Organometallics **2008,** *27,* 5889–5893

Rare-Earth Metal Bis(alkyl)s Supported by a Quinolinyl Anilido-Imine Ligand: Synthesis and Catalysis on Living Polymerization of ε-Caprolactone

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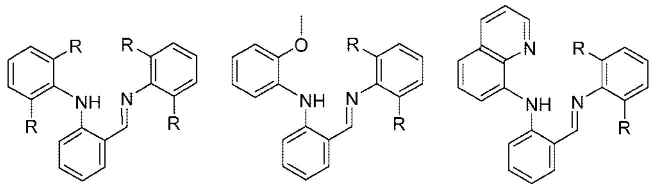
Received June 22, 2008

The tridentate ligand *N*-(2-((2,6-diisopropylphenylimino)methyl)phenyl)quinolin-8-amine (**HL**) was prepared. Treatment of **HL** with 1 equiv of $Ln(CH_2SiMe_3)_3(THF)_2$ afforded the corresponding rare-earth metal bis(alkyl) complexes $\mathbf{L}Ln(CH_2SiMe_3)_2(THF)_n$ (Ln = Sc, *n* = 0 (**1**); Y, *n* = 1 (**2**); Lu, *n* = 0 (**3**)) in high yields. Variable-temperature ^1H NMR spectral analysis showed that these complexes were fluxional at room temperature. Complexes **1** and **3** were THF-free, where the metal center adopted a square-pyramidal geometry, while in **2** the metal center generated a distorted octahedral geometry owing to the coordination of a THF molecule. All these complexes catalyzed the ring-opening polymerization of ε-caprolactone with high activities in living fashion, among which the Lu complex was proved to be more active than its Sc and Y analogues.

Introduction

Rare-earth metal alkyl complexes have attracted considerable interest in the catalytic area and have been widely used as single-component catalysts for the polymerizations of polar monomers or as crucial precursors of cationic counterparts after being activated by MAO or borates for the polymerizations of olefin and conjugated dienes.[1] In the past decades the most studied rare-earth metal alkyl complexes are stabilized by cyclopentadienyl (Cp) ligands.[2] Recently, non-Cp ligands based on N, O, and P heteroatoms[3] have attracted increasing attention by virtue of their strong metal−ligand bonds and exceptional and tunable steric and electronic features required for compensating coordinative unsaturation of metal centers and catalytic activity toward polymerization,[4] whereas formation of solvent or salt adducts, dimerization, or ligand redistribution hinder the isolation of rare-earth metal alkyl complexes, especially bis(alkyl) complexes supported by such ligands. Thus to develop ligands with bulky substitutes and multicoordination sites becomes a major strategy for stabilizing rare-earth metal bis(alkyl) species. Piers and co-workers have employed anilido-imine derivatives (Chart 1, **A**) to stabilize yttrium dialkyl complexes ($\textit{ortho}\text{-}C_6H_4N(C_6H_3{}^iPr_2)CH{=}NC_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(THF)$ (**4**). When bearing bulky substituents on both sides, such ligands can saturate even the organoyttrium cations,[5] whereas stabilized derivatives based on other lanthanide elements with larger ionic radius have not been available. Recently, our group has reported the amino-imino-ligated yttrium complexes ($\textit{ortho}\text{-}C_6H_4N(C_6H_4OMe)CH{=}NC_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(THF)$ (**5**), where the functional methoxy group is coordinated to the metal center to increase the sterics and coordination sites of the ligand (Chart

Chart 1



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10.1021/om800575p CCC: $40.75 © 2008 American Chemical Society
Publication on Web 10/11/2008

