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Bis(β-diketiminate) Rare-Earth-Metal Borohydrides: Syntheses, Structures, and Catalysis for the Polymerizations of L-Lactide, ε-Caprolactone, and Methyl Methacrylate

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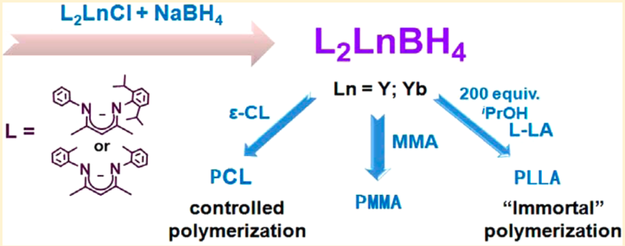
Ⓢ *Supporting Information*

ABSTRACT: Reaction of $LnCl_3$ (Ln = Y, Yb) with 2 equiv of $NaL^{2,6\text{-ipr}2}{}_{Ph}$ ($L^{2,6\text{-ipr}2}{}_{Ph}$ = $[(2,6\text{-}^iPr_2C_6H_3)NC(Me)CHC(Me)N(C_6H_5)]^-$) afforded the chlorides $(L^{2,6\text{-ipr}2}{}_{Ph})_2YCl$ (**1**) and $(L^{2,6\text{-ipr}2}{}_{Ph})_2YbCl$ (**2**). Crystal structure analysis revealed **2** to be the unsolvated monomer. Treatment of the chlorides **1** and **2** with $NaBH_4$ in a 1/1 molar ratio in THF led to the preparation of the monoborohydrides $(L^{2,6\text{-ipr}2}{}_{Ph})_2LnBH_4$ (Ln = Y (**3**), Yb (**4**)) in good yields. Reaction of $LnCl_3$ (Ln = Y, Yb) with 2 equiv of $NaL^{2\text{-Me}}$ ($L^{2\text{-Me}}$ = $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$) in THF, followed by treatment with 1 equiv of $NaBH_4$, afforded the monoborohydrides $(L^{2\text{-Me}})_2LnBH_4$ (Ln = Y (**5**), Yb (**6**)). Complexes **3**−**6** were fully characterized, including X-ray crystal structure analyses. Complexes **3**−**6** are isostructural. The central metal in each complex is ligated by two β-diketiminate ligands and one η^3-BH_4^- group in a distorted trigonal bipyramid. Complexes **3**−**6** were found to be highly active in the ring-opening polymerization of L-lactide (L-LA) and ε-caprolactone (ε-CL) to give polymers with relatively narrow molar mass distributions. The activity depends on both the central metal and the ligand (Y > Yb and $L^{2,6\text{-ipr}2}{}_{Ph}$ > $L^{2\text{-Me}}$). The best control over the molar mass was found for complex **6**. The M_n(obsd) values (M_n = the number-average molar mass) of the resulting PCL are in good agreement with M_n(calcd), with a ratio of monomer to **6** of up to 1000. The polymerization kinetics of L-LA in THF at 20 °C by complex **6** displays a first-order dependence on the monomer concentration. Notably, the binary **6**/^{i}PrOH system exhibited an "immortal" nature and proved able to quantitatively convert 10 000 equiv of L-LA with up to 200 equiv of ^{i}PrOH per metal initiator. All the obtained PLAs showed monomodal, narrow distributions (M_w/M_n = 1.06−1.11), with the M_n values decreasing proportionally with an increasing amount of ^{i}PrOH. Complex **4** can also initiate the polymerization of methyl methacrylate (MMA) at −40 °C with high activity, affording the PMMA with 83.3% syndiotacticity.



■ INTRODUCTION

There is continuing interest in the synthesis of aliphatic polyesters due to their biodegradable and biocompatible characteristics and wide applications in the medical and materials fields.[1] Controlled ring-opening polymerization of cyclic esters is a convenient route for the synthesis of aliphatic polyesters with predictable molar mass, low polydispersity indices, and control over end groups.

Rare-earth-metal borohydrides have been known to be valuable active species for the polymerization of cyclic esters,[2] MMA,[3] and even dienes[4] in reactions together with metal alkyl complexes. Consequently, significant efforts over the past few decades have been made toward the design and synthesis of well-characterized rare-earth-metal monoborohydrides by use of appropriate ancillary ligands as single-site initiators in the ring-opening polymerization of cyclic esters.[2b−d,f,h,3c,5] Remarkable advances have been reported with bulky ligands such as C_5Me_5,[2a,d,f,3c] tetradentate bisphenolate,[2c,h] bridged bisamidinate,[5a] guanidinate,[5b] etc.

β-Diketiminate ligands, as one of the most important non-cyclopentadienyl monoanionic ligands, have proven to be useful in organometallic chemistry of rare-earth metals, due to their easily accessed and tunable steric and electronic effects.[6] Various rare-earth-metal derivatives supported by mono-β-diketiminate ligands have been well documented.[7] However, their application in rare-earth-metal complexes supported by two monoanionic β-diketiminate ligands as single-site initiators has been limited until now. Although a series of bis(β-diketiminate) rare-earth-metal halides L'_2LnX (L' = $\{[N(Ph)C(Me)]_2CH\}$, X = Br, Ln = Sm, Gd; L' = $\{[N(SiMe_3)C(Ph)]_2CH\}$, X = Cl, Ln = Ce, Pr, Nd, Sm, Yb; L' = $[N(SiMe_3)C(Ph)]CHC(Bu^t)]$, X = I, Ln = Tm) were

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successfully prepared,[8] the further transformation of $\{[N(SiMe_3)C(Ph)]_2CH\}CeCl$ with $LiCH(SiMe_3)_2$ did not afford the corresponding monoalkyl complex; $Ce[CH(SiMe_3)_2]_2\{[N(SiMe_3)C(Ph)]_2CH\}$ was obtained instead.[8b] It is suggested that $Ce[CH(SiMe_3)_2]\{[N(SiMe_3)C(Ph)]_2CH\}_2$ would be too sterically hindered. As a result, only two yttrium complexes, $YL'_2(N[SiHMe_3]_2)$[9] and $[Y(L^1)_2O^tBu]$,[10] have been synthesized and structurally characterized up to date. Furthermore, no catalytic activity was found for these kinds of complexes.

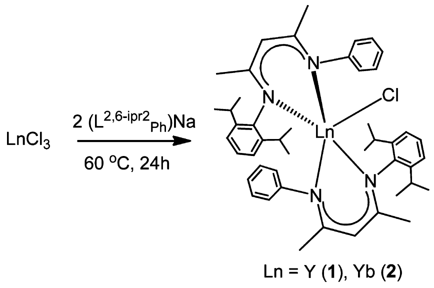
Very recently we became interested in the reaction chemistry of β-diketiminate rare-earth-metal complexes.[11] In a continuation of our work, we focus our attention now on the synthesis of rare-earth-metal derivatives supported by bis(β-diketiminate) ligands, with the aim of exploring the potential of these kind of rare-earth-metal complexes as single-site initiators in the controlled ring-opening polymerization of cyclic esters.

In this contribution, we report the synthesis of the bis(β-diketiminate) rare-earth-metal chlorides $(L^{2,6\text{-ipr2}}_{Ph})_2LnCl$ ($L^{2,6\text{-ipr2}}_{Ph}$ = $[(2,6\text{-}^iPr_2C_6H_3)NC(Me)CHC(Me)N(C_6H_5)]^-$, Ln = Y (**1**), Yb (**2**)) and their transformation with $NaBH_4$ to the monoborohydride complexes $(L^{2,6\text{-ipr2}}_{Ph})_2LnBH_4$ (Ln = Y (**3**), Yb (**4**)) and $(L^{2\text{-Me}})_2LnBH_4$ ($L^{2\text{-Me}}$ = $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$, Ln = Y (**5**), Yb (**6**)) and the molecular structures of complexes **2**–**6**. The catalytic behavior of these new borohydrides toward ε-CL and L-LA polymerizations, including an "immortal" nature in the presence of HO^iPr with up to 200 PAL per metal active center and catalytic activity in the polymerization of MMA, is also presented.

