

Synthesis and Characterization of a Series of New Lanthanide Derivatives Supported by Silylene-Bridged Diamide Ligands and Their Catalytic Activities for the Polymerization of Methyl Methacrylate

Liyang Zhou,[†] Yingming Yao,[†] Cheng Li,[†] Yong Zhang,[†] and Qi Shen^{*,†,‡}

Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received January 18, 2006

The synthesis and structures of a series of new lanthanide complexes supported by silylene-bridged diamide ligands are described. The complex $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{YbCl}(\text{TMEDA})\}_2$ (**1**) can be synthesized by YbCl_3 with $\text{PhLiNSiMe}_2\text{NLiPh}$ in 1:1 molar ratio in good yield. Treatment of $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCl}(\text{THF})_n\}_2$ in situ and $\text{Cp}'\text{Na}$ in 1:2 molar ratio afforded a series of new anionic complexes: $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}[\text{Li}(\text{DME})_3]$ [$\text{Cp}' = \text{C}_5\text{H}_5$, $\text{Ln} = \text{Yb}$ (**2**); Sm (**3**); $\text{Cp}' = \text{MeC}_5\text{H}_4$, $\text{Ln} = \text{Yb}$ (**4**)]. Complexes **2** and **4** can also be synthesized by $\text{Cp}'_2\text{YbCl}$ with $\text{PhLiNSiMe}_2\text{NLiPh}$ in 1:1 molar ratio in good yield. The complex **1** reacted with $\text{PhLiNSiMe}_2\text{NLiPh}$ in 1:1 molar ratio to yield an anionic amide complex, $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{THF})_2\text{Li}(\text{THF})\}$ (**6**). These complexes were characterized by elemental analysis, IR, and ^1H NMR. The molecular structures of **2–4** and **6** were further determined by X-ray diffraction techniques. These anionic complexes showed high activity for the polymerization of methyl methacrylate (MMA) at rt, giving syndiotactic-rich polymers with high molecular weights ($M_n > 10^4$) and relatively narrow molecular weight distributions ($M_w/M_n = 1.54\text{--}1.85$).

Introduction

The application of organolanthanide complexes as single-component catalysts in the polymerization of polar monomers has attracted much attention since H. Yasuda et al. first reported that lanthanide hydride is a highly active catalyst for living syndiotactic polymerization of methyl methacrylate (MMA) in 1992.¹ Many kinds of lanthanide derivatives have been explored to perform polymerization of MMA to give high syndiotactic or high isotactic polymers. Most of the complexes published are the neutral trivalent complexes containing $\text{Ln}-\text{C}$, $\text{Ln}-\text{N}$, and $\text{Ln}-\text{H}$ σ bonds as well as divalent complexes.^{2–15} The anionic complexes of lanthanides are often isolated, especially for the case where a less bulky ligand was used, due to the

large ionic radius and the demand of a high coordination number of the lanthanide element. However, only a few papers are concerned with the catalytic behavior of anionic complexes. Anionic Sm(II) complexes of $[(\text{C}_5\text{Me}_5)(\text{THF})_n\text{Sm}(\text{ER})(\text{C}_5\text{Me}_5)\text{K}(\text{THF})_y]_n$ ($\text{ER} = \text{OAr}$, SAr , NR_2 , SiH_3 , CHR_2) were found to be active for the homopolymerization of ethylene and styrene and their block copolymerization.¹⁶ The analogous complexes of Sm(II) $[(\text{C}_5\text{Me}_5)(\text{THF})\text{Sm}(\text{PHAr})(\text{KC}_5\text{Me}_5)(\text{THF})_n]$ and $(\text{C}_5\text{Me}_5)[(\text{SiMe}_2)_2\text{N}]\text{Sm}[(\text{C}_5\text{Me}_5)\text{Na}(\text{THF})_3]$ are active for the po-

* Corresponding author. Tel: +86-512-6588-0306. Fax: +86-512-6588-0305. E-mail: qshen@suda.edu.cn.

[†] Suzhou University.

[‡] Shanghai Institute of Organic Chemistry.

(1) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.

(2) (a) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134. (b) Ihara, E.; Morimoto, M.; Yasuda, H. *Macromolecules* **1995**, *28*, 7886. (c) Yasuda, H.; Ihara, E.; Nitto, Y.; Kakehi, T.; Morimoto, M.; Nodono, M. *ACS Symp. Ser.* **1998**, *704*, 149. (d) Ihara, E.; Adachi, Y.; Yasuda, H.; Hashimoto, H.; Kanehisa, N.; Kai, Y. *J. Organomet. Chem.* **1998**, *569*, 147. (e) Tanaka, K.; Furo, M.; Ihara, E.; Yasuda, H. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 1382. (f) Yasuda, H. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 1955.

(3) Giardello, M. A.; Yamamoto, Y.; Bard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276.

(4) Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A.; Mashima, K. *Macromolecules* **1996**, *29*, 8014.

(5) (a) Boffa, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494. (b) Boffa, L. S.; Novak, B. M. *Tetrahedron* **1997**, *53*, 15367. (c) Boffa, L. S.; Novak, B. M. *J. Mol. Catal. A: Chem.* **1998**, *133*, 123.

(6) (a) Mao, L. S.; Shen, Q. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 1593. (b) Mao, L. S.; Shen, Q.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 9.

(7) (a) Knjazhanski, S. Y.; Elizalde, L.; Cadenas, G.; Bulychev, B. M. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 1599. (b) Knjazhanski, S. Y.; Elizalde, L.; Cadenas, G.; Bulychev, B. M. *J. Organomet. Chem.* **1998**, *568*, 33.

(8) Lee, M. H.; Hwang, J. W.; Kim, Y.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124.

