Synthesis and Structural Characterization of 2,5-Bis(*N*-aryliminomethyl)pyrrolyl Complexes of Aluminum

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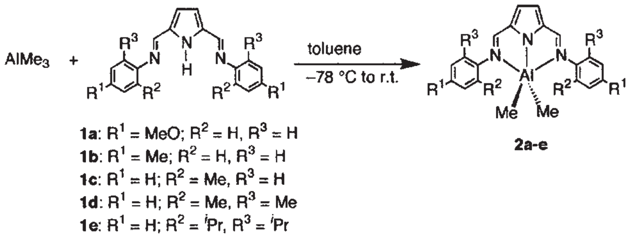
Reaction of tridentate ligands, 2,5-bis(*N*-aryliminomethyl)pyrroles (**1a**–**e**), with 1 equiv of $AlMe_3$ in toluene afforded aluminum dimethyl complexes, $AlMe_2$[2,5-bis(*N*-aryliminomethyl)pyrrolyl] (**2a**–**e**) with the release of one equiv of methane. In solution the aluminum complexes **2a**–**e** showed C_s-symmetry as characterized by their ^1H NMR spectra, while in solid the geometry around the Al atom as crystallographically determined for **2a** and **2b** was found to a tetrahedral by an amido nitrogen atom of the pyrrolyl anion, a nitrogen atom of one of two imino groups and two methyl groups. The aluminum complex **2e** upon activated by one equiv of $B(C_6F_5)_3$ became a catalyst for ethylene polymerization (Activity = 80 g-PE/mol-cat•h).

The chemistry of alkylaluminum bearing nitrogen-based polydentate ligands has recently attracted much attention due to the rich structural chemistry of this class of complexes[1–5] and their applicability as unique catalysts.[6–8] Although there are many examples of monodentate amido and imido alkylaluminum complexes, only a few mononucelar alkylaluminum complexes with bidentate and tridentate amido and imido ligands have been reported.[2,9] We and other groups recently reported that 2-(*N*-aryliminomethyl)pyrroles and 2,5-bis(*N*-aryliminomethyl)pyrroles serve as unique didentate and tridentate monoanionic nitrogen ligands, respectively, and their homoleptic and heteroleptic complexations with early transiton metals were elucidated.[10–14] As an extensiton of our countinuous interest, we have investigated the reactions of trialkylaluminum with these tridentate pyrroles. Here we report syntheses and structures of mononuclear dimethylaluminum complexes bearing 2,5-bis(*N*-aryliminomethyl)pyrrolyl ligands, as well as their possible applications for transition metal-free ethylene polymerization catalysts.

Results and Discussion

Reaction of tridentate ligands, 2,5-bis(*N*-aryliminomethyl)pyrroles **1a**–**e**, with 1 equiv of $AlMe_3$ in toluene afforded the corresponding mononuclear aluminum dimethyl complexes, [Al(Me)$_2${2,5-bis(*N*-aryliminomethyl)pyrrolyl}] (**2a**–**e**), in 85–90% yields with the release of one equiv of methane (Eq. 1). These complexes **2a**–**e** were obtained as yellow air- and moisture-sensitive crystals. The formulation and structure of **2a**–**e** were characterized by NMR spectroscopy and combustion analysis. The ^1H NMR spectra of **2a**–**e** in benzene-d_6 exhibited one singlet due to CH_3 and one set of the pyrrolyl ligand in an exact 2:1 ratio. The singlet signal of $-C\underline{H}=N-$ appeared in a higher field (δ 7.33–7.92) compared with that of the corresponding free ligand (δ 7.81–8.22) and the pyrrolyl ring protons were observed as a singlet signals in the olefinic region (δ 6.65–6.74), suggesting that the pyrrolyl anion and the imino moiety coordinated in an κ-*N*-coordination to the aluminum metal. Thus, the signals of both the CH_3 group and the pyrrolyl ring are consistent with the C_s symmetry of the molecule in solution. In the ^{13}C NMR spectra of **2a**–**e**, the carbon resonance of the iminomethyl moiety was observed in the range of δ 150.2–158.6, a chemical shift value which was shifted to a lower field compared with that found for the free ligand (δ 146.7–151.8).



