Ethylene oligomerization catalyzed by a novel iron complex containing fluoro and methyl substituents

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Abstract

A novel 2,6-bis(imino)pyridyl iron complex, $[2,6\text{-}(2\text{-}F\text{-}4\text{-}CH_3C_6H_3N=CCH_3)_2C_5H_3N]FeCl_2 \cdot H_2O$ (**3**) has been synthesized by the reaction of the corresponding bis(imino)pyridyl ligand with $FeCl_2 \cdot 4H_2O$ in tetrahydrofuran (THF). The activity of complex **3** reaches to 10^7 g/mol Fe h in ethylene oligomerization, and the products are mostly (>90%) 1-butene, 1-hexene and 1-octene. As reaction temperature increases, the activities decrease rapidly and the product distributions shift to the low-molecular-weight part. The product distributions are almost unchanged when the Al/Fe molar ratio increases from 420 to 2500, but the catalytic activities increase rapidly at first and then decrease. Other three complexes $\{2,6\text{-}(2\text{-}X\text{-}4\text{-}Y\text{-}6\text{-}ZC_6H_3N=CCH_3)_2C_5H_3N\}FeCl_2 \cdot nH_2O$ (X = CH_3, Y = CH_3, Z = H, $n = 0$ (**1**), X = F, Y = H, Z = F, $n = 1$ (**2**)) and $\{Fe[2,6\text{-}(2\text{-}FC_6H_3N=CCH_3)_2C_5H_3N]_2\}^{2+}[FeCl_4]^{2-} \cdot H_2O$ (**4**) have been also synthesized for comparison and used for ethylene oligomerization. The *ortho* and *para* substituents on aniline have performed effects on oligomerization activities and distributions of oligomers for 2,6-bis(imino)pyridyl iron complexes.
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Keywords: 2,6-Bis(imino)pyridyl iron complex; Ethylene oligomerization; α-Olefin; Oligomers distribution

1. Introduction

Linear low-molecular-weight α-olefins are used primarily as comonomers for the production of linear low-density polyethylene (LLDPE), plasticizers and synthetic lubricants. Since Ziegler's original work on AlR_3 catalysis of ethylene oligomerization, there has been considerable sustained interest in developing new oligomerization catalysts. In 1998, Small and Brookhart [1–3] and Britovsek et al. [4,5] reported iron and cobalt complexes with mono-alkyl-substituted bis(imino)pyridyl ligands. Compared with traditional Ziegler-Natta catalysts of early transition metals, the novel late transition metal catalysts possess advantages not only in catalytic activity and selectivity, but also in their potential for tolerating heteroatom functionalities. These iron and cobalt catalysts exhibit high activity in ethylene oligomerization, and the oligomers consist of >95% linear α-olefins. Some

other complexes [6–9] were synthesized and reported for oligomerization of ethylene, and most of their ligands contain alkyls on the *ortho* position of aryl rings. But the distributions of oligomers are very wide because of the large steric hindrance of alkyl substituents.

In order to obtain the resulting oligomers with narrow distribution, Bluhm et al. [10] reported some complexes without *ortho* substituents at aryl rings and used for oligomerization of ethylene. The distribution of oligomers obtained is much narrower (mainly C_4–C_{10}), but catalytic activities (TOF $< 2.5 \times 10^4 \, h^{-1}$) and selectivity for α-olefins (<88%) are lower because of too small steric hindrance. Recently, a series of halogen-substituted 2,6-bis(imino)pyridyl iron and cobalt complexes were reported by Chen et al. [11,12]. Their result shows that the oligomer distributions obtained from the complexes are much narrower when the *ortho* position of aryl rings are halogen than those are alkyls. Meanwhile, alkyl in the *meta* or *para* position of aryl rings could improve the catalytic activities evidently as reported in literatures [4–6]. In order to find an oligomerization catalyst with both high activity