RESULTS AND DISCUSSION

Syntheses of Bis(β-diketiminate) Rare-Earth-Metal Chlorides $(L^{2,6\text{-ipr2}}_{Ph})_2LnCl$ (Ln = Y (1), Yb (2)) and the Molecular Structure of Complex 2. The β-diketiminate proligands $L^{2,6\text{-ipr2}}_{Ph}H$ and $L^{2\text{-Me}}H$ were prepared by the published methods.[12] Reaction of YCl_3 with a THF solution of $NaL^{2,6\text{-ipr2}}_{Ph}$, which was formed in situ by the reaction of $L^{2,6\text{-ipr2}}_{Ph}H$ with NaH, in a 1/2 molar ratio at 60 °C was conducted first. After workup the monochloride $(L^{2,6\text{-ipr2}}_{Ph})_2YCl$ (**1**) was isolated as yellow crystals in good yield. The analogous Yb complex, $(L^{2,6\text{-ipr2}}_{Ph})_2YbCl$ (**2**), was also prepared by the same procedure without difficulty (Scheme 1).

Scheme 1. Syntheses of 1 and 2



The elemental analyses of **1** and **2** are consistent with their formulas. The IR spectra exhibited strong absorptions near 1547 and 1516 cm^{-1}, indicative of the partial C=N character of the β-diketiminate ligands.[13] ^1H NMR of **1** revealed signals assigned to the $L^{2,6\text{-ipr2}}Ph$ ligand. The formation of **2** was further confirmed by a single-crystal structure analysis. An attempt to determine the molecular structure of **1** was unsuccessful, due to the poor quality and weak diffraction of the crystals.

The same reactions with a THF solution of $NaL^{2\text{-Me}}$ did not afford the isolable monochloride $(L^{2\text{-Me}})_2LnCl$ (Ln = Y, Yb), but an oil was obtained instead as the product. The oil products prevented further characterization. Fortunately, the further transformation of them with $NaBH_4$ went smoothly with the formation of the monoborohydride complexes of Y and Yb in desired yields (see below), indicating the oil products were the monochlorides $(L^{2\text{-Me}})_2YCl$ and $(L^{2\text{-Me}})_2YbCl$.

Complex **2** crystallizes with two THF molecules and one toluene molecule of solvation: **2**·THF·0.5(toluene). The molecular structure of **2** is shown in Figure 1 with selected bond distances and angles. The molecular structure of **2** is quite similar to those reported for L_2NdCl[8b] and L_2YCl.[10] The coordination geometry around the Yb atom is a distorted trigonal bipyramid formed by four nitrogen atoms from two $L^{2,6\text{-ipr2}}_{Ph}$ ligands and one chlorine atom with the two nitrogen atoms of N(1) and N(1A) occupying axial sites (the angle of N(1)−Yb(1)−N1A = 171.2(2)°) and the three atoms N(2), N(2A), and Cl(1) at the equatorial positions (the sum of the angles of N(2)−Yb(1)−Cl(1), Cl(1)−Yb(1)−N(2A), and N(2A)−Yb(1)−N(2) is 360.04(10)°). The bond parameters in **2**, including Yb−N and Yb−Cl bond distances and the bond angles around the Yb atom, are comparable with those found in the analogues reported previously,[8b,10,14] when the differences in ion radii among them are considered.

Syntheses and Molecular Structures of Bis(β-diketiminate) Rare-Earth-Metal Monoborohydrides $(L^{2,6\text{-ipr2}}_{Ph})_2LnBH_4$ (Ln = Y (3), Yb (4)) and $(L^{2\text{-Me}})_2LnBH_4$ (Ln = Y (5), Yb (6)). The metathesis reaction of **1** with $NaBH_4$ was then tried to see whether the monoborohydride could be prepared. The reaction of **1** with 1 equiv of $NaBH_4$ was carried out in a THF solution at 60 °C. After the mixture was stirred for 5 days, the monoborohydride complex $(L^{2,6\text{-ipr2}}_{Ph})_2YBH_4$ (**3**) was isolated as pale yellow crystals upon crystallization from toluene solution in good yield (Scheme 2). By the same procedure, the Yb complex $(L^{2,6\text{-ipr2}}_{Ph})_2YbBH_4$ (**4**) was also prepared in the desired yield as red crystals (Scheme 2).

Although an isolable monochloride with $L^{2\text{-Me}}$ ligands, $(L^{2\text{-Me}})_2LnCl$ (Ln = Y, Yb), could not be obtained as mentioned above, treatment of the reaction solution of $LnCl_3$ and 2 equiv of $NaL^{2\text{-Me}}$ with 1 equiv of $NaBH_4$ in THF led to the isolation of the corresponding monoborohydride complexes $(L^{2\text{-Me}})_2YBH_4$ (**5**) and $(L^{2\text{-Me}})_2YbBH_4$ (**6**) as pure crystals (Scheme 2).

Complexes **3**–**6** were characterized by standard analytical/spectroscopic techniques. The IR spectra of **3**–**6** exhibited strong absorptions near 1550 and 1510 cm^{-1}, which were consistent with the partial C=N character of the β-diketiminate ligands,[13] and the expected two strong absorptions diagnostic of the η^3-bridging borohydride stretching vibration and terminal borohydride stretching vibration in the range of 2300−2200 cm^{-1}.[15] A resolvable ^1H NMR spectrum for **4** and **6** could not be measured owing to paramagnetism of Yb. In the ^1H NMR spectra of **3** and **5** the signals at 0.97−1.16 ppm for **3** and 1.07−1.33 ppm for **5** assigned to the BH_4 ligand are observed clearly.

Complexes **3**, **4**, and **6** were isolated as the solvates **3**·0.5(toluene), **4**·0.5(toluene), and **6**·2THF, respectively. X-ray diffraction analyses showed that complexes **3**–**6** are isostructural and all are five-coordinate monomers (Figure 2 gives the ORTEP plot of complex **3**, and crystal data are given in Table 1), reflecting that both ligands are sterically more

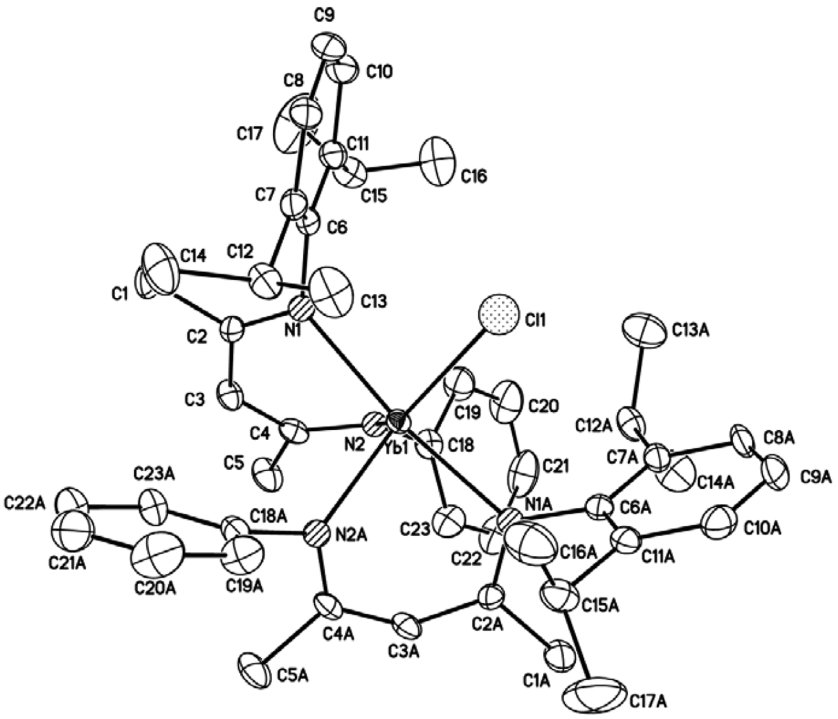
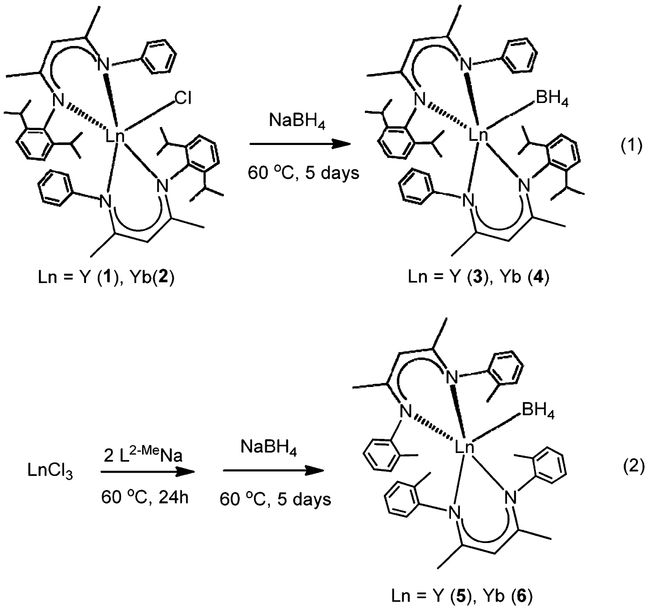


