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Chiral Amido Aluminum and Zinc Alkyls: A Synthetic, Structural, and Polymerization Study

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Reactions of racemic (±)-*trans*-1,2-($NHSiMe_3$)$_2$-cyclohexane ((±)-*trans*-1,2-Cy($NHSiMe_3$)$_2$) with 2 equiv of $AlMe_3$, 2 equiv of $ZnEt_2$, and 1 equiv of $ZnEt_2$ produce the dinuclear aluminum complex {(±)-*trans*-Cy($NSiMe_3$)$_2$}Al_2Me_4 (**1**) in 88% yield, the tetranuclear zinc complex {(±)-*trans*-Cy($NSiMe_3$)$_2$}$_2$$Zn_4Et_4$ (**2**) in 87% yield, and the dinuclear zinc complex {(±)-*trans*-Cy($NHSiMe_3$)($NSiMe_3$)}$_2$$Zn_2Et_2$ (**3**) in 77% yield, respectively. Complex **1** features a puckered four-membered Al_2N_2 ring exhibiting a smaller N−Al−N angle (77.6(1)°) than any other dimeric alkyl aluminum amide reported. Complex **2** consists of four three-coordinate, planar zinc centers, two of which are symmetrically bonded to two amide groups via intramolecular Zn−N coordination, whereas the other two are nearly symmetrically bonded to two amide groups through intermolecular Zn−N coordination. In complex **3**, there are a center of symmetry and a planar four-membered Zn_2N_2 core. The zinc alkyls **2** and **3** are effective initiators for polymerization of ϵ-caprolactone and L-lactide, while **1** and **2**, upon activation with Al(C_6F_5)$_3$, are highly active for polymerization of methyl methacrylate.

Introduction

A wide range of organoaluminum and zinc complexes have been extensively used as efficient catalysts/initiators for ring-opening polymerization of heterocyclic monomers[1] such as lactides,[2] lactones,[3] and epoxides[4] as well as for polymerization of methacrylates.[5] These catalysts/initiators used for the ring-opening polymerization of heterocyclic monomers have a general structural formula of $L_nM{-}X$, where L_n is an inert supporting ligand, M is the metal, and X is an active initiating group such as OR or NR_2 and NRR′. When supported by bulky chelating ligands and constructed in a different general formula of $[X^\frown X]Al{-}R$, we[6] and others[7] found that these discrete, structurally characterized organoaluminum alkyls are also effective catalysts/initiators for ring-opening polymerization of heterocyclic monomers. The R group in the structure formula, however, is now an inert supporting group, and the polymerization is initiated by the covalently linked chelating ligand itself, producing telechelic oligomers/polymers.[6]

Achiral aluminum and zinc amides represent a rich area that has been extensively studied.[8] Our interest has been focused on constructing chiral bisinitiators in the structure formula of $[N^\frown N]^*M{-}R$, by introducing chiral chelating bisamide ligands (denoted by $[N^\frown N]^*$), and on investigating their performance in stereoselective polymerization of polar monomers such as methacrylates. Herein, we report the convenient syntheses and X-ray structures of chiral aluminum (**1**) and zinc (**2** and **3**) alkyl complexes incorporating a chelating (±)-*trans*-1,2-($NHSiMe_3$)$_2$-cyclohexane[9] diamide ligand (Chart 1) as well as their performance in polymerizations of ϵ-caprolactone (CL), L-lactide (LA), and methyl methacrylate (MMA).

Experimental Section

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in

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(1) For representative reviews, see: (a) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1−59. (b) Sugimoto, H.; Inoue, S. *Adv. Polym. Sci.* **1999**, *146*, 39−119. (c) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992.

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(4) For recent examples and reviews, see: (a) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785−2794. (b) Munoz-Hernandez, M.-A.; Mckee, M. L.; Keizer, T. S.; Yearwood, B. C.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **2002**, 410−414. (c) Antelmann, B.; Chisholm, M. H.; Iyer, S.; Huffman, J. C.; Navarro-Llobet, D.; Pagel, M.; Simonsick, W. J.; Zhong, W. *Macromolecules* **2001**, *34*, 3159−3174.

(5) For recent examples, see: (a) Baugh, L. S.; Sissano, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1633−1651. (b) Peace, R. J.; Horton, M. J.; Péron, G. L. N.; Holmes, A. R. *Macromolecules* **2001**, *34*, 8409−8411. (c) Cameron, P. A.; Gibson, V. C.; Irvine, D. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2141−2144.

