



# Iron(III) complexes bearing 2-(benzimidazole)-6-(1-aryliminoethyl)pyridines: Synthesis, characterization and their catalytic behaviors towards ethylene oligomerization and polymerization

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## ABSTRACT

A series of iron(III) complexes ligated by 2-(benzimidazole)-6-(1-aryliminoethyl)pyridines was synthesized and examined by <sup>1</sup>H NMR, ESI-MS, IR spectroscopic, elemental analysis and X-ray photoelectron spectroscopy (XPS). Activated with methylaluminoxane (MAO), all ferric complexes exhibited good activities (up to  $5.38 \times 10^6 \text{ g mol}^{-1}(\text{Fe}) \text{ h}^{-1}$ ) of ethylene oligomerization and polymerization, and resultant oligomers and polyethylene waxes showed high  $\alpha$ -olefin feature, meanwhile the distribution of oligomers mostly resembled Schulz–Flory rules. The various reaction parameters were investigated in detail, and the less bulky and electron-withdrawing substituents of ligands could enhance the catalytic activities of their ferric complexes. The observations explain the cause for unstable activities performed by stored iron(II) complexes.

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## 1. Introduction

Ethylene oligomerization is a major industrial process for producing linear  $\alpha$ -olefins in the range of C<sub>6</sub>–C<sub>20</sub> with about six millions of tons productivities annually, which provide basic feedstocks in the preparation of detergents, plasticizers and copolymerization with ethylene for the linear low-density polyethylene (LLDPE) [1–3]. The iron and cobalt catalysts showed unique properties for the high selectivity of vinyl-type oligomers and polyolefins (polyolefin waxes). The pioneering work was reported by Gibson [4] and Brookhart groups [5] employing bis(imino)pyridyl iron and cobalt complexes as highly active catalyst for ethylene polymerization and oligomerization [6–17]. Extensive research on bis(imino)pyridyl iron complexes has been focused on understanding the active species or intermediates [18–25], controlling the products of polymers or oligomers as well as improving the catalytic activities through adapting steric and electronic characteristics of the complexes [26–33]. Apart from ferrous catalysts ligated by bis(imino)pyridines, a few models of iron catalysts were reported [34–39], but the iron complexes bearing 2-imino-

1,10-phenanthroline [40–42], 2-benzimidazole-6-iminopyridines [43–45], 6-(quinoxalin-2-yl)-2-iminopyridines [46], 2-benzoxazolyl-6-[1-(arylimino)ethyl]pyridines [47], 2-methyl-2,4-bis(6-iminopyridin-2-yl)-1H-1,5-benzodiazepines [48,49], 2-benzimidazole-1,10-phenanthrolines [50], 2-oxazoline/benzoxazole-1,10-phenanthrolines [51] and N-((pyridin-2-yl)methylene)-quinolin-8-amine derivatives [52] provided alternative models performing high catalytic activities [53]. Despite great interest in designing new iron(II) based catalysts, unstable catalytic activities of stored iron(II) catalysts were often observed, however, commonly within one-order or less than ten times. The part oxidation of ferrous into ferric was imaged, and the nature of the active species as iron(III) or iron(II) were not settled [54–57]. Recently ferric pre-catalysts ligated by bis(imino)pyridines have generated from iron(II) precursors and shown the catalytic behavior towards ethylene oligomerization [17,21,58,59]. The detail investigation of ferric complexes will extend novel catalytic model for ethylene oligomerization and polymerization and explain the cause in various activities of stored iron(II) catalysts.

In this paper, a series of ferric complexes based on 2-(benzimidazole)-6-(1-aryliminoethyl)pyridines was synthesized and fully investigated for their catalytic behaviors in ethylene reactivity. Good catalytic activities toward ethylene oligomerization and polymerization could be observed in the presence of methylaluminoxane (MAO), which exhibited similar trend in catalytic behaviors but a little lower reactivity than that of their ferrous analogues

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[43]. The catalytic reaction parameters and the steric and electronic effects of ligands were investigated in detail on the influence of their catalytic activities.

