Lithium, Magnesium, and Zinc Iminophosphorano(8-quinolyl)methanide Complexes: Syntheses, Characterization, and Activity in ϵ-Caprolactone Polymerization

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Received November 12, 2006

Lithiation of $R_2P(CH_2C_9H_6N\text{-}8)$═$NBu^t$ (R = Ph, **3**; R = Pr^i, **4**) with an equivalent of Bu^nLi afforded lithium iminophosphorano(8-quinolyl)methanide [Li{CH(8-C_9H_6N)P(Ph_2)═NBu^t}(THF)] (**5**) and [Li{CH(8-C_9H_6N)P(Pr^i_2)═NBu^t}]$_2$ (**6**), respectively. Reaction of **4** with Et_2Mg yielded magnesium iminophosphorano(8-quinolyl)methanide complex (**7**). Treatment of **6** with $ZnCl_2$ gave [Zn(Cl){CH(8-C_9H_6N)P(Pr^i_2)═NBu^t}] (**8**), which was transformed into alkylated zinc complexes [Zn(R^1){CH(8-C_9H_6N)P(Pr^i_2)═NBu^t}] (R^1 = Ph, **9**; R^1 = Me, **10**) by treating with R^1Li or R^1MgX. Ethylzinc complexes [Zn(Et){CH(8-C_9H_6N)P(R_2)═NBu^t}] (R = Ph, **11**; R = Pr^i, **12**) were obtained by reaction of **3** or **4** with an equivalent of Et_2Zn. Compounds **2** and **4**−**12** were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analyses. Structures of complexes **6**−**8** and **10** were further characterized by single-crystal X-ray diffraction techniques. The catalytic behaviors of complexes **7** and **9**−**12** in the ring-opening polymerization of ϵ-caprolactone was studied. Complex **7** exhibited high catalytic activity in the presence or absence of benzyl alcohol. Complexes **9**−**12** catalyzed the ring-opening polymerization of ϵ-CL in the presence of benzyl alcohol and exhibited first-order dependence on monomer concentration.

Introduction

Poly(ϵ-caprolactone) (PCL), polylactide (PLA), and their copolymers are important materials for biomedical, pharmaceutical, and agricultural applications due to their biodegradable, biocompatible, and permeable properties.[1,2] The major method to synthesize the polymers is ring-opening polymerization (ROP) of lactones or lactides by a coordination, anoinic or cationic initiator.[3] Metal-complex-catalyzed ROP of cyclic esters is one of the promising methodologies because it provides control on molecular weight, molecular weight distribution, polymer architecture, and end functionality.[4] Some excellent metal catalysts or initiators have been reported, including aluminum,[5] tin,[6] magnesium,[7] zinc,[8] transition metal,[9] and rare earth metal[10] complexes supported by various ligands. Nitrogen based ligand−metal complexes are widely applied as catalysts/initiators for ring-opening polymerization of cyclic esters. For example, some of the β-diketiminate complexes of zinc and magnesium demonstrated excellent catalytic lactide polymerization behavior.[11] Among the nitrogen based ligands, iminophosphorano ligands have attracted considerable attention recently. A range of complexes supported by iminophosphorano ligands has been synthesized and characterized.[12] Some of them exhibited good catalytic activity in the ROP of cyclic esters.[13] We previously reported synthesis of aluminum complexes bearing iminophosphorano ligands [CH(8-C_9H_6N){P(Ph_2)═NBu^t}]$^-$ and [C(8-

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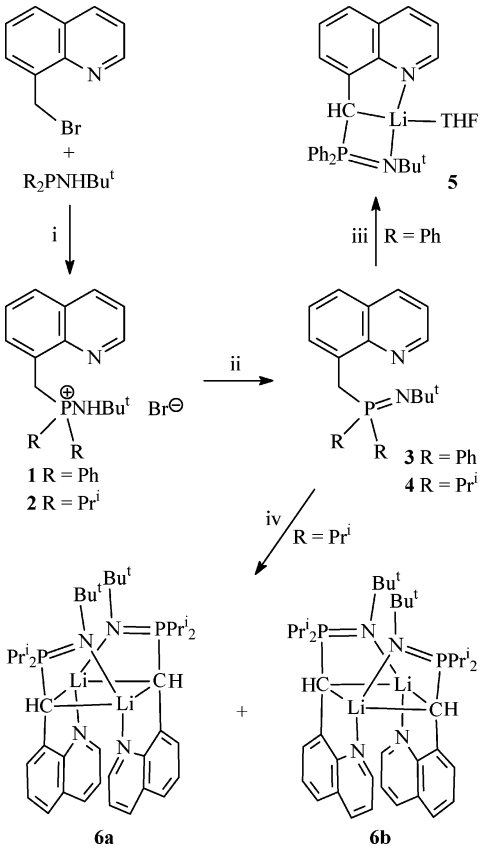
10.1021/om0610400 CCC: $37.00
Publication on Web 03/23/2007

$C_9H_6N)\{P(Ph_2)=NBu^t\}]^{2-}$ through reaction of $Ph_2P(CH_2C_9H_6N$-8)$=NBu^t$ with $AlMe_3$.[12h] We now describe synthesis and characterization of Li, Mg, and Zn complexes supported by [CH-(8-$C_9H_6N)\{P(R_2)=NBu^t\}]^-$ (R = Ph, Pr^i) ligands and the use of the Mg and Zn complexes in the ring-opening polymerization of ϵ-caprolactone.

Results and Discussion

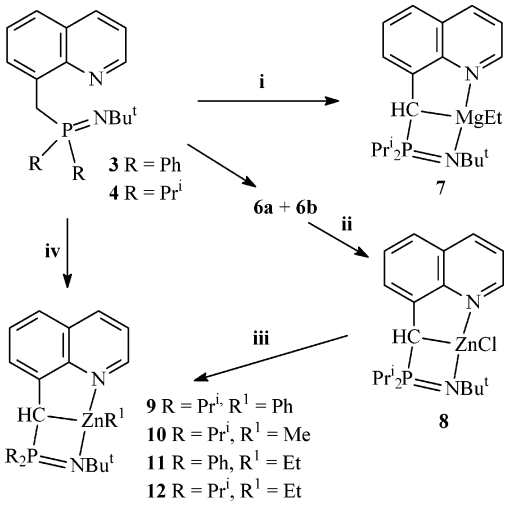
Syntheses and Characterization of Compounds 2 and 4−12. Syntheses of compounds **1**−**6** have been summarized in Scheme 1. Compounds **1** and **3** were prepared according to our previously reported methods.[12h] Compound **2** was prepared in quantitative yield by a similar procedure through reaction of 8-(bromomethyl)quinoline with $Pr^i_2PNHBu^t$. Treatment of **2** with excess NaH afforded $Pr^i_2P(CH_2C_9H_6N$-8)$=NBu^t$ (**4**). Compound **2** was almost insoluble in toluene, benzene, hexane, and Et_2O and soluble in CH_2Cl_2 and $CHCl_3$, while **4** was soluble in hexane and very soluble in toluene and Et_2O. Both **2** and **4** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. Reaction of **3** or **4** with an equivalent of Bu^nLi in tetrahydrofuran (THF) formed lithiated products **5** and **6**, respectively, as red crystalline solids. Complex **5** was crystallized from THF, and complex **6** was crystallized from Et_2O. Complexes **5** and **6** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. The variable-temperature ^1H NMR spectra of **5** in C_6D_6 (until 333 K) showed no changes compared with that at room temperature, proving its coordination mode to be kept at higher temperature. The ^1H NMR spectrum of complex **6** gave broad signals in the region of Pr^i groups. Two CH signals of Pr^i were attributed to the presence of diastereotopic Pr^i in the enantiomeric dimeric structures of **6** (on the basis of the single-crystal X-ray diffraction result; see below). The variable-temperature ^1H NMR spectra of **6** in C_6D_6 showed that the two broad CH signals of Pr^i coalesced into a very broad signal at 313 K and became a broad signal centered at δ 2.30 ppm at 323 K. The aromatic proton signals also became broad at higher temperature. These are attributed to the dissociation and recombination of the dimeric structures at elevated temperature. The solid structure of complex **6** was characterized by single-crystal X-ray diffraction techniques. Complex **6** is dimeric in the solid state and consists of two enantiomers (**6a**,**b**, Figure 1). It crystallizes with three independent molecules in the asymmetric unit, two **6a** and one **6b**. For each of the enantiomers **6a**,**b**, the two lithium atoms are bridged by two carbon atoms, forming a 1,3-Li_2C_2 four-membered ring. With the 1,3-Li_2C_2 ring as the base, the CPNLi and C_3NLi rings form the flaps of an "open box"-like structure

Scheme 1. Synthesis of Compounds 1−6[a]



[a] Reagents and conditions: i, CH_2Cl_2, room temperature, 15 h.; ii, NaH, THF, room temperature, 2 h. and then reflux for 4 h.; iii, Bu^nLi, THF, −80 °C to room temperature, 15 h., crystallized from THF; iv, Bu^nLi, THF, −80 °C to room temperature, 15 h., crystallized from Et_2O.

