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Rapid and Controlled Polymerization of *rac*-Lactide Using N,N,O-Chelate Zinc Enolate Catalysts

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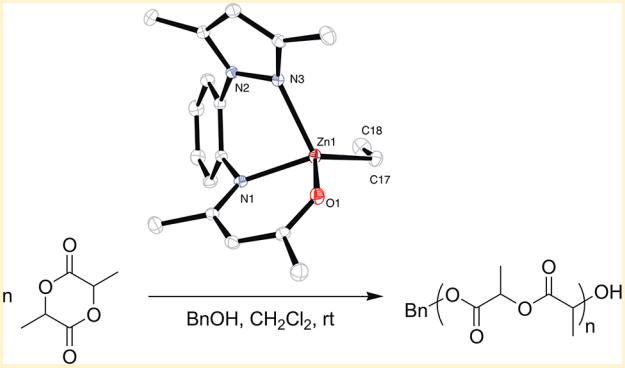
Supporting Information

ABSTRACT: The synthesis and characterization of N,N,O-chelate zinc enolate complexes and the catalysis of the complexes for the ROP of *rac*-lactide are reported. The pyrazole-based ligand precursors *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=C(Me)CH=C(OH)R^1 (R^1 = Me, **1**; R^1 = Ph, **2**; R^1 = *t*-Bu, **3**; R^1 = CF_3, **4**) were synthesized by reaction of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-benzenamine with 1,3-diketones, including pentane-2,4-dione, 1-phenylbutane-1,3-dione, 5,5-dimethylhexane-2,4-dione, and 1,1,1-trifluoropentane-2,4-dione. Treatment of **1**−**4** with $ZnEt_2$ generated the N,N,O-coordinated zinc complexes [Zn(Et)-{*o*-(OC(R^1)=CHC(Me)=N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (R^1 = Me, **5**; R^1 = Ph, **6**; R^1 = *t*-Bu, 7; R^1 = CF_3, **8**). The imino-phosphoranyl-moiety-containing ligand precursors *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=P(Ph_2)CH_2C(O)R^2 (R^2 = Ph, **9**; R^2 = *t*-Bu, **10**) were synthesized by reaction of 1-(2-azidophenyl)-3,5-dimethyl-1*H*-pyrazole with 1-phenyl-2-(diphenylphosphino)-ethanone and 3,3-dimethyl-1-(diphenylphosphino)butan-2-one, respectively. Treatment of **9** and **10** with $ZnEt_2$ afforded the zinc complexes [Zn(Et){*o*-(OC(R^2)=CHP(Ph_2)=N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (R^2 = Ph, **11**; R^2 = *t*-Bu, **12**). The ligand precursors and complexes were characterized by NMR spectroscopy and elemental analyses. Complexes **5** and **11** were also characterized by single-crystal X-ray diffraction techniques. In the presence of BnOH complexes **5**−**8** efficiently catalyzed the ring-opening polymerization of *rac*-lactide in a controlled fashion, whereas complexes **11** and **12** showed much lower catalytic activity under the same conditions.



INTRODUCTION

Polylactide (PLA) as an important class of biodegradable and biocompatible polymer has attracted considerable attention due to its biomedical, pharmaceutical, and agricultural applications.[1] PLA is also a promising and practical material for an attractive alternative to petrochemical-derived polyolefin because its monomer is derived from naturally renewable resources such as corn and sugar beets.[2] PLA is typically produced by the ROP of lactide catalyzed by metal complexes such as Sn,[3] Al,[4] Zn,[5] Ca,[6] and Mg[5a,b,7] complexes. In this context, zinc-based catalysts have been extensively employed and are among the highly active metal-based catalysts used to date for the controlled polymerization of lactide. For instance, in 2003 Tolman et al. found a highly active zinc catalyst supported by an amino-phenolate-based N,N,O-tridentate ligand, which can lead to 96% conversion of *rac*-lactide in 13 min at 25 °C at a monomer to catalyst ratio of 1000.[8] Lin et al. developed a catalyst system and demonstrated a zinc complex bearing an N,N,O-tridentate Schiff base ligand with hindered substituents to lead to good stereocontrol at low temperature, producing highly heterotactic PLA from the polymerization of *rac*-lactide.[9] Several other N,N,O-chelate zinc complexes were also proven to be active catalysts for the ROP of lactides.[10] We wished to modify N,N,O-ligands by changing the coordination groups or ligand skeleton to tune the catalytic properties of their metal complexes in the ROP of cyclic esters. For this reason we designed two classes of pyrazole-based N,N,O-tridentate enolate ligands containing a ketiminate moiety and an iminophosphoranyl moiety, respectively, synthesized and characterized zinc complexes of the ligands, and studied the catalysis of the complexes in the ROP of *rac*-lactide. Herein we report the results.

RESULTS AND DISCUSSION

Synthesis and Characterization of N,N,O-Chelate Zinc Enolate Complexes. As shown in Scheme 1, ligand precursors **1**−**3** were synthesized in good yields through reactions of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine with the corresponding 1,3-diketones in refluxing toluene in the presence of 4 Å molecular sieves and a catalytic amount of formic acid. The crude products were purified by column chromatography. Compound **4** was synthesized by grinding a mixture of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)benzenamine and 1,1,1-trifluoropentane-2,4-dione using sulfuric acid as catalyst under solventless conditions. Respective treatment of **1**−**4** with $ZnEt_2$ in toluene at room temperature generated N,N,O-chelate zinc complexes **5**−**8**.

