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Alkylaluminum Complexes Containing Pyridyl Amido Ligands. Syntheses, Structures, and NMR Spectroscopic Studies of [Al(CH$_3$)$_2$(NHCH$_2$-2-Py)]$_2$, [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)]$_2$, [Al(CH$_3$)$_2$(HNCH$_2$-4-Py)Al(CH$_3$)$_3$]$_2$, and Al(CH$_3$)$_3$(NH$_2$CH$_2$-4-Py)Al(CH$_3$)$_3$

Steven J. Trepanier and Suning Wang*

Department of Chemistry & Biochemistry, University of Windsor,
Windsor, Ontario N9B 3P4, Canada

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The reactions of Al(CH$_3$)$_3$ with 2-(aminomethyl)pyridine and 4-(aminomethyl)pyridine have been investigated. The reaction of Al(CH$_3$)$_3$ with 2-(aminomethyl)pyridine in a 1:1 ratio in toluene yields a *cis* dinuclear compound [Al(CH$_3$)$_2$(NHCH$_2$-2-Py)]$_2$ (**1**), where the aluminum center is five-coordinate. The reaction of Al(CH$_3$)$_3$ with 4-(aminomethyl)pyridine in a 1:1 ratio in toluene yields a four-coordinate dinuclear compound [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)]$_2$ (**2**), while the reaction in a 2:1 ratio yields the adduct Al(CH$_3$)$_3$(NH$_2$CH$_2$-4-Py)Al(CH$_3$)$_3$ (**4**) initially which changes to the tetranuclear compound [Al(CH$_3$)$_2$(HNCH$_2$-4-Py)Al(CH$_3$)$_3$]$_2$ (**3**) in solution and in the solid state. Compound **3** can also be obtained by the reaction of Al(CH$_3$)$_3$ with **2** in a 2:1 ratio in toluene. Both *cis* and *trans* isomers are present in solution for compounds **2** and **3**, but only the crystals of the *trans* products were obtained. The structures of compound **1** and the *trans* products of **2** and **3** were determined by X-ray diffraction analyses.

Introduction

The chemistry of organoaluminum amides and imides has attracted much attention because of their interesting structural features and reactivities and their potential applications in materials and catalysis.[1] Earlier work in organoaluminum amides and imides focused mostly on the complexes involving monodentate amido or imido ligands. Some alkylaluminum complexes containing polydentate aliphatic amido or imido ligands have been reported.[2] Our group has been investigating the synthesis of polynuclear alkylaluminum complexes by using polydentate arylamido and arylimido ligands or polydentate amido and imido ligands with aryl coordination groups such as a pyridyl. We described recently the unusual structures and reactivity of alkylaluminum complexes containing *N*-phenyl-(2-aminoethyl)amido and 8-quinolylimido ligands.[3] We report herein the structures and chemistry of methylaluminum complexes containing 2-(pyridylmethyl)amido and 4-(pyridylmethyl)amido ligands.

Experimental Section

The reactions were conducted under an atmosphere of dry, oxygen-free nitrogen or argon, employing either a Vacuum Atmosphere inert-atmosphere glovebox or standard Schlenk-line techniques. Solvents were distilled from the appropriate drying agents under nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, on a Bruker AC-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ, or Canadian Microanalytical Service, Delta, British Columbia, Canada. Trimethylaluminum, 2-(aminomethyl)pyridine, and 4-(aminomethyl)pyridine were purchased from Aldrich Chemical Co. The ligands were distilled prior to use.

Synthesis of [Al(CH$_3$)$_2$(NHCH$_2$-2-Py)]$_2$ (1). A 2.0 M solution of Al(CH$_3$)$_3$ (4.0 mL, 8.0 mmol) in toluene was added to 2-(aminomethyl)pyridine (0.866 g, 8.0 mmol) dissolved in 10 mL of toluene at 23 °C. The solution immediately became pink and was stirred for 1 h. (The pink color was caused by the trace amount of impurities.) Concentration of the solution afforded compound **1** as a colorless solid. Yield: 72%. ^{1}H NMR (C$_6$D$_6$, 298 K, δ, ppm): −0.33 (br, 6H, CH$_3$), 0.45 (t, $^3J_{H-H}$ = 9.9 Hz, 1H, NH), 3.77 (d, $^3J_{H-H}$ = 9.9 Hz, 2H, CH$_2$), 6.32 (d, 1H, 2-Py), 6.46 (m, 1H, 2-Py), 6.82 (m, 1H, 2-Py), 8.27 (d, 1H, 2-Py). ^{13}C NMR (C$_6$D$_6$, 298 K, δ, ppm): −7.83 (CH$_3$), 46.58 (CH$_2$), 120.83, 121.73, 136.83, 145.64, 161.60 (CH, Py). Anal. Calcd for C$_{16}$H$_{26}$Al$_2$N$_4$: C, 58.49; H, 7.92; N, 17.06. Found: C, 58.29; H, 7.85; N, 16.86.