Scheme 2. Synthesis of Complexes 7−12[a]



[a] Reagents and Conditions: i, Et_2Mg, THF, −80 °C to room temperature, 15 h. and then reflux for 4 h.; ii, $ZnCl_2$, Et_2O, −80 °C to room temperature, 15 h.; iii, R^1Li or R^1MgX, toluene, −80 °C to room temperature, 15 h.; iv, Et_2Zn, toluene, −80 °C to room temperature, 15 h. and then reflux for 7 h.

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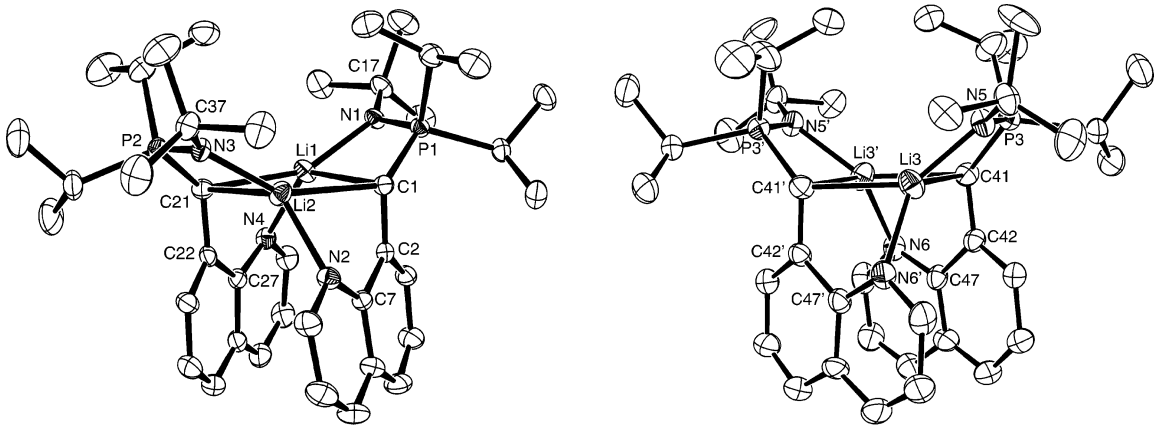

a **b**

Figure 1. ORTEP drawings of **6a**,**b** shown with 20% thermal ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 6a,b

compound **6a**							
Li1−N1	1.966(8)	Li1−N4	2.101(8)	Li2−N2	2.058(9)	Li2−N3	1.946(8)
Li1−C1	2.410(9)	Li1−C21	2.417(8)	Li2−C1	2.355(8)	Li2−C21	2.432(9)
Li1···Li2	2.856(11)	P1−C1	1.739(4)	P1−N1	1.584(4)	P2−C21	1.753(4)
P2−N3	1.585(4)	C1−C2	1.446(6)	C21−C22	1.439(6)		
N1−Li1−N4	128.0(4)	N1−Li1−C1	73.6(3)	N4−Li1−C1	126.8(4)	N1−Li1−C21	152.0(4)
N4−Li1−C21	75.3(3)	C1−Li1−C21	106.2(3)	N2−Li2−N3	127.5(4)	N3−Li2−C1	149.4(4)
N2−Li2−C1	77.2(3)	N3−Li2−C21	74.1(3)	N2−Li2−C2 1	126.2(4)	C1−Li2−C21	107.5(3)
Li1−C1−Li2	73.6(3)	Li1−C21−Li2	72.2(3)	C2−C1−P1	124.1(3)	C22−C21−P2	124.9(3)
compound **6b**							
Li3−N5	1.924(9)	Li3−N6′	2.078(10)	Li3−C41	2.443(11)	Li3−C41′	2.311(10)
P3−C41	1.734(5)	C41−C42	1.437(6)	Li3···Li3′	2.782(17)	P3−N5	1.585(4)
C41−Li3−C41′	108.4(4)	N5−Li3−C6′	134.2(5)	C41−Li3−N6′	124.5(5)	C41′−Li3−N6′	78.2(3)
Li3−C41−Li3′	71.6(4)	Li3−C41−P3	79.5(3)	Li3−C41−C42	87.0(4)	Li3′−C41−P3	127.1(3)
P3−C41−C42	126.5(4)	Li3′−C41−C42	95.6(4)				

framework. The two $Pr^i_2P{=}NBu^t$ groups lie on one side of the base, and the two quinolyl groups lie on the other side of the base. Each of the four-coordinated lithium centers adopts a very distorted tetrahedral geometry. The average distance of 2.079 Å between the lithium atoms and the quinolyl nitrogen atoms (Table 1) is longer than those between the lithium atoms and the imino nitrogen atoms (average, 1.940 Å), and both lie within the normal range as observed for lithiated iminophosphoranes, amidolithium, and diketiminatolithium complexes.[14] The Li−C distances ranging from 2.311(10) to 2.443(11) Å (average, 2.390 Å) are similar to those in the dilithium cluster $[Li_2C(PPh_2{=}NSiMe_3)_2]_2$ [2.312(9)−2.45(1) Å],[15] but longer than those in $[Li(CH(SiMe_3)\{Ph(1,2\text{-}C_6H_4)P{=}NSiMe_2\})]_2$ [2.232(6) Å][16] and $[Li\{CH(SiMe_3)PPh_2{=}NSiMe_3\}]_2$ [2.122(9) and 2.190(9) Å, respectively],[17] and shorter than those found in $[Li\{CH(PPh_2{=}NSiMe_3)_2\}]_2$ (average, 2.615 Å)[18] and $[Li\{CH(PR_2{=}NSiMe_3)_2\}(L)]$ (R = Ph, L = THF; R = Cy, L = Et_2O) [2.560(8), 2.622(9), and 2.633(7) Å, respectively].[19]

Syntheses of magnesium and zinc iminophosphorano(8-quinolyl)methanide complexes are presented in Scheme 2. Treatment of **4** with Et_2Mg in THF afforded dark-red magnesium complex **7**. Reaction of complex **6** with $ZnCl_2$ in Et_2O gave yellow $[Zn(Cl)\{CH(8\text{-}C_9H_6N)P(Pr^i_2){=}NBu^t\}]$ (**8**) in relatively low yield. Compound **8** was transformed into phenylated or methylated zinc complexes $[Zn(R^1)\{CH(8\text{-}C_9H_6N)P(Pr^i_2){=}NBu^t\}]$ (R^1 = Ph, **9**; R^1 = Me, **10**) by treating with R^1Li or R^1MgX (R^1 = Ph or Me). Ethyl zinc iminophosphorano(8-quinolyl)methanide complexes **11** and **12** were obtained by reaction of **3** or **4** with Et_2Zn in toluene under reflux conditions. Each of the complexes **7**−**12** was an air-sensitive crystalline solid and was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analyses. The data were consistent with their respective structure. In addition, the variable-temperature ^1H NMR spectra of complexes **7**, **11**, and **12** (**7**, **11**, and **12** in C_6D_6 and **12** in C_5D_5N) proved that the coordination mode of each of the complexes was retained at higher temperature (until 333 K in C_6D_6 and 353 K in C_5D_5N).

The single-crystal X-ray diffraction structure of complex **7** is displayed in Figure 2; selected bond distances and bond angles are listed in Table 2. Complex **7** is monomeric in the solid state. The four-coordinated Mg is bonded to the methanide carbon atom C1, ethyl carbon atom C21, quinolyl nitrogen atom N1, and imino nitrogen atom N2 to form two metallacycles sharing

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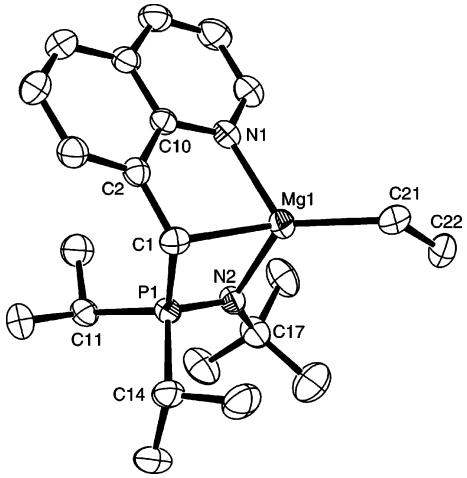

Figure 2. ORTEP drawing of complex **7** shown with 30% thermal ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 7