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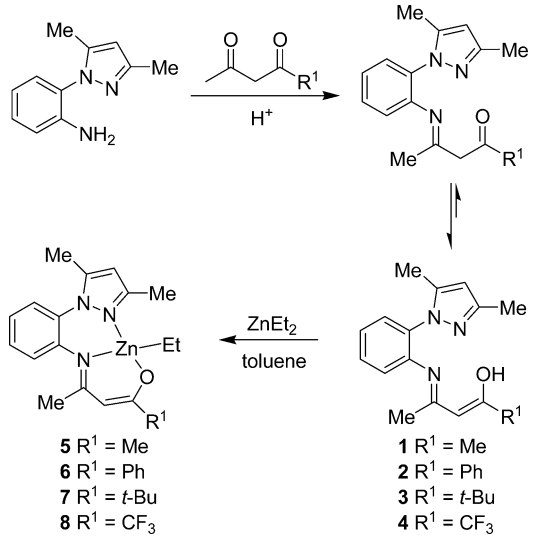
Scheme 1. Synthesis of Zinc Complexes 5−8



Compounds **1**, **3**, and **4** are pale yellow (**1** and **3**) or purplish pink oils (**4**), and **2** is yellow crystals. They gave satisfactory elemental analytical results. The ^{1}H and ^{13}C NMR spectra match their respective structures. The ^{19}F NMR spectrum of compound **4** displayed a single signal at δ −76.85 ppm. This showed that the CF_3 group is adjacent to the carbonyl carbon rather than the imine carbon, in comparison with the ^{19}F NMR spectra of similar systems (the chemical shift of ^{19}F NMR spectra in $CF_3C(=NAr)CH=(OH)R$ is about −63 ppm).[11] It should be noted that the ^{1}H NMR spectra showed each of the compounds to exist as an equilibrium mixture of keto and enol forms in $CDCl_3$ solution, the ratio of keto to enol form ranging from about 1:5 (**1**, **2**, and **4**) to 1:15 (**3**). Complexes **5**−**8** are air-sensitive pale yellow (**5** and **7**), yellow (**6**), or yellowish gray crystals (**8**). They were characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of the complexes, the OH signals in the ligand precursors were not observed and ZnEt signals appeared at 0.65−0.93 and 1.51−1.61 ppm, respectively. ^{13}C NMR spectra of complexes **5**−**8** showed that the signals of $ZnCH_2$ appeared at high field (−2.09, −2.04, −2.16, and −2.34 ppm, respectively). The ^{19}F NMR spectrum of complex **8** was also determined, the chemical shift being −74.57 ppm. The structure of complex **5** was additionally characterized by single-crystal X-ray diffraction. The ORTEP drawing is depicted in Figure 1, along with selected bond lengths and angles. The central zinc atom is four-coordinate and has a distorted-tetrahedral geometry. The difference between the angles C17−Zn−N1 (129.3(2)°) and N1−Zn−N3 (84.13(16)°) is illustrative of the distortion from an ideal tetrahedral topology. In comparison with several N,N,O-coordinate zinc complexes, the Zn−O distance of 1.991(4) Å in complex **5** is longer than the corresponding distance in LZnEt (L = 2,4-di-*tert*-butyl-6-{[(2′-dimethylaminoethyl)-methylamino]methyl}phenolate) (1.956(2) Å).[8] The Zn−N1 distance of 2.051(4) Å is shorter than the Zn−N(imine) distance in $[L^1ZnEt]_2$ (L^1 = 2-[(2-(dimethylamino)ethylimino)methyl]-4-chlorophenolate) (2.168(3) Å).[9a] The longer bond distance of the latter is probably due to the higher coordination number of the zinc atom. The Zn−N3 distance of 2.159(4) Å in complex **5** is longer than the Zn−N(pyrazolyl) distances in $[Zn(Me)(bpa^{tBu_2,Me_2})]$ (bpa^{tBu_2,Me_2} = (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetate) (2.085(7) and 2.104(6) Å).[12] The Zn−C

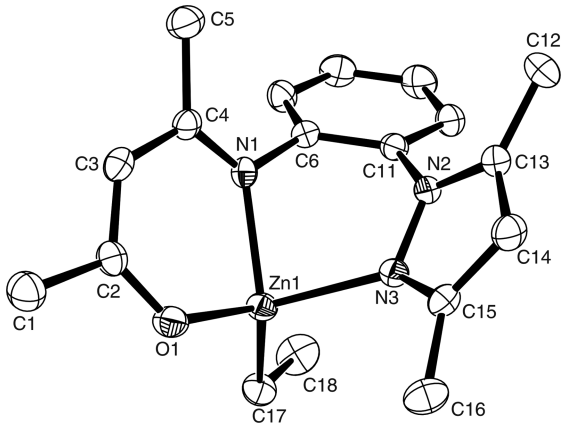
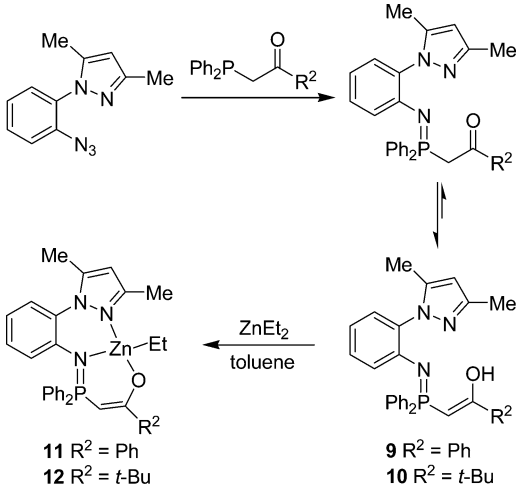


Figure 1. ORTEP drawing (30% probability) of complex **5**. Selected bond lengths (Å) and angles (deg): Zn(1)−C(17) = 1.973(6), Zn(1)−O(1) = 1.991(4), Zn(1)−N(1) = 2.051(4), Zn(1)−N(3) = 2.159(4), O(1)−C(2) = 1.265(7), N(1)−C(4) = 1.299(7), N(1)−C(6) = 1.427(7), C(2)−C(3) = 1.395(8); C(17)−Zn(1)−O(1) = 118.5(2), C(17)−Zn(1)−N(1) = 129.3(2), O(1)−Zn(1)−N(1) = 92.17(17), C(17)−Zn(1)−N(3) = 116.5(2), O(1)−Zn(1)−N(3) = 110.01(18), N(1)−Zn(1)−N(3) = 84.13(16), C(2)−O(1)−Zn(1) = 123.6(4).

distance of 1.973(6) Å is slightly shorter than those in LZnEt (1.997(4) Å)[8] and $[L^1ZnEt]_2$ (1.985(4) Å)[9a] and slightly longer than that in $[Zn(Me)(bpa^{tBu_2,Me_2})]$ (1.962(8) Å).[12] The C2−C3 distance of 1.395(8) Å is slightly longer than a typical C−C double bond due to electron delocalization.

