_2$-2,5}$^-$ are summarized in Scheme 1.

Compound **1** was prepared in 84% yield by reacting $AlCl_3$ and 1 equiv of Li{$C_4H_2N(CH_2NMe_2)_2$-2,5} in diethyl ether at −78 °C. The five-coordinate aluminum compound **1** shows a geometry in solution that is

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10.1021/om000951l CCC: $20.00
Publication on Web 05/15/2001

Table 1. Summary of Crystallographic Data for Compounds 1, 2, and 3

	1	**2**	**3**
formula	$C_{10}H_{18}AlCl_2N_3$	$C_{14}H_{22}AlClN_4$	$C_{12}H_{24}AlN_3$
fw	278.12	308.79	237.32
temp, K	150(1)	150(1)	150(1)
wavelength, Å	0.71073	0.71073	0.71073
diffractometer used	SMART CCD	SMART CCD	SMART CCD
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	*Pbca*	$P2_12_12_1$	*Pbca*
a, Å	11.9929(8)	8.4637(2)	12.1410(2)
b, Å	14.6956(9)	9.2139(2)	14.9987(2)
c, Å	15.6033(9)	20.1903(3)	15.6734(1)
volume (Å ^{3}), *Z*	2750.0(3), 8	1574.51(6), 4	2854.11(6), 8
density (cald), Mg/m^3	1.344	1.303	1.105
absorp coeff, mm^{-1}	0.515	0.295	0.124
F(000)	1168	656	1040
cryst size, mm	0.20 × 0.15 × 0.13	0.20 × 0.20 × 0.16	0.60 × 0.60 × 0.40
θ range, deg	2.55 to 25.00	2.02 to 26.38	2.52 to 27.50
no. of reflns collected	8595	7497	19 162
no. of indep reflns	2394 (R_{int}=0.0767)	3190 (R_{int}=0.0503)	3266 (R_{int}=0.0266)
absorp corr		empirical used SADABS	
max. and min. trans	0.9280 and 0.8154	0.9280 and 0.7818	0.9280 and 0.8057
refinement method		full-matrix least-squares on F^2	
no. of data/restraints/params	2394/0/146	3190/0/182	3266/0/152
goodness-of-fit on F^2	1.185	1.056	1.142
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0726, wR2 = 0.0949	R1 = 0.0502, wR2 = 0.0887	R1 = 0.0470, wR2 = 0.1168
R indices (all data)	R1 = 0.1102, wR2 = 0.1038	R1 = 0.0670, wR2 = 0.0943	R1 = 0.0526, wR2 = 0.1198
extinction coeff	0.0031(5)	0.0033(9)	0.0030(7)
largest diff peak and hole, e Å^{-3}	0.343 and −0.260	0.292 and −0.218	0.339 and −0.281
structure determined program		SHELXTL	

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1, 2, and 3

1		**2**		**3**	
Al−N(2)	1.827(3)	Al−N(3)	1.896(3)	Al−N(2)	1.8617(13)
Al−Cl(1)	2.135(2)	Al−N(1)	1.906(3)	Al−C(1)	1.980(2)
Al−Cl(2)	2.146(2)	Al−N(4)	2.105(3)	Al−C(2)	2.000(2)
Al−N(3)	2.211(3)	Al−N(2)	2.110(3)	Al−N(3)	2.426(2)
Al−N(1)	2.257(3)	Al−Cl	2.1907(12)	Al−N(1)	2.2838(14)
N(2)−Al−Cl(1)	130.61(11)	N(3)−Al−N(1)	143.93(12)	N(2)−Al−C(1)	126.45(7)
N(2)−Al−Cl(2)	118.20(11)	N(3)−Al−N(4)	81.18(11)	N(2)−Al−C(2)	116.99(6)
Cl(1)−Al−Cl(2)	111.17(6)	N(1)−Al−N(4)	95.66(11)	C(1)−Al−C(2)	116.54(7)
N(2)−Al−N(3)	77.63(12)	N(3)−Al−N(2)	95.45(11)	N(2)−Al−N(1)	76.55(5)
Cl(1)−Al−N(3)	96.31(9)	N(1)−Al−N(2)	81.79(11)	C(1)−Al−N(1)	98.54(6)
Cl(2)−Al−N(3)	96.05(9)	N(4)−Al−N(2)	170.48(11)	C(2)−Al−N(1)	97.05(6)
N(2)−Al−N(1)	77.12(12)	N(3)−Al−Cl	108.94(9)	N(2)−Al−N(3)	74.42(5)
Cl(1)−Al−N(1)	97.26(9)	N(1)−Al−Cl	107.12(9)	C(1)−Al−N(3)	95.21(6)
Cl(2)−Al−N(1)	99.04(9)	N(4)−Al−Cl	94.34(8)	C(2)−Al−N(3)	99.78(6)
N(3)−Al−N(1)	154.49(12)	N(2)−Al−Cl	95.17(8)	N(1)−Al−N(3)	150.66(5)

