Dialkyllanthanide Complexes Containing New Tridentate Monoanionic Ligands with Nitrogen Donors

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Three new tridentate NNN ligand precursors, $CH_3C(2,6\text{-}(^iPr)_2C_6H_3NH)CHC(CH_3)(NCH_2CH_2-D)$ (D = NMe_2, NEt_2, $N((CH_2CH_2)_2CH_2)$), were synthesized. Subsequent metalations with in situ generated $Ln(CH_2SiMe_3)_3(THF)_n$ (Ln = Nd, Sm, Y, Lu) provided six solvent-free dialkyllanthanide complexes. Five of the lanthanide complexes were characterized by single-crystal X-ray diffraction, which showed that the pendant arm D bonds to the lanthanide ion in the solid state. The NMR spectra of these complexes in C_6D_6 showed that such coordination is retained in solution. These dialkyllanthanide complexes show high activities for the ring-opening polymerization of ϵ-caprolactone, in which narrow-polydispersity polymers were produced. The size of the pendant arm has a significant effect on the molecular weight of the polymer obtained. In comparison to the Y complex with a $-NMe_2$ group, the Y complexes with $-NEt_2$ and $-N((CH_2CH_2)_2CH_2)$ groups yield much higher molecular weight polymer (60 000 vs 20 000).

Introduction

Organolanthanide complexes are useful catalysts in many polymer[1] and organic syntheses.[2] The most widely investigated organolanthanides are those bearing Cp-type ligands. The search for new-generation organolanthanide catalysts has led to the exploration of organolanthanide complexes with ancillary ligands beyond Cp and its derivatives.[3] In this connection, ligands with nitrogen donor atoms have received much attention, as they form strong N−Ln bonds with the acidic and hard Ln^{3+} ions and are expected to stabilize the highly electrophilic organolanthanide complexes. One promising set of nitrogen-containing ligands is the family of β-diketiminato ligands.[4] The precursors for these ligands can be readily prepared by condensation of β-diketones with anilines. The steric and electronic properties of these types of ligands can be easily tuned by an appropriate choice of β-diketone and aniline starting materials, and they can coordinate to lanthanide ions in different bonding modes ranging from purely σ to a combination of σ and π donation. Therefore, numerous β-diketiminato lanthanide complexes have been prepared in the past few years.[5–8] Some of them show good activities in polymer synthesis, such as ring-opening polymerization of ϵ-caprolactone or lactides,[7f,8c] methyl methacrylate polymerization,[7b] ethylene polymerization,[6c] and copolymerization of cyclohexene oxide and CO_2.[8e] Among β-diketiminato lanthanide complexes, the dialkyl derivatives are of the greatest interest, as they provide highly reactive Ln−C bonds. However, examples of these complexes are few in number. Piers and co-workers reported several Sc dialkyl

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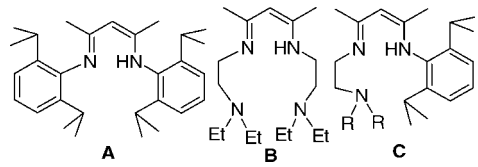
Chart 1



complexes stabilized by the bulky β-diketiminato ligand derived from **A**[6b] (Chart 1), and Lappert's group synthesized a Ce complex, $[(CH(C(Ph)NSiMe_3)_2)Ce(CH(SiMe_3)_2)_2]$, having the bulky and less reactive $-CH(SiMe_3)_2$ substituent.[5a] Generally, β-diketiminato lanthanide dialkyl complexes are difficult to synthesize, due to their tendency to undergo ligand redistribution, dimerization, and elimination reactions.[8c]

Usually, introducing neutral pendant arms is a useful strategy for stabilizing the organolanthanide complexes.[9] Roesky and co-workers developed the β-diketiminato derivative **B**, which contains two dangling arms with nitrogen donors incorporated. With the tetradentate ligand derived from **B**, they prepared a series of salt- and solvent-free lanthanide complexes, such as $LLnX_2$ (X = Cl, Br, I) and $LLn(BH_4)_2$.[10] However, the preparation of the corresponding dialkyl complxes is very difficult, and only $LTb(CH_2SiMe_3)_2$ has been obtained.[10b] After considering both steric and electronic features of the ligand, which are crucial to the stabilization of organolanthanide complexes, we designed a new type of tridentate NNN ligands derived from **C**. The ligand precursors **C** can be conveniently prepared from 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one and the appropriate diamine, and these precursors have proved to be ideal for ancillary ligands for the organolanthanide dialkyl complexes, including those of larger metal ions, such as Nd^{3+} and Sm^{3+}. Herein we report the preparation of these ligand precursors, the preparation and structures of organolanthanide dialkyl complexes containing these ligands, and their application in the ring-opening polymerization of ϵ-caprolactone.

Results and Discussion

Synthesis and Characterization. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one was prepared by condensation of acetylacetone with 2,6-diisopropylaniline.[11] Subsequent treatment of this product with an appropriate diamine in benzene or toluene using a catalytic amount of *p*-toluenesulfonic acid provided the desired tridentate ligand precursors **HL1**−**HL3** in 56–67% yield (Scheme 1). These were characterized by NMR and mass spectroscopy and by elemental analysis.