The synthesis of ligand precursors **9** and **10** and complexes **11** and **12** is shown in Scheme 2. The reaction of 1-(2-azidophenyl)-

Scheme 2. Synthesis of Zinc Complexes 11 and 12



3,5-dimethyl-1*H*-pyrazole with 1-phenyl-2-(diphenylphosphino)-ethanone and 3,3-dimethyl-1-(diphenylphosphino)butan-2-one, respectively, in CH_2Cl_2 afforded compounds **9** and **10**. Treatment of **9** and **10** with $ZnEt_2$ in toluene gave the corresponding zinc complexes **11** and **12**. Compounds **9** and **10** are yellow crystals or powders, and **11** and **12** are colorless crystals. Both **11** and **12** are air sensitive and stable under a nitrogen atomsphere. Each compound was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **9** and **10** showed that each of them also exists as an equilibrium mixture of keto and enol forms in solution and the enol form is predominant. The ^{1}H NMR spectra of **11** and **12** revealed ZnEt

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signals. The ^{31}P NMR spectra showed the chemical shifts of the complexes slightly shifted to higher fields in comparison with those of the corresponding ligand precursors in enol form. The coordination mode of complex **11** was confirmed by single-crystal X-ray diffraction analysis. An ORTEP drawing is presented in Figure 2, along with selected bond lengths and angles.

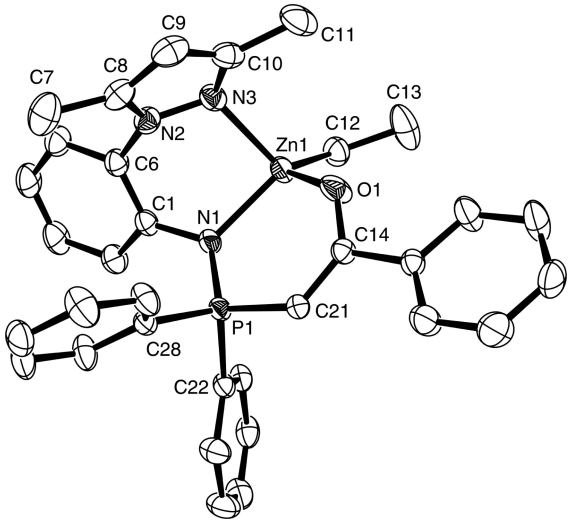

Figure 2. ORTEP drawing (30% probability) of complex **11**. Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) = 2.0336(17), Zn(1)−N(3) = 2.141(2), Zn(1)−C(12) = 1.982(3), Zn(1)−O(1) = 2.0006(17), P(1)−N(1) = 1.6100(18), C(14)−C(21) = 1.369(3); C(12)−Zn(1)−O(1) = 114.58(10), C(12)−Zn(1)−N(1) = 128.57(10), C(12)−Zn(1)−N(3) = 124.79(10), O(1)−Zn(1)−N(1) = 97.65(7), O(1)−Zn(1)−N(3) = 95.45(8), N(1)−Zn(1)−N(3) = 88.05(7).

The structural skeleton is similar to that of complex **5**. Thus, the central zinc atom is surrounded by N, N, O, and C atoms and has a distorted-tetrahedral geometry. The C12−Zn−N1 angle (128.57(10)°) is much wider than that of N1−Zn−N3 (88.05(7)°). The N3−Zn−O angle of 95.45(8)° is narrower than the corresponding angle in complex **5**, which is 110.01(18)°. The Zn−O distance of 2.0006(17) Å and Zn−C distance of 1.982(3) Å are slightly longer than the corresponding distances in complex **5** [(1.991(4) and 1.973(6) Å, respectively), and the Zn−C distance is close to that of $[L^1ZnEt]_2$ (1.985(4) Å).[9a] The Zn−N distances of 2.0336(17) and 2.141(2) Å are shorter than the corresponding distances in complex **5** (2.051(4) and 2.159(4) Å, respectively). The C14−C21 distance of 1.369(3) Å is indicative of a C−C double bond.

Catalysis of the Zinc Complexes in the ROP of *rac*-Lactide. Catalysis of zinc complexes **5**−**8**, **11**, and **12** toward the ROP of *rac*-lactide was evaluated, and the results showed that each of these zinc complexes can catalyze the polymerization of *rac*-lactide at ambient temperature in the presence of benzyl alcohol (Table 1). Complexes **5**−**8** exhibited high activity. They led to polymerization of 100 equiv of *rac*-LA in 1−3 min, giving 90−98% monomer conversions (entries 1−5, Table 1). Such activity is lower than that of the amino-phenolate-based N,N,O-chelate zinc complex reported by Tolman and co-workers, which leads to 96% conversion of *rac*-LA in 5 min at 25 °C at a monomer to catalyst ratio of 650.[8] However, the activity of **5**−**8** is comparable to or higher than those of other known zinc-based catalyst systems.[5,9] For example, a zinc complex bearing an N,N,O-tridentate Schiff base ligand,

Table 1. Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Complexes 5−8, 11, and 12[a]

entry	cat.	time (min)	conversn[b] (%)	M_n(calcd)[c]	M_n(GPC)[d]	PDI[e]
1	**5**	1	96	13901	11200	1.17
2	**6**	1	83	12114	10400	1.08
3	**6**	3	97	14045	13500	1.06
4	**7**	1	90	13137	10000	1.11
5	**8**	1	98	14200	13000	1.07
6	**11**	858	92	13324	11500	1.08
7	**12**	1668	93	13440	11900	1.11

[a]All polymerizations were carried out in CH_2Cl_2 at 25 °C; $[LA]_0$ = 0.5 M and $[LA]_0/[Zn]/[BnOH]$ = 100/1/1. [b]Measured by ^1H NMR spectra. [c]Calculated from the molecular weight of LA times the conversion of monomer plus the molecular weight of BnOH. [d]Obtained from GPC analysis and calibrated against a polystyrene standard, multiplied by 0.58.[15] [e]Obtained from GPC analysis.

