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Synthesis of Bimetallic Bis(phenolate) N-Heterocyclic Carbene Lanthanide Complexes and Their Applications in the Ring-Opening Polymerization of L-Lactide

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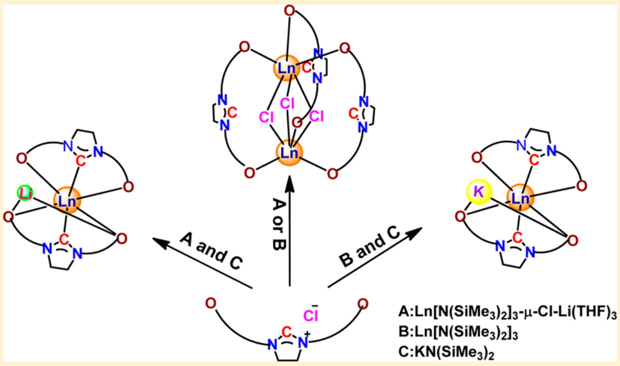
Supporting Information



ABSTRACT: The bis(phenolate) N-heterocyclic carbene (NHC) lanthanide complexes [Ln(**L**)$_2$M] (**L** = 1,3-bis[O-4,6-di-tBu-C_6H_2-2-CH_2][C(NCH_2CH_2N)], M = Li, Ln = Nd (**1a**); M = K, Ln= Nd (**2a**), Sm (**2b**), La (**2c**), Y (**2d**)) were synthesized by the reaction of **L** with KN$(SiMe_3)_2$ and Nd[N$(SiMe_3)_2$]$_3$-μ-Cl-Li(THF)$_3$ or Ln[N$(SiMe_3)_2$]$_3$ (Ln = Nd, Sm, La, Y). The imidazolinium-bridged bis(phenolate) lanthanide complexes [Ln$_2$(**L3**)$_3$Cl$_3$] (**L3** = 1,3-bis[O-4,6-di-tBu-C_6H_2-2-CH_2][CH(NCH_2CH_2N)]$^+$Cl$^-$, Ln = Sm (**3a**), Dy (**3b**), Er (**3c**)) were synthesized by the amine elimination reaction of **L3** with Ln[N$(SiMe_3)_2$]$_3$ or Ln[N$(SiMe_3)_2$]$_3$-μ-Cl-Li(THF)$_3$. All complexes were characterized by elemental analysis. Complex **1a**, **2a**,**c**, and **3a**−**c** were characterized by X-ray crystallography, and complexes **2c**,**d** were characterized by ^{1}H and ^{13}C NMR spectroscopy. The NHC complexes were efficient initiators for the ring-opening polymerization (ROP) of L-lactide (L-LA), with **2a** giving the best catalytic activity. Imidazolinium-bridged lanthanide complexes **3a**−**c** were inert in the ROP of L-LA. The influences of ligand structural factors and the cooperative effects between metals and the reaction medium on the catalytic activity were discussed for the ROP of L-LA.

INTRODUCTION

N-heterocyclic carbene transition-metal complexes have exhibited remarkable success in areas such as metathesis and coupling reactions[1] and have showed enhanced catalytic activity in comparison to the phosphine analogues. The number of reviews on NHC lanthanides is far less than that for the transition-metal counterparts.[2] Recently, lanthanide complexes bearing an NHC ligand have attracted research interest,[3] and their catalytic uses are being described with increasing frequency. Pioneering work was carried out by Arduengo et al. in 1994, who synthesized the first NHC lanthanide complexes,[4] but most of the work has come out in the past decade.[5]

Chelate NHCs with a pendent anionic functionalized group have undergone an upsurge of interest due to the ease of tuning their steric and electronic properties and the possibility of a reduced tendency for ligand dissociation,[6] which means stronger metal−NHC binding by chelating effects. Complexes supported by this class of NHCs show a constrained geometry. Moreover, lanthanide complexes bearing alkali metals are popular in lanthanide chemistry, since there is a cooperative effect between lanthanide and alkali metals, and they have potential in the area of homogeneous catalysis.[7]

Most of the NHC ligands used have been five-membered functionalized imidazolylidenes due to the easy access of their precursors (imidazolium salts). Comparatively, functionalized imidazolidinylidene (the backbone of NHC is saturated) ligands,[8] which are common ligands for transition-metal complexes, are rarely seen used in lanthanide chemistry. Dagorne[6c,9] and Zi[10] etc. have reported the applications of bis(phenolate) NHC transition-metal complexes in the ROP of cyclic monomers; to the best of our knowledge, no bis(phenolate) NHC lanthanide complexes have been applied in the ROP of cyclic monomers before this work. Herein we report the synthesis of lanthanide complexes bearing backbone-saturated tridentate dianionic bis(phenolate) NHC ancillary ligands and the coordination modes of sterically demanding **L** and **L3** to the metal center. The bis(phenolate) NHC lanthanide complexes were found as efficient initiators for the ROP of L-lactide (L-LA). In addition, the catalytic properties of the complexes in quest of the role of the NHC moiety were studied.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes 1a, 2a−d, and 3a−c. The ligand **L3** used in this work was prepared according to the general pathway depicted in Scheme 1.

