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ScienceDirect
Journal of Molecular Catalysis A: Chemical 269 (2007) 85–96
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Iron(II) complexes ligated by 2-imino-1,10-phenanthrolines: Preparation and catalytic behavior toward ethylene oligomerization

Suyun Jie [a], Shu Zhang [a], Wen-Hua Sun [a,*], Xiaofei Kuang [a], Tianfu Liu [a], Jianping Guo [b]

[a] *Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b] *Institute of Modern Chemistry, Shanxi University, Taiyuan 030006, China*

Received 4 September 2006; received in revised form 9 January 2007; accepted 10 January 2007
Available online 13 January 2007

Abstract

A series of *N*,*N*,*N*-tridentate iron (II) complexes bearing 2-imino-1,10-phenanthrolines, [2-{(2,6-R^1,R^3-4-R^2-C_6H_2)N=C(R)}-1,10-phen]$FeCl_2$, was synthesized and characterized by IR spectroscopy and elemental analysis. One of these complexes (**18b**) was determined by single-crystal X-ray crystallography for its unambiguous structure. These iron(II) complexes were found to exhibit remarkable activities for ethylene oligomerization in the presence of MAO or MMAO cocatalyst affording α-olefins with high selectivity and the composition of oligomers followed the Schluz–Flory distribution. The effects of substituents on imino fragment on the activity were explored in detail; complexes with mono substituent at the *ortho*-position of the phenyl ring showed high activities with low *K* values, suggesting that fine tuning of the steric bulk of substituents on the imino fragment directly affects both the activity and the selectivity.

Keywords: 2-Imino-1,10-phenanthroline; Iron complex; Ethylene reactivity; α-Olefins; Polyethylene wax

1. Introduction

Ethylene oligomerization is currently one of the major industrial processes for producing linear α-olefins [1], which are attractive and valuable for their wide applications, such as feedstocks for detergents, lubricants, plasticizers, and oil field chemicals as well as monomers for copolymers of ethylene and α-olefins. Since the pioneering work by Ziegler in the presence of AlR_3 [2], considerable attention has been paid to the development of the new catalyst systems with various transition metals (Ti, Zr, Cr, Fe, Ni, etc.) exhibiting high activities toward ethylene (oligomerization and/or polymerization) in both academic and industrial fields [3–7]. Especially in recent years, substantive progress has been made in iron and cobalt complexes bearing 2,6-bis(imino)pyridines as highly active catalysts by the groups of Brookhart [8] and Gibson [9,10]. As a way of promoting this system, iron and cobalt complexes containing new ligands have been designed; however, they could not provide satisfactory results [11–19]. Considering the frameworks of iron complexes bearing tridentate ligands, we previously reported a limited number of iron (II) complexes bearing 2-imino-1,10-phenanthrolines as highly active catalysts for ethylene oligomerization with high selectivity for the formation of linear α-olefins [20] while their nickel analogues showed good activities for ethylene oligomerization with low selectivity for linear α-olefins [21]. In the same period, their cobalt analogues were reported to show good catalytic activities for ethylene oligomerization with good selectivity for linear α-olefins [22]. Compared with the different metal analogues, iron complexes could be the best candidates for ethylene oligomerization with high catalytic activity and selectivity for linear α-olefins [20]. Consequently, these iron complexes could be of great potential commercially for the conversion of ethylene into linear α-olefins. For this purpose, we believe that it is necessary to establish the effects of substituents on the catalytic activities as well as the distributions of products in ethylene oligomerization using iron(II) complexes containing 2-imino-1,10-phenanthroline ligands of this type, [2-{(2,6-R^1,R^3-4-R^2-C_6H_2)N=C(R)}-1,10-phen]$FeCl_2$, in the

* Corresponding author. Tel.: +86 10 62557955; fax: +86 10 62618239.
E-mail address: whsun@iccas.ac.cn (W.-H. Sun).

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doi:10.1016/j.molcata.2007.01.008

presence of cocatalyst. In this paper, we prepared various iron analogues (18 complexes) and explored the reaction with ethylene in the presence of Al cocatalyst such as MAO and MMAO. The effects of substituents on the ligand, cocatalysts, the Al/Fe molar ratio, reaction temperature on the activity and selectivity have also been described.

2. Experimental

2.1. General considerations and materials

All manipulations for air or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Melting points (mp) were measured with a digital electrothermal apparatus without calibration. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 spectrometer by using KBr disc in the range of 4000–400 cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 300 or 400 MHz instruments with tetramethylsilane (TMS) as the internal standard. Splitting patterns are designated as follows—s: singlet; d: doublet; dd: double doublet; t: triplet; quad: quadruplet; sept: septet; m: multiplet. Elemental analysis was performed on a Flash EA1112 micro-analyzer. The GC analysis was performed with a Carlo Erba gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) DM-1 silica capillary column, while the GC–MS analysis was performed with a HP 5890 Series II and a HP 5971 Series mass detector. ^1H and ^{13}C NMR spectra of the waxes were recorded on a Bruker DMX 400 MHz instrument at 135 °C in *o*-dichlorobenzene-d_4 using TMS as the internal standard.

Toluene and tetrahydrofuran (THF) were refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Corp (USA). Trimethylaluminum (2 M in toluene), diethylaluminum chloride (Et_2AlCl, 1 M in hexane) and ethylaluminum dichloride ($EtAlCl_2$, 1 M in hexane) were purchased from Acros Chemicals. 2-Acetyl-1,10-phenanthroline, 2-formyl-1,10-phenanthroline and 2-benzoyl-1,10-phenanthroline were prepared according to our previous report [20]. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

2.2. Synthesis of 2-imino-1,10-phenanthroline ligands (*1a–18a*)

2.2.1. 2-Acetyl-1,10-phenanthroline(2-methylanil) (*1a*)

A reaction mixture of 2-acetyl-1,10-phenanthroline (0.445 g, 2.0 mmol), 2-methylaniline (0.289 g, 2.7 mmol), *p*-toluenesulfonic acid (0.040 g) and anhydrous sodium sulfate in 30 mL toluene were refluxed under nitrogen for 30 h. After filtration, the solvent was removed by a rotary evaporator and the resulting solid was eluted with petroleum ether/ethyl acetate (4:1, v/v) on an alumina column. The second eluting fraction was collected and concentrated to give a yellow solid in 23% yield (0.143 g). mp: 94–96 °C. IR (KBr disc, cm^{-1}): 2988, 2908, 1635, 1595, 1551, 1485, 1456, 1389, 1363, 1320, 1283, 1227, 1189, 1114, 1079, 1042, 850, 829, 789, 746, 657. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 4.5 Hz, 1H); 8.70 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.7 Hz, 1H); 8.30 (d, J = 8.1 Hz, 1H); 7.88 (s, 2H); 7.68 (dd, J = 8.1 Hz, 1H); 7.23 (m, 2H); 7.06 (t, J = 7.5 Hz, 1H); 6.74 (d, J = 7.8 Hz, 1H); 2.65 (s, 3H, CH_3); 2.17 (s, 3H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 156.6, 150.9, 150.6, 150.1, 146.3, 145.1, 136.5, 136.3, 130.4, 129.4, 129.0, 127.5, 127.1, 126.4, 123.7, 122.9, 121.0, 118.0, 17.8, 17.0. Anal. Calc. for $C_{21}H_{17}N_3$ (311.38): C, 81.00; H, 5.50; N, 13.49. Found: C, 80.82; H, 5.72; N, 13.27.

2.2.2. 2-Acetyl-1,10-phenanthroline(2-ethylanil) (*2a*)

In a similar manner with **1a**, the ligand **2a** was prepared as a yellow solid in 23% yield. mp: 122–124 °C. IR (KBr disc, cm^{-1}): 2961, 2928, 2869, 1633, 1592, 1551, 1484, 1446, 1416, 1390, 1363, 1321, 1283, 1241, 1221, 1186, 1113, 1079, 1050, 850, 821, 788, 770, 752, 658. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 3.9 Hz, 1H); 8.70 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.4 Hz, 1H); 8.30 (dd, J = 7.5 Hz, 1H); 7.87 (s, 2H); 7.67 (d, J = 8.1 Hz, 1H); 7.29 (d, J = 7.8 Hz, 1H); 7.22 (d, J = 7.2 Hz, 1H); 7.14 (t, J = 7.2 Hz, 1H); 6.72 (d, J = 8.1 Hz, 1H); 2.68 (s, 3H, CH_3); 2.56 (m, 2H, CH_2CH$_3$); 1.18 (t, J = 7.5Hz, 3H, CH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 156.6, 150.6, 149.3, 146.2, 145.0, 136.4, 136.2, 133.3, 129.3, 128.9, 128.5, 127.4, 126.4, 126.3, 123.8, 122.8, 120.9, 118.1, 24.6, 16.9, 14.0. Anal. Calc. for $C_{22}H_{19}N_3$ (325.41): C, 81.20; H, 5.89; N, 12.91. Found: C, 81.55; H, 5.72; N, 12.74.

