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Article

Lanthanide Borohydride Complexes Supported by Diaminobis(phenoxide) Ligands for the Polymerization of ϵ-Caprolactone and L- and *rac*-Lactide

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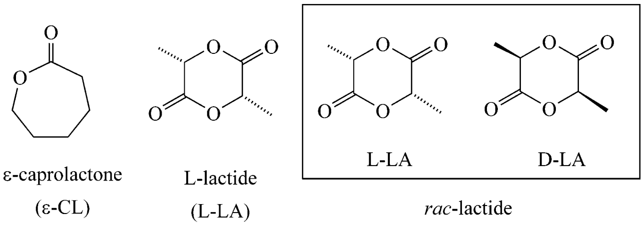
Reaction of Na_2O_2NN' [$H_2O_2NN' = (2\text{-}C_5H_4N)CH_2N\{2\text{-}HO\text{-}3,5\text{-}C_6H_2{}^tBu_2\}_2$] with $M(BH_4)_3(THF)_3$ afforded the dimeric, rare-earth borohydride compounds $[M(O_2NN')(\mu\text{-}BH_4)(THF)_n]_2$ [$M = Y^{III}$, $n = 0.5$ (**1-Y**); $M = Nd^{III}$, $n = 1$ (**1-Nd**); $M = Sm^{III}$, $n = 0$ (**1-Sm**)]. For comparison the chloride analogues $[M(O_2NN')(\mu\text{-}Cl)(THF)_n]_2$ (**2-M**; $M = La^{III}$ or Sm^{III}, $n = 0$; $M = Nd^{III}$, $n = 1$) and the corresponding pyridine adducts $[M(O_2NN')(\mu\text{-}X)(py)]_2$ [$X = BH_4$ (**3-M**) or Cl (**4-M**); $M = La^{III}$, Nd^{III}, or Sm^{III}] were prepared and structurally characterized for **4-La**. Compounds **1-M** initiated the ring-opening polymerization of ϵ-caprolactone. The best molecular weight control (suppression of chain transfer) for all three monomers was found for the samarium system **1-Sm**. The most effective heterotactic enrichment (P_r) in the polymerization of *rac*-lactide was found for **1-Y** ($P_r = 87\%$). Compound **1-Nd** catalyzed the block copolymerization of ϵ-caprolactone and L- and *rac*-lactide provided that ϵ-caprolactone was added first. Attempted block polymerization by the addition of L-lactide first, or random copolymerization of a ca. 1:1 mixture of ϵ-caprolactone and L-lactide, gave only a poly(L-lactide) homopolymer.

Introduction

There is presently much interest in the controlled ring-opening polymerization (ROP) of cyclic esters such as lactones and lactides because of the biodegradability and biocompatibility of the resulting polyesters.[1,2] A wide range of main group complexes have been employed in this area with impressive results.[3] Of particular interest to our present contribution is the ability of discrete, non-cyclopentadienyl group 3 and lanthanide complexes $(L)_xLn{-}R$ [where $(L)_x$ = dianionic supporting ligand set; Ln = group 3 or lanthanide metal][4] to act as ROP catalysts for the cyclic esters shown in Chart 1[2a−d] and, in particular, those with chelating phenoxide supporting ligands.[5]

The initiating functional group Ln-R in lanthanide ROP catalysts, in general, is typically an aryl oxide or alkoxide, secondary amide, or alkyl moiety.[2,3] Recently, however, pioneering work by Guillaume et al. has shown that

Chart 1



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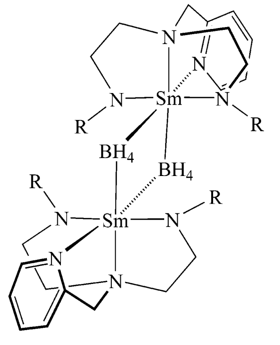
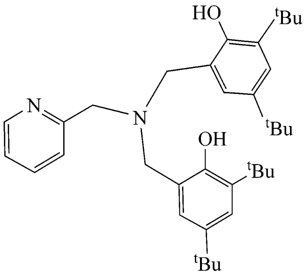
10.1021/ic051316g CCC: $30.25

Chart 2



I (R = $SiMe_3$ or 2,4,6-$C_6H_2Me_3$)



H_2O_2NN'

borohydride compounds can initiate the ROP of ε-caprolactone (ε-CL), either without supporting ancillary ligands [namely, $Nd(BH_4)_3(THF)_3$][6a,b] or as the metallocene complex $Cp^*_2Sm(BH_4)(THF)$.[6c] In complimentary work, the groups of Barbier-Baudry and Visseaux showed that dialkylmagnesium-activated lanthanide borohydride complexes allowed for the stereospecific polymerization of isoprene.[6d−f] We very recently reported that the diaminobis(amide)-supported samarium borohydride compounds $[Sm(N_2NN')(\mu\text{-}BH_4)]_2$ [**I**; see Chart 2; $N_2NN' = (2\text{-}C_5H_4N)CH_2N(CH_2CH_2NR)_2$, R = $SiMe_3$ or 2,4,6-$C_6H_2Me_3$] are catalysts for the living ROP of ε-CL and the well-controlled polymerization of methyl methacrylate (MMA; this being the first example of a borohydride compound effecting this process).[6g] So far, no rare-earth borohydride initiator for the polymerization of lactides has been reported. Unfortunately, although **I** and other N_2NN'-supported borohydride complexes showed reasonable activity for the polymerization of L-lactide (L-LA), no stereocontrol was achieved with *rac*-lactide (*rac*-LA, or D,L-lactide).[7]

Carpentier et al. have recently reported the stereoselective opening of *rac*-LA using group 3 alkyl and amide complexes supported by a bis(phenoxide) ether ligand.[5c] We therefore anticipated that the formal replacement of the amide "arms" of N_2NN' in **I** by methyl phenoxide groups might allow for a more successful catalytic system and so turned to the related diaminobis(phenoxide) ligand O_2NN' [$H_2O_2NN' = (2\text{-}C_5H_4N)CH_2N\{2\text{-}HO\text{-}3,5\text{-}C_6H_2{}^tBu_2\}_2$; see Chart 2]. The O_2NN' ligand and a number of tetradentate bis(phenoxide) analogues have been used with considerable effect in group 4 Ziegler−Natta polymerization in the past few years[4a,8] but have received somewhat less attention in rare-earth chemistry and polar monomer catalysis.[4b−d,5,9]

In this contribution, we describe the synthesis and characterization of a new, non-cyclopentadienyl rare-earth metal borohydride complex containing the diaminobis(phenoxide) ligand O_2NN'. We report the polymerization of ε-CL and, for the first time with any borohydride complex, the polymerization of L- and *rac*-LA. Comparative studies of the corresponding chloride complexes $[Ln(O_2NN')(\mu\text{-}Cl)(L)_n]_2$ (L = py or THF, $n = 0$ or 1) are also described.

Results and Discussion

Syntheses. The starting compounds Na_2O_2NN',[10a] $Ln(BH_4)_3(THF)_3$,[10b] and $LnCl_3(THF)_2$[10c] were prepared as described previously. The syntheses and proposed structures of the new rare-earth borohydride and chloride compounds are summarized in Scheme 1.

Reaction of $Sm(BH_4)_3(THF)_3$ with Na_2O_2NN' in THF at room temperature followed by toluene extraction afforded the compound $[Sm(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Sm**) as a pale-yellow solid in 87% isolated yield. The corresponding reaction with $Nd(BH_4)_3(THF)_3$ gave pale-blue-green $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**; 70% yield) containing an additional THF per metal center. Interestingly, with $Y(BH_4)_3(THF)_3$, the pale-yellow product $[Y(O_2NN')(\mu\text{-}BH_4)(THF)_{0.5}]_2$ (**1-Y**) contained 0.5 equiv of THF per metal center according to NMR spectroscopy and elemental analysis. The coordinated THF in **1-Y** or **1-Nd** could not be removed even upon prolonged drying in vacuo. Attempted synthesis of the lanthanum and scandium analogues of **1-Y**, **1-Sm**, and **1-Nd** was unsuccessful and gave unidentified mixtures of products.

The reactions of Na_2O_2NN' with $ScCl_3$ [or $ScCl_3(THF)_3$] or YCl_3 in THF have been reported to give intractable

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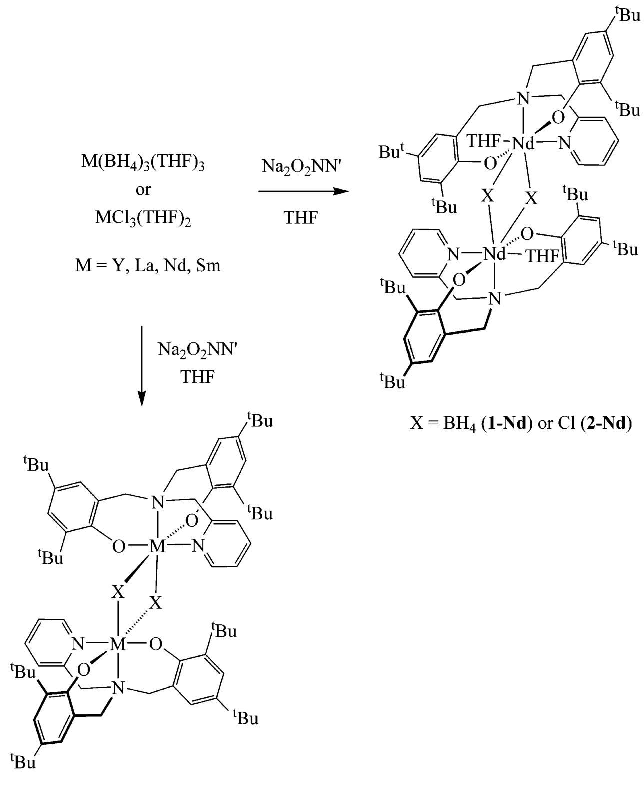
Scheme 1. Synthesis of Some of the New Rare-Earth Borohydride or Chloride Compounds[a]



X = BH_4 (**1-Nd**) or Cl (**2-Nd**)