Synthesis of [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)]$_2$ (2). A 2.0 M solution of Al(CH$_3$)$_3$ (4.0 mL, 8.0 mmol) in toluene was added to 4-(aminomethyl)pyridine (0.866 g, 8.0 mmol) dissolved in

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Table 1. Crystallographic Data

formula	$C_{16}H_{26}N_4Al_2$ (**1**)	$C_{16}H_{26}N_4Al_2$ (**2**)	$C_{22}H_{44}N_4Al_4$ (**3**)
fw	328.38	328.38	472.54
space group	$C2/c$	$P2_1/c$	$P2_1/n$
a/Å	18.549(8)	7.617(1)	11.134(1)
b/Å	7.894(3)	11.655(6)	11.667(1)
c/Å	15.351(8)	10.967(3)	12.146(2)
β/deg	122.14(3)	97.16(2)	107.664(9)
V/Å^3	1903(1)	966.1(5)	1503.4(3)
Z	4	2	2
D_c/g cm^{-3}	1.15	1.13	1.04
T/°C	23	23	23
μ(Mo Kα)/cm^{-1}	1.50	1.50	1.70
2θ range/deg	3−47	3−45	3−50
reflcns measd	$+h,+k,\pm l$, 1594	$+h,+k,\pm l$, 1255	$+h,+k,\pm l$, 2790
reflcns obsd	790 ($I > 3.00\sigma(I)$)	756 ($I > 3.00\sigma(I)$)	852 ($I > 1.5\sigma(I)$)
no of variables	100	100	139
largest shift/esd in final cycle	0.00	0.00	0.00
largest electron-density peak/e Å^{-3}	0.20	0.47	0.37
R^a	0.057	0.087	0.088
$R_w{}^b$	0.048	0.071	0.047
goodness-of-fit,^{c} S	2.53	2.48	1.49

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2}$, $w = 1/\sigma^2(F_o)$. [c] $S = (\sum w(|F_o| - |F_c|)^2/(N_o - N_v))^{1/2}$, where N_o = number of observations and N_v = number of variables.

10 mL of toluene at 23 °C. The solution became light blue after being stirred for 1 h. (The blue color was caused again by unknown impurities.) Concentration of the solution afforded compound **2** as a light blue solid. Yield: 53%. ^{1}H NMR (C_6D_6, 298 K, δ, ppm): −0.68 (s, 3H, CH_3), −0.63 (s, 6H, CH_3), −0.57 (s, 3H, CH_3), 0.91 (br, 2H, NH), 3.37 (d, 4H, CH_2, $^3J_{H-H}$ = 7.8 HZ), 6.51 (d, 4H, 4-Py), 8.47 (d, 4H, 4-Py). ^{13}C NMR (C_6D_6, 298 K, δ, ppm): 45.85 (CH_2), 121.11, 148.97, 150.30 (4-Py) (the methyl resonance appears to be a broad signal at about −9.0 ppm but could not be determined accurately). Anal. Calcd for $C_{16}H_{26}Al_2N_4$: C, 58.49; H, 7.92; N, 17.06. Found: C, 57.27, 57.58; H, 7.86, 7.83; N, 16.78, 16.76. The pure compound **2** is colorless. However, the surfaces of crystals of **2** almost always are coated with a blue-colored unidentified substance which is difficult to remove completely and may contribute to the low carbon value of the CHN analysis.

Synthesis of [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)Al(CH$_3$)$_3$]$_2$ (3). [Al(CH_3)$_2$(NHCH$_2$-4-Py)$_2$]$_2$ (**2**) (320 mg, 0.975 mmol) was dissolved in 8 mL of toluene at 23 °C A 1 mL (2.0 mmol) solution of $AlMe_3$ (2.0 M in toluene) was added. The light blue color of the solution disappeared immediately. The mixture was stirred for approximately 2 h. Upon concentration, colorless solids of compound **3** precipitated in 80% yield. The ^{1}H NMR spectrum of the colorless solid showed the complete conversion of **2** to **3**. Compound **3** can also be obtained by the direct reaction of $Al(CH_3)_3$ with 4-(aminomethyl)pyridine in a 2:1 ratio in toluene at 23 °C for a few days in nearly quantitative yield. Anal. Calcd for $C_{22}H_{44}Al_4N_4$: C, 55.94; H, 9.32; N, 11.86. Found: C, 55.88; H, 9.04; N, 12.02. ^{1}H NMR (C_6D_6, 298 K, δ, ppm): −0.82 (s, 3H, $Al(CH_3)_2$, *cis* isomer), −0.70 (s, 6H, $Al(CH_3)_2$, *trans* isomer), −0.57 (s, 3H, $Al(CH_3)_2$, *cis* isomer), −0.14 (s, 18H, $Al(CH_3)_3$), 0.67 (br, d, 2H, NH), 3.22 (br, t, 4H, CH_2), 6.30 (d, 4H, 4-Py), 8.25 (d, 4H, 4-Py). ^{13}C NMR (C_6D_6, 298 K, δ, ppm): 45.49 (CH_2), 122.09, 147.72 (4-Py) (the methyl resonance could not be detected).

