1438 *Organometallics* **2002,** *21,* 1438−1442

Neutral, Three-Coordinate, Chelating Diamide Aluminum Complexes: Catalysts/Initiators for Synthesis of Telechelic Oligomers and High Polymers

Debashis Chakraborty and Eugene Y.-X. Chen*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

Received December 11, 2001

Reaction of the bulky chelating diamine ligand ArNH(CH$_2$)$_3$NHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with AlMe$_3$ cleanly affords the monomeric, three-coordinate, chelating diamide aluminum complex [N$^\cap$N]AlMe (**1**). The isobutyl derivative [N$^\cap$N]Al^{i}Bu (**2**) is prepared in the same manner using triisobutylaluminum. The Al/B alkyl/aryl ligand exchange between **1** and B(C$_6$F$_5$)$_3$ in refluxing toluene cleanly produces the pentafluorophenyl-substituted derivative [N$^\cap$N]AlC$_6$F$_5$ (**3**). Studies of model reactions between **1** and ϵ-caprolactone as well as analyses of low-molecular-weight oligomers demonstrate the ability of **1** to produce telechelic oligomers. At high monomer/initiator ratios, all three complexes are active for ring-opening polymerization of ϵ-caprolactone and cyclohexene oxide, producing high-molecular-weight polymers. The isobutyl derivative **2** exhibits the highest activity for both polymerizations in this catalyst series and produces poly(ϵ-caprolactone) having a number-average molecular weight over 1,000,000 Da.

Introduction

In polymer synthesis and polymerization catalysis, aluminum compounds have been extensively used as potent olefin polymerization activators,[1] as efficient initiators for ring-opening polymerization (ROP) of heterocyclic monomers such as lactides,[2] lactones,[3] and epoxides,[4] and as activators/catalysts/modifiers for living or controlled polymerization of polar vinyl monomers such as methacrylates.[5] We are interested in developing new aluminum-based catalyst systems for the synthesis of telechelic polymers: polymers that carry reactive/functional groups at both polymer chain ends. Such polymers are important building blocks for the production of segmented copolymers and polymer networks.[6] Typical aluminum initiators used for ROP of heterocyclic monomers have the structure form of L$_n$AlOR, where L$_n$ is a supporting ligand and OR is an initiating group, and they are not suitable for the direct synthesis of telechelic polymers.

Simple organoaluminum compounds have been shown to be dimeric in the solid state,[7] and only a handful of monomeric, neutral three-coordinate aluminum complexes have been reported and structurally characterized.[8,9] We reasoned that, if carrying suitable initiating groups, these neutral, three-coordinate aluminum complexes would be ideal candidates for coordination ROP of heterocyclic monomers such as lactones and lactides due to their high Lewis acidity for effective monomer

---

(1) For recent reviews, see: (a) Pédeutour, J.-N.; Radhakrishnan, K.; Cramail, H.; Deffieux, A. *Macromol. Rapid Commun.* **2001**, *22*, 1095−1123. (b) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

(2) For recent examples and reviews, see: (a) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2215−2224. (b) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4686−4692. (c) Radano, C. R.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552−1553. (d) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2927−2637.

(3) For recent examples and reviews, see: (a) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196−6201. (b) Wu, B.; Lenz, R. W.; Hazer, B. *Macromolecules* **1999**, *32*, 6856−6859. (c) Miola-Delaite, C.; Hamaide, T.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1771−1778. (d) Wu, B.; Lenz, R. W. *Macromolecules* **1998**, *31*, 3473−3477. (e) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992. (f) Wu, B.; Harlan, C. J.; Lenz, R. W.; Barron, A. R. *Macromolecules* **1997**, *30*, 316−318.

(4) For recent examples, see: (a) 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. (b) Sarbu, T.; Beckman, E. J. *Macromolecules* **1999**, *32*, 6904−6912. (c) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599−3608. (d) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39−48. (e) Gal, Y.-S.; Jung, B.; Lee, W.-C.; Choi, S.-K. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30*, 531−540.