(9) (a) Qian, C. T.; Nie, W. L.; Sun, J. *Organometallics* **2000**, *19*, 4134. (b) Qian, C. T.; Zou, G.; Chen, Y. F.; Sun, J. *Organometallics* **2001**, *20*, 3106. (c) Qian, C. T.; Zou, G.; Jiang, W. H.; Chen, Y. F.; Sun, J.; Li, N. *Organometallics* **2004**, *23*, 4980.

(10) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Carpentier, J. F. *Organometallics* **2003**, *22*, 4467.

(11) Zhou, S. L.; Wang, S. W.; Yang, G. S.; Liu, X. Y.; Sheng, E. H.; Zhang, K. H.; Cheng, L.; Huang, Z. X. *Polyhedron* **2003**, *22*, 1019.

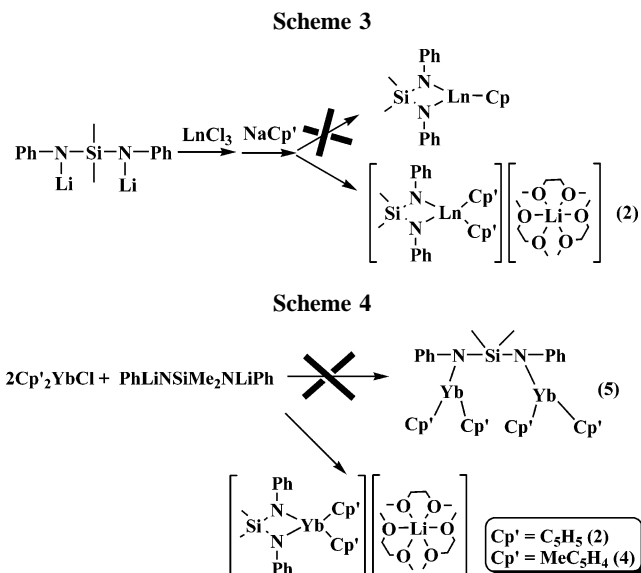
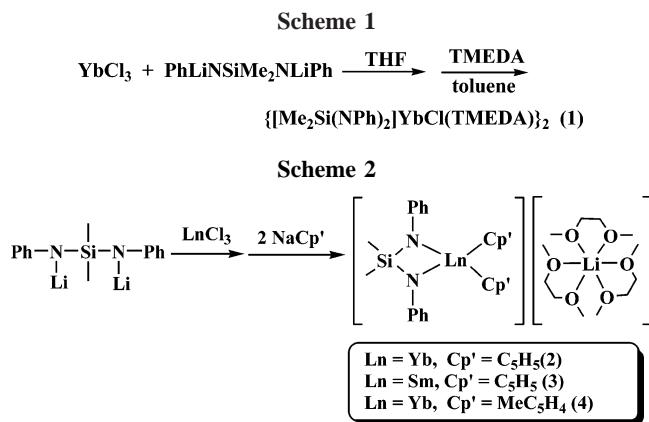
(12) (a) Woodman, T. J.; Schormann, M.; Bochmann, M. *Organometallics* **2003**, *22*, 2938. (b) Woodman, T. J.; Schormann, M.; Hughes, M., D.; Bochmann, L. M. *Organometallics* **2003**, *22*, 3028. (c) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2004**, *23*, 2972.

(13) Yuan, F. G.; Wang, H. Y.; Zhang, Y. *Chin. J. Chem.* **2005**, *23*, 409.

(14) Luo, Y. J.; Yao, Y. M.; Li, W. J.; Chen, J. L.; Zhang, Z. Q.; Zhang, Y.; Shen, Q. *J. Organomet. Chem.* **2003**, *679*, 125.

(15) Simpson, C. K.; White, R. E.; Carlson, C. N.; Wroblewski, D. A.; Kuehl, C. J.; Croce, T. A.; Steele, I. M.; Scott, B. L.; Young, V. G.; Hanusa, T. P.; Sattelberger, A. P.; John, K. D. *Organometallics* **2005**, *24*, 3685.

(16) (a) Hou, Z. M.; Tezuka, H.; Zhang, Y. G.; Yamazaki, H.; Wakatsuki, Y. *Macromolecules* **1998**, *31*, 8650. (b) Hou, Z. M.; Zhang, Y. G.; Tezuka, H.; Xie, P.; Tardif, O.; Koizumi, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10533. (c) Hou, Z. M.; Zhang, Y. G.; Tardif, O.; Yamazaki, H. *J. Am. Chem. Soc.* **2001**, *123*, 9216.



lymerization of ethylene.^{16b} Recently, the “ate” allyl complexes of lanthanides $\text{K}[\text{Ln}\{\text{C}_3\text{H}_3(\text{SiMe}_3)_2\}_4]$ and $[\text{Ln}\{\text{C}_3\text{H}_3(\text{SiMe}_3)_2\text{SiMe}_2\}_2\{\mu\text{-K}(\text{THF})\}(\text{THF})_x]_\infty$ were reported to exhibit much higher activity for the polymerization of MMA than the corresponding neutral one, $\text{Ln}[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]_3$, and to work as a single-component catalyst, not the combined catalyst of two fragments; even $\text{K}[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]$ itself shows very high activity.¹⁵

To further understand the catalytic behavior of anionic lanthanide complexes, we synthesized the anionic complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}[\text{Li}(\text{DME})_3]$ (Cp' = C₅H₅, Ln = Yb, Sm; Cp' = MeC₅H₄, Ln = Yb), $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{THF})_2\text{Li}(\text{THF})\}$, and $\text{Cp}_4\text{YbLi}(\text{THF})_n$. In these complexes only the ancillary ligands of Cp' and chelating diamido groups, which were recently developed as alternatives to Cp in organometallic chemistry, existed around the central metals. The study on their catalytic activity demonstrated that all the anionic complexes synthesized exhibit high activity for the polymerization of MMA at 30 °C to yield the syndiotactic-rich polymers (53–59% rr) with high molecular weights and moderate polydispersity (M_w/M_n 1.54–1.85). In contrast, **1**, Cp₃Ln, CpLi, and PhLiNSiMe₂NLiPh are almost inactive under the same conditions. Here we would like to report the results.

