2-Ethyl-ketimino-1,10-phenanthroline iron(II) complexes as highly active catalysts for ethylene oligomerization☆

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ABSTRACT

A series of 2-(1-aryliminopropyl)-1,10-phenanthrolines (**L1**–**L7**) and their corresponding iron(II) chlorides (**Fe1**–**Fe7**) are synthesized and characterized by elemental and spectroscopic analyses. The molecular structures of 2-[1-(2,6-diisopropy1phenylimino)propyl]-1,10-phenanthroline (**L3**) and {2-[1-(2,6-diethylphenylimino)propyl]-1,10-phenanthroline}·$FeCl_2$ (**Fe2**) are determined by the single crystal X-ray diffraction. All iron complexes, activated with methylaluminoxane (MAO), exhibit high activities in ethylene oligomerization with high selectivity for α-olefins produced. Compared with other 2-imino-phenanthrolines, the title complexes show better thermal stability, and their oligomerization products are potentially more useful due to lower contents of butenes and waxes observed.

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1. Introduction

α-Olefins are major industrial substances extensively used for preparing detergents, lubricants, plasticizers and oil field chemicals, and as monomers for copolymerization. The annual demand of α-olefins is more than 6 million tons with growing rate around 5% per year. The industrial processes include the full range process such as the original Ziegler process [1] and the shell higher olefin process (SHOP) [2], and chromium-based on-purpose process for 1-hexene [3]. Beyond the recent progress of on-purpose process towards trimerization or tetramerization of ethylene by newly designed Cr (III) complexes [2c,4], there are numerous papers of N∧N∧N tridentate iron(II) complexes showing high activities in ethylene polymerization and oligomerization, which are reviewed in relative articles [5]. Regarding the scientific advantages such as high linearity and high selectivity of α-olefins produced, and considering of the most abundant transition metal in the earth and non-toxic and sustainable metal, iron catalytic systems are highly promising for the commercial application in ethylene oligomerization on the base of their high catalytic activities. In view of this, a multi-million dollars joint-adventure between DuPont and PetroChina on ethylene oligomerization using bis(imino)pyridine iron catalysts has been initiated. In review articles [5], most researchers have focused on iron complexes bearing bis(imino)pyridines. We have also been involved in the research of the bis(imino)pyridine iron dihalides for a number of years. A few of our results are documented [6], serious problems are found within our experiences of the bis(imino)pyridine iron catalytic systems: their catalytic activities would be decreased along with increasing reaction temperatures. Regarding ethylene oligomerization, the polyethylene waxes formed contain some polymers with high molecular weights, which would cause trouble in the commercial process. To target alternative catalyst models, new N∧N∧N tridentate ligands and their late-transition metal complexes have been designed with promising properties [7]. The polymerization reaction is a highly exothermal reaction; therefore, an important property of an applicable catalyst should be to maintain high activity during the ethylene polymerization at elevated temperature. To the best of our knowledge, there is only one model of a cobalt catalyst reported for improved ethylene polymerization at increased reaction temperature [8]. In general, ethylene oligomerization by late-transition metal catalysts is promising [7], however, it is important that the polyethylene waxes obtained should be without fractions of high molecular weights.

It is of special interest that the iron complexes ligated by 2-imino-1,10-phenanthrolines (model **A**, R′ = H, Me or Ph, Chart 1) have high activities for ethylene oligomerization [7a,d]. Their catalytic activities are generally good for being scaled-up, but it would be better to reduce amounts of by-products such as polyethylene waxes or butenes. Checking the previous data carefully [7a,d], the variation of the substituent on the imino-C of 2-imino-1,10-phenanthroline ligands results in
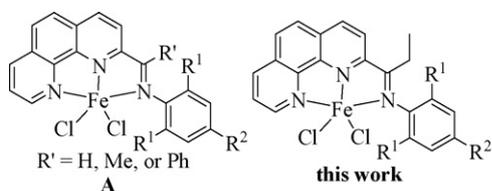
Chart 1. Modified catalyst models.

changing their catalytic performance with the active order of aldimine < phenyl-ketimine < methyl-ketimine. Therefore, the transition metal complex model with ethyl-ketimine group is worthy of investigation (this work, Chart 1). The title complexes indeed perform high catalytic activities towards ethylene oligomerization, which is comparable to the analogues of methyl-ketimine. In addition, their oligomers distributions are narrower with lower content of butenes among oligomer products and less amount of polyethylene waxes compared with those of their analogues. Herein we report in detail the synthesis and characterization of the title iron complexes and their catalytic behaviors towards ethylene oligomerization.