Figure 1. ORTEP diagram of complex **2** (one of the two independent molecules) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and the free toluene and THF molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Yb(1)−N(1) = 2.295(5), Yb(1)−N(2) = 2.256(5), Yb(1)−Cl(1) = 2.501(2); N(1)−Yb(1)−N(1A) = 171.2(2), N(2)−Yb(1)−Cl(1) = 126.82(13), Cl(1)−Yb(1)−N(2A) = 126.82(13), N(2)−Yb(1)−N(2A) = 106.4(3). Symmetry transformations used to generate equivalent atoms: (#1) $-x + {}^{1}/_{2}$, y, $-z + {}^{1}/_{2}$.

Scheme 2. Syntheses of Complexes 3−6



demanding than the C_5Me_5 ligand.[2a] For clarity the molecular cores of complexes **4**−**6** are shown in Figure 3.

Each central metal in complexes **3**−**6** is ligated by one BH_4^- group and two *β*-diketiminate ligands. The coordination polyhedron around the five-coordinate metal center can be described as a distorted trigonal bipyramid with two nitrogen atoms from two ligands respectively occupying the axial sites in an distorted setup to form an N(1)−Ln(1)−N(3) angle of 177.10(15)° for **3**, and N(1)−Ln(1)−N(1A) angles of 176.9(6)° for **4**, 170.39(19)° for **5**, and 168.45(16)° for **6** (Table 2). The average Ln−N bond distances of **3**−**6** are 2.340(4), 2.282(4), 2.337(4), and 2.302(3) Å, respectively, which are comparable with each other when the differences in ionic radii among these metals are considered.

The N−C and C−C bond distances of each anionic NCCCN unit in the *β*-diketiminate ligand in each complex are almost consistent (Table 2), reflecting the electron delocalization within the anionic NCCCN unit. The Ln−B distances (2.524(8) Å for **3**, 2.471(9) Å for **4**, 2.544(10) Å for **5**, 2.480(8) Å for **6**) are quite comparable to the corresponding values found in the monoborohydride complexes of rare-earth metals with a η^3-BH_4 group but are significantly shorter than those with a η^2-BH_4 group.[15c,16] The average Ln−H bond distances of complexes **3**−**6** are 2.27(8), 2.40(11), 2.27(6), and 2.16(8) Å, respectively, which are comparable with those for the complexes reported.[15c] Thus, the boron atoms in **3**−**6** are linked to the rare-earth-metal center via the three bridging hydrogen atoms.

Ring-Opening Polymerization of L-LA. The catalytic behaviors of **3**−**6** for polymerization of L-LA were assessed at room temperature with a molar ratio of monomer to initiator of 1000 ($[M]_0$ = 1.0 M). The results are given in Table 3. An almost complete conversion of the monomer was achieved after 4 min for complexes **3** (93%) and **5** (96%), while an 82% yield for complex **4** and 73% yield for complex **6** were obtained. The slightly lower activity for Yb compared to that for Y may be attributed to the small ionic radius of Yb. The borohydride complexes with $L^{2,6\text{-ipr2}}{}_{Ph}$ are more active than the complexes with $L_{2\text{-Me}}$ (Table 3, entries 1−4). The polymerization can proceed either in THF or in toluene (Table 3, entries 4 and 6). A control experiment with the chloride **1** was carried out. Even

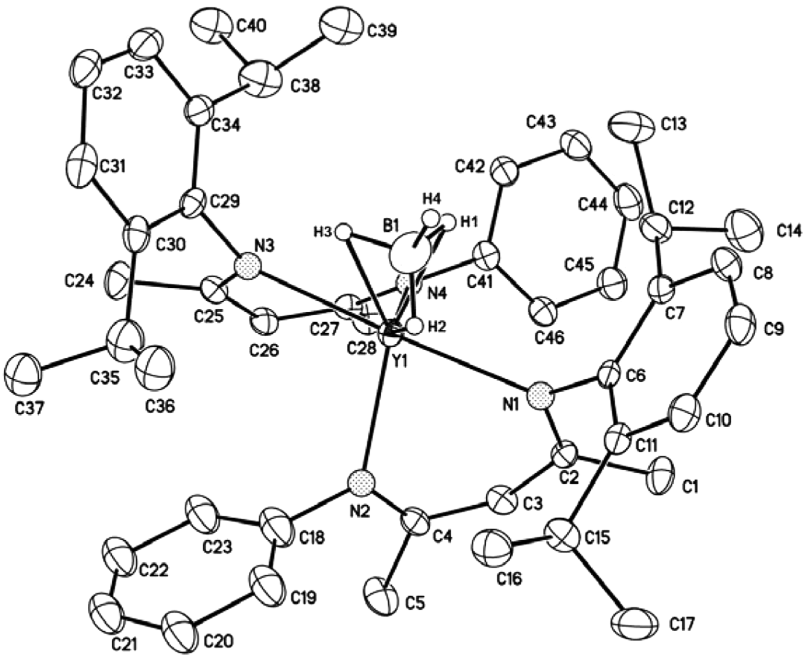


Figure 2. ORTEP diagram of complex **3** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and the free toluene molecule are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (#1) $-x$, $-y + 1$, $-z + 1$.

