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Phosphinimino-amino Magnesium Complexes: Synthesis and Catalysis of Heteroselective ROP of *rac*-Lactide

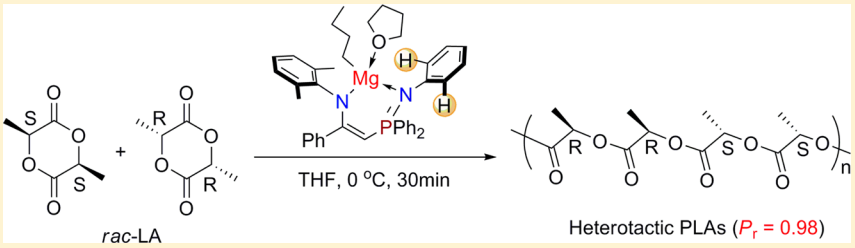
Hongyan Xie,[†,‡] Zehuai Mou,[†,‡] Bo Liu,[†] Ping Li,[§] Weifeng Rong,[†,‡] Shihui Li,[†] and Dongmei Cui*[,†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

[‡]University of Chinese Academy of Sciences, Changchun Branch, Changchun 130022, People's Republic of China

[§]Jinzhou City Health School, Beijing Road 4-26, Jinzhou, Liaoning 121001, People's Republic of China

Supporting Information

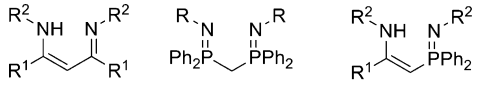


ABSTRACT: Alkane elimination reactions of phosphinimino-amine ligands HL^{1-8} ((2,6-Me_2-C_6H_3NH)C(Ph)=CHPPh_2(NAr) (Ar = C_6H_5 (HL^1); 2,6-Me_2-C_6H_3 (HL^2); 2,6-Et_2-C_6H_3 (HL^3); 2,6-^{i}Pr$_2$-C_6H_3 (HL^4); 2-OMe-C_6H_4 (HL^5); 2-Cl-C_6H_4 (HL^6); 3-CF_3-C_6H_4 (HL^7); 4-MeO-C_6H_4 (HL^8)) with Mg^nBu_2, respectively, afforded a series of phosphinimino-amine-based complexes L^{1-8}Mg^{n}Bu(THF) (**1**−**8**) by releasing butane. Complexes **1**−**8** are phosphinimino-amine-ligated THF-solvated mono(alkyl)s, among which **1**−**4** adopt twisted tetrahedral geometries, whereas **5** contains a trigonal bipyramido geometry core. Complexes **1**−**8** all display high activity for the ring-opening polymerization of *rac*-lactide. The molecular weights of the resulting PLA are close to the theoretic values, and the molecular weight distributions are narrow. Moreover, these complexes show medium to high heteroselectivity, which, interestingly, increases with the decrease of the ligand steric hindrance; thus, complex **1**, bearing a less bulky ligand, exhibits a heteroselectivity of P_r = 0.98, the highest value of a magnesium-based initiator achieved to date. The kinetics study showed that the polymerization rate is first-order dependent on both monomer and initiator concentrations, and the overall rate equation is $-d[LA]/dt = 3.78\ M^{-1}\ s^{-1}\ [LA][Mg]$.

INTRODUCTION

The development of environmentally benign and renewable materials has become more and more urgent because of white pollution and shortages of source and energy problems encountered by our society.[1] Polylactides (PLAs) are one of the most promising biodegradable and biocompatible synthetic materials arising from biosources, having been widely used in packaging, agriculture, medicine, pharmaceutics, and tissue engineering.[1c,2] The applications are strongly dependent on the microstructures of PLA.[1e] Ring-opening polymerization (ROP) of lactide (LA) catalyzed by single-site catalysts has been adopted as the most important manner in which to obtain PLAs with tailor-made microstructures such as controllable molecule weight and narrow molecule weight distribution as well as stereoregularity when *rac*-LA or *meso*-LA is employed, in particular, multiblocks and topological microstructures.[3] Therefore for the past decades, many efforts have been made to develop novel organometallic complexes that facilitate enhancing catalytic activity and specific selectivity.[4] *β*-Diketiminato compounds (Chart 1, BDI) and their derivatives have been widely used as "hard" donor ligands in the synthesis of organometallic precursors,[5] because they are monoanionic chelating ligands having similar electronics to the cyclopentadienyl anion, and their steric and electronic effects can be swiftly tuned via choosing appropriate starting reagents.[6] BDI-supported zinc[7] and magnesium[8] complexes, whether in the dimeric or monomeric THF-solvate coordination mode, have been proved to be highly active and heteroselective for the ROP of *rac*-LA. Recently, modifying *β*-diketiminato frameworks by replacing the carbon atoms in BDI with "large" and "soft" phosphorus atoms to increase the steric bulk and lower the electron density of the metal centers has led to generating bis(phosphinimino)methane (Chart 1, BPI) and phosphinimino-amine (Chart 1, PIA) ligands. The BPI-stabilized zinc aryloxyl and triphenylmethoxyl complexes have been reported

Chart 1



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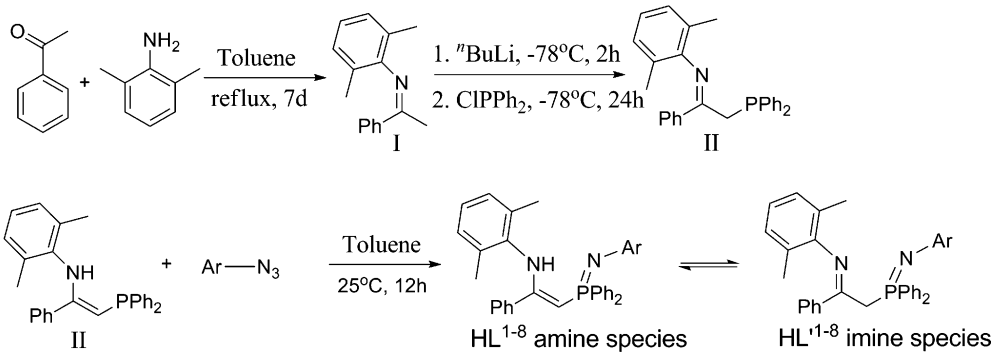
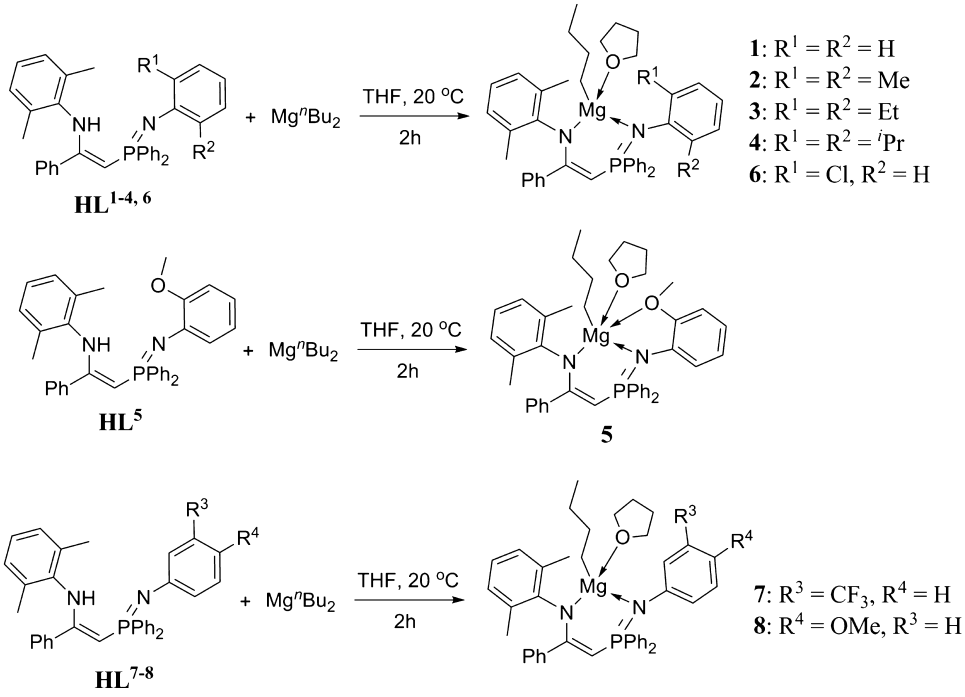
Scheme 1. Synthesis of Ligands HL^{1-8}



Ar = Ph, HL^1; Ar = 2,6-Me_2-Ph, HL^2;
Ar = 2,6-Et_2-Ph, HL^3; Ar = 2,6-$^i Pr_2$-Ph, HL^4;
Ar = *o*-MeOPh, HL^5; Ar = *o*-ClPh, HL^6;
Ar = *m*-CF_3Ph, HL^7; Ar = *p*-MeOPh, HL^8.

