

Synthesis, structure of functionalized N-heterocyclic carbene complexes of Fe(II) and their catalytic activity for ring-opening polymerization of ϵ -caprolactone

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Abstract

The reaction of anhydrous FeBr_2 with two equivalents of in situ generated anionic aryloxo-functionalized N-heterocyclic carbene $[\text{NaO}-4,6\text{-di-}C(\text{CH}_3)_3\text{-C}_6\text{H}_2\text{-2-CH}_2\{\text{C}(\text{NCHCHNR})\}]$ ($\text{R} = \text{CH}(\text{CH}_3)_2, \text{NaL}^1$; $\text{R} = \text{CH}_2\text{Ph}, \text{NaL}^2$) affords two bis-ligand Fe(II) complexes FeL_2^1 (**1**) and FeL_2^2 (**2**) in good yield, respectively. Attempt to synthesize mono-ligand Fe(II) bromide by the 1:1 molar ratio of NaL to FeBr_2 is unsuccessful, the same complexes of **1** and **2** were obtained. Both of **1** and **2** have been fully characterized by elemental analysis, ^1H NMR spectra and X-ray structure determination. Preliminary studies show that **1** can catalyze the ring-opening polymerization of ϵ -caprolactone as a single component catalyst. The mechanism of the present ROP of ϵ -caprolactone has been investigated by the end group analysis.

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1. Introduction

Late transition metal complexes with N-heterocyclic carbenes (NHCs) are currently intensively investigated for their good stabilities and high activities in a variety of homogeneous catalysis [1]. For example, the NHC complexes of ruthenium show excellent catalytic activity in the atom transfer radical polymerization (ATRP) of styrene [2], the ring-opening metathesis polymerizations (ROMP) of norbornene [3] and 1,5-cyclooctadiene [4], the acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene [5]. NHC-Pd(II) complexes can also efficiently catalyze the ring-opening metathesis polymerizations (ROMP) of norbornene [6] and the copolymerizations of carbon monoxide with ethylene [7a] or bisphenol A [7b], and the NHC-Ni(II) complexes show catalytic activity in dimerizations of ethylene [8], propene and 1-butene [9],

the addition polymerization of norbornene and the polymerization of ethylene [10]. However, the NHC complexes of iron to date are less developed. The first mononuclear NHC-Fe(II) halides, $\text{Fe}(\text{NHC})_2\text{X}_2$, were synthesized in 2000 [11]. Since then, the piano-stool Fe(II) complexes of the type $\text{CpFe}(\text{CO})_2(\text{NHC})\text{X}$ [12] and pincer Fe(II)/Fe(III) complexes of $\text{Fe}(2,6\text{-bis}(\text{NHC})\text{pyridine})\text{X}_n$ ($n = 2$ or 3) [13] were reported by Siebert, Guerchais and Gibson et al., respectively. Very recently, binuclear NHC-Fe(II) complexes, $[\text{Fe}_2(\mu\text{-S}(\text{CH}_2)_3\text{S})(\text{CO})_{6-x}(\text{NHC})_x]$ ($x = 1, 2$), were synthesized as bio-inspired derivatives by Capon et al. [14]. Among these NHC complexes of iron, only the complex $\text{Fe}(\text{NHC})_2\text{X}_2$ has been found to show good catalytic activity for the ATRP of styrene and methyl methacrylate [11]. So, further study on the synthesis of iron-based complexes with NHC ligand and their reactivity in homogeneous catalysis is valuable.

The functionalized NHCs have attracted increasing attentions in recent years, as the introduction of pendant functional group will give an opportunity to better control

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the stability of the active species and improve the catalytic activity. Moreover, the use of anionic functionalized NHC, such as amido, aryloxo, alkoxo-tethered NHCs, can efficiently reduce the ligand dissociation not only in complexes of early metals (Cu) [15a] and rare earth metals (Sm, Yb) [15b], but also in complexes of early transition metals (Ti, Zr) [15c] and late transition metals (Pd) [15d,15e]. Recently, we have designed two novel anionic functionalized NHCs, i.e. salicylaldiminato- or aryloxo-functionalized NHC ligands, and successfully synthesized the corresponding complexes of Ni(II) with them [16,17]. In order to further extend the application of the anionic functionalized NHC in iron complex, we study the metathesis reaction of FeBr₂ with aryloxo-functionalized NHC sodium salt, [NaO-4,6-di-C(CH₃)₃-C₆H₂-2-CH₂{C(NCH-CHNR)}] (R = CH(CH₃)₂, NaL¹; R = CH₂Ph, NaL²), and successfully synthesized the first bis-aryloxo-functionalized NHC Fe(II) complexes, L₂¹Fe, **1** and L₂²Fe, **2**. Preliminary study indicated that complex **1** shows high catalytic activity for the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). Here we report the results.

