Achiral Lanthanide Alkyl Complexes Bearing N,O Multidentate Ligands. Synthesis and Catalysis of Highly Heteroselective Ring-Opening Polymerization of *rac*-Lactide

Xinli Liu,[†] Xiaomin Shang,[†,‡] Tao Tang,[†] Ninghai Hu,[†] Fengkui Pei,[†] Dongmei Cui,*[,†] Xuesi Chen,[†] and Xiabin Jing[†]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China, and Department of Chemical Engineering, Changchun University of Technology, Changchun 130012, People's Republic of China

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Alkane elimination reactions of amino-amino-bis(phenols) $\mathbf{H_2L^{1-4}}$, Salan $\mathbf{H_2L^5}$, and methoxy-β-diimines $\mathbf{HL^{6,7}}$ with lanthanide tris(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu), respectively, afforded a series of lanthanide alkyl complexes **1**−**8** with the release of tetramethylsilane. Complexes **1**−**6** are THF-solvated mono(alkyl)s stabilized by *O*,*N*,*N*,*O*-tetradentate ligands. Complexes **1**−**3** and **5** adopt twisted octahedral geometry, whereas **4** contains a tetragonal bipyramidal core. Bearing a monoanionic moiety $\mathbf{L^6}$ ($\mathbf{L^7}$), complex **7** (**8**) is a THF-free bis(alkyl). In complex **7**, the *O*,*N*,*N*-tridentate ligand combined with two alkyl species forms a tetrahedral coordination core. Complexes **1**, **2**, and **3** displayed modest activity but high stereoselectivity for the polymerization of *rac*-lactide to give heterotactic polylactide with the racemic enchainment of monomer units P_r ranging from 0.95 to 0.99, the highest value reached to date. Complex **5** exhibited almost the same level of activity albeit with relatively low selectivity. In contrast, dramatic decreases in activity and stereoselectivity were found for complex **4**. The Salan yttrium alkyl complex **6** was active but nonselective. Bis(alkyl) complexes **7** and **8** were more active than **1**−**3** toward polymerization of *rac*-LA, however, to afford atactic polylactides due to di-active sites. The ligand framework, especially the "bridge" between the two nitrogen atoms, played a significant role in governing the selectivity of the corresponding complexes via changing the geometry of the metal center. The NMR spectrum of the active species of the *rac*-lactide oligomer attached to complex **1** demonstrated a coordination−insertion mechanism. In addition it also confirmed that the geometry of the metal center of complex **1** in the solid state was retained in solution (THF) during the polymerization, which contributed significantly to the high selectivity of the complex.

Introduction

Polylactides (PLAs) are the most promising biodegradable and biocompatible synthetic macromolecules, possessing versatile physical properties and having been widely used in medicine, pharmaceutics, and tissue engineering such as media for the controlled release of drugs, scaffolds, and the delivery of antibodies and genes.[1] The applications are strongly dependent on the microstructures of PLAs. Ring-opening polymerization (ROP) of lactide (LA) by single-site catalysts is the most efficient manner to obtain PLAs with predicted molecular weight and narrow molecular weight distribution and, significantly, tacticity. The past two decades have witnessed the development of catalysts for such aims. Metal alkoxides are well-known highly active initiators albeit with less stereocontrol due to the aggregation nature of the active species.[2,3] Multidentate ligands containing heteroatoms are intended to encapsulate metal ions and thus control the geometry of complexes to form discrete single-site complexes of the formula L_mMR.[4] L_m is the ancillary ligand, the steric and electronic character of which tune the properties of the metal center, the catalytic activity, and the selectivity of the complexes; R is the initiation group, usually being alkoxide, phenoxide, and amide, or in some cases alkyl species, which is supposed to affect the activity of the complexes. Appropriate combinations of L_m with M and R have generated highly active initiators for the ROP of LA, such as

* Corresponding author. E-mail: dmcui@ciac.jl.cn. Fax: (+86) 431 85262773. Tel: +86 431 85262773.

† Changchun Institute of Applied Chemistry.

‡ Changchun University of Technology.

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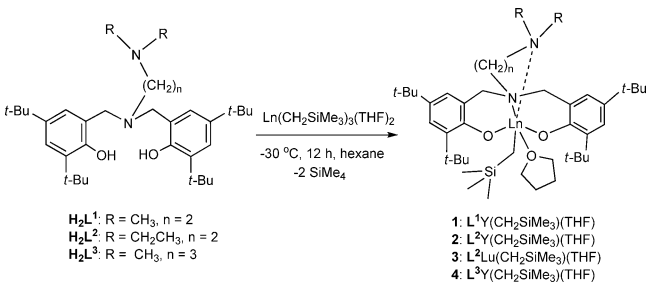
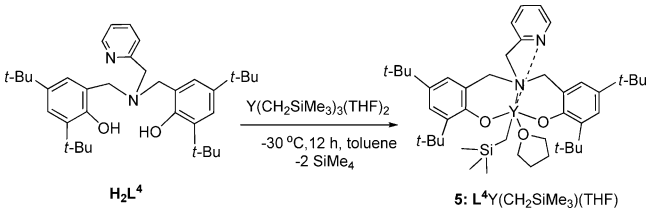
Schiff-base (Salen)-ligated aluminum alkoxides,[5] β-diiminate (BDI)-stabilized zinc, magnesium, and lanthanide alkoxides,[6] *N*,*N*-bidentate guandinate-[7] or amidinate[8]-supported lanthanide complexes, and *N*,*N*,*N*-multidentate calcium and zinc alkoxides.[9] The phenolate[10] and bisphenolate[11] ligated metal complexes also occupy important positions in the catalyst list. Most of catalysts mentioned above have been explored to initiate the ROP of optically pure D-LA or L-LA to yield isotactic PLA with the retention of configuration; however, for the racemic lactide (*rac*-LA), atactic PLA is usually isolated. Stereoselective polymerization of *rac*-LA is initially accessed by employing an optically pure Salen aluminum initiator to afford isotactic PLA when the conversion is below 50%.[5a] Thorough developments have been achieved by using homochiral or racemic Salen aluminum initiators that can completely transfer *rac*-LA to stereoblock P(L-LA)-*b*-P(D-LA) via ligand exchange or polymer chain transfer mechanism.[5b−h] Recent investigations demonstrate strikingly that the stereoblock PLA can be obtained by using achiral Salen aluminum alkoxides via polymer-chain-end control. The alkyl bridge between the two imido nitrogen atoms in the ligands is crucial to govern the selectivity of the complexes.[5i−k] Contrarily, studies on the synthesis of heterotactic PLA have remained less explored. This polymerization is extremely sensitive to the sterics of the ligands, because the environment of the last unit of the propagating active species must be sterically proper to incorporate the configurationally opposite enantiomer. β-Diiminate zinc or magnesium alkoxide or amide[6a−c] and Salan (C═N reduction derivative of Salen) aluminum alkyls[12] represent rare examples of heteroselective initiators. Complexes based on rare earth metals, unfortunately, have demonstrated to be less stereocontrolled.[5f] Breakthroughs have been achieved very recently by Carpentier,[13] Mountford,[14] and Okuda,[15] who employed modified bis(phenolate)-ligated lanthanide amide, alkoxide, or borohydride to realize heteroselective polymerization of *rac*-LA. The tacticity of the resulting PLA varies from medium to very high level depending on the ligand framework. Recently, our group has been engaged in preparing a new family of rare earth metal alkyl complexes stabilized by non-cyclopentadienyl (nonCp) ligands.[16] The amino-amino-bisphenols are one type of moiety we used, which have been applied to prepare group 4 metal complexes that catalyze living polymerization of olefins[17] and cyclic esters[18] and stereoselective polymerization of *rac*-LA.[19] Here, we wish to report that the combination of these ligands with lanthanide alkyl units afforded initiators for

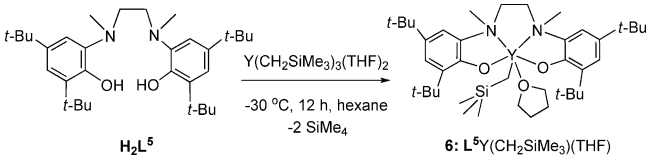
Scheme 1. Preparation of Complexes 1−4



Scheme 2. Preparation of Complex 5



Scheme 3. Preparation of Complex 6



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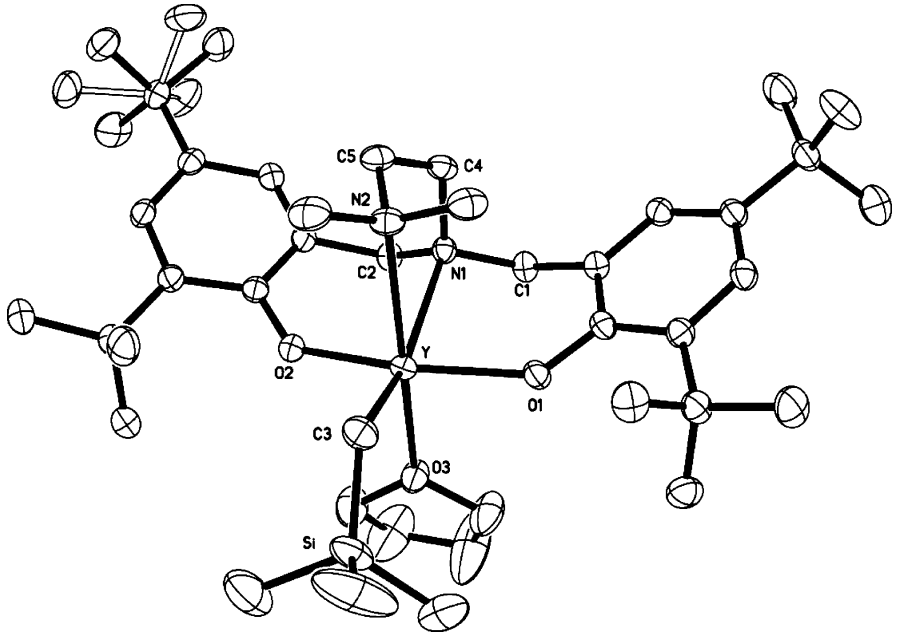

