Aluminum and zinc complexes supported by functionalized phenolate ligands: Synthesis, characterization and catalysis in the ring-opening polymerization of ε-caprolactone and *rac*-lactide

Cheng Zhang, Zhong-Xia Wang *

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ABSTRACT

A series of aluminum and zinc complexes supported by functionalized phenolate ligands were synthesized and characterized. Reaction of 2-(3,5-$R_2C_3N_2$)$C_6H_4NH_2$ (R = Me, Ph) with salicylaldehyde or 3,5-di-*tert*-butylsalicylaldehyde afforded 2-((2-(1H-pyrazol-1-yl)phenylimino)methyl)phenol derivatives **2a–2d**. Treatment of **2a–2d** with an equiv. of AlR_3^2 (R^2 = Me, Et) gave corresponding aluminum aryloxides **3a–3e**, while reaction with an equiv. of $ZnEt_2$ afforded zinc aryloxides **4a–4d**. Treatment of **2c** with 0.5 equiv. of $ZnEt_2$ formed diphenolato zinc complex **5**. All new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses. The structures of complexes **3a**, **4a** and **5** were further characterized by single crystal X-ray diffraction techniques. The catalytic activity of complexes **3–5** toward the ring-opening polymerization of ε-caprolactone was studied. The zinc complexes (**4a–4d**) exhibited higher catalytic activity than the aluminum complexes (**3a–3e**). The diphenolato zinc complex **5** showed lower catalytic activity than the ethylzinc complexes **4a–4d**. The aluminum complex (**3b**) is inactive to initiate the ROP of *rac*-lactide, while the zinc complex (**4d**) is active initiator for the ROP of *rac*-lactide, giving atactic polylactide.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Synthetic aliphatic polyesters derived from ε-caprolactone (ε-CL), lactide and glycolide are of great interest for their biomedical applications due to their biodegradable, biocompatible and permeable properties [1,2]. Ring-opening polymerization (ROP) of cyclic esters initiated by metal complexes is an efficient way to produce the polyesters. This method can enable control of polymer molecular weight and polymer architecture and can yield macromolecular samples with narrow molecular weight distributions [3]. A range of main group and transition metal complexes have been reported to be effective catalysts/initiators for the ROP of lactones/lactides, giving polymers with both high and controlled molecular weights [4]. Among the metals, magnesium, calcium, zinc, aluminum, and tin(II) are attractive due to their low toxicity [1d,2c,5]. The choice of supporting ligands on central metals is crucial to the catalytic behavior of the complexes. Alkoxides are the most widely used ligands. Other chelate ligands are often used as ancillary ligands. These ancillary ligands are not directly involved in the polymerization but do tune the properties of the metallic center and minimize the aggregation processes and side reactions [2c,5i,6]. For example, the metal complexes featuring SALEN or SALAN-type ligands exhibited excellent stereocontrol in the ROP of lactide [7]; the aluminum complexes

featuring biphenolate and methylenebiphenolate ligands showed high catalytic activity in the ROP of lactones and lactides [1d,8]. Recently it was reported that salicylaldiminato-aluminum and -zinc complexes (**I**) were active catalysts in the ROP of ε-CL or lactides [5f,9]. The aluminum and zinc complexes bearing pendant arm tridentate Schiff base (**II**) [10] and related ligand (**III**) [11] were also active catalysts for the ROP of cyclic esters and exhibited good molecular weight control of polymer. In order to compare catalysis with **I–III**, we synthesized aluminum and zinc complexes supported by ligand **IV** and evaluated their catalysis toward ε-CL and *rac*-lactide. Here we report the results.
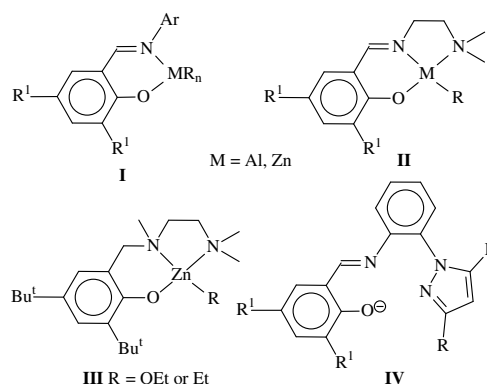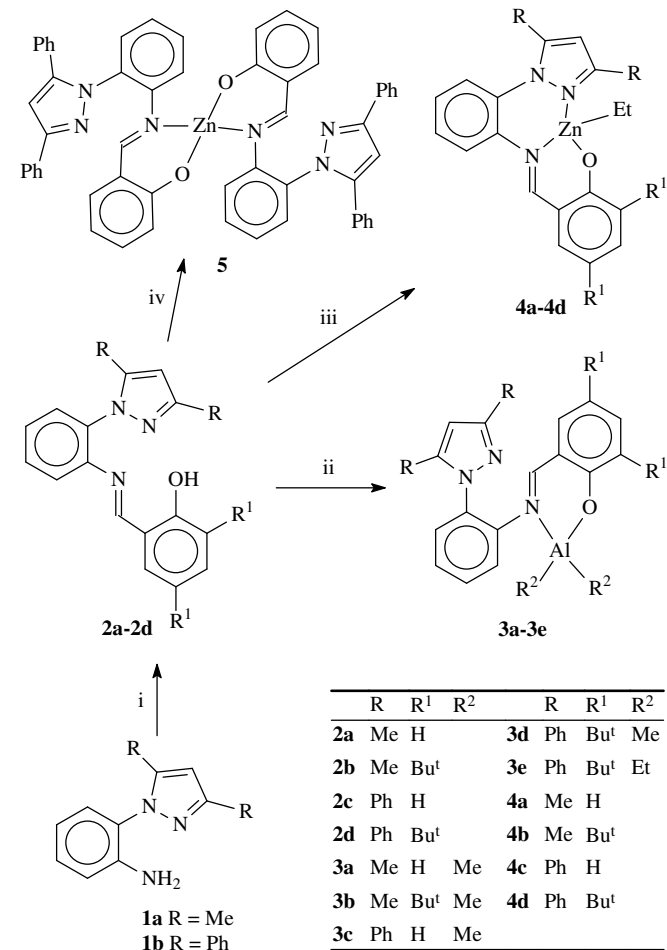

* Corresponding author. Tel.: +86 551 360 3043; fax: +86 551 360 1592.
E-mail address: zxwang@ustc.edu.cn (Z.-X. Wang).

2. Results and discussion

2.1. Synthesis and characterization of compounds 2a–5

Synthesis of compounds **2a–5** are presented in Scheme 1. Acid catalyzed reaction of **1a** and **1b** with salicylaldehyde and 3,5-di-tert-butylsalicylaldehyde, respectively, in the presence of 4A molecular sieves afforded 2-((2-(1H-pyrazol-1-yl)phenylimino)methyl)- phenol derivatives **2a–2d** in high yields. Treatment of **2a-2d** with AlR_3 (R = Me, Et) in toluene afforded N,O-chelate aluminum complexes **3a–3e**. Reaction of **2a–2d** with an equiv. of $ZnEt_2$ gave N,N,O-chelate ethylzinc complexes **4a–4d**; whereas reaction of **2c** with 0.5 equiv. of $ZnEt_2$ formed diphenolato zinc complex **5**. The neutral compounds **2a–2d** are air-stable yellow oil (**2a**) or orange (**2b**) or yellow (**2c** and **2d**) solids. They were characterized by elemental analyses and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The proton signals of the OH groups of **2a–2d** appeared at low field regions (from δ 11.89 to δ 12.67 ppm), showing the existence of intramolecular hydrogen bonds. The other NMR spectral signals were consistent with the respective structure. The aluminum (**3a–3e**) and zinc complexes (**4a–4d**) are air-sensitive crystalline solids. Each of them gave satisfactory elemental analysis. The ^1H and $^{13}C\{^1H\}$ NMR spectra were consistent with their structures. Complex **5** is air-stable yellow crystals and was characterized by
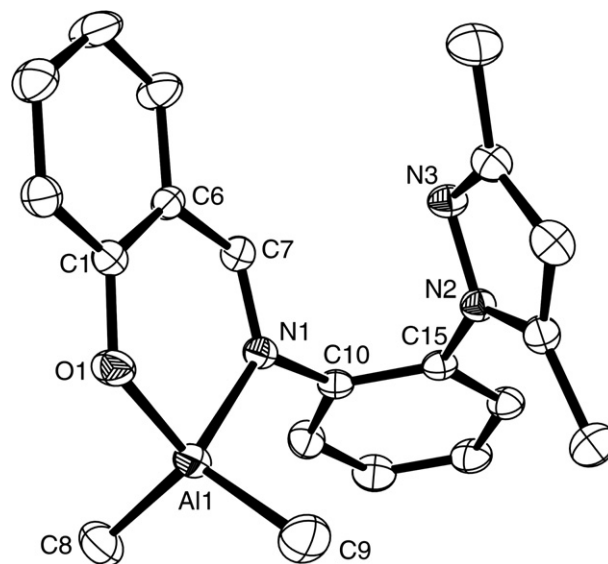