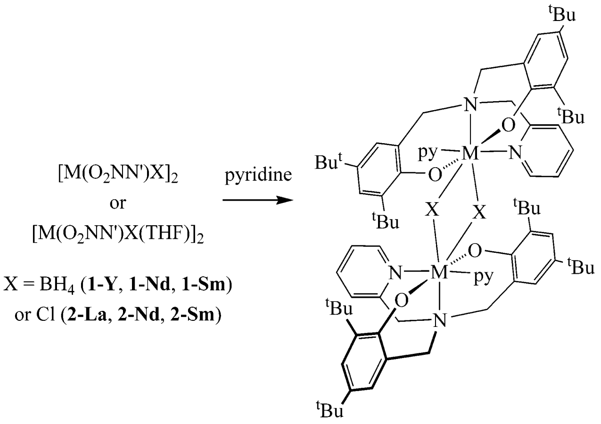
X = BH_4, M = Y (**1-Y**) or Sm (**1-Sm**)
X = Cl, M = La (**2-La**) or Sm (**2-Sm**)

[a] The additional THF for **1-Y** is not shown.

products.[9a] For comparison with these reactions and the borohydride compounds **1-Y**, **1-Sm**, and **1-Nd**, the reactions of Na_2O_2NN' with the trichlorides $MCl_3(THF)_2$ (M = La, Nd, and Sm) were carried out in THF as summarized in Scheme 1. For M = La^{III} and Sm^{III}, the THF-free products $[M(O_2NN')(\mu\text{-}Cl)]_2$ [**2-La** (76%) and **2-Sm** (80%)] were obtained after toluene extraction, whereas with $NdCl_3(THF)_2$, the pale-blue THF adduct $[Nd(O_2NN')(\mu\text{-}Cl)(THF)]_2$ [**2-Nd** (60%)] was obtained.

The new compounds $[M(O_2NN')(\mu\text{-}X)(THF)_n]_2$ [X = BH_4 (**1-M**) or Cl (**2-M**); n = 0, 0.5, or 1] are proposed to exist as BH_4- or Cl-bridged dimers in the solid state. Scheme 1 suggests likely structures. Those proposed for the six-coordinate, THF-free compounds $[M(O_2NN')(\mu\text{-}X)]_2$ are related to that found recently for the μ-oxo-bridged dititanium compound $[Ti(O_2NN')(\mu\text{-}O)]_2$.[9a] The structures proposed for the adducts $[M(O_2NN')(\mu\text{-}X)(THF)]_2$ are based on that of the chloride-bridged pyridine adduct $[La(O_2NN')(\mu\text{-}Cl)(py)]_2$ (**4-La**). In accordance with several structurally authenticated rare-earth borohydride dimers, the complex IR spectra (ca. 2160−2460 cm^{-1} region) of compounds **1-M** suggest μ−η^3,η^3-bridging (as opposed to η^3-bound terminal) borohydride ligands.[11] The mono(THF) adduct **1-Y** is proposed to have a structure analogous to those illustrated in Scheme 1 but with a single THF bound to only one yttrium center.

Consistent with their proposed dimeric structures, the borohydride and chloride compounds are rather insoluble and NMR data (C_6D_6) could only be obtained with the aid of several drops of added pyridine-d_5. The NMR spectra of the new compounds showed the presence of coordinated O_2NN' and (for **1-M**) borohydride ligands (the spectra for the neodymium compounds were very broad indeed as expected). To gain evidence of the possible pyridine adducts formed under these conditions, we prepared the compounds $[M(O_2NN')(\mu\text{-}BH_4)(py)]_2$ (**3-M**; M = Y^{III}, Sm^{III}) and $[M(O_2NN')(\mu\text{-}Cl)(py)]_2$ (**4-M**; M = La^{III}, Nd^{III}, Sm^{III}) according to eq 1. Dimeric solid-state structures are again proposed on the basis of the IR data for **3-M** (consistent with μ-BH_4 groups) and the X-ray structure of $[La(O_2NN')(\mu\text{-}Cl)(py)]_2$ (**4-La**). It was not possible to prepare a fully characterized Nd^{III} analogue of **3-M** (further details are given in the Supporting Information).



(1)

X = BH_4, M = Y (**3-Y**) or Sm (**3-Sm**)
X = Cl, M = La (**4-La**), Nd (**4-Nd**) or Sm (**4-Sm**)

The molecular structure of **4-La** is shown in Figure 1, and selected bond distances and angles are given in Table 1. Compound **4-La** consists of two seven-coordinate lanthanum centers linked through μ-Cl bridges. The central La_2Cl_2 moiety is slightly puckered, and the fold angle between the individual $LaCl_2$ units [folded along the Cl(1)···Cl(2) vector] is 162.3°. The La atoms possess approximate face-capped, trigonal-prismatic geometries [with the face-capping atoms being N(2) and N(5) for La(1) and La(2), respectively]. There is some disorder in certain of the phenyl ring and *tert*-butyl carbon atoms of the O_2NN' ligand of La(1), and this was satisfactorily resolved (see the Experimental Section). Crystals of the homologues **4-Nd** and **4-Sm** were also obtained. However, the disorder in these was very severe, and only the unit cell parameters (all isostructural with **4-La**) and the heavy-atom positions could be determined with confidence. The average M−Cl distances of 2.914 Å (**4-La**), 2.85 Å (**4-Nd**), and 2.82 Å (**4-Sm**) are in keeping with the trends in atomic radii for La, Nd, and Sm.[12]

Polymerization Studies. As mentioned, group 3 and lanthanide compounds supported by tetradentate bis(phenoxide) ligands have recently attracted attention as polar monomer polymerization catalysts.[5] However, none so far has featured a M−BH_4 unit as the initiating group. Indeed

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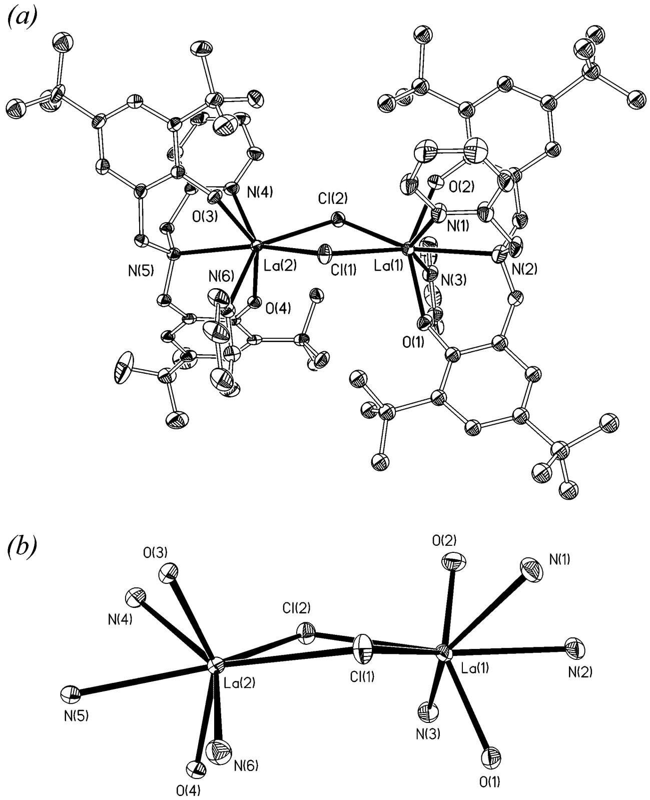

Figure 1. Displacement ellipsoid plots of [La(O_2NN′)(μ-Cl)(py)]$_2$ (**4-La**) drawn at the 25% probablility level with C_6H_6 molecules of crystallization omitted. (a) General view with H atoms omitted. The predominant position is shown for the disordered atoms. (b) View of the $La_2O_4N_6Cl_2$ central coordination sphere with C, H, and O atoms omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [La(O_2NN′)(μ-Cl)(py)]$_2$ (**4-La**)

La(1)−Cl(1)	2.8871(15)	La(2)−Cl(1)	2.9410(14)
La(1)−Cl(2)	2.9312(14)	La(2)−Cl(2)	2.8802(15)
La(1)−O(1)	2.281(4)	La(2)−O(3)	2.282(4)
La(1)−O(2)	2.270(5)	La(2)−O(4)	2.262(4)
La(1)−N(1)	2.673(5)	La(2)−N(4)	2.669(5)
La(1)−N(2)	2.739(5)	La(2)−N(5)	2.740(4)
La(1)−N(3)	2.714(6)	La(2)−N(6)	2.690(5)
Cl(1)−La(1)−Cl(2)	73.53(4)	Cl(1)−La(2)−Cl(2)	73.48(4)
Cl(1)−La(1)−O(1)	92.46(12)	Cl(1)−La(2)−O(3)	90.64(10)
Cl(2)−La(1)−O(1)	123.80(11)	Cl(2)−La(2)−O(3)	120.19(11)
Cl(1)−La(1)−O(2)	119.92(13)	Cl(1)−La(2)−O(4)	114.76(10)
Cl(2)−La(1)−O(2)	80.65(13)	Cl(2)−La(2)−O(4)	90.61(11)
O(1)−La(1)−O(2)	145.26(16)	O(3)−La(2)−O(4)	145.40(14)
Cl(1)−La(1)−N(1)	79.78(13)	Cl(2)−La(2)−N(4)	78.95(12)
Cl(2)−La(1)−N(1)	129.33(13)	Cl(1)−La(2)−N(4)	138.62(12)
O(1)−La(1)−N(1)	99.22(18)	Cl(2)−La(2)−N(4)	78.95(12)
O(2)−La(1)−N(1)	76.6(2)	O(3)−La(2)−N(4)	77.16(16)
Cl(1)−La(1)−N(2)	136.39(13)	O(4)−La(2)−N(4)	95.52(15)
Cl(2)−La(1)−N(2)	148.45(14)	Cl(1)−La(2)−N(5)	150.94(11)
O(1)−La(1)−N(2)	72.81(17)	Cl(2)−La(2)−N(5)	135.57(11)
O(2)−La(1)−N(2)	74.72(18)	O(3)−La(2)−N(5)	75.06(14)
N(1)−La(1)−N(2)	63.24(16)	O(4)−La(2)−N(5)	71.54(14)
Cl(1)−La(1)−N(3)	134.53(13)	N(4)−La(2)−N(5)	63.41(16)
Cl(2)−La(1)−N(3)	74.59(12)	Cl(1)−La(2)−N(6)	71.70(12)
O(1)−La(1)−N(3)	79.32(17)	Cl(2)−La(2)−N(6)	136.78(12)
O(2)−La(1)−N(3)	85.33(19)	O(3)−La(2)−N(6)	85.07(17)
N(1)−La(1)−N(3)	145.54(17)	O(4)−La(2)−N(6)	81.54(16)
N(2)−La(1)−N(3)	83.93(16)	N(4)−La(2)−N(6)	143.87(17)
La(1)−Cl(1)−La(2)	104.48(5)	La(1)−Cl(2)−La(2)	104.91(5)

