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Zinc and Aluminum Complexes Supported by Quinoline-Based N,N,N-Chelate Ligands: Synthesis, Characterization, and Catalysis in the Ring-Opening Polymerization of ε-Caprolactone and *rac*-Lactide

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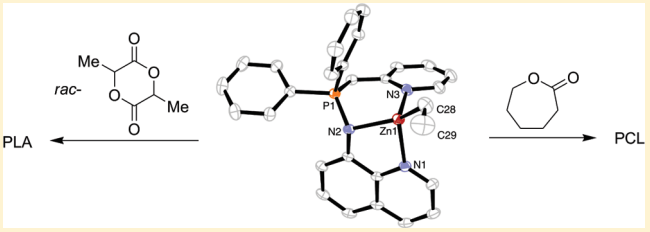
Supporting Information

ABSTRACT: A series of zinc and aluminum complexes supported by quinoline-based N,N,N-chelate ligands were synthesized and characterized. The reaction of 2-$PyCH_2PPh_2$ or $ArN{=}C(Ph)CH_2PPh_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) with 8-azidoquinoline in dichloromethane gave the iminophosphoranes 2-$PyCH_2P(Ph_2){=}N(8\text{-}C_8H_6N)$ (**1**; C_8H_6N = quinolyl) and $ArN{=}C(Ph)CH_2P(Ph_2){=}N(8\text{-}C_8H_6N)$, respectively. Treatment of the iminophosphoranes with 1 equiv of $ZnEt_2$ afforded the corresponding zinc complexes $[Zn(Et)\{2\text{-}PyCHP(Ph_2){=}N(8\text{-}C_8H_6N)\}]$ (**2**) and $[Zn(Et)\{ArNC(Ph){=}CHP(Ph_2){=}N(8\text{-}C_8H_6N)\}]$ (**5a**, Ar = Ph; **5b**, Ar = *p*-MeC_6H_4; **5c**, Ar = *p*-$MeOC_6H_4$). Similar reactions between the iminophosphoranes and an equimolar amount of $AlMe_3$ generated the aluminum complexes $[Al(Me_2)\{2\text{-}PyCHP(Ph_2){=}N(8\text{-}C_8H_6N)\}]$ (**3**) and $[Al(Me_2)\{ArNC(Ph){=}CHP(Ph_2){=}N(8\text{-}C_8H_6N)\}]$ (**6a**, Ar = Ph; **6b**, Ar = *p*-MeC_6H_4). Compounds **1**−**6** were all characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. The molecular structures of complexes **2**, **3**, **5a**, and **6b** were determined by single-crystal X-ray diffraction techniques. In the presence of benzyl alcohol (BnOH) each of the zinc and aluminum complexes is the active catalyst in the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL), leading to polymers with good molecular weight control and narrow molecular weight distribution. The zinc complexes catalyze the ROP of *rac*-lactide (*rac*-LA) efficiently in the presence of BnOH, and the polymerizations are well controlled. However, the aluminum complexes are inactive toward the ROP of *rac*-lactide under the same conditions.



INTRODUCTION

Synthetic aliphatic polyesters such as poly(lactide) (PLA), poly(glycolide) (PGA), poly(ε-caprolactone) (PCL), and their copolymers have attracted considerable attention due to their biocompatible, biodegradable, and permeable properties, which are important in biomedical and pharmaceutical applications.[1] Among these polymers, PLA, whose starting materials can be derived from renewable resources, has found wide applicability, including medical, agricultural, and packaging applications,[1,2] while PCL is ideally suited for long-term drug delivery due to its slow degradation in comparison to other polymers.[3] The most promising method for the synthesis of polyesters is the ring-opening polymerization (ROP) of ε-CL and LA catalyzed by metal complexes.[1,2] Numerous catalyst systems for the polymerizations have been developed. However, different catalysts can lead to different microstructures and physical and mechanical properties of the polymers. Therefore, it is still of great interest to develop new catalysts for the preparation of PCL and PLA. Zinc and aluminum complexes have been among the most extensively studied catalysts for this purpose.[1,2] For example, a range of salen-Al complexes were found to catalyze the stereoselective polymerization of *rac*-LA.[2c] β-Diiminate zinc complexes catalyzed the polymerization of *rac*-LA in high activity and selectivity.[4] Tridentate N,N,N- and N,N,O-chelate aluminum and zinc complexes were also proven to be efficient catalysts for the ROP of ε-CL or LA.[5] Recently, we reported aluminum and tin(II) complexes supported by quinoline-based N,N,O-chelate ligands and found that the aluminum complexes have good catalytic activity in the ROP of ε-CL, giving polymers with good control over the molecular weight and distribution.[6] Sun and co-workers also found several aluminum complexes bearing quinoline-based ligands to be active catalysts for the ROP of ε-CL.[7] We wished to further investigate the potential of quinoline based ligand stabilized aluminum and zinc complexes in catalyzing the ROP of ε-CL or *rac*-LA. Hence, we designed quinoline-based N,N,N-tridentate ligands, synthesized their aluminum and zinc complexes, and studied catalysis of the complexes in the ROP of ε-CL and *rac*-LA. Herein we report the results.

RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds 1−6. The synthesis of compounds **1**−**3** is summarized in Scheme 1.

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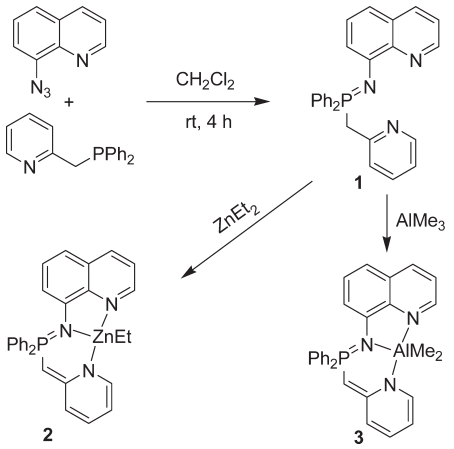
Scheme 1. Synthesis of Compounds 1−3



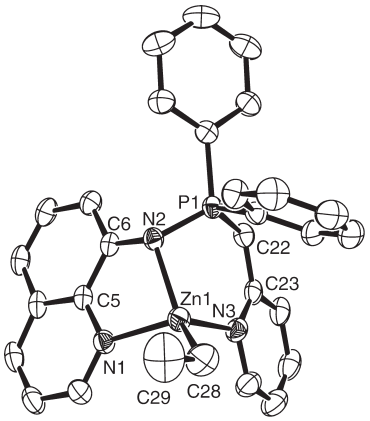


Figure 1. ORTEP diagram of complex **2** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) = 2.093(3), Zn(1)−N(2) = 2.068(3), Zn(1)−N(3) = 2.148(4), Zn(1)−C(28) = 1.953(5), P(1)−N(2) = 1.630(3), P(1)−C(22) = 1.704(4), C(22)−C(23) = 1.413(6); C(28)−Zn(1)−N(2) = 137.7(2), C(28)−Zn(1)−N(1) = 120.1(2), N(1)−Zn(1)−N(2) = 81.38(13), C(28)−Zn(1)−N(3) = 114.8(2), N(2)−Zn(1)−N(3) = 94.60(14), N(1)−Zn(1)−N(3) = 99.16(14), C(6)−N(2)−P(1) = 121.1(3), C(6)−N(2)−Zn(1) = 110.3(3), P(1)−N(2)−Zn(1) = 104.17(17).

Compound **1** was prepared in high yield by reaction of 8-azidoquinoline with 2-PyCH$_2$PPh$_2$ in CH$_2$Cl$_2$. Treatment of **1** with ZnEt$_2$ in toluene gave a zinc complex (**2**) in 80% yield. In order to make the reaction to go to completion, the reaction mixture was heated at 110 °C for 12 h after it was stirred at room temperature overnight. Treating **1** with AlMe$_3$ in toluene at room temperature and then refluxing for 12 h generated aluminum complex **3** in 76% yield. Both **2** and **3** are air-sensitive yellow crystals and are stable under a nitrogen atmosphere. They are soluble in toluene and can be purified by recrystallization from toluene.