Mg1−C1	2.339(4)	Mg1−C21	2.183(14)
Mg1−N1	2.187(3)	Mg1−N2	2.108(3)
P1−C1	1.804(3)	P1−N2	1.633(3)
C1−C2	1.515(4)		
C1−Mg1−N1	80.51(12)	C1−Mg1−N2	75.43(11)
N1−Mg1−N2	101.45(12)	N1−Mg1−C21′	114.7(3)
N2−Mg1−C21′	127.4(2)	C1−Mg1−C21′	144.6(3)
C2−C1−Mg1	103.70(19)	P1−C1−Mg1	83.43(12)
P1−N2−Mg1	95.39(12)	C10−N1−Mg1	114.0(2)
C2−C1−P1	121.5(2)		

the Mg1−C1 edge. The magnesium atom exhibits a distorted tetrahedral geometry. The Mg1−C21 distance of 2.183(14) Å is slightly longer than those found in [Mg(CH_2Ph){[N(2,6-$Pr^i_2C_6H_3$)C(Me)]$_2$CH}(THF)] [2.1325(18) Å],[20] [Mg(Et)-{PhTpBu^t}] (PhTpBu^t = phenyltris(3-*tert*-butylpyrazolyl)borato) [2.163(2) Å],[21] and [Mg(R){N(R)C_5H_3[ArN=C(Me)]$_2$-2,6}] (R = Me, Et, Pr^i) [2.122(2)−2.157(2) Å].[22] The Mg1−C1 distance of 2.339(4) Å is significantly longer than that of Mg1−C21. This is probably a consequence of ring strain. A similar structural feature is also found in [Mg(Cl){CH(P(Ph_2)=$NSiMe_3$)$_2$}]$_2$ in which the Mg−C distance is 2.460(8) Å.[12e] The Mg1−N1 distance of 2.187(3) Å is slightly longer than that of Mg1−N2 [2.108(3) Å], and both are comparable to the dative Mg−N bond distances in quinolyl, pyridyl, and iminophosphorane nitrogen atom coordinated magnesium complexes such as [Mg{8-N($SiMe_3$)C_9H_6N}$_2$], [Mg{2-C($SiMe_3$)$_2$(C_5H_5N)}(Cl)]$_2$, [Mg_2{{N($SiMe_3$)C(Bu^t)C(H)}$_2$$C_4H_2$N-2,3}$Br_2(THF)_4$], and [Mg-{($Me_3$SiN=P$Pr^i_2$CH)$_2$$C_5H_3$N-2,6}THF] [2.061(19)−2.220(2) Å].[23] The phosphorus atom adopts a distorted tetrahedral geometry. The P1−N2 diatance of 1.633(3) Å is normal for a coordinated iminophosphorane[24] and shows that the P−N bond has a bond order that is larger than unity.[25] The P1−C1 distance of 1.804-(3) Å is indicative of a P−C single bond.

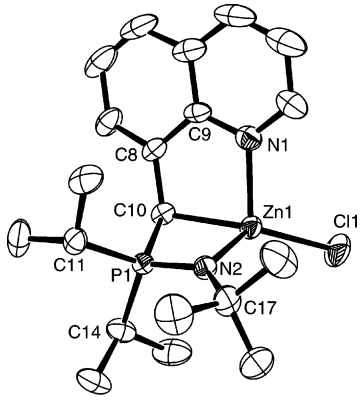

Figure 3. ORTEP drawing of complex **8** shown with 30% thermal ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) of 8

Zn1−N1	2.076(4)	Zn1−N2	2.011(4)
Zn1−C10	2.122(4)	Zn1−Cl1	2.1913(15)
P1−N2	1.601(4)	P1−C10	1.787(4)
C8−C10	1.499(6)		
N1−Zn1−N2	102.90(15)	N1−Zn1−C10	84.71(16)
N2−Zn1−C10	78.71(14)	N1−Zn1−Cl1	110.02(12)
N2−Zn1−Cl1	126.88(11)	C10−Zn1−Cl1	143.17(13)
N2−P1−C10	101.28(19)	C8−C10−P1	122.2(3)
C8−C10−Zn1	104.3(3)	P1−C10−Zn1	84.50(17)
P1−N2−Zn1	93.23(17)		

Complex **8** is monomeric and crystallizes with two molecules in the unit cell. An ORTEP structural drawing of a single molecule is shown in Figure 3, and selected bond distances and bond angles are listed in Table 3. The skeletal structure of complex **8** is similar to that of complex **7**. The Zn1−N1 distance of 2.076(4) Å is slightly longer than the Zn1−N2 distance [2.011(4) Å], and the latter represents a relatively short interaction when compared with the corresponding distances for other dative zinc−nitrogen bonds [2.070(4)−2.191(2) Å].[23a,26] The Zn1−C10 distance of 2.122(4) Å is longer than the Zn−C σ-bond distances seen in [Zn(Br){C($SiMe_3$)$_2$-($SiMe_2C_5H_4$N-2)}]$_2$ [2.037(4) Å],[26c] [Zn(Br){C($SiMe_3$)$_2$($SiMe_2$-NMe_2)}]$_2$ [2.045(3) Å],[27] and [Zn(*o*-$C_6H_4PPh_2NSiMe_3$)$_2$] [2.008-(5) Å].[28] Both P1−N2 and P1−C10 distances [1.601(4) and 1.787(4) Å, respectively] are shorter than those in complex **7**.

The ORTEP drawing of complex **10** is presented in Figure 4. Selected bond distances and bond angles are listed in Table 4. Complex **10** is a monomer in the solid state. It has similar structural skeleton to complex **8**. However, the two structures show some differences in bond lengths and angles. For example, each of the N1−Zn1−N2, C3−Zn1−N1, C3−Zn1−N2, and P1−C3−C9 bond angles in complex **10** is narrower than that in complex **8**. The Zn−N distances in complex **10** are longer than those in complex **8**. The Zn1−C3 distance of 2.172(2) Å in complex **10** is also slightly longer than that in complex **8** [2.122(4) Å], and the former is comparable to the Zn−C distance

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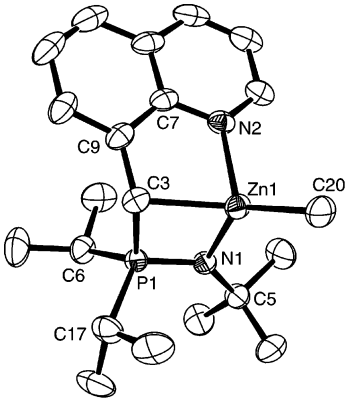


Figure 4. ORTEP drawing of complex **10** shown with 30% thermal ellipsoids.

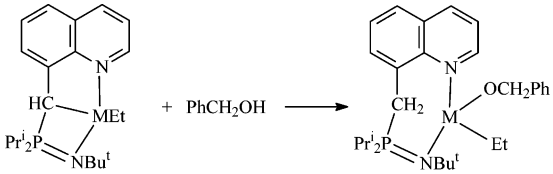
Table 4. Selected Bond Distances (Å) and Angles (deg) of 10

Zn1−N1	2.0584(15)	Zn1−N2	2.1651(17)
Zn1−C3	2.172(2)	Zn1−C20	1.975(2)
P1−N1	1.5853(16)	P1−C3	1.7737(19)
C3−C9	1.477(3)		
N1−Zn1−N2	96.15(6)	N1−Zn1−C3	76.90(6)
N2−Zn1−C3	80.97(7)	N1−Zn1−C20	128.44(10)
N2−Zn1−C20	115.49(10)	C3−Zn1−C20	143.99(11)
N1−P1−C3	103.04(9)	C9−C3−P1	120.51(14)
C9−C3−Zn1	105.90(15)	P1−C3−Zn1	84.80(8)
P1−N1−Zn1	93.65(7)		

for the η^1-ring of [Zn($Pr^i_4C_5H)_2$] [(2.223(4) Å)].[29] The Zn1−C20 distance of 1.975(2) Å in complex **10** is in the expected range for terminal zinc alkyl complexes.[22,30]

Ring-Opening Polymerization of ϵ-CL Catalyzed by 7 and 9−12. Organomagnesium complex **7** was highly active for the ring-opening polymerization of ϵ-CL in the presence or absence of benzyl alcohol (BnOH) in toluene or THF. In the presence of BnOH, the polymerization was found to be an exothermic reaction and proceeded extremely fast. When polymerization was performed at a $[CL]_0$/**7** ratio of 200:1 in 7 mL of toluene at 25 °C, the lactone became gum rapidly during the period of dropwise addition. This led to the catalyst being wrapped, and the polymerization reaction could not go to completion. The conversion of the monomer stopped at 67%, indicated by ^{1}H NMR spectrum. The poly(ϵ-caprolactone) was identified by gel permeation chromatography (GPC) with M_n = 213 399 kg/mol and polydispersity indice (PDI) = 1.30 (Table 5, entry 1). To reduce the reaction rate, we performed the polymerization at 0 °C in 20 mL of toluene or THF and the results are listed in Table 5 (entries 2 and 3, respectively). Under these conditions, the polymerization could achieve completion and gave high yields of polymers. If the reaction was carried out in 40 mL of toluene at 0 °C, the reaction proceeded more smoothly and formed polymer with higher molecular weight (Table 5, entry 4). We further tried the polymerization reactions with a different ratio of ϵ-CL to **7**. When the molar ratio of ϵ-CL to **7** was about 500, the reaction in 20 mL of toluene at 0 °C or in 30 mL of toluene at −25 °C gave gum, which resulted in low conversion of monomer and low yields of polymers but much larger molecular weights (determined by GPC) (Table 5, entries 7 and 8). In 70 mL of toluene, the polymerization gave 100% conversion and 97% yield with wider PDI. When the molar ratio of ϵ-CL to **7** was 99, the polymerization could go to completion within 3 min in 30 mL of toluene at 0 °C. The molecular weights (M_n) determined by GPC are much higher than the calculated M_n (based on the hypothesis of "living" polymerization). This may be due to the presence of transesterifications in the process of reaction. The intermolecular chain-transfer (via transesterification) results in formation of higher molecular weights. A similar situation was also observed in the ROP of ϵ-CL catalyzed by [Mg(1,2-{N(PPh_2)}$_2$$C_6H_4$-$\kappa^2N,N'$)-($THF)_2$] and [ZnPr{1-N($PMes_2$)-2-N($PHMes_2$)$C_6H_4$-$\kappa^2N,N'$}].[31]

The active catalyst was studied by ^{1}H NMR spectroscopy. To the solution of complex **7** in toluene was added dropwise an equivalent of BnOH at 0 °C, and the mixture was stirred for 10 min ^{1}H NMR spectrum showed that the reaction was complete and the product formed was **Ia** (eq 1). The reason that the reaction occurred on CH rather than CH_2CH_3 is probably due to the existence of a strong ring strain in **7**.