The dialkyllanthanide complexes usually were prepared via salt[5a,6b,10b,12] or alkane elimination.[13] The addition of 1 equiv of $Y(CH_2SiMe_3)_3(THF)_2$ to the ligand precursor **HL1** was monitored by ^1H NMR spectroscopy in C_6D_6. Alkane elimination occurred, and the target Y complex was formed nearly quantitatively in 10 min. A C_6D_6 solution of the Y complex formed is quite stable and showed no sign of decomposition over 1 day. Accordingly, the alkane elimination method was applied for the synthesis of dialkyl complexes **4**−**9**. Reactions between in situ generated Ln trialkyl complexes (Ln = Y, Lu, Sm) and the ligand precursors **HL1**−**HL3** in hexane at 0 °C provided dialkyl complexes **4**−**6**, **8**, and **9** in 38–73% isolated yields. Attempts to prepare the $L1NdR_2$ complex **7** by the same procedure failed, probably due to the instability of the in situ generated Nd trialkyl complex in hexane.[14] Therefore, the Nd trialkyl complex was prepared and reacted with **HL1** in THF. The THF was evaporated under vacuum after the reaction was complete. Recrystallization of the residue from hexane provided the desired Nd complex as greenish blue crystals in 33% yield.

Single crystals of the complexes **4**−**7** and **9** were grown from hexane solutions and characterized by X-ray diffraction. ORTEP diagrams are shown in Figures 1 and 2,[15] and selected bond lengths and angles are given in Table 1. One interesting feature of these complexes is that they are all solvent-free, five-coordinate monomers, even those of large lanthanide ions, such as Nd^{3+} and Sm^{3+}. In the complexes, ligand **L1** or **L3** serves as a tridentate ligand and the five-coordinate center is completed by a pair of $-CH_2SiMe_3$ substitutents. The geometry at the metal centers is best described as distorted square pyramidal with one of the $-CH_2SiMe_3$ substitutents taking the apical station. The backbone of the ligands is bonded to the metal ions at Ln−N separations from 2.28 to 2.42 Å, which fall in the range of 2.04−2.49 Å observed for Ln−N bonds in other reported β-diketiminato lanthanide complexes,[5–7] and those values are closely dependent on the central metal ions and increase as the lanthanide ion size becomes larger. As expected, the Ln−N bond lengths of the pendant arms (2.50–2.66 Å) are longer than those of the backbone, because the pendant arm acts as a neutral donor while the backbone is an anionic donor. The C−N and C−C bond lengths of the β-diketiminato backbone are intermediate between those of typical single and double bonds, and N1, C2, C3, C4, and N2 atoms are coplanar, indicating a delocalized electronic structure. The metal ions sit above the C_3N_2 ligand plane from 1.17 to 1.37 Å, and the deviation values are larger than that in $[(CH(C(Me)NCH_2CH_2NEt_2)_2)Tb(CH_2SiMe_3)_2]$ (0.81 Å),[10b] less than that in $[(CH(C(Ph)NSiMe_3)_2)Ce(CH(SiMe_3)_2)_2]$ (1.84 Å),[5a] and close to those in $[(CH(C(R)N(2,6\text{-}(^iPr)_2Ph)_2)\text{-}ScR'_2]$ (1.11–1.26 Å).[6b] Although the lanthanide ions are situated out of the ligand plane significantly, distances from metal ions to the ligand backbone carbon atoms C2, C3 and C4 are too long for effective interaction (>3.15 Å). Thus, the bonding mode of the ligands is best described as 2-σ-electron donors. The size of the metal ion is considered to be a potential contributing factor to out-of-plane bonding. The characterization of the solid-state structures of complexes **4**−**7**, which differ only in the metal ions, provides direct crystallographic information of the metal size's effect on the out-of-plane bonding. It was found that the degrees of the metal's deviation from the ligand plane in these complexes are almost the same if the difference in Ln^{3+} radii

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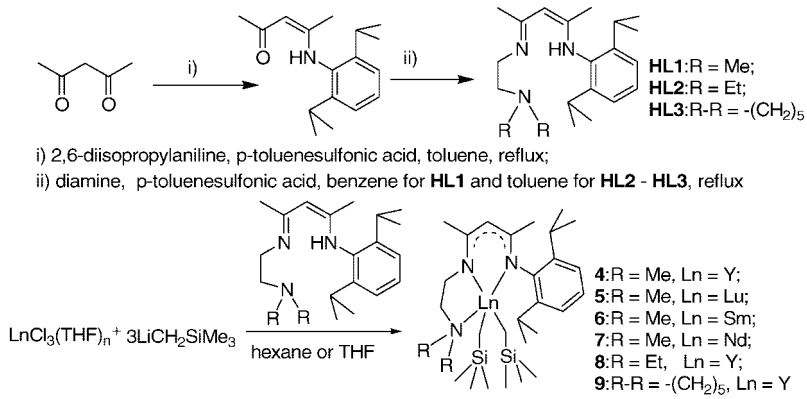
(15) Since the structures of **4**–**7** are very similar, only the ORTEP figure of **7** is shown in the main text; others are given in the Supporting Information.

Scheme 1



is counted; this phenomenon reveals that the metal size hardly plays a role in the complexes' adoption of the out-of-plane bonding mode. The size of the pendant arm affects the alkyl−Ln−alkyl angle, and the complex **9**, with bulkier N substituents, displays a larger alkyl−Ln−alkyl angle (117.22(19)°) compared to those in complexes **4**−**7** (average 111.4°).

