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A series of novel 2,6-bis(imino)pyridyl iron catalysts: synthesis, characterization and ethylene oligomerization

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Abstract

A series of novel 2,6-bis(imino)pyridyl iron complexes $\{2,6\text{-}(2\text{-X-}4\text{-Y-}5\text{-Z}C_6H_2N{=}CCH_3)_2C_5H_3N\}FeCl_2$ (X = Cl, Y = CH_3, Z = H (**2**); X = Br, Y = CH_3, Z = H (**3**); X = F, Y = H, Z = CH_3 (**4**); X = Cl, Y = H, Z = CH_3 (**5**); X = Cl, Y = F (**7**)) have been synthesized and characterized with elemental analysis and IR. These iron coordinative complexes, activated with methylaluminoxane (MAO), lead to highly active ethylene oligomerization (>10^7 g/mol Fe h) and the products are mostly linear α-olefins (>90%). The catalytic activities and product properties depend on the substituents on aryl rings and the reaction conditions. As reaction temperature increases, the catalytic activities decrease rapidly and more low-molar-mass products are produced. The product distributions are almost independent of the Al/Fe molar ratio, but the catalytic activities change in different trends when the *ortho*-substituents on the aryl rings are different. The other three complexes have also been synthesized for comparison to investigate the steric hindrance and electronic effect on the properties of complexes. The complex with adaptable steric hindrance and electronic properties exhibits the highest catalytic activities.

Keywords: 2,6-Bis(imino)pyridyl iron complex; Oligomerization; α-Olefin; Distribution

1. Introduction

Oligomerization of ethylene presents one of the major processes for the production of linear α-olefins in the range C_4–C_{20}. Such linear oligomers are extensively used for preparation of detergents, plasticizers and as co-monomers for the preparation of linear low-density polyethylene (LLDPE). 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 Gibson and co-workers [4,5] independently discovered that mono-alkyl-substituted [2,6-bis(imino)pyridyl]iron and -cobalt dihalides, which are activated by MAO, are effective catalysts for the oligomerization of ethylene to oligomers with high catalytic activity (>10^7 g/mol Fe h) and high selectivity for linear α-olefins (>95%). The size and regio-chemistry of the substituents in the imino-aryl groups are of crucial importance in controlling the oligomerization of ethylene. But when the *ortho*-substituents on ligands are alkyls, the carbon number distributions of oligomers obtained are very wide [1–9]. Bluhm et al. [10] reported on some complexes without *ortho*-substituents on aryl rings. The distribution of oligomers obtained is much narrower (mainly C_4–C_{10}), but both catalytic activities (TOF < 2.5×10^4/h) and selectivity for α-olefins (<88%) are low because of small steric hindrance.

Compared to the little difference in electronic effect and large steric hindrance originated from changing the alkyl groups, the electronic effect and steric bulk from varying

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halogens are much more significant due to the big differences in their electronegativities and covalent radius (Å). When there are only halogen substituents at aryl rings of ligands, detailed work has been carried out by Qian and co-workers [11,12]. Their results show that steric bulk of halogen substituents and the positive charge of central metal are two important factors that influence the activities of complexes greatly. The results obtained by Gibson and co-workers [5] show that the introduction of alkyl group at the *para*- or *meta*-position of aryl rings could improve catalytic activities markedly. The introduction of bromine in the *para*-position of aryl rings has also been reported to improve the catalytic activity in ethylene polymerization [13]. Combining these two kinds of substituents in the same catalyst are expected to give a series of novel oligomerization catalysts. Recently, a complex with a fluoro-substituent at the *ortho*-position and a methyl substituent at the *para*-position of aryl rings was reported by our group [14], which exhibited high activity and selectivity for α-olefins. In this paper, other five novel bis(imino)pyridyl iron complexes bearing halogen and alkyl substituents are synthesized and used for ethylene oligomerization. Their structures and synthetic route are presented in Scheme 1. Meanwhile, the relationship between the structures of the complexes and the catalytic activities and product properties are discussed in detail.

2. Experimental

2.1. Materials

2,6-Diacetylpyridine and all the anilines with different substituents were purchased from Acros. Polymerization-grade ethylene was obtained from Yanshan Petrochemical Company, Sinopec, China. Methylaluminoxane (MAO) solution in toluene (1.4 mol/L) was purchased from Albemarle Corp. Toluene, THF and ether (Et_2O) were distilled from solidum/benophenone and degassed before use. All other chemicals were obtained commercially and used without further purification.

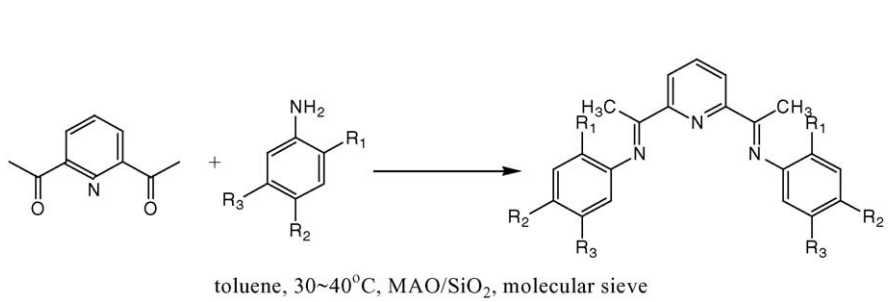
Qian and co-workers [11] reported that silica–alumina catalyst support was an effective catalyst for the preparation of 2,6-bis(imino)pyrdyl ligand containing halogen substituents on aryl rings. Recently, we found that MAO supported on SiO_2 (MAO/SiO_2) was another effective catalyst for the synthesis of ligands of this kind. MAO/SiO_2 was prepared in the following procedure: in a 50 mL dried Schlenk flask with a stirring bar, 4 g dried SiO_2 was purged with dry nitrogen two to three times and then 16 mL MAO were injected. The reaction system was magnetically stirred at 50 °C for 12 h. The precipitate was filtered and washed with toluene for three times and then dried under reduced pressure to give a white solid. Finally, the resulting product obtained was preserved in nitrogen atmosphere.