2. Experimental

2.1. General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. Isopropylimidazole was obtained commercially and used as received. Benzyl-imidazole was prepared according to the literature method [18]. Imidazolium chloride salt [HO-4,6-di-C(CH₃)₃-C₆H₂-2-CH₂{CH(NCHCHNR)}]Cl (R = CH(CH₃)₂, H₂L¹Cl; R = CH₂Ph, H₂L²Cl) were prepared according to the literature [17]. ε-Caprolactone was purchased from Across and dried by stirring with CaH₂ for 48 h, then distilled under reduced pressure before use. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. ¹H NMR (400 MHz, C₆D₆) spectra were measured on a Unity Inova-400 spectrometer at 25 °C. Molecular weight and molecular weight distribution were determined against PSt standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-3, HR-4).

2.2. Synthesis of L₂¹Fe (**1**)

2.2.1. Procedure A

A Schlenk flask was charged with H₂L¹Cl (0.73 g, 2 mmol), THF (20 mL) and a stir bar. To the suspension was added dropwise Na[N(SiMe₃)₂] (1.05 M, 4.2 mL) in THF at –20 °C. The reaction was stirred for 20 min and gradually warmed to room temperature for additional 10 min. The mixture was added to a suspension of FeBr₂ (0.216 g, 1 mmol) in THF (10 mL) under stirring and the

mixture was stirred for additional 16 h, the color of the solution was changed from yellow to grey-green gradually. The suspension was pumped to dryness and extracted with toluene. Colorless crystals suitable for elemental analysis and X-ray diffraction determination were obtained by crystallization from diethyl ether/hexane at 0 °C (0.48 g, 68%). Decomposition temperature: 145–147 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C) δ: 7.23 (s, 2H, Ph-H), 6.96 (s, 2H, Ph-H), 6.91 (s, 2H, NCH), 6.84 (s, 2H, NCH), 4.58 (s, 4H, ArCH₂N), 3.45–3.50 (m, 2H, CH(CH₃)₂), 1.50 (s, 12H, CH(CH₃)₂), 1.23 (s, 18H, C(CH₃)₃), 0.89 (s, 18H, C(CH₃)₃). Anal. Calc. for C₄₂H₆₂N₄O₂Fe: C, 70.97; H, 8.79; N, 7.88. Found: C, 70.95; H, 8.78; N, 7.86%.

2.2.2. Procedure B

The procedure is analogous to that described above, but the molar ratio of H₂L¹Cl to FeBr₂ was 1:1. The same complex **1** was isolated with the yield of 36% (0.25 g).

2.3. Synthesis of L₂²Fe (**2**)

2.3.1. Procedure A

By the procedure analogous to that described above, into the suspension of H₂L²Cl (0.83 g, 2 mmol) in THF (20 mL) was added dropwise Na[N(SiMe₃)₂] (1.05 M, 4.2 mL) in THF at –20 °C and then the mixture was added to the suspension of FeBr₂ (0.216 g, 1 mmol) in THF (10 mL). After workup, complex **2** was obtained by crystallization in diethyl ether/hexane at 0 °C as light green-yellow crystals (0.56 g, 70%). Decomposition temperature: 163–166 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 7.35–7.42, 6.79–7.16 (10H, Ph-H, 4H, Ph-H, 4H, NCH), 3.63 (s, 4H, ArCH₂N), 3.33 (s, 4H, NCH₂Ph), 1.47 (s, 18H, C(CH₃)₃), 0.95 (s, 18H, C(CH₃)₃). Anal. Calc. for C₅₀H₆₂N₄O₂Fe: C, 74.42; H, 7.74; N, 6.94. Found: C, 74.40; H, 7.78; N, 6.95%.

2.3.2. Procedure B

The procedure is analogous to that described above, but the molar ratio of H₂L²Cl to FeBr₂ was 1:1. The same complex **2** was isolated with the yield of 37% (0.29 g).

2.4. X-ray structural determination of **1** and **2**

Suitable crystals of complexes **1** and **2** were each sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structure was solved by direct methods and refined by full-matrix least squares procedures based on *F*². All non-hydrogen atoms were refined with isotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXL-97 program. Crystal data and collection and main refinement parameters are given in Table 1. Selected bond lengths (Å) and angles (°) for **1** and **2** are given in Table 2.

