Full Paper

Applied Organometallic Chemistry

Received: 26 April 2008 Revised: 13 July 2008 Accepted: 28 August 2008 Published online in Wiley Interscience: 10 October 2008

(www.interscience.com) DOI 10.1002/aoc.1461

N,O-chelate aluminum and zinc complexes: synthesis and catalysis in the ring-opening polymerization of ε-caprolactone

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Reaction between 2-(1*H*-pyrrol-1-yl)benzenamine and 2-hydroxybenzaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde afforded 2-(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (HOL^1NH, 1a) or 2,4-di-*tert*-butyl-6-(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (HOL^2NH, 1b). Both 1a and 1b can be converted to 2-(*H*-pyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (HOL^3N, 2a) and 2,4-di-*tert*-butyl-6-(*H*-pyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (HOL^4N, 2b), respectively, by heating 1a and 1b in toluene. Treatment of 1b with an equivalent of $AlEt_3$ afforded [$Al(Et_2)(OL^2NH)$] (3). Reaction of 1b with two equivalents of AlR_3 (R = Me, Et) gave dinuclear aluminum complexes [$(AlR_2)_2(OL^2N)$] (R = Me, 4a; R = Et, 4b). Refluxing the toluene solution of 4a and 4b, respectively, generated [$Al(R_2)(OL^4N)$] (R = Me, 5a; R = Et, 5b). Complexes 5a and 5b were also obtained either by refluxing a mixture of 1b and two equivalents of AlR_3 (R = Me, Et) in toluene or by treatment of 2b with an equivalent of AlR_3 (R = Me, Et). Reaction of 2a with an equivalent of $AlMe_3$ afforded [$Al(Me_2)(OL^3N)$] (5c). Treatment of 1b with an equivalent of $ZnEt_2$ at room temperature gave [$Zn(Et)(OL^2NH)$] (6), while reaction of 1b with 0.5 equivalent of $ZnEt_2$ at 40 °C afforded [$Zn(OL^2NH)_2$] (7). Reaction of 1b with two equivalents of $ZnEt_2$ from room temperature to 60 °C yielded [$Zn(Et)(OL^4N)$] (8). Compound 8 was also obtained either by reaction between 6 and an equivalent of $ZnEt_2$ from room temperature to 60 °C or by treatment of 2b with an equivalent of $ZnEt_2$ at room temperature. Reaction of 2b with 0.5 equivalent of $ZnEt_2$ at room temperature gave [$Zn(OL^4N)_2$] (9), which was also formed by heating the toluene solution of 6. All novel compounds were characterized by NMR spectroscopy and elemental analyses. The structures of complexes 3, 5c and 6 were additionally characterized by single-crystal X-ray diffraction techniques. The catalysis of complexes 3, 4a, 5a–c, 6 and 8 toward the ring-opening polymerization of ε-caprolactone was evaluated.

Keywords: N,O-ligands; aluminum; zinc; synthesis; ring-opening polymerization; catalysis

Introduction

Organoaluminum and -zinc compounds have attracted considerable attention due to their widespread use in organic synthesis[1] and in polymerization chemistry, e.g. organoaluminum compounds as catalysts or co-catalysts for olefin polymerization[2] and organoaluminum and -zinc compounds as initiators for the ring-opening polymerization (ROP) of cyclic esters.[3] The foundation of the applications is a fundamental understanding of the chemistry of these compounds. Hence it is essential to explore the structural features, stability and reactivities of the complexes. On the other hand, properties of complexes strongly rely on supporting ligands besides the metal itself. Therefore the choice of ligands is also crucial. N,O-chelate ligands are one of the most often used ligands in main group and transition metal coordination chemistry. Aluminum complexes with N,O-ligands show versatile coordination mode and unique applications.[4] For example, tris(8-quinolinolato)aluminum is one of the most widely used complexes for organic light emitting devices.[5] A series of N,O-chelate aluminum complexes such as ketiminate, salicylaldimine, SALAN and SALEN aluminum complexes exhibited excellent catalytic behavior in the ring-opening polymerization of cyclic esters.[6] N,O-bidentate ligands were also found to be able to stabilize cationic monoalkylaluminum species.[7] Some N,O-chelate zinc complexes were also reported, including structures, reactivity and uses as asymmetric catalysts.[1e,8] Here we report synthesis and characterization of aluminum and zinc complexes bearing novel N,O-chelate ligands as well as catalysis of the complexes in the ROP of ε-caprolactone.

Results and Discussion

Synthesis and characterization of compounds 1a-9

Synthesis of the N,O-chelate ligands and their aluminum complexes are summarized in Scheme 1. Reaction of 2-(1*H*-pyrrol-1-yl)benzenamine with 2-hydroxybenzaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in refluxing EtOH afforded 2-(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl)phenol derivatives, **1a** and **1b**, respectively. This is a Mannich type of reaction and has been reported before.[9] Both **1a** and **1b** could be transformed to 2-(*H*-pyrrolo[1,2-*a*]quinoxalin-4-yl)phenol derivatives, **2a** and **2b**, by refluxing in toluene in the presence of 4 Å molecular sieves. Treatment of **1b** with 1 equiv of $AlEt_3$ gave complex **3**, which was transformed to a dinuclear aluminum complex **4b** by reaction with another equivalent of $AlEt_3$. Attempts to prepare the methylaluminum analog of **3** by treatment of **1b** with 1 equiv of $AlMe_3$

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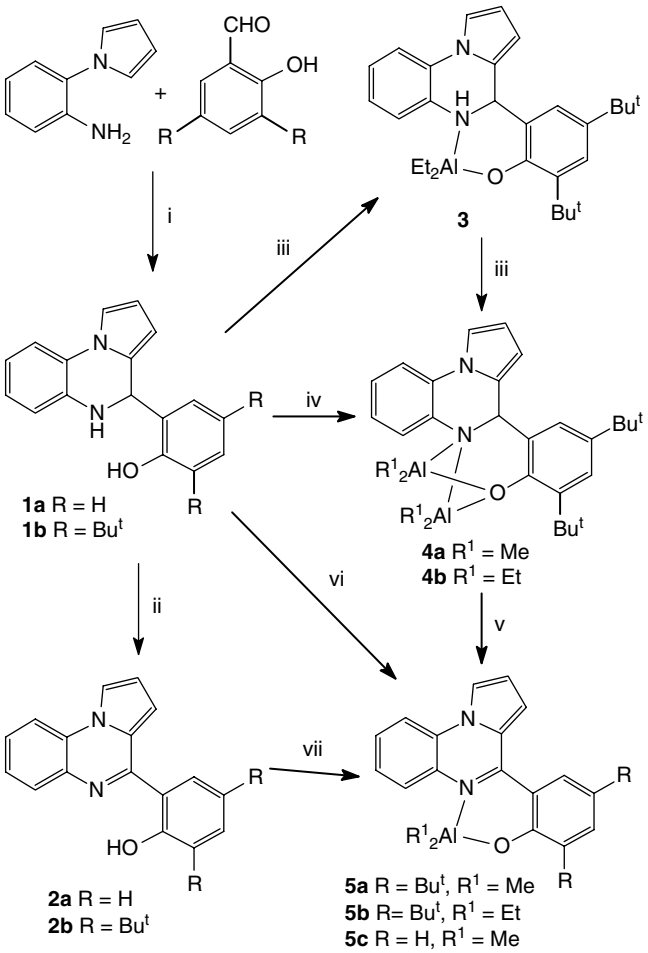


Scheme 1. Synthesis and reactions of compounds **1a**–**5c**. Reagents and conditions: (i) anhydrous ethanol, reflux, 3 h (for **1a**) or 8 h (for **1b**); (ii) toluene, molecular sieves, reflux, 48 h (for **2a**) or 72 h (for **2b**); (iii) 1 equiv of $AlEt_3$, −80 °C to room temperature (r.t.)., 12 h; (iv) 2 equiv of AlR_3 (R = Me, Et), −80 °C to r.t., 10 h; (v) toluene, reflux, 8 h (for **5a**) or 20 h (for **5b**); (vi) 2 equiv of AlR_3, toluene, −80 °C to r.t., 10 h, then reflux 8 h (for **5a**) or 20 h (for **5b**); (vii) 1 equiv of AlR_3 (R = Me, Et), −80 °C to r.t., 12 h.

were unsuccessful. The reaction gave a mixture indicated by the ^{1}H NMR spectrum. Reaction of **1b** with 2 equiv of AlR_3 (R = Me, Et) afforded dinuclear aluminum complexes **4a** and **4b**, respectively. A similar reaction between **1a** and 2 equival of AlR_3 (R = Me, Et) led to a mixture under either room temperature or heating conditions. Both **4a** and **4b** could be converted to **5a** and **5b**, respectively, by refluxing in toluene. Transformation of **4b** was slower than that of **4a**, the former requiring much longer reaction time. This reaction seems to undergo $AlHR^1_2$ elimination from the dinuclear aluminum complexes under heating. Complex **5a** was also obtained by treatment of **1b** with 2 equiv of $AlMe_3$ in reflux toluene. In addition, reaction of **2a** and **2b** with 1 equiv of $AlMe_3$ or $AlEt_3$ afforded complexes **5a**–**c**.

Both **1a** and **1b** are white solids that slowly oxidize when exposed to air. Compounds **2a** and **2b** are air-stable yellow crystals. The aluminum complexes are air-sensitive yellowish (**3**) or yellow (**4a**–**5c**) crystals or powder. **1a** is a known compound and was identified by ^{1}H NMR spectroscopy.[9] Each of compounds **1b**–**5c** was characterized by elemental analysis, as well as ^{1}H and ^{13}C NMR spectroscopy. Additionally, single crystal X-ray diffraction data established the molecular structures of complexes **3** and **5c**.