(1)

The discrete structure of these aluminum complexes in solid state was elucidated by X-ray crystallographic analyses for the complexes **2a** and **2b**. Figures 1 and 2 show the crystal structures of **2a** and **2b**, respectively, and selected bond distances and angles are listed in Table 1. Both complexes adopt the same tetrahedral geometry around the aluminum center: the pyrrolyl ligand chelates to the aluminum atom through the

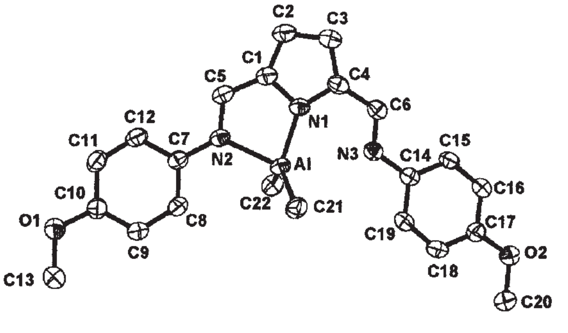


Fig. 1. Molecular structure of **2a** with the numbering scheme. Hydrogen atoms are omitted for clarity.

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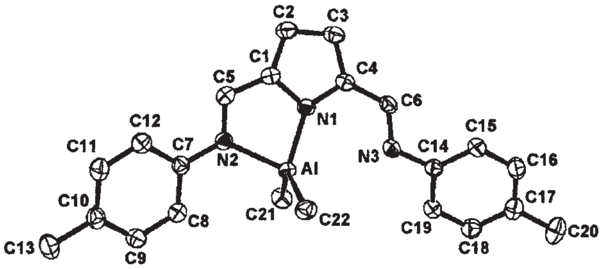

Fig. 2. Molecular structure of **2b** with the numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles of **2a** and **2b**

	2a	**2b**
	Bond distances (Å)	
Al–N1	1.8899(17)	1.8977(11)
Al–N2	2.0582(17)	2.0368(11)
Al–C21	1.952(2)	1.9590(13)
Al–C22	1.951(2)	1.9505(13)
N1–C1	1.368(3)	1.3708(16)
N1–C4	1.360(3)	1.3635(16)
N2–C5	1.302(3)	1.3006(17)
N3–C6	1.286(3)	1.2816(17)
C1–C2	1.398(3)	1.4013(18)
C1–C5	1.424(3)	1.4228(18)
C2–C3	1.390(3)	1.389(2)
C3–C4	1.406(3)	1.4083(18)
C4–C6	1.439(3)	1.442(2)
	Bond angles (°)	
N1–Al–N2	81.69(7)	82.34(5)
N1–Al–C21	117.05(10)	114.94(5)
N1–Al–C22	113.70(10)	118.03(5)
N2–Al–C21	107.41(10)	107.53(5)
N2–Al–C22	103.41(9)	106.91(5)
C21–Al–C22	123.19(12)	119.23(7)
Al–N1–C1	107.55(17)	114.05(8)
Al–N1–C4	137.02(15)	139.25(9)
C1–N1–C4	107.55(17)	106.38(10)
Al–N2–C5	111.02(14)	111.25(9)
Al–N2–C7	127.33(13)	127.06(8)
C5–N2–C7	121.62(17)	121.66(11)
Sum of around N1 atom	360.0	359.7
Sum of around N2 atom	360.0	360.0

amido nitorogen atom of the pyrrolyl anion and the nitrogen atom of one of two imino groups, and hence the nitrogen atom of the other imino group is coordinatively free. In contrast, when we observed ^{1}H NMR spectra due to C_s symmetry of aluminum compounds in the temperature range of 213–308 K, we did not observe any fluxionality. Some mononuclear dialkyl aluminum complexes with a tetrahedral Al–C_2N_2 core have been reported so far.[3,9] The ligand in both complexes is essentially planar and the Al atom is coplanar with the ligand plane. Two methyl carbon atoms are nearly symmetrically bisected by the plane of the ligand. The bond distance (1.8899(17) Å for **2a** and 1.8977(11) Å for **2b**) of Al–N1 is significantly shorter than that (2.0582(17) Å for **2a** and 2.0368(11) Å for **2b**) of Al–N2 and the known Al–N(amido) bond distances, indicative of the participation of the lone pair of the pyrrolyl nitrogen in the Al–N1 bond.[2,4]

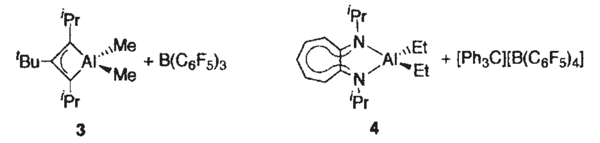

Fig. 3. Aluminum ethylene polymerization catalyst systems.