(5) For recent examples and reviews, see: (a) Peace, R. J.; Horton, M. J.; Péron, G. L. N.; Holmes, A. R. *Macromolecules* **2001**, *34*, 8409−8411. (b) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943−7944. (c) Hatada, K. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 245−260. (d) Sugimoto, H.; Inoue, S. *Adv. Polym. Sci.* **1999**, *146*, 39−119. (e) Kitayama, T.; Hirano, T.; Hatada, K. *Tetrahedron* **1997**, *53*, 15263−15279. (f) Schlaad, H.; Muller, A. H. E. *Macromol. Symp.* **1996**, *107*, 163−176.

(6) For reviews and examples, see: (a) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1−59. (b) van Caeter, P.; Goethals, E. J. *Trends Polym. Sci.* **1995**, *3*, 223−233. (c) Dubois, Ph.; Degee, P.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1993**, *26*, 2730−2735. (d) Tezuka, Y. *Prog. Polym. Sci.* **1992**, *17*, 471−514. (e) Jerome, R.; Henrioulle-Granville, M.; Boutevin, B.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837−906. (f) Goethals, E. J., Ed. *Telechelic Polymers: Synthesis and Applications*; CRC Press: Boca Raton, FL, 1989.

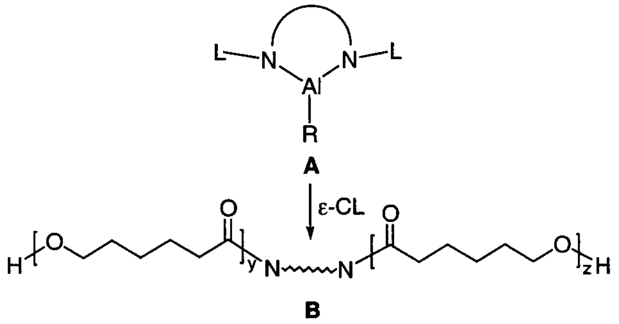
(7) For a comprehensive review, see: Eisch, J. J. In *Comprehensive Organometallic Chemistry*, 2nd ed.; Housecroft, C. E., Ed.; Pergamon: Oxford, U.K., 1995; Vol. 1, pp 431−502.

(8) For examples, see: (a) Atwood, D. A.; Rutherford, D. *Main Group Chem.* **1996**, *1*, 431−442. (b) Healy, M. D.; Mason, M. R.; Gravelle, P. W.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441−454. (c) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385−3393. (d) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633−2637. (e) Shreve, A.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409−416. (f) Jerius, J. J.; Hahn, J. M.; Rahman, A. F. M. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986**, *5*, 1812−1814.

(9) For examples of cationic, three-coordinate aluminum complexes, see: (a) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673−8674. (b) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125−8126.

10.1021/om011051n CCC: $22.00
Publication on Web 03/03/2002

Scheme 1



activation via σ-bond coordination between one of the monomer's heteroatoms and the three-coordinate, highly Lewis acidic aluminum center. Furthermore, for production of telechelic polymers, the initiating groups in a complex must be covalently linked together. To this end, we focus on utilizing bulky chelating diamide ligation (**A**, where L is a bulky supporting ligand and R is not a initiating group; Scheme 1) in the preparation of monomeric, neutral three-coordinate aluminum complexes carrying linked biinitiating groups for synthesis of telechelic polymers such as telechelic poly(ϵ-caprolactone) (**B**). We wish to report the synthesis and structure of three monomeric, three-coordinate aluminum complexes incorporating a bulky chelating ArN(CH$_2$)$_3$NAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) diamide ligand. Model reactions and polymerization studies demonstrate the ability of these complexes to produce telechelic, oligomeric, and polymeric ϵ-caprolactones (PCL), depending on the monomer and initiator ratio. These complexes also exhibit high activities for the ROP of cyclohexene oxide (CHO).