Table 1. Crystallographic Data for Complexes 2−6

param	**2**·C_4H_8O·$0.5C_7H_8$	**3**·$0.5C_7H_8$	**4**·C_4H_8O	**5**	**6**·$2C_4H_8O$
empirical formula	$C_{53.50}H_{70}ClN_4OYb$	$C_{49.50}H_{66}BN_4Y$	$C_{50}H_{71}BN_4OYb$	$C_{38}H_{47}BN_4Y$	$C_{46}H_{63}BN_4O_2Yb$
formula wt	993.63	816.78	927.96	659.52	886.85
temp (K)	293(2) K	223(2)	223(2)	223(2)	223(2)
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2/n$	$P\bar{1}$	$C2$	$Fdd2$	$C2/c$
cryst size (mm)	0.80 × 0.80 × 0.50	0.36 × 0.26 × 0.10	0.40 × 0.20 × 0.20	0.50 × 0.35 × 0.10	0.80 × 0.60 × 0.45
a (Å)	23.123(5)	9.0620(6)	22.0087(17)	22.685(5)	21.2509(17)
b (Å)	8.9946(18)	12.4085(12)	8.4890(4)	38.486(6)	12.8271(10)
c (Å)	24.820(5)	20.938(2)	16.4327(13)	8.1013(13)	16.7357(13)
α (deg)	90	86.514(6)	90	90	90
β (deg)	94.149(5)	81.914(5)	129.7710(10)	90	105.687(2)
γ (deg)	90	82.017(6)	90	90	90
V (Å^3)	5148.4(18)	2306.4(3)	2359.7(3)	7073(2)	4394.2(6)
Z	4	2	2	8	4
$D_{calcd.}$ (mg cm^{-3})	1.282	1.176	1.306	1.239	1.341
abs coeff (mm^{-1})	1.907	1.300	2.020	1.680	2.168
$F(000)$	2056	870	964	2776	1828
no. of collected/unique rflns (R(int))	36 764/9316 (0.0507)	19 887/8513 (0.0700)	6122/3895 (0.0283)	5600/2851 (0.0558)	10 849/4060 (0.0262)
no. of data/restraints/params	9316/19/538	8513/15/466	3895/11/264	2851/4/212	4060/13/246
goodness of fit on F^2	1.151	1.061	1.026	0.920	1.078
final R1 ($I > 2\sigma(I)$)	0.0540	0.0870	0.0314	0.0470	0.0336
wR2 (all data)	0.1192	0.2134	0.0669	0.0670	0.0870

after 10 min, no ROP was observed (Table 3, entry 5). This confirms that the M−BH_4 unit in each complex is the only active site. The molar mass distributions of the polymers formed with these borohydride complexes range from 1.33 to 1.44 (Table 3, entries 1−4). The best control over the molar mass was found for complex **6**. The M_n(obsd) values of PLAs obtained with complex **6** either in THF or in toluene are in good agreement with the M_n(calcd) fvalues or one chain growing per metal center (Table 3, entries 4, 6, and 7). In contrast, the M_n(obsd) values of the polymers obtained with complexes **3**−**5** are somewhat lower than those calculated. This can be attributed to transesterification reactions.

The polymerization kinetics of L-LA with complex **6** at a molar ratio of monomer to **6** of 1000 was further investigated at 20 °C in THF. The conversion increases with time, and a first-order dependence on the monomer concentration, without any induction period, was observed (Figure 4). The number-average molar mass (M_n) of the polymers increased linearly with the monomer conversion, while the values of M_w/M_n stayed relatively narrow (M_w/M_n = 1.31−1.38) (Figure 5),

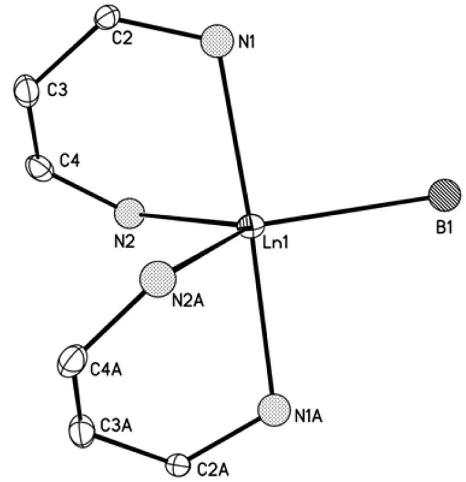


Figure 3. ORTEP drawing of the molecular core of complexes **4**−**6**.

which demonstrated that the polymerization in this system occurs in a living manner.

The end groups of the oligomer of L-LA, which was prepared by the polymerization of L-LA using complex **6** as the initiator in a 1/10 molar ratio and quenched by wet *n*-hexane, were determined by ^{1}H NMR. The ^{1}H NMR spectrum exhibited the quartet characteristic of a −C*H*(Me)OH terminal group at δ 4.33 ppm. The −C*H*(Me)OH group was formed by hydrolysis of the metal−alkoxide bond. An additional resonance at δ 4.16 ppm assigned to the CH_2OH end group[2e,h] was also observed. The results indicate that the polymerization proceeds by a classical coordination/insertion mechanism with an initial ring opening through acyl−oxygen bond cleavage, as described previously for the catalyst systems with rare-earth-metal borohydride complexes.[2e,h]

To address the possibility of achieving immortal polymerization with these systems by introducing several equivalents of a chain-transfer agent, polymerizations with complex **6** were conducted in the presence of isopropyl alcohol (^{i}PrOH). Representative results are summarized in Table 4. Immortal polymerization with complex **6** and ^{i}PrOH could be obtained either at 60 °C or at room temperature (Table 4, entries 2 and 3). Remarkably, the binary **6**/^{i}PrOH system was able to quantitatively convert 10 000 equivalents of L-LA with up to 200 equiv of chain-transfer agent per metal initiator. All the obtained PLAs at various ^{i}PrOH/**6** ratios (from 6 to 200) showed monomodal, narrow distributions (M_w/M_n = 1.06−1.11) with M_n values decreasing proportionally with increasing amounts of ^{i}PrOH.

The results indicated that the β-diketiminate ligands used here appear to be suitable ligands for stabilizing the Ln−alkoxide active species; thereby, an excess amount of ^{i}PrOH did not lead to deactivation but behaved as a chain transfer agent, in particular, arousing a living chain transfer polymerization to give PLAs with a chain end-capped by a OH group. To the best of our knowledge, metal catalysts which allow "immortal" ring-opening polymerization of LA, that is, to grow as many as 200 polymer chains per metal center, remain quite uncommon.[17] The resulting polymer with an end group of OH was further confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of PLAs obtained at $[\text{L-LA}]_0/[^i\text{PrOH}]_0/[\mathbf{6}]_0$ = 500/50/1 in $CDCl_3$ showed a multiplet resonance at 5.03 ppm and a doublet of doublets (or a quartet) resonance at 1.22 ppm assigned to the isopropoxide chain end $-OCH(CH_3)_2$ a quartet resonance around 4.33 ppm and a doublet resonance around 1.47 ppm indicative of the $-CH(CH_3)OH$ chain end, and a quartet resonance at 5.14 ppm and a doublet resonance around 1.56 ppm attributed to $\{-C(O)CH(CH_3)O-\}_n$.

Ring-Opening Polymerization of ε-CL. The catalytic activities of complexes **3**−**6** for ring-opening polymerization of ε-CL were evaluated at room temperature in toluene. All complexes are highly active. The activities depend on both the metal and the ligand with the same active sequences as those for the polymerization of L-LA (Table 5, entries 1−4). The systems with complexes **3**−**6** gave polymers with M_w/M_n values ranging from 1.29 to 1.48. The best molar mass control was found for complex **6**. Decreasing the polymerization temperature from 20 to 10 °C led to a greater deviation between the M_n(obsd) and M_n(calcd) values (for one chain growing per metal center) of the resulting polymers. This may be attributed to a slow initiation step in comparison to propagation. Indeed,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3−6

	3		4	5	6
		Bond Lengths			
Ln(1)−N(1)	2.382(5)	Ln(1)−N(1)	2.312(3)	2.365(3)	2.325(3)
Ln(1)−N(2)	2.293(4)	Ln(1)−N(2)	2.252(4)	2.309(4)	2.278(3)
Ln(1)−N(3)	2.371(5)	Ln(1)−N(1A)	2.312(3)	2.365(3)	2.325(3)
Ln(1)−N(4)	2.315(4)	Ln(1)−N(2A)	2.252(4)	2.309(4)	2.278(3)
Ln−N(av)	2.340(4)	Ln−N(av)	2.282(4)	2.337(4)	2.302(3)
Ln(1)−B(1)	2.524(8)	Ln(1)−B(1)	2.471(9)	2.544(10)	2.480(8)
Ln−H(av)	2.27(8)	Ln−H(av)	2.40(11)	2.27(6)	2.16(8)
C(2)−C(3)	1.421(8)	C(2)−C(3)	1.417(9)	1.395(7)	1.394(6)
C(3)−C(4)	1.387(9)	C(3)−C(4)	1.396(8)	1.391(7)	1.397(6)
N(1)−C(2)	1.325(7)	N(1)−C(2)	1.368(13)	1.328(6)	1.327(5)
N(2)−C(4)	1.342(8)	N(2)−C(4)	1.347(7)	1.334(5)	1.325(5)
		Bond Angles			
N(1)−Ln(1)−N(3)	177.10(15)	N(1)−Ln(1)−N(1A)	176.9(6)	170.39(19)	168.45(16)
N(2)−Ln(1)−N(4)	102.95(16)	N(2)−Ln(1)−N(2A)	106.3(2)	103.2(2)	108.31(16)
N(2)−Ln(1)−B(1)	124.5(3)	N(2)−Ln(1)−B(1)	126.83(11)	128.39(10)	125.85(8)
B(1)−Ln(1)−N(4)	132.4(3)	B(1)−Ln(1)−N(2A)	126.83(11)	128.39(10)	125.85(8)