Fig. 1. ORTEP drawing (30% probability) of complex **3a**. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.765(3), Al(1)–N(1) 1.965(3), Al(1)–C(8) 1.943(4), Al(1)–C(9) 1.939(5), O(1)–C(1) 1.331(4), N(1)–C(7) 1.305(4), N(1)–C(10) 1.438(4), O(1)–Al(1)–N(1) 95.31(13), O(1)–Al(1)–C(8) 110.43(18), O(1)–Al(1)–C(9) 112.94(19), C(8)–Al(1)–N(1) 109.01(18), C(9)–Al(1)–N(1) 108.99(18), C(9)–Al(1)–C(8) 117.8(2).

elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In addition, the structures of complexes **3a**, **4a** and **5** were additionally characterized by single crystal X-ray diffraction techniques.

The ORTEP drawing of complex **3a** is presented in Fig. 1, along with selected bond lengths and angles. Crystalline **3a** is monomeric. The ligand coordinates to the central aluminum atom in a bidentate N,O-chelate mode. The aluminum atom is four-coordinate and has a distorted tetrahedral geometry with angles ranging from 95.31(13)° to 117.8(2)°. The most acute angle is associated with the bite angle of the chelate ligand, which is close to corresponding those in [{Sal(Bu^t)}AlEt$_2$] [94.97(6)°] [12] and [Me$_2$-AlOC(Ph)CH{(3,5- Me$_2$C$_3$HN$_2$)-1}] [94.81(13)°] [13]. The fused six-membered ring Al(1)O(1)C(1)C(6)C(7)N(1) is almost coplanar with the phenylene moiety. The Al(1)–O(1) distance of 1.765(3) Å is comparable to those in [{Sal(Bu^t)}AlEt$_2$] [1.772(1) Å], [{Sal(Bu^t)}-Al(Me)Cl] [1.750(5) Å] [12] and [Me$_2$AlOC(Ph)CH{(3,5-Me$_2$C$_3$HN$_2$)-1}] [1.747(3) Å] [13]. The Al(1)–N(1) distance of 1.965(3) Å is close to that in [Et$_2$Al{OC(Me)CHC(Me)N(2,6- Pr$_2^i$C$_6$H$_3$)}] [1.958(2) Å] [14]. The N(1)–C(7) distance of 1.305(4) Å shows a double bond between the atoms. The Al(1)–N(3) distance of 4.645 Å is too far to bond.

The ORTEP drawing of complex **4a** is presented in Fig. 2, along with selected bond lengths and angles. Crystalline **4a** exists in a monomeric form. The ligand bonds to the central zinc atom in a tridentate manner. The Zn atom presents a distorted tetrahedral coordinate geometry with an acute N1(bridge)–Zn–N(pyrazolyl) angle (N(1)–Zn(1)–N(3), 82.55(7)°). The Zn(1)–N(1) distance of 2.0629(19) Å is within the normal range for the bidentate Schiff base zinc complexes such as [Zn{OC$_6$H$_4$(CH=NAr)-o}$_2$] (Ar = m-NO$_2$C$_6$H$_4$ or p-MeOC$_6$H$_4$) [2.006(2)–2.027(3) Å] [15] and [(SalenMe)-ZnEt] [2.012(7) and 2.200(9) Å, respectively] [10b]. The Zn(1)–N(3) distance of 2.105(2) Å is close to that of the Zn–N distances in a pyrazolyl coordinated zinc complex [Zn(Me){OC(O)C(N$_2$C$_3$Me$_2$-3,5)-(N$_2$C$_3$Bu$_2^t$-3′, 5′)}] [2.085(7) and 2.104(6) Å, respectively] [16]. The Zn–O and Zn–C distances are also normal for a four-coordinate zinc complex [15–17].

The ORTEP drawing of complex **5** is displayed in Fig. 3, along with selected bond lengths and angles. The complex is monomeric in the solid state. Each ligand combines the zinc atom in a biden-

Scheme 1. Synthesis of the ligands and aluminum and zinc complexes. *Reagents and conditions:* (i) salicylaldehyde or 3,5-di-tert-butylsalicylaldehyde, 4A molecular sieves, CH$_3$COOH (cat. amount), toluene, refluxed 20 h; (ii) an equiv. of AlR$_3^2$ (R^2 = Me, Et), toluene, −80 °C to r.t., 12 h; (iii) an equiv of ZnEt$_2$, toluene, 0 °C, 2 h, and then r.t., 15 h; (iv) 0.5 equiv. of ZnEt$_2$, toluene, 0–60 °C, 12 h.

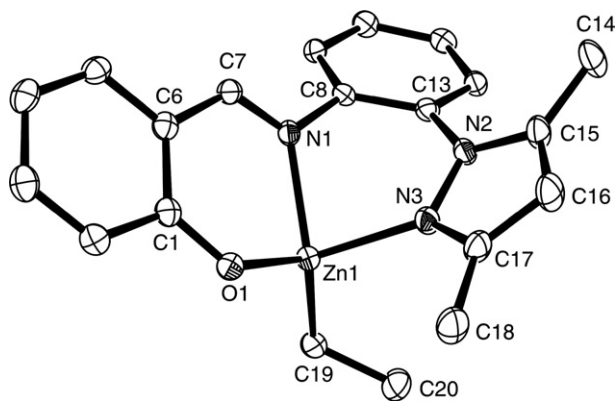|	R	R^1	R^2		R	R^1	R^2
2a	Me	H		**3d**	Ph	Bu^t	Me
2b	Me	Bu^t		**3e**	Ph	Bu^t	Et
2c	Ph	H		**4a**	Me	H	
2d	Ph	Bu^t		**4b**	Me	Bu^t	
3a	Me	H	Me	**4c**	Ph	H	
3b	Me	Bu^t	Me	**4d**	Ph	Bu^t	
3c	Ph	H	Me				

Fig. 2. ORTEP drawing (50% probability) of complex **4a**. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 1.9728(16), Zn(1)–N(1) 2.0629(19), Zn(1)–N(3) 2.105(2), Zn(1)–C(19) 1.981(2), O(1)–C(1) 1.302(3), N(1)–C(7) 1.287(3), N(1)–C(8) 1.428(3), C(6)–C(7) 1.449(3), N(2)–C(13) 1.428(3), N(2)–N(3) 1.376(3), O(1)–Zn(1)–C(19) 121.18(8), O(1)–Zn(1)–N(1) 90.63(7), C(19)–Zn(1)–N(1) 133.93(9), O(1)–Zn(1)–N(3) 108.07(7), C(19)–Zn(1)–N(3) 113.07(9), N(1)–Zn(1)–N(3) 82.55(7), N(1)–C(7)–C(6) 125.3(2), C(7)–N(1)–Zn(1) 124.90(15).
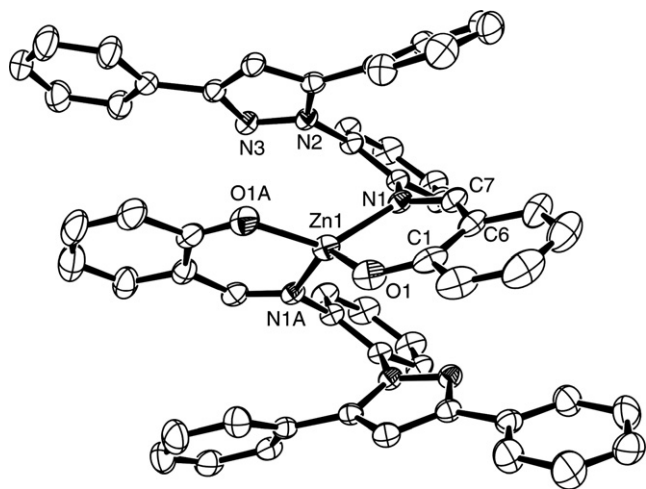