consistent with meridional bonding of the $\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$. The methylene protons of **1** give rise to a sharp singlet in the proton NMR spectrum at 3.68 ppm. Similar proton NMR spectral patterns have been observed for analogous Ti[8] and Zr[9] derivatives with $\{C_6H_3(CH_2NMe_2)_2\text{-}2,5\}^-$ as the ancillary ligand. The ^{13}C gated-decoupling NMR spectrum shows a triplet for the methylene carbon at 60.6 ppm with a normal sp^3 coupling constant at 137 Hz. A crystal obtained from a saturated methylene chloride/diethyl ether solution of compound **1** was characterized by single-crystal X-ray structure analysis. The crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2, and an ORTEP plot is depicted in Figure 1.

Compound **1** is best described as distorted trigonal bipyramidal with the tridentate monoanionic $\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}^-$ attached to aluminum in a meridional geometry. The pyrrolate nitrogen atom is σ-bonded to aluminum with an Al−N distance of 1.827(3) Å, which is approximately 0.4 Å shorter than the mean bond distance of the dimethylamino nitrogen atoms coordinated to aluminum. The two dimethylamino nitrogen atoms occupy axial positions, while the pyrrolate nitro-

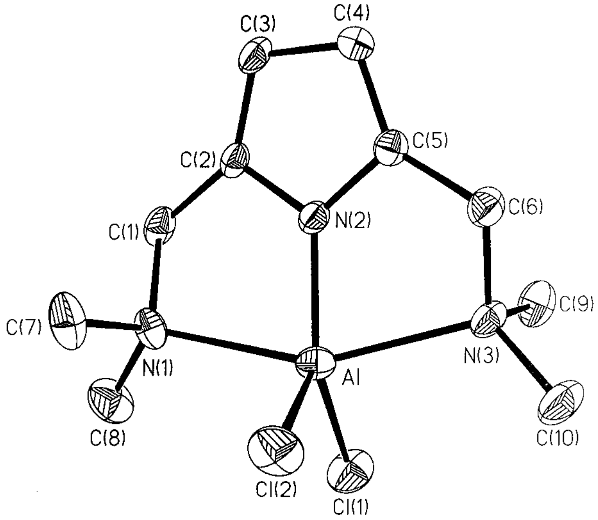

Figure 1. ORTEP plot of compound **1**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

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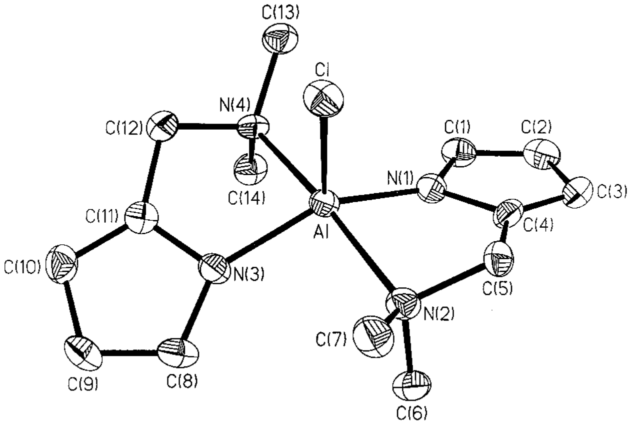

Figure 2. ORTEP plot of compound **2**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

gen and two chlorides occupy the equatorial positions forming two five-membered rings with bond angles of N(2)−Al−N(3) and N(2)−Al−N(1) of 77.63(12)° and 77.12(12)°, respectively.