Table 3. Polymerization of L-LA by 3−6[a]

entry	initiator	solvent	$[M]_0/[I]_0$	time (min)	yield (%)[b]	$10^{-4}M_n$(obsd)[c]	$10^{-4}M_n$(calcd)[d]	M_w/M_n
1	**3**	toluene	1000	4	93	12.01	13.42	1.44
2	**4**	toluene	1000	4	82	10.45	11.76	1.35
3	**5**	toluene	1000	4	96	12.66	13.76	1.35
4	**6**	toluene	1000	4	73	10.03	10.57	1.33
5	**1**	toluene	1000	10	<3			
6	**6**	THF	1000	4	80	10.47	11.54	1.33
7	**6**	THF	1000	8	96	13.32	13.86	1.34

[a] Conditions: [L-LA] = 1.0 M, temp 20 °C. [b] Yield = (weight of polymer obtained)/(weight of monomer used). [c] Measured by SEC calibrated with standard MMA samples. [d] M_n(calcd) = ([M]/[I]) × 144 × (polymer yield).

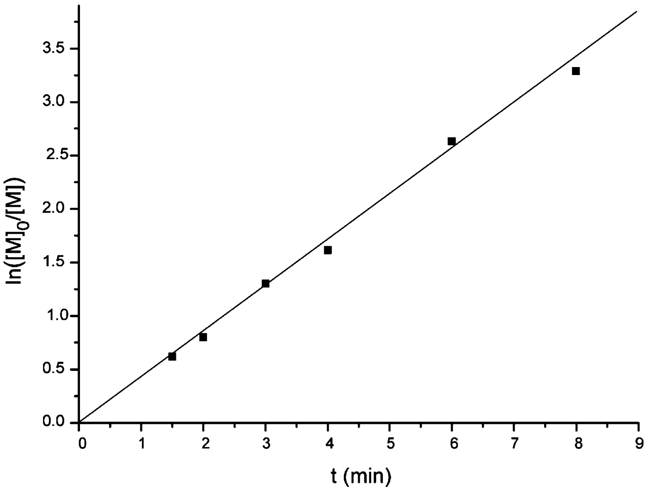


Figure 4. Plot of $\ln([M]_0/[M])$ versus time for the polymerization of L-LA by **6**. Conditions: $[M]_0/[I]_0$ = 1000, $[\text{L-LA}]_0$ = 1.0 M, in THF, 20 °C.

raising the reaction temperature to 40 °C led to the improvement of the controllability of the system with complex **6**, as judged by the resulting polymer with narrower M_w/M_n (1.16; entry 6, Table 5). Toluene is a better solvent compared to THF (entries 6 and 7, Table 5). The polymerizations of ε-CL with complex **6** were further investigated at various ratios of monomer to **6**. All polymerizations were complete within 2 min, giving polymers with M_n(obsd) values in good agreement with M_n(calcd) values and low polydispersities (M_w/M_n = 1.15−1.17) (Figure 6), indicating that complex **6** can serve as a single-site initiator initiating the controlled ring-opening polymerization of ε-CL in the present cases.

The ^{1}H NMR spectra of the oligomer of ε-CL obtained by complex **6** display, in addition to the polymer chain peaks, a triplet resonance at 3.64 ppm, assigned to the $-CH_2OH$ chain end which was formed by hydrolysis of the metal−alkoxide bond. No other chain end signals were observed, and there is no evidence of a −C(O)OH linkage. This supports the view that both chain ends of the polymers prepared from initiator **6** are hydroxyl groups, and the ring-opening process occurs by a coordination insertion mechanism via an oxygen−acyl bond cleavage.[2a,d,f,19]

Polymerization of MMA. Rare-earth-metal borohydride complexes are well-known to be active initiators for MMA polymerization.[3] Thereby the polymerization of MMA by complex **4**, as an example, was examined. The preliminary results are shown in Table 6. Complex **4** showed high activity in toluene, giving the polymers in quantitative yield at 0 °C within 2 h at a MMA/**4** molar ratio of 1000 (entry 3, Table 6). The polymerization can still give the polymer in 85% yield, with even the MMA/**4** molar ratio increasing to 1500 (entry 4, Table 6). The activity depends greatly on the reaction temperature. The polymer yields increased with a decrease in

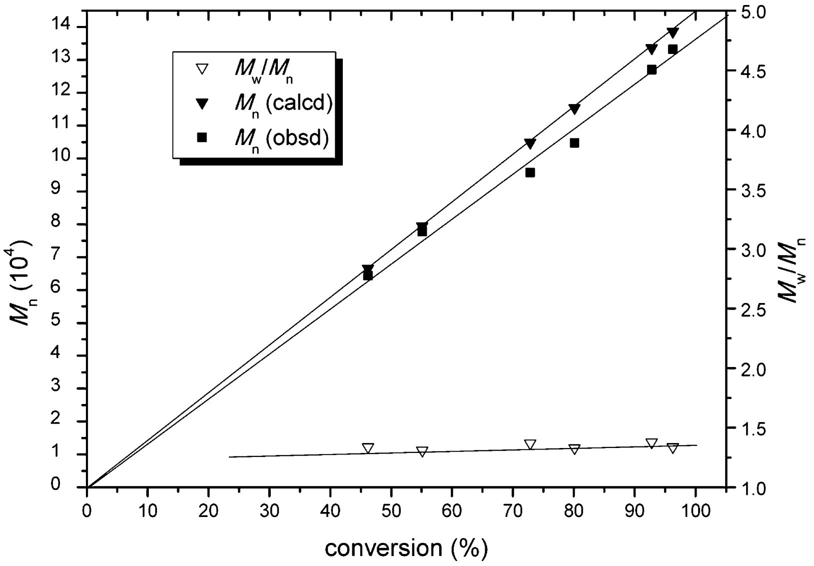


Figure 5. Relationship between conversion and M_n and M_w/M_n for the polymerization of L-LA by **6**. For the conditions, see Figure.4.

Table 4. Immortal Ring-Opening Polymerization of L-LA in the Presence of a Binary 6/^{i}PrOH System[a]

entry	[6]/[^{i}PrOH]/[L-LA]	temp (°C)	time (h)	yield (%)[b]	$10^{-4}M_n$(obsd)[c]	$10^{-4}M_n$(calcd)[d]	M_w/M_n
1	1/6/1000	60	1	99	2.51	2.38	1.11
2	1/20/3000	60	1	99	1.89	2.14	1.08
3	1/20/3000	25	1	93	2.04	2.01	1.04
4[e]	1/50/500	60	1	99	0.15	0.14	1.09
5[e]	1/100/5000	60	1	99	0.74	0.71	1.08
6[e]	1/100/10000	60	2	99	1.38	1.43	1.06
7[e]	1/200/10000	60	2	99	0.62	0.71	1.07

[a]Conditions: in THF; [L-LA] = 1.0 M. [b]Yield = (weight of polymer obtained)/(weight of monomer used). [c]Measured by SEC calibrated with standard polystyrene samples and corrected with a coefficient of 0.58.[18] [d]M_n(calcd) = ([M]/[OH]) × 144 × (polymer yield). [e][L-LA] = 2.0 M.