## 2. Experimental

### 2.1. General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. All the organic compounds used as ligands for the ferric complexes were prepared by employing our developed procedure [43,60]. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp., diethylaluminum chloride ( $\text{Et}_2\text{AlCl}$ , 1.7 M in hexane) was purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals.  $^1\text{H}$  NMR spectra were recorded on JOEL 300 NMR spectrometer with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al  $K\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. GC analysis was performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) DM-1 silica capillary column. The yield of oligomers was calculated by referencing with the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated areas in the GC trace.

### 2.2. Synthesis of title iron(III) complexes

#### 2.2.1. General procedure

A solution of the ligand in THF was added dropwise to an equimolar amount of  $\text{FeCl}_3$  in THF solution. Immediately, the color of the solution changed and some precipitate formed. The reaction mixture was stirred at room temperature for 8 h then diluted with diethyl ether. The resulting precipitate was collected, washed with diethyl ether and dried in vacuum. All of the complexes were prepared in high yield in this manner. Data for these complexes are as follows.

**2.2.1.1.  $\text{L}^1\text{FeCl}_3$ .** Obtained as brown powder in 82% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.50 (1H, -Py), 8.43 (1H, -Py), 8.21 (1H, -Ph), 7.76 (m, 2H), 7.53 (2H, -Ph), 7.12 (2H, -Ph), 6.96 (1H, -Ph), 4.34 (3H, -CH<sub>3</sub>), 2.23 (3H, -CH<sub>3</sub>), 2.01 (s, 6H, -CH<sub>3</sub>). ESI-MS: 481.0 (M-Cl<sup>-</sup>), 355.3 (M-FeCl<sub>3</sub>+H<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 2968, 1594 ( $\nu_{\text{C}=\text{N}}$ ); 1489; 1403; 1368; 1332; 1305; 1282; 1256; 1205; 1156; 1100; 793; 750. *Anal. Calc.* for  $\text{C}_{23}\text{H}_{22}\text{Cl}_3\text{N}_4\text{Fe}$ : C, 53.47; H, 4.29; N, 10.84. Found: C, 53.86; H, 4.68; N, 10.34%.

**2.2.1.2.  $\text{L}^2\text{FeCl}_3$ .** Obtained as yellow powder in 79% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.51 (1H, -Py), 8.42 (1H, -Py), 8.20 (1H, -Ph), 7.74 (m, 2H), 7.34 (2H, -Ph), 7.14 (2H, -Ph), 7.03 (1H, -Ph), 4.34 (3H, -CH<sub>3</sub>), 2.35 (3H, -CH<sub>3</sub>), 2.25 (4H, -CH<sub>2</sub>), 1.10 (6H, -CH<sub>3</sub>). ESI-MS: 383.4 (M-FeCl<sub>3</sub>+H<sup>+</sup>), 421.2 (M-FeCl<sub>3</sub>+K<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 3428, 2964, 1593 ( $\nu_{\text{C}=\text{N}}$ ); 1491; 1455; 1403; 1371; 1332; 1283; 1258; 1200; 1160; 1091; 1025; 791; 749. *Anal. Calc.* for

$\text{C}_{25}\text{H}_{26}\text{Cl}_3\text{N}_4\text{Fe}$ : C, 55.12; H, 4.81; N, 10.29. Found: C, 55.23; H, 5.02; N, 10.02%.

**2.2.1.3.  $\text{L}^3\text{FeCl}_3$ .** Obtained as yellow powder in 79% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.52 (1H, -Py), 8.41 (1H, -Py), 8.21 (1H, -Ph), 7.74 (m, 2H), 7.35 (2H, -Ph), 7.20 (2H, -Ph), 7.10 (1H, -Ph), 4.35 (3H, -CH<sub>3</sub>), 2.27 (3H, -CH<sub>3</sub>), 2.10 (2H, -CH), 1.14 (12H, -CH<sub>3</sub>). ESI-MS: 537.1 (M-Cl<sup>-</sup>), 411.5 (M-FeCl<sub>3</sub>+H<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 3423, 2964, 1594 ( $\nu_{\text{C}=\text{N}}$ ); 1492; 1463; 1423; 1402; 1369; 1330; 1307; 1284; 1258; 1197; 1105; 1025; 792; 753. *Anal. Calc.* for  $\text{C}_{27}\text{H}_{30}\text{Cl}_3\text{N}_4\text{Fe}$ : C, 56.62; H, 5.28; N, 9.78. Found: C, 56.86; H, 5.44; N, 9.58%.