(1)

Ia M = Mg
Ib M = Zn

Complex **7** was also effective for the ROP of ϵ-CL in the absence of benzyl alcohol. A 100% conversion was achieved within 3 min at a $[CL]_0$/**7** ratio of 200 in toluene at 0 °C. This gave PCL with high M_n and narrow PDI (Table 5, entry 10). From the ^{1}H NMR spectrum of PCL we cannot judge which of the CH and CH_2CH_3 groups inserts to ϵ-CL due to the high molecular weight of the PCL obtained.

Complexes **9−12** were also investigated on their catalytic behavior in the ROP of ϵ-CL in the presence of benzyl alcohol. Experimental results indicated that each of the complexes **9−12** had lower activity than the **7**/BnOH system. The reactions were carried out at 60 °C, and more than 90% conversions were achieved in 60−156 min (Table 6, entries 1−7). These reactions gave PCLs with relatively low molecular weights (M_n = 26 200−39 321) and narrow PDIs (1.01−1.09). The catalytic active species of complex **12** in the presence of BnOH was studied by ^{1}H NMR spectroscopy, and the result proved to be **Ib** (eq 1), similar to that of complex **7**. Due to the catalytic reactions run at 60 °C, we carried out a variable-temperature ^{1}H NMR spectral study in C_6D_6 for **Ib** to see if the structure was retained at higher temperature. The result revealed that the structure was unchanged until 333 K.

The catalytic behavior of complex **12** was also studied in the absence of benzyl alcohol, and the results showed that it had very low catalytic activity in the ROP of ϵ-CL (Table 6, entry 8).

The kinetics of the ROPs catalyzed by **9−12** in the presence of BnOH was determined in toluene. Plots of ln($[M]_0$/[M]) vs time are shown in Figure 5. For each of complexes **9−12** the plot of ln($[M]_0$/[M]) vs time exhibited well a linear relationship, which indicated that the polymerization proceeded with first-order dependence on the monomer concentration. The first-order kinetics implied that the concentration of active species remained unchanged, or, in other words, the growing polymer chain

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Table 5. Ring-Opening Polymerization of ϵ-CL Catalyzed by Complex 7[a]

entry	temp (°C)	cat. (mmol)	BnOH (mmol)	$[M]_0/[BnOH]_0$	solvent vol (mL)	time (min)	conv. (%)	M_n[b] (GPC)	yield (%)	PDI
1[c]	25	0.104	0.104	199	7	<1	67	213 399	62	1.30
2	0	0.104	0.104	201	20	4	100	121 800	87	1.32
3	0	0.104	0.104	199	20[d]	<1	93	141 839	91	1.26
4	0	0.102	0.103	203	40	4	100	196 000	93	1.04
5	0	0.105	0.104	99	30	3	100	91 162	93	1.16
6	0	0.099	0.099	400	60	10	99	151 311	97	1.14
7[c]	0	0.099	0.1	498	20	<1	66	314 093	65	1.03
8[c]	−25	0.101	0.1	506	30	<1	57	303 203	54	1.88
9	0	0.102	0.104	488	70	7	100	209 889	97	1.54
10	0	0.107			30	3	100	255 200	95	1.16

[a] Catalytic polymerization was carried out in toluene except entry 3. [b] Obtained from GPC analysis and calibrated polystyrene standard. [c] Gum was formed during the period of addition of ϵ-caprolactone. [d] THF solvent.

Table 6. Ring-Opening Polymerization of ϵ-CL Catalyzed by Complexes 9−12 in the Presence of Benzyl Alcohol at 60 °C

entry	cat. (mmol)	BnOH (mmol)	$[M]_0/[BnOH]_0$	solvent vol. (mL)	time (min)	conv. (%)	M_n[a] (calcd)	M_n[b] (NMR)	M_n[c] (GPC)	yield (%)	PDI
1	**9** (0.105)	0.105	198	12	156	90	20 400	22 200	26 200	82	1.01
2	**10** (0.105)	0.105	199	7	61	71	16 200	19 100	28 114	67	1.03
3	**10** (0.107)	0.104	200	12	89	92	21 100	22 200	35 300	88	1.01
4	**11** (0.105)	0.105	202	7	34	67	15 500	20 100	29 620	62	1.03
5	**11** (0.101)	0.102	202	12	60	100	23 100	22 800	39 121	96	1.09
6	**12** (0.104)	0.104	200	7	47	74	16 800	24 300	33 410	65	1.05
7	**12** (0106)	0.107	197	12	120	100	22 500	26 100	34 036	92	1.01
8	**12** (0.105)			30	57	20			30 415	13	1.92

[a] Calculated from the molecular weight of ϵ-caprolactone times the conversion of monomer and the ratio of $[M]_0/[BnOH]_0$ plus the molecular weight of BnOH. [b] Obtained from the ^{1}H NMR spectral analysis. [c] Obtained from GPC analysis and calibrated polystyrene standard.

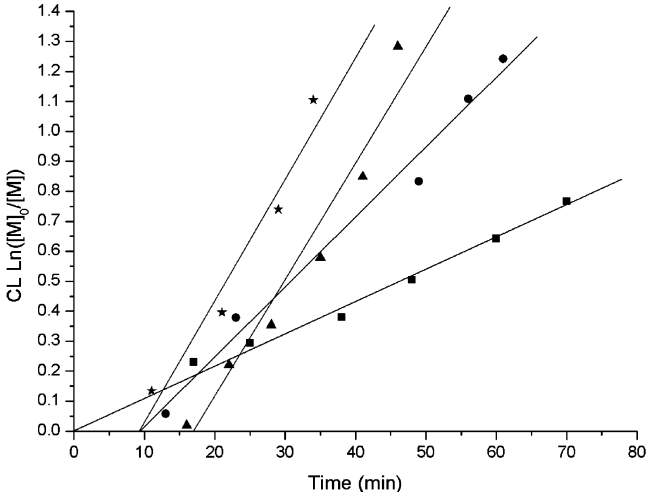

Figure 5. Plots of $\ln([M]_0/[M])$ vs time for the polymerization of ϵ-caprolactone catalyzed by (■) **9**, (●) **10**, (★) **11**, and (▲) **12** in toluene in the presence of an equivalent of BnOH at 60 °C.

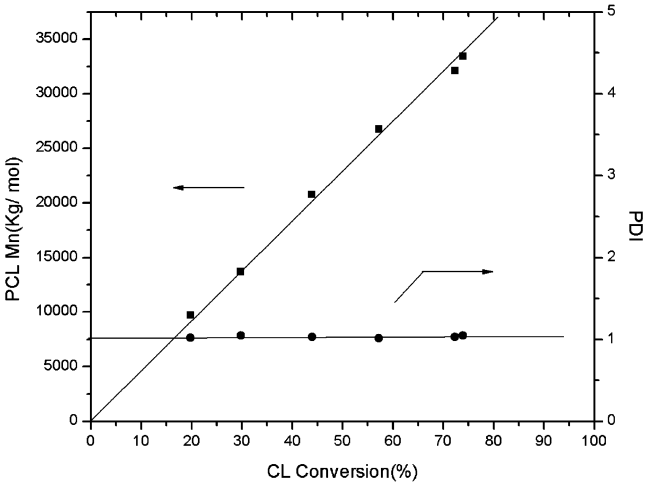

Figure 6. Plot of PCL M_n (■) and polydispersity (●) as a function of conversion with ϵ-caprolactone and **12** in the presence of an equivalent of BnOH in toluene at 60 °C.

remained alive during the entire polymerization. The plot also revealed that there was an induction period before each of **10**−**12** initiated the ROP reaction, while **9** did not require an induction period. The lack of an induction period for **9** may be mainly related to the electronic effect of the phenyl group on the central metal because a more sterically hindered phenyl group should lead to a longer induction period based on the tendency seen in complexes **10** and **12**. The plots also showed that the two lines of $\ln([M]_0/[M])$ vs time for the ROP catalyzed by **11** and **12** are almost parallel. This indicated that the substisuents on the phosphorus atom affected mainly the induction period rather than reaction rates.

The relationship between the number average molecular weight and ϵ-CL conversion was also studied for the complex **12**/BnOH system (Figure 6). The linear relationship of M_n vs ϵ-CL conversion and the low polydispersities of the PCLs obtained (1.02−1.05) showed that the polymerization proceeded in a living fashion.