2.2. Synthesis and characterization of ligands and complexes

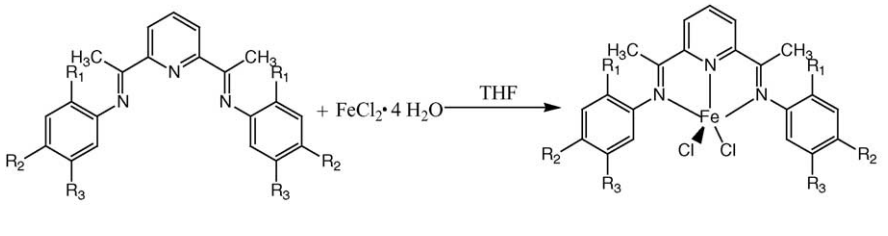
The structures of ligands and complexes **1**–**5** are shown in Scheme 1.

All the ligands were synthesized by the method reported in [11], and the silica–aluminum catalyst support was displaced with MAO/SiO_2.

Ligand **1** (**L1**, $C_{23}H_{17}F_2N_3$): a solution of 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-fluoro-4-methylaniline



	R_1	R_2	R_3
L1	F	CH_3	H
L2	Cl	CH_3	H
L3	Br	CH_3	H
L4	F	H	CH_3
L5	Cl	H	CH_3
L6	Cl	H	H
L7	Cl	F	H
L8	F	F	H



	R_1	R_2	R_3
C1	F	CH_3	H
C2	Cl	CH_3	H
C3	Br	CH_3	H
C4	F	H	CH_3
C5	Cl	H	CH_3
C6	Cl	H	H
C7	Cl	F	H
C8	F	F	H

Scheme 1.

(0.84 g, 7 mmol), MAO/SiO_2 (0.3 g), and molecular sieve 4 Å (2.0 g) in toluene (10 mL) was stirred at 30–40 °C for 24 h. Then the reaction mixture was filtered, and the molecular sieve was washed with toluene several times. The toluene of the combined filtrates was removed under vacuum. Anhydrous methanol was added to the residue. A yellow solid was filtered off to give ligand **1** in 55% 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: calcd. (%): C, 73.19; H, 5.61; N, 11.13; found (%): C, 73.37; H, 5.66; N, 10.89. IR (KBr): 1645 ($\nu_{C=N}$), 1570, 1499, 1423, 1364, 1324, 1270, 1242, 1212, 1119, 1080, 940, 872, 826, 778 and 724 cm^{-1}.

Ligand **2** (**L2**, $C_{23}H_{17}Cl_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-chloro-4-methylaniline (0.92 g, 7 mmol), MAO/SiO_2 (0.3 g) and molecular sieve 4 Å (2.0 g) were used. **L2** was obtained as a yellow powder in 62% yield. ^{1}H NMR ($CDCl_3$) δ: 8.23 (d, 2H, PyrH^3), 7.99 (t, 1H, PyrH^4), 7.07 (s, 2H, ArH), 6.88 (d, 2H, ArH), 6.69 (d, 2H, ArH), 2.80 (s, 6H, N=C–CH_3), 2.22 (s, 6H, aryl-CH_3). EI mass spectrum: *m/z* 409 [M^+]. Elemental analysis ($C_{23}H_{17}Cl_2N_3$): calcd. (%): C, 67.32; H, 5.16; N, 10.24; found (%): C, 67.21; H, 5.21; N, 9.97. IR (KBr): 1643 ($\nu_{C=N}$), 1574, 1486, 1452, 1419, 1362, 1321, 1257, 1225, 1120, 1100, 1081, 970, 880, 824, 772 and 739 cm^{-1}.

Ligand **3** (**L3**, $C_{23}H_{17}Br_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-bromo-4-methylaniline (1.31 g, 7 mmol), MAO/SiO_2 (0.3 g) and molecular sieve 4 Å (2.0 g) were used. **L3** was obtained as a yellow crystal in 63% yield. ^{1}H NMR ($CDCl_3$) δ: 8.23 (d, 2H, PyrH^3), 7.99 (t, 1H, PyrH^4), 7.24 (s, 2H, ArH), 6.92 (d, 2H, ArH), 6.70 (d, 2H, ArH), 2.80 (s, 6H, N=C–CH_3), 2.22 (s, 6H, aryl-CH_3). EI mass spectrum: *m/z* 497 [M^+]. Elemental analysis ($C_{23}H_{17}Br_2N_3$): calcd. (%): C, 55.33; H, 4.24; N, 8.42; found (%): C, 55.33; H, 4.31; N, 8.27. IR (KBr): 1638 ($\nu_{C=N}$), 1570, 1482, 1450, 1422, 1365, 1321, 1256, 1223, 1121, 1100, 1075, 964, 885, 827, 768 and 741 cm^{-1}.

Ligand **4** (**L4**, $C_{23}H_{17}F_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-fluoro-5-methylaniline (0.84 g, 7 mmol), MAO/SiO_2 (0.3 g) and molecular sieve 4 Å (2.0 g) were used. **L4** was obtained as a light yellow powder in 64% yield. ^{1}H NMR ($CDCl_3$) δ: 8.23 (d, 2H, PyrH^3), 7.93 (t, 1H, PyrH^4), 7.02 (d, 2H, ArH), 6.85 (s, 2H, ArH), 6.73 (d, 2H, ArH), 2.80 (s, 6H, N=C–CH_3), 2.23 (s, 6H, aryl-CH_3). EI mass spectrum: *m/z* 377 [M^+]. Elemental analysis ($C_{23}H_{17}F_2N_3$): calcd. (%): C, 73.19; H, 5.61; N, 11.13; found (%): C, 72.92; H, 5.63; N, 10.84. IR (KBr): 1642 ($\nu_{C=N}$), 1572, 1501, 1452, 1424, 1366, 1322, 1258, 1209, 1120, 1098, 1077, 980, 876, 820, 777 and 742 cm^{-1}.