Results and Discussion

Synthesis and Characterization of Lanthanide Complexes.

To synthesize the desired anionic complex in high yield, the less bulky bridged diamide ligand is chosen. Thus, the silylene-bridged diamide ligand PhNHSi(Me)₂NHPh was synthesized according to the literature procedure,¹⁷ and the corresponding lithium salt was prepared by its reaction with *n*-BuLi in hexane.

The reaction of YbCl₃ with PhLiNSiMe₂NLiPh in THF at rt followed by crystallization from toluene with tetramethylethyldiamine (TMEDA) yields the corresponding chloride $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{YbCl}(\text{TMEDA})\}_2$ (**1**) as red crystals in 85% yield (Scheme 1).

The anhydrous lanthanide trichloride reacts with PhLiNSiMe₂NLiPh, then Cp'Na in 1:1:2 molar ratio to afford the corresponding anionic complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}[\text{Li}(\text{DME})_3]$ [Cp' = C₅H₅, Ln = Yb (**2**); Sm(**3**); Cp' = MeC₅H₄, Ln = Yb (**4**)] in high yields (Scheme 2). The cation in each complex is Li(DME)₃, not Na(DME)₃.

Even when the reaction was carried out in the 1:1 molar ratio of complex **1** to CpNa, the anionic complex **2** is still isolated in reasonable, lower yield, instead of the neutral one (Scheme 3).

When PhLiNSiMe₂NLiPh reacts with Cp₂YbCl and (MeC₅H₄)₂YbCl in 1:1 molar ratio, respectively, the same complexes **2** and **4**, not the bimetallic complex **5** (Scheme 4), were obtained.

The results indicated that the anionic lanthanide complexes are much more stable, as the less bulky ligand provides a larger coordination sphere around the lanthanide atom.

Complex **1** reacts with PhLiNSiMe₂NLiPh in 1:1 molar ratio to yield the expected anionic amide complex $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{THF})_2\text{Li}(\text{THF})\}$ (**6**) in high yield (Scheme 5).

All these complexes are air- and moisture-sensitive. They are soluble in tetrahydrofuran (THF) and dimethylethyl ether (DME), but hardly so in toluene and hexane.

Crystal Structure Analyses. The molecular structures of complexes **2–4** and **6** were determined by X-ray diffraction. Crystals of complexes **2–4** suitable for X-ray diffraction were grown from DME, while **6** was grown from toluene. Because complexes **2–4** have an analogous solid structure and the same monoclinic space groups, only the crystal structure of **2** is depicted in Figure 1 as a representation. The molecular structure of **6** is shown in Figure 2. Selected bond lengths and angles are given in Tables 1, 2, and 3, and details of the crystallographic data in Table 4.

As shown in Figure 1, the molecule contains the crystallographically independent anion $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}^-$ and the cation $[\text{Li}(\text{DME})_3]^+$. The lanthanide ion is ligated by two nitrogen atoms of the chelating diamide ligand and two cyclopentadienyl groups in η^5 -fashion. The coordination geometry around the lanthanide ion is best described as a pseudodistorted tetrahedron. The lithium atom in the cation is coordinated to six oxygen atoms from three DME molecules and adopts a distorted octahedral geometry.

The average lanthanide–carbon (ring) bond lengths for **2**, **3**, and **4** are 2.628, 2.727, and 2.640 Å, respectively. These values are comparable when the difference in the ionic radii between Sm and Yb is considered. The Ln–N bond lengths in complexes **2** and **4** are similar (2.250(4), 2.232(7) Å for **2** and 2.242(4), 2.254(4) Å for **4**), which are somewhat longer than those in

(17) Patent U.S. Nat. Aeronautics and Space Administration, U.S. 3433818.

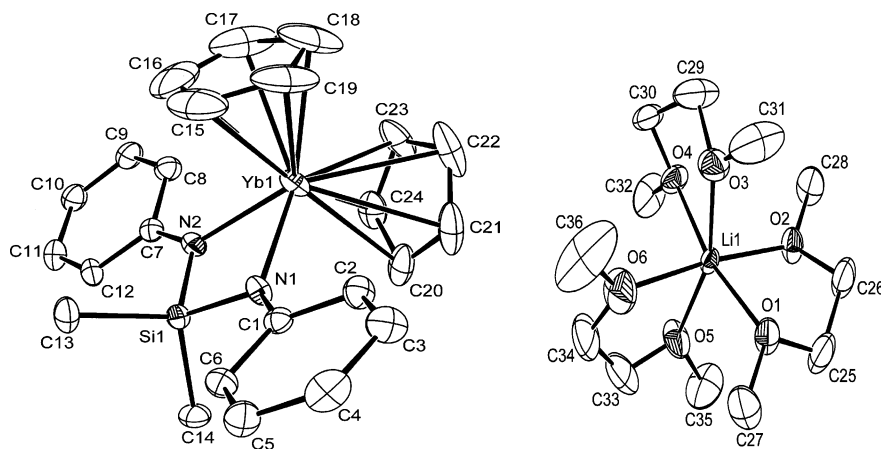


Figure 1. Molecular structure of complex 2.

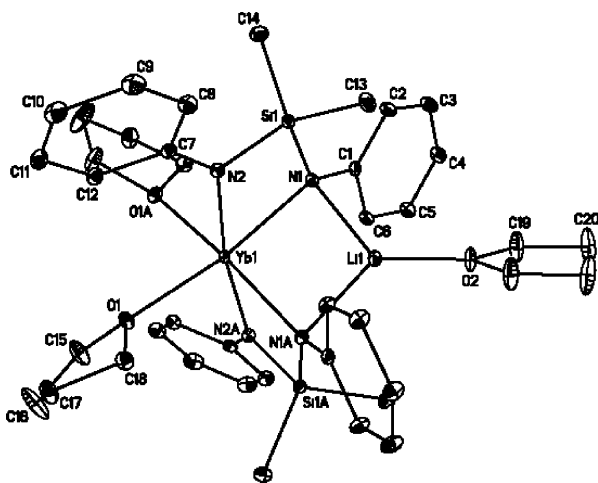


Figure 2. Molecular structure of complex 6.