The ^{1}H NMR spectrum of complexes **4**, **5**, **8**, and **9** in C_6D_6 shows an AB system for the Y−CH_2 methylene protons, indicating a C_s-symmetric structure in solution, and in all Y complexes, the signals for M−CH_2 are further split into doublets with a coupling constant of 3 Hz due to the Y−H coupling. For the ligand precursor **HL2**, the methylene units of −N(CH_2CH_3)$_2$ display one peak at 2.30 ppm. In the Y complex **8**, however, an AB pattern was observed for those −CH_2− units: one signal at 2.83 ppm and the other at 2.47 ppm, the latter being partly overlapped with the signal of −NCH_2CH_2N− (2.44 ppm). However, the former clearly shows a sextet. This is consistent with a coordination interaction between Y and the pendant group, and two hydrogen atoms on the −CH_2− unit become diastereotopic as the rotation around the N−C bond is hindered after the pendant arm bonds to the metal. The −CH_2− signal is split into a doublet with a J value of 14 Hz due to the H−H coupling between two diastereotopic hydrogen atoms, and each of these two doublets is further split into a quartet with $^3J_{H-H} = 7$ Hz; two quartets partially overlap to form the sextet observed. A similar change was observed in the ^{1}H NMR spectrum of Y complex **9** as compared to that of **HL3**. The ^{1}H NMR spectrum of **HL3** features one broad signal at 2.19 ppm for N(−CH_2−)$_2$ in the N((−CH_2CH_2)$_2CH_2$) group, while for the Y complex **9**, the N(−CH_2−)$_2$ group displays two broad signals at 2.10 and 3.16 ppm, respectively.

Polymerization of ϵ-Caprolactone. The complexes **4**−**9** were used for the ring-opening polymerization of ϵ-caprolactone (ϵ-CL), and the results are summarized in Table 2. All of these complexes are highly active initiators for the ϵ-caprolactone ring-opening polymerization in toluene. Over 85% yields were achieved at room temperature in 20 min using a very small mount of initiator (ϵ-CL/initiator molar ratio 2000), and activities of the initiators range up to 570–670 kg of PCL/((mol of Ln) h). The M_w values of the polymers obtained are between 20 000 and 70 000, and the polydispersities are narrow (<1.4).

The M_w values of polymers obtained when complexes **4**, **6**, and **7** were used are very similar (Table 2, entries 1, 3, and 4) and are much lower than the predicted values. The lower M_w values of polymers obtained using complexes **4**, **6**, and **7** are mainly due to transesterification reactions during the polymerization process, as observed in other ϵ-CL polymerization systems.[7g] In comparison with the cases for the Nd, Sm, and Y initiators, the Lu initiator **5** produces a polymer with a higher M_w value (Table 2, entry 2). The most interesting observation of the present catalytic system is that the transesterification reaction can be efficiently suppressed by using a bulkier substituent on the pendant nitrogen atom (Table 2, entries 5 and 6). The Y complexes **8** and **9** with −NEt_2 and −N((CH_2CH_2)$_2CH_2$) groups provide a polymer with a much higher M_w value than does the Y complex **1** with −NMe_2.

Conclusion

A series of dialkylorganolanthanide complexes containing tridentate monoanionic ligands with nitrogen donors have been prepared by alkane elimination from in situ generated Ln(CH_2SiMe_3)$_3$(THF)$_n$ with the ligand precursors. The addition

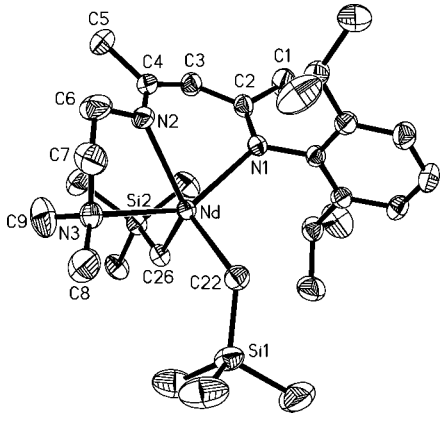


Figure 1. Molecular structure of **7** with thermal ellipsoids at the 30% probability level.

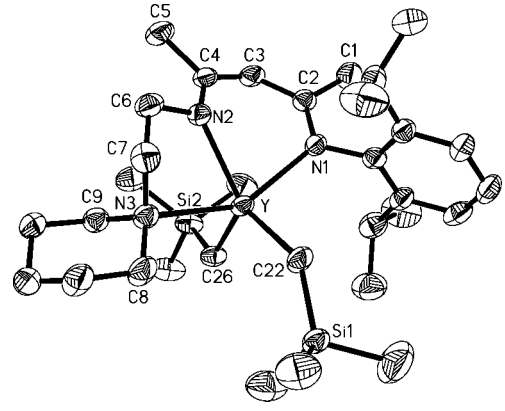


Figure 2. Molecular structure of **9** with thermal ellipsoids at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4–7 and 9

	4 (Ln = Y)	**5** (Ln = Lu)	**6** (Ln = Sm)	**7** (Ln = Nd)	**9** (Ln = Y)
Ln−N1	2.338(4)	2.289(4)	2.381(2)	2.405(3)	2.352(4)
Ln−N2	2.340(4)	2.279(5)	2.394(3)	2.421(3)	2.339(4)
Ln−N3	2.555(4)	2.499(5)	2.625(3)	2.656(3)	2.543(4)
Ln−C22	2.403(5)	2.368(5)	2.451(4)	2.485(4)	2.410(5)
Ln−C26	2.406(5)	2.339(5)	2.441(3)	2.471(4)	2.397(5)
C2−N1	1.329(6)	1.322(7)	1.315(4)	1.319(5)	1.361(6)
C4−N2	1.319(6)	1.326(8)	1.313(5)	1.310(5)	1.328(7)
C2−C3	1.394(6)	1.393(8)	1.407(5)	1.409(5)	1.402(7)
C3−C4	1.403(7)	1.389(8)	1.402(5)	1.393(5)	1.395(7)
N_2C_3 plane−Ln	1.229(7)	1.166(7)	1.320(4)	1.374(5)	1.147(6)
N1−Ln−N2	78.07(14)	79.46(15)	76.63(9)	76.17(10)	77.72(14)
N1−Ln−N3	143.91(15)	145.97(16)	140.84(10)	139.16(11)	145.84(14)
N2−Ln−N3	69.27(15)	69.86(16)	67.75(10)	66.85(11)	71.01(15)
C22−Ln−C26	111.11(18)	111.2(2)	111.56(12)	111.95(13)	117.22(19)
N1−C2−C3	124.3(5)	124.5(5)	124.4(3)	123.5(3)	123.6(5)
C2−C3−C4	128.5(5)	128.3(6)	128.6(4)	129.3(4)	129.1(5)
C3−C4−N2	123.8(5)	123.2(5)	123.4(3)	124.4(4)	123.2(5)
Ln−N1−C2	120.0(3)	119.9(3)	119.5(2)	119.0(2)	121.9(3)
Ln−N2−C4	119.2(3)	119.9(4)	118.5(2)	116.9(3)	121.8(3)
Ln−N3−C7	103.4(3)	102.8(4)	103.1(2)	103.8(3)	99.9(3)

