

Syntheses and Structures of Tris- β -Diketimate Lanthanide Complexes and Their High Activity for Ring-Opening Polymerization of ϵ -Caprolactone and L-Lactide

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Keywords: Synthetic methods / Lanthanides / Lactones / Ring-opening polymerization / Metathesis

Metathesis of $[(4\text{-XC}_6\text{H}_4)\text{NC}(\text{Me})_2\text{CH}]\text{Li}$ with anhydrous lanthanide trichlorides (LnCl_3) in a 3:1 molar ratio yielded a series of tris- β -diketimate complexes with the general formula $[\text{LnL}_3^X]$ [$X = \text{Cl}$, L^{Cl} : $\text{Ln} = \text{Pr}$ (**1**), Nd (**2**), Sm (**3**); $X = \text{H}$, L : $\text{Ln} = \text{Nd}$ (**4**); $X = \text{Me}$, L^{Me} : $\text{Ln} = \text{Nd}$ (**5**)]. Reaction of sodium salt of β -diketimate with anhydrous LnCl_3 in a 1:1 molar ratio in thf afforded the corresponding β -diketimate lanthanide dichlorides $[\text{L}^{\text{Cl}}\text{PrCl}_2(\text{thf})_2]$ (**6**), $[\text{L}^{\text{Me}}\text{NdCl}_2(\text{thf})_2]$ (**7**), and $[\text{L}^{\text{iPr}_2}\text{NdCl}_2(\text{thf})_2]$ [$\text{L}^{\text{iPr}_2} = [(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2\text{CH}^-]$ (**8**)], respectively. Each of these complexes was characterized, and the molecular structures of complexes **1–5** and **8** were determined by X-ray single-crystal structure analysis. Complexes

1–5 were found to be very active single-component initiators for the ring-opening polymerization of ϵ -caprolactone (ϵ -CL) and L-lactide (L-LA) under mild conditions, giving polymers with high molecular weight and moderate polydispersities, whereas complexes **6–8** displayed no activity under the same polymerization conditions. The high catalytic activity shown by tris- β -diketimate lanthanide complexes may be attributed to the activated Ln- β -diketimate bond caused by the crowded coordination sphere around the central metal.

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Introduction

β -Diketimate anions, the alternatives to cyclopentadienyl ligands, have widely been used in coordination chemistry and organometallic chemistry of lanthanide metals, as they can act as versatile spectator ligands by virtue of their strong metal–ligand bonds and their exceptional and tunable steric demands by variation of the substituents.^[1,2] A variety of derivatives, such as alkylides,^[3] allylides,^[4] amides,^[2h,2k] borohydrides,^[5] alkoxides,^[6] and so on, was synthesized and found to serve as highly active initiators in homogeneous catalyses. In these catalytic reactions, β -diketimate groups act as inert ancillary ligands to stabilize an active species. In fact, the Ln- β -diketimate bond in β -diketimate lanthanide dichloride was proven to be inactive or much less active in the ring-opening polymerization of ϵ -caprolactone.^[2h,2k]

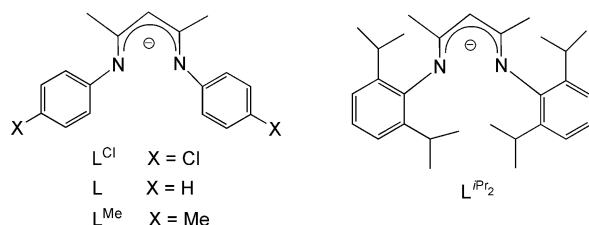
Recently, it was explored by the Evans group that the normally inert $(\text{C}_5\text{Me}_5)^-$ group in the sterically crowded $[(\text{C}_5\text{Me}_5)_3\text{Ln}]$ shows remarkable sterically induced reactivity.^[7] We are interested in understanding the chemical behavior of the Ln- β -diketimate bond in a sterically

crowded tris- β -diketimate lanthanide complex. In this regard, we are beginning to study the synthesis of tris- β -diketimate lanthanide complexes and their reactivity.

Tris- β -diketimate lanthanide complexes are rare; only two kinds of complexes have been reported to date: one is the complex bearing the β -diketimate with a neighboring, fused six-membered heterocyclic ring and the other is that with *N,N*-diphenyl β -diketimate ligands.^[8] An attempt to synthesize tris- β -diketimate lanthanide complexes with the bulky β -diketimate group resulted in a series of novel complexes containing a “normal” and a deprotonated ligand through ligand deprotonation induced by steric demand.^[2b] In this paper, we synthesized a series of tris- β -diketimate lanthanide complexes by using various β -diketimate anions (Scheme 1), including $[\text{LnL}_3^{\text{Cl}}]$ [$\text{L}^{\text{Cl}} = [4\text{-CIPhNC}(\text{Me})_2\text{CH}^-]$; $\text{Ln} = \text{Pr}$ (**1**), Nd (**2**), Sm (**3**)], $[\text{NdL}_3]$ [$\text{L} = [\text{PhNC}(\text{Me})_2\text{CH}^-]$ (**4**), and $[\text{NdL}_3^{\text{Me}}]$ [$\text{L}^{\text{Me}} = [4\text{-MePhNC}(\text{Me})_2\text{CH}^-]$ (**5**)], and tested their catalytic activity for ring-opening polymerization of ϵ -caprolactone and L-lactide. The corresponding β -diketimate lanthanide dichlorides, $[\text{L}^{\text{Cl}}\text{PrCl}_2(\text{thf})_2]$ (**6**), $[\text{L}^{\text{Me}}\text{NdCl}_2(\text{thf})_2]$ (**7**), and $[\text{L}^{\text{iPr}_2}\text{NdCl}_2(\text{thf})_2]$ [$\text{L}^{\text{iPr}_2} = [(2,6\text{-iPr}_2\text{Ph})\text{NC}(\text{Me})_2\text{CH}^-]$ (**8**)], were also prepared for comparison with their catalytic activity. It was found that tris- β -diketimate lanthanide complexes showed extremely high activity for ring-opening polymerization of ϵ -caprolactone and L-lactide, whereas the corresponding dichlorides were inactive. The much higher activity of these tris- β -diketimate lanthanide complexes compared to their dichlorides might be attributed to

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“steric-induced activation”. Here we would like to report these results. The effect of central metals and β -diketiminate ligands was also discussed.

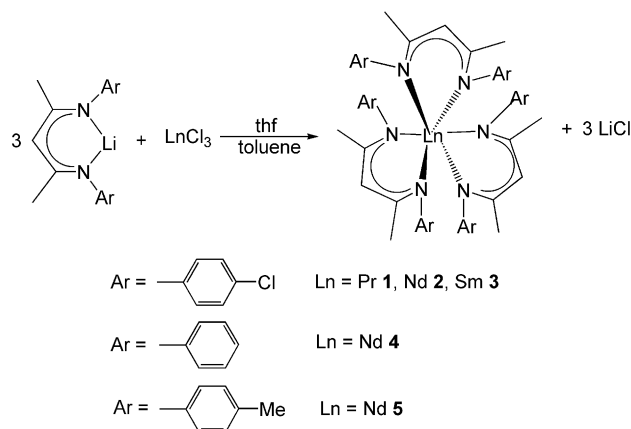


Scheme 1.