Figure 1. ORTEP drawing of complex **1** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1−5

	1·C_6H_{14} (Ln = Y)	**2**·C_6H_{14} (Ln = Y)	**3**·C_6H_{14} (Ln = Lu)	**4** (Ln = Y)	**5**·C_6H_{14} (Ln = Y)
Ln−O(1)	2.1379(16)	2.138(2)	2.1279(10)	2.154(2)	2.113(5)
Ln−O(2)	2.1441(17)	2.168(2)	2.1239(9)	2.141(2)	2.159(5)
Ln−O(3)	2.3866(17)	2.375(3)	2.3596(9)	2.378(2)	2.354(5)
Ln−C(3)	2.424(3)	2.432(3)	2.3593(15)	2.423(3)	2.445(7)
Ln−N(1)	2.574(2)	2.576(3)	2.5118(11)	2.614(2)	2.582(6)
Ln−N(2)	2.588(2)	2.651(3)	2.5838(11)	2.536(3)	2.525(6)
O(1)−Ln−O(2)	150.94(7)	148.77(10)	151.03(4)	155.66(8)	152.57(18)
O(1)−Ln−O(3)	83.87(6)	81.57(10)	80.39(4)	84.14(8)	85.39(18)
O(2)−Ln−O(3)	81.98(6)	80.65(9)	80.92(3)	88.83(8)	83.16(18)
O(1)−Ln−C(3)	102.92(8)	102.44(11)	103.50(4)	109.32(10)	102.2(2)
O(2)−Ln−C(3)	105.32(8)	106.21(11)	102.60(5)	93.71(10)	105.0(2)
O(3)−Ln−C(3)	105.94(8)	101.89(11)	104.99(4)	88.52(11)	107.4(2)
O(1)−Ln−N(1)	78.08(6)	78.90(9)	81.86(3)	79.62(7)	77.07(17)
O(2)−Ln−N(1)	79.52(6)	79.58(9)	79.64(4)	76.96(7)	79.92(17)
O(3)−Ln−N(1)	99.86(7)	101.03(10)	99.55(3)	88.81(8)	97.91(18)
C(3)−Ln−N(1)	154.15(8)	156.98(11)	155.41(4)	170.35(10)	154.6(2)
O(1)−Ln−N(2)	97.72(7)	92.83(10)	95.87(4)	91.43(8)	102.28(19)
O(2)−Ln−N(2)	91.27(7)	100.13(10)	98.40(3)	93.02(9)	81.88(18)
O(3)−Ln−N(2)	167.99(7)	169.23(10)	169.17(4)	172.96(8)	160.25(19)
C(3)−Ln−N(2)	85.37(8)	88.26(11)	85.73(4)	98.13(12)	88.9(2)
N(1)−Ln−N(2)	69.01(6)	68.73(9)	69.77(3)	84.99(9)	66.78(19)

ROP of *rac*-LA with unprecedented heteroselectivity. The resulting PLA has a P_r of 0.99, the highest value reached to date, as far as we are aware. (P_r: probability of racemic enchainment of monomer units calculated according to the methine region of the homonuclear decoupled ^{1}H NMR spectrum.) The syntheses and full characterizations of these complexes and investigations on the correlation between catalytic performances and molecular structure, and the mechanism of polymerization, will be presented. The primary polymerization results by using the rare earth metal bis(alkyl)s bearing modified β-diiminate ligands are also described as a comparison.

Results and Discussion

Synthesis and Characterization of Lanthanide Alkyl Complexes 1−8. Reactions between the neutral compounds of amino-amino-bisphenols, $\mathbf{H_2L^{1-4}}$, and lanthanide tris(alkyl)s, $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu), took place immediately upon addition by release of tetramethylsilane. The reaction was maintained at −30 °C for 12 h in hexane, then the volatiles were removed under reduced pressure to afford oily residues. The residues were carefully washed with a minimum amount of cold hexane to extrude unreacted reagents to give white crystalline solids of lanthanide mono(alkyl) complexes **1**−**5** (Schemes 1 and 2). It is crucial to control the reaction temperature below −25 °C and avoid prolonging the reaction time to increase the yield; otherwise, some unknown complexes would be produced. Following a similar procedure, treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with Salan compound $\mathbf{H_2L^5}$ afforded complex **6** selectively (Scheme 3). All complexes **1**−**6** except **5** have good solubility in solvents such as THF, ether, toluene, benzene, and hexane. Therefore, pure solids or good single crystals for X-ray analysis were isolated only from a concentrated mixture of toluene and hexane (1:10 v/v) at −30 °C within several days. An alternative pathway for the preparation of complexes **1**−**6** is through metathesis reaction of lithium salts

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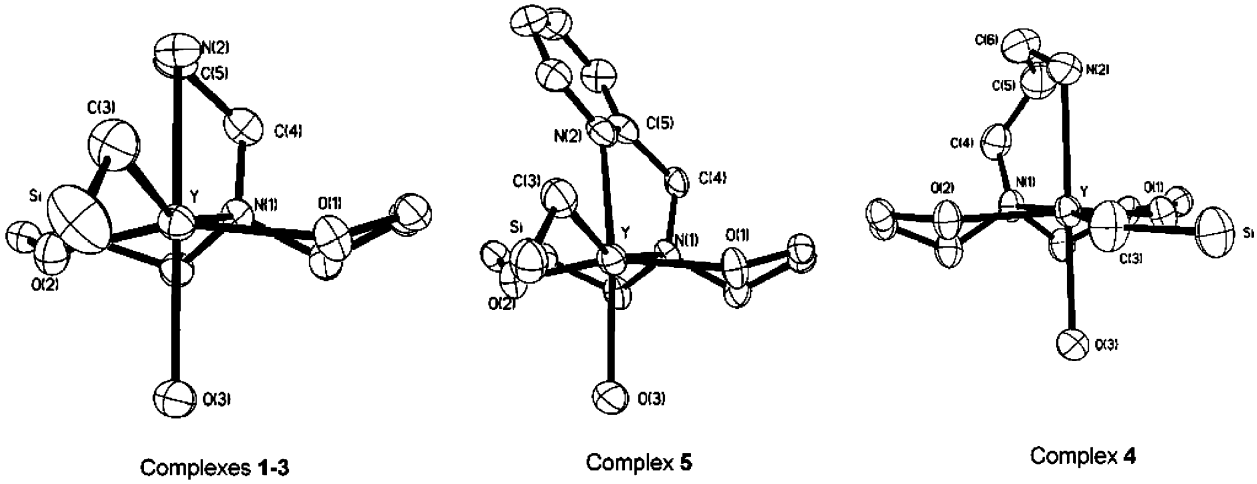
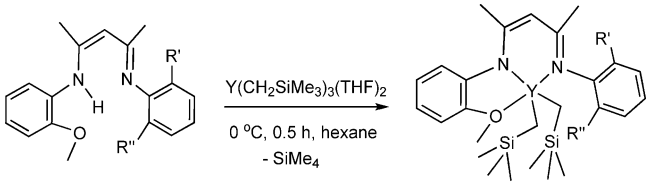


Figure 2. ORTEP drawings of the molecule cores of complexes **1**−**5**.

of the ligands with lanthanide trichlorides followed by alkylation. However, lithium adduct or ate complexes are usually isolated. The NMR spectra for complexes **1**−**6** were informative for the formation of mono(alkyl) species. The methylene protons of the metal alkyl species in **1**−**6** gave resonances around δ 0−0.5, downfield shifted compared to that at δ −0.60 in metal tris(alkyl)s. The pendent nitrogen atom was found to attach a metal center in solution, because the proton resonances of the groups $-N(CH_3)_2$ in **1** and **4**, $-N(CH_2CH_3)_2$ in **2** and **3**, and $-NC_5H_4$ in **5** shifted approximately 0.3−0.5 ppm, respectively, compared to those in the free ligands $\mathbf{H_2L^1}$−$\mathbf{H_2L^4}$. The benzylic protons in each complex were diastereotopic, giving a ^{1}H AB spin in contrast to the singlet resonance in free ligands; moreover, the methylene protons were equivalent, showing doublets with coupling constants of 3−5 Hz in all yttrium complexes **1**, **2**, **4**, and **5**, indicating monomeric and C_s symmetric molecular structures in solution.

X-ray diffraction analyses displayed that the overall structures of **1**−**5** are analogous six-coordinate monomers (Figure 1, ORTEP plot of complex **1**).[20] For complexes **1**−**3** and **5**, each metal ion bonds to an alkyl moiety, a THF molecule, and the dianionic amino−amino-modified bisphenolato ligand in an *O*,*N*,*N*,*O*-tetradentate mode, adopting a twisted octahedral geometry. In complex **4**, the *O*,*N*,*N*,*O*-tetradentate ligand combined with a THF molecule and the alkyl species forms a tetragonal bipyramidal geometry core. The pendent nitrogen and THF oxygen atoms occupy the axial positions, while the phenolate oxygen, the nitrogen, and the carbon atoms are located at equatorial positions. The average bond distance of $Ln-O_{phenol}$ (Ln−O(1): av 2.134 Å; Ln−O(2): av 2.147 Å) is comparable to that formed by a lanthanide metal ion and phenol oxygen,[13b,21,22] which is noticeably shorter than Ln−O(3), averaging 2.371 Å (Table 1), whereas the bond distances from lanthanide ions to the equatorial nitrogen (Ln−N(1)) and the pendent nitrogen (Ln−N(2)) atoms are similar, falling in a narrow range of 2.5118(11)−2.651(3) Å, which are comparable to other yttrium complexes containing these groups,[21,23] but longer than

Scheme 4. Preparation of Complexes 7 and 8



$Ln-N_{terminal}$ (av 2.286 Å).[13b,21] The bond distance of Ln−C, with an average of 2.417 Å, is typical for those found in nonCp-ligated rare earth metal alkyl complexes.[24] The bond angle of O(1)−Y−O(2), 155.66(8)°, in **4** is larger than 152.57(18)° in **5** and the average of 150.25° in **1**−**3**, while the bond angle of O(3)−Ln−N(1) is 99.86(7)° for **1**, 101.03(10)° for **2**, 99.55(3)° for **3**, 97.91(18)° for **5**, and only 88.81(8)° for **4** (Table 1); an obvious difference is found for the deviation angle of the alkyl ligand from the LnONO plane, being 29.39° for **1**, 29.97° for **2**, 31.45° for **3**, and a slightly smaller 26.77° for **5**; however, a much smaller 2.72° was found for **4** (Figure 2). This suggested that the short ethylene bridge between the two nitrogen atoms N(1) and N(2) in **1**−**3** and the stiff piconyl bridge in **5** cause a more distorted geometry of these molecular cores than the longer, flexible trimethylene bridge in **4**, which might contribute significantly to the different activity and selectivity among these complexes (*vide infra*).