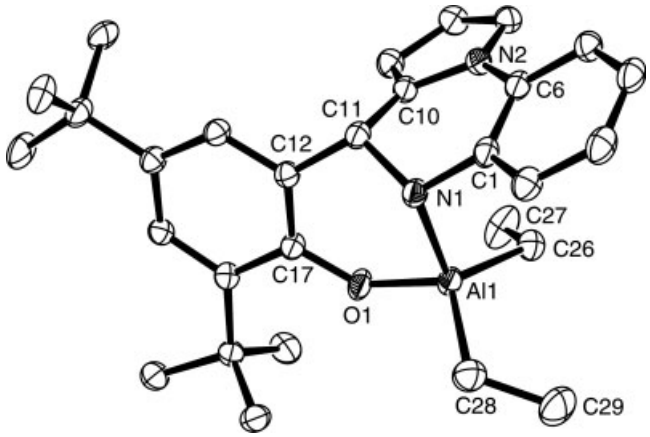


Figure 1. ORTEP drawing of complex **3** (50% probability). Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 2.0376(17), Al(1)–O(1) 1.7445(14), Al(1)–C(26) 1.965(2), Al(1)–C(28) 1.974(2), N(1)–C(1) 1.462(2), N(1)–C(11) 1.516(2), C(11)–C(12) 1.518(2), O(1)–C(17) 1.334(2), O(1)–Al(1)–N(1) 93.55(7), C(11)–N(1)–Al(1) 113.17(11), C(17)–O(1)–Al(1) 134.89(12).

The ^{1}H NMR spectra of both **1a** and **1b** exhibited the proton signals of OH, NH, tertiary CH, and other corresponding groups. The ^{13}C NMR spectrum of **1b** displayed the tertiary carbon signal at 57.91 ppm. These spectral features are consistent with those of the reported analogs.[9] The ^{1}H NMR spectra of **2a** and **2b** showed OH signals at 13.48 and 13.50 ppm, respectively. The ^{13}C NMR spectra revealed the imine carbon signals at 160.23 (for **2a**) and 156.49 ppm (for **2b**), respectively. The ^{1}H NMR spectrum of **3** displayed two sets of $AlEt_2$ signals, which showed that the two ethyl groups were in the different chemical environments. The ^{1}H NMR spectrum also proved the existence of NH group, the NH signal appearing at 4.08 ppm. The ^{13}C NMR spectrum showed a tertiary carbon signal at 59.83 ppm. Crystalline **3** is monomeric and the aluminum atom is four-coordinate with a distorted tetrahedral geometry (Fig. 1). Both C(11) and N(1) atoms display tetrahedral geometries. The C(11)–N(1) distance of 1.516(2) Å is indicative of a single bond. The Al(1)–N(1) distance of 2.0376(17) Å is longer than those found in $[Al(Me_2)\{3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2CH{=}NR\}]$[7] and $[Al(Et_2)\{3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2CH{=}NBu^t\}]$[10] [1.972(3)-1.976(2) Å], but close to that of $[Al(Me_2)\{2\text{-}(CH_2NMe_2)\text{-}6\text{-}Bu^t\text{-}(O)C_6H_3\}]$ [2.036(1) Å].[6] The Al(1)–O(1) distance of 1.7445(14) Å is comparable to corresponding ones found in $[Al(Me_2)\{3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2CH{=}NR\}]$,[7] $[Al(Et_2)\{3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2CH{=}NBu^t\}]$[11] and $[Al(Me_2)OC(Ph)CH\text{-}\{(3,5\text{-}Me_2C_3HN_2)\text{-}1\}]$[12] [1.747(3)–1.755(3) Å]. The bite angle of the N,O-bonded aminophenolate [N(1)–Al(1)–O(1) = 93.55(7)°] is normal for a six-membered N,O-chelate aluminum ring.[12–14]

The ^{1}H and ^{13}C NMR spectra of each of **4a** and **4b** showed the existence of four sets of signals for the AlR_2 (R = Me, Et) groups, revealing that the R groups are in different chemical environments. The other signals were consistent with the respective structure. The ^{1}H and ^{13}C NMR spectra of **5a**–**5c** showed that the two R groups on the Al atom were equivalent in each complex. The crystal structure of **5c** is displayed in Fig. 2. Crystalline **5c** is monomeric. The aluminum atom exhibits a distorted tetrahedral geometry. The aluminum-containing six-membered ring Al(1)N(1)C(7)C(6)C(1)O(1) is not planar, showing a twist conformation. The Al(1)–N(1) distance of 1.980(3) Å is shorter than that of complex **3** [2.0376(17) Å], reflecting the difference in the coordination between amine and imine ligands. This is consistent with the data of amine and imine aluminum complexes

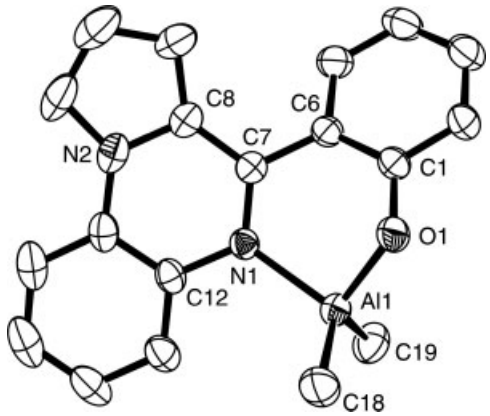
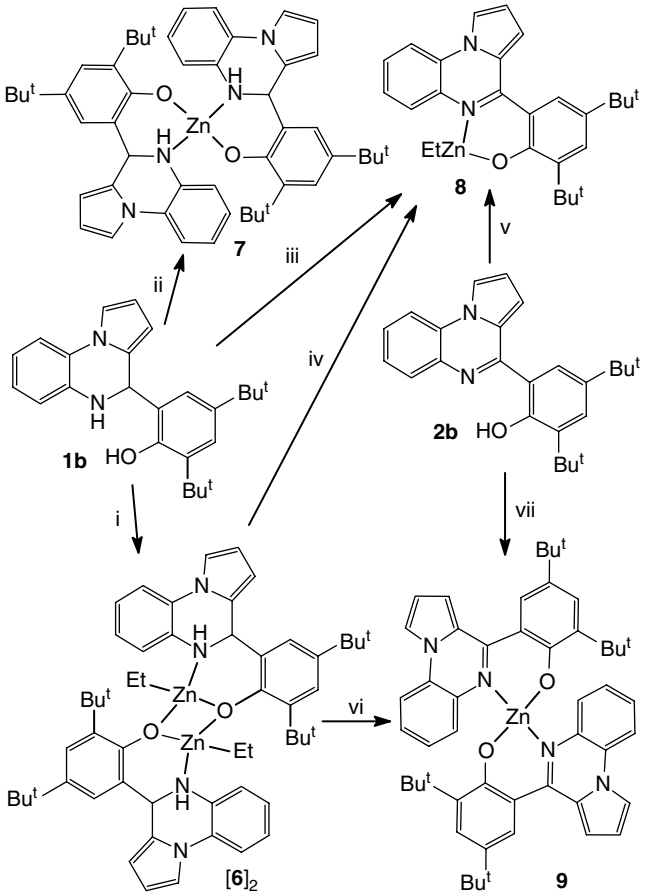


Figure 2. ORTEP drawing of complex **5a** (30% probability). Selected bond lengths (Å) and angles (deg): Al(1)–N(1) 1.980(3), Al(1)–O(1) 1.765(2), Al(1)–C(18) 1.943(4), Al(1)–C(19) 1.953(4), N(1)–C(7) 1.340(4), O(1)–C(1) 1.339(4), C(6)–C(7) 1.472(4), C(7)–C(8) 1.413(4), O(1)–Al(1)–N(1) 94.54(11), C(7)–N(1)–Al(1) 119.6(2), C(1)–O(1)–Al(1) 122.6(2), N(1)–C(7)–C(6) 120.8(3), N(1)–C(7)–C(8) 120.7(3).

reported in the literature.[7,10] The Al(1)–O(1) distance of 1.765(2) Å is typical of an alkoxide.[7] The O(1)–Al(1)–N(1) angle of 94.54(11)° is unexceptional compared with the complexes with similar structures.[7,10,12]

Reaction of **1b** and **2b** with $ZnEt_2$ is showed in Scheme 2. Treatment of **1b** with 1 equiv of $ZnEt_2$ in toluene at room temperature afforded complex **6**, while with 0.5 equiv of $ZnEt_2$ in toluene at 40 °C gave complex **7**. If the latter reaction was carried out at room temperature, a mixture of **7** and starting material **1b** was obtained. If 2 equiv of $ZnEt_2$ were employed, **1b** was converted to **8** at 60 °C. Complex **8** was also formed when treatment of **6** with 1 equiv of $ZnEt_2$ at 60 °C. It seems that reaction of **6** with 1 equiv of $ZnEt_2$ generates a dinuclear zinc complex, which further converted to **8** upon heating. However, attempts to isolate the zinc intermediate were unsuccessful. Heating **6** at 100 °C in toluene formed complex **9**. If **6** was heated at 60 °C for 48 h or the solution of **6** in C_6D_6 in a sealed NMR tube was kept at room temperature for a month, a mixture of **9** and another species, **10**, was formed (Scheme 3). In the ^{1}H NMR spectra of the mixture, the components except **9** showed the presence of the tertiary C–H signal and disappearance of the ZnEt signal compared with complex **6**. Further heating the mixture formed a single component of complex **9**. This proves that the conversion from **6** to **9** is via complex **10** (Scheme 3). Thus, complex **6** was converted to **10** through elimination of C_2H_6 upon heating. Complex **10** was further transformed to **9**, possibly through elimination of ZnH_2. An example of ZnH_2 elimination from a 1,4-dihydro-1-pyridylzinc molecule has been reported.[15] In addition, complexes **8** and **9** were also prepared by reaction of **2b** with $ZnEt_2$ in 1 to 1 and 2 to 1 molar ratios, respectively.