Scheme 2. Preparation of Complexes 1−8



to be highly active for ROP of *rac*-LA, although providing atactic PLA.[9] The coordination chemistry of PIA ligands to Li, Pd, Ni, Sc, and Al metals has been investigated recently in olefin polymerization and the ROP of ε-caprolactone;[10] however, the analogous magnesium complexes have remained unexplored. In addition, although aluminum, zinc, and lanthanide-element-based complexes have been reported to be highly active,[11] and in some cases specifically selective,[4f−h,12] abundant, cheap, and biobenign magnesium-based precursors possessing high activity and specific selectivity are still scarce.[4c,13] Herein, we report the synthesis of magnesium complexes bearing PIA ligands ((2,6-Me_2-C_6H_3NH)C(Ph)═CHPPh_2(═NAr)), which exhibit unique structures and excellent heteroselectivity for the ROP of *rac*-LA.

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes 1−6. Compound **I** was generated by the condensation reaction of 2,6-dimethylaniline and acetophenone. Lithiation of compound **I** by ^{n}BuLi and further treatment with $ClPPh_2$ gave compound **II**. Staudinger reaction between compound **II** and the corresponding azides afforded the PIA ligands HL^{1-8} (Scheme 1, HL'^{1-8} are the isomers).[10a,11] In the ^{1}H NMR spectrum of HL^1, two doublets at 4.68 (major) and 3.89 (minor) ppm are arising from the methide proton C*H*PPh_2; the methyl protons CH_3-Ph give two singlet signals at 1.91 (major) and 1.85 (minor) ppm; the singlet at 9.75 ppm can be attributed to a N-H proton. In the ^{31}P NMR spectrum, there are also two singlets at 16.47 (major) and 14.72 (minor) ppm. These weak resonances are attributed to the imine species (HL'^1). The amine species HL^1 and imine species HL'^1 exist in a HL^1-to-

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HL′[1] ratio of 87:13 (Scheme 1). The ratio of amine-to-imine species varies with the substituents; thus, HL[2−5]-to-HL′[2−5] is 86:14 and HL[6]-to-HL′[6] is 93:7, while HL[7,8]-to-HL′[7,8] is 87:13.

Treatment of these ligands with 1.1 equiv of Mg^{n}Bu$_2$ afforded the corresponding PIA-supported magnesium complexes [L[1−8]Mg^{n}Bu(THF)] (**1**−**8**) in 53−78% yields (Scheme 2). Complexes **1**−**8** are soluble in THF and toluene but insoluble in *n*-hexane. The NMR spectrum analyses of complexes **1**−**8** are informative for the formation of mono(alkyl) species. The *α*-methylene protons of Mg-C*H*$_2$(CH$_2$)$_2$CH$_3$ give an AA′XX′ spin resonance centered at *δ* 0.28 (**1**), 0.26 (**2**), 0.18 (**3**), −0.11 (**4**), −0.30 (**5**), −0.06 (**6**), 0.27 (**7**), and 0.24 (**8**) ppm, respectively, which are comparable to that in the BDI-Mg^{n}Bu complex.[8b] The methine proton C*H*-PPh$_2$ gives a doublet resonance ($^2J_{P-H}$ = 20.6−24.5 Hz) due to coupling with the phosphorus atom. The coupling constants of complexes **1**−**8** are comparable to the complexes PIA-Al (PIA = Ar-NC(Ph)═CHP(Ph$_2$)═N-Ar) and LZnEt (L = *o*-(OC(R)═CHP(Ph$_2$)═N)C$_6$H$_4$(3,5-Me$_2$C$_3$HN$_2$)) (23−26 Hz).[10a,14] For complex **5**, the methoxyl group −OC*H*$_3$ shows a singlet at *δ* 3.25 ppm, shifting downfield slightly compared to the free HL[5] at *δ* 3.10 ppm in C$_6$D$_6$, suggesting the weak coordination of the methoxyl oxygen to the central metal in solution.[5f] Complexes **1**−**8** reveal singlet resonances in their ^{31}P NMR spectra at *δ* 33.28 (**1**), 29.35 (**2**), 30.01 (**3**), 31.55 (**4**), 31.71 (**5**), 34.66 (**6**), 34.09 (**7**), and 33.74 (**8**) ppm, respectively, however, which are close to each other, suggesting the electronics around the phosphorus atom in these molecules is similar.

The solid-state structures of complexes **1**−**5** were established by single-crystal X-ray diffraction analyses as shown in Figures 1, 2 (complexes **1**, **5**), and S1−3 (complexes **2**−**4**) along with the selected bond lengths and bond angles. Complexes **1**−**4** are structural analogues, where the magnesium ion bonds to an alkyl moiety, a THF molecule, and a PIA ligand in an *N,N*-bidentate chelating mode, adopting a twisted tetrahedral geometry. The ligand nitrogen atoms, THF oxygen atom, and alkyl carbon atom occupy the apexes, while the Mg^{2+} ion sits in

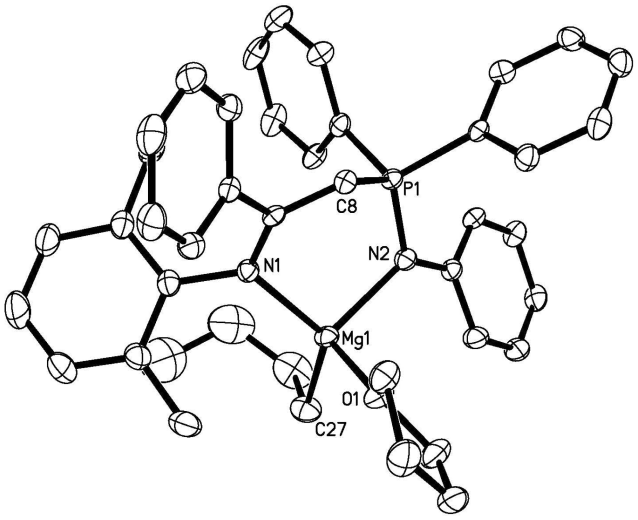

Figure 1. X-ray structure of complex **1** (thermal ellipsoids at the 35% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) 2.093(2), Mg(1)−N(2) 2.106(3), Mg(1)−C(27) 2.130(3), Mg(1)−O(1) 2.076(2), P(1)−N(2) 1.619(2); N(1)−Mg(1)−N(2) 101.79(9), O(1)−Mg(1)−C(27) 108.76(12), C(7)−C(8)−P(1) 126.6(2).