N,*N*′-Bis(3,5-di-*tert*-2-hydroxyphenylmethyl)ethylenediimine (**L1**) was reduced by sodium borohydride to give *N*,*N*′-bis(3,5-di-*tert*-2-hydroxyphenylmethyl)ethylenediamine (**L2**) and fur-

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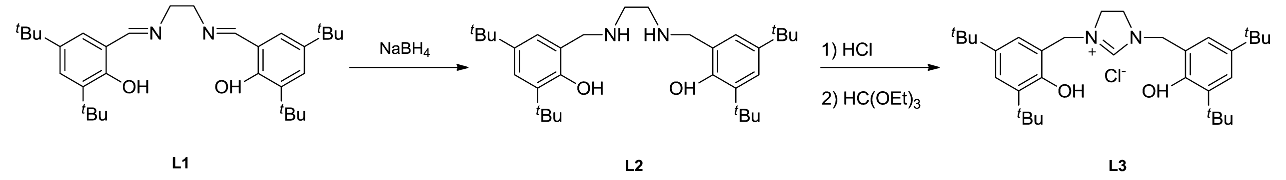
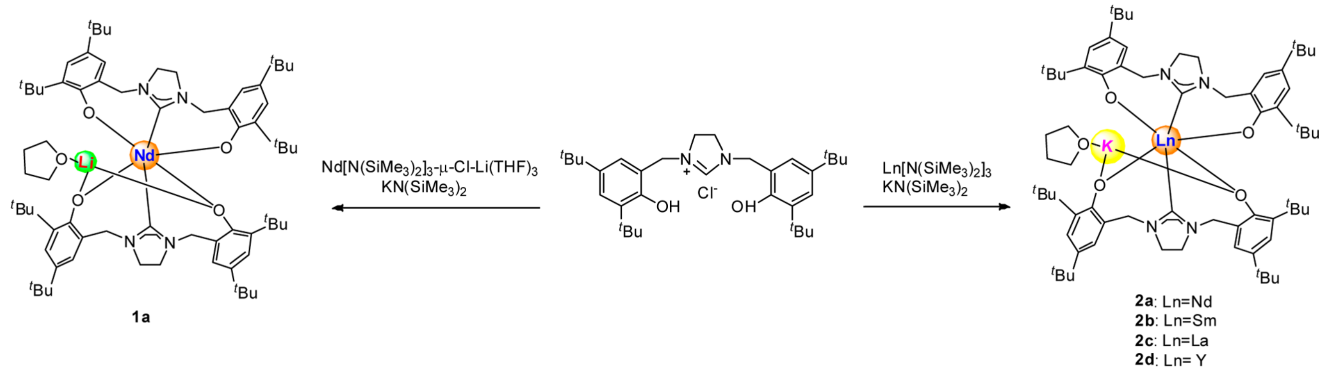
Scheme 1. Synthesis of L3



Scheme 2. Synthesis of NHC Lanthanide Complexes



ther reduced using a classical procedure (HCl and then $CH(OEt)_3$) to accomplish the ring-closing procedure.[11] *N*,*N*′-Bis(3,5-di-*tert*-butyl-2-hydroxyphenylmethyl)imidazolinium chloride (**L3**) was obtained as an NHC precursor. NHC ligand **L** was obtained in situ by treatment of **L3** with $KN(SiMe_3)_2$ for deprotonation.

Complex **1a** was synthesized by treatment of $Nd[N(SiMe_3)_2]_3$-*μ*-Cl-Li(THF)$_3$ with 2 equiv of **L3** and 6 equiv of $KN(SiMe_3)_2$ in THF at room temperature for 5 h (Scheme 2). Suitable crystals for X-ray analysis were grown from a hexane/THF solvent mixture at room temperature. Complex **1a** is soluble in THF and toluene and partially soluble in hexane. The paramagnetism of the complex precludes $^{1}H(^{13}C)$ NMR spectroscopic identification, but the solid structure revealed by X-ray diffraction analysis and the results of elemental analysis indicated that complex **1a** was successfully prepared. An ORTEP diagram of complex **1a** is depicted in Figure 1. It can be seen that the ligand of the "ate" complex adopts a tridentate coordination mode: carbon from the imidazolinium ring and two oxygens from the aryloxo groups. The coordination number of the metal center Nd is 6, and the geometry can be best described as a trigonal antiprism with two oxygens and one $C_{carbene}$ from one ligand on one plane and the other two oxygens and one $C_{carbene}$ on the other plane. Hydrogen on the imidazolinium ring was deprotonated by $KN(SiMe_3)_2$, thus forming an N-heterocyclic carbene structure. The geometry of the Li ion is planar and the atom is three-coordinated, with two phenoxide oxygens and one oxygen from THF. The Nd−$C_{carbene}$ bond length of 2.686 Å falls in the range published in the literature.[5b,d,12] The $C_{carbene}$−Nd−$C_{carbene}$ bond angle is 91.05°, and the two NHC ligands are bent to half a circle as a force of the coordination of two oxygens to lithium. The Nd−O bond lengths are around 2.28 Å, which falls in the range published in the literature.[13] The Li−O(Ar) bond lengths are around 2.23−2.24 Å, longer than that reported (Li−O 1.93 Å),[14] and the Li−O(THF) bond length is 1.88 Å.