Table 5. Polymerization of ε-CL by 3–6[a]

entry	initiator	solvent	T (°C)	t (min)	yield (%)[b]	$10^{-4}M_n$(obsd)[c]	$10^{-4}M_n$(calcd)[d]	M_w/M_n
1	**3**	toluene	20	3	99	10.65	11.29	1.48
2	**4**	toluene	20	3	96	9.50	10.96	1.47
3	**5**	toluene	20	3	98	9.87	11.17	1.35
4	**6**	toluene	20	3	57	6.56	6.53	1.29
5	**6**	toluene	10	12	65	8.04	7.45	1.38
6[e]	**6**	toluene	40	2	90	10.23	10.53	1.16
7[e]	**6**	THF	40	4.5	93	12.48	10.63	1.34

[a]Conditions: $[M]_0/[I]_0$ = 1000/1,V_{CL}/V_{Sol} = 1/10. [b]Yield = (weight of polymer obtained)/(weight of monomer used). [c]Measured by SEC calibrated with standard MMA samples. [d]M_n(calcd) = ([M]/[I]) × 114 × (polymer yield). [e]V_{CL}/V_{Sol} = 1/20.

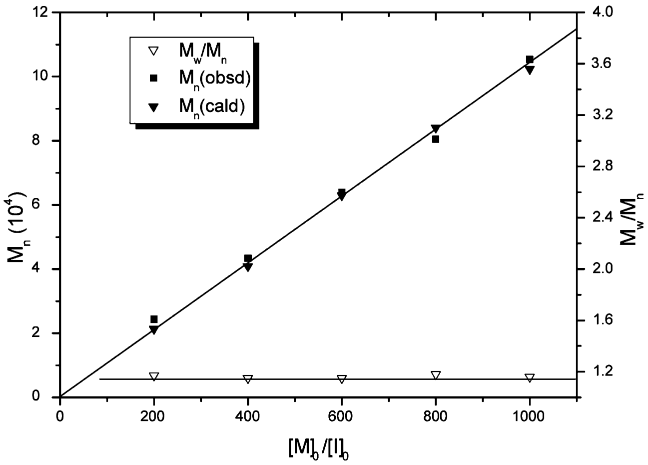


Figure 6. M_n vs $[M]_0/[I]_0$ for the polymerization of ε-CL by **6**. Conditions: $V_{ε\text{-CL}}/V_{sol}$ = 1/20, in toluene, 40 °C.

temperature from 40 to 0 °C and then decreased when the temperature was decreased to −40 °C (entries 1, 3, and 5, Table 6). The highest activity was obtained at 0 °C. The lower activity at 40 °C, in comparison to that at 0 °C, can be attributed to the occurrence of a side reaction concomitant with the polymerization reaction, leading to the destruction of the active species, which was often found in the polymerization systems with rare-earth-metal amide and alkyl complexes.[20] The polymerization initiated by **4** at 0 °C afforded PMMA with a syndiotacticity of ~80% (entries 3–5, Table 6). The syndiotacticity of PMMA obtained at −40 °C increases to 83.3% (entry 6). The molar mass distributions of the resulting polymers range from 1.50 to 2.65, indicating the present polymerization is out of control.

■ CONCLUSIONS

The monoborohydrides **3–6** were synthesized by the metathesis reactions of monochlorides with 1 equiv of $NaBH_4$ and structurally characterized. All monoborohydrides can serve as highly active initiators for ring-opening polymerizations of ε-CL and L-LA to give polymers with relatively narrow molar mass distributions. The polymerizations of both ε-CL and L-LA with complex **6** proceed in a controlled manner. Interestingly, the initiator **6** appears to be well suited for achieving immortal polymerization of L-LA by addition of isopropyl alcohol as a chain transfer agent, up to 200 equiv of HO^{i}Pr per metal initiator. Complex **4** can also initiate MMA polymerization at

Table 6. Polymerization of MMA Catalyzed by 4[a]

entry	$[M]_0/[I]_0$	T (°C)	t (min)	yield (%)[b]	$10^{-4}M_n$[c]	M_w/M_n	tacticity (%)[d]		
							mm	*mr*	*rr*
1	1000	40	120	8.1	12.13	1.45	2.4	24.5	73.1
2	600	0	120	>99.0	42.66	1.80			
3	1000	0	120	>99.0	52.49	1.81	1.3	21.4	77.3
4	1500	0	120	85.1	67.59	1.54	~0	21.2	78.8
5	2500	0	120	54.1	72.09	1.50	~0	20.6	79.4
6	1000	−40	240	26.2	17.29	2.65	1.0	15.7	83.3

[a]Conditions: in toluene, V_{MMA}/V_{sol} = 1/2. [b]Yield = (weight of polymer obtained)/(weight of monomer used). [c]Measured by SEC calibrated with standard MMA samples. [d]^{1}H NMR spectra in $CDCl_3$ at 25 °C.

−40 °C, giving PMMA with 83.3% syndiotacticity content. Further study on the application of diketiminate ligands in the synthesis of single-site rare-earth-metal catalysts is proceeding in our laboratory.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. The ligands were synthesized by the published procedure.[12] Solvents were degassed and distilled from sodium benzophenone ketyl before use. Rare-earth-metal analyses were performed by ethylenediaminetetraacetic acid (EDTA) titration with a xylenol orange indicator and a hexamine buffer.[21] Element analyses were performed by direct combustion using a CarloErba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. ^{1}H NMR spectra were measured on an INOVA-400 MHz apparatus. The number-average molar masses (M_n) and molar mass distributions (M_w/M_n) were determined against a MMA standard by size exclusion chromatography (SEC) on a PL-50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C.

Synthesis of Complexes 1−6. *$(L^{2,6\text{-ipr2}}{}_{Ph})_2YCl$ (1).* A THF solution of $NaL^{2,6\text{-ipr2}}{}_{Ph}$ (28.7 mL, 0.353 M), which was formed by reaction of $L^{2,6\text{-ipr2}}{}_{Ph}H$ with NaH in THF, was added to a slurry of anhydrous YCl_3 (0.99 g, 5.07 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. After the undissolved portion was removed by centrifugation, the yellow solution was concentrated to dry and then about 30 mL of toluene was added. Crystallization at room temperature afforded **1** as pale yellow crystals (1.95 g, 49%). Anal. Calcd for $C_{46}H_{58}ClN_4Y$ (790.341): C, 69.82; H, 7.39; N, 7.08; Y, 11.23. Found: C, 69.32; H, 7.21; N, 6.54; Y, 11.01. ^{1}H NMR (400 MHz, C_6D_6): δ 7.13−6.81 (m, 16H, Ar*H*), 6.52−6.49 (d, 4H, Ar−C*H*(CH$_3$)$_2$), 4.96 (s, 2H, C*H*), 1.81−1.62 (m, 12H, −C*H*$_3$), 1.18−1.11 (m, 24H, Ar−CH(C*H*$_3$)$_2$) ppm. IR (KBr, cm^{-1}): 1744 (m), 1705 (m), 1547 (m), 1516 (m), 1462 (w), 1339 (w), 1223 (w), 1196 (w), 952 (m), 779 (s), 740 (s), 680 (m), 644 (m), 556 (m), 525 (s), 444 (s), 420 (vs).