Table 1. Selected Bond Distances (Å) for Complex 2, 3, and 4

	2	3	4
Ln(1)–N(1)	2.250(4)	2.340(4)	2.242(4)
Ln(1)–N(2)	2.232(7)	2.332(4)	2.254(4)
Ln(1)–C(15)	2.65(1)	2.745(6)	2.661(6)
Ln(1)–C(16)	2.64(1)	2.720(6)	2.635(7)
Ln(1)–C(17)	2.641(9)	2.733(6)	2.637(7)
Ln(1)–C(18)	2.67(1)	2.742(6)	2.628(7)
Ln(1)–C(19)	2.66(1)	2.741(6)	2.639(7)
Ln(1)–C(20/25)	2.59(1)	2.731(7)	2.622(8)
Ln(1)–C(21)	2.60(1)	2.726(7)	2.644(8)
Ln(1)–C(22)	2.61(1)	2.707(8)	2.632(7)
Ln(1)–C(23)	2.610(9)	2.703(7)	2.630(8)
Ln(1)–C(24)	2.610(8)	2.722(8)	2.611(8)
O(1)–Li(1)	2.11(1)	2.180(12)	2.178(14)
O(2)–Li(1)	2.07(2)	2.107(10)	2.121(11)
O(3)–Li(1)	2.21(1)	2.087(11)	2.254(17)
O(4)–Li(1)	2.11(1)	2.148(13)	1.969(14)
O(5)–Li(1)	2.08(2)	2.133(11)	2.163(17)
O(6)–Li(1)	2.14(1)	2.073(11)	2.034(14)

$[\text{N}(\text{C}_6\text{H}_3\text{-}^i\text{Pr}_2\text{-}2,6)(\text{SiMe}_3)_2\text{LnCH}_3(\mu\text{-CH}_3)\text{Li}(\text{THF})_3]$ (2.224(6) and 2.227(6) Å).¹⁴ The corresponding Ln–N bond lengths in complex 3 are 2.340(4) and 2.332(4) Å; these values are comparable to those of 2 and 4, when the difference in the ionic radii between the two metals is considered. The angles of N–Si–N bonds are 96.5(3)° for 2, 97.5(2)° for 3, and 97.0(2)° for 4, respectively, which are almost equal. The N–Ln–N angles in complexes 2 (70.0(2)°) and 4 (70.17(17)°) are almost the same and smaller than that of $[\text{N}(\text{C}_6\text{H}_3\text{-}^i\text{Pr}_2\text{-}2,6)(\text{SiMe}_3)_2\text{-LnCH}_3(\mu\text{-CH}_3)\text{Li}(\text{THF})_3]$ (121.3(2)°),¹⁴ indicating that the bridged

Table 2. Selected Bond Angles (deg) for Complexes 2, 3, and 4

	2	3	4
N(2)–Ln(1)–N(1)	70.0(2)	67.13(15)	70.17(17)
N(2)–Si(1)–N(1)	96.5(3)	97.5(2)	97.0(2)
N(2)–Si(1)–Ln(1)	48.6(2)	48.61(15)	48.66(15)
N(1)–Si(1)–Ln(1)	48.0(2)	48.93(15)	48.29(15)
Si(1)–N(1)–Ln(1)	96.3(2)	97.33(19)	96.5(2)
Si(1)–N(2)–Ln(1)	97.0(3)	98.0(2)	96.4(2)
O(1)–Li(1)–O(2)	78.5(6)	76.5(4)	78.1(4)
O(3)–Li(1)–O(4)	76.0(5)	77.1(4)	79.6(6)
O(5)–Li(1)–O(6)	77.4(5)	78.5(4)	73.8(6)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 6

Bond Distances			
Yb(1)–N(2)	2.281(2)	Si(1)–Li(1)	3.139(4)
Yb(1)–N(1)	2.300(2)	O(2)–Li(1)	1.847(8)
Yb(1)–O(1)	2.3361(19)	N(1)–Li(1)	2.093(5)
Yb(1)–Li(1)	2.965(7)	C(1)–Li(1)	2.575(3)
Yb(1)–Si(1)	3.0455(8)		
Bond Angles			
N(2)#1–Yb(1)–N(2)	170.66(12)	N(2)–Si(1)–N(1)	96.28(11)
N(2)#1–Yb(1)–N(1)	104.43(8)	N(1)–Li(1)–Yb(1)	50.57(17)
N(2)–Yb(1)–N(1)	68.59(8)	N(2)–Yb(1)–Li(1)	85.33(6)
N(1)–Yb(1)–N(1)#1	89.31(11)	N(1)–Yb(1)–Li(1)	44.65(6)
O(2)–Li(1)–Yb(1)	180.0	N(1)–Yb(1)–Si(1)	34.66(6)
Si(1)#1–Li(1)–Si(1)	119.6(2)	Li(1)–N(1)–Yb(1)	84.78(17)
Si(1)–Yb(1)–Si(1)#1	125.90(3)	N(1)–N(2)–Yb(1)	98.15(10)
N(2)–Si(1)–Yb(1)	47.84(8)	Si(1)–N(1)–Yb(1)	96.75(10)
N(1)–Si(1)–Yb(1)	48.58(7)	Yb(1)–Li(1)–Si(1)	59.78(12)

diamide ligand provides a more open coordination environment. The corresponding N–Ln–N angle in 3 (67.13(15)°) is smaller than those in 2 and 4, resulting from the difference in ionic radii between Sm and Yb.