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and narrow oligomer distributions, a novel iron (II) complex [2,6-(2-F-4-CH$_3$C$_6$H$_3$N=CCH$_3$)$_2$C$_5$H$_3$N]FeCl$_2$·H$_2$O (**3**) will be reported in the present paper, on which there are a methyl substituted on *para* and a fluoro substituted on *ortho* position of aryl rings respectively. {Fe[2,6-(2-FC$_6$H$_3$ N=CCH$_3$)$_2$C$_5$H$_3$N]$_2$}$^{2+}$ [FeCl$_4$]$^{2-}$·H$_2$O (**4**) and the other two complexes ({2,6-(2,4-(CH$_3$)$_2$C$_6$H$_3$N=CCH$_3$)$_2$C$_5$H$_3$N} FeCl$_2$ (**1**) and ({2,6-(2,6-F$_2$C$_6$H$_3$N=CCH$_3$)$_2$C$_5$H$_3$N} FeCl$_2$ (**2**) are synthesized for comparison. The relation between the structures of the complexes and their activity and selectivity is also discussed.

2. Experimental

2.1. Materials

2,6-Diacetylpyridine, 2-fluoro-4-methylaniline, 2,4-dimethylaniline, 2,6-difluoroaniline and 2-fluoroaniline were purchased from Acros. Polymerization grade ethylene was obtained from Yanshan Petro-chemical Company Sinopec China. Methylaluminoxane (MAO) solution (1.4 mol/L) of toluene was purchased from Albemarle Corp. Toluene, THF and ether were distilled from solidum/benophenone and degassed. All other chemicals were obtained commercially and used without further purification.

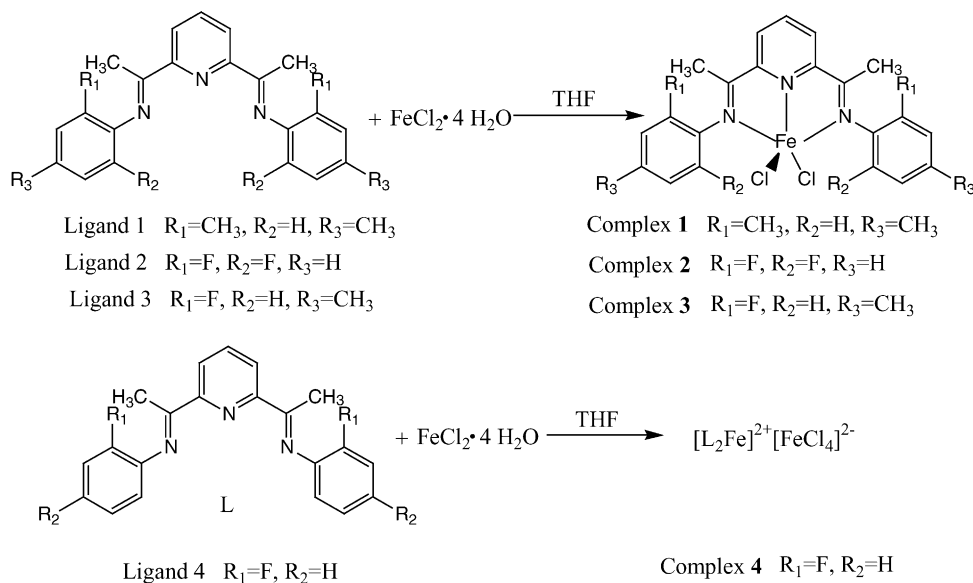### 2.2. Synthesize and characterization of catalysts

The structures of ligands and complexes **1**–**4** were shown in Scheme 1.

Ligand 1 (C$_{25}$H$_{27}$N$_3$) was synthesized according to the method reported in literature [1]. ^{1}H NMR (CDCl$_3$): δ = 8.42 (d, Py-*m*-H), 7.91 (t, Py-*p*-H), 7.24 (m, Aryl),

7.07 (t, Aryl), 6.70 (d, Aryl), 2.36 (s, N=C–CH$_3$), 2.14 (s, Aryl-CH$_3$); Elemental analysis: Calc. (%): C, 80.90; H, 6.79; N, 12.31; Found (%): C, 80.75; H, 6.73; N, 12.42.