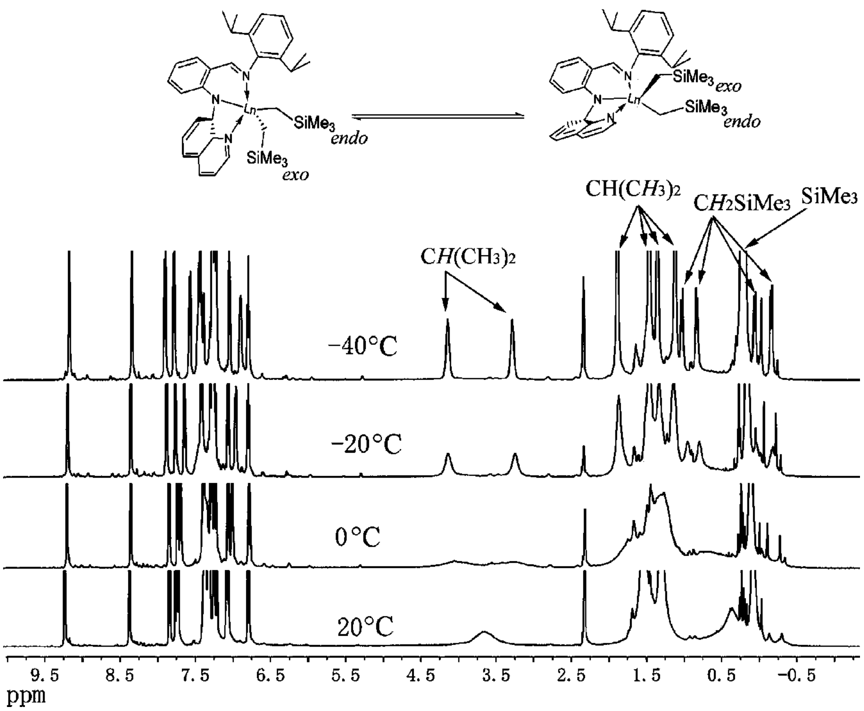

Figure 1. Variable-temperature ^{1}H NMR spectrum of **1**.

1, **B**).[6] This yttrium complex exhibited a single-site nature to initiate the polymerization of lactide, avoiding back-biting. Keeping in mind that a more rigid backbone would protect the metal center as well, we introduced the quinolinyl group into the amino-imine compound, which is more rigid than the methoxy group, to form NNN tridentate pincer ligands. Here we report the synthesis of rare-earth metal alkyl complexes bearing such ligands. The catalytic behavior of these complexes toward the polymerization of ε-caprolactone will also be presented.

Result and Discussion

Synthesis and Characterization. The NNN-tridentate ligand *N*-(2-((2,6-diisopropylphenylimino)methyl)phenyl)quinolin-8-amine (**HL**) was prepared by the reaction of 8-aminoquinolinelithium with 1 equiv of $o\text{-}C_6H_4F(CH{=}NC_6H_3{}^i\mathrm{Pr}_2\text{-}2,6)$ in THF in a moderate yield. The ^{1}H NMR spectrum shows an NH signal at δ 12.05 ppm, which is typical for amino-imino ligands and β-diimine ligands.[4h,5]

Abstracting the amino proton of **HL** with rare-earth metal tri(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$, took place immediately at room temperature upon addition, with the color changing from yellow to deep red. Evaporating the solvent afforded red powders of the corresponding complexes $LLn(CH_2SiMe_3)_2(THF)_n$ (Ln = Sc, *n* = 0 (**1**); Y, *n* = 1 (**2**); Lu, *n* = 0 (**3**)). The complexes **1**−**3** were characterized by ^{1}H NMR spectral analyses, which displayed similar topology. The singlets within 8.12−8.28 ppm were assigned to the *H*C=N protons, and the signals arising from the silylmethyl groups were comparable to other related complexes. The methylene protons of the alkyl groups CH_2SiMe_3 and the methyl and methine protons of $CH(CH_3)_2$ from the ligands were highly fluxional in solution to give broadened resonances. This has been found in the [ONO]-type rare-earth metal alkyl complexes and their cationic counterparts[7] and some transition metal complexes.[8] Variable-temperature ^{1}H NMR studies revealed the flip between two enantiomers, which could be frozen out on the NMR time scale at −20 °C. The two sharp singlets at δ 3.05 and 3.91 ppm and the four singlets around δ 0.90−1.65 ppm were assignable to the methine and methyl protons of $C\mathit{H}(CH_3)_2$, respectively, while the four doublet signals at δ −0.379, −0.159, 0.612, and 0.789 ppm arose from *exo* and *endo* $C\mathit{H}_2SiMe_3$ groups (Figure 1).