The ^{1}H NMR spectral studies of the PCLs revealed that the polymer chains were capped with one benzyl ester (δ 7.28 and 5.05 ppm, respectively, for OCH_2Ph) and one hydroxyl end (δ 3.58 ppm for CH_2OH). This indicated that the polymerization reaction was initiated through the insertion of the benzyl alkoxyl group to ϵ-CL followed by ring opening via acyl−oxygen cleavage.

Conclusion

We have synthesized and characterized lithium, magnesium, and zinc iminophosphorano(8-quinolyl)methanide complexes. The single-crystal X-ray diffraction result shows that lithium complex **6** is dimeric and consists of two enantiomers. The magnesium complex exhibited excellent catalytic activity in the ROP of ϵ-CL in the presence or absence of BnOH, yielding PCL with high molecular weights. The zinc complexes also showed good catalytic activity in the ROP of ϵ-CL in the presence of BnOH. The kinetic studies revealed that the

catalytic reactions were first-order-dependent on monomer concentration and showed "living" characters. Investigation by ^{1}H NMR spectroscopy showed that the active species of the Mg and Zn complexes in the presence of BnOH were $[M(R^1)OCH_2Ph\{N(Bu^t)=P(R_2)CH_2(8\text{-}C_9H_6N)\}]$ (M = Mg, Zn).

Experimental Section

General Procedures. All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene, dioxane), sodium/benzophenone (THF, Et_2O, and *n*-hexane) or CaH_2 (CH_2Cl_2) and degassed prior to use. PhLi, Et_2-Mg, $Pr^i_2PNHBu^t$, and 8-bromomethylquinoline were prepared according to literature methods.[32−35] Compounds **1** and **3** were prepared according to our previously reported methods.[12h] Bu^nLi, MeLi, and Et_2Zn were purchased from Alfa Aesar and used as received. $CDCl_3$ and C_6D_6, purchased from Acros Organics, were degassed and stored over 4A molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). ϵ-Caprolactone, purchased from Acros Organics, was dried over 4A molecular sieves. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analyses were performed by the Analytical Center of the University of Science and Technology of China. Gel permeation chromatography (GPC) measurements were performed on a Waters 150C instrument equipped with UltraStyragel columns (10^3, 10^4, and 10^5 Å) and 410 refractive index detector, using monodispersed polystyrene as calibration standard. THF (HPLC grade) was used as eluent at a flow rate of 1 mL/min.

Preparation of $[Pr^i_2P(CH_2C_9H_6N\text{-}8)NHBu^t]^+Br^-$ (2). A solution of 8-bromomethylquinoline (7.88 g, 35.5 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a solution of $Pr^i_2PNHBu^t$ (6.72 g, 35.50 mmol) in CH_2Cl_2 (40 mL) at room temperature with stirring. Stirring of the mixture was continued overnight, and then the solvent was removed under vacuum. The residue was washed with benzene and dried under vacuum to give white powder **2** (14.57 g, 99.8%), mp 194−196 °C. ^{1}H NMR ($CDCl_3$): δ 1.13 (dd, J = 7.5, 17.1 Hz, 6H, CHMe_2), 1.31 (dd, J = 6.9, 17.7 Hz, 6H, CHMe_2), 1.37 (s, 9H, CMe_3), 2.89−3.02 (m, 2H, CHMe$_2$), 4.65 (d, J = 14.1 Hz, 2H, CH_2), 6.64 (s, 1H, NH), 7.47−7.57 (m, 2H, C_9H_6N) 7.79 (d, J = 8.1 Hz, 1H, C_9H_6N), 8.23 (dd, J = 1.5 Hz, J = 8.4 Hz, 1H, C_9H_6N), 8.46 (d, J = 6.9 Hz, 1H, C_9H_6N), 8.84−8.86 (m, 1H, C_9H_6N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.96 (CHMe_2), 16.10 (CHMe_2), 23.41 (d, J = 58.9 Hz, CHMe$_2$), 24.87 (d, J = 51.8 Hz, CHMe$_2$), 32.22 (CMe_3), 53.59 (d, J = 5.1 Hz, CMe$_3$), 121.74 (C_9H_6N), 126.90 (C_9H_6N), 128.33 (d, J = 3 Hz, C_9H_6N), 128.42 (d, J = 1.7 Hz, C_9H_6N), 128.70 (d, J = 8.7 Hz, C_9H_6N), 133.28 (d, J = 6.6 Hz, C_9H_6N), 137.45 (C_9H_6N), 145.88 (C_9H_6N), 149.41 (C_9H_6N). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 58.56. Anal. Calcd for $C_{20}H_{32}N_2PBr$: C, 58.40; H, 7.84; N, 6.81. Found: C, 58.58; H, 7.61; N, 6.80.

Preparation of $Pr^i_2P(CH_2C_9H_6N\text{-}8)=NBu^t$ (4). A mixture of **2** (3.58 g, 8.7 mmol), NaH (1 g, 57−63%, 23−26 mmol), and THF (30 mL) was stirred for 2 h at room temperature and then refluxed for 4 h. The mixture was filtered, and the solvent was removed from the filtrate under vacuum. The residue was dissolved in hexane, concentrated under vacuum, and stored at 0 °C to form yellowish crystals of **4** (2.31 g, 80.5%), mp 58−60 °C. ^{1}H NMR ($CDCl_3$): δ 0.78 (dd, J = 7.2, 14.6 Hz, 6H, CHMe_2), 0.92 (dd, J = 7.1, 14.3 Hz, 6H, CHMe_2), 1.40 (d, J = 0.9 Hz, 9H, CMe_3), 1.68−1.85 (m, 2H, CHMe$_2$), 3.83 (d, J = 12.4 Hz, 2H, CH_2), 6.68 (dd, J = 4.1, 8.2 Hz, 1H, C_9H_6N), 7.19−7.22 (m, 2H, C_9H_6N), 7.45 (dd, J = 1.8, 8.4 Hz, 1H, C_9H_6N), 8.25−8.29 (m, 1H, C_9H_6N), 8.60−8.62 (m, 1H, C_9H_6N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 16.90 (d, J = 2.4 Hz, CHMe_2), 17.33 (d, J = 2.8 Hz, CHMe_2), 27.17 (d, J = 63.1 Hz, CHMe$_2$), 27.93 (d, J = 57.7 Hz, PCH$_2$), 36.67 (d, J = 7.1 Hz, CMe_3), 50.55 (d, J = 3.7 Hz, CMe$_3$), 120.72 (C_9H_6N), 125.94 (d, J = 2.5 Hz, C_9H_6N), 126.28 (d, J = 2.7 Hz, C_9H_6N), 128.64 (d, J = 1.5 Hz, C_9H_6N), 131.49 (d, J = 4 Hz, C_9H_6N), 135.39 (d, J = 7.7 Hz, C_9H_6N), 136.28 (C_9H_6N), 147.35 (d, J = 4.7 Hz, C_9H_6N), 149.10 (C_9H_6N). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 9.34. Anal. Calcd for $C_{20}H_{31}N_2P$: C, 72.69; H, 9.46; N, 8.48. Found: C, 72.64; H, 9.42; N, 8.38.

Preparation of $[Li\{CH(8\text{-}C_9H_6N)(R_2P=NBu^t)\}(L)]$ (R = Ph, L = THF, 5; R = Pr^i, L = Absent, 6). Bu^nLi (0.51 mL, 2.89 M solution in hexanes, 1.47 mmol) was added dropwise to a stirred solution of **3** (0.58 g, 1.46 mmol) in THF (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The solution was filtered, and then the filtrate was concentrated under vacuum to give red crystalline **5** (0.46 g, 66.3%), mp 132−136 °C. ^{1}H NMR (C_6D_6): δ 1.40−1.44 (m, 4H, C_4H_8O), 1.51 (s, 9H, CMe_3), 3.55−3.59 (m, 5H, CH + C_4H_8O), 6.02 (b, 1H, C_9H_6N + *Ph*), 6.22 (b, 1H, C_9H_6N + *Ph*), 6.67 (dd, J = 4.5, 8.1 Hz, 1H, C_9H_6N + *Ph*), 6.96−7.33 (m, 8H, C_9H_6N + *Ph*), 7.99 (b, 4H, C_9H_6N + *Ph*), 8.49 (d, J = 2.7 Hz,1H, C_9H_6N + *Ph*). ^{13}C-{^{1}H} NMR (C_6D_6): δ 25.82 (THF), 35.91 (d, J = 10.3 Hz, PCH), 51.50 (d, J = 8.1 Hz, CMe$_3$), 67.84 (THF), 112.94 (C_9H_6N), 114.8 (C_9H_6N), 120.28 (C_9H_6N), 127.19 (C_9H_6N), 127.86 (C_9H_6N), 127.92 (C_9H_6N), 128.17, 128.23, 129.33, 129.74, 130.11, 132.39 (d, J = 9.3 Hz), 132.91, 137.34 (C_9H_6N), 145.79 (C_9H_6N). ^{31}P{^{1}H} NMR (C_6D_6): δ 6.00. Anal. Calcd for $C_{26}H_{26}N_2PLi\cdot THF$: C, 75.62; H, 7.19; N, 5.88. Found: C, 75.29; H, 7.00; N, 6.17.