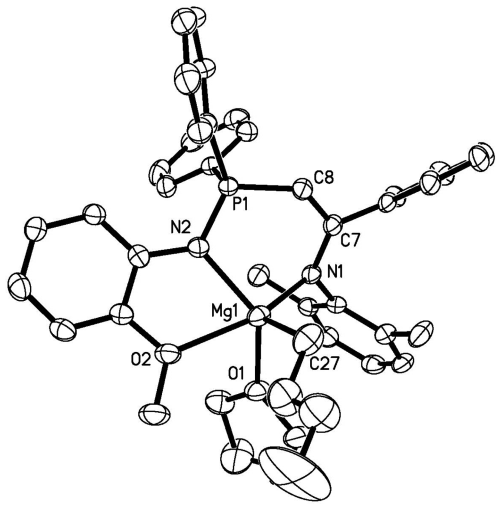

Figure 2. X-ray structure of complex **5** (thermal ellipsoids at the 35% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−N(1) 2.202(4), Mg(1)−N(2) 2.110(3), Mg(1)−C(27) 2.167(5), Mg(1)−O(1) 2.118(3), Mg(1)−O(2) 2.305(3), P(1)−N(2) 1.617(3); N(1)−Mg(1)−N(2) 101.79(9), O(1)−Mg(1)−C(27) 108.76(12), N(2)−Mg(1)−O(2) 71.36(12), C(27)−Mg(1)−O(2) 99.25(17), C(7)−C(8)−P(1) 126.6(2).

the center of the tetrahedron. For complex **5**, the Mg^{2+} ion *σ*-bonds to an alkyl moiety, a coordinating *N,N,O*-tridentate ligand, and a solvated THF molecule, generating a trigonal bipyramidal geometry core. All the metal alkyl bond distances Mg(1)−C(27) of these complexes (**1**, 2.130(3) Å; **2**, 2.156(4) Å; **3**, 2.136(4) Å; **4**, 2.134(3) Å; **5**, 2.167(5) Å) fall in the reasonable range of those reported in the literatures.[8b,11f] The phosphinimine P═N double-bond lengths (1.619(2) Å (**1**), 1.603(3) Å (**2**), 1.597(4) Å (**3**), 1.601(2) Å (**4**), 1.617(3) Å (**5**)) are comparable to the P═N bonds in PIA-Al complexes [Me$_2$Al(N(Ar)C(R)═CHP(Ph$_2$)═N(Ar))] (av P═N double-bond length 1.62 Å) and in the other previously reported literature,[10a,15] which are also similar to that in the amino isomer of the neutral PIA compound [(2,6-^{i}Pr$_2$-C$_6$H$_3$NH)C(Me)═CHP(Ph$_2$)═N(2,6-^{i}Pr$_2$-C$_6$H$_3$)] (1.590(3) Å),[16] but longer than that in the localized imine isomer [(2,6-^{i}Pr$_2$-C$_6$H$_3$)N═C(Me)CH$_2$P(Ph$_2$)═N(2,6-Me$_2$-C$_6$H$_3$)] (1.562(2) Å),[10c] suggesting the partial delocalization of the electrons over the NPCCN skeleton.[17] The bond angle of N(1)−Mg(1)−N(2), 101.79(9)° for **1**, 96.14(11)° for **2**, 96.20(14)° for **3**, 97.58(9)° for **4**, and 93.11(13)° for **5**, varies significantly with the substituents of the ligands; the bigger the substituents, the smaller the angle, which might be attributed to the steric repulsion between the substituents and the alkyl ligand and the coordinated THF molecule. Noteworthy was that the smaller the N1−Mg1−N2 bond angle, the more open the environment around the central metal ion, which affects significantly the specific selectivity of the metal center (*vide infra*).

ROP of *rac*-LA. The catalytic performances of complexes **1**−**8** toward the ROP of *rac*-LA in THF were investigated, the representative polymerization results of which are summarized in Table 1. Complexes **1**−**6** and **8** displayed similar catalytic activity, suggesting that the substituents such as the bulky −^{i}Pr, the electron-donating group −OMe, and the weak electron-withdrawing group −Cl hardly affected the activity of the initiators (Table 1, entries 1−8). However, by using complex **7**, the polymerization became sluggish, which might be attributed

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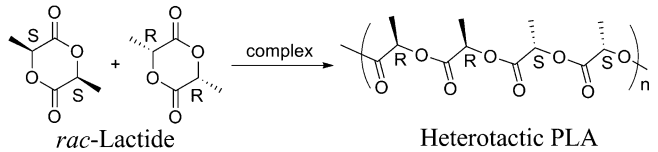
Table 1. ROP of *rac*-LA Initiated by Complexes 1−8[a]



entry	cat	[LA]/[Mg]	temp (°C)	time (min)	conv[b] (%)	$M_{n,cacld}$[c] × 10^{-4}	$M_{n,\ found}$[d] × 10^{-4}	M_w/M_n[d]	P_r[e]
1	**1**	200	25	10	94	2.71	3.09	1.60	0.92
2	**2**	200	25	10	95	2.74	3.44	1.69	0.79
3	**3**	200	25	10	95	2.74	3.92	1.55	0.77
4	**4**	200	25	10	96	2.76	3.48	1.77	0.67
5	**5**	200	25	10	96	2.76	2.76	1.51	0.62
6	**6**	300	25	10	96	4.15	3.77	1.76	0.87
7	**7**	200	25	120	73	2.11	3.45	1.60	0.72
8	**8**	200	25	10	93	2.68	3.25	1.72	0.93
9[f]	**1**	300	25	60	88	3.80	2.80	1.87	0.53
10[g]	**1**	300	25	1440	trace				
11	**1**	300	0	30	89	3.84	8.99	2.28	0.96
12	**1**	100	0	30	81	1.17	3.55	1.63	0.98
13[h]	**1**	50	25	10	97	0.70	1.17	1.59	0.93
14	**1**	100	25	10	92	1.32	2.11	1.70	0.93
15	**1**	300	25	10	95	4.10	4.21	1.59	0.92
16	**1**	400	25	10	94	5.41	5.08	1.58	0.91
17	**1**	500	25	10	94	6.77	6.47	1.45	0.92
18[i]	**1**	800	25	60	90	10.37	8.50	1.54	0.90
19[i]	**1**	1000	25	60	92	13.25	10.01	1.38	0.90

[a]Polymerization conditions: THF 5 mL, $[Mg]_0$ 10 μmol. [b]Determined by ^{1}H NMR spectroscopy. [c]$M_{n,cald}$ = [LA]/[Mg] × 144.13 × conv (%) + 57.12(−^{n}Bu). [d]Determined by size exclusion chromatography (SEC) against polystyrene standard. M_n values were obtained using a correction factor for polylactides (0.58). [e]P_r is the probability of racemic linkages between monomer units determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum. [f]In toluene. [g]In dichloromethane. [h]$[Mg]_0$ = 30 μmol, 20 min. [i]$[Mg]_0$ = 5 μmol, 60 min.