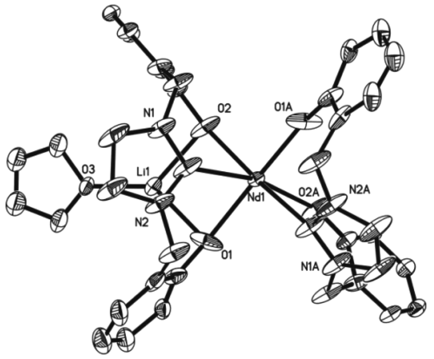


Figure 1. X-ray structure of complex **1a**, with 30% probability thermal ellipsoids. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. The lithium ion is distributed statistically on each ligand, and one lithium ion is depicted.

Lanthanide bis(trimethylsilyl)amides are important starting materials in preparing lanthanide complexes and are known as strong bases. Complex **2a** was obtained by treating $Nd[N(SiMe_3)_2]_3$ with 2 equiv of **L3** and 6 equiv of $KN(SiMe_3)_2$ in THF at room temperature. Complexes **2a**−**d** are soluble in THF and toluene and partially soluble in hexane. The X-ray structure analysis of complex **2a** revealed a structure similar to that of complex **1a**, also forming an "ate" structure. The difference in structure is the alkali metal, with potassium ion in **2a** and lithium ion in **1a**. Complexes **2b**−**d** were prepared in a way similar to that for **2a**. Attempts to obtain suitable crystals of **2b**,**d** for X-ray analysis were not successful.

In complex **2a**, as shown in Figure 2, the Nd−$C_{carbene}$ bond length of 2.707 Å is consistent with that in **1a** and shorter than the La−$C_{carbene}$ bond length of 2.798 Å. The La−O bond lengths in **2c** separate from 2.31 to 2.36 Å, slightly larger than that of Nd−O in **2a** from 2.27 to 2.32 Å. The Nd−O lengths in **1a** and **2a** are the same. The K−O(Ar) bond lengths in **2a** are around 2.79−2.94 Å, and that of K−O(THF) is 2.584 Å, slightly shorter than those in **2c** (K−O(Ar) 2.81−2.96 Å, K−O(THF) 2.595 Å). The $^{1}H(^{13}C)$ NMR spectra for **2c**,**d** were also indicative of the formation of the bis(phenolate) NHC complex. The ^{1}H NMR of **L3** showed the resonance of hydrogen at the imidazolinium ring (C2) at δ 8.42, and the resonance peak was diminished after the formation of the NHC lanthanide complexes. Moreover, the ^{13}C

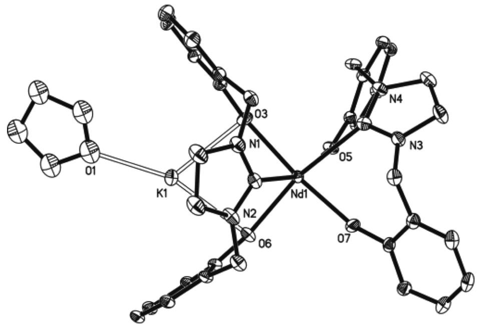
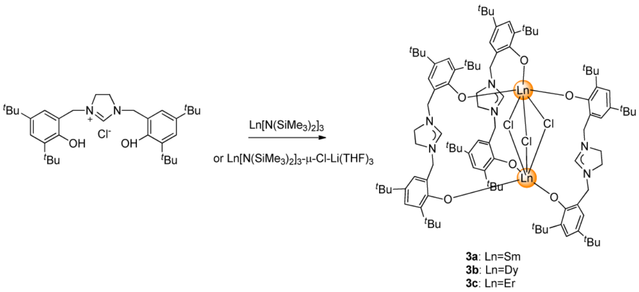


Figure 2. X-ray structure of complex **2a**, with 30% probability thermal ellipsoids. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. The potassium ion is distributed statistically on each ligand, and one potassium ion is depicted. Complex **2c** is isomorphous with complex **2a**.

NMR spectra contain high $C_{carbene}$ resonances at δ 225.57 and 220.26 for **2c** and δ 220.77 and 214.61 for **2d**, suggesting that the $C_{carbene}$ atoms are bound to the metal centers. Owing to the electron-withdrawing effect of the potassium ion, the signals of the hydrogens and carbons on the ligand linking to the alkali metal tend to be shifted downfield.

Complexes **3a−c** were prepared by treating 3 equiv of **L3** with 2 equiv of $Ln[N(SiMe_3)_2]_3$ or $Ln[N(SiMe_3)_2]_3$-μ-Cl- Li(THF)$_3$ in THF at room temperature for 1 day (Scheme 3). Attempts to synthesize a monomeric structure by adding 1 equiv of lanthanide amido complexes and **L3** were unsuccessful. Colorless crystals suitable for X-ray analysis were grown from hexane at room temperature. Complexes **3a−c** are soluble in THF and partially soluble in toluene and hexane and are also paramagnetic. The X-ray structure of **3a** is given in Figure 3. Yao and Luo[15] reported imidazolidine-bridged bis(phenolate) rare-earth-metal amido complexes and analyzed the role of ^{i}PrOH in the ROP of L-LA. The complexes they obtained had a solvated monomeric structure. Complexes **3a−c** synthesized in this work exhibit an imidazolinium-bridged dinuclear structure.