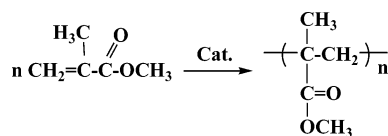
As shown in Figure 2, the space group of complex 6 is orthorhombic. The six-coordinate lanthanide center is ligated by four nitrogen atoms of two chelating diamide ligands and two oxygen atoms from two THF molecules and adopts a distorted octahedral geometry. The lithium atom is coordinated to two nitrogen atoms of two chelating diamide ligands and one oxygen atom from the THF molecule, and the structure adopts a trigonal geometry. The three coordinated lithium atom is scarcely found.

The Yb–N bond lengths in complex 6 are 2.281(2) and 2.300(2) Å, which are somewhat longer than those in complexes 2 and 4. The angle of N–Si–N is 96.28(11)°, which is almost equal to that in complex 2 (96.5(3)°). The two N–Yb–N angles in complex 6 are equal to 68.59(2)°, which is somewhat smaller than those in 2 and 4 (70.0(2)° and 70.17(17)°), indicating that two bridged diamide ligands make the central metal very

Table 4. Details of the Crystallographic Data of Complexes 2, 3, 4, and 6

	2	3	4	6
empirical formula	C ₃₆ H ₅₆ LiN ₂ O ₆ SiYb	C ₃₆ H ₅₆ LiN ₂ O ₆ SiSm	C ₃₈ H ₆₀ LiN ₂ O ₆ SiYb	C ₄₀ H ₅₆ LiN ₄ O ₃ Si ₂ Yb
fw	820.91	798.21	848.95	877.05
cryst color	red	yellow	red	yellow
temperature (K)	193.1	193(2)	193(2)	193(2)
wavelength (Å)	0.7107	0.7107	0.7107	0.7107
size (mm)	0.38 × 0.35 × 0.55	0.54 × 0.48 × 0.30	0.32 × 0.30 × 0.12	0.70 × 0.31 × 0.27
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>Pn</i> (#7)	<i>Pn</i>	<i>P2₁/c</i>	<i>pbcn</i>
<i>a</i> (Å)	17.038(1)	16.8941(16)	17.4946(18)	12.4130(5)
<i>b</i> (Å)	15.6124(10)	15.6116(14)	15.9091(13)	18.8362(8)
<i>c</i> (Å)	16.9013(13)	17.1362(19)	16.973(2)	17.8812(7)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	117.499(3)	117.361(2)	118.801(3)	90.00
γ (deg)	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	3987.9(5)	4014.0(7)	4139.7(7)	4180.9(3)
<i>Z</i>	4	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.367	1.321	1.362	1.393
absorp coeff (mm ⁻¹)	2.417	1.534	2.331	2.334
<i>F</i> (000)	1684.00	1652	1748	1796
θ (deg)	3.0–27.5	3.0–25.3	3.0–25.3	3.01–27.48
no. of reflns collected	88 030	39 202	40 642	43 594
no. of indep reflns	9450	13 781	7564	4802
no. of variables	959	849	417	235
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.029 [<i>I</i> > 3σ(<i>I</i>)]	0.0368	0.0499	0.0291
<i>R</i> _w	0.065	0.0861	0.1117	0.0644
GOF on <i>F</i> ²	1.001	1.063	1.116	1.117

Scheme 6

Table 5. Polymerization of MMA Initiated by Anionic Lanthanide Complexes^a

	init	[M]/[I]	conv ^b (%)	<i>M</i> _n (× 10 ⁴)	<i>M</i> _w / <i>M</i> _n ^c	tacticity ^d (%)		
						mm	rm	rr
1	2	500:1	96.8	3.40	1.54	6.1	34.6	59.3
2	2	1000:1	83.4	4.65	1.57	15.6	30.9	53.5
3	2	1500:1	72.0	5.37	1.60			
4	3	500:1	100	3.50	1.70	12.9	34.3	52.9
5	3	1000:1	69.9	4.30	1.78	14.8	31.0	54.3
6	3	1500:1	44.1	5.39	1.85			
7	4	500:1	100	3.11	1.58	13.5	30.5	56.0
8	4	1000:1	69.9	3.82	1.70	13.5	32.6	54.0
9	4	1500:1	48.4	4.21	1.77			
10	6	500:1	49.3	4.44	1.45			
11	7	500:1	73.0	3.23	1.50			

^a Polymerization conditions: sol/MMA = 2v/v, THF, 30 °C, 3 h. ^b Conv = weight of polymer obtained/weight of monomer used. ^c Measured by GPC calibrated with standard polystyrene samples. ^d Carried out using ¹H NMR spectra in CDCl₃ at 25 °C.

congested. Each chelating diamide ligand binds to Yb through two nitrogen atoms to yield a planar tetragon (sum of angles, 359.77°).

Catalytic Activity of 2–4 for the Polymerization of MMA.

The catalytic activity of 2–4 for the polymerization of MMA (Scheme 6) was first examined, and various conditions were explored.

Interestingly, all the complexes are able to initiate the polymerization of MMA in high activity under mild conditions as shown in Table 5. For example, the conversion reaches 96.8% in the case of [M]/[I] = 500 at 30 °C in 3 h using 2 as the initiator (entry 1, Table 5).

The central metal has a great influence on the activity. For example, the conversion reaches 83.4% in the loading of [M]/[I] = 1000 at 30 °C in 3 h using 2 as the initiator, while it is 69.9%

for 3 (entries 2 and 5, Table 5). The increasing order of Sm < Yb in activity is observed, which is just the opposite of the ionic radii, Sm (1.079 Å) > Yb (0.985 Å). The activity order contrasts that published for the catalyst systems of lanthanocene methyl complexes.^{2a} The reason for this is still not well understood. The substituent on the cyclopentadienyl ligand exerts a dramatic influence. A methyl substituent on the cyclopentadienyl ligand led to a decrease in the activity (entries 2, 3, 8, and 9).