Table 2. Polymerization of ϵ-CL Catalyzed by [Y(O_2NN′)(μ-BH$_4$)(THF)$_{0.5}$]$_2$ (**1-Y**), [Sm(O_2NN′)(μ-BH$_4$)]$_2$ (**1-Sm**), or [Nd(O_2NN′)(μ-BH$_4$)(THF)]$_2$ (**1-Nd**) and the Corresponding Control Reaction in the Presence of [Sm(O_2NN′)(μ-Cl)]$_2$ (**2-Sm**)[a]

run	initiator	time	[ϵ-CL]$_0$/[M]$_0$	yield[b] (%)	M_n(obsd)[c] (g mol^{-1})	PDI	M_n(calcd)[d] (g mol^{-1})
1	**1-Y**	2 min	290	84	24 710	1.74	27 800
2	**1-Sm**	0.5 min	275	90	26 920	1.76	28 250
3	**1-Nd**	0.5 min	275	89	24 000	1.57	27 900
4	**2-Sm**	16 h	250	0			

[a] Polymerization conditions: $T = 25$ °C; solvent = toluene (4 mL) with a few drops of THF to solubilize **1-M**; weight of ϵ-CL = 0.50 g; [M] corresponds to the total lanthanide metal concentration. [b] Isolated yield. [c] Measured by GPC at 30 °C in THF relative to polystyrene standards with Mark−Houwink corrections[14] for M_n [M_n(obsd) = 0.56M_n(GPC)]. [d] Calculated from MW$_{\epsilon\text{-CL}}$([ϵ-CL]$_0$/[M]$_0$) × conversion.

only a few examples of the use of lanthanide borohydride compounds in polar monomer polymerization catalysis have been reported.[6a,b,f] In the second part of this contribution, we describe the activity of the new compounds [M(O_2NN′)(μ-BH$_4$)(THF)$_n$] (**1-M**) as initiators for the polymerization of ϵ-CL, L-LA, and *rac*-LA (also often referred to as D,L-lactide). These monomers are illustrated in Chart 1. The polymerization of ϵ-CL by cyclopentadienyl- and non-cyclopentadienyllanthanide borohydrides has been reported previously,[6a,b,f] but the polymerization of lactides has not yet been achieved. Unfortunately (unlike the N_2NN′-supported samarium systems **I**[6g]), the compounds **1-M** were ineffective for the polymerization of MMA.

ROP of ϵ-CL. ROP of ϵ-CL has been well established for a wide number of lanthanide compounds[2] including borohydride species,[6a−c,g] and so serves as an appropriate benchmark for the new compounds synthesized above. The catalytic activities of the new borohydride complexes **1-Y**, **1-Sm**, and **1-Nd** toward the ROP of ϵ-CL (275−290 equiv per metal center) were assessed in a toluene solution at room temperature. A rapid increase in the viscosity of the solution was immediately observed, and after quenching with wet toluene, the mixture was poured into ethanol to precipitate poly(ϵ-CL). The results are shown in Table 2. For **1-Sm** and **1-Nd**, a ca. 90% yield of poly(ϵ-CL) was obtained after 30 s, and with **1-Y**, a 84% yield was obtained after 2 min. The polydispersity indexes (PDIs, evaluated by gel permeation chromatography, GPC) of the polyesters formed with these O_2NN′ complexes (runs 1−3) range from 1.57 to 1.76, and the molecular weights (M_n) are in accordance with the calculated ones (also reported in Table 2) for one polymer chain growing per metal center. Therefore, the polymerization is fairly well controlled, and negligible chain-transfer reactions occur. The slightly lower activity for **1-Y** compared to that of **1-Sm** and **1-Nd** is attributed to the smaller radius of yttrium. Because it is well-known[2] that ROP of ϵ-CL can be initiated by insertion into Ln−OR bonds, a control experiment with the chloride compound [Sm(O_2NN′)(μ-Cl)]$_2$ (**2-Sm**) was carried out (Table 2, run 4). Even after 16 h, no ROP was observed, confirming that the M−BH$_4$ units in the compounds **1-M** are the active sites rather than the M−O bonds of the supporting ligand.

ROP of L-LA. The ROP of L-LA to form poly(lactic acid) (PLA) was investigated with the complexes **1-M**. The reactions were carried out either in THF at room temperature or in toluene at 70 °C, as shown in Table 3. At the end of the reaction, a small sample of the viscous mixture was taken

Table 3. Polymerization of L-LA Catalyzed by $[M(O_2NN')(\mu\text{-}BH_4)]_2$ [M = Y (**1-Y**) or Sm (**1-Sm**)] and $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**)[a]

run	initiator	time (min)	solvent	temp (°C)	yield[b] (%)	M_n(obsd)[c] (g mol^{-1})	PDI	M_n(calcd)[d] (g mol^{-1})
1	**1-Y**	180	THF	25	28	3850	1.37	7780
2	**1-Y**	120	toluene	70	24	2980	1.34	13900
3	**1-Sm**	45	THF	25	74	15200	1.63	14400
4	**1-Sm**	120	toluene	70	88	14090	1.73	25370
5	**1-Nd**	180	THF	25	34	6330	1.31	9790
6	**1-Nd**	120	toluene	70	66	6090	1.46	18170

[a] Polymerization conditions: weight of L-LA = 0.30 g; $[\text{L-LA}]_0/[M]_0 = 200$ ([M] corresponds to the total lanthanide metal concentration); solvent = THF (2.5 mL) or toluene (3.5 mL). [b] By ^{1}H NMR in $CDCl_3$. [c] Determined by GPC at 30 °C in THF relative to polystyrene standards with Mark−Houwink corrections[14] for M_n [M_n(obsd) = 0.58M_n(GPC)]. [d] Calculated from $MW_{\text{L-LA}}([\text{L-LA}]_0/[M]_0) \times$ conversion.

and dried to determine the yield by ^{1}H NMR in $CDCl_3$, and the polymerization mixture was quenched with methanol and poured into hexanes. All three complexes **1-M** are efficient catalysts for the ROP of L-LA. **1-Sm** was found to be the most active system either in THF or in toluene (runs 3 and 4), affording 74% yield of poly(L-LA)s in 45 min in THF at room temperature. The PDIs of the poly(L-LA)s are in the same range as those obtained with ϵ-CL with the same complexes. However, the observed molecular weights (M_n) of the poly(L-LA)s are generally lower than those calculated for one chain growing per metal center [e.g., M_n(obsd) = 3850 g mol^{-1} vs M_n(calcd) = 7780 g mol^{-1} for run 1]. This can be attributed to transesterification reactions frequently observed with cyclic esters[13] or to a slow initiation step compared to propagation. Notably, the samarium initiator **1-Sm** is the exception because it gives good control of the molecular weight in THF [M_n(obsd) = 15 200 g mol^{-1} vs M_n(calcd) = 14 400 g mol^{-1} for run 3). Furthermore, because **1-Sm** is the fastest system, the rates of initiation and propagation are apparently much faster than that of chain transfer, thus accounting for the better control of M_n. It is important to mention that the GPC-measured M_n values reported in Table 2 are those obtained after applying the appropriate Mark−Houwink corrections[14] (actual M_n = 0.58M_n estimated from calibration with polystyrene standards) and so are proportionately lower than the values usually reported in the literature when calculated with respect to polystyrene standards.[15]

Further studies were undertaken of the **1-M**/L-LA systems. Figure 2 shows semilogarithmic plots of L-LA conversion vs time for **1-Y** and **1-Sm**. Under these conditions, the reaction kinetics display a first-order dependence on the monomer concentration (for **1-Y**, $k_{app} = 0.31 \times 10^{-4}$ s^{-1}; for **1-Sm**, $k_{app} = 4.96 \times 10^{-4}$ s^{-1}), without any induction period. Figure 3 shows a linear increase of M_n with L-LA conversion for **1-Sm**, which indicates that in this system the polymerization occurs in a living fashion [consistent with the very similar observed and theoretical M_n values (Table 3, run 3)]. However, a surprising (and reproducible) result was obtained with the Nd complex **1-Nd**. First-order semilogarithmic plots were highly nonlinear, and instead this system displays a second-order kinetic dependence on [L-LA] (Figure 4).

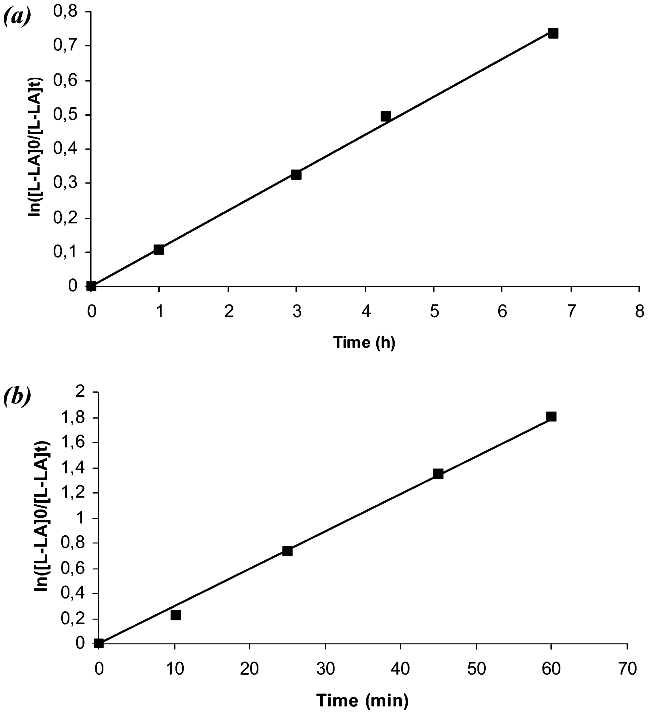

Figure 2. Semilogarithmic plots of L-LA conversion vs time using (a) $[Y(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Y**) or (b) $[Sm(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Sm**). Conditions: THF, 20 °C, $[\text{L-LA}]_0/[\textbf{1-M}]_0 = 200$, and $[\text{L-LA}]_0 = 0.83$ M. For **1-Y**, k_{app}= 0.31 × 10^{-4} s^{-1} (linear fit, R = 0.999), and for **1-Sm**, k_{app}= 4.96 × 10^{-4} s^{-1} (linear fit, R = 0.998).

