Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2013, **42**, 1278

Bis(imino)diphenylamido rare-earth metal dialkyl complexes: synthesis, structure, and catalytic activity in living ring-opening ε-caprolactone polymerization and copolymerization with γ-butyrolactone†

Gaixia Du,‡[a,b] Yanling Wei,‡[a] Wei Zhang,[a] Yuping Dong,[b] Zhengguo Lin,[a] Huan He,[a] Shaowen Zhang*[a] and Xiaofang Li*[a]

Received 24th August 2012,
Accepted 18th October 2012

DOI: 10.1039/c2dt31932b

www.rsc.org/dalton

Bis(imino)diphenylamido rare-earth metal dialkyl complexes [*o*-(2,6-$^{i}Pr_2$-C_6H_3–N=C–C_6H_4)$_2$–N]Ln-(CH_2SiMe_3)$_2$ (**1**: Ln = Sc; **2**: Ln = Lu; **3**: Ln = Y) have been synthesized in good yields and structurally characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction studies. They serve as highly efficient single-component catalysts both for the living ring-opening ε-caprolactone polymerization and random copolymerization with γ-butyrolactone, with the activity being dependent on the steric hindrance around the metal center, yielding high molecular weight PCLs or P(CL-*co*-BL)s with narrow molecular weight distributions.

Introduction

Biodegradable polymers have received much current interest because of increasing demand for plastic materials and some serious disadvantages of oil-based poly(olefin)s such as environmental problem, economic pressure and petroleum resource shortage. Poly(ε-caprolactone) (PCL), which has main characteristics of biodegradability, biocompatibility and potential availability from renewable resource starch,[1] is one of the most promising, environmentally friendly commodity plastic for numerous biomedical and pharmaceutical applications. Since the first synthesis of PCL was reported by more than half a century ago,[2] extensive studies have been carried out in this area. A variety of ways such as polycondensation,[3] enzymatic polymerization,[4] cationic polymerization,[5] anionic polymerization,[6] or coordination/insertion polymerization[7] have been adopt for the synthesis of PCL. Among them, the coordination/insertion polymerization catalyzed by metal complexes based on magnesium,[8] calcium,[9] aluminium,[10] zinc,[11] titanium,[12] zirconium,[13] vanadium,[14] iron,[15] tin,[16] lanthanides and rare earth metals[17] offers a means from control over the polymer structure to kinetic enhancement, producing PCLs with high molecular weights. By comparison, low toxic rare earth metal catalysts bearing alkoxides,[18] beta-diketiminate,[19] bis(amidinate),[20] aryloxide[21] ligands usually exhibited higher activities than other metal catalysts in the ring opening polymerization of ε-caprolactone. However, few cases exhibit exceptional activity and living mode.[22] Therefore, there is an impetus to develop highly efficient rare-earth metal catalysts, producing biodegradable PCL at low cost with improved property.

In view that the use of bulky ligand for metal complex reduces transesterification reactions and usually yields PCL with narrow polydispersity in the coordination/insertion polymerization of ε-caprolactone (CL), the sterically demanding pincer ligand is considered to be good choice for the design of new rare-earth metal catalyst. Pincer ligand represents one of the most widely utilized tridentate chelating ligand in organometallic chemistry. Until now, metal pincer complexes are widely used in olefin polymerization, catalysis and bond activation.[23] Early examples of pincer ligand are monoanionic PCP in which a carbanion is located in the central site and two phosphines are placed in flank.[24] Subsequently, variations have been developed where the phosphines are replaced by thioethers and tertiary amines or the nitrogenous donors such as pyridines are introduced at the central position.[25] Despite these extensive efforts, however, the

[a]*Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China. E-mail: xfli@bit.edu.cn, swzhang@bit.edu.cn; Fax: +86 10-68914780; Tel: +86 10; Fax: -68914780*

[b]*School of Materials Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China*

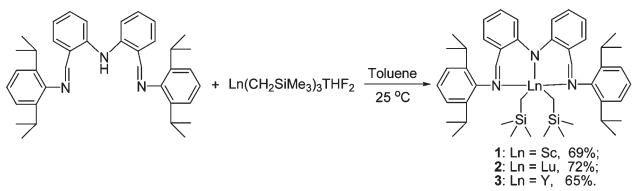
†Electronic supplementary information (ESI) available: GPC, DSC, and NMR (^{1}H and ^{13}C) spectra of representative polymer products. CCDC 857397 (**1**), 857396 (**2**), and 857398 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31932b

‡G. Du and Y. Wei contributed equally to this paper.

monoanionic NNN pincer ligands are less exploited.[26] The metal complexes bearing a monoanionic bis(imino)diphenylamido pincer ligand have not been reported previously.[27] Their catalytic potential for the olefin polymerization has remained unexplored to date, as far as we are aware. We report herein the synthesis and structural characterization of novel bis(imino)diphenylamido rare-earth metal dialkyl complexes. They serve as highly efficient single-component catalysts in the living ring-opening polymerization of CL, with the activity being significantly dependent on the steric hindrance around the metal center, yielding high molecular weight PCLs with narrow molecular weight distributions. Moreover, the random copolymerization of CL and γ-butyrolactone (BL) can be also carried out by these complexes, yielding high molecular weight copolymers with BL contents up to 18 mol%.[28]

Results and discussion

The monoanionic bis(imino)diphenylamido NNN pincer ligand was synthesized according to the literature.[29] The acid–base reaction between the rare-earth metal trialkyl complex Ln-$(CH_2SiMe_3)_3(THF)_2$[30] and the bis(imino)diphenylamido pincer ligand in toluene at 25 °C afforded in high yields the corresponding bis(imino)diphenylamido rare-earth metal dialkyl complexes **1–3** [*o*-(2,6-^{i}Pr$_2$-C$_6$H$_3$–N=C–C$_6$H$_4$)$_2$–N]Ln-$(CH_2SiMe_3)_2$ (**1**: Ln = Sc, 69%; **2**: Ln = Lu, 72%; **3**: Ln = Y, 65%) (Scheme 1). All complexes **1–3** are soluble in THF, toluene, and benzene. ^{1}H NMR spectra of complexes **1–3** indicated that four similar doublets for the isopropyl-methyl group between 0.8–2.0 ppm integrating for twenty-four protons and another singlet for the imino-methine groups at 8.20 ppm integrating for two protons were observed, implying a symmetry in the chelating pincer ligand. No THF molecule which showed signals at 1.70 and 3.50 ppm was found. Two double signals for the methylene protons of the Ln–CH_2SiMe_3 groups at high field (**1**: 0.04 ppm (d, 2 H, J = 11.6 Hz), 0.18 ppm (d, 2 H, J = 11.6 Hz); **2**: −0.70 ppm (d, 2 H, J = 12.0 Hz), −0.59 ppm (d, 2 H, J = 12.0 Hz); **3**: −0.47 ppm (d, 2 H, J = 11.2 Hz), −0.42 ppm (d, 2 H, J = 11.6 Hz)) indicated that the metal alkyl species in **1–3** are fixed in the solution state, which could not rotate freely. That the ^{1}H NMR spectra of complex **3** had no changes according to the temperature range 25 to −40 °C (Fig. 1) also ascertained this conclusion. These results suggested that the complexes **1–3** bearing bis(imino)diphenylamido pincer ligand have large steric hindrance around metal center.



Scheme 1 Synthesis of bis(imino)diphenylamido rare-earth metal dialkyl complexes.

