# Synthesis, Characterization, and Catalysis in ϵ-Caprolactone Polymerization of Aluminum and Zinc Complexes Supported by *N*,*N*,*N*-Chelate Ligands

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A series of aluminum and zinc complexes supported by pyridine-based *N*,*N*,*N*-chelate ligands have been synthesized and characterized. Treatment of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-((trimethylsilyl)methyl)pyridine (**2**) with LiBu$^n$/tmeda and then PhCN afforded a lithium complex [Li{2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)═CH}$C_5H_3N$}] ([LiL]) (**3**). Reaction of **3** with $ZnCl_2$ formed corresponding zinc chloride complex [Zn(Cl)L] (**4**), which was transformed to methyl- or ethylzinc complex [Zn(R)L] (R = Me, **5a**; R = Et, **5b**) by treatment with methyl- or ethyllithium. The ethylzinc complex (**5b**) was also generated by reaction of **4** with $LiHBEt_3$. Reaction of **4** with $AlR_3$ (R = Me, Et) gave alkyl aluminum chloride complexes [Al(Cl)(R)L] (R = Me, **6a**; R = Et, **6b**). Structurally similar *N*,*N*,*N*-chelate zinc complex [Zn(Et){2-(3,5-$Me_2C_3HN_2$)-6-{N(Ph)P($Ph_2$)═CH}$C_5H_3N$}] (**9**) was obtained by reaction of 2-(3,5-$Me_2C_3HN_2$)-6-{PhN═P($Ph_2$)$CH_2$}$C_5H_3N$ (**8**) with $ZnEt_2$. The aluminum and zinc complexes bearing [{2-{N($SiMe_3$)═P($Ph_2$)}-6-{N($SiMe_3$)P($Ph_2$)═CH}$C_5H_3N$}]$^-$ ligand, **14** and **15**, were similarly prepared by reaction of 2-{$Me_3SiN$═P($Ph_2$)}-6-{$Me_3SiN$═P($Ph_2$)$CH_2$}$C_5H_3N$ with $AlEt_3$ and $ZnEt_2$, respectively. The new compounds were characterized by NMR spectroscopy and elemental analyses. The molecular structures of complexes **5a**, **9**, **14**, and **15** were determined by single-crystal X-ray diffraction techniques. The catalysis of complexes **5a**, **6a**, **14**, and **15** in the ring-opening polymerization of ϵ-caprolactone was evaluated.

## Introduction

Organoaluminum and zinc complexes have been widely explored due to their rich structural chemistry[1] and importance in organic synthesis[2] and in polymerization chemistry,[3] e.g., as well-defined catalysts for the ring-opening polymerization of cyclic esters.[4] A range of ligands have been used to stabilize the metal complexes and tune the properties of the complexes. Among them, nitrogen-based polydentate ligands have attracted considerable attention.[5] For example, β-diketiminate ligands were used to stabilize cationic aluminum complexes which are active catalysts for olefin polymerization.[6] The zinc complexes bearing β-diketiminate ligands exhibited excellent catalytic activity and highly steric selectivity in catalyzing the ROP of cyclic esters.[5a,7] Tridentate *N*,*N*,*N*-chelate aluminum and zinc

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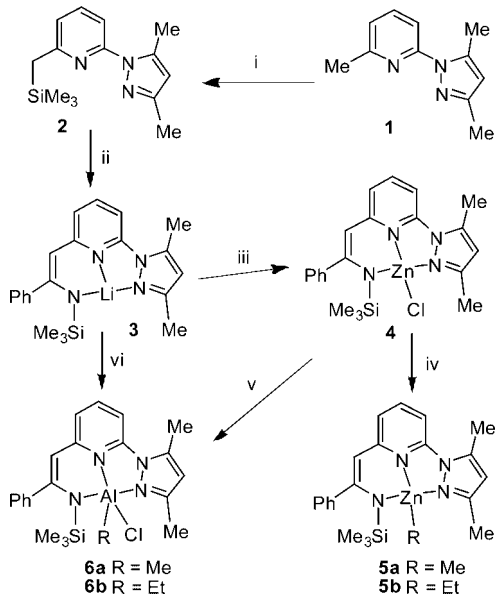
**Scheme 1. Synthesis of Compounds 2–6b**[a]

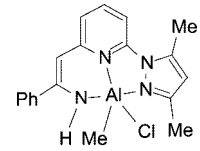



[a] Reagents and conditions: (i) LDA, THF, −40 °C, 0.5 h, then $Me_3SiCl$, −60 °C to rt, 15 h; (ii) $LiBu^n$/tmeda, $Et_2O$, −80 °C to rt, 6 h, then PhCN, −80 °C to rt, 15 h; (iii) $ZnCl_2$, $Et_2O$, −80 °C to rt, 15 h; (iv) LiR (R = Me, Et), toluene, −20 °C to rt, 15 h; or $LiHBEt_3$, THF, −80 °C to rt, 15 h; (v) $AlR_3$ (R = Me, Et), toluene, −80 °C to rt, 15 h; (vi) $MeAlCl_2$, toluene, −80 °C to rt, 15 h, then 90 °C, 6 h.

complexes were also reported[8] and some of the complexes showed catalysis toward ethylene polymerization or the controlled polymerization of polar monomers such as (meth)acrylates, propylene oxide, and lactones.[8a–d] The applications depend on a fundamental understanding of the chemistry of these compounds. Hence it is of interest to study the coordination modes, structural features, stability, and reactivity of the complexes. In this paper we report synthesis and characterization of aluminum and zinc complexes bearing pyridine-based *N*,*N*,*N*-chelate ligands.

## Results and Discussion

**Synthesis and Characterization of Compounds 1−15.** Syntheses of lithium, zinc, and aluminum complexes of the anionic ligand [2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)═CH}$C_5H_3N$]$^-$ ([L]$^-$) are summarized in Scheme 1. Treatment of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (**1**) with LDA and then $Me_3SiCl$ afforded 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-((trimethylsilyl)methyl)pyridine (**2**) in excellent yield. Reaction of **2** with $LiBu^n$/tmeda and then PhCN gave [LiL] (**3**). In the reaction of lithiated **2** with PhCN a 1,3-trimethylsilyl C → N migration was observed, as that occurred in a similar reaction reported previously.[9] Reaction of **3** with $ZnCl_2$ yielded a 1:1 adduct of zinc chloride complex **4** and LiCl, [Zn(Cl)L]·LiCl, which could be transformed to LiCl-free **4** by recrystallizing from toluene. [Zn(Cl)L] reacted readily with LiMe or LiEt to produce corresponding methyl- or ethylzinc complex [Zn(R)L] (R = Me, **5a**; R = Et, **5b**). Surprisely, treatment of [Zn(Cl)L] with 1 equiv of $LiHBEt_3$ gave **5b** as the sole isolated product, rather than a zinc hydride complex. An attempt to prepare [Zn(H)L] by reaction of [Zn(Cl)L] with $LiAlH_4$ was also unsuccessful. The reaction yielded a mixture. Reaction of [Zn(Cl)L] with a little excess $AlR_3$ (R = Me, Et) afforded [Al(Cl)(R)L] (R = Me, **6a**; R = Et, **6b**). In this reaction, the zinc atom in [Zn(Cl)L] was replaced by the aluminum atom, and one of the R groups on aluminum was replaced by a chloride atom. Complex **6a** was also obtained by reaction of **3** with 1 equiv of $MeAlCl_2$ (prepared in situ by reaction between $AlMe_3$ and $AlCl_3$ in a 1:2 ratio in toluene). Compound **2** is a colorless oil, whereas the complexes are yellow (**3**, **4** and **5a**), yellow orange (**5b** and **6b**), or orange (**6a**) crystals or powder. Complexes **3**, **6a**, and **6b** are soluble in toluene and $Et_2O$, slightly soluble in hexane. Complex **4** is soluble in toluene and very soluble in $CH_2Cl_2$ and THF. Each of **5a** and **5b** is soluble in hexane, and very soluble in toluene and $Et_2O$. Compounds **2**−**6b** were characterized by $^1H$ and $^{13}C$ NMR spectroscopy and elemental analyses. The analytical and spectral data of complex **3** proved no coordinate tmeda or solvent molecules in the complex. The $^1H$ NMR spectra of both **6a** and **6b** showed only one R group on the aluminum atom in each molecule, consistent with the results of elemental analyses. From the mother liquor of **6a**, trace **6a′** was obtained as yellow orange