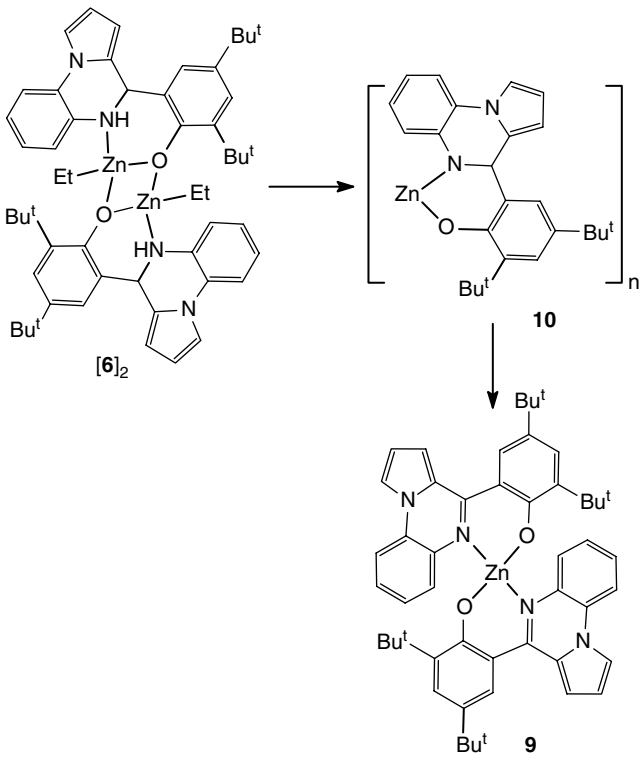
Complexes **6**–**9** are colorless (**6**), pale yellow (**7**) or yellow (**8** and **9**) solid. Complexes **6** and **8** are air-sensitive, while **7** and **9** are air stable in the solid state. Each of complexes **6**–**9** gave satisfactory elemental analytical results. In complex **6**, the ligand contains a chiral center. Hence dimeric **6** (single crystal X-ray diffraction result, see below) should exist as isomers. However, its ^{1}H NMR spectrum showed only one set of signals. The ^{13}C NMR spectral data gave consistent results. This may be attributed to the rapid conversion between dimer and monomer in solution.[8f] Single-crystal X-ray diffraction data revealed that complex **6** exists in a dimeric form in the solid state (Fig. 3). The two oxygen atoms bridge the two



Scheme 2. Synthesis of zinc complexes **6**–**9**. Reagents and conditions: (i) 1 equiv of $ZnEt_2$, toluene, −80 °C to r.t., 18 h; (ii) 0.5 equiv of $ZnEt_2$, toluene, 40 °C, 48 h; (iii) 2 equiv of $ZnEt_2$, toluene, −80 °C to r.t., 8 h, then 60 °C, 15 h; (iv) 1 equiv of $ZnEt_2$, toluene, −80 °C to r.t., 1 h, then 60 °C, 15 h; (v) 1 equiv of $ZnEt_2$, toluene, −80 °C to r.t., 15 h; (vi) toluene, 100 °C, 15h; (vii) 0.5 equiv of $ZnEt_2$, −80 °C to r.t., 15 h.

zinc atoms, the skeletal structure being ladder-shaped. The central Zn(1)O(1)Zn(1A)O(1A) ring is planar, with the angle at Zn narrower [82.10(14)°] than that at O [97.90(14)°]. The terminal $ZnOC_3N$ rings are boat-shaped. The two ethyl groups on the zinc centers are oriented in a *trans* fashion. The four-coordinate zinc atom presents a distorted tetrahedral geometry, with the angle ranging from 82.10(14)° to 129.4(2)°. The Zn–N distance of 2.165(4) Å is within normal range for amine coordinated zinc complexes.[1e,16] The Zn–O distances [2.010(3) and 2.056(3) Å, respectively] are also unexceptional.[1e,16b,c]

The NMR spectra of complex **7** displayed two sets of ligand signals. This was attributed to the existence of isomers due to use of racemic ligand. Reaction of $ZnEt_2$ with racemic ligand [(*R*)- and (*S*)-ligands] should yield a mixture of (i) [(*R*)-L]$_2$Zn (L = ligand), (ii) [(*S*)-L]$_2$Zn, (iii) [(*R*)-L]Zn[(S)-L] and (iv) [(*S*)-L]Zn[(*R*)-L]. Complexes (i) and (ii) gave a set of NMR signals and (iii) and (iv) gave another set of NMR signals [(iii) and (iv) are the same species]. The NMR spectra of complex **8** displayed one set of ligand signals and were consistent with the structure. However, we cannot judge that **8** is a monomer or a dimer based on the NMR spectral data. Attempts to grow single crystals of complexes **7** and **8** for X-ray diffraction analyses were unsuccessful. The NMR spectra of complex **9** presented one set of ligand signals, which proves that the two ligands adopt the same coordinate mode. The ^{1}H



Scheme 3. Transformation of **6** to **9**.

NMR spectrum showed the absence of NH and tertiary CH proton signals compared with **6**, being consistent with the existence of the C–N double bonds in **9**. The ^{13}C NMR spectrum also revealed the presence of the carbon signal of the C–N double bonds at 164.44 ppm.

Catalysis of complexes 3, 4a, 5a–c, 6 and 8 in the ROP of ε-caprolactone in the absence and presence of $PhCH_2OH$

We first determined catalytic activities of complexes **3, 4a, 5a–c, 6** and **8** in the absence of $PhCH_2OH$. The catalyzed ring-opening polymerization of ε-CL was carried out at a $[\varepsilon\text{-CL}]_0$/cat. ratio of 200 : 1 in 20 ml of toluene. The monomer conversion was determined by ^{1}H NMR spectroscopy and the M_n and PDI were determined by GPC. The data are listed in Table 1. Complexes **3, 4a** and **8** showed low catalytic activity at 20 °C. At a higher temperature (60 °C) the reaction rate increased obviously. For example, in the polymerization reaction catalyzed by complex **3**, at 20 °C the monomer was converted 26.1% in 780 min, while at 60 °C the monomer was converted 55.7% in 180 min. In the polymerization reactions except entry 7 (Table 1) the measured molecular weights of polymers were much higher than calculated values (based on living polymerization). For example, the polymerization reaction catalyzed by **3** at 20 °C gave polymer with M_n = 232 000, which means that the polymer chains contain more than 2000 ε-CL units. This and the narrow PDI value imply that the number of active sites of the catalyst is rather small. Complexes **3, 4a, 5a–c** and **8** gave similar results. It is also seen that at higher reaction temperatures the polymers have wider molecular weight distributions (entries 2 and 4–6, Table 1). This may mean the existence of intermolecular chain-transfer via transesterification, which can also lead to an increase in the molecular weights of polymers.

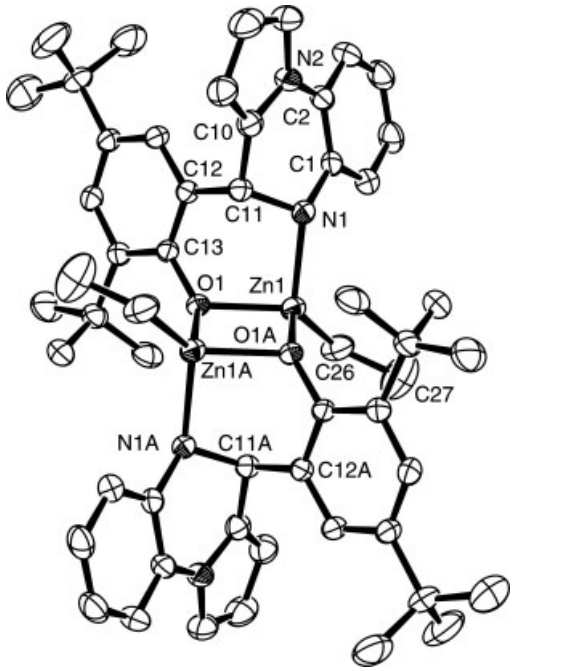


Figure 3. ORTEP drawing of complex **6** dimer (30% probability). Selected bond lengths (Å) and angles (deg): Zn(1)–N(1) 2.165(4), Zn(1)–O(1) 2.010(3), Zn(1)–O(1A) 2.056(3), Zn(1)–C(26) 1.966(6), Zn(1)–Zn(1A) 3.0669(13), N(1)–C(11) 1.507(7), C(10)–C(11) 1.489(7), C(11)–C(12) 1.515(7), Zn(1)–O(1)–Zn(1A) 97.90(14), C(26)–Zn(1)–O(1) 127.4(3), C(26)–Zn(1)–O(1A) 120.2(2), O(1)–Zn(1)–O(1A) 82.10(14), C(26)–Zn(1)–N(1) 129.4(2), O(1)–Zn(1)–N(1) 90.59(15), O(1A)–Zn(1)–N(1) 94.02(15), N(1)–C(11)–C(12) 110.7(4), C(1)–N(1)–C(11) 112.4(4), C(1)–N(1)–Zn(1) 118.7(3).