to the strong electron-withdrawing substituent $-CF_3$ in the molecule to reduce the electron density around the central metal. The polymerization when complex **1** was chosen as the initiator proceeded smoothly under various monomer-to-initiator ratios ranging from 50 to 1000 to provide PLAs with molecular weights close to the theoretic values and moderate molecular weight distributions (M_w/M_n = 1.38−1.70) (Table 1, entries 13−19), indicating a controlled process. In contrast to their negligible effect on the catalytic activity, the substituents aroused significant change to the specific selectivity of the attached central metal. Complex **1**, bearing the less bulky ligand, exhibited the highest heteroselectivity for the polymerization of *rac*-LA to give heterotactic PLA with a racemic enchainment of monomer units of P_r = 0.92. When the polymerization was carried out at a lower temperature (0 °C), the selectivity increased up to P_r = 0.98, the highest value of a magnesium-based catalyst achieved to date (Table 1, entry 12). For complexes **2**−**4**, the steric hindrance increased from the methyl-substituted ligand to the bulky ^{i}Pr-substituted ligand and the heterotactic selectivity dropped from 0.79 to 0.67 (Table 1, entries 2−4), which was in contrast to many lanthanide-element-based complexes that display high heteroselectivity when bearing bulky ligands.[4h,18] This might be ascribed to the crystallographic geometry of the complexes where the more bulkier the ligand, the more open the steric environment around the central metal ion, due to the steric repulsion (evidenced by the bite-angle N(1)−Mg(1)−N(2): 101.79(9)° for **1**, 96.14(11)° for **2**, 96.20(14)° for **3**, and 97.58(9)° for **4**, *vide supra*), which allows the coordination of the *rac*-LA monomer to the initiation center more freely, to result in a specifically irregular product. This could explain why complex **6** also displayed a higher specific selectivity because of the smaller chloride-substituted ligand. As expected, complex **8** was highly heteroselective (P_r = 0.93, Table 1, entry 8), because the methoxyl substituent is on the *para* position of the aromatic ring, which hardly impacts the steric environment of the ligand. The case of complex **5** was complicated: it has the smallest N(1)−Mg(1)−N(2) bond angle of 93.11(13)°, which was the main reason for its lowest selectivity (P_r = 0.62, Table 1, entry 5), while it also has a ligand with a methoxyl side arm coordinating to the Mg^{2+} center that was designed to increase the selectivity to mimic the role of THF (from the polymerization medium). It has been demonstrated previously through the amino−amino-bis(phenols) yttrium alkyl initiation systems that the reversible coordination of the THF molecule to the central metal active species facilitates the orientation of the coordination of *rac*-LA and thus increases the heteroselectivity.[4e,g,h,18a−c] Thus, the low selectivity of complex **5** means that the interaction between the methoxyl group and Mg^{2+}, which is stronger and irreversible, is different from THF.[4e] This could be proved further by performing the polymerization in toluene and dichloromethane, whereupon both the catalytic activity and heteroselectivity decreased dramatically (Table 1, entries 9, 10). The end-group of a PLA oligomer produced by complex **1** ($[LA]_0/[1]_0$ = 20, THF, 20 °C) was analyzed by its ^{1}H NMR spectrum (Figure S30), which revealed the resonances from a hydroxyl group and ^{n}Bu group (from the initiator), respectively, suggesting that the ring-opening polymerization of *rac*-LA took place in the coordination−insertion mechanism.

Kinetics Studies of Polymerization of *rac*-LA. Fixing the initial concentration of monomer *rac*-LA at $[LA]_0$ = 0.333 M,

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polymerizations under various concentrations of complex **1** ([Mg] = 0.834−2.09 mM) were performed in THF at 20 °C. The conversions at different polymerization times were recorded according to ^{1}H NMR spectroscopy analysis. The results showed that the plots of $\ln[LA]_0/[LA]_t$ vs time are linear in a wide range of $[LA]_0$, indicating they proceeded with first-order dependence on monomer concentration (Figure 3,

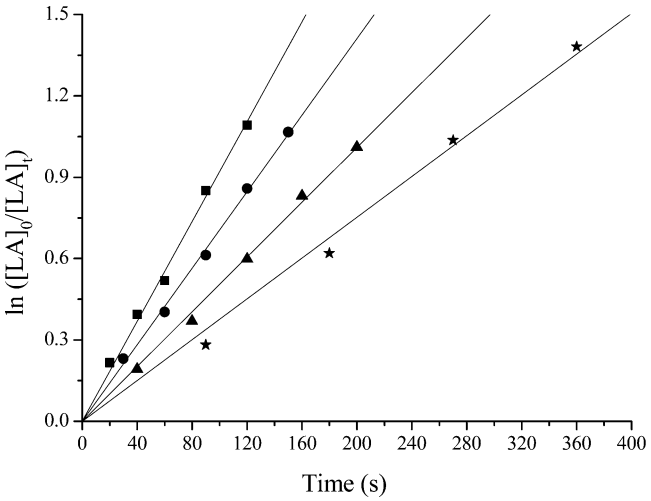

Figure 3. First-order kinetic plots for *rac*-LA polymerizations versus time in THF at 20 °C with different concentrations of complex **1** as initiator ($[LA]_0$ = 0.333 M, squares, [Mg] = 2.09 mM, k_{app} = 9.21 × 10^{-3} s^{-1}, R^2 = 0.998; circles, [Mg] = 1.67 mM, k_{app} = 7.06 × 10^{-3} s^{-1}, R^2 = 0.999; triangles, [Mg] = 1.25 mM, k_{app} = 5.05 × 10^{-3} s^{-1}, R^2 = 0.999; stars, [Mg] = 0.834 mM, k_{app} = 3.76 × 10^{-3} s^{-1}, R^2 = 0.997).

the apparent rate constants k_{app} = (3.76−9.18) × 10^{-3} s^{-1}). Thus, the polymerization rate equation can be depicted as $-d[LA]/dt = k_{app}[LA]$, where $k_{app} = k_p[Mg]^x$ and k_p is the rate constant. Plotting ln k_{app} vs ln[Mg] allowed us to determine the order in initiator concentration from the slope of the fitted line, x = 0.98, as shown in Figure 4 (R^2 = 0.982). Eventually, the polymerization of *rac*-LA initiated by complex **1** showed first-order dependence on both monomer and initiator concentrations: $-d[LA]/dt = k[LA][Mg]$. The intercept of the regression line deduces a polymerization rate constant of k_p = 3.78 M^{-1} s^{-1} at 20 °C in THF, which is comparable to those for

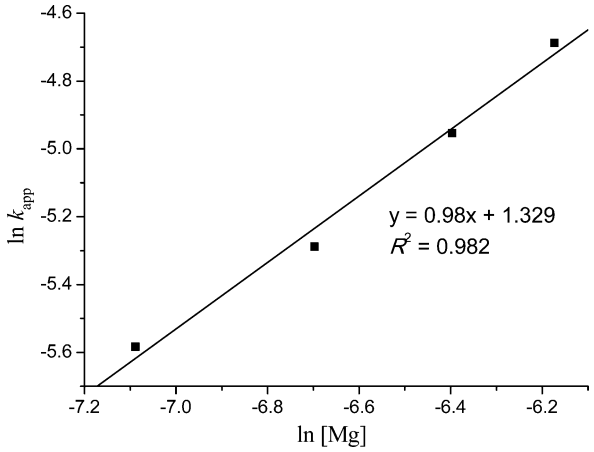

Figure 4. Plot of ln k_{app} versus ln[Mg] for the polymerization of *rac*-LA with complex **1** as the initiator (THF, 20 °C, $[LA]_0$ = 0.333 M).

the β-diketiminato Mg alkyl system (k_p = 10.7 M^{-1} s^{-1}, 25 °C in dichloromethane)[8b] and the heteroscorpionate magnesium alkyls [Mg(κ^3-pbp^{t}amd)(CH_2SiMe_3)] and [Mg(κ^3-tbp^{t}amd)-(CH_2SiMe_3)] systems (1.73 and 1.27 M^{-1} s^{-1}, 20 °C in THF),[19] but much higher than that for the magnesium alkoxide ($NNONNMg_2$)OEt system (3.9 × 10^{-3} M^{-1} s^{-1} in dichloromethane at 20 °C),[20] positioning the current magnesium-based initiators at top high activity, and moreover, with unprecedented high selectivity.

CONCLUSION

We have demonstrated that the phosphinimino-amine-stabilized magnesium complexes are extremely active toward the ROP of *rac*-LA to provide PLAs with controllable molecular weights and narrow molecular weight distributions, in particular a heterotacticity of up to P_r = 0.98, the highest value reported to date by using a magnesium-based initiator. The change of ligand steric hindrance and bulkiness seems to have a negligible influence on the catalytic activity of these complexes but affects the specific selectivity significantly: the smaller the steric bulkiness of the ligand, the higher the selectivity of the attached active magnesium center, because the repulsion of the large substituents on the ligands leaves more open space for the metal center to allow the monomer to coordinate to the active centers more randomly. This work sheds new light on designing catalyst precursors for specifically selective polymerizations and focuses on the geometry of the ligand generated around the metal center.