Treatment of ligands $\mathbf{HL^6}$ with $Y(CH_2SiMe_3)_3(THF)_2$ generated the corresponding yttrium bis(alkyl) complex **7** (Scheme 4). The molecular structure of **7** is shown in Figure 3. The yttrium atom coordinates to the *N*,*N*,*O*-tridentate ligand and two alkyl species arranged in *cis*-positions, generating a tetrahedral geometry core. The complex is solvent-free. The bond lengths of Y(1)−N(1) and Y(1)−N(2) (2.310(2) and 2.338(2) Å) are

(20) The ^{1}H and ^{13}C NMR spectra for complexes **6**−**8**, crystallographic data and structure refinements of complexes **1**−**5** and **7**, and ORTEP drawings of complexes **2**−**5**; see Supporting Information.

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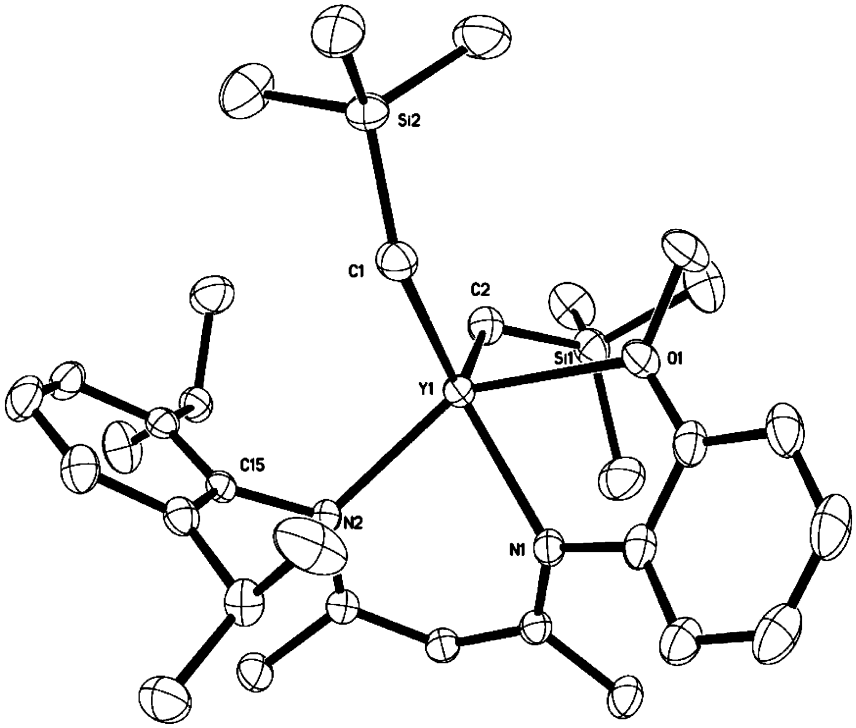

Figure 3. ORTEP drawing of complex **7** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

slightly shorter than Ln−N, averaging 2.572 Å in complexes **1**−**5**, but the bond length of Y(1)−O(1) (2.4394(16) Å) is longer than Ln−O(1) (av 2.134 Å) in complexes **1**−**5**. The bond angle of C(1)−Y(1)−C(2), 115.92(9)°, is larger than those found in bis(alkyl) yttrium complexes stabilized by anilido imine (108.90(6)°),[24g] tetradentate triamine (av 101.4°),[24b,c,h] and Salen compounds (110.97(7)°),[24d] but smaller than that in the amidinato yttrium bis(alkyl) complex (140.56(6)°).[24f] Complex **7** is asymmetric in the solid state, consistent with that in solution, which is evidenced in the NMR spectrum, because the methylene protons YCH_2SiMe_3 are diastereotopic, showing four discrete signals that further split into a doublet due to coupling with the Y atom (SI, Figure 7). Treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with **HL**[7] afforded complex **8** (Scheme 4). The ^1H and ^{13}C NMR spectral analyses indicate a symmetric monomer of bis(alkyl) species in solution.[20]

Ring-Opening Polymerization of *rac*-Lactide. All these lanthanide alkyl complexes **1**−**8** can initiate the ROP of *rac*-LA. The catalytic activity and stereoselectivity are strongly dependent on the molecular structures of the complexes and the polymerization conditions. For mono(alkyl) complexes **1**−**3**, **5**, and **6**, almost complete conversion was reached within 1 h at room temperature. The molecular weights of the resulting PLAs were close to the theoretic values, and the molecular weight distributions were narrow. Strikingly, complexes **1**−**3** showed similar high stereoselectivity for *rac*-LA to afford heterotactic PLA with P_r over 0.94 (Table 2, entries 1, 4, 6).[6b,25] Complex **5** showed the same level of catalytic activity as complexes **1**−**3**, albeit with relatively low selectivity (Table 2, entry 9). In contrast, dramatic decreases in catalytic activity and stereocontrol ability were found for complex **4** even though it is an analogue of complex **1** (Table 2, entries 7, 8). The Salan-ligated mono(alkyl) complex **6** showed no selectivity ($P_r = 0.65$, Table 2, entry 10), although its aluminum counterpart was reported to be highly heteroselective ($P_r = 0.96$).[12] Using bis(alkyl) complexes **7** and **8** as initiators, a complete conversion could be achieved in 30 min. The molecular weight of the resultant PLA was close to the theoretic value calculated on the basis of di-active sites. Thus, we suggested that both metal alkyl species participated in the initiation, leading to the relatively broad molecular weight distribution and atactic microstructure of the isolated PLA (Table 2, entries 11, 12).

At various monomer-to-initiator ratios ranging from 100 to 500, polymerization of *rac*-lactide initiated by complexes **1** and **2** proceeded smoothly. The molecular weight of the resulting PLA increased with the ratio, while the molecular weight distribution did not change obviously (PDI = 1.25−1.48) (Table 3, entries 1−4 and 7−10). When the ratio was raised to over 500, the reaction became sluggish because of too low concentration of the initiator, and complete conversion could not be reached even for long reaction times (entries 5, 6, 11). Strikingly, the high heteroselectivity of complexes **1** and **2** was not influenced or even slightly increased with the ratio and also showed no relationship with the conversion. The resulting heterotactic PLA had a P_r of 0.99, the highest value reached up to date, as far as we aware. This result indicated the absence of transesterification that would cause a decrease in selectivity.

Reaction conditions also affected the catalytic performance of the complexes. With complex **2**, if the polymerization was performed at 70 °C, 85% conversion could be achieved in 5 min (Table 4, entry 1), whereas, the heterotacticity of the resultant PLA dropped slightly ($P_r = 0.93$). This also indicated that **2** was stable at high temperature, at least, in the initiation time scale. Polymerization medium played an important role in influencing the activity and stereocontrol ability of the catalysts. THF was the optimum solvent (Table 4, entry 2).[9e,f,12,15] Contrarily, polymerization performed in CH_2Cl_2 at room temperature for a long time (12 h) led to low conversion and isolation of low-tacticity PLA ($P_r = 0.75$, Table 4, entry 3). This could be due to the competitive coordination between the polar CH_2Cl_2 molecule and monomer lactide, which changed the environment of the initiator.[26] Toluene was such a poor

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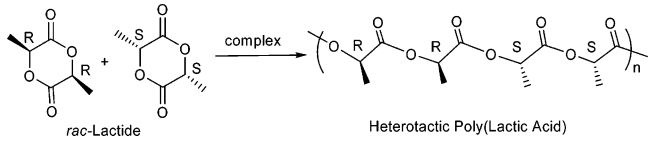
Table 2. Polymerization of *rac*-Lactide with Various Lanthanide Alkyl Complexes[a]



entry	initiator [Ln]	[LA] (mol·L^{-1})	[LA]/[Ln]	t (h)	T (°C)	conv	$M_{calcd} \times 10^{-4}$ [b]	$M_n \times 10^{-4}$ [c]	PDI	P_r [d]
1	**1**	1.7	300	1	20	100	4.32	5.66	1.32	0.96
2	**1** + $C_6H_5NH_2$ (1:1)	1.7	300	1	20	96	4.15	4.69	1.44	0.95
3	**1** + HO*i*Pr (1:1)	1.7	300	24	20	trace	n.d.[f]	n.d.	n.d.	0.94
4	**2**	1.7	300	1	20	100	4.32	3.96	1.43	0.97
5	**2**$^{-Me}$ [e]	1.7	300	2	20	68	2.93	1.54	1.29	0.90
6	**3**	1.7	300	1	20	100	4.32	3.86	1.59	0.94
7	**4**	1.7	300	6	20	trace	n.d.	n.d.	n.d.	n.d.
8	**4**	1.7	300	1	70	70	3.02	2.10	1.44	0.75
9	**5**	1.7	300	1	20	91	3.89	2.12	1.51	0.90
10	**6**	1.7	300	1	20	100	4.32	3.74	1.64	0.65
11	**7**	1.0	500	0.5	20	100	3.60[g]	4.57	1.72	0.69
12	**8**	1.0	300	0.5	20	100	2.16[g]	2.67	1.96	0.64