Results and Discussion

Synthesis and Characterization of $[LnL_3^{Cl}]$ $\{L^{Cl} = [4-ClPhNC(Me)]_2CH^-$; $Ln = Pr$ (1), Nd (2), Sm (3)}, $[NdL_3]$ $\{L = [PhNC(Me)]_2CH^-$ (4), and $[NdL_3^{Me}]$ $\{L^{Me} = [4-MePhNC(Me)]_2CH^-$ (5)

The β -diketiminate L^{Cl} was chosen as the ligand and a series of complexes with different lanthanide metals $[LnL_3^{Cl}]$ [$Ln = Pr$ (1), Nd (2), Sm (3)] were synthesized in desired yields by metathesis reaction of $LnCl_3$ with the lithium salt of L^{Cl} in a 1:3 molar ratio (Scheme 2).



Scheme 2.

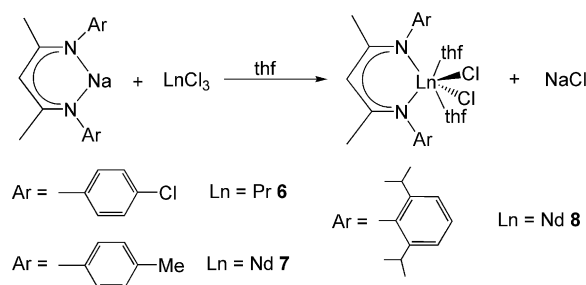
To examine the influence of the electronic effects of the ligand on the reactivity of tris- β -diketiminate lanthanide complexes, the β -diketiminate with a Me electron-donating group and no substituent at the *para*-position on the phenyl ring, L^{Me} and L , were also used as ligands. Thus, the same reaction of $NdCl_3$ was conducted with these β -diketiminate lithium salts. The reactions went smoothly, after workup, to yield the corresponding complexes $[NdL_3]$ (4) and $[NdL_3^{Me}]$ (5) as blue crystals in good yields upon crystallization (Scheme 2). Elemental analysis revealed that all these complexes consist of three β -diketiminate ligands around the metal center. The IR spectra of complexes 1–5 exhibited strong absorptions near 1551 and 1528 cm^{-1} , which were consistent with partial $C=N$ character.^[9] These complexes

did not provide any resolvable 1H NMR spectra; the resonances are broad and shifted due to the strong paramagnetic nature of the lanthanide ion.

All the complexes are moderately sensitive to air and moisture, and the crystals can be exposed to air for a few hours without apparent decomposition, but the color of the solution changes immediately when the solution is exposed to air. They are freely soluble in donor solvents such as tetrahydrofuran (thf) and dimethoxyethane (dme) and moderately soluble in toluene and sparingly soluble in hexane.

Synthesis and Characterization of $[L^{Cl}PrCl_2(thf)_2]$ (6), $[L^{Me}NdCl_2(thf)_2]$ (7), and $[L^{Pr_2}NdCl_2(thf)_2]$ $\{L^{Pr_2} = [(2,6-iPr_2)PhNC(Me)]_2CH^-$ (8)

The corresponding β -diketiminate lanthanide dichlorides were also synthesized for comparison. Generally, the metathesis reaction of $LnCl_3$ with lithium salts often yields an ate complex of β -diketiminate lanthanide dichloride with $LiCl$, whereas the same reaction with sodium salts gives the dichloride without $NaCl$ conveniently. Thus, reaction of anhydrous lanthanide trichlorides with in situ formed sodium salts of β -diketiminate in a 1:1 molar ratio in thf, after workup, gave the corresponding β -diketiminate lanthanide dichlorides, $[L^{Cl}PrCl_2(thf)_2]$ (6), $[L^{Me}NdCl_2(thf)_2]$ (7), and $[L^{Pr_2}NdCl_2(thf)_2]$ (8) (Scheme 3), respectively, which were characterized by elemental analyses and IR spectroscopy and X-ray structural analysis for 8.



Scheme 3.

Complex $[LSmCl_2(thf)_2]$ was synthesized according to a literature procedure.^[10] An attempt to determine the molecular structures of 6 and 7 was unsuccessful because of the decay of diffracted intensity of the crystals during data collection. Complexes 6–8 are very soluble in thf and moderately soluble in dme.

Molecular Structures of Complexes 1–5 and 8

The molecular structures of complexes 1–5 and 8 were further determined by X-ray diffraction. Their molecular structures are shown in Figures 1, 2, 3, and 4. Selected bond lengths and angles and the crystallographic data are summarized in Tables 1, 2, and 5.

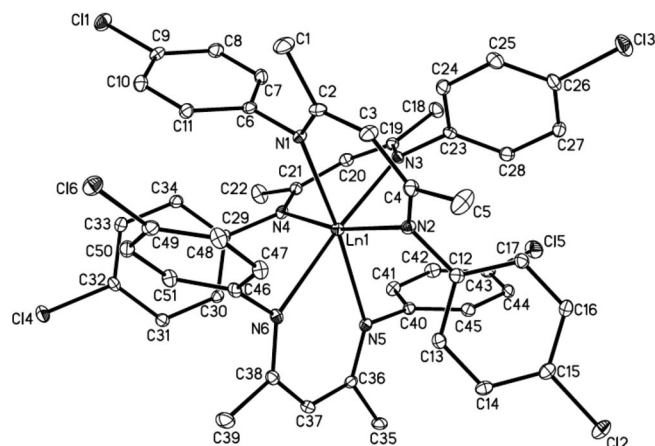


Figure 1. ORTEP diagram of complexes **1**, **2**, **3** (Ln = Pr **1**, Nd **2**, Sm **3**) showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

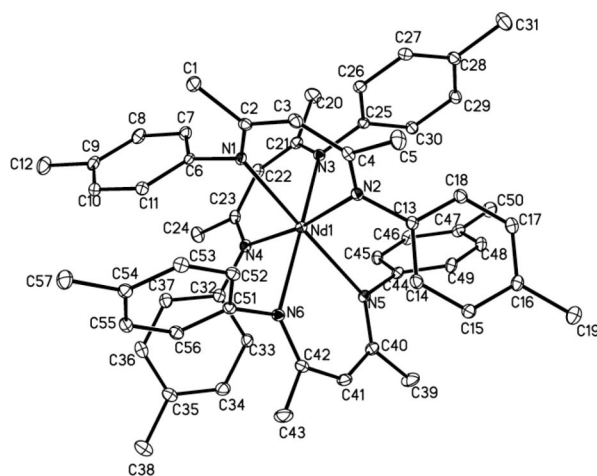


Figure 3. ORTEP diagram of complexes **5** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 10% probability level. Hydrogen atoms are omitted for clarity.

