Iron Complexes Bearing 2-Imino-1,10-phenanthrolinyl Ligands as Highly Active Catalysts for Ethylene Oligomerization

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A series of iron complexes ligated by 2-imino-1,10-phenanthrolinyl ligands, $LFeCl_2$ (L = 2-(ArN=CR)-1,10-phen), were synthesized and sufficiently characterized by elemental and spectroscopic analysis along with X-ray diffraction analysis. Activated with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), these iron(II) complexes show high catalytic activities up to 8.95×10^7 g mol^{-1}(Fe) h^{-1} for ethylene oligomerization. The distribution of oligomers produced follows Schluz−Flory rules with high selectivity for α-olefins. Both the steric and electronic effects of coordinative ligands affect the catalytic activity and the properties of the catalytic products. The parameters of the reaction conditions were also investigated to explore the catalytic potentials of these complexes.

1. Introduction

α-Olefins are major industrial reactants that are extensively used in the preparation of detergents, lubricants, plasticizers, oil field chemicals, and monomers for copolymerization. The α-olefin industry's increasing demand for higher fractions has been growing at around 5% per year, and the oligomerization of ethylene is currently one of the major industrial processes for the production of α-olefins. α-Olefin production falls into two categories: the full range process of ethylene oligomerization with a range of C_4/C_6 up to $C_{20}+$ generated, and the deliberate dimerization and trimerization of ethylene. The selective dimerization reaction was first described in 1954 by Ziegler,[1] and later the selectivity was improved by modification of the catalysts and optimization of the reaction conditions.[2] Phillips has developed chromium-based catalysts, which can selectively trimerize ethylene to 1-hexene with high selectivity.[3] On the basis of chromium catalysts, the tetramerization of ethylene has also been developed with reasonable selectivity.[4] However, these processes could not provide higher order α-olefins, and the full-range process of ethylene oligomerization provides various chemical substances and plays a more important role in large-scale industry. The full-range process of ethylene oligomerization was originally achieved with the Ziegler (Alfen) process, while currently the catalysts widely employed in industrial processes are alkylaluminum compounds, a combination of alkylaluminum compounds with early transition metal compounds, or nickel(II) complexes.[5] Homogeneous nickel-based catalysts with monoanionic [P,O] ligands (**A**, Chart 1) for ethylene oligomerization were developed as the well-known Schell Higher Olefin Process (SHOP) and have been extensively investigated.[6] In the past decade significant progress was achieved in the development of late transition metal catalysts for the oligomerization of ethylene. Nickel and palladium complexes based on α-diimine ligands (**B**, Chart 1)[7]

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(1) Zieger, K.; Martin, H. US Patent 2.943.125, 1954.

(2) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M. *Catal. Today* **1992**, *14*, 1−121.

(3) (a) Reagen, W. K. *Am. Chem. Soc. Symp., Div. Pet. Chem.* **1989**, *34*, 583, 3. (b) Phillips Petroleum (Reagen, W. K.; Conroy, B. K.), US Patent 5.288.823, 1994. (c) *Eur. Chem. News* **2000**, 2−8 October, 29.

(4) (a) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712−14713. (b) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. *Chem. Commun.* **2005**, 622−624.

(5) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 2002; Vol. 1, pp 240−253.

(6) (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1978**, *90*, 493−494; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466−468. (b) Keim, W.; Behr, A.; Limbacker, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503. (c) Keim, W.; Behr, A.; Kraus, G. *J. Organomet. Chem.* **1983**, *251*, 377−391. (d) Grenouillet, P.; Neibecker, D.; Tkatchenko, I. *J. Organomet. Chem.* **1983**, *243*, 213−222. (e) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594−597. (f) Peuckert, M.; Keim, W. *J. Mol. Catal.* **1984**, *22*, 289−295. (g) Keim, W. *New J. Chem.* **1987**, *11*, 531−534. (h) Klabunde, U.; Itten, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134. (i) Ostoja Starzewski, K. A.; Witte, J. *Angew. Chem.* **1987**, *99*, 76−77; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 63−74. (j) Keim, W. *Angew. Chem.* **1990**, *102*, 251−260; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235−244. (k) Hirose, K.; Keim, W. *J. Mol. Catal.* **1992**, *73*, 271−276. (l) Keim, W. *Macromol. Chem. Macromol. Symp.* **1993**, *66*, 225−230. (m) Matt, D.; Huhn, M.; Fischer, J.; De Cian, A.; Kläui, W.; Tkatchenlo, I.; Bonnet, M. C. *J. Chem. Soc., Dalton Trans.* **1993**, 1173−1178. (n) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994**, *92*, 21−33. (o) Braunstein, P.; Chauvin, Y.; Mecier, S.; Saussine, L.; De Cian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2203−2204.

(7) (a) Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65−74. (b) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005−2007.

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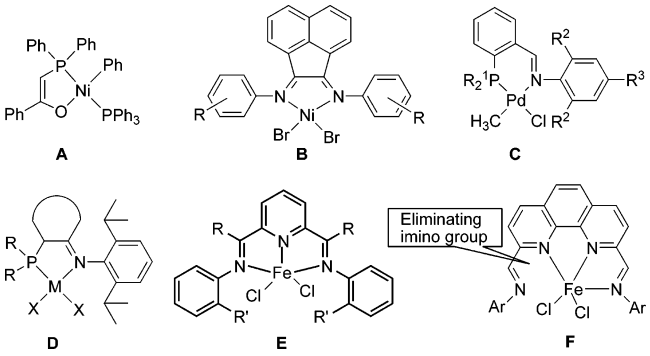
Chart 1. Complex Models of Ethylene Oligomerization Catalyst



and iminophosphines (**C** and **D**, Chart 1)[8] were reported to be very active and selective catalysts for ethylene oligomerization. In 1998, extremely active iron- and cobalt-based catalysts bearing 2,6-bis(imino)pyridyl ligands for the linear polymerization of ethylene were reported independently by Brookhart[9] and Gibson.[10] By tuning the steric and electronic properties of the ligands, the catalytic products of these metal complexes varied from polyethylene to oligomers (**E**, Chart 1),[11] in which both the catalytic activity and selectivity of α-olefins are highly interesting.

Extending the iron complexes including other tridentate ligands, however, commonly leads to lower catalytic activities for ethylene oligomerization and polymerization.[12] In scanning suitable tridentate metal complexes, the late transition metal complexes ligated by 2,9-bis(imino)-1,10-phenanthrolinyl ligands were investigated in our group.[13] The nickel and cobalt complexes showed considerable to good catalytic activities for ethylene oligomerization and polymerization, but the iron complexes (**F**, Chart 1) showed only negligible activities for ethylene polymerization. This result was confirmed by Gibson's group.[14] It could be argued that the nitrogen atom of the additional imino group can coordinate to the active catalytic center (iron), which is a necessary site for the coordination of ethylene for oligomerization and polymerization.[15] To verify this hypothesis, the additional imino group in **F** should be eliminated. The synthesis of 2-formyl-, 2-acetyl-, and 2-benzoyl-1,10-phenanthrolines would be required for this work, but the multistep syntheses have thus blocked further work. Fortunately, a convenient synthetic method for 2-acetyl-1,10-phenanthroline has been developed in our group, and accordingly the various 2-imino-1,10-phenanthrolinyl ligands and their corresponding iron(II) complexes have been synthesized. The catalytic investigation showed that these iron(II) complexes could oligomerize ethylene to linear α-olefins with high activity and selectivity. Herein the syntheses of 2-formyl-, 2-acetyl-, and 2-benzoyl-1,10-phenanthrolines are reported along with an improved synthetic method for 2-acetyl-1,10-phenanthroline. The 2-imino-1,10-phenanthrolinyl ligands and corresponding iron(II) complexes are investigated and discussed regarding ethylene oligomerization with various catalytic reaction parameters.

2. Results and Discussion

2.1. Preparation of 2-Formyl-, 2-Acetyl-, and 2-Benzoyl-1,10-phenanthroline. The 2-formyl, 2-acetyl, and 2-benzoyl 1,10-phenanthroline derivatives are not commercially available, nor are their synthetic intermediates, except 1,10-phenanthroline. Therefore the literature procedures and improved synthetic methods have been explored to prepare the three reactants (Scheme 1). First, 1,10-phenanthroline was oxidized with 30% hydrogen peroxide in glacial acetic acid to form 1,10-phenanthroline 1-oxide.[16] (Caution: An explosion easily happened during the concentration of the resulting acetic acid solution. The modified method included the least amount of acetic acid to dissolve 1,10-phenanrhroline and no rotary evaporation before being neutralized and extracted.) Following the procedure in the same report,[16] the oxide was converted to 2-cyano-1,10-phenanthroline through cyanation using KCN and benzoyl chloride. Further treatment gave 2-carbomethoxy-1,10-phenanthroline. Subsequently the ester was reduced to the carbinol with $NaBH_4$,[17] and the resulting carbinol was oxidized by SeO_2 to produce the aldehyde, 2-formyl-1,10-phenanthroline.[18] The attempts to convert 2-cyano-1,10-phenanthroline into the aldehyde by employing the reported one-step reaction employing Raney nickel and sodium hypophosphite were not successful.[19] In the preparation of 2-acetyl-1,10-phenanthroline, the literature procedure through a Claisen condensation reaction of 2-carbomethoxy-1,10-phenanthroline gave the highest total yield of 36% from 2-cyano-1,10-phenanthroline due to multistep reactions and manipulations.[20] To shorten the synthetic route and improve the total yield, an alternative synthetic methodology was established through the direct reaction of 2-cyano-1,10-phenanthroline and trimethylaluminum (Scheme 1) for preparing 2-acetyl-1,10-phenanthroline in 60% yield in a somewhat scaled-up reaction. However, other methyl metal reagents such as methyllithium or methylmagnesium iodide did not work well.

(8) (a) van den Beuken, E. K.; Smeets, W. J. J.; Spek, A. L.; Feringa, B. L. *Chem. Commun.* **1998**, 223−224. (b) Guan, Z.; Marshall, W. J. *Organometallics* **2002**, *21*, 3580−3586.

(9) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049−4050.

(10) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849−850.

(11) (a) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143−7144. (b) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728−8740. (c) Britovsek, G. J. P.; Mastroianni, S.; Solan, G. A.; Baugh, S. P. D.; Redshaw, C.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J. *Chem. Eur. J.* **2000**, *6*, 2221−2231. (d) Chen, Y.; Chen, R.; Qian, C.; Dong, X.; Sun, J. *Organometallics* **2003**, *22*, 1231−1236. (e) Chen, Y.; Chen, R.; Qian, C.; Dong, X.; Sun, J. *Organometallics* **2003**, *22*, 4312−1321.

(12) (a) Qian, M.; Wang, M.; He, R. *J. Mol. Catal. A* **2000**, *160*, 243−247. (b) Qian, M.; Wang, M.; Zhou, B.; He, R. *Appl. Catal. A* **2001**, *209*, 11−15. (c) LePichon, L.; Stephan, D. W.; Gao, X.; Wang, Q. *Organometallics* **2002**, *21*, 1362−1366. (d) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. *Organometallics* **2003**, *22*, 2545−2547. (e) Zhou, M.-S.; Huang, S.-P.; Weng, L.-H.; Sun, W.-H.; Liu, D.-S. *J. Organomet. Chem.* **2003**, *665*, 237−245. (f) Britovsek, G. J. P.; Gibson, V. C.; Hoarau, O. D.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2003**, *42*, 3454−3465. (g) Cowdell, R.; Davies, C. J.; Hilton, S. J.; Maréchal, J.-D.; Solan, G. A.; Thomas, O.; Fawcett, J. *Dalton Trans.* **2004**, 3231−3240.

(13) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.* **2002**, *658*, 62−70.

(14) Britovsek, G. J. P.; Baugh, S. P. D.; Hoarau, O.; Gibson, V. C.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Inorg. Chim. Acta* **2003**, *345*, 279−291.

(15) Ameerunisha, S.; Schneider, J.; Meyer, T.; Zacharias, P. S.; Bill, E.; Henkel, G. *Chem. Commun.* **2000**, 2155−2156.

(16) Corey, E. J.; Borror, A. L.; Foglia, T. *J. Org. Chem.* **1965**, *30*, 288−290.