$[Zn(OBn)\{OC_6H_4\{2\text{-}(CH{=}NCH_2CH_2NMe_2)\}\}]_2$, drives 96% conversion of *rac*-LA in 4 h at 25 °C at a monomer to catalyst ratio of 100;[9a] $[(IMes)Zn(OBn)_2]_2$ (IMes = 1,3-dimesitylimidazol-2-ylidene) initiates 96% *rac*-LA monomer consumption after 20 min at 25 °C at a monomer to catalyst ratio of 130.[13] The lower activity of complex **7** in comparison to that of **5** may be due to the steric hindrance of the *t*-Bu group in complex **7**, which hampers the incorporation of monomer into the growing polymer chain. Complex **8** showed activity close to that of complex **5**. Hence, it does not seem that the electronic effect difference of the ligands is the decisive factor for the catalytic activity in the present catalytic systems.[9,11,14] However, the fact that complex **6** has the lowest activity among the complexes cannot be reasonably explained on the basis of electronic effects. It is probably a composite result of steric and electronic effects. The PDIs of polymers, ranging from 1.06 to 1.17, are narrow. The molecular weights of the polymers determined by GPC approximately match those calculated (entries 1−5, Table 1). These facts show that the polymerizations are controlled. A linear relationship between the number average molecular weight (M_n) and $([LA]_0\text{-}[LA])/[Zn]_0$, as shown in Figure 3, implies the "living" character of the polymerization process catalyzed by **5**-BnOH. The polylactide molecular weight in each *rac*-LA to catalyst ratio also approximately matches the theoretical value (Table 2). However, it was also noted that M_n values determined by GPC were somewhat lower than the predicted polymer molecular weights. This might imply the possibility of a certain degree of chain transfer. The ^1H NMR spectra of PLAs indicated that the polymer chain was capped with a benzyl ester on one end and a hydroxyl group on the other end (Figures S1 and S2 in the Supporting Information). The observed results suggest that the polymerization may be initiated through insertion of the benzyloxy group to LA, followed by ring opening via acyl oxygen cleavage, and the BnOZnL formed in situ is the real catalyst (Scheme S1 in the Supporting Information). The polymers so obtained are atactic, as indicated by ^1H NMR spectral analysis. Lin et al. indicated that the tacticity of the polymer was significantly influenced by the steric hindrance of the ligand in N,N,O-chelate Schiff base zinc catalyst systems, a sterically bulky ligand resulting in an increase in *Pr*.[9a] These tactics may also be suitable for our catalytic systems. Further investigation is in progress.

The catalytic activity of complexes **11** and **12** is much lower than that of complexes **5**−**8**, as seen in Table 1. The polymerization went to completion in hours using complex **11** or **12** in

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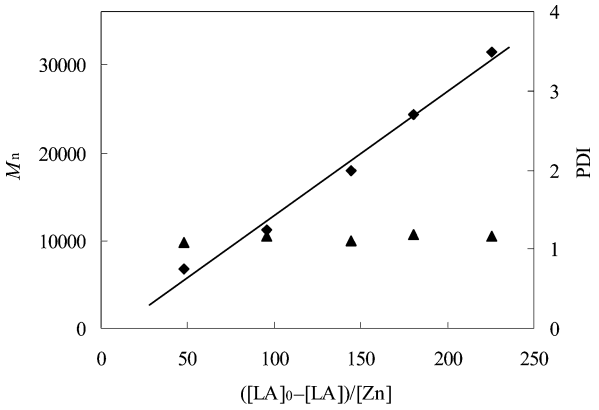

Figure 3. Plots of M_n (◆, obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of $([LA]_0 - [LA])/[Zn]$ for the polymerization catalyzed by **5**/BnOH at 25 °C. Conditions: $[Zn]_0/[BnOH]_0 = 1/1$; $[LA]_0 = 0.5$ M; solvent CH_2Cl_2.

Table 2. Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Complex 5/BnOH[a]

entry	$[LA]_0/[Zn]$	time (min)	conversn (%)[b]	M_n(calcd)[c]	M_n(GPC)[d]	PDI[e]
1	50	0.5	96	7055	6800	1.09
2	100	1	96	13901	11200	1.17
3	150	3	96	20927	18000	1.11
4	200	4	90	26079	24400	1.19
5	250	7.5	90	32608	31500	1.17

[a]Polymerizations were carried out in CH_2Cl_2 at 25 °C; $[LA]_0 = 0.5$ M and $[Zn]/[BnOH] = 1/1$. [b]Measured by ^1H NMR spectra. [c]Calculated from the molecular weight of LA times the conversion of monomer plus the molecular weight of BnOH. [d]Obtained from GPC analysis and calibrated against a polystyrene standard, multiplied by 0.58.[15] [e]Obtained from GPC analysis.

the presence of benzyl alcohol (entries 6 and 7, Table 1). This contrast of catalytic activity is probably caused by the difference in electronic effects between iminophosphoranyl and imino groups in the two classes of ligands.[16] It seems that the combination of imino, pyrazolyl, and alkenoxy groups provides a proper electronic environment at the metal center for the catalysis. The lower activity of complex **12** in comparison to that of **11** is ascribed to the greater steric hindrance of the ligand in complex **12** and the difference of electron effects between phenyl and *tert*-butyl

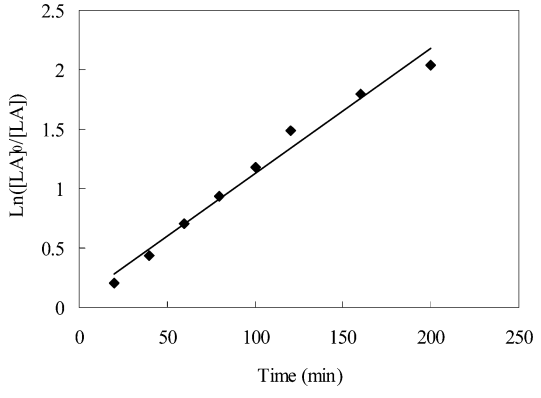

Figure 4. Plot of $\ln([LA]_0/[LA])$ versus time for the polymerization of *rac*-lactide catalyzed by **11**/BnOH. Conditions: $[LA]_0/[\mathbf{11}]/[BnOH] = 100/1/1$; $[LA]_0 = 0.5$ M; solvent CH_2Cl_2; polymerization temperature 38 °C.

groups. The determined molecular weights of the PLAs obtained by catalysis with **11** and **12** in the presence of BnOH are close to the calculated values, and the polymers have a low polydispersity (1.08 and 1.11, respectively; Table 1). A plot of $\ln([LA]_0/[LA])$ versus time in a **11**/BnOH-catalyzed *rac*-LA polymerization exhibits a linear relationship (Figure 4), indicating that the polymerization proceeds with first-order dependence on monomer concentration. The number average molecular weight (M_n) follows a linear relationship in monomer conversion, and polydispersity (PDI) values remain low (Figure 5), proving the