Complex **6** was prepared using similar procedure. Thus, treatment of the solution of **4** (1.38 g, 4.18 mmol) in THF (15 mL) with Bu^nLi (1.45 mL, 2.89 M solution in hexanes, 4.19 mmol) gave, after crystallizing from Et_2O, red crystalline solid **6** (1.11 g, 79%), mp 138−142 °C. ^{1}H NMR (C_6D_6): δ 0.88−1.30 (m, 12H, CHMe_2), 1.66 (s, 9H, CMe_3), 1.98−2.21 (b, 1H, CHMe$_2$), 2.49−2.77 (b, 1H, CHMe$_2$), 3.16 (d, J = 11.7 Hz, 1H, CH), 6.02 (d, J = 7.5 Hz, 1H, C_9H_6N), 6.29 (t, J = 7.5 Hz, 1H, C_9H_6N), 6.66 (d, J = 7.2 Hz, 1H, C_9H_6N), 6.73−6.77 (m,1H, C_9H_6N), 7.39 (d, J = 8.1 Hz, 1H, C_9H_6N), 8.53 (s, 1H, C_9H_6N). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.44 (CHMe_2), 20.48 (CHMe_2), 28.01 (d, J = 57.9 Hz, CHMe$_2$), 30.21 (CMe_3), 35.84 (d, J = 9.1 Hz, PCH), 51.17 (d, J = 7.2 Hz, CMe$_3$), 111.37 (C_9H_6N), 113.02 (d, J = 2.5 Hz, C_9H_6N), 120.22 (C_9H_6N), 127.24 (C_9H_6N), 127.85 (C_9H_6N), 128.17 (C_9H_6N), 137.34 (C_9H_6N), 145.14 (C_9H_6N), 146.59 (C_9H_6N). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.34. Anal. Calcd for $C_{20}H_{30}N_2PLi$: C, 71.41; H, 8.99; N, 8.33. Found: C, 71.31; H, 9.00; N, 8.15.

Preparation of $[Mg(Et)\{CH(8\text{-}C_9H_6N)(Pr^i_2P=NBu^t)\}]$ (7). $MgEt_2$ (0.14 g, 1.70 mmol) was dissolved in THF (5 mL), and the resulting solution was transferred into a stirred solution of **4** (0.28 g, 0.85 mmol) in THF (10 mL) at about −80 °C. Stirring of the mixture was continued overnight at room temperature, and then it was refluxed for 4 h. Solvents were removed under vacuum. The residue was dissolved in hexane and then filtered. Concentration of the filtrate afforded dark-red crystals of **7** (0.22 g, 67.8%), mp 98−100 °C. ^{1}H NMR (C_6D_6): δ 0.14 (dd, J = 7.2, 13.5 Hz, 3H, CHMe_2), 0.41 (q, J = 8.4 Hz, 2H, CH_2CH$_3$), 0.71 (dd, J = 6.9, 15.6 Hz, 3H, CHMe_2), 1.00 (dd, J = 7.2, 14.7 Hz, 3H, CHMe_2), 1.30 (dd, J = 6.9, 13.8 Hz, 3H, CHMe_2), 1.34 (s, 9H, CMe_3), 1.70−1.94 (m, 2H, CHMe$_2$), 2.07 (t, J = 8.1 Hz, 3H, CH$_2$CH_3), 2.33 (d, J = 2.4 Hz, 1H, CH), 6.61 (dd, J = 4.5, 8.4 Hz, 1H, C_9H_6N), 7.04−7.08 (m, 1H, C_9H_6N), 7.21−7.27 (m, 1H, C_9H_6N), 7.36−7.39 (m, 1H, C_9H_6N), 7.56 (dd, J = 1.5, 8.4 Hz, 1H, C_9H_6N), 8.38 (dd, J = 1.2, 4.2 Hz, 1H, C_9H_6N). ^{13}C{^{1}H} NMR (C_6D_6): δ −1.87 (CH_2CH_3), 14.59 (CH_2CH_3), 16.21 (d, J = 2.6 Hz, CHMe_2), 16.39

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(CH*Me*$_2$), 16.61 (d, J = 3.2 Hz, CH*Me*$_2$), 16.83 (d, J = 2.1 Hz, CH*Me*$_2$), 28.01 (d, J = 74.8 Hz, P*C*H), 28.37 (d, J = 51 Hz, *C*HMe$_2$), 28.45 (d, J = 41.4 Hz, *C*HMe$_2$), 35.46 (d, J = 7.4 Hz, C*Me*$_3$), 50.75 (d, J = 7.2 Hz, *C*Me$_3$), 119.69 (d, J = 4.3 Hz, *C*$_9$H$_6$N), 120.75 (*C*$_9$H$_6$N), 127.89 (d, J = 3.6 Hz, *C*$_9$H$_6$N), 129.86 (d, J = 2.9 Hz, *C*$_9$H$_6$N), 131.17 (d, J = 8.4 Hz, *C*$_9$H$_6$N), 138.36 (*C*$_9$H$_6$N), 146.51 (*C*$_9$H$_6$N), 148.41 (d, J = 1.3 Hz, *C*$_9$H$_6$N), 148.44 (d, J = 4.3 Hz, *C*$_9$H$_6$N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 34.61. Anal. Calcd for C$_{22}$H$_{35}$N$_2$PMg: C, 69.03; H, 9.22; N, 7.32. Found: C, 68.17; H, 9.28; N, 7.42.

Preparation of [Zn(Cl){CH(8-C$_9$H$_6$N)(Pr$^i_2$P=NBu^t)}] (8). A solution of **6** prepared from **4** (2.18 g, 6.60 mmol) and LiBu^n (2.3 mL, 2.89 M solution in hexanes, 6.65 mmol) in Et$_2$O (30 mL) was added into a stirred suspension of ZnCl$_2$ (0.99 g, 7.26 mmol) in Et$_2$O (10 mL) at about −80 °C. The mixture was stirred overnight at room temperature and then filtered. The residual solid was dried under vacuum and then extracted with toluene (2 × 30 mL). The extract was concentrated to afford yellow crystals of **8** (1.41 g, 49.7%), mp 156−160 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.24 (dd, J = 7.4, 13.7 Hz, 3H, CH*Me*$_2$), 0.78 (dd, J = 7.1, 15.6 Hz, 3H, CH*Me*$_2$), 1.16 (dd, J = 7.3, 15 Hz, 3H, CH*Me*$_2$), 1.50 (dd, J = 6.9, 14.2 Hz, 3H, CH*Me*$_2$), 1.54 (s, 9H, C*Me*$_3$), 1.84−2.04 (m, 2H, C*H*Me$_2$), 2.83 (s, 1H, C*H*), 6.81 (dd, J = 4.5, 8.3 Hz, 1H, C$_9$*H*$_6$N), 7.25−7.36 (m, 2H, C$_9$*H*$_6$N), 7.45−7.49 (m, 1H, C$_9$*H*$_6$N), 7.66 (dd, J = 1.6, 8.3 Hz, 1H, C$_9$*H*$_6$N), 8.77−8.79 (m, 1H, C$_9$*H*$_6$N). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 15.82 (d, J = 2.9 Hz, CH*Me*$_2$), 16.37 (d, J = 1 Hz, CH*Me*$_2$), 16.65 (d, J = 2.6 Hz, CH*Me*$_2$), 16.81 (d, J = 3.1 Hz, CH*Me*$_2$), 27.34 (d, J = 65.1 Hz, *C*HMe$_2$), 27.92 (d, J = 73.1 Hz, *C*HMe$_2$), 29.32 (d, J = 77.6 Hz, P*C*H), 34.96 (d, J = 7.2 Hz, C*Me*$_3$), 51.56 (d, J = 7.5 Hz, *C*Me$_3$), 121.35 (d, J = 1 Hz, *C*$_9$H$_6$N), 122.66 (d, J = 4.2 Hz, *C*$_9$H$_6$N), 127.52 (d, J = 3.9 Hz, *C*$_9$H$_6$N), 129.22 (d, J = 2.6 Hz, *C*$_9$H$_6$N), 132.73 (d, J = 7.5 Hz, *C*$_9$H$_6$N), 138.70 (*C*$_9$H$_6$N), 144.52 (d, J = 5.9 Hz, *C*$_9$H$_6$N), 147.22 (d, J = 3.9 Hz, *C*$_9$H$_6$N), 147.79 (*C*$_9$H$_6$N). ^{31}P {^{1}H} NMR (C$_6$D$_6$): δ 82.67. Anal. Calcd for C$_{20}$H$_{30}$N$_2$PZnCl: C, 55.83; H, 7.03; N, 6.51. Found: C, 55.66; H, 6.97; N, 6.38.