EXPERIMENTAL SECTION

General Methods. All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen gas filled MBraun glovebox. Toluene, tetrahydrofuran, and *n*-hexane were distilled under nitrogen from sodium/benzophenone. Deuterated NMR solvents were purchased from Cambridge Isotopes, dried over Na (for C_6D_6) and molecular sieves (for $CDCl_3$), and stored in the glovebox. Acetophenone, chlorodiphenylphosphine, aniline, 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, 2-methoxyaniline, 2-choloaniline, 3-$CF_3C_6H_4$, and 4-methoxyaniline were obtained from commercial sources and distilled under nitrogen prior to use. Compounds 2,6-Me_2-C_6H_3N=C(Me)Ph and 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and all the azides[21] were synthesized via a modified procedure according to the literature. Mg^nBu_2 was purchased from Sigma-Aldrich. *rac*-Lactide (Aldrich) was recrystallized three times in dry ethyl acetate.

Instruments and Measurements. Organometallic samples for NMR measurements were prepared in NMR tubes and sealed with paraffin film in the glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P) spectrometer. Homonuclear decoupled ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). The number-average molar mass (M_n) and the molecular weight distributions (M_w/M_n) of the polymer were measured by size exclusion chromatography (SEC) on a TOSOH HLC-8220 SEC instrument (column: Super HZM-H × 3) at 40 °C using THF as eluent with a flow rate of 0.35 mL/min; the values were relative to polystyrene standards.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 °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

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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 calculated positions and were included in the structure calculations without further refinement of the parameters.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=NPh (HL^1). To a THF (25 mL) solution of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 was added dropwise 1.43 g (12 mmol) of PhN_3. N_2 evolution commenced immediately, and the mixture was stirred at 50 °C for 24 h. Removal of THF under vacuum left a yellow, oily solid. The solid was washed with 30 mL of hexane, and then the suspension was stirred for 1 h at ambient temperature. Filtering, washing with 2 × 20 mL of hexane, and evaporating the residual solvents afforded HL^1 as a pale yellow solid (4.28 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.75 (s, 1H, N*H*), 7.94−7.90 (m, 4H, *o*-PPh_2), 7.50−7.42 (m, 6H, *o*-C_6H_5, *m*-PPh_2), 7.27−7.24 (m, 2H, *p*-PPh_2), 7.20−7.18 (m, 3H, *m,p*-C_6H_5), 7.03−6.99 (m, 2H, *m*-$C_6H_3Me_2$), 6.87−6.79 (m, 5H, *o,m,p*-NC_6H_5), 6.64 (m, 1H, *p*-$C_6H_3Me_2$), 4.68 (d, $^2J_{P-H}$ = 21.2 Hz, 1H, P*CH*), 1.91 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 16.47 ppm (s). Anal. Calcd for $C_{34}H_{31}N_2P$: C, 81.90; H, 6.27; N, 5.62. Found: C, 81.72; H, 6.23; N, 5.65.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(2,6-Me_2-C_6H_3) (HL^2). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^2 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 1.76 g (12 mmol) of (2,6-Me_2-C_6H_3)N_3 as a pale yellow solid (4.48 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.97 (br, 1H, N*H*), 7.78−7.73 (m, 4H, ArH), 7.43−7.35 (m, 5H, ArH), 7.27−7.25 (m, 2H, ArH), 7.21−7.12 (m, 4H, ArH), 6.87−6.68 (m, 5H, ArH), 6.61−6.56 (m, 1H, ArH), 4.72 (d, $^2J_{P-H}$ = 22.2 Hz, 1H, P*CH*), 2.07 (s, 6H, $C_6H_3(CH_3)_2$), 2.00 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 8.38 ppm (s). Anal. Calcd for $C_{36}H_{35}N_2P$: C, 82.10; H, 6.70; N, 5.32. Found: C, 81.95; H, 6.76; N, 5.28.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(2,6-Et_2-C_6H_3) (HL^3). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^3 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 2.11 g (12 mmol) of (2,6-Et_2-C_6H_3)N_3 as a pale yellow solid (4.65 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.13 (br, 1H, N*H*), 7.73−7.68 (m, 4H, ArH), 7.42−7.34 (m, 5H, ArH), 7.28−7.26 (m, 2H, ArH), 7.23−7.13 (m, 5H, ArH), 6.90−6.88 (m, 2H, ArH), 6.81−6.78 (m, 2H, ArH), 6.73−6.70 (m, 1H, ArH), 4.64 (d, $^2J_{P-H}$ = 22.3 Hz, 1H, P*CH*), 2.50 (q, $^3J_{H-H}$ = 7.6 Hz, 4H, $C_6H_3(CH_2Me)_2$), 2.03 (s, 6H, $C_6H_3(CH_3)_2$), 0.92 (t, $^3J_{H-H}$ = 7.5 Hz, 6H, $C_6H_3(CH_2CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ −4.45 ppm (s). Anal. Calcd for $C_{38}H_{39}N_2P$: C, 82.28; H, 7.09; N, 5.05. Found: C, 81.98; H, 7.03; N, 5.07.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(2,6-^{i}Pr_2-C_6H_3) (HL^4). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^4 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 2.44 g (12 mmol) of (2,6-^{i}Pr_2−C_6H_3)N_3 as a pale yellow solid (4.72 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.35 (br, 1H, N*H*), 7.71−7.66 (m, 4H, ArH), 7.43−7.35 (m, 6H, ArH), 7.42−7.29 (m, 2H, ArH), 7.21−7.14 (m, 4H, ArH), 6.91−6.89 (m, 2H, ArH), 6.80−6.78 (m, 3H, ArH), 4.56 (d, $^2J_{P-H}$ = 22.1 Hz, 1H, P*CH*), 3.45 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, *CH*Me_2), 2.04 (s, 6H, $C_6H_3(CH_3)_2$), 0.76 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $C_6H_3(CH(CH_3)_2)_2$. ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ −3.63 ppm (s). Anal. Calcd for $C_{40}H_{43}N_2P$: C, 82.44; H, 7.44; N, 4.81. Found: C, 82.56; H, 7.35; N, 4.77.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(2-OMe-C_6H_4) (HL^5). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^5 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 1.79 g (12 mmol) of (2-OMe-C_6H_4)N_3 as a yellow solid (4.66 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 11.34 (s, 1H, N*H*), 7.88−7.83 (m, 4H, ArH), 7.49−7.41 (m, 5H, ArH), 7.27−7.08 (m, 7H, ArH), 6.88−6.84 (m, 2H, ArH), 6.67−6.52 (m, 4H, ArH), 4.26 (d, $^2J_{P-H}$ = 23.7 Hz, 1H, P*CH*), 3.32 (s, 3H, OCH_3), 2.13 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 6.93 ppm (s). Anal. Calcd for $C_{35}H_{33}N_2OP$: C, 79.52; H, 6.29; N, 5.30. Found: C, 79.27; H, 6.22; N, 5.35.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(C_6H_4-2-Cl) (HL^6). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^6 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 1.84 g (12 mmol) of (2-OMe-C_6H_4)N_3 as a pale yellow solid (4.66 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.22 (s, 1H, N*H*), 7.94−7.89 (m, 4H, ArH), 7.52−7.44 (m, 6H, ArH), 7.23−7.06 (m, 6H, ArH), 6.87−6.75 (m, 4H, ArH), 6.63−6.52 (m, 2H, ArH), 4.45 (d, $^2J_{P-H}$ = 22.7 Hz, 1H, P*CH*), 2.03 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 5.97 ppm (s). Anal. Calcd for $C_{34}H_{33}ClN_2P$: C, 76.61; H, 5.67; N, 6.65. Found: C, 76.75; H, 5.61; N, 6.62.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(C_6H_4-3-CF_3) (HL^7). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^7 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 2.24 g (12 mmol) of (3-CF_3-C_6H_4)N_3 as a yellow solid (4.73 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.17 (s, 1H, N*H*), 7.95−7.90 (m, 4H, ArH), 7.50−7.44 (m, 6H, ArH), 7.30−7.05 (m, 6H, ArH), 6.99−6.77 (m, 6H, ArH), 4.77 (d, $^2J_{P-H}$ = 20.8 Hz, 1H, P*CH*), 1.83 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 3.48 ppm (s). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ −62.68 ppm (s). Anal. Calcd for $C_{35}H_{30}N_2F_3P$: C, 74.19; H, 5.34; N, 4.94. Found: C, 74.28; H, 5.30; N, 4.96.