In **1** and **3** the flip might take place directly between the two conformations. As complex **2** was a THF solvate, the disassociation and recoordination of the THF molecule on a time scale should be considered; thus a pseudo-five-coordinate model of the complexes was favored during the flip.[7d]

Complexes **1**, **2**, and **3** have been characterized by X-ray diffraction analysis. The ORTEP diagrams are shown in Figures 2 and 3, and the crystallographic data are summarized in Table 1. Complexes **1** and **3** are THF-free monomers. This could be attributed to the rigid and bulky tridentate coordinating quinolinyl-imino ligand. The metal centers are five-coordinate, adopting a distorted square-pyramidal geometry with atoms N(1), N(2), N(3), and an alkyl carbon in the square plane with the other alkyl carbon as the apex. Thus the two metal alkyl groups are *exo* and *endo* to the C1−C6 ring. Complex **2** is a THF solvate. The yttrium ion is six-coordinate, and the geometry around it can be well described as distorted octahedral. The average bond length of Ln−C is 2.219 Å in **1** and 2.341 Å in **3**, similar to those found in other lutetium bis(alkyl)s.[2c,4c,d,5,9]

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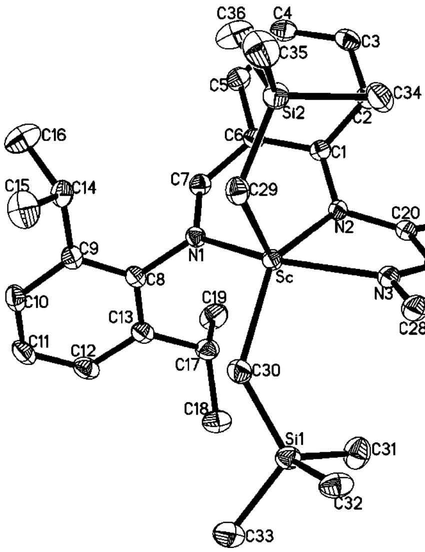

Figure 2. X-ray structure of **1** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−Sc = 2.271(2), N(2)−Sc = 2.172(2), N(3)−Sc 2.290(2), C(29)−Sc = 2.209(3), C(30)−Sc = 2.230(3); N(1)−Sc−N(2) = 79.90(7), N(2)−Sc−N(3) = 73.07(8), C(29)−Sc−C(30) = 106.46(10).

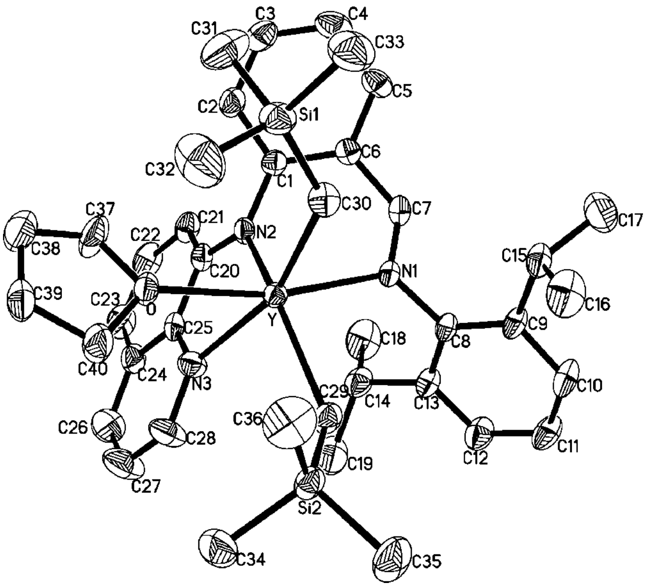

Figure 3. X-ray structure of **2** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−Y = 2.494(4), N(2)−Y = 2.332(4), N(3)−Y = 2.540(4), O(1)−Y = 2.400(4), C(29)−Y = 2.414(5), C(30)−Y = 2.412(5); N(1)−Y−N(2) = 71.96(14), N(2)−Y−N(3) = 66.12(15), C(29)−Y−C(30) = 104.31(19).

The Ln−N(2) bond lengths of 2.172(2) Å in **1**, 2.332(4) Å in **2**, and 2.286 Å in **3** are well consistent with their ionic radii and are comparable to those found in [2-(2,6-$R_2C_6H_3N$=CH)-C_4H_3N]Ln$(CH_2SiMe_3)_2(THF)_2$.[4d] The dihedral angle between quinolinyl (C_{20}−C_{28}, N_3) and the parent coordinate plane (C_1, C_6, C_7, N_1, N_2) of 43.69(10)° in **1** and 44.36(18)° in **3**, respectively, is smaller than that of 51.84(24)° in **2** due to the crowded environment in the metal center arising from the coordinated THF molecule. As compared to complexes **4** and **5**, the metal centers in **1**, **2**, and **3** are more crowded, and these differences in the solid-state structures contribute significantly to their different catalytic performances.