2.2.3. 2-Acetyl-1,10-phenanthroline(2-isopropylanil) (*3a*)

In a similar manner with **1a**, the ligand **3a** was prepared as a yellow solid in 40% yield. mp: 125–127 °C. IR (KBr disc, cm^{-1}): 2958, 2926, 2866, 1630, 1591, 1551, 1483, 1446, 1417, 1388, 1362, 1313, 1279, 1223, 1188, 1115, 1082, 1032, 849, 783, 754, 659. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.2 Hz, 1H); 8.71 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.4 Hz, 1H); 8.30 (d, J = 7.5 Hz, 1H); 7.87 (s, 2H); 7.67 (dd, J = 8.1 Hz, 1H); 7.36 (d, J = 8.1 Hz, 1H); 7.23 (m, 1H); 7.14 (t, J = 7.2 Hz, 1H); 6.70 (d, J = 7.5 Hz, 1H); 3.08 (sept, J = 6.6 Hz, 1H, CH(CH$_3$)$_2$); 2.70 (s, 3H, CH_3); 1.21 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 157.0, 151.0, 149.1, 146.7, 145.4, 138.5, 136.8, 136.6, 129.8, 129.3, 127.8, 126.8, 126.5, 126.0, 124.5, 123.3, 121.4, 118.7, 28.8, 23.3, 17.4. Anal. Calc. for $C_{23}H_{21}N_3$ (339.43): C, 81.38; H, 6.24; N, 12.38. Found: C, 81.10; H, 6.40; N, 12.20.

2.2.4. 2-Acetyl-1,10-phenanthroline(2-ethyl-6-methylanil) (*4a*)

In a similar manner with **1a**, the ligand **4a** was prepared as a yellow solid in 56% yield. mp: 154–156 °C. IR (KBr disc, cm^{-1}): 3059, 3014, 2966, 2930, 2870, 1636, 1587, 1551, 1490, 1456, 1417, 1389, 1362, 1322, 1283, 1248, 1202, 1137, 1115, 887, 864, 821, 782, 743, 661. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.9 Hz, 1H); 8.80 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.4 Hz, 1H); 8.29 (d, J = 7.8 Hz, 1H); 7.89 (s, 2H); 7.67 (dd, J = 8.1 Hz, 1H); 7.12 (t, J = 7.5 Hz, 2H); 7.02 (t, J = 7.5 Hz, 1H); 2.58 (s, 3H, CH_3); 2.45 (m, 2H, CH_2CH$_3$); 2.08 (s, 3H, PhCH_3);

1.17 (t, J = 7.5Hz, 3H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 154.9, 149.4, 147.2, 145.1, 143.9, 135.2, 135.0, 130.1, 128.3, 127.7, 126.7, 126.3, 125.2, 124.8, 123.8, 122.0, 121.7, 119.6, 23.4, 16.8, 15.9, 12.5. Anal. Calc. for $C_{23}H_{21}N_3$ (339.43): C, 81.38; H, 6.24; N, 12.38. Found: C, 81.30; H, 6.27; N, 12.11.

*2.2.5. 2-Acetyl-1,10-phenanthroline(2-bromoanil) (**5a**)*

In a similar manner with **1a**, the ligand **5a** was prepared as a yellow solid in 40% yield. mp: 138–140 °C. IR (KBr disc, cm^{-1}): 3045, 2994, 1643, 1584, 1552, 1489, 1462, 1393, 1363, 1320, 1276, 1221, 1115, 1078, 1023, 886, 853, 818, 776, 745, 659. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (d, J = 4.1 Hz, 1H); 8.70 (dd, J = 8.4 Hz, 1H); 8.36 (dd, J = 8.4 Hz, 1H); 8.29 (d, J = 7.8 Hz, 1H); 7.87 (s, 2H); 7.68 (d, J = 4.5 Hz, 1H); 7.65 (d, J = 9.0 Hz, 1H); 7.34 (t, J = 7.5 Hz, 1H); 7.01 (t, J = 7.5 Hz, 1H); 6.86 (d, J = 7.8 Hz, 1H); 2.67 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 156.0, 150.4, 149.5, 146.1, 144.9, 136.3, 136.0, 132.7, 129.3, 128.7, 127.8, 127.4, 126.2, 124.4, 122.7, 121.0, 119.7, 113.3, 17.3. Anal. Calc. for $C_{20}H_{14}BrN_3$ (376.25): C, 63.84; H, 3.75; N, 11.17. Found: C, 63.84; H, 3.76; N, 11.09.

*2.2.6. 2-Acetyl-1,10-phenanthroline(2-bromo-4-methylanil) (**6a**)*

In a similar manner with **1a**, the ligand **6a** was prepared as a yellow solid in 30% yield. mp: 166–168 °C. IR (KBr disc, cm^{-1}): 3204, 2917, 1641, 1556, 1506, 1361, 1313, 1271, 1117, 853, 818, 739, 657. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (s, 1H); 8.70 (d, J = 8.4 Hz, 1H); 8.36 (d, J = 8.4 Hz, 1H); 8.30 (d, J = 7.8 Hz, 1H); 7.87 (s, 2H); 7.68 (m, 1H); 7.49 (s, 1H); 7.15 (d, J = 7.5 Hz, 1H); 6.76 (t, J = 7.8 Hz, 1H); 2.68 (s, 3H, CH_3), 2.36 (s, 3H, $PhCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 156.3, 150.6, 147.1, 146.3, 145.1, 136.6, 136.3, 134.7, 133.2, 129.5, 129.0, 128.8, 127.6, 126.5, 123.0, 121.3, 120.0, 113.4, 20.5, 17.5. Anal. Calc. for $C_{21}H_{16}BrN_3$ (390.28): C, 64.63; H, 4.13; N 10.77. Found: C, 64.64; H, 4.22; N, 10.48.

*2.2.7. 2-Acetyl-1,10-phenanthroline(2-bromo-4-fluoroanil) (**7a**)*

In a similar manner with **1a**, the ligand **7a** was prepared as a yellow solid in 39% yield. mp: 206–208 °C. IR (KBr disc, cm^{-1}): 3045, 1641, 1589, 1554, 1479, 1396, 1366, 1321, 1253, 1234, 1193, 1118, 1078, 854, 825, 763, 740, 654. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.2 Hz, 1H); 8.63 (d, J = 8.4 Hz, 1H); 8.36 (d, J = 8.1 Hz, 1H); 8.29 (dd, J = 7.5 Hz, 1H); 7.88 (s, 2H); 7.69 (q, J = 4.5 Hz, 1H); 7.34 (t, J = 7.5 Hz, 2H); 6.86 (t, J = 8.7 Hz, 1H); 2.72 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 155.8, 150.6, 149.5, 146.2, 150.0, 136.5, 136.2, 129.5, 128.9, 127.7, 127.5, 126.3, 123.0, 121.0, 119.7, 119.4, 17.6. Anal. Calc. for $C_{20}H_{13}BrFN_3$ (394.24): C, 60.93; H, 3.32; N, 10.66. Found: C, 61.08; H, 3.41; N, 10.46.

*2.2.8. 2-Acetyl-1,10-phenanthroline(2,4-dibromoanil) (**8a**)*

In a similar manner with **1a**, the ligand **8a** was prepared as a yellow solid in 45% yield. mp: 150–152 °C. IR (KBr disc, cm^{-1}): 3419, 3054, 1636, 1587, 1551, 1488, 1458, 1391, 1365, 1319, 1284, 1253, 1219, 1116, 1077, 1042, 859, 831, 742, 686. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.2 Hz, 1H); 8.67 (d, J = 8.1 Hz, 1H); 8.37 (d, J = 8.4 Hz, 1H); 8.31 (dd, J = 8.1 Hz, 1H); 7.88 (s, 2H); 7.80 (s, 1H); 7.68 (q, J = 4.2 Hz, 1H); 7.47 (dd, J = 8.4 Hz, 1H); 6.74 (d, J = 8.4 Hz, 1H); 2.68 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 155.7, 153.1, 150.6, 148.8, 146.2, 145.0, 136.6, 136.2, 135.0, 134.3, 131.0, 128.9, 127.7, 126.3, 123.0, 121.1, 116.4, 114.3, 17.5. Anal. Calc. for $C_{20}H_{13}Br_2N_3$ (455.15): C, 52.78; H, 2.88; N, 9.23. Found: C, 52.71; H, 2.97; N, 9.25.

*2.2.9. 2-Acetyl-1,10-phenanthroline (2,4,6-trifluoroanil) (**9a**)*

In a similar manner with **1a**, the ligand **9a** was prepared as a yellow solid in 40% yield. mp: 211–213 °C. IR (KBr disc, cm^{-1}): 3102, 3033, 1629, 1595, 1553, 1492, 1444, 1391, 1368, 1320, 1284, 1216, 1119, 1080, 1036, 998, 856, 804, 778, 728, 659. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.2 Hz, 1H); 8.67 (d, J = 8.4 Hz, 1H); 8.36 (d, J = 8.4 Hz, 1H); 8.30 (dd, J = 8.4 Hz, 1H); 7.87 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 6.81 (m, 2H); 2.76 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 159.7, 147.6, 146.5, 141.5, 139.5, 137.8, 129.9, 128.8, 125.9, 124.8, 123.3, 122.0, 117.8, 35.3, 34.2, 31.3, 29.5. Anal. Calc. for $C_{20}H_{12}F_3N_3$ (351.32): C, 68.37; H, 3.44; N, 11.96. Found: C, 68.00; H, 3.51; N, 11.67.