Table 1
X-ray crystallographic data for **1** and **2**

	1	2
Empirical formula	C ₄₂ H ₆₂ FeN ₄ O ₂ · 0.5C ₄ H ₁₀ O	C ₅₀ H ₆₂ FeN ₄ O ₂ · C ₆ H ₁₄
Formula weight	747.87	893.06
Temperature (K)	193(2)	193(2)
λ (Mo Kα) (Å)	0.71070	0.71070
Crystal system	Tetragonal	Monoclinic
Space group	<i>p</i> 43 21 2	<i>c</i> 2/ <i>c</i>
<i>a</i> (Å)	16.7327(11)	29.773(6)
<i>b</i> (Å)	16.7327(11)	12.688(2)
<i>c</i> (Å)	32.370(2)	15.714(4)
β (°)	90.00	117.055(4)
<i>V</i> (Å ³)	9063.1(11)	5287.3(18)
<i>Z</i>	8	4
<i>D</i> _{calc} (g/cm ³)	1.096	1.122
Absorption coefficient (mm ⁻¹)	0.371	0.327
<i>F</i> (000)	3240	1928
Crystal size (mm ³)	0.48 × 0.32 × 0.14	0.40 × 0.35 × 0.24
2θ _{max} (°)	3.05–25.35	30.7–25.35
No. of reflections collected	86060	25783
No. of independent reflections	8288	4829
Goodness-of-fit on <i>F</i> ²	1.156	1.075
Final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0643, 0.1497	0.0825, 0.2055

Table 2
Selected bond distances (Å) and angles (°) for **1** and **2**

1			
Fe–O1	1.918(2)	Fe–O2	1.918(3)
Fe–C8	2.076(4)	Fe–C29	2.094(4)
O1–Fe–C8	101.0(1)	O1–Fe–C29	105.0(1)
O2–Fe–C8	109.1(1)	O2–Fe–C29	99.6(1)
N1–C7–C6	113.8(3)	N3–C28–C27	114.2(3)
H ₁ ^a	67.64(0.13)	H ₂ ^b	63.80(0.15)
2			
Fe–O1	1.910(2)	Fe–O1A	1.910(2)
Fe–C8	2.085(3)	Fe–C8A	2.085(3)
O1–Fe–C8	109.0(1)	O1A–Fe–C8A	109.0(1)
C1–Fe–C8A	98.1(1)	C1A–Fe–C8	98.1(1)
N1–C7–C6	114.4(2)	N1A–C7A–C6A	114.4(2)
F ₁ ^c	65.56(0.14)	F _{1A} ^d	65.56(0.14)

^a H₁ is the angle formed between the planes formed by the atoms C₁, C₂, C₃, C₄, C₅, C₆ and C₈, N₁, C₉, C₁₀, N₂.

^b H₂ is the angle formed between the planes formed by the atoms C₂₂, C₂₃, C₂₄, C₂₅, C₂₆, C₂₇ and C₂₉, N₃, C₃₀, C₃₁, N₄.

^c F₁ is the angle formed between the planes formed by the atoms C₁, C₂, C₃, C₄, C₅, C₆ and C₈, N₁, C₉, C₁₀, N₂.

^d F_{1A} is the angle formed between the planes formed by the atoms C_{1A}, C_{2A}, C_{3A}, C_{4A}, C_{5A}, C_{6A} and C_{8A}, N_{1A}, C_{9A}, C_{10A}, N_{2A}.

2.5. A typical procedure for the ROP of ε-CL

A typical polymerization reaction is given as follows. Under dry argon, the solid initiator **1** (12.8 mg, 0.018 mmol), toluene (0.2 mL) and ε-CL (0.6 mL, 5.4 mmol) were added into a dry glass ampoule in turn. The ampoule was sealed and placed into a water bath held at 80 °C. After a definite reaction time, the polymerization was stopped by adding 1 mL of 5% HCl/methanol. The solvent was evaporated and the resulted polymer was dissolved in THF, followed by precipitation in a large access of metha-

nol. After filtration, the white polymer was obtained and dried in vacuum at room temperature overnight. The polymer yield was determined gravimetrically.