**2.2.1.4.  $\text{L}^4\text{FeCl}_3$ .** Obtained as brown powder in 69% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.57 (1H, -Py), 8.37 (1H, -Py), 8.24 (1H, -Ph), 7.74 (m, 2H), 7.29 (m, 4H), 6.87 (1H, -Ph), 4.35 (3H, -CH<sub>3</sub>), 2.54 (3H, -CH<sub>3</sub>). ESI-MS: 487.9 (M-Cl<sup>-</sup>), 363.4 (M-FeCl<sub>3</sub>+H<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 3406, 3048, 1593 ( $\nu_{\text{C}=\text{N}}$ ); 1491; 1424; 1405; 1368; 1308; 1284; 1254; 1183; 1154; 1094; 1025; 873; 782; 749. *Anal. Calc.* for  $\text{C}_{21}\text{H}_{16}\text{Cl}_3\text{F}_2\text{N}_4\text{Fe}$ : C, 48.08; H, 3.07; N, 10.68. Found: C, 47.93; H, 3.33; N, 10.37%.

**2.2.1.5.  $\text{L}^5\text{FeCl}_3$ .** Obtained as brown powder in 71% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.56 (1H, -Py), 8.42 (1H, -Py), 8.24 (1H, -Ph), 7.65 (m, 4H), 7.37 (m, 2H), 7.20 (1H, -Ph), 4.35 (3H, -CH<sub>3</sub>), 2.40 (3H, -CH<sub>3</sub>). ESI-MS: 397.2 (M-FeCl<sub>3</sub>+H<sup>+</sup>), 418.5 (M-FeCl<sub>3</sub>+Na<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 3432, 3069, 1596 ( $\nu_{\text{C}=\text{N}}$ ); 1483; 1433; 1370; 1306; 1254; 1226; 1188; 1158; 1024; 931; 802; 783; 745. *Anal. Calc.* for  $\text{C}_{21}\text{H}_{16}\text{Cl}_5\text{FeN}_4$ : C, 45.24; H, 2.89; N, 10.05. Found: C, 45.10; H, 2.99; N, 10.03%.

**2.2.1.6.  $\text{L}^6\text{FeCl}_3$ .** Obtained as yellow powder in 73% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.57 (1H, -Py), 8.45 (1H, -Py), 8.24 (1H, -Ph), 7.76 (m, 4H), 7.36 (m, 2H), 7.07 (1H, -Ph), 4.36 (3H, -CH<sub>3</sub>), 2.35 (3H, -CH<sub>3</sub>). ESI-MS: 485.1 (M-FeCl<sub>3</sub>+H<sup>+</sup>), 507.1 (M-FeCl<sub>3</sub>+Na<sup>+</sup>). IR (KBr; cm<sup>-1</sup>): 3425, 3067, 1594 ( $\nu_{\text{C}=\text{N}}$ ); 1492; 1429; 1368; 1282; 1259; 1228; 1186; 1160; 1025; 928; 830; 779; 751. *Anal. Calc.* for  $\text{C}_{21}\text{H}_{16}\text{Cl}_3\text{Br}_2\text{FeN}_4$ : C, 39.02; H, 2.49; N, 8.67. Found: C, 39.13; H, 2.67; N, 8.31%.

### 2.3. Procedure for oligomerization and polymerization with 1 atm of ethylene

Ethylene oligomerization and polymerization were carried out as follows: the catalyst precursor (Fe(III) complex) was dissolved in toluene in a Schlenk tube stirred with a magnetic stirrer under an ethylene atmosphere (1 atm), and the reaction temperature was controlled by a water bath. The reaction was initiated by adding the desired amount of cocatalyst. After the desired period of time, a small amount of the reaction solution was collected with a syringe and was quenched by the addition of 5% hydrochloric acid in an ice-water bath in accordance with the oligomers produced. An analysis by gas chromatography (GC) was carried out to determine the distribution of oligomers obtained. The remaining solution was quenched with hydrochloric acid in ethanol (5%), and the precipitated polyethylene was collected by filtration, washed with ethanol, dried under vacuum at 60 °C to constant weight, weighed and finally characterized.