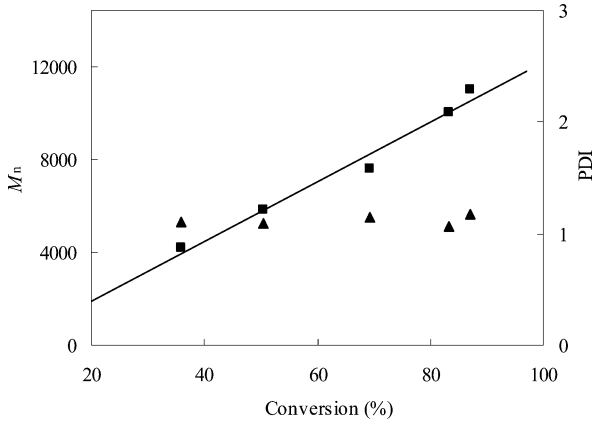

Figure 5. Plots of M_n (■, obtained from GPC analysis) and polydispersity (▲, M_w/M_n) as a function of *rac*-LA conversion using complex **11**/BnOH as the catalyst. Conditions: $[LA]_0/[Al]_0/[BnOH]_0 = 100/1/1$; $[LA]_0 = 0.5$ M; solvent CH_2Cl_2; polymerization temperature 38 °C.

controlled character of the polymerization.[17] The polymers formed by catalysis with **11** and **12** are also atactic.

CONCLUSIONS

In summary, we have synthesized and characterized several zinc complexes supported by novel pyrazolyl-based NNO-tridentate enolate ligands. In the presence of BnOH the complexes bearing ligands containing a ketiminate unit (**5**–**8**) are extremely active catalysts for the ring-opening polymerization of *rac*-lactide, whereas the complexes bearing ligands containing an iminophosphoranyl unit (**11** and **12**) show much lower catalytic activity. The approximate activity order is **5** ≈ **8** > **7** > **6** ≫ **11** > **12**. The electron effect difference between the two types of ligands may be the decisive factor determining the catalytic activity of the complexes. The polymerizations are controlled and give PLAs with an atactic microstructure. Future work will involve further modification of ligands to improve stereocontrol.

EXPERIMENTAL SECTION

All air- or moisture-sensitive manipulations were performed under dry N_2 using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane and diethyl ether), or calcium hydride (CH_2Cl_2). $ZnEt_2$ was purchased from Acros Organics and used as received. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories and stored over activated molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). 1-(2′-Aminophenyl)-3,5-dimethylpyrazole,[18] 1-(2′-azidophenyl)-3,5-dimethylpyrazole,[19] and 1-phenyl-2-(diphenylphosphino)ethanone[20] were prepared according to reported methods. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85%

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H_3PO_4, and the ^{19}F NMR spectra were referenced to external CF_3COOH. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. Molecular weights and molecular weight distributions were determined on a Waters 150C gel permeation chromatograph (GPC) equipped with UltraStyragel columns (10^3, 10^4, and 10^5 Å) and a 410 refractive index detector, using monodispersed polystyrene as the calibration standard. THF (HPLC grade) was used as eluent at a flow rate of 1 mL/min.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=C(Me)CH=C(OH)Me (1). A mixture of 1-(2′-aminophenyl)-3,5-dimethylpyrazole (2.68 g, 14.31 mmol), 2,4-pentanedione (2.86 g, 28.56 mmol), activated 4 Å molecular sieves (30 g), toluene (50 mL), and several drops of formic acid was refluxed for 40 h and then cooled to room temperature. The molecular sieves were filtered out and washed with CH_2Cl_2 (3 × 20 mL). The resulting solution was washed two times with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum to give an oil. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 1/1) to afford a light yellow oil (2.63 g, 70%). ^1H NMR ($CDCl_3$): δ 1.83 (s, 3H, Me), 2.03 (s, 3H, Me), 2.13 (s, 3H, Me), 2.28 (s, 3H, Me), 5.09 (s, 1H, CH), 5.97 (s, 1H, pyrazolyl), 7.23−7.42 (m, 4H, C_6H_4), 12.05 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 11.13, 13.41, 19.47, 28.97, 98.24, 105.87, 126.16, 126.35, 128.83, 128.86, 134.67, 135.46, 140.69, 149.53, 159.41, 195.95. Anal. Calcd for $C_{16}H_{19}N_3O$: C, 71.35; H, 7.11; N, 15.60. Found: C, 71.86; H, 7.18; N, 15.72.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=C(Me)CH=C(OH)Ph (2). A mixture of 1-(2′-aminophenyl)-3,5-dimethylpyrazole (2.00 g, 10.68 mmol), benzoylacetone (2.07 g, 12.76 mmol), activated 4 Å molecular sieves (30 g), toluene (50 mL), and several drops of formic acid was refluxed for 40 h and then cooled to room temperature. The molecular sieves were filtered out and washed with CH_2Cl_2 (3 × 20 mL). The solution was washed two times with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was recrystallized from toluene to give yellow crystals of **2** (3.06 g, 86%), mp 130−132 °C. ^1H NMR ($CDCl_3$): δ 1.91 (s, 3H), 2.15 (s, 3H), 2.28 (s, 3H), 5.78 (s, 1H, CH), 5.94 (s, 1H, pyrazolyl), 7.30−7.45 (m, 7H, Ar), 7.84−7.88 (m, 2H, Ar), 12.70 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 11.60, 13.72, 20.26, 94.71, 106.31, 127.06, 127.25, 128.35, 129.17, 131.03, 135.49, 135.59, 140.09, 141.10, 150.02, 162.34, 188.89. Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.00; H, 6.39; N, 12.64.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=C(Me)CH=C(OH)*t*-Bu (3). A mixture of 1-(2′-aminophenyl)-3,5-dimethylpyrazole (2.20 g, 11.75 mmol), 5,5-dimethylhexane-2,4-dione (1.96 g, 13.78 mmol), activated 4 Å molecular sieves (30 g), toluene (50 mL), and several drops of formic acid was refluxed for 40 h and then cooled to room temperature. The molecular sieves were filtered out and washed with CH_2Cl_2 (3 × 20 mL). The solution was washed two times with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum to give an oil. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 1/1) to afford a light yellow oil (2.53 g, 69%). ^1H NMR ($CDCl_3$): δ 1.12 (s, 9H, *t*-Bu), 1.77 (s, 3H, Me), 2.09 (s, 3H, Me), 2.27 (s, 3H, Me), 5.23 (s, 1H, CH), 5.91 (s, 1H, pyrazolyl), 7.24−7.27 (m, 1H, Ar), 7.30−7.33 (m, 1H, Ar), 7.36−7.41 (m, 2H, Ar), 12.22 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 11.53, 13.68, 20.04, 27.78, 41.72, 93.28, 106.09, 126.69, 127.32, 128.93, 129.01, 129.52, 135.48, 135.68, 141.05, 149.82, 160.97. Anal. Calcd for $C_{19}H_{25}N_3O{\cdot}0.1CH_3COOEt$: C, 72.76; H, 8.12; N, 13.12. Found: C, 72.52; H, 8.09; N, 13.07.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N=C(Me)CH=C(OH)CF_3 (4). 1-(2′-Aminophenyl)-3,5-dimethylpyrazole (1.0 g, 5.34 mmol) and 1,1,1-trifluoropentane-2,4-dione (0.86 g, 5.58 mmol) were mixed in a mortar. To the mixture was added 2 drops of concentrated sulfuric acid. The mixture was ground for 10 min and left to stand for 10 min under an infrared lamp. Then 1,1,1-trifluoropentane-2,4-dione (0.86 g, 5.58 mmol) was added to the mortar and grinding was continued for an additional 10 min. After that, the process of addition of 1,1,1-trifluoropentane-2,4-dione (0.86 g, 5.58 mmol) and grinding was repeated once again. The resultant species was extracted with CH_2Cl_2 (20 mL) and filtered. The filtrate was dried over $MgSO_4$, and then solvent was removed under vacuum to afford an oil (1.10 g, 64%). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.95 (s, 3H, Me), 2.14 (s, 3H, Me), 2.26 (s, 3H, Me), 5.42 (s, 1H, CH), 5.98 (s, 1H, CH), 7.32 (d, J = 7.6 Hz, 1H, C_6H_4), 7.42−7.51 (m, 3H, C_6H_4), 12.18 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.46, 13.47, 20.31, 91.23, 106.61, 117.40 (q, J = 287 Hz), 127.28, 128.28, 128.87, 129.33, 134.05, 135.36, 140.76, 150.33, 167.95, 176.82 (q, J = 33 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −76.85. Anal. Calcd for $C_{16}H_{16}F_3N_3O$: C, 59.44; H, 4.99; N, 13.00. Found: C, 59.58; H, 4.82; N, 13.20.