We preliminary tested the catalytic activity of aluminum complexes for ethylene polymerization because some cationic organoaluminum complexes have been utilized as unique initiators of ethylene polymerization (Fig. 3); dimethylaluminum complexes (L)$AlMe_2$ reacted with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ to afford catalytically active cationic monomethylaluminum complexes (L)$AlMe^+$.[8] Treatment of **2e** with 1 equiv of $B(C_6F_5)_3$ in toluene under ethylene atmosphere (1 atm) for 1 h gave solid polyethylene (Eq. 2). The activity of **2e**/$B(C_6F_5)_3$ (80 g-PE/mmol-cat•h) was found to be high for the ethylene polymerization, but the value was lower than those of imidinate–aluminum system (Fig. 3, **3**/$B(C_6F_5)_3$) (700 g-PE/mmol-cat•h)[8a] and aminotroponiminate–aluminum system (Fig. 3, **4**/$[Ph_3C][B(C_6F_5)_4]$) (2600 g-PE/mmol-cat•h)[8c] (Fig. 1).

$$\text{n } CH_2{=}CH_2 \xrightarrow[\text{toluene, ethylene 1 atm}]{\textbf{2e} + B(C_6F_5)_3} \text{polyethylene} \qquad (2)$$

activity: 80 g-PE/mol-cat.·h

In summary, we have demonstrated that aluminum complexes **2a–e** bearing 2,5-bis(N-aryliminomethyl)pyrrolyl ligands can be readily prepared by reactions of $AlMe_3$ with free ligands **1a–e**. The aluminum complexes **2a–e** were found to have C_s-symmetry in solution, while they adopted dissymmetric structure in solid state. In the presence of one equiv of $B(C_6F_5)_3$, the aluminum complex **2e** was found to be an active catalyst for ethylene polymerization.

Experimental

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using the standard Schlenk techniques under argon. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium diphenyl ketyl under argon. Benzene-d_6 was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. 2,5-bis{N-(4-methoxyphenyl)iminomethyl}pyrrole (**1a**), 2,5-bis{N-(4-methylphenyl)iminomethyl}pyrrole (**1b**), 2,5-bis{N-(2-methylphenyl)iminomethyl}pyrrole (**1c**), 2,5-bis{N-(2,6-dimethylphenyl)iminomethyl}pyrrole (**1d**), and 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (**1e**) were prepared according to the literature method.[11,14]

The ^{1}H (500, 400, 300, and 270 MHz) and ^{13}C (125, 100, 75, and 68 MHz) NMR spectra were measured on a VARIAN Unity Inova-500, a JEOL JNM-AL400, a VARIAN Mercury-300, or a JEOL GSX-270 spectrometer. When benzene-d_6 was used as the solvent, the spectra were referenced to the residual solvent protons at δ 7.20 in the ^{1}H NMR spectra and to the residual solvent carbons at δ 128.0 in the ^{13}C NMR spectra. Assignments for ^{1}H and ^{13}C NMR peaks for some complexes were aided by 2D ^{1}H–^{1}H COSY, 2D ^{1}H–^{1}H NOESY, 2D ^{1}H–^{13}C HMQC, and 2D ^{1}H–^{13}C HMBC spectra. Elemental analyses were recorded by Perkin Elmer 2400. All melting points were measured in sealed tubes under argon atmosphere and were not corrected.

Table 2. Crystal Data and Data Collection Parameters of **2a** and **2b**

Complex	**2a**	**2b**
Formula	$C_{22}H_{24}AlN_3O_2$	$C_{22}H_{24}AlN_3$
Formula weight	389.42	357.43
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca* (No. 61)	$Pna2_1$ (No. 33)
a/Å	12.7468(4)	19.4940(2)
b/Å	28.2110(9)	7.3050(1)
c/Å	11.5848(5)	13.7841(1)
V/Å^3	4165.9(3)	1962.90(4)
Z	8	4
No. of refl. for cell det. (θ range)	47534 (2.15–27.47 deg)	33107 (2.79–27.48 deg)
D_{calcd}/g cm^{-3}	1.242	1.209
$F(000)$	1648	760
μ[Mo Kα]/mm^{-1}	0.119	0.113
Diffractometer	R-AXIS RAPID	R-AXIS RAPID
T/K	153(1)	153(1)
Crystal size/mm	0.43 × 0.37 × 0.25	0.55 × 0.35 × 0.27
No. of images	65	90
Total oscillation angles/deg	260.0	270.0
Exposure time/min deg^{-1}	1.00	1.50
$2\theta_{\mathrm{max}}$/deg	55.0	55.0
No. of reflections measured	44572	19684
Unique data (R_{int})	4778 (0.0954)	4465 (0.0248)
Completeness to $\theta = 27.48$/%	99.9	100
No. of observations	3213	4252
Max and min transmission	0.9788, 0.8413	0.9887, 0.9106
No. of variables	349	330
$R1$, $wR2$ (all data)	0.0873, 0.1183	0.0300, 0.0733
$R1$, $wR2$ ($I > 2.0\sigma(I)$)	0.0482, 0.1003	0.0276, 0.0749
Flack parameter (χ)	—	−0.05(9)
GOF on F^2	1.025	1.044
$\Delta\rho$/e Å^{-3}	0.296, −0.242	0.169, −0.178