Table 2. Polymerization of ϵ-Caprolactone with Complexes 4−9[a]

entry	initiator	yield (%)	activity[b]	M_w[c]	M_w/M_n
1	**4**, Y(Ll)	89	610	23 700	1.37
2	**5**, Lu(Ll)	95	618	46 900	1.35
3	**6**, Sm(Ll)	85	575	28 700	1.35
4	**7**, Nd(Ll)	89	610	29 400	1.35
5	**8**, Y(L2)	97	664	62 500	1.39
6	**9**, Y(L3)	98	671	67 800	1.34

[a] Polymerization conditions: 6.8 μmol of initiator, ϵ-CL/initiator molar ratio 2000, 6 mL of toluene, T = 26 °C, polymerization time 20 min. [b] In units of kg of polymer/((mol of Ln) h). [c] Determined by GPC relative to polystyrene standards.

of a neutral pendant arm to the commonly used β-diketiminato ligand has a dramatic effect on the stabilization of the highly reactive dialkylorganolanthanide complexes. Therefore, those of larger metal ions, such as Nd^{3+} and Sm^{3+}, were accessible. These dialkylorganolanthanide complexes are highly active initiators for the ϵ-caprolactone ring-opening polymerization. It is worth noting that the molecular weight of the polymer obtained is greatly affected by the substituent on the pendant nitrogen atom, which could provide a convenient way to control the molecular weight of the polymer by an appropriate choice of pendant arm.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen-filled glovebox. THF was distilled from Na−benzophenone ketyl; toluene and hexane were dried over Na/K alloy. $CDCl_3$ was purchased from Cambridge Isotopes and dried over 4 Å molecular sieves; C_6D_6 was purchased from Cambridge Isotopes, dried over Na/K alloy, distilled under vacuum, and stored in the glovebox. Acetylacetone, 2,6-diisopropylaniline, *N*,*N*-dimethylethylenediamine, *N*,*N*-diethylethylenediamine, and *N*-(2-aminoethyl)piperidine were purchased from Acros and used without purification. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one was synthesized by following the literature procedure.[11] $LiCH_2SiMe_3$ was prepared according to a standard procedure.[16] ϵ-CL (Acros) was dried by stirring with CaH_2 for 48 h and then distilled under reduced pressure and degassed prior to the polymerization experiment. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at room temperature, and the chemical shifts are reported in δ (ppm) units referenced to the residual solvent resonances of the deuterated solvents. Gel permeation chromatographic analysis was performed on a Waters 1515 apparatus equipped with a set of Waters Styragel columns (HR3, HR4, and HR5) at 35 °C. THF was used as the eluent, and the system was calibrated using polystyrene standards. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points of the complexes were determined on an SWG X-4 digital melting point apparatus in a sealed capillary and are uncorrected.

HL1. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one (8.20 g, 31.6 mmol), *N*,*N*-dimethylethylenediamine (2.79 g, 31.6 mmol), and a catalytic amount of *p*-toluenesulfonic acid in benzene (30 mL) were combined and heated at reflux overnight. The water produced during the reaction was removed as a benzene azeotrope using a water separator. The benzene was removed in vacuo after the reaction was complete. Distillation of the residue under reduced pressure (bp 120 °C, 8 Pa) provided **HL1** as a light yellow oil (7.02 g, 67% yield). Anal. Calcd for $C_{21}H_{35}N_3$: C, 76.54; H, 10.71; N, 12.75. Found: C, 76.65; H, 10.86; N, 12.76. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 11.04 (br s, 1H, N*H*), 7.24–7.14 (m, 3H, Ar*H*), 4.71 (s, 1H, MeC(N)C*H*), 3.20 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.97 (t, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2), 2.18 (t, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2), 1.95 (s, 6H, N*Me*$_2$), 1.69 (s, 3H, *Me*C(NHAr)), 1.66 (s, 3H, *Me*C(NCH$_2$CH$_2$NMe$_2$)), 1.27 (t, $^3J_{HH}$ = 7.8 Hz, 12H, ArCH*Me*$_2$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.83 (br s, 1H, N*H*), 7.12–7.01 (m, 3H, Ar*H*), 4.65 (s, 1H, MeC(N)C*H*), 3.33 (q, 2H, NCH_2), 2.88 (sp, $^3J_{HH}$ = 7.2 Hz, 2H, ArC*H*Me$_2$), 2.39 (t, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2), 2.21 (s, 6H, N*Me*$_2$), 2.02 (s, 3H, *Me*C(NHAr)), 1.62 (s, 3H, *Me*C(NCH$_2$CH$_2$NMe$_2$)), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 165.9 (1C, Me*C*(NCH$_2$CH$_2$NMe$_2$)), 155.3 (1C, Me*C*(NHAr)), 146.9 (1C, C_{ipso}), 137.9 (2C, C_{ortho}), 122.5 (2C, C_{meta}), 122.3 (1C, C_{para}), 93.1 (1C, MeC(N)*C*H), 59.8 (1C, N *C*H$_2$), 45.7 (2C, N*Me*$_2$), 41.5 (1C, N*C*H$_2$), 27.9 (2C, Ar*C*HMe$_2$), 23.8 (2C, ArCH*Me*$_2$), 22.7 (2C, ArCH*Me*$_2$), 21.5 (1C, *Me*C(NHAr)), 19.4 (1C, *Me*C(NCH$_2$CH$_2$NMe$_2$)). EIMS: *m*/*z* 329 (M^+, 1.30), 271 (100), 58 (48.53).