[a] Polymerizations were performed in THF. [b]Calculated by ([LA]/[Ln]) × 144.14 × X (X = conv). [c]Determined by GPC against polystyrene standard. [d]P_r is the probability of racemic linkages between monomer units determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum. [e]Complex **2**$^{-Me}$ is an analogue of **2** with methyl substituents on the *ortho*-positions of phenyl rings. [f]n.d.: not determined. [g]Calculated by ([LA]/2[Ln]) × 144.14 × X (X = conv).

medium that almost no polymerization of *rac*-LA took place at room temperature. The reaction became obviously rapid at 70 °C, but gave atactic PLA with low molecular weight and broad molecular weight distribution (Table 4, entries 4, 5). This is in striking contrast to the methoxy-amino-bisphenolato lanthanide alkoxide systems, which initiate the equally rapid ROP of *rac*-LA in toluene and THF.[13]

The effect of the type of initiator was also investigated. **L^1**-ligated yttrium amide and alkoxide initiators, *in situ* generated by addition of equivalent aniline and 2-propanol to yttrium alkyl complex **1**, respectively, were employed to catalyze the polymerization of *rac*-LA. Both exhibited similar selectivity to the parent alkyl species. The slight drop in heterotacticity for the resulting PLAs might be attributed to the impurities in the systems, such as the unreacted lanthanide tris(alkyl)s and the ligand-redistribution byproduct, which were active initiators but nonselective (Table 2, entries 2, 3). It should be noted that the alkoxide species displayed extremely low activity; only a trace amount of polymer could be isolated from the polymerization carried out for 24 h at room temperature, which might be due to the too electron-negative metal center. This is in contrast to the literature results that lanthanide alkoxide species are slightly less or equally active initiators compared to the corresponding alkyl congeners and initiate very controllable polymerization.[13b,15]

In fact, the catalytic performance of a complex is affected by the concerted influence of the ligand framework and Lewis acidity of the central metal[27] and the nucleophilicity of initiation species.[11d,e] Complex L^{1-OMe}Y(CH$_2$SiMe$_3$)(THF) containing a pendent OMe functional group in the ligand skeleton displays modest selectivity[13b] compared to complex **1** (L^{1}Y(CH$_2$SiMe$_3$)(THF)), having a pendent N(CH$_3$)$_2$ functionality. The same L^1-attached ytterbium methyl shows activity to caprolactone,[28] whereas the yttrium amido counterpart is highly active to *rac*-LA but ambiguous in selectivity owing to the existence of competitive initiators (impurities).[13b] The titanium bis(alkoxo) complexes bearing a L^1 moiety can initiate the polymerization of caprolactone and L-LA.[18] L^4-attached titanium bis(alkoxide)s are active toward the ROP of *rac*-LA, although it is nonselective, whereas their zirconium and hafnium counterparts belong to the rare examples of group 4 metal complexes that show modest iso- or heteroselectivity (P_r/P_m = 0.3/0.7; P_r/P_m = 0.5/0.5).[19] Much higher selectivity has been found for the dimeric L^4-stabilized yttrium borohydrides (P_r = 0.87).[14]

Mechanistic Aspect. A computational investigation of the mechanism for the stereoselective ROP of *rac*-LA with (BDI)-Mg(O*i*Pr) reported by Rzepa demonstrates that the clashes between the methyl of the first insertion lactide and the *ortho* substituent of *N*-aryl of the BDI ligand represent the most significant contribution to the stereoselectivity.[29] The larger the *ortho* substituent is, the higher the selectivity of the complex. This can well explain some experimental results. For instance, substituting the *ortho* CH$_3$ unit of the *N*-aryl in (BDI)Zn(O*i*Pr) by a larger *i*Pr group or substituting the *ortho* CH$_3$ group of the bisphenolate in the lanthanide alkoxide complexes by a larger C(CH$_3$)$_2$Ph group leads to a dramatic increase in the selectivity of the corresponding complexes.[6b,13b] For our system, the sterics of the *ortho* position, indeed, influenced the selectivity, however not as obviously as the above-mentioned systems. The less bulky complex **2**$^{-Me}$ [30] (*ortho* CH$_3$) showed slightly lower selectivity (P_r = 0.90, Table 2, entry 5) than the spacially steric analogue

(26) The NMR spectrum (see Supporting Information) for complex **5** in CD_2Cl_2 showed a different pattern from that in C_6D_6 especially the yttrium alkyl group, shifting to lower-field region at δ = 0.09 from −0.6 ppm, indicating the change of geometry of the metal center.

(27) The Lewis acidity of the central metal ion influences the catalytic activity of the complex toward the polymerization of cyclohexene oxide with CO_2; see: (a) Cui, D.; Nishiura, M.; Hou, Z. *Macromolecules* **2005**, *38*, 4089−4095. (b) Darensbourg, D. J.; Niezgoda, S. A.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 4690−4698. (c) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342.

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(30) Methyl-substituted phenol reacted with dimethylamino ethylene amine to afford **H$_2$L^{2-Me}**, treatment of which by Y(CH$_2$SiMe$_3$)$_2$THF$_2$ gave L^{2-Me}Y(CH$_2$SiMe$_3$)(THF) (**2**$^{-Me}$), an analogue of **2**. NMR data: δ 7.11 (s, 1H, C$_6$H$_2$), 6.88 (s, 1H, C$_6$H$_2$), 6.86 (s, 1H, C$_6$H$_2$), 6.82 (s, 1H, C$_6$H$_2$), 5.42 (s, 1H, ArC*H*$_2$N), 5.39(s, 1H, ArC*H*$_2$N), 5.07(s, 1H, ArC*H*$_2$N), 5.04(s, 1H, ArC*H*$_2$N), 3.69 (m, 4H, THF), 3.38 (s, 1H, ArC*H*$_2$N), 3.35 (s, 1H, ArC*H*$_2$N), 3.08 (s, 1H, ArC*H*$_2$N), 3.05 (s, 1H, ArC*H*$_2$N), 2.80 (m, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.66 (m, 2H, N(CH$_2$)$_2$N), 2.51 (s, 3H, ArCH$_3$), 2.44 (s, 3H, ArCH$_3$), 2.40 (s, 3H, ArCH$_3$), 2.32 (m, 2H, N(CH$_2$)$_2$N), 2.22 (m, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.20 (s, 3H, ArCH$_3$), 1.53 (m, 4H, THF), 0.69 (br, 3H, N(CH$_2$C*H*$_3$)$_2$), 0.43 (br, 3H, N(CH$_2$C*H*$_3$)$_2$, 9H, CH$_2$Si(C*H*$_3$)$_3$), −0.10, −0.57 (AB, d, J(H, H) = 12 Hz, J(Y, H) = 3.2 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$)).

Table 3. Polymerization of *rac*-Lactide with Complexes 1 and 2 at Various Monomer-to-Initiator Ratios[a]

entry	initiator [Ln]	[LA] (mol·L^{-1})	[LA]/[Ln]	t (h)	conv	$M_{cal} \times 10^{-4}$ [b]	$M_n \times 10^{-4}$ [c]	PDI	P_r [d]
1	**1**	1.7	100	1	100	1.44	1.93	1.25	0.95
2	**1**	1.7	200	1	100	2.88	2.11	1.41	0.97
3	**1**	1.7	300	1	100	4.32	5.66	1.32	0.96
4	**1**	1.7	500	1	100	7.20	9.25	1.33	0.96
5	**1**	1.7	700	3	86	8.67	3.77	1.48	0.99
6	**1**	2.2	1000	18	36	5.18	3.51	1.47	0.98
7	**2**	1.0	100	1	100	1.44	1.78	1.38	0.96
8	**2**	1.0	200	1	100	2.88	2.68	1.28	0.97
9	**2**	1.7	300	1	100	4.32	3.96	1.43	0.97
10	**2**	1.0	500	1	100	7.20	6.69	1.39	0.97
11	**2**	1.7	700	3	95	10.08	8.04	1.59	0.98

[a] Polymerizations were performed in THF at 20 °C. [b]Calculated by ([LA]/[Ln]) × 144.14 × X (X = conv). [c]Determined by GPC against polystyrene standard. [d]P_r is the probability of racemic linkages between monomer units determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum.

Table 4. Polymerization of *rac*-Lactide with Complex 2: Influence of the Reaction Conditions

entry	solvent	[LA] (mol·L^{-1})	[LA]/[Ln]	t (h)	T (°C)	conv	$M_{cal} \times 10^{-4}$ [a]	$M_n \times 10^{-4}$ [b]	PDI	P_r [c]
1	THF	1.0	300	5 min	70	85	3.67	3.07	1.47	0.93
2	THF	1.7	300	1	20	100	4.32	3.96	1.43	0.97
3	CH_2Cl_2	1.0	300	12	20	70	4.32	3.98	1.57	0.75
4	toluene	0.5	300	12	20	trace	n.d.[d]	n.d.	n.d.	n.d.
5	toluene	0.5	300	1	70	86	4.32	1.83	1.67	0.63

[a] Calculated by ([LA]/[Ln]) × 144.14 × X (X = conv). [b]Determined by GPC against polystyrene standard. [c]P_r is the probability of racemic linkages between monomer units determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum. [d]n.d. = not determined.