Table 1. Summary of Crystallographic Data for Complexes 1, 2, and 3

	1	**2**	**3**
formula	$C_{36}H_{50}N_3ScSi_2$	$C_{40}H_{58}N_3OSi_2Y$	$C_{36}H_{50}LuN_3Si_2$
fw	625.93	741.98	755.94
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a (Å)	10.0455(10)	11.2166(14)	10.1020(8)
b (Å)	10.5478(10)	20.184(3)	10.6056(9)
c (Å)	18.0428(17)	20.545(3)	17.9299(14)
α (deg)	84.010(2)	90	84.1090(10)
β (deg)	82.350(2)	64.610(3)	81.7550(10)
γ (deg)	73.292(2)	90	74.0980(10)
V (Å^3)	1810.4	4202.0(9)	1824.3(3)
Z	2	4	2
μ (mm^{-1})	0.297	1.476	2.798
R_{int}	0.0210	0.1343	0.0325
GOOF	1.026	0.927	0.989
R_1	0.0532	0.0678	0.0447
wR_2	0.1221	0.1115	0.0824

Table 2. Polymerization of ε-Caprolactone with Complexes 1−3[a]

entry	initiator	M/I	time (min)	conversion (%)	$M_{n\,calcd}{}^{b} \times 10^{-4}$	$M_n{}^{c} \times 10^{-4}$	M_w/M_n
1	**1**	945	30	99	10.7	9.45	1.18
2	**2**	945	5	100	10.8	9.91	1.41
3	**3**	945	2	100	10.8	11.2	1.41
4	**2**	94.5	5	100	1.1	1.31	1.24
5	**2**	283	5	100	3.24	2.47	1.30
6	**2**	472	5	100	5.4	4.46	1.38
7	**2**	1890	10	98	21.2	25.34	1.43
8	**4**	945	5	93	5.0[d]	4.5	1.39
9	**5**	945	5	100	10.8	9.1	1.87

[a] Polymerization condition: 10 μmol of initiator; T = 25 °C; 20 mL of toluene. [b] Calculated from $MW_{\varepsilon\text{-CL}}$ ([ε-CL]$_0$/[Ln]$_0$) × conversion. [c] Determined by GPC relative to polystyrene standards, multiplied by 0.56. [d] Calculated from $MW_{\varepsilon\text{-CL}}$ ([ε-CL]$_0$/[Ln]$_0$) × conversion × 0.5.

Ring-Opening Polymerization of ε-Caprolactone. The ring-opening polymerization (ROP) of ε-caprolactone provides a biocompatible and biodegradable polymer used widely as a delivery system for the controlled release of drugs and tissue engineering.[10] Many catalytic systems have been investigated to initiate such polymerizations, for instance ionic initiators and coordination initiators.[11] Both types of systems usually encounter the back-biting and transesterification problems, which impede isolation of the polymer with high molecular weight and narrow molecular weight distribution.[12] Complexes **1**−**3** were applied to initiate the polymerization of ε-caprolactone as shown in Table 2 and exhibited high activities at room temperature. When using complexes **2** and **3** as the initiators, full conversions could be achieved within 5 min, whereas the Sc complex **1** showed lower activity compared with its Y and Lu analogues, such that completion could be reached by prolonging the reaction time to 30 min. It was noteworthy that for all these systems the polymer obtained had an M_n value close to the theoretic one,

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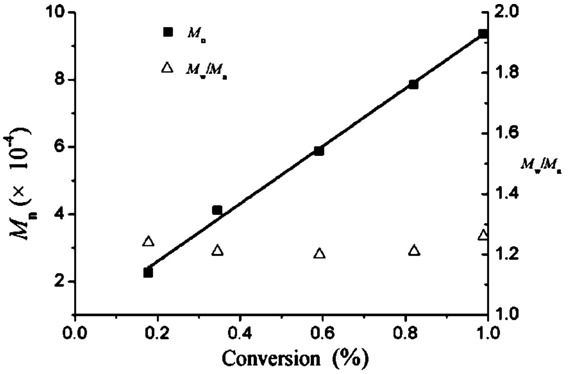