Synthesis of [Zn(Et){*o*-(OC(Me)=CHC(Me)=N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (5). $ZnEt_2$ (1.90 mL, 1 M solution in hexane, 1.90 mmol) was added dropwise to a stirred solution of **1** (0.50 g, 1.86 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature, stirred overnight at that temperature, and concentrated under vacuum. A small amount of diethyl ether was added to the concentrated solution to give pale yellow crystals of **5** (0.57 g, 84%), mp 156−157 °C. ^1H NMR (C_6D_6): δ 0.65−0.82 (m, 2H, ZnEt), 1.50 (s, 3H), 1.58 (t, J = 8 Hz, 3H, ZnEt), 1.68 (s, 3H, Me), 2.01 (s, 3H, Me), 2.29 (s, 3H, Me), 4.82 (s, 1H, CH), 5.45 (s, 1H, pyrazolyl), 6.62 (d, J = 8.1 Hz, 1H, Ar), 6.68−6.75 (m, 1H, Ar*H*), 6.82 (d, J = 7.8 Hz, 1H, Ar), 6.87−6.95 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −2.09, 11.90, 13.24, 13.78, 21.25, 28.37, 97.34, 106.97, 123.90, 125.81, 126.34, 128.64, 130.88, 141.10, 145.39, 149.99, 166.99, 185.58. Anal. Calcd for $C_{18}H_{23}N_3OZn$: C, 59.59; H, 6.39; N, 11.58. Found: C, 59.12; H, 6.14; N, 11.94.

Synthesis of [Zn(Et){*o*-(OC(Ph)=CHC(Me)=N)C_6H_4(3,5-Me_2-C_3HN_2)}] (6). $ZnEt_2$ (1.20 mL, 1 M solution in hexane, 1.20 mmol) was added dropwise to a stirred solution of **2** (0.38 g, 1.15 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature, stirred overnight, and concentrated under vacuum. A small amount of *n*-hexane was added to the solution to give yellow crystals of **6** (0.38 g, 78%), mp 229−230 °C. ^1H NMR (C_6D_6): δ 0.73−0.93 (m, 2H, ZnEt), 1.56 (s, 3H, Me), 1.61 (t, J = 8.1 Hz, 3H, $ZnCH_2CH_3$), 1.68 (s, 3H, Me), 2.28 (s, 3H, Me), 5.39 (s, 1H, CH), 5.57 (s, 1H, pyrazole), 6.63 (dd, J = 1.2, 7.8 Hz, 1H, Ar), 6.74 (dt, J = 1.2, 7.2 Hz, 1H, Ar), 6.83 (dd, J = 1.5, 7.8 Hz, 1H, Ar), 6.94 (dt, J = 1.2, 7.5 Hz, 1H, Ar), 7.12−7.25 (m, 3H, Ar), 8.09 (dd, J = 1.6, 7.8 Hz, 2H, Ar). ^{13}C NMR (C_6D_6): δ −2.04, 11.90, 13.18, 13.74, 21.72, 94.86, 106.65, 127.17, 127.55, 127.85, 128.32, 129.38 130.42, 140.67, 142.09, 145.02, 149.64, 167.78, 178.77. Anal. Calcd for $C_{23}H_{25}N_3OZn$: C, 65.02; H, 5.93; N, 9.89. Found: C, 64.90; H, 5.91; N, 9.68.

Synthesis of [Zn(Et){*o*-(OC(*t*-Bu)=CHC(Me)=N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (7). $ZnEt_2$ (1.90 mL, 1 M solution in hexane, 1.90 mmol) was added dropwise to a stirred solution of **3** (0.55 g, 1.77 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The resulting solution was concentrated to afford pale yellow crystals of **7** (0.67 g, 93%)., mp 111−113 °C. ^1H NMR (C_6D_6): δ 0.74−0.79 (m, 2H, $ZnCH_2CH_3$), 1.26 (s, 9H, *t*-Bu), 1.47 (s, 3H, Me), 1.51 (t, J = 8.2 Hz, 3H, ZnEt), 1.57 (s, 3H, Me), 2.24 (s, 3H, Me), 5.02 (s, 1H, CH), 5.37 (s, 1H, pyrazolyl), 6.54 (d, J = 8 Hz, 2H, Ar), 6.64 (t, J = 7.6 Hz, 1H, Ar), 6.77 (d, J = 8 Hz, 1H, Ar), 6.84 (t, J = 7.6 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −2.16, 11.72, 11.87, 13.12, 13.70, 21.87, 28.73, 29.03, 40.99, 92.19, 106.82, 125.59, 125.50, 125.98, 127.19, 128.41, 140.99, 145.75, 149.74, 167.78, 194.45. Anal. Calcd for $C_{21}H_{29}N_3OZn$: C, 62.30 H, 7.22; N, 10.38. Found: C, 61.92; H, 7.17; N, 10.70.