### 2.4. Procedure for oligomerization and polymerization at higher ethylene pressure

Ethylene oligomerization and polymerization were performed in a 250-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller. A 100 mL amount of toluene containing the catalyst precursor was transferred to the

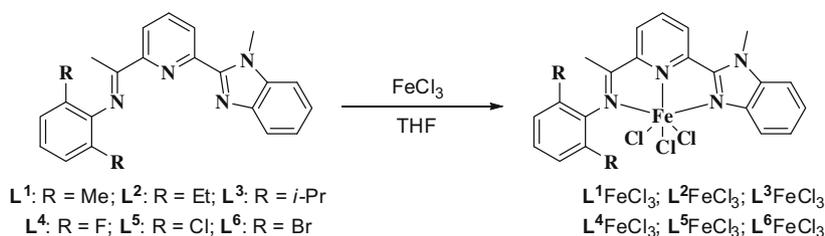
fully dried reactor under an ethylene atmosphere. The required amount of cocatalyst (MAO, MMAO or Et<sub>2</sub>AlCl) was then injected into the reactor via a syringe. At the reaction temperature, the reactor was sealed and pressurized to high ethylene pressure, and the ethylene pressure was maintained with feeding of ethylene. After the reaction mixture was stirred for the desired period, the pressure was released and a small amount of the reaction solution was collected, which was then analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained. Then the residual reaction solution was quenched with 5% hydrochloric acid in ethanol. The precipitated low-molecular-weight waxes were collected by filtration, washed with ethanol and water and dried under vacuum to constant weight.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the iron(III) complexes containing 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines

The 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines (L<sup>1</sup>–L<sup>6</sup>) were prepared according to our reported procedures [43,60]. The iron(III) complexes (L<sup>1</sup>FeCl<sub>3</sub>–L<sup>6</sup>FeCl<sub>3</sub>) were obtained by treating the THF solution of FeCl<sub>3</sub> with an equimolar corresponding ligand (L<sup>1</sup>–L<sup>6</sup>) at room temperature in satisfying yields (69–82%) (Scheme 1). These complexes showed high stability in both solution and solid state, such behaviors were different from their iron(II) complexes [43,60]. These iron(III) complexes were identified by <sup>1</sup>H NMR, ESI-MS, FT-IR and elemental analysis. From <sup>1</sup>H NMR, the chemical shift to a higher field for the pyridyl ring was observed because of the coordination with iron center. The IR spectra of the ligands L<sup>1</sup>–L<sup>6</sup> gave the C=N<sub>imino</sub> stretching frequencies in the range of 1639–1650 cm<sup>-1</sup> [43,60], while the C=N<sub>imino</sub> stretching vibrations of the complexes L<sup>1</sup>FeCl<sub>3</sub>–L<sup>6</sup>FeCl<sub>3</sub> shifted toward lower frequencies between 1593 and 1596 cm<sup>-1</sup> with weak intensities which indicates the effective coordination between the imino nitrogen atom and the iron center. It has been tried hard in getting the single crystals of those iron(III) complexes in different solution parameters for their absolute molecular structures, however, likely crystals are not suitable for X-ray diffraction and the differences of both ionic radius and electronic effects of ferrous and ferric cores would be considered. Further investigation for direct molecular structures of ferric complexes is still worthy to study.

In order to confirm the oxidation state of Fe(III) core in the title complexes, XPS experiments for the title Fe(III) complexes and their iron(II) analogues are carried out to observe their binding energies of Fe 2p<sub>3/2</sub> (Table 1). According to the results, the obvious differences indicate the difference between the Fe(III) complexes and their Fe(II) analogues. The Fe(III) complexes clearly show the characteristic peaks coinciding with literature data of Fe(III) [61]. In addition, the significant difference for Fe(II) complex bearing 6-difluoro-N-(1-(6-(1-methyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethylidene)benzenamine (L<sup>4</sup>) is caused by different coordination mode in resulting its molecular structure as L<sub>2</sub><sup>4</sup>Fe-FeCl<sub>4</sub> [60].