Experimental Section

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line (10^{-6}–10^{-7} Torr), or in an argon-filled glovebox (<0.5 ppm of O$_2$ and moisture). NMR-scale reactions were conducted in Teflon-valve-sealed sample J. Young tubes. Organic solvents were first saturated with nitrogen and then dried by passage through activated alumina and Q-5 catalyst (Englehardt Chemicals Inc.) stainless steel columns prior to use. Toluene used for polymerization was further dried over Na/K alloy. Deuterated benzene and toluene were dried over Na/K alloy and distilled and/or filtered prior to use. CDCl$_3$ was dried over activated Davison 4 Å molecular sieves. ϵ-Caprolactone (ϵ-CL) and cyclohexene oxide (CHO) were degassed and dried over CaH$_2$ overnight and then freshly vacuum-distilled before use. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or a Varian Inova 400 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external CFCl$_3$ standard. Electrospray mass spectrometry was carried out on a Fisons VG Quattro-SQ mass spectrometer operated in the positive-ion mode. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, and by Desert Analytics, Tucson, AZ.

Tris(perfluorophenyl)borane was obtained as a research gift from Boulder Scientific Co. and used without further purification for preparative reactions or purified by recrystallization from hexane at −35 °C for NMR-scale reactions. Triisobutylaluminum (TIBA, neat), 2,6-diisopropylaniline, TMEDA, and 1,3-dibromopropane were purchased from Aldrich Chemical Co. and used as received. Trimethylaluminum (TMA, neat) was obtained from Strem Chemicals, Inc. The bulky chelating diamine ligand ArNH(CH$_2$)$_3$NHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) was prepared from LiNHAr and 1,3-dibromopropane according to the literature procedure.[10]

Synthesis of [ArN(CH$_2$)$_3$NAr]AlMe ([N∩N]AlMe, 1). In an Ar-filled glovebox, to a stirred solution of ArNH(CH$_2$)$_3$NHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1.93 g, 4.89 mmol) in 15 mL of hexanes at −20 °C was added slowly TMA (2.45 mL, 2.0 M in hexanes, 4.89 mmol). The reaction mixture was warmed to ambient temperature and stirred for a period of 20 h. The solvent was removed in vacuo, and the residue was redissolved in 2 mL of hexanes and stored at −35 °C for 2 days, yielding 1.0 g of a crystalline solid. When the mother liquor was cooled, an additional crop of 0.85 g of the pure product was obtained. The total yield is 1.85 g (86.9%). Anal. Calcd for C$_{28}$H$_{43}$AlN$_2$: C, 77.37; H, 9.97; N, 6.45. Found: C, 77.03; H, 9.89; N, 6.37.

^{1}H NMR (C$_7$D$_8$, 23 °C): δ 7.10 (s, 6H, Ar), 3.68 (sept, J = 6.9 Hz, 4H, −CHMe$_2$), 3.17 (t, J = 5.1 Hz, 4H, −NCH_2CH$_2$), 2.09 (pent, 2H, −NCH$_2$$CH_2$), 1.33 (d, J = 7.2 Hz, 12H, −CHMe_2), 1.24 (d, J = 7.2 Hz, 12H, −CHMe_2), −0.76 (s, 3H, Al−CH$_3$). ^{13}C NMR (C$_7$D$_8$, 23 °C): δ 147.40, 145.54, 126.06, 124.23 (Ar), 56.26 (−NCH_2CH$_2$), 34.95, 29.02, 25.76, 25.22 (−CHMe$_2$, −CHMe_2, −NCH$_2$$CH_2$), −16.61 (Al−$CH_3$).