Table 1. The ring-opening polymerization of ε-CL catalyzed by complexes **3, 4a, 5a–c, 6** and **8** in the absence of an alcohol[a]

Entry	Complex	Temperature (°C)	Time (min)	Conversion (%)[b]	Yield (%)	M_n[c,d]	PDI
1	**3**	20	780	26.1	22.5	232 000	1.05
2	**3**	60	180	55.7	53.5	87 500	1.48
3	**4a**	20	780	88.4	83.2	47 800	1.19
4	**5a**	60	680	22.2	19.4	94 500	1.32
5	**5b**	60	680	28.0	25.7	41 000	1.40
6	**5c**	60	680	32.6	29.8	74 000	1.32
7	**6**	20	450	93.2	90.3	23 800	1.01
8	**8**	20	460	46.9	43.1	199 500	1.08
9	**8**	60	130	40.4	35.2	95 000	1.12

[a] $[\varepsilon\text{-CL}]_0/[M]$ = 200 : 1, [ε-CL] = 20 mmol, solvent = toluene (20 ml).
[b] Obtained from the ^{1}H NMR spectral data.
[c] Obtained from GPC analysis and calibrated polystyrene standard.
[d] Using a correcting factor 0.58 for M_n, see Ma and Okuda.[17]

Then we determined catalytic activities for the ROP of ε-CL of the complexes in the presence of $PhCH_2OH$. Thus, a complex was reacted with 1 equiv of $PhCH_2OH$ (2 equiv of $PhCH_2OH$ for dinuclear complexes **4a** and $[\mathbf{6}]_2$) in toluene at room temperature for 6 h and then 200 equiv of ε-CL was added at a preset temperature. The monomer conversion was determined by ^{1}H NMR spectroscopy and the M_n and PDI were determined by GPC. The data are listed in Table 2. From Table 2 it can be seen that catalytic activity of the complexes–$PhCH_2OH$ system is much

Table 2. The ring-opening polymerization of ε-CL catalyzed by complexes **3, 4a, 5b–c, 6** and **8** in the presence of $PhCH_2OH$[a]

Entry	Complex	Temperature (°C)	Time (min)	Conversion (%)[b]	Yield (%)	M_{calc}[c]	M (NMR)[b]	M_n (GPC)[d,e]	PDI[d]
1	**3**	20	120	83	77	19 000	10 500	8 100	1.19
2	**3**	60	60	100	97	22 900	21 000	17 500	1.20
3	**4a**	20	60	79	76	18 200	13 500	12 500	1.32
4	**4a**	20	120	100	97	22 900	17 000	15 500	1.21
5	**5b**	20	120	18					
6	**5b**	45	560	93	89	21 300	23 500	19 000	1.15
7	**5b**	60	180	100	95	22 900	13 500	11 000	1.27
8	**5c**	60	540	91	86	20 700	6 800	6 600	1.18
9	**5c**	60	900	100	95	22 900	11 000	8 700	1.32
10	**6**	20	60	94	91	21 600	13 500	11 000	1.03
11	**8**	20	120	31					
12	**8**	60	60	100	96	21 900	20 500	16 900	1.18

[a] $[\varepsilon\text{-CL}]_0/[M] = 200 : 1$, $[\varepsilon\text{-CL}]_0 = 20$ mmol, solvent: toluene (20 ml).
[b] Obtained from the ^{1}H NMR spectral data.
[c] Calculated from the molecular weight of CL times the conversion of monomer and the ratio of $[M]_0/[BnOH]_0$ plus the molecular weight of BnOH.
[d] Obtained from GPC analysis and calibrated polystyrene standard.
[e] Using a correcting factor 0.58 for M_n, see Ma and Okuda.[17]

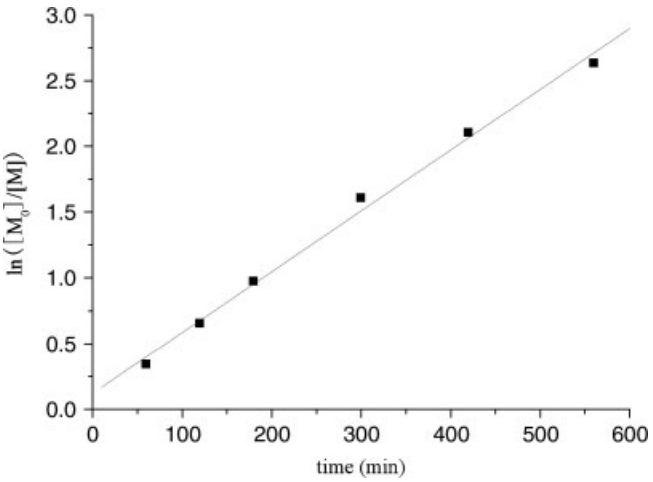


Figure 4. Plot of $\ln([M]_0/[M])$ vs time for the ROP of ε-CL catalyzed by complex **5b** in the presence of 1 equiv of $PhCH_2OH$. Conditions: $[\varepsilon\text{-CL}]_0/[\mathbf{5b}] = 200$; $[\varepsilon\text{-CL}]_0 = 1.0$ M, 45 °C, toluene.

higher than that of pure complexes. The activity of complex **3** is higher than that of **5b**, which means that the O,N(amine)-chelate aluminum complex has higher catalytic activity than the O,N (imine)-chelate aluminum complex. The O,N(imine)-chelate zinc complex **8** is more active than the corresponding aluminum complex **5b**. The dinuclear aluminum complex **4a** displays higher activity than the mononuclear aluminum complexes, **3, 5b** and **5c**. Dinuclear zinc complex **6** is also more active than mononuclear zinc complex **8**, as well as the aluminum complexes. This is possibly because of a synergistic effect of the two metal centers. The bimetal synergistic effect in the ROP of cyclic esters or in CO_2/CHO copolymerization has been reported.[18] The approximate activity order is **6** > **4a** > **3** > **8** > **5b** > **5c**. Catalytic activity of the aluminum complex–$PhCH_2OH$ systems is also comparable to that of salicylaldimine–Al–$PhCH_2OH$ systems.[6f] The ^{1}H NMR spectrum of each PCL showed one benzyl ester signal, suggesting that the initiation occurred through the insertion of the benzyl alkoxy group from the metal complexes into ε-CL. Most examples show that the determined molecular weights of PCL match the calculated values well. However, in some cases the determined molecular weight is lower than the calculated ones (entries 1, 8 and 9, Table 2). This may be caused by intramolecular transesterification. On the basis of the molecular weights of PCLs and the $[M]_0$/complex ratio, we guessed that the two $PhCH_2O$ groups in the alkoxy complexes formed from **4a** and **6**, respectively, could be used as initiators, but other possibilities cannot be ruled out.

For the polymerization of ε-CL catalyzed by complex **5b**-$PhCH_2OH$, conversion of ε-CL with time was monitored by ^{1}H NMR spectroscopy at 45 °C ($[\varepsilon\text{-CL}]_0/[\mathbf{5b}] = 200$; $[\varepsilon\text{-CL}]_0 = 1$ M in toluene). The plot of $\ln([M]_0/[M])$ vs time exhibited well a linear relation (Fig. 4), 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 remained alive during the entire polymerization.

Conclusions

We have synthesized and characterized aluminum and zinc complexes bearing N,O-chelate ligands. Transformation of these complexes was also studied. It has been demonstrated that compounds **1a** and **1b** were converted to complexes **5** via mononuclear aluminum complexes of type **3** and dinuclear aluminum complexes of type **4** successively. Similarly, **1b** was converted to **8** through complex **6**. Complex **6** can be transformed to **9** through intermediate **10**. These aluminum and zinc complexes are active initiators in the ROP of ε-CL. In the presence of $PhCH_2OH$, the polymerization seems to be alive. The dinuclear complexes, **4a** and **6**, exhibited higher catalytic activity compared with the mononuclear derivatives. Amine donor complex **3** also showed higher catalytic activity than corresponding imine donor complex **5**.

Experimental

General remarks

All air- or moisture-sensitive manipulations were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene) or sodium/benzophenone (*n*-hexane and diethyl ether) and degassed prior to use. $AlMe_3$, $AlEt_3$ and $ZnEt_2$ were purchased from Alfa Aesar and used as received. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories Inc., and C_6D_6 was degassed and stored over Na/K alloy. 2-(1*H*-pyrrol-1-yl)benzenamine was prepared according to the reported methods.[19] NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China.

Preparation of 2-(4,5-dihydropyrrolo[1,2-*a*]quinoxalin-4-yl) phenol (HOL^1NH, 1a)

A mixture of 2-(1*H*-pyrrol-1-yl)benzenamine (3.5 g, 22.12 mmol), salicylaldehyde (2.7 g, 22.12 mmol) and ethanol (40 ml) was refluxed for 5 h. Solvent was removed *in vacuo*. The residue was recrystallized from a mixed solvent of methanol and water. The precipitates were filtered and the solid was dried *in vacuo* to give white powder of **1a** (3.47 g, 60%), m.p. 174–176 °C. (lit.[9] 169–171 °C). ^1H NMR ($CDCl_3$): δ 4.32 (b, 1H, NH), 5.48 (s, 1H, CH), 5.50–5.52 (m, 1H, C_4H_3N), 6.17 (t, $J = 2.4$ Hz, 1H, C_4H_3N), 6.78–6.88 (m, 2H, Ar), 6.90–6.97 (m, 2H, Ar), 7.06–7.08 (m, 1H, Ar), 7.13–7.14 (m, 1H, Ar), 7.18 (s, 1H, Ar), 7.20–7.24 (m, 1H, Ar), 7.28–7.30 (m, 1H, Ar).