Ligand 2 (C$_{21}$H$_{15}$F$_4$N$_3$) was synthesized by the method reported in reference [11]. A solution of 2,6-diacetylpyridine (0.49 g, 3 mmol), 2,6-difluoroaniline (0.9 g, 7 mmol), silica-alumina catalyst support (0.3 g), and molecular sieves 4A (1.0 g) in toluene (10 mL) was stirred at 30–40 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieves were washed with toluene several times. The toluene of the combined filtrates was removed in vacuum. Some anhydrous methanol was added to the residue. A yellow solid was filtered off to give Ligand 2 in 62% yield. ^{1}H NMR(CDCl$_3$): δ = 8.47 (d, 2H, Py-*m*-H), 7.93 (t, ^{1}H, Py-*p*-H), 7.07 (t, 4H, Aryl), 6.99 (d, 2H, Aryl), 2.46 (s, 6H, N=C–CH$_3$). EI mass spectrum: *m/z* 385 [*M*$^+$]. Elemental analysis: Calc. (%): C, 65.45; H, 3.92; N, 10.90; Found (%): C, 65.61; H, 4.02; N, 10.78.IR (KBr): 1636 (νC=N), 1576, 1465, 1369, 1277, 1237, 1215, 1126, 1032, 1002, 827, 789, 759 cm^{-1}.

Ligand 3 (C$_{23}$H$_{21}$F$_2$N$_3$) was synthesized following the above procedure. 2,6-Diacetylpyridine (0.49 g, 3 mmol), 2-fluoro-4-methylaniline (0.84 g, 7 mmol), silica-alumina catalyst support (0.3 g), and molecular sieves 4A (2.0 g) were used. Ligand 3 was obtained as a yellow crystal in 65% yield. ^{1}H NMR(CDCl$_3$): δ = 8.26 (d, 2H, Py-*m*-H), 8.05 (t, 1H, Py-*p*-H), 6.88 (d, 2H, Aryl), 6.85 (d, 2H, Aryl), 6.80 (s, 2H, Aryl), 2.82 (d, 6H, Aryl-CH$_3$), 2.29 (s, 6H, N=C–CH$_3$). EI mass spectrum: *m/z* 377 [*M*$^+$]. Elemental analysis: Calc. (%): C, 73.19; H, 5.61; N, 11.13; Found (%): C, 73.37; H, 5.66; N, 10.89. IR (KBr): 1645 (νC=N), 1570, 1499, 1423, 1364, 1324, 1270, 1242, 1212, 1119, 1080, 940, 872, 826, 778, 724 cm^{-1}.

Ligand 1 R$_1$=CH$_3$, R$_2$=H, R$_3$=CH$_3$
Ligand 2 R$_1$=F, R$_2$=F, R$_3$=H
Ligand 3 R$_1$=F, R$_2$=H, R$_3$=CH$_3$

Complex **1** R$_1$=CH$_3$, R$_2$=H, R$_3$=CH$_3$
Complex **2** R$_1$=F, R$_2$=F, R$_3$=H
Complex **3** R$_1$=F, R$_2$=H, R$_3$=CH$_3$

Ligand 4 R$_1$=F, R$_2$=H

Complex **4** R$_1$=F, R$_2$=H

Scheme 1.

Ligand 4 ($C_{21}H_{17}F_2N_3$) was synthesized following the above procedure. 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-fluoroaniline (0.92 g, 7 mmol), silica-alumina catalyst support (0.3 g), and molecular sieves 4 A (2.0 g) were used. Ligand 4 was obtained as a yellow crystal in 55% yield. ^1H NMR(CDCl$_3$): δ = 8.22 (d, 2H, Py-*m*-H), 8.03 (t, 1H, Py-*p*-H), 7.26 (t, 2H, Aryl), 6.98 (t, 2H, Aryl), 6.80 (d, 2H, Aryl), 6.67 (d, 2H, Aryl), 2.42 (s, 6H, N=C–CH$_3$). EI mass spectrum: *m/z* 349 [M^+]. Elemental analysis: Calc. (%): C, 72.19; H, 4.90; N, 12.03; Found (%): C, 71.98; H, 4.97; N, 11.97. IR (KBr): 1634 (νC=N), 1601, 1575, 1482, 1365, 1237, 1194, 1123, 1102, 1079, 1031, 842, 825, 780, 762, 743 cm^{-1}.