Figure 4. Polymerization of ε-caprolactone with complex **1** as initiator: molecular weight vs conversion. Conditions: [M]/[Sc] = 1000, 10 mL of toluene, 25 °C.

which was calculated on the basis of one alkyl participating in the initiation, indicating that these complexes were "single-site". This could be explained by the geometry of the metal alkyl moieties that are arranged in *endo* and *exo* positions (*vide supra*). During the polymerization process, the monomer prefers to insert into the *exo* alkyl, which is sterically less shielded than the *endo* alkyl. As the insertion of the monomer makes the metal center more crowded, impeding the flip between the *endo* and *exo* moieties, the polymerization is performed in a "single-site" model. Such a phenomenon has been observed in other rare-earth metal bis(alkyl) complexes, where only one of the two alkyl species initiates polymerization.[6] In addition by using complex **2** polymerization could perform fluently under various monomer-to-initiator ratios ranging from 100 to 2000; the molecular weight of the resultant polymer showed an approximately linear increase with the ratio, suggesting that this system could initiate controlled polymerization of ε-caprolactone. Dynamic study of the polymerization with **1** demonstrated that the conversion increased with polymerization time, which had a linear correlation with the number-average molecular weight (M_n) of the obtained polymer, while the molecular weight distribution (M_w/M_n) was narrow and remained almost unchanged (1.18−1.26) (Figure 4). This result was indicative of the living nature of the present catalyst systems and the controlled nature of the ROP of ε-caprolactone. In order to evaluate the influence of ligands on the catalytic performances of the attached complexes, the analogues to **1**−**3** bearing amino-imine auxiliaries, complexes **4** and **5** reported previously by Piers and our group, were employed to initiate the polymerization of ε-caprolactone. The results showed that in the case of **4** being the initiator the molecular weight of the resultant PCL was halved compared with that of using **2** as initiator, suggesting that both metal-alkyl species participated in the initiation. This could probably be attributed to the less steric coordination sphere of the ligand. While with **5** as the initiator, the molecular weight of the PCL obtained was close to the value calculated based on the one-alkyl model albeit with broader molecular weight distribution. This result indicated that the introduction of the NNN-tridentate, rigid ligand into the lanthanide bis(alkyl) complexes **1**−**3** had obviously impeded the back-biting and chain-transfer reactions in the polymerization of ε-caprolactone.

Conclusion

Sc, Y, and Lu bis(alkyl) complexes supported by an NNN-tridentate quinolinyl anilindo-imine ligand have been synthesized by treatment of rare-earth metal tris(alkyl)s with quinolinyl anilindo-imine and well characterized. All these complexes can initiate the polymerization of ε-caprolactone in living mode under broad monomer-to-initiator ratios to afford high molecular weight polymer with low polydispersity. The lutetium complex has a much higher catalytic activity as compared with its scandium and yttrium counterparts.

Experimental Section

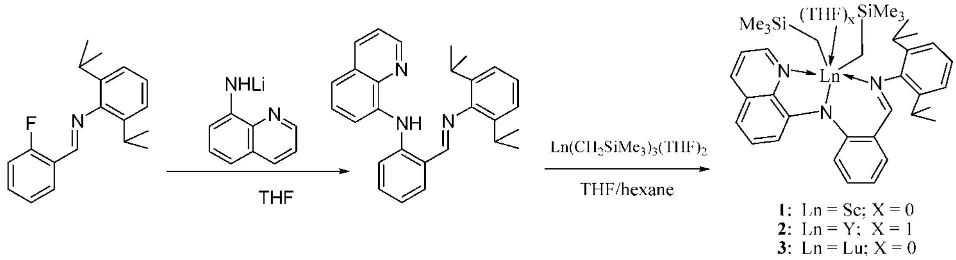
General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. All solvents were purified from an SPS system. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC experiments when necessary. The molecular weight and molecular weight distribution of the polymers were measured by a GPC Tosoh-8220. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). 2,6-Diisopropylaniline was obtained from Aldrich and purified by distillation before use. o-$C_6H_4F(CH{=}NC_6H_3{}^iPr_2$-2,6),[5] *ortho*-$C_6H_4\{N(C_6H_3{}^iPr_2)\}(CH{=}NC_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(THF)$,[5] and *ortho*-$C_6H_4\{N(C_6H_4OMe)\}(CH{=}NC_6H_3{}^iPr_2)Y(CH_2SiMe_3)_2(THF)$[6] were synthesized according to the literature.[5]