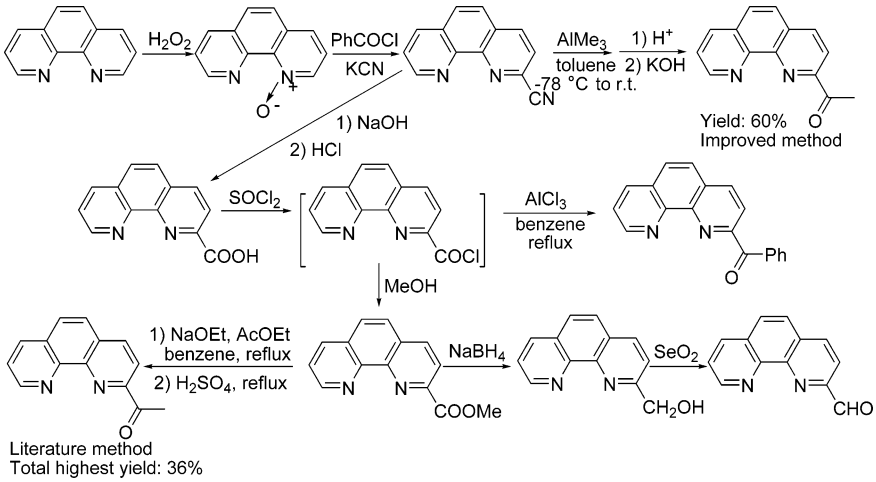
(17) Sigman, D. S.; Wahl, G. M.; Greighton, D. J. *Biochemistry* **1972**, *11*, 2236−2242.

(18) Greighton, D. J.; Hajdu, J.; Sigman, D. S. *J. Am. Chem. Soc.* **1976**, *98*, 4619−4624.

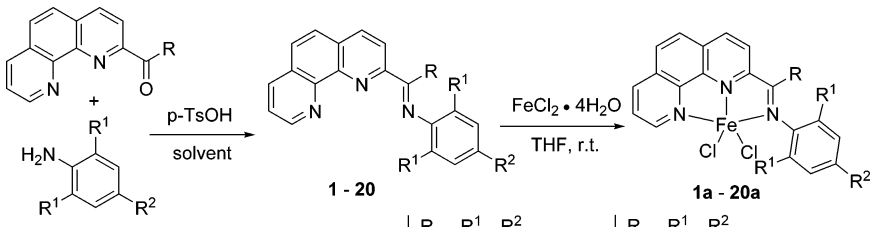
(19) (a) Backeberg, O. G.; Ataskun, B. *J. Chem. Soc.* **1962**, 3961−3963. (b) Staskun, B.; Backeberg, O. G. *J. Chem. Soc.* **1964**, 5880−5881. (c) van Es, T.; Staskun, B. *J. Chem. Soc.* **1965**, 5775−5777.

(20) Case, F. H.; Schilt, A. A. *J. Heterocycl. Chem.* **1979**, *16*, 1135−1139.

Scheme 1. Synthesis of 2-Formyl-, 2-Acetyl-, and 2-Benzoyl-1,10-phenanthroline



Scheme 2. Synthesis of the Ligands 1−20 and the Iron(II) Complexes 1a−20a



	R	R^1	R^2		R	R^1	R^2
1(**a**)	Me	Me	H	**11**(**a**)	Me	Br	Br
2(**a**)	Me	Et	H	**12**(**a**)	H	Me	H
3(**a**)	Me	*i*-Pr	H	**13**(**a**)	H	Et	H
4(**a**)	Me	Me	Me	**14**(**a**)	H	*i*-Pr	H
5(**a**)	Me	Me	Br	**15**(**a**)	H	F	H
6(**a**)	Me	F	H	**16**(**a**)	H	Cl	H
7(**a**)	Me	Cl	H	**17**(**a**)	H	Br	H
8(**a**)	Me	Br	H	**18**(**a**)	Ph	Me	H
9(**a**)	Me	Br	Me	**19**(**a**)	Ph	Et	H
10(**a**)	Me	Br	Cl	**20**(**a**)	Ph	*i*-Pr	H

2-Benzoyl-1,10-phenanthroline was first synthesized from 1,-10-phenanthroline-2-carbonyl chloride followed by a Friedel−Crafts acylation reaction of benzene with $AlCl_3$ as catalyst.

2.2. Synthesis of 2-Imino-1,10-phenanthrolinyl Ligands and Their Iron Complexes. The 2-imino-1,10-phenanthrolinyl ligands (**1**−**20**, 2-(ArN═CR)-1,10-phen) were prepared through the condensation reaction of aldehydes or ketones and the corresponding substituted anilines using *p*-toluenesulfonic acid as catalyst (Scheme 2). Because of the difference in the reactive nature between aldehydes and ketones and alkyl- and halogen-substituted anilines, various solvents such as ethanol, toluene, and tetraethyl silicate were employed in order to improve the product yields. The 2-imino-1,10-phenanthrolinyl ligands can be classified according to the nature of R on the imino-C as methyl-ketimine (R = Me, **1**−**11**), aldimine (R = H, **12**−**17**), and phenyl-ketimine (R = Ph, **18**−**20**), and all compounds were sufficiently characterized and confirmed by the analysis of IR and ^{1}H and ^{13}C NMR spectra as well as their elemental analysis.

The iron(II) complexes **1a**−**20a** were easily prepared by mixing the corresponding ligand and 1 equiv of $FeCl_2 \cdot 4H_2O$ in THF at room temperature under argon (Scheme 2). The resulting complexes were precipitated from the reaction solution and separated as blue, purple, or brown air-stable powders. All the complexes were characterized by FT-IR spectra and elemental analysis. In the IR spectra, the stretching vibration bands of C═N of these iron(II) complexes (1602−1614 cm^{-1}) apparently shifted to lower wavenumber and the peak intensity was greatly reduced, as compared to the corresponding ligands (1618−1656 cm^{-1}), indicating the coordination interaction between the imino nitrogen atom and the metal cation. Some elemental data of complexes showed incorporation of a solvent molecule because the samples were prepared through the recrystallization. These iron(II) complexes are paramagnetic. As one representative species, complex **2a** was characterized in its methanol-d_4 solution by the Evans method[21] and afforded a magnetic moment of 5.5 μ_B, consistent with four unpaired electrons of the high-spin iron(II). Their unambigious structures were confirmed by single-crystal X-ray diffraction analysis.

2.3. Crystal Structures. Single crystals of complexes **2a**, **4a**, **7a**, and **8a** suitable for X-ray diffraction analysis were individually obtained by slow diffusion of diethyl ether into their methanol solutions under argon atmosphere, while crystals of **14a** suitable for X-ray diffraction analysis were grown through slow layering of the chloroform solution of ligand **14** over the ethanol solution of $FeCl_2$ in a Schlenk tube under argon atmosphere. According to their structures, the coordination geometry around the iron center can be described as distorted trigonal bipyramidal, in which the nitrogen (next to the imino-C) of the phenanthrolinyl group and two chlorides compose an equatorial plane. Their crystal structures are shown in Figures

(21) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005. (b) Löliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646−647. (c) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.

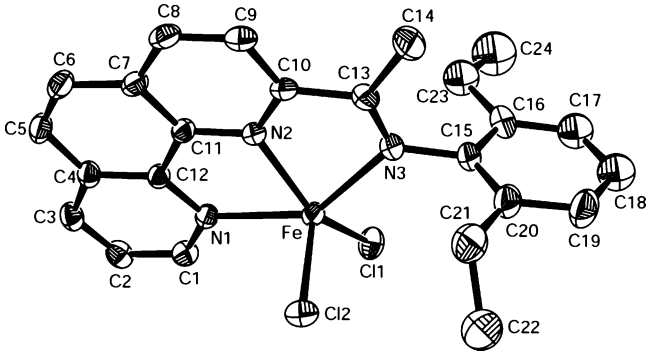


Figure 1. ORTEP drawing of complex **2a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

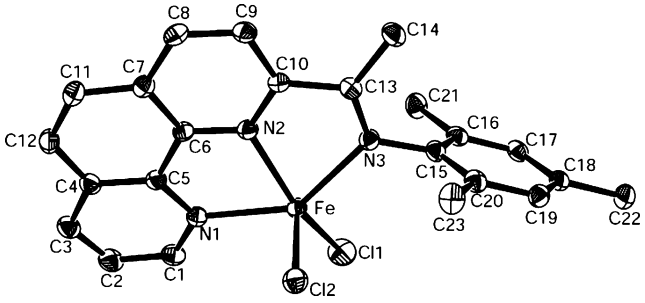


Figure 2. ORTEP drawing of complex **4a** with thermal ellipsoids at the 60% probability level. Hydrogen atoms have been omitted for clarity.

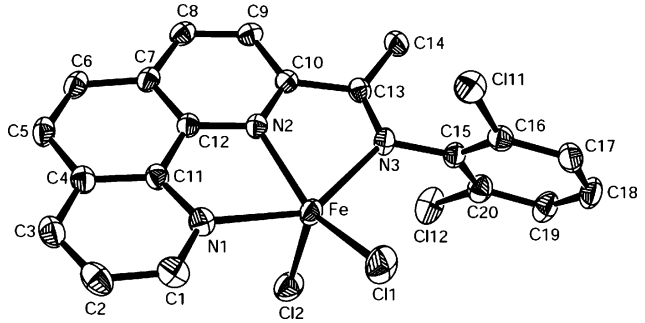


Figure 3. ORTEP drawing of complex **7a** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

1−5, individually, and selected bond lengths and angles are collected in Table 1.

In the structure of **2a** (Figure 1), the iron atom slightly deviates by 0.0465 Å from the triangular plane of N2, Cl1, and Cl2 with equatorial angle ranges between 103.06(8)° and 146.74(8)°, deviating from 120°. This equatorial plane is nearly perpendicular to the phenanthrolinyl plane, with a dihedral angle of 91.2°. The dihedral angle between the phenyl ring and the phenanthrolinyl plane is 79.8°. The Fe−N(2)(phenanthrolinyl) bond (2.110(3) Å) is shorter by about 0.16 Å than the Fe−N(1)(phenanthrolinyl) (2.271(3) Å) and Fe−N(3)(imino) (2.275(3) Å) bonds, which is similar to the 2,6-bis(imino)pyridyl iron(II) complexes.[10] The two Fe−Cl bond lengths show a slight difference between the Fe−Cl(2) (2.3046(13) Å) and Fe−Cl(1) (2.2806(11) Å). The imino N(3)−C(13) bond length is 1.273(5) Å, with the typical character of a C═N double bond.

According to complex **4a** (Figure 2), the phenanthrolinyl nitrogen atom (N2) and two chlorides form the equatorial plane, and the iron atom slightly deviates by 0.0330 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 respectively 150.53(5)°, 99.54(4)°, and 109.86(2)°, with the larger distortion of N(2)−Fe−Cl(1), and the axial Fe−N bonds subtend an angle of 143.38(6)° (N(1)−Fe−N(3)). The dihedral angles between the equatorial plane and the phenanthrolinyl plane, and the phenyl plane and the phenanthrolinyl plane, are 85.5° and 77.3°, respectively. Their two axial Fe−N bond lengths, 2.2643(16) and 2.2296(16) Å, are longer than that of Fe−N(2) of the equatorial plane (2.1262(15) Å), which is similar to that observed in the bis-(2,4,6-trimethylphenylimino)pyridyliron(II) complex,[11b] also with a trigonal bipyramical geometry at the iron center. The difference of the two Fe−Cl linkages, Fe−Cl(2) (2.3321(5) Å) and Fe−Cl(1) (2.2923(5) Å), is about 0.04 Å. The imino N(3)−C(13) bond length is 1.286(2) Å with the typical character of a C═N double bond, but slightly longer than that of **2a** (1.273(5) Å). The difference is probably due to the less bulky methyl at the *ortho*-positions of the phenyl ring in **4a**. This steric effect of the substituents also influences the Fe−N(imino) bonds. For instance, the Fe−N(imino) bond length of **4a** (2.2296(16) Å) is noticeably shorter than that of **2a** (2.275(3) Å), with the relatively bulkier ethyl groups at the *ortho*-positions of the phenyl ring.