Scheme 1. Synthesis of iron(III) complexes with 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines.

Table 1  
Fe 2p<sub>3/2</sub> binding energies from XPS analysis.

Ligand	Fe 2p <sub>3/2</sub> (eV)	
	Fe(III) complexes	Fe(II) complexes
L <sup>1</sup>	711.1	710.6
L <sup>2</sup>	711.1	710.6
L <sup>3</sup>	711.2	710.8
L <sup>4</sup>	711.2	708.7, 710.8
L <sup>5</sup>	710.6	710.2

#### 3.2. Ethylene activation behaviors of the N<sup>^</sup>N<sup>^</sup>N coordinated iron(III) complexes

##### 3.2.1. Cocatalysts selection

The influences of various cocatalysts on the ethylene activation were evaluated with the catalytic systems formed from L<sup>1</sup>FeCl<sub>3</sub> at 10 atm of ethylene pressure in the presence of methylaluminoxane (MAO), modified methylaluminoxane (MMAO) or diethylaluminum chloride (Et<sub>2</sub>AlCl) as cocatalyst. The results summarized in Table 2 indicated that L<sup>1</sup>FeCl<sub>3</sub>/MAO system showed remarkable catalytic activity in the order of 10<sup>5</sup> g mol<sup>-1</sup>(Fe) h<sup>-1</sup>, which was nearly 13 times and 30 times higher than that of L<sup>1</sup>FeCl<sub>3</sub>/MMAO system and L<sup>1</sup>FeCl<sub>3</sub>/Et<sub>2</sub>AlCl system, the distribution of oligomers was ranged from C<sub>4</sub> to C<sub>28</sub> with high  $\alpha$ -olefin selectivity.

##### 3.2.2. Ethylene oligomerization at ambient pressure

L<sup>1</sup>FeCl<sub>3</sub> and L<sup>3</sup>FeCl<sub>3</sub> were investigated for their ethylene catalytic behaviors at ambient pressure and the results were collected in Table 3. Under different conditions, the oligomer products were obtained in moderate catalytic activity with high  $\alpha$ -olefin selectivity. The amount of cocatalyst was found to have significant influences on the catalytic behaviors of L<sup>1</sup>FeCl<sub>3</sub>/MAO system. When the Al/Fe molar ratio was varied from 300 to 1500, the catalytic activities initially increased and then decreased (entries 1–4 in Table 3). Notably, the catalytic activity increased sharply from the Al/Fe molar ratio of 300–500, which may be attributed that MAO scavenged adventitious water and impurities in the solvent at the Al/Fe ratio of 300 and the iron catalysts require more cocatalyst to be active. At the Al/Fe ratio of 500, the catalytic activity was at a peak (entries 2 in Table 3). Increase the Al/Fe molar ratio to 1000 and 1500 led to lower activity (entries 3–4 in Table 3). This observation could be traced to the impurities in commercial MAO such as alkyl aluminum, which led to the deactivation of active catalytic sites [48]. If the reaction temperature was elevated to 40 °C, it resulted in a sharp decrease of activity (entry 5 in Table 3), which is possible due to the decomposition of active species and lower ethylene solubility at higher temperature [7,21], but the oligomer distribution was not changed evidently.

##### 3.2.3. Ethylene oligomerization at 10 atm of ethylene

3.2.3.1. Effect of ethylene pressure. Ethylene activation with iron(III) catalysts were conducted at 10 atm of ethylene as shown in Table 4.

**Table 2**  
Selection of the suitable cocatalyst based on  $L^1FeCl_3$ .

Entry	Cocatalyst	Al/Fe	Oligomer activity <sup>a</sup>	Oligomer distribution
1	MAO	1000	21.8	C <sub>4</sub> –C <sub>28</sub>
2	MMAO	1000	1.64	C <sub>4</sub> –C <sub>28</sub>
3	Et <sub>2</sub> AlCl	500	0.75	C <sub>4</sub>

Condition: 5  $\mu$ mol catalyst; 10 atm ethylene; 30 min; 20 °C; 100 mL toluene.<sup>a</sup> Unit of activity:  $10^4$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>.**Table 3**  
Oligomerization of ethylene with  $L^1FeCl_3$ ,  $L^3FeCl_3$ /MAO at 1 atm.