Scheme 3. Synthesis of Imidazolinium-Bridged Bis(phenolate) Lanthanide Complexes



3a: Ln=Sm
3b: Ln=Dy
3c: Ln=Er

As shown in Figure 3, each ligand adopts a bidentate coordination mode, and the two samariums are bridged by three chlorides. The geometry at the metal center can be best described as a trigonal antiprism with oxygens on one plane and chlorides on the other plane. Most likely, the structures of complexes **3a−c** are isomorphous. One interesting feature is that all these complexes are solvent-free and are six-coordinated. The backbone of the ligand is bonded to the metal ions at Ln−O separations from 2.18 to 2.20 Å for Sm−O, from 2.14 to 2.16 Å for Dy−O, and from 2.11 to 2.13 Å for Er−O. The decreasing bond length from Sm−O to Er−O is in good agreement with lanthanide contraction (the ionic radius decreases from La to Lu). The C−N bond length is around 1.31 Å, which is intermediate between the lengths of typical single and double bonds, reflecting a delocalized electronic structure. C−H···Cl interactions, which have attracted increasing attention,[16] are detected in these complexes. The hydrogens (NC*H*N, part of NCH_2-Ar) have interactions with chlorides. The C−H···Cl hydrogen bond length (H84···Cl3 = 2.50 Å, H18···Cl3 = 2.63 Å, H19B···Cl3 = 2.86 Å, etc.) is shorter than the sum of the van der Waals radii of H and Cl (3.0 Å),[17] and bond angles range from 113.96 to 155.5°.

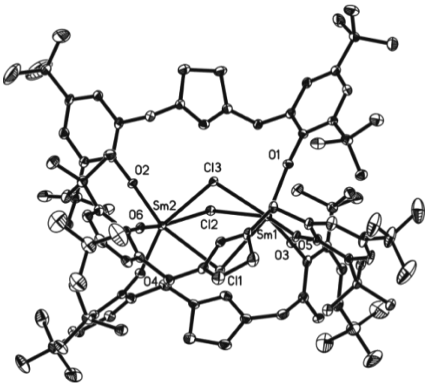


Figure 3. X-ray structure of complex **3a**, with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Complexes **3b**,**c** are isomorphous with complex **3a**.

All of the complexes are air- and moisture-sensitive, and the crystals of these complexes are stable and can be stored in a sealed flask for over 1 year without decomposition.

ROP of L-Lactide. Polylactide is one of the most desirable biodegradable polymers, and it has received great attention for its biodegradability as well as its practical applications.[15,18] Lanthanide[19] and other metal[20] complexes have proven to be efficient initiators for the ROP of cyclic monomers, and a possible polymerization mechanism toward the ROP of L-LA has been reported. Our previous work has been on the phenolate lanthanide complexes in the application of the ROP of cyclic monomers,[21] and the complexes showed moderate activity toward the ROP of L-LA. The ROP of L-LA was carried out with the prepared complexes, and the relationship between structure and activity was studied. Polymerization data were collected in Table 1. Two kinds of complexes supported by **L** and **L3**, with **1a** and **2a−d** containing an NHC structure and **3a−c** containing an imidazolinium-bridged structure, have been designed to evaluate the donation of the NHC moiety to the catalytic activity of the complexes. The polymerization results indicate that imidazolinium-bridged bis(phenolate) lanthanide complexes **3a−c** show no activity toward the ROP of L-LA, whereas bis(phenolate) NHC lanthanide complexes **1a** and **2a−d** show comparatively high catalytic activity, much higher than that of benzoxazine-functionalized amine bridged bis(phenolate) lanthanide complexes we reported before;[21a] thus, the NHC moiety may play a crucial role in improving the catalytic activity.

The polymerization medium has profound effects on the polymerization, and toluene is a much better solvent than the polar solvent THF. When complex **1a** was used as initiator, polymerization conversion of L-LA could reach 90% in 30 min in toluene (entry 5), but it dropped to 40% using THF as the solvent (entry 7). This case is identical with those reported in several works.[22] The high affinity of oxophilic lanthanide causes the THF molecule to compete with cyclic monomer for

Table 1. ROP of L-Lactide by Complexes **1a** and **2a**−**d**[a]

entry	initiator	$[I]_0/[M]_0$	t (min)	yield (%)[b]	$10^{-4}M_n$[c]	$10^{-4}M_n^{\text{theor}}$	PDI
1	**1a**	1/1000	5	35	0.7	5.0	1.19
2	**1a**	1/1000	7	45	0.9	6.5	1.19
3	**1a**	1/1000	11	56	1.0	8.1	1.22
4	**1a**	1/1000	18	70	1.4	10.1	1.24
5	**1a**	1/1000	30	90	1.7	13.0	1.33
6	**1a**	1/1000	60	92	1.8	13.3	1.38
7[d]	**1a**	1/1000	30	40	0.7	5.8	1.18
8	**1a**	1/1500	60	86	2.1	18.6	1.41
9	**1a**	1/2000	120	61	2.1	17.6	1.40
10	**2a**	1/1000	5	80	1.3	11.5	1.31
11	**2a**	1/1000	20	90	1.6	13.0	1.52
12	**2a**	1/1000	30	93	1.7	13.4	1.57
13[d]	**2a**	1/1000	60	50	0.8	7.1	1.34
14	**2a**	1/2000	120	80	1.5	23.0	1.25
15	**2b**	1/1000	30	69	1.4	10.0	1.32
16	**2b**	1/1500	60	68	1.5	14.8	1.29
17	**2c**	1/1000	5	57	1.0	8.14	1.43
18	**2d**	1/1000	60	67	1.3	9.7	1.44

[a] General polymerization conditions: toluene as the solvent, [L-lactide] = 1 M, polymerization temperature 70 °C. [b] Yield: (weight of polymer obtained)/(weight of monomer used). [c] Measured by GPC relative to polystyrene standards using a correcting factor of 0.58 for polylactides. [d] Polymerized in THF.