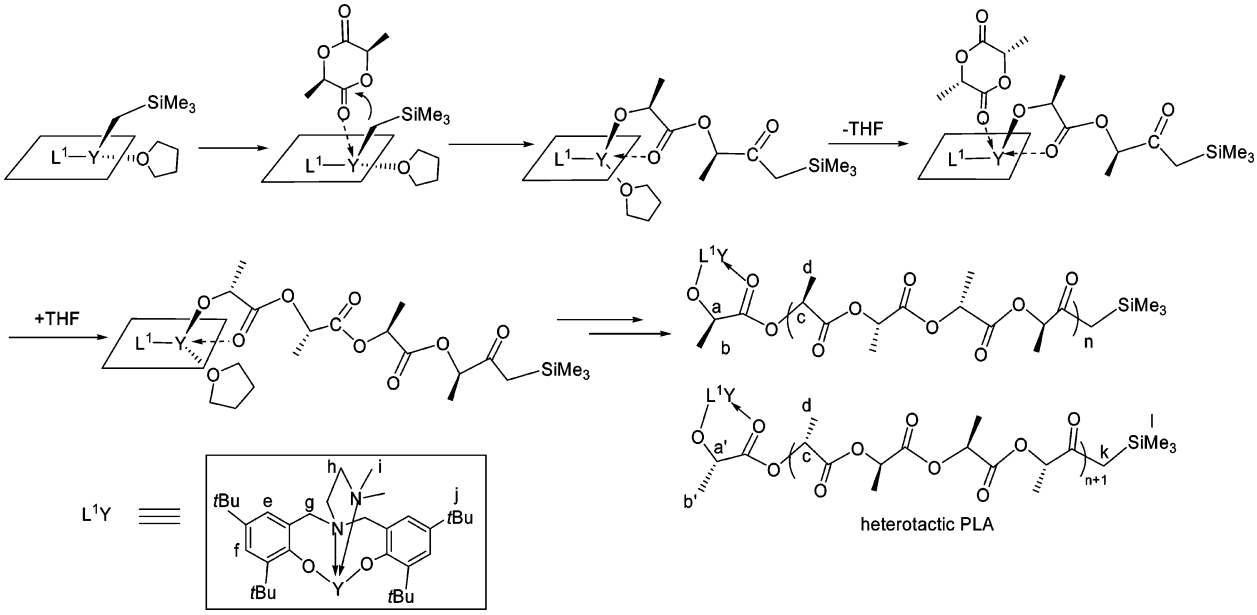
2 (*ortho t*Bu, P_r = 0.97, Table 2, entry 4). This result was consistent with the *O,S,S,O*-type scandium alkoxide systems reported by Okuda et al. that showed that the sterics of the *ortho* substituent of the bisphenolate does not greatly influence the selectivity.[15] They attribute the high selectivity to a dynamic monomer-recognition process involving interconversion of the ligand configuration. The structure of Salan yttrium complex **6** is much close to these *O,S,S,O*-type scandium alkoxide systems; however, it is a nonselective initiator, which might be due to the lesser constraint of the ligand framework and the absence of the exchange of ligand configuration.

It was noteworthy that the major differences in molecular structures of complexes **1**−**5** were the bridge between the two nitrogen atoms of the ligand, the type of lanthanide element, and the pendent amino alkyl group. X-ray crystallographic data had shown that the bridge significantly influenced the geometry of the metal center. The more flexible trimethylene bridge resulted in a less distorted tetragonal bipyramid in **4**, while the short ethylene in **1**−**3** and the rigid pyconyl in **5** generated a more twisted octahedral geometry. This was reflected in the deviation angles of the alkyl ligand from the LnONO plane, being 29.39° for **1**, 29.97° for **2**, 31.45° for **3**, and a slightly smaller 26.77° for **5**, but very small 2.72° for **4** (*vide supra*), in a trend of **1** ≈ **2** ≈ **3** > **5** ≫ **4**, which was fairly coincident with the catalytic activity[31] and stereoselectivity. This indicated that changing the substituent of the pendent nitrogen atom from methyl (**1**) to ethyl (**2**), or switching the central metal from yttrium (**2**) to lutetium (**3**), caused negligible differences in catalytic behavior. In contrast, the bridge between the two nitrogen atoms was crucial in governing the catalytic performance via tuning the geometry of the metal center.

Obviously, it is important to know whether the geometry of the molecular core is retained in solution especially during the polymerization process and what are the mechanistic aspects of the ROP of *rac*-LA initiated by these Ln−C species. Thus, we designed a polymerization performed in C_4D_8O at a monomer-to-initiator ratio of 15:1 (10 min) and successfully isolated the active propagating species of *rac*-LA oligomer attached to complex **1**. The process could be described as shown in Scheme 5. The *S,S*-LA (or *R,R*-LA) enantiomer first coordinated to a yttrium ion via its O_{acyl} from the back-side of the alkyl moiety with respect to the steric environment of the metal center in the cases of complexes **1**−**3** and **5** being catalysts. For complex **4**, the coordination of monomer was more random due to the less distorted geometry of the metal center. The following nucleophilic addition of Y−CH_2SiMe_3 species to the $C_{cabonyl}$ led to the ring-opening of *S,S*-LA (or *R,R*-LA) to form five-membered metal-lactate active species with C(O)-CH_2SiMe_3 as the end group. The NMR spectrum was clear and informative (Figure 4). There were two sets of ideal quartet/doublet resonances at 5.01/1.59 and 4.82/1.53,[11e] respectively, with an integral intensity ratio of 1:3 and a J(H, H) of 3.6 Hz, which were assigned to the methine (H_a, $H_{a'}$) and methyl (H_b, $H_{b'}$) protons derived from two different enantiomeric lactate units bonding to the yttrium ion. This indicated that two types of active propagating species were present, consistent with the alternating arrangement of two enantiomers in the polymer chain. More strikingly, the ligand also showed two sets of chemical shifts. The benzylic proton H_g (PhCH_2N) gave two ^{1}H AB spins compared to one in complex **1** (SI, Figure 12); the amino methyl protons H_i (−N(CH_3)$_2$) displayed two singlet resonances compared to one in complex **1**. This suggested that the ligand and the pendent nitrogen atom kept attaching to the metal ion and the geometry of the central metal of complex **1** did not collapse but remained in solution upon monomer coordination and insertion. It further confirmed that the metal ion was bonded to two different enantiomeric lactate units. Thus the environment of the resulting propagating sites was spacially steric. Incorporation of a configurationally opposite enantiomer *R,R*-LA (*S,S*-LA) should be favored to lower this transition-state energy. The following nucleophilic addition of the newly formed metal alkoxy propagating species to the $C_{cabonyl}$ led to the ring-opening of *R,R*-LA (*S,S*-LA) to form a racemic enchainment. This coordination−insertion mechanism was proved by the presence of the end group C(O)CH_2SiMe_3, giving a singlet resonance at δ 1.49 assignable to the methylene protons

(31) The activities of complexes **1**−**5** were 73.5, 73.5, 73.5, 0, and 66.9 kg·mol^{-1}·h^{-1}, respectively.

Scheme 5 . Formation of Active Propagating Species of *rac*-LA Oligomer Initiated by Complex 1



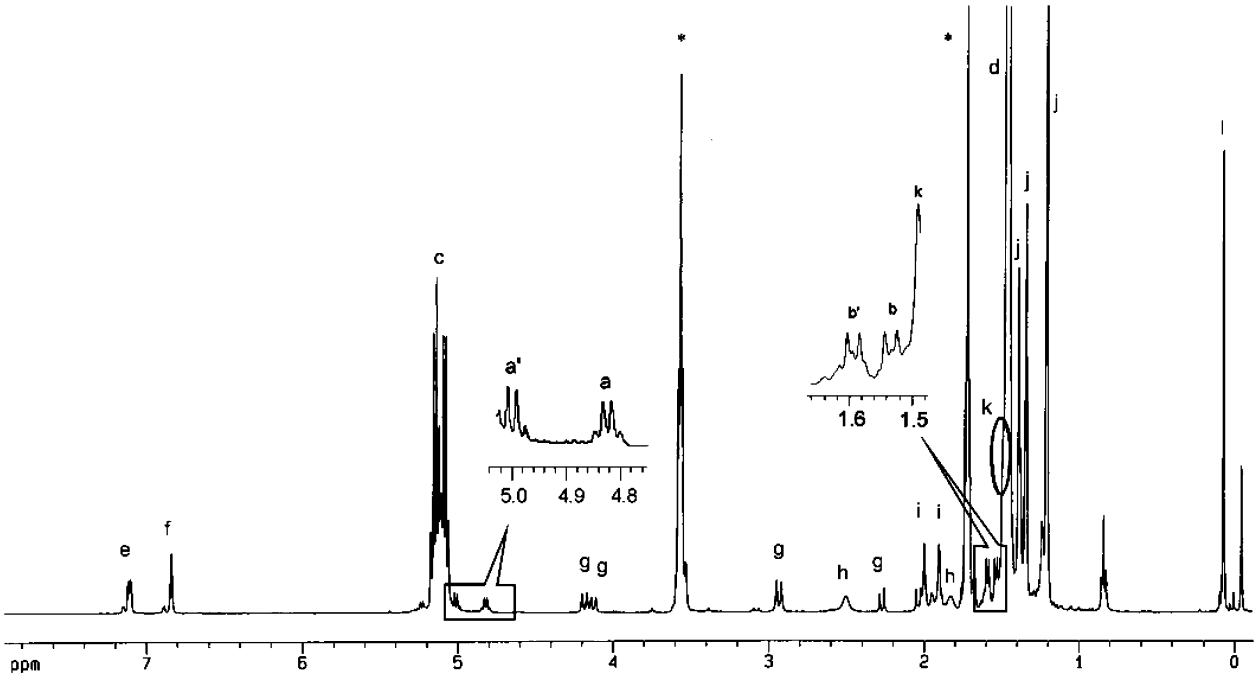


Figure 4. ^{1}HNMR spectrum (400 MHz) of the active species of *rac*-lactide oligomer initiated by complex **1** (*C_4D_8O, $[LA]_0$:[Y] = 15:1, 25 °C).