Synthesis of Al(CH$_3$)$_3$(NH$_2$CH$_2$-4-Py)Al(CH$_3$)$_3$ (4). A 4.7 mL (9.4 mmol) solution of $Al(CH_3)_3$ (2.0 M in toluene) was placed in 5 mL of toluene at 23 °C. A 0.40 mL (3.9 mmol) volume of 4-(aminomethyl)pyridine was added to the solution. After the mixture was stirred for 1 h, a colorless solid precipitated. The ^{1}H NMR spectrum confirmed that >95% of the product is compound **4** and a small amount of compound **3** is present. ^{1}H NMR (C_6D_6, 298 K, δ, ppm): −0.32 (s, 18H, $Al(CH_3)_3$), 1.25 (br, t, 2H, NH_2), 2.77 (t, 2H, CH_2, $^3J_{H-H}$ = 7.8 Hz), 5.69 (d, 2H, 4-Py), 8.08 (d, 2H, 4-Py). ^{13}C NMR (C_6D_6, 298 K, δ, ppm): −8.11 (br, CH_3), 43.28 (CH_2), 123.18, 147.22, 151.07 (4-Py).

Conversion of 4 to 3. Compound **4** undergoes conversion to compound **3** in solution and in the solid state. The solution of **4** was monitored by ^{1}H NMR spectra which indicated that compound **4** was converted to compound **3** completely after a few days in solution. In fact compound **3** was obtained in quantitative yield from the solution of **4** after a few days standing. The ^{1}H NMR spectra also showed that compound **4** gradually changed to compound **3** even in the solid state. Due to the poor stability of **4**, satisfactory elemental analysis results could not be obtained.

X-ray Crystallographic Analysis. All crystals for single-crystal X-ray diffraction were obtained from concentrated toluene/hexane solutions, mounted and flame sealed in glass capillaries. Data were collected at 23 °C on a Rigaku AFC6S diffractometer with a graphite-monochromated Mo Kα radiation, operated at 50 kV and 35 mA. Three standard reflections were measured every 147 reflections. At the end of data collection, the intensity of the standards of compound **2** decreased by 8%, while no decay was observed for **1** and **3**. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic package and corrected for decay and Lorentz−polarization effects. Neutral scattering factors were taken from Cromer and Waber.[4] The crystals of **2** and **3** belong to the monoclinic space group $P2_1/c$ and $P2_1/n$, respectively, uniquely determined by the systematic absences ($0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, for **2**; $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, for **3**). The crystal of **1** belongs to the monoclinic space group $C2/c$, determined by the systematic absences (hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$) and the successful solution and refinement of the structure. All structures were solved by direct methods. Full-matrix least-square refinements minimizing the functions $\sum w(|F_o| - |F_c|)^2$ were applied. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were either calculated or located directly from the differences Fourier maps and not refined except H(22) in compound **3**, whose positional parameters were refined. The contributions of hydrogen atoms in structure factor calculations were included. The data for the crystallographic analysis are given in Table 1.

Results and Discussion

Synthesis and Structure of *cis*-Al$_2$(2-NHCH$_2$Py)$_2$(CH$_3$)$_4$ (1). Compound **1** was obtained from the reaction of $Al(CH_3)_3$ with 2-(aminomethyl)pyridine in a 1:1 ratio in toluene. Compound **1** is insoluble in hexane and slightly soluble in benzene and toluene. The composi-

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Table 2. Positional Parameters and *B*(eq) Values ($Å^2$)

atom	*x*	*y*	*z*	*B*(eq)[a]
		Compound **1**		
Al	0.4246(1)	0.0491(2)	0.7619(1)	4.92(4)
N(1)	0.4474(2)	0.0883(5)	0.6522(3)	4.7(1)
N(2)	0.2949(3)	0.0293(5)	0.6175(3)	5.2(1)
C(1)	0.3905(4)	0.2429(7)	0.8141(4)	6.7(2)
C(2)	0.4164(4)	−0.1835(7)	0.8031(4)	6.3(2)
C(3)	0.3866(4)	0.0061(6)	0.5537(4)	5.9(2)
C(4)	0.2977(4)	0.0055(6)	0.5324(4)	4.9(1)
C(5)	0.2255(4)	−0.0177(7)	0.4379(4)	6.4(2)
C(6)	0.1483(4)	−0.0154(7)	0.4277(5)	7.0(2)
C(7)	0.1437(4)	0.0093(7)	0.5123(6)	6.9(2)
C(8)	0.2184(4)	0.0301(7)	0.6060(5)	6.5(2)
		Compound **2**		
Al	0.0793(3)	0.9216(2)	0.0887(2)	2.98(6)
N(1)	−0.1612(9)	0.9760(5)	0.0339(5)	3.0(2)
N(2)	−0.402(1)	0.7676(7)	0.3873(7)	4.6(2)
C(1)	0.160(1)	0.9769(9)	0.2542(8)	5.2(3)
C(2)	0.105(1)	0.7607(8)	0.044(1)	5.6(3)
C(3)	−0.270(1)	1.0209(7)	0.1259(7)	3.2(2)
C(4)	−0.317(1)	0.9333(8)	0.2172(8)	2.8(2)
C(5)	−0.389(1)	0.8285(9)	0.1827(7)	3.4(2)
C(6)	−0.426(1)	0.7500(8)	0.268(1)	4.5(3)
C(7)	−0.332(1)	0.872(1)	0.414(8)	5.2(3)
C(8)	−0.292(1)	0.9554(7)	0.3417(8)	3.8(3)
		Compound **3**		
Al(1)	0.0532(2)	0.0089(3)	0.6210(2)	3.87(7)
Al(2)	0.7240(2)	0.0010(3)	0.8952(2)	5.02(8)
N(1)	0.1129(6)	0.0270(6)	0.4862(6)	3.5(2)
N(2)	0.5719(6)	−0.0066(8)	0.7525(6)	3.8(2)
C(1)	0.1245(7)	−0.1291(8)	0.7068(7)	4.8(3)
C(2)	0.0516(8)	0.1557(8)	0.6948(8)	6.3(3)
C(3)	0.2219(7)	−0.0426(8)	0.4768(7)	4.8(3)
C(4)	0.3435(7)	−0.0249(8)	0.5742(7)	3.3(2)
C(5)	0.4375(7)	−0.1051(8)	0.5902(8)	4.2(3)
C(6)	0.5471(8)	−0.0931(9)	0.6785(8)	4.5(3)
C(7)	0.4814(9)	0.0726(8)	0.7342(8)	5.2(3)
C(8)	0.3697(8)	0.0677(8)	0.6466(8)	5.2(3)
C(9)	0.667(1)	−0.080(1)	1.0110(8)	8.7(4)
C(10)	0.8555(9)	−0.083(1)	0.852(1)	12.6(5)
C(11)	0.752(1)	0.164(1)	0.921(1)	12.5(4)
H(22)	0.148(7)	0.104(6)	0.480(7)	5.2