Preparation of 2,4-di-*tert*-butyl-6-(4,5-dihydropyrrolo[1,2-*a*] quinoxalin-4-yl)phenol (HOL^2NH, 1b)

A mixture of 2-(1*H*-pyrrol-1-yl)benzenamine (2.8 g, 17.7 mmol), 3,5-di-*tert*-butylsalicylaldehyde (4.17 g, 17.8 mmol) and ethanol (30 ml) was refluxed for 8 h. The solution was cooled to room temperature and the product gradually crystallized. The precipitates were collected and dried *in vacuo* to give white powder of **1b** (5.83 g, 88%), m.p. 160–162 °C. ^1H NMR ($CDCl_3$): δ 1.24 (s, 9H, Bu^t), 1.33 (s, 9H, Bu^t), 4.30 (s, 1H, NH), 5.44 (s, 1H, CH), 5.46 (s, 1H, C_4H_3N), 6.15 (s, 1H, C_4H_3N), 6.77 (s, 1H, C_4H_3N), 6.92 (s, 3H, Ar), 7.11 (s, 1H, Ar), 7.27 (s, 2H, Ar), 8.39 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 29.85 (CMe_3), 31.82 (CMe_3), 34.36 (CMe_3), 35.28 (CMe_3), 57.91 (CH), 106.57 (pyrrolyl), 110.69 (pyrrolyl), 115.20 (pyrrolyl), 115.27 (Ar), 117.17 (Ar), 121.54 (Ar), 121.99 (Ar), 124.44 (Ar), 124.65 (Ar), 124.72 (Ar), 127.14 (Ar), 128.82 (Ar), 135.02 (Ar), 137.24 (Ar), 141.16 (Ar), 153.56 (Ar). Anal. calcd for $C_{25}H_{30}N_2O$: C, 80.17; H, 8.07; N, 7.48. Found: C, 80.12; H, 8.14; N, 7.38.

Preparation of 2-(*H*-pyrrolo[1,2-*a*]quinoxalin-4-yl)phenol (HOL^3N, 2a)

A mixture of **1a** (1.4 g, 5.34 mmol), 4 Å molecular sieves (15 g) and toluene (30 ml) was refluxed for 2 days. The solution was cooled to room temperature and filtered. The molecular sieves were washed with dichloromethane (3 × 20 ml). Solvents were removed from the combined organic phase and anhydrous ethanol was added to the residue to form yellow crystals of compound **2a** (0.69 g, 50%), m.p. 155–156 °C. ^1H NMR ($CDCl_3$): δ 6.93–7.02 (m, 2H, Ar), 7.11–7.16 (m, 1H, Ar), 7.33–7.54 (m, 4H, Ar), 7.81–7.89 (m, 2H, Ar), 7.98–8.01 (m, 1H, Ar), 8.19 (d, $J = 7.8$ Hz, Ar), 13.48 (b, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 110.73 (pyrrolyl), 113.92 (pyrrolyl), 114.68 (pyrrolyl), 115.71 (Ar), 118.40 (Ar), 118.80 (Ar), 119.44 (Ar), 123.89 (Ar), 125.76 (Ar), 127.14 (Ar), 128.01 (Ar), 128.57 (Ar), 129.28 (Ar), 132.19 (Ar), 133.31 (Ar), 153.73 (Ar), 160.23 (*C*=N). Anal. calcd for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.58; H, 4.51; N, 10.61.

Preparation of 2,4-di-*tert*-butyl-6-(*H*-pyrrolo[1,2-*a*] quinoxalin-4-yl)phenol (HOL^4N, 2b)

A mixture of **1b** (0.80 g, 2.14 mmol), 4 Å molecular sieves (10 g) and toluene (20 ml) was refluxed for 3 days. The solution was cooled to room temperature and filtered. The molecular sieves were washed with dichloromethane (3 × 20 ml). Solvents were removed from the combined organic phase and then petroleum ether was added to the residue to form yellow crystals of compound **2b** (0.32 g, 40%), m.p. 150–152 °C. ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, Bu^t), 1.45 (s, 9H, Bu^t), 6.86–6.88 (m, 1H, Ar), 7.18 (d, $J = 4.4$ Hz, 1H, Ar), 7.34–7.45 (m, 3H, Ar), 7.78 (d, $J = 8.1$ Hz, 1H, Ar), 7.84 (d, $J = 7.8$ Hz, 1H, Ar), 7.92–7.96 (m, 2H, Ar), 13.50 (b, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 29.83 (CMe_3), 31.81 (CMe_3), 34.58 (CMe_3), 35.52 (CMe_3), 110.84 (pyrrolyl), 113.79 (pyrrolyl), 114.51 (pyrrolyl), 115.50 (Ar), 118.64 (Ar), 124.11 (Ar), 124.43 (Ar), 125.59 (Ar), 126.74 (Ar), 127.00 (Ar), 127.66 (Ar), 128.49 (Ar), 133.43 (Ar), 137.41 (Ar), 139.91 (Ar), 154.94 (Ar), 156.49 (*C*=N). Anal. calcd for $C_{25}H_{28}N_2O$ requires C, 80.61; H, 7.58; N, 7.52. Found: C, 80.86; H, 7.52; N, 7.14.

Preparation of $[Al(Et_2)(OL^2NH)]$ (3)

$AlEt_3$ (1 ml, a 1.82 M solution in hexane, 1.82 mmol) was added to a stirred solution of **1b** (0.68 g, 1.82 mmol) in toluene (10 ml) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under vacuum and the residue was dissolved in *n*-hexane (20 ml). The resultant solution was filtered and the filtrate was concentrated to afford yellowish crystals of compound **3** (0.69 g, 82.2%), m.p. 182–184 °C. ^1H NMR (C_6D_6): δ −0.65 to −0.42 (m, 2H, $AlCH_2$), −0.09–0.12 (m, 2H, $AlCH_2$), 0.84 (t, $J = 8.1$ Hz, 3H, Me), 1.22 (t, $J = 8.1$ Hz, 3H, Me), 1.43 (s, 9H, Bu^t), 1.71 (s, 9H, Bu^t), 4.08 (s, 1H, NH), 4.58 (s, 1H, CH), 5.77–5.78 (m, 1H, Ar), 6.11 (t, $J = 3$ Hz, 1H, Ar), 6.39(d, $J = 7.8$ Hz, 1H, Ar), 6.62–6.68 (m, 1H, Ar), 6.82–6.88 (m, 4H, Ar), 7.67 (d, $J = 2.4$ Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ −3.45 ($AlCH_2$), −0.43 ($AlCH_2$), 8.56 ($AlCH_2CH_3$), 9.73 ($AlCH_2CH_3$), 30.19 (CMe_3), 32.11 (CMe_3), 34.38 (CMe_3), 35.80 (CMe_3), 59.83 (CH), 109.12 (pyrrolyl), 112.11 (pyrrolyl), 116.02 (pyrrolyl), 116.12 (Ar), 120.02 (Ar), 120.26 (Ar), 120.85 (Ar), 124.02 (Ar), 125.36 (Ar), 127.45 (Ar), 129.02 (Ar), 130.82 (Ar), 138.62 (Ar), 140.13 (Ar), 156.93 (Ar). Anal. calcd for $C_{29}H_{39}AlN_2O$: C, 75.95; H, 8.57; N, 6.11. Found: C, 75.64; H, 8.53; N, 5.95.

Preparation of $[(AlMe_2)_2(OL^2N)]$ (4a)

$AlMe_3$ (0.85 ml, a 2.2 M solution in hexane, 1.87 mmol) was added to a solution of **1b** (0.35 g, 0.93 mmol) in toluene (8 ml) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under vacuum and the residue was dissolved in *n*-hexane. The solution was filtered and the filtrate was concentrated to afford pale yellow powder of compound **4a** (0.38 g, 84%), m.p. 100–102 °C. ^1H NMR (C_6D_6): δ −0.88 (s, 3H, AlMe), −0.78 (s, 3H, AlMe), −0.35 (s, 3H, AlMe), 0.16 (s, 3H, AlMe), 1.26 (s, 9H, Bu^t), 1.42 (s, 9H, Bu^t), 5.30 (s, 1H, CH), 6.12–6.13 (m,

1H, C_4H_3N), 6.31 (t, J = 3.3 Hz, 1H, C_4H_3N), 6.83–6.88 (m, 3H, Ar), 6.96–6.99 (m, 1H, Ar), 7.27–7.28 (m, 1H, Ar), 7.42 (d, J = 2.1 Hz, 1H, Ar), 7.65–7.68 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −10.52 (AlMe), −9.32 (AlMe), −8.44 (AlMe), −4.34 (AlMe), 30.02 (CMe_3), 31.49 (CMe_3), 34.65 (CMe_3), 35.32 (CMe_3), 60.31 (*C*H), 108.05 (pyrrolyl), 111.14 (pyrrolyl), 115.56 (pyrrolyl), 116.44 (Ar) 122.82 (Ar), 123.48 (Ar), 124.65 (Ar), 124.94 (Ar), 125.43 (Ar), 126.47 (Ar), 130.16 (Ar), 131.51 (Ar), 135.28 (Ar), 141.07 (Ar), 146.25 (Ar), 151.13 (Ar). Anal. calcd for $C_{29}H_{40}Al_2N_2O$: C, 71.58; H, 8.29; N, 5.76. Found: C, 71.48; H, 8.41; N, 6.10.