H_k, which was comparable with $C(O)CH_2SiMe_3$ in $[(C_5Me_4SiMe_3)Y(OC(O)CH_2SiMe_3)_2]_2$,[27a] and also evidenced in the ^{13}C DEPT spectrum (SI, Figures 13 and 15). During the process, the THF molecule might be extruded from or rebonded to the Y ion to satisfy a six-coordination sphere and also contributed partially to lower the transition-state energy.[29] This might be the reason that THF was the optimum medium for the polymerization.

Conclusion

We have demonstrated that the combinations of amino-amine-modified bisphenolate ligands with lanthanide alkyl units generated unprecedented stereoselective initiators for the ring-opening polymerization of *rac*-LA to give heterotactic polylactide with P_r up to 0.99. The bridge between the two nitrogen atoms of the ligand played a critical role in governing the stereoselectivity via tuning the geometry of the molecular core of the complexes, while the mono(alkyl) complex bearing a Salan ligand was an active initiator, unfortunately without stereocontrol due to the less constrained ligand. The monoanionic β-diiminate-ligated lanthanide bis(alkyl) complexes were also active but nonselective due to the di-active sites. A more important implication of the current work is that single-site catalysts offer new opportunities for microstructural control of polymers if new reaction pathways are accessed through catalyst design and control of reaction conditions.

Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or

under a nitrogen atmosphere in an MBraun glovebox. Solvents were purified by an MBraun SPS system. Ligands $\mathbf{H_2L^1}$−$\mathbf{H_2L^5}$, $\mathbf{HL^6}$ and $\mathbf{HL^7}$ were synthesized according to modified literature procedures.[6e,17b,32] The phenols and amines were purchased from Aldrich or Fluka. All liquids were dried over 4 Å molecular sieves for a week and distilled before use, and solid materials were used without purification. The synthesis of lanthanide tris(alkyl)s followed the established method with minor alteration.[33]

Instruments and Measurements. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by use of NMR tubes and then sealed by paraffin film. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H−^{1}H (COSY), ^{1}H−^{13}C (HMQC), and ^{13}C NMR (DEPT) experiments when necessary. The molecular weight and molecular weight distribution of the polymers were measured by a GPC Waters 410. Crystals for X-ray analysis were obtained as described in the Experimental Section. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. IR spectra were obtained on a Bruker Vertex 70 FTIR spectrometer. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry.

$\mathbf{L^1Y(CH_2SiMe_3)(THF)}$ (1). To a hexane (5 mL) solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.181 g, 0.37 mmol) was added an equimolar amount of $\mathbf{H_2L^1}$ (0.19 g, 0.37 mmol, in 10 mL of hexane). The reaction mixture was stirred at −30 °C for 12 h. Removal of the volatiles afforded a residue, which was carefully washed with cold hexane to remove nonreacted lanthanide tris(alkyl)s and then cooled to −30 °C again. White solids of complex **1** were deposited on the bottom of the flask in 1 day (0.19 g, 70%). Good crystals for X-ray analysis were isolated by recrystallizing the solids from a mixture of toluene (0.5 mL) and hexane (2.5 mL) at −30 °C for several days. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.72 (d, ^4J(H, H) = 2.7 Hz, 2H, C_6H_2), 7.23 (d, ^4J(H, H) = 2.72 Hz, 2H, C_6H_2), 4.06 (br, 4H, THF), 3.86 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 3.00 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 2.39 (br, 2H, N(CH$_2$)$_2$N), 1.90 (s, 18H, C(CH$_3$)$_3$), 1.83 (s, 6H, N(CH$_3$)$_2$), 1.70 (br, 2H, N(CH$_2$)$_2$N), 1.57 (s, 18H, C(CH$_3$)$_3$), 1.27 (br, 4H, THF), 0.62 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), −0.35 (d, ^2J(Y, H) = 3.2 Hz, 2H, C*H*$_2$SiMe$_3$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 162.3 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 137.4 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 136.9 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 126.3 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$), 125.2(2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$) 125.1 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 72.3 (2C, THF), 65.9 (2C, Ar*C*H$_2$N), 60.47 (1C, N(CH$_2$)$_2$N), 48.9 (1C, N(CH$_2$)$_2$N), 46.8 (2C, N(CH$_3$)$_2$), 36.2 (2C, *C*(CH$_3$)$_3$), 34.7 (2C, *C*(CH$_3$)$_3$), 32.7 (6C, C(*C*H$_3$)$_3$), 31.1 (6C, C(*C*H$_3$)$_3$), 26.1 (1C, *C*H$_2$SiMe$_3$), 25.6 (2C, THF), 5.4 (3C, Si(*C*H$_3$)$_3$) ppm. IR (KBr pellet): ν 2956(m), 2903(m), 2870(m), 1606(m), 1480(m), 1446(m), 1417(m), 1388(m), 1363(m), 1307(m), 1255(m), 1240(m), 1205(m), 1169(m), 1136(m), 1113(w), 1087(w), 1031(m), 996(w), 963(w), 940(w), 915(m), 879(m), 839(m), 808(m), 781(w), 668(m) cm^{-1}. Anal. Calcd for $C_{42}H_{73}N_2O_3SiY$ (%): C, 65.43; H, 9.54; N, 3.63. Found: C, 65.35; H, 9.48; N, 3.56.

$\mathbf{L^2Y(CH_2SiMe_3)(THF)}$ (2). Following a similar procedure to that described for the preparation of complex **1**, treatment of $Y(CH_2SiMe_3)_3(THF)_2$ (0.181 g, 0.37 mmol) with equimolar $\mathbf{H_2L^2}$ (0.20 g, 0.37 mmol) afforded complex **2** as white powders (0.18 g, 64%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.71 (d, ^4J(H, H) = 2.7 Hz, 2H, C_6H_2), 7.23 (d, ^4J(H, H) = 2.7 Hz, 2H, C_6H_2), 4.05 (m, 4H, THF), 3.87 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 3.02 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 2.75 (m, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.47 (br, 2H, N(CH$_2$)$_2$N), 2.22 (br, 2H, N(C*H*$_2$CH$_3$)$_2$), 1.99 (br, 2H, N(CH$_2$)$_2$N), 1.91 (s, 18H, C(C*H*$_3$)$_3$), 1.56 (s, 18H, C(C*H*$_3$)$_3$), 1.32 (m, 4H, THF), 0.63 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), 0.56 (t, ^3J(H, H) = 7.3 Hz, 6H, N(CH$_2$C*H*$_3$)$_2$), −0.29 (d, ^2J(Y, H) = 3.2 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): 162.2 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 137.4 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 136.9 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 126.2 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 125.2 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 125.1 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 72.1 (2C, THF), 66.0 (2C, Ar*C*H$_2$N), 52.8 (1C, N(CH$_2$)$_2$N), 49.0 (1C, N(CH$_2$)$_2$N), 45.9 (2C, N(*C*H$_2$CH$_3$)$_2$), 36.2 (2C, *C*(CH$_3$)$_3$), 34.7 (2C, *C*(CH$_3$)$_3$), 32.7 (6C, C(*C*H$_3$)$_3$), 31.3 (6C, C(*C*H$_3$)$_3$), 26.3 (1C, *C*H$_2$SiMe$_3$), 25.6 (2C, THF), 9.0 (2C, N(CH$_2$*C*H$_3$)$_2$), 5.5 (3C, Si(*C*H$_3$)$_3$) ppm. IR (KBr pellet): ν 2954(m), 2901(m), 2867(m), 1603(m), 1559(w), 1478(m), 1443(m), 1415(m), 1385(m), 1361(m), 1304(m), 1248(m), 1238(m), 1203(m), 1167(m), 1134(m), 1115(w), 1089(w), 1059(w), 1026(m), 959(w), 912(m), 876(m), 862(m), 838(m), 806(m), 782(w), 694(m) cm^{-1}. Anal. Calcd for $C_{44}H_{77}N_2O_3SiY$ (%): C, 66.13; H, 9.71; N, 3.51. Found: C, 65.78; H, 9.66; N, 3.40.

$\mathbf{L^2Lu(CH_2SiMe_3)(THF)}$ (3). Following the same procedure as that of complex **1**, complex **3** was isolated by treatment of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.213 g, 0.37 mmol) with equimolar $\mathbf{H_2L^2}$ (0.20 g, 0.37 mmol) as white powders (0.22 g, 71%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.74 (d, ^4J(H, H) = 2.8 Hz, 2H, C_6H_2), 7.22 (d, ^4J(H, H) = 2.8 Hz, 2H, C_6H_2), 4.09 (m, 4H, THF), 3.91 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 3.00 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 2.79 (m, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.46 (br, 2H, N(CH$_2$)$_2$N), 2.27 (br, 2H, N(C*H*$_2$CH$_3$)$_2$), 2.02 (br, 2H, N(CH$_2$)$_2$N), 1.90 (s, 18H, C(C*H*$_3$)$_3$), 1.56 (s, 18H, C(C*H*$_3$)$_3$), 1.28 (m, 4H, THF), 0.62 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), 0.55 (t, ^3J(H, H) = 7.3 Hz, 6H, N(CH$_2$C*H*$_3$)$_2$), −0.41 (br, 2H, C*H*$_2$Si(CH$_3$)$_3$) ppm. ^{13}C NMR(100 MHz, C_6D_6, 25 °C): δ 162.6(2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 137.4 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 137.3 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 126.0 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 125.2 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 125.0 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 72.5 (2C, THF), 66.0 (2C, Ar*C*H$_2$N), 52.7 (1C, N(CH$_2$)$_2$N), 49.3 (1C, N(CH$_2$)$_2$N), 46.5 (2C, N(*C*H$_2$CH$_3$)$_2$), 36.2 (2C, *C*(CH$_3$)$_3$), 34.7 (2C, *C*(CH$_3$)$_3$), 32.7 (6C, C(*C*H$_3$)$_3$), 31.4 (6C, C(*C*H$_3$)$_3$), 31.0 (1C, *C*H$_2$SiMe$_3$), 25.7 (2C, THF), 9.1 (2C, N(CH$_2$*C*H$_3$)$_2$), 5.6 (3C, CH$_2$Si(*C*H$_3$)$_3$) ppm. IR (KBr pellets): ν 2954(m), 2901(m), 2865(m), 1605(m), 1477(m), 1445(m), 1415(m), 1383(m), 1361(m), 1308(m), 1240(m), 1203(m), 1167(m), 1133(m), 1115(w), 1071(w), 1018(m), 913(m), 876(m), 839(m), 809(m), 772(w), 670(m) cm^{-1}. Anal. Calcd for $C_{44}H_{77}N_2O_3SiLu$ (%): C, 59.70; H, 8.77; N, 3.16. Found: C, 59.55; H, 8.78; N, 3.11.