(6) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 1438−1442.

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(8) For comprehensive reviews, see: (a) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K. 1st ed.; 1982; Vol. 1, pp 555−682; 2nd ed.; 1995; Vol. 1, pp 431−502. (b) Boersma, J. In *Comprehensive Organometallic Chemistry*, 1st ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 2, pp 823−862. (c) O'Brien, P. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 2, pp 175−206. (d) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980.

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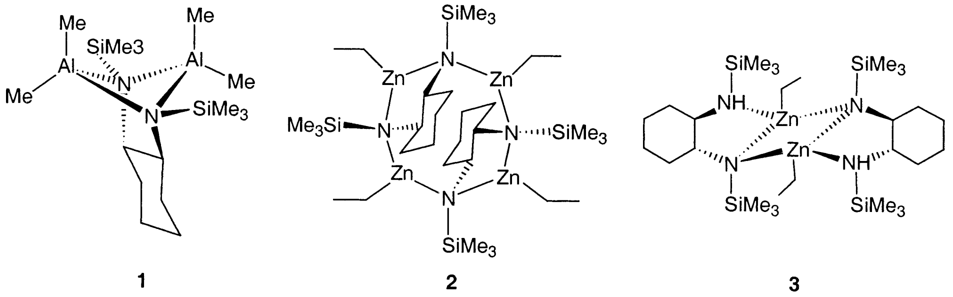
Chart 1



flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon-filled glovebox. HPLC-grade organic solvents were first saturated with nitrogen and then dried by passage through activated alumina and Q-5 catalyst in stainless steel columns prior to use. Benzene-d_6 and toluene-d_8 were dried over Na/K alloy and distilled and/or filtered prior to use. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C) or a Varian Inova 400 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to TMS. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

CL, MMA, LA, diethyl zinc, chlorotrimethylsilane, (±)-*trans*-1,2-diaminocyclohexane, and triethylamine were purchased from Aldrich. CL and MMA were degassed and dried over CaH_2 overnight and then vacuum-distilled before use, whereas LA was purified by sublimation on the high-vacuum line. $B(C_6F_5)_3$ was obtained as a research gift from Boulder Scientific Co. and further purified by recrystallization from hexanes at −35 °C. $Al(C_6F_5)_3$ (as a 0.5•toluene adduct) was prepared according to the literature procedure.[10] *Extra caution should be exercised when handling this material due to its thermal and shock sensitivity.* The chelating diamine ligand (±)-*trans*-1,2-$(NHSiMe_3)_2$-cyclohexane {(±)-*trans*-Cy$(NHSiMe_3)_2$} was prepared according to the literature procedure.[9]

Synthesis of {(±)-*trans*-Cy$(NSiMe_3)_2$}Al_2Me_4 (1). To a stirred solution of (±)-*trans*-1,2-Cy$(NHSiMe_3)_2$ (0.500 g, 1.93 mmol) in 15 mL of toluene at −30 °C was added $AlMe_3$ (1.93 mL, 2.0 M in hexanes, 3.86 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred overnight. The resulting mixture was concentrated to about half of its original volume and stored at −30 °C for 2 days to afford 0.45 g of the product. Upon concentration and cooling, the filtrate produced an additional 0.18 g of the product. Total yield is 0.63 g; 88%. ^{1}H NMR (C_6D_6, 23 °C): δ 3.44 (m, 2H, methine H, Cy), 1.94, 1.48, 1.05 (m, 8H, methylene H, Cy), 0.14 (s, 18H, Si*Me*$_3$), −0.14 (s, 6H, Al−CH_3), −0.38 (s, 6H, Al−CH_3). ^{13}C NMR (C_6D_6, 23 °C): δ 61.44 (−N*C*H), 34.18, 26.64 (*C*H_2), 1.75 (Si*Me*$_3$), −2.48, −4.27 (Al-*C*H_3). Anal. Calcd for $C_{16}H_{40}Al_2N_2Si_2$: C, 51.85; H, 10.88; N, 7.56. Found: C, 51.25; H, 10.45; N, 7.20.