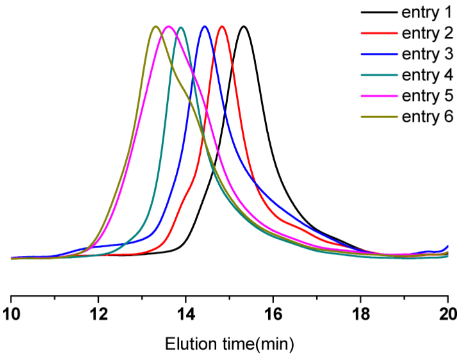


Figure 5. GPC curves of polymers obtained from entries 1−6 in Table 1.

coordination at the metal center. Polymerizations were carried out at 70 °C in toluene, and this indicated the thermal stability of the complexes.

Complex **2a** exhibited a higher activity but slightly wider molecular weight distribution in comparison with complex **1a**. An 80% conversion of the polymerization could be achieved in 5 min with a molar ratio of monomer to initiator of 1000 (entry 10), and 80% conversion could be achieved with a ratio of 2000 (entry 14). The structural difference of the two complexes lies in the alkali metals: lithium in complex **1a** and potassium in complex **2a**. The same phenomenon was also reported in ROP initiated by heterometallic complexes containing transition-metal and alkali-metal cations, and the alkali-metal cations in the heterometallic complexes played important roles in the catalytic process.[23] The reason for the difference in activity of complexes **1a** and **2a** may be attributed to the difference in electronic configurations and charge densities of lithium and potassium cations,[23c] and their steric effect may also play a role in ROP. K^+ has a larger radius than Li^+, which would cause the bending ligands to open wider, and this may favor the insertion of monomers. Complexes **2b**−**d** showed lower activity in comparison with **2a**, with the activity in the order Nd > La > Sm > Y. **2c** is slightly lower in activity than **2a**. The ionic radius (La > Nd > Sm > Y) should have much influence, resulting in differences in activity. The Nd complex had the most suitable radius and room for L-LA to insert. For **2b**,**d**, the environment around the metal center is more hindered, thus making the coordination and insertion of L-LA difficult.[19e]

Polymerization results show that the produced poly(L-lactide) (PL-LA) exhibits M_n values lower than the theoretically predicted molecular weight. This may be due to extensive transesterification reactions during the polymerization process. Monomodal symmetric GPC curves of polymers obtained from entries 1−6 are shown in Figure 5; the molecular weight distribution (MWD) widened with longer polymerization time, which provided evidence for the transesterification reactions in this system. This was also substantiated by MALDI-TOF analyses of the produced PLLA samples, with the peaks spaced by 72 au (see Figures s1−s3 in the Supporting Information). However, the MWDs of polymers prepared are still acceptable.

A kinetic study for the ROP of L-LA has been investigated employing **1a** as the initiator with respect to the concentration of L-LA (1 M) in toluene at 70 °C ($[M]_0/[I]_0 = 1000$). The rather good control by complex **1a** was exemplified by linear correlations between M_n and conversion as well as between time and conversion (Figure 6). Figure 6a shows that the reaction kinetics display a first-order dependence on the monomer concentration with $k_{app} = 0.073\ \text{min}^{-1}$, and Figure 6b shows a linear increase of M_n with L-LA conversion. This indicates that the polymerization in this system occurs in a controllable fashion. In addition, complex **2d** was chosen for kinetic study and a similar result was obtained (see Figure s4 in the Supporting Information).

According to the influences of reaction medium and lanthanide radius on the polymerization and the polymerization features, it can be concluded that the ROP of L-LA with NHC complexes is undergoing a monomer coordination−insertion mechanism, which involves an activation process via monomer coordination to the metal center. The NHC and non-NHC complexes are both bis(phenolate) lanthanide complexes, and they differ in the coordination mode. The non-NHC complexes

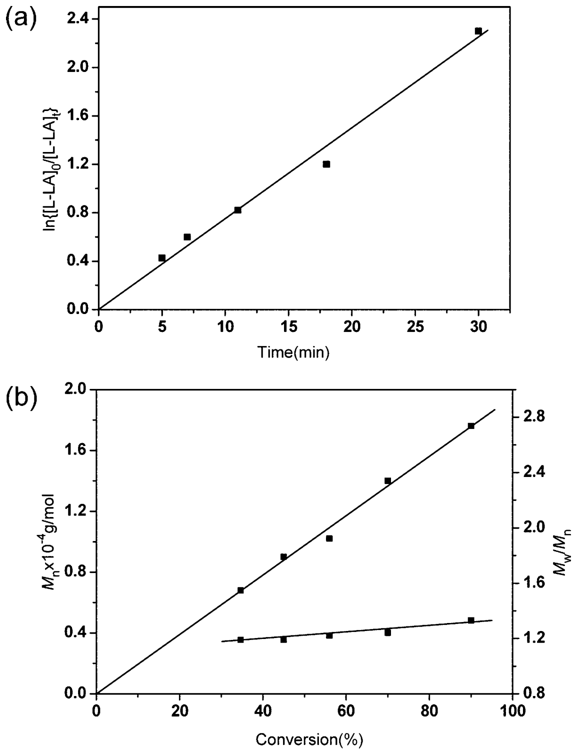


Figure 6. (a) Semilogarithmic plot of L-LA conversion versus time using complex **1a** as the initiator (linear fit, $R = 0.981$). (b) M_n versus L-LA conversion using complex **1a** as the initiator (linear fit, $R = 0.988$). Conditions: toluene, 70 °C, $[\text{L-LA}]_0/[\text{Ln}]_0 = 1000$, and $[\text{L-LA}]_0 = 1$ M.