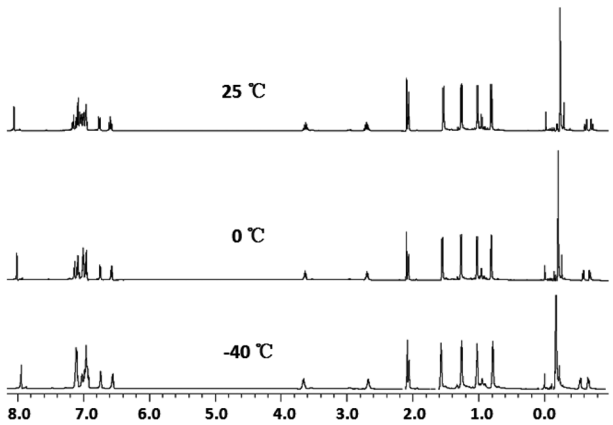


Fig. 1 Variable temperature ^{1}H NMR (600 MHz, C_7D_8) of complex **3**.

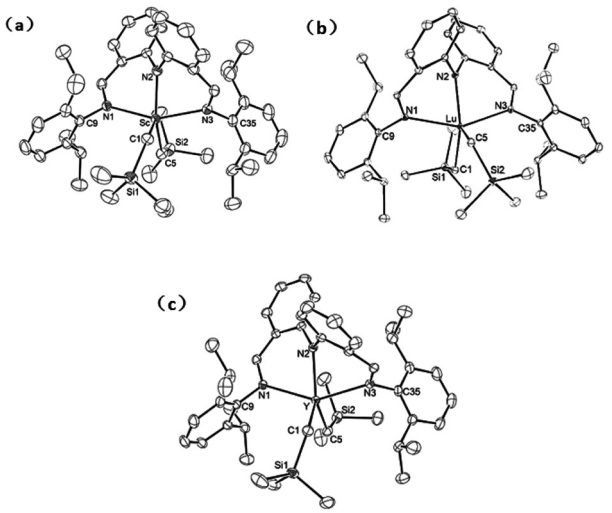


Fig. 2 ORTEP drawings of **1** (a), **2** (b) and **3** (c) with 30% thermal ellipsoids. The hydrogen atoms in **1**, **2** and **3** and one toluene solvent molecule are omitted for clarity.

Single crystals of complexes **1–3** suitable for an X-ray determination were grown from a concentrated toluene–hexane mixture solution at −30 °C. The X-ray diffraction study revealed that complexes **1–3** are isostructural and isomorphous (Fig. 2, Table 1). Table 2 provides selected bond lengths and angles for complex **1–3**. Each of complex **1–3** (τ = 0.2–0.3) adopts a distorted square pyramidal geometry, in which the rare-earth metal center is boned with one monoanionic bis(imino)diphenylamido unit and two trimethylsilylmethyl groups. The Ln–N bond with the negatively charged amido nitrogen N(2) is significantly shorter at 2.141(2)–2.282(2) Å than the Ln–N bonds with the neutral imino nitrogens N(1) and N(3) at 2.327(2)–2.457(2) Å. Because of the ionic radius of the metal center in a trend of Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å), the bond distances of the chelating Ln–N(1), Ln–N(2), Ln–N(3), Ln–C(1) as well as Ln–C(5) bond increase in order of **1** < **2** < **3**.

The Ln–N(2) bonds of complexes **1–3** divide the angles of N(1)–Ln–N(3) (147.2(1)–154.0(1)°) into two almost equal parts

Table 1 Crystallographic data and structure refinement details for complex **1–3**

	1	**2**	**3**
Formula	$C_{53}H_{74}N_3ScSi_2$	$C_{53}H_{74}N_3LuSi_2$	$C_{53}H_{74}N_3YSi_2$
f_w	854.29	984.30	898.24
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	13.661(2)	13.3938(8)	13.506(1)
b (Å)	18.871(3)	18.7363(12)	18.827(1)
c (Å)	20.672(3)	20.5867(13)	20.695(1)
B (°)	97.225(5)	97.4890(10)	9 7.347(1)
V (Å^3)	5286.9(1)	5122.2(6)	5219.0(5)
Z	4	4	4
D_c (Mg m^{-3})	1.073	1.276	1.143
μ (mm^{-1})	0.219	2.010	1.198
F (000)	1848	2048	1920
θ range	2.01 to 25.02°	1.53 to 25.02°	3.23 to 25.02°
No. of reflns collected	58 700	24 877	24 387
No. of indep reflns	9346 (R_{int} = 0.0446)	8997 (R_{int} = 0.0176)	9178 (R_{int} = 0.0259)
Completeness to θ	100.0%	99.5%	99.7%
Max. and min. transmn	0.9273/0.9079	0.4857/0.4649	0.6791/0.6146
No. of data/restraints/params	9346/0/579	8997/0/543	9178/0/548
Goodness-of-fit on F^2	1.055	1.198	1.017
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0446, wR_2 = 0.1060	R_1 = 0.0204, wR_2 = 0.0731	R_1 = 0.0329, wR_2 = 0.0725
R indices (all data)	R_1 = 0.0648, wR_2 = 0.1232	R_1 = 0.0229, wR_2 = 0.0870	R_1 = 0.0488, wR_2 = 0.0782
Largest diff. Peak and hole, e Å^{-3}	0.302/−0.283	1.039/−0.882	0.293/−0.242

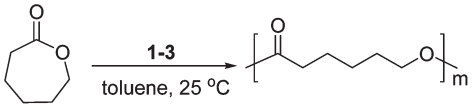
Table 2 Selected bond lengths [Å] and angles [°] for complex **1–3**

	1	**2**	**3**
Ln=	Sc	Lu	Y
Ln–N1	2.342(2)	2.407(2)	2.457(2)
Ln–N2	2.141(2)	2.239(2)	2.282(2)
Ln–N3	2.327(2)	2.382(2)	2.429(2)
Ln–C1	2.226(2)	2.345(3)	2.383(2)
Ln–C5	2.224(2)	2.333(3)	2.390(2)
∠N1–Ln–N2	77.5(1)	75.4(1)	73.8(1)
∠N2–Ln–N3	77.7(1)	74.9(1)	74.6(1)
∠N1–Ln–N3	154.0(1)	149.2(1)	147.2(1)
∠N2–Ln–C1	112.6(1)	112.7(1)	113.3(1)
∠N2–Ln–C5	135.7(1)	134.9(1)	134.2(1)
∠C1–Ln–C5	111.7(1)	112.2(1)	112.4(1)
∠N1–Ln–C1	99.9(1)	96.4(1)	103.4(1)
∠N1–Ln–C5	97.4(1)	96.3(1)	99.1(1)
∠N3–Ln–C1	96.4(1)	102.5(1)	97.1(1)
∠N3–Ln–C5	95.2(1)	98.8(1)	96.3(1)
∠C9–N1–Ln	124.5(1)	130.9(2)	120.5(1)
∠C35–N3–Ln	131.8(1)	120.9(2)	131.5(1)
Ln–N1N2N3	−0.195(2)	0.230(2)	−0.262(2)
C1–N1N2N3	−2.318(3)	−2.459(4)	−2.540(4)
C5–N1N2N3	1.207(4)	1.252(5)	1.250(5)
C9–N1N2N3	−0.793(3)	0.766(4)	−0.755(3)
C35–N1N2N3	0.858(4)	−0.861(4)	0.839(3)
∠N1LnN3–N1N2N3	21.5(1)	22.3(1)	21.1(1)
∠C1LnC5–N1N2N3	88.9(1)	87.8(1)	87.7(1)
∠C9–C14–N1N2N3Ln	67.4(1)	70.2(1)	70.5(1)
∠C35–C40–N1N2N3Ln	53.8(1)	53.0 (1)	52.3 (1)

N(1)–Ln–N(2) and N(2)–Ln–N(3) (73.8(1)–77.7(1)°), suggesting the N(1), N(2), N(3) and Ln atom are almost planar. These angles decrease in order of **1** > **2** > **3**. Whereas the angles of C(35)–N(3)–Ln increased in a trend of **1** (114.7(1)°) < **2** (130.9(2)°) < **3** (131.5(1)°). These results show that this pincer ligand occupy the less steric space around the larger metal center. The Ln, C(1), and C(5) atoms have slightly folded geometry with the NNN plane. The Ln–NNN distances in complexes **1–3** are much shorter, only lying 0.195(2)–0.262(2) Å out of the NNN plane. The dihedral angels of the best planes of N(1)–Ln–N(3) and NNN are around 21.1(1)–22.3(1)°, consistent with an almost planar four-membered metallacyclic ring (NNNLn) in complexes **1–3**. In contrast, the distances of C(1) and C(5) to the NNN plane in complexes **1–3** are much longer (about 1.207(4)–1.250(5) Å and 2.318(3)–2.540(4) Å, respectively) and increase in order of **1** < **2** < **3**. As a result, the steric environment around rare-earth metal center decreases as the follow: **1** > **2** > **3**.

