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Bis(imino)aryl NCN Pincer Aluminum and Zinc Complexes: Synthesis, Characterization, and Catalysis on L-Lactide Polymerization

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Reactions of 2,6-$(ArN{=}CH)_2C_6H_3Li$ with $AlEt_2Cl$ afford a number of NCN pincer aluminum complexes (2,6-$(ArN{=}CH)_2C_6H_3)AlEt_2$ (Ar = Ph (**1**), 2,6-$Me_2C_6H_3$ (**2**), 2,6-$Et_2C_6H_3$ (**3**), 2,6-$^iPr_2$-C_6H_3 (**4**)). Similar reactions of 2,6-$(ArN{=}CH)_2C_6H_3Li$ with ZnEtCl produce bisligated zinc complexes (2,6-$(ArN{=}CH)_2C_6H_3)_2Zn$ (Ar = Ph (**5**), 2,6-$Me_2C_6H_3$ (**6**), 2,6-$Et_2C_6H_3$ (**7**)) and monoligated NCN pincer zinc complex (2,6-$(ArN{=}CH)_2C_6H_3$)ZnEt (Ar = 2,6-$^iPr_2C_6H_3$ (**8**)). All complexes were characterized by ^1H and ^{13}C NMR spectroscopy, and the molecular structures of complexes **3**, **4**, **6**, **7**, and **8** were determined by X-ray crystallography. The X-ray diffraction analysis reveals that both complexes **3** and **4** adopt a distorted trigonal-bipyramidal geometry around the aluminum central metal with three carbon atoms in the equator and the two imine nitrogen atoms in the apical positions. Complexes **6** and **7** adopt a distorted tetrahedral geometry around their zinc metal centers, while complex **8** adopts a square-planar geometry around its metal center. All these Al and Zn complexes are efficient initiators for L-lactide ring-opening polymerization in the presence of benzyl alcohol, and the polymerization reaction takes place in an immortal manner. The productivity of the Zn complexes is generally higher than that of the Al complexes under similar conditions.

Introduction

In the past decades, polylactides (PLAs) prepared from renewable sources have received considerable attention as important biodegradable materials for biomedical, pharmaceutical, and agricultural applications.[1] Although various methods have been exploited and used, the most efficient route for the synthesis of PLAs is the lactide ring-opening polymerization employing the metal alkoxides as initiators. Many kinds of structurally well-defined alkoxides of Sn,[2] Al,[3] Zn,[3d,4] Mg,[5,4d] Fe,[6] Ti,[7] In,[8] and the rare earth metals[9] have been investigated, in which the aluminum- and zinc-based systems seem to be the best candidates in the preparation of PLAs due to their high Lewis acidity, low toxicity and good abilities in controlling the molecular weight and molecular weight distribution. In general, most of the investigated aluminum and zinc complexes have a formula

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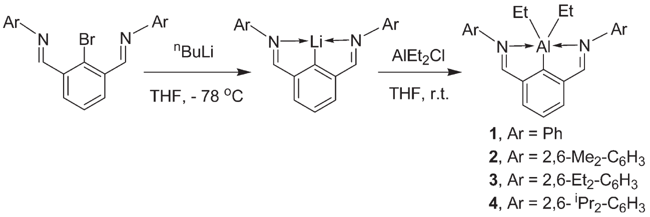
of L_nMR in which M is the central metal atom (Al or Zn) coordinated by one or two ancillary ligand(s) L and an alkoxy or alkyl ligand R. The ancillary ligand has been proved to play an important role in tuning the steric and electronic properties of the initiator and, in turn, determining the productivities and even stereoselectivity of the ring-opening polymerization. Over the past decades significant efforts have been devoted to the design and synthesis of appropriate ancillary ligands to improve the performance of the initiators, and many main group and transition metal complexes with various ligands have been developed. It has been reported that some Al and Zn complexes with achiral/chiral salen or salan ligands show significant stereocontrol over the ring-opening polymerization of lactides.[10] Along with the development of the salen and salan complexes, some Al and Zn complexes with a β-diketiminate ligand[11] were also investigated. Recently, Lin's group and our group also reported some alkyl complexes of Al and Zn chelated by an anilindo-aldimine ligand show high productivities for ε-caprolactone and L-lactide ring-opening polymerization in the presence of benzyl alcohol and the polymerizations take place in a controlled fashion.[12]

Pincer ligands have attracted widespread interest in the area of new catalyst design and synthesis for their unique structural feature. Complexes of Ru, Os, Ni, Pd, Pt, and Rh with a pincer ligand[13−18] have been extensively studied as catalysts for Heck coupling and other C−C bond formation reactions. More recently, we reported the bis(imino)aryl NCN pincer lanthanide complexes as catalysts for the polymerization of dienes with good catalytic activities and high cis-1,4 selectivities.[19] Although some Al dichloride, dialkyl,[20] and dihydride[20,21] complexes chelated by a diamine NCN pincer ligand have been reported, to the best of our knowledge, Al and Zn complexes supported by a bis(imino)aryl NCN pincer ligand have not been seen in the literature. In this contribution, we report the synthesis and characterization of several new pincer aluminum and zinc complexes, $(2,6\text{-}(ArN{=}CH)_2C_6H_3)AlEt_2$ (Ar = Ph (**1**), $2,6\text{-}Me_2C_6H_3$ (**2**), $2,6\text{-}Et_2C_6H_3$ (**3**), $2,6\text{-}{}^iPr_2C_6H_3$ (**4**)), $(2,6\text{-}(ArN{=}CH)_2C_6H_3)_2Zn$ (Ar = Ph (**5**), $2,6\text{-}Me_2C_6H_3$ (**6**), $2,6\text{-}Et_2C_6H_3$ (**7**)) and $(2,6\text{-}(ArN{=}CH)_2C_6H_3)ZnEt$ (Ar = $2,6\text{-}{}^iPr_2C_6H_3$ (**8**)), as well as their catalytic behavior as initiators for the ring-opening polymerization of L-lactide.

Scheme 1. Synthetic Route for the κ^3N,C,N'-NCN Pincer Aluminum Complexes



1, Ar = Ph
2, Ar = $2,6\text{-}Me_2\text{-}C_6H_3$
3, Ar = $2,6\text{-}Et_2\text{-}C_6H_3$
4, Ar = $2,6\text{-}{}^iPr_2\text{-}C_6H_3$

Results and Discussion

Synthesis and Characterization of Aluminum Complexes. A primary approach to the synthesis of the NCN pincer transition metal complexes is through the oxidation addition of the middle aryl C−X bond in the ligand to low-valent metal precursors.[18a,13g] However, this approach is limited to the precursors with high reactivity such as $[RhCl(COD)]_2$, $Pt(dipdba)_2$, and $[Ni(PPh_3)_4]$. We have found that the lithium salt elimination reaction is an efficient method for the synthesis of bis(imino)aryl NCN pincer lanthanide complexes in high yields.[19] The new NCN pincer aluminum complexes **1**−**4** were synthesized in a similar way. The lithium salts of the ligands were prepared first *in situ* by treatment of the ligands with ⁿBuLi in THF at low temperature. Reactions of the *in situ* formed lithium salts of the ligands with $AlEt_2Cl$ afforded the target complexes in moderate yields, as shown in Scheme 1.