Ligand **5** (**L5**, $C_{23}H_{17}Cl_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-chloro-5-methylaniline (0.92 g, 7 mmol), MAO/SiO_2 (0.3 g), and molecular sieve 4 Å (2.0 g) were used. **L5** was obtained as a light yellow crystal in 54% yield. ^{1}H NMR ($CDCl_3$) δ: 8.23 (d, 2H, PyrH^3), 8.00 (t, 1H, PyrH^4), 7.27 (d, 2H, ArH), 6.63 (s, 2H, ArH), 6.55 (d, 2H, ArH), 2.81 (s, 6H, N=C–CH_3), 2.25 (s, 6H, aryl-CH_3). EI mass spectrum: *m/z* 409 [M^+]. Elemental analysis ($C_{23}H_{17}Cl_2N_3$): calcd. (%): C, 67.32; H, 5.16; N, 10.24; found (%): C, 66.92; H, 5.20; N, 9.95. IR (KBr): 1643 ($\nu_{C=N}$), 1571, 1475, 1453, 1365, 1320, 1237, 1121, 1103, 1080, 995, 873, 821, 764 and 738 cm^{-1}.

Ligand **6** (**L6**, $C_{21}H_{17}Cl_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-chloroaniline (0.89 g, 7 mmol), MAO/SiO_2 (0.15 g), and molecular sieve 4 Å (1.0 g) were used. **L6** was obtained as a yellow crystal in 56% yield. ^{1}H NMR ($CDCl_3$) δ: 8.44 (d, 2H, PyrH^3), 7.94 (t, 1H, PyrH^4), 7.43 (dd, 2H, ArH), 7.28 (pseudo t, 2H, ArH), 7.07 (pseudo t, 2H, ArH), 6.86 (dd, 2H, ArH), 2.38 (s, 6H, N=C–CH_3). EI-MS: *m/z* 381 [M^+]. Elemental analysis ($C_{21}H_{17}Cl_2N_3$) (382.3): calcd. (%): C 65.97, H 4.48, N 10.99; found (%): C 65.64, H 4.69, N 10.89. IR (KBr): 1635 ($\nu_{C=N}$), 1582, 1465, 1436, 1362, 1252, 1222, 1120, 1054, 1032, 816, 772, 756, 743, 735 and 687 cm^{-1}.

Ligand **7** (**L7**, $C_{21}H_{15}Cl_2F_2N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2-chloro-4-fluoroaniline (1.02 g, 7 mmol), MAO/SiO_2 (0.3 g), and molecular sieve 4 Å (2.0 g) were used. **L7** was obtained as a yellow powder in 61% yield. ^{1}H NMR ($CDCl_3$) δ: 8.22 (d, 2H, PyrH^3), 7.94 (t, 1H, PyrH^4), 7.25 (s, 2H, ArH), 7.00 (d, 2H, ArH), 6.72 (d, 2H, ArH), 2.79 (s, 6H, N=C–CH_3). EI-MS: *m/z* 417 [M^+]. Elemental analysis ($C_{21}H_{15}Cl_2F_2N_3$) (418.3): calcd. (%): C 60.30, H 3.61, N 10.05; found (%): C 60.54, H 3.68, N 10.19. IR (KBr): 1645 ($\nu_{C=N}$), 1575, 1482, 1426, 1368, 1322, 1254, 1191, 1124, 1102, 1075, 972, 861, 822, 769 and 741 cm^{-1}.

Ligand **8** (**L8**, $C_{21}H_{15}F_4N_3$): 2,6-diacetylpyridine (0.49 g, 3 mmol), 2,4-difluoroaniline (0.91 g, 7 mmol), MAO/SiO_2 (0.15 g), and molecular sieve 4 Å (3.0 g) were used. **L8** was obtained as a yellow powder in 65% yield. ^{1}H NMR ($CDCl_3$) δ: 8.38 (d, 2H, PyrH^3), 7.90 (t, 1H, PyrH^4), 6.93 (m, 6H, ArH), 2.41 (s, 6H, N=C–CH_3). EI-MS: *m/z* 385 [M^+]. Elemental analysis ($C_{21}H_{15}F_4N_3$) (385.4): calcd. (%): C 65.45, H 3.92, N 10.90; found (%): C 65.76, H 4.13, N 10.79. IR (KBr): 1639 ($\nu_{C=N}$), 1596, 1575, 1497, 1426, 1366, 1322, 1261, 1199, 1140, 1094, 1080, 960, 848, 825, 778 and 726 cm^{-1}.

All the complexes were synthesized as reported in literature [11]. Ligand was added to a solution of $FeCl_2{\cdot}4H_2O$ in THF at room temperature with rapid stirring. After being stirred for 12 h, the reaction mixture was filtered and the product was washed with Et_2O and dried in a vacuum.

Complex **1** (**C1**, {2,6-(2-F-4-$CH_3C_6H_3N$=CCH_3)$_2C_5H_3N$}$FeCl_2{\cdot}H_2O$): ligand **L1** (190 mg, 0.50 mmol), $FeCl_2{\cdot}4H_2O$ (110 mg, 0.55 mmol) and THF (12 mL) were used. The desired product (210 mg) was obtained as a purple powder in 83% yield. Elemental analysis ($C_{23}H_{17}N_3F_2FeCl_2{\cdot}H_2O$): calcd. (%): C 52.90, H 4.44, N 8.05; found (%): C 53.41, H 4.38, N 7.57. IR (KBr): 1623 ($\nu_{C=N}$), 1584, 1502, 1424, 1377, 1323, 1267, 1223, 1113, 1031, 943, 842, 808 and 729 cm^{-1}.