3a−c are inactive, while the NHC complexes are highly active in the ROP of L-LA, and this would indicate the involvement of the NHC moiety in the ROP process. Arnold and co-workers[24] reported that NHC yttrium complexes initiated lactide polymerization and suggested that the initiating group was the NHC moiety; further chain growth occurred via monomer insertion at the metal. This mechanism has been confirmed by several scholars.[25] Dagorne and co-workers[26] proposed the anionic mechanism for the ROP of β-BL initiated by NHC zinc complexes. The complexes most likely dissociate to produce a free NHC, which abstracts the hydrogen of the β-BL, and then crotonates may initiate the ROP of β-BL by alkyl cleavage and subsequent chain growth by an anionic mechanism. To further understand the polymerization mechanism, we conducted the in situ polymerization of L-LA initiated by complex **2d** in toluene-d_8 in a NMR tube with online ^{1}H NMR analysis. It was evidenced that the lanthanide−NHC bond was broken and the free NHC abstracted the methine hydrogen of L-LA. The carbanion was regarded as the propagating species of the ROP, and further chain growth occurred via a similar monomer coordination−insertion at the rare-earth metal, as reported.[19j,k] The proposed mechanism of the polymerization and the ^{1}H NMR spectrum are included in the Supporting Information (Scheme s1, Figure s5). The polymerization was terminated by methanol, and due to the methanolysis reaction after the ROP, proton and methoxyl groups are at the two chain ends, respectively. This was also supported by MALDI-TOF mass (Figures s1−3, Supporting Information) and ^{1}H NMR (Figure 7) measurements.

CONCLUSION

In conclusion, a series of bis(phenolate) NHC lanthanide complexes and imidazolinium-bridged bis(phenolate) lanthanide complexes were synthesized via metathesis reactions, and their structural features have been determined by X-ray diffraction. The catalytic activity of the complexes was evaluated in the ROP of L-LA. Imidazolinium-bridged bis(phenolate) complexes show no catalytic activity, while bis(phenolate) NHC complexes are efficient initiators for the controlled ROP of L-LA. For NHC lanthanide complexes, the reaction medium, cooperative effects between metal elements, and lanthanide radii affect the activity for the ROP of L-LA. The NHC moiety was found to be involved in the initiation of the ROP of L-LA, and a coordination−insertion polymerization mechanism was proposed. These results may provide insights into the design and synthesis of lanthanide complexes.

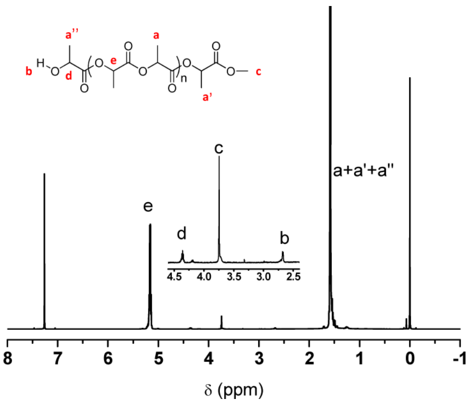


Figure 7. ^{1}H NMR spectrum of PL-LA terminated by MeOH in $CDCl_3$. Conditions: complex **2a** as the initiator, toluene, 70 °C, $[\text{L-LA}]_0/[\text{Ln}]_0 = 200$, and $[\text{L-LA}]_0 = 1$ M.

EXPERIMENTAL SECTION

General Procedures. All experiments except ligand synthesis were carried out under purified argon using Schlenk techniques. Hexane, THF, and toluene were distilled from sodium benzophenone ketyl prior to use. Lanthanide chlorides were prepared from lanthanide oxides according to the literature.[27] All other reagents and solvents were commercially available and were used without further purification. Metal analyses were performed by complexometric titration. NMR spectra were recorded on a Bruker Avance DMX 400 spectrometer or Agilent 600 MHz Direct Drive 2. Elemental analyses were performed by direct combustion with a Flash EA-1112 instrument. The mass measurement sample was investigated in positive ion mode on a Varian 500-MS ion trap mass spectrometer equipped with an electrospray ionization (ESI) source. Matrix-assisted laser desorption/ionization time of fight (MALDI-TOF) mass spectra were collected on a Bruker UltraFLEX MALDI-TOF mass spectrometer. Polylactide samples were dissolved in THF (5 mg/mL), and CCA was used as the matrix. $Nd[N(SiMe_3)_2]_3$-μ-Cl-$Li(THF)_3$[28] and $Ln[N(SiMe_3)_2]_3$[29] were prepared according to literature procedures. 2,2′-Ethylidenebis(4,6-di-*tert*-butylphenol) (**L2**)[30] was synthesized according to the literature.