Synthesis of {(±)-*trans*-Cy$(NSiMe_3)_2$}$_2Zn_4Et_4$ (2). To a stirred solution of (±)-*trans*-1,2-Cy$(NHSiMe_3)_2$ (1.07 g, 4.12 mmol) in 20 mL of toluene at −35 °C was added dropwise $ZnEt_2$ (8.24 mL, 1.0 M in hexanes, 8.24 mmol). The reaction mixture was gradually warmed to ambient temperature and stirred overnight. The volume of the mixture was reduced to about 10 mL under vacuum and stored at −35 °C for 2 days, during which the product crystallized. The crystals were separated and washed with 2 × 3 mL of cold hexanes and dried to afford 1.20 g of the pure product. Upon concentration and cooling, the toluene filtrate produced a second crop of the product (0.40 g). Total yield is 1.60 g; 87%. ^{1}H NMR (C_6D_6, 23 °C): δ 2.42 (m, 4H, methine H, Cy), 1.95, 1.44, 1.07, 0.95 (m, 16H, methylene H, Cy), 1.47 (t, J = 8.1 Hz, 12H, Zn−CH_2*C*H_3), 0.65 (q, J = 8.4 Hz, 8H, Zn-*C*H_2CH_3), 0.17 (s, 36H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 23 °C): δ 65.85 (−N*C*H), 36.51, 26.04 (*C*H_2, Cy), 12.68, 2.79 (Et), 2.70 (Si*Me*$_3$). Anal. Calcd for $C_{32}H_{76}N_4Si_4Zn_4$: C, 43.14; H, 8.60; N, 6.29. Found: C, 42.86; H, 8.75; N, 6.27.

Synthesis of {(±)-*trans*-Cy$(NHSiMe_3)(NSiMe_3)$}$_2Zn_2Et_2$ (3). To a stirred solution containing (±)-*trans*-1,2-Cy$(NHSiMe_3)_2$ (0.537 g, 2.07 mmol) in 10 mL of hexanes at −35 °C was added dropwise $ZnEt_2$ (2.07 mL, 1.0 M in hexanes, 2.07 mmol). Precipitates appeared within the first 5 min of addition and slowly disappeared when the reaction mixture was warmed to ambient temperature. The reaction mixture was stirred for an additional 2 h at this temperature. All volatiles were removed under reduced pressure; the residue was crystallized from 5 mL of toluene at −35 °C over a period of 3 days to afford 0.48 g of the product. Upon concentration and cooling of the toluene filtrate, an additional crop of the product was obtained (0.08 g). Total yield is 0.56 g; 77%. ^{1}H NMR (C_6D_6, 23 °C): δ 2.69, 2.38 (m, 4H, methine H, Cy), 1.85, 1.57, 1.32, 1.15 (m, 16H, methylene H, Cy), 1.55 (t, J = 8.0 Hz, 6H, Zn−CH_2*C*H_3), 0.69 (br, 2H, NH), 0.56 (q, J = 8.1 Hz, 4H, Zn-*C*H_2CH_3), 0.43, −0.05 (s, 36H, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 23 °C): δ 64.91, 64.04 (−N*C*H), 38.83, 36.07, 26.90, 26.30 (*C*H_2, Cy), 13.00, 3.00 (Et), 4.86, 0.96 (Si*Me*$_3$). Anal. Calcd for $C_{28}H_{68}N_4Si_4Zn_2$: C, 47.77; H, 9.74; N, 7.96. Found: C, 46.89; H, 10.33; N, 7.40.

Polymerization Procedures and Polymer Characterizations. Polymerization of CL was carried out in an argon-filled glovebox. In a typical polymerization, 22.5 μmol of the zinc complex was first dissolved in 3 mL of toluene and CL was added (0.50 mL, $[CL]_o/[Zn]_o$ = 200:1). The solution was stirred at the box temperature for the measured time interval to produce a gel-like polymer product. The bottle was taken out of the box, and methylene chloride was added to dissolve the polymer gel. The solution was then precipitated into cold methanol (50 mL), filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Polymerization of LA was performed in 50 mL Schlenk flasks on a Schlenk line. In the glovebox, the dried flask was charged with LA (0.215 g, 1.50 mmol) and 4 mL of toluene. The flask was tightly capped with a septum, brought out of the box, and fixed on the Schlenk line. After a desired temperature (25 or 70 °C) was reached using the external temperature-controlled bath, 1.0 mL of the catalyst solution in toluene (7.5 μmol, $[LA]_o/[Zn]_o$ = 200:1) was injected into the flask via a gastight syringe. The reaction was stirred for the measured time interval, and an aliquot taken from the reaction was injected into a tube containing a small amount of methanol. The tube was evacuated and residue was redissolved in $CDCl_3$ for determining the conversion based on the integration of the methyl resonances of the monomer and polymer product. The remaining reaction mixture was treated with 1 mL of methanol, and the solvents were removed in vacuo. The polymer product was precipitated with excess methanol, filtered, and dried in a vacuum oven at 50 °C overnight to a constant weight.