Complexes **1**–**4** were synthesized according to literature [12].

Complex **3**: [2,6-(2-F-4-CH$_3$C$_6$H$_3$N=CCH$_3$)$_2$C$_5$H$_3$N] FeCl$_2$·H$_2$O. Elemental analysis: Calc. (%): C, 52.90; H, 4.44; N, 8.05; Found (%): C, 53.33; H, 4.35; N, 7.97. TOF mass spectrum: *m/z* 810 [M^+]. IR (KBr): 3481, 1623 (νC=N), 1584, 1502, 1424, 1377, 1323, 1267, 1223, 1113, 1031, 943, 842, 808, 729 cm^{-1}.

Complex **4**: {Fe[2,6-(2-FC$_6$H$_3$N=CCH$_3$)$_2$C$_5$H$_3$N]$_2$}$^{2+}$ [FeCl$_4$]$^{2-}$·H$_2$O. Elemental analysis: Calc. (%): C, 52.04; H, 3.64; N, 8.67; Found (%): C, 52.22; H, 3.83; N, 8.17. TOF mass spectrum: *m/z* 754 [M^+]. IR (KBr): 3448, 1624 (νC=N), 1584, 1529, 1487, 1402, 1322, 1246, 1104, 807, 764 cm^{-1}.

2.3. Oligomerization of ethylene at atmosphere pressure

A 250 mL dried three-necked flask with a stir ring bar was purged with dry nitrogen two to three and then ethylene once. Then, 50 mL of toluene and a prescribed amount of MAO were injected in it and the mixture was magnetically stirred at different temperatures. The ethylene monomer was continuously fed in and its pressure was maintained at 0.1 MPa by an electromagnetic valve, and 2 min later, oligomerization was started by adding a catalyst. The reaction was terminated by the addition of wt.10% acidified ethanol after 30 min and catalytic activities were computed by pressure changes in the buffer storage. The samples used for GC-MS were prepared in the following procedure: 3 mL water was injected into the reactor to terminate the reaction, and then the resulting product was stocked in the close reactor for more than 2 h at 0 °C before subjected to GC–MS analysis, which could prevent the evaporation of C$_4$ and C$_6$. The distribution of oligomers and selectivity for α-olefins could be obtained with high reliability.

2.4. Measurements

^1H NMR spectra were recorded on a Bruker DMX (300 M Hz) spectrometer. Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. IR spectra were recorded using a Perkin-Elmer system 2000 FT-IR spectrometer. EI and TOF mass spectra were carried out with GCT-MS (Micromass UK) and BIFLFX III (Bruker) spectrometers, respectively. The distribution of oligomers was determined by GC–MS analysis using an HP-5890 apparatus with an HP-1 capillary column (30 m × 0.25 mm) and an HP-5971 mass spectrometer. The column temperature started with 35 °C (10 min), heated at 10 °C/min to 220 °C and kept at 220 °C for 10 min.

3. Results and discussion

2,6-Diacetylpyridinebis(2,6-difluoroanil) (L2), 2,6-diacetylpyridinebis(2-fluoro-4-methylanil) (L3) and 2,6-diacetylpyridinebis(2-fluoroanil) (L4) were synthesized in good yield by condensation of 2,6-diacetylpyridine with the corresponding aniline using silica-alumina catalyst support as the catalyst and molecular sieves as the water adsorbent [11]. 2,6-Diacetylpyridinebis(2,4-dimethylanil) (L1) was synthesized for comparison. Elemental analysis, ^1H NMR, IR and mass spectrometry were used for characterization of ligands. Iron complexes of these ligands were synthesized by dissolving the ligands in tetrahydrofuran (THF) (Scheme 1), followed by the addition of 1.1 equiv of FeCl$_2$·4H$_2$O. The complexes were characterized with elemental analysis, IR and mass spectrometry. The IR spectra of the free ligands shows that the C=N stretching frequencies appear at 1634–1645 cm^{-1}. In complexes **2**–**4**, the C=N stretching vibrations shift toward lower frequencies around 1624 cm^{-1} and were greatly reduced in intensity, which indicated the coordination interaction between the imino nitrogen atoms and the metal ions. Elemental analysis results also show good accordance with corresponding ligands and complexes.