Complex **2** (**C2**, {2,6-(2-Cl-4-$CH_3C_6H_3N$=CCH_3)$_2C_5H_3N$}$FeCl_2{\cdot}$THF): ligand **L2** (410 mg, 1.0 mmol), $FeCl_2{\cdot}4H_2O$ (219 mg, 1.1 mmol) and THF (12 mL) were

used. **C2** (462 mg) was obtained as a light blue powder in 86% yield. Elemental analysis ($C_{23}H_{17}N_3Cl_2FeCl_2$·THF): calcd. (%): C 53.32, H 4.64, N 6.91; found (%): C 53.43, H 4.78, N 6.72. IR (KBr): 1624 ($\nu_{C=N}$), 1588, 1490, 1428, 1374, 1320, 1270, 1233, 1151, 1060, 889, 840, 814 and 716 cm^{-1}.

Complex **3** (**C3**, {2,6-(2-Br-4-$CH_3C_6H_3N$=CCH_3)$_2$ C_5H_3N}$FeCl_2$·THF): ligand **L3** (499 mg, 1.0 mmol), $FeCl_2$·$4H_2O$ (219 mg, 1.1 mmol) and THF (12 mL) were used. **C3** (564 mg) was obtained as a light blue powder in 90% yield. Elemental analysis ($C_{23}H_{17}N_3Br_2FeCl_2$·THF): calcd. (%): C 46.52, H 4.05, N 6.03; found (%): C 46.33, H 4.22, N 5.95. IR (KBr): 1623 ($\nu_{C=N}$), 1588, 1485, 1427, 1373, 1321, 1270, 1231, 1152, 1049, 888, 842, 813 and 714 cm^{-1}.

Complex **4** (**C4**, {2,6-(2-F-5-$CH_3C_6H_3N$=CCH_3)$_2$ C_5H_3N}$FeCl_2$·THF): ligand **L4** (378 mg, 1.0 mmol), $FeCl_2$·$4H_2O$ (219 mg, 1.1 mmol) and THF (12 mL) were used. **C4** (490 mg) was obtained as a purple powder in 90% yield. Elemental analysis ($C_{23}H_{17}N_3F_2FeCl_2$·THF): calcd. (%): C 52.90, H 4.44, N 8.05; found (%): C 53.11, H 4.29, N 7.89. IR (KBr): 1628 ($\nu_{C=N}$), 1593, 1501, 1377, 1263, 1216, 1160, 1115, 815, 768 and 715 cm^{-1}.

Complex **5** (**C5**, {2,6-(2-Cl-5-$CH_3C_6H_3N$=CCH_3)$_2$ C_5H_3N}$FeCl_2$): ligand **L5** (410 mg, 1.0 mmol), $FeCl_2$·$4H_2O$ (219 mg, 1.1 mmol) and THF (12 mL) were used. **C5** (430 mg) was obtained as a light blue powder in 80% yield. Elemental analysis ($C_{23}H_{17}N_3Cl_2FeCl_2$): calcd. (%): C 51.43, H 3.94, N 7.82; found (%): C 51.15, H 4.12, N 7.69. IR (KBr): 1624 ($\nu_{C=N}$), 1590, 1478, 1430, 1375, 1268, 1205, 1169, 1144, 1109, 815 and 713 cm^{-1}.

Complex **6** (**C6**, {2,6-(2-ClC_6H_4N=CCH_3)$_2C_5H_3$ N}$FeCl_2$): ligand **L6** (382 mg, 1.0 mmol), $FeCl_2$·$4H_2O$ (219 mg, 1.1 mmol) and THF (10 mL) were used. **C6** was obtained as a light blue powder in 76% yield. Elemental analysis ($C_{21}H_{17}N_3Cl_2FeCl_2$) (509.0): calcd. (%): C 49.55, H 3.37, N 8.25; found (%): C 49.76, H 3.56, N 7.98. IR (KBr): 1623 ($\nu_{C=N}$), 1587, 1470, 1440, 1373, 1262, 1228, 1060, 1033, 820, 778, 759, 745, 730 and 688 cm^{-1}.

Complex **7** (**C7**, {2,6-(2-Cl-4-FC_6H_3N=CCH_3)$_2C_5$ H_3N}$FeCl_2$·THF): ligand **L7** (418 mg, 1.0 mmol), $FeCl_2$·$4H_2O$ (219 mg, 1.1 mmol) and THF (10 mL) were used. **C7** was obtained as a light blue powder in 70% yield. Elemental analysis ($C_{21}H_{15}N_3Cl_2F_2FeCl_2$·THF) (616.1): calcd. (%): C 48.66, H 3.76, N 6.81; found (%): C 48.76, H 3.68, N 6.55. IR (KBr): 1625 ($\nu_{C=N}$), 1588, 1485, 1429, 1375, 1262, 1205, 1106, 1049, 908, 813 and 713 cm^{-1}.

Complex **8** (**C8**, {2,6-(2,4-$F_2C_6H_3N$=CCH_3)$_2C_5$ H_3N}$FeCl_2$·THF): ligand **L8** (231 mg, 0.60 mmol), $FeCl_2$·$4H_2O$ (132 mg, 0.66 mmol) and THF (6 mL) were used. **C8** was obtained as a light blue powder in 66% yield. Elemental analysis ($C_{21}H_{15}F_4N_3FeCl_2$·THF) (584.2): calcd. (%): C 51.40, H 3.97, N 7.19; found (%): C 51.36, H 4.16, N 7.27. IR (KBr): 1619 ($\nu_{C=N}$), 1587, 1502, 1429, 1374, 1266, 1219, 1145, 1093, 966, 875, 806 and 715 cm^{-1}.