2.6. Oligomers for end group characterization

The oligomerization of ε-CL was carried out with **1** in toluene at 80 °C when [ε-CL]/[**1**] is 5(M). The reaction was terminated by adding 5% HCl/methanol after 3 h of oligomerization. The quenched reaction solution was evaporated to dryness to give a solid product, which was subsequently dissolved in THF (ca. 5 mL), then precipitated in a large access of methanol. After filtration, the product was dissolved in THF and then precipitated in a large access of methanol twice more to remove unconsumed monomer and catalyst. Then the product obtained and dried in vacuum at room temperature overnight for ¹H NMR spectra.

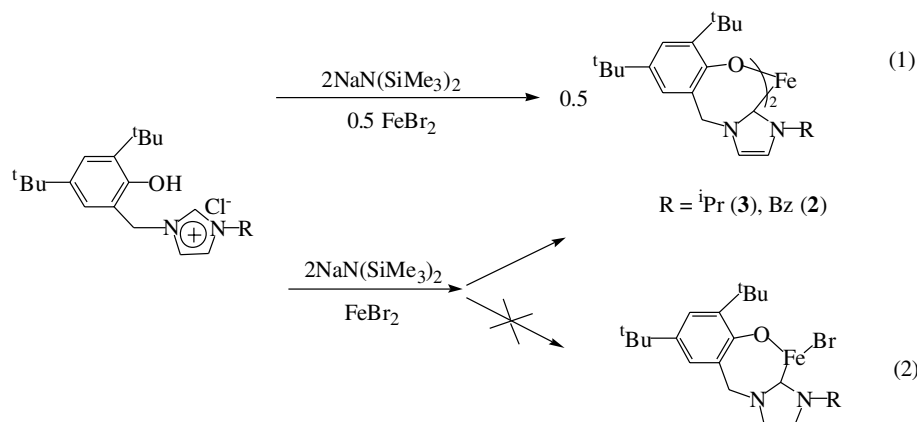
3. Results and discussion

3.1. Synthesis and characterization of **1** and **2**

Taking into consideration that anionic aryloxo-functionalized NHCs are capable of binding metal atom through the aryloxo oxygen and the carbene carbon to provide an [O, C_{carbene}]-type chelation, we are interested to use this kind of NHC ligand stabilizing Fe(II) complex. The aryloxo-functionalized NHC precursors used here, [HO-4,6-di-C(CH₃)₃-C₆H₂-2-CH₂{CH(NCHCHNR)}]Cl (R = CH(CH₃)₂, H₂L¹Cl, R = CH₂Ph, H₂L²Cl) were synthesized via the nucleophilic attack of a 1-alkylimidazole on an alkyl halide by the published method [17] in 85% or 80% yields, respectively.

H₂L¹Cl and H₂L²Cl reacted with two equivalents of Na[N(SiMe₃)₂] in THF at the temperature of –20 °C, respectively, to give the corresponding Na derivatives, which react directly with anhydrous FeBr₂ in 2:1 molar ratio at room temperature. After workup, mononuclear Fe(II) complexes **1** and **2** possessing the bi-chelating NHC ligands were obtained as colorless (for **1**) or light green yellow (for **2**) crystalline solids in good yield (68% for **1** and 70% for **2**), respectively (Scheme 1, eq. 1). It is worthy of mention that the both NaL¹ and NaL² show considerable thermal stability and no obviously 1,2-migration is observed at room temperature. In fact, the 1,2-migration is a relatively common reaction for singlet carbenes, i.e. the Na derivative of 1,3-bis(4,6-di-tert-butyl-2-hydroxybenzyl)imidazolium bromide was thermolabile and readily decomposing to the 2-alkylated imidazole at room temperature via the 1,2-benzyl migration [15d].

Attempt to synthesize the corresponding mono-ligand complex of iron by the same reaction in the molar ratio of 1:1 (NaLⁿ:FeBr₂) is unsuccessful (Scheme 1, eq. 2). Still the bis-ligand complexes **1** and **2** were isolated in reasonable lower yields of 36% and 37%, respectively. The situation is quite similar to that in the synthesis of Ni(II) complex with the same ligand [17]. The results might be contributed to either the additional of the second ligand

Scheme 1. Synthesis of **1** and **2**.

being faster than the first one or the disproportionation of mono-ligand Fe(II) halide to a more stable bis-ligand complex [17,19].