Complex **7a** (Figure 3) with 2,6-dichlorophenyl and complex **8a** (Figure 4) with 2,6-dibromophenyl almost have the same structural characters, as shown in Figures 3 and 4 (their bond distances and angles are listed in Table 1). One nitrogen atom

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 2a, 4a, 7a, 8a, and 14a

	2a	4a	7a	8a	14a
			Bond Lengths		
Fe−N(1)	2.271(3)	2.2643(16)	2.2387(17)	2.241(4)	2.259(3)
Fe−N(2)	2.110(3)	2.1262(15)	2.1223(17)	2.128(4)	2.097(2)
Fe−N(3)	2.275(3)	2.2296(16)	2.2750(17)	2.279(4)	2.276(2)
Fe−Cl(1)	2.2806(11)	2.2923(5)	2.2760(6)	2.2727(16)	2.2496(12)
Fe−Cl(2)	2.3046(13)	2.3321(5)	2.3292(7)	2.3228(17)	2.2921(12)
N(3)−C(13)	1.273(5)	1.286(2)	1.288(3)	1.283(6)	1.277(3)
N(3)−C(15)	1.438(4)	1.437(2)	1.419(3)	1.419(6)	1.449(3) (N3−C14)
			Bond Angles		
N(2)−Fe−N(1)	73.80(10)	73.36(6)	74.34(6)	74.19(16)	73.83(10)
N(2)−Fe−N(3)	71.86(10)	71.86(6)	71.30(6)	71.21(15)	72.58(9)
N(1)−Fe−N(3)	144.10(10)	143.38(6)	144.52(6)	144.14(16)	145.10(10)
N(1)−Fe−Cl(1)	97.95(7)	99.57(4)	101.91(5)	101.21(12)	101.26(8)
N(2)−Fe−Cl(1)	146.74(8)	150.53(5)	148.63(5)	148.98(12)	139.89(8)
N(3)−Fe−Cl(1)	104.97(8)	105.01(4)	102.72(5)	103.49(11)	98.26(7)
N(1)−Fe−Cl(2)	98.20(8)	98.35(4)	93.62(5)	93.87(12)	94.10(8)
N(2)−Fe−Cl(2)	103.06(8)	99.54(4)	100.50(5)	99.02(11)	103.50(8)
N(3)−Fe−Cl(2)	99.37(8)	98.32(4)	100.97(5)	100.47(11)	102.63(7)
Cl(1)−Fe−Cl(2)	110.04(4)	109.86(2)	110.85(3)	111.96(7)	116.60(5)

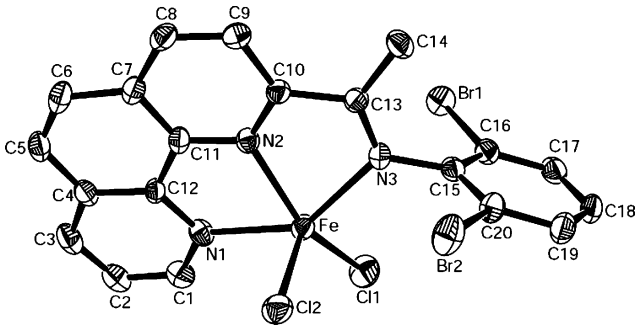


Figure 4. ORTEP drawing of complex **8a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

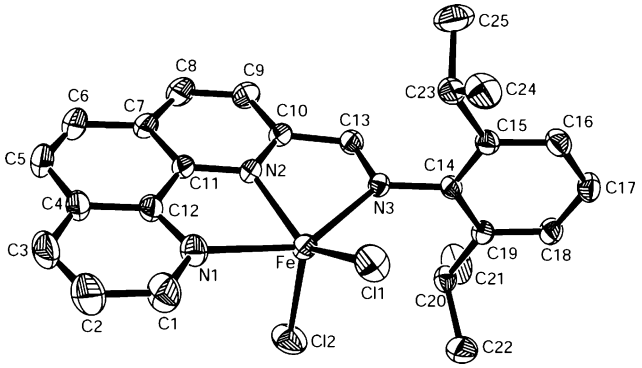


Figure 5. ORTEP drawing of complex **14a** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

(N2) of the phenanthrolinyl group and two chlorides form the equatorial plane, while the iron atom lies 0.0155 and 0.0246 Å out of the equatorial plane in **7a** and **8a**, respectively. The bond angles N(1)−Fe−N(3) are nearly identical for the two complexes, (144.52(6)° (**7a**) and 144.14(16)° (**8a**)), as well as the N(2)−Fe−Cl angles of **8a** (148.98(12)° and 99.02(11)°) and those of **7a** (148.63(5)° and 100.50(5)°) and the angles Cl(1)−Fe−Cl(2) of **7a** and **8a** (110.85(3)° and 111.96(7)°, respectively). The equatorial planes of these two complexes are nearly orthogonal to the phenanthrolinyl plane, with dihedral angles of 83.3° in **7a** and 84.7° in **8a**. The dihedral angles between the phenyl plane and the phenanthrolinyl plane are 103.9° in **7a** and 102.0° in **8a**, which are different from the corresponding alkyl-substituted analogues **2a** (79.8°) and **4a** (77.3°). The difference in bond distance is about 0.05 Å between the Fe−Cl(1) and Fe−Cl(2) bonds, such as 2.2760(6) and 2.3292(7) Å in **7a** and 2.2727(16) and 2.3228(17) Å in **8a**, respectively. Interestingly, the Fe−Cl distances on the same sides of the complex frame are almost equal. The two imino C═N bonds have distinctive double-bond character, with C−N distances of 1.288(3) Å (**7a**) and 1.283(6) Å (**8a**). The electronic properties of the substituents at the *ortho*-positions of the phenyl ring also have some influence on the adjacent N(3)−C(15)(phenyl) bond length. The N(3)−C(15) bonds of **7a** (1.419(3) Å) and **8a** (1.419(6) Å) with 2,6-dihalogenphenyl are shorter by 0.02 Å than those of **2a** (1.438(4) Å) and **4a** (1.437(2) Å) with 2,6-dialkylphenyl.

Complex **14a** (Figure 5) has a structural character similar to complex **2a**. One phenanthrolinyl nitrogen atom and two chlorides form the equatorial plane, with the iron atom slightly deviating by 0.012 Å from this plane. The three equatorial angles are respectively 139.89(8)°, 103.50(8)°, and 116.60(5)°, with a smaller N(2)−Fe−Cl(1) angle and a larger Cl(1)−Fe−Cl(2) angle than those of the ketimine analogues, while the axial N(1)−Fe−N(3) angle is 145.10(10)°. Both the equatorial plane and the phenyl plane are almost perpendicular to the phenanthrolinyl plane, with dihedral angles of 87.3° and 81.3°, respectively. The two axial Fe−N bond lengths, 2.259(3) and 2.276(2) Å, are longer than that of Fe−N(2) in the equatorial plane (2.097(2) Å). The two Fe−Cl distances show an obvious difference, 2.2496(12) and 2.2921(12) Å. Furthermore, they are shorter than those of the ketimine complexes, as shown in Table 1. The imino C(13)−N(3) bond has typical C═N double-bond character, with a bond length of 1.277(3) Å, and it also has a longer N(3)−C(14)(phenyl) (1.449(3) Å), which is slightly longer than that of the ketimine analogues.

Table 2. Results of Ethylene Oligomerization by Complexes 1a−20a/MAO[a]

				oligomers			waxes
entry	cat.	Al/Fe	T^b(°C)	A_o[c]	α	% α-O[e]	A_w[d]
1	**2a**	200	40	1.20	0.68	>99	1.01
2	**2a**	500	40	21.2	0.64	>96	1.56
3	**2a**	1000	40	49.1	0.62	>94	14.6
4	**2a**	1500	40	25.5	0.62	>97	9.13
5	**2a**	2000	40	7.50	0.64	>98	1.25
6	**2a**	1000	20	16.4	0.49	>96	10.1
7	**2a**	1000	30	21.4	0.55	>95	26.3
8	**2a**	1000	50	35.5	0.61	>93	5.87
9	**2a**	1000	60	14.4	0.44	>95	4.88
10	**1a**	1000	40	38.9	0.67	>96	102
11	**3a**	1000	40	9.42	0.50	>98	0.21
12	**4a**	1000	40	12.4	0.72	>96	138
13	**5a**	1000	40	48.2	0.67	>91	174
14	**6a**	1000	40	23.7	0.37	>79	trace
15	**7a**	1000	40	35.1	0.52	>79	trace
16	**8a**	1000	40	40.6	0.61	>80	65.5
17	**9a**	1000	40	38.9	0.73	>80	241
18	**10a**	1000	40	19.6	0.49	>90	14.6
19	**11a**	1000	40	22.2	0.64	>87	64.1
20	**12a**	1000	40	13.3	0.58	>94	48.6
21	**13a**	1000	40	1.60	0.54	>99	trace
22	**14a**	1000	40	9.00	0.48	>97	0.88
23	**15a**	1000	40	6.99	0.39	>97	trace
24	**16a**	1000	40	7.30	0.59	>97	4.51
25	**17a**	1000	40	1.08	0.62	>99	trace
26	**18a**	1000	40	12.7	0.57	>91	304
27	**19a**	1000	40	23.0	0.52	>95	3.25
28	**20a**	1000	40	1.31	0.50	>98	3.18

[a] General conditions: cat.: 2 μmol; reaction time: 1 h; solvent: toluene (100 mL); ethylene pressure: 10 atm. [b] Reaction temperature. [c] Activity for oligomers: 10^6 g mol^{-1}(Fe) h^{-1}. [d] Activity for low-molecular-weight waxes: 10^5 g mol^{-1}(Fe) h^{-1}. [e] % α-olefin content determined by GC and GC-MS.

2.4. Ethylene Oligomerization. All the synthesized iron(II) complexes, when activated with methylaluminoxane (MAO), display high catalytic activities for ethylene oligomerization with high selectivity for α-olefins at 10 atm of ethylene pressure. The detailed results are summarized in Table 2. The distribution of oligomers obtained in all cases follows Schulz−Flory rules, which is characteristic of the constant α, where α represents the probability of chain propagation (α = rate of propagation/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of Cn)).[22] The α values are determined by the molar ratio of C_{12} and C_{14} fractions.

2.4.1. Effects of the Molar Ratio of Al/Fe and Reaction Temperature. The catalytic system of **2a**/MAO was typically investigated with varying reaction conditions, such as the molar ratio of Al/Fe and reaction temperature. When the Al/Fe molar ratio was enhanced from 200 to 2000, the catalytic activities of

(22) (a) Schulz, G. V. Z. *Phys. Chem., Abt. B* **1935**, *30*, 379−398. (b) Schulz, G. V. Z. *Phys. Chem., Abt. B* **1939**, *43*, 25−46. (c) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561−1565. (d) Henrici-Olivé, G.; Olivé, S. *Adv. Polym. Sci.* **1974**, *15*, 1−30.

2a for both oligomers and low-molecular-weight waxes initially increased and then decreased, while the α value showed little change. With increasing reaction temperature, both the catalytic activity and α value initially increased and then decreased; however, the activity showed no great change. Complex **2a** exhibited an activity of 4.91×10^7 g mol^{-1}(Fe) h^{-1} at the Al/Fe molar ratio of 1000:1 and 40 °C under 10 atm of ethylene pressure.

2.4.2. Effect of the Ligand Environment. The variation of the R substituent on the imino-C of ligands, 2-(ArN═CR)-1,-10-phen, resulted in changes of the catalytic performance. Aldimine (R = H) and phenyl-ketimine (R = Ph) complexes showed relatively lower catalytic activities than the corresponding methyl-ketimine (R = Me) complexes. Furthermore, the R substituent had different influences on the catalytic performances of methyl- or phenyl-ketimine and aldimine analogues. Consider the 2,6-dialkyl-substituted ketimine and aldimine complexes as examples. Both the methyl-ketimine complex **2a** and the phenyl-ketimine complex **19a** have 2,6-diethyl groups on the phenyl ring of the imino nitrogen and showed the highest activity among their analogues. However, the corresponding aldimine complex **13a** showed much lower activity under the same reaction conditions (entries 3, 27, and 21 in Table 2). Comparing the complexes ligated by the ketimine or aldimine containing the 2,6-diisopropylphenyl group on the imino nitrogen, both **3a** and **14a** (entries 11 and 22 in Table 2) showed much better catalytic activity than **20a** (entry 28 in Table 2), which also showed lower activity than its analogues (entries 26 and 27 in Table 2), perhaps due to the bulky phenyl-ketimine. In general, all methyl-ketimine complexes bearing electron-donating alkyl groups showed high catalytic activity and good selectivity for α-olefins. On the contrary, relatively lower selectivity was observed with the complexes containing electron-withdrawing halogen groups, such as complexes **6a**−**9a**, despite their good productivity.