Fig. 3. ORTEP drawing (30% probability) of complex **5**. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.0225(16), Zn(1)–O(1) 1.9092(15), N(1)–C(7) 1.297(3), Zn(1)···N(3) 3.841, O(1)–Zn(1)–N(1) 95.79(7), O(1)–Zn(1)–N(1A) 133.54(7), N(1)–Zn(1)–N(1A) 102.49(9), O(1)–Zn(1)–O(1A) 101.77(10).

tate N,O-chelate manner. The zinc atom is four-coordinate, having a distorted tetrahedral coordinate geometry. The Zn(1)–N(3) distance of 3.841 Å shows no bond interaction between the atoms. The N(1)–Zn(1)–O(1) angle of 95.79(7)° is normal for a N,O-chelate six-membered metallacycle [15]. Both Zn(1)–N(1) and Zn(1)–O(1) distances are shorter than corresponding those in complex **4a**, but close to those found in [Zn{OC₆H₄(CH=NAr)-o}₂] (Ar = m-NO₂C₆H₄ or p-MeOC₆H₄) [15].

2.2. Catalysis of complexes **3a–5** in the ROP of ε-caprolactone

Metal alkoxides are often efficient initiators for the ring-opening polymerization of cyclic esters [1d,2a,2b]. We attempted to prepare aluminum and zinc alkoxides by reaction of the alkyl aluminum and alkyl zinc complexes mentioned in Scheme 1 with an alcohol such as PhCH₂OH and PrⁱOH. However, each reaction gave a mixture. Hence catalysis of complexes **3a–3e** and **4a–4d** in the ring-opening polymerization of ε-caprolactone was tested. The catalytic activities for the ROP of ε-CL of the complexes were deter-

Table 1
The ring-opening polymerization of ε-CL catalyzed by complexes **3a–3e**[a]

Entry	Cat.	Solvent vol. (mL)	Temperature (°C)	Time (min)	Conv. (%)[b]	M_n[c,d]	Yield (%)	PDI[c]
1	**3a**	16	80	780	55.6	39 000	42.8	1.08
2	**3a**	16	110	100	88.5	163 000	73.6	1.05
3	**3a**	20	110	200	100	96 000	81.7	1.02
4	**3b**	16	80	220	69.1	123 000	51	1.07
5	**3b**	20	110	80	96.1	109 000	80.9	1.03
6	**3c**	16	80	290	46.5	120 000	32.4	1.04
7	**3c**	16	110	70	71.7	211 000	60.6	1.07
8	**3c**	20	110	160	94.4	98 000	80.8	1.11
9	**3d**	16	80	240	100	87 000	84.7	1.08
10	**3e**	16	80	200	100	143 000	87.5	1.05

[a] [ε-CL]₀/[Al] = 200:1, [ε-CL] = 13 mmol, solvent:toluene.
[b] Obtained from the ¹H NMR spectral data.
[c] Obtained from GPC analysis and calibrated polystyrene standard.
[d] Using a correcting factor 0.58 for M_n, see Ref. [18].

mined at a [ε-CL]₀/cat. ratio of 200:1 in toluene. The polymerization process was monitored by ¹H NMR spectroscopy, and the monomer conversion was also determined by ¹H NMR spectroscopy. The catalysis of the aluminum complexes **3a–3e** was determined at first. The data are listed in Table 1. In the catalysis of complexes **3b–3c** the conversion of ε-CL can not reach completion in 16 mL of toluene even at elevated reaction temperature and in longer reaction time. In 20 mL of toluene these reaction can go to completion. However, in the reaction catalyzed by **3d** and **3e**, the conversion of the monomer can reach 100% in 16 mL of solvent. The polymerization of ε-CL catalyzed by **3a** proceeded much slower compared with those of **3b–3e**. All these complexes have lower catalytic activity compared with the reported salicylaldiminatoaluminum alkoxides [5f]. In each polymerization reaction the measured molecular weight of polymer was much higher than calculated value (based on living polymerization). For example, the polymerization reaction catalyzed by **3a** in 20 mL of toluene gave polymer with M_n = 96 000, which means that the polymer chains contain about 840 ε-CL units. This and narrow PDI values imply the number of active sites of the catalyst is rather small. The other aluminum complexes gave similar results. It is also seen that the M_n values do not increase with increase of the ε-CL conversion (entries 2, 3, 7 and 8, Table 1). Hence the polymerization reactions did not take place in a living manner. Due to high molecular weights of the polymers, we did not observe the signals of the initiating group in the ¹H NMR spectra of the PCLs. In this case we can not obtain the information of the initiating species. In addition, the catalysis of **3b** toward the ROP of rac-lactide was also tested and the result showed that the complex was inactive for the polymerization of rac-lactide.

The catalysis of the zinc complexes (**4a–4d**) was determined as above and the results are listed in Table 2. It was noticed that the zinc complexes displayed higher catalytic activity than the aluminum complexes. However, the polymerization catalyzed by the zinc complexes also gave high molecular weight polymers. This means that the number of active sites of the catalysts is rather small. For example, the polymerization reaction catalyzed by **4d** in 28 mL of toluene gave polymer with M_n = 167 000, which means that the polymer chains contain about 1450 ε-CL units. That the M_n value did not increase with increase of the ε-CL conversion (entries 4–10, Table 2) indicates that the polymerization reactions were not living.

Complex **5** showed much lower catalytic activity compared with **4a–4d** (Table 3). At 80 °C in 36.5 h only 42.9% of monomer was converted. At a higher temperature (110 °C) the reaction rate increased obviously, 90.6% ε-CL conversion being reached in 430 min. Higher polymerization temperature also led to higher molecular weights of PCLs. The low activity of **5** may be due to

Table 2
The ring-opening polymerization of ε-CL catalyzed by complexes **4a**–**4d**[a]

Entry	Cat.	Solvent vol. (mL)	Time (min)	Conv. (%)[b]	M_n[c,d]	Yield (%)	PDI
1	**4a**	16	90	69	–	–	–
2	**4a**	16	110	86	98 000	75.6	1.06
3	**4a**	24	66	11.1	–	–	–
4	**4b**	16	90	51.6	115 000	38.7	1.01
5	**4b**	24	160	100	101 000	73.7	1.04
6	**4c**	16	37	57.8	138 000	48.3	1.10
7	**4c**	24	64	69.6	125 000	57.3	1.05
8	**4c**	28	160	100	124 000	80.6	1.10
9	**4d**	16	34	76.6	181 000	71.4	1.11
10	**4d**	28	75	100	167 000	82.5	1.06

[a] [ε-CL]$_0$/[Zn] = 200:1, [ε-CL] = 13 mmol, solvent:toluene, reaction temperature: 80 °C.
[b] Obtained from the ^1H NMR spectral data.
[c] Obtained from GPC analysis and calibrated polystyrene standard.
[d] Using a correcting factor 0.58 for M_n, see Ref. [18].

Table 3
The ring-opening polymerization of ε-CL catalyzed by complex **5**[a]

Entry	Temperature (°C)	Time (min)	Conv. (%)[b]	M_n[c,d]	Yield (%)	PDI
1	80	2190	42.9	25,000	30.4	1.03
2	110	430	90.6	166,000	80.9	1.05

[a] Polymerization were performed in 10 mL toluene, [ε-CL]$_0$/[Zn] = 200:1, [ε-CL] = 13 mmol.
[b] Obtained from the ^1H NMR spectral data.
[c] Obtained from GPC analysis and calibrated polystyrene standard.
[d] Using a correcting factor 0.58 for M_n, see Ref. [18].

either the steric hindrance around the zinc atom or the low reactivity of the zinc–oxygen bonds in the complex. Formation of high molecular weight polymers also indicates that the number of active sites of the catalyst remains rather small.