A preliminary study showed that the complexes **1–3** alone exhibited very high activities in the ring-opening polymerization of ε-caprolactone (Table 3). Moreover, their activities depended on the steric hindrance around the metal center. The sterically demanding scandium complex **1** showed the lowest activities *ca.* 1.0 × 10^5 g mol^{-1} h^{-1}, which converted 4000 equiv. of CL in 4 h at room temperature (Table 3, entries 1–2). By contrast, the relatively bulky lutetium complex **2** exhibited much higher activities up to 1.6 × 10^6 g mol^{-1} h^{-1} under the same condition (Table 3, entries 3–8). It could completely convert 12 000 equiv. of CL in 3 h, yielding high molecular weight PCL (M_n = 310 000 g mol^{-1}) with relatively narrow molecular weight distribution (M_w/M_n = 1.57) (Table 3, entry 8). It is noteworthy that the less bulky yttrium complex **3** exhibited exceptional activities up to 5.5 × 10^7 g mol^{-1} h^{-1} in the ring-opening polymerization of CL (Table 3, entries 9–23). Only 2 hours was needed to completely convert 12 000 equiv. of monomer, producing high molecular weight PCL (M_n = 920 000 g mol^{-1}) with narrow molecular weight distribution (M_w/M_n = 1.39) (Table 3, entry 16). The order of the gradually increased activities from **1** to **3** is consistent with the increased trend of their ionic radius of the metal center. Such an "ionic radius effect" on the catalytic activity was also observed

Table 3 Polymerization of ε-caprolactone by bis(imino)diphenylamido rare-earth metal dialkyl complexes **1–3**[a]



Entry	Cat. (Ln)	CL (mmol)	[CL]/[Cat.]	t (min)	T (°C)	Yield (%)	Act.[b]	M_n[c] (10^4)	M_w/M_n[c]	T_m[d] (°C)
1	**1**(Sc)	10	2000	120	25	100	0.1	17	1.26	59
2	**1**(Sc)	20	4000	240	25	100	0.1	26	1.35	57
3	**2**(Lu)	10	2000	15	25	100	0.9	17	1.35	57
4	**2**(Lu)	20	4000	20	25	100	1.4	25	1.45	58
5	**2**(Lu)	30	6000	25	25	100	1.6	54	1.41	57
6	**2**(Lu)	40	8000	60	25	100	0.9	58	1.50	58
7	**2**(Lu)	50	10 000	120	25	100	0.6	60	1.51	56
8	**2**(Lu)	60	12 000	180	25	100	0.5	31	1.57	56
9	**3**(Y)	5	1000	2	25	100	3.4	10	1.21	57
10[e]	**3**(Y)	5 + 5	2000	5	25	100	2.7	25	1.22	57
11	**3**(Y)	10	2000	5	25	100	2.7	24	1.25	57
12	**3**(Y)	20	4000	10	25	100	2.7	36	1.26	57
13	**3**(Y)	30	6000	15	25	100	2.7	54	1.36	56
14	**3**(Y)	40	8000	20	25	100	2.7	69	1.39	57
15	**3**(Y)	50	10 000	40	25	100	1.7	80	1.40	57
16	**3**(Y)	60	12 000	120	25	100	0.7	92	1.39	57
17	**3**(Y)	40	8000	1	25	56	30.7	53	1.26	55
18	**3**(Y)	40	8000	3	25	76	13.9	59	1.32	56
19	**3**(Y)	40	8000	5	25	86	9.5	63	1.31	57
20	**3**(Y)	40	8000	15	25	96	3.5	67	1.34	55
21	**3**(Y)	40	8000	10	50	100	5.5	63	1.37	56
22	**3**(Y)	40	8000	5	70	100	11.0	73	1.51	55
23	**3**(Y)	40	8000	1	90	100	54.8	44	1.58	56

[a] Conditions: 5 μmol of catalyst, 30 mL of toluene. [b] Activity in 10^6 g mol^{-1} h^{-1}. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Measured by DSC. [e] Polymerization of 1000 equiv. of CL in 30 mL of toluene for 2 min followed by the addition of 1000 equiv. of CL for another 3 min.

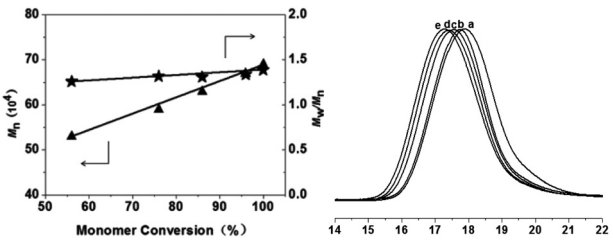


Fig. 3 Plot of monomer conversions *vs.* molecular weights and molecular weight distributions of the PCLs (a–e: Table 3, entries 14, 17–20).

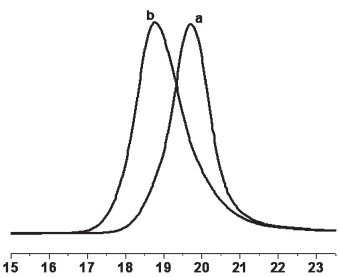


Fig. 4 Plot of molecular weights and molecular weight distributions of the PCLs (a: Table 3, entry 9; b: Table 3, entry 10).

previously in the rare-earth-metal-catalyzed ε-caprolactone polymerization.[31] These catalysts also behaved living nature in the ring-opening polymerization of CL. For complex **3**, with an increase in the monomer conversion, the molecular weight of the resultant PCL increased linearly from 530 000 to 690 000 g mol^{-1}, whereas the molecular weight distribution remained very narrow (M_w/M_n = 1.26–1.39) (Fig. 3, Table 3, entries 14, 17–20). Moreover, after complete consumption of the first 1000 equiv. of CL in 2 min, the polymer chain ends are still active and continually concerted the second 1000 equiv. of CL to PCL in 3 min (Table 3, entries 9–10). The molecular weight of the resulting PCL increased from 100 000 g mol^{-1} (M_w/M_n = 1.21) to 250 000 g mol^{-1} (M_w/M_n = 1.22), whereas the molecular weight distributions remained unchanged (Fig. 4). These results demonstrated that the complex **3** indeed has the living character. In addition, the temperature has significant influence on the activity. With the temperature increasing from 25 to 90 °C, the activity of complex **3** gradually increased from 2.7 to 54.8 × 10^6 g mol^{-1} h^{-1} (Table 3, entries 14, 21–23).

The GPC curves of the resulting PCLs are all unimodal with narrow molecular weight distributions (M_w/M_n = 1.21–1.58), in consistence with the predominance of a homogeneous single-site catalytic species. The ^{1}H NMR spectrum of PCL (Fig. 5, complex **3**, [CL]/[Y] = 100) displays the presence of an end group of $HOCH_2$– which assigns its methylene protons signal at 3.64 ppm. The resonances for the other end group –$COCH_2SiMe_3$ derived from the coordination/insertion of CL into metal alkyl species Ln–CH_2SiMe_3 are observed at 0.07 (SiMe_3) and 0.11 (CH_2) ppm.