[a] $B_{eq} = {}^{8}/_{3}\,\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 3. Important Bond Lengths (Å) and Angles (deg)

	Compound **1** Bond Lengths		
Al−N(1)	1.965(4)	N(2)−C(8)	1.333(6)
Al N(1′)	2.035(4)	C(3)−C(4)	1.502(6)
Al−N(2)	2.248(4)	C(4)−C(5)	1.365(7)
Al−C(1)	1.981(5)	C(5)−C(6)	1.357(7)
Al−C(2)	1.974(5)	C(6)−C(7)	1.360(7)
N(1)−C(3)	1.472(6)	C(7)−C(8)	1.376(7)
N(2)−C(4)	1.348(5)		
	Compound **1** Bond Angles		
N(1)−Al−N(1′)	79.8(2)	Al−N(1)−C93)	126.2(3)
N(1)−Al−N(2)	76.8(2)	Al−N(2)−C(4)	113.1(4)
N(1)−Al−C(1)	119.1(2)	Al−N(2)−C(8)	129.5(4)
N(1)−Al−C(2)	120.6(2)	C(4)−N(2)−C(8)	117.4(5)
N(1′)−Al−N(2)	156.6(2)	N(1)−C(3)−C(4)	112.2(4)
N(1′)−Al−C(1)	97.7(2)	N(2)−C(4)−C(3)	113.1(5)
N(1′)−Al−C(2)	101.3(2)	N(2)−C(4)−C(5)	121.8(5)
N(2)−Al−C(1)	92.8(2)	C(3)−C(4)−C(5)	125.0(5)
N(2)−Al−C(2)	91.5(2)	C(4)−C(5)−C(6)	119.9(6)
C(1)−Al−C(2)	119.5(2)	C(5)−C(6)−C(7)	119.4(6)
Al−N(1)−Al′	97.4(2)	C(6)−C(7)−C(8)	118.3(5)
Al−N(1)−C(3)	114.5(3)	N(2)−C(8)−C(7)	123.2(5)
	Compound **2** Bond Lengths		
Al−N(1)	1.961(7)	N(2)−C(7)	1.36(1)
Al−N(1′)	1.957(6)	C(3)−C(4)	1.50(1)
Al−C(1)	1.952(9)	C(4)−C(5)	1.37(1)
Al−C(2)	1.955(9)	C(4)−C(8)	1.38(1)
N(1)−C(3)	1.477(9)	C(5)−C(6)	1.36(1)
N(2)−C(6)	1.31(1)	C(7)−C(8)	1.37(1)
	Compound **2** Bond Angles		
N(1)−Al−N(1′)	87.6(3)	C(6)−N(2)−C(7)	114.5(8)
N(1)−Al−C(1)	110.7(3)	N(1)−C(3)−C(4)	114.4(7)
N(1)−Al−C(2)	110.7(4)	C(3)−C(4)−C(5)	122.7(8)
N(1)−Al−C(1′)	110.2(4)	C(3)−C(4)−C(8)	121.2(8)
N(1)−Al−C(2)	111.2(4)	C(5)−C(4)−C(8)	116.0(8)
C(1)−l−C(2)	121.3(4)	C(4)−C(5)−C(6)	121.1(8)
Al−N(1)−Al′	92.4(3)	N(2)−C(6)−C(5)	124.3(9)
Al−N(1)−C(3)	119.0(5)	N(2)−C(7)−C(8)	123.8(9)
Al−N(1′)−C(3)	120.4(5)	C(4)−C(8)−C(7)	119.1(8)
	Compound **3** Bond Lengths		
Al(1)−N(1)	1.957(7)	N(1)−C(3)	1.49(1)
Al(1)−N(1′)	1.947(7)	N(2)−C(6)	1.32(1)
Al(1)−C(1)	1.950(9)	N(2)−C(7)	1.33(1)
Al(1)−C(2)	1.936(9)	C(3)−C(4)	1.52(1)
Al(2)−N(2)	2.025(7)	C(4)−C(5)	1.37(1)
Al(2)−C(9)	1.95(1)	C(4)−C(8)	1.37(1)
Al(2)−C(10)	1.96(1)	C(5)−C(6)	1.37(1)
Al(2)−C(11)	1.94(1)	C(7)−C(8)	1.37(1)
N(1)−H(22)	0.99(7)		
	Compound **3** Bond Angles		
N(1)−Al(1)−N(1′)	87.6(3)	Al(1)−N(1)−C(3)	119.7(6)
N(1)−Al(1)−C(1)	110.5(3)	Al(1)−N(1′)−C(3′)	117.3(5)
N(1)−Al(1)−C(2)	110.1(4)	Al(2)−N(2)−C(6)	124.2(7)
N(1′)−Al(1)−C(1)	109.2(3)	Al(2)−N(2)−C(7)	120.3(7)
N(1′)−Al(1)−C(2)	111.0(4)	N(2)−Al(2)−C(9)	103.1(3)
C(1)−Al(1)−C(2)	122.9(4)	N(2)−Al(2)−C(10)	104.4(4)
N(2)−Al(2)−C(11)	103.5(4)	C(9)−Al(2)−C(10)	112.3(6)
C(9)−Al(2)−C(11)	115.4(6)	N(1)−C(3)−C(4)	114.9(7)
C(10)−Al(2)−C(11)	116.1(6)	C(3)−C(4)−C(5)	118.6(9)
Al(1)−N(1)−Al(1′)	92.4(3)	C(3)−C(4)−C(8)	125.0(8)