**6a'**

crystals. Single-crystal X-ray diffraction analysis showed that the central aluminum atom is five coordinate in the complex (its structural data are not reported here due to relatively poor data quality). From the structure of **6a′** we deduce that the aluminum atoms in **6a** and **6b** adopt similar coordination modes. The molecular structure of **5a** was established by single-crystal X-ray diffraction data. The ORTEP diagram is presented in Figure 1, along with selected bond lengths and angles. Complex **5a** is monomeric in the solid state. The ligand exhibits a *N*,*N*,*N*-tridentate coordinate mode and the zinc atom has a distorted tetrahedral geometry. The C6−C7 distance of 1.373(6) Å indicates the existence of a C−C double bond. The C5−C6−C7−N2 atoms are approximately in a plane, but they are not coplanar with the pyridyl ring. The Zn1−N4 distance of 2.266(4) Å is longer than those of Zn1−N1 and Zn1−N2 [2.014(4) and 2.064(4) Å, respectively]. It is also longer than those observed in most four-coordinate zinc complexes,[1f,8g,10,11] but still within the range for dative Zn−N bonds.[4k,12]

Synthesis of compounds **7–9** is showed in Scheme 2. Lithiated **1** was treated with $Ph_2PCl$ from about −80 °C to room

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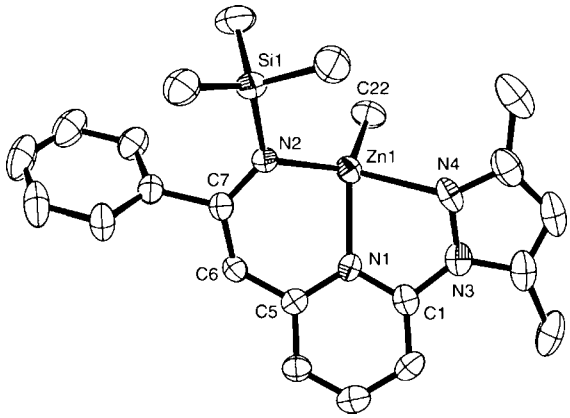
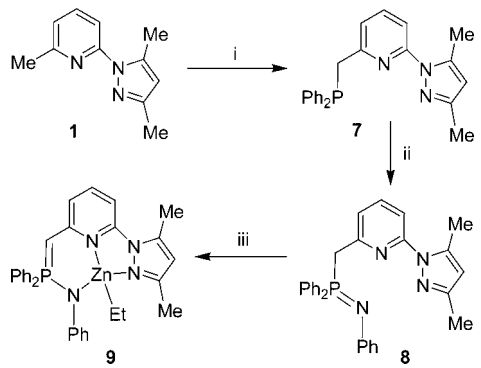



**Figure 1.** ORTEP diagram of complex **5a** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) 2.064(4), Zn(1)−N(2) 2.014(4), Zn(1)−N(4) 2.266(4), Zn(1)−C(22) 1.972(5), C(5)−C(6) 1.414(6), C(6)−C(7) 1.373(6), N(2)−C(7) 1.347(5), C(22)−Zn(1)−N(2) 120.3(2), C(22)−Zn(1)−N(1) 136.94(19), N(2)−Zn(1)−N(1) 91.35(14), C(22)−Zn(1)−N(4) 101.1(2), N(2)−Zn(1)−N(4) 130.04(15), N(1)−Zn(1)−N(4) 73.30(15), N(2)−C(7)−C(6) 126.4(4), C(7)−N(2)−Zn(1) 114.2(3), N(3)−N(4)−Zn(1) 107.3(3), C(1)−N(1)−Zn(1) 120.9(3), C(5)−N(1)−Zn(1) 121.5(3).

**Scheme 2. Synthesis of Compounds 7–9**[a]




[a] Reagents and conditions: (i) LDA, THF, −60 to −20 °C, 20 min, then $Ph_2PCl$, −80 °C to rt, 15 h; (ii) $PhN_3$, THF, rt, 3 h; (iii) $ZnEt_2$, toluene, −80 °C to rt, 15 h, then 100 °C, 5 h.

temperature to form **7**. Reaction of **7** with $PhN_3$ at room temperature yielded **8**. Treatment of **8** with $ZnEt_2$ afforded complex **9**. Both compounds **7** and **8** are white solid and soluble in toluene and THF. Complex **9** is red orange crystals. It is soluble in toluene and slightly soluble in hexane and $Et_2O$. The compounds have been characterized by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy and elemental analyses. The structure of complex **9** was established by single-crystal X-ray diffraction data. The ORTEP view is shown in Figure 2, along with selected bond lengths and bond angles. The complex crystallizes as a monomer in which the zinc atom exhibits a distorted tetrahedral geometry. The Zn1−N1 distance [2.059(2) Å] is comparable to the corresponding distance of complex **5a**, while the Zn1−N3 distance [2.184(2) Å] is significantly shorter than that of **5a** [2.266(4) Å]. This shows that the change of the coordinate groups from an imine in **5a** to an iminophosphorane in **9** affects the Zn−N(pyrazolyl) bonds much more than the Zn−N(pyridyl) bonds. The Zn1−N4 distance of 2.039(2) Å is shorter than those of the Zn−N(P═N) in four-coordinated zinc complex [ZnMe{CH{C(O)NAd}($Ph_2P$═N$SiMe_3$)$_2$}] [2.132(2) and 2.191(2) Å, respectively].[1f] The N1−Zn1−N3 angle of 74.26(9)° is close to the corresponding angle in complex **5a** [73.30(15)°], while the N1−Zn1−N4 angle of 97.12(8)° is wider than that in **5a**

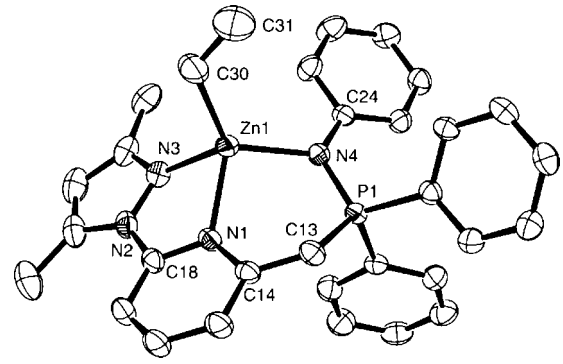
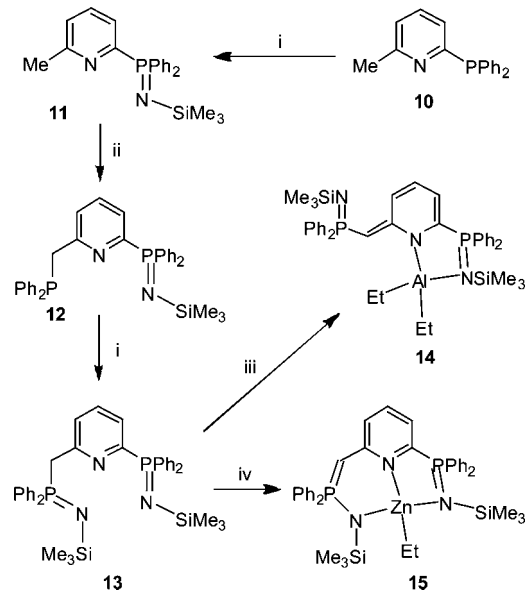



**Figure 2.** ORTEP diagram of complex **9** (30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) 2.059(2), Zn(1)−N(3) 2.184(2), Zn(1)−N(4) 2.039(2), Zn(1)−C(30) 1.986(4), P(1)−N(4) 1.623(2), P(1)−C(13) 1.729(3), N(1)−Zn(1)−N(3) 74.26(9), N(1)−Zn(1)−N(4) 97.12(8), N(4)−Zn(1)−N(3) 120.90(9), C(30)−Zn(1)−N(1) 129.43(15), C(30)−Zn(1)−N(3) 106.66(16), C(30)−Zn(1)−N(4) 121.11(12), P(1)−N(4)−Zn(1) 115.60(10), N(4)−P(1)−C(13) 112.41(12), C(14)−C(13)−P(1) 127.4(2).