In addition, Chen et al. [11] reported that the complexes would be formed in two structures depending on the solvent selected. The structure of FeLCl$_2$ would be formed when THF was used and an ion pair structure would appear in strong polar solvent such as CHCl$_3$ and CH$_3$CN. The TOF mass spectrum shows that complexes **2** and **3** have the same ion pair structure as complex **4**, even when they are synthesized in THF. This could be attributed to the transformation of complex (Scheme 2) happening during the process of characterization by mass spectrometer, in which some strong polar solvents is used. The structure of complex **1**, whose *ortho* substituents of aryl rings is methyl, could be characterized with a mass spectrum in close accord with FeLCl$_2$. So the transformation only happened in the complexes with very small steric hindrance, such as F and H *ortho* substituted aryl rings.

Complexes **1**–**4** were used in the oligomerization of ethylene in order to investigate the effect of steric bulk and electronic effect on the catalytic properties. It is very difficult

$$FeLCl_2 \xrightarrow{\text{strong polar solvent}} [FeL_2]^{2+}[FeCl_4]^{2-}$$
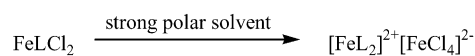
Scheme 2.

Table 1
Effect of temperature on oligomerization result of complexes **1**–**4**

Run	Complex	Temperature (°C)	Yield (g)	Activity (10^6 g/molFe·h)	α-Olefin (%)	α
1	**1**	20	8.15	16.3	97	0.87
2	**1**	30	7.75	15.5	98	0.83
3	**1**	40	6.55	13.1	99	0.78
4	**1**	50	5.25	10.5	99	0.71
5	**1**	60	4.93	9.85	99	0.69
6	**2**	40	5.20	10.4	96	0.64
7	**2**	50	3.29	6.57	97	0.52
8	**2**	60	2.46	3.83	98	0.48
9	**2**	70	0.89	1.78	99	0.45
10	**3**	30	9.15	18.3	95	0.42
11	**3**	40	7.55	15.1	95	0.39
12	**3**	50	5.90	11.8	96	0.36
13	**3**	60	3.08	6.15	98	0.29
14	**3**	70	1.17	2.33	98	0.32
15	**4**	30	Inactive			

Reaction conditions: Fe = 1 μmol; ethylene pressure = 0.1 MPa; reaction time = 30 min; 50 mL toluene as solvent; MAO as cocatalyst, Al/Fe = 1500.

to compare results obtained by different authors since reaction conditions are usually different. The typical results of oligomerization by complexes **1**–**4** under different temperatures are summarized in Table 1. It is clear that the catalytic activity and selectivity for α-olefins formation catalyzed by complex **2** are much higher than those reported by Qian et al. [11]. It is well known that the evaporation of C_4 and C_6 at room temperature makes it very difficult to accurately measure the content and distribution of oligomers with GC–MS. We keep the reactor closed at 0 °C until the products were measured which could prevent the evaporation of C_4 and C_6 and make the results more reliable. This could account for the difference of results between ours and those reported in literature. These complexes exhibit high activity to ethylene oligomerization and high selectivity for α-olefins except complex **4**, as shown in Table 1. Very interesting by the complex **3** exhibits high activity to ethylene oligomerization, but complex **4**, where there is no substituent on other aryl positions, shows no product detected. This could be attributed to the ion pair structure of complex **4** [12].