Compounds **1**−**3** were all characterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The analytical results are in accord with their respective formulas. In the ^{1}H NMR spectrum of compound **1** one set of proton signals was observed and is consistent with the structure of **1**. The ^{31}P NMR spectrum exhibits a single signal at δ 15.15 ppm. The ^{1}H NMR spectrum of

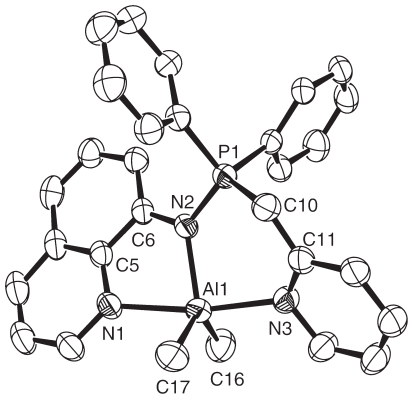


Figure 2. ORTEP diagram of complex **3** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 2.189(3), Al(1)−N(2) = 1.952(3), Al(1)−N(3) = 2.100(3), Al(1)−C(16) = 1.987(5), Al(1)−C(17) = 1.982(4), P(1)−N(2) = 1.638(3), P(1)−C(10) = 1.710(4), C(10)−C(11) = 1.400(5); N(2)−Al(1)−C(17) = 121.84(17), N(2)−Al(1)−C(16) = 111.87(17), C(17)−Al(1)−C(16) = 124.9(2), N(2)−Al(1)−N(3) = 93.03(12), C(17)−Al(1)−N(3) = 92.94(17), C(16)−Al(1)−N(3) = 95.83(17), N(2)−Al(1)−N(1) = 77.53(12), C(17)−Al(1)−N(1) = 91.54(17), C(16)−Al(1)−N(1) = 88.43(16), N(1)−Al(1)−N(3) = 170.54(12), P(1)−N(2)−Al(1) = 122.38(15), C(6)−N(2)−Al(1) = 115.6(2), C(5)−N(1)−Al(1) = 110.3(2), C(11)−N(3)−Al(1) = 122.1(2).

complex **3** exhibits only a single Al−Me signal at δ −0.08 ppm, implying the molecule undergoes possibly fast structural isomerization in solution. The ^{31}P NMR spectra of the complexes show resonance signals at δ 16.78 ppm for complex **2** and δ 22.57 ppm for complex **3**.

The structures of complexes **2** and **3** were further characterized by single crystal X-ray diffraction techniques. The ORTEP drawing of **2** is displayed in Figure 1, along with selected bond lengths and angles. The ligand bonds to the central zinc atom in a tridentate manner. The central zinc atom has a distorted-tetrahedral coordination geometry with an acute N(quinolyl)−Zn−N(bridge) angle (N(1)−Zn(1)−N(2) = 81.38(13)°). The N(2)−Zn−N(3) angle is wider (N(2)−Zn(1)−N(3) = 94.60(14)°) than that of N(1)−Zn(1)−N(2), which corresponds with the metal ring sizes. The Zn−N(1) distance of 2.093(3) Å is shorter than the Zn−N(quinolyl) distance in [Zn(Et){Bu^{t}N=P(Pr^i)$_2$CH(8-C$_8$H$_6$N)}] (2.1651(17) Å), while the Zn(1)−N(2) distance (2.068(3) Å) is comparable to the Zn−N(P=N) distance in [Zn(Et){Bu^{t}N=P(Pr^i)$_2$CH(8-C$_8$H$_6$N)}] (2.0584(15) Å).[8] The Zn(1)−N(3) distance (2.148(4) Å) is longer than the Zn−N(pyridyl) distances in [Zn(Et){2-(3,5-Me$_2$C$_3$HN$_2$)-6-{N(SiMe$_3$)C(Ph)=CH}C$_5$H$_3$N}] (2.064(4) Å) and [Zn(Et){2-{N(SiMe$_3$)=P(Ph)$_2$}-6-{N(SiMe$_3$)P(Ph)$_2$=CH}-C$_5$H$_3$N}] (2.103(2) Å) but is still within the normal range.[9] The P(1)−N(1) distance of 1.630(3) Å is slightly longer than a typical P−N double bond[10] but is normal for a coordinated iminophosphorane,[11] while the P(1)−C(22) distance of 1.704(4) Å is between a single and double bond.[10]

The ORTEP drawing of **3** is shown in Figure 2, along with selected bond lengths and angles. The central aluminum atom is five-coordinated and has a distorted-trigonal-bipyramidal geometry in which the iminophosphoranyl nitrogen atom and two methyl carbon atoms occupy the equatorial positions and the quinolyl nitrogen atom and the pyridyl nitrogen atom occupy the axial positions. The arrangement of the N(1)Al(1)N(3) atoms is

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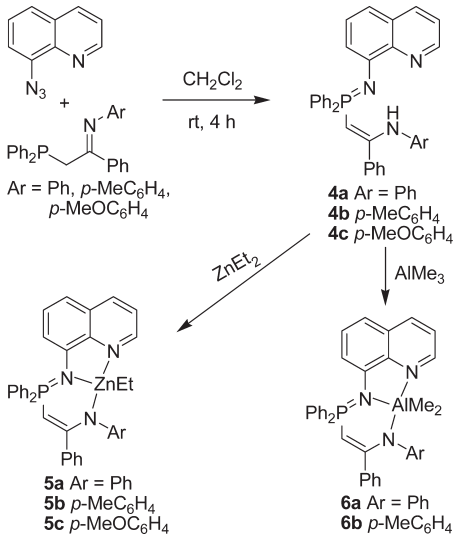
Scheme 2. Synthesis of Compounds 4−6



close to a line, the N(1)−Al(1)−N(3) angle being 170.54(12)°. The N(2)Al(1)C(16)C(17) atoms are approximately coplanar, the sum of the angles at aluminum being 358.61°. The Al−N(1) distance of 2.189(3) Å is slightly longer than the Al−N(quinolyl) distance in [Al(Me$_2$){OC(Bu^t)=CHP(Ph$_2$)=N(8-C$_9$H$_6$N)}] (2.162(3) Å) and in [Al(Me$_2$){OC(Me)=CHC(Me)=N(8-C$_9$H$_6$N)}] (2.1448(19) Å).[6] The Al−N(2) distance of 1.952(3) Å is normal for an iminophosphorane-coordinated aluminum complex.[6,12] The Al−N(3) distance of 2.100(3) Å is shorer than the Al−N(pyridyl) distance in [Al(Me$_2$){3,5-Bu$^t_2$-2-(O)-C$_6$H$_2$CH=N(2-C$_5$H$_4$N)}] (2.254(2) Å)[13] but is still within the normal range.[9a,14] The P(1)−N(2) and P(1)−C(10) distances are comparable to the corresponding distances in complex **2**.

The synthesis of compounds **4**−**6** is shown in Scheme 2. Compounds **4a**−**c** were synthesized through reaction of 8-azidoquinoline with ArN=C(Ph)CH$_2$PPh$_2$ (Ar = Ph, *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$) under the same conditions as for **1**. Treatment of **4a**−**c** with ZnEt$_2$ in toluene gave zinc complexes **5a**−**c** as yellow crystalline solids. In order to drive the reactions to reach completion, it is necessary to heat the reaction mixture for a few hours. The complexes were purified by recrystallization from toluene (for **5a**,**c**) or diethyl ether (for **5b**). Reaction of **4a**,**b** with AlMe$_3$ in toluene gave the yellow aluminum complexes **6a**,**b**, respectively. Complex **6a** can be recrystallized from toluene. Complex **6b** is very soluble in toluene and was recrystallized from diethyl ether. Compounds **4a**−**c** are air stable and gave satisfactory microanalytical results. The ^{1}H NMR spectral data reveal that each of the compounds exists in an enamine form. The chemical shifts of NH at 12.46, 12.43, and 12.48 ppm, respectively, prove the presence of a hydrogen bond in each compound. The ^{13}C and ^{31}P NMR spectral data are also consistent with their respective structures. Complexes **5a**−**c** and **6a**,**b** were characterized by elemental analyses and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The ^{1}H NMR spectra of complexes **5a**−**c** show that in each molecule the chemical shift of the CH$_2$ group appears in the low-frequency region, proving the presence of a zinc−C bond. The ^{13}C NMR spectra give results consistent with the ^{1}H NMR spectra. The ^{31}P NMR spectrum appears as a single signal at about δ 16.30 ppm for each complex, shifting slightly toward low

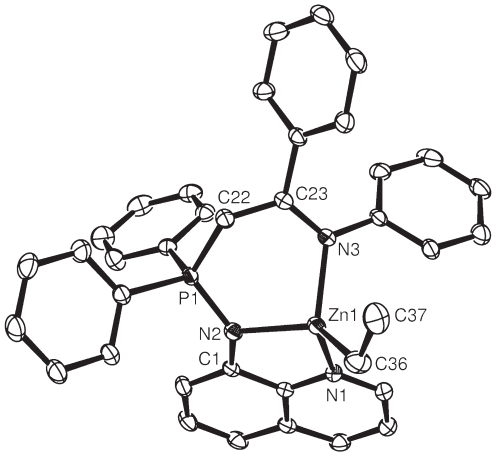


Figure 3. ORTEP diagram of complex **5a** (30% probability thermal ellipsoids; the toluene molecule is omitted). Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) = 2.108(3), Zn(1)−N(2) = 2.062(3), Zn(1)−N(3) = 2.037(3), Zn(1)−C(36) = 1.993(4), P(1)−N(2) = 1.615(3), P(1)−C(22) = 1.740(3), C(22)−C(23) = 1.390(4), N(3)−C(23) = 1.343(4); C(36)−Zn(1)−N(3) = 117.54(14), C(36)−Zn(1)−N(2) = 134.00(15), N(3)−Zn(1)−N(2) = 96.23(113), C(36)−Zn(1)−N(1) = 112.03(15), N(3)−Zn(1)−N(1) = 110.99(10), N(2)−Zn(1)−N(1) = 79.93(11), P(1)−N(2)−Zn(1) = 116.27(15), C(23)−C(22)−P(1) = 126.4(3), N(3)−C(23)−C(22) = 123.5(3), C(23)−N(3)−Zn(1) = 117.1(2).