Remarkably, the complexes **2** and **3** also showed good activities in the ring-opening copolymerization of ε-caprolactone and γ-butyrolactone (BL), even though these catalysts could not promote the ring-opening polymerization of BL. Some representative results are summarized in Table 4. The complex **2** showed higher activity (1.4×10^5 g mol^{-1} h^{-1}) than complex **3** (0.6×10^5 g mol^{-1} h^{-1}) in the equal amount of CL and BL at room temperature. Whereas the resulting poly(CL-*co*-BL) has less BL content (*ca*. 12 mol%) than that obtained by complex **3** (BL content *ca.* 15 mol%) (Table 4, entries 1 and 6). Moreover, the resulting copolymer by complex **2** has bad solubility in THF, as a result the molecular weight could not been obtained. For the complex **3**, with the increased mole ratio of CL and BL monomer from 3 : 1 and 1 : 3, the BL contents of the resulting copolymers also increased from 6 mol% to 18 mol% (Table 4, entries 2–7).

The copolymers obtained by complex **3** show good solubilities in THF and benzene. The ^{1}H NMR and ^{13}C NMR spectrum suggest random distribution of the monomer moieties in the copolymer products (Fig. 6 and 7). The GPC curves of the copolymers are all unimodal with moderate polydispersities (M_w/M_n = 1.31–1.71), in consistence with the predominance of a homogeneous single-site catalytic species. The metal temperature (T_m) of the copolymers shows a decreased tendency correlation with the increased γ-butyrolactone content.

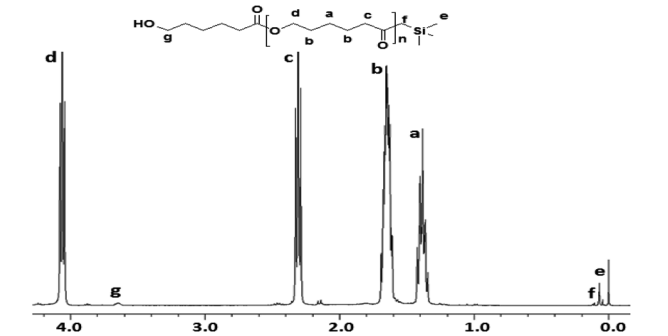


Fig. 5 ^{1}H NMR spectrum of PCL.

Experimental section

General methods

All manipulations of air and moisture-sensitive compounds were performed under a nitrogen atmosphere in an Mbraun glovebox. Anhydrous toluene, THF and hexane were purified by use of a SPS-800 solvent purification system (Mbraun), and dried over fresh Na chips in the glovebox. ε-Caprolactone was purchased from J&K Chemical, dried over CaH_2, vacuum-transferred, and degassed by two freeze–pump–thaw cycles prior to polymerization experiments. $LnCl_3$ was purchased from Strem. $LiCH_2SiMe_3$ (1.0 M solution in pentane) was purchased from Aldrich and used as received. The anionic NNN bis(imino)-diphenylamide pincer ligand [*o*-(2,6-^{i}Pr$_2$-C$_6$H$_3$–N=C–C$_6$H$_4$)$_2$–NH] and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ were synthesized according to the literature.[29,30] The deuterated solvents C_6D_6 (99.6 atom% D), $CDCl_3$ (99.8 atom% D) and C_7D_8 (99.6 atom% D) were obtained from Cambridge Isotope.

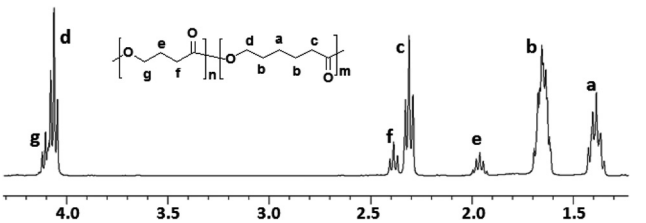


Fig. 6 ^{1}H NMR spectrum of poly(CL-*co*-BL).

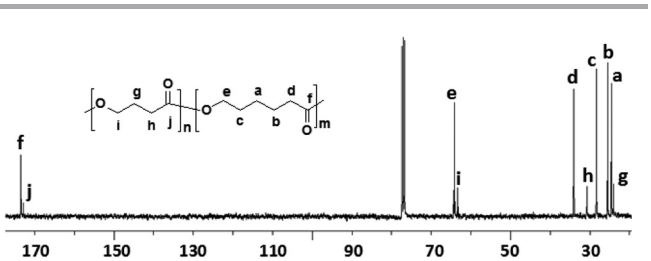
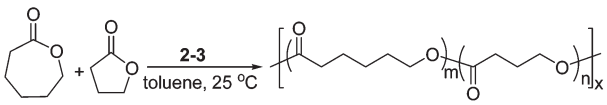


Fig. 7 ^{13}C NMR spectrum of poly(CL-*co*-BL).

Table 4 Random copolymerization of ε-caprolactone with γ-butyrolactone by bis(imino)diphenylamido rare-earth metal dialkyl complexes **2–3**[a]



Entry	Cat. (Ln)	CL (mmol)	BL (mmol)	CL/BL	*t* (h)	Yield (g)	Act[b]	Cont. of BL[c] (mol%)	M_n (10^3)[d]	M_w/M_n[d]	T_m[e] (°C)
1	**2**(Lu)	30	30	1/1	3	2.1	1.4	12	—	—	48
2	**3**(Y)	45	15	3/1	3	3.7	2.5	6	81	1.50	52
3	**3**(Y)	40	20	2/1	3	1.3	0.9	7	65	1.63	53
4	**3**(Y)	30	30	1/1	3	0.9	0.6	15	85	1.30	48
5	**3**(Y)	30	10	3/1	1	3.7	7.4	6	88	1.51	51
6	**3**(Y)	20	20	1/1	1	1.8	3.6	12	106	1.31	49
7	**3**(Y)	10	30	1/3	1	0.5	1.4	18	25	1.71	45

[a] Conditions: 5 μmol of catalyst, 30 mL of toluene, 25 °C. [b] Activity in 10^5 g mol^{-1} h^{-1}. [c] Determined by ^{1}H NMR. [d] Determined by GPC in THF at 40 °C against polystyrene standard. [e] Measured by DSC.

Samples of rare-earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker 400 or 600 spectrometer at a suitable temperature in $CDCl_3$, C_6D_6 or C_7D_8 as a solvent. Elemental analyses were performed on an Elementar Vario MICRO CUBE (Germany). The molecular weights and molecular weight distributions of polymerization were determined at 40 °C by gel permeation chromatography on a Waters 1515 HPLC using THF as an eluent at a flow rate of 1 mL min^{-1} against polystyrene standards. The DSC measurements were performed on a Q2000 (TA Co.) Differential Scanning Calorimeter at a rate of 20 °C min^{-1}. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 10 °C min^{-1} to −90 °C, and then recording the second DSC scan.

Synthesis of *o*-$(C_6H_4$–$COOCH_3)_2$–NH. The *o*-$(C_6H_4$–$COOH)_2$–NH (5.02 g, 19.50 mmol) was added to stirring methanol solvent (50 mL), then concentrated H_2SO_4 (5 mL) was dropped in. The reaction mixture was refluxed for 3 hours. After removing the methanol, the reaction mixture was poured into water and treated by Na_2CO_3 solution. The solution was extracted with EtOAc (2 × 20 mL) and the combined organic solvent was removed under reduced pressure to obtain the pure *o*-$(C_6H_4$–$COOCH_3)_2$–NH as pale yellow solid (5.34 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ/ppm): 3.94 (s, 6H, CH_3), 6.88–8.00 (m, 8H, Ar*H*), 11.06 (s, 1H, N*H*).