All aluminum complexes **1**−**4** were characterized by elemental analyses and ^1H and ^{13}C NMR spectroscopy. For all complexes, similar resonances in the regions of −0.01 to 0.05 ppm and 0.70−0.75 ppm for the methylene and methyl protons of the $Al\text{-}CH_2CH_3$ group, respectively, can be observed in the ^1H NMR spectra. At the low-field region, a singlet signal at 8.35−8.62 ppm can be assigned to the *H*C=N proton, which shifts downfield with respect to the corresponding signal for their free ligands. For these complexes, the resonances for the two aryl groups on the two imine N atoms are the same, which indicates these molecules have a C_{2v} symmetry in solution and the two imine groups equivalently coordinate to the aluminum atom, as evidenced by the observation of only one *H*C=N proton resonance. Since different Al−N bond lengths were determined in the solid state for both complexes, it is possible that the Al atom in these complexes moves quickly between the two imine N atoms in solution. Attempts to confirm this dynamic procedure by variable-temperature ^1H NMR experiments were not successful (Figure S3 in the Supporting Information).

Single crystals of complexes **3** and **4** suitable for X-ray diffraction study were grown from hexane. Their molecular

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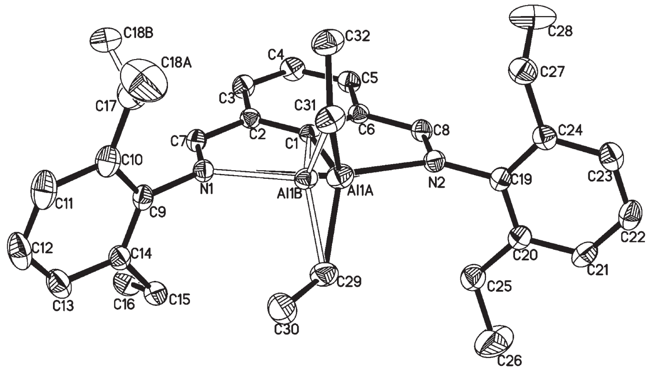


Figure 1. Perspective view of complex **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1A−C1 1.963(2), Al1A−N2 2.1637(19), Al1A−C29 2.038(8), Al1A−C31 2.033(7); C1−Al1A−C29 124.9(6), C1−Al1A−C31 113.4(4) N2−Al1A−C1 84.4(5), C31−Al1A−C29 109.4(5).

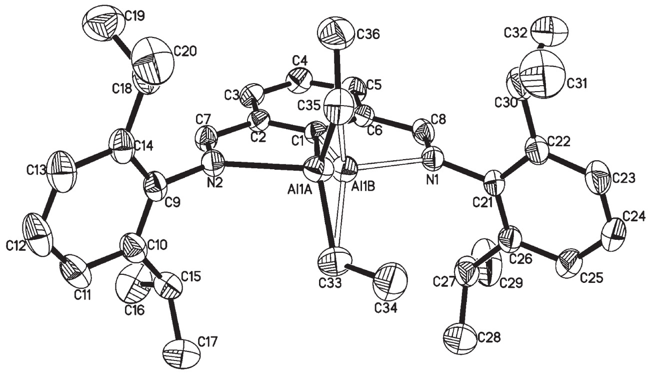
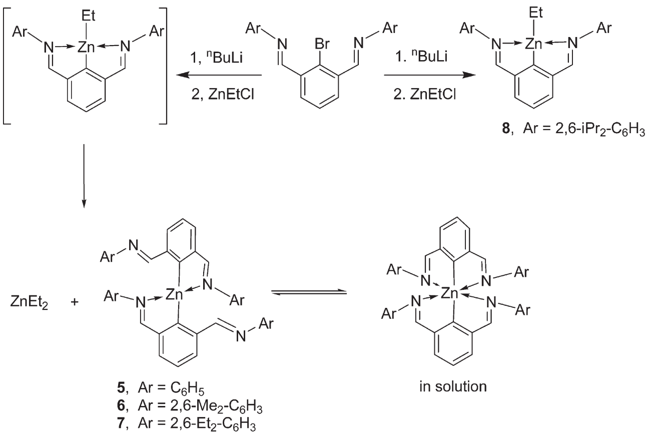


Figure 2. Perspective view of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1A−C1 1.977(7), Al1B−C1 2.012(9), Al1A−C(33) 1.988(6), Al1B−C(33) 1.984(6), Al1A−C(35) 1.976(5), Al1B−C(35) 1.987(6), Al1A−N2 2.25(2), Al1B−N2 2.1862(19), C33−Al1A−C35 113.5(3), C33−Al1B−C35 113.2(3), C1−Al1A−N2 80.1(5), C1−Al1B−N1 81.4(3).

Scheme 2. Synthetic Route for the κ^2C,N- and κ^3N,C,N′-NCN Zn Complexes



structures and some selected bond lengths and angles, determined by X-ray diffraction analysis, are depicted in Figures 1 and 2, respectively. In both complexes, the monoanionic NCN pincer ligand coordinates to the central metal in a tridentate fashion. The Al atom is disordered over two positions, and the geometry around the disordered Al atom can be described as a distorted trigonal bipyramid with three carbon atoms in the equator and the two imine nitrogen atoms in the apical positions. The Al atom in both complexes is essentially coplanar with the NCN plane with a deviation of 0.1136 Å (av) for **3** and 0.1358 Å (av) for **4**. The Al−C_{ipso} bond lengths of 1.963 Å (av) in **3** and 1.977 Å (av) in **4** are similar to those observed in neutral aryl aluminum complexes bis(8-methoxynaphthyl)AlR (R = Me, Et)[22] but slightly longer than those found in cationic aryl aluminum complexes $[(2,6\text{-}Mes_2C_6H_3)_2Al]^+[B(C_6F_5)_4]^-$.[23] In contrast to the observation by NMR experiments in solution, different Al−N bond lengths were determined for both complexes **3** and **4**. The short Al−N bond lengths of 2.1637 Å (av) in **3** and 2.1862 Å (av) in **4** are slightly longer than the one (1.972(3) Å) reported for $\{2,4\text{-}{}^tBu_2\text{-}6\text{-}(CH{=}NC_6H_3{}^iPr_2\text{-}2,6)C_6H_2O\}AlMe_2$,[24] while the long Al−N bond lengths of 2.84 Å (av) in **3** and 2.73 Å (av) in **4** are apparently longer than typical Al−N coordination bond lengths. These values are shorter than the sum of the van der Waals radii of N and Al atoms [$r_v(N) + r_m(Al) = 1.55 + 1.43 = 2.98$ Å], suggesting the presence of the imine N coordination to the Al atom.[25] The two aryl rings on the imine N atoms dispose the vertical positions against the parent plane, and the ethyl groups on the Al atom arrange in *trans* positions to form a large Et−Al−Et angle (111.99° (av) in complex **3** and 113.35° (av) in complex **4**).