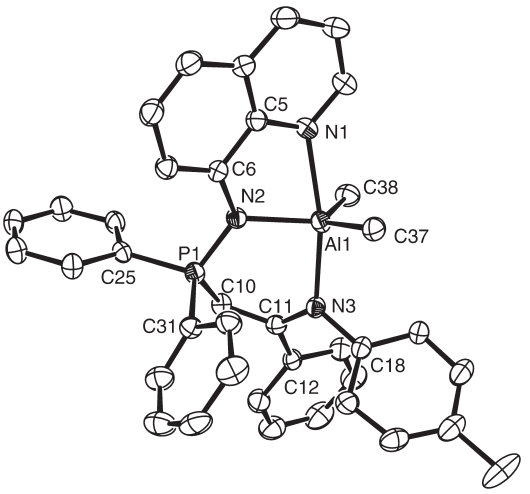


Figure 4. ORTEP diagram of complex **6b** (30% probability thermal ellipsoids; benzene molecules are omitted). Selected bond lengths (Å) and angles (deg): Al(1)−C(37) = 1.996(6), Al(1)−C(38) = 1.985(6), Al(1)−N(1) = 2.222(6), Al(1)−N(2) = 1.986(5), Al(1)−N(3) = 2.044(6), P(1)−N(2) = 1.634(5), P(1)−C(10) = 1.719(6), C(10)−C(11) = 1.376(7), N(3)−C(11) = 1.372(7); C(38)−Al(1)−N(2) = 121.4(3), C(38)−Al(1)−C(37) = 123.5(3), N(2)−Al(1)−C(37) = 112.1(3), C(38)−Al(1)−N(3) = 96.2(2), N(2)−Al(1)−N(3) = 92.7(2), C(37)−Al(1)−N(3) = 98.2(3), C(38)−Al(1)−N(1) = 89.4(3), N(2)−Al(1)−N(1) = 75.7(2), C(37)−Al(1)−N(1) = 87.1(2), N(3)−Al(1)−N(1) = 168.3(3), C(5)−N(1)−Al(1) = 112.2(5), C(6)−N(2)−Al(1) = 116.8(4), P(1)−N(2)−Al(1) = 118.9(3), C(11)−N(3)−Al(1) = 120.5(4), C(11)−C(10)−P(1) = 120.8(5), N(3)−C(11)−C(10) = 118.7(6).

frequency compared with those of **4a**−**c** and being very close to that of **2**. The ^{1}H NMR spectra of **6a**,**b** both exhibit a single

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Table 1. Ring-Opening Polymerization of ε-Caprolactone Catalyzed by Complexes 2, 3, 5a−c, and 6a,b[a]

entry	cat.	T (°C)	time (min)	conversn (%)[c]	yield (%)	$10^4 M_{n,calc}$[c]	$10^4 M_{n,NMR}$[d]	$10^4 M_{n,GPC}$[e]	PDI[f]
1	**2**	90	10	96	92	2.20	1.74	1.62	1.37
2	**2**	70	30	98	94	2.25	2.11	2.19	1.37
3[b]	**2**	70	30	15					
4	**2**	50	75	96	93	2.20	2.23	2.00	1.38
5	**2**	30	220	35					
6	**3**	70	8	89	84	2.04	2.04	2.32	1.10
7	**3**	50	30	86	75	1.97	1.69	1.95	1.10
8	**3**	30	75	78	69	1.79	1.61	1.69	1.14
9	**3**	30	90	89	85	2.04	2.00	2.35	1.14
10	**5a**	90	120	93	85	2.13	2.05	1.93	1.33
11	**5a**	70	180	53	48	1.22	0.99	1.22	1.38
12	**5b**	90	15	97	93	2.22	2.33	1.87	1.33
13	**5b**	70	45	98	95	2.25	2.24	2.11	1.33
14	**5c**	90	30	96	93	2.20	2.01	2.13	1.34
15	**5c**	70	60	78	76	1.79	1.83	3.63	1.23
16	**6a**	70	8	95	85	2.18	2.11	2.74	1.10
17	**6a**	50	18	88	80	2.02	2.15	2.78	1.08
18	**6a**	30	75	98	95	2.25	2.23	2.55	1.08
19	**6b**	70	6	93	92	2.13	2.76	3.31	1.11
19	**6b**	50	9	81	75	1.86	3.06	2.51	1.06
20	**6b**	30	75	88	82	2.02	1.84	2.88	1.06

[a] All polymerizations were carried out in toluene. Conditions: $[\varepsilon\text{-CL}]_0 = 2$ M, $[\varepsilon\text{-CL}]_0:[\text{cat.}]_0:[\text{BnOH}]_0 = 200:1:1$, except for entry 3. [b] BnOH was not employed: $[\varepsilon\text{-CL}]_0:[\text{cat.}]_0 = 200:1$. [c] Calculated from the molecular weight of ε-CL times the conversion of monomer and the ratio of $[\varepsilon\text{-CL}]_0$ to $[\text{BnOH}]_0$ plus the molecular weight of BnOH. [d] Measured by ^{1}H NMR spectra. [e] Obtained from GPC analysis and calibrated against polystyrene standard, multiplied by 0.56.[15] [f] Obtained from GPC analysis.

resonance at δ 0.09 ppm. In the ^{13}C NMR spectra, the signals for the methyls appear at −3.03 ppm (for **6a**) and −3.07 ppm (for **6b**), respectively. These results are consistent with those of complex **3**. The ^{31}P NMR spectra of complexes **6a**,**b** show resonance signals at 21.62 and 21.57 ppm, respectively, being very close to that of **3** at 22.57 ppm.

The structures of complexes **5a** and **6b** were also determined by single-crystal X-ray diffraction techniques. The ORTEP diagram of complex **5a** is depicted in Figure 3, along with selected bond lengths and angles. The skeletal structure is similar to that of complex **2**. The central zinc atom has a distorted-tetrahedral geometry. The acute N(quinolyl)−Zn−N(bridge) angle of 79.93(11)° is close to the corresponding angle in complex **2** (81.38(13)°). The Zn−N(P═N) and Zn−N(quinolyl) distances of 2.062(3) and 2.108(3) Å, respectively, are comparable to those in complex **2**. However, the Zn−N(3) distance of 2.037(3) Å is shorter than that in complex **2** (2.148(4) Å). The former is slightly longer than the Zn−N(enamide) distance in [Zn(Et){2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)═CH}C_5H_3N}] (2.014(4) Å).[9a] The P(1)−N(2) distance of 1.615(3) Å is slightly shorter than that in complex **2** (1.630(3) Å), and the former is closer to the distance of a P−N double bond.[10]

Complex **6b** crystallizes with two molecules in the asymmetric unit (Figure 4; one molecule is presented). The skeletal structure of **6b** is similar to that of complex **3**. The central aluminum atom has a distorted-trigonal-bipyramidal geometry with the iminophosphorane nitrogen atom and two methyl carbon atoms occupying the equatorial positions and the quinolyl nitrogen atom and the enamide nitrogen atoms occupying the axial positions. However, the aluminum atom deviates slightly from the plane composed of N(2), C(37), and C(38) atoms, and the N(1)−Al(1)−N(3) angle of 168.3(3)° is slightly smaller than the corresponding angle in complex **3** (170.54(12)°). The Al−N(P═N) and Al−N(quinolyl) distances (1.986(5) Å and 2.222(6) Å, respectively) are both longer than the corresponding distances in complex **3**. The Al−N(enamide) distance of 2.044(6) Å is shorter than the Al−N(pyridyl) distance (2.100(3) Å) in complex **3** but longer than the Al−N(enamide) distance (1.901(3) Å) in [Al(Me_2){N(Ph)C(Ph)═CHP(Ph_2)═N(*p*-MeC_6H_4)}].[12] The P(1)−N(2) and P(1)−C(10) distances are very close to the corresponding distances in complex **3**.