Synthesis of *o*-$(C_6H_4$–$CHO)_2$–NH. The *o*-$(C_6H_4$–$COOCH_3)_2$–NH (6.70 g, 23.48 mmol) was added to a suspension of $LiAlH_4$ (2.00 g, 52.70 mmol) in anhydrous ether (200 mL) during 1 hour. The resulting mixture was refluxed for 4 hours. After cooling, the reaction mixture was treated sequentially by water (3 mL), NaOH (3 mL, 15%) and water (50 mL), and then filtered. The precipitate was extracted by boiling chloroform (4 × 100 mL) and the combined extracts and filtrate were concentrated to afford the white solid *o*-$(C_6H_4$–$CH_2OH)_2$–NH was afforded. The *o*-$(C_6H_4$–$CH_2OH)_2$–NH (5.00 g, 21.81 mmol) in anhydrous ether (100 mL) and active MnO_2 (38.00 g, 437.08 mmol) were stirred and refluxed together for 8 hours. The MnO_2 was filtered off and extracted with boiling chloroform (3 × 100 mL). The combined extracts and filtrate were concentrated to afford the *o*-$(C_6H_4$–$CHO)_2$–NH as yellow crystal (3.29 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ/ppm): 7.02–7.71 (m, 8H, Ar*H*), 10.02 (s, 2H, C*H*O), 11.34 (s, 1H, N*H*).

Synthesis of [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–NH]. 2,6-^{i}Pr$_2$-C_6H_3–NH_2 (0.66 g, 3.70 mmol), *o*-$(C_6H_4$–$CHO)_2$–NH (0.42 g, 1.85 mmol), 10 mL methanol, 2 drops of methane acid, and 5 Å molecular sieves (approximately 50% by volume) were added to a 25 mL round bottom flask. The mixture was heated to reflux and allowed to react overnight. The reaction mixture was hot filtrated. Filtrate was removed under pressure and the residue was purified by flash silica gel column chromatography with a petroleum ether–EtOAc mixture (15/1, v/v) to obtain the pure product as bright yellow crystals (0.72 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ/ppm): 0.98 (d, 24H, CH_3), 2.87 (m, 4H, CH($CH_3)_2$), 7.03–7.79 (m, 14H, Ar*H*), 8.36 (s, 2H, C*H*N), 11.19 (s, 1H, N*H*). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, δ/ppm): 23.2 (s, *C*H_3), 27.9 (s, *C*H($CH_3)_2$), 119.5, 121.3, 122.9, 124.2, 124.7, 131.7, 132.1, 137.7, 144.5, 149.1 (m, Ar*C*), 162.5 (s, N=*C*).

Synthesis of [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–N]Sc$(CH_2SiMe_3)_2$ (1). A toluene solution (5 mL) of *o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–NH (1.55 g, 2.85 mmol) was added to a hexane solution (5 mL) of $Sc(CH_2SiMe_3)_3(THF)_2$ (1.29 g, 2.85 mmol) at room temperature. The yellow mixture was stirred at room temperature for 1.5 hours. After removal of all volatiles *in vacuo*, the residue was recrystallized from hexane at −30 °C to give **1** as orange-yellow crystals (1.50 g, 69% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.08 (s, 18H, $CH_2Si(CH_3)_3$), 0.04 (d, J = 11.60, 2H, CH_2SiMe$_3$), 0.18 (d, J = 11.60, 2H, CH_2SiMe$_3$), 0.93 (d, 6H, CH(C$H_3)_2$), 1.11 (d, 6H, CH(C$H_3)_2$), 1.45 (d, 6H, CH-(C$H_3)_2$), 1.75 (d, 6H, CH(C$H_3)_2$), 2.83 (m, 2H, CH($CH_3)_2$), 4.08 (m, 2H, CH($CH_3)_2$), 6.76–7.35 (m, 14H, Ar*H*), 8.32 (s, 2H, C*H*=N,). ^{13}C NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): 3.8 (s, Si-(*C*$H_3)_3$), 21.4, 22.5, 22.9, 23.4, 26.3, 26.5, 28.1, 29.1 (m, *C*H-($CH_3)_2$, CH(*C*$H_3)_2$), 44.4 (s, Sc*C*H_2Si$(CH_3)_3$), 119.9, 123.4, 124.6, 125.0, 125.7, 127.4, 128.5, 129.3, 133.9, 134.7, 141.0, 141.9, 149.0, 150.4 (m, Ar*C*), 167.9 (s, *C*=N). Anal. Calcd for $C_{53}H_{74}N_3ScSi_2$: C, 63.50; H, 9.56; N, 4.36. Found: C, 63.35; H, 9.88; N, 4.20.

Synthesis of [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–N]Lu$(CH_2SiMe_3)_2$ (2). A toluene solution (5 mL) of *o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–NH (2.72 g, 5.00 mmol) was added to a hexane solution (5 mL) of $Lu(CH_2SiMe_3)_3(THF)_2$ (2.90 g, 5.00 mmol) at room temperature. The yellow mixture was stirred for 0.5 hours. After removal of all volatiles *in vacuo*, the residue was recrystallized from hexane at −30 °C to give **2** as orange-yellow crystals (3.21 g, 72% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.70 (d, J = 12.00, 2H, CH_2SiMe$_3$), −0.59 (d, J = 12.00, 2H, CH_2SiMe$_3$), −0.01 (s, 18H, $CH_2Si(CH_3)_3$), 0.94 (d, 6H, CH-(C$H_3)_2$), 1.17 (d, 6H, CH(C$H_3)_2$), 1.41 (d, 6H, CH(C$H_3)_2$), 1.71 (d, 6H, CH(C$H_3)_2$), 2.87 (m, 2H, CH($CH_3)_2$), 3.86 (m, 2H, C*H*-($CH_3)_2$), 6.70–7.30 (m, 14H, Ar*H*), 8.18 (s, 2H, C*H*=N). ^{13}C NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): 4.1 (s, Si(*C*$H_3)_3$), 21.4, 22.4, 23.0, 26.1, 26.2, 28.5, 29.2, 31.9 (m, *C*H($CH_3)_2$, CH-(*C*$H_3)_2$), 44.9 (s, Lu*C*H_2Si$(CH_3)_3$), 119.6, 124.4, 124.6, 124.7, 125.7, 127.5, 128.5, 129.3, 134.2, 135.2, 141.0, 141.7, 148.1, 151.6 (m, Ar*C*), 169.0 (s, *C*=N). Anal. Calcd for $C_{53}H_{74}N_3ScSi_2$: C, 52.82; H, 7.95; N, 3.62. Found: C, 52.77; H, 7.85; N, 3.43.

Synthesis of [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–N]Y$(CH_2SiMe_3)_2$ (3). A toluene solution (5 mL) of *o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–$C_6H_4)_2$–NH (1.63 g, 3.00 mmol) was added to a hexane solution (5 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (1.48 g, 3.00 mmol) at room temperature. The yellow mixture was stirred for 3.5 hours. After removal of all volatiles *in vacuo*, the residue was recrystallized from hexane at −30 °C to give **3** as orange-yellow crystals (1.57 g, 65% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.47 (d, J = 11.20, 2H, CH_2SiMe$_3$), −0.42 (d, J = 11.60, 2H, CH_2SiMe$_3$), −0.02 (s, 18H, $CH_2Si(CH_3)_3$), 0.95 (d, 6H, CH-(C$H_3)_2$), 1.19 (d, 6H, CH(C$H_3)_2$), 1.41 (d, 6H, CH(C$H_3)_2$), 1.71 (d, 6H, CH(C$H_3)_2$), 2.91 (m, 2H, CH($CH_3)_2$), 3.85 (m, 2H, C*H*-($CH_3)_2$), 6.74–7.30 (m, 14H, Ar*H*), 8.20 (s, 2H, C*H*=N,). ^{13}C

NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): 4.0 (s, Si(CH_3)$_3$), 21.4, 22.4, 23.1, 26.0, 26.2, 28.8, 29.3, 31.9 (m, $CH(CH_3)_2$, CH-(CH_3)$_2$), 38.2, 38.6 (d, Y $CH_2Si(CH_3)_3$), 119.6, 124.3, 124.6, 124.7, 125.7, 127.5, 128.5, 129.3, 134.2, 135.4, 140.9, 141.3, 147.8, 151.9 (m, Ar*C*), 169.0 (s, *C*=N). Anal. Calcd for $C_{53}H_{74}N_3ScSi_2$: C, 59.44; H, 8.95; N, 4.08. Found: C, 59.60; H, 9.06; N, 4.22.