Entry	Catalyst	Al/Fe	T (°C)	Activity <sup>a</sup>	$\alpha$ -olefin <sup>b</sup> (%)	Oligomer distribution (%)		
						C <sub>4</sub> / $\Sigma$ C	C <sub>6</sub> / $\Sigma$ C	C <sub>8</sub> / $\Sigma$ C
1	$L^1FeCl_3$	300	20	2.78	>99	77.0	4.9	18.1
2	$L^1FeCl_3$	500	20	8.37	>99	60.2	8.4	31.4
3	$L^1FeCl_3$	1000	20	5.19	>99	40.6	20.2	39.2
4	$L^1FeCl_3$	1500	20	5.01	>99	77.2	13.0	9.8
5	$L^1FeCl_3$	500	40	3.62	>99	55.5	5.5	39.0
6	$L^3FeCl_3$	500	20	4.08	>99	73.6	8.7	17.7

Condition: 5  $\mu$ mol catalyst; 1 atm ethylene; 30 min; 30 mL toluene.<sup>a</sup> Unit of activity:  $10^3$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>.<sup>b</sup> Percent  $\alpha$ -olefin content determined by GC and GC-MS.

It is observed that the catalytic activities were dramatically improved along with increasing ethylene pressure attributable to the higher monomer concentration around active iron centers. The product properties were also significantly affected. Much longer carbon chain oligomers and polymer wax could be obtained at high ethylene pressure. Comparing with the catalytic behavior at ambient pressure (Table 3), the activities were increased by nearly two order of magnitude at 10 atm of ethylene and the distribution of oligomers resembled Schulz–Flory rules, the chain propagation is represented with the constant  $K$ , where  $K$  = rate of propagation/(rate of propagation + rate of chain transfer) = (moles of  $C_{n+2}$ )/(moles of  $C_n$ ), the  $K$  values are determined by the molar ratio of  $C_{12}$  and  $C_{14}$  fractions [62–65].

**3.2.3.2. Effects of the molar ratio of Al/Fe and reaction temperature.** The influences of different molar ratio of MAO to iron(III) complex on catalytic activities were investigated in detail with

$L^1FeCl_3$  and  $L^4FeCl_3$ , and the results were collected in Table 4. For complex  $L^1FeCl_3$ , when the Al/Fe molar ratio was enhanced from 100 to 1000, the oligomerization activity initially increased and then decreased (entries 1–5 in Table 4), the highest activity was obtained at Al/Fe = 500 (entry 3 in Table 4). For the Al/Fe molar ratio was 100, the activity was very low and only 1-butene was produced (entry 1 in Table 4). The distribution of the oligomers was nearly as a constant with different Al/Fe molar ratio from 300 to 1000, which could be observed from the  $K$  value (0.68–0.71) (entries 2–5 in Table 4). The polymerization activity was changed with the similar trend but got the peak value at Al/Fe = 300 (entry 2 in Table 4). Similar to the effects of the molar ratio of Al/Fe on  $L^1FeCl_3$ ,  $L^4FeCl_3$  showed the same trend and the activity was also peaked at Al/Fe = 500 (entry 10 in Table 4). Differently, the  $K$  value was decreased gradually with the increase of cocatalyst molar ratio from 300 to 1000 probably due to the fast  $\beta$ -hydrogen elimination (entries 9–12 in Table 4).