*2.2.10. 2-Acetyl-1,10-phenanthroline (2,4,6-trichloroanil) (**10a**)*

2-Acetyl-1,10-phenanthroline (0.445 g, 2.0 mmol), 2,4,6-trichloroaniline (0.491 g, 2.5 mmol) and *p*-toluenesulfonic acid (0.040 g) were combined with tetraethyl orthosilicate (5 mL) in a flask. The flask was equipped with a condenser along with a water knockout trap, and the mixture was heated at 140–150 °C under nitrogen for 36 h. Tetraethyl orthosilicate was removed at reduced pressure and the resulting solid was eluted with petroleum ether/ethyl acetate (4:1, v/v) on an alumina column. The second eluting fraction was collected and concentrated to give a yellow solid in 15% yield (0.120 g). mp: 188–190 °C. IR (KBr disc, cm^{-1}): 3049, 1643, 1587, 1543, 1490, 1450, 1430, 1362, 1322, 1285, 1229, 1135, 1114, 854, 798, 706. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (d, J = 4.2 Hz, 1H); 8.74 (d, J = 8.4Hz, 1H); 8.38 (d, J = 8.4 Hz, 1H); 8.31 (dd, J = 7.8 Hz, 1H); 7.89 (s, 2H); 7.69 (dd, J = 7.8 Hz, 1H); 7.41 (s, 2H); 2.67 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 155.4, 151.1, 145.6, 145.0, 137.1, 136.7, 130.2, 129.4, 129.0, 128.5, 128.4, 126.8, 125.3, 121.7, 18.5. Anal. Calc. for $C_{20}H_{12}Cl_3N_3$ (400.69): C, 59.95; H, 3.02; N, 10.49. Found: C, 59.65; H, 3.07; N, 10.20.

*2.2.11. 2-Acetyl-1,10-phenanthroline (2-bromo-4,6-difluoroanil) (**11a**)*

In a similar manner with **10a**, the ligand **11a** was prepared as a yellow solid in 40% yield. mp: 173–175 °C. IR (KBr disc, cm^{-1}): 3041, 1631, 1603, 1583, 1553, 1489, 1464, 1419, 1366, 1324, 1290, 1206, 1164, 1109, 1080, 992, 886, 851, 793, 739, 659. ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (d, J = 3.6 Hz, 1H); 8.71 (d, J = 8.4 Hz, 1H); 8.34 (d, J = 8.4 Hz, 1H); 8.26 (d, J = 8.1 Hz, 1H); 7.84 (s, 2H); 7.66

(dd, J = 7.8 Hz, 1H); 7.24 (s, 1H); 6.94 (m, 1H); 2.70 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 155.1, 151.9, 146.0, 144.8, 136.3, 135.9, 129.4, 128.7, 127.6, 126.0, 122.7, 121.0, 115.4, 115.1, 103.8, 103.6, 103.3, 17.8. Anal. Calc. for $C_{20}H_{12}BrF_2N_3$ (412.20): C, 58.27; H, 2.93; N, 10.19. Found: C, 57.94; H, 3.06; N, 10.13.

*2.2.12. 2-Acetyl-1,10-phenanthroline(2-bromo-6-chloro-4-fluoroanil) (**12a**)*

In a similar manner with **10a**, the ligand **12a** was prepared as a yellow solid in 39% yield. mp: 197–198 °C. IR (KBr disc, cm^{-1}): 3076, 2986, 1657, 1586, 1562, 1491, 1440, 1389, 1362, 1319, 1284, 1252, 1195, 1137, 1115, 928, 858, 772, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.3 Hz, 1H); 8.76 (d, J = 8.4Hz, 1H); 8.37 (d, J = 8.4 Hz, 1H); 8.30 (d, J = 7.8 Hz, 1H); 7.88 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 7.35 (d, J = 6.9 Hz, 1H); 7.23 (d, J = 8.1 Hz, 1H); 2.66 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4, 155.5, 151.1, 146.7, 145.6, 137.1, 136.7, 130.2, 129.4, 128.3, 126.8, 124.6, 123.4, 121.7, 119.3, 118.9, 117.0, 116.6, 114.2, 18.4. Anal. Calc. for $C_{20}H_{12}BrClFN_3$ (428.68): C, 56.04; H, 2.82; N, 9.80. Found: C, 55.76; H, 2.78; N, 9.64.

*2.2.13. 2-Acetyl-1,10-phenanthroline(2-bromo-4-chloro-6-fluoroanil) (**13a**)*

In a similar manner with **10a**, the ligand **13a** was prepared as a yellow solid in 43% yield. mp: 117–118 °C. IR (KBr disc, cm^{-1}): 3061, 2919, 1639, 1587, 1554, 1504, 1490, 1455, 1418, 1401, 1392, 1372, 1323, 1286, 1266, 1246, 1212, 1170, 1136, 1118, 1080, 921, 887, 857, 822, 775, 762, 742, 710, 659, 625. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.3 Hz, 1H); 8.71 (d, J = 7.5 Hz, 1H); 8.36 (d, J = 7.8 Hz, 1H); 8.30 (d, J = 7.2 Hz, 1H); 7.87 (s, 2H); 7.68 (s, 1H); 7.48 (s, 1H); 7.18 (d, J = 8.1 Hz, 1H); 2.70 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 155.3, 150.7, 146.3, 145.1, 137.1, 136.7, 136.3, 129.8, 129.2, 129.0, 128.1, 128.0, 126.4, 123.1, 121.4, 116.1, 115.9, 115.6, 18.3. Anal. Calc. for $C_{20}H_{12}BrClFN_3$ (428.68): C, 56.04; H, 2.82; N, 9.80. Found: C, 55.78; H, 2.83; N, 9.71.

*2.2.14. 2-Formyl-1,10-phenanthroline(2-methylanil) (**14a**)*

A reaction mixture of 2-formyl-1,10-phenanthroline (0.208 g, 1.0 mmol), 2-methylaniline (0.129 g, 1.2 mmol), *p*-toluenesulfonic acid (0.040 g) and absolute ethanol (10 mL) was refluxed under nitrogen for 6 h. The solvent was thereafter removed by a rotary evaporator and the resulting solid was eluted with petroleum ether/ethyl acetate (1:1, v/v) on an alumina column. The second eluting fraction was collected and concentrated to afford a yellow solid in 41% yield (0.122 g). mp: 196–198 °C. IR (KBr disc, cm^{-1}): 3255, 3061, 2912, 1637, 1591, 1555, 1495, 1461, 1412, 1128, 861, 823, 751. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.18 (d, J = 3.0 Hz, 1H); 8.27 (d, J = 7.8 Hz, 2H); 7.83 (s, 2H), 7.67 (dd, J = 4.2 Hz, 1H); 7.06–6.78 (m, 5H); 6.58 (d, J = 7.5 Hz, 1H); 2.24 (s, 3H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.3, 154.6, 150.5, 146.0, 145.6, 136.2, 133.2, 129.9, 129.0, 128.6, 127.7, 126.3, 126.0, 125.9, 125.8, 125.7, 125.6, 123.3, 122.1, 18.6. Anal. Calc. for $C_{20}H_{15}N_3$ (297.35): C, 80.78; H, 5.08; N, 14.13. Found: C, 80.54; H, 5.38; N, 13.97.

*2.2.15. 2-Formyl-1,10-phenanthroline(2,4,6-trimethylanil) (**15a**)*

In a similar manner with **14a**, the ligand **15a** was prepared as a yellow solid in 82% yield. mp: 99–101 °C. IR (KBr disc, cm^{-1}): 3445, 2915, 2856, 1635, 1587, 1554, 1485, 1394, 1210, 1144, 1091, 855, 835, 739. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (s, 1H); 8.85 (s, 1H, CH=N); 8.70 (d, J = 8.4 Hz, 1H); 8.37 (d, J = 8.1 Hz, 1H); 8.28 (d, J = 7.8 Hz, 1H); 7.88 (s, 2H), 7.67 (dd, J = 8.1 Hz, 1H); 6.92 (s, 2H); 2.31 (s, 3H, PhCH_3); 2.17 (s, 6H, PhCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 154.8, 150.7, 147.9, 146.1, 145.8, 136.8, 136.3, 133.4, 129.8, 129.0, 128.8, 127.7, 126.6, 126.5, 123.2, 120.3, 20.8, 18.3. Anal. Calc. for $C_{22}H_{19}N_3$·EtOH (371.47): C, 77.60; H, 6.78; N, 11.31. Found: C, 77.83; H, 6.63; N, 11.44.