2. Results and discussions

2.1. Syntheses and characterization of ligands and iron complexes

The 2-(1-aryliminopropyl)-1,10-phenanthrolines (2-ethyl-ketimino-1,10-phenanthrolines, **L1**–**L7**) are routinely synthesized from the condensation reaction of 2-propionyl-1,10-phenanthrolines with corresponding anilines. Because of the difference in the reactive nature between ketones and alkyl- or halogen-substituted anilines, various solvents or the water absorption reagent of tetraethyl silicate were employed in order to improve the yields of imino products. All compounds were characterized by the analysis of FT-IR and ^{1}H and ^{13}C NMR spectra as well as elemental analysis.

The iron complexes **Fe1**–**Fe7** are routinely synthesized by mixing the corresponding ligands with one equivalent of FeCl$_2$·4H$_2$O in THF at room temperature under nitrogen. The resulting complexes are precipitated from the reaction solution and separated as blue or purple solids. All the complexes were characterized by FT-IR spectra and elemental analysis. Compared with the corresponding ligands (C=N absorption, 1625–1645 cm^{-1}), the stretching vibration bands of C=N of these iron(II) complexes in the IR spectra (1604–1608 cm^{-1}) apparently shift to lower wave number along with their peak intensities greatly reduced, indicating the coordination interaction of nitrogen with metal center. Their ^{1}H NMR spectra were acquired in N$_2$ atmosphere at 20 °C on a 600 MHz instrument and Fig. 1 showed the ^{1}H NMR spectra of **Fe1** and **Fe3** (all ^{1}H NMR spectra of iron complexes were collected in supporting information). All protons chemical shifts significantly different from those of the corresponding protons in the free ligands, which is consistent with the paramagnetic compound. On the basis of integration and proximity to the paramagnetic center, some peaks could be assigned. The protons of phenanthroline could be assigned as H$_a$–H$_g$ (shown in Fig. 1). The differences between complexes are caused by the different distance between the aryl substituents and the iron center on the NMR timescale (Scheme 1).

The molecular structures of representative ligand **L3** and iron complex **Fe2** are further confirmed by the single-crystal X-ray diffraction analysis. Molecular structures of ligand **L3** and complex **Fe2** are shown in Figs. 2 and 3, respectively, along with selected bond lengths and angles. Similar to the 2-imino-9-phenyl-1,10-phenanthroline ligand [7e], the imino nitrogen atom in **L3** display a *trans*-format to the phenanthroline nitrogen atoms with a typical C=N double bond length of 1.275(3) Å (Fig. 2). However, unlike
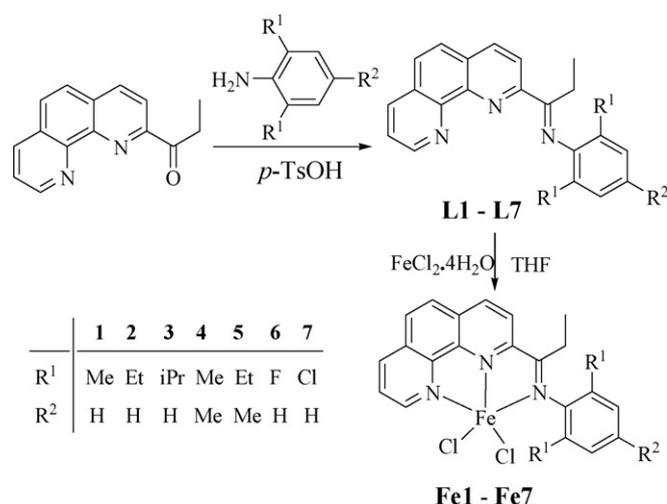
Scheme 1. Synthesis procedure.

other 2-imino-9-phenyl-1,10-phenanthroline ligand in which the aryl ring on the imino nitrogen atom is approximately perpendicular to the plane of the phenanthroline moiety with a dihedral angle of 92.1° [7e], the corresponding dihedral angle in ligand **L3** is much wider (115.3°).