Synthesis and Characterization of Zinc Complexes. The zinc complexes **5**−**8** were prepared in a similar procedure to that for the aluminum complexes **1**−**4** as shown in Scheme 2. Reactions of the *in situ* formed lithium salts of the ligands with ZnEtCl produced complexes **5**−**7** in yields of 40−50%, while complex **8** was obtained in a yield of 70%. Complexes **5**−**8** were all characterized by elemental analyses and ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR analysis on complexes **5**−**7** shows no resonance in the upfield region for the assumed ethyl group attached to the Zn atom in these complexes. As seen for the aluminum complexes **1**−**4**, the resonances for the two *H*C=N protons and the corresponding protons in the two aryl groups on the imine N atoms are the same for complexes **5**−**7**, which indicates the two imine groups in the NCN pincer ligand equivalently coordinate to the central zinc atom at room temperature. X-ray diffraction analysis on complexes **6** and **7** reveals that the Zn atoms in these complexes are chelated by two κ^2*C,N*-NCN ligands, in which each NCN ligand coordinates to the zinc atom with the C_{ipso} atom and one of the two imine N atoms. No obvious fluxionality was detected in variable-temperature ^{1}H NMR experiments with complex **7**, suggesting that the complex should be six-coordinated in solution (see Figure S4 in the Supporting Information). ^{1}H NMR analysis of complex **8** demonstrates the existence of the ethyl group on the Zn

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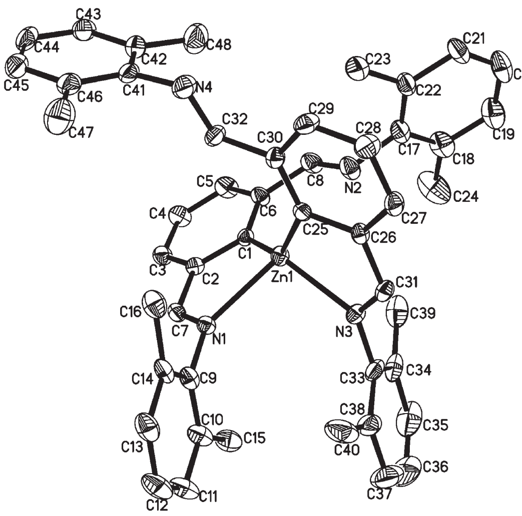

Figure 3. Perspective view of complex **6** with thermal ellipsoids drawn at the 30% probability level. One molecular of two independent molecules in a unit cell is presented. Hydrogens and uncoordinated solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C1 1.963(2), Zn1−C25 2.1637(19), Zn1−N12 2.1862(19), Zn1−N3 2.3116(7); C1−Zn1−N1 178.83(3), C25−Zn1−N3 155.31(7).

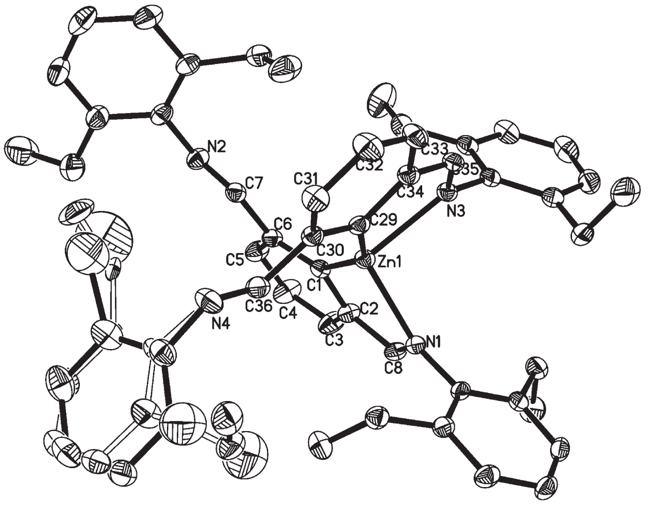

Figure 4. Perspective view of complex **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C1 1.963(2), Zn1−C29 2.1637(19), Zn1−N12 2.1862(19), Zn1−N3 2.3116(7); C1−Zn1−N1 178.83(3), C29−Zn1−N3 155.31(7).

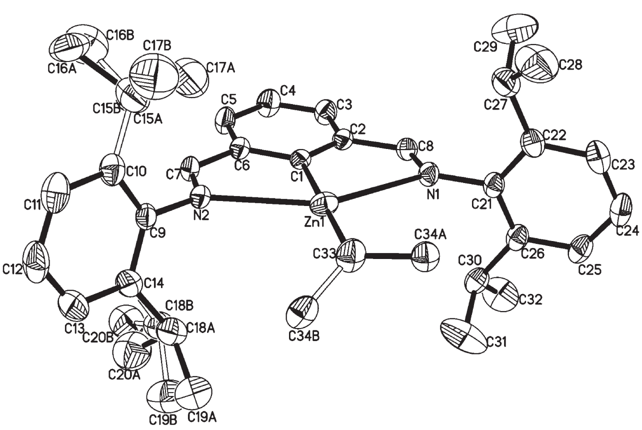

Figure 5. Perspective view of complex **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogens and uncoordinated solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C1 1.963(2), Zn1−C29 1.963(2), Zn1−N1 2.1637(19), Zn1−N2 2.1862(19); C1−Zn1−C33 178.61(14), N1−Zn1−N2, 149.24(7).

atom, and the whole molecule has a C_{2v} symmetry in solution, as discussed above for complexes **1**−**4**. X-ray diffraction analysis confirms that the Zn atom in complex **8** is ligated by a κ^3*N,C,N′*-NCN pincer ligand and an ethyl group. It is possible that monoligated ethyl zinc complexes similar to **8** are formed first in these reactions and then disproportionate rapidly to the bisligated complexes **5**−**7** and $ZnEt_2$ (Scheme2). Similar disproportionation was observed in the zinc complexes supported by β-diketiminato,[26] fluorous imino-alkoxide,[27] and tris(pyrazolyl)borate ligands.[28] It was believed that a decrease in the electron density at the Zn center is one of the driving forces for this disproportionation, while an increase in the bulk of the ligands around the Zn center may inhibit such disproprotionation. The fact that complex **8** can be synthesized in high yield supports such an assumption.