Preparation of [Zn(Ph){CH(8-C$_9$H$_6$N)(Pr$^i_2$P=NBu^t)}] (9). LiPh (2.45 mL, 0.48 M solution in Et$_2$O, 1.18 mmol) was added dropwise to a stirred solution of **8** (0.49 g, 1.14 mmol) in toluene (10 mL) at about −80 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The precipitate was filtered off, and the solvent was removed from the filtrate under vacuum. The residue was dissolved in Et$_2$O, and the solution was concentrated to form orange crystals of **9** (0.35 g, 65.1%), mp 136−140 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.19 (dd, J = 7.2, 13.2 Hz, 3H, CH*Me*$_2$), 0.78 (dd, J = 6.9, 15.3 Hz, 3H, CH*Me*$_2$), 1.09 (dd, J = 6.9, 14.4 Hz, 3H, CH*Me*$_2$), 1.48 (dd, J = 6.9, 13.8 Hz, 3H, CH*Me*$_2$), 1.41 (s, 9H, C*Me*$_3$), 1.78−1.98 (m, 2H, C*H*Me$_2$), 2.74 (s, 1H, C*H*), 6.72 (dd, J = 4.2, 7.8 Hz, 1H, C$_9$*H*$_6$N), 7.14−7.29 (m, 2H, C$_9$*H*$_6$N), 7.41−7.48 (m, 2H, C$_9$*H*$_6$N), 7.55−7.63 (m, 3H, *Ph*), 8.18 (d, J = 7.2 Hz, 2H, *Ph*), 8.58 (d, J = 3.9 Hz, 1H, C$_9$*H*$_6$N). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.01 (d, J = 2.5 Hz, CH*Me*$_2$), 16.46 (CH*Me*$_2$), 16.81 (d, J = 2 Hz, CH*Me*$_2$), 16.96 (d, J = 3 Hz, CH*Me*$_2$), 28.26 (d, J = 33.1 Hz, *C*HMe$_2$), 28.33 (d, J = 54.2 Hz, *C*HMe$_2$), 28.70 (d, J = 80.6 Hz, P*C*H), 35.31 (d, J = 7.4 Hz, C*Me*$_3$), 51.05 (d, J = 6.9 Hz, *C*Me$_3$), 121.04 (*C*$_9$H$_6$N), 121.26 (d, J = 4.4 Hz, *C*$_9$H$_6$N), 125.80 (*C*$_9$H$_6$N), 127.38 (*Ph*), 127.59 (*Ph*), 127.64 (*Ph*), 127.91 (*Ph*), 128.59 (*C*$_9$H$_6$N), 131.66 (d, J = 8.1 Hz, *C*$_9$H$_6$N), 137.71 (*C*$_9$H$_6$N), 139.85 (*C*$_9$H$_6$N), 147.52 (*C*$_9$H$_6$N), 157.65 (*C*$_9$H$_6$N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 47.66. Anal. Calcd for C$_{26}$H$_{35}$N$_2$PZn: C, 66.17; H, 7.48; N, 5.94. Found: C, 65.99; H, 7.51; N, 5.71.

Preparation of [Zn(Me){CH(8-C$_9$H$_6$N)(Pr$^i_2$P=NBu^t)}] (10). MeLi (0.6 mL, 1.6 M solution in Et$_2$O, 0.96 mmol) was added dropwise to a stirred solution of **8** (0.41 g, 0.95 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room trmperature and stirred overnight. Solvents were removed under reduced pressure, and the residue was dissolved in Et$_2$O. After filtration, concentration of the filtrate afforded orange crystals of **10** (0.30 g, 76.8%), mp 82−86 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.12 (s, 3H, *Me*), 0.14 (dd, J = 7.5, 13.5 Hz, 3H, CH*Me*$_2$), 0.70 (dd, J = 6.9, 15 Hz, 3H, CH*Me*$_2$), 1.02 (dd, J = 7.2, 14.4 Hz, 3H, CH*Me*$_2$), 1.34 (s, 9H, C*Me*$_3$), 1.36 (dd, J = 6.9, 13.8 Hz, 3H, CH*Me*$_2$), 1.71−1.87 (m, 2H, C*H*Me$_2$), 2.60 (s, 1H, C*H*), 6.64 (dd, J = 4.5, 8.4 Hz, 1H, C$_9$*H*$_6$N), 7.03−7.07 (m, 1H, C$_9$*H*$_6$N), 7.15−7.21 (m, 1H, C$_9$*H*$_6$N), 7.31−7.34 (m, 1H, C$_9$*H*$_6$N), 7.48 (dd, J = 1.6, 8.2 Hz, 1H, C$_9$*H*$_6$N), 8.39−8.41 (m, 1H, C$_9$*H*$_6$N). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ −13.20 (*Me*), 16.08 (d, J = 2 Hz, CH*Me*$_2$), 16.50 (CH*Me*$_2$), 16.90 (CH*Me*$_2$), 16.92 (d, J = 3.3 Hz, CH*Me*$_2$), 28.22 (d, J = 48.8 Hz, *C*HMe$_2$), 28.38 (d, J = 38 Hz, *C*HMe$_2$), 29.14 (d, J = 81.8 Hz, P*C*H), 35.17 (d, J = 7.5 Hz, C*Me*$_3$), 50.99 (d, J = 7.1 Hz, *C*Me$_3$), 120.89 (d, J = 4.5 Hz, *C*$_9$H$_6$N), 120.02 (*C*$_9$H$_6$N), 127.53 (d, J = 3.8 Hz, *C*$_9$H$_6$N), 129.53 (d, J = 2.6 Hz, *C*$_9$H$_6$N), 131.20 (d, J = 8.2 Hz, *C*$_9$H$_6$N), 137.38 (*C*$_9$H$_6$N), 146.87 (*C*$_9$H$_6$N), 147.83 (d, J = 5.6 Hz, *C*$_9$H$_6$N), 148.27 (d, J = 3.5 Hz, *C*$_9$H$_6$N). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 44.12. Anal. Calcd for C$_{21}$H$_{33}$N$_2$PZn: C, 61.54; H, 8.12; N, 6.83. Found: C, 60.83; H, 8.05; N, 6.72.

Preparation of [Zn(Et){CH(8-C$_9$H$_6$N)(R$_2$P=NBu^t)}] (R = Ph, 11; R = Pr^i, 12). ZnEt$_2$ (4.9 mL, 0.882 M solution in hexane, 4.32 mmol) was added dropwise to a stirred solution of **3** (0.85 g, 2.13 mmol) in toluene (30 mL) at about −80 °C. The mixture was stirred overnight at room temperature and then refluxed for 7 h. Solvents were removed under vacuum. The residue was dissolved in hexane and filtered. Concentration of the filtrate afforded yellow crystals of **11** (0.94 g, 89.6%), mp 128−134 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.21 (dq, J = 1.8, 8.1 Hz, C*H*$_2$CH$_3$), 1.38 (s, 9H, C*Me*$_3$), 2.07 (t, J = 8.1 Hz, 3H, CH$_2$C*H*$_3$), 3.27 (d, J = 2.4 Hz, 1H, C*H*), 6.74−6.88 (m, 4H, C$_9$*H*$_6$N + *Ph*), 7.01−7.14 (m, 5H, C$_9$*H*$_6$N + *Ph*), 7.26−7.28 (m, 3H, C$_9$*H*$_6$N + *Ph*), 7.53 (dd, J = 1.2, 8.1 Hz, 1H, C$_9$*H*$_6$N + *Ph*), 8.07−8.14 (m, 2H, C$_9$*H*$_6$N + *Ph*), 8.61−8.64 (m, 1H, C$_9$*H*$_6$N + *Ph*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 1.16 (*C*H$_2$CH$_3$), 14.47 (CH$_2$*C*H$_3$), 34.53 (d, J = 9.3 Hz, C*Me*$_3$), 36.36 (d, J = 84.2 Hz, P*C*H), 51.66 (d, J = 7.7 Hz, *C*Me$_3$), 120.78 (*C*$_9$H$_6$N), 121.47 (d, J = 5.3 Hz, *C*$_9$H$_6$N), 127.15 (d, J = 10.5 Hz, *Ph*), 128.53 (*Ph*), 129.28 (d, J = 3.4 Hz, *C*$_9$H$_6$N), 129.46 (d, J = 2.9 Hz, *Ph*), 130.53 (d, J = 2.6 Hz, *Ph*), 131.73 (d, J = 8.7 Hz, *C*$_9$H$_6$N), 131.88 (d, J = 9.2 Hz, *Ph*), 132.24 (d, J = 8.6 Hz, *Ph*), 134.58 (d, J = 68.4 Hz, *Ph*), 137.11 (*C*$_9$H$_6$N), 137.61 (*C*$_9$H$_6$N), 138.09 (*Ph*), 145.81 (d, J = 5.5 Hz, *C*$_9$H$_6$N), 147.23 (*C*$_9$H$_6$N), 148.05 (d, J = 4.3 Hz, *C*$_9$H$_6$N). ^{31}P-{^{1}H} NMR (C$_6$D$_6$): δ 20.04. Anal. Calcd for C$_{28}$H$_{31}$N$_2$PZn: C, 68.36; H, 6.35; N, 5.69. Found: C, 68.03; H, 6.35; N, 5.61.