Preparation of [($AlEt_2$)$_2$(OL^2N)] (4b) from 1b

$AlEt_3$ (1.00 ml, a 1.82 M solution in hexane, 1.82 mmol) was added to a solution of **1b** (0.34 g, 0.91 mmol) in toluene (8 ml) at about −80 °C. The mixture was warmed to room temperature and stirred for 18 h. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane and the resultant solution was filtered. The filtrate was concentrated and the residual solution was stored at 5 °C for 5 days to form yellow crystals of compound **4b** (0.35 g, 72%), m.p. 126–128 °C. ^{1}H NMR (C_6D_6): δ −0.35 to −0.04 (m, 4H, $AlCH_2$), 0.22–0.35 (m, 2H, $AlCH_2$), 0.44–0.57 (m, 2H, $AlCH_2$), 0.70 (t, 3H, J = 8.4 Hz, $AlCH_2CH_3$), 0.89 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), 1.18 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), 1.25 (s, 9H, Bu^t), 1.46 (s, 9H, Bu^t), 1.53 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), 5.36 (s, 1H, CH), 6.13–6.14 (m, 1H, C_4H_3N), 6.32 (t, J = 3 Hz, 1H, C_4H_3N), 6.82–6.89 (m, 3H, Ar), 6.94–6.97 (m, 1H, Ar), 7.26–7.27 (m, 1H, Ar), 7.41 (d, J = 2.1 Hz, 1H, Ar), 7.56–7.59 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −0.57 ($AlCH_2$), 0.63 ($AlCH_2$), 1.44 ($AlCH_2$), 4.95 ($AlCH_2$), 8.12 ($AlCH_2CH_3$), 8.62 ($AlCH_2CH_3$), 8.98 ($AlCH_2CH_3$), 9.88 ($AlCH_2CH_3$), 30.25 (CMe_3), 31.49 (CMe_3), 34.67 (CMe_3), 35.54 (CMe_3), 60.46 (*C*H), 107.96 (pyrrolyl), 111.38 (pyrrolyl), 115.51 (pyrrolyl), 116.30 (Ar), 122.77 (Ar), 123.71 (Ar), 124.80 (Ar), 124.91 (Ar), 125.45 (Ar), 126.36 (Ar), 130.04 (Ar), 131.25 (Ar), 135.37 (Ar), 141.19 (Ar), 146.29 (Ar) 150.97 (Ar). Anal. calcd for $C_{33}H_{48}Al_2N_2O$: C, 73.03; H, 8.91; N, 5.16. Found: C, 72.30; H, 8.70; N, 5.66.

Preparation of [($AlEt_2$)$_2$(OL^2N)] (4b) from 3

$AlEt_3$ (0.38 ml, a 1.82 M solution in hexane, 0.68 mmol) was added to a solution of **3** (0.31g, 0.67 mmol) in toluene (8 ml) at about −80 °C. The solution was warmed to room temperature and stirred for 18 h. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane (10 ml) and the resultant solution was filtered. The filtrate was concentrated and stored at 5 °C for 5 days to form yellow crystals of compound **4b** (0.28 g, 78.2%). ^{1}H NMR (C_6D_6): δ −0.36 to −0.05 (m, 4H, $AlCH_2$), 0.21–0.34 (m, 2H, $AlCH_2$), 0.43–0.56 (m, 2H, $AlCH_2$), 0.69 (t, 3H, J = 8.1 Hz, $AlCH_2CH_3$), 0.88 (t, J = 8.4 Hz, 3H, $AlCH_2CH_3$), 1.17 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), 1.25 (s, 9H, Bu^t), 1.45 (s, 9H, Bu^t), 1.52 (t, J = 8.1 Hz, 3H, $AlCH_2CH_3$), 5.36 (s, 1H, CH), 6.12–6.14 (m, 1H, C_4H_3N), 6.32 (t, J = 3.3 Hz, 1H, C_4H_3N), 6.82–6.89 (m, 3H, Ar), 6.94–6.97 (m, 1H, Ar), 7.25 (d, J = 2.1 Hz, 1H, Ar), 7.40 (d, J = 2.4 Hz, 1H, Ar), 7.55–7.58 (m, 1H, Ar).

Preparation of [Al(Me_2)(OL^4N)] (5a) from 4a

A solution of **4a** (0.25 g, 0.51 mmol) in toluene (6 ml) was heated at 120 °C (bath temperature) for 8 h. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane and the resultant solution was filtered. Concentration of the filtrate formed yellow crystals of compound **5a** (0.16 g, 72.4%), m.p. 236–238 °C. ^{1}H NMR (C_6D_6): δ −0.07 (s, 6H, AlMe), 1.36 (s, 9H, Bu^t), 1.78 (s, 9H, Bu^t), 6.40–6.42 (m, 1H, Ar), 6.89 (s, 3H, Ar), 7.06–7.12 (m, 2H, Ar), 7.77–7.82 (m, 2H, Ar), 8.14–8.17 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −8.48 ($AlCH_3$), 30.11 (CMe_3), 31.77 (CMe_3), 34.47 (CMe_3), 36.01 (CMe_3), 114.38 (pyrrolyl), 115.54 (pyrrolyl), 117.34 (pyrrolyl), 117.69 (Ar), 120.85 (Ar), 125.41 (Ar), 125.59 (Ar), 125.67 (Ar), 126.69 (Ar), 127.51 (Ar), 127.91 (Ar), 129.09 (Ar), 131.63 (Ar), 138.36 (Ar) 141.23 (Ar), 157.63 (Ar), 159.80 (*C*═N). Anal. calcd for $C_{27}H_{33}AlN_2O$: C, 75.67; H, 7.76; N, 6.54. Found: C, 75.39; H, 7.72; N, 6.49.

Preparation of [Al(Me_2)(OL^4N)] (5a) from 1b

$AlMe_3$ (1.02 ml, a 2.2 M solution in hexane, 2.24 mmol) was added to a solution of **1b** (0.42 g, 1.12 mmol) in toluene (10 ml) at about −80 °C. The mixture was warmed to room temperature and stirred for 10 h. Then the mixture was heated at 120 °C (bath temperature) for 8 h. Solvent was removed under vacuum. The residue was dissolved in n-hexane and the resultant solution was filtered. Concentration of the filtrate gave yellow crystals of compound **5a** (0.31 g, 64.5%). ^{1}H NMR (C_6D_6): δ −0.08 (s, 6H, AlMe), 1.35 (s, 9H, Bu^t), 1.77 (s, 9H, Bu^t), 6.39–6.41 (m, 1H, Ar), 6.86–6.92 (m, 3H, Ar), 7.05–7.11 (m, 2H, Ar), 7.79 (dd, J = 2.4, 13 Hz, 2H, Ar), 8.13–8.16 (m, 1H, Ar).

Preparation of [Al(Me_2)(OL^4N)] (5a) from 2b

$AlMe_3$ (0.38 ml, a 2.2 M solution in hexane, 0.83 mmol) was added to a solution of **2b** (0.31 g, 0.83 mmol) in toluene (6 ml) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under vacuum. The residue was dissolved in n-hexane and the resultant solution was filtered. Concentration of the filtrate yielded yellow crystals of compound **5a** (0.31 g, 86.9%). ^{1}H NMR (C_6D_6): δ −0.09 (s, 6H, AlMe), 1.33 (s, 9H, Bu^t), 1.76 (s, 9H, Bu^t), 6.38–6.41 (m, 1H, Ar), 6.87–6.92 (s, 3H, Ar), 7.05–7.11 (m, 2H, Ar), 7.77 (dd, J = 2.7, 15 Hz, 2H, Ar), 8.11–8.14 (m, 1H, Ar).

Preparation of [Al(Et_2)(OL^4N)] (5b) from 4b

A solution of compound **4b** (0.31 g, 0.57 mmol) in toluene (5 ml) was heated at 120 °C (bath temperature) for 20 h. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane and the resultant solution was filtered. Concentration of the filtrate afforded yellow crystals of compound **5b** (0.17 g, 65.2%), m.p. 170–172 °C. ^{1}H NMR (C_6D_6): δ 0.45–0.65 (m, 4H, $AlCH_2$), 1.35 (s, 9H, Bu^t), 1.42 (t, J = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.78 (s, 9H, Bu^t), 6.38 (t, J = 3.5 Hz, 1H, Ar), 6.88–6.99 (m, 3H, Ar), 7.06–7.07 (m, 2H, Ar), 7.77 (dd, J = 2.4, 15.6 Hz, 2H, Ar), 8.14 (d, J = 8.4 Hz, 1H, Ar). ^{13}C NMR (C_6D_6): δ 1.56 ($AlCH_2CH_3$), 9.91 ($AlCH_2CH_3$), 30.09 (CMe_3), 31.77 (CMe_3), 34.46 (CMe_3), 36.01 (CMe_3), 114.42 (pyrrolyl), 115.58 (pyrrolyl), 117.36 (pyrrolyl), 117.75 (Ar), 120.73 (Ar), 125.18 (Ar), 125.37 (Ar), 125.80 (Ar), 126.38 (Ar), 126.60 (Ar), 127.63 (Ar), 129.07 (Ar), 131.70 (Ar), 138.41 (Ar), 141.03 (Ar), 157.72 (Ar), 160.27 (C═N). Anal. calcd for $C_{29}H_{37}AlN_2O$: C, 76.28; H, 8.17; N, 6.14. Found: C, 76.39; H, 8.19; N, 6.13.