The molecular structures of complexes **6**, **7**, and **8**, together with some selected bond lengths and angles, are given in Figures 3, 4, and 5, respectively. The geometry around the metal center for complexes **6** and **7** can be described as distorted tetrahedral. The Zn−C bond lengths (1.963(2) and 2.1637(19) Å in **6**, 2.1637(19) and 2.411(4) Å in **7**) are similar to the ones (2.05 Å (av)) observed in Li(thf)-$Zn(C_6H_4CH_2NMe_2\text{-}2)_3$[29] and slightly longer than that (1.971(3) Å) in $Cp_2Zr(ZnC_6H_3\text{-}2,6\text{-}(2,4,6\text{-}{}^iPr_3C_6H_2)_2)_2$.[30] Complex **8** adopts a square-planar geometry around the zinc metal center with a κ^3*N,C,N′*-NCN pincer ligand and an ethyl group attached to the Zn(II) ion. The Zn atom is essentially coplanar with the NCN plane. As seen in complexes **3** and **4**, the two aryl rings on the imine N atoms in complex **8** also take the vertical positions against the parent NCN plane. The Zn−C bond length of 1.963 Å is shorter than the ones in complexes **6** and **7** and those observed in the above-mentioned Zn complexes.[29,30]

Polymerization of L-Lactide. All aluminum complexes **1**−**4** and zinc complexes **5**−**8** were investigated as initiators for the ring-opening polymerization of L-lactide. The polymerizations were carried out in toluene at 70 °C, and the representative polymerization results are summarized in Table 1. All aluminum complexes show very low productivities in the absence of benzyl alcohol. Low conversions of L-lactide (21.1% for **2** and 28.2% for **3**) were achieved from reactions initiated by complexes **2** and **3**, while no polymer was obtained from the complexes **1** and **4** initiated reactions after 24 h (entries 1−4). The number averaged molecular

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Table 1. Polymerization Results of L-Lactide Initiated with Pincer Aluminium and Zinc Complexes[a]

entry	initiator	[M]/[I]/[BnOH]	time (min)	yield (%)[b]	M_c[c] ($\times 10^4$)	M_n[d] ($\times 10^4$)	PDI[d]
1	**1**	100/1/0	1440				
2	**2**	100/1/0	1440	21.1	0.30	0.20	1.12
3	**3**	100/1/0	1440	28.2	0.40	0.31	1.13
4	**4**	100/1/0	1440				
5	**5**	100/1/0	30	21.1	0.30	0.24	1.13
6	**6**	100/1/0	30	52.1	0.75	8.72	1.57
7	**7**	100/1/0	30	37.6	0.54	4.14	1.37
8	**8**	100/1/0	30	47.8	0.69	4.85	1.31
9	**1**	100/1/2	1440				
10	**2**	100/1/2	1440	71.3	0.51	0.69	1.09
11	**3**	100/1/2	1440	93.8	0.68	0.74	1.07
12	**4**	100/1/2	1440	82.6	0.59	0.73	1.04
13	**5**	100/1/1	30	86.5	1.24	1.17	1.09
14	**6**	100/1/1	30	96.2	1.39	1.29	1.02
15	**7**	100/1/1	30	97.1	1.40	1.34	1.02
16	**8**	100/1/1	30	92.6	1.33	1.24	1.02
17	**8**	300/1/1	120	99.2	4.29	4.17	1.65
18	**8**	500/1/1	120	95.0	6.84	5.41	1.63
19	**8**	700/1/1	180	91.7	9.24	8.14	1.49
20	**8**	900/1/1	240	71.9	9.32	7.19	1.56
21	**8**	100/1/2	30	97.1	0.70	0.60	1.07
22	**8**	100/1/3	30	98.0	0.47	0.53	1.05
23	**8**	500/1/5	120	100	1.44	1.24	1.12
24	**8**	500/1/10	120	97.1	0.70	0.67	1.19

[a] Polymerization conditions: 30 μmol of initiator; T = 70 °C; 15 mL of toluene. [b] Detemined by ^{1}H NMR. [c] Calculated from ($[\mathrm{LA}]_0/[\mathrm{I}]_0$) × conversion × 144 or ($[\mathrm{LA}]_0/[\mathrm{BnOH}]_0$) × conversion × 144. [d] Determined by GPC against polystyrene standards in THF, multiplied by 0.58.[32]

weight (M_n) values of the resulting polymers from the complexes **2** and **3** initiated reactions are in agreement with the calculated molecular weight (M_c) values with relatively narrow polydispersity indexes (PDIs) (1.12−1.13). In comparison to the aluminum complexes, the Zn complexes are much more productive under the same conditions. Conversions of 21.2−52.1% could be obtained in 30 min (entries 5−8) with complexes **5**−**8** as activators. However, the measured M_n values of the polymers produced by complexes **6**−**8** are several times larger than the calculated M_c values with broader PDIs. The uncontrollable behavior of these single-component systems may be attributed to the poor nucleophilicity of the alkyl or aryl groups and inefficient initiation.[31] Upon activation with benzyl alcohol (BnOH), the productivity of most of these complexes is drastically improved except complex **1** (entries 9−16). The inactivity of the complex **1** system may result from poor stability of the intermediates formed from the reaction of complex **1** with L-lactide or BnOH. Considering that complex **4** itself could not initiate the ring-opening polymerization of L-lactide, it is especially remarkable to achieve a high conversion of 82.6% from the **4**/BnOH-initiated reaction (entry 12). These results imply that the inactivity of the BnOH-free complex **4** system may be caused by the difficult approach of L-lactide to the metal center of complex **4** shielded by its bulky ligand. The M_n values of the polymers obtained from these BnOH-activated reactions are close to the M_c values calculated according to the monomer/BnOH (M/B) molar ratio, and the PDIs are all quite narrow, ranging from 1.02 to 1.09, which is indicative of single-site catalyst or initiator systems. As observed above for the BnOH-free reactions, the Zn initiator systems are also much more productive than the Al initiator systems in the presence of BnOH.