ROP of ε-CL and *rac*-LA Catalyzed by the Zinc or Aluminum Complexes. The catalysis of the zinc and aluminum complexes toward the ROP of ε-CL was evaluated first, and the results are given in Table 1. Each of the complexes initiated the ROP of 200 equiv of ε-CL at elevated temperature in the presence of BnOH. The polymerization catalyzed by **2**/BnOH at 90 °C proceeded rapidly. The monomer conversion reached 96% in 10 min (entry 1, Table 1). At 70 °C the monomer conversion reached 98% in 30 min using the same catalyst system (entry 2, Table 1). In sharp contrast, in the absence of BnOH complex **2** led to only 15% monomer conversion at 70 °C in 30 min (entry 3, Table 1). At lower temperature the polymerization is much slower. At 30 °C only 35% of the monomer was converted to polymer in 220 min using **2**/BnOH as the catalyst (entry 5, Table 1). The complex **3**/BnOH system exhibits higher catalytic activity than **2**/BnOH. The former led to 89% conversion of ε-CL in 8 min at 70 °C and 78% monomer conversion in 75 min at 30 °C (entries 6 and 8, Table 1). **5a**−**c** show different catalytic activities. Among them, **5b** exhibits the highest catalytic activity and **5a** shows the lowest activity (entries 10−15, Table 1). It

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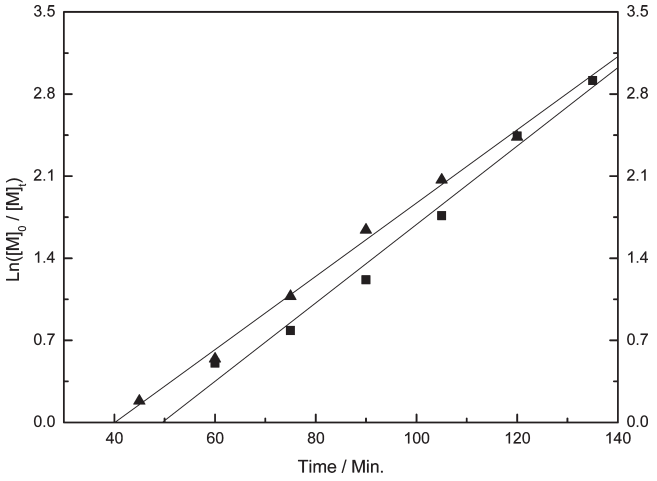
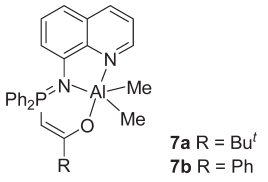


Figure 5. Plots of $\ln([M]_0/[M])$ versus time for the polymerization of ε-CL catalyzed by **2** (■) and **5b** (▲). Conditions: $[M]_0/[Al]/[BnOH]_0$ = 200:1:1; $[M]_0$ = 2 M; solvent toluene; polymerization temperature 40 °C for **2** and 65 °C for **5b**.

seems that the *p*-MeC_6H_4 group on the imine nitrogen atom in **5b** causes the ligand to provide a proper electronic environment at the metal center for catalysis. However, the activities of complexes **5a**−**c** are all lower than that of complex **2**. For example, **5b**/BnOH drives 98% monomer conversion in 45 min at 70 °C, while **2**/BnOH requires 30 min for the same conversion at 70 °C. Complex **6a** exhibits almost the same activity as **6b** at 70 °C (entries 16 and 19, Table 1). However, at 30 °C complex **6a** is slightly more active than **6b** (entries 18 and 21, Table 1). It is also noted that **6a,b** are both more active than either **3** or **5b**. Hence, an approximate activity order is **6a** ≥ **6b** > **3** > **2** > **5b** > **5c** > **5a**. In other words, the aluminum complexes exhibit higher catalytic activity than the zinc complexes in the ROP of ε-CL. In most cases the determined molecular weights of the polymers by GPC closely match the calculated values. The polydispersities are also relatively narrow, ranging from 1.08 to 1.38. These results imply that the catalytically active species are quite stable during the reaction process and the polymerizations are well controlled. In addition, the aluminum complexes **3** and **6a,b** show higher catalytic activity and better control than the N,N,O-chelate aluminum complexes **7a,b** that we previously reported.[6]



7a R = Bu^t
7b R = Ph

In order to establish the reaction order in monomer and metal concentration, we also carried out kinetic studies of ε-CL polymerization catalyzed by complexes **2** and **5b** in the presence of BnOH. Plots of $\ln([CL]_0/[CL])$ versus time using each catalyst exhibits a good linear relationship (Figure 5), which shows that the polymerization proceeds with first-order dependence on monomer concentration. The reaction rate remains constant with reaction time, indicating a constant number of active sites throughout the polymerization. This implies that the polymerizations catalyzed by **2** and **5b**, respectively, are

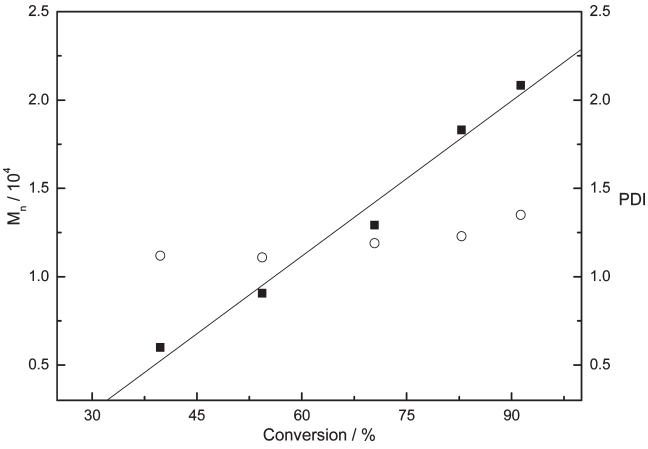


Figure 6. Plots of PCL M_n (■, obtained from GPC analysis) and polydispersity (○, M_w/M_n) as a function of ε-CL conversion using complex **2** at 40 °C. Conditions: $[M]_0$:$[Al]_0$:$[BnOH]_0$ = 200:1:1; $[M]_0$ = 2 M; solvent toluene.

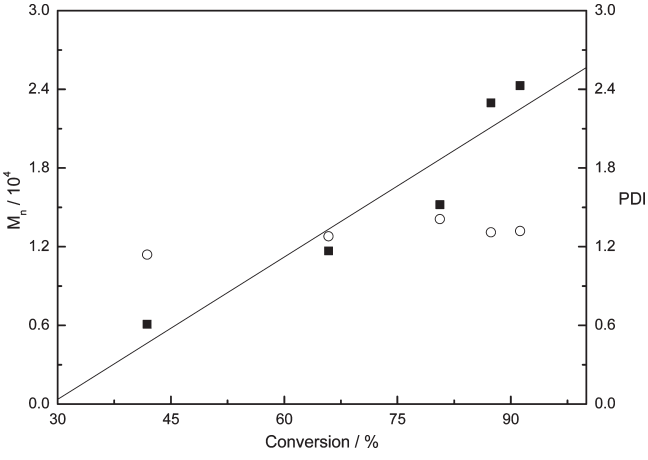


Figure 7. Plots of PCL M_n (■ ,obtained from GPC analysis) and polydispersity (○, M_w/M_n) as a function of ε-CL conversion using complex **5b** at 65 °C. Conditions: $[M]_0$:$[Al]_0$:$[BnOH]_0$ = 200:1:1; $[M]_0$ = 2 M; solvent toluene.

controlled. The controlled polymerization is further proven by the linear relationship of molecular weight with monomer conversion in each catalytic reaction, along with relatively low PDI values (Figures 6 and 7).

We next evaluated catalysis of the zinc and aluminum complexes toward the ROP of *rac*-lactide. Surprisingly, the aluminum complexes are inactive in the presence or absence of BnOH. Each zinc complex is an active catalyst toward the ROP of *rac*-lactide in the presence of BnOH at elevated temperature (Table 2). At 70 °C the complex **2**/BnOH system exhibits high catalytic activity. It drives 50−300 equiv of *rac*-LA to polymerize within 15 min, giving 93−97% monomer conversions (entries 1−6, Table 2). The PDIs of polyesters ranging from 1.18 to 1.38 are relatively narrow. A linear relationship between the number average molecular weight (M_n) and $([LA]_0 - [LA])/[Zn]_0$ as shown in Figure 8 implies the "living" character of the polymerization process. However, the polylactide molecular weights are lower than expected at higher monomer loading. In the presence of 2 equiv of BnOH complex **2** exhibited a catalytic activity

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Table 2. Ring-Opening Polymerization of *rac*-Lactide Catalyzed by Complexes 2 and 5a−c[a]

entry	cat.	$[cat.]_0/[BnOH]_0/[LA]_0$	conversn (%)[c]	$10^4M_{n,calc}$[c]	$10^4M_{n,NMR}$[d]	$10^4M_{n,GPC}$[e]	PDI[f]
1	**2**	1:1:50	97	0.71	0.58	1.01	1.18
2	**2**	1:1:100	97	1.41	0.75	1.20	1.38
3	**2**	1:1:150	97	2.11	1.43	1.49	1.33
4	**2**	1:1:200	96	2.78	1.90	1.82	1.26
5	**2**	1:1:250	94	3.40	2.10	1.89	1.28
6	**2**	1:1:300	93	4.03	3.20	2.05	1.22
7	**2**	1:2:200	97	2.78	1.42		
8	**5a**	1:1:100	95	1.38	1.85	1.34	1.16
9	**5a**	1:1:200	71	2.06	1.66	2.00	1.18
10	**5b**	1:1:100	96	1.39	1.80	1.41	1.21
11	**5b**	1:1:200	95	2.75	2.17	2.16	1.23
12	**5b**	1:1:250	83	3.00	2.64	1.63	1.10
13[b]	**5c**	1:1:200	88	2.55	1.67	1.16	1.08
14	**5c**	1:1:100	95	1.38	2.37	1.85	1.19
15	**5c**	1:1:150	96	2.09	2.86	2.12	1.20
16	**5c**	1:1:200	95	2.75	3.73	2.84	1.22
17	**5c**	1:1:250	96	3.47	3.56	3.09	1.22

[a] All polymerizations were carried out in toluene at 70 °C and run for 15 min, except for entry 12. Conditions: $[LA]_0$ = 0.5 M. [b] Polymerization was carried out at 20 °C and run for 216 min. [c] Calculated from the molecular weight of LA times the conversion of monomer and the ratio of $[LA]_0/[BnOH]_0$ plus the molecular weight of BnOH. [d] Measured by ^{1}H NMR spectra. [e] Obtained from GPC analysis and calibrated against polystyrene standard, multiplied by 0.58.[17] [f] Obtained from GPC analysis.