Synthesis of [ArN(CH$_2$)$_3$NAr]Al(^{i}Bu) ([N∩N]Al^{i}Bu, 2). In an Ar-filled glovebox, to a stirred solution of ArNH(CH$_2$)$_3$NHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (0.52 g, 1.32 mmol) in 10 mL of hexane at −35 °C was added slowly a precooled solution (−35 °C) of TIBA (0.26 g, 1.32 mmol) in 5 mL of hexanes. The reaction mixture was warmed to ambient temperature and stirred for a period of 20 h. All volatiles were removed in vacuo, and the resulting viscous yellow oil was redissolved in 2 mL of hexanes and stored at −35 °C for 2 days. The crystallized product was separated and dried under reduced pressure to afford 0.35 g of crude product; yield 55.6%. The sample submitted for the elemental analysis was obtained by further washing the product with 2 mL of cold hexanes and drying. Anal. Calcd for C$_{31}$H$_{49}$AlN$_2$: C, 78.10; H, 10.36; N, 5.87. Found: C, 77.50; H, 10.37; N, 5.64.

^{1}H NMR (C$_6$D$_6$, 23 °C): δ 7.13 (s, 6H, Ar), 3.75 (sept, J = 6.8 Hz, 4H, −CHMe$_2$), 3.19 (t, J = 5.2 Hz, 4H, −NCH_2CH$_2$), 2.07 (pent, 2H, −NCH$_2$$CH_2$), 1.45 (m, 1H, Al−CH$_2$$CHMe_2$), 1.33 (d, J = 7.2 Hz, 12H, −CHMe_2), 1.30 (d, J = 7.2 Hz, 12H, −CHMe_2), 0.63 (d, 1H, J = 6.0 Hz, 6H, Al−CH$_2$CHMe_2), 0.16 (d, 1H, J = 6.8 Hz, 2H, Al−CH_2CHMe$_2$). ^{13}C NMR (C$_6$D$_6$, 23 °C): δ 147.32, 146.45, 125.93, 124.37 (Ar), 56.50 (−NCH_2CH$_2$), 34.61, 29.08, 25.44, 25.24 (−CHMe$_2$, −CHMe_2, −NCH$_2$$CH_2$), 28.34, 26.17, 17.63 (Al−^{i}Bu).

Synthesis of [ArN(CH$_2$)$_3$NAr]Al(C$_6$F$_5$) ([N∩N]Al(C$_6$F$_5$), 3). In an Ar-filled glovebox, **1** (0.35 g, 1.03 mmol) and B(C$_6$F$_5$)$_3$ (0.22 g, 0.43 mmol, B/Al molar ratio 1/2.4) were mixed as solids and 40 mL of toluene was added. The reaction mixture was heated to mild reflux for a period of 10 h. The ^{1}H NMR spectrum of an aliquot taken from the reaction mixture revealed ~98% completion of the reaction. The reaction mixture was concentrated to 5 mL and stored at −35 °C overnight to yield 0.35 g of the pure product as a crystalline solid; yield 58.5%. Attempts to grow single crystals by repeated recrystallization from toluene resulted in a low yield (18.4%). Anal. Calcd for C$_{33}$H$_{40}$AlN$_2$F$_5$: C, 67.56; H, 6.87; N, 4.78. Found: C, 67.68; H, 7.08; N, 4.72.

^{1}H NMR (C$_7$D$_8$, 23 °C): δ 7.02 (s, 6H, Ar), 3.78 (sept, J = 7.2 Hz, 4H, −CHMe$_2$), 3.25 (t, J = 5.1 Hz, 4H, −NCH_2CH$_2$), 2.10 (pent, 2H, −NCH$_2$$CH_2$), 1.30 (pseudo t, 24H, −CHMe_2). ^{13}C NMR (C$_7$D$_8$, 23 °C): δ 146.86, 143.63, 126.17, 124.07 (Ar), 56.35 (−NCH_2CH$_2$), 34.28, 28.94, 26.00, 24.44 (−CHMe$_2$,

---

[10] Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415−4420.