The performance of the zinc complex/BnOH initiating systems was further investigated using the **8**/BnOH initiating system. To examine the effect of the monomer/initiator (M/I) molar ratio on the ring-opening polymerization of L-lactide, a number of experiments with a constant initiator/BnOH (I/B) molar ratio (1:1) and different M/I molar ratios (from 300:1 to 900:1) were carried out (entries 17−20). As can be seen from the results listed in Table 1, the molecular weight M_n of the resulting polymer increases with the increase in the M/I molar ratio. Meanwhile, the PDI gets broad and the monomer conversion decreases. The broad PDIs may be attributed to intermolecular transesterification and intramolecular transesterification (cyclization) due to the lengthening reaction time. The intermolecular and intramolecular transesterifications have been observed in magnesium phenoxides[5b] and silylamido lanthanide[9g] initiating systems. The effect of the M/B molar ratio on the ring-opening polymerization of L-lactide was also examined with the **8**/BnOH initiating system (entries 21−24). It was found that the molecular weight M_n of the resulting polymer increases linearly with the increase in the M/B molar ratio. The corresponding PDIs are narrow and the measured M_n values are in agreement with the M_c values calculated

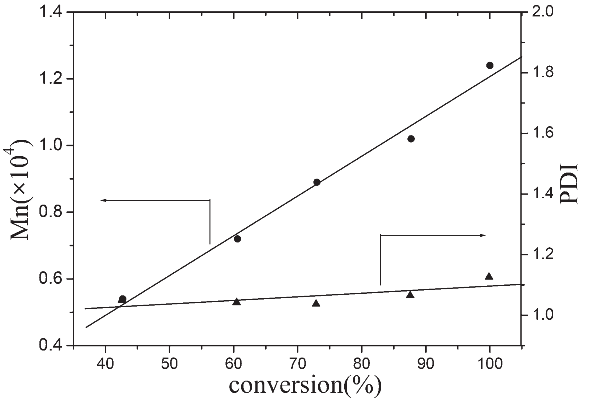

Figure 6. Plot of molecular weight M_n vs monomer conversion for **8**/BnOH-initiated polymerization of L-lactide. Conditions: 30 μmol of initiator, M/I/B = 500:1:5, 10 mL of toluene, 70 °C.

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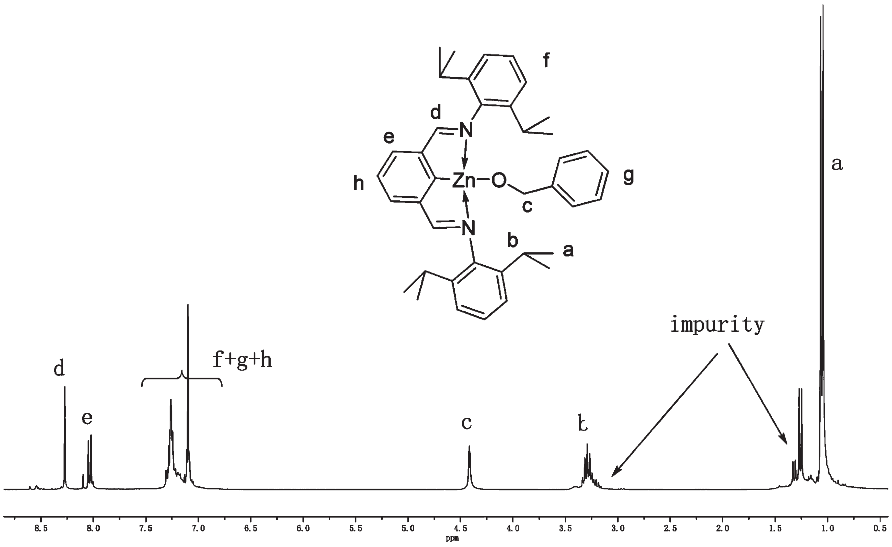
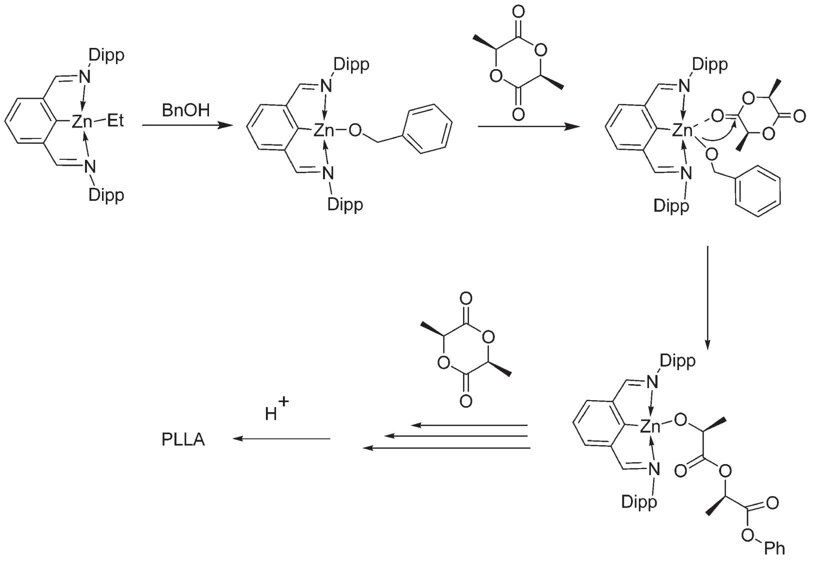


Figure 7. *In situ* ^{1}H NMR spectrum of the reaction mixture of **8** with BnOH (1:1) in C_6D_6.

Scheme 3. Proposed Mechanism for the ROP of L-Lactide Initiated by 8/BnOH



according to the M/B molar ratio, indicating somewhat "immortal" behavior of the binary initiating system at low monomer to initiator ratios. To further investigate the behavior of this initiating system, polymerization experiments for different times with a monomer/**8**/BnOH = 500:1:5 system were carried out. It was found that the molecular weight M_n of the resultant polymers increases linearly with the increase of the monomer conversion, and the PDIs of these polymers are narrow (1.02−1.14), as shown in Figure 6. These results further demonstrate the immortal characterization of the binary initiating system.

In order to further understand the polymerization reaction of lactide initiated by the binary system, the reaction of complex **8** with BnOH (1:1) was monitored *in situ* by ^{1}H NMR at room temperature. The ^{1}H NMR spectrum shows the disappearance of the resonances for protons of $ZnCH_2CH_3$ in the high-field region and the appearance of a broad $PhCH_2OZn$ signal in the region 4.0−4.5 ppm, demonstrating the formation of a benzyloxy zinc complex.