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Table 1. Crystal Data and Structure Refinements for 1, 2, and 3

	1	**2**	**3**
empirical formula	$C_8H_{20}AlNSi$	$C_{16}H_37N2Si_2Zn_2$	$C_{14}H_34N_2Si_2Zn$
fw	185.32	444.40	351.98
temperature/K	178(2)	55.2(2)	183.2(2)
wavelength/Å	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Ibca*	$P2_1/n$	$P\bar{1}$
a/Å	13.716(6)	13.365(2)	10.398(6)
b/Å	16.340(7)	10.579(2)	10.572(6)
c/Å	20.915(9)	15.255(3)	10.840(8)
α/deg	90	90	60.878(7)
β/deg	90	96.336(3)	65.318(11)
γ/deg	90	90	87.509(8)
volume/Å^3	4687(4)	2143.6(6)	926.5(10)
Z	16	4	2
density(calcd)/Mg/m^3	1.050	1.377	1.262
abs coeff/mm^{-1}	0.226	2.349	1.447
F(000)	1632	940	380
cryst size/mm^3	0.25 × 0.20 × 0.08	0.20 × 0.50 × 0.50	0.30 × 0.25 × 0.20
θ range for data collection/deg	3.37 to 23.32	3.62 to 23.27	3.45 to 23.31
index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$ $-23 \leq l \leq 23$	$-14 \leq h \leq 14$, $-11 \leq k \leq 11$ $-16 \leq l \leq 16$	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$ $-12 \leq l \leq 12$
no. of reflns collected	13 989	13 041	5807
no. of ind reflns	1700[$R_{int} = 0.0568$]	3064[$R_{int} = 0.0418$]	2652[$R_{int} = 0.0290$]
no. of data/restraints/params	1700/0/100	3064/0/199	2652/0/177
goodness-of-fit on F^2	1.085	1.034	1.017
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0476$ $wR_2 = 0.1339$	$R_1 = 0.0310$ $wR_2 = 0.0822$	$R_1 = 0.0381$ $R_2 = 0.1003$
R indices (all data)	$R_1 = 0.0677$ $wR_2 = 0.1419$	$R_1 = 0.0385$ $wR_2 = 0.0848$	$R_1 = 0.0393$ $wR_2 = 0.1016$
largest diff peak and hole/e Å^{-3}	0.634 and −0.209	0.702 and −0.468	0.678 and −0.656

MMA polymerizations were performed in 50 mL Schlenk flasks with a septum and an external temperature-controlled bath on a Schlenk line or in a glovebox. In a typical procedure, the complex (46.7 μmol) and the activator $M(C_6F_5)_3$ (M = B, Al) in a proper ratio were loaded into the flask in a glovebox, and toluene was added (10 mL total volume). The flask was removed from the box and put on the Schlenk line. MMA (1.00 mL, 9.35 mmol, $[MMA]_o/[Zn]_o = [MMA]_o/[Al]_o = 200{:}1$) was added through the septum via a gastight syringe after stirring the catalyst and activator mixture for 10 min. The polymerization was quenched by adding 2 mL of acidified methanol after the measured time interval. The polymer product was precipitated into 50 mL methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 40 °C using THF as the eluent on a Polymer Laboratory-210 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL/min. Number-average molecular weight (M_n) and polydispersity (PDI) of polymers were given relative to PS standards. The ^{1}H and ^{13}C NMR spectra for examining PMMA microstructures in terms of triad distributions were recorded in $CDCl_3$ and analyzed according to the literature.[11]

X-ray Crystallography. Single crystals suitable for X-ray diffraction studies were obtained from slow recrystallization from a mixture of toluene and hexanes solvents at −35 °C in the glovebox over a period of several days. In each case, the solvent was decanted in the glovebox, and the crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C/10^{-6} Torr for 24 h). The crystals were then mounted on thin glass fibers and transferred into the cold-steam of a Siemens SMART CCD diffractometer. The structures were solved by direct methods and refined using the Siemens SHELXTL program library.[12] The structure was refined by full-matrix weighted least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the structure factor calculations at idealized positions. Selected crystal data and structural refinement parameters are collected in Table 1.