tion and structure of **1** were established by elemental, NMR, and X-ray diffraction analyses. The positional and isotropic thermal parameters of non-hydrogen atoms are given in Table 2. Important bond lengths and angles are listed in Table 3. An ORTEP diagram showing the crystal structure of **1** is given in Figure 1.

Compound **1** contains two aluminum(III) ions bridged by two amido nitrogen atoms. Each of these two aluminum ions is also coordinated by the pyridyl nitrogen atom and two methyl ligands in a distorted trigonal bipyramidal geometry, as evidenced by the bond angle of N(1′)−Al−N(2) = 156.6(2)° and the sum of bond angles surrounding the Al atom on the basal plane, 359.2°. This distorted geometry could be attributed to the constraint of the chelating five-membered ring. The pyridyl N(2)−Al distance (2.248(4) Å) is much longer than the amido N(1)−Al and N(1′)−Al distances (1.965(4) and 2.035(4) Å), indicating that the negatively charged amido nitrogen atom is a stronger donor to the aluminum center than the neutral pyridyl nitrogen atom. X-ray diffraction analysis unambiguously established that the molecule of **1** has a C_2 symmetry and a *cis* structure; i.e., the two N−H groups are *cis* to each other. As a result, there are two distinct methyl environments in **1**, one being *cis* to the N−H group and the other being *trans* to the N−H group. If compound **1** exists as the *cis* isomer only in solution, two methyl resonances with equal intensity should be observed in the ^1H NMR spectrum of **1**. To confirm it, we examined the solution behavior of compound **1** by variable-temperature ^1H NMR analysis. At 23 °C, the solution of the *cis* isomer of compound **1** dissolved in toluene has a broad methyl signal at −0.43 ppm. At −10 °C, the broad methyl signal becomes two sharp signals with equal intensity (−0.25 and −0.49 ppm). The further decrease of temperature results in no change of the

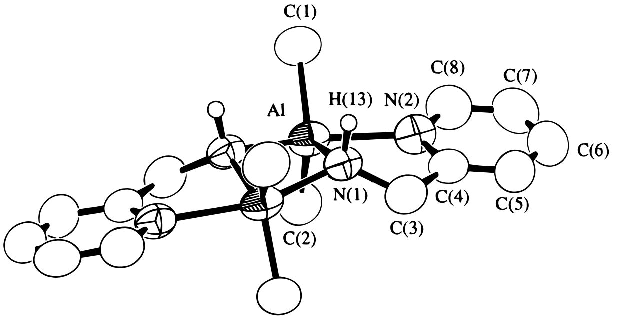
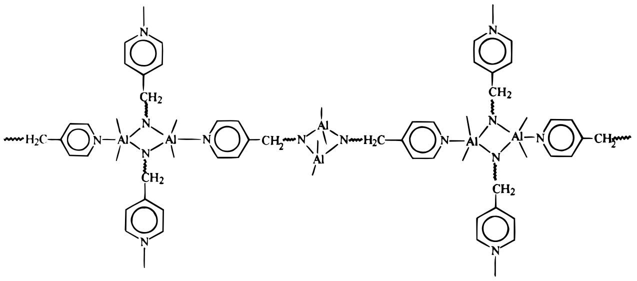


Figure 1. ORTEP diagram showing the structure of **1** with labeling scheme and 50% thermal ellipsoids.