The analogous reaction of $AlCl_3$ with 2 equiv of Li{$C_4H_3N(CH_2NMe_2)$-2} in diethyl ether at −78 °C yielded an off-white compound, AlCl{$C_4H_3N(CH_2NMe_2)$-2}$_2$ (**2**), which was isolated in 84% yield. The ^1H NMR spectrum of **2** highlights the diasterotopic nature of the methylene protons, showing doublets at 4.10 and 3.79 ppm, while the dimethylamino protons give rise to doublets at 2.64 and 2.56 ppm. Crystals of **2** suitable for X-ray structure analysis were obtained from a diethyl ether solution. The crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2, and an ORTEP plot is depicted in Figure 2.

Similar to **1**, compound **2** can be described as a distorted trigonal bipyramid with the two dimethylamino nitrogen atoms occupying axial positions and with an angle of 170.48(11)°. The two pyrrolate nitrogen atoms and the chlorine atom form a trigonal plane with the sum of angles N(1)−Al−Cl, N(1)−Al−N(3), and N(3)−Al−Cl at nearly 360°. The aluminum to axial nitrogen bond distances (ca.. 2.1 Å) are 0.2 Å longer than aluminum to equatorial nitrogen distance (ca. 1.9 Å), indicating the σ-bonded anionic pyrrolate nitrogen atoms are bound more strongly than are the axial nitrogen atoms, which are bonded through lone-pair N→Al interactions.

Compound **2** is not thermally stable and is converted within 2 days to uncharacterized products when heated to 80 °C in deuterated chloroform in an NMR tube under an inert atmosphere. To eliminate the possible reaction of compound **2** with chloroform, benzene was used as solvent, and the same result was observed. However, the rate of decomposition of compound **2** in chloroform is much faster than that in benzene. Alkylation of compound **2** by MeLi or n-BuLi in diethyl ether was not successful, and Li{$C_4H_3N(CH_2NMe_2)$-2} was recovered.

Alkylation of **1** with 2 equiv of MeLi afforded $AlMe_2${$C_4H_2N(CH_2NMe_2)_2$-2,5}, **3**, in 85% yield. The ^1H NMR spectrum of **3** is consistent with a C_{2v} symmetric structure with the two methyl groups observed as a singlet in the ^1H NMR spectrum at −0.85 ppm. The region of the ^{13}C NMR spectrum associated with the methyl groups attached to aluminum shows a very weak quartet due to the quadrupole interaction of aluminum ($I = 5/2$),[10] which also has a low J_{CH} coupling constant at 111 Hz. Compound **3** is extremely air-sensitive and decomposes rapidly when exposed to the atmosphere. Colorless cube crystals were obtained from saturated diethyl ether solution, and X-ray analysis was performed. Crystallographic data and selected bond distances and angles of compound **3** are summarized in Tables 1 and 2, respectively. An ORTEP plot of compound **3** is shown in Figure 3.

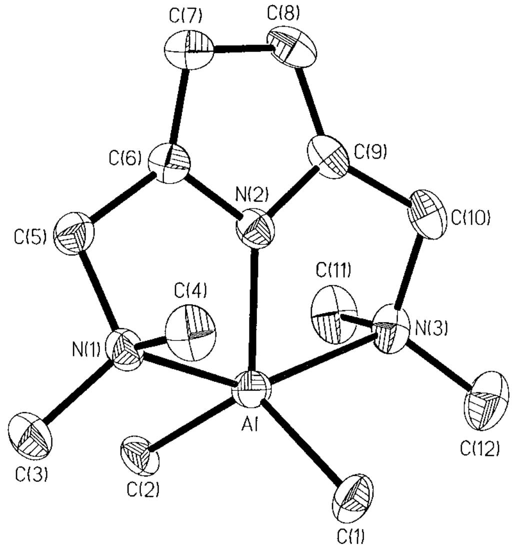

Figure 3. ORTEP plot of compound **3**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