The substituents on the imino-N aryl ring had a great influence on the catalytic performances of both the ketimine and aldimine complexes. For the 2,6-dialkyl-substituted methyl-ketimine complexes **1a**−**3a**, somewhat reduced catalytic activity was observed for the sterically bulkier catalyst systems. This could be demonstrated by comparing the 2,6-diisopropyl-substituted **3a** with the 2,6-dimethyl-substituted **1a** or 2,6-diethyl-substituted **2a** (entry 11 vs entry 10 or 3 in Table 2). The greater bulkiness of the isopropyl groups at the *ortho*-positions of the imino-N aryl ring of complex **3a** may prevent the access of ethylene to the active center in the catalytic system, therefore resulting in the decrease of catalytic activity. Furthermore, the bulkier the substituents, the smaller α value and a smaller amount of low-molecular-weight waxes produced. Complexes **5a**−**11a**, which bear mono- or multi-halogen groups, exhibited comparable catalytic activity and relatively lower selectivity for α-olefins in the oligomerization of ethylene than complexes **1a**−**4a**, bearing only alkyl groups. In the catalytic systems of complexes **6a**−**8a**, containing a 2,6-dihalogen-substituted ligand, the bulkier substituents at the *ortho*-positions of the imino-N aryl ring resulted in higher catalytic activities as well as higher α values (bromo- > chloro- > fluoro-, entries 14−16 in Table 2). In addition, the substituent at the 4-position of the aryl ring had an obvious influence on the catalytic activity and α value. The 2,6-dibromo-substituted complex **9a**, which also bears an electron-donating methyl group at the 4-position of the aryl ring, exhibited higher catalytic activity and a larger α value than the corresponding complexes **10a** (4-chloro) and **11a** (4-bromo), which bear an electron-withdrawing halogen group at the 4-position of the aryl ring. However, complex **5a**, bearing 4-bromo-2,6-dimethyl groups, showed higher oligomerization activity than 2,4,6-trimethyl-substituted complex **4a**.

Table 3. Ethylene Oligomerization with Complexes 1a−4a and 6a−8a/MMAO[a]

			oligomers			waxes	
entry	cat.	*t* (min)	A_o[b]	a	% α-O[d]	yield (g)	A_w[c]
1	**1a**	5	8.95	0.67	>98	0.67	40.2
2	**1a**	10	4.77	0.65	>98	0.73	22.1
3	**1a**	20	2.99	0.67	>98	1.88	28.2
4	**1a**	30	2.97	0.68	>97	2.63	26.3
5	**1a**	60	1.22	0.70	>97	3.99	20.0
6	**2a**	30	1.70	0.64	>97	0.06	0.61
7	**3a**	30	1.37	0.46	>98	trace	
8	**4a**	30	2.07	0.55	>98	2.55	25.5
9	**6a**	30	1.72	0.42	>95		
10	**7a**	30	1.80	0.65	>96	0.13	1.32
11	**8a**	30	1.87	0.62	>93	0.15	1.45

[a] General conditions: cat.: 2 μmol; reaction temperature: 40 °C; solvent: toluene (100 mL); ethylene pressure: 10 atm. [b] Activity for oligomers: 10^7 g mol^{-1}(Fe) h^{-1}. [c] % α-olefin content determined by GC and GC-MS. [d] Activity for low-molecular-weight waxes: 10^5 g mol^{-1}(Fe) h^{-1}.

For the aldimine complexes **12a**−**17a**, 2,6-dimethyl-substituted complex **12a** displayed the higher catalytic activity of 1.33×10^7 g mol^{-1}(Fe) h^{-1} (entry 20 in Table 2), while a much lower catalytic activity was obtained for 2,6-diethyl-substituted complex **13a** (entry 21 in Table 2) under the same reaction conditions. For the 2,6-dihalogen-substituted complexes **15a**−**17a**, complex **17a**, with bromine atoms at the *ortho*-positions of the imino *N*-aryl ring, gave the lower activity, while the 2,6-dichloro-substituted complex **16a** displayed a higher oligomerization activity with some waxes produced and 2,6-difluoro-substituted complex **15a** showed comparable oligomerization activity with a lower α value. This probably resulted from the interaction of their steric and electronic effects. For the phenyl-ketimine complexes, complex **20a**, bearing bulkier isopropyl groups at the *ortho*-positions of the aryl ring, had much lower oligomerization activity than the 2,6-dimethyl-substituted **18a** and the 2,6-diethyl-substituted **19a**, probably because of the cooperative interaction of bulkier isopropyl groups on the imino-N aryl ring and bulkier phenyl on the imino-C.

2.4.3. Effect of Different Cocatalysts. When modified methylaluminoxane (MMAO) was employed as cocatalyst, methyl-ketimine complexes **1a**−**4a** and **6a**−**8a** also displayed high catalytic activity for ethylene oligomerization with high selectivity for α-olefins at 10 atm, and the distribution of oligomers obtained in all cases followed Schulz−Flory rules. The detailed results are listed in Table 3.

In the presence of MMAO, ethylene was consumed very quickly over the first 5 min, but after this time, the consumption rate slowed gradually. In the presence of MAO, the consumption rate of ethylene slightly decreased during the reaction time. As an example, the lifetime of the complex **1a**/MMAO system was studied by varying the reaction time from 5 to 60 min. The highest activity of 8.95×10^7 g mol^{-1}(Fe) h^{-1} was obtained at 5 min (entry 1 in Table 3). With prolonged reaction time, the oligomerization activity decreased and the yield of low-molecular-weight waxes increased progressively, while the α value and the activity for waxes had no remarkable change (entries 1−5 in Table 3). However, under the same reaction conditions, complex **1a** showed a lower catalytic activity (1.22×10^7 g mol^{-1}(Fe) h^{-1}) than that using MAO as cocatalyst (3.89×10^7 g mol^{-1}(Fe) h^{-1}, entry 5 in Table 3 and entry 10 in Table 2). On treatment with MMAO, the other alkyl- and halogen-substituted methyl-ketimine complexes displayed comparable

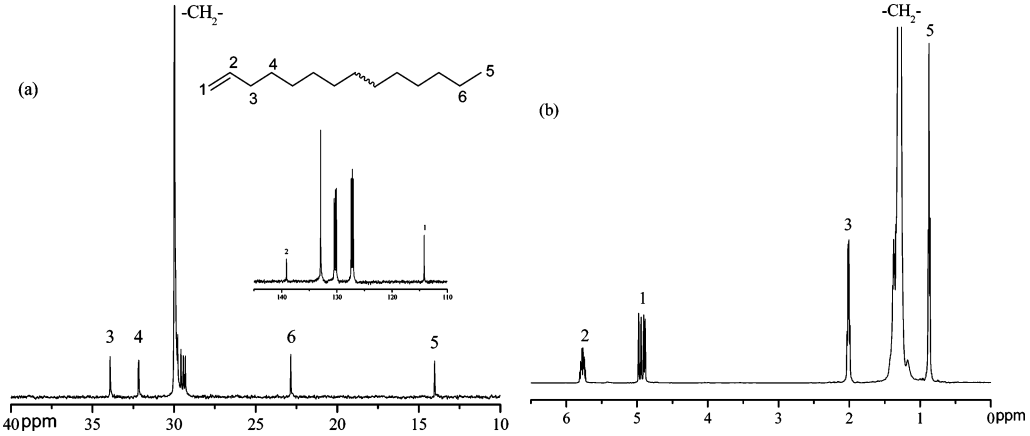


Figure 6. NMR spectra of the waxes obtained by complex **1a**/MAO. (a) ^{13}C NMR; (b) ^{1}H NMR.

ethylene oligomerization activities and high selectivities for α-olefins. However, the 2,6-diisopropyl-substituted complex **3a** and the 2,6-difluoro-substituted complex **6a** gave lower α values and no waxes were formed.

2.4.4. Characterization of Low-Molecular-Weight Waxes. In many cases, some low-molecular-weight waxes as higher oligomers were obtained in addition to lower oligomers. Characterized by IR spectra recorded using KBr disks in the range 4000−400 cm^{-1}, the waxes can be confirmed to be mainly linear α-olefins from the characteristic vibration absorption bands of C═C and various C−H bonds. ^{1}H and ^{13}C NMR spectra of the waxes obtained by complex **1a**/MAO were recorded in *o*-dichlorobenzene-d_4 using TMS as the internal standard. NMR spectra of the waxes are shown in Figure 6, and the assignments were determined according to the literature.[23,24] The ^{13}C NMR spectra further demonstrated that linear α-olefins of the waxes absolutely predominated in the waxes, and the single peaks at δ 139.14 and 114.17 ppm showed the property of a vinyl-unsaturated chain end. The obtained average molecular weight from ^{1}H NMR indicated that the carbon number of the waxes was about 40.

3. Conclusions

A series of tridentate iron(II) complexes bearing 2-imino-1,-10-phenanthrolinyl ligands have been synthesized and fully characterized. Upon treatment with MAO or MMAO, these iron(II) complexes showed high catalytic activities of up to 8.95 × 10^7 g mol^{-1}(Fe) h^{-1} for ethylene oligomerization with high selectivity for α-olefins. However, MAO was found to be a more effective cocatalyst than MMAO. Both the R on the imino-C and the substituents on the N-aryl rings had an obvious influence on the catalytic activity, distribution of oligomers, and selectivity for α-olefins due to their different steric and electronic properties. The methyl ketimine complexes were proved to be relatively more active than either the corresponding aldimine or phenyl ketimine complexes under the same reaction conditions. Electron-donating groups placed on the N-aryl rings increased the selectivity for α-olefins. The placement of bulkier *o*-alkyl groups on the N-aryl rings led to reduced activity because of steric interaction; however, bulkier halogen groups gave the reverse effect.

4. Experimental Section

4.1. General Considerations. All manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of argon 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 disks in the range 4000−400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-300 instrument with 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 microanalyzer. 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.

Toluene and tetrahydrofuran were refluxed over sodium-benzophenone and distilled under argon prior to use. Trimethylaluminum was purchased from Acros Chemicals and diluted to 2 M with dried toluene. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. (Gallipolis Ferry, WV). All the anilines were purchased from Aldrich or Acros Chemicals. Iron(II) chloride tetrahydrate was synthesized from reduced iron power and aqueous hydrogen chloride and kept under inert atmosphere. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

4.2. Preparation of the Starting Materials (aldehyde and ketones). 4.2.1. Preparation of 2-Formyl-1,10-phenanthroline. 1,10-Phenanthroline 1-oxide. A 30 mL portion of 30% hydrogen peroxide was added dropwise to a solution of 50.0 g (0.25 mol) of 1,10-phenanthroline monohydrate in 60 mL of glacial acetic acid. The reaction mixture was maintained at 70−75 °C for 3 h, after which an addition 30 mL of 30% hydrogen peroxide was added dropwise and the heating continued for 3 h. After cooling, the mixture was neutralized to pH ≈ 10 with saturated aqueous potassium hydroxide and then was extracted repeatedly with chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate and evaporated to give a yellow solid (39.0 g) in 79% yield. Mp: 178−180 °C [lit.[16] 176−179 °C].

2-Cyano-1,10-phenanthroline. To a solution consisting of 25.0 g (0.13 mol) of 1,10-phenanthroline 1-oxide and 25.0 g of potassium cyanide dissolved in 200 mL of water was added dropwise 25 mL of benzoyl chloride under magnetic stirring. The total addition required 1 h, and the reaction mixture was stirred for an additional 2 h. The resulting precipitate was collected by suction filtration, washed with water, and dried as a brown solid in 87% yield. Mp: 230−232 °C [lit.[16] 233−234 °C].