*2.2.16. 2-Formyl-1,10-phenanthroline(4-bromo-2,6-dimethylanil) (**16a**)*

In a similar manner with **14a**, the ligand **16a** was prepared as a yellow solid in 36% yield. mp: 190–192 °C. IR (KBr disc, cm^{-1}): 3443, 2966, 2911, 1635, 1587, 1553, 1492, 1465, 1393, 1191, 856, 815, 742. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.3 Hz, 1H); 8.82 (s, 1H, CH=N); 8.68 (d, J = 8.4 Hz, 1H); 8.40 (d, J = 8.4 Hz, 1H); 8.31 (d, J = 7.5 Hz, 1H); 7.90 (s, 2H); 7.69 (dd, J = 8.1 Hz, 1H); 7.24 (s, 2H); 2.15 (s, 6H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 154.3, 150.8, 149.4, 146.0, 145.9, 136.9, 136.3, 130.7, 129.9, 129.0, 128.9, 128.0, 126.4, 123.3, 120.2, 116.7, 18.1. Anal. Calc. for $C_{21}H_{16}BrN_3$ (390.28): C, 64.63; H, 4.13; N, 10.77. Found: C, 64.34; H, 4.07; N, 10.52.

*2.2.17. 2-Benzoyl-1,10-phenanthroline(2,4,6-trimethylanil) (**17a**)*

In a similar manner with **10a**, while 2-benzoyl-1,10-phenanthroline and 2,4,6-trimethylaniline were alternatively used, the ligand **17a** was prepared as a yellow solid in 44% yield. mp: 210–212 °C. IR (KBr disc, cm^{-1}): 3054, 2913, 1623, 1589, 1551, 1487, 1447, 1389, 1322, 1215, 1140, 967, 877, 845, 789, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.20–6.59 (m, 14H); 2.22 (d, J = 8.4 Hz, 6H), 2.25 (d, J = 8.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 156.8, 151.4, 147.2, 146.9, 146.5, 138.8, 137.3, 136.7, 136.6, 132.8, 131.6, 130.8, 130.2, 129.8, 129.4, 129.1, 128.8, 128.3, 128.1, 127.1, 127.0, 126.2, 123.9, 122.7, 21.5, 19.7, 19.3. Anal. Calc. for $C_{28}H_{23}N_3$·0.5H_2O (410.51): C, 81.92; H, 5.89; N, 10.24. Found: C, 82.21; H, 5.63; N, 10.12.

*2.2.18. 2-Benzoyl-1,10-phenanthroline(4-bromo-2,6-dimethylanil) (**18a**)*

In a similar manner with **17a**, the ligand **18a** was prepared as a yellow solid in 25% yield. mp: 194–196 °C. IR (KBr disc, cm^{-1}): 3056, 2918, 1625, 1588, 1574, 1551, 1487, 1465, 1447, 1388, 1321, 1206, 1159, 966, 878, 845, 785, 692. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (d, J = 4.0 Hz, 1H); 8.18 (d, J = 8.0Hz, 1H); 8.07 (d, J = 8.0 Hz, 1H); 7.95 (d, J = 7.6 Hz, 2H); 7.74 (d, J = 8.8 Hz, 1H); 7.67 (d, J = 8.8 Hz, 1H); 7.59 (dd, J = 8.0 Hz, 1H); 7.46 (t, J = 7.2 Hz, 1H); 7.39 (t, J = 7.2 Hz, 2H); 7.30 (dd, J = 8.4 Hz, 2H); 6.89 (s, 2H); 2.24 (s, 6H, PhCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 154.9, 150.1, 147.4, 145.8, 145.2,

137.1, 136.1, 135.7, 135.5, 130.7, 130.1, 129.6, 129.0, 128.6, 128.3, 127.9, 127.1, 125.8, 122.8, 123.0, 114.9, 18.4. Anal. Calc. for $C_{27}H_{20}BrN_3$ (466.37): C, 69.53; H, 4.32; N, 9.01. Found: C, 69.45; H, 4.46; N, 8.89.

2.3. Preparation of iron(II) complexes

2.3.1. General procedure

The ligand and $FeCl_2{\cdot}4H_2O$ were added together in a Schlenk tube, previously purged three times with argon and then charged with THF. The reaction mixture was stirred at room temperature for 9 h. The resulting precipitate was filtered, washed with diethyl ether and dried in vacuum. All of the complexes were prepared in high yield in this manner.

2.3.2. Synthesis of complexes *1b–18b*

1b: Dark blue powder in 70% yield. IR (KBr disc, cm^{-1}): 3420, 3056, 2918, 1667, 1605, 1578, 1511, 1488, 1401, 1287, 1260, 1226, 1150, 864, 742, 656. Anal. Calc. for $C_{21}H_{17}Cl_2FeN_3$ (438.13): C, 57.57; H, 3.91; N, 9.59. Found: C, 57.80; H, 3.54; N, 9.24. **2b**: Dark blue powder in 90% yield. IR (KBr disc, cm^{-1}): 3482, 3059, 2966, 2934, 2876, 1608, 1579, 1513, 1484, 1447, 1405, 1370, 1337, 1286, 1223, 1147, 858, 786, 742, 657. Anal. Calc. for $C_{22}H_{19}Cl_2FeN_3$ (489.22): C, 58.44; H, 4.24; N, 9.29. Found: C, 58.19; H, 4.36; N, 8.93. **3b**: Dark blue powder in 95% yield. IR (KBr disc, cm^{-1}): 3447, 3060, 2962, 2922, 2869, 1610, 1578, 1514, 1486, 1445, 1406, 1371, 1286, 1228, 1195, 1145, 1089, 1033, 858, 835, 790, 756, 741, 656. Anal. Calc. for $C_{23}H_{21}Cl_2FeN_3$ (466.18): C, 59.26; H, 4.54; N, 9.01. Found: C, 58.89; H, 4.54; N, 8.83. **4b**: Dark blue powder in 88% yield. IR (KBr disc, cm^{-1}): 3446, 1974, 2912, 1609, 1581, 1509, 1489, 1456, 1403, 1372, 1285, 1203, 1143, 1095, 894, 862, 783, 741, 656. Anal. Calc. for $C_{24}H_{23}Cl_2FeN_3$ (480.21): C, 60.03; H, 4.83; N, 8.75. Found: C, 59.91; H, 4.61; N, 8.62. **5b**: Gray blue powder in 79% yield. IR (KBr disc, cm^{-1}): 3468, 3059, 3015, 2910, 1612, 1580, 1514, 1492, 1464, 1426, 1406, 1373, 1333, 1287, 1223, 1149, 1137, 1027, 862, 834, 789, 762, 739, 657. Anal. Calc. for $C_{20}H_{14}BrCl_2FeN_3$ (503.00): C, 47.76; H, 2.81; N, 8.35. Found: C, 47.43; H, 2.56; N, 8.05. **6b**: Dark green powder in 89% yield. IR (KBr disc, cm^{-1}): 3440, 3058, 2917, 1610, 1578, 1512, 1485, 1398, 1337, 1288, 1232, 1154, 1047, 843, 857, 739, 655. Anal. Calc. for $C_{21}H_{16}BrCl_2FeN_3$ (517.03): C, 48.78; H, 3.12; N, 8.13. Found: C, 48.42; H, 3.34; N, 8.25. **7b**: Dark blue powder in 87% yield. IR (KBr disc, cm^{-1}): 3449, 3055, 2912, 1614, 1596, 1513, 1479, 1405, 1374, 1289, 1260, 1193, 1039, 856, 787, 740, 655. Anal. Calc. for $C_{20}H_{13}BrCl_2FFeN_3$ (520.99): C, 46.11; H, 2.52; N, 8.07. Found: C, 45.83; H, 2.73; N, 7.87. **8b**: Dark green powder in 92% yield. IR (KBr disc, cm^{-1}): 3449, 3065, 1607, 1586, 1516, 1465, 1425, 1399, 1375, 1287, 1213, 1174, 1114, 1063, 996, 861, 738, 658. Anal. Calc. for $C_{20}H_{13}Br_2Cl_2FeN_3$ (581.90): C, 41.28; H, 2.25; N, 7.22. Found: C, 40.97; H, 2.38; N, 7.14. **9b**: Dark blue powder in 92% yield. IR (KBr disc, cm^{-1}): 3452, 3051, 2910, 1631, 1599, 1579, 1514, 1495, 1447, 1404, 1285, 1227, 1124, 1043, 998, 847, 741, 660. Anal. Calc. for $C_{20}H_{12}Cl_2F_3FeN_3$ (478.08): C, 50.25; H, 2.53; N, 8.79. Found: C, 49.97; H, 2.81; N, 8.48. **10b**: Dark blue powder in 75% yield. IR (KBr disc, cm^{-1}): 3466, 3061, 2910, 1613, 1578, 1548, 1514, 1491, 1438, 1405, 1375, 1286, 1232, 1152, 859, 799, 739, 656. Anal. Calc. for $C_{20}H_{12}Cl_5FeN_3$ (527.44): C, 45.54; H, 2.29; N, 7.97. Found: C, 45.29; H, 2.34; N, 7.89. **11b**: Dark blue powder in 81% yield. IR (KBr disc, cm^{-1}): 3449, 3065, 1607, 1586, 1516, 1465, 1425, 1398, 1287, 1213, 1174, 1114, 1063, 996, 861, 738, 658. Anal. Calc. for $C_{20}H_{12}BrCl_2F_2FeN_3$ (538.98): C, 44.57; H, 2.24; N, 7.80. Found: C, 44.82; H, 2.31; N, 7.52. **12b**: Dark purple powder in 99% yield. IR (KBr disc, cm^{-1}): 3482, 3059, 2969, 2908, 1612, 1589, 1570, 1515, 1493, 1448, 1407, 1376, 1286, 1266, 1200, 1178, 936, 861, 779, 734, 657. Anal. Calc. for $C_{20}H_{12}BrCl_3FFeN_3$ (555.44): C, 43.25; H, 2.18; N, 7.57. Found: C, 43.60; H, 2.51; N, 7.23. **13b**: Dark blue powder in 85% yield. IR (KBr disc, cm^{-1}): 3459, 3060, 2909, 1612, 1562, 1513, 1491, 1454, 1405, 1374, 1587, 1216, 1174, 928, 860, 791, 740, 657. Anal. Calc. for $C_{20}H_{12}BrCl_3FFeN_3$ (555.44): C, 43.25; H, 2.18; N, 7.57. Found: C, 43.46; H, 2.46; N, 7.28. **14b**: Dark blue powder in 64% yield. IR (KBr disc, cm^{-1}): 3431, 3059, 3016, 1603, 1580, 1512, 1487, 1405, 1296, 1185, 1143, 1116, 965, 862, 760. Anal. Calc. for $C_{20}H_{15}Cl_2FeN_3{\cdot}0.5H_2O$ (433.11): C, 55.46; H, 3.72; N, 9.70. Found: C, 55.29; H, 3.64; N, 9.44. **15b**: Dark blue powder in 70% yield. IR (KBr disc, cm^{-1}): 3436, 3053, 2917, 1608, 1582, 1512, 1481, 1406, 1297, 1198, 1142, 964, 860, 738, 646. Anal. Calc. for $C_{22}H_{19}Cl_2FeN_3{\cdot}H_2O$ (470.17): C, 56.20; H, 4.50; N, 8.94. Found: C, 56.52; H, 4.31; N, 8.88. **16b**: Gray blue powder in 95% yield. IR (KBr disc, cm^{-1}): 3436, 3056, 2976, 1606, 1582, 1512, 1494, 1470, 1436, 1406, 1297, 1182, 1140, 963, 859, 840, 738, 644. Anal. Calc. for $C_{21}H_{16}BrCl_2FeN_3$ (517.03): C, 48.78; H, 3.12; N, 8.13. Found: C, 49.04; H, 3.26; N, 7.94. **17b**: Dark brown powder in 89% yield. IR (KBr disc, cm^{-1}): 3443, 3060, 2913, 1601, 1583, 1510, 1491, 1442, 1402, 1289, 1223, 1000, 866, 701. Anal. Calc. for $C_{28}H_{23}Cl_2FeN_3{\cdot}0.5EtOH$ (551.29): C, 63.18; H, 4.75; N, 7.62. Found: C, 62.94; H, 4.49; N, 7.58. **18b**: Dark brown powder in 95% yield. IR (KBr disc, cm^{-1}): 3447, 3043, 2966, 1619, 1590, 1509, 1494, 1463, 1441, 1404, 1290, 1217, 1158, 1113, 1000, 856, 701. Anal. Calc. for $C_{27}H_{20}BrCl_2FeN_3{\cdot}CH_3OH$ (625.16): C, 53.79; H, 3.87; N, 6.72. Found: C, 53.71; H, 3.97; N, 6.51.