The structure of the methylaluminum compound **3** is very similar to that of compound **1**, exhibiting a distorted trigonoal bipyramidal structure with the two dimethylamino nitrogen atoms occupying axial positions. The pyrrolate nitrogen and the two methyl groups form a trigonal plane with the sum of bond angles of N(2)−Al−C(1), N(2)−Al−C(2), and C(1)−Al−C(2) at 359.98°. Surprisingly, compound **3** is quite thermally stable in $CDCl_3$, showing no decomposition at 70 °C during 24 h. An attempt to synthesize AlMeCl{$C_4H_2N(CH_2NMe_2)_2$-2,5} by reacting **1** with 1 equiv of MeLi in diethyl ether resulted in the formation of the dimethyl compound **3** and left unreacted **1**. Moreover, upon mixing equimolar amounts of compounds **1** and **3** in C_6D_6 in an NMR tube fitted with a J. Young adapter and heated to 80 °C for 3 days, no reaction was observed.

On careful examination of the ^1H NMR spectrum of compound **3**, a small amount of isomer (ca. 5%) was found to be present, identified by a broad resonance at 2.10 ppm. This species could be converted to **3** in deuterated benzene or chloroform at 50 °C within 30 min. We suggest that this compound is the kinetic product, *fac*-coordinated $AlMe_2${$C_4H_2N(CH_2NMe_2)_2$-2,5}, which can be converted to *mer*-coordinated compound **3**. Similar results have been observed for gallium and indium complexes with the same ligand systems.[11]

Experimental Section

General Procedure. All the reactions were performed using standard Schlenk techniques in an atmosphere of high-

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[10] Similar phenomena have been seen, for example: Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 5183.

purity nitrogen or in glovebox. $AlCl_3$ was purchased from Lancaster and used directly. Heptane and diethyl ether were dried over Na/benzophenone ketyl and distilled before use. $\{C_4H_4N(CH_2NMe_2)\text{-}2\}$ and $\{C_4H_3N(CH_2NMe_2)_2\text{-}2,5\}$ were synthesized according to published literature.[7] The lithium salts were prepared by adding 1 molar equiv of n-BuLi to the substituted pyrrole at −78 °C followed by stirring at room temperature for 4 h. $CDCl_3$ was degassed by using freeze-and-thaw cycles and dried over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were measured on a Bruker AC200 instrument. Elemental analysis was performed on a Perkin-Elmer CHN-2400 or Heraeus CHN-OS Rapid. Due to the moisture sensitivity of the Al compounds, we could not get better elemental analysis data. The ^1H NMR spectra of compounds **1**, **2**, and **3** are included in the Supporting Information.

$AlCl_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$, 1. A 100 mL Schlenk flask containing $AlCl_3$ (3.0 g, 22 mmol) was cooled to −78 °C, and 20 mL of diethyl ether was added. To the $AlCl_3$/ether solution was added dropwise $Li\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$ (4.2 g, 22 mmol) in 20 mL of diethyl ether with stirring. The reaction mixture was stirred at room temperature for 12 h after the addition was completed. The resulting suspension was filtered through Celite, and the residue was extracted with 15 mL of diethyl ether in three portions and filtered through Celite again. The combined filtrate was concentrated to about 5 mL, and the product was crystallized at −20 °C to yield 5.26 g of white solid in 84% yield. ^1H NMR ($CDCl_3$): 5.90(s, 2H, C_4H_2N), 3.68(s, 4H, CH_2NMe_2), 2.56(s, 12H, NMe_2). ^{13}C NMR ($CDCl_3$): 129.7(s, C_{ipso}), 105.2(d, $J_{CH} = 167$ Hz, CH), 60.3(t, $J_{CH} = 137$ Hz, CH_2), 47.9(q, $J_{CH} = 137$ Hz, CH_3). Anal. Calcd for $C_{10}H_{18}AlCl_2N_3$: C, 43.18; H, 6.52; N, 15.10. Found: C,42.15; H, 7.74; N, 15.64.