(23) Galland, G. B.; De Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620−1625.
(24) Galland, G. B.; Quijada, R.; Rojas, R.; Bazan, G. C.; Komon, Z. J. A. *Maromolecules* **2002**, *35*, 339−345.

2-Carboxy-1,10-phenanthroline. A solution of 10.0 g of sodium hydroxide in 60 mL of water was added to a solution of 12.0 g (59.0 mmol) of 2-cyano-1,10-phenanthroline in 120 mL of 95% ethanol, and the reaction mixture was refluxed for 2 h. Some of ethanol was removed at reduced pressure, and the residue was made slightly acidic with concentrated hydrochloric acid in an ice−water bath. The precipitate was filtrated, washed with water, and dried in a vacuum, and a yellow-brown solid (10.4 g) was obtained in 79% yield. Mp: 212−214 °C [lit.[16] 209−210 °C].

2-Carbomethoxy-1,10-phenanthroline. A 6.10 g (27.0 mmol) amount of 2-carboxy-1,10-phenanthroline was suspended in 250 mL of thionyl chloride and refluxed until the solid had dissolved to give a red solution (about 4 h), and then the residual $SOCl_2$ was removed at reduced pressure. To the residue was added 200 mL of anhydrous methanol, and the mixture was stirred overnight at room temperature. The resulting red solution was eluted through a basic alumina column, and the methanol effluent was then concentrated to approximately 10 mL on a rotatory evaporator. The addition of 200 mL of water caused the ester to precipitate from the solution. And the product was collected by filtration, washed with water, and dried as a yellow solid (5.10 g) in 80% yield. Mp: 110−112 °C [lit.[17] 112−114 °C].

2-Carbinol-1,10-phenanthroline. To a red solution of 6.30 g (26.4 mmol) of 2-carbomethoxy-1,10-phenanthroline dissolved in 60 mL of anhydrous methanol was slowly added 7.0 g of sodium borohydride over 30 min at 0−5 °C. The reaction solution was stirred for 1 h at room temperature and then refluxed for 2 h. After the solution was allowed to cool, 100 mL of distilled water was added, and methanol was removed on the rotatory evaporator. The resulting solution was then extracted four times with chloroform, and the extracts were combined and dried over sodium sulfate. The chloroform was evaporated and the residue was eluted with ethanol on an alumina column. The second eluting part was collected and concentrated to give an orange solid (4.0 g) in 72% yield. Mp: 136−138 °C [lit.[17] 139−143 °C].

2-Formyl-1,10-phenanthroline. A 1.40 g (12.5 mmol) portion of selenium dioxide was added to a solution of 5.25 g (25.0 mmol) of 2-carbinol-1,10-phenanthroline in 200 mL of pyridine with constant stirring. The mixture was then heated for 4 h at 80−90 °C, and the color changed from orange to a dirty brown, characteristic of selenium metal precipitate. After cooling to room temperature, the selenium precipitate was removed by filtration. Pyridine of the filtrate was removed at reduced pressure, and the residue was eluted with methanol on an alumina column. The eluent was concentrated to give a yellow solid (4.70 g) in 90% yield. Mp: 152−154 °C [lit.[18] 152−153 °C]. FT-IR (KBr disk, cm^{-1}): 1705 ($\nu_{C=O}$).

4.2.2. Preparation of 2-Acetyl-1,10-phenanthroline. To a suspension of 2-cyano-1,10-phenanthroline (2.10 g, 10.0 mmol) in 50 mL of toluene was added dropwise 2 equiv of trimethylaluminum (10 mL, 20.0 mmol) toluene solution at −78 °C, and then the temperature was slowly elevated to room temperature. After stirring for 12 h at room temperature, a small amount of water was added dropwise to the reaction mixture in an ice−water bath and a yellow precipitate appeared. Then the mixture was extracted with dilute aqueous hydrogen chloride. The combined water layer was made alkaline with solid potassium hydroxide, and the resulting precipitate was filtered, dried, and then purified through a basic alumina column. The desired product was obtained as an ivory-white solid (1.37 g) in 60% yield. Mp: 152−154 °C. FT-IR (KBr disk, cm^{-1}): 1693 ($\nu_{C=O}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (d, J = 3.9 Hz, 1H); 8.37 (s, 2H); 8.29 (d, J = 8.1 Hz, 1H); 7.87 (dd, J = 8.7 Hz, 2H); 7.69 (dd, J = 7.8 Hz, 1H); 3.09 (s, 3H, CH_3). Anal. Calc for $C_{19}H_{10}N_2O$ (222.24): C, 75.66; H, 4.54; N, 12.60. Found: C, 75.50; H, 4.64; N, 12.41.

4.2.3. Preparation of 2-Benzoyl-1,10-phenanthroline. 1,10-Phenanthroline-2-carboxylic acid (12.0 g, 53.0 mmol) was refluxed with thionyl chloride (250 mL) for 6 h, and the residual $SOCl_2$ was removed at reduced pressure. The resulting yellowish solid was refluxed with anhydrous aluminum chloride (9.00 g, 66.0 mmol) in benzene (70 mL) for 4 h. The resulting red solution was cooled to room temperature, and it was stirred for 12 h and then refluxed for 6 h. After the solution was cooled to room temperature, it was poured into distilled water (125 mL) at 0 °C. The aqueous layer was extracted with chloroform (20 mL × 4). The combined organic phases were dried over anhydrous sodium sulfate and evaporated in a vacuum to afford a white solid in 48% yield. Mp: 110−112 °C. FT-IR (KBr disk, cm^{-1}): 1655 ($\nu_{C=O}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.18 (dd, J = 2.1 Hz, 1H); 8.44 (s, 1H); 8.41 (s, 1H); 8.39 (d, J = 3.3 Hz, 1H); 8.27−8.23 (m, 2H); 7.86−7.83 (m, 2H), 7.66−7.58 (m, 2H); 7.54−7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 154.8, 150.7, 146.3, 144.8, 136.9, 136.1, 135.9, 133.1, 131.8, 129.5, 129.0, 128.4, 128.2, 126.0, 123.1, 122.9. Anal. Calc for $C_{19}H_{12}N_2O$ (284.31): C, 80.27; H, 4.25; N, 9.85. Found: C, 80.24; H, 4.24; N, 9.83.

4.3. Synthesis of the 2-Imino-1,10-phenanthroline Ligands 1−20. 2-Acetyl-1,10-phenanthroline(2,6-dimethylanil) (1). A reaction mixture of 2-acetyl-1,10-phenanthroline (0.445 g, 2.00 mmol), 2,6-dimethylaniline (0.315 g, 2.60 mmol), *p*-toluenesulfonic acid (0.040 g), and absolute ethanol (20 mL) was refluxed under N_2 atmosphere for 2 days. The solvent was rotary evaporated and the resulting solid was eluted with petroleum ether/ethyl acetate (v/v = 2:1) on an alumina column. The second eluting part was collected and concentrated to give a yellow solid in 72% yield. Mp: 170−172 °C. FT-IR (KBr disk, cm^{-1}): 3435, 2970, 2933, 1645, 1590, 1553, 1490, 1469, 1446, 1366, 1324, 1207, 1138, 1117, 1091, 866, 777, 747. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.24 (t, J = 2.1 Hz, 1H); 8.80 (dd, J = 8.7 Hz, 1H); 8.34 (dd, J = 8.4 Hz, 1H); 8.27 (d, J = 7.8 Hz, 1H); 7.85 (s, 2H); 7.65 (m, 1H); 7.10 (d, J = 7.5 Hz, 2H); 6.96 (t, J = 7.5 Hz, 1H); 2.56 (s, 3H, CH_3); 2.08 (s, 6H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 156.0, 150.6, 148.9, 146.2, 145.0, 136.4, 136.2, 129.4, 128.9, 127.8, 127.5, 126.4, 125.2, 123.0, 122.9, 120.8, 17.9, 16.9. Anal. Calc for $C_{22}H_{19}N_3$ (325.41): C, 81.20; H, 5.89; N, 12.91. Found: C, 80.99; H, 5.94; N, 12.87.

2-Acetyl-1,10-phenanthroline(2,6-diethylanil) (2). In a manner similar to that described for **1**, the ligand **2** was prepared as a yellow solid in 68% yield. Mp: 188−190 °C. FT-IR (KBr disk, cm^{-1}): 3424, 2966, 2930, 2870, 1639, 1587, 1553, 1491, 1453, 1363, 1322, 1257, 1197, 1138, 1116, 1079, 867, 824, 782, 747. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 3.0 Hz, 1H); 8.80 (d, J = 8.3 Hz, 1H); 8.35 (d, J = 8.3 Hz, 1H); 8.27 (dd, J = 7.8 Hz, 1H); 7.86 (s, 2H); 7.66 (m, 1H); 7.15 (d, J = 7.6 Hz, 2H); 6.96 (t, J = 7.5 Hz, 1H); 2.58 (s, 3H, CH_3); 2.43 (m, 4H, CH_2CH$_3$), 1.16 (t, J = 7.5 Hz, 6H, CH$_2$CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 156.2, 150.7, 148.0, 146.4, 145.2, 136.5, 131.1, 129.5, 129.0, 127.5, 126.5, 126.0, 123.4, 122.9, 120.8, 24.6, 17.3, 13.7. Anal. Calc for $C_{24}H_{23}N_3$ (353.46): C, 81.55; H, 6.56; N, 11.89. Found: C, 80.88; H, 6.59; N, 11.78.

2-Acetyl-1,10-phenanthroline(2,6-diisopropylanil) (3). In a manner similar to that described for **1**, the ligand **3** was prepared as a yellow solid in 72% yield. Mp: 196−198 °C. FT-IR (KBr disk, cm^{-1}): 3434, 2961, 2870, 1646, 1588, 1552, 1490, 1459, 1363, 1321, 1191, 1115, 861, 821, 772, 745. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 2.7 Hz, 1H); 8.82 (d, J = 8.7 Hz, 1H); 8.33 (m, 2H); 7.85 (s, 2H); 7.65 (m, 1H); 7.17 (m, 3H); 2.86 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 2.60 (s, 3H, CH_3); 1.17 (d, 12H, CH-(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 156.1, 150.7, 146.7, 146.4, 145.2, 136.5, 136.3, 135.7, 129.5, 129.0, 127.5, 126.5, 123.7, 123.0, 122.9, 120.9, 28.3, 23.3, 22.9, 17.6. Anal. Calc for $C_{26}H_{27}N_3$ (381.51): C, 81.85; H, 7.13; N, 11.01. Found: C, 81.82; H, 7.25; N, 10.71.

2-Acetyl-1,10-phenanthroline(2,4,6-trimethylanil) (4). In a manner similar to that described for **1**, the ligand **4** was prepared

as yellow solid in 80% yield. Mp: 146−148 °C. FT-IR (KBr disk, cm^{-1}): 2937, 1634, 1586, 1551, 1480, 1364, 1323, 1216, 1136, 1115, 824, 773, 744. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.5 Hz, 1H); 8.80 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.4 Hz, 1H); 8.30 (dd, J = 8.1 Hz, 1H); 7.88 (s, 2H); 7.68 (quad, J = 4.5 Hz, 1H); 6.93 (s, 2H); 2.56 (s, 3H, CH_3); 2.32 (s, 3H, PhCH_3); 2.05 (s, 6H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 156.2, 150.5, 146.4, 146.2, 145.0, 136.4, 136.3, 132.2, 129.4, 128.9, 128.5, 127.4, 126.4, 125.1, 122.9, 120.9, 20.7, 17.9, 16.9. Anal. Calc for $C_{23}H_{21}N_3$ (339.43): C, 81.38; H, 6.24; N, 12.38. Found: C, 81.42; H, 6.26; N, 12.14.