(16) Tessier-Youngs, C.; Beachley, O. T. *Inorg. Synth.* **1986**, *24*, 95.

HL2. The procedure described for **HL1** was used, but with 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one (5.79 g, 22.3 mmol), *N*,*N*-diethylethylenediamine (2.59 g, 22.3 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (30 mL). The product **HL2** (4.51 g, 56% yield) was obtained as a yellow oil by distillation under reduced pressure (bp 140–142 °C, 8 Pa). Anal. Calcd for $C_{23}H_{39}N_3$: C, 77.26; H, 10.99; N, 11.75. Found: C, 77.45; H, 10.95; N, 11.64. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 10.95 (br s, 1H, N*H*), 7.23–7.13 (m, 3H, Ar*H*), 4.72 (s, 1H, MeC(N)C*H*), 3.21 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.99 (q, 2H, NCH_2), 2.38 (t, $^3J_{HH}$ = 6.9 Hz, 2H, NCH_2), 2.30 (q, 4H, N(CH_2CH$_3$)$_2$), 1.70 (s, 6H, *Me*C(NHAr) and *Me*C(NCH$_2$CH$_2$NEt$_2$)), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.24 (d, $^3J_{HH}$ = 6.2 Hz, 6H, ArCH*Me*$_2$), 0.83 (t, $^3J_{HH}$ = 6.9 Hz, 6H, N(CH$_2$CH_3)$_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.76 (br s, 1H, N*H*), 7.13–7.01 (m, 3H, Ar*H*), 4.64 (s, 1H, MeC(N)C*H*), 3.30 (q, 2H, NCH_2), 2.88 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 2.52 (ov, m, 6H, NCH_2 and N(CH_2CH$_3$)$_2$), 2.02 (s, 3H, *Me*C(NHAr)), 1.61 (s, 3H, *Me*C(NCH$_2$CH$_2$NEt$_2$)), 1.15 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.95 (t, $^3J_{HH}$ = 6.9 Hz, 6H, N(CH$_2$CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 165.9 (1C, Me*C*(NCH$_2$CH$_2$NEt$_2$)), 155.4 (1C, Me*C*(NHAr)), 147.1 (1C, C_{ipso}), 137.9 (2C, C_{ortho}), 122.6 (2C, C_{meta}), 122.3 (1C, C_{para}), 92.9 (1C, MeC(N)*C*H), 53.5 (1C, NCH_2), 47.3 (2C, N(*C*H$_2$CH$_3$)$_2$), 41.7 (1C, NCH_2), 27.9 (2C, Ar*C*HMe$_2$), 23.8 (2C, ArCH*Me*$_2$), 22.8 (2C, ArCH*Me*$_2$), 21.6 (1C, *Me*C(NHAr)), 19.5 (1C, *Me*C(NCH$_2$-CH$_2$NEt$_2$)), 11.7 (2C, N(CH$_2$*C*H$_3$)$_2$). EIMS: *m*/*z* 357 (M$^+$, 2.84), 271 (100), 86 (96.57).

HL3. The procedure described for **HL1** was used, but with 2-((2,6-diisopropylphenyl)imido)-2-penten-4-one (5.01 g, 19.3 mmol), *N*-(2-aminoethyl)piperidine (2.47 g, 19.3 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (25 mL). The product **HL3** (4.19 g, 59% yield) was obtained as a yellow oil by distillation under reduced pressure (bp 130–132 °C, 5 Pa). Anal. Calcd for $C_{24}H_{39}N_3$: C, 77.99; H, 10.64; N, 11.37. Found: C, 78.01; H, 10.46; N, 10.93. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 11.01 (br s, 1H, N*H*), 7.24–7.16 (m, 3H, Ar*H*), 4.71 (s, 1H, MeC(N)C*H*), 3.20 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 3.03 (t, $^3J_{HH}$ = 6.9 Hz, 2H, NCH_2), 2.27 (t, $^3J_{HH}$ = 6.6 Hz, 2H, NCH_2), 2.19 (m, 4H, N(CH_2CH$_2$)$_2$CH$_2$), 1.69 (s, 3H, *Me*C(NHAr)), 1.67 (s, 3H, *Me*C(NCH$_2$CH$_2$NC$_5$H$_{10}$)), 1.39 (m, 4H, N(CH$_2$CH_2)$_2$CH$_2$), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$), 1.17 (m, 2H, N(CH$_2$CH$_2$)$_2$CH_2). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ(ppm) 10.79(br s, 1H, N*H*), 7.13–7.01 (m, 3H, Ar*H*), 4.63 (s, 1H, MeC(N)C*H*), 3.35 (q, 2H, NCH_2), 2.87 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.40 (ov, m, 6H, NCH_2 and N(CH_2CH$_2$)$_2$CH$_2$), 2.01 (s, 3H, *Me*C(NHAr)), 1.61 (s, 3H, *Me*C(NCH$_2$CH$_2$NC$_5$H$_{10}$)), 1.50 (m, 4H, N(CH$_2$CH_2)$_2$CH$_2$), 1.37 (m, 2H, N(CH$_2$CH$_2$)$_2$CH_2), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) 165.9 (1C, Me*C*(NCH$_2$CH$_2$NC$_5$H$_{10}$)), 155.4 (1C, Me*C*(NHAr)), 147.0 (1C, C_{ipso}), 138.0 (2C, C_{ortho}), 122.6 (2C, C_{meta}), 122.3 (1C, C_{para}), 93.0 (1C, MeC(N)*C*H), 60.0 (1C, NCH_2), 54.9 (2C, N(*C*H$_2$CH$_2$)$_2$CH$_2$), 40.9 (1C, N *C*H$_2$), 28.0 (2C, Ar*C*HMe$_2$), 25.8 (2C, N(CH$_2$*C*H$_2$)$_2$CH$_2$), 24.2 (1C, N(CH$_2$CH$_2$)$_2$*C*H$_2$), 23.8 (2C, ArCH*Me*$_2$), 22.8 (2C, ArCH*Me*$_2$), 21.6 (1C, *Me*C(NHAr)), 19.5 (1C, *Me*C(NCH$_2$CH$_2$NC$_5$H$_{10}$)). EIMS: *m*/*z* 369 (M$^+$, 1.37), 271 (100), 98 (87.3).