The PMMAs obtained with these complexes have high molecular weights (*M*_n > 10⁴) and relatively narrow molecular weight distributions (*M*_w/*M*_n = 1.54–1.85), which is comparable with that obtained with Bochmann's anionic initiators of [Li(OEt₂)(THF)₃]⁺[Ln{3-(*η*³-C₃H₃SiMe₃-1)₂SiMe₂}₂]⁻ (1.85)¹² and better than that of the anionic complex [(3,6-^tBu₂C₁₃H₆)-SiMe₂N^tBu]₂La]⁻[Li(THF)₄]⁺ (2.8).¹⁰ In all cases, gel permeation chromatography shows a unimodal pattern, indicating only one kind of active species existed in the polymerization systems.

Triad microstructural analysis of the resulting polymers was carried out using ¹H NMR spectra in CDCl₃ according to the reported triad.¹⁸ The present polymerization systems all yielded the syndiotactic-rich PMMA, and the amount of syndiotacticity ranges from 53 to 59%.

Among all these complexes used here, complex 2 exhibits the highest catalytic activity. Thus, the effects of the solvent on both the activity and stereoselectivity were examined by using complex 2 as the initiator. The activity in THF solvent is much higher than that in toluene (entries 1 and 3, Table 6), and the polymerization in THF yielded the syndiotactic polymer, while the atactic polymer occurred in toluene. The change of stereospecificity may contribute to the coordination of THF, which favors the polymers with syndiotacticity. Such a solvent effect on the microstructure of PMMA is often observed in the anionic polymerization of MMA.^{9a,11,12c}

To understand further the possible polymerization mechanism, the polymerizations of MMA with the complexes Cp₃Yb, 1, CpLi, and PhLiNSi(Me)₂NLiPh, respectively, were first conducted under the same conditions (sol/MMA = 2v/v, [M]/[I]

Table 6. Effect of Solvent on Polymerization of MMA^a

solv	conv (%)	$M_n (\times 10^4)$	M_w/M_n	tacticity ^b (%)		
				mm	rm	rr
1 THF	96.8	3.40	1.54	6.1	34.6	59.3
2 THF:toluene = 1:1	100	2.70	1.60	6.7	36.8	56.5
3 toluene	15.7	2.59	1.45	29.0	41.7	29.3

^a Polymerization conditions: complex **2**, sol/MMA = 2v/v, [M]/[I] = 500, 30 °C, 3 h. ^b Carried out using ¹H NMR spectra in CDCl₃ at 25 °C.

= 500, THF, 30 °C, 3 h). The results show that all these complexes show no or very low activity (yield: 0, 0, 6.5, and 10.8%, respectively). Then, the anionic complex Cp₄YbLi-(THF)_n (**7**) was synthesized by the reaction of YbCl₃ with 4 equiv of CpLi in THF. The polymerization of MMA with the anionic complexes **6** and **7**, respectively, was performed under the above conditions. The two complexes both can initiate the polymerization of MMA with moderate activities, and the activity of **7** is higher than that of **6** (entries 10 and 11, Table 5). The results tell us that the polymerization might be initiated by either the amide or the Cp ligand present in the anionic complex. If the reaction goes by the former way, the end group of the polymer should be connected with the amide group, while with Cp group by the latter one. To answer the question, an oligomer of MMA was prepared from the oligomerization of MMA with a [MMA]/[initiator] mole ratio of 10 and characterized by ¹H NMR (CDCl₃, without TMS). A single peak at 0.06 ppm is assigned to the signal of the silylene group, while multiplets around 6.7–7.6 ppm might belong to the protons of the benzene of the amino group. According to the value of the molecular weights of the resulting polymer, it could be supposed that the polymerization of MMA is initiated by one Ln–N bond of the chelating diamide group. The postulated anionic polymerization of MMA is shown in Scheme 7. In the initiation step, the N of the amide attacks the CH₂ group of MMA to generate a transient species, and then the incoming MMA molecule may participate in a 1,4-addition to afford an eight-membered-ring intermediate. In the propagation step, another MMA molecule may attack the growing end, liberating the coordinated ester group. The polymerization should proceed by repeating these pathways. Further study on the reactivity of anionic complexes of lanthanides is proceeding.

Conclusion

In summary, a series of anionic lanthanocene complexes supported by silylene-bridged diamide ligand have been successfully synthesized for the first time. The structural features of **2–4** and **6** have been determined by an X-ray diffraction study. These anionic complexes can serve as single-component catalysts to initiate the polymerization of MMA at rt with high activity. The polymerization systems yield syndiotactic-rich polymers with high molecular weights ($M_n > /10^4$) and relatively narrow molecular weight distributions ($M_w/M_n = 1.54–1.85$). The results indicated that the anionic complexes of lanthanides should have potential in homogeneous catalysis. Further study on the reactivity of anionic complexes of lanthanides is proceeding in our laboratory.

Experimental Section

General Procedures. All manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone

ketyl prior to use. The silylene-bridged diamide ligand PhNHSi-(Me)₂NHPh¹⁷ and anhydrous LnCl₃¹⁹ were prepared according to the literature procedures. Melting points were determined in sealed Ar-filled capillary tubes. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Analysis of Ln was carried out by complexometric titration of EDTA. The IR spectra were recorded on a Magna-IR 550 spectrometer. Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography (GPC) on a waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4); THF was used as an eluent at 30 °C. ¹H NMR spectra were measured on a Unity Inova-400 spectrometer in C₆D₆ or CDCl₃.