X-ray Crystallographic Study. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

***N*-(2-((2,6-Diisopropylphenylimino)methyl)phenyl)quinolin-8-amine (HL).** An *n*-BuLi solution of hexane (15 mL, 25.0 mmol) was added to a THF (40 mL) solution of 8-aminoquinoline (2.0 g, 22 mmol) at −78 °C, and the mixture was allowed to warm to room temperature overnight. The resulting solution of LiNHAr was cannula-transferred into a solution of o-$C_6H_4F(CH{=}NC_6H_3{}^iPr_2$-2,6) (4.0 g, 20.0 mmol) in 45 mL of THF at room temperature. After stirring for 4 h, the reaction mixture was quenched with 10 mL of H_2O, extracted with *n*-hexane, and evaporated to dryness *in vacuo*, and the desired product was obtained by chromgraphy in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, 12H, J_{H-H} = 6.9 Hz, $CH(CH_3)_2$), 3.23 (m, 2H, $CH(CH_3)_2$), 6.92 (m, 1H), 7.39−7.47 (m, 1H), 7.84 (t, 2H), 7.98 (d, 1H), 8.37 (s, 1H, *H*C=N), 8.67 (d, 1H, J_{H-H} = 1.2 Hz, 2-quinolinyl), 12.05 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 24.07 (s, 4C, $CH(CH_3)_2$), 28.47 (s, 2C, $CH(CH_3)_2$), 113.74 (s, 1C, Ph), 115.56 (s, 1C, Ph), 119.13 (s, 1C, Ph), 119.85 (s, 1C, Ph), 121.68 (s, 1C, Ph), 121.95 (s, 1C, Ph), 123.42 (s, 2C, Ph), 124.74 (s, 2C, Ph), 127.08 (s, 2C, Ph), 129.54 (s, 1C, Ph), 132.18 (s, 1C, Ph), 135.26 (s, 1C, Ph), 136.24 (s, 1C, Ph), 138.79 (s, 1C, Ph), 139.54 (s, 1C, Ph), 141.29 (s, 1C, Ph), 144.80 (s, 1C, Ph), 148.89 (s, 1C, Ph), 149.74 (s, 2C, Ph), 165.15 (s, 1C, *C*H=N) ppm.

[2-(2,6-^{i}Pr$_2$C$_6$H$_3$NC(H)C$_6$H$_4$-C$_9$H$_6$N)Sc(CH$_2$SiMe$_3$)$_2$ (1). To a hexane solution (5.0 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.246 g, 0.55 mmol) was added dropwise 1 molar equiv of **HL** (0.20 g, 0.5 mmol) in 5 mL of THF at room temperature, and the resulting red mixture was stirred for 20 min. Removal of the volatiles gave a deep yellowish, oily residue. The residue was dissolved with 3 mL of