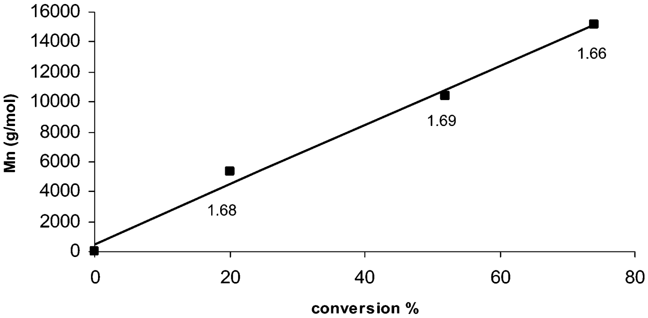

Figure 3. M_n vs L-LA conversion using $[Sm(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Sm**). Conditions: THF, 20 °C, $[\text{L-LA}]_0/[\textbf{1-Sm}]_0 = 200$, and $[\text{L-LA}]_0 = 0.60$ M. PDI values are indicated.

ROP of *rac*-(D,L)-LA. To investigate the influence of the ligand structure on the stereochemistry of the polymerization process, we also tested the three complexes **1-M** as initiators for the ROP of *rac*-LA (racemic mixture of L- and D-LA; Chart 1) to PLA. Polymerizations were carried out either in THF at 20 °C or in toluene at 70 °C, and the results are summarized in Table 4. The O_2NN' complexes of Y, Sm, and Nd are all active for *rac*-LA ROP. For comparison, the previously reported[9a] complex $Sc(O_2NN')(CH_2SiMe_3)(THF)$ was also tested under these conditions and was found to be

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(13) (a) Spassky, N.; Simic, V.; Montaudo, M. S.; Hubert-Pfalzgraf, L. G.; *Macromol. Chem. Phys.* **2000**, *201*, 2432. (b) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F.; Spassky, N.; LeBorgne, A.; Wisniewski, *Macromolecules* **1996**, *29*, 6461. (c) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Symp.* **1997**, *123*, 93. (d) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325. (e) Dubois, P.; Jacobs, C.; Jérome, R.; Teysieé, P. *Macromolecules* **1991**, *24*, 2266.

(14) Barakat, I.; Dubois, P.; Jérome, R.; Teyssie, P. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505.

(15) See, for example, refs 3a and 5c.

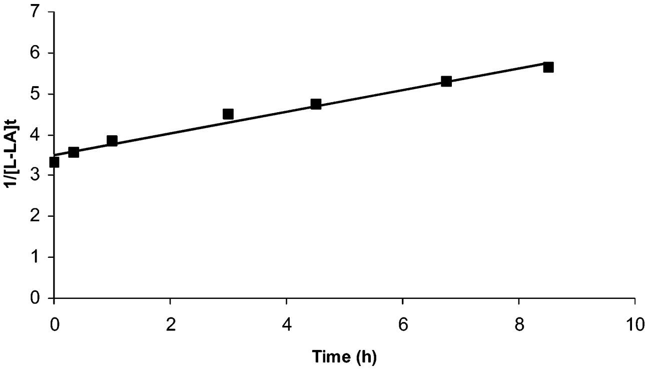

Figure 4. L-LA conversion vs time using $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**). Conditions: THF, 20 °C, $[L\text{-}LA]_0/[\mathbf{1\text{-}Nd}]_0 = 200$, $[L\text{-}LA]_0 = 0.83$ M, and $k_{app} = 7.33 \times 10^{-5}$ L mol^{-1} s^{-1} (linear fit, $R = 0.980$).

completely inactive, possibly because of the small radius of scandium, which (when surrounded by such a bulky ligand) does not favor the coordination of the monomer. As for the ϵ-CL polymerizations (Table 2, run 4), a control experiment found the samarium chloride analogue **2-Sm** to be completely unreactive, which is consistent with the BH_4 group initiating the polymerization and the inertness of the Sm−OAr linkages.

The **1-Sm** system in THF at a $[rac\text{-}LA]_0/[Sm]_0$ ratio of 90 (Table 4, run 4) reaches 95% conversion to PLA in 1 h and shows the best agreement between observed M_n and that calculated for one chain growing per metal center. Thus, as for L-LA polymerization with **1-Sm**, *rac*-LA polymerization proceeds in a living fashion with little chain transfer. For the initiators **1-M** in general, the use of higher $[rac\text{-}LA]_0/[M]_0$ ratios and/or the use of toluene as a solvent lead to poorer agreement between the observed and calculated M_n decreases.

Polymerization of *rac*-LA with **1-M** also follows first-order kinetic dependence on [*rac*-LA] with $k_{app} = 1.20 \times 10^{-4}$ s^{-1} (**1-Y**), 9.96×10^{-4} s^{-1} (**1-Sm**), and 4.9×10^{-5} s^{-1} (**1-Nd**) without any significant induction time (see the Supporting Information). It is not clear why **1-Nd** shows different kinetic behavior with L-LA (Figure 4; second order in [monomer]) and *rac*-LA (first order; see the Supporting Information). Although the observed and calculated M_n values (Table 4, run 8) for **1-Nd** indicate that some chain transfer occurs under these conditions, the polymerization occurs in a living fashion over the entire conversion range, in the sense that there is a linear increase of M_n with conversion (Figure 5), with PDIs ranging from 1.30 to 1.84.

Structure of PLA Obtained with 1-M. The homonuclear-decoupled ^{1}H NMR spectra at 0 °C show that PLA synthesized in THF with the compounds **1-M** are heterotactic-enriched by up to 87% (for **1-Y**). There is little dependence of P_r on the $[rac\text{-}LA]_0/[M]_0$ ratio (e.g., runs 1 and 2 or runs 4 and 5 in Table 4) or the extent of monomer conversion ($P_r = 87\%$ after 1 h and 83% after 7 h for complex **1-Y**). The extent of stereocontrol achieved with **1-Y** is comparable or, in fact, slightly superior to that reported very recently for a related “O_3N”-donor bis(phenoxide) ether supported yttrium bis(dimethylsilyl)amide initiator.[5c] PLA obtained for all three **1-M** systems in toluene at 70 °C was atactic, either as a result of the higher temperature or the change in solvent. The IR spectrum of a dried polymer clearly shows the presence of ν(OH) stretching bands between 3650 and 3200 cm^{-1} attributed to chain ends following the methanolysis workup and consistent with the PLA being linear rather than cyclic.[1b] Guillaume and coworkers have previously proposed a mechanism for the lanthanide borohydride initiated ROP of ϵ-CL,[6a,b] and on the basis of the current data, it is likely that the ROP of L- and *rac*-LA (also being cyclic esters) follows an analogous pathway.

Synthesis of Diblock PLA/PCL Copolymers. Table 5 summarizes our efforts in the block and random copolymerization of L-LA and ϵ-CL using **1-Nd**. A PCL/PLA block copolymer was obtained by sequential addition of the two monomers (Table 5, run 1). ϵ-CL (62 equiv) was polymerized as before in toluene (cf. Table 2) using **1-Nd**. After formation of the first PCL block (as indicated by a rapid increase of the viscosity), a solution of L-LA (120 equiv) in toluene was added, and the solution was stirred at room temperature for another 16 h, giving a further visible increase in the viscosity. The use of a higher number of equivalents of ϵ-CL to synthesize the PCL block gave a very thick gel, which did not allow the addition of the second monomer.[16] The ^{1}H NMR spectrum of the polymer in $CDCl_3$ clearly showed the presence of the two blocks. GPC analysis [either by UV or refractive index (RI) detection] revealed a monomodal peak ($M_n = 14\,400$ g mol^{-1}; PDI = 1.85) in accordance with the formation of a diblock copolymer and not a mixture of two homopolymers of PCL and PLA.

Another diblock copolymer was obtained by using *rac*-LA as the second monomer (Table 5, run 2). The ^{1}H NMR spectrum shows the presence of the two blocks, namely, PCL and poly(*rac*-LA). However, the GPC analysis displayed a bimodal distribution with a main fraction with $M_n = 20\,170$ g mol^{-1}. This can be attributed to the PCL/PLA diblock polymer because the molecular weight is higher than that for a pure PCL block on its own (maximum estimated $M_n = 6390$ g mol^{-1}) and a second, minor peak with $M_n = 1537$ g mol^{-1} assigned to some PLA formed through transesterification. In this diblock copolymer, the poly(*rac*-LA) chain is not heterotactically enriched [cf. homopolymerization of *rac*-LA with **1-Nd** under the same conditions, which also gave atactic polymer (Table 4, run 9)].

When L-LA was added as the first monomer and ϵ-CL was added after formation of the poly(L-LA) block, no additional polymerization occurred even after 16 h and only PLA was obtained after isolation of the polymer (Table 5, run 3). Analogous results have previously been described in the literature for a number of systems.[17]

Finally, a random copolymerization of ϵ-CL and L-LA (Table 5, run 4; equimolar quantities of the two monomers)

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(16) In principle, the Nd-bound ϵ-CL can be dissolved in a large amount of solvent, but at such high volumes, trace impurities lead to catalyst deactivation.

(17) (a) Simic, V.; Pensec, S.; Spassky, N. *Macromol. Symp.* **2000**, *153*, 109. (b) Duda, A.; Biela, T.; Libiszowski, J.; Penczek, S.; Dubois, P.; Mecerreyes, D.; Jérôme, R. *Polym. Degrad. Stab.* **1998**, *59*, 215. (c) Song, C. X.; Feng, X. D. *Macromolecules* **1984**, *17*, 2764.