L1Y(CH$_2$SiMe$_3$)$_2$ (4). A suspension of anhydrous YCl_3 (450 mg, 2.3 mmol) in 5 mL of THF was stirred overnight. The THF solvent was removed in vacuo, and 5 mL of hexane was added. To the above suspension was added a solution of $LiCH_2SiMe_3$ (640 mg, 6.8 mmol in 15 mL of hexane) at ambient temperature. After 2 h, the precipitate was separated by centrifugation, and the resulting clear solution was added to an **HL1** solution (622 mg, 1.9 mmol in 5 mL of hexane) at 0 °C. After 1 h, the reaction solution was concentrated to approximately 5 mL and cooled to −10 °C to give **4** as a pale yellow crystalline solid (448 mg, 40% yield). Mp: 117–120 °C without decomposition. Anal. Calcd for $C_{29}H_{56}N_3Si_2Y$: C, 58.85; H, 9.54; N, 7.10. Found: C, 58.64; H, 9.26; N, 7.05. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.17–7.13 (m, 3H, Ar*H*), 4.88 (s, 1H, MeC(N)C*H*), 3.25 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 2.88 (t, $^3J_{HH}$ = 5.8 Hz, 2H, NCH_2), 2.21 (t, $^3J_{HH}$ = 6.1 Hz, 2H, NCH_2), 2.07 (s, 6H, N*Me*$_2$), 1.69 (s, 3H, *Me*C), 1.63 (s, 3H, *Me*C), 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.22 (s, 18H, Y(CH$_2$Si*Me*$_3$)$_2$), −0.67 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$), −0.92 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 166.4 (1C, imine *C*), 165.7 (1C, imine *C*), 144.1 (1C), 142,7 (2C), 126.1 (1C), 124.5 (2C) (Ar*C*), 98.0 (1C, MeC(N)*C*H), 58.0 (1C, N*C*H$_2$), 47.3 (1C, N*C*H$_2$), 44.9 (2C, N*Me*$_2$), 35.6 (d, $^1J_{YC}$ = 39.8 Hz, 2C, *C*H$_2$SiMe$_3$), 28.3 (2C, Ar*C*HMe$_2$), 25.3 (2C, ArCH*Me*$_2$), 24.6 (2C, ArCH*Me*$_2$), 24.1 (1C, *Me*C), 23.3 (1C, *Me*C), 4.6 (6C, CH$_2$Si*Me*$_3$).

L1Lu(CH$_2$SiMe$_3$)$_2$ (5). Following the procedure described for **4**, reaction of anhydrous $LuCl_3$ (510 mg, 1.8 mmol), $LiCH_2SiMe_3$ (503 mg, 5.3 mmol), and **HL1** (489 mg, 1.5 mmol) gave **5** as a pale yellow crystalline solid (732 mg, 73% yield). Mp: 105–109 °C without decomposition. Anal. Calcd for $C_{29}H_{56}N_3Si_2Lu$: C, 51.38; H, 8.33; N, 6.20. Found: C, 51.18; H, 8.21; N, 6.14. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.17–7.15 (m, 3H, Ar*H*), 4.86 (s, 1H, MeC(N)C*H*), 3.28 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, ArC*H*Me$_2$), 2.88 (t, $^3J_{HH}$ = 5.7 Hz, 2H, NCH_2), 2.15 (t, $^3J_{HH}$ = 6 Hz, 2H, NCH_2), 2.04 (s, 6H, N*Me*$_2$), 1.66 (s, 3H, *Me*C), 1.62 (s, 3H, *Me*C), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.6 Hz, 6H, ArCH*Me*$_2$), 0.21 (s, 18H, Lu(CH$_2$Si*Me*$_3$)$_2$), −0.88 (d, $^2J_{HH}$ = 12 Hz, 2H, CH_2SiMe$_3$), −1.08 (d, $^2J_{HH}$ = 12 Hz, 2H, CH_2SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm): 166.8 (1C, imine *C*), 166.5 (1C, imine *C*), 145.3 (1C), 142.7 (2C), 126.0 (1C), 124.4 (2C) (Ar*C*), 98.6 (1C, MeC(N)*C*H), 57.7 (1C, N*C*H$_2$), 47.4 (1C, N*C*H$_2$), 45.0 (2C, N*Me*$_2$), 43.0 (2C, *C*H$_2$SiMe$_3$), 28.2 (2C, Ar*C*HMe$_2$), 25.3 (2C, ArCH*Me*$_2$), 24.8 (2C, ArCH*Me*$_2$), 24.5 (1C, *Me*C), 23.3 (1C, *Me*C), 4.8 (6C, CH$_2$Si*Me*$_3$).