2.3. Oligomerization of ethylene at atmospheric pressure

A 250 mL dried three-necked flask with a stirring bar was purged with dry nitrogen two to three times and then ethylene once. Then 50 mL of toluene and a prescribed amount of MAO were injected into 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 1 μmol catalyst suspension in toluene. The reaction was terminated by the addition of 3 mL water after 30 min and catalytic activities were calculated by pressure change in the buffer storage. The product was stocked in the sealed 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.

2.4. Measurements

^{1}H NMR spectra were recorded on a Bruker DMX (300 MHz) 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 discussions

3.1. Preparation and characterization of ligands and complexes

All the ligands were synthesized in good yields by condensation of 2,6-diacetylpyridine with the corresponding aniline using MAO/SiO_2 as the catalyst and molecular sieve as the water adsorbent [11] (Scheme 1). Elemental analysis, ^{1}H NMR, IR and mass spectrometry were used for characterization of ligands. Iron complexes were synthesized by dissolving the ligands in tetrahydrofuran (THF) (Scheme 1), followed by the addition of 1.1 equiv. of $FeCl_2$·$4H_2O$. The complexes were characterized with elemental analysis and IR. The IR spectra of the free ligands show that the C=N stretching frequencies appear at 1638–1645 cm^{-1}. In complexes **2**–**4**, the C=N stretching vibrations shift toward lower frequencies around 1619–1628 cm^{-1} and are 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.

Table 1
Results of ethylene oligomerizations by iron complexes with different *ortho*-substituents

Run	Complex	Yield (g)	Activity (10^6 g/mol Fe h)	α	α-Olefin (%)
1	**1** [13]	9.15	18.30	0.42	>93
2	**2**	12.10	24.20	0.55	>94
3	**3**	7.75	15.50	0.61	>95
4	**4**	11.30	22.60	0.29	>91
5	**5**	14.45	28.90	0.52	>95

Reaction conditions: reaction temperature = 30 °C; Al/Fe = 1400.

3.2. Catalysis of ethylene oligomerization

Ethylene oligomerizations catalyzed by these iron coordinative complexes using MAO as co-catalyst have been systematically investigated. The aim of this research is to gain a preliminary insight into the effects of the *ortho*-substituents, electronic effect, the Al/Fe molar ratios and the reaction temperatures on ethylene oligomerization.

3.2.1. Effect of ortho-substituent on the catalytic activity and oligomer distribution

The steric bulk and electronic effect of *ortho*-substituents play important roles in the complex activities and product properties. The activities of complexes are influenced greatly by the steric bulk and electronegativities of *ortho*-substituents as shown in Table 1. The activities of complex **2** (the *ortho*-substituent is chloro) at different reaction temperatures are the highest, and complex **3** has the lowest activities and the activities of complex **1** are between those of complexes **2** and **3** as shown in Fig. 1(a). The activities of complex **4** are lower than those of complex **5**. The results obtained by Gibson and co-workers [5] show that larger steric bulk of the *ortho*-substituent at aryl rings could improve the activities of complexes. In addition, the results of Qian and co-workers [12] show that electron-withdrawing groups at the *ortho*-position of aryl rings could lead to high activities by increasing the central metal positive charge. Alternatively, complexes with both large steric bulk and high electron-withdrawing effect will have the highest activities. Halogens are a family of interesting substituents. The electronegativities of fluorine, chlorine and bromine atom are 4.0, 3.0 and 2.8 while the covalent radius (Å) increases in this order: 0.72, 0.99 and 1.14, respectively. This could explain why the complex **2** has the highest activities, and complexes **1** and **3** have the lower activities because of smaller steric bulk and lower electron-withdrawing ability.

The distributions of products obtained from complexes with different *ortho*-substituents are illustrated in Fig. 1(b). 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 percent of low-molar-mass products decreases and α value (as shown in Table 1) increases in the order of fluoro-, chloro- and bromo-substituents, which is in the same order with the covalent radius (Å). Meanwhile, complexes with the same *ortho*-substituents (such as complex **1** corresponding to complex **4** and complex **2** to complex **5**) have almost the same oligomer distributions. With the increasing in steric bulk, the selectivity for linear α-olefin increases as shown in Table 1. The result indicates that steric bulk is the main factor that influences the product distribution and reducing the steric bulk will result in more low-molar-mass products, which agrees well with the results obtained in literatures [5].

3.2.2. Influence of electronic effect on the catalytic activity and oligomer distribution

Complexes **2**, **6** and **7**, and complexes **1** and **8** have the same *ortho*-substituents but different *para*- ones in the aryl rings, respectively. The change of *para*-substituents from F, H to CH_3 is not expected to obtain significant change in