Table 4. Polymerization of *rac*-LA Catalyzed by $[M(O_2NN')(\mu\text{-}BH_4)]_2$ [M = Y (**1-Y**) or Sm (**1-Sm**)] or $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**) and Some Corresponding Experiments with $Sc(O_2NN')(CH_2SiMe_3)(THF)$[9a] (Indicated by an Asterisk) and $[Sm(O_2NN')(\mu\text{-}Cl)]_2$ (**2-Sm**)[a]

run	initiator	solvent	time (h)	$[rac\text{-}LA]_0/[M]_0$	yield[b] (%)	M_n(obsd)[c] (g mol^{-1})	PDI	M_n(calcd)[d] (g mol^{-1})	P_r (%)[e]
1	**1-Y**	THF	1	90	91	8300	1.44	11800	83.3
2	**1-Y**	THF	1	200	72	10600	1.59	18300	87
3	**1-Y**	toluene	2	200	25	2000	1.34	6740	atactic
4	**1-Sm**	THF	1	90	95	11300	1.59	12660	68.5
5	**1-Sm**	THF	1	200	66	15700	1.47	18000	71.5
6	**1-Sm**	toluene	2	200	68	6780	1.97	19600	atactic
7	**1-Nd**	THF	1	100	56	5500	1.72	8070	61
8	**1-Nd**	THF	2	200	33	4800	1.41	9500	64
9	**1-Nd**	toluene	2	200	25	4140	1.41	11400	atactic
10	*	THF	5	200	0				
11	**2-Sm**	THF	24	200	0				

[a] Polymerization conditions: weight of *rac*-LA = 0.30 g; $T = 25$ °C in THF (3.5 mL) excepted for runs 3, 6, and 9, which were at 70 ° C in toluene (5 mL); [M] corresponds to the total lanthanide metal concentration. [b] By ^1H NMR in $CDCl_3$. [c] Determined by GPC at 30 °C in THF relative to polystyrene standards with Mark−Houwink corrections[14] for M_n. [d] Calculated from $MW_{rac\text{-}LA}([rac\text{-}LA]_0/[M]_0) \times$ yield conversion. [e] P_r corresponds to the ratio of the mrm and rmr units toward all of the other types of units.

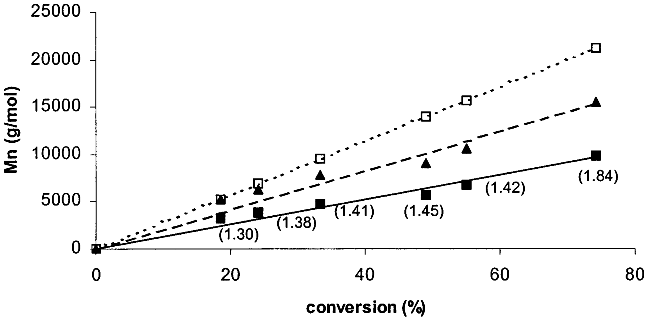

Figure 5. Plots of M_n vs *rac*-LA conversion using $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**) in THF at 20 °C with $[rac\text{-}LA]_0/[\mathbf{1\text{-}Nd}]_0 = 200$ and $[rac\text{-}LA]_0 = 0.60$ M: (i, ■) M_n (measured by GPC, after Mark−Houwink corrections[14] with PDI values in parentheses); (ii, ▲) M_n (measured by GPC against polystyrene standards); (iii, □) theoretical values assuming no chain transfer and every metal site catalytically active.

was attempted under the same experimental conditions as those for the homopolymerization of L-LA in THF (Table 3, runs 1, 3, and 5). After 16 h at room temperature, the NMR spectrum of the crude reaction mixture showed the complete conversion of L-LA but no conversion of ϵ-CL. Workup of the polymer afforded pure poly(L-LA). Again, analogous results have previously been described for a number of systems.[17]

Summary

We have reported the synthesis and characterization of a series of new rare-earth borohydride and chloride complexes of O_2NN'. The X-ray structure of $[La(O_2NN')(\mu\text{-}Cl)(py)]_2$ (**4-La**) established this as a dimeric species, and (on the basis of the available data) this is also conserved for **4-Sm** and **4-Nd**. The IR data for the borohydride compounds **1-M** and **3-M** suggest that they too are dimeric in the solid state. Nonetheless, the borohydride compounds **1-M** are efficient initiators for the ROP of ϵ-CL, with the highest productivity being found for **1-Sm** and **1-Nd**. Of the three compounds, **1-Sm** gave the best control of the molecular weight as judged by comparison of observed and expected M_n values, and the other two were comparable. The compounds **1-M** also initiate the ROP of L- and *rac*-LA, the first lanthanide borohydride compounds to do so. These polymerizations are accompanied by greater degrees of chain transfer, but for the samarium compound **1-Sm**, this process is reasonably well inhibited. In addition, poly(*rac*-LA) obtained with **1-M** in THF has up to 87% heterotactic enrichment, with the best values being for **1-Y**. The ROP of *rac*-LA shows first-order kinetics with respect to [lactide] for all three compounds **1-M**, and this is also the case for ROP of L-LA with **1-Y** and **1-Sm**. Surprisingly, there is a second-order dependence on [L-LA] for polymerization initiated by **1-Nd**.

Compound **1-Nd** catalyzed the block copolymerization of ϵ-CL and L- and *rac*-LA, provided that ϵ-CL was added first. Attempted block copolymerization by adding the L-LA first, or random copolymerization of a ca. 1:1 mixture of ϵ-CL and L-LA, gave pure poly(L-LA).

Detailed DFT computational studies of the mechanism of the ROP of lactide (and other polar monomers) by lanthanide borohydride compounds with N_2NN', O_2NN', and related supporting ligands are underway and will be reported in due course.

Experimental Section

General Methods and Instrumentation. All experiments were carried out on a Schlenk line under argon or in a glovebox under nitrogen. The solvents were deoxygenated, dried over sodium/benzophenone ketyl, and distilled just before use. NMR solvents were dried over a sodium/potassium amalgam. NMR spectra were recorded in Teflon-valved NMR tubes on Varian Mercury VX 300 and Varian Unity Plus 500 spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are expressed in ppm versus $SiMe_4$ and are referenced to the residual solvent peaks. Combustion analyses were recorded by the elemental analysis service at the London Metropolitan University.

GPC was carried out using Plgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min^{-1}. Molecular weight and molecular weight distributions were calculated using polystyrene as standard and Mark−Houwink corrections were applied.[14]

Starting materials. The compounds Na_2O_2NN',[10a] metal borohydride compounds,[10b] metal chloride THF adducts,[10c] and $Sc(O_2NN')(CH_2SiMe_3)(THF)$[9a] were prepared according to the literature methods. Anhydrous salts YCl_3, $SmCl_3$, and $NdCl_3$ were purchased from Strem. ϵ-CL (99%, Sigma-Aldrich) was dried over CaH_2 and molecular sieves and distilled just before use. L-LA (98%, Sigma-Aldrich) and D,L-LA (Aldrich) were purified by sublimation.

Table 5. Block and Random Copolymerization of ϵ-CL and Lactide (L-LA or *rac*-La) Catalyzed by $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**)[a]

run	$[m_1]_0/[\mathbf{1\text{-}Nd}]_0$ (m_1)	t_1	$[m_2]_0/[\mathbf{1\text{-}Nd}]_0$ (m_2)	t_2	yield (%)[b]	M_n(copolymer)[c] (g mol^{-1})	PDI	m_1/m_2 in copolymer[d] (mol %/mol %)
1	62 (ϵ-CL)	1 h	120 (L-LA)	16 h	89	14400	1.85	23/77
2	56 (ϵ-CL)	30 min	114 (*rac*-LA)	16 h	91	20170[e]	1.31[e]	27/73[f]
						1537[e]	1.15[e]	
3	121 (L-LA)	2 h	127 (ϵ-CL)	16 h	7.5	3330	1.46	100 (PLA)/0
4	120, 115 (ϵ-CL, L-LA)	16 h	120, 115 (ϵ-CL, L-LA)		49	4290	1.58	100 (PLA)/0

[a] Polymerization conditions: Runs 1 and 2 were performed in toluene (4.5 mL with 4 drops of THF) at room temperature for the ϵ-CL and L-LA polymerization and at 70 °C for the *rac*-LA polymerization; m_1 and m_2 refer to the first and second added monomer, respectively. Runs 3 and 4 performed in THF (2.5 mL) at room temperature. [b] By ^1H NMR in $CDCl_3$. [c] By GPC at 30 °C in THF relative to polystyrene standards. Mark−Houwink corrections[14] for L-LA [$M_n(\text{obsd}) = 0.58M_n(\text{GPC})$] were applied to runs 1, 3, and 4. Corrections for *rac*-LA were applied to M_n in run 2. [d] Calculated by integration of the respective signals in the ^1H NMR spectrum. [e] Bimodal. [f] For both fractions.

$[Y(O_2NN')(\mu\text{-}BH_4)(THF)_{0.5}]_2$ (1-Y). To a mixture of $Y(BH_4)_3(THF)_3$ (162 mg, 0.463 mmol) and Na_2O_2NN' (272 mg, 0.462 mmol) in an ampule was added 30 mL of THF by vacuum distillation. The cold solution was allowed to warm to room temperature to afford a white-beige solution and a precipitate, and the mixture was stirred for 16 h. The solution was filtered, and the volatiles were removed under reduced pressure to give a yellow oil. The target compound was extracted into toluene to afford 257 mg (86% yield) of **1-Y** as a pale-yellow solid. Elem anal. Calcd for $[Y(O_2NN')(\mu\text{-}BH_4)(THF)_{0.5}]_2$, $C_{76}H_{116}B_2N_4O_5Y_2$: C, 66.8; H, 8.7; N, 3.9. Found: C, 66.4; H, 8.0; N, 3.8. ^1H NMR (C_6D_6 with 4 drops of pyridine-d_5 to aid solubility, 300 MHz, 293 K): δ 8.65 (d, 2H, 6-$NC_5\mathit{H}_4$), 7.37 (d, 4H, 4-$C_6\mathit{H}_2{}^tBu_2$), 6.93 (d, 4H, 6-$C_6\mathit{H}_2{}^tBu_2$), 6.54 (m, 2H, 4-$NC_5\mathit{H}_4$), 6.20 (t, 2H, 5-$NC_5\mathit{H}_4$), 5.85 (d, 2H, 3-$NC_5\mathit{H}_4$), 3.97 (d, 4H, $NC\mathit{H}_2Ar$ distal to C_5H_4N), 3.30 (s, 4H, $NC\mathit{H}_2C_5H_4N$), 2.83 (d, 4H, $NC\mathit{H}_2Ar$ proximal to C_5H_4N), 1.73 (s, 36H, 3-$C_6H_2{}^t\mathit{Bu}_2$), 1.38 (s, 36H, 5-$C_6H_2{}^t\mathit{Bu}_2$), between 1 and 2 (m, 8H, BH_4). $^{13}C\{^1H\}$ NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 290 K): δ 161.80 (2-$\mathit{C}_6H_2{}^tBu_2$), 159.10 (2-C_5H_4N), 149.68 (6-C_5H_4N), 137.95 (4-C_5H_4N), 136.76 (5-$\mathit{C}_6H_2{}^tBu_2$), 136.49 (3-$\mathit{C}_6H_2{}^tBu_2$), 125.43 (4-$\mathit{C}_6H_2{}^tBu_2$), 124.19 (6-$\mathit{C}_6H_2{}^tBu_2$), 123.68 (1-$\mathit{C}_6H_2{}^tBu_2$), 122.25 (5-C_5H_4N), 121.55 (3-C_5H_4N), 64.62 ($N\mathit{C}H_2Ar$), 57.74 ($N\mathit{C}H_2C_5H_4N$), 35.44 (3-$C_6H_2(\mathit{C}Me_3)_2$), 34.12 (5-$C_6H_2(\mathit{C}Me_3)_2$), 32.22 (5-$C_6H_2(C\mathit{Me}_3)_2$), 30.28 (3-$C_6H_2(C\mathit{Me}_3)_2$). Resonances for displaced THF were also observed. IR (Nujol, cm^{-1}): 2456, 2364, 2310, 2280, 2224, 2162 (BH_4).