**Scheme 3. Synthesis of compounds 11–15**[a]




[a] Reagents and conditions: (i) $Me_3SiN_3$, 140 to 160 °C, 12 h; (ii) LDA, THF, −60 to −20 °C, 20 min, then $Ph_2PCl$, −80 °C to rt, 15 h; (iii) $AlEt_3$, toluene, −80 °C to rt, 72 h; (iv) $ZnEt_2$, toluene, −80 °C to rt, 15 h, then 100 °C, 5 h.

[91.35(14)°]. The wider N1−Zn1−N4 angle in **9** may be caused by the larger atom radius of the phosphorus atom.

Synthesis of compounds **11**–**15** is presented in Scheme 3. A mixture of 2-(diphenylphosphino)-6-methylpyridine and $Me_3SiN_3$ was heated at 140–160 °C for 12 h to yield an iminophosphorane **11** in excellent yield. Treatment of **11** with LDA and then $Ph_2PCl$ afforded compound **12**, which was further transformed to **13** by reaction with $Me_3SiN_3$. Reaction of **13** with $AlEt_3$ gave complex **14**, and with $ZnEt_2$ produced complex **15**. Both **11** and **12** are colorless oils and were characterized by $^1H$, $^{13}C$, and $^{31}P$ NMR spectroscopy and elemental analyses. Complex **13** was purified by recrystallizing from a mixed solvent of $CH_2Cl_2$ and hexane, and gave satisfactory elemental analytical data, as well as $^1H$, $^{13}C$, and $^{31}P$ NMR spectra. Both **14** and **15** are red crystals. Complex **14** is soluble in hexane and very soluble in toluene and $Et_2O$. Complex **15** is slightly soluble in hexane and soluble in toluene and $Et_2O$. The $^1H$ NMR spectrum

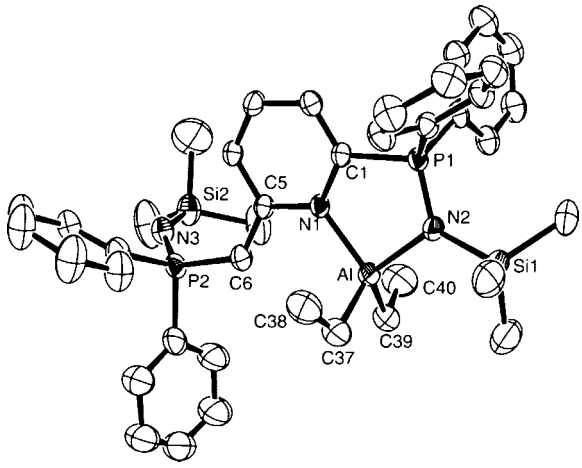



**Figure 3.** ORTEP diagram of complex **14** (30% probability thermal ellipsoids). C(38)′, C(39)′, and C(40)′, which represent alternative orientations of C(38), C(39), and C(40) in the disordered ethyl groups, have been omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Al−N(1) 1.933(5), Al−N(2) 1.943(5), Al−C(37) 1.947(9), N(1)−C(1) 1.355(7), N(1)−C(5) 1.396(6), C(5)−C(6) 1.385(8), P(1)−C(1) 1.797(6), P(1)−N(2) 1.595(5), P(2)−N(3) 1.530(5), P(2)−C(6) 1.758(6), N(1)−Al−C(39) 120.6(9), N(1)−Al−N(2) 91.4(2), C(39)−Al−N(2) 117.8(7), N(1)−Al−C(37) 110.7(3), C(39)−Al−C(37) 105.3(9), N(2)−Al−C(37) 110.8(3), N(2)−P(1)−C(1) 104.8(3), P(1)−N(2)−Al 112.8(2).

of **14** exhibited one set of triplets for the methyl groups of $AlEt_2$ and one set of multiplets for the $CH_2$. Its $^{13}C$ NMR spectrum also gave only one set of $AlEt_2$ signals. These results showed that the two ethyl groups on the aluminum atom have the same chemical environments. The $^1H$ NMR spectrum of **15** also revealed one set of methyl signals of $ZnCH_2CH_3$. However, the protons of the $CH_2$ were inequivalent, giving two sets of multiplets at 0.40−0.51 and 0.58−0.69 ppm, respectively. The structures of complexes **14** and **15** were further characterized by single-crystal X-ray diffraction techniques. The ORTEP diagram of **14** is displayed in Figure 3, along with selected bond lengths and angles. Crystalline **14** is monomeric and the aluminum atom is four-coordinate with a distorted tetrahedral geometry. In the molecule the N1 atom is still $sp^2$ hybrid and the pyridyl ring is approximately planar. C6 and P2 atoms are approximately coplanar with the pyridyl ring, which shows C6 to be a $sp^2$ hybrid atom. The C5−C6 distance of 1.385(8) Å is also indicative of a C−C double bond. The Al1−N1 distance of 1.933(5) Å is slightly shorter than that of Al1−N1 [1.943(5) Å], and both are within the normal range for a four-coordinate aluminum complex.[13] The bite angle of 91.4(2)° is wider than those of the five-membered cyclic imine aluminum complex due to the larger atom radius of the phosphorus atom in **14**.[5c,d,14]

The ORTEP drawing of complex **15** is displayed in Figure 4, along with selected bond lengths and angles. The complex is monomeric in the solid state. The difference in skeletal structures between **15** and **9** is that the pyrazolyl group in **9** is replaced by the $P(Ph_2)$═$NSiMe_3$ group in **15**. The Zn1−N1 and Zn1−N3 distances [2.103(2) and 2.057(2) Å, respectively] are longer than the corresponding distances in **9** [2.059(2) and 2.039(2) Å, respectively]. The Zn1−C37 distance of 2.044(3)

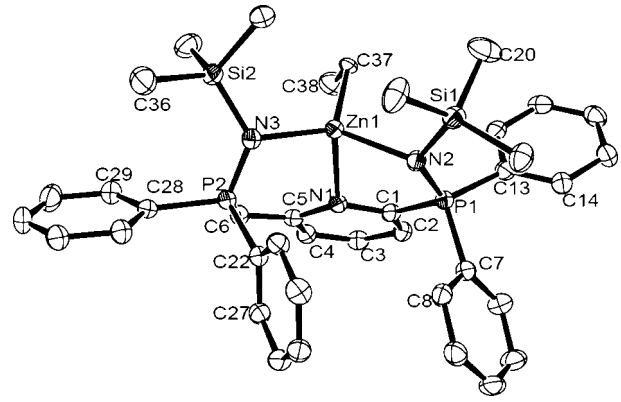



**Figure 4.** ORTEP diagram of complex **15** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Zn(1)−N(1) 2.103(2), Zn(1)−N(2) 2.167(2), Zn(1)−N(3) 2.057(2), Zn(1)−C(37) 2.044(3), P(1)−C(1) 1.813(3), P(1)−N(2) 1.583(3), P(2)−C(6) 1.741(3),P(2)−N(3)1.613(3),N(1)−Zn(1)−N(2)83.45(9),N(1)−Zn(1)−N(3) 98.70(9), N(2)−Zn(1)−N(3) 125.26(10), C(37)−Zn(1)−N(1) 107.99(10), C(37)−Zn(1)−N(2) 111.66(10), C(37)−Zn(1)−N(3) 119.10(11), P(1)−N(2)−Zn(1) 108.00(13), P(2)−N(3)−Zn(1) 107.76(13), N(2)−P(1)−C(1) 108.20(13), N(3)−P(2)−C(6) 117.85(14).