2.4. General procedure for ethylene reactivity

Ethylene oligomerization under atmospheric pressure of ethylene was carried out as follows: the catalyst precursor was dissolved in toluene in a Schlenk tube. The mixture was intensively stirred at a controlled temperature under one atmospheric ethylene. The reaction was thereafter initiated by the addition of the desired amount of cocatalyst. After the set period of time, an aliquot amount of the solution was collected with a syringe and quenched by the addition of 5% aqueous hydrogen chloride. The composition and distribution of obtained oligomers were analyzed by gas chromatography (GC).

Ethylene oligomerization at 10 atm of ethylene was carried out as follows: a 250-mL autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller was heated in *vacuo* for at least 2 h over 80 °C. On cooling to the required reaction temperature under ethylene, it was charged with toluene solution (100 mL total volume) of catalyst

Table 1
Crystal data and structure refinement for [2-{(2,6-Me_2-4-Br–C_6H_2)N=C(Ph)}-1,10-phen]$FeCl_2$ (**18b**)

Formula	$C_{27}H_{20}BrCl_2FeN_3 \cdot CH_3OH$	Formula weight	624.15
Temperature(K)	293(2)	Wavelength (Å)	0.71073
Crystal system	Triclinic	Space group	*P*-1
a (Å)	8.2536(16)	*b* (Å)	8.5313(16)
c (Å)	19.678(4)	α (°)	84.533(4)
β (°)	88.482(4)	γ (°)	75.124(3)
Volume (Å^3)	1333.0(4)	*Z*	2
D_{calc} (Mg m^{-3})	1.555	μ (mm^{-1})	2.292
F(0 0 0)	630	Crystal size (mm)	0.20 × 0.15 × 0.10
θ range (°)	2.08–25.01	Limiting indices	$-9 \le h \le 8$, $-10 \le k \le 6$, $-22 \le 1 \le 23$
Reflections collected	5524	Unique reflections	4598
Completeness to θ (%)	98.0 (θ = 25.01°)	Number of parameters	327
Goodness-of-fit on F^2	1.053	Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0891$, $wR2 = 0.1795$
R indices (all data)	$R1 = 0.1579$, $wR2 = 0.2103$	Largest diffraction peak, hole (einstein Å^{-3})	0.815, −0.351

precursor and the desired amount of cocatalyst. Ethylene at 10 atm pressures was then introduced to start the reaction. At the lapse of the reaction set time, the pressure was released and an aliquot amount of the solution was collected, terminated by the addition of 5% aqueous hydrogen chloride and then analyzed by gas chromatography (GC) for composition and distribution of oligomers. The residual solution was finally quenched with 5% hydrochloric acid ethanol. The precipitated low-molecular-weight waxes were collected by filtration, washed with ethanol, dried in vacuum at 60 °C to constant weight.

2.5. X-ray crystallography measurements

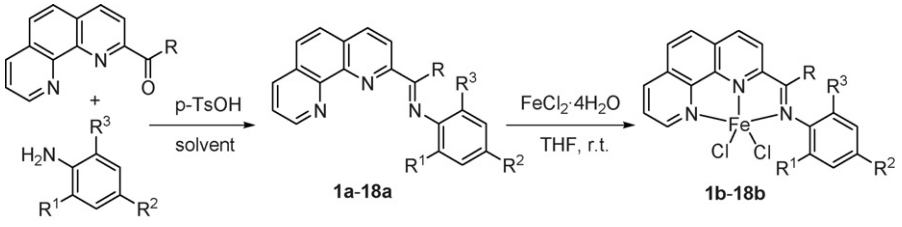
Single-crystal X-ray diffraction studies for **18b** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 Package [23]. Its crystallographic data and processing parameters are summarized in Table 1. The crystallographic data have been deposited within the Cambridge Crystallographic Data Center, CCDC 624452.

3. Results and discussion

3.1. Synthesis and characterization of the ligands and iron(II) complexes

The 2-formyl, 2-acetyl and 2-benzoyl-1,10-phenanthroline derivatives were prepared according to our previous work [20]. The 2-imino-1,10-phenanthrolines, 2-{(2,6-R^1,R^3-4-R^2-C_6H_2)N=C(R)}-1,10-phen (**1a–18a**), were conveniently prepared through the condensation reaction of the aldehyde or ketones of 1,10-phenanthroline with the corresponding substituted anilines using *p*-toluene sulfonic acid as a catalyst (Scheme 1). The reaction solvents were varied according to different substances in order to improve the yields of products. All the compounds were characterized and confirmed by IR, ^{1}H and ^{13}C NMR spectra as well as their elemental analysis.