A typical procedure for ε-caprolactone polymerization by complex 3 (Table 3, entry 14). In the glovebox, [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–C_6H_4)$_2$–N]Y(CH_2SiMe_3)$_2$ (4.03 mg, 5 μmol) was dissolved in 30 mL of toluene in a 100 ml flask that was equipped with a magnetic stir bar. Then ε-caprolactone (4.57 g, 40 mmol) was added immediately. The color of the mixture changed immediately from dark yellow to pale yellow, and the resulting pale yellow solution quickly became very viscous. After 20 min, no solvent was left and the flash was taken outside. The polymerization was quenched by addition of alcohol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). The precipitated polymer was filtered and dried under vacuum at 60 °C overnight to a constant weight (4.57 g, 100% yield).

A typical procedure for copolymerization of ε-caprolactone with γ-butyrolactone by complex 3 (Table 4, entry 6). In the glovebox, [*o*-(2,6-^{i}Pr$_2$-C_6H_3–N=C–C_6H_4)$_2$–N]Y(CH_2SiMe_3)$_2$ (4.03 mg, 5 μmol) was dissolved in 30 mL of toluene in a 100 ml flask that was equipped with a magnetic stir bar. Then a mixture of ε-caprolactone (2.28 g, 20 mmol) and γ-Butyrolactone (1.72 g, 20 mmol) was added immediately. After 60 min, the polymerization was quenched by addition of alcohol (50 mL, containing 5% butylhydroxytoluene (BHT) as a stabilizing agent). The precipitated polymer was filtered and dried under vacuum at 60 °C overnight to a constant weight (1.80 g colorless polymer was obtained).

X-ray crystallographic studies

A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at −100 °C on a Bruker Smart-Apex CCD diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[32] The raw frame data were processed using SAINT[33] and SADABS[34] to yield the reflection data file. The structures were solved by using SHELXTL-97 program.[35] Refinements were performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. CCDC 857397 (**1**), 857396 (**2**), and 857398 (**3**).†

Conclusions

In summary, we have demonstrated that the novel bis(imino)-diphenylamido rare-earth metal dialkyl complexes **1–3** can be easily prepared by reaction of the rare-earth metal trialkyl complexes with the bis(imino)diphenylamido NNN pincer ligand. With the increased ionic radius of the metal center in a trend of Sc (0.89 Å) < Lu (1.00 Å) < Y (1.04 Å), the complexes **1–3** have the steric hindrance around the metal center decreasing in order of **1** > **2** > **3**. An "ionic radius effect" on the catalytic activity of these complexes is observed in the ring-opening polymerization of ε-caprolactone. The less bulky yttrium complex **3** shows exceptional activity not only in the living ring-opening polymerization of CL but also in the random copolymerization of CL and BL, yielding high molecular weight PCLs or P(CL-*co*-BL) with narrow molecular weight distributions. These results indicate that the introduction of the monoanionic NNN pincer ligand into the rare-earth metal dialkyl complex has obviously impeded the transesterification reactions and yields PCL with narrow polydispersity in the polymerization of ε-caprolactone. Further studies on the detailed polymerization mechanism and related transition metal catalysts bearing bis(imino)diphenylamido ligand are in progress.

Acknowledgements

We gratefully acknowledge the support from the National Natural Science Foundation of China (No. 20974014, 21173022, 21274012), the 111 project (B07012) and Basic Research Fund of Beijing Institute of Technology (20111942018).

Notes and references

1 M. Minami and S. Kozaki, *US patent*, 2003/0023026 A1, 2003.
2 F. J. VanNatta, J. W. Hill and W. H. Carothers, *J. Am. Chem. Soc.*, 1934, **56**, 455.
3 W. H. Carothers, *Chem. Rev.*, 1931, **8**, 353.
4 (*a*) R. A. Gross, A. Kumar and B. Kalra, *Chem. Rev.*, 2001, **101**, 2097; (*b*) R. T. MacDonald, S. K. Pulapura, Y. Y. Svirkin, R. A. Gross, D. L. Kaplan, J. Akkara, G. Swift and S. Wolk, *Macromolecules*, 1995, **28**, 73; (*c*) A. Córdova, T. Iversen, K. Hult and M. Martinelle, *Polymer*, 1998, **39**, 6519; (*d*) S. Kobayashi, K. Takeya, S. Suda and H. Uyama, *Macromol. Chem. Phys.*, 1998, **199**, 1729.
5 (*a*) P. Kubisa and S. Penczek, *Prog. Polym. Sci.*, 1999, **24**, 1409; (*b*) Y. Shibasaki, H. Sanada, M. Yokoi, F. Sanda and T. Endo, *Macromolecules*, 2000, **33**, 4316.
6 (*a*) S. Dumitriu, *Polymeric Biomaterials*, Marcel Dekker, New York, 2002; (*b*) B. A. Rozenberg, *Pure Appl. Chem.*, 1981, **53**, 1715; (*c*) K. Ito, Y. Hashizuka and Y. Yamashita, *Macromolecules*, 1977, **10**, 821; (*d*) K. Ito and Y. Yamashita,

Macromolecules, 1978, **11**, 68; (*e*) M. Bero, G. Adamus, J. Kasperczyk and H. Janeczek, *Polym. Bull.*, 1993, **31**, 9.

7 (*a*) W. Yao, Y. Mu, A. Gao, W. Gao and L. Ye, *Dalton Trans.*, 2008, 3199; (*b*) A.-C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466.

8 (*a*) A. Amgoune, L. Lavanant, C. M. Thomas, Y. Chi, R. Welter, S. Dagorne and J.-F. Carpentier, *Organometallics*, 2005, **24**, 6279; (*b*) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2006, **25**, 1012; (*c*) L. E. Breyfogle, C. K. Williams, V. G. Young, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2006, 928; (*d*) L. F. Sánchez-Barba, A. Garcés, M. Fajardo, C. Alonso-Moreno, J. Fernández-Baeza, A. Otero, A. Antiñolo, J. Tejeda, A. Lara-Sánchez and M. I. López-Solera, *Organometallics*, 2007, **26**, 6403; (*e*) W.-Y. Lee, H.-H. Hsieh, C.-C. Hsieh, H. M. Lee, G.-H. Lee, J.-H. Huang, T.-C. Wu and S.-H. Chuang, *J. Organomet. Chem.*, 2007, **692**, 1131.

9 Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340.