Synthesis of L3. **L3** was synthesized similarly to the literature procedure,[31] which reported the synthesis of the similar compound *N*,*N*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)imidazolinium chloride. Concentrated HCl (4.3 mL, 44 mmol) was added dropwise to a stirred solution of **L2** (9.62 g, 20 mmol, 100 mL of ethanol/EtOAc) for 30 min. Then the solvent was evaporated under reduced pressure, leaving a white solid in the flask. $HC(OEt)_3$ (95 mL) and HCOOH (18 drops) were added and refluxed at 120 °C overnight. After the mixture was cooled and stood for 1 day, a white crystalline solid was filtered and washed three times with ethyl ether. Mass measurements, calculated for $C_{33}H_{51}N_2O_2^+$ (**L3**-Cl^-):, m/z 507.7; found, 507.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (1H, s, C2−H(imid)), 7.32 (2H, d, Ar−H), 6.90 (2H, d, Ar−H), 4.74 (4H, s, CH_2), 3.86 (4H, s, $N(CH_2)_2N$), 1.41 (18H, s, tBu), 1.25 (18H, s, tBu).

Synthesis of $L3_2NdLi(thf)$ (1a). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Nd[N(SiMe_3)_2]_3$-*μ*-Cl-Li$(THF)_3$ (0.16 g, 0.18 mmol) and $KN(SiMe_3)_2$ (0.22g, 1.11 mol). The reaction mixture was stirred for 5 h at room temperature, and then the solvent was removed under vacuum. A hexane/THF solvent mixture was added to extract complex **1a**. Blue block crystals were obtained at room temperature in 1−2 days. Anal. Calcd for $C_{70}H_{104}N_4O_5NdLi$: C, 68.19; H, 8.50; N, 4.54. Found: C, 68.54; H, 8.57; N, 4.44.

Synthesis of $L3_2NdK(thf)$ (2a). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Nd[N(SiMe_3)_2]_3$ (0.11 g, 0.18 mmol) and $KN(SiMe_3)_2$ (0.22 g, 1.11 mol). The reaction mixture was stirred for 5 h at room temperature, and then solvent was removed under vacuum. A hexane/THF solvent mixture was added to extract complex **2a**. Blue needle crystals were obtained at room temperature in 1−2 days. Anal. Calcd for $C_{70}H_{104}N_4O_5NdK$: C, 66.46; H, 8.28; N, 4.43. Found: C, 66.65; H, 8.47; N, 4.11.

Synthesis of $L3_2SmK(thf)$ (2b). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Sm[N(SiMe_3)_2]_3$ (0.11 g, 0.18 mmol) and $KN(SiMe_3)_2$ (0.22 g, 1.11 mol). The reaction mixture was stirred for 5 h at room temperature, and then solvent was removed under vacuum. A hexane/THF solvent mixture was added to extract complex **2b**. Colorless crystals were obtained at room temperature in 1−2 days. Anal. Calcd for $C_{70}H_{104}N_4O_5SmK$: C, 66.14; H, 8.24; N, 4.41. Found: C, 66.71; H, 8.05; N,4.38.

Synthesis of $L3_2LaK(thf)$ (2c). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $La[N(SiMe_3)_2]_3$ (0.11 g, 0.18 mmol) and $KN(SiMe_3)_2$ (0.22 g, 1.11 mol). The reaction mixture was stirred for 5 h at room temperature, and then solvent was removed under vacuum. A hexane/THF solvent mixture was added to extract complex **2c**. Colorless block crystals were obtained at room temperature in 1−2 days. ^1H NMR (600 MHz, C_6D_6): δ 1.36, 1.49 (36H, s, tBu); 1.54, 1.75 (36H, s, tBu); 1.40 (4H, t, THF); 2.70, 2.85 (8H, t, $N(CH_2)_2N$); 3.30, 3.60, 5.84, 5.97 (8H, s, NCH_2−Ar); 3.50 (4H, s, THF); 6.84, 7.01 (4H, s, Ar−H); 7.41, 7.59 (4H, s, Ar−H). ^{13}C NMR (600 MHz, C_6D_6): δ 25.94 (THF); 30.85, 31.10 ($-C(CH_3)_3$); 32.32, 32.64 ($-C(CH_3)_3$); 34.37 ($-C(CH_3)_3$); 35.88 ($-C(CH_3)_3$); 47.72, 48.35 ($N(CH_2)_2N$); 53.56, 53.98 (NCH_2−Ar); 67.95 (THF); 123.82, 124.36 (tBu-Ar); 124.87, 125.61 (tBu-Ar); 125.84, 126.26 (CH_2−Ar); 134.84, 135.91 (H−Ar); 137.02, 138.01 (H−Ar); 163.97, 164.82 (O−Ar); 225.57, 220.26 (carbene C). Anal. Calcd for $C_{70}H_{104}N_4O_5LaK$: C, 66.74; H, 8.31; N, 4.45. Found: C, 66.93; H, 8.52; N, 4.46.