Å is also longer than that of complex **9** [1.986(4) Å]. The N1−Zn1−N3 angle of 98.70(9)° is comparable to the corresponding angle of complex **9** [97.12(8)°]. The distance of Zn1−N2 in complex **15** is shorter than that of Zn1−N3 in complex **9** or that of Zn1−N4 in complex **5a**, showing a stronger coordination of the nitrogen atom to zinc in **15**. The distances of both Zn1−N2 and Zn1−N3 are within the range found in the iminophosphorane−Zn complexes such as [Zn(Me){CH-$(Ph_2P$═$NR)_2$}] and [ZnCl{$CH(8\text{-}C_9H_6N)P(Pr^i_2)$═$NBu^t$}].[1f,15]

**Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by Complexes 5a, 6a, 14, and 15.** Metal alkoxides are often efficient initiators for the ring-opening polymerization of cyclic esters.[3a,16] We attempted to prepare aluminum and zinc alkoxides by reaction of the alkyl aluminum and alkyl zinc complexes mentioned in Schemes 1−3 with an alcohol. However, the reactions could not give expected alkoxides. In this case, catalysis of complexes **5a**, **6a**, **14**, and **15** in the ring-opening polymerization of ϵ-caprolactone was tested. Each of the polymerization reactions at room temperature was very slow, but accelerated on heating to 60 °C. Representative results are given in Table 1. The result of the polymerization catalyzed by **5** showed that both monomer conversion and the polymer molecular weight increase with time. After 480 min the solution became very viscous and the monomer conversion achieved 80.6% (entry 2 in Table 1). Complex **6a** behaves similarly to **5a** (entries 3 and 4 in Table 1). However, both the monomer conversion and the polymer molecular weight increase more rapidly with time compared with those catalyzed by **5**. The polymerization catalyzed by **14** gave higher molecular weights of polymer under the same conditions. The catalysis of complex **15** was tested at 60 and 90 °C, respectively. The reaction at 90 °C was much faster than that at 60 °C. The lactone became gummy in 70 min at 90 °C. However, the conversion of the monomer was only 38.4%. The relatively low conversion in

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**Table 1. Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by Complexes 5a, 6a, 14, and 15[a]**

| entry | initiator[b] | temp (°C) | time (min) | conv (%)[c] | yield (%) | $M_n$[d] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | **5a** | 60 | 350 | 27.5 | 18 | 37000 | 1.07 |
| 2 | **5a** | 60 | 480 | 80.6 | 74.6 | 115500 | 1.20 |
| 3 | **6a** | 60 | 350 | 17.1 | 10.2 | 11500 | 1.18 |
| 4 | **6a** | 60 | 420 | 79.1 | 73.6 | 107500 | 1.16 |
| 5 | **14** | 60 | 350 | 73.6 | 68.4 | 174000 | 1.07 |
| 6 | **15** | 60 | 350 | 51.6 | 43.5 | 37500 | 1.06 |
| 7 | **15** | 90 | 70 | 38.4 | 26.7 | 36000 | 1.08 |

[a] Polymerization reaction was carried out in 20 mL of toluene. [b] 0.1 mmol of initiator, initiator to ϵ-caprolactone ratio 1:200. [c] Obtained from the $^1$H NMR spectral analysis. [d] Obtained from GPC analysis and calibrated polystyrene standard.

each polymerization reaction can be attributed to the higher viscosity of the obtained polymer impeding the approach of new monomers to the active center. It was also noted that in each polymerization reaction the measured molecular weight of polymer was higher than the calculated value (based on the hypothesis of "living" polymerization). This may be caused by intermolecular chain transfer (via transesterification).

## Conclusions

We have synthesized and characterized lithium, aluminum, and zinc complexes supported by [2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)=CH}$C_5H_3N$]$^-$, [2-(3,5-$Me_2C_3HN_2$)-6-{N(Ph)P(Ph$_2$)=CH}$C_5H_3N$]$^-$, and [2-{N(SiMe$_3$)=P(Ph)$_2$}-6-{N(SiMe$_3$)P(Ph)$_2$=CH}$C_5H_3N$]$^-$ ligands. In the crystalline aluminum complexes, the [2-(3,5-$Me_2C_3HN_2$)-6-{N(H)-C(Ph)=CH}$C_5H_3N$]$^-$ ligand exhibits a tridentate coordination mode, whereas the [2-{N(SiMe$_3$)=P(Ph)$_2$}-6-{N(SiMe$_3$)P(Ph)$_2$=CH}$C_5H_3N$]$^-$ ligand reveals a bidentate coordination mode. In the crystalline zinc complexes, each ligand acts in a tridentate coordinate form and the central zinc atoms exhibit distorted tetrahedral coordination geometries. Reactions of [Zn(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)=CH}$C_5H_3N$}]-(**4**) with LiR afforded normal substituted products, [Zn(R){2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)=CH}$C_5H_3N$}] (R = Me, **5a**; R = Et, **5b**), whereas with LiHBEt$_3$ they gave ethyl-substituted product, **5b**, rather than a zinc hydride complex. In addition, the reaction of **4** with AlR$_3$ generated [Al(R)(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)=CH}$C_5H_3N$}] (R = Me, **6a**; R = Et, **6b**). Complexes **5a**, **6a**, **14**, and **15** are active in initiating the ring-opening polymerization of ϵ-caprolactone at elevated temperature, but the polymerizations may be accompanied by the intermolecular chain-transfer reactions.

## Experimental Section

**General Procedures.** All reactions were performed under nitrogen atmosphere with standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene) or sodium/benzophenone (THF, Et$_2$O, and hexane) and degassed prior to use. 2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine,[17] 2-(diphenylphosphino)-6-methylpyridine,[18] and phenyl azide[19] were prepared according to literature methods. AlMe$_3$, AlEt$_3$, ZnEt$_2$, LiHBEt$_3$, LiBu$^n$, Me$_3$SiN$_3$, and ϵ-caprolactone were purchased from Alfa Aesar or Acros Organics and used as received. $CDCl_3$ and $C_6D_6$, purchased from Cambridge Isotope Laboratories, Inc., were degassed and stored over 4A molecular sieves ($CDCl_3$) or Na/K alloy ($C_6D_6$). 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 TMS or 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 chromatograph (GPC) measurements were performed in the Department of Polymer Science and Engineering, University of Science and Technology of China, 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 the calibration standard. THF (HPLC grade) was used as eluent at a flow rate of 1 mL/min.

**Preparation of 2-(3,5-$Me_2C_3HN_2$)-6-($Me_3SiCH_2$)$C_5H_3N$ (2).** To a solution of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methylpyridine (0.48 g, 2.56 mmol) in THF (20 mL) was added dropwise a Et$_2$O solution of LDA (2.87 mmol, prepared from Pr$^i_2$NH and LiBu$^n$ in Et$_2$O) at −40 °C with stirring. After being stirred at −40 °C for 30 min, the solution was cooled to −60 °C and Me$_3$SiCl (0.5 mL, 3.94 mmol) was added dropwise. The solution was warmed to room temperature and stirring was continued overnight. Solvents and unreacted Me$_3$SiCl were removed in vacuo and the residue was extracted with Et$_2$O. The mixture was filtered and solvent was removed in vacuo from the filtrate. The residue was distilled under reduced pressure to afford colorless oil (0.60 g, 90%), bp 80−81 °C/0.2 mmHg. $^1$H NMR ($CDCl_3$): $\delta$ 0.03 (s, 9H, SiMe$_3$), 2.29 (s, 3H, Me), 2.32 (s, 2H, CH$_2$), 2.63 (s, 3H, Me), 5.96 (s, 1H, pyrazolyl), 6.78−6.81 (m, 1H, Py), 7.51−7.61(m, 2H, Py). $^{13}$C NMR ($CDCl_3$): $\delta$ −1.58, 13.58, 14.68, 30.09, 108.56, 110.83, 118.94, 137.95, 141.30, 149.25, 152.96, 159.66. Anal. Calcd for $C_{14}H_{21}N_3Si$: C, 64.82; H, 8.16; N, 16.20. Found: C, 64.32; H, 8.28; N, 15.93.

**Preparation of [Li{2-{N(SiMe$_3$)C(Ph)=CH}-6-(3,5-$Me_2C_3HN_2$)-$C_5H_3N$}] (3).** Compound **2** (0.35 g, 1.35 mmol) was dissolved in Et$_2$O (10 mL) and the solution was cooled to about −80 °C. To the solution was added successively tmeda (0.22 mL, 1.46 mmol) and LiBu$^n$ (0.65 mL, 2.25 M solution in hexanes, 1.45 mmol) with stirring. The resulting solution was warmed to room temperature and stirred for 6 h. The formed red solution was recooled to about −80 °C and PhCN (0.15 mL, 1.47 mmol) was added. The mixture was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated in vacuo to afford yellow crystals of **3** (0.32 g, 64%), mp 184−185 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.22 (s, 9H, SiMe$_3$), 1.89 (s, 3H, Me), 1.99 (s, 3H, Me), 5.50 (s, 1H, pyrazolyl), 5.58 (s, 1H, CH), 6.00 (d, $J$ = 7.5 Hz, 1H, Py), 6.63 (d, $J$ = 8.1 Hz, 1H, Py), 6.98 (t, $J$ = 8.1 Hz, 1H, Py), 7.19−7.33 (m, 3H, Ph), 7.65−7.70 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 3.63, 13.49, 14.42, 98.09, 98.40, 109.72, 119.10, 126.75, 136.27, 140.41, 148.76, 149.37, 150.39, 158.67, 171.60. Anal. Calcd for $C_{21}H_{25}LiN_4Si$: C, 68.45; H, 6.84; N, 15.20. Found: C, 68.23; H, 6.90; N, 15.27.