Scheme 1. Synthesis of Ligand and Complexes



hexane and then cooled to −30 °C for 12 h to give a yellow solid. The solid was washed carefully by a small amount of hexane (0.5 mL) and then dried *in vacuo* to afford complex **1** in 85% yield (0.26 g). Red crystals for X-ray analysis grew from a mixture of toluene and hexane at −30 °C within a week. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.02 (s, 18H, Sc-CH_2SiMe_3), 0.31(b, 4H, Sc-CH_2SiMe_3), 0.98−1.40 (b, 12H, CH-$CH(CH_3)_2$), 3.56 (b, 2H, $CH(CH3)_2$), 6.68 (t, 1H, $^3J_{H-H}$ = 6 Hz, Ar-H), 6.92 (q, 1H, $^3J_{H-H}$ = 4.8 Hz, Ar-H), 6.98 (d, 1H, $^3J_{H-H}$ = 8 Hz, 3-quinolinyl), 7.10−7.27(m, 6H, Ar-H), 7.63 (s, 1H, 7-quinolinyl), 7.65 (s, 1H, $^3J_{H-H}$ = 6 Hz, 4-quinolinyl), 7.75 (d, 1H, $^3J_{H-H}$ = 6 Hz, 5-quinolinyl), 8.28 (s, 1H, N═C*H*), 9.13 (d, 1H, $^3J_{H-H}$ = 2.7 Hz, 2-quinolinyl) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 3.96 (6C, $SiMe_3$), 23.21 (1C, *C*HMe$_2$), 26.39 (s, 4C, CH(CH_3)), 44.32 (b, 2C, CH_2SiMe_3), 117.30 (s, 1C, 7-quinolinyl), 118.42 (s, 1C, Ar), 119.45 (s, 1C, Ar), 121.67 (s, 1C, 3-quinolinyl), 122.28 (s, 1C, 5-quinolinyl), 124.84 (s, 1C, Ar), 129.50 (s, 1C, Ar), 130.86 (s, 1C, Ar), 135.22 (s, 1C, Ar), 136.81 (s, 1C, Ar), 140.28 (s, 1C, Ar), 141.96 (s, 1C, Ar), 142.90 (s, 1C, 4-quinolinyl), 148.81 (s, 1C, Ar), 149.26 (1C, 2-quinolinyl), 149.60 (s, 1C, 9-quinolinyl), 153.68 (s, 1C, 10-quinolinyl), 171.27 (1C, N═*C*H) ppm. Anal. Calcd for $C_{36}H_{50}N_3ScSi_2$ (%): C, 69.08; H, 8.05; N, 6.71. Found: C, 69.04; H, 8.01; N, 6.68.

[2-(2,6-^{i}Pr$_2$C$_6$H$_3$NC(H)C$_6$H$_4$-C$_9$H$_6$N)Y(CH$_2$SiMe$_3$)$_2$(THF) (2). Following a similar procedure to that described for the preparation of **1**, treatment of a toluene solution (5.0 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.26 g, 0.52 mmol) with 1 equiv of **HL** (0.20 g, 0.5 mmol) in 5 mL of THF afforded complex **2** (0.28 g, 76%) as a red powder. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.36 (s, 4H, CH_2SiMe_3), 0.21 (s, 18H, CH_2SiMe_3), 1.02 (b, 12H, $CH(CH_3)_2$), 1.38 (s, 4H, THF), 3.14 (br, 2H, *CH*Me$_2$), 3.71 (s, 4H, THF), 6.79 (t, 1H, $^3J_{H-H}$ = 6 Hz, Ar-H), 6.89 (d, 1H, $^3J_{H-H}$ = 6 Hz, Ar-H), 6.92 (t, 1H, $^3J_{H-H}$ = 6 Hz, 3-quinolinyl), 7.18−7.27 (m, 6H, Ar-H), 7.45 (d, 1H, $^3J_{H-H}$ = 6 Hz, 7-quinolinyl), 7.66 (d, 1H, $^3J_{H-H}$ = 6 Hz, 4-quinolinyl), 7.81 (d, 1H, $^3J_{H-H}$ = 6 Hz, 5-quinolinyl), 8.12 (s, 1H, N═C*H*), 9.10 (d, 1H, $^3J_{H-H}$ = 2.7 Hz, 2-quinolinyl) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.80 (6C, $Si(CH)_3$), 25.74 (2C, *C*HMe$_2$), 29.50 (s, 2C, THF), 35.32 (d, 2C, CH_2SiMe_3), 69.55 (s, 2C, THF), 112.38 (s, 1C, 7-quinolinyl), 114.84 (s, 1C, Ar), 120.06 (s, 1C, Ar), 121.29 (s, 1C, 3-quinolinyl), 124.53 (s, 1C, 5-quinolinyl), 125.03 (s, 1C, Ar), 125.83 (s, 1C, Ar), 127.51 (s, 1C, Ar), 129.88 (s, 1C, Ar), 131.24 (s, 1C, Ar), 134.07 (s, 1C, Ar), 135.53 (s, 1C, Ar), 139.76 (s, 1C, 4-quinolinyl), 140.94 (s, 1C, Ar), 143.50 (s, 1C, Ar), 148.58 (1C, 2-quinolinyl), 152.06 (s, 1C, 9-quinolinyl), 152.27 (s, 1C, 10-quinolinyl), 169.63 (1C, N═*C*H) ppm. Anal. Calcd for $C_{40}H_{57}N_3OSi_2Y$ (%): C, 64.84; H, 7.75; N, 5.67. Found: C, 64.81; H, 7.72; N, 5.64.