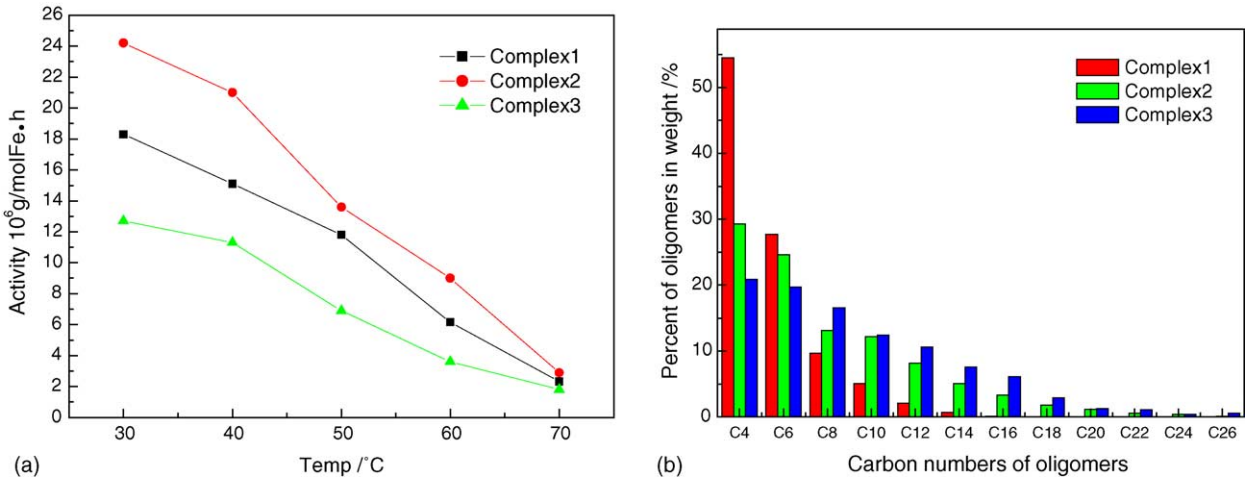


Fig. 1. Catalytic activities: (a) (Al/Fe = 1400) and distribution (b) of oligomers (reaction temperature = 60 °C; Al/Fe = 1400) obtained by complexes with different *ortho*-substituents.

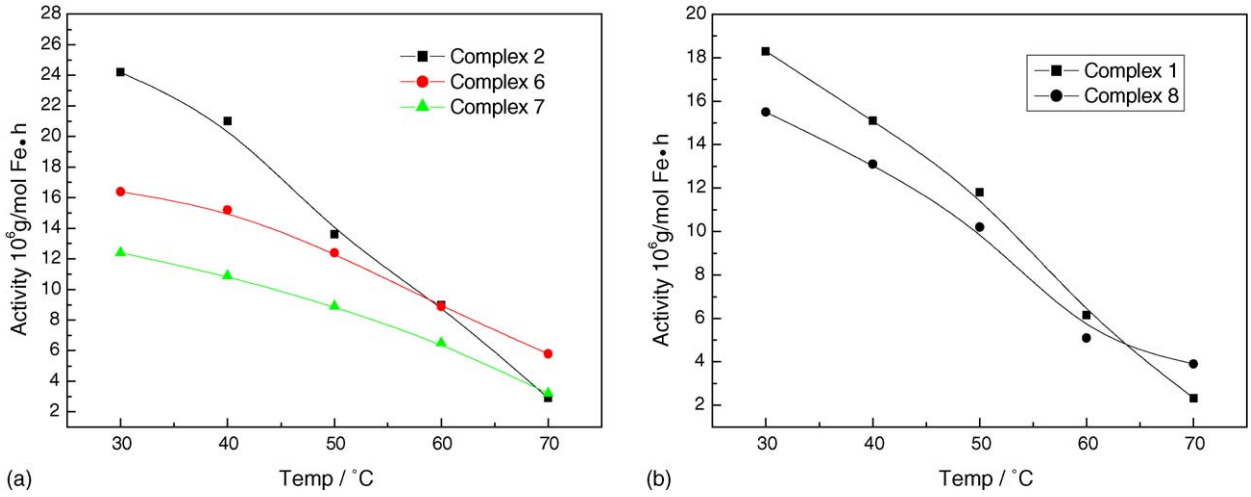


Fig. 2. The catalytic activities of complexes with the same *ortho*-substituents. Reaction conditions: Al/Fe = 1400.

steric bulk. For these complexes we can consider that the electronic effect is more important than the steric effect. As reported before, the *para*-substituents dramatically influence the catalytic activities by changing the positive charge of center metal, which could accelerate or decelerate the ethylene coordination and chain transfer [12]. The catalytic activities of these complexes at different reaction temperatures are given in Fig. 2. The catalytic activities are in the following orders: complex **2** > complex **6** > complex **7** and complex **1** > complex **8**, which is in the contrary order with the electronegativities of the *para*-substituents on the aryl rings. This means the introduction of electron-withdrawing groups will decrease the catalytic activities and vice versa. It has also been reported that the introduction of electronic-withdrawing bromo group in the *para*-position of the aryl rings increases the catalytic activity if the *ortho*-substituents are electron-donating groups [12]. All the results indicate that the combination of substituents with contrary electronic character favors the increase of catalytic activity.

In order to study the effect of different *para*-substituents on the properties of products, the results of ethylene oligomerization obtained by these complexes at the same reaction conditions are summarized in Table 2. The *para*-substituents do not exhibit obvious effect on the selectivity of α-olefins. It is interesting to find that the α values increase as the *para*-substituents change from CH_3, H to F, which indicates the increase in chain-transfer rate. This could be also proved by the distribution of oligomers obtained by these complexes as shown in Fig. 3. The oligomers shift to the lower mass weight part as the electron-donating ability of the *para*-substituents increases. All results mean that the *para*-substituents influence the chain transfer by changing the electronic character of the aryl rings and then the metallic center.

In addition, if methyl substituent is changed from the fourth position to the fifth position (such as complex **1** corresponding to complex **4** and complex **2** corresponding to complex **5**), the catalytic activities increase and the α values decrease more or less as shown in Table 2. When the *ortho*-substituent is fluoro, the activities of complexes are higher than when the *ortho*-substituent is chloro. As an electron-donating group, methyl could provide different positive charge of center metal when depending on the positions of aryl rings, which is one of the important factors in the activation of complexes as discussed above.