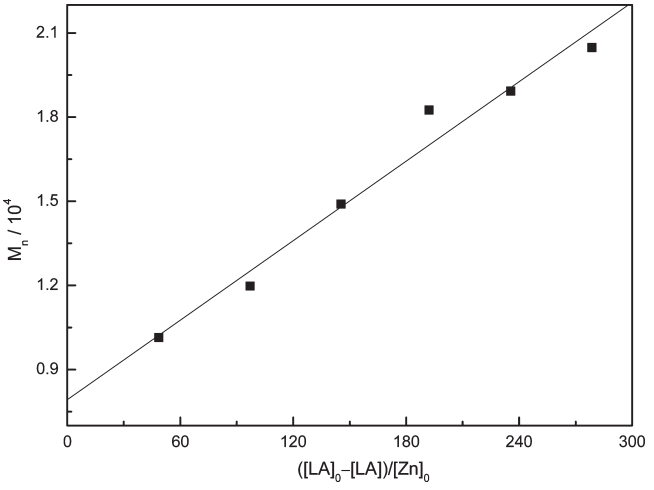

Figure 8. Plot of M_n versus $([LA]_0 - [LA])/[Zn]_0$ for the polymerization of LA by **2**. Conditions: $[LA]_0$ = 0.5 M, toluene, 70 °C.

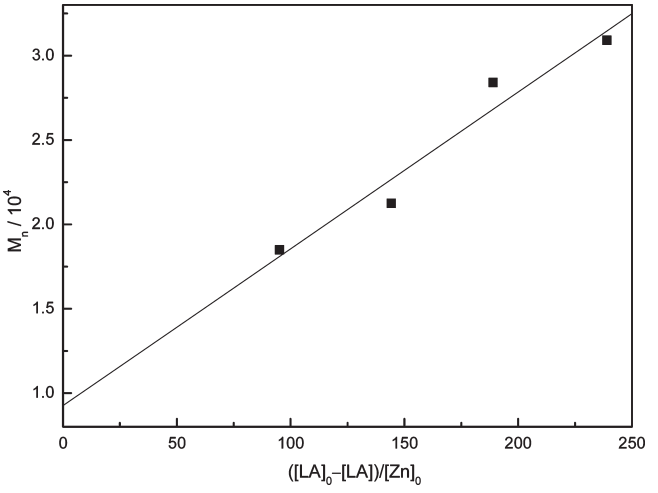

Figure 9. Plot of M_n versus $([LA]_0 - [LA])/[Zn]_0$ for the polymerization of LA by **5c**. Conditions: $[LA]_0$ = 0.5 M, toluene, 70 °C.

similar to that using 1 equiv of BnOH. However, the molecular weights of the polymers determined by ^{1}H NMR spectroscopy are about half of the theoretical values (entry 7, Table 2). This is attributed to the fact that all the added alcohol molecules contribute to the immortal polymerization. When 100 equiv of *rac*-LA was employed, complexes **5a**−**c** all displayed excellent catalytic activity. They led to 95−96% monomer conversion in 15 min at 70 °C. However, when more *rac*-LA was loaded, complex **5c** showed higher catalytic activity than either **5a** or **5b**. Good molecular weight control using **5c** is demonstrated by a linear increase in M_n with LA conversion (Figure 9) and relatively narrow molecular weight distributions of the polymers (polydispersity index, PDI = 1.19−1.22). It should be noted that the PLAs obtained by these zinc catalysts have an atactic microstructure, identified by ^{1}H NMR spectroscopic analysis.[16] In addition, complex **5c**/BnOH is also able to catalyze the ROP of *rac*-LA at 20 °C (entry 13, Table 1), but the reaction is much slower than that at a higher temperature.

CONCLUSIONS

We have synthesized and characterized a series of zinc and aluminum complexes supported by novel quinoline-based N,N,N-chelate ligands. In the presence of benzyl alcohol all the zinc and aluminum complexes are able to catalyze the ROP of ε-CL and the reactions lead to polymers with good molecular weight control and narrow molecular weight distribution. The zinc complexes catalyze the ROP of *rac*-lactide efficiently in the presence of BnOH. The polymerizations are well controlled

and give PLAs with an atactic microstructure. However, the aluminum complexes are inactive toward the ROP of *rac*-lactide under the same conditions.

EXPERIMENTAL SECTION

General Procedures. All air- or moisture-sensitive manipulations were performed under a nitrogen atmosphere using standard Schlenk and vacuum-line techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (*n*-hexane, THF, and Et_2O), or CaH_2 (CH_2Cl_2) and degassed prior to use. Chlorodiphenylphosphine was purchased from Acros Organics and distilled prior to use. Diisopropylamine was dried with NaOH and distilled prior to use. $LiBu^n$, $ZnEt_2$, and $AlMe_3$ were purchased from Acros Organics or Alfa-Aesar and used as received. $CDCl_3$ and C_6D_6, purchased from Cambridge Isotope Laboratories, Inc., were degassed and stored over Na/K alloy (C_6D_6) or 4 Å molecular sieves ($CDCl_3$). ε-Caprolactone, purchased from Acros Organics, was stirred over CaH_2 for 24 h and distilled under vacuum. *rac*-Lactide was purchased from Beijing Yuanshengrong, Inc. and recrystallized three times from toluene prior to use. 8-Azidoquinoline,[18] 2-((diphenylphosphino)methyl)pyridine,[19] *N*-(1-phenyl-2-(diphenylphosphino)ethylidene)benzenamine,[12] and 4-methyl-*N*-(1-phenyl-2-(diphenylphosphino)ethylidene)benzenamine[12] were prepared using the procedures described in the literature. 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 or TMS; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. Gel permeation chromatograph (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (103, 104, and 105 Å) and 410 refractive index detector, using monodispersed polystyrene as calibration standard. THF was used as eluent at a flow rate of 1 mL/min.

Synthesis of 2-PyCH$_2$P(Ph$_2$)=N(8-C$_8$H$_6$N) (1). A solution of 8-azidoquinoline (1.35 g, 7.933 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of 2-$PyCH_2PPh_2$ (2.00 g, 7.212 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then at room temperature for 4 h. Solvent was removed under reduced pressure. The residue was washed with *n*-hexane and dried in vacuo to give a brown powder of **1** (2.632 g, 87%), mp146−148 °C. The product was pure enough for the next step. The sample for analysis was further purified by recrystallization of the crude product from diethyl ether. Anal. Calcd for $C_{27}H_{22}N_3P$: C, 77.31; H, 5.29; N, 10.02. Found: C, 76.91; H, 5.24; N, 10.18. ^1H NMR ($CDCl_3$): δ 4.49 (d, J = 14.6 Hz, 2H, CH_2), 6.88−7.00 (m, 2H, Ar), 7.05−7.15 (m, 2H, Ar), 7.23−7.43 (m, 9H, Ar), 7.74−7.86 (m, 4H, Ar), 7.96 (dd, J = 1.5, 8.4 Hz, 1H, Ar), 8.22−8.32 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 40.99 (d, J = 64.5 Hz), 113.83 (d, J = 3.7 Hz), 119.43, 120.72, 121.75, 123.29, 127.18, 128.47, 128.64, 128.89 (d, J = 13 Hz), 131.92 (d, J = 10.2 Hz), 132.27 (d, J = 2.5 Hz), 133.01, 136.28, 136.35, 137.81, 148.10, 149.17. ^{31}P NMR ($CDCl_3$): δ 15.15 (m).