Preparation of [Al(Et_2)(OL^4N)] (5b) from 1b

$AlEt_3$ (0.80 ml, a 1.82 M solution in hexane, 1.45 mmol) was added to a solution of **1b** (0.27 g, 0.72 mmol) in toluene (10 ml) at about

−80 °C. The mixture was stirred at room temperature for 10 h and then heated at 120 °C (bath temperature) for 20 h. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane and the resultant solution was filtered. Concentration of the filtrate *in vacuo* gave yellow crystals of compound **5b** (0.17 g, 51.6%). ^{1}H NMR (C_6D_6): δ 0.45–0.65 (m, 4H, $AlCH_2$), 1.35 (s, 9H, Bu^t), 1.42 (t, J = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.78 (s, 9H, Bu^t), 6.38–6.40 (m, 1H, Ar), 6.88–6.99 (m, 3H, Ar), 7.06–7.09 (m, 2H, Ar), 7.77 (dd, J = 2.7, 15.6 Hz, 2H, Ar), 8.15 (d, J = 7.8 Hz, 1H, Ar).

Preparation of [Al(Et$_2$)(OL^{4}N)] (5b) from 2b

$AlEt_3$ (0.52 ml, a 1.82 M solution in hexane, 0.94 mmol) was added to a solution of **2b** (0.35 g, 0.94 mmol) in toluene (8 ml) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under vacuum. The residue was dissolved in *n*-hexane and the resultant solution was filtered. Concentration of the filtrate formed yellow crystals of compound **5b** (0.36 g, 85.3%). ^{1}H NMR (C_6D_6): δ 0.44–0.65 (m, 4H, $AlCH_2$), 1.34 (s, 9H, Bu^t), 1.42 (t, J = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.78 (s, 9H, Bu^t), 6.38 (dd, J = 2.7, 4.2 Hz, 1H, Ar), 6.85–6.98 (m, 3H, Ar), 7.04–7.07 (m, 2H, Ar), 7.76 (dd, J = 2.7, 17.1 Hz, 2H, Ar), 8.13 (d, J = 8.1 Hz, 1H, Ar).

Preparation of [Al(Me$_2$)(OL^{3}N)] (5c)

$AlMe_3$ (0.53 ml, a 2.2 M solution in hexane, 1.16 mmol) was added to a solution of **2a** (0.30 g, 1.15 mmol) in toluene (6 ml) at about −80 °C. The mixture was warmed to room temperature and stirred overnight. Solvent was removed under vacuum. The residue was dissolved in Et_2O and the resultant solution was filtered. Concentration of the filtrate produced yellow powder of compound **5c** (0.32 g, 87.7%), m.p. 178–180 °C. ^{1}H NMR (C_6D_6): δ 0.19 (s, 6H, AlMe), 6.60–6.62 (m, 1H, Ar), 6.91–6.97 (m, 1H, Ar), 7.11–7.18 (m, 4H, Ar), 7.28–7.29 (m, 1H, Ar), 7.50 (dt, J = 1.5, 6.9 Hz, 1H, Ar), 7.59–7.61 (m, 1H, Ar), 7.89 (dd, J = 1.5, 7.8 Hz, 1H, Ar), 8.37–8.40 (m, 1H, Ar). ^{13}C NMR (C_6D_6): δ −8.41 ($AlCH_3$), 114.38 (pyrrolyl), 115.61 (pyrrolyl), 117.21 (pyrrolyl), 117.30 (Ar), 117.80 (Ar), 120.97 (Ar), 123.02 (Ar), 124.65 (Ar), 125.61 (Ar), 126.50 (Ar), 131.49 (Ar), 131.71 (Ar), 134.80 (Ar), 156.21 (Ar), 163.39 (*C*=N). Anal. calcd for $C_{19}H_{17}AlN_2O$: C, 72.14; H, 5.42; N, 8.86. Found: C, 72.06; H, 5.33; N, 8.85.

Preparation of [Zn(Et)(OL^{2}NH)] (6)

A solution of **1b** (0.40 g, 1.07 mmol) in toluene (8 ml) was added to a stirred solution of $ZnEt_2$ (1.17 ml, 1 M solution in hexane, 1.17 mmol) in toluene (4 ml) at about −80 °C. The resultant mixture was warmed to room temperature and stirred for 18 h. White precipitates were formed. Solvents were removed under vacuum. The residue was dissolved in Et_2O (40 ml) and filtered. Concentration of the filtrate formed colorless crystals of compound **6** (0.41 g, 82%), m.p. 130 °C (dec.). ^{1}H NMR (C_6D_6): δ 0.76–0.94 (m, 2H, $ZnCH_2$), 1.06 (s, 9H, Bu^t), 1.48 (s, 9H, Bu^t), 1.49 (t, J = 8.3 Hz, 3H, Me), 4.96 (s, 1H, CH), 6.45–6.51 (m, 2H, Ar), 6.57–6.62 (m, 2H, Ar), 6.82(t, J = 7.5 Hz, 1H, Ar), 6.99–7.04 (m, 2H, Ar), 7.33 (d, J = 2.2 Hz, 1H, Ar), 7.69 (d, J = 7.9 Hz, 1H, Ar). ^{13}C NMR (C_6D_6 + CH_2Cl_2): δ 2.48 ($ZnCH_2$), 12.86 ($ZnCH_2CH_3$), 30.43 (CMe_3), 31.52 (CMe_3), 34.09 (CMe_3), 35.18 (CMe_3), 53.02 (CH), 107.38 (pyrrolyl), 111.90 (pyrrolyl), 115.30 (pyrrolyl), 115.39 (Ar), 124.30 (Ar), 125.01 (Ar), 128.94 (Ar), 133.99 (Ar), 138.13 (Ar), 139.64 (Ar), 158.12 (Ar). Anal. calcd for $C_{27}H_{34}N_2OZn$: C, 69.30; H, 7.32; N, 5.99. Found: C, 69.05; H, 7.11; N, 6.12.

Preparation of [Zn(OL^{2}NH)$_2$] (7)

$ZnEt_2$ (0.46 ml, a 1 M solution in hexane, 0.46 mmol) was added to a solution of compound **1b** (0.35 g, 0.93 mmol) in toluene (8 ml) at 10 °C. The solution was stirred at 10 °C for 10 min and at 40 °C for two days. Solvent was removed under vacuum and Et_2O (15 ml) was added to solve the residue. The resultant solution was filtered and the filtrate was concentrated to form pale yellow crystals of compound **7** (0.23 g, 62.1%), m.p. 170 °C (dec.). ^{1}H NMR (C_6D_6): δ 1.12 (s, 9H, Bu^t), 1.49 (s, 9H, Bu^t), 1.78 (s, 9H, Bu^t), 1.89 (s, 9H, Bu^t), 3.01 (s, 1H, NH), 4.15 (s, 1H, NH), 4.41 (d, J = 2 Hz, 1H, CH), 4.57 (s, 1H, CH), 5.59 (t, J = 3 Hz, 1H, Ar), 5.78 (d, J = 2.1 Hz, 1H, Ar), 5.82 (d, J = 3.2 Hz, 1H, Ar), 5.95 (s, 1H, Ar), 6.37 (t, J = 3.1 Hz, 1H, Ar), 6.42 (s, 1H, Ar), 6.59 (dt, J = 0.9, 7.8 Hz, 1H, Ar), 6.67–6.81 (m, 6H, Ar), 6.88 (dd, J = 0.9, 7.8 Hz, 1H, Ar), 6.97 (d, J = 1.5 Hz, 1H, Ar), 7.32 (d, J = 2.4 Hz, 1H, Ar), 7.77 (d, J = 2.4 Hz, 1H, Ar), 8.10 (b, 1H, Ar). ^{13}C NMR (C_6D_6): δ 30.26 (CMe_3), 30.46 (CMe_3), 33.91 (CMe_3), 34.31 (CMe_3), 35.80 (CMe_3), 36.10 (CMe_3), 61.31 (CH), 65.91 (CH), 106.83 (pyrrolyl), 109.29 (pyrrolyl), 110.85 (pyrrolyl), 112.79 (pyrrolyl), 114.55 (pyrrolyl), 114.68 (pyrrolyl), 115.19 (Ar), 115.78 (Ar), 118.55 (Ar), 120.60 (Ar), 122.54 (Ar), 123.87 (Ar), 124.30 (Ar), 125.14 (Ar), 125.49 (Ar), 125.63 (Ar), 125.77 (Ar), 127.03 (Ar), 128.81 (Ar), 130.21 (Ar), 133.11 (Ar) 134.10 (Ar), 135.47 (Ar), 136.25 (Ar), 138.03 (Ar), 140.79 (Ar), 162.76 (Ar), 163.37 (Ar). Anal. calcd for $C_{50}H_{58}N_4O_2Zn$: C, 73.92; H, 7.19; N, 6.90. Found: C, 73.92; H, 6.79; N, 6.83.

Preparation of [Zn(Et)(OL^{4}N)] (8) from 6

$ZnEt_2$ (0.78ml, a 1 M solution in hexane, 0.78 mmol) was added to a stirred solution of **6** (0.33 g, 0.71 mmol) in toluene (8 ml) at about −80 °C. The solution was warmed to room temperature and then was heated at 60 °C for 15 h. The solution was cooled to room temperature and filtered. Solvents were removed under vacuum and then Et_2O (25 ml) was added. The resultant solution was concentrated to afford yellow crystals of compound **8** (0.16 g, 50.6%), m.p. 258–260 °C. ^{1}H NMR (C_6D_6): δ 0.78–0.95 (m, 2H, $ZnCH_2$), 1.27 (s, 9H, Bu^t), 1.33 (t, J = 8.1 Hz, 3H, Me), 2.00 (s, 9H, Bu^t), 6.24–6.26 (m, 1H, Ar), 6.31 (d, J = 3.2 Hz, 1H, Ar), 6.54–6.62 (m, 3H, Ar), 6.77 (s, 1H, Ar), 7.43 (d, J = 2.4 Hz, 1H, Ar), 7.72–7.75 (m, 2H, Ar). ^{13}C NMR (C_6D_6): δ 1.15 ($ZnCH_2$), 13.02 ($ZnCH_2CH_3$), 31.07 (CMe_3), 31.72 (CMe_3), 34.36 (CMe_3), 36.28 (CMe_3), 113.01 (pyrrolyl), 113.82 (pyrrolyl), 114.03 (pyrrolyl), 115.42 (Ar), 124.70 (Ar), 125.53 (Ar), 125.87 (Ar), 126.73 (Ar), 126.88 (Ar), 127.01 (Ar), 132.83 (Ar), 138.23 (Ar), 141.83 (Ar), 156.08 (Ar), 160.78 (*C*=N). Anal. calcd for $C_{27}H_{32}N_2OZn$: C, 69.60; H, 6.92; N, 6.01. Found: C, 69.61; H, 7.32; N, 5.97.