Table 2
Results of ethylene oligomerizations by iron complexes with different *para*-substituents

Run	Complex	Yield (g)	Activity (10^6 g/mol Fe h)	α	α-Olefin (%)
1	**2**	12.10	24.20	0.55	>94
2	**6**	8.20	16.40	0.62	>94
3	**7**	6.20	12.40	0.65	>95
4	**1** [13]	9.15	18.30	0.42	>93
5	**8**	7.70	15.40	0.52	>92
6	**4**	11.30	22.60	0.29	>91
7	**5**	14.45	28.90	0.52	>95

Reaction conditions: reaction temperature = 30 °C; Al/Fe = 1400.

3.2.3. *Effect of reaction temperature on the catalytic activity and oligomer distribution*

As other complexes reported before [1–10], the catalytic activities of these complexes are influenced strongly by reaction temperature as shown in Fig. 1(a). The catalytic activities of all the complexes decrease by almost one order of magnitude when reaction temperature increases from 30 to 70 °C. Generally, an increase in temperature is expected to result in overall enhanced propagation rate and therefore increased productivities. However, a decrease in ethylene solubility and increased rates of catalyst deactivation at higher temperatures may result in a decline in the catalytic activity.

The product distributions of complex **2** at different reaction temperatures are given in Fig. 4. As reaction temperature

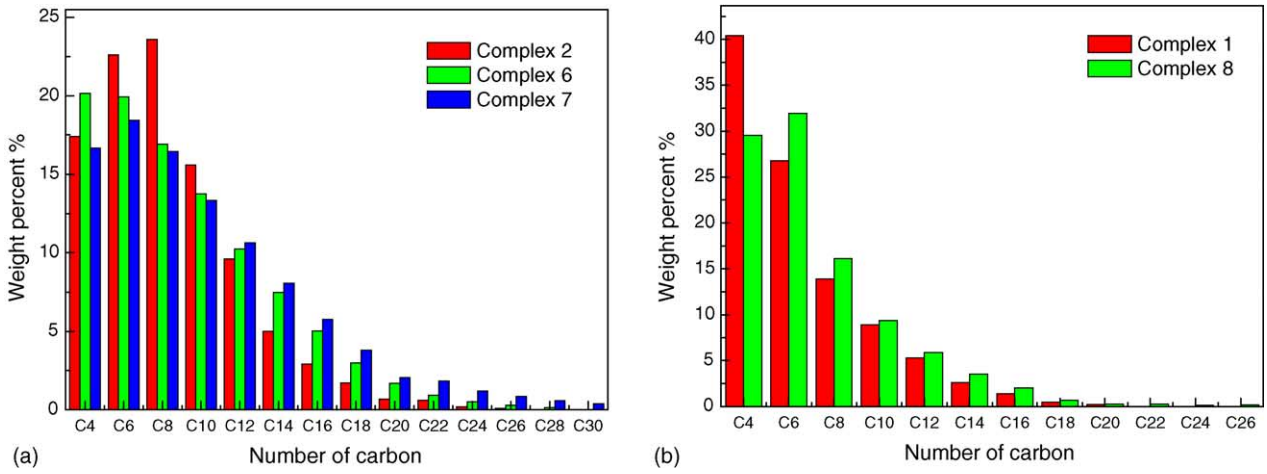


Fig. 3. The distributions of the oligomers obtained by complexes **1**–**5** with different *para*-substituents. Reaction conditions: Al/Fe = 1400; reaction temperature = 30 °C.

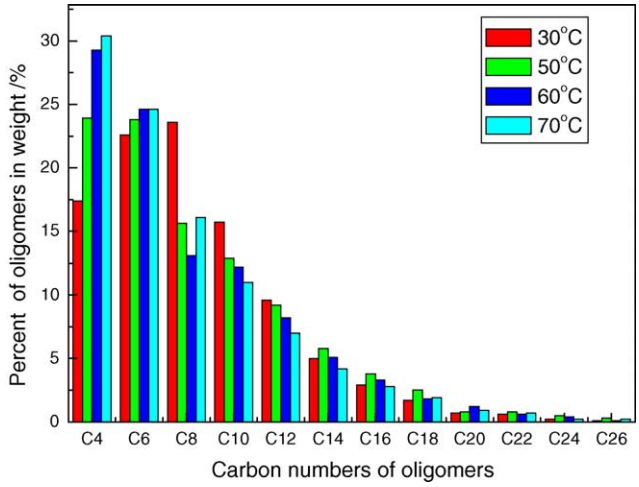


Fig. 4. Effect of reaction temperature on product distribution (obtained by complex **2**, reaction conditions: Al/Fe = 1400).

increases from 30 to 70 °C, the products shift to lower mass weight part and the α value decreases as shown in Table 3. Increasing reaction temperature will result in overall higher propagation and transfer rates. The dependence of α value on temperature indicates that the rate of chain transfer increases more than the rate of propagation, which is expected to afford lower molecular weight products.

Table 3
Results of ethylene oligomerizations by complex **2** at different reaction temperatures

Run	Temperature (°C)	Yield (g)	Activity (10^6 g/mol Fe h)	α	α-Olefin (%)
1	30	12.10	24.2	0.55	>94
2	40	10.05	21.0	0.55	>94
3	50	7.80	13.6	0.54	>96
4	60	4.50	9.00	0.53	>96
5	70	1.45	2.90	0.51	>95

Reaction conditions: Al/Fe = 1400.