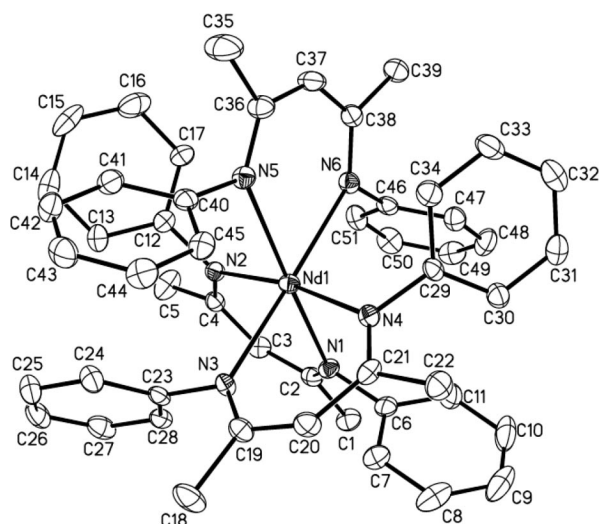


Figure 2. ORTEP diagram of complexes **4** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Complexes **1–5** are isostructural. They have unsolvated monomeric structure with a six-coordinate lanthanide metal ligated by six nitrogen atoms of three chelating bidentate β -diketiminate ligands. The coordination geometry around the lanthanide ion can be described as a distorted octahedron. Four nitrogen atoms, N2, N3, N4, and N6, from three β -diketiminate ligands can be considered to occupy equatorial positions within the octahedron about the lanthanide ion [the sum of these bond angles is $360.53(16)^\circ$ for **1**, $360.52(8)^\circ$ for **2**, $360.48(7)^\circ$ for **3**, $360.34(11)^\circ$ for **4**, and $360.4(10)^\circ$ for **5**], and the other two nitrogen atoms, N1 and N5, occupy axial positions [the angle of N1–Ln1–N5 is $171.14(16)^\circ$ for **1**, $171.70(8)^\circ$ for **2**, $172.30(7)^\circ$ for **3**, $170.41(11)^\circ$ for **4**, and $171.57(10)^\circ$ for **5**]. The molecular structures are similar to those for the analogous $\text{Ln}[\{\text{PhNC}(\text{Me})_2\text{CH}\}_3]$ (Ln = Sm and Gd) complexes reported previously.^[8a] Complex **8** is a two-thf-solvated

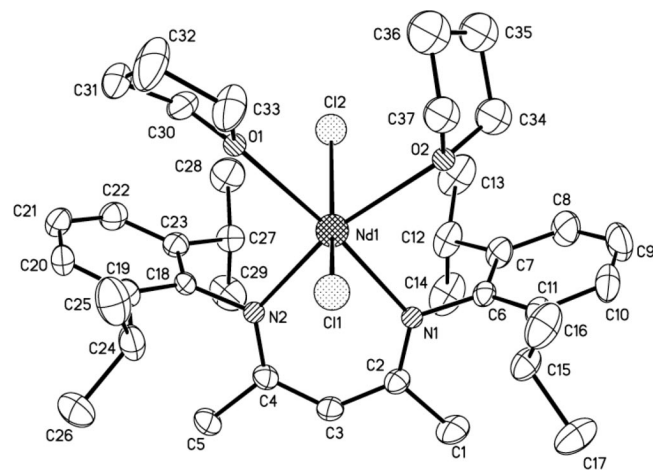


Figure 4. ORTEP diagram of complexes **8** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

monomer, in which a six-coordinate neodymium ion is coordinated by one β -diketiminate ligand, two chlorine atoms, and two oxygen atoms from two thf molecules forming a distorted octahedron. The molecular structure of **8** is quite similar to those of monomeric β -diketiminate–lanthanide dichlorides reported.^[2g,2k,10,11]

The C–N distances within the chelating β -diketiminate ligands for all the complexes (see Tables 1 and 2) are approximately equivalent and are significantly shorter than C–N single bond lengths and longer than the general double bond lengths, indicating that the π -electrons in these complexes are delocalized within the N–C–C–N fragment. The quite long distances between the lanthanide center and the carbon atoms of the backbone of the β -diketiminate ligands reveal that all the β -diketiminate ligands in these complexes only act as an N,N' -bonded chelate anion.

The values of the bite angle of N–Ln–N in tris- β -diketiminate lanthanide complexes **1–5** are comparable to each other (Table 1). However, these angles are more acute than

Table 1. Selected bond lengths (Å) and bond angles (°) for complexes **1–5**.

	1 (Ln = Pr)	2 (Ln = Nd)	3 (Ln = Sm)	4 (Ln = Nd)	5 (Ln = Nd)
Ln1–N1	2.508(5)	2.500(3)	2.473(2)	2.499(3)	2.475(3)
Ln1–N2	2.493(5)	2.486(3)	2.458(2)	2.481(3)	2.503(3)
Ln1–N3	2.536(5)	2.520(2)	2.487(2)	2.495(3)	2.475(3)
Ln1–N4	2.485(5)	2.474(2)	2.446(2)	2.484(3)	2.510(3)
Ln1–N5	2.479(5)	2.473(2)	2.448(2)	2.487(3)	2.499(3)
Ln1–N6	2.522(5)	2.507(2)	2.475(2)	2.491(3)	2.492(3)
N1–C2	1.338(8)	1.335(4)	1.334(4)	1.322(5)	1.328(4)
N2–C4	1.332(8)	1.331(4)	1.329(3)	1.325(5)	1.324(5)
C2–C3	1.387(9)	1.401(5)	1.396(4)	1.411(6)	1.395(5)
C3–C4	1.396(9)	1.396(5)	1.396(4)	1.406(6)	1.401(5)
N1–Ln1–N2	74.89(16)	75.56(8)	76.46(7)	74.91(11)	72.52(10)
N3–Ln1–N4	74.12(16)	74.78(8)	75.89(7)	74.03(11)	74.28(10)
N5–Ln1–N6	71.57(16)	72.14(8)	73.15(7)	74.66(11)	75.58(10)
N1–Ln1–N5	171.14(16)	171.70(8)	172.30(7)	170.41(11)	171.57(10)
N2–Ln1–N3	96.10(16)	95.82(8)	95.62(7)	99.53(11)	101.36(9)
N4–Ln1–N6	102.90(16)	102.15(8)	101.25(7)	101.99(11)	97.44(10)
N2–Ln1–N6	87.41(16)	87.77(8)	87.72(7)	84.79(11)	87.32(9)

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **8**.