The 2-imino-1,10-phenanthrolines as ligands reacted with one equivalent of $FeCl_2 \cdot 4H_2O$ to form their corresponding iron complexes precipitately at room temperature under nitrogen (Scheme 1). The resultant precipitates were collected and separated by filtration and subsequently washed with diethyl ether to obtain the complexes as blue, green or brown air-stable



Scheme 1. Synthesis of **1a–18a** and their iron (II) complexes **1b–18b**.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
R	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me	H	H	H	Ph	Ph
R^1	Me	Et	*i*-Pr	Me	Br	Br	Br	Br	F	Cl	Br	Br	Br	Me	Me	Me	Me	Me
R^2	H	H	H	H	H	Me	F	Br	F	Cl	F	F	Cl	H	Me	Br	Me	Br
R^3	H	H	H	Et	H	H	H	H	F	Cl	F	Cl	F	H	Me	Me	Me	Me

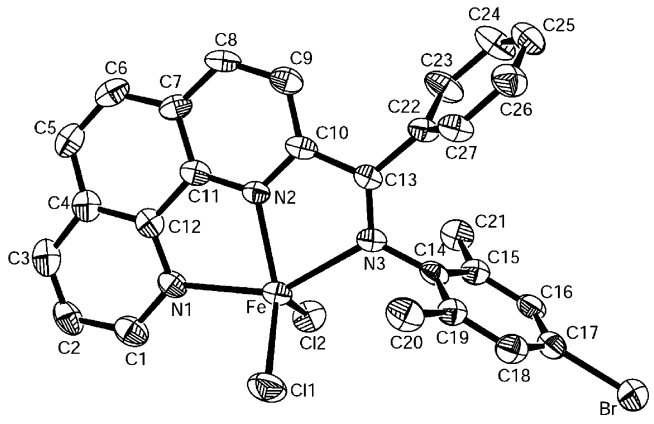


Fig. 1. ORTEP drawing of **18b** with thermal ellipsoids at 30% probability level. One methanol molecule and all hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for [2-{(2,6-Me_2-4-Br-C_6H_2)N=C(Ph)}-1,10-phen]$FeCl_2$ (**18b**)

Bond lengths	
Fe–N(1)	2.223(7)
Fe–N(2)	2.107(6)
Fe–N(3)	2.303(6)
Fe–Cl(1)	2.275(3)
Fe–Cl(2)	2.304(3)
N(3)–C(13)	1.269(9)
N(3)–C(14)	1.431(1)
Br–C(17)	1.893(9)
Bond angles	
N(2)–Fe–N(1)	74.6(3)
N(2)–Fe–N(3)	71.9(2)
N(1)–Fe–N(3)	146.4(2)
N(1)–Fe–Cl(1)	95.9(2)
N(2)–Fe–Cl(1)	136.74(2)
N(3)–Fe–Cl(1)	106.24(2)
N(1)–Fe–Cl(2)	97.24(2)
N(2)–Fe–Cl(2)	110.84(2)
N(3)–Fe–Cl(2)	97.35(2)
Cl(1)–Fe–Cl(2)	112.21(1)

powders in good yields and in high purity. All the complexes were characterized by IR spectra and elemental analysis. In addition, the solid structure was confirmed by the single-crystal X-ray diffraction analysis of complex **18b**.

Single crystals of complex **18b** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its methanol solution under nitrogen. The crystal structure is shown in Fig. 1 and the selected bond lengths and angles are collected in Table 2.

In the structure of complex **18b**, the coordination geometry around the iron center can be described as a distorted trigonal bipyramidal. The nitrogen atom (N(2) in Fig. 1) of the phenanthrolinyl group and two chlorine atoms compose an equatorial plane and the central iron atom slightly deviates by 0.0567 Å from this plane. The three equatorial angles N(2)–Fe–Cl(1), N(2)–Fe–Cl(2) and Cl(1)–Fe–Cl(2) are 106.24(18)°, 110.84(19)° and 112.21(11)°, respectively and the axial Fe–N bonds subtend an angle of 146.4(2)° (N(1)–Fe–N(3)). The dihedral angle between the equatorial plane and the phenanthrolinyl plane is 87.2°. The two phenyl rings are nearly perpendicular to the equatorial plane with the dihedral angles of 89.2° and 90.4°. The two axial Fe–N bonds, 2.223(7) (Fe–N(1)) and 2.303(6) Å (Fe–N(3)), are much longer than Fe–N(2) of the equatorial plane (2.107(6) Å), which is similar to that observed in the aldimine or methyl-ketimine analogues [20]. Differently, Fe–N(1)(phenanthroline) is shorter by about 0.08 Å than that of Fe–N(3)(imino) probably due to the existence of the phenyl group on the imino-C. The difference of the two Fe–Cl linkages is that Fe–Cl(2) (2.304(3) Å) is about 0.03 Å longer than Fe–Cl(1) (2.275(3) Å). The imino N(3)–C(13) bond length is 1.269(9) Å with the typical character of C=N double bond.

Table 3
Ethylene oligomerization using [2-{(2-*i*-Pr-C_6H_4)N = C(Me)}-1,10-phen]$FeCl_2$ (**3b**) with different co-catalysts[a]

Entry	Co-catalyst	Al/Fe	*t* (min)	A_o[b]	% α-O[c]	Distribution of oligomers (%)[d]		
						$C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$
1	$EtAlCl_2$	20	30	–	–	–	–	–
2	$EtAlCl_2$	100	30	–	–	–	–	–
3	Et_2AlCl	100	30	–	–	–	–	–
4	Et_2AlCl	200	30	–	–	–	–	–
5	$AlEt_3$	100	30	4.47	>99	100	–	–
6	$AlEt_3$	200	30	8.17	>99	100	–	–
7	$AlEt_3$	500	30	10.3	>99	100	–	–
8	$AlEt_3$	750	30	7.90	>99	100	–	–
9	$AlEt_3$	1000	30	4.57	>99	100	–	–
10	MAO	500	30	8.93	>96	57.6	31.1	11.3
11	MMAO	500	5	385	>81	64.6	35.4	–
12	MMAO	500	10	291	>83	64.0	36.0	4.0
13	MMAO	500	20	158	>87	57.6	35.4	7.0
14	MMAO	500	30	87.2	>87	55.7	34.6	9.7

[a] General conditions—catalyst: 5 μmol; solvent: toluene (30 mL); reaction temperature: 20 °C; ethylene pressure: 1 atm.
[b] Activity for oligomers: 10^4 g mol^{-1} (Fe) h^{-1}.
[c] % α-olefin content determined by GC and GC–MS.
[d] $\sum C$: total amount of oligomers.

3.2. Ethylene oligomerization under atmospheric pressure of ethylene

3.2.1. Effects of different co-catalysts and reaction time

Complex **3b**, [2-{(2-*i*-Pr–C_6H_4)N=C(Me)}-1,10-phen]$FeCl_2$, has been chosen to explore the effect of Al cocatalyst for ethylene oligomerization and the results are summarized in Table 3. Negligible catalytic activities were observed when Et_2AlCl or $EtAlCl_2$ was used as cocatalyst even at various Al/Fe molar ratios. In contrast, remarkable catalytic activities were seen in the presence of MMAO; whereas moderate activities were observed in the presence of MAO or $AlEt_3$. In particular, MMAO was the best one among the series of Al cocatalysts employed in the oligomerization. Time course plots for ethylene oligomerization with **3b**/MMAO catalyst were employed (entries 11–14) and the observed activities turned out to be high especially at the beginning (<10 min) and then decreased gradually. The product in the oligomerization with **3b**/$AlEt_3$ catalyst was C4 olefin as the major product, and the **3b**/MAO catalyst afforded higher oligomers with a similar α-olefin selectivity and distribution.

3.2.2. Effects of Al/Fe molar ratio and reaction temperature

The influence of the Al/Fe molar ratio and reaction temperature was investigated in detail with the precursor **2b** and MMAO as cocatalyst (Table 4). In many cases, the composition of obtained oligomers follows the Schulz–Flory distribution which is characteristic of the constant K, where K represents the probability of chain propagation (K = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n)) [24–27]. The K values are determined by the molar ratio of C_{12} and C_{14} fractions. By fixing the reaction temperature at room temperature (20 °C) and changing the Al/Fe molar ratio from 100 to 2000, the catalytic activity was observed increasing initially with increasing molar ratio and later decreasing with further increment. The optimum activity was up to 9.1×10^5 g mol^{-1} (Fe) h^{-1} at the ratio of 500 (entry 4). At the lower Al/Fe molar ratios (such as 100), complex **2b** showed lower catalytic activity and the oligomers produced consisted of only butene and hexene (entry 2). In addition, by fixing the Al/Fe molar ratio at 500 and changing the reaction temperature in the range of −10 to 60 °C, the highest activity (1.34×10^6 g mol^{-1} (Fe) h^{-1}) was observed at 0 °C with larger

Table 4
Ethylene reactivity with [2-{(2,6-R^1,R^3-4-R^2-C_6H_2)N=C(R)}-1,10-phen]$FeCl_2$ (**1b–18b**)/MMAO under atmospheric pressure of ethylene[a]