The effect of temperature on activity of complexes **1**–**3** and the distribution of oligomers obtained from complex **3** are given in Figs. 1 and 2, respectively. The catalytic activities and product distributions of complexes **1**, **2** and **3** for ethylene oligomerization are strongly affected by reaction temperature. As temperature increases, the activity of complex **3** decreases from 1.83×10^7 g/mol Fe h (30 °C) to 2.33×10^6 g/mol Fe h (70 °C). The distribution of oligomers obtained follows Schulz–Flory rules, which could be characterized by a constant α, where α represents the probability of chain propagation [α = rate of propagation/(rate of propagation + rate of chain transfer) = mol of C_{n+2}/mol of C_n]. The α value can be determined by the molar ratio of C_{12} and C_{14}. The α value of complex **3** decreases from 0.39 to 0.29 as reaction temperature increases from 30 °C to 70 °C. The other two complexes (**1** and **2**) exhibit the same trend as described in Table 1 and Fig. 1. Meanwhile, complex **1**
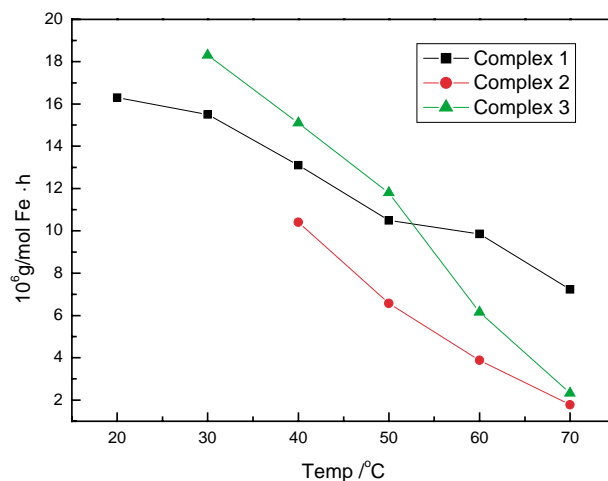

Fig. 1. Effect of temperature on activity of complexes **1**–**3**. Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst, Al/Fe = 1500.
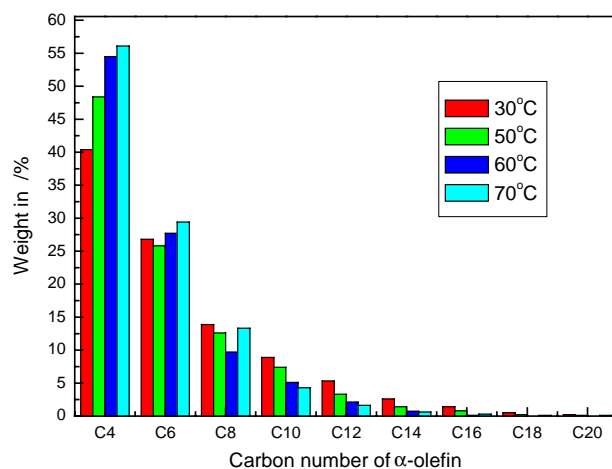

Fig. 2. Effect of temperature on distribution of oligomers obtained from complex **3**. Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst, Al/Fe = 1500.

Table 2
Effect of Al/Fe ratio on oligomerization result of complex **2** and complex **3**

Run	Complex	Al/Fe	Yield (g)	Activity (10^6 g/mol Fe h)	α-Olefin (%)	α
1	**2**	300	1.03	2.06	98	0.51
2	**2**	500	2.59	5.18	98	0.47
3	**2**	1000	1.93	3.85	98	0.52
4	**2**	3000	1.69	3.38	99	0.51
5	**2**	5000	1.74	3.48	99	0.48
6	**3**	420	2.07	4.13	98	0.26
7	**3**	750	3.51	7.01	99	0.30
8	**3**	1000	3.72	7.44	99	0.29
9	**3**	2500	2.23	4.45	99	0.26

Reaction conditions: Fe = 1 μmol; ethylene pressure = 0.1 MPa; reaction time = 30 min; reaction temperature = 60 °C; 50 mL toluene as solvent; MAO as cocatalyst.