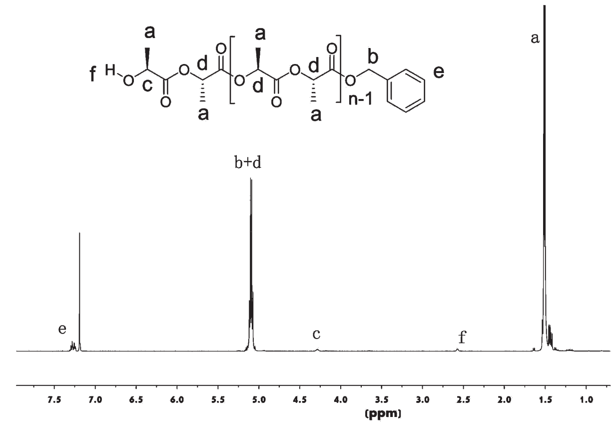


Figure 8. ^{1}H NMR spectrum of a polymer sample obtained from the **8**/BnOH system with M/I/B = 25:1:1 (in $CDCl_3$).

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

The benzyloxy complex can survive for several hours in solution and then decomposes gradually to unidentified compounds. The ^{1}H NMR spectrum of a PLLA oligomer obtained from the **8**/BnOH initiating system with a M/I/B molar ratio of 25:1:1 shows that the polymer chains are capped with a benzyl ester group, indicating that the alkyl zinc complex has been converted to benzyloxy zinc species before the polymerization begins and the real initiator is the benzyloxy zinc species as shown in Scheme 3.

Conclusion

A series of aluminum and zinc complexes **1**−**8** chelated by bis(imino)aryl NCN ligands have been synthesized and structurally characterized. All aluminum complexes **1**−**4** were obtained in a monoligated form in which the Al atom is chelated by a $\kappa^3 N,C,N'$-NCN pincer ligand. The zinc complexes **5**, **6**, and **7** were proved to be bisligated with the zinc being chelated by two $\kappa^2 N,C$-NCN ligands, while complex **8** possesses a structure similar to those of complexes **1**−**4**, with the central zinc atom being chelated by a $\kappa^3 N,C,N'$-NCN pincer ligand. All these Al and Zn complexes are efficient initiators for L-lactide ring-opening polymerization in the presence of benzyl alcohol, and the polymerization reaction takes place in an immortal manner. The productivity of the Zn complexes is generally higher than that of the Al complexes under similar conditions.

Experimental Section

General Considerations. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or drybox techniques. Toluene and hexane were dried over sodium/benzophenone and distilled under nitrogen prior to use. Elemental analyses were performed on a Varian EL microanalyzer. NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer at room temperature in CDCl$_3$ or C$_6$D$_6$. The molecular weight and molecular weight distribution of the polymers were measured on a TOSOH HLC 8220 GPC at 40 °C using THF as eluent against polystyrene standards. ZnEtCl,[33] 2-bromoisophthalaldehyde, and the ligands[19] were synthesized according to literature procedures. 2,6-Dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, and AlEt$_2$Cl were purchased from Aldrich.

(2,6-(C$_6$H$_5$N=CH)$_2$C$_6$H$_3$)AlEt$_2$ (1). A ^{n}BuLi solution in hexane (0.98 mL, 1.35 mmol) was added dropwise to a THF (20 mL) solution of 2,6-(C$_6$H$_5$N=CH)$_2$C$_6$H$_3$-1-Br (0.47 g, 1.29 mmol) at −78 °C. The reaction mixture was stirred for 1 h before the addition of AlEt$_2$Cl (0.16g, 1.35 mmol). The mixture was allowed to warm to room temperature gradually and stirred overnight. The solvents were removed under reduced pressure, and the residue was extracted with hexane. The volume of the solvent was reduced to precipitate the product as a yellow powder. Yield: 0.22 g (46%). Anal. Calcd for C$_{24}$H$_{25}$AlN$_2$ (%): C, 78.23; H, 6.84; N, 7.60. Found: C, 78.34; H, 6.88; N, 7.53. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ −0.01 (q, $J_{\mathrm{H-H}}$ = 8.1 Hz, 4H, Al-CH_2CH$_3$), 0.70 (t, $J_{\mathrm{H-H}}$ = 8.1 Hz, 6H, Al-CH$_2$CH_3), 7.31−7.47 (m, 11H, N-C$_6$H$_5$, *p*-Al-C$_6$H$_3$), 7.65 (d, $J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, *m*-Al-C$_6$H$_3$), 8.62 (s, 2H, CH=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ −0.81 (s, 2C, Al-CH$_2$CH$_3$), 9.89 (s, 2C, Al-CH$_2$$CH_3$), 121.65 (s, 2C, *p*-N-C$_6$H$_5$), 126.96 (s, 1C, *p*-Al-C$_6$H$_3$), 128.13 (s, 4C, *m*-N-C$_6$H$_5$), 129.27 (s, 2C, C=N-C), 131.38 (s, 2C, *m*-Al-C$_6$H$_3$), 141.95 (s, 2C, *o*-Al-C$_6$H$_3$), 148.52 (s, 4C, *o*-N-C$_6$H$_5$), 164.22 (s, 2C, C=N-C) ppm.

(2,6-(2,6-Me$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)AlEt$_2$ (2). Complex **2** was synthesized in the same manner as **1** with 2,6-(2,6-Me$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.49 g, 1.17 mmol), ^{n}BuLi (1.21 mmol), and AlEt$_2$Cl (0.14 g, 1.16 mmol) as starting materials or reagents. Pure **2** was obtained as a yellow powder. Yield: 0.26 g (52%). Anal. Calcd for C$_{28}$H$_{33}$AlN$_2$ (%): C, 79.21; H, 7.83; N, 6.60. Found: C, 79.34; H, 7.91; N, 6.49. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ −0.02 (q, $J_{\mathrm{H-H}}$ = 8.1 Hz, 4H, Al-CH_2CH$_3$), 0.75 (t, $J_{\mathrm{H-H}}$ = 8.1 Hz, 6H, Al-CH$_2$CH_3), 2.20 (s, 12H, CH$_3$), 7.00−7.11 (m, 6H, N-C$_6$H$_3$), 7.50 (t, $J_{\mathrm{H-H}}$ = 7.5 Hz, 1H, *p*-Al-C$_6$H$_3$), 7.73 (d, $J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, *m*-Al-C$_6$H$_3$), 8.35 (s, 2H, CH=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ −0.88 (s, 2C, Al-CH$_2$CH$_3$), 9.47 (s, 2C, Al-CH$_2$CH$_3$), 19.34 (s, 4C, CH$_3$), 124.95 (s, 2C, *p*-N-C$_6$H$_3$), 128.01 (s, 1C, *p*-Al-C$_6$H$_3$), 128.19 (s, 4C, *m*-N-C$_6$H$_3$), 128.90 (s, 2C, C=N-C), 132.40 (s, 2C, *m*-Al-C$_6$H$_3$), 141.92 (s, 2C, *o*-Al-C$_6$H$_3$), 148.98 (s, 4C, *o*-N-C$_6$H$_3$), 169.68 (s, 2C, C=N−C) ppm.