Synthesis of $L3_2YK(thf)$ (2d). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Y[N(SiMe_3)_2]_3$ (0.10 g, 0.18 mmol) and $KN(SiMe_3)_2$ (0.22 g, 1.11 mol). The reaction mixture was stirred for 5 h at room temperature, and then solvent was removed under vacuum. A hexane/THF solvent mixture was added to extract complex **2d**. Colorless crystals were obtained at room temperature in 1−2 days. ^1H NMR (600 MHz, C_6D_6) δ 1.37, 1.51 (36H, s, tBu); 1.58, 1.71, 1.94 (36H, s, tBu); 1.41 (4H, t, THF); 2.69, 2.91 (8H, t, $N(CH_2)_2N$); 3.25, 3.40, 3.67, 5.69, 5.95, 6.07 (8H, s, NCH_2−Ar); 3.53 (4H, s, THF); 6.75, 6.91, 7.01 (4H, s, Ar−H); 7.45, 7.62 (4H, s, Ar−H). ^{13}C NMR (600 MHz, C_6D_6) δ 25.95 (THF); 31.14, 31.41, 31.62, 31.83 ($-C(CH_3)_3$); 32.31, 32.64 ($-C(CH_3)_3$); 34.23, 35.89, 36.28 ($-C(CH_3)_3$); 47.82, 48.18, 48.38, 48.48 ($N(CH_2)_2N$); 52.76, 53.52, 53.67, 54.10 (NCH_2−Ar); 67.94 (THF); 123.53, 124.14, 124.29, 124.77 (tBu-Ar); 125.01, 125.38, 125.60, 125.82 (tBu-Ar); 126.05, 126.31 (CH_2−Ar); 134.79, 134.89, 135.69, 136.44 (H−Ar); 137.24, 138.16, 138.55, 138.94 (H−Ar); 162.70, 163.10, 164.12, 164.30 (O−Ar); 220.77, 214.61 (carbene C). Anal. Calcd for $C_{70}H_{104}N_4O_5YK$: C, 69.50; H, 8.66; N, 4.63. Found: C, 69.60; H, 8.65; N, 4.15.

Synthesis of $L3_3Sm_2Cl_3$ (3a). A stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Sm[N(SiMe_3)_2]_3$ (0.15 g, 0.24 mmol). Alternatively, a stirred solution of **L3** (0.20 g, 0.37 mmol) in THF was treated with $Sm[N(SiMe_3)_2]_3$-*μ*-Cl-Li$(THF)_3$ (0.21 g, 0.24 mmol). The reaction mixture was stirred for 5 h at room temperature, and then solvent was removed under vacuum. Hexane was added to extract complex **3a**. Colorless block crystals were obtained at room temperature in 1−2 days. Anal. Calcd for $C_{99}H_{147}N_6C_{l13}O_6Sm_2$: C, 61.79; H, 7.70; N, 4.37. Found: C, 61.89; H, 7.99; N, 4.16.

Synthesis of $L3_3Dy_2Cl_3$ (3b). A procedure similar to that described for complex **3a** was followed, but $Dy[N(SiMe_3)_2]_3$ (0.15 g, 0.24 mmol) was used instead of $Sm[N(SiMe_3)_2]_3$. Colorless block crystals were obtained in hexane at room temperature in 1−2 days. Anal. Calcd for $C_{99}H_{147}N_6C_{l13}O_6Dy_2$: C, 61.02; H, 7.60; N, 4.31. Found: C, 61.01; H, 8.11; N, 4.12.

Synthesis of $L3_3Er_2Cl_3$ (3c). A procedure similar to that described for complex **3a** was followed, but $Er[N(SiMe_3)_2]_3$ (0.16 g, 0.24 mmol) was used instead of $Sm[N(SiMe_3)_2]_3$. Pink block crystals were obtained in hexane at room temperature in 1−2 days. Anal. Calcd for $C_{99}H_{147}N_6C_{l13}O_6Er_2$: C, 60.73; H, 7.57; N, 4.29. Found: C, 60.46; H, 7.96; N, 3.94.

Typical Procedure for the ROP of L-Lactide. The procedures for the ROP of L-lactide initiated by complexes **1a** and **2a**−**d** were similar. A typical procedure is given below. All of the reactions were carried out under argon using Schlenk techniques. The desired amounts of L-lactide and toluene were placed in a 20 mL flask and dissolved at 70 °C. Then a toluene solution of complex **1a** was added. The system became viscous in a few minutes, and after the prescribed time, the reaction solution was quenched by pouring into excess methanol. The polymer was precipitated, dried under vacuum, and weighed.

X-ray Crystallographic Study. Single crystals of complexes **1a**, **2a**,**c**, and **3a**−**c** were sealed in liquid paraffin oil. Data collections were performed at 140 K on a CrysAlisPro instrument from Oxford Diffraction Ltd. using graphite-monochromated Mo K*α* radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined by full-matrix least-squares methods based on $|F|^2$. The structures were solved and refined using SHELX-97 programs. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. Crystal and refinement data for complexes **1a**, **2a**,**c**, and **3a**−**c** are given in Table s2 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving a kinetic study of complex **2d**, $^1H(^{13}C)$ NMR spectra of complexes **2c**,**d** and yttrium complex **3d**, a proposed mechanism for polymerization and ^1H NMR spectrum of in situ polymerization, MALDI-TOF mass spectra, and selected bond lengths and angles, crystal and structure refinement data, and X-ray crystallographic data for complexes **1a**, **2a**,**c** and **3a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org. The Cambridge Crystallgraphic Database also contains supporting information with file nos. CCDC-994413 for **1a**, CCDC-994412 for **2a**, CCDC-1012411 for **2c**, CCDC-931174 for **3a**, CCDC-931175 for **3b**, and CCDC-931176 for **3c**.

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Notes

The authors declare no competing financial interest.

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