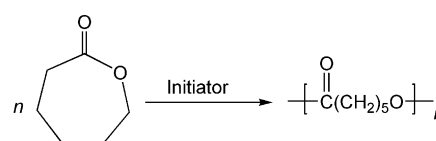
Nd1–N1	2.459(4)	Nd1–N2	2.444(4)
Nd1–Cl1	2.6531(18)	Nd1–Cl2	2.6357(18)
Nd1–O1	2.528(4)	Nd1–O2	2.540(6)
N1–C2	1.328(6)	N2–C4	1.326(6)
C2–C3	1.399(8)	C3–C4	1.388(7)
N1–Ln1–N2	75.81(13)	N2–Nd1–O1	99.41(13)
N1–Nd1–O1	174.45(13)	N2–Nd1–O2	166.52(17)
N1–Nd1–O2	90.71(17)	O1–Nd1–O2	94.06(17)
N2–Nd1–Cl2	98.73(11)	N1–Nd1–Cl2	102.98(10)
O1–Nd1–Cl2	80.38(11)	O2–Nd1–Cl2	84.03(15)
N2–Nd1–Cl1	100.60(11)	N1–Nd1–Cl1	96.98(10)
O1–Nd1–Cl1	81.00(11)	O2–Nd1–Cl1	80.84(14)
Cl2–Nd1–Cl1	155.03(6)		

the corresponding angles in mono- β -diketiminato lanthanide complexes. For example, the average bond angle of N–Nd–N in **2** is 74.16(8)°, whereas the values are 76.9(2)° for [L^{Me2}NdCl(thf)(μ -Cl)₂Li(thf)] {L^{Me2} = [(2,6-Me₂Ph)NC(Me)]₂CH[–]}^[2g] and 75.81(13)° for **8**; the value is 75.17(7)° for **3**, whereas it is 79.5(4)° for [LSmCl₂(thf)₂]^[10]. Hence, the Ln–N bond lengths in complexes **1–5** are longer than those in [L'LnX₂(thf)₂] (L' = β -diketiminato ligand; X = anion) complexes. For example, the average bond length of Sm–N is 2.465(2) Å for **3**, which is 0.135 Å longer than 2.33(1) Å in [LSmCl₂(thf)₂]^[10] the average Nd–N bond length 2.492(3) Å for **2**, **4**, and **5** is 0.059 Å and 0.040 Å longer than 2.433(7) Å in [L^{Me2}NdCl(thf)(μ -Cl)₂Li(thf)]^[2g] and 2.452(4) Å in complex **8**, respectively, although these structurally characterized mono- β -diketiminato neodymium complexes contain a more bulky β -diketiminato ligand.

Catalytic Activity of Complexes **1–8** and [LSmCl₂(thf)₂] for Ring-Opening Polymerization of ϵ -Caprolactone (CL) and L-Lactide (LA)

To examine the reactivity of the Ln- β -diketiminato bond in complexes **1–5**, the polymerization of CL with complex **1** as the initiator was first tested. It was found that complex **1** showed extremely high activity at room temperature as

a single-component initiator to yield polymers with high molecular weights and moderate polydispersities (Table 3). For example, the polymerization of CL gave complete conversion of 4000 equivalents of CL within 30 min at room temperature in toluene (Table 3, Entry 2). The very high activity was still observed when the polymerization proceeded even at 0 °C (Table 3, Entry 4). The high activity shown by complex **1** encouraged us to further screen complexes **2–5** with varied central metals and ligands. As shown in Table 3, all the tris- β -diketiminato lanthanide complexes can serve as highly active initiators for ring-opening polymerization of CL, yielding polymers with high molecular weight and moderate molecular weight distributions (M_w/M_n) ranging from 1.38 to 1.89. The activity depended strongly on the central metals, and the active trend of Sm < Nd < Pr, which is consistent with the sequence of ionic radii, was observed (Table 3, Entries 1, 5, and 9).



In comparison, the catalytic activity of mono- β -diketiminato lanthanide dichlorides **6–8** and [LSmCl₂(thf)₂] were tested for ring-opening polymerization of ϵ -CL under the same reaction conditions. The results indicated that these complexes were inactive: even when the molar ratio of monomer to complex was decreased to 100 and the polymerization time prolonged to 180 min no polymer was obtained (Table 3, Entries 20–23). From the comparative polymerization results and the bond angles and bond length data between the two kinds of complexes, it can be supposed that the high catalytic activity shown by tris- β -diketiminato lanthanide complexes may be attributed to the activation of the Ln- β -diketiminato bond induced by steric demand of the three β -diketiminato ligands.

The electronic factor of the β -diketiminato ligand has a great effect on the catalytic activity of tris- β -diketiminato lanthanide complexes. Complex **2** containing a ligand with

Table 3. Polymerization of ϵ -caprolactone initiated by complexes **1–8**.^[a]

Entry	Initiator	[M]/[I] ^[b]	<i>T</i> (°C)	<i>t</i> (min)	Yield (%) ^[c]	<i>M</i> _{n,theo} (10 ^{−4}) ^[d]	<i>M</i> _{n,exp} (10 ^{−4}) ^[e]	PDI
1	1	4000	25	15	64	29.2	27.7	1.59
2	1	4000	25	30	100	45.6	41.6	1.81
3	1	2000	25	15	100	22.8	21.9	1.77
4	1	2000	0	30	100	22.8	29.7	1.85
5	2	4000	25	15	39	17.8	16.8	1.38
6	2	2000	25	15	100	22.8	20.7	1.84
7	2	2000	0	20	70	16.0	21.8	1.56
8	2	2000	0	30	100	22.8	27.5	1.81
9	3	4000	25	60	0	—	—	—
10	3	1500	25	60	90	10.3	10.6	1.48
11	3	1000	25	60	100	11.4	9.68	1.78
12	3	500	25	30	100	5.70	5.05	1.68
13	4	2000	25	15	54	12.3	11.2	1.42
14	4	2000	25	30	100	22.8	19.7	1.89
15	4	1000	25	15	100	11.4	12.5	1.77
16	4	1000	0	60	90	10.3	16.6	1.43
17	5	2000	25	15	0	—	—	—
18	5	1000	25	15	97	11.1	11.6	1.69
19	5	500	25	5	100	5.70	7.78	1.73
20	6	100	25	180	0	—	—	—
21	7	100	25	180	0	—	—	—
22	8	100	25	180	0	—	—	—
23	X ^[f]	100	25	180	0	—	—	—

[a] Polymerization conditions: in toluene; ϵ -CL = 0.82 mol L^{−1}. [b] [M]/[I] = [monomer]/[initiator]. [c] Yield = weight of polymer obtained/weight of monomer used. [d] $M_{n,theo} = ([CL]/[I]) \times 114.14 \times (\text{polymer yield})$. [e] Measured by GPC calibrated with standard polystyrene samples and corrected with the coefficient of 0.56. [f] X = [LSmCl₂(thf)₂].

an electron-withdrawing group, Cl, showed the highest activity, whereas complex **5** bearing a ligand with an electron-donating group, Me, exhibited the lowest activity. For example, **2** gave complete conversion in the case of [M]/[I] = 2000 at 25 °C in 15 min (Table 3, Entry 6), whereas only 54% conversion (Table 3, Entry 13) and no polymer (Table 3, Entry 17) were obtained for complexes **4** and **5**, respectively. The conversion was still 100% even when the temperature was decreased to 0 °C with **2** as the initiator (Table 3, Entry 8). Therefore, a decrease in the electron density of the ligand around the metal center was beneficial to the increase in the activity of the Ln–N bond for ϵ -CL polymerization in the present systems. This may be because the electron-withdrawing substituents on the ligand make the central metal more electron-deficient, which favors the coordination of the monomer.