L1Sm(CH$_2$SiMe$_3$)$_2$ (6). Following the procedure described for **4**, reaction of $SmCl_3$ (478 mg, 1.9 mmol), $LiCH_2SiMe_3$ (517 mg, 5.5 mmol), and **HL1** (502 mg, 1.5 mmol) gave **6** as a yellow crystalline solid (486 mg, 49% yield). Mp: 115–117 °C without decomposition. Anal. Calcd for $C_{29}H_{56}N_3Si_2Sm$: C, 53.32; H, 8.64; N, 6.43. Found: C, 52.71; H, 8.41; N, 6.66. **6** is paramagnetic. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 8.49 (s, 1H), 7.13 (br s, 2H), 6.56 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 5.96 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 4.77 (br s, 2H), 3.22 (s, 3H), 2.41 (s, 3H), 1.24 (s, 18H), 0.47 (d, $^3J_{HH}$ = 6.3 Hz, 6H), −0.58 (br s, 2H), −0.63 (d, $^3J_{HH}$ = 6.3 Hz, 6H), −1.46 (s, 6H), −1.55 (br s, 2H), −5.54 (s, 2H). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 176.1, 171.3, 138.6, 138.5, 124.4, 123.4, 104.3, 47.3, 44.1, 39.9, 25.8, 23.3, 23.0, 21.9, 4.1.

L1Nd(CH$_2$SiMe$_3$)$_2$ (7). Anhydrous $NdCl_3$ (537 mg, 2.1 mmol) was suspended in 10 mL of THF and the suspension stirred overnight. A solution of $LiCH_2SiMe_3$ (595 mg, 6.3 mmol in 10 mL of THF) was added to the above suspension at ambient temperature, and a bright blue solution formed in 10 min. The reaction mixture was stirred for 2 h and then cooled to 0 °C. **HL1** (578 mg, 1.8 mmol) in 5 mL of THF then was added. The reaction solution was stirred for 2 h at 0 °C. The volatiles were removed under vacuum, and the residue was extracted with 30 mL of hexane. Concentration of the extract solution in vacuo to approximately 5 mL and cooling to −10 °C afforded **7** as greenish blue crystals (374 mg, 33% yield). Mp: 110–112 °C without decomposition. Anal. Calcd for $C_{29}H_{56}N_3Si_2Nd$: C, 53.82; H, 8.72; N, 6.49. Found: C, 52.98; H, 7.94; N, 6.36. **7** is paramagnetic. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 20.77 (s), 17.36 (br s), 13.48 (s), 11.76 (s), 6.45 (s), 4.59 (s), 3.06 (br s), 1.38 (d, $^3J_{HH}$ = 6.9 Hz), −0.18 (s), −4.27 (s), −8.97 (s), −20.16 (s), −24.58 (br s), −26.85 (s). ^{13}C

Table 3. Crystallographic Data and Refinement for Complexes 4–7 and 9

	4 (Ln = Y)	**5** (Ln = Lu)	**6** (Ln = Sm)	**7** (Ln = Nd)	**9** (Ln = Y)
formula	$C_{29}H_{56}N_3Si_2Y$	$C_{29}H_{56}N_3Si_2Lu$	$C_{29}H_{56}N_3Si_2Sm$	$C_{29}H_{56}N_3Si_2Nd$	$C_{32}H_{60}N_3Si_2Y$
fw	591.86	677.92	653.30	647.19	631.92
color	pale yellow	pale yellow	yellow	greenish blue	pale yellow
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.6359(18)	9.613(3)	9.5972(7)	9.6033(8)	10.989(5)
b, Å	11.092(2)	10.999(3)	11.0827(7)	11.1048(9)	11.935(6)
c, Å	17.373(3)	17.249(5)	17.2952(12)	17.3163(14)	14.662(8)
α, deg	87.918(3)	87.576(4)	88.2900(10)	88.3720(10)	89.934(9)
β, deg	75.102(3)	74.846(4)	75.1190(10)	75.2940(10)	84.979(10)
γ, deg	81.202(3)	80.946(5)	81.2510(10)	81.2820(10)	82.763(11)
V, Å^3	1773.3(6)	1738.6(8)	1757.1(2)	1765.4(2)	1900.3(16)
Z	2	2	2	2	2
D_{calcd}, g/cm^3	1.108	1.295	1.235	1.217	1.104
$F(000)$	636	700	682	678	680
θ range, deg	2.21–26.00	1.87–27.00	2.21–26.50	1.22–26.00	1.72–26.00
no. of rflns collected	9458	10 187	9993	9556	10 460
no. of unique rflns	6797	7349	7103	6804	7331
no. of obsd rflns ($I > 2\sigma(I)$)	3757	6370	6355	5830	3644
no. of params	330	330	339	330	355
goodness of fit	0.861	0.976	0.992	1.009	0.820
final R, R_w ($I > 2\sigma(I)$)	0.0607, 0.1301	0.0433, 0.1055	0.0335, 0.0790	0.0342, 0.0741	0.0646, 0.1501
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.053, −0.877	2.910, −1.359	1.232, −0.801	1.222, −0.469	0.828, −0.928

NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 154.2, 131.8, 125.1, 111.0, 37.1, 17.5, 12.8, 5.9.