spectrum. When the solution of **1** was heated to about 50 °C, one sharp methyl signal was observed and no methane elimination was detected. The methylene signal is a doublet from 23 to −85 °C, while the NH signal is a triplet in the same temperature range. Irradiation on the NH resonance in a HOMODECOUPLING experiment resulted in a singlet methylene signal, suggesting that the CH_a and CH_b coupling constant of the methylene group is essentially zero. The change of the ^1H NMR spectrum of **1** with temperature is fully reversible. We therefore believe that compound **1** has the *cis* structure in solution at the temperature range −10 to −85 °C. At higher temperature, the Al−N bond rupture occurs which leads to the average of the two methyl environments at the NMR time scale. A similar temperature dependence of the ^1H NMR spectrum was observed in the dinuclear compound $\{Al(CH_3)_2[N(CH_3)CH_2CH_2N(CH_3)_2]\}_2$ reported by Beachley and co-workers[5] and the optically active compound $\{Me_2Al[OCH(Ph)CH(CH_3)(NHCH_3)]\}_2$ reported by Oliver and co-workers,[6] which was attributed to the presence of a rapid equilibrium between the dimer and a chelated four-coordinate monomer. Although the same monomer/dimer equilibrium is also likely to be responsible for the temperature dependence of the ^1H NMR spectrum of **1** at a temperature above −10 °C, it is puzzling why the *trans* isomer was not observed at all. Simple molecular modeling can illustrate that there is no significant kinetic difference between the *cis* and *trans* approaching of two monomers in the formation of the dimer **1**. The *cis* isomer could be considered as the thermodynamically preferred product, but we could not find a good explanation for the relatively poor thermodynamic stability of the unidentified *trans* isomer.

Synthesis and Structure of $Al_2(4\text{-}NHCH_2Py)_2(CH_3)_4$ (2). The structure of **1** demonstrates that 2-(aminomethyl)pyridine cannot be used to build higher nuclearity aluminum complexes due to its chelating tendency. In contrast, the pyridyl nitrogen atom of the 4-(aminomethyl)pyridine ligand cannot bind to the same aluminum center with the amido nitrogen because of the geometrical restriction. We therefore anticipated that the 4-(aminomethyl)pyridine ligand could be used to form polymeric complexes such as **A** via the formation of interdimer Al−N bonds. The reaction of $Al(CH_3)_3$ with 4-(aminomethyl)pyridine was therefore investigated. Compound **2** was obtained readily from the reaction of $Al(CH_3)_3$ with 4-(aminomethyl)pyridine in a 1:1 ratio in toluene. The structure of the *trans*-isomer of **2** has been determined by a single-crystal X-ray diffraction analysis. The positional and isotropic thermal parameters of non-hydrogen atoms are given in Table 2. Selected bond lengths and angles are listed in Table 3. The molecular structure of **2** is shown in Figure 2.



A

As observed in compound **1**, there are two aluminum(III) ions bridged by two amido nitrogen atoms in **2**. However, each aluminum center in **2** is only four-coordinate with a tetrahedral geometry. The aluminum−amido nitrogen bond lengths in **2** are similar to those in **1**. In contradiction to our anticipation, the pyridyl nitrogen atom does not form an intermolecular Al−N bond, perhaps due to some steric factors. The crystal structure of **2** has an inversion center with the two N−H groups being *trans* to each other. Although the methyl environments are not exactly identical in the crystal structure because of the tilted orientation of the pyridyl ring, we believe that, in the *trans* isomer, all the methyl groups should be identical in solution since the C_{2h} symmetry with the Al−Al′ vector being the C_2 axis should be achieved readily in solution. Interestingly, the ^1H NMR spectrum of **2** obtained by dissolving the crystals of the *trans* isomer in toluene shows three broad overlapping resonances of the methyl groups at 23 °C (centered at −0.74 ppm). At 10 °C, these signals become three sharp and well-resolved resonances with a relative integral ratio of 1:2:1. The pattern and the relative integral ratio of the methyl resonances do not change with the further decrease of temperature. The doublet methylene resonance (6.43 ppm), however, becomes a pseudotriplet at about −20 °C. A possible explanation for the ^1H NMR spectra of **2** is the presence of both *cis* and *trans* isomers in solution in a 1:1 ratio. Two of the methyl resonances (0.83 and −0.65 ppm at 10 °C) can be related to the *cis* isomer while the resonance at −0.70 ppm can be attributed to the *trans* isomer. The NMR data are consistent with the presence of a equilibrium between the *cis* and *trans* isomers of **2** in solution. Such an equilibrium or interconversion of *cis* and *trans* isomers have been observed previously in monodentate amido-bridged four-coordinate dinuclear aluminum complexes.[7] Since the *trans* and *cis* interconversion requires the breaking of the aluminum−amido nitrogen bond, the presence of trace amount donor ligands has been proposed to be responsible for the isomerization process of the monodentate amido-bridged dinuclear aluminum

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[5] (a) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1975**, *14*, 2534. (b) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110.

[6] Sierra, M. L.; Srini J. de Mel, V.; Oliver, J. P. *Organometallics* **1989**, *8*, 2486.

[7] (a) Choquette, D. M.; Timm, M. J.; Hobbs, J. L.; Rahim, M. M.; Ahmed, K. J.; Planalp, R. P. *Organometallics* **1992**, *11*, 529. (b) Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J. Z.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377. (c) Gosling, K.; Smith, J. D.; Wharmby, D. H. W. *J. Chem. Soc. A.* **1969**, 1738.