2-Acetyl-1,10-phenanthroline(4-bromo-2,6-dimethylanil) (5). A reaction mixture of 2-acetyl-1,10-phenanthroline (0.445 g, 2.00 mmol), 4-bromo-2,6-dimethylaniline (0.520 g, 2.60 mmol), *p*-toluenesulfonic acid (0.040 g), and anhydrous sodium sulfate in 30 mL of toluene was refluxed under N_2 atmosphere for 30 h. After filtration, the solvent was removed through rotary evaporation and the resulting solid was eluted with petroleum ether/ethyl acetate (v/v = 4:1) on an alumina column. The second eluting part was collected and concentrated to give a yellow solid in 65% yield. Mp: 196−198 °C. FT-IR (KBr disk, cm^{-1}): 3036, 2969, 2913, 1641, 1584, 1550, 1462, 1397, 1366, 1323, 1284, 1201, 1113, 1077, 997, 880, 853, 780, 743, 710, 661. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd., J = 4.2 Hz, 1H); 8.76 (d, J = 8.4 Hz, 1H); 8.37 (d, J = 8.4 Hz, 1H); 8.31 (dd, J = 7.8 Hz, 1H); 7.89 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 7.25 (d, J = 5.7 Hz, 2H); 2.55 (s, 3H, CH_3); 2.05 (s, 6H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 155.5, 150.4, 147.7, 146.0, 1449, 136.3, 136.0, 130.2, 129.3, 128.7, 127.4, 127.3, 126.1, 122.7, 120.5, 115.3, 17.5, 16.8. Anal. Calc for $C_{22}H_{18}BrN_3$ (404.30): C, 65.36; H, 4.49; N, 10.39. Found: C, 64.97; H, 4.49; N, 10.39.

2-Acetyl-1,10-phenanthroline(2,6-difluoroanil) (6). In a manner similar to that described for **5**, the ligand **6** was prepared as a yellow solid in 54% yield. Mp: 180−182 °C. FT-IR (KBr disk, cm^{-1}): 3429, 3015, 1637, 1585, 1556, 1473, 1421, 1391, 1368, 1322, 1277, 1237, 1121, 1066, 1027, 999, 888, 852, 821, 766, 744, 697, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.2 Hz, 1H); 8.70 (d, J = 8.4 Hz, 1H); 8.36 (d, J = 8.7 Hz, 1H); 8.30 (dd, J = 8.7 Hz, 1H); 7.88 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 7.11−6.97 (m, 3H); 2.76 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 155.7, 154.5, 151.3, 151.2, 150.7, 146.3, 145.1, 136.6, 136.3, 129.7, 129.0, 127.8, 126.4, 124.1, 123.0, 121.4, 111.8, 111.5, 18.2. Anal. Calc for $C_{20}H_{13}F_2N_3$ (333.33): C, 72.06; H, 3.93; N, 12.61. Found: C, 71.89; H, 3.90; N, 12.87.

2-Acetyl-1,10-phenanthroline(2,6-dichloroanil) (7). 2-Acetyl-1,10-phenanthroline (0.445 g, 2.00 mmol), 2,6-dichloroaniline (0.388 mg, 2.40 mmol), and *p*-toluenesulfonic acid (0.040 g) were combined with tetraethyl silicate (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 silicate was removed at reduced pressure, and the resulting solid was eluted with petroleum ether/ethyl acetate (v/v = 4:1) on an alumina column. The second eluting part was collected and concentrated to give a yellow solid in 32% yield. Mp: 184−186 °C. FT-IR (KBr disk, cm^{-1}): 2966, 2926, 1641, 1629, 1585, 1554, 1489, 1448, 1432, 1390, 1367, 1324, 1285, 1260, 1223, 1119, 1079, 854, 782, 761, 738, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (d, J = 4.2 Hz, 1H); 8.78 (d, J = 8.4 Hz, 1H); 8.38 (d, J = 8.4 Hz, 1H); 8.31 (d, J = 7.8 Hz, 1H); 7.89 (s, 2H); 7.69 (dd, J = 8.1 Hz, 1H); 7.39 (d, J = 8.1 Hz, 2H); 7.02 (t, J = 8.1 Hz, 1H); 2.68 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 155.4, 150.7, 136.7, 136.4, 129.8, 129.0, 128.3, 127.9, 126.5, 124.4, 123.1, 121.5, 18.1. Anal. Calc for $C_{20}H_{13}Cl_2N_3$ (366.24): C, 65.59; H, 3.58; N, 11.47. Found: C, 65.29; H, 3.70; N, 11.28.

2-Acetyl-1,10-phenanthroline(2,6-dibromoanil) (8). In a manner similar to that described for **7**, the ligand **8** was prepared as a yellow solid in 22% yield. Mp: 170−172 °C. FT-IR (KBr disk, cm^{-1}): 3011, 2966, 1639, 1625, 1587, 1550, 1503, 1489, 1448, 1426, 1391, 1365, 1323, 1284, 1263, 1220, 1194, 1137, 1118, 1080, 889, 855, 818, 775, 759, 739, 725, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (d, J = 4.2 Hz, 1H); 8.81 (d, J = 8.4 Hz, 1H); 8.39 (d, J = 8.4 Hz, 1H); 8.31 (d, J = 8.1 Hz, 1H); 7.89 (s, 2H); 7.69 (dd, J = 8.1 Hz, 1H); 7.60 (d, J = 8.1 Hz, 2H); 6.88 (t, J = 8.1 Hz, 1H); 2.67 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 155.2, 150.7, 148.3, 146.3, 145.2, 136.7, 136.4, 132.0, 129.9, 129.0, 127.9, 126.5, 125.3, 123.1, 121.5, 113.5, 18.1. Anal. Calc for $C_{20}H_{13}Br_2N_3$ (455.15): C, 52.78; H, 2.88; N, 9.23. Found: C, 52.78; H, 2.92; N, 9.16.

2-Acetyl-1,10-phenanthroline(2,6-dibromo-4-methylanil) (9). In a manner similar to that described for **7**, the ligand **9** was prepared as a yellow solid in 37% yield. Mp: 213−215 °C. FT-IR (KBr disk, cm^{-1}): 2966, 2921, 1628, 1585, 1551, 1486, 1449, 1388, 1363, 1319, 1284, 1229, 1195, 1116, 1079, 853, 775, 740, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (dd, J = 4.2 Hz, 1H); 8.80 (d, J = 8.4 Hz, 1H); 8.38 (d, J = 8.4 Hz, 1H); 8.31 (dd, J = 7.5 Hz, 1H); 7.89 (s, 2H); 7.68 (d, J = 8.1 Hz, 1H); 7.43 (s, 2H); 2.66 (s, 3H, CH_3); 2.18 (s, 3H, PhCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 155.4, 150.7, 146.3, 145.7, 145.2, 136.7, 136.3, 135.4, 132.5, 129.8, 129.0, 127.8, 126.5, 123.0, 121.4, 113.1, 20.2, 18.0. Anal. Calc for $C_{21}H_{15}Br_2N_3$ (469.17): C, 53.76; H, 3.22; N, 8.96. Found: C, 53.95; H, 3.49; N, 8.80.

2-Acetyl-1,10-phenanthroline(4-chloro-2,6-dibromoanil) (10). In a manner similar to that described for **7**, the ligand **10** was prepared as a yellow solid in 22% yield. Mp: 214−216 °C. FT-IR (KBr disk, cm^{-1}): 3070, 3045, 2987, 1656, 1619, 1587, 1552, 1531, 1491, 1450, 1439, 1425, 1390, 1365, 1322, 1285, 1229, 1190, 1137, 1117, 1081, 858, 821, 773, 742, 699, 659. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.3 Hz, 1H); 8.77 (d, J = 8.4 Hz, 1H); 8.38 (d, J = 8.4 Hz, 1H); 8.31 (d, J = 7.8 Hz, 1H); 7.89 (s, 2H); 7.69 (dd, J = 7.8 Hz, 1H); 7.62 (s, 2H); 2.66 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 155.0, 150.7, 147.2, 146.3, 145.2, 136.7, 136.4, 131.6, 129.9, 129.2, 129.0, 128.0, 126.4, 123.1, 121.4, 113.6, 18.2. Anal. Calc for $C_{20}H_{12}Br_2ClN_3$ (489.59): C, 49.06; H, 2.47; N, 8.58. Found: C, 49.17; H, 2.49; N, 8.43.

2-Acetyl-1,10-phenanthroline(2,4,6-tribromoanil) (11). In a manner similar to that described for **7**, the ligand **11** was prepared as a yellow solid in 22% yield. Mp: 206−208 °C. FT-IR (KBr disk, cm^{-1}): 3066, 1644, 1586, 1551, 1529, 1489, 1450, 1421, 1393, 1363, 1323, 1286, 1225, 1192, 1136, 1114, 1079, 887, 854, 829, 775, 741, 681, 658. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.3 Hz, 1H); 8.77 (d, J = 8.4 Hz, 1H); 8.38 (d, J = 8.4 Hz, 1H); 8.30 (d, J = 7.8 Hz, 1H); 7.88 (s, 2H); 7.75 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 2.66 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 154.9, 150.7, 147.6, 146.3, 145.2, 136.7, 136.3, 134.3, 129.9, 129.0, 128.0, 126.4, 123.1, 121.3, 116.0, 113.9, 18.2. Anal. Calc for $C_{20}H_{12}Br_3N_3$ (534.04): C, 44.98; H, 2.26; N, 7.87. Found: C, 45.16; H, 2.32; N, 7.94.

2-Formyl-1,10-phenanthroline(2,6-dimethylanil) (12). In a manner similar to that described for **1**, the ligand **12** was prepared as a yellow solid in 78% yield. Mp: 164−166 °C. FT-IR (KBr disk, cm^{-1}): 3513, 3446, 2956, 2917, 1628, 1590, 1556, 1490, 1470, 1394, 1192, 1089, 855, 764, 743. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.23 (s, 1H); 8.89 (s, 1H, CH═N); 8.69 (d, J = 8.4 Hz, 1H); 8.32 (d, J = 8.4 Hz, 1H); 8.21 (d, J = 7.8 Hz, 1H); 7.79 (s, 2H), 7.63 (s, 1H); 7.10 (d, J = 7.2 Hz, 2H); 7.00 (dd, J = 6.9 Hz, 1H); 2.21 (s, 6H, PhCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 154.7, 150.8, 150.5, 146.2, 146.0, 137.0, 136.4, 129.9, 129.1, 128.3, 128.0, 126.7, 126.6, 124.2, 123.4, 120.4, 18.5. Anal. Calc for $C_{21}H_{17}N_3 \cdot 0.5H_2O$ (320.39): C, 78.72; H, 5.66; N, 13.12. Found: C, 78.23; H, 5.70; N, 12.84.

2-Formyl-1,10-phenanthroline(2,6-diethylanil) (13). In a manner similar to that described for **1**, the ligand **13** was prepared as a yellow solid in 70% yield. Mp: 94−96 °C. FT-IR (KBr disk, cm^{-1}): 3507, 3436, 2964, 2933, 2875, 1631, 1589, 1556, 1505,

1491, 1454, 1395, 1324, 1185, 1093, 867, 748. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.31 (dd, J = 4.2 Hz, 1H); 8.85 (s, 1H, C*H*═N); 8.72 (d, J = 8.4 Hz, 1H); 8.40 (d, J = 8.4 Hz, 1H); 8.36 (d, J = 7.8 Hz, 1H); 7.90 (s, 2H), 7.72 (dd, J = 8.1 Hz, 1H); 7.12 (m, 2H); 6.98 (d, J = 7.5 Hz, 1H); 2.57 (q, J = 7.5 Hz, 4H, C*H*$_2$CH$_3$), 1.15 (t, J = 7.5 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 154.8, 150.2, 149.4, 145.2, 137.1, 136.9, 132.5, 129.9, 129.0, 127.6, 126.8, 126.2, 126.1, 124.3, 123.3, 120.6, 24.7, 14.4. Anal. Calc for $C_{23}H_{21}N_3$·0.5EtOH (362.47): C, 79.53; H, 6.67; N, 11.59. Found: C, 79.45; H, 6.45; N, 11.47.