Synthesis of [Zn(Et){2-PyCHP(Ph$_2$)=N(8-C$_8$H$_6$N)}] (2). $ZnEt_2$ (0.79 mL, 1 M solution in hexane, 0.79 mmol) was added dropwise to a stirred solution of **1** (0.30 g, 0.72 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature, stirred overnight at that temperature, and heated to 110 °C (bath temperature) for 12 h. The resulting solution was cooled to room temperature and filtered. Concentration of the filtrate generated yellow crystals of **2** (0.2935 g, 80%), mp 174−176 °C. Anal. Calcd for $C_{29}H_{26}N_3PZn\cdot 0.5C_7H_8$: C, 69.83; H, 5.41; N, 7.52. Found: C, 69.87; H, 5.42; N, 7.58. ^1H NMR (C_6D_6): δ 0.69 (q, J = 8.1 Hz, 2H, CH_2), 1.61 (t, J = 8.1 Hz, 3H, CH_3), 2.24 (s, $PhCH_3$), 3.94 (d, J = 22.5 Hz, 1H, PCH), 6.03−6.08 (m, 1H, Ar), 6.56−6.66 (m, 2H, Ar), 6.77−6.87 (m, 3H, Ar), 7.05−7.11 (m, 1H, Ar), 7.15−7.35 (m, 6H, Ar), 7.45 (dd, J = 1.5, 8.4 Hz, 1H, Ar), 7.65−8.80 (b, 4H, Ar), 7.88−7.95 (m, 1H, Ar), 8.22 (dd, J = 1.5, 8.4 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −1.13, 13.72, 48.73 (d, J = 132.3 Hz), 108.08, 116.65, 120.16 (d, J = 8.8 Hz), 120.69 (d, J = 17.4 Hz), 121.04, 128.77 (d, J = 11.8 Hz), 130.13, 131.41, 133.00, 134.61 (d, J = 3.6 Hz), 138.37, 145.92, 146.34. ^{31}P NMR (C_6D_6): δ 16.78 (m).

Synthesis of [Al(Me$_2$){2-PyCHP(Ph$_2$)=N(8-C$_8$H$_6$N)}] (3). $AlMe_3$ (0.35 mL, 2.3 M solution in hexane, 0.81 mmol) was added dropwise to a stirred solution of **1** (0.30 g, 0.72 mmol) in toluene (10 mL) at room temperature. The mixture was stirred overnight at room temperature and then refluxed for 12 h. The resulting solution was cooled to room temperature and filtered. Concentration of the filtrate formed yellow crystals of **3** (0.2585 g, 76%), mp 222−224 °C. Anal. Calcd for $C_{29}H_{27}AlN_3P$: C, 73.25; H, 5.72; N, 8.84. Found: C, 73.01; H, 5.68; N, 8.74. ^1H NMR (C_6D_6): δ −0.08 (s, 6H, $AlCH_3$), 3.54 (d, J = 24 Hz, 1H, PCH), 5.90−5.99 (m, 1H, Ar), 6.48 (d, J = 8.4 Hz, 1H, Ar), 6.57−6.81 (m, 5H, Ar), 6.85−7.19 (m, 6H, Ar), 7.33 (dd, J = 1.5, 8.1 Hz, 1H, Ar), 7.86−8.00 (m, 4H, Ar), 8.23 (d, J = 6 Hz, 1H, Ar), 8.45 (dd, J = 1.5, 4.5 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −3.17, 53.14 (d, J = 141.86 Hz), 109.02, 115.81, 116.30 (d, J = 9.4 Hz), 119.80 (d, J = 17.3 Hz), 121.95, 128.02, 128.44, 128.60, 128.98, 130.15, 131.42, 131.58 (d, J = 2.5 Hz), 133.32 (d, J = 10.1 Hz), 135.24 (d, J = 3.2 Hz), 136.99, 144.00, 145.54, 164.75. ^{31}P NMR (C_6D_6): δ 22.57 (m).

Synthesis of PhN=C(Ph)CH$_2$P(Ph$_2$)=N(8-C$_8$H$_6$N) (4a). The synthesis of **4a** followed the same procedure as for **1**. Thus, reaction of 8-azidoquinoline (0.9866 g, 5.798 mmol) with $PhN{=}C(Ph)CH_2PPh_2$ (2.00 g, 5.271 mmol) in CH_2Cl_2 (30 mL) gave **4a** (2.31 g, 84%), mp 176−178 °C. The product was pure enough for the next step. The sample used for analysis was further purified by recrystallization of the crude product from diethyl ether. Anal. Calcd for $C_{35}H_{28}N_3P$: C, 80.60; H, 5.41; N, 8.06. Found: C, 80.36; H, 5.42; N, 7.94. ^1H NMR ($CDCl_3$): δ 4.50 (d, J = 24.3 Hz, 1H, PCH), 6.72−6.90 (m, 2H, Ar), 6.94−7.14 (m, 6H, Ar), 7.16−7.30 (m, 4H, Ar), 7.35−7.54 (m, 8H, Ar), 7.78−8.00 (m, 5H, Ar), 8.70−8.81 (m, 1H, Ar), 12.46 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 86.67 (d, J = 134.6 Hz), 115.68, 117.16 (d, J = 14 Hz), 120.81, 121.68, 123.02, 127.10, 128.23 (d, J = 5 Hz), 128.47, 128.54, 128.62, 128.94, 129.83, 131.28, 131.31, 132.07 (d, J = 9.9 Hz), 133.31, 135.89, 139.13 (d, J = 16.5 Hz), 142.53, 147.50, 160.22. ^{31}P NMR ($CDCl_3$): δ 5.63 (m).

Synthesis of *p*-MeC$_6$H$_4$N=C(Ph)CH$_2$P(Ph$_2$)=N(8-C$_8$H$_6$N) (4b). The synthesis of **4b** followed the same procedure as for **1**. Treatment of 8-azidoquinoline (0.9515 g, 5.591 mmol) with *p*-$MeC_6H_4N{=}C(Ph)CH_2PPh_2$ (2.00 g, 5.083 mmol) in CH_2Cl_2 (30 mL) generated compound **4b** (2.48 g, 91%), mp 158−160 °C. The product was pure enough for the next step. The sample used for analysis was further purified by recrystallization of the crude product from diethyl ether. Anal. Calcd for $C_{36}H_{30}N_3P$: C, 80.73; H, 5.65; N, 7.85. Found: C, 80.51; H, 5.66; N, 7.80. ^1H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 4.42 (d, J = 24.6 Hz, 1H, PCH), 6.75 (d, J = 7.2 Hz, 1H, Ar), 6.90 (s, 4H, Ar), 6.95−7.06 (m, 2H, Ar), 7.15−7.27 (m, 5H, Ar), 7.30−7.47 (m, 7H, Ar), 7.79−7.96 (m, 5H, Ar), 8.68−8.76 (m, 1H, Ar), 12.43 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.80, 85.54 (d, J = 135.4 Hz), 115.57, 117.07 (d, J = 13.9 Hz), 120.75, 123.12, 127.05, 128.18, 128.41, 128.55, 128.80, 131.20, 131.22, 132.03 (d, J = 9.9 Hz), 135.82, 139.96, 147.50, 160.49. ^{31}P NMR ($CDCl_3$): δ 5.72 (m).

Synthesis of *p*-MeOC$_6$H$_4$N=C(Ph)CH$_2$P(Ph$_2$)=N(8-C$_8$H$_6$N) (4c). $LiBu^n$ (3.9 mL, 2.5 M solution in hexane, 9.75 mmol) was added dropwise to a solution of diisopropylamine (0.9936 g, 9.819 mmol) in THF (20 mL) at −20 °C. The mixture was stirred at that temperature for 20 min and then added dropwise to a solution of 4-methoxy-*N*-(1-phenylethylidene)benzenamine (2.00 g, 8.877 mmol) in THF (15 mL) at about −80 °C. The mixture was stirred for an additional 2 h at that temperature. A solution of chlorodiphenylphosphine (1.76 mL, 9.803 mmol) in THF (10 mL) was added dropwise to the reaction mixture. The resulting solution was warmed to room temperature and stirred for

16 h. Volatiles were removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (60 mL). The extract was concentrated to about 30 mL and was added dropwise to a solution of 8-azidoquinoline (1.6617 g, 9.765 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then at room temperature for 4 h. Solvents were removed under vacuum, and the residue was dissolved in diethyl ether (40 mL). The resulting solution was filtered. Concentration of the filtrate generated light brown crystals of **4c** (2.4971 g, 51% based on 4-methoxy-*N*-(1-phenylethylidene)benzenamine), mp 168−170 °C. Anal. Calcd for $C_{36}H_{30}N_3OP$: C, 78.39; H, 5.48; N, 7.62. Found: C, 78.34; H, 5.61; N, 7.48. ^{1}H NMR ($CDCl_3$): δ 3.68 (s, 3H, OCH_3), 4.36 (d, J = 24.6 Hz, 1H, PCH), 6.66 (d, J = 8.7 Hz, 2H, C_6H_4), 6.74 (d, J = 6.9 Hz, 1H, Ar), 6.95 (d, J = 8.7 Hz, 2H, C_6H_4), 6.98−7.10 (m, 2H, Ar), 7.17−7.25 (m, 4H, Ar), 7.33−7.47 (m, 8H, Ar), 7.85 (dd, J = 7.8, 11.7 Hz, 4H, Ar), 7.94 (d, J = 8.4 Hz, 1H, Ar), 8.63−8.70 (m, 1H, Ar), 12.48 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 55.45, 84.00 (d, J = 136.4 Hz), 113.56, 115.55, 116.98 (d, J = 13.3 Hz), 120.77, 124.90, 127.08, 127.97, 128.16, 128.44, 128.59, 128.66, 128.73, 129.81, 131.23, 132.07 (d, J = 9.8 Hz), 135.87, 147.63, 148.98, 155.02, 161.01. ^{31}P NMR ($CDCl_3$): δ 5.72 (m).