$(L^{2,6\text{-ipr2}}{}_{Ph})_2YbCl\cdot C_4H_8O\cdot 0.5C_7H_8$ (2). A THF solution of $NaL^{2,6\text{-ipr2}}{}_{Ph}$ (17.43 mL, 0.460 M), which was formed by reaction of $L^{2,6\text{-ipr2}}{}_{Ph}H$ with NaH in THF, was added to a slurry of anhydrous $YbCl_3$ (1.12 g, 4.01 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. After the undissolved portion was removed by centrifugation, the brown solution was concentrated to dry and then about 0.5 mL of THF and 20 mL of toluene were added. Crystallization at room temperature afforded yellow crystals of **2** (1.09 g, 31%). Anal. Calcd for $C_{46}H_{58}ClN_4Yb$ (875.37): C, 63.11; H, 6.68; N, 6.40; Yb, 19.77; Found: C, 62.71; H, 6.42; N, 6.14; Yb, 19.25. IR (KBr, cm^{-1}): 1794 (m), 1744 (s), 1705 (s), 1678 (s), 1647 (s), 1616 (w), 1516 (vs), 1462 (m), 1423 (m), 1396 (w), 1339 (w), 1196 (w), 1018 (w), 976 (w), 880 (m), 780 (s), 648 (s), 598 (s), 540 (vs), 482 (vs), 428 (s).

$(L^{2,6\text{-ipr2}}{}_{Ph})_2YBH_4\cdot 0.5C_7H_8$ (3). A THF solution of $(L^{2,6\text{-ipr2}}{}_{Ph})_2YCl$ (3.33 g, 4.21 mmol) was added to a solution of $NaBH_4$ (0.16 g, 4.21 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at 60 °C for 5 days. After the undissolved portion was removed by centrifugation, the solution was concentrated to dryness and then 4 mL of toluene was added. Crystallization at room temperature gave complex **3** as pale yellow crystals (0.85 g, 38%). Anal. Calcd for $C_{46}H_{62}BN_4Y$ (770.41): C, 71.68; H, 8.11; N, 7.27; Yb, 11.54. Found: C, 70.90; H, 8.14; N, 6.96; Yb, 10.85. ^{1}H NMR (400 MHz, C_6D_6) δ 7.14−7.06 (m, 6H, ArH), 7.02 (t, 4H, Ar*H*), 6.90 (t, 2H, Ar*H*), 6.85 (d, 4H, Ar*H*), 4.85 (s, 2H, −C*H*−), 3.19 (m, 4H, Ar−C*H*(CH$_3$)$_2$), 1.69 (s, 6H, −C*H*$_3$), 1.67 (s, 6H, −C*H*$_3$), 1.15 (d, 12H, Ar−CH(C*H*$_3$)$_2$), 1.10 (d, 12H, Ar−CH(C*H*$_3$)$_2$), 0.97−1.16 (m, 4H, B*H*$_4$) ppm. IR (KBr, cm^{-1}): 2355 (m), 2294 (m), 1631 (s), 1549 (m), 1501 (m), 746 (vs).

$(L^{2,6\text{-ipr2}}{}_{Ph})_2YbBH_4\cdot C_4H_8O$ (4). Complex **4** was prepared in a manner similar to that used for the preparation of **3**, but $(L^{2,6\text{-ipr2}}{}_{Ph})_2YbCl$ (2.73 g, 3.12 mmol) and $NaBH_4$ (0.17 g, 4.47 mmol) were used. After the undissolved portion was removed by centrifugation, the solution was concentrated to dryness and then 4 mL of THF was added. Crystallization at room temperature gave complex **4** as orange crystals (1.21 g, 45%). Anal. Calcd for $C_{46}H_{62}BN_4Yb$ (855.45): C, 64.63; H, 7.31; N, 6.55; Yb, 20.24. Found: C, 64.08; H, 7.41; N, 6.52; Yb, 19.11. IR (KBr, cm^{-1}): 2336 (m), 2294 (w), 2227 (w), 1625 (s), 1600 (s), 1556 (vs), 1507 (s), 750 (s).

$(L^{2\text{-Me}})_2YBH_4$ (5). A THF solution of $NaL^{2\text{-Me}}$ (14.82 mL, 0.452 M), which was formed by reaction of $L^{2\text{-Me}}H$ with NaH in THF, was added to a slurry of anhydrous YCl_3 (3.35 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at 60 °C for 24 h. Then $NaBH_4$ (0.17 g, 4.47 mmol) was added. The reaction mixture was stirred at 60 °C for 5 days. After the undissolved portion was removed by centrifugation, the solution was concentrated to dryness and then 3 mL of DME was added. Crystallization at room temperature gave complex **5** as yellow crystals (0.91 g, 41.2%). Anal. Calcd for $C_{38}H_{46}BN_4Y$ (658.51): C, 69.31; H, 7.04; N, 8.51; Y, 13.50. Found: C, 69.05; H, 6.88; N, 8.24; Y, 13.11. ^{1}H NMR (400 MHz, C_6D_6) δ 7.02 (d, 4H, Ar*H*), 6.92 (m, 8H, Ar*H*), 6.83 (t, 4H, Ar*H*), 4.81 (d, 2H, −C*H*−), 2.01 (s, 12H, Ar−C*H*$_3$), 1.58 (d, 12H, −C*H*$_3$), 1.07−1.33 (m, 4H, B*H*$_4$) ppm. IR (KBr, cm^{-1}): 2342 (m), 2294 (w), 2226 (w), 1627 (s), 1604 (m), 1558 (s), 1508 (m), 744 (s).

$(L^{2\text{-Me}})_2YbBH_4\cdot 2C_4H_8O$ (6). This complex was prepared in a manner similar to that used for the preparation of **5**, but $NaL^{2\text{-Me}}$ (15.31 mL, 0.452 M), $YbCl_3$ (3.46 mmol), and $NaBH_4$ (0.18 g, 4.74 mmol) were used instead. After the undissolved portion was removed by centrifugation, the solution was concentrated to dryness and then 6 mL of THF was added. Crystallization at room temperature gave complex **6** as red crystals (1.48 g, 57.5%). Anal. Calcd for $C_{38}H_{46}BN_4Yb$ (743.32): C, 61.46; H, 6.24; N, 7.54; Yb, 23.30. Found: C, 60.82; H, 6.28; N, 7.45; Yb, 23.14. IR (KBr, cm^{-1}): 2350 (m), 2293 (m), 2226 (w), 1628 (s), 1604 (m), 1555 (s), 1509 (m), 743 (s).

General Procedure for the Polymerization of ε-CL and L-LA. The procedures for the polymerization of ε-CL and L-LA initiated by complexes **3**−**6** are similar, and a typical polymerization procedure is given below. To a stirred solution of ε-CL or L-LA in THF was added a THF solution of the initiator using a syringe. The polymerization mixture was stirred for a definite time at the desired temperature and then quenched with an ethanol solution containing a small amount of hydrochloric acid (5%). The polymer was precipitated from ethanol, washed with ethanol three times, and dried under vacuum.

X-ray Crystallography. Suitable single crystals of complexes **2**−**6** were sealed in thin-walled glass capillaries. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode by using Mo Kα radiation (λ = 0.710 70 or 0.710 75 Å). The diffracted intensities were corrected for Lorentz and polarization effects, and empirical methods were used to correct for absorption. Details of the intensity data collection and crystal data are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the 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 the 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 the SHELXL-97 program.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray crystallographic data for complexes **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature (London)* **1997**, *388*, 860. (b) Calandrelli, L.; Calarco, A.; Laurienzo, P.; Malinconico, M.; Petillo, O.; Peluso, G. *Biomacromolecules* **2008**, *9*, 1527. (c) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11. (d) Labet, M.; Thielemans, W. *Chem. Soc. Rev.* **2009**, *38*, 3484.