It has been reported that complex **IIIa** was very active catalyst for the ROP of lactide and exhibited good molecular weight control of polylactide, whereas **IIIb** was inactive [11a]. The complexes we have synthesized (**4a**–**4d**) have similar skeletal structure to **III**. It is of interest to compare their catalytic activity toward the ROP of lactide. However, as indicated above, we could not obtain zinc alkoxide derivatives (**6**). Hence, we tested the catalysis of complex **4d** toward the ROP of *rac*-lactide. The reaction was carried out in 8 mL of toluene at 80 °C with 8.17 mM of catalyst concentration and a 1:60 of catalyst to lactide ratio. After 400 min the ^1H NMR spectrum showed that conversion of the monomer reached 91.7%. Gel-permeation chromatography (GPC, *versus* polystyrene standards) analysis revealed an M_n of 12000 g/mol and a molecular weight distribution of 1.03. The homonuclear decoupled ^1H NMR spectrum of methine region of the polymer showed an atactic microstructure.

IIIa R = OEt
IIIb R = Et
6
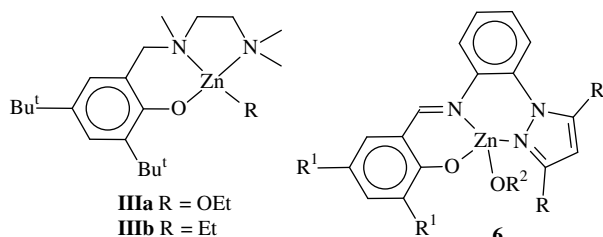
3. Conclusions

We have synthesized novel functionalized phenolate ligands and their aluminum and zinc complexes, including N,O-chelate aluminum complexes, N,N,O-chelate zinc complexes and a bis(N,O-chelate)zinc complex. These complexes exhibited catalytic activity toward the ROP of ε-CL. N,N,O-Chelate zinc complexes behaved higher catalytic activity than the aluminum complexes. Bis(N,O-chelate)zinc complex **5** displayed relatively low catalytic activity. The zinc complex (**4d**) is also active initiator for the ROP of *rac*-lactide, giving atactic polylactide. Each polymerization led to polymer of high molecular weight, and the polymerization did not take place in a living manner.

4. Experimental

4.1. General remarks

All air or moisture sensitive manipulations were performed under 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. ε-Caprolactone, purchased from Acros Organics, was dried over molecular sieves and distilled under reduced pressure prior to use. *rac*-Lactide, purchased from Beijing Yuanshengrong Company, was recrystallized three times from toluene prior to use. CDCl$_3$ and C$_6$D$_6$, purchased from Cambridge Isotope Laboratories, Inc., were degassed and stored over activated 4A molecular sieves (CDCl$_3$) or Na/K alloy (C$_6$D$_6$). Compounds **1a** and **1b** were prepared according to literature methods [19]. All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a Bruker Avance300 spectrometer at ambient temperature. The chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to internal solvent resonances. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China. Molecular weight and the molecular weight distribution were determined on a Waters 150C gel-permeation chromatograph (GPC) equipped with Ultra-Styragel columns (103, 104 and 105 Å) and 410 refractive index detector, using monodispersed polystyrene as calibration standard. THF (HPLC grade) was used as eluent at a flow rate of 1 mL/min.

4.2. Preparation of compounds

4.2.1. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)- phenylimino)methyl)-phenol (**2a**)

To a three necked flask was added successively activated 4A molecular sieves (30 g), 1-(2'-aminophenyl)-3,5-dimethylpyrazole (2.48 g, 13.25 mmol), *o*-hydroxylbenzaldealdehyde (1.65 g, 13.55 mmol), toluene (30 mL) and several drops of anhydrous acetic acid. The mixture was refluxed for 20 h and then cooled to room temperature. The molecular sieves were filtered off and washed with dichloromethane (3 × 20 mL). The combined organic solution were washed with water and then dried over MgSO$_4$. MgSO$_4$ was removed by filtration and volatiles were removed from the filtrate by rotary evaporation to give yellow oil (3.47 g, 90%), which was used without further purification. Anal. Calc. for C$_{18}$H$_{17}$N$_3$O: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.08; H, 5.91; N, 14.49%. δ_H (CDCl$_3$) 1.93 (3H, s, CH$_3$), 2.15 (3H, s, CH$_3$), 5.86 (1H, s, CH), 6.70 (1H, t, J 7.2, C$_6$H$_4$), 6.78 (1H, d, J 8.1, C$_6$H$_4$), 7.11–7.22 (4H, m, C$_6$H$_4$), 7.28–7.33 (2H, m, C$_6$H$_4$), 8.36 (1H, s, CH), 12.14 (1H, s, OH). δ_C (CDCl$_3$) 11.18, 13.42, 105.54, 117.06, 118.82, 118.93, 119.16, 127.10, 128.84, 129.73, 132.41, 133.30, 133.76, 140.59, 144.92, 149.03, 160.83, 163.85.

4.2.2. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenol (**2b**)

Synthesis of compound **2b** followed the same procedure as for **2a**. Thus, a mixture of activated 4A molecular sieves (30 g), 1-(2'-amino-phenyl)-3,5-dimethylpyrazole (2.78 g, 14.86 mmol), 3,5-di-*tert*-

butylsalicyaldehyde (3.56 g, 15.20 mmol), toluene (40 mL) and several drops of anhydrous acetic acid was refluxed for 20 h and then cooled to room temperature. The molecular sieves were filtered off and washed with dichloromethane (3 × 20 mL). The combined organic layers were washed with water and then dried over $MgSO_4$. $MgSO_4$ was removed by filtration and volatiles were removed from the filtrate by rotary evaporation. The residue was dissolved in n-hexane and concentration of the hexane solution afforded orange powder (5.09 g, 85%). M.p. 93–94 °C. Anal. Calc. for $C_{26}H_{33}N_3O$: C, 77.38; H, 8.24; N, 10.41. Found: C, 77.44; H, 8.16; N, 10.20%. δ_H (CDCl$_3$) 1.23 (9H, s, Bu^t), 1.34 (9H, s, Bu^t), 2.00 (3H, s, Me), 2.22 (3H, s, Me), 5.87 (1H, s, CH), 7.04 (1H, d, J 2.4, Ar), 7.24–7.29 (2H, m, Ar), 7.34–7.44 (3H, m, Ar), 8.40 (1H, s, CH), 12.67 (1H, s, OH). δ_C (CDCl$_3$) 11.54, 13.62, 29.44, 31.55, 34.24, 35.21, 105.79, 118.28, 119.87, 126.87, 127.09, 128.46, 128.95, 129.95, 133.78, 137.11, 140.43, 141.05, 145.80, 149.35, 158.47, 165.31.

4.2.3. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)- phenylimino)methyl)-phenol (2c)

Synthesis of compound **2c** followed the same procedure as for **2a**. Thus, a mixture of activated 4A molecular sieves (30 g), 1-(2′-aminophenyl)-3,5-diphenylpyrazole (2.50 g, 8.03 mmol), o-hydroxylbenzaldealdehyde (1.02 g, 8.36 mmol), toluene (30 mL) and several drops of anhydrous acetic acid was refluxed for 20 h and then cooled to room temperature. The molecular sieves were filtered off and washed with dichloromethane (3 × 20 mL). The combined organic layers was washed with water and dried over $MgSO_4$. $MgSO_4$ was removed by filtration and volatiles were removed from the filtrate by rotary evaporation. The residue was crystallized from toluene to afford yellow crystals (2.80 g, 84%). M.p. 151–152 °C. Anal. Calc. for $C_{28}H_{21}N_3O$: C, 80.94; H, 5.09; N, 10.11. Found: C, 81.10; H, 5.08; N, 10.02%. δ_H (CDCl$_3$) 6.68–6.73 (2H, m, Ar+CH), 6.79 (1H, d, J 8.4, Ar), 6.93–7.04 (7H, m, Ar), 7.17–7.24 (2H, m, Ar), 7.27–7.37 (4H, m, Ar), 7.63 (1H, dd, J 1.8 and 7.2, Ar), 7.81–7.83 (3H, m, Ar+CH), 11.89 (1H, s, OH). δ_C (CDCl$_3$) 103.96, 117.24, 118.87, 119.24, 119.97, 126.06, 127.41, 127.83, 128.00, 128.02, 128.32, 128.66, 128.86, 129.97, 130.58, 132.53, 133.22, 133.47, 134.22, 144.91, 146.55, 152.52, 160.91, 164.43.