Synthesis of 2,6-Me_2-C_6H_3NHC(Ph)=CHP(Ph_2)=N(C_6H_4-4-OMe) (HL^8). Following a similar procedure to that described for the preparation of ligand HL^1, the ligand HL^8 was isolated from the Staudinger reaction of 4.07 g (10 mmol) of 2,6-Me_2-C_6H_3N=C(Ph)CH_2PPh_2 and 1.79 g (12 mmol) of (4-OMe-C_6H_4)N_3 as a yellow solid (4.42 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.76 (s, 1H, N*H*), 7.93−7.88 (m, 4H, ArH), 7.48−7.40 (m, 5H, ArH), 7.26−7.09 (m, 7H, ArH), 6.82−6.77 (m, 4H, ArH), 6.64−6.61 (m, 2H, ArH), 4.69 (d, $^2J_{P-H}$ = 21.0 Hz, 1H, P*CH*), 3.69 (s, 3H, OCH_3), 1.92 (s, 6H, $C_6H_3(CH_3)_2$). ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ 2.43 ppm (s). Anal. Calcd for $C_{35}H_{33}N_2OP$: C, 79.52; H, 6.29; N, 5.30. Found: C, 79.36; H, 6.23; N, 5.26.

Synthesis of $L^1Mg^nBu(THF)$ (1). To a hexane solution (3 mL) of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) was added dropwise HL^1 (0.498 g, 1 mmol in 10 mL of THF) at room temperature. The mixture was stirred for 2 h at room temperature to afford a clear yellow solution. Evaporation of solvent gave crystalline solids, which were washed with a small amount of hexane to remove impurities and dried *in vacuo* to give yellow solids of complex **1** (0.475 g, 73%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.92−7.87 (m, 4 H, *o*-PPh_2), 7.42−7.40 (m, 2H, ArH), 7.16 (m, 1H, ArH), 7.12−7.07 (m, 7H, ArH), 7.01 (m, 2H, ArH), 6.95−6.86 (m, 3H, ArH), 6.80 (m, 2H, ArH), 6.69 (m, 2H, ArH), 3.92 (d, $^2J_{P-H}$ = 22.9 Hz, 1H, P*CH*), 3.60 (m, 4H, THF), 2.17−2.10 (m, 8H, β-^{n}Bu and $C_6H_3(CH_3)_2$), 1.81 (m, 2H, γ-^{n}Bu), 1.24 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, δ-^{n}Bu), 1.17 (m, 4H, THF), 0.29 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 174.97 (s, N-C), 150.20 (C-Ar), 149.92 (d, J_{PC} = 7.1 Hz, *ipso*-PPh2), 143.58 (d, J_{PC} = 15.4 Hz, *ipso*-PPh_2), 133.90 (C-Ar), 133.28 (d, J_{PC} = 9.6 Hz, C-Ar), 133.00 (C-Ar), 132.77 (C-Ar), 131.34 (d, J_{PC} = 2.6 Hz, C-Ar), 128.93 (C-Ar), 128.48 (C-Ar), 128.39 (C-Ar), 128.37 (C-Ar), 128.23 (C-Ar), 128.06 (C-Ar), 127.46 (C-Ar), 123.98 (d, J_{PC} = 13.9 Hz, C-Ar), 122.76 (C-Ar), 119.74 (C-Ar), 69.66 (d, J_{PC} = 132.8 Hz, P*CH*), 68.55 (THF), 33.65 (δ-^{n}Bu), 32.34 (γ-^{n}Bu), 25.40 (THF), 19.88 ($C_6H_3(CH_3)_2$), 14.88 (β-^{n}Bu), 9.93 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 33.28 ppm (s). Anal. Calcd for $C_{88}H_{102}Mg_2N_4O_3P_2$: C, 76.91; H, 7.48; N, 4.08. Found: C, 76.68; H, 7.42; N, 4.05.

Synthesis of $L^2Mg^nBu(THF)$ (2). Following a similar procedure to that described for the preparation of complex **1**, complex **2** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^2 (0.526 g, 1 mmol in 10 mL of THF) as a yellow solid

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(0.359 g, 53%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.87−7.86 (m, 4H, *o*-PPh_2), 7.72−7.70 (m, 2H, ArH), 7.16 (m, 1H, ArH), 7.11−7.05 (m, 5H, ArH), 7.02−6.95 (m, 2H, ArH), 6.95−6.90 (m, 1H, ArH), 6.86 (m, 4H, ArH), 6.82−6.75 (m, 1H, ArH), 6.71 (m, 1H, ArH), 3.70 (d, $^2J_{P-H}$ = 20.7 Hz, 1H, P*CH*), 3.15 (m, 4H, THF), 2.57 (s, 6H, P=N$C_6H_3(CH_3)_2$), 2.13 (s, 6H, $C_6H_3(CH_3)_2$), 1.88 (m, 2H, γ-^{n}Bu), 1.34 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, δ-^{n}Bu), 0.99 (m, 4H, THF), 0.26 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 176.01 (s, N-C), 150.85 (C-Ar), 146.11 (d, J_{PC} = 9.8 Hz, *ipso*-PPh_2), 144.68 (d, J_{PC} = 16.0 Hz, *ipso*-PPh_2), 136.34 (d, J_{PC} = 6.3 Hz, C-Ar), 132.77 (d, J_{PC} = 9.1 Hz, C-Ar), 130.88 (d, J_{PC} = 2.4 Hz, C-Ar), 128.72 (C-Ar), 128.69 (C-Ar), 128.57 (C-Ar), 128.54 (C-Ar), 128.44 (C-Ar), 128.15 (C-Ar), 127.94 (C-Ar), 127.59 (C-Ar), 122.49 (C-Ar), 122.44 (C-Ar), 68.87 (THF), 66.60 (d, J_{PC} = 133.4 Hz, P*CH*), 33.99 (δ-^{n}Bu), 32.92 (γ-^{n}Bu), 24.90 (THF), 20.95 ($C_6H_3(CH_3)_2$), 20.58 ($C_6H_3(CH_3)_2$), 14.80 (β-^{n}Bu), 10.94 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 29.35 ppm (s). Anal. Calcd for $C_{44}H_{51}MgN_2OP$: C, 77.81; H, 7.57; N, 4.12. Found: C, 77.63; H, 7.62; N, 4.08.