L2Y(CH$_2$SiMe$_3$)$_2$ (8). Complex **8** was prepared according to the same procedure as that for **4** by reaction of anhydrous YCl_3 (286 mg, 1.5 mmol), $LiCH_2SiMe_3$ (406 mg, 4.3 mmol), and **HL2** (428 mg, 1.3 mmol) as a pale yellow crystalline solid (319 mg, 43% yield). Mp: 108–111 °C without decomposition. Anal. Calcd for $C_{31}H_{60}N_3Si_2Y$: C, 60.06; H, 9.76; N, 6.78. Found: C, 59.17; H, 9.53; N, 7.01. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.17–7.14 (m, 3H, Ar*H*), 4.90 (s, 1H, MeC(N)C*H*), 3.29 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 2.93 (t, $^3J_{HH}$ = 5.7 Hz, 2H, NCH_2), 2.83 (sextet, 2H, N(CH_2CH$_3$)$_2$), 2.51–2.42 (overlapped, m, 4H, N(CH_2CH$_3$)$_2$ and NCH_2), 1.69 (s, 3H, *Me*C), 1.64 (s, 3H, *Me*C), 1.44 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.78 (t, $^3J_{HH}$ = 7.1 Hz, 6H, N(CH$_2$CH_3)$_2$), 0.19 (s, 18H, Y(CH$_2$Si*Me*$_3$)$_2$), −0.62 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$), −0.84 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ(ppm) 165.9 (1C, imine *C*), 165.8 (1C, imine *C*), 145.1 (1C), 142.7 (2C), 126.0 (1C), 124.4 (2C) (Ar*C*), 98.0 (1C, MeC(N)*C*H), 49.9 (1C, N*C*H$_2$), 46.7 (1C, N*C*H$_2$), 44.3 (2C, N(*C*H$_2$CH$_3$)$_2$), 36.0 (d, $^1J_{YC}$ = 38.3 Hz, 2C, *C*H$_2$SiMe$_3$), 28.2 (2C, Ar*C*HMe$_2$), 25.4 (2C, ArCH*Me*$_2$), 24.8 (2C, ArCH*Me*$_2$), 24.3 (1C, *Me*C), 22.9 (1C, *Me*C), 8.4 (2C, N(CH$_2$*C*H$_3$)$_2$), 4.5 (6C, CH$_2$Si*Me*$_3$).

L3Y(CH$_2$SiMe$_3$)$_2$ (9). Complex **9** was prepared according to the same procedure as that for **4** by reaction of anhydrous YCl_3 (230 mg, 1.2 mmol), $LiCH_2SiMe_3$ (327 mg, 3.5 mmol), and **HL3** (369 mg, 1.0 mmol) as a pale yellow crystalline solid (240 mg, 38% yield). Mp: 119–121 °C without decomposition. Anal. Calcd for $C_{32}H_{60}N_3Si_2Y$: C, 60.82; H, 9.57; N, 6.65. Found: C, 61.79; H, 9.82; N, 6.66. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (ppm) 7.18–7.14 (m, 3H, Ar*H*), 4.91 (s, 1H, MeC(N)C*H*), 3.29 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 3.16 (m, 2H, N(CH_2CH$_2$)$_2$CH$_2$), 2.94 (t, $^3J_{HH}$ = 5.8 Hz, 2H, NCH_2), 2.49 (t, $^3J_{HH}$ = 5.6 Hz, 2H, NCH_2), 2.10 (m, 2H, −N(CH_2CH$_2$)$_2$CH$_2$), 1.69 (s, 3H, *Me*C), 1.65 (s, 3H, *Me*C), 1.44 (d, $^3J_{HH}$ = 7.2 Hz, 6H, ArCH*Me*$_2$), 1.25 (m, 6H, N(CH$_2$CH_2)$_2$CH$_2$ and N(CH$_2$CH$_2$)$_2$CH_2), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCH*Me*$_2$), 0.20 (s, 18H, Y(CH$_2$Si*Me*$_3$)$_2$), −0.55 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$), −0.81 (dd, $^2J_{HH}$ = 12 Hz, $^2J_{YH}$ = 3 Hz, 2H, CH_2SiMe$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (ppm) 165.9 (1C, imine *C*), 165.6 (1C, imine *C*), 145.0 (1C), 142.6 (2C), 126.0 (1C), 124.4 (2C) (Ar*C*), 98.1 (1C, MeC(N)*C*H), 52.3 (1C, N(CH$_2$CH$_2$)$_2$*C*H$_2$), 52.0 (1C, N*C*H$_2$), 46.2 (1C, N*C*H$_2$), 36.5 (d, $^1J_{YC}$ = 40.5 Hz, 2C, *C*H$_2$SiMe$_3$), 28.2 (2C, Ar*C*HMe$_2$), 25.4 (2C, ArCH*Me*$_2$), 24.7 (2C, ArCH*Me*$_2$), 24.2 (1C, *Me*C), 23.9 (1C, *Me*C), 22.7 (2C, N(*C*H$_2$CH$_2$)$_2$CH$_2$), 21.8 (2C, N(CH$_2$-*C*H$_2$)$_2$CH$_2$), 4.5 (6C, CH$_2$Si*Me*$_3$).

Polymerization of ϵ-Caprolactone. In a glovebox, 6.8 μmol of initiator in 0.5 mL of toluene was added to a toluene solution of ϵ-caprolactone (13.6 mmol in 5.5 mL of toluene). After 20 min, the reaction vessel was taken out of the glovebox and the polymerization was quenched with 2 mL of acidic methanol. The reaction mixture was poured into 20 mL of methanol to precipitate the polymer. The resulting polymer was isolated, washed with methanol, and dried under vacuum for 1 day.

X-ray Crystallography. Suitable single crystals of **4**−**7** and **9** were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. Crystallographic data and refinement details are given in Table 3.

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Supporting Information Available: ORTEP diagrams of the molecular structures of **4**–**6** and CIF files giving X-ray crystallographic data for **4**–**7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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