**Preparation of [Zn(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N(SiMe$_3$)C(Ph)=CH}$C_5H_3N$}] (4).** To a stirred suspension of $ZnCl_2$ (0.11 g, 0.81 mmol) in Et$_2$O (10 mL) was added dropwise a solution of **3** (0.24 g, 0.65 mmol) in Et$_2$O (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. The mixture was filtered and the residual solid was dissolved in hot toluene. The solution was filtered and the filtrate was concentrated to afford yellow powder **4**·LiCl identified by elemental analysis. **4**·LiCl was dissolved in toluene and then filtered. The filtrate was concentrated to give yellow crystals of **4** (0.17 g, 56%), mp 259−260 °C. $^1$H NMR ($CDCl_3$): $\delta$ 0.04 (s, 9H, SiMe$_3$), 2.52 (s, 3H, Me), 2.64 (s, 3H, Me), 5.13 (s, 1H, pyrazolyl), 6.21 (s, 1H, CH), 6.68 (d, $J$ = 8.4 Hz, 1H, Py), 6.75 (d, $J$ = 7.8 Hz, 1H, Py), 7.32−7.34 (m, 3H,

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Ph), 7.41−7.50 (m, 3H, Ph + Py). $^{13}$C NMR ($CDCl_3$): δ 3.77, 13.94, 15.13, 98.01, 100.43, 112.59, 119.85, 127.69, 128.05, 128.51, 138.48, 141.49, 144.97, 145.98, 151.46, 158.06, 170.33. Anal. Calcd for $C_{21}H_{25}ClN_4SiZn$: C, 54.55; H, 5.45; N, 12.12. Found: C, 54.39; H, 5.47; N 11.92.

**Preparation of [Zn(Me){2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)-C(Ph)=CH}$C_5H_3N$}] (5a).** To a stirred solution of **4** (0.20 g, 0.43 mmol) in toluene (10 mL) was added dropwise a solution of LiMe (0.28 mL, a 1.6 M solution in $Et_2O$, 0.45 mmol) at about −20 °C. The resulting solution was warmed to room temperature and stirred overnight. Solvents were removed in vacuo and the residue was dissolved in hexane. The solution was filtered and the filtrate was concentrated to give yellow crystals of **5a** (0.12 g, 63%), mp 159−161 °C. $^1$H NMR ($C_6D_6$): δ −0.25 (s, 3H, ZnMe), 0.31 (s, 9H, $SiMe_3$), 1.71 (s, 3H, Me), 2.29 (s, 3H, Me), 5.37 (s, 1H, pyrazolyl), 5.54 (s, 1H, CH), 5.90 (d, $J$ = 7.5 Hz, 1H, Py), 6.35 (d, $J$ = 8.4 Hz, 1H, Py), 6.78 (t, $J$ = 8.1 Hz, 1H, Py), 7.14−7.22 (m, 3H, Ph), 7.57−7.60 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): δ −11.64, 3.93, 13.56, 13.66, 98.68, 101.75, 111.09, 118.79, 127.92, 128.79, 137.29, 140.18, 147.45, 150.46, 159.06, 170.15. Anal. Calcd for $C_{22}H_{28}N_4SiZn$: C, 59.79; H, 6.39; N, 12.68. Found: C, 59.66; H, 6.32; N, 12.51.

**Preparation of [Zn(Et){2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)=CH}$C_5H_3N$}] (5b).** To a stirred solution of **4** (0.11 g, 0.24 mmol) in toluene (10 mL) was added dropwise a solution of LiEt (0.32 mmol, prepared from EtBr and Li in $Et_2O$) at about −20 °C. The resulting solution was warmed to room temperature and stirred overnight. Solvents were removed in vacuo and the residue was dissolved in hexane. The solution was filtered and the filtrate was concentrated to give yellow orange crystals of **5b** (0.07 g, 65%), mp 112−114 °C. $^1$H NMR ($C_6D_6$): δ 0.31 (s, 9H, $SiMe_3$), 0.62 (q, $J$ = 8.1 Hz, 2H, $CH_2$), 1.52 (t, $J$ = 8.1 Hz, 3H, $CH_3$), 1.75 (s, 3H, Me), 2.28 (s, 3H, Me), 5.37 (s, 1H, pyrazolyl), 5.56 (s, 1H, CH), 5.93 (d, $J$ = 7.5 Hz, 1H, Py), 6.34 (d, $J$ = 8.1 Hz, 1H, Py), 6.79 (t, $J$ = 8.1 Hz, 1H, Py), 7.14−7.22 (m, 3H, Ph), 7.60−7.63 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): δ 2.20, 3.87, 13.57, 13.69, 13.74, 98.85, 101.51, 111.09, 118.66, 127.92, 127.96, 128.84, 137.38, 140.08, 146.32, 147.49, 150.50, 158.98, 170.31. Anal. Calcd for $C_{23}H_{30}N_4SiZn$: C, 60.58; H, 6.63; N, 12.29. Found: C, 60.27; H, 6.57; N 12.32.

**Reaction of [Zn(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)=CH}$C_5H_3N$}] with $LiHBEt_3$.** To a stirred solution of **4** (0.17 g, 0.37 mol) in THF (10 mL) was added dropwise a solution of $LiHBEt_3$ (0.38 mL, a 1 M solution in THF, 0.38 mmol) at about −80 °C. The resulting solution was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue was dissolved in hexane. The solution was filtered and the filtrate was concentrated to give yellow orange crystals of **5b** (0.11 g, 66%), mp 110−112 °C. $^1$H NMR ($C_6D_6$): δ 0.31 (s, 9H, $SiMe_3$), 0.63 (q, $J$ = 8.1 Hz, 2H, $CH_2$), 1.53 (t, $J$ = 8.1 Hz, 3H, Me), 1.73 (s, 3H, Me), 2.28 (s, 3H, Me), 5.38 (s, 1H, pyrazolyl), 5.55 (s, 1H, CH), 5.92 (d, $J$ = 7.5 Hz, 1H, Py), 6.34 (d, $J$ = 8.1 Hz, 1H, Py), 6.79 (t, $J$ = 8.1 Hz, 1H, Py), 7.17−7.25 (m, 3H, Ph), 7.61−7.67 (m, 3H, Ph).

**Reaction of [Zn(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)=CH}$C_5H_3N$}] with $AlMe_3$.** To a stirred solution of **4** (0.20 g, 0.43 mol) in toluene (10 mL) was added dropwise a solution of $AlMe_3$ (0.22 mL, a 2.2 M solution in hexane, 0.48 mmol) at about −80 °C. The resulting solution was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated to give orange crystals of **6a** (0.12 g, 63%), mp 204−206 °C dec. $^1$H NMR ($C_6D_6$): δ −0.13 (s, 3H, AlMe), 0.43 (s, 9H, $SiMe_3$), 1.54 (s, 3H, Me), 2.89 (s, 3H, Me), 5.35 (s, 1H, pyrazolyl), 5.98 (d, $J$ = 7.8 Hz, 1H, Py), 6.04 (s, 1H, CH), 6.49 (d, $J$ = 8.1 Hz, 1H, Py), 6.84 (t, $J$ = 7.8 Hz, 1H, Py), 7.14−7.22 (m, 3H, Ph), 7.88−7.90 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): δ 1.44, 4.73, 14.05, 17.02, 101.31, 102.74, 114.60, 119.70, 128.87, 129.34, 130.14, 137.80, 140.55, 143.04, 145.33, 155.41, 156.16, 170.18. Anal. Calcd for $C_{22}H_{28}AlClN_4Si$: C, 60.19; H, 6.43; N, 12.76. Found: C, 60.07; H, 6.41; N, 13.08.