3.2.4. *Effect of Al/Fe molar ratio on the catalytic activity and oligomer distribution*

The effect of Al/Fe ratio on activities of complexes is studied and the results are given in Fig. 5. It is very interesting to find that as the Al/Fe ratio increases the activities of complexes change in the same trend when the *ortho*-substituent is the same. The activities of complexes **1** and **4**, which have a fluorine atom at the *ortho*-position of aryl rings, increase and reach the maximum at Al/Fe ratio of 1000 and 420, respectively, then decrease rapidly. But the activities of complexes **2** and **5**, which bear a chlorine atom at the *ortho*-position of aryl rings, decrease monotonously. The activity of complex **3**, whose *ortho*-substituent is displaced with bromine, increases gradually and reaches the maximum at about 3000 Al/Fe. In addition, the product distribution is almost unchanged when the Al/Fe ratio is altered as shown in Fig. 6, which is similar with the results we reported before [14]. More active species are formed when more MAO is introduced to the reaction system, which results in the increase in activities, but too

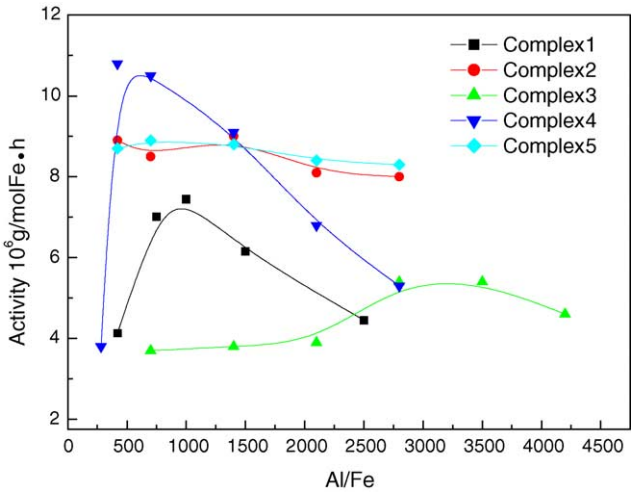


Fig. 5. Effect of Al/Fe ratio on activities of complexes **1**–**5** (at 60 °C).

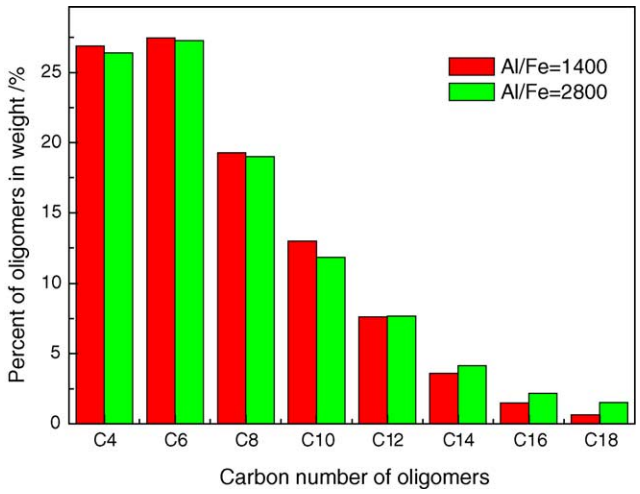


Fig. 6. Effect of Al/Fe ratio on distribution of product (obtained from complex **5** at 60 °C).

much MAO could deactivate the active species through the reaction with trimethylaluminium (TMA) contained in commercial MAO. The results indicate that the reaction between these complexes and TMA occurs more easily in the order: F > Cl > Br, which is in the same order with the steric bulk of their ligands. Alternatively, the reaction occurs more readily with complexes containing a fluoro substituent on the *ortho*-position of aryl rings, which could not provide sufficient protection of central metal. This result is well in agreement with that obtained by Gibson and co-workers [5].

4. Conclusions

In summary, all the complexes exhibit high catalytic activities for ethylene oligomerization. The iron complexes bearing a 2,6-bis(imino)pyridyl ligand with a chloro substituent at the *ortho*-position and a methyl one at the *para*- or *meta*-position have higher catalytic activity than other complexes. The steric bulk and positive charge of center metal caused by different substituents at aryl rings are main factors that influence the activities of complexes. The percent of low-molar-mass products decreases with increase the steric bulk at the *ortho*-position. The steric bulk is one of the most important factors that influence the distribution of oligomers. As reaction temperature increases, the activities decrease and low-molar-mass products increase. As the Al/Fe ratio increases, the activities change more or less, depending on the different *ortho*-substituents at aryl rings, and the distribution of products is almost unchanged.

Acknowledgments

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References

[1] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143–7144.
[2] B.L. Small, M. Brookhart. US Patent 6,150,482 (2000) to E.I. du Pont de Nemours and Company.
[3] B.L.Small, M. Brookhart. US Patent 6,103,946 (2000) to E. I. du Pont de Nemours and Company.
[4] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. Mctavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849–850.
[5] G.J.P. Britovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J. Williams, J. Chem. Eur. J. 6 (2000) 2221–2231.
[6] R. Schmidt, U. Hammon, S. Gottfried, M.B. Welch, H.G. Alt, J. Appl. Polym. Sci. 88 (2003) 476–482.
[7] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Zanobini, F. Laschi, A. Sommazzi, Eur. J. Inorg. Chem. (2003) 1620–1631.
[8] H. Wang, W. Yan:, T. Jiang, B. Liu, W. Xu, J. Ma, Y. Hu, Chin. Sci. Bull. 47 (2002) 1616–1618.
[9] T. Jiang, W. Yan, H. Wang, B. Liu, W. Xu, J. Ma, Y. Hu, Acta Polym. Sinica (2002) 293–295.
[10] M. Bluhm, C. Folli, M. Döring, J. Mol. Catal. A: Chem. 212 (2004) 13–18.
[11] Y. Chen, C. Qian, J. Sun, Organometallics 22 (2003) 1231–1236.
[12] Y. Chen, R. Chen, C. Qian, X. Dong, J. Sun, Organometallics 22 (2003) 4312–4321.
[13] I.S. Paulino, U. Schuchardt, J. Mol. Catal. A: Chem. 211 (2004) 55–58.
[14] Z. Zhang, J. Zou, N. Cui, Y. Ke, Y. Hu, J. Mol. Catal. A: Chem. 219 (2004) 249–254.