Synthesis of [Zn(Et){PhNC(Ph)═CHP(Ph$_2$)═N(8-C$_8$H$_6$N)}] (5a). $ZnEt_2$ (0.64 mL, 1 M solution in hexane, 0.64 mmol) was added dropwise to a stirred solution of **4a** (0.30 g, 0.58 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature, stirred overnight at room temperature, and heated to 110 °C for 8 h. The resulting solution was cooled to room temperature and then filtered. Concentration of the filtrate gave yellow crystals of **5a** (0.2052 g, 58%), mp 218−220 °C. Anal. Calcd for $C_{37}H_{32}N_3PZn\cdot 0.8\,C_7H_8$: C, 74.29; H, 5.62; N, 6.10. Found: C, 74.34; H, 5.44; N, 6.12. ^{1}H NMR (C_6D_6): δ 0.98 (q, J = 8.1 Hz, 2H, CH_2), 1.83 (t, J = 8.1 Hz, 3H, CH_3), 2.11 (s, $PhCH_3$), 4.16 (d, J = 27 Hz, 1H, PCH), 6.48 (dd, J = 4.5, 8.4 Hz, 1H, Ar), 6.64−6.78 (m, 3H, Ar), 6.84−7.21 (m, 16H, Ar+$PhCH_3$), 7.30 (d, J = 8.1 Hz, 1H, Ar), 7.55−7.64 (m, 2H, Ar), 7.67−8.13 (b, 4H, Ar), 8.40 (dd, J = 1.2, 4.2 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ 0.78, 14.59, 21.42, 73.51 (d, J = 127.7 Hz), 116.71, 119.22 (d, J = 9 Hz), 119.77, 121.39, 124.36, 125.70, 127.99, 128.28, 128.57, 128.71, 128.82, 129.34, 130.28, 131.47, 132.29 (d, J = 9.8 Hz), 138.00, 147.19, 153.47. ^{31}P NMR (C_6D_6): δ 16.30 (m).

Synthesis of [Zn(Et){*p*-MeC$_6$H$_4$NC(Ph)═CHP(Ph$_2$)═N(8-C$_8$H$_6$N)}] (5b). $ZnEt_2$ (0.62 mL, 1 M solution in hexane, 0.62 mmol) was added dropwise to a stirred solution of **4b** (0.30 g, 0.56 mmol) in toluene (10 mL) at about −80 °C. The mixture was stirred overnight at room temperature and heated to 110 °C for 8 h. The resulting solution was cooled to room temperature and filtered. Solvents were removed under vacuum. Recrystallization of the residue from diethyl ether afforded yellow crystals of **5b** (0.1973 g, 56%), mp 202−204 °C. Anal. Calcd for $C_{38}H_{34}N_3PZn$: C, 72.55; H, 5.45; N, 6.68. Found: C, 72.11; H, 5.44; N, 6.68. ^{1}H NMR (C_6D_6): δ 0.97 (q, J = 8.1 Hz, 2H, CH_2), 1.83 (t, J = 8.1 Hz, 3H, CH_3), 2.09 (s, 3H, CH_3), 4.12 (d, J = 27 Hz, 1H, PCH), 6.50 (dd, J = 4.5, 8.1 Hz, 1H, Ar), 6.64−6.78 (m, 2H, Ar), 6.82−7.15 (m, 14H, Ar), 7.31 (d, J = 8.1 Hz, 1H, Ar), 7.54−7.64 (m, 2H, Ar), 7.67−8.21 (b, 4H, Ar), 8.42 (d, J = 4.5 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ 0.78, 14.57, 20.79, 72.13 (d, J = 127.4 Hz), 116.66, 119.36 (d, J = 9 Hz), 121.35, 124.38, 127.94, 128.68, 128.82, 129.49, 130.26, 131.43, 132.32 (d, J = 9.7 Hz), 137.98, 147.15. ^{31}P NMR (C_6D_6): δ 16.30 (m).

Synthesis of [Zn(Et){*p*-MeOC$_6$H$_4$NC(Ph)═CHP(Ph$_2$)═N(8-C$_8$H$_6$N)}] (5c). $ZnEt_2$ (1.0 mL, 1 M solution in hexane, 1.0 mmol) was added dropwise to a stirred solution of **4c** (0.50 g, 0.91 mmol) in toluene (20 mL) at about −80 °C. The mixture was stirred overnight at room temperature and heated to 110 °C for 8 h. The resulting solution was cooled to room temperature and filtered. Concentration of the filtrate gave yellow crystals of **5c** (0.4861 g, 83%), mp 160−162 °C. Anal. Calcd for $C_{38}H_{34}N_3OPZn\cdot C_7H_8$: C, 73.32; H, 5.74; N, 5.70. Found: C, 73.19; H, 5.76; N, 5.68. ^{1}H NMR (C_6D_6): δ 0.91 (q, J = 8.1 Hz, 2H, CH_2),1.78 (t, J = 8.1 Hz, 3H, CH_3), 2.11 (s, $PhCH_3$), 3.27 (s, 3H, OCH_3), 4.08 (d, J = 26.6 Hz, 1H, PCH), 6.50 (dd, J = 4.5, 8.3 Hz, 1H, Ar), 6.70 (d, J = 8.8 Hz, 3H, Ar), 6.74 (d, J = 8.3 Hz, 1H, Ar), 6.86−7.17 (m, 12H, Ar), 7.33 (dd, J = 1.4, 8.3 Hz, 1H, Ar), 7.53−7.62 (m, 2H, Ar), 7.69−8.24 (b, 4H, Ar), 8.36 (dd, J = 1.4, 4.5 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ 0.73, 14.49, 21.42, 54.89, 70.20 (d, J = 126.4 Hz), 114.31, 116.68, 119.46 (d, J = 8.8 Hz), 121.32, 125.32, 125.70, 127.92, 128.16, 128.57, 128.68, 128.84, 129.34, 130.21, 131.46, 132.37 (d, J = 9.2 Hz), 138.02, 147.04, 154.26. ^{31}P NMR (C_6D_6): δ 16.28 (m).

Synthesis of [Al(Me$_2$){PhNC(Ph)═CHP(Ph$_2$)═N(8-C$_8$H$_6$N)}] (6a). $AlMe_3$ (0.28 mL, 2.3 M solution in hexane, 0.64 mmol) was added dropwise to a stirred solution of **4a** (0.30 g, 0.58 mmol) in toluene (10 mL) at room temperature. The mixture was stirred overnight at room temperature and heated to 110 °C for 12 h. The resulting solution was cooled to room temperature and filtered. Concentration of the filtrate afforded yellow crystals of **6a** (0.1561 g, 47%), mp 258−260 °C. Anal. Calcd for $C_{37}H_{33}AlN_3P$: C, 76.93; H, 5.76; N, 7.27. Found: C, 76.66; H, 5.77; N, 7.01. ^{1}H NMR (C_6D_6): δ 0.09 (s, 6H, $AlCH_3$), 4.43 (d, J = 30.9 Hz, 1H, PCH), 6.58 (dd, J = 2.4, 6.3 Hz, 1H, Ar), 6.60−6.67 (m, 1H, Ar), 6.71 (dd, J = 4.5, 8.1 Hz, 1H, Ar), 6.76−6.85 (m, 4H, Ar), 6.86−7.00 (m, 9H, Ar), 7.03 (dd, J = 1.8, 7.5 Hz, 2H, Ar), 7.38 (dd, J = 1.2, 8.1 Hz, 1H, Ar), 7.57 (d, J = 6.9 Hz, 2H, Ar), 7.87 (d, J = 6.9 Hz, 2H, Ar), 7.91 (d, J = 6.9 Hz, 2H, Ar), 8.70 (dd, J = 1.2, 4.5 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −3.03, 75.53 (d, J = 128.5 Hz), 115.93 (d, J = 9.4 Hz), 116.62, 122.11, 127.62, 128.60, 128.76, 130.46, 132.07 (d, J = 2.3 Hz), 133.43 (d, J = 10.2 Hz), 136.46, 144.73, 152.74. ^{31}P NMR (C_6D_6): δ 21.62 (m).