exhibits higher catalytic activities than complexes **2** and **3** at 60 °C and 70 °C. Larger steric bulk could provide more protection for central metal from reaction with trimethylaluminium (TMA) in commercial MAO, which would deactivate the active species and decrease the catalytic activities dramatically as reported in literature [5]. All the results indicate that although enhanced temperatures are expected to result in overall higher propagation and transfer rates, the rate of chain transfer increases more than the rate of propagation, which could result in more low-molecular-weight products. In addition, a decrease in ethylene solubility and higher rates of catalyst deactivation at higher temperatures may result in a decline of catalytic activity and productivity. Therefore, a combination of above effects is likely to account for the obtained temperature dependence of the activity and products distribution.

The effect of MAO on catalytic activity of complexes (**2** and **3**) and product distribution is given in Table 2, Figs. 3 and 4, respectively. The catalytic activity of the complex **2** is enhanced dramatically as the molar ratio of Al/Fe
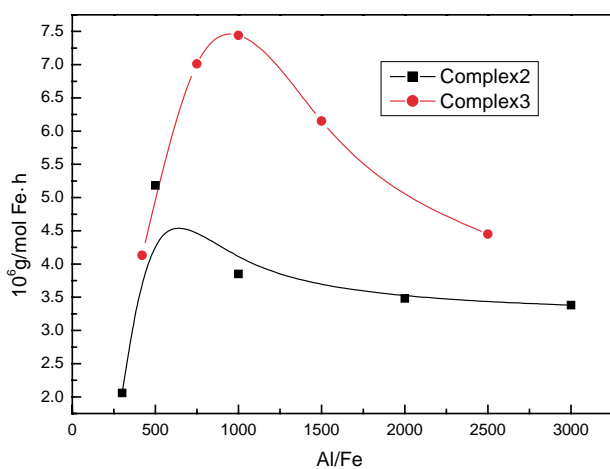

Fig. 3. Effect of Al/Fe molar ratio on catalytic activity of complexes (**2** and **3**). Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst; reaction temperature = 60 °C.
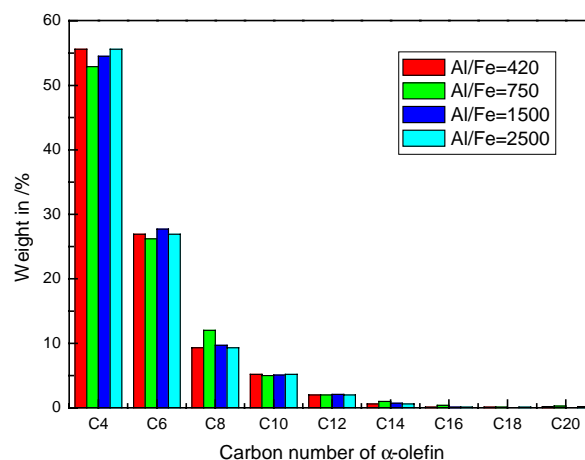

Fig. 4. Effect of Al/Fe molar ratio on product distribution obtained from complex **3**. Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst; reaction temperature = 60 °C.

increases from 300 to 500, and then decreases gradually when the Al/Fe ratio increases from 500 to 3000. Dissimilarly, the activity of complex **3** is increased to a maximum when the Al/Fe ratio is 1000 and then decreases rapidly with an increase in the Al/Fe ratio. In other words, less MAO is needed for complex **3** to reach the highest catalytic activity than complex **2**. But the product distributions are almost unchanged with different Al/Fe ratios as shown in Fig. 4, and the α values of complexes **2** and **3** are around 0.50 and 0.30, respectively. More active species are formed when more MAO is introduced to the reaction system, which conduce to the increase of activities, but too much MAO could make the active species deactivate because of the reaction of active species with TMA. This indicates that the reaction between TMA and active species is easier to happen in complex **3** than that in complex **2**, which could be attributed to the different protection provided by *ortho* substituents in complexes **2** and **3** as described in literature [5].