Synthesis of L^{3}Mg^{n}Bu(THF) (3). Following a similar procedure to that described for the preparation of complex **1**, complex **3** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^3 (0.554 g, 1 mmol in 10 mL of THF) as a yellow solid (0.459 g, 65%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.87−7.82 (m, 4H, *o*-PPh_2), 7.71−7.68 (m, 2H, ArH), 7.16 (m, 1H, ArH), 7.11−7.05 (m, 5H, ArH), 7.00−6.97 (m, 5H, ArH), 6.94−6.90 (m, 1H, ArH), 6.87 (m, 4H, ArH), 6.72 (m, 1H, ArH), 3.66 (d, $^2J_{P-H}$ = 20.6 Hz, 1H, P*CH*), 3.12 (m, 4H, THF), 2.92 (m, 2H, CH_2Me), 2.58 (s, 6H, $C_6H_3(CH_3)_2$), 2.54 (m, 2H, CH_2Me), 2.08 (m, 2H, β-^{n}Bu), 1.83 (m, 2H, γ-^{n}Bu), 1.30 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, δ-^{n}Bu), 0.97−0.92 (m, 10H, THF and CH_2CH_3), 0.18 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 175.64 (s, N-C), 150.73 (C-Ar), 144.87 (C-Ar), 144.71 (d, J_{PC} = 15.8 Hz, *ipso*-PPh_2), 141.30 (d, J_{PC} = 6.2 Hz, *ipso*-PPh_2), 132.76 (d, J_{PC} = 9.0 Hz, C-Ar), 132.65 (C-Ar), 130.86 (d, J_{PC} = 2.6 Hz, C-Ar), 128.65 (d, J_{PC} = 8.8 Hz, C-Ar), 128.36 (C-Ar), 128.13 (C-Ar), 127.94 (C−Ar), 127.58 (C-Ar), 125.44 (d, J_{PC} = 3.0 Hz, C-Ar), 69.07 (THF), 66.67 (d, J_{PC} = 133.1 Hz, P*CH*), 33.87 (δ-^{n}Bu), 32.87 (γ-^{n}Bu), 25.10 (CH_2CH_3), 24.82 (THF), 20.36 ($C_6H_3(CH_3)_2$), 14.77 (CH_2CH_3), 13.96 (β-^{n}Bu), 10.46 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 30.01 ppm (s). Anal. Calcd for $C_{46}H_{55}MgN_2OP$: C, 78.12; H, 7.84; N, 3.96. Found: C, 77.89; H, 7.80; N, 3.93.

Synthesis of L^{4}Mg^{n}Bu(THF) (4). Following a similar procedure to that described for the preparation of complex **1**, complex **4** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^4 (0.582 g, 1 mmol in 10 mL of THF) as a pale yellow solid (0.446 g, 61%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.75−7.70 (m, 4H, *o*-PPh_2), 7.76 (m, 2H, ArH), 7.16 (m, 2H, ArH), 7.06−6.88 (m, 12H, ArH), 6.75 (m, 1H ArH), 3.87 (m, 2H, $CHMe_2$), 3.69−3.58 (m, 5H, P*CH* and THF), 2.54 (s, 6H, $C_6H_3(CH_3)_2$), 1.71−1.51 (m, 4H, β-^{n}Bu and γ-^{n}Bu), 1.25 (m, 10H, THF and $CH(CH_3)_2$), 1.14 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, δ-^{n}Bu), 0.61 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), −0.11 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 175.21 (N-C), 150.61 (C-Ar), 146.03 (d, J_{PC} = 6.4 Hz, C-Ar), 144.68 (d, J_{PC} = 15.9 Hz, C-Ar), 142.51 (d, J_{PC} = 10.4 Hz, C-Ar), 135.73 (C-Ar), 134.83 (C-Ar), 132.91 (d, J_{PC} = 8.9 Hz, C-Ar), 132.53 (C-Ar), 130.82 (d, J_{PC} = 2.3 Hz, C-Ar), 128.76 (d, J_{PC} = 13.3 Hz, C-Ar), 128.53 (C-Ar), 128.18 (C-Ar), 127.94 (C-Ar), 127.63 (C-Ar), 124.20 (d, J_{PC} = 3.2 Hz, C-Ar), 123.84 (d, J_{PC} = 3.7 Hz, C-Ar), 122.70 (C-Ar), 69.40 (THF), 67.73 (d, J_{PC} = 132.4 Hz, P*CH*), 33.39 (δ-^{n}Bu), 32.73 (γ-^{n}Bu), 28.73 ($CH(CH_3)_2$), 25.43 ($CH(CH_3)_2$), 25.19 (THF), 23.68 ($CH(CH_3)_2$), 20.27 ($C_6H_3(CH_3)_2$), 14.53 (β-^{n}Bu), 10.10 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 31.55 ppm (s). Anal. Calcd for $C_{48}H_{59}MgN_2OP$: C, 78.41; H, 8.09; N, 3.81. Found: C, 78.64; H, 8.01; N, 3.78.

Synthesis of L^{5}Mg^{n}Bu(THF) (5). Following a similar procedure to that described for the preparation of complex **1**, complex **5** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^5 (0.528 g, 1 mmol in 10 mL of THF) as a pale yellow solid (0.531 g, 78%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.01−7.96 (m, 4H, *o*-PPh_2), 7.30−7.28 (m, 2H, ArH), 7.16 (m, 1H, ArH), 7.11−7.10 (m, 5H, ArH), 6.92−6.74 (m, 7H, ArH), 6.67−6.58 (m, 2H, ArH), 6.42−6.40 (m, 1H, ArH), 4.08 (d, $^2J_{P-H}$ = 24.5 Hz, 1H, P*CH*), 3.55 (m, 4H, THF), 3.25 (s, 3H, −O*Me*), 2.02 (s, 6H, $C_6H_3(CH_3)_2$), 1.73 (m, 2H, β-^{n}Bu), 1.58 (m, 2H, γ-^{n}Bu), 1.38 (m, 4H, THF), 1.16 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, δ-^{n}Bu), −0.30 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 174.94 (d, J_{PC} = 3.1 Hz, N-C), 151.03 (d, J_{PC} = 15.8 Hz, C-Ar), 149.25 (C-Ar), 143.71 (d, J_{PC} = 15.2 Hz, C-Ar), 139.77 (d, J_{PC} = 4.7 Hz, C-Ar), 133.61 (C-Ar), 132.70 (C-Ar), 132.59 (d, J_{PC} = 9.8 Hz, C-Ar), 131.76 (d, J_{PC} = 2.5 Hz, C-Ar), 128.98 (d, J_{PC} = 11.7 Hz, C-Ar), 127.67 (C-Ar), 127.38 (C-Ar), 123.02 (d, J_{PC} = 43.4 Hz, C-Ar), 121.47 (d, J_{PC} = 10.0 Hz, C-Ar), 118.71 (C-Ar), 110.33 (C-Ar), 68.03 (THF), 62.06 (d, J_{PC} = 120.7 Hz, P*CH*), 55.30 (OCH_3), 33.36 (δ-^{n}Bu), 32.33 (γ-^{n}Bu), 25.59 (THF), 19.70 ($C_6H_3(CH_3)_2$), 14.81 (β-^{n}Bu), 8.01 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 31.71 ppm (s). Anal. Calcd for $C_{43}H_{49}MgN_2O_2P$: C, 75.82; H, 7.25; N, 4.11. Found: C, 75.67; H, 7.19; N, 4.15.