10 (*a*) P. A. Cameron, D. Jhurry, V. C. Gibson, A. J. P. White, D. J. Williams and S. Williams, *Macromol. Rapid Commun.*, 1999, **20**, 616; (*b*) L. S. Baugh and J. A. Sissano, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1633; (*c*) W. Braune and J. Okuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 64; (*d*) N. Nomura, T. Aoyama, R. Ishii and T. Kondo, *Macromolecules*, 2005, **38**, 5363; (*e*) H. Zhu and E. Y.-X. Chen, *Organometallics*, 2007, **26**, 5395; (*f*) M. Bouyahyi, E. Grunova, N. Marquet, E. Kirillov, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2008, **27**, 5815; (*g*) S. G. Gong and H. Y. Ma, *Dalton Trans.*, 2008, 3345; (*h*) N. Iwasa, J. Liu and K. Nomura, *Catal. Commun.*, 2008, **9**, 1148; (*i*) J. Liu, N. Iwasa and K. Nomura, *Dalton Trans.*, 2008, 3978; (*j*) N. Iwasa, M. Fujiki and K. Nomura, *J. Mol. Catal. A: Chem.*, 2008, **292**, 67; (*k*) N. Iwasa, S. Katao, J. Liu, M. Fujiki, Y. Furukawa and K. Nomura, *Organometallics*, 2009, **28**, 2179; (*l*) D. Pappalardo, L. Annunziata and C. Pellecchia, *Macromolecules*, 2009, **42**, 6056.

11 (*a*) H.-Y. Chen, B.-H. Huang and C.-C. Lin, *Macromolecules*, 2005, **38**, 5400; (*b*) Z.-X. Wang and C.-Y. Qi, *Organometallics*, 2007, **26**, 2243; (*c*) C. Alonso-Moreno, A. Garcés, L. F. Sánchez-Barba, M. Fajardo, J. Fernández-Baeza, A. Otero, A. Lara-Sánchez, A. Antiñolo, L. Broomfield, M. I. López-Solera and A. M. Rodríguez, *Organometallics*, 2008, **27**, 1310; (*d*) Z.-Y. Chai, C. Zhang and Z.-X. Wang, *Organometallics*, 2008, **27**, 1626; (*e*) C. Zhang and Z.-X. Wang, *J. Organomet. Chem.*, 2008, **693**, 3151.

12 (*a*) Y. Takashima, Y. Nakayama, T. Hirao, H. Yasuda and A. Harada, *J. Organomet. Chem.*, 2004, **689**, 612; (*b*) L. I. Strunkina, M. K. Minacheva, K. A. Lyssenko, V. V. Burlakov, W. Baumann, P. Arndt, B. N. Strunin and V. B. Shur, *J. Organomet. Chem.*, 2006, **691**, 557; (*c*) J. Cayuela, V. Bounor-Legare, P. Cassagnau and A. Michel, *Macromolecules*, 2006, **39**, 1338; (*d*) Y. Perez, I. del Hierro, I. Sierra, P. Gomez-Sal, M. Fajardo and A. Otero, *J. Organomet. Chem.*, 2006, **691**, 3053; (*e*) C. J. Chuck, M. G. Davidson, M. D. Jones, G. Kociok-Köhn, M. D. Lunn and S. Wu, *Inorg. Chem.*, 2006, **45**, 6595; (*f*) M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Inorg. Chem.*, 2006, **45**, 2282; (*g*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2006, 887; (*h*) S.-D. Mun, Y. Hong and Y. Kim, *Bull. Korean Chem. Soc.*, 2007, **28**, 698; (*i*) M. H. Cho, J. S. Yoon and I.-M. Lee, *Bull. Korean Chem. Soc.*, 2007, **28**, 2471; (*j*) L. Postigo, J. Sanchez-Nieves, P. Royo and M. E. G. Mosquera, *Dalton Trans.*, 2009, 3756.

13 (*a*) H. Wang, H.-S. Chan, J. Okuda and Z. Xie, *Organometallics*, 2005, **24**, 3118; (*b*) V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics*, 2006, **25**, 519; (*c*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250; (*d*) K.-C. Hsieh, W.-Y. Lee, L.-F. Hsueh, H. M. Lee and J.-H. Huang, *Eur. J. Inorg. Chem.*, 2006, 2306; (*e*) F. Gornshtein, M. Kapon, M. Botoshansky and M. S. Eisen, *Organometallics*, 2007, **26**, 497; (*f*) R. F. Munha, L. G. Alves, N. Maulide, M. T. Duarte, I. E. Marko, M. D. Fryzuk and A. M. Martins, *Inorg. Chem. Commun.*, 2008, **11**, 1174.

14 (*a*) J. Yamada and K. Nomura, *Organometallics*, 2005, **24**, 3621; (*b*) Y. Mahha, A. Atlamsani, J.-C. Blais, M. Tessier, J.-M. Bregeault and L. Salles, *J. Mol. Catal. A: Chem.*, 2005, **234**, 63; (*c*) A. Arbaoui, C. Redshaw, D. M. Homden, J. A. Wright and M. R. J. Elsegood, *Dalton Trans.*, 2009, 8911.

15 (*a*) D. M. Kurtz, *Chem. Rev.*, 1990, **90**, 585; (*b*) M.-Z. Chen, H.-M. Sun, W.-F. Li, Z.-G. Wang, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2006, **691**, 2489; (*c*) R. R. Gowda and D. Chakraborty, *J. Mol. Catal. A: Chem.*, 2009, **301**, 84; (*d*) A. Arbaoui, C. Redshaw, M. R. J. Elsegood, A. Yoshizawa and T. Yamato, *Chem.–Asian J.*, 2010, **5**, 621.

16 (*a*) S. Penczek, A. Duda, A. Kowalski, J. Libiszowski, K. Majerska and T. Biela, *Macromol. Symp.*, 2000, **157**, 61; (*b*) F. Stassin and R. Jérôme, *Chem. Commun.*, 2003, 232; (*c*) M. Sobczak and W. Kolodziejski, *Molecules*, 2009, **14**, 621.

17 (*a*) X. Deng, M. Yuan, C. Xiong and X. Li, *J. Appl. Polym. Sci.*, 1999, **73**, 1401; (*b*) Y. Wu, S. Wang, C. Qian, E. Sheng, M. Xie, G. Yang, Q. Feng, L. Zhang and X. Tang, *J. Organomet. Chem.*, 2005, **690**, 4139; (*c*) J. Chai, V. Jancik, S. Singh, H. Zhu, C. He, H. W. Roesky, H. G. Schmidt, M. Noltemeyer and N. S. Hosmane, *J. Am. Chem. Soc.*, 2005, **127**, 7521; (*d*) H. Sun, S. Chen, Y. Yao, Q. Shen and K. Yu, *Appl. Organomet. Chem.*, 2006, **20**, 310; (*e*) R. M. Gauvin, T. Chenal, R. A. Hassan, A. Addad and A. Mortreux, *J. Mol. Catal. A: Chem.*, 2006, **257**, 31; (*f*) S. Wang, X. Tang, A. Vega, J. Y. Saillard, S. Zhou, G. Yang, W. Yao and Y. Wei, *Organometallics*, 2007, **26**, 1512; (*g*) S. Zhou, S. Wang, G. Yang, Q. Li, L. Zhang, Z. Yao, Z. Zhou and H.-B. Song, *Organometallics*, 2007, **26**, 3755; (*h*) S. Zhou, S. Wang, E. Sheng, L. Zhang, Z. Yu, X. Xi, G. Chen, W. Luo and Y. Li, *Eur. J. Inorg. Chem.*, 2007, 1519; (*i*) S. Wang, S. Wang, S. Zhou, G. Yang, W. Luo, N. Hu, Z. Zhou and H. Song,

J. Organomet. Chem., 2007, **692**, 2099; (*j*) Y. Wei, Z. Yu, S. Wang, S. Zhou, G. Yang, L. Zhang, G. Chen, H. Qian and J. Fan, *J. Organomet. Chem.*, 2008, **693**, 2263.

18 (*a*) Y. Yao, X. Xu, B. Liu, Y. Zhang, Q. Shen and W. Wong, *Inorg. Chem.*, 2005, **44**, 5133; (*b*) H. Sheng, J. Li, Y. Zhang, Y. Yao and Q. Shen, *Polyhedron*, 2008, **27**, 1665; (*c*) H. Sheng, J. Li, Y. Zhang, Y. Yao and Q. Shen, *J. Appl. Polym. Sci.*, 2009, **112**, 454.