All of the polymers obtained have high molecular weights. Although a roughly linear relationship between monomer-to-initiator ratio and molecular weight can be observed, the molecular weight distributions of the resulting polymers are relatively broad (from 1.38 to 1.89). These results indicate that these polymerization systems are not well controlled.

The catalytic behavior of complexes **1–8** for L-LA polymerization was also examined, and the preliminary results are summarized in Table 4. Complexes **1–5** proved to be highly active initiators for L-LA polymerization. The catalytic activity also depended strongly on the size of the center metal and the electronic factor of the β -diketiminato ligands. Praseodymium complex **1** has been found to be the most active catalyst among these complexes: almost com-

plete conversion was achieved in thf in 15 min at 65 °C when the molar ratio of monomer to initiator ([M]/[I]) was 500 (Table 4, Entry 1). A decrease in the ionic radii of the metals resulted in a marked decrease in the catalytic activity. For example, by using complex **1** as the initiator, 90% yield could be obtained within 5 min at 40 °C when the molar ratio of monomer to initiator was 300 (Table 4, Entry 4), whereas the yield was 68% within 15 min for **2** (Table 4, Entry 6) and only 38% for **3** even when the polymerization time was prolonged to 60 min (Table 4, Entry 9). Therefore, the active order for central metals is Sm < Nd < Pr. A similar active trend was also observed when bis(allyl)(diketiminato)lanthanide complexes^[4] or the β -ketoiminato rare-earth metal aryloxido complexes^[12] were used as the catalysts for lactide polymerization.

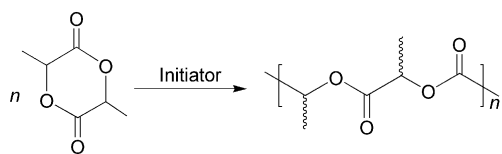
Similarly, mono- β -diketiminato lanthanide dichlorides **6–8** and [LSmCl₂(thf)₂] were inactive for L-LA polymerization under the same polymerization conditions (thf as solvent, L-LA = 1 mol L^{−1}, 40 °C). Even when the molar ratio of monomer to initiator was decreased to 100 and the polymerization time extended to 180 min, still no polymerization occurred (Table 4, Entries 14–17). The results once again indicated that the Ln– β -diketiminato bond in a tris- β -diketiminato lanthanide complex is much more active than that in a less bulky dichloride, which is consistent with the data of Ln–N bond lengths for the two kinds of complexes.

In general, by using the ligands with better electron-donating ability, one can expect to hamper the coordination of the monomer and to slow polymerization process down.^[13a] Gibson and co-workers showed that modification of the

Table 4. Polymerization of L-lactide initiated by complexes **1–8**.^[a]

Entry	Initiator	[M]/[I] ^[b]	<i>T</i> (°C)	<i>t</i> (min)	Yield (%) ^[c]	<i>M_{n,theo}</i> (10 ^{−4}) ^[d]	<i>M_{n,exp}</i> (10 ^{−4}) ^[e]	PDI
1	1	500	65	15	98	7.06	12.0	1.49
2	1	500	40	15	84	6.05	23.5	1.53
3	1	500	20	15	44	3.17	19.4	1.38
4	1	300	40	5	90	3.89	24.6	1.61
5	1	300	20	15	80	3.46	34.6	1.43
6	2	300	40	15	68	2.94	17.3	1.36
7	2	300	40	30	98	4.23	13.6	1.42
8	2	300	20	30	50	2.16	20.7	1.35
9	3	300	40	60	38	1.64	3.64	1.24
10	3	200	40	60	84	2.42	16.5	1.64
11	4	300	40	30	86	3.72	24.3	1.41
12	5	300	40	30	58	2.51	13.1	1.23
13	5	200	40	5	81	2.33	26.2	1.37
14	6	100	40	180	0	—	—	—
15	7	100	40	180	0	—	—	—
16	8	100	40	180	0	—	—	—
17	X ^[f]	100	40	180	0	—	—	—

[a] Polymerization conditions: thf as solvent; L-LA = 1.0 mol L^{−1}. [b] [M]/[I] = [monomer]/[initiator]. [c] Yield = weight of polymer obtained/weight of monomer used. [d] $M_{n,theo} = ([LA]/[I]) \times 144.13 \times (\text{polymer yield})$. [e] Measured by GPC calibrated with standard polystyrene samples and corrected with the coefficient of 0.58. [f] X = [LSmCl₂(thf)₂].



supporting ligand by introduction of electron-withdrawing substituents furnishes a more active aluminium catalyst for the polymerization of lactide.^[13b] In the present cases, a similar effect of the electronic factor of the β-diketiminato ligand on the catalytic activity was also observed. The active sequence is **2** > **4** > **5**, which is consistent with the electron-deficiency of the ligand (Table 4, Entries 7, 11, and 12).

It was noticed that no correlation could be found between the calculated and the GPC measured M_n . In order to get the correct M_n value of PLA the experimental value, which is obtained from the GPC traces by using polystyrene standards, has to be multiplied by 0.58.^[14] All the number-averaged molecular weights corrected by the coefficient 0.58 of the polymers produced are far greater than theoretical ones. This may be due to faster propagation related to initiation,^[15] or not all of the complexes participated in the polymerization as active initiators. As expected, raising the polymerization temperature led to an increase in the polymerization rate. For example, if the polymerization was performed at 65 °C, 98% conversion could be achieved in 15 min, whereas only 84 and 44% were obtained at 40 and 20 °C (Table 4, Entries 1–3), respectively. Moreover, the resulting polymers at 65 °C have the molecular weights more close to theoretical ones in comparison with those obtained at 40 °C or at 20 °C.