$\mathbf{L^3Y(CH_2SiMe_3)(THF)}$ (4). Reaction of $Y(CH_2SiMe_3)_3(THF)_2$ (0.181 g, 0.37 mmol) with equimolar $\mathbf{H_2L^3}$ (0.199 g, 0.37 mmol) by the same manner as described previously for the formation of complex **1** afforded complex **4** (0.08g, 30.7%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.72 (d, ^4J(H, H) = 2.8 Hz, 2H, C_6H_2), 7.23 (d, ^4J(H, H) = 2.8 Hz, 2H, C_6H_2), 3.99 (m, 4H, THF), 3.89 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 2.88 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 2.55 (m, 2H, NC*H*$_2$CH$_2$CH$_2$N(CH$_3$)$_2$), 2.09 (s, 6H, N(CH$_3$)$_2$, 1.90 (s, 18H, C(C*H*$_3$)$_3$), 1.57 (s, 18H, C(C*H*$_3$)$_3$), 1.50 (s, 2H, NCH$_2$CH$_2$C*H*$_2$N(CH$_3$)$_2$), 1.32 (m, 4H, THF), 0.90 (br, 2H, NCH$_2$C*H*$_2$CH$_2$N(CH$_3$)$_2$), 0.59 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), −0.39 (d, ^2J(Y, H) = 3.2 Hz, 2H, C*H*$_2$Si(CH$_3$)$_3$) ppm. ^{13}C NMR(100 MHz, C_6D_6,

(32) (a) Burke, W.; Smith, R.; Weatherbee, C. *J. Am. Chem. Soc*. **1952**, *74*, 602−605. (b) Burke, W.; Kolbezen, M.; Stephens, C. *J. Am. Chem. Soc*. **1952**, *74*, 3601−3605. (c) Carey, D.; Cope-Eatough, E.; Vilaplana-MaféMair, E.; Mair, F.; Pritchard, R.; Warren, J.; Wood, R. *Dalton Trans.* **2003**, 1083−1093.

(33) Lappert, M.; Pearce, R. *Chem. Commun*. **1973**, 126−127.

25 °C): 162.4 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 137.3 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 136.6 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 126.5 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 125.6 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 124.9 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 71.9 (2C, THF), 66.7 (2C, Ar*C*H$_2$N), 63.4 (1C, N*C*H$_2$CH$_2$-CH$_2$N(CH$_3$)$_2$), 56.6 (1C, NCH$_2$CH$_2$*C*H$_2$N(CH$_3$)$_2$), 48.0 (2C, N(*C*H$_3$)$_2$), 36.2 (2C, *C*(CH$_3$)$_3$), 34.7 (2C, *C*(CH$_3$)$_3$), 32.7 (6C, C(*C*H$_3$)$_3$), 31.5 (6C, C(*C*H$_3$)$_3$), 25.6 (2C, THF), 25.0 (1C, *C*H$_2$SiMe$_3$), 14.9 (1C, *C*H$_2$*C*H$_2$CH$_2$), 5.4 (3C, CH$_2$Si(*C*H$_3$)$_3$) ppm. IR (KBr pellet): ν 2954(m), 2866(m), 2784(m), 1604(m), 1478(m), 1442(m), 1415-(m), 1386(m), 1361(m), 1305(m), 1266(m), 1238(m), 1202(m), 1167(m), 1134(m), 1099(w), 1057(m), 1027(m), 970(w), 914(m), 876(m), 838(m), 808(m), 777(w), 694(m) cm^{-1}. Anal. Calcd for C$_{43}$H$_{75}$N$_2$O$_3$SiY (%): C, 65.79; H, 9.63; N, 3.57. Found: C, 65.69; H, 9.61; N, 3.57.

L^{4}Y(CH$_2$SiMe$_3$)(THF) (5). To a stirred solution of ligand **H$_2$L^4** (0.22 g, 0.04 mmol) in toluene (10 mL) was added a toluene (5 mL) solution of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.20 g, 0.04 mmol) at −30 °C. The reaction mixture was stirred for 12 h, and the volatiles were removed under vacuum. The residue was washed with hexane and dried under vacuum, to give complex **5** as white powders (0.24 g, 75%). Good crystals for X-ray analysis were grown from a toluene solution. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 8.73 (d, ^3J(H, H) = 5.1 Hz, 1H, Py-α*H*), 7.46 (d, ^4J(H, H) = 2.5 Hz, 2H, C$_6$H$_2$), 7.09 (d, ^4J(H, H) = 2.5 Hz, 2H, C$_6$H$_2$), 6.55 (d, d, d, ^3J(H, H) = 1.6 Hz, 1.7 Hz, 1.5 Hz, 1H, *β*-Py), 6.26 (t, ^3J(H, H) = 6.4 Hz, 1H, *γ*-Py), 5.90 (d, ^3J(H, H) = 8.0 Hz, 1H, *δ*-Py), 4.10 (br, 4H, THF), 4.06 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 3.36 (s, 2H, PyC*H*$_2$N), 3.06 (d, ^2J(H, H) = 12.0 Hz, 2H, ArC*H*$_2$N), 1.82 (s, 18H, C(CH$_3$)$_3$), 1.52 (s, 18H, C(CH$_3$)$_3$), 1.36 (m, 4H, THF), 0.70 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), 0.09 (d, ^2J(Y, H) = 3.0 Hz, 2H, C*H*$_2$-SiMe$_3$) ppm. ^{13}C NMR(100 Hz, C$_6$D$_6$, 25 °C): 162.6 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 160.5 (1C, *ipso*-*C*$_6$H$_4$N), 149.8 (1C, *C*$_6$H$_4$N), 138.1 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 136.8 (2C, *ipso*-2,4-*t*Bu$_2$*C*$_6$H$_2$O), 126.1 (1C, *C*$_6$H$_4$N), 126.0 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 124.6 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 124.1 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$O), 122.5 (1C, *C*$_6$H$_4$N), 121.7 (1C, *C*$_6$H$_4$N), 72.0 (2C, THF), 64.9 (2C, Ar*C*H$_2$N), 57.5 (1C, Py*C*H$_2$N), 36.0 (2C, *C*(CH$_3$)$_3$), 34.6 (2C, *C*(CH$_3$)$_3$), 32.8 (6C, C(*C*H$_3$)$_3$), 30.8 (6C, C(*C*H$_3$)$_3$), 26.8 (1C, *C*H$_2$SiMe$_3$), 25.6 (2C, THF), 5.40 (3C, CH$_2$Si(*C*H$_3$)$_3$) ppm. IR (KBr pellet): ν 2955(m), 2905(m), 2869(m), 1607(m), 1574(m), 1520(w), 1479(m), 1443-(m), 1417(m), 1388(m), 1362(m), 1307(m), 1240(m), 1204(m), 1169(m), 1156(m), 1136(m), 1101(w), 1070(w), 1057(m), 1029-(w), 1016(w), 975(w), 932(w), 915(w), 877(m), 838(m), 809(m), 754(m), 697(m) cm^{-1}. Anal. Calcd for C$_{44}$H$_{69}$N$_2$O$_3$SiY (%): C, 66.81; H, 8.79; N, 3.54. Found: C, 66.66; H, 8.71; N, 3.50.

L^{5}Y(CH$_2$SiMe$_3$)(THF) (6). Treatment of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.181 g, 0.37 mmol) with Salan ligand **H$_2$L^5** (0.20 g, 0.37 mmol) according to the procedure described for the preparation of **1** afforded complex **6** as white powders (0.18 g, 64%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.76 (s, 2H, C$_6$H$_2$), 7.06 (s, 2H, C$_6$H$_2$), 4.70 (br, 1H, THF), 4.09 (br, 4H, ArC*H*$_2$N), 3.75 (br, 1H, THF), 2.95 (br, 2H, THF), 2.83 (br, 2H, THF), 2.17 (br, 3H, NC*H*$_3$), 1.94 (br, 7H, NC*H*$_3$, N(C*H*$_2$)$_2$N), 1.82 (s, 18H, C(CH$_3$)$_3$), 1.53 (s, 18H, C(CH$_3$)$_3$), 1.24 (br, 1H, THF), 1.05 (br, 1H, THF), 0.44 (s, 9H, CH$_2$Si(C*H*$_3$)$_3$), −0.35, −0.38 (AB, ^2J(H, H) = 12.0 Hz, ^2J(Y, H) = 4.0 Hz, 2H, C*H*$_2$SiMe$_3$) ppm. ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 162.4 (1C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 161.6 (1C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 138.3 (1C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 137.2 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 136.7 (1C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 126.7 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$), 125.7 (2C, 2,4-*t*Bu$_2$-*C*$_6$H$_2$), 124.7 (2C, *ipso*-2,4-*t*Bu$_2$-*C*$_6$H$_2$), 72.3 (2C, THF), 65.7 (2C, Ar*C*H$_2$N), 64.7 (1C, N(CH$_2$)$_2$N), 52.0 (1C, N(CH$_2$)$_2$N), 46.0 (1C, NCH$_3$), 45.0 (1C, NCH$_3$), 36.1 (2C, *C*(CH$_3$)$_3$), 34.7 (2C, *C*(CH$_3$)$_3$), 32.7 (6C, C(*C*H$_3$)$_3$), 31.0 (6C, C(*C*H$_3$)$_3$), 29.7 (1C, *C*H$_2$SiMe$_3$), 25.6 (2C, THF), 5.2 (3C, Si(*C*H$_3$)$_3$). IR (KBr pellet): ν 2955(m), 2902(m), 2865(m), 1605(m), 1477(m), 1444-(m), 1415(m), 1389(m), 1361(m), 1308(m), 1283(m), 1239(m), 1203(m), 1167(m), 1133(m), 1071(w), 1014(w), 981(w), 963(w), 946(w), 915(w), 876(m), 839(m), 809(m), 795(w), 772(w), 680-(m) cm^{-1}. Anal. Calcd for C$_{42}$H$_{73}$N$_2$O$_3$SiLu (%): C, 58.86; H, 8.59; N, 3.27. Found: C, 58.65; H, 8.55; N, 3.20.