Results and Discussion

Synthesis of Chiral Complexes 1−3. Reaction of (±)-*trans*-1,2-$Cy(NHSiMe_3)_2$ with 2 equiv of $AlMe_3$ in toluene cleanly produces the dinuclear aluminum complex {(±)-*trans*-$Cy(NSiMe_3)_2$}Al_2Me_4 (**1**) in 88% isolated yield. The 1:1 ratio reaction is less clean, but **1** can be identified as the major product. Consistent with the structure imposing C_2 symmetry, both ^{1}H and ^{13}C NMR spectra of **1** show only one type of $SiMe_3$ group but two diastereotopic Al-CH_3 groups at each aluminum center (^{1}H in C_6D_6: δ −0.14 and −0.38 ppm; ^{13}C in C_6D_6: δ −2.48 and −4.27 ppm).

The outcome of the protonolysis of $ZnEt_2$ by (±)-*trans*-1,2-$Cy(NHSiMe_3)_2$ depends on the ratio of the two reactants. The 1:2 ligand/$ZnEt_2$ ratio reaction produces the tetranuclear zinc complex {(±)-*trans*-$Cy(NSiMe_3)_2$}$_2$-Zn_4Et_4 (**2**) in 87% isolated yield. The NMR spectra of the isolated pure product show only one type of $SiMe_3$ group, indicating formation of a single diastereomer. Steric considerations may be attributable for suppressing formation of the other diastereomer.

The 1:1 ligand/$ZnEt_2$ ratio reaction, on the other hand, produces the dinuclear zinc complex {(±)-*trans*-Cy-$(NHSiMe_3)(NSiMe_3)$}$_2Zn_2Et_2$ (**3**) in 77% isolated yield. Similar to the 1:2 ligand/$ZnEt_2$ ratio reaction, only a single diastereomer is seen in the isolated product. Because of the presence of both covalently bonded $-NSiMe_3$ and datively bonded $-NHSiMe_3$ moieties to the zinc centers in **3**, two different types of $-SiMe_3$ and

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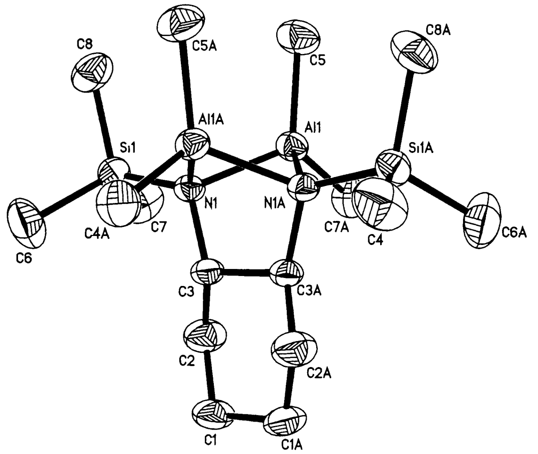

Figure 1. X-ray crystal structure of **1**. Selected bond distances (Å) and bond angles (deg): Al1−C5 1.954(4), Al1−C4 1.964(3), Al1−N1 1.973(3), Al1−N1A 2.017(3), Al1−Al1A 2.763(2), Al1A−N1 2.017(3); C5−Al1−C4 108.99(16), C5−Al1−N1 116.72(13), C4−Al1−N1 117.09(15), C5−Al1−N1A 118.70(14), C4−Al1−N1A 115.15(14), N1−Al1−N1A 77.60(12), Al1−N1−Al1A 87.63(11).