4.2.4. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenol (2d)

Synthesis of compound **2d** followed the same procedure as for **2a**. Thus, a mixture of activated 4A molecular sieves (30 g), 1-(2′-aminophenyl)-3,5-diphenylpyrazole (3.22 g, 10.34 mmol), 3,5-di-$tert$-butylsalicylaldehyde (2.52 g, 10.75 mmol), toluene (50 mL) and several drops of anhydrous acetic acid was refluxed for 20 h. The molecular sieves were filtered off and washed with dichloromethane (3 × 20 mL). The combined solution was washed with water and dried over $MgSO_4$. The $MgSO_4$ was removed by filtration and volatiles were removed from the filtrate by rotary evaporation. Methanol was added to the residue to give yellow powder (4.80 g, 88%). M.p. 175–176 °C. Anal. Calc. for $C_{36}H_{37}N_3O$: C, 81.94; H, 7.07; N, 7.96. Found: C, 81.84; H, 7.05; N, 7.90%. δ_H (CDCl$_3$) 1.19 (9H, s, Bu^t), 1.31 (9H, s, Bu^t), 6.70 (1H, s, CH), 6.80 (1H, d, J 2.1, Ar), 6.95–7.07 (6H, m, Ar), 7.22–7.39 (6H, m, Ar), 7.62 (1H, dd, J 1.2 and 7.5, Ar), 7.83–7.86 (2H, m, Ar), 7.92 (1H, s, CH), 12.44 (1H, s, OH). δ_C (CDCl$_3$) 29.42, 31.55, 34.18, 35.14, 103.97, 118.36, 120.21, 126.16, 126.96, 127.16, 127.95, 128.19, 128.26, 128.65, 128.80, 129.88, 130.60, 133.38, 134.08, 136.91, 140.28, 145.24, 146.62, 152.56, 158.13, 165.66.

4.2.5. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)-phenylimino)methyl)phenato dimethyl aluminum (3a)

AlMe$_3$ (0.78 mL, a 2.2 M solution in hexane, 1.72 mmol) was added to a solution of **2a** (0.50 g, 1.72 mmol) in toluene (10 mL)

at about −80 °C. The solution was warmed to room temperature and stirred overnight. Solvent was removed under vacuum and the residue was dissolved in Et$_2$O. The mixture was filtered and the filtrate was concentrated to yield yellow crystals of **3a** (0.42 g, 70.4%). M.p. 124–125 °C. Anal. Calc. for $C_{20}H_{22}AlN_3O$: C, 69.15; H, 6.38; N, 12.10. Found: C, 69.19; H, 6.37; N, 12.00%. δ_H (C$_6$D$_6$) −0.36 (6H, s, AlMe), 1.80 (3H, s, Me), 2.07 (3H, s, Me), 5.54 (1H, s, CH), 6.46 (1H, t, J 6.9, C$_6$H$_4$), 6.78–7.05 (6H, m, C$_6$H$_4$), 7.33 (1H, d, J 8.1, C$_6$H$_4$), 8.16 (1H, s, CH). δ_C (C$_6$D$_6$) −8.86, 11.50, 13.37, 106.67, 117.57, 119.11, 122.52, 125.57, 127.92, 129.35, 129.87, 133.68, 135.86, 138.22, 140.93, 143.53, 149.41, 165.71, 175.85.

4.2.6. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butyl phenato dimethyl aluminum (3b)

AlMe$_3$ (0.73 mL, a 2.2 M solution in hexane, 1.61 mmol) was added to a solution of **2b** (0.65 g, 1.61 mmol) in toluene (10 mL) at about −80 °C. The solution was warmed to room temperature and stirred overnight. Volatiles were removed under vacuum and the residue was dissolved in Et$_2$O. The mixture was filtered and the filtrate was concentrated to about 1 mL. To the solution n-hexane (1 mL) was added. The resultant solution was stored at about −30 °C for several days to yield yellow crystals of complex **3b** (0.45 g, 60.9%). M.p. 85–86 °C. Anal. Calc. for $C_{28}H_{38}AlN_3O$: C, 73.17; H, 8.33; N, 9.14. Found: C, 72.94; H, 8.31; N, 9.14%. δ_H (C$_6$D$_6$) −0.32 (6H, s, AlMe), 1.29 (9H, s, Bu^t), 1.51 (9H, s, Bu^t),1.81 (3H, s, Me), 2.13 (3H, s, Me), 5.49 (1H, s, CH), 6.80–7.03 (4H, m, Ar), 7.41 (1H, d, J 7.8, Ar), 7.65 (1H, d, J 2.4, Ar), 8.20 (1H, s, CH). δ_C (C$_6$D$_6$) −8.76, 11.43, 13.49, 29.59, 31.49, 34.12, 35.54, 106.66, 118.93, 125.54, 127.57, 129.53, 130.24, 130.39, 133.17, 133.78, 139.22, 140.91, 140.92, 143.91, 149.29, 162.88, 176.62.

4.2.7. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-phenato dimethyl aluminum (3c)

Complex **3c** was synthesized using a similar procedure to that of **3a**. Thus, reaction of AlMe$_3$ (0.66 mL, a 2.2 M solution in hexane, 1.44 mmol) with **2c** (0.60 g, 1.44 mmol) in toluene (10 mL) from about −80 °C to room temperature afforded, after work-up, yellow crystals of **3c** (0.56 g, 82.3%). M.p. 182–183 °C. Anal. Calc. for $C_{28}H_{38}AlN_3O$: C, 76.42; H, 5.56; N, 8.91. Found: C, 76.50; H, 5.55; N, 8.77%. δ_H (C$_6$D$_6$) −0.44 (6H, s, AlMe), 6.45–6.51 (1H, m, Ar), 6.59 (1H, s, CH), 6.80 (1H, dd, J 1.5 and 7.8, Ar), 6.86–7.15 (9H, m, Ar), 7.24–7.39 (5H, m, Ar), 7.73 (1H, s, CH), 7.74 (1H, d, Ar), 8.01–8.04 (1H, m, Ar). δ_C (C$_6$D$_6$) −9.46, 105.51, 117.43, 119.53, 122.47, 126.00, 126.25, 127.92, 128.24, 128.46, 128.87, 129.01, 129.47, 130.02, 130.23, 133.40, 134.00, 136.11, 138.41, 142.72, 146.54, 153.24, 165.89, 174.87.

4.2.8. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenato dimethyl aluminum (3d)

Complex **3d** was synthesized using a similar procedure to that of **3b**. Thus, reaction of AlMe$_3$ (0.50 mL, a 2.2 M solution in hexane, 1.10 mmol) with **2 d** (0.58 g, 1.10 mmol) in toluene (10 mL) from about −80 °C to room temperature afforded, after similar work-up, yellow crystals of **3d** (0.40 g, 62.4%). M.p. 169–170 °C. Anal. Calc. for $C_{38}H_{42}AlN_3O$: C, 78.19; H, 7.25; N, 7.20. Found: C, 78.23; H, 7.52; N, 7.23%. δ_H (C$_6$D$_6$) −0.55 (6H, s, AlMe), 1.16 (9H, s, Bu^t), 1.53 (9H, s, Bu^t), 6.45 (1H, s, CH), 6.64 (1H, d, J 2.4, Ar), 6.80 (1H, dt, J 1.5 and 7.8, Ar), 6.89 (1H, dt, J 1.8 and 7.8, Ar), 6.98–7.07 (5H, m, Ar), 7.13–7.18 (1H, m, Ar), 7.23–7.30 (4H, m, Ar), 7.65 (1H, d, J 2.7, Ar), 7.67 (1H, s, CH), 7.93–7.97 (2H, m, Ar). δ_C (C$_6$D$_6$) −9.56, 29.58, 31.32, 34.03, 35.53, 105.27, 119.39, 125.78, 126.20, 128.48, 128.93, 128.99, 129.01, 129.68, 129.92, 130.53, 133.35, 133.38, 134.18, 139.17, 140.93, 143.20, 146.89, 153.09, 163.02, 175.54.