$-\mathrm{CH}Me_2$, $-\mathrm{NCH_2}CH_2$). ^{19}F NMR (C_7D_8, 23 °C): δ −118.76 (dd, 6F, *o*-F), −147.72 (t, 3F, *p*-F), −159.60 (tt, 6F, *m*-F).

Polymerization Procedures. Polymerization of ϵ-caprolactone was carried out in an argon-filled glovebox. In a typical experiment, **1** (9.78 mg, 22.5 μmol) was first dissolved in 3 mL of toluene and ϵ-caprolactone monomer was added (0.50 mL, [M]/[I] = 200). The solution was stirred at room temperature for 4 h to produce a gel-like polymer. 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. Yield: 73.8%.

For the preparation of low-molecular-weight oligomers, a ratio of [M]/[I] = 10 was used. The reaction was quenched with methanol. A small amount of solution was taken for electrospray MS analysis. The solvent was removed under vacuum, the residue was dissolved in methylene chloride, and this solution was filtered. The solvent of the filtrate was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR.

For polymerization of CHO, an initiator was first dissolved in toluene in a glovebox and loaded into the Schlenk tube. This tube was taken out of the box and attached to the high-vacuum line. Monomer was then quickly injected into the solution via a gastight syringe once the external bath temperature was stabilized. The polymerization was terminated by addition of acidic methanol after the measured time interval. The polymer product was precipitated into 50 mL of methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. Typical conditions for CHO polymerization: 9.88 μmol of initiator; 0.5 mL of CHO (4.94 mmol); [M]/[I] = 500; 2 mL of toluene.

Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 40 °C using THF as 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 and polydispersity of polymers were given relative to PS standards.

X-ray Crystallography. Colorless single crystals suitable for X-ray diffraction studies were obtained from slow recrystallization of **1** from hexanes at −35 °C in the glovebox over a period of 1 week. Data were collected at 173(2) K on a Siemens SMART CCD diffractometer. The structure was solved by direct methods and refined using the Siemens SHELXTL program library.[11] 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.

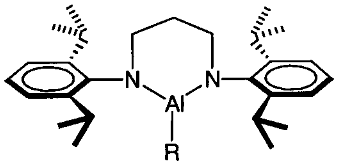
Results and Discussion

Synthesis of Three-Coordinate Aluminum Complexes 1−3. The methyl substituted complex **1** (R = Me; Chart 1) was synthesized in 87% yield from the reaction of $AlMe_3$ with the known ligand $ArNH(CH_2)_3NHAr$ (Ar = 2,6-^{i}$Pr_2C_6H_3$).[10] Solution ^{1}H NMR spectra of **1** reveal a sharp singlet for the Al−Me group and two doublets for the diastereotopic isopropyl methyl groups on the phenyl ring, suggesting that the rotations about the N−C_{ipso} bond are restricted (assuming the two nitrogen centers are sp^2-hybridized, vide infra). The corresponding isobutyl derivative **2** was synthesized in the same manner using triisobutylaluminum.

Table 1. Crystal Data and Structure Refinement for 1

empirical formula	$C_{28}H_{43}AlN_2$
fw	434.62
temp	173(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	9.807(2) Å
b	17.067(4) Å
c	17.426(4) Å
α	108.628(5)°
β	90.792(4)°
γ	90.356(5)°
V	2763.3(10) Å^3
Z	4
density (calcd)	1.045 Mg/m^3
abs coeff	0.089 mm^{-1}
F(000)	952
cryst size	0.2 × 0.3 × 0.3 mm^3
θ range for data collection	1.26−23.30°
index ranges	$-10 \le h \le 10$, $-15 \le k \le 18$, $-19 \le l \le 19$
no. of rflns collected	13 071
no. of indep rflns	7915 (R_{int} = 0.0646)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	7915/0/559
goodness of fit on F^2	0.803
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0609, wR2 = 0.1097
R indices (all data)	R1 = 0.1763, wR2 = 0.1359
largest diff peak and hole	0.314 and −0.346 e Å^{-3}