Synthesis of L^{6}Mg^{n}Bu(THF) (6). Following a similar procedure to that described for the preparation of complex **1**, complex **6** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^6 (0.533 g, 1 mmol in 10 mL of THF) as a pale yellow solid (0.431 g, 63%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.97−7.92 (m, 4H, *o*-PPh_2), 7.57−7.55 (m, 2H, ArH), 7.29−7.27 (m, 1H, ArH), 7.19−7.16 (m, 2H, ArH), 7.10−7.07 (m, 5H, ArH), 7.01−6.91 (m, 3H, ArH), 6.82−6.81 (m, 2H, ArH), 6.74−6.69 (m, 2H, ArH), 6.51−6.47 (m, 1H, ArH), 3.93 (d, $^2J_{P-H}$ = 22.4 Hz, 1H, P*CH*), 3.32 (m, 4H, THF), 2.36 (s, 6H, $C_6H_3(CH_3)_2$), 1.89 (m, 2H, β-^{n}Bu), 1.68 (m, 2H, γ-^{n}Bu), 1.21 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, δ-^{n}Bu), 1.04 (m, 4H, THF), −0.06 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 174.92 (d, J_{PC} = 2.5 Hz, N−C), 150.28 (C-Ar), 146.80 (d, J_{PC} = 6.6 Hz, C-Ar), 144.40 (d, J_{PC} = 15.5 Hz, C-Ar), 134.44 (C-Ar), 133.50 (C-Ar), 133.19 (C-Ar), 132.76 (d, J_{PC} = 9.6 Hz, C-Ar), 131.29 (d, J_{PC} = 2.1 Hz, C-Ar), 129.86 (C-Ar), 128.95 (C-Ar), 128.87 (C-Ar), 128.50 (C-Ar), 128.44 (C-Ar), 128.39 (C-Ar), 128.18 (C-Ar), 127.53 (C-Ar), 127.08 (C-Ar), 122.90 (C-Ar), 122.21 (d, J_{PC} = 2.4 Hz, C-Ar), 68.09 (THF), 64.70 (d, J_{PC} = 125.6 Hz, P*CH*), 33.63 (δ-^{n}Bu), 32.58 (γ-^{n}Bu), 25.01 (THF), 20.30 ($C_6H_3(CH_3)_2$), 14.78 (β-^{n}Bu), 9.81 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 34.66 ppm (s). Anal. Calcd for $C_{42}H_{46Cl}MgN_2OP$: C, 73.58; H, 6.76; N, 4.09. Found: C, 73.76; H, 6.70; N, 4.04.

Synthesis of L^{7}Mg^{n}Bu(THF) (7). Following a similar procedure to that described for the preparation of complex **1**, complex **7** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1 mmol) and HL^7 (0.566 g, 1 mmol in 10 mL of THF) as a pale yellow solid (0.527 g, 73%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.86−7.81 (m, 4H, *o*-PPh_2), 7.42 (s, 1H, ArH), 7.37−7.35 (m, 2H, ArH), 7.13−7.03 (m, 6H, ArH), 6.94−6.85 (m, 4H, ArH), 6.81−6.75 (m, 3H, ArH), 6.68−6.65 (m, 1H, ArH), 3.92 (d, $^2J_{P-H}$ = 23.5 Hz, 1H, P*CH*), 3.63 (m, 4H, THF), 2.13−2.02 (m, 8H, β-^{n}Bu and $C_6H_3(CH_3)_2$), 1.84−1.71 (m, 2H, γ-^{n}Bu), 1.21 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, δ-^{n}Bu), 1.12 (m, 4H, THF), 0.27 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 175.95 (d, J_{PC} = 2.2 Hz, N-C), 151.22 (d, J_{PC} = 6.7 Hz, C-Ar), 150.18 (C-Ar), 143.50 (d, J_{PC} = 15.3 Hz, C-Ar), 133.59 (d, J_{PC} = 9.7 Hz, C-Ar), 133.07 (C-Ar), 132.94 (C-Ar), 132.17 (C-Ar), 132.12 (C-Ar), 132.10 (C-Ar), 129.64 (C-Ar), 129.05 (C-Ar), 128.82 (C-Ar), 128.30 (C-Ar), 127.87 (C-Ar), 123.34 (C-Ar), 120.35 (CF_3), 115.62 (*ipso*-$C_6H_4CF_3$), 69.50 (THF), 69.36 (d, J_{PC} = 132.9 Hz, PCH), 33.90 (δ-^{n}Bu), 32.61 (γ-^{n}Bu), 25.43 (THF), 20.08 ($C_6H_3(CH_3)_2$), 15.16 (β-^{n}Bu), 10.03 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 34.09 ppm (s). ^{19}F NMR (376 MHz, C_6D_6, 25 °C): δ −62.44 ppm (s). Anal. Calcd for $C_{43}H_{46}MgN_2OPF_3$: C, 71.82; H, 6.45; N, 3.90. Found: C, 71.97; H, 6.39; N, 3.87.

Synthesis of L^{8}Mg^{n}Bu(THF) (8). Following a similar procedure to that described for the preparation of complex **1**, complex **8** was isolated from the metathesis reaction of Mg^nBu_2 (1.1 mL, 1 M, 1.1

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mmol) and HL[8] (0.528 g, 1 mmol in 10 mL of THF) as a pale yellow solid (0.454 g, 67%). Single crystals suitable for X-ray analysis were obtained from a THF/hexane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.94−7.89 (m, 4H, *o*-PPh_2), 7.45 (m, 2H, ArH), 7.16 (m, 1H, ArH), 7.12−7.10 (m, 6H, ArH), 7.07−6.99 (m, 2H, ArH), 6.96−6.87 (m, 3H, ArH), 6.83−6.81 (m, 2H, ArH), 6.72−6.68 (m, 1H, ArH), 6.63−6.61 (m, 2H, ArH), 3.89 (d, $^2J_{P-H}$ = 22.3 Hz, 1H, P*CH*), 3.58 (m, 4H, THF), 3.23 (s, 3H, O*Me*), 2.23 (s, 6H, $C_6H_3(CH_3)_2$), 2.11 (m, 2H, β-^{n}Bu), 1.81 (m, 2H, γ-^{n}Bu), 1.22 (m, 7H, THF and δ-^{n}Bu), 0.24 (m, 2H, α-^{n}Bu). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 174.69 (d, J_{PC} = 2.1 Hz, N-C), 154.23 (C-Ar), 150.44 (C-Ar), 143.91 (d, J_{PC} = 15.7 Hz, C-Ar), 142.40 (d, J_{PC} = 7.8 Hz, C-Ar), 134.65 (C-Ar), 133.75 (C-Ar), 133.21 (d, J_{PC} = 9.5 Hz, C-Ar), 132.84 (C-Ar), 131.22 (d, J_{PC} = 2.1 Hz, C-Ar), 128.42 (C-Ar), 127.45 (C-Ar), 125.68 (d, J_{PC} = 11.9 Hz, C-Ar), 122.70 (C-Ar), 114.42 (C-Ar), 69.29 (d, J_{PC} = 132.8 Hz, P*CH*), 68.57 (THF), 54.93 (OCH_3), 33.69 (δ-^{n}Bu), 32.41 (γ-^{n}Bu), 25.38 (THF), 20.04 ($C_6H_3(CH_3)_2$), 14.91 (β-^{n}Bu), 9.80 (α-^{n}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 33.74 ppm (s). Anal. Calcd for $C_{43}H_{49}MgN_2O_2P$: C, 75.82; H, 7.25; N, 4.11. Found: C, 75.72; H, 7.14; N, 4.07.

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 *rac*-LA (0.288 g, 2 mmol) in 4 mL of THF was added a THF solution (1 mL) of complex **1** (6.5 mg, 10 μmol, [LA]/[Mg] = 200:1, [LA] = 0.4 mol/L). The polymerization took place immediately at room temperature. The system became viscous in a few minutes, was kept stirring for 10 min, and then was terminated by 0.5 mL of ethanol. 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 (0.271 g, 94%). 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, and ^{31}P NMR spectra of all complexes, homonuclear decoupling ^{1}H NMR spectrum for resulting PLA, and X-ray structures of complexes **2**−**4** as well as the crystallographic data for complexes **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif using accession codes CCDC-965841 (**1**), 965842 (**2**), 965843 (**3**), 965844 (**4**), and 965845 (**5**).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dmcui@ciac.ac.cn. Fax: +86 431 85262774. Tel: +86 431 85262773.

Notes

The authors declare no competing financial interest.

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