19 (*a*) M. Endo, T. Aida and S. Inoue, *Macromolecules*, 1987, **20**, 2982; (*b*) L. F. Sanchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Organometallics*, 2005, **24**, 3792; (*c*) M. Xue, Y. Yao, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2005, **690**, 4685; (*d*) Y. Yao, Z. Zhang, H. Peng, Y. Zhang, Q. Shen and J. Lin, *Inorg. Chem.*, 2006, **45**, 2175; (*e*) X. Xu, X. Xu, Y. Chen and J. Sun, *Organometallics*, 2008, **27**, 758; (*f*) A. Arbaoui, C. Redshaw and D. L. Hughes, *Chem. Commun.*, 2008, 4717.

20 (*a*) W. Gao, D. Cui, X. Liu, Y. Zhang and Y. Mu, *Organometallics*, 2008, **27**, 5889; (*b*) J. Wang, H. Sun, Y. Yao, Y. Zhang and Q. Shen, *Polyhedron*, 2008, **27**, 1977; (*c*) J. Wang, Y. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2009, **48**, 744.

21 (*a*) Y. Yao, M. Ma, X. Xu, Y. Zhang, Q. Shen and W.-T. Wong, *Organometallics*, 2005, **24**, 4014; (*b*) F. Peng, J. Ling, Z. Shen and W. Zhu, *J. Mol. Catal. A: Chem.*, 2005, **230**, 135; (*c*) I. Westmoreland and J. Arnold, *Dalton Trans.*, 2006, 4155; (*d*) X. Xu, Z. Zhang, Y. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, **46**, 9379; (*e*) H. Zhou, H. Guo, Y. Yao, L. Zhou, H. Sun, H. Sheng, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, **46**, 958; (*f*) L. Zhang, Y. Niu, Y. Wang, P. Wang and L. Shen, *J. Mol. Catal. A: Chem.*, 2008, **287**, 1.

22 A. Arbaoui and C. Redshaw, *Polym. Chem.*, 2010, **1**, 801.

23 (*a*) V. Gómez-Benítez, R. Redón and D. Morales-Morales, *Rev. Soc. Quim. Mex.*, 2003, **47**, 124; (*b*) J. T. Singleton, *Tetrahedron*, 2003, **59**, 1837; (*c*) N. Selander and K. J. Szabó, *Chem. Rev.*, 2011, **111**, 2048; (*d*) J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761; (*e*) H. Zhang and A. Lei, *Dalton Trans.*, 2011, **40**, 8745; (*f*) Z. Wang and N. Liu, *Eur. J. Inorg. Chem.*, 2012, 901.

24 For example: (*a*) H. Rimml and L. M. Venanzi, *J. Organomet. Chem.*, 1983, **259**, C6; (*b*) M. Gupta, C. Hagen, W. C. Kaska, R. E. Crammer and C. M. Jensen, *J. Am. Chem. Soc.*, 1997, **119**, 840; (*c*) M. Gupta, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1997, 461; (*d*) X. Zhang, J. M. Longmire and M. Shang, *Organometallics*, 1998, **17**, 4374; (*e*) P. Dani, T. Karlen, R. A. Gossage, S. Gladiali and G. van Koten, *Angew. Chem., Int. Ed.*, 2000, **39**, 743; (*f*) R. B. Bedford, S. M. Draper, P. N. Scully and S. L. Welch, *New J. Chem.*, 2000, **24**, 745; (*g*) D. Morales-Morales, R. Redón, C. Yung and C. M. Jensen, *Chem. Commun.*, 2000, 1619; (*h*) M. Albrecht and G. van Koten, *Angew. Chem.*, 2001, **113**, 3866; (*i*) M. W. Haenel, S. Oevers, K. Angermund, W. C. Kaska, H. J. Fan and M. B. Hall, *Angew. Chem., Int. Ed.*, 2001, **40**, 3596; (*j*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750.

25 For example: (*a*) R. A. Gossage, A. D. Ryabov, A. L. Spek, D. J. Stufkens, J. A. M. van Beek, R. van Eldik and G. van Koten, *J. Am. Chem. Soc.*, 1999, **121**, 2488; (*b*) G. Rodriguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 2002, **124**, 5127; (*c*) E. Ben-Ari, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 4714; (*d*) C. A. Kruithof, M. A. Casado, G. Guillena, M. R. Egmond, A. van Kerk-van Hoof, A. J. R. Heck, R. J. M. Klein Gebbink and G. van Koten, *Chem.–Eur. J.*, 2005, **11**, 6869; (*e*) K. Okamoto, T. Kanbara, T. Yamamoto and A. Wada, *Organometallics*, 2006, **25**, 4026; (*f*) F. E. Michael and B. M. Cochran, *J. Am. Chem. Soc.*, 2006, **128**, 4246; (*g*) C. Scriban and D. S. Glueck, *J. Am. Chem. Soc.*, 2006, **128**, 2788.

26 (*a*) A. R. Wills and P. G. Edwards, *J. Chem. Soc., Dalton Trans.*, 1989, 1253; (*b*) Y. Jiang, Q. Jiang and X. Zhang, *J. Am. Chem. Soc.*, 1998, **120**, 3817; (*c*) T. Suzuki, A. Kinoshita, H. Kawada and M. Nakada, *Synlett*, 2003, 570; (*d*) M. Inoue, T. Suzuki and M. Nakada, *J. Am. Chem. Soc.*, 2003, **125**, 1140; (*e*) K. C. Jantunen, B. L. Scott, P. J. Hay, J. C. Gordon and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2006, **128**, 6322; (*f*) J. D. Masuda, K. C. Jantunen, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2008, **27**, 803.

27 Only one patent mentioned that the bis(imino)diphenylamide iron complex $[\{2\text{-}(ArNdCH)C_6H_4\}_2N]FeCl_2$ was synthesized and served as low active catalyst for ethylene polymerization. See: S. Matsui, M. Nitabaru, K. Tsuru, T. Fujita, Y. Suzuki, Y. Takagi and H. Tanaka, *PCT Int. Appl.* WO9954364, Mitsui Chemicals Inc., Japan, 1999.

28 D. St. C. Black and N. E. Rothnie, *Aust. J. Chem.*, 1983, **36**, 2395.

29 (*a*) M. Nishiura, Z. Hou, T. Koizumi, T. Imamoto and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 8245; (*b*) S. Li, M. Pignol, F. Gasc and M. Vert, *Macromolecules*, 2004, **37**, 9798; (*c*) J. E. Báez and A. Martínez-Richa, *Polymer*, 2005, **46**, 12118.

30 (*a*) S. Arndt, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 5075; (*b*) Y. Luo, J. Baldamus and Z. Hou, *J. Am. Chem. Soc.*, 2004, **126**, 13910; (*c*) X. Li, J. Baldamus and Z. Hou, *Angew. Chem., Int. Ed.*, 2005, **44**, 962.

31 (*a*) M. Yamashita, Y. Takemoto, E. Ihara and H. Yasuda, *Macromolecules*, 1996, **29**, 1798; (*b*) H. Sheng, F. Xu, Y. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, **46**, 7722.

32 *SMART Software Users Guide, Version 4.21*, Bruker AXS, Inc., Madison, WI, 1997.

33 *SAINT+, Version 6.02*, Bruker AXS, Inc., Madison, WI, 1999.

34 G. M. Sheldrick, *SADABS*, Bruker AXS, Inc., Madison, WI, 1998.

35 G. M. Sheldrick, *SHELXTL, Version 5.1*, Bruker AXS, Inc., Madison, WI, 1998.