Synthesis of [Zn(Et){*o*-(OC(CF_3)=CHC(Me)=N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (8). $ZnEt_2$ (2.5 mL, a 1.5 M solution in toluene, 3.75 mmol) was added dropwise to a stirred solution of **4** (0.79 g, 2.46 mmol) in toluene (10 mL) at about −80 °C. The mixture was then warmed to room temperature and stirred overnight at that temperature. The resulting solution was concentrated in vacuo. *n*-Hexane (20 mL) was added to the concentrated solution to afford complex **8** as a yellowish gray solid (0.93 g, 91%), mp 116−118 °C. ^1H NMR (C_6D_6): δ 0.64−0.80 (m, 2H, $ZnCH_2$), 1.23 (s, 3H, Me), 1.46 (t, J = 8 Hz, 3H, $ZnCH_2CH_3$), 1.58 (s, 3H, Me), 2.18 (s, 3H, Me), 5.26 (s, 1H, CH), 5.33 (s, 1H, CH), 6.50 (dd, J = 1.2, 8.0 Hz, 1H, C_6H_4), 6.56 (d, J = 1.2, 8.0 Hz, 1H, C_6H_4), 6.68 (dt, J = 1.2, 8.0 Hz, 1H, C_6H_4), 6.84 (dt, J = 1.2, 8.0 Hz, 1H, C_6H_4). ^{13}C NMR (C_6D_6): δ −2.34, 11.79, 12.91, 13.35, 21.05, 93.52 (q, J = 2.6 Hz), 107.35, 120.76 (q, J = 282.6

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Hz), 124.91, 125.14, 125.79, 127.94, 128.87, 129.96, 141.37, 143.62, 150.59, 166.02 (q, J = 30.9 Hz), 170.81. ^{19}F NMR (C_6D_6): δ −74.57. Anal. Calcd for $C_{18}H_{20}F_3N_3OZn$: C, 51.88; H, 4.84; N, 10.08. Found: C, 51.59; H, 4.68; N, 9.83.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N═P(Ph_2)CH_2C(O)Ph (9). A solution of 1-(2′-azidophenyl)-3,5-dimethylpyrazole (1.80 g, 8.44 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $Ph_2PCH_2C(O)Ph$ (2.56 g, 8.41 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (20 mL), and the solution was concentrated to give yellow crystals of **9** (3.38 g, 82%), mp 64−66 °C. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, Me), 2.14 (s, Me), 2.23 (s, Me), 4.07 (d, J = 15.3 Hz, CH), 4.37 (d, J = 15.3 Hz, CH), 5.79 (s, pyrazolyl), 5.95 (s, pyrazolyl), 6.40 (d, J = 7.8 Hz, Ar), 6.63 (t, J = 7.5 Hz, Ar), 6.84 (t, J = 7.5 Hz, Ar), 6.96 (t, J = 7.8 Hz, Ar), 7.07 (d, J = 7.5 Hz, Ar), 7.10−7.17 (m, Ar), 7.19−7.26 (m, Ar), 7.29−7.44 (m, Ar), 7.51−7.62 (m, Ar), 7.69−7.80 (m, Ar). ^{13}C NMR ($CDCl_3$): δ 11.66, 12.10, 13.52, 13.86, 40.77 (d, J = 50 Hz), 50.94 (d, J = 125 Hz), 104.29, 106.77, 118.18, 120.60 (d, J = 4.6 Hz), 121.54, 123.62 (d, J = 10.6 Hz), 126.47, 126.84, 127.74, 128.28, 128.33, 128.37, 128.40, 128.58, 128.73, 128.93, 129.10, 129.48, 129.69, 129.89, 129.99, 131.65, 131.80, 132.07 (d, J = 10 Hz), 132.22 (d, J = 2.6 Hz), 133.22, 137.10, 141.27 (d, J = 14.6 Hz), 141.81, 141.96, 146.96, 147.61, 149.92, 185.63. ^{31}P NMR ($CDCl_3$): δ −4.42, 23.71. Anal. Calcd for $C_{31}H_{28}N_3OP$: C, 76.06; H, 5.76; N, 8.58. Found: C, 75.74; H, 5.71; N, 8.85.

Synthesis of *o*-(3,5-$Me_2C_3HN_2$)C_6H_4N═P(Ph_2)CH_2C(O)-*t*-Bu (10). A solution of 1-(2′-azidophenyl)-3,5-dimethylpyrazole (2.00 g, 9.38 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $Ph_2PCH_2C(O)$*t*Bu (2.67g, 9.39 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under reduced pressure, and the residue was dissolved in *n*-hexane. The resulting solution was concentrated and kept at −20 °C to form a yellow powder of **10** (3.00 g, 68%), mp 110−112 °C. ^{1}H NMR ($CDCl_3$): δ 0.78 (s, *t*-Bu), 0.92 (s, *t*-Bu), 2.13 (s, Me), 2.18 (s, Me), 2.23 (s, Me), 3.59 (d, J = 14.7 Hz, CH), 3.72 (d, J = 32.4 Hz, CH), 5.87 (s, pyrazolyl), 5.93 (b, pyrazolyl), 6.37 (d, J = 7.8 Hz, Ar), 6.51−6.82 (m, Ar), 6.88 (t, J = 7.2 Hz, Ar), 6.92−7.80 (m, Ar). ^{13}C NMR ($CDCl_3$): δ 11.85, 12.10, 13.56, 13.91, 25.70, 28.50, 38.29 (d, J = 55.6 Hz), 47.50 (d, J = 122.5 Hz), 104.35, 106.73, 118.11, 120.95 (d, J = 4.5 Hz), 121.23, 123.79 (d, J = 10.6 Hz), 126.49, 127.90, 128.50 (d, J = 12.1 Hz), 128.85, 128.97 (d, J = 12.4 Hz), 131.54 (d, J = 10.5 Hz), 131.86 (d, J = 4.7 Hz), 132.33 (d, J = 0.6 Hz), 137.61, 141.90, 147.39, 147.64, 149.77, 179.86. ^{31}P NMR ($CDCl_3$): δ −2.25, 24.44. Anal. Calcd for $C_{29}H_{32}N_3OP$: C, 74.18; H, 6.87; N, 8.95. Found: C, 74.06; H, 7.04; N, 8.69.