$[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (1-Nd). To a mixture of $Nd(BH_4)_3(THF)_3$ (200 mg, 0.493 mmol) and Na_2O_2NN' (290 mg, 0.493 mmol) in an ampule was added 30 mL of THF by vacuum distillation. The cold solution was allowed to warm to room temperature to afford a bright-blue solution with a precipitate, and the mixture was stirred for 16 h. The solution was filtered, and the volatiles were removed under reduced pressure to give a bright-blue foaming oil. The target compound was extracted into toluene to afford 266 mg (70% yield) of **1-Nd** as a pale-blue-green solid. Elem anal. Calcd for $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$, $C_{80}H_{124}B_2N_4Nd_2O_6$: C, 62.1; H, 8.1; N, 3.6. Found: C, 61.9; H, 7.7; N, 3.6. ^1H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 293 K): very broad spectrum. Only the peaks due to the *tert*-butyl groups (3.29 ppm, br s, 64 H), coordinated THF (2.52 and 1.02 ppm, 2 × m, 2 × 8H) and the borohydride (35 ppm, m, 8H, BH_4) could be identified. IR (Nujol, cm^{-1}): 2462, 2316, 2224, 2174 (BH_4).

$[Sm(O_2NN')(\mu\text{-}BH_4)]_2$ (1-Sm). To a mixture of $Sm(BH_4)_3(THF)_3$ (150 mg, 0.365 mmol) and Na_2O_2NN' (245 mg, 0.401 mmol) in an ampule was added 30 mL of THF by vacuum distillation. The cold solution was allowed to warm to room temperature to afford a bright-yellow solution with a precipitate, and the mixture was stirred for 16 h. The solution was filtered, and the volatiles were removed under reduced pressure to give a pale-yellow foaming oil. The target compound was extracted into benzene to afford 225 mg (87% yield) of **1-Sm** as a pale-yellow solid. Elem anal. Calcd for $[Sm(O_2NN')(\mu\text{-}BH_4)]_2$, $C_{72}H_{108}B_2N_4O_4Sm_2$: C, 61.1; H, 7.7; N, 3.9. Found: C, 62.3; H, 7.7; N, 3.8. ^1H NMR (toluene-d_8, 300 MHz, 293 K): δ 8.37 (d, 4H, 4-$C_6\mathit{H}_2{}^tBu_2$), 7.32 (d, 4H, 6-$C_6\mathit{H}_2{}^tBu_2$), 6.04 (t, 2H, 5-$NC_5\mathit{H}_4$), 5.71 (d, 2H, 3-$NC_5\mathit{H}_4$), 4.62 (m, 2H, 4-$NC_5\mathit{H}_4$), 3.86 (s, 36H, 3-$C_6H_2{}^t\mathit{Bu}_2$), 3.45 (s, 4H, $NC\mathit{H}_2C_5H_4N$), 1.69 (s, 36H, 5-$C_6H_2{}^t\mathit{Bu}_2$), −1.05 (br, 4H, $NC\mathit{H}_2Ar$), between −8 and −9.5 (m, 8H, BH_4, 3-$C_6H_2(\mathit{C}Me_3)_2$). IR (Nujol, cm^{-1}): 2459, 2363, 2330, 2280, 2214, 2200 (BH_4).

$[La(O_2NN')(\mu\text{-}Cl)]_2$ (2-La). To a mixture of $LaCl_3(THF)_2$ (85 mg, 0.256 mmol) and Na_2O_2NN' (150 mg, 0.256 mmol) was added 20 mL of THF by vacuum distillation. The cold solution was allowed to warm to room temperature to afford a colorless solution with a white precipitate, and this was stirred for 4 days. The volatiles were removed under reduced pressure to give a white oil. The target compound was extracted into 20 mL of toluene, and the volatiles were removed under reduced pressure to afford 140 mg (76% yield) of **2-La** as a white solid. Elem anal. Calcd for $[La(O_2NN')(\mu\text{-}Cl)]_2$, $C_{72}H_{100}Cl_2La_2N_4O_4$: C, 60.3; H, 7.0; N, 3.9. Found: C, 59.9; H, 7.0; N, 3.4. ^1H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 353 K): δ 9.20 (d, 2H, 6-$NC_5\mathit{H}_4$), 7.32 (d, 4H, 4-$C_6\mathit{H}_2{}^tBu_2$), 6.95 (d, 4H, 6-$C_6\mathit{H}_2{}^tBu_2$), 6.74 (m, 2H, 4-$NC_5\mathit{H}_4$), 6.45 (t, 2H, 5-$NC_5\mathit{H}_4$), 6.20 (d, 2H, 3-$NC_5\mathit{H}_4$), 4.05 (d, 4H, $NC\mathit{H}_2Ar$ distal to C_5H_4N), 3.64 (s, 4H, $NC\mathit{H}_2C_5H_4N$), 3.32 (d, 4H, $NC\mathit{H}_2Ar$ proximal to C_5H_4N), 1.55 (s, 36H, 3-$C_6H_2{}^t\mathit{Bu}_2$), 1.38 (s, 36H, 5-$C_6H_2{}^t\mathit{Bu}_2$). $^{13}C\{^1H\}$ NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 290 K): δ 162.59 (2-$\mathit{C}_6H_2{}^tBu_2$), 159.50 (2-C_5H_4N), 149.90 (6-C_5H_4N), 136.83 (4-C_5H_4N), 136.09 (5-$\mathit{C}_6H_2{}^tBu_2$), 135.32 (3-$\mathit{C}_6H_2{}^tBu_2$), 126.13 (4-$\mathit{C}_6H_2{}^tBu_2$), 124.84 (6-$\mathit{C}_6H_2{}^tBu_2$), 123.73 (1-$\mathit{C}_6H_2{}^tBu_2$), 122.51 (5-C_5H_4N), 120.93 (3-C_5H_4N), 64.28 ($N\mathit{C}H_2Ar$), 57.14 ($N\mathit{C}H_2C_5H_4N$), 35.27 (3-$C_6H_2(\mathit{C}Me_3)_2$), 34.08 (5-$C_6H_2(\mathit{C}Me_3)_2$), 32.29 (5-$C_6H_2(C\mathit{Me}_3)_2$), 30.61 (3-$C_6H_2(C\mathit{Me}_3)_2$).

$[Nd(O_2NN')(\mu\text{-}Cl)(THF)]_2$ (2-Nd). $NdCl_3(THF)_2$ (137 mg, 0.34 mmol) and Na_2O_2NN' (200 mg, 0.339 mmol) were weighed in the glovebox in an ampule. A total of 20 mL of THF was added by distillation. The cold solution was allowed to warm to room temperature to afford a bright-blue solution with insolubles, and the mixture was stirred for 2 days. The volatiles were removed under reduced pressure to give a bright-blue oil. The target compound was extracted into 30 mL of toluene, and the volatiles were removed under reduced pressure to afford 161 mg (60% yield) of **2-Nd** as a pale-blue powder. Elem anal. Calcd for $[Nd(O_2NN')(\mu\text{-}Cl)(THF)]_2$, $C_{80}H_{116}Cl_2N_4Nd_2O_6$: C, 60.5; H, 7.4; N, 3.5. Found: C, 60.8; H, 7.4; N, 3.5. ^1H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 293 K): very broad spectrum. Only a broad resonance due to the *tert*-butyl groups (3.07 ppm) could be identified.

$[Sm(O_2NN')(\mu\text{-}Cl)]_2$ (2-Sm). To a mixture of $SmCl_3(THF)_2$ (140 mg, 0.342 mmol) and Na_2O_2NN' (214 mg, 0.339 mmol) in an ampule was added 20 mL of THF by vacuum distillation. The cold solution was allowed to warm to room temperature to afford a bright-blue solution with a precipitate, and this was stirred for 2 h to afford a pale-yellow solution with some precipitates. The volatiles were removed under reduced pressure to give a bright-yellow oil. The target compound was extracted in 30 mL of toluene, and the volatiles were removed under reduced pressure to afford 218 mg (80% yield) of **2-Sm** as a pale-yellow powder. Elem anal. Calcd for $[\text{Sm(O}_2\text{NN}')(\mu\text{-Cl})]_2$, $\text{C}_{72}\text{H}_{100}\text{Cl}_2\text{N}_4\text{O}_4\text{Sm}_2$: C, 59.3; H, 6.9; N, 3.8. Found: C, 59.4; H, 6.9; N, 3.8. ^{1}H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 333 K): δ 7.93 (d, 4H, $\text{4-C}_6H_2{}^t\text{Bu}_2$), 7.43 (d, 4H, $\text{6-C}_6\text{H}_2{}^t\text{Bu}_2$), 6.02 (t, 2H, 5-NC_5H_4), 5.81 (m, 2H, 4-NC_5H_4), 4.91 (d, 2H, 6-NC_5H_4), 2.31 (s, 4H, $\text{NC}H_2\text{C}_5\text{H}_4\text{N}$), 2.64 (s, 36H, $\text{3-C}_6\text{H}_2{}^tBu_2$), 1.57 (s, 36H, $\text{5-C}_6\text{H}_2{}^tBu_2$), 0.93 (br, 2H, 3-NC_5H_4).