Chart 1



1, R = Me; **2**, R = ^{i}Bu; **3**, R = C_6F_5

Upon heating in toluene, **1** undergoes facile Al/B alkyl/aryl ligand exchange[12] with $B(C_6F_5)_3$[13] to produce the pentafluorophenyl derivative **3** (eq 1). The optimized

$$\underset{\mathbf{1}}{[\mathrm{N}^\cap\mathrm{N}]\mathrm{AlMe}} + {}^1\!/_3\mathrm{B}(\mathrm{C_6F_5})_3 \xrightarrow[\text{reflux}]{\text{tolune}} \underset{\mathbf{2}}{[\mathrm{N}^\cap\mathrm{N}]\mathrm{AlC_6F_5}} + {}^1\!/_3\mathrm{BMe_3}\uparrow \quad (1)$$

B/Al ratio for quantitative conversion by NMR is 1/2.4, which was the ratio used for preparative isolation. Using this ratio, the borane $B(C_6F_5)_3$ and methylborane species ($MeB(C_6F_5)_2$ and $Me_2B(C_6F_5)$)[12a] were not seen upon the completion of the reaction; rather, a clean conversion to **2** and BMe_3 was observed (δ 0.73 ppm in C_7D_8).[12d]

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The monomeric, three-coordinate structure in the solid

---

(11) Sheldrick, G. M. SHELXTL, Version 5; Siemens, Madison, WI, 1996.

(12) (a) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686. (b) Chen, E. Y.-X.; Kruper, W. J.; Roof, G. R. PCT Int. Appl. WO 0009515, 2000. (c) Lee, C. H.; Lee, S. J.; Park, J. W.; Kim, K. H.; Lee, B. Y.; Oh, J. S. *J. Mol. Catal., A: Chem.* **1998**, *132*, 231−239. (d) Carnahan, E. M.; Chen, E. Y.-X.; Jacobsen, G. B.; Stevens, J. C. PCT Int. Appl. WO 9915534, 1999. (e) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912. (f) Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U.S. Patent 5,602,269, 1997.

(13) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

Table 2. Results for Ring-Opening Polymerization of ϵ-Caprolactone (ϵ-CL) and Cyclohexene Oxide (CHO)

entry	initiator	monomer	[M]/[I] ratio	T_p (°C)	t_p (h)	isolated yield (%)	$10^4 M_n$	M_w/M_n
1	$[\mathrm{N^\frown N}]$AlMe (**1**)	ϵ-CL	200	23	4.0	74	17.0	3.19
2	$[\mathrm{N^\frown N}]\mathrm{Al^{i}Bu}$ (**2**)	ϵ-CL	200	23	1.5	74	121	2.55
3	$[\mathrm{N^\frown N}]\mathrm{Al(C_6F_5)}$ (**3**)	ϵ-CL	200	23	18.5	62	22.7	7.83
4	$[\mathrm{N^\frown N}]$AlMe (**1**)	CHO	500	23	1.0	74	6.44	4.35
5	$[\mathrm{N^\frown N}]$AlMe (**1**)	CHO	500	0	1.0	70	9.67	4.23
6	$[\mathrm{N^\frown N}]\mathrm{Al^{i}Bu}$ (**2**)	CHO	500	0	0.25	98	7.31	5.65
7	$[\mathrm{N^\frown N}]\mathrm{Al(C_6F_5)}$ (**3**)	CHO	500	23	0.5	99	2.56	4.89
8	$[\mathrm{N^\frown N}]\mathrm{Al(C_6F_5)}$ (**3**)	CHO	500	0	0.5	97	3.28	4.31