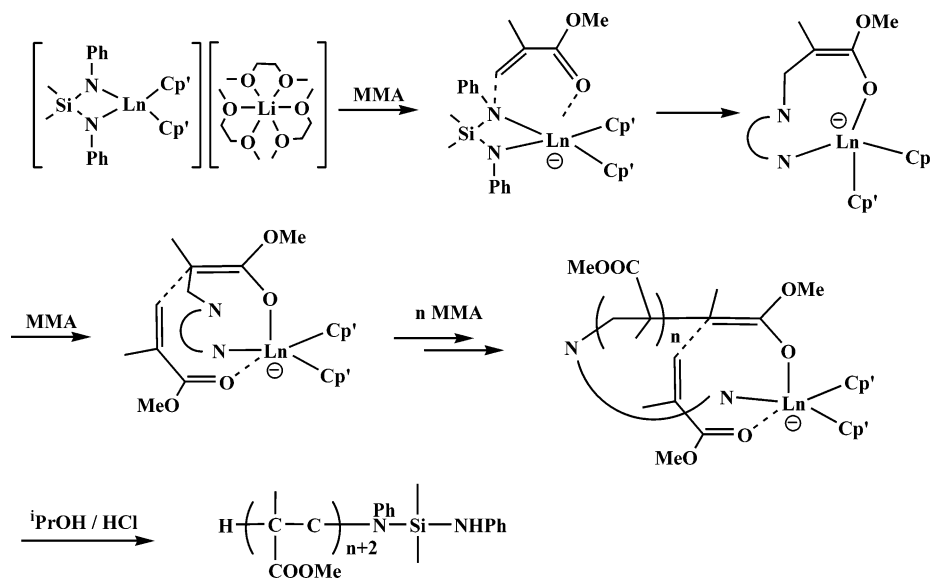
{[Me₂Si(NPh)₂]YbCl(TMEDA)}₂ (**1**). A Schlenk flask was charged with PhNHSi(Me)₂NHPh (1.00 g, 4.10 mmol), THF (15 mL), and a stir bar. The solution was cooled to 0 °C, and n-BuLi (8.20 mL, 8.2 mmol, 1.00 M in hexane) was added. The solution was slowly warmed to room temperature and stirred for 1 h. Then this solution was added slowly to a pale gray slurry of YbCl₃ (1.15 g, 4.12 mmol) in 15 mL of THF. The resulting red solution was then stirred for another 24 h and removed under vacuo. The residue was extracted with toluene, and LiCl was removed by centrifugation. After the extracts were concentrated and TMEDA added, red crystals of {[Me₂Si(NPh)₂]YbCl(TMEDA)}₂·3C₇H₈ (2.45 g, 85%) were obtained at –30 °C for few days. Mp: 165–166 °C (dec). The ¹H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of Yb metal. Anal. Calc for C₆₁H₈₈Cl₂N₈Si₂Yb₂: C, 52.09; H, 6.31; N, 7.97; Yb, 24.60. Found: C, 52.01; H, 6.51; N, 7.85; Yb, 24.76. IR (KBr pellet, cm⁻¹): 3036 (w), 2963 (w), 2832 (w), 2782 (w), 2627 (w), 2458 (w), 1605 (s), 1501 (s), 1397 (m), 1242 (s), 1157 (s), 1096 (m), 1026 (m), 976 (w), 802 (m), 756 (m), 694 (m), 625 (w), 556 (w), 505 (m).

{[Me₂Si(NPh)₂]YbCp₂}{Li(DME)₃} (**2**). **Path A.** A Schlenk flask was charged with YbCl₃ (0.78 g, 2.80 mmol, 15 mL of THF) and PhNLSi(Me)₂NLiPh (2.80 mmol, 20 mL of THF), and the solution was stirred for 4 h at room temperature. Then CpNa (5.60 mL, 5.60 mmol, 1.00 M in THF) was added. The resulting solution was then stirred for another 48 h and removed under vacuo. The residue was extracted with DME, and LiCl was removed by centrifugation. Concentration of the extracts and crystallization at rt for a few days gave **1** as red crystals (1.73 g, 75%). Mp: 127 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 6.37–7.22 (br, 20H, H-Ph, H-Cp); 2.00–4.00 (br, 30H, OCH₂, OCH₃); 0.18–0.36 (br, 6H, SiCH₃). Anal. Calc for C₃₆H₅₆LiN₂O₆SiYb: C, 52.67; H, 6.88; N, 3.41; Yb, 21.08. Found: C, 52.34; H, 6.95; N, 3.29; Yb, 20.85. IR (KBr pellet, cm⁻¹): 2959 (w), 2928 (w), 2859 (w), 1628 (s), 1609 (s), 1389 (m), 1262 (m), 1084 (m), 1026 (m), 910 (w), 802 (m), 752 (w), 694 (w), 469 (w).

Path B. A Schlenk flask was charged with a pale gray slurry of YbCl₃ (0.63 g, 2.26 mmol) in 15 mL of THF, and then CpNa (4.52 mL, 4.52 mmol, 1.00 M in THF) was added by a syringe. The solution was stirred for 4 h at room temperature, and then the fresh dilithium PhLiSiMe₂NLiPh (2.26 mmol) was added. The resulting solution was then stirred for another 48 h and removed under vacuo. Treatment as path A and crystallization from DME yielded red crystals (1.35 g, 73%).

{[Me₂Si(NPh)₂]SmCp₂}{Li(DME)₃} (**3**). Following a procedure similar to the synthesis of complex **2** (path A), using 2.65 mmol of PhNLSi(Me)₂NLiPh, 0.68 g of SmCl₃ (2.65 mmol), 5.30 mmol of CpNa (5.30 mL, 1.00 M), and 45 mL of THF, followed by crystallization from DME, yielded yellow crystals of **3** (1.65 g, 78%). Mp: 120 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 7.15–7.20 (m, 10H, H-Ph); 6.74–6.82 (m, 10H, H-Cp); 3.17 (m, 12H, OCH₂); 3.04 (m, 18H, OCH₃), 0.17 (s, 6H, SiCH₃). Anal. Calc for C₃₆H₅₆LiN₂O₆SiSm: C, 54.17; H, 7.07; N, 3.51; Sm, 18.84.