$[\text{Y(O}_2\text{NN}')(\mu\text{-BH}_4)(\text{py})]_2$ (3-Y). To a solution of $\text{Y(BH}_4)_3(\text{THF})_3$ (100 mg, 0.286 mmol) in 10 mL of THF was added dropwise a solution of $\text{Na}_2\text{O}_2\text{NN}'$ (167 mg, 0.285 mmol) in 10 mL of THF to afford a pale-yellow solution with a precipitate, and this was stirred for 16 h. The volatiles were removed under reduced pressure to give a yellow foaming oil. The presumed intermediate compound **1-Y** was extracted into benzene, and the solution was filtered. A total of 1 mL of pyridine was then added, and the solution was stirred for 30 min. The volatiles were removed under reduced pressure to afford 180 mg (87% yield) of **3-Y** as a yellow solid. ^{1}H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 293 K): δ 8.66 (d, 2H, 6-NC_5H_4), 8.53 (d, 4H, $\text{2-NC}_5\text{H}_5$), 7.37 (d, 4H, $\text{4-C}_6H_2{}^t\text{Bu}_2$), 7.03 (t, 2H, $\text{4-NC}_5\text{H}_5$), 6.93 (d, 4H, $\text{6-C}_6H_2{}^t\text{Bu}_2$), 6.71 (td, 4H, $\text{3-NC}_5\text{H}_5$), 6.53 (m, 2H, 4-NC_5H_4), 6.20 (t, 2H, 5-NC_5H_4), 5.85 (d, 2H, 3-NC_5H_4), 3.97 (d, 4H, $\text{NC}H_2\text{Ar}$ distal to $\text{C}_5\text{H}_4\text{N}$), 3.30 (s, 4H, $\text{NC}H_2\text{C}_5\text{H}_4\text{N}$), 2.83 (d, 4H, $\text{NC}H_2\text{Ar}$ proximal to $\text{C}_5\text{H}_4\text{N}$), 1.73 (s, 36H, $\text{3-C}_6\text{H}_2{}^tBu_2$), 1.38 (s, 36H, $\text{5-C}_6\text{H}_2{}^tBu_2$), between 1 and 2 (m, 8H, BH_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 290 K): δ 161.82 ($\text{2-}C_6\text{H}_2{}^t\text{Bu}_2$), 159.10 ($\text{2-}C_5\text{H}_4\text{N}$), 150.24 ($\text{2-C}_5\text{H}_5\text{N}$), 149.70 ($\text{6-}C_5\text{H}_4\text{N}$), 137.94 ($\text{4-C}_5\text{H}_5\text{N}$), 136.76 ($\text{4-}C_5\text{H}_4\text{N}$), 136.51 ($\text{5-}C_6\text{H}_2{}^t\text{Bu}_2$), 135.30 ($\text{3-}C_6\text{H}_2{}^t\text{Bu}_2$), 125.42 ($\text{4-}C_6\text{H}_2{}^t\text{Bu}_2$), 124.19 ($\text{2-C}_5\text{H}_5\text{N}$), 123.69 ($\text{6-}C_6\text{H}_2{}^t\text{Bu}_2$), 123.51 ($\text{1-}C_6\text{H}_2{}^t\text{Bu}_2$), 122.24 ($\text{5-}C_5\text{H}_4\text{N}$), 121.55 ($\text{3-}C_5\text{H}_4\text{N}$), 64.62 ($\text{N}C\text{H}_2\text{Ar}$), 57.75 ($\text{N}C\text{H}_2\text{C}_5\text{H}_4\text{N}$), 35.43 ($\text{3-C}_6\text{H}_2(C\text{Me}_3)_2$), 34.10 ($\text{5-C}_6\text{H}_2(C\text{Me}_3)_2$), 32.21 ($\text{5-C}_6\text{H}_2(C\text{Me}_3)_2$), 30.22 ($\text{3-C}_6\text{H}_2(C\text{Me}_3)_2$). IR (Nujol, cm^{-1}): 2437, 2370, 2310, 2280, 2215, 2162 (BH_4). EI MS: *m/z* 646 $[\text{Y(O}_2\text{NN}')\text{BH}_4]^+$, 30%. Despite repeated attempts, a satisfactory elemental analysis could not be obtained.

$[\text{Sm(O}_2\text{NN}')(\mu\text{-BH}_4)(\text{py})]_2$ (3-Sm). To a solution of $\text{Sm(BH}_4)_3(\text{THF})_3$ (150 mg, 0.364 mmol) in 10 mL of THF was added dropwise a solution of $\text{Na}_2\text{O}_2\text{NN}'$ (245 mg, 0.401 mmol) in 10 mL of THF to afford a pale-yellow solution with a precipitate, and this was stirred for 16 h. The volatiles were removed under reduced pressure to give a yellow foaming oil. The presumed intermediate compound **1-Sm** was extracted into benzene, and the solution was filtered. A total of 1 mL of pyridine was then added, and the solution was stirred for 30 min. The volatiles were removed under reduced pressure to afford 257 mg (89% yield) of **3-Sm** as a yellow solid. Elem anal. Calcd for $[\text{Sm(O}_2\text{NN}')(\mu\text{-BH}_4)(\text{py})]_2$, $\text{C}_{82}\text{H}_{118}\text{B}_2\text{N}_6\text{O}_4\text{Sm}_2$: C, 62.6; H, 7.6; N, 5.3. Found: C, 62.5; H, 7.6; N, 5.4. The NMR spectra were extremely broad and could not be meaningfully interpreted. IR (Nujol, cm^{-1}): 2430, 2363, 2280, 2214, 2154 (BH_4).

$[\text{La(O}_2\text{NN}')(\mu\text{-Cl})(\text{py})]_2$ (4-La). $[\text{La(O}_2\text{NN}')(\mu\text{-Cl})]_2$ (**2-La**; 50 mg, 0.0698 mmol) was dissolved in 10 mL of pyridine to give immediately a clear yellow solution. After the solution was stirred for 30 min, the volatiles were removed under reduced pressure to afford 45 mg of **4-La** as a yellow solid (82% yield). Elem anal. Calcd for $[\text{La(O}_2\text{NN}')(\mu\text{-Cl})(\text{py})]_2$, $\text{C}_{82}\text{H}_{110}\text{Cl}_2\text{La}_2\text{N}_6\text{O}_4$: C, 61.8; H, 7.0; N, 5.3. Found: C, 61.8; H, 7.0; N, 5.2. ^{1}H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 353 K): δ 9.18 (d, 2H, 6-NC_5H_4), 8.54 (d, 4H, NC_5H_4), 7.31 (d, 4H, $\text{4-C}_6H_2{}^t\text{Bu}_2$), 7.10 (m, 2H, NC_5H_4), 6.95 (d, 4H, $\text{6-C}_6H_2{}^t\text{Bu}_2$), 6.76 (m, 4H, NC_5H_4), 6.73 (m, 2H, 4-NC_5H_4), 6.46 (t, 2H, 5-NC_5H_4), 6.21 (d, 2H, 3-NC_5H_4), 4.04 (d, 4H, $\text{NC}H_2\text{Ar}$ distal to $\text{C}_5\text{H}_4\text{N}$), 3.65 (s, 4H, $\text{NC}H_2\text{C}_5\text{H}_4\text{N}$), 3.33 (d, 4H, $\text{NC}H_2\text{Ar}$ proximal to $\text{C}_5\text{H}_4\text{N}$), 1.54 (s, 36H, $\text{3-C}_6\text{H}_2{}^tBu_2$), 1.38 (s, 36H, $\text{5-C}_6\text{H}_2{}^tBu_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 290 K): δ 162.59 ($\text{2-}C_6\text{H}_2{}^t\text{Bu}_2$), 159.55 ($\text{2-}C_5\text{H}_4\text{N}$), 150.26 ($\text{2-}C_5\text{H}_5\text{N}$), 149.85 ($\text{6-}C_5\text{H}_4\text{N}$), 136.84 ($\text{4-}C_5\text{H}_4\text{N}$), 136.09 ($\text{5-}C_6\text{H}_2{}^t\text{Bu}_2$), 135.32 ($\text{3-}C_6\text{H}_2{}^t\text{Bu}_2$), 126.11 ($\text{4-}C_6\text{H}_2{}^t\text{Bu}_2$), 124.84 ($\text{6-}C_6\text{H}_2{}^t\text{Bu}_2$), 123.73 ($\text{1-}C_6\text{H}_2{}^t\text{Bu}_2$), 123.51 ($\text{3-}C_5\text{H}_5\text{N}$), 122.53 ($\text{5-}C_5\text{H}_4\text{N}$), 120.94 ($\text{3-}C_5\text{H}_4\text{N}$), 35.28 ($\text{3-C}_6\text{H}_2(C\text{Me}_3)_2$), 34.08 ($\text{5-C}_6\text{H}_2(C\text{Me}_3)_2$), 32.29 ($\text{5-C}_6\text{H}_2(C\text{Me}_3)_2$), 30.61 ($\text{3-C}_6\text{H}_2(C\text{Me}_3)_2$).

$[\text{Nd(O}_2\text{NN}')(\mu\text{-Cl})(\text{py})]_2$ (4-Nd). $[\text{Nd(O}_2\text{NN}')(\mu\text{-Cl})(\text{THF})]_2$ (**2-Nd**; 43 mg, 0.0543 mmol) was dissolved in 7 mL of pyridine to give immediately a blue-green solution and a small quantity of a precipitate. After it was stirred for 2 h, the solution was filtered and the volatiles were removed under reduced pressure to afford 31 mg of **4-Nd** as a blue-green solid (71% yield). Elem anal. Calcd for $[\text{Nd(O}_2\text{NN}')(\mu\text{-Cl})(\text{py})]_2$, $\text{C}_{82}\text{H}_{110}\text{Cl}_2\text{N}_6\text{Nd}_2\text{O}_4$: C, 61.4; H, 6.9; N, 5.2. Found: C, 61.3; H, 6.8; N, 5.2. ^{1}H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 333 K): very broad spectrum. Only a broad resonance due to coordinated pyridine at 8.32, 6.91, and 6.58 ppm and the *tert*-butyl groups (ca. 3.03 ppm) could be indentified.