**Reaction of [Zn(Cl){2-(3,5-$Me_2C_3HN_2$)-6-{N($SiMe_3$)C(Ph)=CH}$C_5H_3N$}] with $AlEt_3$.** To a stirred solution of **4** (0.17 g, 0.37 mmol) in toluene (10 mL) was added dropwise a solution of $AlEt_3$ (0.22 mL, a 1.8 M solution in hexane, 0.40 mmol) at about −80 °C. The resulting solution was warmed to room temperature and stirred overnight. The solution was filtered and the filtrate was concentrated to give yellow orange crystals of **6b** (0.10 g, 60%), mp 128−130 °C. $^1$H NMR ($C_6D_6$): δ 0.44 (s, 9H, $SiMe_3$), 0.47 (q, $J$ = 8.1 Hz, 2H, $CH_2$), 1.29 (t, $J$ = 8.1 Hz, 3H, Me), 1.51 (s, 3H, Me), 2.93 (s, 3H, Me), 5.33 (s, 1H, pyrazolyl), 5.98 (d, $J$ = 8.1 Hz, 1H, Py), 6.06 (s, 1H, CH), 6.50 (d, $J$ = 8.1 Hz, 1H, Py), 6.82 (d, $J$ = 8.1 Hz, 1H, Py), 7.18−7.24 (m, 3H, Ph), 7.91−7.95 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): δ 4.73, 4.88, 11.31, 14.05, 17.22, 101.06, 102.74, 114.69, 119.63, 127.91, 128.23, 129.34, 129.44, 130.24, 137.68, 140.48, 143.12, 145.20, 155.75, 156.20, 170.32. Anal. Calcd for $C_{23}H_{30}AlClN_4Si$: C, 60.98; H, 6.67; N, 12.37. Found: C, 60.34; H, 6.80; N 11.90.

**Reaction of [Li{2-{N($SiMe_3$)C(Ph)=CH}-6-(3,5-$Me_2C_3HN_2$)-$C_5H_3N$}] (3) with $Al(Me)Cl_2$.** $AlMe_3$ (0.17 mL, a 2.2 M solution in hexane, 0.37 mmol) was added to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in toluene (10 mL) at room temperature with stirring. The mixture was stirred for 5 h and added to a stirred solution of **3** (0.37 g, 1 mmol) in toluene (15 mL) at about −80 °C. The resulting solution was stirred at room temperature for 15 h and heated at 90 °C (bath temperature) for 6 h. The solution was cooled to room temperature and filtered. The filtrate was concentrated to form orange crystals of **6a** (0.24 g, 55%). $^1$H NMR ($C_6D_6$): δ −0.13 (s, 3H, AlMe), 0.41 (s, 9H, $SiMe_3$), 1.47 (s, 3H, Me), 2.87 (s, 3H, Me), 5.29 (s, 1H, pyrazolyl), 5.91 (d, $J$ = 7.8 Hz, 1H, Py), 6.02 (s, 1H, CH), 6.45 (d, $J$ = 8.1 Hz, 1H, Py), 6.77 (t, $J$ = 7.8 Hz, 1H, Py), 7.12−7.22 (m, 3H, Ph), 7.86−7.89 (m, 2H, Ph).

**Preparation of 2-(3,5-$Me_2C_3HN_2$)-6-($Ph_2PCH_2$)$C_5H_3N$ (7).** To a stirred solution of 2-methyl-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine (0.43 g, 2.3 mmol) in THF (10 mL) was added dropwise a solution of LDA (2.5 mmol, prepared from $Pr^i_2NH$ and $LiBu^n$ in THF) at about −60 °C. The resulting solution was stirred at −20 °C for 20 min and then recooled to about −80 °C. To the solution $Ph_2PCl$ (0.47 mL, 2.5 mmol) dissolved in THF (5 mL) was added. The resulting solution was stirred at −80 °C for 15 min and then at room temperature overnight. Solvents were removed in vacuo and the residue was extracted with toluene. The extract was filtered and the solvent was removed from the filtrate. The residual oil was dissolved with $Et_2O$ and concentrated to afford colorless crystals of **7** (0.45 g, 53%), mp 119−120 °C. $^1$H NMR ($CDCl_3$): δ 2.15 (s, 3H, Me), 2.36 (s, 3H, Me), 3.47 (s, 2H, $CH_2$), 5.79 (s, 1H, pyrazolyl), 6.73 (d, $J$ = 7.5 Hz, 1H, Py), 7.15−7.17 (m, 6H, Ph), 7.27−7.31 (m, 4H, Ph), 7.40 (t, $J$ = 7.8 Hz, 1H, Py), 7.52 (d, $J$ = 8.1 Hz, 1H, Py). $^{13}$C NMR ($CDCl_3$): δ 13.51, 14.56, 38.41 (d, $J$ = 16.5 Hz), 108.66, 112.52, 120.13 (d, $J$ = 6 Hz), 128.24 (d, $J$ = 6.5 Hz), 128.55, 132.53, 132.78, 137.97, 138.13, 138.18, 141.57, 149.35, 152.93, 156.11 (d, $J$ = 8.2 Hz). $^{31}$P NMR ($CDCl_3$): δ −14.84. Anal. Calcd for $C_{23}H_{22}N_3P$: C, 74.38; H, 5.97; N, 11.31. Found: C, 75.07; H, 6.18; N, 11.12.

**Preparation of 2-(3,5-$Me_2C_3HN_2$)-6-{PhN=P(Ph)$_2CH_2$}$C_5H_3N$ (8).** To a stirred solution of **7** (0.30 g, 0.81 mmol) in THF (10 mL) was added dropwise $PhN_3$ (0.12 g, 1.00 mmol) at room temperature. The mixture was stirred for 3 h and then solvent was removed in vacuo. The residue was dissolved in toluene and filtered. The filtrate was concentrated to give colorless crystals of **8** (0.30 g, 80%), mp 209−211 °C. $^1$H NMR ($C_6D_6$): δ 2.39 (s, 6H, Me), 3.99 (d, $J$ = 13.5 Hz, 2H, $CH_2$), 5.93 (s, 1H, pyrazolyl), 6.98−7.18 (m, 9H, Ph + Py), 7.25−7.40 (m, 4H, Ph + Py), 7.80−7.87 (m, 4H, Ph), 8.03 (d, $J$ = 8.1 Hz, 1H, Py). $^{13}$C NMR ($C_6D_6$): δ 13.84, 14.83, 38.58 (d, $J$ = 60.1 Hz), 109.18, 113.33 (d, $J$ = 2.7 Hz), 117.80, 122.17

(d, $J$ = 3.8 Hz), 123.76, 124.01, 128.60, 128.75, 129.34, 130.94, 131.49 (d, $J$ = 2.8 Hz), 132.10, 132.22, 138.24 (d, $J$ = 2.5 Hz), 141.46, 149.47, 150.73, 150.82, 152.15 (d, $J$ = 2.2 Hz), 153.83. $^{31}$P NMR ($CDCl_3$): $\delta$ −3.74. Anal. Calcd for $C_{29}H_{27}N_4P$: C, 75.31; H, 5.88; N, 12.11. Found: C, 75.25; H, 5.87; N, 11.77.

**Preparation of [ZnEt{2-(3,5-Me$_2$C$_3$HN$_2$)-6-{N(Ph)P(Ph)$_2$=CH}C$_5$H$_3$N}] (9).** To a stirred solution of **8** (0.21 g, 0.45 mmol) in toluene (10 mL) was added dropwise $ZnEt_2$ (0.60 mL, a 0.882 M solution in hexane, 0.53 mmol) at about −80 °C. The mixture was stirred overnight at room temperature and then heated at 100 °C (bath temperature) for 5 h. After being cooled to room temperature, the mixture was filtered. Concentration of the filtrate afforded red orange crystals of **9** (0.16 g, 63%), mp 186−187 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.73 (q, $J$ = 8.1 Hz, 2H, $CH_2$), 1.49 (t, $J$ = 8 Hz, 3H, $CH_3$), 1.68 (s, 3H, Me), 2.20 (s, 3H, Me), 3.43 (d, $J$ = 20.6 Hz, 1H, CH), 5.43 (s, 1H, pyrazolyl), 5.57 (d, $J$ = 7.4 Hz, 1H, Py), 6.33 (d, $J$ = 8.5 Hz, 1H, Py), 6.61−6.74 (m, 2H, Ph + Py), 6.97−7.06 (m, 8H, Ph + Py), 7.31 (d, $J$ = 8.1 Hz, 2H, Ph), 7.88−7.95 (m, 4H, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 0.31, 13.53, 13.87, 14.17, 58.03 (d, $J$ = 143 Hz), 93.56, 110.36, 117.14 (d, $J$ = 15.9 Hz), 119.41, 124.00 (d, $J$ = 13.6 Hz), 128.26, 129.03, 130.74, 132.66 (d, $J$ = 9.5 Hz), 134.00, 135.22, 135.44, 140.32, 146.80, 149.11, 150.79, 165.18. $^{31}$P NMR ($C_6D_6$): $\delta$ 16.44 (m). Anal. Calcd for $C_{31}H_{31}N_4PZn$: C, 66.97; H, 5.62; N, 10.08. Found: C, 67.21; H, 5.67; N, 10.41.