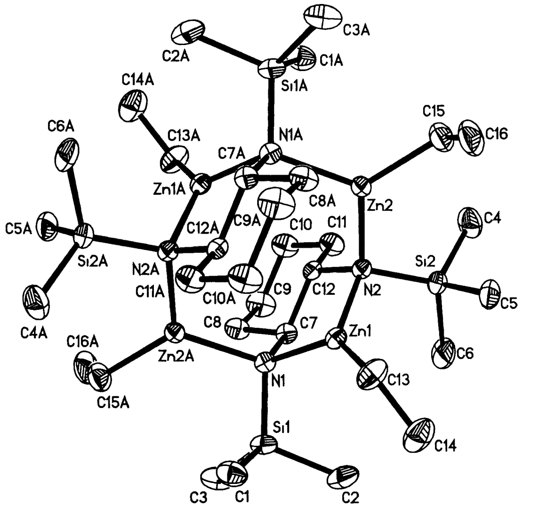

Figure 2. X-ray crystal structure of **2**. Selected bond distances (Å) and bond angles (deg): Zn1−C13 1.984(3), Zn1−N1 2.041(3), Zn1−N2 2.041(3), Zn2−C15 1.998(3), Zn2−N2 2.058(2), Zn2−N1A 2.073(3), N1−C7 1.503(4), N1−Zn2A 2.073(3), N2−C12 1.504(4); C13−Zn1−N1 135.02(14), C13−Zn1−N2 133.98(13), N1−Zn1−N2 90.95(10), C15−Zn2−N2 122.11(13), C15−Zn2−N1A 122.66(13), N2−Zn2−N1A 115.20(10), Zn1−N1−Zn2A 115.57(12), Zn1−N2−Zn2 103.28(11).

−NCH (methine group in Cy) groups are now seen in both ^{1}H and ^{13}C NMR spectra (^{1}H in C_6D_6: δ 2.69, 2.38 ppm for −NC*H* and 0.43, −0.05 ppm for −Si*Me*$_3$; ^{13}C in C_6D_6: δ 64.91, 64.04 ppm for −N*C*H and 4.86, 0.96 ppm for −Si*Me*$_3$).

X-ray Crystal Structures of 1, 2, and 3. The molecular structures of **1**, **2**, and **3** in the solid state are shown in Figures 1, 2, and 3, respectively. In complex **1**, the two Al atoms lie on a 2-fold axis that passes through the centers of the C1−C1A and C3−C3A bonds, and subsequently **1** has C_2 symmetry. The cyclohexane ring in **1** adopts a chair conformation with the −N(SiMe$_3$)Al$_2$ groups placed in equatorial positions, while the two five-membered Al−N−C−C−N rings adopt envelope conformations. The four-membered Al$_2$N$_2$ ring is puckered and shows a butterfly geometry, which is attributable to chelation of the bisamide ligand that distorts the commonly planar Al$_2$N$_2$[13] ring out of its planarity. The chelating effect of the bisamide ligand also results in a very acute N−Al−N angle of only 77.6(1)°, which, to our knowledge, represents the smallest N−Al−N angle for dimeric alkyl aluminum amides reported in the literature.[13−15] The geometry about Al is a distorted tetrahedron with angles about Al widely varying from 77.6(1)° to 118.7(1)°. The amide nitrogen centers are also distorted tetrahedra with a small Al−N−Al angle of 87.6(1)° and correspondingly larger values for the remaining bond angles about the nitrogens. The Al−C and Al−N bond lengths are typical of those found in dimeric alkyl aluminum amides;[13−15] however, the two Al−N bond distances between the aluminum and two chelating amide nitrogens in **1** differ from each other by 0.044(3) Å (Al−N1 = 1.973(3) Å, Al−N1A = 2.017(3) Å).

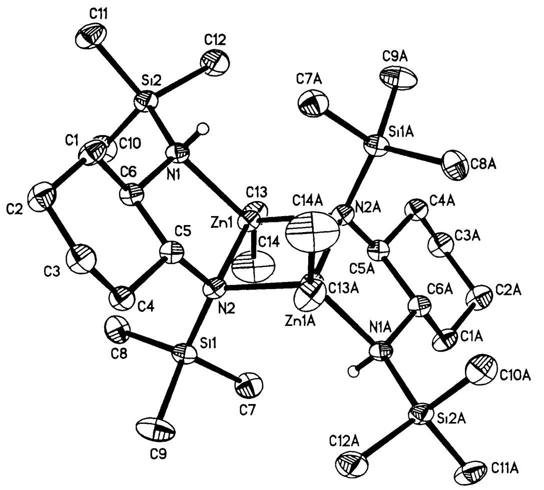

Figure 3. X-ray crystal structure of **3**. Selected bond distances (Å) and bond angles (deg): Zn1−C13 2.019(3), Zn1−N2 2.076(3), Zn1−N2A 2.174(3), Zn1−N1 2.228(3), Zn1−Zn1A 2.937(2), N1−C6 1.497(4), N2−C75 1.488(4), N2−Zn1A 2.174(3); C13−Zn1−N2 136.50(12), C13−Zn1−N2A 112.85(12), N2−Zn1−N2A, 92.55(9), C13−Zn1−N1 114.14(11), N2−Zn1−N1 85.67(9), N2A-Zn1−N1 111.35(11), Zn1−N2−Zn1A 87.45(9).