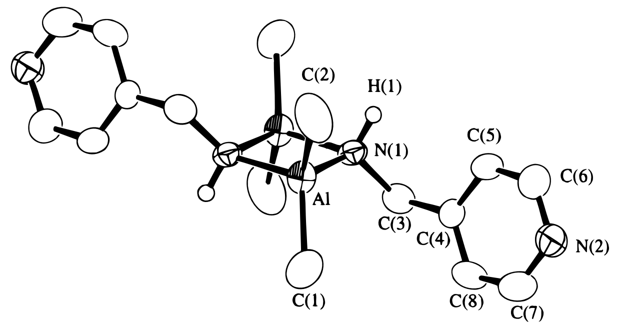

Figure 2. ORTEP diagram showing the structure of **2** with labeling scheme and 50% thermal ellipsoids.

complexes.[8] It is conceivable that the facile isomer interconversion observed in **2** was facilitated by the uncoordinated pyridyl group which could attack the aluminum center and break the Al−amido bond via an intermolecular process. In contrast to compound **1** where the *cis* isomer appears to be the thermodynamically favored, the *cis* and *trans* isomers of compound **2** seem to have the same thermodynamic stability in solution. Despite the fact that NMR spectra confirmed the presence of the *cis* isomer of **2** in solution, we have not been able to isolate and identify the crystals of the *cis* isomer.

Syntheses and Structures of [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)Al(CH$_3$)$_3$]$_2$ (3) and Al(CH$_3$)$_3$(NH$_2$CH$_2$-4-Py)Al(CH$_3$)$_3$ (4). In compound **2** there are two uncoordinated pyridyl groups which could be used to incorporate two additional aluminum centers into the complex. Indeed, when compound **2** was reacted with 2 equiv of Al(CH$_3$)$_3$, a new tetranuclear species [Al(CH$_3$)$_2$(NHCH$_2$-4-Py)Al(CH$_3$)$_3$]$_2$ (**3**) was obtained in quantitative yield. Compound **3** can also be obtained by the direct reaction of Al(CH$_3$)$_3$ with 4-(aminomethyl)pyridine in a 2:1 ratio in toluene at 23 °C for several days. Compound **3** is soluble in toluene and benzene and has been fully characterized by elemental, ^{1}H NMR, and X-ray diffraction analyses. Important atomic coordinates and isotropic thermal parameters are given in Table 2. Selected bond lengths and angles are listed in Table 3. An ORTEP diagram illustrating the structure of **3** is shown in Figure 3.

The central portion of **3** resembles the structure of **2**. The bond distances and angles surrounding the Al(1) center are essentially identical to those found in **2**. As observed in **2**, compound **3** has a crystallographically imposed inversion center and the dinuclear unit has a *trans* geometry. Each of the pyridyl nitrogen atoms is attached by a Al(CH$_3$)$_3$ moiety. The Al(2) center has a typical tetrahedral geometry.

The behavior of compound **3** in solution appears to be similar to that of **2**. The ^{1}H NMR spectrum of the *trans* isomer of **3** dissolved in benzene or toluene at 23 °C shows three sharp methyl resonances of the Al(CH$_3$)$_2$ groups with a relative integral ratio of 1:2:1, consistent with the isomerization of the *trans* isomer to the *cis* isomer and the presence of equal portions of *cis* and *trans* isomers in solution. The pattern of the ^{1}H NMR spectrum of **3** does not change in the temperature range 23 to −85 °C, suggesting that both isomers have similar thermodynamic stability. Because there is no uncoordinated ligand present in **3**, the isomerization mechanism involving the Al−N bond breaking by external ligands seems quite unlikely for compound **3**. The absence of chelate ligands in **3** also rules out the monomer/dimer equilibrium mechanism leading to the isomerization, since a three-coordinate aluminum center without sterically bulky ligands would be highly thermodynamically unfavorable due to the electron deficiency of the Al center. It is however possible that instead of breaking two Al−N bonds simultaneously to form two monomers, only one Al−N bond is broken in the dimer to allow the rotation of the NH group, thus achieving the *cis* and *trans* isomerization.

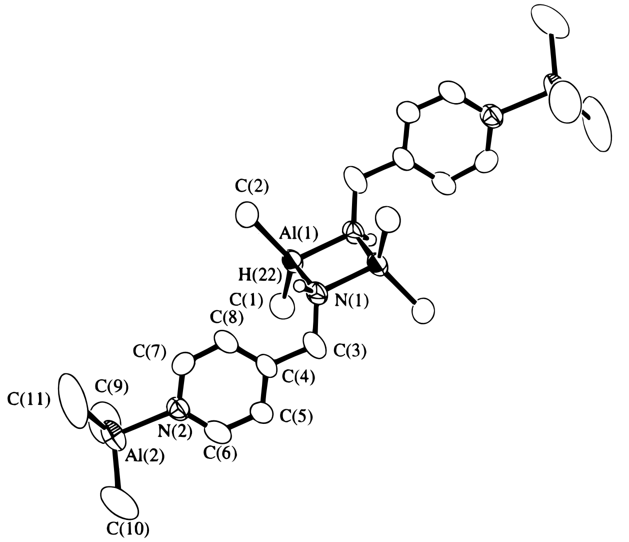

Figure 3. ORTEP diagram showing the structure of **3** with labeling scheme and 50% thermal ellipsoids.

Several examples of tetranuclear alkylaluminum amido complexes with interesting structural features have been reported earlier.[2,3] Compound **3** is, however, the first example demonstrating that dinuclear aluminum amido complexes with functional groups such as pyridyl can be used as building blocks for the formation of larger aggregates. Efforts to build new polynuclear compounds by using compounds such as **2** are being taken in our laboratory.