**Preparation of 2-{Me$_3$SiN=P(Ph)$_2$}-6-MeC$_5$H$_3$N (11).** A mixture of 2-methyl-6-(diphenylphosphino)pyridine (1.0 g, 3.61 mmol) and $Me_3SiN_3$ (0.6 mL, 4.4 mmol) was heated at 140−160 °C for 12 h with stirring. The resulting mixture was dissolved with hexane and then filtered. Volatiles were removed in vacuo from the filtrate to afford **11** as colorless oil (1.19 g, 91%). $^1$H NMR ($CDCl_3$): $\delta$ 0.20 (s, 9H, $SiMe_3$), 2.72 (s, 3H, Me), 7.34 (d, $J$ = 7.5 Hz, 1H, Py), 7.54−7.66 (m, 6 H, Ph + Py), 7.83−7.90 (m, 1H, Ph), 7.98−8.04 (m, 4H, Ph), 8.31 (t, $J$ = 6.9 Hz, 1H, Py). $^{13}$C NMR ($CDCl_3$): $\delta$ 3.89 (d, $J$ = 3.2 Hz), 24.69, 124.13 (d, $J$ = 3.1 Hz), 125.36, 125.64, 127.88 (d, $J$ = 10.9 Hz), 130.74 (d, $J$ = 2.7 Hz), 132.45 (d, $J$ = 9.9 Hz), 134.65, 135.88, 135.96, 156.84, 158.33, 158.58, 158.63. $^{31}$P NMR ($CDCl_3$): $\delta$ −7.70. Anal. Calcd for $C_{21}H_{25}N_2PSi$: C, 69.20; H, 6.91; N, 7.69. Found: C, 69.47; H, 7.23; N 7.40.

**Preparation of 2-{Me$_3$SiN=P(Ph)$_2$}-6-(Ph$_2$PCH$_2$)C$_5$H$_3$N (12).** To a stirred solution of **11** (1.19 g, 3.26 mmol) in THF (20 mL) was added LDA (3.7 mmol, prepared from Pr$^i_2$NH and LiBu$^n$ in $Et_2O$) at −60 °C. The resulting solution was stirred at −20 °C for 20 min and recooled to about −80 °C. To the cooled solution was added dropwise a solution of $Ph_2PCl$ (0.71 mL, 3.8 mmol) in THF (5 mL). The mixture was stirred at −80 °C for 15 min and at room temperature overnight. Solvents were removed in vacuo and the residue was extracted with hot hexane. The extract was filtered and solvent was removed from the filtrate to give colorless oil (1.20 g, 67%). $^1$H NMR ($CDCl_3$): $\delta$ 0.05 (s, 9H, $SiMe_3$), 3.70 (s, 2H, $CH_2$), 7.21−7.52 (m, 16H, Ph + Py), 7.68−7.82 (m, 6H, Ph + Py), 8.21 (t, $J$ = 6.8 Hz, 1H, Py). $^{13}$C NMR ($CDCl_3$): $\delta$ 3.73 (d, $J$ = 3.5 Hz), 38.68 (d, $J$ = 17 Hz), 124.37 (d, $J$ = 2.9 Hz), 124.45 (d, $J$ = 2.8 Hz), 125.64, 125.88, 127.67, 127.83, 128.28 (d, $J$ = 6.8 Hz), 128.52, 130.56 (d, $J$ = 2.8 Hz), 132.29, 132.43, 132.57, 132.82, 134.27, 135.60, 135.76, 135.89, 138.27 (d, $J$ = 15.4 Hz), 156.91, 158.16, 158.42, 158.71. $^{31}$P NMR ($CDCl_3$): $\delta$ −15.03 (m), −7.60. Anal. Calcd for $C_{33}H_{34}N_2P_2Si$: C, 72.24; H, 6.25; N, 5.10. Found: C, 72.44; H, 6.32; N 4.72.

**Preparation of 2-{Me$_3$SiN=P(Ph)$_2$}-6-{Me$_3$SiN=P(Ph)$_2$CH$_2$}-C$_5$H$_3$N] (13).** A mixture of **12** (1.68 g, 3.1 mmol) and $Me_3SiN_3$ (0.6 mL, 4.4 mmol) was heated at 140−160 °C for 12 h with stirring. The resulting mixture was cooled to room temperature, dissolved with hexane, and filtered. The filtrate was concentrated to give colorless crystals of **13** (1.40 g, 72%), mp 91−93 °C. $^1$H NMR ($CDCl_3$): $\delta$ −0.21 (s, 9H, $SiMe_3$), −0.14 (s, 9H, $SiMe_3$), 3.74 (d, $J$ = 14.1 Hz, 2H, $CH_2$), 7.08−7.12 (m, 4H, Ph + Py), 7.24−7.26 (m, 5H, Ph), 7.33−7.37 (m, 3H, Ph + Py), 7.43−7.64 (m, 10H, Ph), 8.08 (t, $J$ = 6.6 Hz, 1H, Py). $^{13}$C NMR ($CDCl_3$): $\delta$ 3.82 (d, $J$ = 3.3 Hz), 3.97 (d, $J$ = 3.2 Hz), 42.70 (d, $J$ = 66.7 Hz), 126.32 (d, $J$ = 1.8 Hz), 126.44, 126.58 (d, $J$ = 1.7 Hz), 127.91 (d, $J$ = 12 Hz), 128.14 (d, $J$ = 11.9 Hz), 128.56 (d, $J$ = 12.7 Hz), 130.74 (d, $J$ = 2.5 Hz), 131.15 (d, $J$ = 10 Hz), 131.83, 131.90, 131.95, 132.47 (d, $J$ = 9.9 Hz), 134.23, 134.89, 135.55, 135.66 (d, $J$ = 1.2 Hz), 136.17, 154.28 (d, $J$ = 7.1 Hz), 154.55 (d, $J$ = 7.1 Hz), 156.76 (d, $J$ = 1.1 Hz), 158.55 (d, $J$ = 1.1 Hz). $^{31}$P NMR ($CDCl_3$): $\delta$ −6.93, −3.86 (m). Anal. Calcd for $C_{36}H_{43}N_3P_2Si_2$: C, 68.09; H, 6.81; N, 12.22. Found: C, 67.75; H, 6.74; N, 11.97.

**Preparation of [Al(Et$_2$){2-{N(SiMe$_3$)=P(Ph)$_2$}-6-{N(SiMe$_3$)-P(Ph)$_2$=CH}C$_5$H$_3$N}] (14).** To a stirred solution of **13** (0.20 g, 0.31 mmol) in toluene (10 mL) was added $AlEt_3$ (0.26 mL, a 1.8 M solution in hexane, 0.47 mmol) at about −80 °C. The resulting solution was warmed to room temperature and stirred for 3 days. The solution was filtered and the filtrate was concentrated to afford red crystals of complex **14** (0.13 g, 57%), mp 57−58 °C. $^1$H NMR ($C_6D_6$): $\delta$ −0.06 (s, 9H, $SiMe_3$), 0.57 (s, 9H, $SiMe_3$), 0.62−0.76 (m, 4H, $CH_2$), 1.52 (t, $J$ = 8.1 Hz, 6H, Me), 5.03 (s, 1H, CH), 5.05−5.08 (m, 1H, Py), 5.94−6.01 (m, 1H, Py), 6.81−6.90 (m, 4H, Ph + Py), 6.96−7.01 (m, 2H, Ph), 7.03−7.08 (m, 2H, Ph), 7.15−7.21 (m, 4H, Ph), 7.40−7.47 (m, 4H, Ph), 7.55−7.59 (m, 1H, Ph), 8.30−8.37 (m, 4H, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 2.16, 2.76 (d, $J$ = 3.2 Hz), 4.82 (d, $J$ = 3.5 Hz), 10.11, 78.25 (d, $J$ = 121.9 Hz), 108.69 (d, $J$ = 19.9 Hz), 124.34 (d, $J$ = 3.4 Hz), 124.43 (d, $J$ = 3.3 Hz), 126.44, 127.92, 28.25, 128.61, 128.95, 129.11, 129.44, 129.64 (d, $J$ = 2.8 Hz), 131.67 (d, $J$ = 9.8 Hz), 133.28 (d, $J$ = 11 Hz), 133.57 (d, $J$ = 2.9 Hz), 140.52, 141.91, 142.68 (d, $J$ = 3.3 Hz), 144.36 (d, $J$ = 3.3 Hz), 158.52, 158.66, 158.84. $^{31}$P NMR ($CDCl_3$): $\delta$ −7.82 (m), 26.97 (m). The sample for elemental analysis was recrystallized from $Et_2O$ and the crystallized sample was found to be **14**·$C_4H_{10}O$. Anal. Calcd for $C_{38}H_{47}N_3P_2Si_2Zn \cdot C_4H_{10}O$: C, 66.55; H, 7.87; N, 5.29. Found: C, 66.66; H, 7.54; N, 5.24.