2-Formyl-1,10-phenanthroline(2,6-diisopropylanil) (14). In a manner similar to that described for **1**, the ligand **14** was prepared as a yellow solid in 88% yield. Mp: 192−194 °C. FT-IR (KBr disk, cm^{-1}): 3426, 3063, 2960, 2868, 1639, 1587, 1555, 1490, 1455, 1395, 1321, 1182, 1090, 859, 787, 751. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 1.5 Hz, 1H); 8.84 (s, 1H, C*H*═N); 8.73 (d, J = 8.4 Hz, 1H); 8.39 (d, J = 8.1 Hz, 1H); 8.29 (d, J = 7.8 Hz, 1H); 7.87 (s, 2H), 7.67 (m, 1H); 7.17 (m, 3H); 3.06 (sept, J = 3.3 Hz, 2H, C*H*(CH$_3$)$_2$); 1.17 (d, J = 4.5 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 154.6, 150.7, 148.2, 146.1, 145.9, 136.8, 136.3, 129.8, 128.9, 127.8, 126.4, 124.3, 123.4, 123.1, 122.8, 120.4, 27.9, 23.2. Anal. Calc for $C_{25}H_{25}N_3$ (367.49): C, 81.71; H, 6.86; N, 11.43. Found: C, 81.36; H, 6.82; N, 11.31.

2-Formyl-1,10-phenanthroline(2,6-difluoroanil) (15). In a manner similar to that described for **5**, the ligand **15** was prepared as a yellow solid in 36% yield. Mp: 156−158 °C. FT-IR (KBr disk, cm^{-1}): 3072, 3037, 1634, 1584, 1555, 1469, 1397, 1316, 1274, 1239, 1012, 970, 793, 741. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.32 (s, 1H, C*H*═N); 9.26 (d, J = 3.6 Hz, 1H); 8.67 (d, J = 8.4 Hz, 1H); 8.35 (d, J = 8.4 Hz, 1H); 8.28 (d, J = 7.5 Hz, 1H); 7.85 (s, 2H); 7.67 (dd, J = 8.1 Hz, 1H); 7.14 (m, 1H); 7.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 156.5, 152.2, 150.6, 146.0, 145.9, 137.3, 136.7, 131.1, 129.4, 128.0, 126.4, 123.6, 123.2, 120.5, 119.6, 116.5. Anal. Calc for $C_{19}H_{11}F_2N_3$ (319.31): C, 71.47; H, 3.47; N, 13.16. Found: C, 70.64; H, 3.56; N, 12.76.

2-Formyl-1,10-phenanthroline(2,6-dichloroanil) (16). In a manner similar to that described for **5**, the ligand **16** was prepared as a yellow solid in 58% yield. Mp: 116−118 °C. FT-IR (KBr disk, cm^{-1}): 3523, 3419, 1634, 1619, 1586, 1558, 1507, 1492, 1434, 1395, 1216, 1083, 856, 781, 743. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (d, J = 3.9 Hz, 1H); 9.00 (s, 1H, C*H*═N); 8.70 (d, J = 8.1 Hz, 1H); 8.39 (d, J = 8.1 Hz, 1H); 8.29 (d, J = 8.1 Hz, 1H); 7.87 (s, 2H); 7.68 (dd, J = 7.8 Hz, 1H); 7.38 (d, J = 8.1 Hz, 2H); 7.04 (t, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 152.2, 150.9, 146.0, 140.0, 137.3, 136.3, 131.1, 129.3, 129.0, 128.3, 127.7, 126.1, 123.6, 119.6, 119.5, 118.0. Anal. Calc for $C_{19}H_{11}Cl_2N_3$ (352.22): C, 64.79; H, 3.15; N, 11.93. Found: C, 65.14; H, 3.50; N, 11.79.

2-Formyl-1,10-phenanthroline(2,6-dibromoanil) (17). In a manner similar to that described for **5**, the ligand **17** was prepared as a yellow solid in 51% yield. Mp: 198−200 °C. FT-IR (KBr disk, cm^{-1}): 3417, 3043, 1639, 1614, 1585, 1550, 1504, 1490, 1451, 1426, 1390, 1334, 1211, 854, 781, 737. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.25 (dd, J = 4.8 Hz, 1H); 8.93 (s, 1H, C*H*═N); 8.71 (d, J = 8.4 Hz, 1H); 8.38 (d, J = 8.1 Hz, 1H); 8.27 (dd, J = 8.4 Hz, 1H); 7.85 (s, 2H); 7.67 (dd, J = 8.1 Hz, 1H); 7.59 (d, J = 8.1 Hz, 2H); 6.89 (t, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 156.0, 153.1, 151.5, 148.4, 148.3, 139.3, 138.7, 134.5, 132.5, 131.3, 130.6, 128.7, 128.6, 125.7, 123.1, 116.6. Anal. Calc for $C_{19}H_{11}Br_2N_3$ (441.12): C, 51.73; H, 2.51; N, 9.53. Found: C, 51.28; H, 2.45; N, 9.34.

2-Benzoyl-1,10-phenanthroline(2,6-dimethylanil) (18). In a manner similar to that described for **7**, the ligand **18** was prepared as a yellow solid in 56% yield. Mp: 206−208 °C. FT-IR (KBr disk, cm^{-1}): 3420, 3057, 2917, 1618, 1589, 1550, 1487, 1446, 1387, 1323, 1208, 1161, 1091, 969, 851, 777, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21−6.67 (m, 15H); 2.26 (s, 6H, PhC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 155.6, 150.5, 148.6, 146.2, 145.6, 137.7, 136.4, 135.8, 135.7, 130.8, 129.9, 129.3, 128.9, 128.2, 127.8, 127.4, 127.2, 126.3, 126.1, 125.4, 123.2, 123.0, 122.7, 121.6, 18.9, 18.5. Anal. Calc for $C_{27}H_{21}N_3$ (387.48): C, 83.69; H, 5.46; N, 10.84. Found: C, 83.56; H, 5.47; N, 10.68.

2-Benzoyl-1,10-phenanthroline(2,6-diethylanil) (19). In a manner similar to that described for **7**, the ligand **19** was prepared as a yellow solid in 76% yield. Mp: 178−180 °C. FT-IR (KBr disk, cm^{-1}): 3433, 3058, 2966, 2931, 1618, 1587, 1552, 1489, 1449, 1324, 1159, 964, 854, 695. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.17−6.80 (m, 15H); 2.85−2.71 (m, 2H, C*H*$_2$CH$_3$); 2.56−2.44 (m, 2H, C*H*$_2$CH$_3$); 1.17 (t, J = 7.5 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 155.5, 150.5, 147.7, 146.3, 145.6, 137.9, 136.5, 135.9, 135.7, 131.9, 130.8, 130.1, 129.5, 129.0, 128.3, 127.9, 127.5, 127.3, 126.3, 125.6, 125.1, 123.7, 123.1, 122.0, 24.9, 24.6, 13.5. Anal. Calc for $C_{29}H_{25}N_3$ (415.53): C, 83.82; H, 6.06; N, 10.11. Found: C, 83.56; H, 6.10; N, 9.98.

2-Benzoyl-1,10-phenanthroline(2,6-diisopropylanil) (20). In a manner similar to that described for **7**, the ligand **20** was prepared as a yellow solid in 82% yield. Mp: 224−226 °C. FT-IR (KBr disk, cm^{-1}): 3060, 2963, 1630, 1449, 1285, 1159, 974, 850, 766, 698. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21−6.84 (m, 15H); 3.30 (sept, J = 6.6 Hz, 2H, C*H*(CH$_3$)$_2$); 1.19 (d, J = 6.3 Hz, 6H, CH(C*H*$_3$)$_2$); 0.98 (d, J = 6.3 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 155.3, 150.4, 146.1, 145.6, 137.9, 136.4, 135.9, 135.6, 130.6, 129.2, 128.9, 128.2, 127.7, 127.4, 127.2, 126.2, 123.4, 123.0, 122.4, 122.2, 28.4, 24.0, 21.7. Anal. Calc for $C_{31}H_{29}N_3$ (443.58): C, 83.94; H, 6.59; N, 9.47. Found: C, 82.99; H, 6.59; N, 9.29.

4.4. Synthesis of the Complexes 1a−20a. General Procedure. The ligand and 1 equiv of $FeCl_2$·4H$_2$O were added together in a Schlenk tube that was 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 a vacuum. All the iron(II) complexes were prepared in high yield in this manner.

2-Acetyl-1,10-phenanthroline(2,6-dimethylanil)FeCl$_2$ (1a). This complex was isolated as a dark blue powder in 96% yield. FT-IR (KBr disk, cm^{-1}): 3436, 3407, 2978, 2915, 1612, 1584, 1512, 1491, 1467, 1406, 1374, 1287, 1209, 1153, 1093, 864, 790, 772, 742, 657. Anal. Calc for $C_{22}H_{19}Cl_2FeN_3$ (452.16): C, 58.44; H, 4.24; N, 9.29. Found: C, 58.51; H, 4.49; N, 9.07.

2-Acetyl-1,10-phenanthroline(2,6-diethylanil)FeCl$_2$ (2a). This complex was isolated as a dark blue powder in 89% yield. FT-IR (KBr disk, cm^{-1}): 3436, 2965, 2933, 2876, 1609, 1583, 1513, 1493, 1447, 1406, 1374, 1287, 1194, 874, 836, 786, 741, 658. Anal. Calc for $C_{24}H_{23}Cl_2FeN_3$ (480.21): C, 60.03; H, 4.83; N, 8.75. Found: C, 59.86; H, 4.88; N, 8.58.

2-Acetyl-1,10-phenanthroline(2,6-diisopropylanil)FeCl$_2$ (3a). This complex was isolated as a dark blue powder in 89% yield. FT-IR (KBr disk, cm^{-1}): 3440, 2967, 2928, 2869, 1605, 1512, 1464, 1446, 1407, 1289, 1191, 1146, 850, 789, 759, 655. Anal. Calc for $C_{26}H_{27}Cl_2FeN_3$ (508.26): C, 61.44; H, 5.35; N, 8.27. Found: C, 61.44; H, 5.58; N, 8.05.

2-Acetyl-1,10-phenanthroline(2,4,6-trimethylanil)FeCl$_2$ (4a). This complex was isolated as a dark blue powder in 63% yield. FT-IR (KBr disk, cm^{-1}): 2915, 1606, 1580, 1513, 1480, 1406, 1286, 1221, 1161, 857, 785, 741, 657. Anal. Calc for $C_{23}H_{21}Cl_2FeN_3$ (466.18): C, 59.26; H, 4.54; N, 9.01. Found: C, 58.24; H, 4.54; N, 8.56.

2-Acetyl-1,10-phenanthroline(4-bromo-2,6-dimethylanil)-FeCl$_2$ (5a). This complex was isolated as a purple powder in 80% yield. FT-IR (KBr disk, cm^{-1}): 3048, 2952, 2911, 1618, 1580, 1515, 1494, 1466, 1436, 1406, 1286, 1206, 854, 796, 738, 657. Anal. Calc for $C_{22}H_{18}BrCl_2FeN_3$ (531.05): C, 49.76; H, 3.42; N, 7.91. Found: C, 49.89; H, 3.53; N, 7.83.