In the structure of complex **Fe2** (Fig. 3), the iron atom slightly deviates by 0.0396 Å from the triangular plane of N2, Cl1 and Cl2 with equatorial angle ranges between 105.84(1)° and 143.85(1)°. This equatorial plane is nearly perpendicular to the phenanthrolinyl plane, with a dihedral angle of 89.8°. The dihedral angle between the phenyl ring and the phenanthrolinyl plane is 79.6°, which is very close to that of 2-acetyl-1,10-phenanthroline(2,6-diethylanil) iron(II) dichloride complex (79.8°, model **A**, R′ = Me, R = Et) [7a]. The Fe–N(2)(phenanthrolinyl) bond (2.112(4) Å) is shorter by about 0.16 Å than the Fe–N(1)(phenanthrolinyl) (2.279(4) Å) and Fe–N(3)(imino) (2.269(4) Å) bonds, which is similar to the 2,6-bis(imino)pyridyl iron(II) complexes [9] and 2-imino-1,10-phenanthrolinyl iron(II) complexes [7a]. The two Fe–Cl bond lengths show a slight difference between the Fe–Cl(2) (2.2949(2) Å) and Fe–Cl(1) (2.3080(2) Å). The imino N(3)–C(13) bond length is 1.295(7) Å, with the typical character of a C=N double bond.

2.2. Catalytic behavior toward ethylene reactivity

Oligomerizations are carried out in toluene under different reaction conditions, and the resulting mixtures are evaluated for soluble oligomers via GC and insoluble waxes via a filtration/gravimetric method (Table 1). Inspired by the highest activities observed with 2-imino-phenanthrolinyl iron(II) complexes at 40 °C and 10 atm ethylene [7a], the complex **Fe1** has been used in selecting suitable ratios of MAO at 40 °C and 10 atm ethylene. Adapting Al/Fe molar ratios within the range of 1000–2000 (entries 1–3, Table 1), the optimum activities for both oligomers and waxes are observed at the Al/Fe ratio 1500, in which it is observed their activities of 1.39×10^7 g mol^{-1}(Fe) h^{-1} for oligomers and 1.03×10^6 g mol^{-1}(Fe) h^{-1} for wax, respectively (entry 3, Table 1). There is a slight decrease of selectivity for α-olefins with the enhancement of cocatalyst concentration (entries 4 and 5, Table 1). However, there is no significant difference of the chain propagation, which is represented with the constant K, and K = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n), the K values are determined by the molar ratio of C_{12} and C_{14} fractions [10,11].

An increase of the reaction temperature to 50 °C results in better activities for ethylene oligomerization and polymerization (entry 6
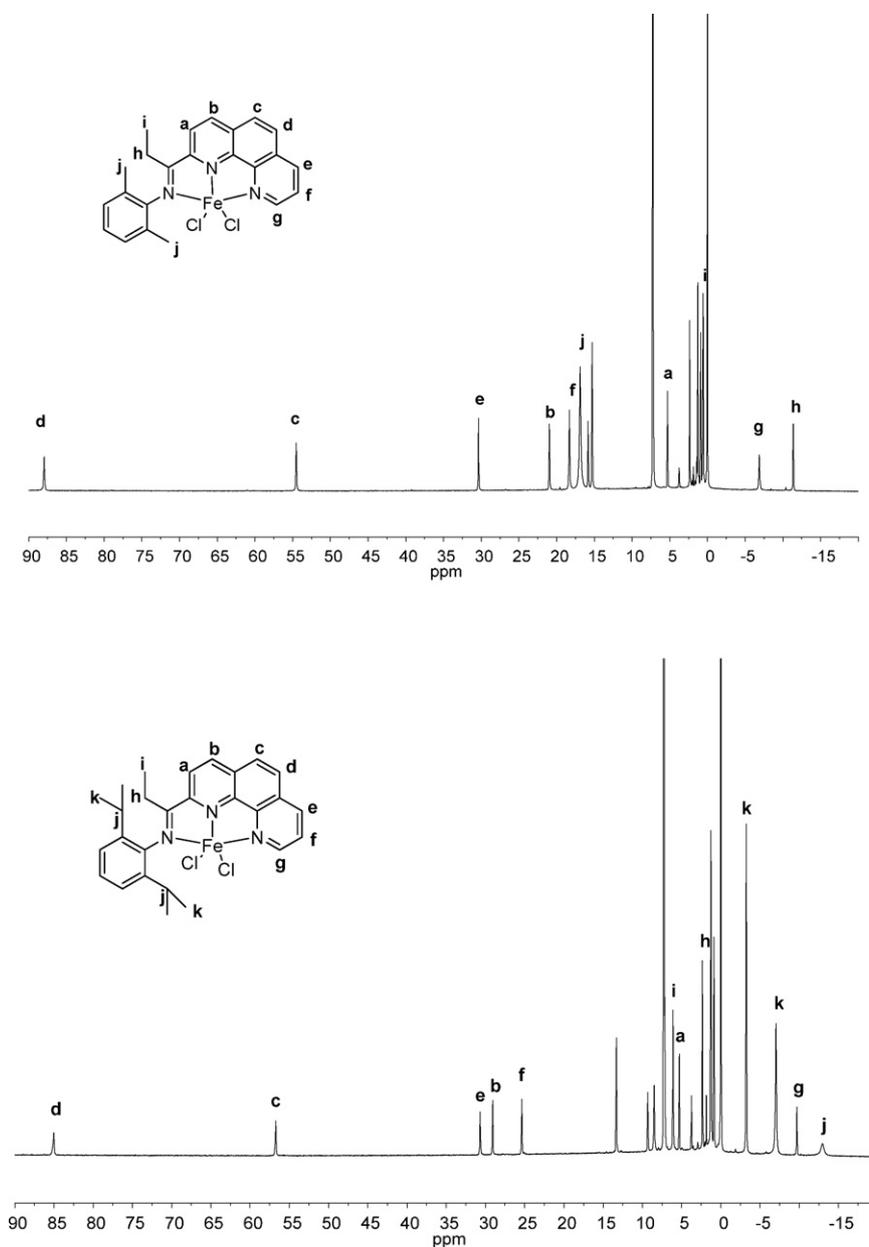
Fig. 1. ¹H NMR spectra of complexes **Fe1** and **Fe3** in CDCl₃ at 293 K.