The solid-state structure of **2** features four unique three-coordinate, planar zinc centers, two of which (Zn1 and Zn1A) are symmetrically bonded to two amide groups from the same cyclohexane ring (i.e., *intramolecular* Zn−N coordination), whereas the other two (Zn2 and Zn2A) are nearly symmetrically bonded to two amide groups from two different cyclohexane rings (i.e., *intermolecular* Zn−N coordination). Two of the four Zn atoms (Zn1 and Zn1A) lie on a 2-fold axis that passes through the centers of the C7−C12, C9−C10, C7A−C12A, and C9A−C10A bonds within two cyclohexane

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rings, and subsequently **2** has C_2 symmetry. Both cyclohexane rings in **2** adopt chair conformations with the $-N(SiMe_3)Zn_2$ groups placed in equatorial positions, while the two five-membered Zn−N−C−C−N rings adopt envelope conformations. All four Zn atoms are three-coordinate and planar, as evidenced by the sum of the angles about the zinc centers of 360.0°. However, there are two types of zinc centers; the first type including Zn1 and Zn1A has symmetric bonding to the amide nitrogens (Zn1−N1 = Zn1−N2 = 2.041(3) Å) and an acute N1−Zn1−N2 angle of 90.95(10)°, whereas the second type, including Zn2 and Zn2A, has slightly unsymmetrical bonding to the amide nitrogens (Zn2−N2 = 2.058(2) Å, Zn2−N1A = 2.073(3) Å) and a larger N2−Zn1−N1A angle of 115.20(10)°. These differences are obviously a result of intramolecular versus intermolecular Zn−N coordination between the two amide nitrogen centers and the ethyl zinc moiety. Consequently, two different Zn−N−Zn angles are evident: Zn1−N1−Zn2A = 115.57(12)°; Zn1−N2−Zn2 = 103.28(11)°. The Zn−C and Zn−N bonds are normal as compared to other rare examples of three-coordinate, planar alkyl Zn amides.[16] The slightly different Zn2−N (intermolecular coordination) distances perhaps indicate a tendency of this complex to dissociate at these sites for catalytic reactions.

The molecular structure of the dimeric **3** exhibits a center of symmetry and a planar four-membered Zn_2N_2 core. All Zn and N atoms are four-coordinate; the Zn atoms are each bonded to three N atoms having different bond distances (Zn1−N2 = 2.076(3) Å, Zn1−N2A = 2.174(3) Å, Zn1−N1 = 2.228(3) Å), and these can be qualitatively correlated to characterizations of covalent Zn−N, dative Zn←N (intermolecular), and dative Zn←NH (intramolecular) bonds, respectively. The cyclohexane and five-membered Zn−N−C−C−N rings in **3** adopt the same conformations as those described for **2**. The geometry about Zn is a distorted tetrahedron with a sum of the three N−Zn−N angles of 289.6°; the N1−Zn1−N2 angle (85.67(9)°) is considerably smaller than the ideal tetrahedral value due to the chelation of Zn to two N atoms on the same cyclohexane ring, while the rest of the angles about Zn are correspondingly larger. Because of increased ring strain in the planar four-membered Zn_2N_2 ring, the Zn−N−Zn angle (87.45(9)°) in complex **3** is significantly smaller than that observed in complex **2** (vide supra).

Polymerizations of CL, LA, and MMA by 1, 2, and 3. Results of CL, LA, and MMA polymerizations by **1**, **2**, and **3** are summarized in Table 2. In CL polymerization, both the tetranuclear Zn **2** and the dinuclear **3** are effective initiators, although the three-coordinate **2** is considerably more active than the four-coordinate **3** (entry 1 vs 2). To investigate the effect of chain-transfer reagents on the polymerization, an addition of 4 equiv of ^{i}PrOH drastically decreases polymerization activity (entry 3), presumably due to decomposition of the zinc complex.