Compound **4** was isolated as a colorless powder from the reaction of Al(CH$_3$)$_3$ with 4-(aminomethyl)pyridine in a 2:1 ratio in toluene at 23 °C for a short period (1 h). ^{1}H NMR spectrum of **4** in C$_6$D$_6$ at 23 °C shows a methyl resonance (18H), a broad triplet NH$_2$ signal (2H), a triplet CH$_2$ resonance (2H), and two doublets due to the protons on the 4-pyridyl group (4H). The pattern of the ^{1}H NMR spectrum of **4** does not change in the temperature range 23 to −50 °C. The only logical explanation for the ^{1}H NMR spectrum of **4** is that this compound has the formula of Al(CH$_3$)$_3$(NH$_2$CH$_2$-4-Py)-Al(CH$_3$)$_3$, and the structure as shown in Figure 4. Primary amine adducts with Al(CH$_3$)$_3$ are known to have poor thermal stability due to their tendency to eliminate methane, forming amido or imido complexes.[1a−c] Therefore, unsurprisingly we have observed that this compound has poor stability both in solution and in the solid state. In fact, ^{1}H NMR spectroscopic study established unambiguously that compound **4** changes to compound **3** in solution and in the solid state (Figure 4). The complete conversion of **4** to **3** in solution can be achieved over a few days period. We therefore believe that compound **4** is the precursor of compound **3** in the direct synthesis of compound **3** via the reaction

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[8] Wakatsuki, K.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1475.

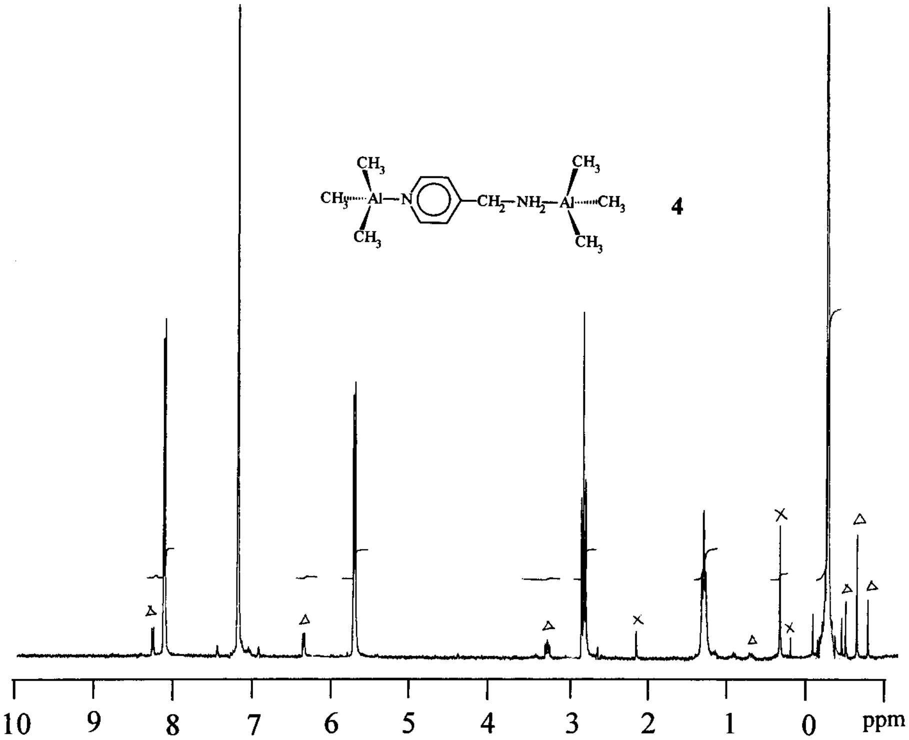
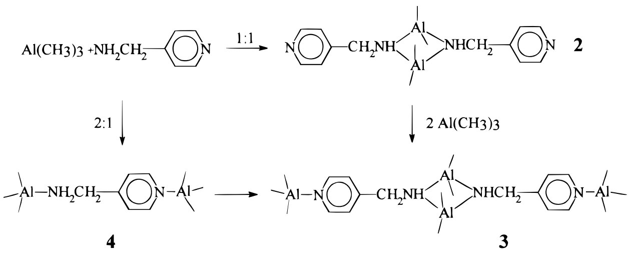


Figure 4. Possible structure of **4** and ^{1}H NMR spectrum of **4** taken immediately after compound **4** was dissolved in C_6D_6 at 23 °C. The peaks marked with a triangle belong to compound **3**. The peaks marked with a cross are due to impurities.

Scheme 1



of $Al(CH_3)_3$ with 4-(aminomethyl)pyridine in a 2:1 ratio. The relationship among compounds **2**–**4** is illustrated in Scheme 1.

Conclusion. Amido ligands containing a pyridyl functional group can be used to synthesize a variety new aluminum complexes. The geometry of the pridyl amido ligand dictates the structure and the nuclearity of the product. The 4-(aminomethyl)pyridine ligand is valuable in the synthesis of new polynuclear alkylaluminum amido complexes. These new complexes display complicated dynamic behaviors in solution which requires further investigation to be understood.

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Supporting Information Available: Tables of complete positional and isotropic and anisotropic thermal parameters and bond lengths and angles (17 pages). Ordering information is given on any current masthead page.

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