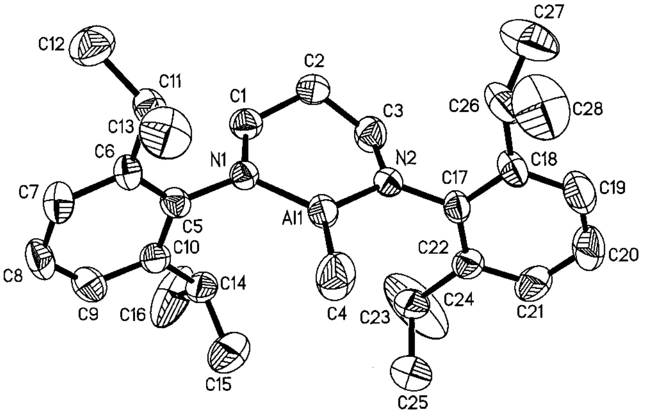


Figure 1. Crystallographic structure of **1**. Selected bond lengths (Å) and angles (deg): Al(1)−C(4) = 1.915(4); Al(1)−N(1) = 1.760(3); Al(1)−N(2) = 1.766(3); N(1)−C(1) = 1.473(5); N(1)−C(5) = 1.438(5); N(2)−C(3) = 1.455(5); N(2)−C(17) = 1.445(4); N(1)-A(l1)−N(2) = 109.2(2); N(1)−Al(1)−C(4) = 125.5(2), N(2)−Al(1)−C(4) = 125.3(2); C(1)−N(1)−Al(1) = 119.8(3); C(5)−N(1)−C(1) = 112.6(3); C(5)−N(1)−Al(1) = 126.2(3); C(3)−N(2)−Al(1) = 118.7(3); C(3)−N(2)−C(17) = 113.3(3); C(17)−N(2)−Al(1) = 127.8(3).

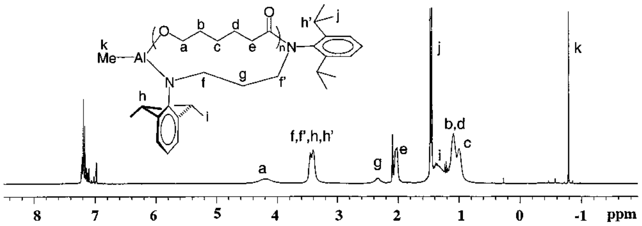


Figure 2. ^{1}H NMR spectrum for reaction of **1** + ϵ-CL after 15 min in toluene-d_8.

state is confirmed by X-ray diffraction studies, featuring an sp^2-hybridized aluminum center, as evidenced by the sum of the angles about the aluminum of 360.0° (Figure 1). The two amide centers are also sp^2-hybridized, with the sums of the angles about the nitrogen centers of 358.6° (N1) and 359.8° (N2), and the 2,6-isopropyl-substituted aryl rings are substantially twisted out of the N$_2$Al plane with dihedral angles of 78.4 and 80.9°, respectively.

Oligomerization and Polymerization of ϵ-Caprolactone. Reaction of **1** with ϵ-CL was monitored by ^{1}H NMR with 1/1, 1/2, and 1/10 M (monomer)/I (initiator) ratios. It is clear from these NMR-scale reaction spectra (Figures 2 and 3) that when **1** is mixed with ϵ-CL, the methyl group remains attached to Al and initiation involves monomer insertion into an Al−N bond, resulting in free rotation about N−C$_{ipso}$ in one of the aryl rings. The NMR spectra also suggest that consecutive monomer insertions favor the nucleophilic attack onto a monomer by the alkoxy group generated in the initiation step rather than attack by the second bulky amide group. This observation is based on the integrations of the isopropyl methyl groups on the freely rotating aryl ring about the N−C$_{ipso}$ bond (appearing as a single doublet, Figure 2) vs the integration of the Al−Me group. This implies that the rate of insertion by the alkoxy group is faster than that by the second bulky amide group; therefore, the overall reaction sequence should result in formation of predominantly heterotelechelic polymers (two different reactive/functional groups at the polymer chain ends, i.e., hydroxy and amine groups) after quenching the polymerization with methanol. To further verify the formation of such oligomeric structures, the crude oligomers formed by **1** at [M]/[I] = 10 after quenching with methanol were analyzed by electrospray mass spectrometry. The spectrum exhibits oligomers of the formula $\mathrm{H[N(Ar)(CH_2)_3(Ar)N][CO(CH_2)_5O]_nH{\cdot}H^+}$ (n = 1−8) as well as molecular ions corresponding to the methanolyzed ligand (n = 0). The ^{1}H NMR spectrum of the oligomers is consistent with these results.