Scheme 7. Possible Polymerization Mechanism



Found: C, 54.01; H, 6.90; N, 3.63; Sm, 18.75. IR (KBr pellet, cm^{-1}): 3041 (w), 2956 (w), 2925 (w), 1729 (w), 1605 (s), 1497 (s), 1389 (m), 1289 (s), 1173 (w), 1104 (w), 1089 (w), 1027 (w), 911 (m), 834 (w), 795 (m), 756 (m), 695 (w), 664 (w), 471 (w).

$\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{CpMe})_2\}\{\text{Li}(\text{DME})_3\}$ (**4**). Path A. Following a procedure similar to the synthesis of complex **2**, path A, using 2.80 mmol of $\text{PhN}(\text{LiSi}(\text{Me})_2\text{N}(\text{LiPh}))$, 0.78 g of YbCl_3 (2.80 mmol), 5.60 mmol of MeCpNa (5.09 mL, 1.10 M) and 50 mL of THF, followed by crystallization from DME, yielded red crystals of **4** (1.62 g, 68%). Mp: 167–168 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ 6.75–7.20 (m, 20H, *H*-Ph, *H*-Cp); 3.37 (m, 12H, OCH_2); 3.16 (m, 18H, OCH_3); 1.40 (s, 6H, CpCH_3); 0.17 (s, 6H, SiCH_3). Anal. Calc for $\text{C}_{38}\text{H}_{62}\text{LiN}_2\text{O}_6\text{SiYb}$: C, 53.64; H, 7.34; N, 3.29; Yb, 20.33. Found: C, 53.49; H, 7.28; N, 3.46; Yb, 20.13. IR (KBr pellet, cm^{-1}): 3041 (m), 2964 (m), 1605 (s), 1497 (s), 1389 (m), 1289 (s), 1081 (w), 1027 (w), 996 (w), 911 (s), 834 (m), 795 (m), 756 (m), 695 (m), 656 (w), 563 (w), 463 (w).

Path B. Following a procedure similar to the synthesis of complex **2**, path B, using a solution of $(\text{MeCp})_2\text{YbCl}$ (3.00 mmol), $\text{PhN}(\text{LiSi}(\text{Me})_2\text{N}(\text{LiPh}))$ (3.00 mmol), and 45 mL of THF, followed by crystallization from DME, yielded complex **4** as red crystals (1.79 g, 70%).

$\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{THF})_2\text{Li}(\text{THF})\}$ (**6**). A Schlenk flask was charged with YbCl_3 (1.01 g, 3.60 mmol, 15 mL of THF) and $\text{PhN}(\text{LiSi}(\text{Me})_2\text{N}(\text{LiPh}))$ (3.60 mmol, 20 mL of THF), and the solution was stirred for 4 h at rt. Then $\text{PhN}(\text{LiSi}(\text{Me})_2\text{N}(\text{LiPh}))$ (3.60 mmol, 15 mL of THF) was added. The resulting yellow solution was then stirred for another 48 h and removed in vacuo. The residue was extracted with toluene, and LiCl was removed by centrifugation. Concentrating the extracts at rt for few days gave **6** as yellow crystals (2.54 g, 80%). Mp: 114–115 °C (dec). The ^1H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of ytterbium metal. Anal. Calc for $\text{C}_{40}\text{H}_{56}\text{LiN}_4\text{O}_3\text{Si}_2\text{Yb}$: C, 54.78; H, 6.44; N, 6.39; Yb, 19.73. Found: C, 54.33; H, 6.46; N, 6.28; Yb, 20.05. IR (KBr pellet, cm^{-1}): 2963 (w), 2932 (w), 2890 (w), 2168 (w), 1632 (s), 1570 (m), 1385 (m), 1265 (m), 1076 (m), 899 (w), 868 (w), 802 (m), 690 (m), 617 (w), 478 (w).

$\text{Cp}_4\text{YbLi}(\text{THF})_n$ (**7**). A Schlenk flask was charged with a pale gray slurry of YbCl_3 (0.84 g, 3.00 mmol) in 15 mL of THF, and then CpLi (24 mL, 12.00 mmol, 0.50 M in THF) was added by a

syringe. After about 24 h, the solvent was removed under vacuo, and the residue was extracted with 30 mL of toluene to remove the LiCl . The resulting solution was concentrated and cooled at 0 °C. Then the dark green crystals (2.45 g, 85%) were obtained. The ^1H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of ytterbium metal. IR (KBr pellet, cm^{-1}): 2956 (m), 2933 (m), 1628 (m), 1513 (s), 1412 (s), 1258 (w), 1158 (w), 1088 (w), 1019 (w), 895 (w), 664 (s), 617 (s).

X-ray Structure Determination. Owing to air- and moisture-sensitivity, suitable single crystals of complexes **2–4** and **6** were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo $\text{K}\alpha$ ($\lambda = 0.71070$ Å) radiation. Details of the intensity data collection and crystal data are given in Tables 1–4. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined using the SHELXS-97 and SHELXL-97 programs.

Typical Polymerization Procedure. All polymerizations were carried out in a 50 mL Schlenk flask under a dry Ar atmosphere. A typical polymerization reaction is given below (entry 1, Table 5). A 50 mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of 1 mL of MMA in THF (0.14 mL). To this solution was added 1.86 mL of a solution of complex **2** in THF (1.0×10^{-2} M, 1.86×10^{-3} mmol) using rubber septum and syringe. The contents of the flask were then vigorously stirred for 3 h at 30 °C. The polymerization was quenched by ethanol with 5% HCl, precipitated from ethanol, dried under vacuum, and weighed.

Acknowledgment. We are indebted to the Chinese National Natural Science Foundation for financial support.

Supporting Information Available: X-ray crystallographic data for the structure determination of **2–4** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060055V