The formations of **1** and **2** were initially supported by elemental analysis and ¹H NMR spectroscopy. The ¹H NMR spectra of complexes **1** and **2** exhibit the characteristic resonance similar to those of the corresponding salts, except the disappearance of a signal at 10.30 ppm for **1** and at 10.27 ppm for **2**, assigned to the imidazolium C₂–H signals of the preligands [15d,17]. Although the assignment of these signals remains some equivocal, which is due to the up-field chemical shifts [20a] and broadened peaks [20b] observed for the protons of **1** and **2** as compared to their precursors, their positions are consistent with the proposed structural formulas given in Scheme 1. The ¹³C NMR spectra of complexes **1** and **2** are less informative due to the very broad peaks observed and the absence of the carbene carbon signal. The absence of the carbene carbon signal is often observed in NHC–Fe(II) complex [13b,21]. The more direct evidence of the formation of desired NHC–Fe(II) complexes **1** and **2** comes from X-ray structure determination.

Both of **1** and **2** are very air and moisture sensitive, but thermally stable. They decomposed at 145–147 °C for **1** and 163–166 °C for **2**, respectively. The complexes **1** and **2** are soluble in toluene, CH₂Cl₂, DME, THF and diethyl ether, and insoluble in hexane.

3.2. Crystal structures of **1** and **2**

Crystals of **1** and **2** suitable for an X-ray crystal structure determination were grown from diethyl ether/hexane at 0 °C. The crystallographic data for complexes **1** and **2** are given in Table 1. The selected bond lengths (Å) and angles (°) are collected in Table 2. The ORTEP drawings of **1** and **2** are shown in Figs. 1 and 2, respectively.

The X-ray structural analysis revealed that both **1** and **2** are mononuclear bis-ligand Fe(II) complexes and have similar solid-state structure, even they crystallize in different space groups (tetragonal for **1** and monoclinic for **2**). The center iron atom of each complex coordinated to two biden-

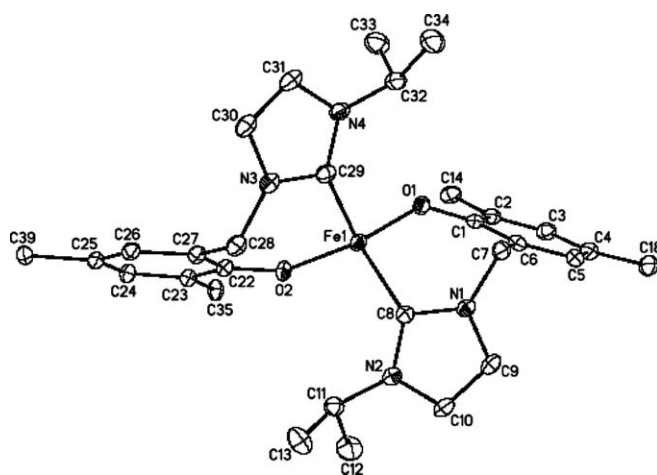


Fig. 1. The crystal structures of complex **1** showing 30% probability ellipsoids. The H atoms and the C atoms of Bu^t (except C39 and C18) are omitted for clarity.

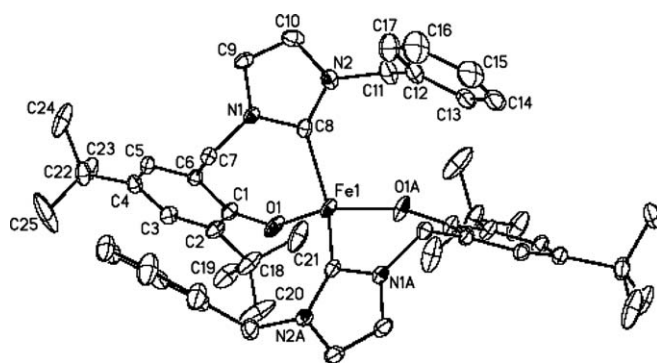


Fig. 2. The crystal structures of complex **2** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

tate ligands to form a distorted tetrahedral geometry, due to the acute O–Fe–C_{carbene} bite angles (101.0° and 99.6° for **1**, 109.0° and 109.0° for **2**) [19,22]. The two chelating rings adopt a *trans* arrangement around the iron atom. The two *trans* Fe–C_{carbene} bonds of 2.076 and 2.094 Å for **1**; 2.085 and 2.085 Å for **2** are indicative of a Fe–C single bond, and within the range of Fe–C_{carbene} bond distances (1.74–