Table 4. Crystal Data and Structure Refinement for Complexes 2a, 4a, 7a, 8a, and 14a

	2a	4a	7a	8a	14a
formula	$C_{24}H_{23}Cl_2FeN_3$	$C_{23}H_{21}Cl_2FeN_3$	$C_{20}H_{13}Cl_4FeN_3$	$C_{20}H_{13}Br_2Cl_2FeN_3$	$C_{25}H_{25}Cl_2FeN_3$
fw	480.20	466.18	492.98	581.90	494.23
temperature (K)	293(2)	293(2)	198(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$Pbca$
a (Å)	8.3051(17)	7.8710(5)	7.925(1)	8.0359(16)	14.974(5)
b (Å)	8.9970(18)	20.0610(11)	18.526(1)	18.611(4)	15.993(5)
c (Å)	16.173(3)	13.3304(8)	13.606(1)	13.788(3)	19.474(6)
α (deg)	103.05(3)	90.00	90.00	90.00	90.00
β (deg)	91.74(3)	104.979(2)	104.17(1)	103.90(3)	90.00
γ (deg)	108.94(3)	90.00	90.00	90.00	90.00
volume (Å^3)	1106.4(4)	2033.3(2)	1936.8(3)	2001.8(7)	4663(3)
Z	2	4	4	4	8
D_{calc} (Mg m^{-3})	1.441	1.523	1.691	1.931	1.408
μ (mm^{-1})	0.939	1.019	1.342	5.024	0.893
F(000)	496	960	992	1136	2048
cryst size (mm)	0.56 × 0.19 × 0.10	0.53 × 0.20 × 0.12	0.15 × 0.15 × 0.10	0.29 × 0.23 × 0.21	0.18 × 0.17 × 0.15
θ range (deg)	1.30−25.01	3.16−27.48	1.90−28.26	1.87−27.48	2.50−27.56
limiting indices	$0 \le h \le 9$, $-10 \le k \le 10$, $-19 \le l \le 19$	$-10 \le h \le 10$, $-25 \le k \le 26$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-22 \le k \le 24$, $-18 \le l \le 17$	$0 \le h \le 10$, $0 \le k \le 24$, $-17 \le l \le 17$	$-19 \le h \le 14$, $-20 \le k \le 20$, $-25 \le l \le 25$
no. of rflns collected	9031	15 428	15 954	14 828	34 649
no. of unique rflns	3616	4611	4747	4448	5373
no. of obsd rflns ($I > 2\sigma(I)$)	3152	4324	3706	2512	3375
R_{int}	0.0317	0.0230	0.029	0.0702	0.0599
completeness to θ (%)	92.8 (θ= 25.01°)	99.1 (θ=27.48°)	98.8 (θ=28.26°)	96.8 (θ=27.48°)	99.7 (θ=27.56°)
absorp corr	empirical	empirical	empirical	empirical	empirical
no. of params	251	262	254	253	280
goodness-of-fit on F^2	1.086	0.940	1.030	0.969	1.079
final R indices [$I > 2\sigma(I)$]	R1=0.0467, wR2=0.1266	R1=0.0353, wR2=0.0947	R1=0.0354, wR2=0.0744	R1=0.0561, wR2=0.1045	R1=0.0565, wR2=0.0925
R indices (all data)	R1=0.0531, wR2=0.1311	R1=0.0379, wR2=0.0969	R1=0.0541, wR2=0.0811	R1=0.1045, wR2=0.1202	R1=0.1102, wR2=0.1130
largest diff peak, hole (e Å^{-3})	0.602, −0.470	0.552, −0.537	0.309, −0.382	0.454, −0.582	0.358, −0.274

2-Acetyl-1,10-phenanthroline(2,6-difloroanil)$FeCl_2$ (6a). This complex was isolated as a dark blue powder in 97% yield. FT-IR (KBr disk, cm^{-1}): 3447, 3056, 2969, 2868, 1612, 1587, 1514, 1472, 1405, 1373, 1284, 1241, 1227, 1150, 1061, 1026, 1005, 861, 775, 743, 658. Anal. Calc for $C_{20}H_{13}Cl_2F_2FeN_3$ (460.08): C, 52.21; H, 2.85; N, 9.13. Found: C, 52.32; H, 3.43; N, 8.83.

2-Acetyl-1,10-phenanthroline(2,6-dichloroanil)$FeCl_2$ (7a). This complex was isolated as a purple powder in 88% yield. FT-IR (KBr disk, cm^{-1}): 3447, 3066, 2992, 2911, 1614, 1580, 1561, 1516, 1495, 1439, 1407, 1376, 1332, 1286, 1231, 1209, 1160, 1150, 1090, 859, 832, 788, 749, 684, 657. Anal. Calc for $C_{20}H_{13}Cl_4FeN_3 \cdot Et_2O$ (567.11): C, 50.83; H, 4.09; N, 7.41. Found: C, 50.86; H, 3.75; N, 7.49.

2-Acetyl-1,10-phenanthroline(2,6-dibromoanil)$FeCl_2$ (8a). This complex was isolated as a purple powder in 96% yield. FT-IR (KBr disk, cm^{-1}): 3462, 3059, 2969, 2909, 1614, 1578, 1551, 1515, 1493, 1432, 1406, 1376, 1331, 1286, 1266, 1231, 1204, 1150, 863, 833, 784, 732, 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, 41.07; H, 2.46; N, 7.15.

2-Acetyl-1,10-phenanthroline(2,6-dibromo-4-methylanil)-$FeCl_2$ (9a). This complex was isolated as a purple powder in 77% yield. FT-IR (KBr disk, cm^{-1}): 3469, 3057, 2911, 1611, 1579, 1537, 1515, 1492, 1449, 1407, 1376, 1333, 1287, 1235, 1149, 860, 744, 658. Anal. Calc for $C_{21}H_{15}Br_2Cl_2FeN_3$ (595.92): C, 42.33; H, 2.54; N, 7.05. Found: C, 41.76; H, 2.68; N, 6.77.

2-Acetyl-1,10-phenanthroline(4-chloro-2,6-dibromoanil)-$FeCl_2$ (10a). This complex was isolated as a purple powder in 95% yield. FT-IR (KBr disk, cm^{-1}): 3449, 3050, 2910, 1613, 1572, 1539, 1512, 1491, 1433, 1407, 1372, 1288, 1263, 1232, 1155, 1138, 875, 858, 842, 792, 747, 732, 699, 658. Anal. Calc for $C_{20}H_{12}Br_2Cl_3FeN_3$ (616.34): C, 38.97; H, 1.96; N, 6.82. Found: C, 39.34; H, 2.30; N, 6.44.

2-Acetyl-1,10-phenanthroline(2,4,6-tribromoanil)$FeCl_2$ (11a). This complex was isolated as a gray powder in 80% yield. FT-IR (KBr disk, cm^{-1}): 3450, 3050, 2910, 1613, 1581, 1562, 1538, 1512, 1491, 1430, 1408, 1369, 1288, 1155, 1138, 876, 856, 789, 746, 732, 692, 658. Anal. Calc for $C_{20}H_{12}Br_3Cl_2FeN_3$ (660.79): C, 36.35; H, 1.83; N, 6.36. Found: C, 35.47; H, 2.11; N, 6.31.

2-Formyl-1,10-phenanthroline(2,6-dimethylanil)$FeCl_2$ (12a). This complex was isolated as a dark blue powder in 94% yield. FT-IR (KBr disk, cm^{-1}): 3436, 3061, 2918, 1607, 1512, 1472, 1406, 1297, 1182, 1142, 1117, 1093, 963, 861, 780, 737. Anal. Calc for $C_{21}H_{17}Cl_2FeN_3$ (438.13): C, 57.57; H, 3.91; N, 9.59. Found: C, 57.09; H, 4.20; N, 9.06.

2-Formyl-1,10-phenanthroline(2,6-diethylanil)$FeCl_2$ (13a). This complex was isolated as a gray-blue powder in 63% yield. FT-IR (KBr disk, cm^{-1}): 3436, 3059, 2965, 2934, 1605, 1584, 1514, 1452, 1405, 1177, 1141, 963, 860, 769, 737. Anal. Calc for $C_{23}H_{21}Cl_2FeN_3$ (466.18): C, 59.26; H, 4.54; N, 9.01. Found: C, 59.05; H, 4.50; N, 8.83.

2-Formyl-1,10-phenanthroline(2,6-diisopropylanil)$FeCl_2$ (14a). This complex was isolated as a dark blue powder in 99% yield. FT-IR (KBr disk, cm^{-1}): 3395, 3.60, 2964, 2868, 1601, 1580, 1514, 1494, 1462, 1447, 1407, 1175, 1117, 849, 806, 766. Anal. Calc for $C_{25}H_{25}Cl_2FeN_3$ (494.24): C, 60.75; H, 5.10; N, 8.50. Found: C, 60.36; H, 5.49; N, 8.00.

2-Formyl-1,10-phenanthroline(2,6-difluoroanil)$FeCl_2$ (15a). This complex was isolated as a gray-green powder in 90% yield. FT-IR (KBr disk, cm^{-1}): 3397, 3060, 3019, 1610, 1588, 1513, 1470, 1434, 1404, 1363, 1342, 1284, 1236, 1198, 1144, 1117, 1058, 1015, 963, 862, 786, 736. Anal. Calc for $C_{19}H_{11}Cl_2F_2FeN_3$ (446.06): C, 51.16; H, 2.49; N, 9.42. Found: C, 51.17; H, 2.90; N, 9.07.

2-Formyl-1,10-phenanthroline(2,6-dichloroanil)$FeCl_2$ (16a). This complex was isolated as a dark blue powder in 56% yield. FT-IR (KBr disk, cm^{-1}): 3370, 3063, 3005, 1607, 1580, 1563, 1513, 1441, 1405, 1360, 1342, 1297, 1200, 1117, 963, 863, 788,

737, 643. Anal. Calc for $C_{19}H_{11}Cl_4FeN_3$ (478.97): C, 47.64; H, 2.31; N, 8.77. Found: C, 47.05; H, 2.66; N, 8.30.

2-Formyl-1,10-phenanthroline(2,6-dibromoanil)$FeCl_2$ (17a). This complex was isolated as a dark gray powder in 86% yield. FT-IR (KBr disk, cm^{-1}): 3420, 3058, 1606, 1579, 1555, 1512, 1435, 1405, 1298, 1199, 1142, 1116, 961, 863, 780, 740, 643. Anal. Calc for $C_{19}H_{11}Br_2Cl_2FeN_3$ (567.87): C, 40.19; H, 1.95; N, 7.40. Found: C, 40.25; H, 2.11; N, 7.35.

2-Benzoyl-1,10-phenanthroline(2,6-dimethylanil)$FeCl_2$ (18a). This complex was isolated as a dark brown powder in 97% yield. FT-IR (KBr disk, cm^{-1}): 3409, 3060, 2908, 1602, 1511, 1492, 1442, 1402, 1297, 1216, 1000, 866, 790, 701. Anal. Calc for $C_{27}H_{21}Cl_2FeN_3 \cdot 0.5H_2O$ (523.24): C, 61.98; H, 4.24; N, 8.03. Found: C, 61.95; H, 4.05; N, 8.03.

2-Benzoyl-1,10-phenanthroline(2,6-diethylanil)$FeCl_2$ (19a). This complex was isolated as a dark brown powder in 87% yield. FT-IR (KBr disk, cm^{-1}): 3436, 3065, 2972, 1605, 1583, 1508, 1444, 1403, 1284, 1001, 881, 783, 703. Anal. Calc for $C_{29}H_{25}Cl_2FeN_3$ (542.28): C, 64.23; H, 4.65; N, 7.75. Found: C, 64.04; H, 4.70; N, 7.66.

2-Benzoyl-1,10-phenanthroline(2,6-diisopropylanil)$FeCl_2$ (20a). This complex was isolated as a dark brown powder in 64% yield. FT-IR (KBr disk, cm^{-1}): 2964, 2867, 1604, 1586, 1510, 1437, 1402, 1292, 1209, 1112, 999, 863, 783, 701. Anal. Calc for $C_{31}H_{29}Cl_2FeN_3 \cdot EtOH$ (616.40): C, 64.30; H, 5.72; N, 6.82. Found: C, 64.27; H, 5.27; N, 7.04.

4.5. General Procedure for Ethylene Oligomerization. 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, allowed to cool to the required reaction temperature under ethylene atmosphere, and then charged with toluene, the desired amount of cocatalyt, and toluene solution of catalytic precursor; the total volume was 100 mL. At the reaction temperature, the reactor was sealed and pressurized to 10 atm of ethylene pressure, and the ethylene pressure was kept with feeding of ethylene. After the reaction was carried out for the required time, the pressure was released and a small amount of the reaction solution was collected and terminated by the addition of 5% aqueous hydrogen chloride, which was then analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained. Then the residual reaction solution was quenched with 5% hydrochloric acid ethanol (5%). The precipitated low-molecular-weight waxes were collected by filtration, washed with ethanol, and dried in a vacuum until constant weight.

4.6. X-ray Crystallography Measurements. Single-crystal X-ray diffraction studies for **2a** and **8a** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data for crystals of **4a** and **14a** were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data set for **7a** was collected with a Nonius Kappa CCD diffractometer, equipped with a Nonius FR591 rotating anode generator. 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.[25] Crystallographic data and processing parameters for complexes **2a**, **4a**, **7a**, **8a**, and **14a** are summarized in Table 4.

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Supporting Information Available: X-ray crystallographic data (CIF) for complexes **2a**, **4a**, **7a**, **8a**, and **14a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Sheldrick, G. M. *SHELXTL-97*, Program for the Refinement of Crystal Structures; University of Gottingen: Germany, 1997.