vs. entry 3, Table 1); however, the further increase of the reaction temperature to 60 °C shows a negative result for ethylene oligomerization but positive result for ethylene polymerization (entry 7 *vs.* entry 3, Table 1). Therefore, the optimum reaction condition is assumed with reaction temperature as 50 °C, which is higher than the optimal temperature of 40 °C for the 2-methyl-ketimino-1,10-phenanthroline iron(II) complexes, indicating a better thermal stability.

With ambient ethylene pressure, its activity of 2.80×10^5 g mol^{-1}(Fe) h^{-1} is observed for ethylene oligomerization (entry 8, Table 1). Relying on the reaction lifetime, the highest productivity is obtained within 30 min (entry 9 *vs.* entries 6 and 10, Table 1), which indicates decaying active sites along with reaction time, however, some of active sites are still remaining in reactive species up to 90 min. Regarding other potential cocatalysts, MMAO is also proved effective (entry 11, Table 1); a good activity of 6.18×10^6 g mol^{-1}(Fe) h^{-1} (entry 11, Table 1) with MMAO is a little lower than that using MAO as

1.39×10^7 g mol^{-1}(Fe) h^{-1} for ethylene oligomerization (entry 9, Table 1).

On the base of the above results, other iron complexes are investigated at the MAO/Fe ratio 1500 with reaction temperature as 50 °C in 60 min, and all results are collected in Table 1 (entries 12–17). The activities by complexes **Fe1**–**Fe3** (entries 6, 12 and 13) show the order as **Fe1** (R^1 = Me) > **Fe2** (R^1 = Et) > **Fe3** (R^1 = ^{i}Pr), suggesting that steric effects play an important role. The bulky groups at the *ortho*-positions of the imino-N aryl ring partly prevent the access of ethylene to the active species, imaging the same active sites of their analogues. The bulkier the substituents used, the smaller are the *K* values and less amounts of low-molecular-weight waxes observed. In their analogues with methyl-ketimine [7a], iron complexes having the ethyl group on the phenyl showed the best activity. Similar to other 2-imino-1,10-phenanthroline iron(II) complexes [7a], complexes **Fe4** and **Fe5** possessing methyl group on the *para*-position of the phenyl show much higher activity in producing polyethylene wax, respectively (entry 14 *vs.* entry 6,

Table 1
Ethylene oligomerization by complexes **Fe1**–**Fe7**.[a]