Preparation of 2a. A solution of **1a** (500 mg, 1.50 mmol) in toluene (15 mL) was added to a solution of $AlMe_3$ (1.50 mmol) in toluene (5 mL) at −78 °C. After evolution of CH_4 gas was completed, the reaction mixture was allowed to warm to room temperature and further stirred for 6 h at room temperature. All volatiles were removed in vacuo. The resulting yellow solid was recrystallized from a mixture of THF and hexane to give yellow crystals of **2a** (504 mg, 1.35 mmol, 90%), mp 178–181 °C. ^{1}H NMR (C_6D_6, 35 °C): δ 0.01 (s, 6H, Al–CH_3), 3.34 (s, 6H, OCH_3), 6.74 (s, 2H, 3,4-pyr), 6.75 (m, 4H, *m*-C_6H_4), 7.30 (m, 4H, *o*-C_6H_4), 7.90 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ −9.44 (q, $^1J_{\text{C–H}} = 114$ Hz, Al–CH_3), 55.0 (q, $^1J_{\text{C–H}} = 144$ Hz, OCH_3), 114.6 (d, $^1J_{\text{C–H}} = 159$ Hz, *m*-C_6H_4), 117.4 (d, $^1J_{\text{C–H}} = 174$ Hz, 3,4-pyr), 122.8 (d, $^1J_{\text{C–H}} = 159$ Hz, *o*-C_6H_4), 140.4 (s, 2,5-pyr), 140.9 (s, *ipso*-C_6H_4), 150.2 (d, $^1J_{\text{C–H}} = 166$ Hz, N=CH), 159.1 (s, *p*-C_6H_4). Anal. Calcd for $C_{22}H_{24}AlN_3O_2$: C, 67.85; H, 6.21; N, 10.79. Found: C, 67.68; H, 6.04; N, 10.79.

2b: 87% yield, mp 180–182 °C. ^{1}H NMR (C_6D_6, 35 °C): δ −0.02 (s, 6H, Al–CH_3), 2.13 (s, 6H, Ar–CH_3), 6.72 (s, 2H, 3,4-pyr), 6.98 (m, 4H, *m*-C_6H_4), 7.26 (m, 4H, *o*-C_6H_4), 7.92 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ −9.66 (q, $^1J_{\text{C–H}} = 114$ Hz, Al–CH_3), 20.9 (q, $^1J_{\text{C–H}} = 126$ Hz, Ar–CH_3), 117.8 (d, $^1J_{\text{C–H}} = 170$ Hz, 3,4-pyr), 121.5 (d, $^1J_{\text{C–H}} = 159$ Hz, *o*-C_6H_4), 130.2 (d, $^1J_{\text{C–H}} = 157$ Hz, *m*-C_6H_4), 136.6 (s, *p*-C_6H_4), 140.4 (s, 2,5-pyr), 145.4 (s, *ipso*-C_6H_4), 151.3 (d, $^1J_{\text{C–H}} = 167$ Hz, N=CH). Anal. Calcd for $C_{22}H_{24}AlN_3$: C, 73.93; H, 6.77; N, 11.76. Found: C, 74.18; H, 6.91; N, 11.83.