Table 2. Results for Polymerization of CL, LA, and MMA[a]

no.	initiator (activator)	M	T_p (°C)	t_p (h)	yield[b] (%)	M_n (10^{-4})	M_w/M_n	[*rr*] (%)
1	**2**	CL	23	1	90	2.84	1.79	
2	**3**	CL	23	2	62	1.66	1.80	
3	**2**/4 ^{i}PrOH	CL	23	3	22	0.56	1.69	
4	**2**	LA	70	2	89	1.39	1.52	
5	**3**	LA	70	2	92	0.96	1.54	
6	**2/4** ^{i}PrOH	LA	70	2	92	0.70	1.49	
7	**2/4** ^{i}PrOH	LA	23	2	72	0.74	1.37	
8	**1** ($Al(C_6F_5)_3$)	MMA	23	2	46			72.9
9	**1** ($2Al(C_6F_5)_3$)	MMA	23	2	100			73.0
10	**1** ($2B(C_6F_5)_3$)	MMA	23	2	0			
11	**1** ($2Ph_3CB(C_6F_5)_4$)	MMA	23	2	0			
12	**2** ($2Al(C_6F_5)_3$)	MMA	23	1	100	4.25	1.25	69.1
13	**2** ($2B(C_6F_5)_3$)	MMA	23	2	0			

[a] $[M]_o/[Al\ or\ Zn]_o$ ratio = 200. [b] For LA polymerization, monomer conversions are shown.

Complexes **2** and **3** have comparable activities for polymerization of LA at 70 °C (entries 4 and 5). In a ratio of $[LA]_o/[Zn]_o = 200:1$, about 90% monomer conversion was achieved for both complexes in 2 h. However, the M_n obtained against polystyrene standards is approximately half of the calculated value (i.e., 28 800 × conversion%). For example, the calculated M_n for entry 4 is 25 600 for an 89% conversion, but the observed M_n is only 13 900, suggesting that there are two Zn amide initiating groups per Zn molecule (i.e., $[LA]_o/2[Zn]_o$). An addition of 4 equiv of ^{i}PrOH did not result in a noticeable increase of activity but a decrease of molecular weight of polylactide (entries 6 and 7).

Complexes **1** and **2**, upon activation with $M(C_6F_5)_3$ (M = Al, B) or $Ph_3CB(C_6F_5)_4$, have been examined for MMA polymerization. Note that both the complexes and activators when used alone are inactive for MMA polymerization. Combining **1** with 1 equiv of $Al(C_6F_5)_3$ generated an active polymerization system, producing syndiotactic PMMA ([*rr*] = 72.9%, entry 8). Doubling the amount of the alane approximately doubles the polymer yield, but the polymer syndiotacticity remains the same (entry 9). When combined with cation-generating reagents such as $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$, **1** is completely inactive (entries 10 and 11). Likewise, combination of the zinc **2** with 2 equiv of $Al(C_6F_5)_3$ generates a highly active polymerization, producing a quantitative yield of the polymer in 1 h (entry 12); the PMMA produced is also syndiotactic ([*rr*] = 69.1%). Again, the use of the borane activator resulted in an inactive system (entry 13). The M_n of PMMA ($M_n = 4.25 \times 10^4$) obtained with **2**/$2Al(C_6F_5)_3$ is approximately double what is calculated based on $[MMA]_o/[\mathbf{2}]_o = 200$ (i.e., $M_n = 2.00 \times 10^4$).

The observations that are consistent with a bimetallic chain propagation involving enolaluminates proposed for the MMA polymerization initiated by zirconocene aluminates[17] include the following: (a) MMA polymerization activity is sensitive to $[Al(C_6F_5)_3]$, (b) PMMA tacticity is practically independent of initiator chirality, and (c) the observed M_n value for PMMA produced is approximately double what is calculated. Details about the chain initiation and propagation steps are currently unknown; however, according to a previous study,[6] initiation presumably involves nucleophilic attack of the metal amide group onto the activated monomer

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(MMA → Al(C_6F_5)$_3$) to generate the enolaluminate[17] that participates in the bimetallic chain propagation.

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Supporting Information Available: Crystallographic data for **1**, **2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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