As the oligomerization and polymerization of ethylene are highly exothermic reactions, the reaction temperature significantly affects the catalytic activity. To understand such influence, the catalytic system of  $L^1FeCl_3$  with 500 eq. MAO at 10 atm of ethylene was investigated with different reaction temperature (entries 3, 15 and 16 in Table 4). Elevation of the reaction temperature from 20 °C to 60 °C resulted in a sharp decrease of productivity separated as oligomerization and polymerization activity, which can be explained as catalyst decomposition and lower ethylene solubility at higher temperature [7,21]. Moreover, the oligomers distribution became narrower along with the decreased reactivity. The proportion of  $C_4$  and other short-chain oligomers were greatly increased at higher temperature because of the faster  $\beta$ -hydrogen elimination than the rate of ethylene propagation and the distribution of obtained oligomers did not resemble Schulz–Flory rules (entry 16 in Table 4). At 60 °C, only 1-butene and 1-hexene could be obtained with very low activity (entry 16 in Table 4). This phenomenon is in consistent with our previous observations [43].

**3.2.3.3. Effect of the ligand environments.** The natural catalytic behaviors of these tridentate ferric complexes are rooted in the characteristics of ligands due to their different substituents, which greatly affected their catalytic behaviors. Fixed the reaction condition, complexes  $L^1FeCl_3$ – $L^6FeCl_3$  showed high activities in ethylene oligomerization (entries 3, 6, 7, 10, 13, 14 in Table 4). Based on these data, their oligomerization activity varied in the orders of

**Table 4**  
Oligomerization and polymerization of ethylene with  $L^1FeCl_3$ – $L^6FeCl_3$ /MAO at 10 atm.

Entry	Catalyst	Al/Fe	T (°C)	$K$	$\alpha$ -olefin <sup>b</sup> (%)	Activity <sup>a</sup>		Oligomer distribution (%)		
						Oligomer	Polymer	C <sub>4</sub> / $\Sigma$ C	C <sub>6</sub> / $\Sigma$ C	C <sub>8</sub> / $\Sigma$ C
1	$L^1FeCl_3$	100	20	–	>99	0.06	–	100	–	–
2	$L^1FeCl_3$	300	20	0.71	99	6.56	1.18	17.2	15.8	67.0
3	$L^1FeCl_3$	500	20	0.68	98	17.5	0.69	16.9	17.0	66.1
4	$L^1FeCl_3$	700	20	0.71	98	4.83	0.23	15.7	15.8	68.5
5	$L^1FeCl_3$	1000	20	0.70	96	2.18	–	18.1	17.3	64.6
6	$L^2FeCl_3$	500	20	0.59	98	10.3	–	28.9	21.6	49.5
7	$L^3FeCl_3$	500	20	0.46	97	7.95	–	42.5	25.7	31.8
8	$L^4FeCl_3$	100	20	–	>99	0.05	–	100	–	–
9	$L^4FeCl_3$	300	20	0.45	99	18.2	–	50.5	28.6	20.9
10	$L^4FeCl_3$	500	20	0.43	99	53.8	–	49.6	29.1	21.3
11	$L^4FeCl_3$	700	20	0.40	99	35.9	–	54.4	28.5	17.1
12	$L^4FeCl_3$	1000	20	0.38	99	8.65	–	51.6	28.3	20.1
13	$L^5FeCl_3$	500	20	0.65	99	19.1	–	21.0	19.4	59.6
14	$L^6FeCl_3$	500	20	0.75	99	8.07	–	10.1	11.4	78.5
15	$L^1FeCl_3$	500	40	0.70	89	0.49	0.14	34.9	21.6	43.5
16	$L^1FeCl_3$	500	60	–	>99	0.04	–	77.3	22.7	–

Condition: 5  $\mu$ mol catalyst; 30 min; 10 atm; 100 mL toluene.<sup>a</sup> Unit of activity:  $10^3$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup>.<sup>b</sup> Percent  $\alpha$ -olefin content determined by GC and GC-MS.

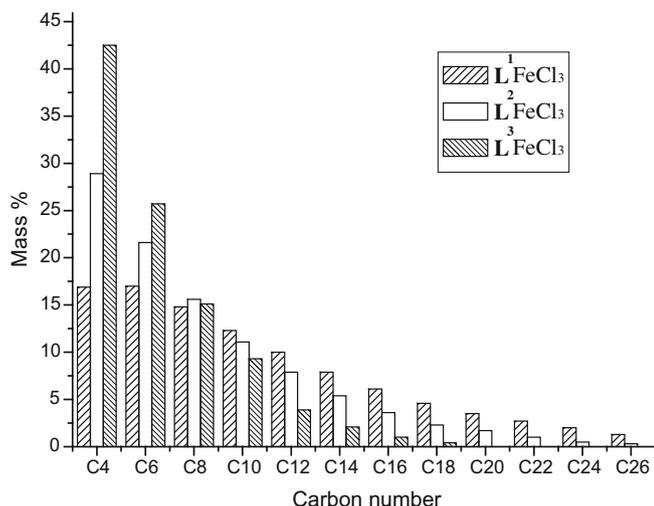


Fig. 1. Oligomer distribution obtained in entries 3, 6, 7 in Table 4.