Entry	Cat.	Al/Fe	T (°C)	t (min)	Oligomer distribution (%)[b]						Wax	
					$C_4/\Sigma C$	$C_6/\Sigma C$	$\geq C_8/\Sigma C$	α-O%[c]	A_o[d]	K	A_p[e]	T_m (°C)
1	Fe1	1000	40	60	21.7	16.5	61.8	>97	9.81	0.62	5.17	60.2
2	Fe1	1200	40	60	34.1	23.5	42.4	>96	9.92	0.60	7.25	61.2
3	Fe1	1500	40	60	20.2	18.1	61.7	>97	11.7	0.63	10.3	69.8
4	Fe1	1800	40	60	28.1	20.8	51.1	>95	9.37	0.64	9.03	65.3
5	Fe1	2000	40	60	42.5	28.1	29.4	>91	8.15	0.62	8.32	63.2
6	Fe1	1500	50	60	19.9	17.1	63.0	>95	13.9	0.70	12.1	59.2
7	Fe1	1500	60	60	40.3	31.4	28.3	>82	6.19	0.52	10.6	55.6
8[f]	Fe1	1500	50	60	12.1	19.8	68.1	>79	0.28	–	Trace	–
9	Fe1	1500	50	30	35.2	27.1	37.7	>96	20.9	0.68	18.4	58.1
10	Fe1	1500	50	90	18.0	15.3	78.6	>94	9.38	0.69	8.21	70.4
11[g]	Fe1	1500	50	30	34.8	27.9	37.3	>94	6.18	0.60	2.91	65.1
12	Fe2	1500	50	60	26.1	20.9	53.0	>95	11.8	0.66	7.14	63.5
13	Fe3	1500	50	60	34.8	23.4	41.8	>93	8.37	0.59	1.06	62.4
14	Fe4	1500	50	60	22.6	18.5	58.9	>94	7.99	0.60	56.2	58.4
15	Fe5	1500	50	60	30.2	23.7	46.1	>94	9.29	0.71	29.3	59.2
16	Fe6	1500	50	60	16.7	14.2	69.1	>81	7.42	0.41	Trace	–
17	Fe7	1500	50	60	15.1	13.3	71.6	>80	10.4	0.44	Trace	–

[a] Conditions: 2 μmol cat., 100 ml toluene, 10 atm ethylene and MAO used except of other indications.
[b] Determined by GC.
[c] Determined by GC and GC–MS.
[d] Oligomer activity: 106 g mol^{-1} (Fe) h^{-1}.
[e] Polymer activity: 105 g mol^{-1} (Fe) h^{-1}.
[f] 30 ml toluene, 1 atm ethylene.
[g] MMAO as cocatalyst.
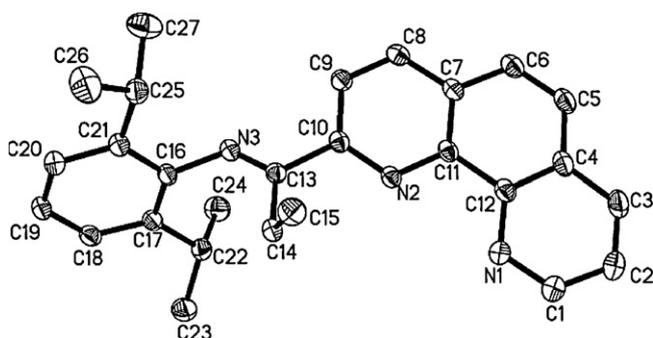
Fig. 2. Molecular structure of ligand **L3** and selected bond lengths [Å] and bond angles [°]: thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

entry 15 *vs.* entry 12, Table 1). Moreover, complexes **Fe6** and **Fe7** bearing electron-withdrawing halogen groups show good activity for ethylene oligomerization, with a trace amount of polyethylene wax produced.

The distribution of oligomers, the portions of α-olefins and the amount of polyethylene waxes are important factors for the consid-
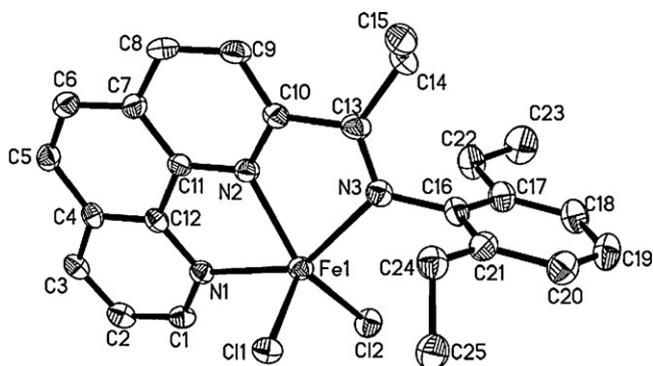
Fig. 3. Molecular structure of complex **Fe2** and selected bond lengths [Å] and bond angles [°]. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