2c: 85% yield, mp 175–178 °C. ^{1}H NMR (C_6D_6, 35 °C): δ −0.22 (s, 6H, Al–CH_3), 2.22 (s, 6H, Ar–CH_3), 6.68 (s, 2H, 3,4-pyr), 6.76 (d, 2H, 6-C_6H_4), 7.02 (d, 2H, 5-C_6H_4), 7.03 (d, 2H, 4-C_6H_4), 7.03 (d, 2H, 3-C_6H_4), 7.56 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ −10.8 (q, $^1J_{\text{C–H}} = 113$ Hz, Al–CH_3), 18.3 (q, $^1J_{\text{C–H}} = 127$ Hz, Ar–CH_3), 118.7 (d, $^1J_{\text{C–H}} = 170$ Hz, 3,4-pyr), 121.7 (d, $^1J_{\text{C–H}} = 160$ Hz, 6-C_6H_4), 126.4 (d, $^1J_{\text{C–H}} = 161$ Hz, 5-C_6H_4), 126.9 (d, $^1J_{\text{C–H}} = 159$ Hz, 4-C_6H_4), 130.9 (s, 2-C_6H_4), 131.2 (d, $^1J_{\text{C–H}} = 157$ Hz, 3-C_6H_4), 140.9 (s, 2,5-pyr), 148.6 (s, 1-C_6H_4), 156.3 (d, $^1J_{\text{C–H}} = 167$ Hz, N=CH). Anal. Calcd for $C_{22}H_{24}AlN_3$: C, 73.93; H, 6.77; N, 11.76. Found: C, 74.03; H, 7.03; N, 11.78.

2d: 87% yield, mp 220–225 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ −0.28 (s, 6H, Al–CH_3), 2.16 (s, 12H, Ar–CH_3), 6.65 (s, 2H, 3,4-pyr), 6.96 (m, 6H, C_6H_3), 7.33 (s, 2H, N=CH). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ −9.3 (q, $^1J_{\text{C–H}} = 114$ Hz, Al–CH_3), 18.6 (q, $^1J_{\text{C–H}} = 127$ Hz, Ar–CH_3), 116.0 (d, $^1J_{\text{C–H}} = 170$ Hz, 3,4-pyr), 125.4 (d, $^1J_{\text{C–H}} = 159$ Hz, *p*-C_6H_3), 128.5 (d, $^1J_{\text{C–H}} = 158$ Hz, *m*-C_6H_3), 129.6 (s, *o*-C_6H_3), 140.4 (s, 2,5-pyr), 148.2 (s, *ipso*-C_6H_3), 158.6 (d, $^1J_{\text{C–H}} = 168$ Hz, N=CH). Anal. Calcd for $C_{24}H_{28}AlN_3$: C, 74.78; H, 7.32; N, 10.90. Found: C, 74.99; H, 7.19; N, 10.89.

2e: 88% yield, mp 185–186 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ −0.22 (s, 6H, Al–CH_3), 1.17 (d, $^3J_{\text{H–H}} = 6.9$ Hz, 24H, $CH(CH_3)_2$), 3.23 (sept, $^3J_{\text{H–H}} = 6.9$ Hz, 4H, $CH(CH_3)_2$), 6.67 (s, 2H, 3,4-pyr), 7.15 (s, 6H, C_6H_3), 7.89 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ −10.4 (q, $^1J_{\text{C–H}} = 114$ Hz, Al–

CH_3), 24.5 (q, $^1J_{C–H} = 126$ Hz, CH(CH_3)$_2$), 28.2 (d, $^1J_{C–H} = 128$ Hz, *C*H(CH_3)$_2$), 118.8 (d, $^1J_{C–H} = 171$ Hz, 3,4-pyr), 123.9 (d, $^1J_{C–H} = 157$ Hz, *m*-C_6H_3), 126.5 (d, $^1J_{C–H} = 159$ Hz, *p*-C_6H_3), 129.3 (s, *o*-C_6H_3), 140.7 (s, 2,5-pyr), 145.5 (s, *ipso*-C_6H_3), 158.0 (d, $^1J_{C–H} = 167$ Hz, N=CH). Anal. Calcd For $C_{32}H_{44}AlN_3$: C, 77.23; H, 8.91; N, 8.44. Found: C, 77.38; H, 8.54; N, 8.43.

Crystallographic Data Collection and Structure Determination of 2a and 2b. Crystals of **2a** and **2b** suitable for the X-ray diffraction study were mounted on glass filers. All measurements were made on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$). Crystal data and data statistics are summarized in Table 2. Indexing was performed from 2 oscillations. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR[15] was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (SIR97)[16] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[17] The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. All hydrogen atoms of **2a** and **2b** were isotropically refined. The function minimized was $[\Sigma w(F_o{}^2 - F_c{}^2)^2]$ ($w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$ with $\sigma^2(F_o{}^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ and $[\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma(wF_o{}^4)]^{1/2}$. All calculations of least-squares refinements were performed with SHELXL-97 programs on an Origin 3400 computer of Silicon Graphics Inc. at the Research Center for Structural Biology Institute for Protein Research, Osaka University. Structural parameters and X-ray structure analysis for **2a** and **2b** are summarized in Table 2. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 213112 for **2a** and 213113 for **2b**.

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