4.2.9. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenato diethyl aluminum (3e)

AlEt$_3$ (0.66 mL, a 1.8 M solution in hexane, 1.19 mmol) was added to a solution of **2d** (0.63 g, 1.19 mmol) in toluene (10 mL) at about −80 °C. The mixture was warmed to room temperature and stirred for 1 h and then at 60 °C overnight. Volatiles were removed under vacuum and the residue was dissolved in *n*-hexane. The mixture was filtered and the filtrate was concentrated to afford yellow crystals of **3e** (0.62 g, 85.2%). M.p. 167–168 °C. Anal. Calc. for C$_{40}$H$_{46}$AlN$_3$O: C, 78.53; H, 7.58; N, 6.87. Found: C, 78.23; H, 7.51; N, 6.95%. δ_H (C$_6$D$_6$) −0.05–0.17 (4H, m, AlCH$_2$), 1.15 (9H, s, Bu^t), 1.26 (3H, t, *J* 8.1, CH$_3$), 1.56 (9H, s, Bu^t), 6.48 (1H, s, CH), 6.68 (1H, d, *J* 2.4, Ar), 6.78 (1H, dt, *J* 1.5 and 7.5, Ar), 6.91 (1H, dt, *J* 1.5 and 7.5 Hz, Ar), 7.00–7.07 (4H, m, Ar), 7.14–7.31 (5H, m, Ar), 7.65 (1H, d, *J* 2.4, Ar), 7.84 (1H, s, CH), 7.94 (1H, s, Ar), 7.96 (1H, d, *J* 1.5, Ar). δ_C (C$_6$D$_6$) 0.14, 9.17, 29.14, 30.82, 33.53, 35.06, 104.75, 118.89, 125.32, 125.69, 127.41, 128.37, 128.46, 128.52, 129.24, 129.42, 130.07, 130.18, 132.86, 132.96, 133.65, 138.65, 140.30, 142.75, 146.38, 152.58, 163.01, 175.54.

4.2.10. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)-phenylimino)methyl)-phenato ethyl zinc (4a)

A solution of **2a** (0.45 g, 1.55 mmol) in toluene (3 mL) was added to a solution of ZnEt$_2$ (0.82 cm^3, a 1.89 M solution in hexane, 1.55 mmol) in toluene (6 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. Volatiles were removed under vacuum and the residue was dissolved in Et$_2$O. The solution was filtered and the filtrate was concentrated to yield yellow crystals of **4a** (0.52 g, 88.3%). M.p. 151–152 °C. Anal. Calc. for C$_{20}$H$_{21}$N$_3$OZn: C, 62.43; H, 5.50; N, 10.92. Found: C, 62.56; H, 5.49; N, 10.81%. δ_H (C$_6$D$_6$) 0.75 (2H, q, *J* 8, ZnCH$_2$), 1.55 (3H, t, *J* 8, CH$_3$), 1.65 (3H, s, CH$_3$), 2.33 (3H, s, CH$_3$), 5.46 (1H, s, CH), 6.43 (1H, dt, *J* 0.9 and 7.1, Ar), 6.56–6.64 (2H, m, Ar), 6.76–6.85 (2H, m, Ar), 6.92 (1H, dt, *J* 0.9 and 7.8, Ar), 7.13-7.25 (2H, m, Ar), 7.63 (1H, s, CH). δ_C (C$_6$D$_6$) −1.43, 12.39, 13.37, 13.73, 107.92, 113.56, 119.86, 121.99, 125.11, 125.21, 125.82, 129.44, 130.53, 135.90, 136.07, 142.09, 145.36, 150.57, 166.47, 173.25.

4.2.11. 2-((2-(3,5-Dimethyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenato ethyl zinc (4b)

A solution of **2b** (0.40 g, 1.00 mmol) in *n*-hexane (5 mL) was added to a solution of ZnEt$_2$ (0.53 mL, a 1.89 M solution in hexane, 1.00 mmol) in *n*-hexane (10 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h and at room temperature overnight. The resultant yellow solution was filtered and the filtrate was concentrated under vacuum to afford yellow crystals of **4b** (0.44 g, 89.7%). M.p. 191–192 °C. Anal. Calc. for C$_{28}$H$_{37}$N$_3$OZn: C, 67.67; H, 7.50; N, 8.45. Found: C, 67.68; H, 7.44; N, 8.31%. δ_H (C$_6$D$_6$) 0.79 (2H, q, *J* 8, ZnCH$_2$), 1.38 (9H, s, Bu^t), 1.64 (3H, t, *J* 8, CH$_3$), 1.65 (3H, s, CH$_3$), 1.77 (9H, s, Bu^t), 2.41 (3H, s, CH$_3$), 5.51 (1H, s, CH), 6.55–6.64 (2H, m, Ar), 6.75 (1H, dt, *J* 1.5 and 7.8, Ar), 6.80 (1H, d, *J* 2.4, Ar), 6.89 (1H, dt, *J* 1.2 and 7.5, Ar), 7.61 (1H, s, CH), 7.66 (1H, d, *J* 2.7, Ar). δ_C (C$_6$D$_6$) −1.65, 12.39, 13.41, 13.87, 29.97, 31.73, 34.03, 36.07, 107.77, 118.88, 122.19, 125.11, 125.35, 129.40, 129.73, 130.58, 134.49, 141.96, 142.55, 145.90, 150.27, 167.16, 170.85.

4.2.12. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-phenato ethyl zinc (4c)

Complex **4c** was synthesized using a similar procedure to that of **4a**. Thus, reaction of **2c** (0.46 g, 1.11 mmol) with ZnEt$_2$ (0.59 mL, a 1.89 M solution in hexane, 1.11 mmol) in toluene (15 mL) afforded, after similar work-up, yellow crystals of **4c** (0.50 g, 89.0%). M.p. 232–234 °C. Anal. Calc. for C$_{30}$H$_{25}$N$_3$OZn: C, 70.80; H, 4.95; N, 8.26. Found: C, 70.43; H, 5.03; N, 8.10%. δ_H (C$_6$D$_6$) 0.71 (2H, q, *J* 8.1, ZnCH$_2$), 1.39 (3H, t, *J* 8.1, CH$_3$), 6.40 (1H, s, CH), 6.42–6.48 (2H, m, Ar), 6.54 (1H, dd, *J* 1.2 and 8.1, Ar), 6.64 (1H, dd, *J* 1.2 and 7.8, Ar), 6.81 (1H, dt, *J* 1.5 and 7.8, Ar), 6.89 (1H, dd, *J* 0.9 and 8.1, Ar), 6.93 (5H, s, Ph), 7.12–7.19 (3H, m, Ar), 7.36 (2H, t, *J* 7.5, Ar), 7.84 (1H, s, CH), 8.19 (2H, dd, *J* 1.2 and 8.4, Ar). δ_C (C$_6$D$_6$) −0.61, 13.43, 107.22, 114.04, 119.89, 122.11, 125.17, 125.79, 128.80, 129.03, 129.10, 129.46, 129.56, 130.13, 131.36, 131.86, 136.02, 136.10, 145.37, 147.34, 154.95, 166.83, 173.11.