Complex **12** was prepared using a similar procedure. Thus, ZnEt$_2$ (4.23 mL, 0.882 M solution in hexane, 3.73 mmol) was reacted with a solution of **4** (0.62 g, 1.88 mmol) in toluene (30 mL), affording, after similar workup, yellow crystals of **12** (0.58 g, 72.9%), mp 118−121 °C. ^{1}H NMR (C$_6$D$_6$): δ 0.23 (dd, J = 7.2, 13.2 Hz, 3H, CH*Me*$_2$), 0.80 (dd, J = 6.9, 15 Hz, 3H, CH*Me*$_2$), 1.05−1.16 (m, 5H, CH*Me*$_2$ + C*H*$_2$CH$_3$), 1.44 (d, J = 0.6 Hz, 9H, C*Me*$_3$), 1.46 (dd, J = 6.9, 13.8 Hz, 3H, CH*Me*$_2$), 1.84−1.95 (m, 2H, C*H*Me$_2$), 2.03 (t, J = 8.1 Hz, 3H, CH$_2$C*H*$_3$), 2.71 (s, 1H, C*H*), 6.75 (dd, J = 4.5, 8.4 Hz, 1H, C$_9$*H*$_6$N), 7.12−7.16 (m, 1H, C$_9$*H*$_6$N), 7.25−7.30 (m, 1H, C$_9$*H*$_6$N), 7.41−7.45 (m, 1H, C$_9$*H*$_6$N), 7.58 (dd, J = 1.5 Hz, J = 8.1 Hz, 1H, C$_9$*H*$_6$N), 8.54−8.56 (m, 1H, C$_9$*H*$_6$N). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 0.66 (*C*H$_2$CH$_3$), 1.44 (CH$_2$*C*H$_3$), 14.62 (CH*Me*$_2$), 16.06 (d, J = 2.3 Hz, CH*Me*$_2$), 16.47 (CH*Me*$_2$), 16.83 (CH*Me*$_2$), 28.24 (d, J = 49.1 Hz, *C*HMe$_2$), 28.41 (d, J = 38 Hz, *C*HMe$_2$), 29.16 (d, J = 82.3 Hz, P*C*H), 35.27 (d, J = 7.5 Hz, C*Me*$_3$), 50.82 (d, J = 6.9 Hz, *C*Me$_3$), 120.75 (d, J = 4.4 Hz, *C*$_9$H$_6$N), 120.89 (*C*$_9$H$_6$N), 127.53 (d, J = 3.8 Hz, *C*$_9$H$_6$N), 129.66 (d, J = 2.9 Hz, *C*$_9$H$_6$N) 131.10 (d, J = 8.3 Hz, *C*$_9$H$_6$N), 137.36 (*C*$_9$H$_6$N), 147.00 (*C*$_9$H$_6$N), 147.93 (d, J = 5.5 Hz), 148.38 (d, J = 3.4 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 38.63. Anal. Calcd for C$_{22}$H$_{35}$N$_2$PZn: C, 62.34; H, 8.32; N, 6.61. Found: C, 61.61; H, 8.31; N, 6.48.

Reaction of Complexes 7 and 12 with BnOH. To a solution of complex **7** (0.0693 g, 0.181 mmol) in toluene (2 mL) was added

Table 7. Details of the X-ray Structure Determinations of Complexes 6−8 and 10

	6	7	8	10
empirical formula	$C_{20}H_{30}LiN_2P$	$C_{22}H_{35}MgN_2P$	$C_{40}H_{60}Cl_2N_4P_2Zn_2$	$C_{21}H_{33}N_2PZn$
fw	336.37	382.80	860.50	409.83
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
a (Å)	33.885(6)	7.951(9)	21.705(5)	9.5809(8)
b (Å)	12.122(2)	9.184(11)	9.564(2)	14.2373(12)
c (Å)	31.117(6)	16.791(19)	21.744(6)	16.3071(14)
α (deg)	90	95.46(2)	90	90
β (deg)	110.123(2)	91.680(19)	99.302(4)	90
γ (deg)	90	94.724(19)	90	90
V (Å^3)	12001(4)	1216(2)	4454.5(19)	2224.4(3)
Z	24	2	4	4
D_{calcd} (g cm^{-3})	1.117	1.046	1.283	1.224
F(000)	4368	416	1808	872
(mm^{-1})	0.140	0.146	1.300	1.182
θ range for data collecn (deg)	1.80−25.00	2.24−25.01	1.23−26.76	1.90−27.89
no. of reflns collected	32157	6220	24826	15005
no. of indep reflns (R_{int})	10566 (0.1102)	4237 (0.0291)	9361 (0.0493)	5270 (0.0198)
no. of data/restraints/params	10566/11/690	4237/27/263	9361/0/465	5270/0/234
goodness of fit on F^2	0.988	1.024	1.054	1.010
final *R* indices[a] [$I > 2\sigma(I)$]				
*R*1	0.0695	0.0522	0.0490	0.0279
*R*w2	0.1544	0.1221	0.1220	0.0670
R indices (all data)				
*R*1	0.1894	0.0974	0.0968	0.0362
*R*w2	0.2052	0.1466	0.1502	0.0700
largest diff peak and hole (e·Å^{-3})	0.543 and −0.388	0.240 and −0.204	0.354 and −0.486	0.331 and −0.173

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|Fo|$; $Rw2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

dropwise a solution of BnOH (0.0193 g, 0.179 mmol) in toluene (0.3 mL) at 0 °C with stirring. Stirring of the mixture was continued for 10 min at 0 °C. Solvent was removed under vacuum. The residue was used to determine the NMR spectrum without further purification. ^{1}H NMR (C_6D_6): *δ* 0.36−0.45 (m, 2H, CH_2, CH_2CH_3), 0.91 (dd, *J* = 7.2, 14.6 Hz, 6H, $CHMe_2$), 1.05 (dd, *J* = 7.1, 14.4 Hz, 6H, $CHMe_2$), 1.12 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 1.55 (s, 9H, CMe_3), 1.83−1.96 (m, 2H, $CHMe_2$), 3.97 (d, *J* = 12.4 Hz, 2H, PCH_2), 4.29−5.34 (b, 2H, OCH_2), 6.79 (dd, *J* = 4.1, 8.2 Hz, 1H, Ar), 6.96−7.14 (m, 5H, Ar), 7.32 (d, *J* = 4. 2 Hz, 3H, Ar), 7.56 (d, *J* = 8.4 Hz, 1H, Ar), 8.42−8.44 (m, 1H, Ar).

Reaction of complex **12** with BnOH was carried out in a NMR tube. Thus, to a solution of complex **12** (0.0553 g, 0.130 mmol) in C_6D_6 (0.7 mL) in a NMR tube was added BnOH (0.0139 g, 0.128 mmol) at 0 °C. The reactants were fully mixed by shaking for a few minutes. After 10 min, the NMR spectrum of the sample was determined and the result showed that the reaction was complete. ^{1}H NMR (C_6D_6): *δ* 0.27 (q, *J* = 8.1 Hz, 2H, CH_2CH_3), 0.91 (dd, *J* = 7.2, 14.5 Hz, 6H, $CHMe_2$), 1.05 (dd, *J* = 7.1, 14.3 Hz, 6H, $CHMe_2$), 1.28 (t, *J* = 8.1 Hz, 3H, CH_2CH_3), 1.54 (s, 9H, CMe_3), 1.81−1.98 (m, 2H, $CHMe_2$), 3.96 (d, *J* = 12.4 Hz, 2H, PCH_2), 4.76 (s, 2H, OCH_2), 6.81 (dd, *J* = 4.1, 8.2 Hz, 1H, Ar), 7.14−7.22 (m, 5H, Ar), 7.29−7.33 (m, 2H, Ar), 7.57 (d, *J* = 8.1 Hz, 1H, Ar), 8.42 (b, 1H, Ar), 8.74 (d, *J* = 2.4 Hz, 1H, Ar).

X-ray Crystallography. Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Bruker Smart CCD area detector (for **7** and **8**) or a Bruker APEX II CCD area detector (for **6** and **10**) with graphite-monochromated Mo Kα radiation (*λ* = 0.710 73 Å) at 293(2) K. The structures were solved by direct methods using SHELXS-97[36] and refined against F^2 by full-matrix least-squares using SHELXL-97.[37] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 7. The *R* indices (for all data) of complex **6** are relatively high. This is due to poor crystal quality resulting in weak diffraction data.

Polymerization of ϵ-Caprolactone Catalyzed by Complexes 7 and 9−12. A typical polymerization procedure was exemplified by the synthesis of PCL catalyzed by complex **9** in the presence of BnOH. Complex **9** (0.0496 g, 0.105 mmol) was added into a Schlenk tube and followed by injection of toluene (2 mL) via a syringe. After the complex dissolved, an equivalent of BnOH (0.0114 g, 0.105 mmol) was added at room temperature. The mixture was stirred for 2 h, and then ϵ-caprolactone (2.38 g, 20.85 mmol) diluted with toluene (10 mL) was added. The flask was put into an oil bath which was preset at 60 °C. The mixture was stirred at 60 °C for 2.6 h during which an increase in viscosity was observed. The polymerization was quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution. After stirring for 0.5 h at room temperature, the resulting viscous solution was poured into methanol with stirring. The white precipitate was washed with hexane three times and dried under vacuum, giving a white solid (1.95 g, 82%).

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant No. 20572106). The authors thank Professors H.-G. Wang and H.-B. Song for determining the crystal structures.

Supporting Information Available: X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **6**−**8** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0610400

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