(2,6-(2,6-Et$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)AlEt$_2$ (3). Complex **3** was synthesized in the same manner as **1** with 2,6-(2,6-Et$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.54 g, 1.14 mmol), ^{n}BuLi (1.20 mmol), and AlEt$_2$Cl (0.14 g, 1.20 mmol) as starting materials or reagents. Pure **3** was obtained as a yellow powder. Yield: 0.33 g, (61%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for C$_{32}$H$_{41}$AlN$_2$ (%): C, 79.96; H, 8.60; N, 5.83. Found: C, 79.52; H, 8.47; N, 5.69. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ −0.06 (q, $J_{\mathrm{H-H}}$ = 8.1 Hz, 4H, Al-CH_2CH$_3$), 0.73 (t, $J_{\mathrm{H-H}}$ = 8.1 Hz, 6H, Al-CH$_2$CH_3), 1.16 (t, $J_{\mathrm{H-H}}$ = 7.5 Hz, 4H, CH$_2$CH_3), 2.55 (q, 4H, $J_{\mathrm{H-H}}$ = 7.5 Hz, CH_2CH$_3$), 7.16 (b, 6H, N-C$_6$H$_3$), 7.51 (t, $J_{\mathrm{H-H}}$ = 7.5 Hz, 1H, *p*-Al-C$_6$H$_3$), 7.76 (d, $J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, *m*-Al-C$_6$H$_3$) 8.35 (s, 2H, CH=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ −1.15 (s, 2C, Al−CH$_2$CH$_3$), 9.40 (s, 2C, Al-CH$_2$$CH_3$), 15.20 (s, 4C, CH$_2$$CH_3$), 24.10 (s, 4C, CH$_2CH_3$), 125.41 (s, 2C, *p*-N-C$_6$H$_3$), 126.11 (s, 4C, *m*-N-C$_6$H$_3$), 128.08 (s, 1C, *p*-Al-C$_6$H$_3$), 132.50 (s, 2C, *m*-Al-C$_6$H$_3$), 135.01 (s, 4C, *o*-N-C$_6$H$_3$), 141.97 (s, 2C, *o*-Al-C$_6$H$_3$), 147.73 (s, 2C, C=N-C), 169.52 (s, 2C, CH=N-C) ppm.

(2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)AlEt$_2$ (4). Complex **4** was synthesized in the same manner as **1** with 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.57 g, 1.07 mmol), ^{n}BuLi (1.12 mmol), and AlEt$_2$Cl (0.14 g, 1.16 mmol) as starting materials or reagents. Pure **4** was obtained as a yellow powder (0.32 g, 55%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for C$_{36}$H$_{49}$AlN$_2$ (%): C, 80.55; H, 9.20; N, 5.22. Found: C, 80.10; H, 9.37; N, 4.99. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ −0.05 (q, $J_{\mathrm{H-H}}$ = 8.1 Hz, 4H, Al-CH_2CH$_3$), 0.75 (t, $J_{\mathrm{H-H}}$ = 8.1 Hz, 6H, Al-CH$_2$CH_3), 1.20 (d, 24H, $J_{\mathrm{H-H}}$ = 6.6 Hz, CH(CH_3)$_2$), 3.04 (hept, $J_{\mathrm{H-H}}$ = 6.6Hz, 4H, CH(CH$_3$)$_2$), 7.22 (m, 6H, N-C$_6$H$_3$), 7.53 (t, $J_{\mathrm{H-H}}$ = 7.5 Hz, 1H, *p*-Al-C$_6$H$_3$), 7.77 (d, $J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, *m*-Al-C$_6$H$_3$) 8.36 (s, 2H, CH=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ −1.85 (s, 2C, Al-CH$_2$CH$_3$), 9.53 (s, 2C, Al-CH$_2$$CH_3$), 24.20 (s, 8C, CH($CH_3$)$_2$) 27.69 (s, 4C, CH(CH$_3$)$_2$), 123.40 (s, 2C, *p*-N-C$_6$H$_3$), 125.74 (s, 4C, *m*-N-C$_6$H$_3$), 128.11 (s, 1C, *p*-Al-C$_6$H$_3$), 132.53 (s, 2C, *m*-Al-C$_6$H$_3$), 139.98 (s, 4C, *o*-N-C$_6$H$_3$), 142.02 (s, 2C, *o*-Al-C$_6$H$_3$), 146.27 (s, 2C, C=N-C), 169.04 (s, 2C, C=N-C).

(2,6-(C$_6$H$_5$N=CH)$_2$C$_6$H$_3$)$_2$Zn (5). A ^{n}BuLi solution in hexane (0.60 mL, 0.83 mmol) was added dropwise to a THF (20 mL) solution of 2,6-(C$_6$H$_5$N=CH)$_2$C$_6$H$_3$-1-Br (0.29 g, 0.80 mmol) at −78 °C. The reaction mixture was stirred for 4 h before the addition of ZnEtCl (0.11 g, 0.85 mmol). The mixture was allowed to warm to room temperature gradually and stirred overnight. The solvents were removed under reduced pressure, and the residue was extracted with hexane. The volume of the solvent was reduced to precipitate the product as an orange powder. Yield: 0.11 g, (43%). Anal. Calcd for C$_{40}$H$_{30}$N$_4$Zn (%): C, 76.01; H, 4.78; N, 8.86. Found: C, 75.89; H, 4.88; N, 8.81. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 7.04 (m, 20H, N-C$_6$H$_5$), 7.41 (t, $J_{\mathrm{H-H}}$ = 7.5 Hz, 2H, *p*-Zn-C$_6$H$_3$), 7.83 (d, $J_{\mathrm{H-H}}$ = 7.5 Hz, 4H, *m*-Zn-C$_6$H$_3$), 8.53 (s, 4H, CH=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ 121.10 (s, 4C, *p*-N-C$_6$H$_3$), 125.85 (s, 2C, *p*-Zn-C$_6$H$_3$),

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[33] Guerrero, A.; Hughes, D. L.; Bochmann, M. *Organometallics* **2006**, *25*, 1525.

126.87 (s, 8C, *m*-N-C$_6$H$_3$), 128.89 (s, 4C, C=N-*C*), 132.02 (s, 4C, *m*-Zn-C$_6$H$_3$), 144.01 (s, 4C, *o*-Zn-C$_6$H$_3$), 150.02 (s, 8C, *o*-N-C$_6$H$_3$), 165.78 (s, 4C, *C*=N-C), ppm.