$AlCl\{C_4H_3N(CH_2NMe_2)\text{-}2\}_2$, 2. A 100 mL Schlenk flask containing $AlCl_3$ (1.0 g, 7 mmol) was cooled to −78 °C, and 20 mL of diethyl ether was added. To the $AlCl_3$/ether solution was added dropwise $Li\{C_4H_3N(CH_2NMe_2)\text{-}2\}$ (2.0 g, 15 mmol) in 20 mL of diethyl ether with stirring. The reaction mixture was stirred at room temperature for 12 h after the addition was completed. The resulting suspension was filtered through Celite, and the residue was extracted with 15 mL of dichloromethane in three portions and filtered through Celite again. The filtrate was concentrated to about 10 mL, and the product was crystallized at −20 °C to yield 1.78 g of white solid in 84% yield. ^1H NMR ($CDCl_3$): 6.87(m, 2H, C_4H_3N), 6.18(m, 2H, C_4H_3N), 6.07(m, 2H, C_4H_3N), 4.10(d, 2H, CH_aNMe_2), 3.79(d, 2H, CH_bNMe_2), 2.64(s, 6H, NMe_2), 2.56(s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$): 134.5(s, pyrrole C_{ipso}), 124.5(d, $J_{CH} = 178$ Hz, pyrrole CH), 110.1(d, $J_{CH} = 167$ Hz, pyrrole CH), 105.8(d, $J_{CH} = 168$ Hz, pyrrole CH), 59.0(t, $J_{CH} = 140$ Hz, CH_2), 47.6(q, $J_{CH} = 138$ Hz, NMe_2), 45.8(q, $J_{CH} = 138$ Hz, NMe_2). Anal. Calcd for $C_{14}H_{22}AlClN_4$: C, 54.45; H, 7.18; N, 18.14. Found: C, 53.81; H, 7.96; N, 17.48.

$AlMe_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$, 3. A 100 mL Schlenk flask containing compound **1** (3.0 g, 10.7 mmol) was cooled to −78 °C, and 20 mL of diethyl ether was added. To this solution was added dropwise MeLi (1.6 M, 13.4 mL, 21.4 mmol) in diethyl ether through Teflon tubing with stirring. The reaction mixture was stirred at room temperature for 4 h. The resulting suspension was filtered through Celite to remove LiCl, the resulting filtrate was vacuum-dried, and the product was recrystallized from diethyl ether at −20 °C to yield 2.18 g of white solid in 85% yield. ^1H NMR($CDCl_3$): 5.86(s, 2H, C_4H_2N), 3.52(s, 4H, $CH2$), 2.34(s, 12H, NMe_2), −0.87(s, 6H, $AlMe_2$). ^{13}C NMR ($CDCl_3$): 131.9(s, C_{ipos}), 103.2(d, $J_{CH} = 165$ Hz, pyrrole CH), 59.5(t, $J_{CH} = 137$ Hz, CH_2), 46.7(q, $J_{CH} = 136$ Hz, NMe_2), −12.1(q, $J_{CH} = 111$ Hz, $AlMe_2$). Anal. Calcd for $C_{12}H_{24}AlN_2$: C, 60.73; H, 10.19 Found: C, 60.78; H, 10.34.

X-ray Structure Determination of Compounds 1, 2, and 3. The crystals were mounted on a glass fiber using epoxy resin, transferred to a goniostat, and cooled to 150 K under liquid nitrogen vapor. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation. Structural determinations were made using the SHELXTL package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are calculated. The crystal data are summarized in Table 1.

Acknowledgment. We thank the National Science Council of Taiwan for financial support and the National Center for High-Performance Computing for database searching. We also thank Dr. Darin Tiedtke for helpful discussions and suggestions.

Supporting Information Available: ^1H NMR spectra and tables of crystal data for **1**, **2**, and **3** including tables of hydrogen coordinates, and *U* values, bond lengths, bond angles, anisotropic parameters, and data collection parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Both of *mer*- and *fac*-coordinated complexes of $InMe_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$ and $GaMe_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$ have been obtained recently in our group. For example, the ratio of *fac*- to *mer*-isomers of $InMe_2\{C_4H_2N(CH_2NMe_2)_2\text{-}2,5\}$ is ca. 1 to 3, and the *fac*-isomer could be converted to the *mer*-isomer under very mild conditions. Manuscript is in preparation: Jui-Hsien Huang, Pei-Cheng Kuo, Gene-Hsiang Lee, Shie-Ming Peng.