2.19 Å) reported [11–14]. The two *trans* Fe–O bond of 1.918 Å for **1**, 1.9102 Å for **2** are very close to these found in a bis-ligand Fe(II) complex of N-isopropylsalicylaldehyde (1.912, 1.916 Å) [19], mostly due to the analogous bis-chelating structure of the two kinds of Fe(II) complexes. However, the length of Fe–O bond in complex **1** or **2** is obviously longer than those in Fe(II) complex with free phenolate ligands, i.e. the three coordinate homoleptic phenoxide of $[\text{Fe}\{\text{O}(2,4,6\text{-}t\text{-BuC}_6\text{H}_2)\}_2]_2$ (1.822 Å) [23], four coordinate trispyrazolylborate phenoxide of $\text{HB}\{(3,5\text{-ipr})\text{pz}\}_3\text{Fe}(\text{OC}_6\text{F}_5)$ (1.876 Å) [24], and a five coordinate iron calixarene adduct of THF (1.895 Å) [25]. In addition, either the length of Fe–C_{carbene} or the length of Fe–O bond in both **1** and **2** is very close no matter the different substituent presented on the nitrogen atom of NHC ligand. However, the difference in dihedral angles between **1** and **2** (67.6° and 63.8° for **1** and 65.6° for **2**) was observed. In complex **1**, the dihedral angles of N-heterocyclic carbene planes (N1–C8–N2–C10–C9 and N3–C29–N4–C31–C30) with the aromatic ring planes (C1–C2–C3–C4–C5–C6 and C22–C23–C24–C25–C26–C27) are slightly different (67.6° and 63.8°), while such angle in complex **2** both are 65.6°. The difference indicated that there is a larger distortion from tetrahedral geometry in **1** as compared with **2**, which may cause from a more bulk isopropyl group [17].

3.3. The ring-opening polymerization (ROP) of ϵ -CL with **1**

The catalytic activity of **1** for the ROP of ϵ -CL was examined. The results are summarized in Table 3. Preliminary experiments show that the present NHC–Fe(II) complex could be used as a single-component initiator for the ROP of ϵ -CL. For example, when the polymerization was carried out in toluene at 80 °C under the conditions of $[\epsilon\text{-CL}]/[\mathbf{1}] = 300:1$ molar ratio, the poly-CL (P-CL) of ca. 100% yield with number-average molecular weight of 4.0×10^4 could be obtained after 12 h. The polymer yield increased with the increasing of polymerization time, while the number-average molecule weight of obtained polymer decreased, and the molecular weight distribution of the polymer slightly broadened. The poor control on the number-average molecular weight as well as the decreasing trend of number-average molecular weight indicate that there is obviously inter- or intramolecular transesterification during the polymerization process [26,27]. Alternatively, the NHC–Fe(II) complex **1** designed herein could not efficiently inhibit these transesterifications in the course of the ϵ -CL polymerization.

Table 3
Catalytic activity of iron(II) complex **1** for the ROP of ϵ -CL

Run	<i>t</i> (h)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1	0.5	20	12.2	2.1
2	1.0	31	8.6	1.9
3	2.0	45	4.7	2.3
4	3.0	66	4.6	2.1
5	12.0	100	4.0	3.1

Conditions: $[\epsilon\text{-CL}] = 6.77$ mol/L, $[\epsilon\text{-CL}]/[\text{Fe}] = 300$, 80 °C, Ar.

In general, the ROP of ϵ -CL initiated with iron-alkoxide or iron-aryloxo complexes has been suggested to proceed via a coordination-insertion mechanism [26–28]. Considering the similarity between the reported iron-aryloxo complexes [26] and the present bis-ligand Fe(II) complex **1**, it is reasonable that the present ROP of ϵ -CL being proceeding by the similar mechanism. According to such mechanism, the obtained PCL chain should be ended by a unit of aryloxo-functionalized imidazolium salt. Thus, an oligomer of ϵ -CL was produced from the oligomerization of ϵ -CL with a $[\epsilon\text{-CL}]/[\mathbf{1}]$ (molar ratio) of 5, and analyzed by ¹H NMR spectra. The ¹H NMR spectra of the oligomer exhibit signals of phenyl and imidazolyl at the range of 6.87–7.76 ppm and that of tert-butyl at 1.28 ppm. So, the present ROP of ϵ -CL should also be occurred via a coordination-insertion mechanism.

4. Conclusion

In summary, two Fe(II) complexes supported by bidentate aryloxo-functionalized NHC ligand, L₂Fe (**1**) and L₂Fe (**2**), were synthesized via the metathesis reaction of FeBr₂ with NaL¹ and NaL² generated in situ. Preliminary experiments show that the present NHC–Fe(II) complex **1** could be used as a single-component initiator for the ROP of ϵ -CL. Further investigations on the detailed structure–activity relationships for these complexes as well as the mechanism are proceeding in our laboratory.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 278136 for complex **1**, and 278137 for **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.031.

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