4.2.13. 2-((2-(3,5-Diphenyl-1H-pyrazol-1-yl)-phenylimino)methyl)-4,6-di-tert-butylphenato ethyl zinc (4d)

Complex **4d** was synthesized using a similar procedure to that of **4a**. Thus, reaction of **2d** (0.44 g, 0.83 mmol) with ZnEt$_2$ (0.45 mL, a 1.89 M solution in hexane, 0.83 mmol) in toluene (10 mL) afforded, after similar work-up, yellow crystals of **4d** (0.42 g, 81.3%). M.p. 230–232 °C. Anal. Calc. for C$_{38}$H$_{41}$N$_3$OZn: C, 73.48; H, 6.65; N, 6.76. Found: C, 73.25; H, 6.68; N, 6.81%. δ_H (C$_6$D$_6$) 0.76 (2H, q, *J* 8.1, ZnCH$_2$), 1.38 (9H, s, Bu^t), 1.51 (3H, t, *J* 8.1, CH$_3$), 1.63 (9H, s, Bu^t), 6.41–6.53 (2H, m, Ar), 6.43 (1H, s, CH), 6.65 (1H, dd, *J* 0.9 and 7.8, Ar), 6.77–6.83 (1H, m, Ar), 6.87 (1H, d, *J* 2.7, Ar), 6.93 (5H, s, Ph), 7.23–7.29 (1H, m, Ar), 7.45 (2H, t, *J* 7.5, Ar), 7.67 (1H, d, *J* 2.4, Ar), 7.85 (1H, s, CH), 8.23 (2H, d, *J* 8.1, Ar). δ_C (C$_6$D$_6$) −0.75, 13.60, 29.87, 31.72, 34.07, 35.91, 107.00, 119.04, 122.09, 125.31, 127.91, 128.74, 129.10, 129.16, 129.46, 129.53, 129.62, 129.68, 130.21, 130.78, 131.17, 134.92, 142.69, 145.72, 147.27, 154.66, 167.14, 170.95.

4.2.14. Bis(2-((2-(3,5-diphenyl-1H-pyrazol-1-yl)-phenylimino)-methyl)phenato)zinc (5)

ZnEt$_2$ (0.32 mL, a 1.89 M solution in hexane, 0.60 mmol) was added to a solution of **2c** (0.50 g, 1.20 mmol) in toluene (20 mL) at 0 °C. The resultant mixture was stirred at 60 °C overnight. The solution was filtered and the filtrate was concentrated to yield yellow crystals of **5** (0.42 g, 80%). M.p. 285–286 °C. Anal. Calc. for C$_{56}$H$_{40}$N$_6$O$_2$Zn: C, 75.21; H, 4.51; N, 9.40. Found: C, 75.26; H, 4.40; N, 9.25%. δ_H (C$_6$D$_6$) 6.15–6.21 (1H, m, Ar), 6.37 (1H, dd, *J* 1.2 and 7.8, Ar), 6.63 (1H, s, CH), 6.67–6.71 (1H, m, Ar), 6.74–6.93 (7H, m, Ar), 7.04–7.08 (2H, m, Ar), 7.12 (1H, s, CH), 7.18–7.27 (3H, m, Ar), 7.33–7.36 (1H, m, Ar), 7.74–7.77 (2H, m, Ar). δ_C (C$_6$D$_6$) 105.88, 113.59, 118.70, 124.26, 125.07, 125.70, 126.02, 126.42, 127.47, 127.85, 127.92, 128.16, 128.23, 128.57, 128.61, 128.72, 129.33, 129.38, 131.55, 133.38, 133.68, 135.97, 136.87, 144.94, 146.18, 153.23, 172.36, 173.12.

4.3. X-Ray crystallography

Single crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A semi-empirical absorption correction was applied to the data. 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 4.

4.4. Polymerization of ε-caprolactone catalyzed by complexes 3a-5

A typical polymerization was exemplified by the synthesis of PCL catalyzed by complex **3b**. Complex **3b** (0.0301 g, 0.065 mmol) was added into a Schlenk tube and followed by injection of a solution of ε-CL (1.49 g, 13.05 mmol) in toluene (16 mL). The flask was put into an oil-bath which was preset at 80 °C. Samples were taken from the reaction mixture using syringe at a desired time interval for ^{1}H NMR spectral analysis. After 220 min the polymerization was quenched by addition of excess glacial acetic acid (0.2 mL) into the solution. After stirring for 0.5 h at room temperature, the

Table 4
Summary of crystal data for complexes **3a**, **4a** and **5**

	3a	4a	5
Empirical formula	$C_{20}H_{22}AlN_3O$	$C_{20}H_{21}N_3OZn$	$C_{56}H_{40}N_6O_2Zn$
Formula weight	347.39	384.77	894.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$	$C2/c$
a (Å)	13.443(3)	25.428(5)	23.583(3)
b (Å)	9.279(2)	9.3262(19)	9.2133(12)
c (Å)	15.742(4)	16.289(3)	20.887(3)
β (°)	90.875(4)	108.32(3)	95.817(2)
V (Å^3)	1963.4(8)	3667.1(13)	4514.8(10)
Z	4	8	4
T (K)	294(2)	113(2)	294(2)
D_{calcd} (g/cm^3)	1.175	1.394	1.316
$F(000)$	736	1600	1856
μ (mm^{-1})	0.115	1.351	0.595
θ range for data collection (°)	1.98 to 25.02	1.69 to 27.87	1.74 to 26.43
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
No. of reflections collected	9650	13739	12481
No. of independent reflections [$R_{(int)}$]	3456 (0.0591)	4370 (0.0373)	4620 (0.0333)
No. of data/restraints/parameters	3456/0/231	4370/0/229	4620/0/294
Goodness-of-fit (GOF) on F^2	1.026	1.067	1.004
Final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0563$, $wR_2 = 0.1253$	$R_1 = 0.0451$, $wR_2 = 0.1044$	$R_1 = 0.0374$, $wR_2 = 0.0829$
R indices (all data)	$R_1 = 0.1306$, $wR_2 = 0.1646$	$R_1 = 0.0509$, $wR_2 = 0.1091$	$R_1 = 0.0621$, $wR_2 = 0.0946$
Largest diff peak and hole [e Å^{-3}]	0.195 and −0.286	0.744 and −0.778	0.202 and −0.238

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

resulting viscous solution was poured into methanol with stirring. The white precipitate was washed three times with hexane and dried under vacuum, giving white solid (0.76 g, 51%).

Acknowledgements

Appendix A. Supplementary material

CCDC 676921, 676921 and 676923 contains the supplementary crystallographic data for **3a**, **4a** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.002.

References

[1] (a) M. Endo, T. Aida, S. Inoue, Macromolecules 20 (1987) 2982;
(b) A. Duda, Z. Florjanczyk, A. Hofman, S. Slomokowski, S. Penczek, Macromolecules 23 (1990) 1640;
(c) B.T. Ko, C.C. Lin, Macromolecules 32 (1999) 8296;
(d) B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, J. Chem. Soc., Dalton Trans. (2001) 2215;
(e) E.P. Wasserman, I. Annis, L.J. Chopin III, P.C. Price, Macromolecules 38 (2005) 322;
(f) G.W. Coates, A.F. Mason, J. Am. Chem. Soc. 126 (2004) 10798.
[2] (a) D. Mecerreyes, R. Jérôme, P. Dubois, Adv. Polym. Sci. 147 (1999) 1;
(b) K.M. Stridsberg, M. Ryner, A.-C. Albertsson, Adv. Polym. Sci. 157 (2002) 41;
(c) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147.
[3] (a) F. Majoumo-Mbe, E. Smolensky, P. Lönnecke, D. Shpasser, M.S. Eisen, E. Hey-Hawkins, J. Mol. Catal. A: Chem. 240 (2005) 91;
(b) K.B. Aubrecht, M.A. Hillmyer, W.B. Tolman, Macromolecules 35 (2002) 644;
(c) J. Wu, T.-L. Yu, C.-T. Chen, C.C. Lin, Coord. Chem. Rev. 250 (2006) 602.
[4] (a) D.K. Han, J.A. Hubbell, Macromolecules 29 (1996) 5233;
(b) B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 3229;