(2,6-(2,6-Me$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)$_2$Zn (6). Complex **6** was synthesized in the same manner as **5** with 2,6-(2,6-Me$_2$-C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.47 g, 1.12 mmol), ^{n}BuLi (1.12 mmol), and ZnEtCl (0.15 g, 1.15 mmol) as starting materials or reagents. Pure **6** was obtained as an orange powder. Yield: 0.20 g, (49%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{48}H_{46}N_4Zn$ (%): C, 77.46; H, 6.23; N, 7.53. Found: C, 77.38; H, 6.19; N, 7.47. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 1.82 (s, 24H, CH$_3$), 6.85−6.94 (m, 12H, N-C$_6$H$_3$), 7.41 (t, J_{H-H} = 7.5 Hz, 2H, *p*-Zn-C$_6$H$_3$), 7.31 (d, J_{H-H} = 7.5 Hz, 4H, *m*-Zn-C$_6$H$_3$), 8.20 (s, 4H, C*H*=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ 18.43 (s, 8C, CH$_3$), 124.25 (s, 4C, *p*-N-C$_6$H$_3$), 127.11 (s, 1C, *p*-Zn-C$_6$H$_3$), 128.13 (s, 4C, *m*-N-C$_6$H$_3$), 128.63 (s, 2C, C=N-*C*), 131.99 (s, 4C, *m*-Zn-C$_6$H$_3$), 143.49 (s, 4C, *o*-Zn-C$_6$H$_3$), 149.60 (s, 8C, *o*-N-C$_6$H$_3$), 170.59 (s, 4C, *C*=N-C), ppm.

(2,6-(2,6-Et$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)$_2$Zn (7). Complex **7** was synthesized in the same manner as **5** with 2,6-(2,6-Et$_2$-C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.48 g, 1.01 mmol), ^{n}BuLi (1.05 mmol), and ZnEtCl (0.14 g, 1.07 mmol) as starting materials or reagents. Pure **7** was obtained as an orange powder. Yield: 0.19 g, (43%). Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{56}H_{62}N_4Zn$ (%): C, 78.53; H, 7.30; N, 6.54. Found: C, 78.47; H, 7.22; N, 6.45. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 0.79 (t, J_{H-H} = 7.5 Hz, 24H, CH$_2$C*H*$_3$), 2.13 (q, J_{H-H} = 7.5 Hz, 16H, C*H*$_2$CH$_3$), 6.91 (m, 12H, N-C$_6$H$_3$), 7.34 (t, J_{H-H} = 7.5 Hz, 2H, *p*-Zn-C$_6$H$_3$), 7.88 (d, J_{H-H} = 7.5 Hz, 4H, *m*-Zn-C$_6$H$_3$) 8.14 (s, 4H, C*H*=N). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ 14.66 (s, 8C, CH$_2$*C*H$_3$), 24.21 (s, 8C, *C*H$_2$CH$_3$), 124.47 (s, 4C, *p*-N-C$_6$H$_3$), 125.90 (s, 8C, *m*-N-C$_6$H$_3$), 126.95 (s, 2C, *p*-Zn-C$_6$H$_3$), 131.79 (s, 4C, *m*-Zn-C$_6$H$_3$), 134.39 (s, 8C, *o*-N-C$_6$H$_3$), 143.41 (s, 4C, *o*-Zn-C$_6$H$_3$), 148.74 (s, 2C, C=N-*C*), 170.40 (s, 4C, *C*H=N-C), ppm.

(2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$_2$C$_6$H$_3$)ZnEt (8). Complex **8** was synthesized in the same manner as **5** with 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N=CH)$_2$C$_6$H$_3$-1-Br (0.54 g, 1.02 mmol), ^{n}BuLi (1.06 mmol), and ZnEtCl (0.15 g, 1.15 mmol) as starting materials or reagents. Pure **8** (0.38 g, 70%) was obtained as an orange powder. Single crystals for X-ray diffraction analysis were obtained from hexane at −30 °C. Anal. Calcd for $C_{34}H_{44}N_2Zn$ (%): C, 74.78; H, 8.12; N, 5.13. Found: C, 74.64; H, 8.08; N, 5.22. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 0.22 (q, 4H, J_{H-H} = 5.1 Hz, Zn-C*H*$_2$CH$_3$), 0.87 (t, 3H, J_{H-H} = 5.1 Hz, Zn-CH$_2$C*H*$_3$), 1.18 (d, 24H, J_{H-H} = 6.9 Hz, CH(C*H*$_3$)$_2$), 2.99 (m, 4H, J_{H-H} = 6.9 Hz, C*H*(CH$_3$)$_2$), 6.99−7.20 (m, 6H, N-C$_6$H$_3$), 7.51 (t, 1H, J_{H-H} = 7.5 Hz, *p*-Zn-C$_6$H$_3$), 7.74 (d, 2H, J_{H-H} = 7.5 Hz, *m*-Zn-C$_6$H$_3$), 8.31 (s, 2H; C*H*=N). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 3.38 (s, 1C, Zn−-*C*H$_2$CH$_3$), 12.00 (s, 1C, Zn-CH$_2$*C*H$_3$), 23.81 (s, 8C, CH(*C*H$_3$)$_2$) 28.82 (s, 4C, *C*H(CH$_3$)$_2$), 123.61 (s, 2C, *p*-N-C$_6$H$_3$), 125.39 (s, 4C, *m*-N-C$_6$H$_3$), 132.45 (s, 1C, *p*-Zn-C$_6$H$_3$), 133.71 (s, 2C, *m*-Zn-C$_6$H$_3$), 138.70 (s, 4C, *o*-N-C$_6$H$_3$), 144.47 (s, 2C, *o*-Zn-C$_6$H$_3$), 148.86 (s, 2C, C=N-*C*), 167.79 (s, 2C, *C*=N-C).

Lactide Polymerization. In a typical polymerization experiment, an aluminum or zinc complex (30 μmol), the required amount of L-lactide, and benzyl alcohol in toluene (15 mL) were loaded in a flame-dried vessel containing a magnetic bar. The vessel was placed in an oil bath thermostated at 70 °C. After a certain reaction time, the polymer was isolated by precipitation with cold methanol. The precipitate was collected and dried under vacuum at 40 °C for 24 h. For some polymerization reactions, samples were taken for determining the monomer conversion by ^{1}H NMR during the reaction.

Crystal Structure Determination. The crystals were mounted on a glass fiber using the oil drop. Data obtained with the $\omega-2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined with full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.

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Supporting Information Available: X-ray crystallographic data and refinements for complexes **3**, **4**, **6**, **7**, and **8** in table and CIF format, ^{1}H NMR spectra of complexes **1**−**8**, and variable-temperature ^{1}H NMR spectra of complexes **3** and **7** are available free of charge via the Internet at http://pubs.acs.org.