Preparation of [Zn(Et)(OL^{4}N)] (8) from 1b

A solution of **1b** (0.40 g, 1.07 mmol) in toluene (8 ml) was added to a stirred solution of $ZnEt_2$ (2.20 ml, a 1 M solution in hexane, 2.20 mmol) in toluene (6 ml) at about −80 °C. The resultant mixture was stirred at room temperature for 8 h and then at 60 °C for 15 h. The solution was cooled to room temperature and filtered. Solvents were removed from the filtrtate under vacuum. Et_2O (25 ml) was added to dissolve the residue. The resultant solution was concentrated to form yellow crystals of compound **8** (0.22 g, 43.7%). ^{1}H NMR (C_6D_6): δ 0.80–0.96 (m, 2H, $ZnCH_2$), 1.27 (s, 9H, Bu^t), 1.33 (t, J = 8.1 Hz, 3H, Me), 2.00 (s, 9H, Bu^t), 6.24–6.26 (m, 1H, Ar), 6.31 (d, J = 3.3 Hz, 1H, Ar), 6.55–6.62 (m, 3H, Ar), 6.77 (dd, J = 1.3, 2.6 Hz, 1H, Ar), 7.43 (d, J = 2.6 Hz, 1H, Ar), 7.73–7.76 (m, 2H, Ar).

Preparation of [Zn(Et)(OL^{4}N)] (8) from 2b

A solution of **2b** (0.22 g, 0.59 mmol) in toluene (8 ml) was added to a solution of $ZnEt_2$ (0.89 ml, 0.89 mmol) in toluene (4 ml) at about −80 °C. The resultant solution was warmed to room temperature and stirred for 15 h. Solvents were removed under vacuum. The residue was dissolved with Et_2O (20 ml) and then the solution was filtered. The filtrate was concentrated to form yellow crystals of compound **8** (0.24 g, 87.3%). ^{1}H NMR (C_6D_6): δ 0.78–0.98 (m, 2H, $ZnCH_2$), 1.27 (s, 9H, Bu^t), 1.33 (t, J = 8 Hz, 3H, Me), 2.00 (s, 9H, Bu^t), 6.24–6.26 (m, 1H, Ar), 6.31 (d, J = 3.3 Hz, 1H, Ar), 6.54–6.62 (m, 3H, Ar), 6.77 (s, 1H, Ar), 7.43 (d, J = 2.5 Hz, 1H, Ar), 7.72–7.77 (m, 2H, Ar).

Preparation of [Zn(OL^{4}N)$_2$] (9) from 6

A solution of compound **6** (0.28 g, 0.60 mmol) in toluene (10 ml) was stirred at 100 °C (bath temperature) for 15 h. The solution was cooled to room temperature and filtered. Solvent was removed under vacuum and Et_2O (10 ml) was added to dissolve the residue. The resultant solution was concentrated to form yellow powder of compound **9** (0.17 g, 70.1%), m.p. 302–304 °C. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 18H, Bu^t), 1.69 (s, 18H, Bu^t), 6.36–6.43 (m, 4H, Ar), 6.57 (t, J = 7.8 Hz, 2H, Ar), 6.72 (d, J = 7.8 Hz, 2H, Ar), 7.00 (s, 2H, Ar), 7.18 (d, J = 3.6 Hz, 2H, Ar), 7.76 (s, 4H, Ar), 7.94 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 29.39 (*C*Me$_3$), 31.52 (C*Me*$_3$), 34.06 (*C*Me$_3$), 35.69 (*C*Me$_3$), 113.19 (pyrrolyl), 114.96 (pyrrolyl), 115.59 (pyrrolyl), 116.53 (Ar), 119.85 (Ar), 124.59 (Ar), 126.02 (Ar), 126.16 (Ar), 126.24 (Ar), 126.37 (Ar), 126.76 (Ar), 127.49 (Ar), 132.88 (Ar), 135.01 (Ar), 140.92 (Ar), 160.39 (Ar), 164.44 (*C*═N). Anal. calcd for $C_{50}H_{54}N_4O_2Zn$: C, 74.29; H, 6.73; N, 6.93. Found: C, 73.91; H, 6.68; N, 6.54.

Preparation of [Zn(OL^{4}N)$_2$] (9) from 2b

$ZnEt_2$ (0.26 ml, 0.26 mmol) was added to a solution of compound **2b** (0.20 g, 0.53 mmol) in toluene (6 ml) at about −80 °C. The resultant solution was warmed to room temperature and stirred for 15 h. Solvents were removed under vacuum and Et_2O (10 ml) was added to dissolve the residue. The solution was concentrated to form yellow powder of compound **9** (0.18 g, 86.2%). ^{1}H NMR (C_6D_6): δ 1.48 (s, 18H, Bu^t), 1.73 (s, 18H, Bu^t), 6.41–6.49 (m, 4H, Ar), 6.61 (t, J = 7.3 Hz, 2H, Ar), 6.76 (d, J = 7.9 Hz, 2H, Ar), 7.05 (s, 2H, Ar), 7.22 (d, J = 4.1 Hz, 2H, Ar), 7.80 (s, 4H, Ar), 7.98 (d, J = 8.2 Hz, 2H, Ar).

X-ray crystallography

Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Rigaku Saturn CCD area-detector (for **3**) or a Bruker Smart CCD area-detector (for **5c** and **6**) with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[20] and refined against F^2 by full-matrix least-squares using SHELXL-97.[21] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 3.

CCDC 665 751 (for **3**), 665 752 (for **5c**) and 677 993 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Details of the X-ray structure determinations of complexes **3, 5c** and **6**

	3	**5c**	**6** · 0.5 Et_2O
Empirical formula	$C_{29}H_{39}AlN_2O$	$C_{19}H_{17}AlN_2O$	$C_{29}H_{39}N_2O_{1.5}Zn$
Fw	458.60	316.33	504.99
T (K)	113(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P2(1)/n$	$P-1$
a (Å)	14.645(3)	9.5804(15)	11.0777(13)
b (Å)	10.929(2)	14.8854(19)	11.2860(14)
c (Å)	16.580(3)	12.3938(16)	13.831(2)
α (deg)	90	90	66.476(2)
β (deg)	101.90(3)	107.845(2)	73.031(2)
γ (deg)	90	90	87.373(3)
V (Å^3)	2596.8(9)	1682.4(4)	1511.5(3)
Z	4	4	2
D_{calcd} (gcm^{-3})	1.173	1.249	1.110
$F(000)$	992	664	538
μ (mm^{-1})	0.101	0.126	0.834
θ range for data collection (deg)	1.69–27.88	2.20–25.01	1.68–25.00
No. of reflections collected	23 849	8082	7940
No. of independent reflections(R_{int})	6176 (R_{int} = 0.0483)	2964 (R_{int} = 0.0396)	5249 (R_{int} = 0.0354)
No. of data/restraints/parameters	6176/0/335	2964/0/209	5249/0/325
Goodness of fit on F^2	1.105	1.036	1.050
Final R indicesa [$I > 2\sigma(I)$]	$R1$ = 0.0617 w$R2$ = 0.1626	$R1$ = 0.0525 w$R2$ = 0.1100	$R1$ = 0.0665 w$R2$ = 0.1950
R indices (all data)	$R1$ = 0.0737 w$R2$ = 0.1725	$R1$ = 0.1037 w$R2$ = 0.1378	$R1$ = 0.0981 w$R2$ = 0.2134
Largest difference peak and hole (e Å^{-3})	0.402 and −0.364	0.222 and −0.449	0.992 and −0.437

[a] $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$; $wR2 = \left[\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^4)\right]^{1/2}$.

General procedure for polymerization of ε-caprolactone catalyzed by complexes 3, 4a, 5a–c, 6 and 8

A typical polymerization was exemplified by the synthesis of PCL catalyzed by complex **5b** in the presence of 1 equiv of $PhCH_2OH$. Complex **5b** (0.0456 g, 0.1 mmol) was added into a Schlenk tube and followed by injection of toluene (6 ml) via a syringe. $PhCH_2OH$ (0.0108 g, 0.1 mmol) was added at 0 °C and the mixture was warmed to room temperature and stirred for 6 h. ε-CL (2.28 g, 20.0 mmol) diluted with toluene (14 ml) was added. The flask was put into an oil bath which was preset at 45 °C. Samples were taken from the reaction mixture using a syringe at a desired time interval for ^{1}H NMR spectral analysis. After 560 min the polymerization reaction was quenched by addition of 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 filtered and washed with hexane and dried under vacuum, giving white solid (2.02 g, 88.6%).

Acknowledgments

We are grateful to the National Natural Science Foundation of China for financial support (Grant No. 20572106) and the Graduate School of University of Science and Technology of China for other support and Professors H.-B. Song, H.-G. Wang and D.-Q. Wang for determining the crystal structures.

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