Synthesis of [Al(Me$_2$){*p*-MeC$_6$H$_4$NC(Ph)═CHP(Ph$_2$)═N(8-C$_8$H$_6$N)}] (6b). $AlMe_3$ (0.27 mL, 2.3 M solution in hexane, 0.62 mmol) was added dropwise to a stirred solution of **4b** (0.30 g, 0.56 mmol) in toluene (10 mL) at room temperature. The mixture was stirred overnight at room temperature and heated to 110 °C for 12 h. The resulting solution was cooled to room temperature and filtered. Solvents were removed under vacuum. Recrystallization of the residue from diethyl ether formed yellow crystals of **6b** (0.1856 g, 56%), mp 248−250 °C. A single crystal of **6b** suitable for an X-ray diffraction determination was grown from benzene. Anal. Calcd for $C_{38}H_{35}AlN_3P\cdot 0.3C_4H_{10}O$: C, 76.69; H, 6.24; N, 6.84. Found: C, 76.31; H, 5.92; N, 7.06. ^{1}H NMR (C_6D_6): δ 0.09 (s, 6H, $AlCH_3$), 1.88 (s, 3H, CH_3), 4.41 (d, J = 30.9 Hz, 1H, PCH), 6.57 (dd, J = 2.4, 6.3 Hz, 1H, Ar), 6.65−6.82 (m, 7H, Ar), 6.83−6.91 (m, 1H, Ar), 6.92−7.01 (m, 6H, Ar), 7.05 (dd, J = 1.8, 7.2 Hz, 2H, Ar), 7.39 (dd, J = 1.5, 8.4 Hz, 1H, Ar), 7.60 (d, J = 6.9 Hz, 2H, Ar), 7.88 (d, J = 7.2 Hz, 2H, Ar), 7.92 (d, J = 6.9 Hz, 2H, Ar), 8.70 (dd, J = 1.5, 4.5 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −3.07, 20.79, 75.01 (d, J = 128.8 Hz), 115.95 (d, J = 9.3 Hz), 116.60, 122.09, 127.51, 127.62, 127.66, 128.40, 128.59, 128.75, 130.44, 132.03 (d, J = 2.6 Hz), 133.45 (d, J = 10.1 Hz), 136.44, 144.74, 150.10. ^{31}P NMR (C_6D_6): δ 21.57 (m).

X-ray Crystallography. Single crystals of complexes **2**, **3**, **5a** and **6b** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data of complexes **2**, **3**, and **5a** were collected on an Oxford Diffraction Gemini S Ultra diffractometer with mirror-monochromated Cu Kα radiation (λ = 1.541 84 Å) (for **2** and **3**) or graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) (for **5a**). Diffraction data of complex **6b** were collected on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods using SHELXS-97[20] and refined against F^2 by full-matrix least squares using SHELXL-97.[21] The disordered solvent molecules in complexes **2** and **3** were removed from the diffraction data using the SQUEEZE program. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are given in Table 3.

Polymerization of ε-Caprolactone Catalyzed by 2, 3, 5a−c, and 6a,b. A typical polymerization procedure was exemplified by the synthesis of PCL using complex **2** as a catalyst in the presence of an

Table 3. Details of the X-ray Structure Deteminations of Complexes 2, 3, 5a, and 6b

	2	3	5a·C_7H_8	6b·$2C_6H_6$
empirical formula	$C_{29}H_{26}N_3PZn$	$C_{29}H_{27}AlN_3P$	$C_{44}H_{40}N_3PZn$	$C_{50}H_{47}AlN_3P$
fw	512.87	475.49	707.13	747.86
T (K)	291(2)	291(2)	150(2)	298(2)
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc
a (Å)	10.1130(4)	9.749(5)	11.6230(4)	22.133(2)
b (Å)	11.3801(5)	10.560(5)	12.7857(6)	11.2770(10)
c (Å)	13.7665(6)	18.134(5)	14.1984(6)	36.196(3)
α (deg)	85.789(4)	104.816(5)	86.513(4)	90
β (deg)	68.959(4)	95.061(5)	68.431(4)	107.595(2)
γ (deg)	73.559(4)	102.460(5)	85.898(3)	90
V (Å^3)	1417.54(10)	1741.9(13)	1955.86(14)	8611.7(14)
Z	2	2	2	8
D_{calcd} (g cm^{-3})	1.202	0.907	1.201	1.154
F(000)	532	500	740	3168
μ (mm^{-1})	1.878	1.061	0.701	0.121
θ range for data collecn (deg)	4.05−68.25	2.55−69.48	2.84−26.37	1.93−25.02
no. of rflns collected	11 836	15 087	16 681	21 334
no. of indep rflns (R_{int})	5122 (0.0237)	6395 (0.0207)	7992 (0.0462)	11 433 (0.0614)
no. of data/restraints/params	5122/12/308	6395/0/305	7992/1/444	11 433/2/997
goodness of fit on F^2	1.052	1.004	1.041	0.854
final R indices ($I > 2\sigma(I)$)				
R1	0.0433	0.0578	0.0578	0.0476
wR2	0.1063	0.1565	0.1473	0.0504
R indices (all data)				
R1	0.0491	0.0664	0.0813	0.1455
wR2	0.1087	0.1591	0.1592	0.0627
largest diff peak and hole (e Å^{-3})	0.716, −0.949	0.50, −0.22	0.635, −0.419	0.140, −0.165

equimolar amount of benzyl alcohol. The conversion of ε-CL was determined by ^{1}H NMR spectroscopic analyses. Complex **2** (0.0174 g, 0.034 mmol) and toluene (3.04 mL) were added successively into a Schlenk tube. Then the Schlenk tube was placed in an oil bath, the temperature of which was preset at 70 °C. After the complex dissolved, benzyl alcohol (0.34 mL, 0.1 M in toluene, 0.034 mmol) and ε-CL (0.7725 g, 6.77 mmol) were added successively into the Schlenk tube. After the solution was stirred for 30 min, the polymerization was terminated by addition of several drops of glacial acetic acid. After it was stirred for 0.5 h at room temperature, the resulting viscous solution was diluted with dichloromethane and then dropped into cool methanol with stirring. The white precipitate was collected by filtration under reduced pressure, washed once with cool methanol, and dried under vacuum, giving a white solid (0.7269 g, 94%). For GPC analysis, the sample was dissolved in dichloromethane, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

Polymerization of *rac*-Lactide Catalyzed by 2 and 5a−c. All the polymerizations were conducted under the same concentration of monomer, which was 0.5 M. A typical polymerization procedure was exemplified by the synthesis of PLA using complex **2** as a catalyst in the presence of an equimolar amount of benzyl alcohol. The conversion of *rac*-lactide was determined by ^{1}H NMR spectroscopic analyses. *rac*-LA (0.9611 g, 6.67 mmol) and toluene (8.0 mL) were added into a Schlenk tube. The Schlenk tube was heated, and the *rac*-LA dissolved. When the solution was cooled to about 70 °C, the Schlenk tube was placed in an oil bath, the temperature of which was preset at 70 °C. After the mixture was stirred at 70 °C for 30 min, benzyl alcohol (0.34 mL, 0.1 M in toluene, 0.034 mmol) and complex **2** (0.0171 g, in 5.0 mL of toluene, 0.033 mmol) were added successively into the mixture. After the solution was stirred for 15 min, the polymerization was terminated by addition of several drops of glacial acetic acid. After it was stirred for 0.5 h at room temperature, the resulting solution was dropped into cool methanol with stirring. The viscous precipitate was collected and dissolved in dichloromethane, and the solution was dropped into *n*-hexane. The white precipitate was collected by filtration, washed with methanol, and dried under vacuum, giving a white solid (0.7201 g, 75%). For GPC analysis, the sample was dissolved in dichloromethane, passed through a short neutral aluminum oxide column, precipitated in methanol, and dried under vacuum.

Kinetic Studies. A typical kinetic study procedure was exemplified by the polymerization of 200 equiv of ε-CL using complex **2** as a catalyst in the presence of an equimolar amount of benzyl alcohol. Complex **2** (0.0174 g, 0.034 mmol) and toluene (3.04 mL) were added successively into a Schlenk tube. After the complex dissolved, the Schlenk tube was placed in an oil bath, the temperature of which was preset at 40 °C. The mixture was stirred for 10 min, and then benzyl alcohol (0.34 mL, 0.1 M in toluene, 0.034 mmol) and ε-CL (0.776 g, 6.8 mmol) were added successively into the Schlenk tube. Samples were taken from the reaction mixture using a syringe at a 15 min interval. The polymerizations of the samples taken from the Schlenk tube were terminated by addition of a drop of glacial acetic acid. Each of the samples was measured by ^{1}H NMR to calculate the conversion of ε-CL and the value of $\ln([M]_0/[M])$. The other part of each sample was diluted with dichloromethane and passed through a short neutral aluminum oxide column. The eluate was concentrated and then dropped into cool methanol with stirring.

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The white precipitates were collected by filtration under reduced pressure, washed with cool methanol, and dried under vacuum. The dried polymer was used for GPC analysis.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray crystal structure data for complexes **2**, **3**, **5a**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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