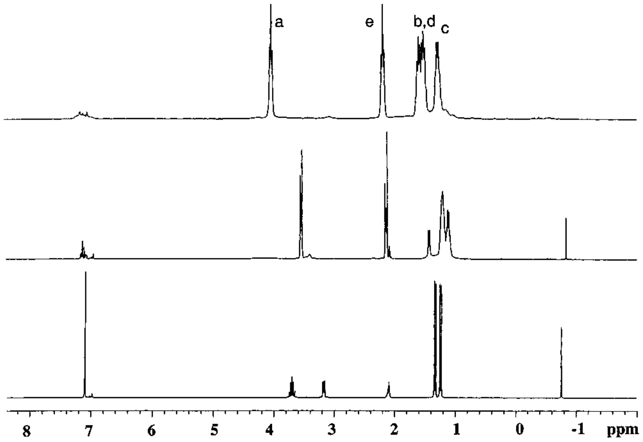


Figure 3. ^{1}H NMR spectra in toluene-d_8 for **1** (bottom), reaction of **1** + 10 ϵ-CL after 15 min (middle), and reaction of **1** + 10 ϵ-CL upon completion of the reaction (top). See the structure drawing in Figure 2 for peak assignments of the labels a−e.

Results of polymerization studies of ϵ-CL and CHO by complexes **1**−**3** are summarized in Table 2. In ϵ-CL polymerization, the isobutyl derivative **2** exhibits the highest activity, producing the polymer with the highest molecular weight. Thus, in a 200/1 [M]/[I] ratio, the polymerization by **2** produced an isolated polymer yield of 74% in 1.5 h of polymerization time (entry 2). Although the activity is lower than those ϵ-CL polymerizations by yttrium and lanthanide alkoxides[14] and samarium complexes,[15] the polymer produced by **2** has a number average molecular weight of over 1,000,000

---

[14] McLain, S.; Drysdale, N. E. *Polym. Prepr.* **1992**, *33*, 174−175.

(1.21×10^6) Da and a polydispersity of 2.55. Surprisingly, the C_6F_5-substituted derivative **3** exhibits the lowest activity and produces PCL with a broad molecular weight distribution (entry 3), while the methyl derivative **1** lies somewhat between **2** and **3** in terms of polymerization activity and the degree of control in polymerization (entry 1).

All complexes are highly active for ROP of CHO (entries 4−8), with **2** again being the most active. For example, in a 500/1 [M]/[I] ratio, the polymerization by **2** produced an isolated polymer yield of 98% in 15 min of polymerization time (entry 6). Poly(cyclohexene oxides) produced by these catalysts typically exhibit broad molecular weight distributions.

In summary, we have developed a catalyst system based on the neutral three-coordinate, chelating diamide aluminum complexes $[N^\cap N]AlR$ for ROP of heterocyclic monomers. Studies of model reactions between the initiator and monomer as well as analyses of the low-molecular-weight oligomers derived from the current catalyst system demonstrate their ability to produce telechelic oligomers. High polymers can also be efficiently produced with high monomer/initiator ratios.

Acknowledgment. We thank Boulder Scientific Co. for the gift of $B(C_6F_5)_3$ and Ms. Susie M. Miller for the X-ray diffraction analysis.

Supporting Information Available: Tables giving crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM011051N

---

(15) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330−2332.