Synthesis of [Zn(Et){*o*-(OC(Ph)═CHP(Ph_2)═N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (11). $ZnEt_2$ (1.60 mL, 1 M solution in hexane, 1.60 mmol) was added dropwise to a stirred solution of **9** (0.73 g, 1.50 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The resulting solution was concentrated under vacuum. A small amount of *n*-hexane was added to the solution to give colorless crystals of **11** (0.78 g, 89%), mp 190−192 °C. ^{1}H NMR (C_6D_6): δ 0.95 (q, J = 8.1 Hz, 2H, ZnEt), 1.46 (s, 3H, Me), 1.80 (t, J = 8.1 Hz, 3H, ZnEt), 2.49 (s, 3H, Me), 4.43 (d, J = 23.4 Hz, 1H, PCH), 5.51 (s, 1H, pyrazolyl), 6.53 (d, J = 3.9 Hz, 2H, Ar), 6.72−6.80 (m, 2H, Ar), 6.97 (b, 5H, Ar), 7.13−7.20 (m, 5H, Ar), 7.58 (b, 3H, Ar), 8.01−8.06 (m, 2H, Ar). ^{13}C NMR (C_6D_6): δ −1.41, 12.27, 13.61, 14.26, 68.11 (d, J = 133.9 Hz), 107.04, 120.94, 126.30, 127.94, 128.18, 128.60, 128.67, 129.27, 131.24 (d, J = 1 Hz), 132.48 (d, J = 9.8 Hz), 133.82 (d, J = 10.8 Hz), 141.02, 142.88 (d, J = 16.2 Hz), 144.86 (d, J = 5.5 Hz), 150.50, 180.81. ^{31}P NMR (C_6D_6): δ 21.87. Anal. Calcd for $C_{33}H_{32}N_3OPZn$: C, 67.99; H, 5.53; N, 7.21. Found: C, 68.03; H, 5.46; N, 7.32.

Synthesis of [Zn(Et){*o*-(OC(*t*-Bu)═CHP(Ph_2)═N)C_6H_4(3,5-$Me_2C_3HN_2$)}] (12). The same procedure as for **11** was used. Thus, reaction of **10** (0.35 g, 0.75 mmol) with $ZnEt_2$ (0.80 mL, 1 M solution in hexane, 0.80 mmol) in toluene afforded, after workup, colorless crystals of **12** (0.32 g, 76%), mp 161−163 °C. ^{1}H NMR (C_6D_6): δ 0.88 (q, J = 8.1 Hz, 2H, ZnEt), 1.33 (s, 9H, *t*-Bu), 1.43 (s, 3H, Me), 1.79 (t, J = 8.1 Hz, 3H, ZnEt), 2.53 (s, 3H, Me), 3.79 (d, J = 24.3 Hz, 1H, PCH), 5.57 (s, 1H, pyrazolyl), 6.48−6.56 (m, 2H, Ar), 6.71−6.79 (m, 1H, Ar), 6.97 (b, 6H, Ar), 7.15−7.24 (m, 1H, Ar), 7.58 (b, 4H, Ar). ^{13}C NMR (C_6D_6): δ −1.52, 12.34, 13.55, 14.34, 29.25, 41.46 (d, J = 13.7 Hz), 63.94 (d, J = 132.8 Hz), 106.82, 120.87 (d, J = 2.9 Hz), 126.29 (d, J = 1.8 Hz), 128.26, 128.58, 128.61, 128.64, 128.72, 131.02 (d, J = 1.7 Hz), 132.29 (d, J = 9.7 Hz), 133.69 (d, J = 10.6 Hz), 141.04, 144.89 (d, J = 5.9 Hz), 150.21, 195.81 (d, J = 1.9 Hz). ^{31}P NMR (C_6D_6): δ 18.17. Anal. Calcd for $C_{31}H_{36}N_3OPZn$: C, 66.13; H, 6.45; N, 7.46. Found: C, 65.71; H, 6.42; N, 7.55.

X-ray Crystallography. Single crystals of complexes **5** and **11** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected at 294(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[21] and refined against F^2 by full-matrix least squares using SHELXL-97.[22] Hydrogen atoms were placed in calculated positions.

Typical Procedure for the ROP of *rac*-Lactide. A typical polymerization procedure is exemplified by the synthesis of PLA using complex **5** as a catalyst precursor. BnOH (0.78 mL, 0.1 M solution in toluene, 0.078 mmol) was added dropwise to a solution of **5** (28.4 mg, 0.078 mmol) in toluene (2 mL), and the mixture was stirred for 2 h. Solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (5 mL) to form a catalyst solution. The catalyst solution (2.5 mL) was injected into a stirred solution of *rac*-LA (0.562 g, 3.90 mmol) in CH_2Cl_2 (5.3 mL) at 25 °C. The solution was stirred for 1 min, and the reaction was quenched by adding several drops of glacial acetic acid into the reaction mixture. A small amount of sample was taken from the mixture to measure the conversion of *rac*-LA by a ^{1}H NMR spectrum. The remaining sample was dropped into *n*-hexane to form white precipitates. The precipitates were collected by filtration and dried under vacuum to give a white solid for GPC analysis.

Kinetic Studies of Polymerization of *rac*-LA Catalyzed by 11-BnOH. A method similar to that used in the typical polymerization procedure was used to prepare a catalyst solution (0.0234 M in CH_2Cl_2) through reaction of **11** with BnOH. A Schlenk tube containing a solution of *rac*-LA (1.35 g, 9.36 mmol) in CH_2Cl_2 (14.7 mL) was kept in an oil bath preset at 38 °C. To the stirred solution was added the catalyst solution (4.0 mL). Samples were taken from the reaction mixture using a syringe at 20 min intervals. The conversion of *rac*-LA in each of the samples was measured by ^{1}H NMR spectra, and the polymer was precipitated in *n*-hexane. The precipitates were collected by filtration and dried under vacuum to afford a white solid for GPC analysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, figures, and a table giving X-ray crystallographic data for complexes **5** and **11**, ^{1}H NMR spectra of PLAs, and the proposed mechanism for the catalytic polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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