The oligomerizations of ε-CL and L-LA were conducted with [PrL₃^C] under the condition of [M]/[I] = 10 and then terminated by isopropyl alcohol. The resulting polymers were examined by ¹H NMR spectroscopic analysis. There

were no peaks for the isopropyl or β-diketiminato groups detected for both oligomers of ε-CL and L-LA, but the peaks of polyCL or polyLA in the ¹H NMR spectra were observed. The same situation was also found for systems with homoleptic lanthanides benzimidinates,^[13a] lanthanides guanidinates complexes,^[16] and chiral heterobimetallic complexes.^[17] Normally, no end-group detection was attributed to the formation of cyclic polymers through intramolecular attack of the Ln–O bond in an active species to the N-bonded acyl carbon atom.^[13a,16,17] Therefore, the formation of cyclic polymers and a similar mechanism as those supposed for the above systems were suggested in our case. As the initial step of the polymerization, ε-CL coordinated to the central metal, which was then followed by nucleophilic attack by one of the β-diketiminato nitrogen atoms at the carbonyl carbon atom of the lactone. Subsequently, acyl bond cleavage occurred with the formation of an alkoxide active species. The cyclic polymer might be formed through intramolecular attack of the Ln–O bond to the N-bonded acyl carbon atom.

Another possibility for no end-group detection may be because the molecular weights of the oligomers obtained are too large to be detected by ¹H NMR spectroscopy.

Conclusions

A series of sterically demanding tris-β-diketiminato lanthanide complexes were successfully synthesized in good yield by a salt metathesis reaction, and their structural features were determined by X-ray diffraction. Tris-β-diketiminato lanthanide complexes were first proven to be highly active initiators for the polymerization of ε-caprolactone and L-lactide. On the basis of the fact that no activity of mono-β-diketiminato lanthanide dichlorides was observed under the same polymerization conditions, the high cata-

lytic activity shown by tris- β -diketiminato lanthanide complexes might be attributed to the activation of Ln–N bonds induced by the steric demand of the three β -diketiminato ligands. Further study on the reactivity of sterically crowded tris- β -diketiminato lanthanide complexes is ongoing in our laboratory.

Experimental Section

General Procedures: All manipulations were performed under a purified argon atmosphere by using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl prior to use. ϵ -Caprolactone was purchased from Acros, dried with CaH_2 for 48 h, and then distilled under reduced pressure. L-Lactide was recrystallized twice with dry toluene. $\text{LLi}^{[18a]}$ and $\text{L}^{\text{Pr}_2}\text{Li}^{[18b]}$ were prepared according to a literature procedure. All glassware for the polymerization was dried in an oven before use. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer.^[19] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo–Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. ^1H NMR spectra were obtained in CDCl_3 for ligands by using a Unity Inova-400 spectrometer. The uncorrected melting points of crystalline samples were determined in sealed argon-filled capillaries. Molecular weights and molecular weight distributions were determined against polystyrene standards by gel permeation chromatography (GPC) at 30 °C with a Waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) by using thf as the eluent.

$\text{L}^{\text{Cl}}\text{H}$: A mixture of *p*-chloroaniline (31.9 g, 0.25 mol), 2,4-pentanedione (12.7 mL, 12.4 g, 0.12 mol), and *p*-toluenesulfonic acid (21.3 g) in toluene (350 mL) was heated at reflux for 24 h in a Dean–Stark apparatus. The toluene was then decanted off, and the solid residue was treated with diethyl ether (250 mL), water (200 mL), and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (53 g). After stirring for 25 min, the ether layer was separated and dried with MgSO_4 , and the solvent was removed in vacuo. The residue was dried in vacuo (10^{-2} bar) at 100 °C for 6 h to remove any remaining free *p*-chloroaniline, and the residue was crystallized from hexane to give 27 g (70%) of $\text{L}^{\text{Cl}}\text{H}$. M.p. 86–87 °C. ^1H NMR (400 MHz, CDCl_3): δ = 12.43 (s, 1 H, NH), 7.11 (d, 4 H, ArH), 6.87 (d, 4 H, ArH), 5.21 (s, 1 H, β -CH), 1.98 (s, 6 H, α -CH₃) ppm. $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{N}_2$ (319.23): calcd. C 63.96, H 5.05, N 8.78; found C 63.77, H 5.02, N 8.80.

$\text{L}^{\text{Me}}\text{H}$: A mixture of *p*-methylaniline (26.8 g, 0.25 mol), 2,4-pentanedione (12.7 mL, 12.4 g, 0.12 mol), and *p*-toluenesulfonic acid (21.3 g) in toluene (350 mL) was heated at reflux for 24 h in a Dean–Stark apparatus. The toluene was then decanted off, and the solid residue was treated with diethyl ether (250 mL), water (200 mL), and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (53 g). After stirring for 25 min, the ether layer was separated and dried with MgSO_4 , and the solvent was removed in vacuo. The residue was dried in vacuo (10^{-2} bar) at 100 °C for 6 h to remove any remaining free *p*-methylaniline, and the residue was crystallized from hexane to give 27.8 g (80%) of $\text{L}^{\text{Me}}\text{H}$. M.p. 73–74 °C. ^1H NMR (400 MHz, CDCl_3): δ = 12.67 (s, 1 H, NH), 7.10 (d, 4 H, ArH), 6.85 (d, 4 H, ArH), 4.85 (s, 1 H, β -CH), 2.31 (s, 6 H, *p*-CH₃), 1.98 (s, 6 H, α -CH₃) ppm. $\text{C}_{19}\text{H}_{22}\text{N}_2$ (278.40): calcd. C 81.97, H 7.96, N 10.06; found C 81.77, H 7.90, N 10.11.

$[\text{PrL}_3^{\text{Cl}}]$ (1): To a slurry of anhydrous PrCl_3 (0.74 g, 3.00 mmol) in thf (ca. 20 mL) was slowly added a solution of $\text{L}^{\text{Cl}}\text{Li}$ (9.00 mmol) in toluene/hexane (4:1, 20 mL) at room temperature. The reaction

mixture was stirred at 40 °C for 48 h, the solvents were stripped off in vacuo, and toluene was added to extract the product. The dissolved portion was removed by centrifugation, and the yellow-green supernatant was then concentrated and cooled to 0 °C to give yellow-green crystals of **1** in 75% yield (2.46 g, 2.25 mmol). M.p. 220–225 °C (decomp.). $\text{C}_{51}\text{H}_{45}\text{Cl}_6\text{N}_6\text{Pr}$ (1095.54): calcd. C 55.91, H 4.14, N 7.67, Pr 12.86; found C 55.71, H 4.34, N 7.62, Pr 12.96. IR (KBr): $\tilde{\nu}$ = 3419 (s), 2964 (m), 2925 (m), 1636 (vs), 1551 (vs), 1482 (vs), 1443 (s), 1382 (vs), 1281 (s), 1189 (s), 1096 (m), 1011 (w), 926 (w), 849 (m), 803 (w), 741 (w), 679 (w), 641 (w), 586 (w), 502 (w) cm^{-1} .