**Preparation of [Zn(Et){2-{N(SiMe$_3$)=P(Ph)$_2$}-6-{N(SiMe$_3$)-P(Ph)$_2$=CH}C$_5$H$_3$N}] (15).** To a stirred solution of **13** (0.20 g, 0.33 mmol) in toluene (10 mL) was added $ZnEt_2$ (0.24 mL, a 1.88 M solution in hexane, 0.45 mmol) at about −80 °C. The resulting solution was stirred overnight at room temperature and then heated at 100 °C for 5 h. The mixture was cooled to room temperature, dissolved with $Et_2O$, and filtered. The filtrate was concentrated to afford red crystals identified as **15** (0.13 g, 53%), mp 158−160 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.10 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$), 0.40−0.51 (m, 1H, $ZnCH_2$), 0.58−0.69 (m, 1H, $ZnCH_2$), 1.49 (t, $J$ = 8.1 Hz, 3H, Me), 3.95 (d, $J$ = 24.4 Hz, 1H, CH), 5.31 (t, $J$ = 7.4 Hz, 1H, Py), 6.06−6.15 (m, 2H, Ph + Py), 6.71−6.92 (m, 14H, Ph + Py), 7.38−7.44 (m, 2H, Ph), 7.52−7.58 (m, 2H, Ph), 7.89−7.95 (m, 2H, Ph). $^{13}$C NMR ($C_6D_6$): $\delta$ 4.70 (d, $J$ = 3.7 Hz), 5.25 (d, $J$ = 3.6 Hz), 7.06, 14.23, 67.09 (d, $J$ = 137 Hz), 109.24, 109.56, 120.18 (d, $J$ = 3.4 Hz), 120.39 (d, $J$ = 3.3 Hz), 130.30, 130.89, 131.28, 132.21, 132.29, 132.43, 132.62, 132.73, 133.01, 133.15, 133.51 (d, $J$ = 10 Hz), 133.87 (d, $J$ = 9.2 Hz), 146.10, 147.86, 165.55, 165.77. $^{31}$P NMR ($C_6D_6$): $\delta$ 12.39, 16.04 (m). Anal. Calcd for $C_{38}H_{47}N_3P_2Si_2Zn$: C, 62.58; H, 6.50; N, 5.76. Found: C, 62.16; H, 6.56; N, 5.77.

**X-Ray Crystallography.** Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Bruker Smart CCD area-detector (for **5a** and **14**) or a Rigaku Saturn CCD area-detector (for **9** and **15**) with graphite-monochromated Mo K$\alpha$ radiation. The structures were solved by direct methods with use of SHELXS-97[20] or SIR92[21] and refined

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**Table 2. Details of the X-ray Structure Determinations of Complexes 5a, 9, 14, and 15**

| | 5a | 9 | 14 | 15 |
|---|---|---|---|---|
| empirical formula | $C_{22}H_{28}N_4SiZn$ | $C_{31}H_{31}N_4PZn$ | $C_{40}H_{52}AlN_3P_2Si_2$ | $C_{38}H_{47}N_3P_2Si_2Zn$ |
| fw | 441.94 | 555.94 | 719.95 | 729.28 |
| $T$ (K) | 298(2) | 293(2) | 298(2) | 113(2) |
| $\lambda$ (Å) | 0.71073 | 0.71070 | 0.71073 | 0.71070 |
| cryst system | triclinic | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $a$ (Å) | 8.0286(16) | 9.056(3) | 27.217(2) | 11.9240(10) |
| $b$ (Å) | 11.2735(18) | 11.133(4) | 9.5120(9) | 12.2017(12) |
| $c$ (Å) | 12.947(2) | 14.071(4) | 34.737(3) | 14.1673(14) |
| α (deg) | 79.004(2) | 78.193(10) | 90 | 87.485(7) |
| $\beta$ (deg) | 80.062(2) | 82.371(10) | 107.876(2) | 69.713(4) |
| $\gamma$ (deg) | 83.476(2) | 81.054(9) | 90 | 83.888(7) |
| $V$ (Å3) | 1129.1(3) | 1364.1(8) | 8558.7(14) | 1922.3(3) |
| $Z$ | 2 | 2 | 8 | 2 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.300 | 1.353 | 1.117 | 1.260 |
| $F$(000) | 464 | 580 | 3072 | 768 |
| $\mu$ (mm$^{-1}$) | 1.155 | 0.986 | 0.208 | 0.814 |
| $\theta$ range for data collection (deg) | 1.62 to 25.01 | 1.89 to 27.85 | 1.57 to 25.01 | 1.53 to 27.89 |
| no. of reflns collected | 5779 | 10405 | 20764 | 24238 |
| no. of indep reflns ($R_{int}$) | 3899 (0.0263) | 6350 (0.0249) | 7491 (0.0919) | 9111 (0.0381) |
| no. of data/ restraints/params | 3899/0/253 | 6350/0/335 | 7491/0/472 | 9111/0/424 |
| goodness of fit on $F^2$ | 1.037 | 1.031 | 1.000 | 1.113 |
| final $R$ indices[a] [$I > 2\sigma(I)$] | $R_1 = 0.0522$; $wR_2 = 0.0915$ | $R_1 = 0.0458$; $wR_2 = 0.1245$ | $R_1 = 0.0785$; $wR_2 = 0.1720$ | $R_1 = 0.0606$; $wR_2 = 0.1327$ |
| $R$ indices (all data) | $R_1 = 0.1016$; $wR_2 = 0.1103$ | $R_1 = 0.0649$; $wR_2 = 0.1386$ | $R_1 = 0.2147$; $wR_2 = 0.2116$ | $R_1 = 0.0671$; $wR_2 = 0.1374$ |
| largest diff peak and hole [e·Å$^{-3}$] | 0.469 and −0.626 | 0.447 and −0.508 | 0.366 and −0.333 | 0.620 and −0.580 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

against $F^2$ by full-matrix least-squares with use of SHELXL-97.[22] Hydrogen atoms were placed in calculated positions. In Figure 3 atoms C(38), C(39), and C(40) exhibit disorder which were modeled by half-carbon atoms C(38), C(39), C(40) and C(38)′, C(39)′, C(40)′. Crystal data and experimental details of the structure determinations are listed in Table 2.

**Polymerization of ϵ-Caprolactone Catalyzed by Complexes 5a, 6a, 14, and 15.** A typical polymerization procedure was exemplified by the synthesis of PCL catalyzed by complex **14**. Complex **14** (0.072 g, 0.1 mmol) was added into a Schlenk tube and followed by injection of toluene (5 mL) via a syringe. After the complex dissolved, ϵ-caprolactone (2.28 g, 20 mmol) diluted with toluene (15 mL) was added. The flask was put into an oil-bath that was preset at 60 °C. The mixture was stirred at 60 °C for 350 min 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 being stirred for 30 min at room temperature, the resulting viscous solution was poured into methanol (60 mL) with stirring. The white precipitate was filtered and washed with hexane three times and dried under vacuum, giving a white solid (1.56 g, 68.4%).

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**Supporting Information Available:** X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **5a**, **9**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Sheldrick, G. M. *SHELXL97, Programs for structure refinement*; Universität Göttingen, 1997.