The effect of steric hindrance and reaction temperatures on the product distributions from different complexes (**1–3**) are given in Table 3 and Fig. 5. The product distributions are greatly affected by reaction temperatures and *ortho* substituents. When temperature increases from 30 °C to 60 °C,

Table 3
Distributions of oligomers obtained from complexes **1–3** at different temperatures

Temperature (°C)	Distribution of oligomers (%)								
	C_4–C_{10}			C_{12}–C_{20}			>C_{20}		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
30	41.2	71.5	90.0	46.7	26.6	10.0	12.1	1.9	0.0
40	42.8	79.3	92.3	46.1	18.9	7.7	11.1	1.8	0.0
50	43.6	84.1	94.2	45.5	14.4	5.8	10.8	1.5	0.0
60	44.4	87.1	96.9	45.6	12.2	3.1	10.0	0.7	0.0

Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst; Al/Fe = 1500.
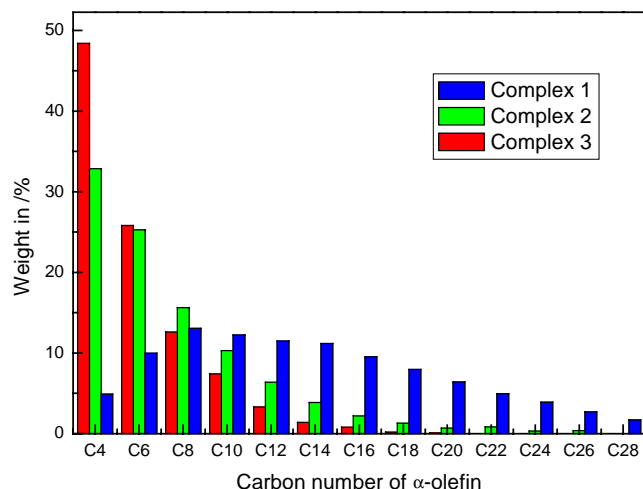
Fig. 5. The product distributions from different complexes (**1**–**3**). Reaction conditions: ethylene pressure = 0.1 MPa; 50 mL toluene as solvent; MAO as cocatalyst; reaction temperature = 60 °C.

the α values of all complexes decrease. More than 90% of oligomers are C_4–C_{10}, when complex **3** was used for ethylene oligomerization at 0.1 MPa ethylene pressure. Less C_4–C_{10} products are detected in oligomers obtained from complex **1** (about 40%) and complex **2** (about 70%) under the same reaction conditions. In addition, the α values decrease from 0.78 to 0.39 with respect to the three complexes with different steric bulk. By comparing of the structures of three complexes, it is not difficult to find that the steric hindrance of substituents in the *ortho* position is in the following series: Me > bisF > F, which could account for the different product distributions of three catalysts as reported in literature [5].

4. Conclusions

A novel 2,6-bis(imino)pyridyl iron complex, [2,6-(2-F-4-$CH_3C_6H_3N$=CCH_3)$_2C_5H_3N$] $FeCl_2\cdot H_2O$ has been synthesized and used for ethylene oligomerization. It exhibits higher catalytic activity than the other two complexes due to methyl in the *para* position of aryl rings. Meanwhile, more than 95% of the whole product is C_4–C_{10}, which is much higher than that obtained from complexes **1** and **2** because of its small steric hindrance in the *ortho* position of aryl rings. The catalytic activity decreases and selectivity for low-molecular-weight oligomers increases as reaction temperature increases. The Al/Fe molar ratio displays no obvious effect on the distribution of products, but the activity increases to the maximum and then decreases with increasing Al/Fe molar ratio. Displacing H with methyl, complex **4**, is inactive for ethylene oligomerization due to its special ion pair structure. All the results show that [2,6-(2-F-4-$CH_3C_6H_3N$=CCH_3)$_2C_5H_3N$]$_2FeCl_2\cdot H_2O$ is an excellent oligomerization catalyst for its high catalytic activity and narrow oligomer distributions.

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