$[\text{Sm(O}_2\text{NN}')(\mu\text{-Cl})(\text{py})]_2$ (4-Sm). $[\text{Sm(O}_2\text{NN}')(\mu\text{-Cl})]_2$ (**2-Sm**; 43 mg, 0.0524 mmol) was dissolved in 7 mL of pyridine to give immediately a green solution along with a small amount of precipitate. After 2 h, the solution was filtered and the volatiles were removed under reduced pressure to afford 31 mg of **4-Sm** as a green solid (71% yield). ^{1}H NMR (C_6D_6 with 4 drops of pyridine-d_5, 300 MHz, 333 K): the spectrum was broad, and only these signals could be assigned. δ 7.94 (d, 4H, $\text{4-C}_6H_2{}^t\text{Bu}_2$), 7.11 (d, 4H, $\text{6-C}_6H_2{}^t\text{Bu}_2$), 6.06 (t, 2H, 5-NC_5H_4), 5.83 (m, 2H, 4-NC_5H_4), 4.95 (d, 2H, 6-NC_5H_4), 2.70 (s, 36H, $\text{3-C}_6\text{H}_2{}^tBu_2$), 2.19 (d, 4H, $\text{NC}H_2\text{Ar}$), 1.57 (s, 36H, $\text{5-C}_6\text{H}_2{}^tBu_2$), 0.89 (br, 2H, $\text{NC}H_2\text{Ar}$). Despite repeated attempts, a satisfactory elemental analysis could not be obtained. Despite this, the compound is assigned as **4-Sm** on the basis of the X-ray structure of **4-La**, the satisfactory elemental analyses for **4-La** and **4-Nd**, and its preliminary X-ray structure determination (see the Supporting Information).

Typical ϵ-CL Polymerization Experiment. In a glovebox, $[\text{Sm(O}_2\text{NN}')(\mu\text{-BH}_4)]_2$ (**1-Sm**; 11.2 mg) was dissolved in 4 mL of toluene. ϵ-CL (0.50 g) was added to the stirring catalyst solution via a syringe. The mixture was magnetically stirred at room temperature for 30 s. The viscous mixture was quenched with wet toluene and poured into ethanol. The white polymer was filtered and dried to a constant weight in vacuo (450 mg, 90% yield).

Typical Ambient-Temperature L-LA and *rac*-LA Polymerization Experiment. In a glovebox, $[\text{Sm(O}_2\text{NN}')(\mu\text{-BH}_4)]_2$ (**1-Sm**; 7.3 mg) was dissolved in 0.5 mL of THF. L-LA (0.30 g) in 2 mL of THF (3 mL for *rac*-LA) was added to the stirring catalyst solution via a syringe. The mixture was magnetically stirred at room temperature for 45 min. After this time, a sample of the mixture was taken and evaporated to dryness to determine the extent of conversion by ^{1}H NMR in CDCl_3 (74%). The viscous reaction mixture was quenched with wet THF and poured into hexanes. The white powder was filtered and dried in vacuo.

Typical High-Temperature L-LA and *rac*-LA Polymerization Experiment. In a glovebox, $[\text{Sm(O}_2\text{NN}')(\mu\text{-BH}_4)]_2$ (**1-Sm**; 8 mg) was dissolved in 1 mL of toluene. L-LA (0.3 g) was dissolved in 3.5 mL of toluene (5 mL for *rac*-LA) at 70 °C, and the catalyst was then added to the monomer solution with stirring. The mixture

Table 6. X-ray Data Collection and Processing Parameters for $[La(O_2NN')(\mu\text{-}Cl)(py)]_2 \cdot 3C_6H_6$ (**4-La·3C$_6$H$_6$**)

empirical formula	$C_{100}H_{128}Cl_2La_2N_6O_4$
fw	1826.87
temp/K	150
wavelength/Å	0.710 73
space group	$P\bar{1}$
a/Å	14.4266(2)
b/Å	17.2972(2)
c/Å	22.1531(2)
α/deg	105.7622(3)
β/deg	106.5123(4)
γ/deg	90.6879(3)
V/Å^3	5076.90(7)
Z	2
d(calcd)/(mg m^{-3})	1.195
abs coeff/mm^{-1}	0.931
R indices R_1, R_w [$I > 3\sigma(I)$][a]	$R_1 = 0.0743$ $R_w = 0.0762$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}}$.

was stirred at 70 °C for 2 h. After this time, a sample of the mixture was taken and evaporated to dryness to determine the extent of conversion by ^{1}H NMR in $CDCl_3$ (88%). The viscous mixture was quenched with wet THF and poured into hexanes. The white powder was filtered and dried in vacuo.

Typical Block Copolymerization of ϵ-CL with L-LA. In a glovebox $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**; 8 mg) was dissolved in 1 mL of toluene and drops of THF, and a solution of ϵ-CL (73 mg, 62 equiv) in 2 mL of toluene was added with stirring. The solution was stirred for 1 h at room temperature, during which time an increase of the viscosity was observed. L-LA (178 mg, 120 equiv) in 1.5 mL of toluene was added to the mixture, which was stirred for 16 h at room temperature. The resultant viscous mixture was quenched with methanol and poured into hexanes. The white powder (228 mg, 89% yield) was filtered and dried in vacuo. An analogous procedure was used for the block copolymerization of ϵ-CL with *rac*-LA, but the polymerization for the second block was carried out at 70 °C because of the poor solubility of *rac*-LA.

Attempted Random Copolymerization of ϵ-CL with L-LA. In a glovebox, $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**; 8 mg) was weighed into a flask and dissolved in 0.5 mL of THF. ϵ-CL (140 mg, 120 equiv) and L-LA (170 mg, 115 equiv) in 2 mL of THF were added with stirring. After 16 h, an increase of the viscosity was observed. A sample of the mixture was taken and evaporated to dryness to determine the extent of conversion by ^{1}H NMR in $CDCl_3$ (100% yield for L-LA, 0% conversion for ϵ-CL, and global yield 49%). The viscous mixture was quenched with methanol and poured into hexanes. The white powder (pure PLA) was filtered and dried in vacuo.

Crystal Structure Determination of $[La(O_2NN')(\mu\text{-}Cl)(py)]_2 \cdot 3C_6H_6$ (4-La·3C$_6$H$_6$). Crystal data collection and processing parameters are given in Table 6. A crystal of **4-La·3C$_6$H$_6$** was mounted on a glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using a Kappa CCD diffractometer, and intensity data were processed using the DENZO−SMN package.[18] Visual examination of the diffraction pattern showed the crystal to be twinned, and this was identified as being due to the presence of two components related by a 180° rotation about the reciprocal vector (0, −1, 1). No attempt was made to resolve the twin at the data processing stage, but instead the contribution of the two components to those reflections where the two diffraction patterns overlapped was incorporated as a parameter in the subsequent refinement. The structure was solved in the space group $P\bar{1}$ using the direct methods program SIR92,[19] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[20] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Examination of the resulting model showed that a number of carbon atoms had unusually high displacement parameters and that the bond lengths and angles concerning these varied substantially from the expected geometry. This was modeled as being due to disorder of the following groups: (i) the $C_6H_2{}^tBu_2$ group C(1)−C(14) over two positions related by a 180° rotation of the *tert*-butyl group C(11)−C(14) about the $C_{quaternary}-C_{phenyl}$ bond and a small displacement of all other C atoms; (ii) the $C_6H_2{}^tBu_2$ group C(1)−C(14) over two positions related solely by a small displacement of all C atoms; (iii) the *tert*-butyl group C(53)−C(55) over two positions related by a 180° rotation about the $C_{quaternary}-C_{phenyl}$ bond, in this instance without any associated disorder of the parent phenyl ring; (iv) the C_6H_6 of crystallization C(89)−C(94) and C(95)−C(100) over two positions related by small displacements of the entire molecules.

The coordinates, isotropic thermal parameters, and site occupancies of the disordered carbon atoms were refined subject to geometric and vibrational restraints. The $C_{phenyl}-C_{phenyl}$ bond lengths were restrained to 1.39(2) Å, $C_{phenyl}-C_{methylene}$ to 1.52(2) Å, $C_{quaternary}-C_{phenyl}$ to 1.55(2) Å, $C_{quaternary}-C_{methyl}$ to 1.54(2) Å, and $C_{phenyl}-O$ to 1.35(2) Å. Bond angles around sp^2-hybridized carbon atoms were restrained to 120(2)° and those around sp^3 to 109°. The carbon atoms of the disordered solvent molecules were restrained to lie 0.000(10) Å from their best least-squares plane. Similarity restraints were applied to the displacement parameters of directly bonded disordered atoms.

The large anisotropic thermal parameters and irregular geometry of the solvent molecule C(83)−C(88) suggest that this is also disordered, but attempts to model this did not lead to any improvement in the agreement with the diffraction data and were abandoned. An attempt to refine the structure in the space group $P1$ failed to converge, suggesting the original assignment of symmetry to be correct. All hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give $R_1 = 0.0743$ and $R_w = 0.0762$.

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Supporting Information Available: X-ray crystallographic data in CIF format for the structure determination of **4-La·3C$_6$H$_6$**; cell parameters and approximate M−Cl distances for $[M(O_2NN')(\mu\text{-}Cl)(py)]_2 \cdot 3C_6H_6$ [M = Nd (**4-Nd·3C$_6$H$_6$**) or Sm (**4-Sm·3C$_6$H$_6$**)]; displacement ellipsoid plot showing the full numbering scheme for **4-La**; semilogarithmic plots of *rac*-LA conversion vs time using (a) $[Y(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Y**), (b) $[Sm(O_2NN')(\mu\text{-}BH_4)]_2$ (**1-Sm**), and (c) $[Nd(O_2NN')(\mu\text{-}BH_4)(THF)]_2$ (**1-Nd**). This material is available free of charge via the Internet at http://pubs.acs.org.

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