$[\text{NdL}_3^{\text{Cl}}]$ (2): To a slurry of anhydrous NdCl_3 (0.95 g, 3.79 mmol) in thf (ca. 30 mL) was slowly added a solution of $\text{L}^{\text{Cl}}\text{Li}$ (11.4 mmol) in toluene/hexane (4:1, 35 mL) at room temperature. The reaction mixture was stirred at room temperature for 48 h, the solvents were stripped off in vacuo, and toluene was added to extract the product. The dissolved portion was removed by centrifugation, and the pale-blue supernatant was then concentrated and cooled to –10 °C to give pale-blue crystals of **2** in 80% yield (3.35 g, 3.05 mmol). M.p. 182–184 °C (decomp.). $\text{C}_{51}\text{H}_{45}\text{Cl}_6\text{N}_6\text{Nd}$ (1098.87): calcd. C 55.74, H 4.13, N 7.65, Nd 13.13; found C 55.96, H 4.08, Nd 13.10. IR (KBr): $\tilde{\nu}$ = 3442 (s), 2987 (m), 2925 (m), 2856 (w), 1636 (vs), 1551 (vs), 1482 (vs), 1443 (s), 1382 (vs), 1281 (s), 1189 (s), 1088 (m), 1011 (m), 834 (v), 841 (m), 764 (m), 679 (w), 633 (w), 579 (w), 509 (w) cm^{-1} .

$[\text{SmL}_3^{\text{Cl}}]$ (3): The synthesis of complex **3** was carried out in the same way as that described for complex **2**, but SmCl_3 (0.90 g, 3.50 mmol) was used instead of NdCl_3 . Orange-yellow microcrystals of **3** were obtained from a concentrated toluene solution in 82% yield (3.17 g, 2.87 mmol). M.p. 178–180 °C (decomp.). $\text{C}_{51}\text{H}_{45}\text{Cl}_6\text{N}_6\text{Sm}$ (1104.98): calcd. C 55.44, H 4.10, N 7.61, Sm 13.61; found C 55.77, H 4.17, N 7.82, Sm 13.39. IR (KBr): $\tilde{\nu}$ = 3442 (s), 2925 (m), 2856 (w), 1628 (s), 1551 (s), 1482 (s), 1436 (m), 1382 (s), 1219 (vs), 1158 (vs), 1096 (m), 1027 (w), 841 (m), 803 (w), 733 (w), 633 (w), 548 (w), 509 (m) cm^{-1} .

$[\text{NdL}_3]$ (4): To a slurry of anhydrous NdCl_3 (1.00 g, 4.00 mmol) in thf (ca. 30 mL) was slowly added a solution of LLi (12.00 mmol) in toluene/hexane (4:1, 30 mL) at room temperature. The reaction mixture was then stirred at 40 °C for 48 h, the solvents were stripped off in vacuo and toluene was added to extract the product. The dissolved portion was removed by centrifugation and the pale-blue solution was then concentrated and cooled to –10 °C to give pale-blue crystals in 75% yield (2.68 g, 3.00 mmol). M.p. 191–194 °C (decomp.). $\text{C}_{51}\text{H}_{51}\text{N}_6\text{Nd}$ (892.22): calcd. C 68.66, H 5.76, N 9.42, Nd 16.17; found C 68.77, H 5.95, N 9.17, Nd 16.02. IR (KBr): $\tilde{\nu}$ = 3064 (s), 2362 (m), 1636 (vs), 1559 (vs), 1490 (vs), 1436 (m), 1366 (s), 1227 (s), 1158 (s), 1073 (w), 1027 (m), 903 (w), 803 (m), 749 (m), 695 (m), 634 (w), 509 (m) cm^{-1} .

$[\text{NdL}_3^{\text{Me}}]$ (5): The synthesis of complex **5** was carried out in the same way as that described for complex **4**, but $\text{L}^{\text{Me}}\text{Li}$ (6.04 mmol) was used instead of LLi . Complex **5** was obtained as pale-blue crystals at –5 °C in 2 d in 65% yield (1.27 g, 1.30 mmol). M.p. 230–233 °C (decomp.). $\text{C}_{57}\text{H}_{63}\text{N}_6\text{Nd}$ (976.37): calcd. C 70.12, H 6.50, N 8.61, Nd 14.77; found C 70.08, H 6.71, N 8.40, Nd 14.50. IR (KBr): $\tilde{\nu}$ = 3427 (s), 3025 (m), 2995 (m), 2925 (m), 2863 (m), 1891 (w), 1628 (vs), 1551 (vs), 1513 (vs), 1436 (s), 1366 (s), 1281 (s), 1189 (s), 1104 (w), 1027 (m), 841 (m), 810 (m), 756 (m), 602 (m), 525 (m) cm^{-1} .

$[\text{L}^{\text{Cl}}\text{PrCl}_2(\text{thf})_2]$ (6): A thf (20 mL) solution of $\text{L}^{\text{Cl}}\text{H}$ (1.32 g, 4.13 mmol) was added dropwise to a NaH suspension (20 mmol) in thf (20 mL) at room temperature. The reaction mixture was stirred overnight, and then the mixture was filtered. The transparent

orange-yellow solution was then slowly added to a slurry of anhydrous PrCl_3 (1.02 g, 4.13 mmol) in thf (20 mL). The color of the solution gradually changed to pale green, and a colorless gel-like precipitate formed gradually. The mixture was stirred at room temperature for 48 h, and the precipitate was removed by centrifugation. To the thf solution was added dme (5 mL), and then the solution was concentrated in vacuo. Green crystals were obtained from a concentrated thf/dme solution (15 mL) at room temperature in 70% yield (1.95 g, 2.89 mmol). M.p. 160–163 °C (decomp.). $\text{C}_{25}\text{H}_{31}\text{Cl}_4\text{N}_2\text{O}_2\text{Pr}$ (674.25): calcd. C 44.53, H 4.63, N 4.15, Pr 21.90; found C 44.83, H 4.50, N 4.28, Pr 21.75. IR (KBr): $\tilde{\nu}$ = 3380 (s), 2987 (s), 2871 (m), 1628 (s), 1605 (s), 1536 (vs), 1489 (vs), 1443 (m), 1382 (m), 1312 (s), 1095 (m), 1034 (m), 834 (m), 712 (m) cm^{-1} .

[$\text{L}^{\text{Me}}\text{NdCl}_2(\text{thf})_2$] (7): A thf (20 mL) solution of $\text{L}^{\text{Me}}\text{H}$ (1.06 g, 3.80 mmol) was added dropwise to a NaH suspension (18 mmol) in thf (20 mL) at room temperature. The reaction mixture was stirred overnight, and then the mixture was filtered. The transparent yellow solution was then slowly added to a slurry of anhydrous NdCl_3 (0.95 g, 3.80 mmol) in thf (20 mL). The color of the solution gradually changed to pale blue, and a colorless gel-like precipitate formed gradually. The mixture was stirred overnight at room temperature, and the precipitate was removed by centrifugation. The solvent was removed under reduced pressure, and the residue was extracted with toluene (50 mL). To the toluene solution was added dme (3 mL), and then the solution was concentrated to about 20 mL. Pale-blue microcrystals were obtained at room temperature in a few days (1.57 g, 65% based on Nd). M.p. 165–168 °C (decomp.). $\text{C}_{27}\text{H}_{37}\text{Cl}_2\text{N}_2\text{NdO}_2$ (636.75): calcd. C 50.93, H 5.86, N 4.40, Nd 22.65; found C 51.20, H 5.78, N 4.50, Nd 22.52. IR (KBr): $\tilde{\nu}$ = 3445 (m), 2986 (s), 2966 (m), 2924 (m), 1632 (m), 1558 (vs), 1485 (vs), 1439 (m), 1381 (m), 1312 (s), 1289 (m), 1090 (m), 837 (m), 718 (m) cm^{-1} .