eration of the potential application of a catalyst. As noted, α-olefins except of butene-1 are targeted in the commercial oligomerization process because of butene-1 separated as by-product in the natural oil refinery process, and polyethylene wax is also less interested due to its low value. Compared with the analogues containing aldimine, phenyl-ketimine or methyl-ketimine [7a,e], the title complexes show the advantages of better thermo-stability with narrower distribution of oligomers and less butenes. Comparing the most active catalytic systems by complex **Fe1** with that by complex **2a** (model **A**, R′ = Me, R = Et) [7a], the best catalytic performance is observed at 50 °C for complex **Fe1**, higher than **2a** (40 °C), along with better selectivity for α-olefins (C_6–C_{16}/ΣC) and less content of butenes (entries 2–4, Table 2). It would be easier for the industrial process with the temperature of 10° higher because of exothermic reaction of ethylene oligomerization. Lower content of butenes in oligomers by using complex **Fe1** in comparison with that by **2a** (30.8% and 33.2%) [7a] will be favorable for value-adding olefins (entry 2 *vs.* entries 3 and 4, Table 2), particularly low amount of butenes as 12.1% at ambient ethylene pressure (entry 1, Table 2). Their distri-
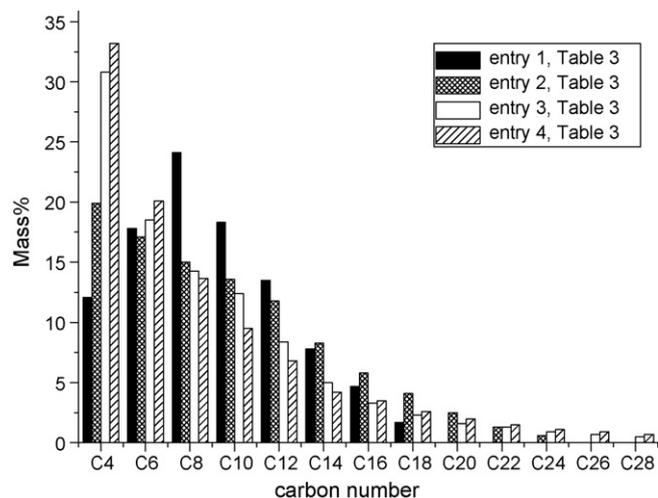

Fig. 4. The distribution comparison of oligomers regarding Table 2.

Table 2
Oligomer distributions by complex **Fe1** and literature **2a**.[a]

Entry	Cat.	Al/Fe	$T(^\circ C)$	Oligomers[b]		$C_4/\Sigma C$	C_6–$C_{16}/\Sigma C$	$\geq C_{16}/\Sigma C$	α-O%	K
				A_0[c]	Distributions					
1[d]	**Fe1**	1500	50	0.28	C_4–C_{18}	12.1	86.2	1.7	>79	–
2	**Fe1**	1500	50	13.9	C_4–C_{24}	19.9	71.8	8.3	>95	0.70
3	**2a**	1000	50	25.5	C_4–C_{28}	30.8	61.9	7.3	>93	0.60
4	**2a**	1000	40	49.1	C_4–C_{28}	33.2	58.0	8.8	>94	0.62

[a] Condition: 2 μmol cat., MAO as cocatalyst, 100 ml toluene, 10 atm ethylene.
[b] Determined by GC and GC–MS.
[c] 10^6 g mol^{-1} (Fe) h^{-1}.
[d] 1 atm ethylene, 30 ml toluene.

butions of oligomers were further illustrated in Fig. 4. Though it is a fact of higher ratio of MAO and a little lower activity, the catalytic systems using the title complexes perform high activity in ethylene oligomerization with competitive distribution of oligomers.

3. Conclusions

The 2-(1-aryliminopropyl)-1,10-phenanthrolines and their corresponding iron(II) complexes have been easily synthesized and characterized. Upon treatment with MAO or MMAO, these iron(II) complexes show high catalytic activities up to 1.39×10^7 g mol^{-1}(Fe) h^{-1} for ethylene oligomerization. Compared with previous analogues [7a,e], the title complexes with a ethyl substituent on the imino-C exhibit a little lower activity for ethylene oligomerization, but show better thermal stability (10° higher in reaction temperature) and have higher content for α-olefins (C_6–C_{16}) and less contents of butanes. In addition, the 2-propionyl-1,10-phenanthroline is commercial available, therefore, the title complexes could be easily prepared and more promising for their consideration in commercial application.

Acknowledgment

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.01.009.

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