Entry	Catalyst	Al/Fe	T[b] (°C)	Oligomers						Waxes
				A_o[c]	K	% α-O[d]	Distribution (%)[e]			A_w[f]
							$C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$	
1	**1b**	500	20	93.3	0.45	>92	31.8	34.1	34.1	–
2	**2b**	100	20	4.90	–	>96	73.2	26.8	-	–
3	**2b**	200	20	46.9	–	>90	48.4	30.8	20.8	–
4	**2b**	500	20	91.0	–	>87	44.3	33.5	22.2	–
5	**2b**	1000	20	73.0	0.44	>89	43.1	32.5	24.4	–
6	**2b**	1500	20	63.8	0.37	>93	53.2	27.6	19.2	–
7	**2b**	2000	20	55.1	0.40	>93	54.6	25.0	20.4	–
8	**2b**	500	-10	34.8	0.47	>93	34.6	45.4	20.0	–
9	**2b**	500	0	134	0.52	>93	30.9	35.6	33.5	–
10	**2b**	500	40	86.2	–	>92	43.2	42.0	14.8	–
11	**2b**	500	60	41.3	–	>92	54.7	44.0	1.3	–
12	**3b**	500	20	87.2	–	>87	55.7	34.6	9.7	–
13	**4b**	500	20	81.5	0.60	>93	20.2	45.0	35.8	5.18
14	**5b**	500	20	99.3	0.48	>90	35.2	43.2	21.6	–
15	**6b**	500	20	41.1	–	>91	36.5	53.5	10.0	–
16	**7b**	500	20	92.4	–	>91	43.6	42.2	14.2	–
17	**8b**	500	20	26.3	–	>92	29.3	61.2	9.5	
18	**9b**	500	20	108	0.40	>90	38.4	40.4	21.2	–
19	**10b**	500	20	46.9	0.45	>91	19.1	40.1	40.8	1.20
20	**11b**	500	20	73.3	–	>94	36.7	50.6	12.7	–
21	**12b**	500	20	79.6	0.52	>89	35.0	46.8	18.2	0.33
22	**13b**	500	20	104	0.42	>91	42.1	44.0	13.9	0.35
23	**14b**	500	20	86.1	0.38	>94	35.7	49.8	14.5	–
24	**15b**	500	20	94.7	0.65	>93	23.7	44.4	31.9	1.84
25	**16b**	500	20	58.9	0.70	>92	18.1	45.0	37.0	2.77
26	**17b**	500	20	80.0	0.62	>95	21.0	29.8	49.2	7.47
27	**18b**	500	20	71.7	0.71	>91	18.8	28.6	52.6	15.9

[a] General conditions—catalyst: 5 μmol; solvent: toluene (30 mL); reaction time: 30 min.
[b] Reaction temperature.
[c] Activity for oligomers: 10^4 g mol^{-1} (Fe) h^{-1}.
[d] % α-olefin content determined by GC and GC–MS.
[e] $\sum C$: total amount of oligomers.
[f] Activity for low-molecular-weight waxes: 10^4 g mol^{-1} (Fe) h^{-1}.

amount of longer oligomers (higher *K* value) (entry 9). When the reaction temperature was increased, both catalytic activity and amount of longer oligomers were gradually decreased.

3.2.3. Effects of ligand environment

All the iron(II) complexes were investigated under atmospheric pressure of ethylene and the variation of R group on the imino-C and substituents on the imino-N aryl rings had significant influences on the catalytic properties (Table 4). For monoalkyl-substituted methylketimine (R = Me) complexes **1b–3b**, the larger the bulkiness of the alkyl group, the lower the oligomerization activity and the less amount of longer oligomers produced. In addition, complex **4b** with two alkyl groups at the *ortho*-positions of the phenyl ring led to a slightly lower oligomerization activity; at the same time, higher *K* value was observed as well as some low-molecular-weight waxes produced with the activity of 5.18×10^4 g mol^{-1} (Fe) h^{-1} (entry 13). Under the same reaction conditions, complexes **5b–13b** bearing mono- or multi-halogen groups on the phenyl ring displayed comparable oligomerization activities to their analogues without obvious regularity. Aldimine (R = H) complexes **14b–16b** and phenylketimine complexes **17b–18b** also showed comparable oligomerization activity and similar α-olefin selectivity. Differently, complex **14b** with only one methyl group gave slightly lower oligomerization activity and a smaller *K* value. However, complex **15b** with three methyl groups resulted in the increase in oligomerization activity and the *K* value along with the production of waxes. Complex **16b** containing a bromine atom at the *para*-position of the phenyl ring displayed higher *K* value along with more waxes although a little lower oligomerization activity was observed, in comparison to its analogues. Phenylketimine (R = Ph) complexes **17b** and **18b** exhibited similar ethylene reactivity with their aldimine analogues except that much more low-molecular-weight waxes obtained.

3.3. Ethylene oligomerization at 10 atm of ethylene

3.3.1. Effects of the amount of catalyst and Al/Fe molar ratio with MMAO

The catalytic system of **3b**/MMAO was examined to determine the optimal amount of catalyst and the Al/Fe molar ratio at 10 atm of ethylene (Table 5). The highest activity for ethylene oligomerization (2.41×10^7 g mol^{-1} (Fe) h^{-1}) was obtained with 2 μmol catalyst at the Al/Fe molar ratio of 1000. When less amount of catalyst (1 μmol) or lower Al/Fe molar ratio (500) was used, the catalytic system produced higher contents of C4 with higher selectivity for α-olefins (entries 1 and 5). However, when the amount of catalyst was increased, the selectivity for α-olefins decreased. It is worthy to note that the amount of catalyst and the Al/Fe molar ratio had no significant influence

Table 5
Ethylene reactivity with [2-{(2,6-R^1,R^3-4-R^2-C$_6$H$_2$)N=C(R)}-1,10-phen]FeCl$_2$ (**1b–18b**)/MMAO at 10 atm of ethylene[a]

Entry	Catalyst (μmol)	Oligomers						Waxes
		A_o[b]	*K*	% α-O[c]	Distribution (%)[d]			A_w[e]
					$C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$	
1	**3b**(1)	21.7	0.27	>93	56.9	30.9	12.2	–
2	**3b**(2)	24.1	0.26	>93	31.2	49.8	19.0	–
3	**3b**(4)	15.1	0.30	>78	33.2	48.8	18.0	–
4	**3b**(5)	11.8	0.28	>76	26.7	52.8	20.5	–
5	**3b**(2)[f]	8.21	0.27	>93	51.6	34.8	13.6	–
6	**3b**(5)[f]	20.8	0.33	>76	31.1	52.1	16.8	–
7	**1b**(2)	18.5	0.46	>96	21.7	37.2	41.1	–
8	**2b**(2)	22.2	0.38	>90	23.7	42.3	34.0	–
9	**4b**(2)	28.6	0.70	>96	15.4	19.1	65.5	37.6
10	**5b**(2)	24.7	0.56	>90	19.6	37.8	42.6	–
11	**6b**(2)	22.6	0.51	>93	21.8	30.6	47.6	–
12	**7b**(2)	24.9	0.54	>95	20.5	33.7	45.8	–
13	**8b**(2)	18.6	0.51	>95	28.0	32.6	39.4	–
14	**9b**(2)	20.6	0.30	>92	44.5	32.8	22.7	–
15	**10b**(2)	29.8	0.65	>89	14.9	21.3	63.8	23.1
16	**11b**(2)	22.3	0.48	>96	21.6	34.4	44.0	–
17	**12b**(2)	22.0	0.60	>93	22.4	26.9	50.7	3.72
18	**13b**(2)	24.3	0.52	>94	31.3	31.7	37.0	0.30
19	**14b**(2)	16.8	0.33	>96	43.7	32.5	23.8	–
20	**15b**(2)	25.7	0.69	>95	12.6	18.4	69.0	40.7
21	**16b**(2)	17.5	0.60	>96	16.6	24.3	59.1	82.0
22	**17b**(2)	19.7	0.67	>98	13.3	15.9	70.8	142
23	**18b**(2)	29.1	0.69	>97	8.8	17.3	73.9	174

[a] General conditions—solvent: toluene (100 mL); Al/Fe: 1000; reaction temperature: 20 °C; reaction time: 30 min; ethylene pressure: 10 atm.
[b] Activity for oligomers: 10^6 g mol^{-1} (Fe) h^{-1}.
[c] % α-olefin content determined by GC and GC–MS.
[d] $\sum C$: total amount of oligomers.
[e] Activity for low-molecular-weight waxes: 10^5 g mol^{-1} (Fe) h^{-1}.
[f] Al/Fe: 500.

on the *K* value. When the amount of catalyst was increased from 2 to 5 μmol with the Al/Fe molar ratio fixed at 1000, the catalytic activities for ethylene reactivity decreased gradually despite similar *K* values, oligomers distribution and α-olefin selectivity (entries 2–4). By fixing the Al/Fe molar ratio at 500, however, a reverse trend was observed (entries 5–6).

3.3.2. Effects of ligand environment with MMAO

All the synthesized iron(II) complexes displayed much higher catalytic activities for ethylene oligomerization with high selectivity for α-olefins when activated with MMAO at 10 atm of ethylene (Table 5). The distribution of oligomers obtained in all cases followed the Schulz–Flory rules. For methylketimine complexes **1b–3b** with monoalkyl group on the imino-N phenyl ring, the catalytic activity was increased with the bulkier group, while the corresponding *K* value went down. With both of *ortho*-positions occupied by alkyl groups, complex **4b** showed higher catalytic activity with a higher *K* value as well as the production of low-molecular-weight waxes (3.76×10^6 g mol^{-1} (Fe) h^{-1}, entry 9). When the substituents on the phenyl ring were changed from alkyl to halogen groups, the complexes showed comparable catalytic activities for ethylene oligomerization. When the *ortho*-position was fixed with a bromine atom in complexes **5b–8b**, the variation of substituent at the *para*-position just had a little influence on the catalytic properties including the oligomerization activity, the distribution of oligomers and the *K* value (entry 10–13). Complexes **9b–13b** with three halogen groups on the phenyl ring also exhibited very high catalytic activity for ethylene oligomerization. However, complex **9b** bearing less bulky fluorine atoms had a much smaller *K* value and higher amount of C4 among the oligomers obtained (entry 14); while 2,4,6-trichloro-subsituted complex **10b** showed the highest activity for ethylene oligomerization (2.98×10^7 g mol^{-1} (Fe) h^{-1}) along with a higher *K* value and the production of low-molecular-weight waxes with the activity of 2.31×10^6 g mol^{-1} (Fe) h^{-1} (entry 15).