(2) (a) Palard, I.; Soum, A.; Guillaume, S. M. *Chem. Eur. J.* **2004**, *10*, 4054. (b) Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. M. *Chem. Eur. J.* **2004**, *10*, 2428. (c) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046. (d) Palard, I.; Schappacher, M.; Soum, A.; Guillaume, S. M. *Polym. Int.* **2006**, *55*, 1132. (e) Skvortsov, G. G.; Yakovenko, M. V.; Castro, P. M.; Fukin, G. K.; Cherkasov, A. V.; Carpentier, J.-F.; Trifonov, A. A. *Eur. J. Inorg. Chem.* **2007**, *2007*, 3260. (f) Barros, N.; Mountford, P.; Guillaume, S. M.; Maron, L. *Chem. Eur. J.* **2008**, *14*, 5507. (g) Mahrova, T. V.; Fukin, G. K.; Cherkasov, A. V.; Trifonov, A. A.; Ajellal, N.; Carpentier, J.-F. *Inorg. Chem.* **2009**, *48*, 4258. (h) Dyer, H. E.; Huijser, S.; Susperregui, N.; Bonnet, F.; Schwarz, A. D.; Duchateau, R.; Maron, L.; Mountford, P. *Organometallics* **2010**, *29*, 3602. (i) Jenter, J.; Roesky, P. W.; Ajellal, N.; Guillaume, S. M.; Susperregui, N.; Maron, L. *Chem. Eur. J.* **2010**, *16*, 4629. (j) Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Ajellal, N.; Roisnel, T.; Kerton, F. M.; Carpentier, J.-F.; Trifonov, A. A. *New J. Chem.* **2011**, *35*, 204. (k) Yakovenko, M. V.; Trifonov, A. A.; Kirillov, E.; Roisnel, T.; Carpentier, J.-F. *Inorg. Chim. Acta* **2012**, *383*, 137. (l) Visseaux, M.; Bonnet, F. *Coord. Chem. Rev.* **2011**, *255*, 374.

(3) (a) Bonnet, F.; Hillier, A. C.; Collins, A.; Dubberley, S. R.; Mountford, P. *Dalton Trans.* **2005**, 421. (b) Yuan, F.; Zhu, Y.; Xiong, L. *J. Organomet. Chem.* **2006**, *691*, 3377. (c) Barros, N.; Schappacher, M.; Dessuge, P.; Maron, L.; Guillaume, S. M. *Chem. Eur. J.* **2008**, *14*, 1881.

(4) Visseaux, M.; Terrier, M.; Mortreux, A.; Roussel, P. *Eur. J. Inorg. Chem.* **2010**, 2867.

(5) (a) Li, W.; Xue, M.; Tu, J.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2012**, *41*, 7258. (b) Zhang, X.; C., W.; Xue, M.; Zhang, Y.; Yao, Y.; Shen, Q. *J. Organomet. Chem.* **2012**, 10.1016/j. jorganchem. 2012.05.011.

(6) (a) Dress, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 814. (b) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699. (c) Deacon, G. B.; Shen, Q. *J. Organomet. Chem.* **1996**, *511*, 1. (d) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (e) Neculai, A. M.; Roesky, H. W.; Neculai, D.; Magull, J. *Organometallics* **2001**, *20*, 5501. (f) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599. (g) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031. (h) Avent, A. G.; Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *Dalton Trans.* **2003**, 1070. (i) Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. *Chem. Commun.* **2005**, 951. (j) Shimokawa, C.; Itoh, S. *Inorg. Chem.* **2005**, *44*, 3010. (k) Jutzi, P.; Leszczyńska, K.; Mix, A.; Neumann, B.; Schoeller, W. W.; Stammler, H.-G. *Organometallics* **2009**, *28*, 1985. (l) Kenward, A. L.; Ross, J. A.; Piers, W. E.; Parvez, M. *Organometallics* **2009**, *28*, 3625. (m) Moreno, A.; Pregosin, P. S.; Laurenczy, G. b.; Phillips, A. D.; Dyson, P. J. *Organometallics* **2009**, *28*, 6432. (n) Oguadinma, P. O.; Schaper, F. *Organometallics* **2009**, *28*, 6721. (o) Drouin, F. d. r.; Oguadinma, P. O.; Whitehorne, T. J. J.; Prud'homme, R. E.; Schaper, F. *Organometallics* **2010**, *29*, 2139. (p) Li, D.; Li, S.; Cui, D.; Zhang, X. *Organometallics* **2010**, *29*, 2186. (q) Phillips, A. D.; Zava, O.; Scopelitti, R.; Nazarov, A. A.; Dyson, P. J. *Organometallics* **2010**, *29*, 417. (r) Azhakar, R.; Sarish, S. P.; Roesky, H. W.; Hey, J.; Stalke, D. *Organometallics* **2011**, *30*, 2897.

(7) (a) Yao, Y.; Zhang, Y.; Shen, Q.; Yu, K. *Organometallics* **2002**, *21*, 819. (b) Xue, M.; Sun, H.; Zhou, H.; Yao, Y.; Shen, Q.; Zhang, Y. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 1147. (c) Chen, H.; Liu, P.; Yao, H.; Zhang, Y.; Yao, Y.; Shen, Q. *Dalton Trans.* **2010**, *39*, 6877.

(8) (a) Dress, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 948. (b) Hitchcock, P. B.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Dalton Trans.* **1997**, 1945.

(9) Lazarov, B. B.; Hampel, F.; Hultzsch, K. C. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2367.

(10) Wei, X.; Cheng, Y.; Hitchcock, P. B.; Lappert, M. F. *Dalton Trans.* **2008**, 5235.

(11) (a) Xue, M.; Jiao, R.; Zhang, Y.; Yao, Y.; Shen, Q. *Eur. J. Inorg. Chem.* **2009**, 4110. (b) Jiao, R.; Shen, X.; Xue, M.; Zhang, Y.; Yao, Y.; Shen, Q. *Chem. Commun.* **2010**, *46*, 4118. (c) Jiao, R.; Xue, M.; Shen, X.; Zhang, Y.; Yao, Y.; Shen, Q. *Eur. J. Inorg. Chem.* **2010**, 2523. (d) Jiao, R.; Xue, M.; Shen, X.; Zhang, Y.; Yao, Y.; Shen, Q. *Eur. J. Inorg. Chem.* **2011**, 1448. (e) Liu, P.; Zhang, Y.; Yao, Y.; Shen, Q. *Organometallics* **2012**, *31*, 1017.

(12) (a) Budzelaar, P. H. M.; Oort, A. B. v.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485. (b) Shen, X.; Zhang, Y.; Xue, M.; Shen, Q. *Dalton Trans.* **2012**, *41*, 3668.

(13) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751.

(15) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1976**, *77*, 263. (b) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193. (c) Makhaev, V. D. *Russ. Chem. Rev.* **2000**, *69*, 727.

(16) Segal, B. G.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 844.

(17) (a) Amgoune, A.; Thomas, C. M.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2007**, *28*, 693. (b) Ajellal, N.; Lyubov, D. M.; Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Thomas, C. M.; Carpentier, J.-F.; Trifonov, A. A. *Chem. Eur. J.* **2008**, *14*, 5440. (c) Mahrova, T. V.; Fukin, G. K.; Cherkasov, A. V.; Trifonov, A. A.; Ajellal, N.; Carpentier, J.-F. *Inorg. Chem.* **2009**, *48*, 4258. (d) Wang, Y.; Zhao, W.; Liu, D.; Li, S.; Liu, X.; Cui, D.; Chen, X. *Organometallics* **2012**, *31*, 4182. (e) Zhao, W.; Wang, Y.; Liu, X.; Cui, D. *Chem. Commun.* **2012**, *48*, 4483. (f) Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363. (g) Guillaume, S. M.; Carpentier, J.-F. *Catal. Sci. Technol.* **2012**, *2*, 898. (h) Poirier, V.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Dalton Trans.* **2009**, 9820.

(18) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.

(19) Wu, G.; Sun, W.; Shen, Z. *J. Appl. Polym. Sci.* **2009**, *112*, 557.

(20) (a) Yasuda, H.; Ihara, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745. (b) Shen, Q.; Yao, Y. *J. Organomet. Chem.* **2002**, *647*, 180.

(21) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115.

(22) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.