L^{6}Y(CH$_2$SiMe$_3$)$_2$ (7). To a stirred suspension of ligand **HL^6** (0.26 g, 0.84 mmol) in hexane (20 mL) was added Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.41 g, 0.84 mmol) in hexane (5 mL) at 0 °C. The mixture was reacted until a clear solution was obtained in 0.5 h. Then, the solution was concentrated to half-volume and cooled to −30 °C. Bright yellow single crystals of complex **7** were isolated after several hours (0.17 g, 75%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 7.22−7.19 (br, 3H, 2,6-*i*Pr$_2$-C$_6$H$_3$), 6.9 (t, ^3J(H, H) = 7.2 Hz, 1H, 2-OMe-C$_6$*H*$_4$-*βH*), 6.82 (t, ^3J(H, H) = 8.0 Hz, 1H, 2-OMe-C$_6$*H*$_4$-*γH*), 6.74 (dd, ^3J(H, H) = 1.2 Hz, 1.2 Hz, 1H, 2-OMe-C$_6$*H*$_4$-α*H*), 6.58 (d, ^3J(H, H) = 8.0 Hz, 1H, 2-OMe-C$_6$*H*$_4$-*δH*), 5.18 (s, 1H, *H*C(C(CH$_3$)NAr)$_2$), 3.86 (s, 3H, ArOC*H*$_3$), 3.31 (m, 2H, ArC*H*-(CH$_3$)$_2$), 2.04 (s, 3H, C(C*H*$_3$)NAr), 1.72 (s, 3H, C(C*H*$_3$)NAr), 1.41 (d, ^3J(H, H) = 8.0 Hz, 6H, ArCH(C*H*$_3$)$_2$), 1.23 (d, ^3J(H, H) = 8.0 Hz, 6H, ArCH(C*H*$_3$)$_2$), 0.23 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), −0.30, −0.33 (d, d, ^2J(H, H) = 12.0 Hz, ^2J(Y, H) = 4.0 Hz, 2H, C*H*$_2$SiMe$_3$), −0.45, −0.48 (d, d, ^2J(H, H) = 12.0 Hz, ^2J(Y, H) = 4.0 Hz, 2H, C*H*$_2$SiMe$_3$). ^{13}C NMR(100 MHz, C$_6$D$_6$, 25 °C): δ 168.8 (1C, HC-(*C*(Me)NAr)$_2$), 160.7 (1C, HC(*C*(Me)NAr)$_2$), 151.4 (1C, *ipso*-2-OMe-*C*$_6$H$_4$), 143.2 (1C, *ipso*-2,6-iPr$_2$-C$_6$H$_3$), 142.5 (2C, *ipso*-2,6-iPr$_2$-C$_6$H$_3$), 138.5 (1C, *ipso*-2-OMe-C$_6$H$_4$), 127.0 (1C, 2,6-*i*Pr$_2$-*C*$_6$H$_3$), 124.9 (2C, 2,6- *i*Pr$_2$-*C*$_6$H$_3$), 124.0 (1C, 2-OMe-*C*$_6$H$_4$), 123.8 (1C, 2-OMe-*C*$_6$H$_4$), 123.5 (1C, 2-OMe-*C*$_6$H$_4$), 111.8 (1C, 2-OMe-*C*$_6$H$_4$), 100.9 (1C, H*C*(C(Me)NAr)$_2$), 58.9 (3C, ArO*C*H$_3$), 36.9 (1C, *C*H$_2$SiMe$_3$), 36.5 (1C, *C*H$_2$SiMe$_3$), 29.3 (2C, Ar*C*H(CH$_3$)$_2$), 25.5 (2C, ArCH(*C*H$_3$)$_2$), 24.7 (2C, ArCH(*C*H$_3$)$_2$), 23.9 (1C, C(*C*H$_3$) NAr), 23.3 (1C, C(*C*H$_3$) NAr), 4.6 (6C, CH$_2$Si(*C*H$_3$)$_3$). IR (KBr pellet): ν 3057(m), 2959(m), 2866(m), 2836(w), 1637(m), 1597-(m), 1560(m), 1516(m), 1478(m), 1462(m), 1437(m), 1384(m), 1363(m), 1327(m), 1284(m), 1241(m), 1227(m), 1177(m), 1117-(m), 1050(w), 1031(m), 935(m), 789(m), 750(m), 735(m) cm^{-1}. Anal. Calcd for C$_{32}$H$_{53}$N$_2$OSi$_2$Y (%): C, 61.31; H, 8.52; N, 4.47. Found: C, 61.10; H, 8.44; N, 4.39.

L^{7}Y(CH$_2$SiMe$_3$)$_2$ (8). Complex **8** was prepared according to the same procedure as that for **7** by reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.41 g, 0.84 mmol) and **HL^7** as light yellow crystals (0.36 g, 85%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 6.91−6.85 (td, ^3J(H, H) = 1.7 Hz, 1.4 Hz, 1.6 Hz, 2H, 2-OMe-C$_6$*H*$_4$-*βH*), 6.83−6.78 (td, ^3J(H, H) = 1.2 Hz, 1.1 Hz, 1.2 Hz, 2H, 2-OMe-C$_6$*H*$_4$-*γH*), 6.65 (d, ^3J(H, H) = 8.0 Hz, 4H, 2-OMe-C$_6$*H*$_4$-α,*δH*), 5.19 (s, 1H, *H*C (C(CH$_3$)-NAr)$_2$), 3.87 (s, 6H, ArOC*H*$_3$), 2.01 (s, 6H, C(C*H*$_3$) NAr), 0.11 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), −0.49 (br, 4H, C*H*$_2$SiMe$_3$). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C): δ 164.0 (2C, HC(*C*(Me)NAr)$_2$), 151.7 (2C, *ipso*-2-OMe-*C*$_6$H$_4$), 138.2 (2C, *ipso*-2-OMe-C$_6$H$_4$), 125.2 (2C, 2-OMe-*C*$_6$H$_4$), 124.4 (2C, 2-OMe-*C*$_6$H$_4$), 123.3 (2C, 2-OMe-*C*$_6$H$_4$), 111.5 (2C, 2-OMe-*C*$_6$H$_4$), 104.1 (1C, H*C*(C(Me)NAr)$_2$). 57.6 (2C, ArO*C*H$_3$), 30.6 (1C, *C*H$_2$SiMe$_3$), 30.2 (1C, *C*H$_2$SiMe$_3$), 23.4 (2C, C(*C*H$_3$) NAr), 4.3 (6C, CH$_2$Si(*C*H$_3$)$_3$). IR (KBr pellet): ν 3061-(w), 2948(m), 2839(w), 1630(w), 1527(m), 1482(m), 1451(m), 1388(m), 1308(w), 1272(m), 1236(m), 1193(w), 1175(m), 1114-(m), 1046(w), 1017(m), 930(m), 858(m), 790(m), 745(m), 695(w) cm^{-1}. Anal. Calcd for C$_{27}$H$_{43}$N$_2$O$_2$Si$_2$Y (%): C, 56.62; H, 7.57; N, 4.89. Found: C, 56.33; H, 7.48; N, 4.64.

Polymerization of *rac*-Lactide. A typical procedure for polymerization of *rac*-LA was performed in a 25 mL round flask in a glovebox. To a stirred solution of D,L-LA (0.50 g, 3.47 mmol) in 1.50 mL of THF was added a THF solution (0.5 mL) of complex **1** (13.37 mg, 0.017 mmol, [LA]/[Y] = 200:1, [LA] = 1.75 mol/L). The polymerization took place immediately at room temperature. The system became viscous in a few minutes and kept stirring for 1 h and then was terminated by 1.0 mL of HCl/CH$_3$OH/CHCl$_3$ (0.1/10/60 v/v). The viscous solution was quenched by an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40 °C for 24 h *in vacuo* to give polymer product (0.50 g, 100%).

The molecular weight and the molecular weight distribution of the resulting polymer were determined by GPC. The tacticity of the PLA was calculated according to the methine region homonuclear decoupling ^{1}H NMR spectrum.

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Supporting Information Available: CIF file and crystallographic data for complexes **1**−**5** and **7** including atomic coordinates and anisotropic thermal parameters, ORTEP drawings of X-ray structures for complexes **2**−**4**, ^{1}H and ^{13}C NMR spectra for complexes **6**−**8**, which have not been characterized by X-ray diffraction analysis, ^{1}H−^{1}H COSY and DEPT ^{13}C NMR spectra for active species of racemic lactide oligomer attaching to complex **1**, and GPC curves and homonuclear decoupled ^{1}H NMR spectra of the represented samples are available free of charge via the Internet at http://pubs.acs.org.

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