The variation of R substituent on the imino-C also resulted in some changes of the catalytic properties. For aldimine (R = H) complexes, **15b** with 2,4,6-trimethyl groups on the phenyl ring displayed higher activity for ethylene oligomerization as well as a much higher *K* value and amount of low-molecular-weight waxes than **14b** with only one methyl group at the *ortho*-position of the phenyl ring. However, when the methyl group at the *para*-position of the phenyl ring was replaced by a bromine atom, complex **16b** gave a little lower oligomerization activity and much more amount of low-molecular-weight waxes (8.20×10^6 g mol^{-1} (Fe) h^{-1}, entry 21). The phenyl-ketimine (R = Ph) complexes bearing the same substituents on the imino-N phenyl ring as the corresponding aldimine complexes showed relatively higher total productivity of oligomers and waxes, in which higher amount of waxes was observed. Complex **18b** with 2,6-dimethyl and 4-bromo groups on the phenyl ring gave higher activity along with higher amount of waxes than complex **17b** bearing 2,4,6-trimethyl groups, which was different from the corresponding aldimine complexes.

3.3.3. Effects of ligand environment with MAO

All the iron (II) complexes were also investigated in the presence of MAO at 10 atm of ethylene (Table 6). These iron complexes also showed higher oligomerization activities with

Table 6
Ethylene reactivity with [2-{(2,6-R^1,R^3-4-R^2-C_6H_2)N=C(R)}-1,10-phen]$FeCl_2$ (**1b–18b**)/MAO at 10 atm of ethylene[a]

Entry	Catalyst	Oligomers						Waxes
		A_o[b]	*K*	% α-O[c]	Distribution (%)[d] $C_4/\sum C$	$C_6/\sum C$	$\geq C_8/\sum C$	A_w[e]
1	**1b**	10.4	0.39	>95	27.7	38.3	34.0	–
2	**2b**	17.8	0.41	>82	22.6	43.4	34.0	–
3	**3b**	18.9	0.30	>83	34.9	46.5	18.6	–
4	**4b**	9.37	0.62	>92	23.3	21.5	55.1	52.4
5	**5b**	26.1	0.42	>88	38.2	43.5	18.3	–
6	**6b**	28.6	0.51	>92	20.7	32.3	47.0	–
7	**7b**	10.6	0.42	>93	26.2	34.7	39.1	–
8	**8b**	22.3	0.44	>94	42.8	39.4	17.8	1.24
9	**9b**	9.93	0.41	>91	39.4	37.8	22.8	–
10	**10b**	44.6	0.58	>87	22.1	25.3	52.7	64.1
11	**11b**	9.65	0.40	>94	24.6	40.1	35.4	–
12	**12b**	27.1	0.48	>86	26.7	35.5	37.8	1.55
13	**13b**	26.4	0.43	>94	41.3	24.7	34.0	1.44
14	**14b**	9.23	0.38	>91	37.3	34.2	28.5	–
15	**15b**	14.7	0.56	>93	17.2	22.4	60.4	19.9
16	**16b**	5.96	0.62	>95	20.4	20.7	58.9	2.55
17	**17b**	5.94	0.58	>96	19.7	21.2	59.2	2.91
18	**18b**	3.66	0.57	>92	18.2	21.2	60.6	24.6

[a] General conditions—catalyst: 2 μmol; solvent: toluene (100 mL); Al/Fe: 1000; reaction temperature: 40 °C; reaction time: 1 h.
[b] Activity for oligomers: 10^6 g mol^{-1} (Fe) h^{-1}.
[c] % α-olefin content determined by GC and GC–MS.
[d] $\sum C$: total amount of oligomers.
[e] Activity for low-molecular-weight waxes: 10^5 g mol^{-1} (Fe) h^{-1}.

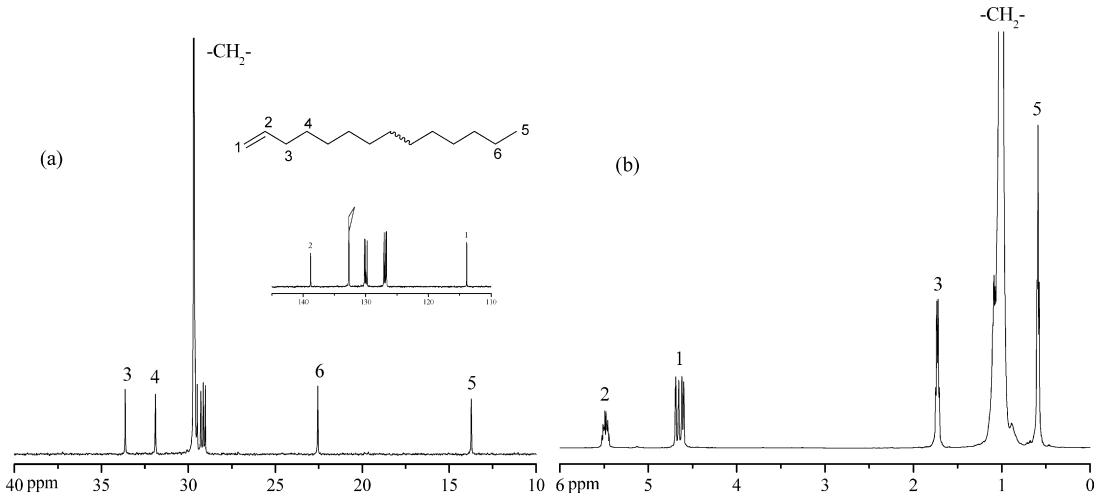


Fig. 2. NMR spectra of the waxes obtained by **18b**/MMAO (entry 23 in Table 5) (a) ^{13}C NMR; (b) ^{1}H NMR.

better selectivity for α-olefins as well as the distribution of oligomers following the Schulz–Flory rules. As in our previous report [20], the consumption rate of ethylene decreased more slowly and the oligomerization reaction could last for a longer time at higher pressure of ethylene. When MAO was employed as cocatalyst, obviously, the variation in the substitution pattern on the phenyl ring significantly influenced the catalyst productivity. Under the same reaction conditions, the highest activity for ethylene oligomerization was achieved with complex **10b** bearing 2,4,6-trichloro groups (4.46×10^7 g mol^{-1} (Fe) h^{-1}, entry 10).

3.3.4. Characterization for low-molecular-weight waxes

In some of catalyst systems examined, low-molecular-weight waxes as higher order oligomers were obtained in large amounts. ^{1}H and ^{13}C NMR spectra of the waxes produced by complex **18b**/MMAO were recorded in *o*-dichlorobenzene-d_4 using TMS as the internal standard. The corresponding spectra are shown in Fig. 2 and the assignments were determined according to the literatures [28,29]. The ^{13}C NMR spectra demonstrated that linear α-olefins absolutely predominated among the produced waxes with the single signals at δ 138.78 and 113.91 ppm, indicating the property of vinyl-unsaturated C=C chain ends.

4. Conclusions

In summary, a series of *N*,*N*,*N*-tridentate iron(II) complexes bearing 2-imino-1,10-phenanthroline ligands were synthesized, characterized and tested for ethylene reactivity after their activation with different cocatalysts. Under atmospheric pressure of ethylene, MMAO was proved to be a more effective cocatalyst than others. Both R group on the imino-C and the substituents on the imino-N phenyl ring had an impact on the catalytic activity and the distribution of oligomers due to their different steric and electronic properties. The results with MMAO or MAO at 10 atm of ethylene proved that these iron(II) complexes were highly active catalysts for ethylene oligomerization with high selectivity for α-olefins (the catalytic activity up to 4.46×10^7 g mol^{-1} (Fe) h^{-1} with complex **10b**/MAO catalyst system) and the distribution of the oligomers obtained followed the Schulz–Flory rules. When MMAO was employed as cocatalyst, methylketimine complexes bearing electron-withdrawing halogen groups and electron-donating alkyl groups displayed comparable catalytic activities, while 2,4,6-trisubstituted aldimine and phenyl-ketimine complexes produced much more low-molecular-weight waxes and higher *K* values with high oligomerization activities kept. The low-molecular-weight waxes obtained as higher order oligomers were predominantly linear α-olefins.

Acknowledgements

The project was supported by NSFC No. 20473099. We thank our CAS-TWAS Postgraduate Fellow, Mr. Sherrif Adewuyi from Nigeria for the English corrections. Prof. Dr. Takashi Tatsumi is gratefully acknowledged for his kindly editorial and English corrections.

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