$L^3FeCl_3$  (with substituent of *i*-Pr) <  $L^2FeCl_3$  (with Et) <  $L^1FeCl_3$  (with Me) and  $L^6FeCl_3$  (with Br) <  $L^5FeCl_3$  (with Cl) <  $L^4FeCl_3$  (with F), and it was consistent with the trend of iron(II) catalytic systems with MAO reported [43]. This could be demonstrated that the bulkiness at the *ortho*-positions of the imino-N aryl ring may prevent the insertion of ethylene to the active center in the catalytic system, therefore resulting in the decrease of catalytic activity. The highest activity could be up to  $5.38 \times 10^6 \text{ g mol}^{-1}(\text{Fe})^{-1} \text{ h}^{-1}$  for complex  $L^4FeCl_3$  (entry 10 in Table 4). According to the *K* value, the distribution of the oligomers was also greatly influenced by the different substitutes on the ligands. For the ligands with electron donating group, the *K* value was increased with small bulkiness substitutes and peaked at 0.68 for complex  $L^1FeCl_3$  (entry 3 in Table 4), the content of longer carbon chain oligomers became decreased with large bulkiness substitutes. For complex  $L^3FeCl_3$ , the oligomers only ranged from C<sub>4</sub> to C<sub>18</sub> (entry 7 in Table 4). What's more, for electron withdrawing group, the *K* value was increased with weaker electro negativities group and peaked at 0.75 for complex  $L^6FeCl_3$  (entry 14 in Table 4). For complex  $L^4FeCl_3$  with *K* value of 0.43, the content of C<sub>4</sub> was nearly half of all the produced oligomers (entry 10 in Table 4). The distributions of the oligomers (entries 3, 6, 7 of Table 4) are shown in detail in Fig. 1. Interestingly, only complex  $L^1FeCl_3$  with small bulkiness substitutes could produce polymer wax because of the faster ethylene propagation than chain termination; the PE waxes obtained demonstrated the linear characteristics and the presence of the vinyl end groups on the base of their IR and NMR spectra. In contrast to the ferrous catalytic systems with the same ligands that we reported previously [43], these ferric analogues exhibited similar trend in catalytic behaviors but a little lower reactivity (entry 5 in Table 4 and literature [43]). The active species generated by either iron(III) or iron(II) complexes could be assumed as the same ones [66], however, better performances are observed with ferrous complexes than their ferric analogues. Therefore, the unstable catalytic behaviors observed by stored ferrous catalysts could be caused by partly oxidizing ferrous species into ferric ones.

#### 4. Conclusions

A series of iron(III) complexes ligated by 2-(1-methyl-2-benzimidazole)-6-(1-aryliminoethyl)pyridines was synthesized and characterized carefully. These complexes could be easily activated and exhibited high activities in ethylene oligomerization and polymerization with MAO as cocatalyst at high ethylene pressure. The

highest catalytic activity was up to  $5.38 \times 10^6 \text{ g mol}^{-1}(\text{Fe})^{-1} \text{ h}^{-1}$  in producing  $\alpha$ -olefins (C<sub>4</sub>–C<sub>28</sub>) with high selectivity. These iron(III) complexes showed the same trend in catalytic behaviors in contrast to the relative iron(II) analogues [43]. The catalysts containing less bulky substituents of ligands enhance ethylene insertion and show better activity. In some cases, the polyethylene waxes have been obtained and confirmed to be linear long-chain vinyl-end alkenes. On the base of current results, iron(III) and iron(II) complexes are assumed to form the same active species for ethylene oligomerization and polymerization.

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