[2-(2,6-^{i}Pr$_2$C$_6$H$_3$NC(H)C$_6$H$_4$-C$_9$H$_6$N)Lu(CH$_2$SiMe$_3$)$_2$ (3). Following the procedure described for the preparation of **1**, treatment of a hexane solution (5.0 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.30 g, 0.52 mmol) with 1 equiv of **HL** (0.20 g, 0.5 mmol) in 5 mL of THF afforded complex **3** (0.26 g, 68%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.40 (b, 4H, CH_2SiMe_3), 0.11 (s, 18H, $CH_2Si(CH_3)_3$), 1.16 (b, 6H, $CH(CH_3)_2$), 1.35 (b, 6H, $CH(CH_3)_2$), 3.41 (b, 2H, *CH*Me$_2$), 6.65 (t, 1H, $^3J_{H-H}$ = 6 Hz, Ar-H), 6.86 (m, 1H, Ar-H), 6.91 (d, 1H, $^3J_{H-H}$ = 6 Hz, 3-quinolinyl), 7.11−7.27 (m, 6H, Ar-H), 7.60 (d, 1H, $^3J_{H-H}$ = 6 Hz, 7-quinolinyl), 7.67 (d, 1H, $^3J_{H-H}$ = 6 Hz, 4-quinolinyl), 7.79 (d, 1H, $^3J_{H-H}$ = 6 Hz, 5-quinolinyl), 8.17 (s, 1H, C*H*═N), 8.98 (d, 1H, $^3J_{H-H}$ = 3.3 Hz, 2-quinolinyl) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.55 (6C, $Si(CH_3)_3$), 23.34 (2C, *C*HMe$_2$), 117.90 (s, 1C, 7-quinolinyl), 117.84 (s, 1C, Ar), 120.79 (s, 1C, Ar), 121.28 (s, 1C, 3-quinolinyl), 121.84 (s, 1C, Ar), 124.84 (s, 1C, Ar), 127.39 (s, 1C, Ar), 129.73 (s, 1C, Ar), 131.18 (s, 1C, Ar), 135.21 (s, 1C, Ar), 136.96 (s, 1C, 4-quinolinyl), 140.66 (s, 1C, Ar), 141.83 (s, 1C, Ar), 143.09 (1C, 2-quinolinyl), 149.08 (s, 1C, 9-quinolinyl), 154.63 (s, 1C, 10-quinolinyl), 171.77 (1C, *C*H═N) ppm. Anal. Calcd for $C_{36}H_{50}LuN_3Si_2$ (%): C, 57.20; H, 6.67; N, 5.56. Found: C, 57.17; H, 6.68; N, 5.53.

Polymerization of ε-Caprolactone. A typical procedure for polymerization of ε-caprolactone was performed in a glovebox. ε-Caprolactone (1.0 mL, 9.45 mmol), 20 mL of toluene, and 10 μmol of complex were added into a 25 mL flask, and the polymerization was initiated. After a given time period, methanol was injected into the system to quench the polymerization. The mixture was poured into a large quantity of methanol to precipitate the white solids of poly ε-caprolactone. The polymer was filtered and dried under vacuum at ambient temperature to constant weight. The molecular weight and the molecular weight distribution of the resulting polymers were determined by GPC.

Details of the Dynamic Study of the Polymerization with 1. In a glovebox, initiator solution in toluene was sequentially added to a series of 25 mL bottles loaded with ε-caprolactone and suitable amounts of toluene. After the specified time intervals each bottle was taken out of the glovebox, the mixture was quenched with methanol, and the polymer was precipitated with a large amount of methanol. The obtained polymer was dried under vacuum at ambient temperature to constant weight.

Acknowledgment. We acknowledge financial support from Jilin Provincial Science and Technology Bureau for project no. 20050555; The National Natural Science Foundation of China for project nos. 20571072 and 20674081; The Ministry of Science and Technology of China for project no. 2005CB623802; and “Hundred Talent Scientist Program” of CAS.

Note Added after ASAP Publication. The version of this paper published on October 11, 2008, was missing three author names. The version published on October 17, 2008 has the correct information.

Supporting Information Available: CIF files of crystallographic data for **1**, **2**, and **3** including atomic coordinates, full bond distances and bond angles, as well as anisotropic thermal parameters are available free of charge via the Internet at http://pubs.acs.org.

OM800575P