(c) M.H. Chisholm, J.C. Huffman, K. Phomphrai, J. Chem. Soc., Dalton Trans. (2001) 222;
(d) M. Cheng, A.B. Attygalle, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 11583.
[5] (a) Z. Zhong, M.J.K. Ankoné, P.J. Dijkstra, C. Birg, M. Westerhausen, J. Feijen, Polym. Bull. 46 (2001) 51;
(b) I. Taden, H.C. Kang, W. Massa, T.P. Spaniol, J. Okuda, Eur. J. Inorg. Chem. (2000) 441;
(c) M.H. Chisholm, N.J. Patmore, Z.P. Zhou, Chem. Commun. (2005) 127;
(d) H.Y. Ma, G. Melillo, L. Oliva, T.P. Spaniol, U. Englert, J. Okuda, Dalton Trans. (2005) 721;
(e) Z.Y. Zhong, P.J. Dijkstra, J. Feijen, Angew. Chem., Int. Ed. 41 (2002) 4510;
(f) N. Nomura, T. Aoyama, R. Ishii, T. Kondo, Macromolecules 38 (2005) 5363;
(g) M.L. Hseueh, B.H. Huang, C.C. Lin, Macromolecules 35 (2002) 5763;
(h) D.J. Darensbourg, P. Ganguly, D. Billodeaux, Macromolecules 38 (2005) 5406;
(i) L.M. Alcazar-Roman, B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, Dalton Trans. (2003) 3082;
(j) Y.C. Liu, B.T. Ko, C.C. Lin, Macromolecules 34 (2001) 6196;
(k) P. Lecomte, F. Stassin, R. Jérôme, Macromol. Symp. 215 (2004) 325;
(l) A. Kowalski, A. Duda, S. Penczek, Macromolecules 33 (2000) 689;
(m) A. Kowalski, J. Libiszowski, A. Duda, S. Penczek, Macromolecules 33 (2000) 1964;
(n) M.H. Chisholm, N.W. Eilerts, J.C. Huffman, S.S. Lyer, M. Pacold, K. Phomphrai, J. Am. Chem. Soc. 122 (2000) 11845;
(o) T.L. Yu, C.C. Wu, C.C. Chen, B.H. Huang, J.C. Wu, C.C. Lin, Polymer 46 (2005) 5909;
(p) H.Y. Chen, B.H. Huang, C.C. Lin, Macromolecules 38 (2005) 5400;
(q) A. Dumitrescu, B. Martin-Vaca, H. Gornitzka, J.B. Cazaux, D. Bourissou, G. Bertrand, Eur. J. Inorg. Chem. (2002) 1948;
(r) W. Yao, Y. Mu, A. Gao, Q. Su, Y. Liu, Y. Zhang, Polymer 49 (2008) 2486;
(s) A. Amgoune, L. Lavanant, C.M. Thomas, Y. Chi, R. Welter, S. Dagorne, J.-F. Carpentier, Organometallics 24 (2005) 6279;
(t) F. Majoumo-Mbe, E. Smolensky, P. Lönnecke, D. Shpasser, M.S. Eisen, E. Hey-Hawkins, J. Mol. Catal. A: Chem. 240 (2005) 91;
(u) N. Iwasa, J. Liu, K. Nomura, Catal. Commun. 9 (2008) 1148.
[6] Y. Sarazin, R.H. Howard, D.L. Hughes, S.M. Humphrey, M. Bochmann, Dalton Trans. (2006) 340.
[7] (a) P. Hormnirun, E.L. Marshall, V.C. Gibson, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 126 (2004) 2688;
(b) T.M. Ovitt, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 4072;
(c) B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 3229;
(d) T.M. Ovitt, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 1316;
(e) Z. Zhong, P.J. Dijkstra, J. Feijen, Angew. Chem., Int. Ed. 41 (2002) 4510;
(f) Z. Zhong, P.J. Dijkstra, J. Feijen, J. Am. Chem. Soc. 125 (2003) 11291;
(g) C.P. Radano, G.L. Baker, M.R. Smith III, J. Am. Chem. Soc. 122 (2000) 1552;
(h) N. Nomura, R. Ishii, M. Akakura, K. Aoi, J. Am. Chem. Soc. 124 (2002) 5938;
(i) K. Majerska, A. Duda, J. Am. Chem. Soc. 126 (2004) 1026;
(j) J. Belleney, M. Wisniewski, A. Le Borgne, Eur. Polym. J. 40 (2004) 523;

(k) Z. Tang, X. Chen, X. Pang, Y. Yang, X. Zhang, X. Jing, Biomacromolecules 5 (2004) 965;

(l) M.R.T. Breteler, Z. Zhong, P.J. Dijkstra, A.R.A. Palmans, J. Peeters, J. Feijen, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 429;

(m) N. Nomura, R. Ishii, Y. Yamamoto, T. Kondo, Chem. -Eur. J. 13 (2007) 4433.

[8] (a) M.-L. Hsueh, B.-H. Huang, C.C. Lin, Macromolecules 35 (2002) 5763;

(b) T.-C. Liao, Y.-L. Huang, B.-H. Huang, C.C. Lin, Macromol. Chem. Phys. 204 (2003) 885;

(c) C.-T. Chen, C.-A. Huang, B.-H. Huang, Macromolecules 37 (2004) 7968;

(d) H.-L. Chen, B.-T. Ko, B.-H. Huang, C.C. Lin, Organometallics 20 (2001) 5076;

(e) B.-H. Huang, C.-N. Lin, M.-L. Hsueh, T. Athar, C.C. Lin, Polymer 47 (2006) 6622;

(f) Y.-C. Liu, B.-T. Ko, C.C. Lin, Macromolecules 34 (2001) 6196.

[9] M.H. Chisholm, J.C. Gallucci, H. Zhen, Inorg. Chem. 40 (2001) 5051.

[10] (a) J. Lewinski, P. Horeglad, M. Dranka, I. Justyniak, Inorg. Chem. 43 (2004) 5789;

(b) J.-C. Wu, B.-H. Huang, M.-L. Hsueh, S.-L. Lai, C.-C. Lin, Polymer 46 (2005) 9784.

[11] (a) C.K. Williams, L.E. Breyfogle, S.K. Choi, W. Nam, V.G. Young Jr., M.A. Hillmyer, W.B. Tolman, J. Am. Chem. Soc. 125 (2003) 11350;

(b) D. Zhang, J. Xu, L. Alcazar-Roman, L. Greenman, C.J. Cramer, M.A. Hillmyer, W.B. Tolman, Macromolecules 37 (2004) 5274;

(c) K.M. Schreck, M.A. Hillmyer, Tetrahedron 60 (2004) 7177.

[12] M.S. Hill, A.R. Hutchison, T.S. Keizer, S. Parkin, M.A. VanAelstyn, D.A. Atwood, J. Organomet. Chem. 628 (2001) 71.

[13] Z.-X. Wang, D. Yang, J. Organomet. Chem. 690 (2005) 4080.

[14] R.-C. Yu, C.-H. Hung, J.-H. Huang, H.-Y. Lee, J.-T. Chen, Inorg. Chem. 41 (2002) 6450.

[15] L. Tatar, D. Ülkü, O. Atakol, Acta Crystallogr., Sect. C 55 (1999) 508.

[16] I. Hegelmann, A. Beck, C. Eichhorn, B. Weibert, N. Burzlaff, Eur. J. Inorg. Chem. (2003) 339.

[17] (a) A. Dumitrescu, B. Martin-Vaca, H. Gornitzka, J.-B. Cazaux, D. Bourissou, G. Bertrand, Eur. J. Inorg. Chem. (2002) 1948;

(b) W. Kläui, M. Berghahn, W. Frank, G.J. Reiß, T. Schönherr, G. Rheinwald, H. Lang, Eur. J. Inorg. Chem. (2003) 2059.

[18] H. Ma, J. Okuda, Macromolecules 39 (2006) 128.

[19] A. Mukherjee, U. Subramanyam, V.G. Puranik, T.P. Mohandas, A. Sarkar, Eur. J. Inorg. Chem. (2005) 1254.

[20] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[21] G.M. Sheldrick, SHELXL97, Programs for Structure Refinement, Universität Göttingen, 1997.