[$\text{L}^{\text{Pr}_2}\text{NdCl}_2(\text{thf})_2$] (8): The synthesis of complex **8** was carried out in the same way as that described for complex **7**, but $\text{L}^{\text{Pr}_2}\text{H}$ (1.47 g, 3.51 mmol) was used instead of $\text{L}^{\text{Me}}\text{H}$. Blue-green microcrystals were obtained from a toluene/dme solution at 0 °C in 72% yield (1.96 g, 2.52 mmol). M.p. 182–185 °C (decomp.). $\text{C}_{37}\text{H}_{57}\text{Cl}_2\text{N}_2\text{NdO}_2$ (776.99): calcd. C 57.20, H 7.39, N 3.61, Nd

18.56; found C 57.00, H 7.12, N 3.70, Nd 18.75. IR (KBr): $\tilde{\nu}$ = 3412 (s), 2961 (s), 2928 (m), 2868 (m), 2360 (m), 2341 (m), 1623 (vs), 1553 (vs), 1487 (m), 1464 (m), 1439 (m), 1380 (m), 1363 (m), 1324 (m), 1277 (m), 1221 (m), 1175 (m), 1101 (m), 1058 (m), 1023 (m), 953 (w), 759 (w), 668 (w) cm^{-1} . Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of a hot toluene/dme solution.

Typical Procedure for the Polymerization Reaction: Polymerizations of L-lactide (L-LA) were performed under an atmosphere of argon in flame-dried round-bottom flasks. To a stirred solution of L-LA (0.50 g, 3.47 mmol) in thf (1.47 mL) was added a thf solution (2.00 mL) of complex **1** (12.71 mg, 0.0116 mmol, $[\text{LA}]/[\text{Pr}] = 300:1$, $[\text{LA}] = 1.00 \text{ mol L}^{-1}$). Temperature equilibration was ensured by stirring the flasks for 15 min in an oil bath thermostatted at 40 °C, followed by the injection of the initiator into the monomer solution. Polymerizations were stopped by injecting a solution of HCl (5 vol.-%) in ethanol. Polymers were precipitated in ethanol, filtered, washed with ethanol, and then dried at 40 °C for 24 h in vacuo to constant weight.

The procedure for the polymerization of ϵ -caprolactone was similar, and a typical polymerization procedure is given below. A 50-mL Schlenk flask, equipped with a magnetic stirring bar, was charged with a solution of initiator in toluene. To this solution was added the desired amount of ϵ -caprolactone by syringe. The contents of the flask were then stirred vigorously at the desired temperature for a fixed time, during which time an increase in viscosity was observed. The reaction mixture was quenched by the addition of 1 M HCl/ethanol solution and then poured into ethanol to precipitate the polymer, which was dried in vacuo and weighed.

X-ray Crystallography: Suitable single crystals of complexes **1–5** and **8** were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode by using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 5. The structures were solved by direct methods

Table 5. Crystallographic data for complexes **1–5** and **8**.

	1	2	3	4	5	8
Empirical formula	$\text{C}_{51}\text{H}_{45}\text{N}_6\text{Cl}_6\text{Pr}$	$\text{C}_{51}\text{H}_{45}\text{N}_6\text{Cl}_6\text{Nd}$	$\text{C}_{51}\text{H}_{45}\text{N}_6\text{Cl}_6\text{Sm}$	$\text{C}_{51}\text{H}_{51}\text{N}_6\text{Nd}$	$\text{C}_{57}\text{H}_{63}\text{N}_6\text{Nd}$	$\text{C}_{37}\text{H}_{57}\text{Cl}_2\text{N}_2\text{NdO}_2$
Formula mass	1095.54	1098.87	1104.98	892.22	976.37	776.99
Temperature (K)	223(2)	193(2)	193(2)	223(2)	223(2)	223(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$Pbca$
Crystal size (mm)	$0.29 \times 0.21 \times 0.12$	$0.37 \times 0.32 \times 0.16$	$0.45 \times 0.43 \times 0.17$	$0.75 \times 0.38 \times 0.20$	$0.60 \times 0.42 \times 0.20$	$0.80 \times 0.69 \times 0.40$
<i>a</i> (Å)	12.2362(15)	12.2368(11)	12.2461(9)	18.7300(19)	12.6186(14)	20.5053(18)
<i>b</i> (Å)	19.433(2)	19.401(2)	19.3441(13)	10.6620(9)	19.3441(18)	15.6086(14)
<i>c</i> (Å)	20.928(2)	20.921(2)	20.9205(16)	22.747(2)	21.108(2)	24.136(2)
β (°)	100.176(3)	100.235(3)	100.344(3)	104.159(2)	99.411(2)	90
<i>V</i> (Å ³)	4898.1(10)	4887.8(8)	4875.3(6)	4404.5(7)	5082.9(9)	7725.0(12)
<i>Z</i>	4	4	4	4	4	8
<i>D</i> _{calcd.} (g cm ^{−3})	1.486	1.493	1.505	1.346	1.276	1.336
μ (mm ^{−1})	1.364	1.432	1.575	1.220	1.063	1.514
<i>F</i> (000)	2216	2220	2228	1836	2028	3224
θ range (°)	3.01–25.35	3.01–25.35	3.01–25.35	3.06–25.35	3.12–25.35	3.02–25.35
Reflns. collected	47281	48029	47755	41462	49299	71617
Reflns. observed [<i>I</i> > 2 σ (<i>I</i>)]	7105	7917	8165	6534	7968	6430
Data/restraints/parameters	8952/0/584	8918/0/584	8905/0/584	8040/0/530	9294/0/590	7067/10/403
Goodness-of-fit on <i>F</i> ²	1.172	1.134	1.120	1.151	1.170	1.146
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0706	0.0347	0.0287	0.0512	0.0450	0.0569
<i>wR</i> ₂ (all data)	0.1229	0.0708	0.0669	0.0872	0.0845	0.1110

and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined by using SHELEXL-97 program. CCDC-725486 (for **1**), -725487 (for **2**), -725488 (for **3**), -725489 (for **4**), -725490 (for **5**), and -725491 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We are indebted to the Chinese National Natural Science Foundation for financial support (20632040).

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Received: April 5, 2009

Published Online: August 11, 2009