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Article

Ferrous and Cobaltous Chlorides Bearing 2,8-Bis(imino)quinolines: Highly Active Catalysts for Ethylene Polymerization at High Temperature

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A series of 2,8-bis(1-aryliminoethyl)quinolines [2,8-(2,6-R^1_2-4-$R^2C_6H_2N{=}CCH_3)_2C_9H_5N$ (**L**), R^1 = Me, Et, or *i*-Pr, R^2 = H or Me] is synthesized and used in the reaction with ferrous or cobaltous chlorides. The corresponding complexes **L**MCl$_2$ are limitedly formed with ligands containing *ortho*-methyl groups of the imino phenyl rings (R = H, M = Fe (**Fe1**), M = Co (**Co1**); R = Me, M = Fe (**Fe2**), M = Co (**Co2**). The X-ray diffraction study reveals a distorted pyramidal geometry of **Co1** around the cobalt atom. These complexes, activated with methylaluminoxane (MAO), show unique properties toward ethylene polymerization: no activity observed at low temperature, but high activity achieved at temperatures higher than 80 °C (up to 7.61×10^6 g·mol^{-1}·h^{-1} at 100 °C). Moreover, the polyethylenes obtained are high molecular weight with narrow molecular distribution. This is the first example of iron and cobalt procatalysts with high activity for ethylene polymerization at high temperature.

1. Introduction

The advent of the bis(imino)pyridine ferrous and cobaltous complexes is a milestone of late transition metal complexes as highly active catalysts for ethylene reactivity.[1–4] In addition to their high productivity, the ferrous and cobaltous catalysts commonly produce α-olefins and/or long-chain α-olefin waxes.[3,5,6] Recognizing the advantages of the high productivity and linear α-olefins, many scientists have modified the ligands of complex catalysts through changing substituents of aryl groups[7] or direct substituents[8] linked to imino groups of bis(imino)pyridines. These modifications modify the steric and electronic influences of ligands in order to control the catalytic activities and products of complex catalysts in ethylene oligomerization and/or polymerization.[4,7,8] In addition, there are extensive modifications with,

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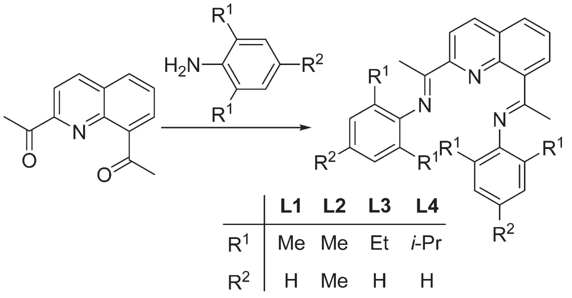
instead of the pyridine or the imino groups, heteroatomic cycles.[6,9-11] The ferrous and cobaltous complexes with modified ligands are obtained with high activities. Although some catalytic systems had high activities in ethylene polymerization, the reaction conditions are limited at relatively low temperature. While most reported late transition metal catalysts with ethylene polymerization activity produce more oligomers or low molecular polyolefins when the reaction temperature was elevated, thermostable nickel and palladium procatalysts bearing modified bidentate ligands were reported for ethylene polymerization.[12] Regarding oligomers and/or polyethylene with low molecular weights, considering the highly exothermic reaction of ethylene polymerization, the late transition catalysts reported are hardly considerable for the potential application in industrial polymerization of commercial common operating temperatures about 80 °C. Beyond the academic interest in late transition metal complexes as catalysts for olefin polymerization, the critical problem must be solved of finding novel complex catalysts with high polymerization activity at commercial operating temperatures. In such catalytic systems, there is no appreciable byproduct of oligomers and/or polyolefin waxes observed.

Cobaltous complexes bearing 2-(2-benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines as catalysts are promising; they perform ethylene oligomerization at room temperature but ethylene polymerization at higher than 40 °C.[13] Encouraged with this achievement, numerous *N^N^N* tridentate ligands are designed and used for their late transition metal complexes, which are expected to be highly active catalysts for ethylene polymerization at commercial operating temperatures. A series of 2,8-bis(1-aryliminoethyl)quinolines was synthesized; however, there are only limited ferrous and cobaltous complexes formed containing ligands having methyl groups at the *ortho*-positions of the imino phenyl rings. The title complexes, activated with methylaluminoxane (MAO), show uncommon catalytic behaviors of ethylene polymerization: no activity at ambient temperature and high activity at elevated temperature. These ferrous and cobaltous complexes have high activities toward ethylene polymerization at high reaction temperature, producing polyethylenes with narrow molecular weight distribution. This is the first example of an iron complex catalyst and the second case for a cobalt complex catalyst. Herein the syntheses and characterization of 2,8-bis(imino)quinolines and the title complexes are reported, along with the ethylene polymerization results of the title complexes.

2. Results and Discussion

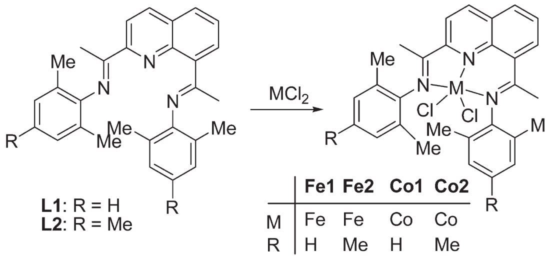
2.1. Preparation of 2,8-Bis(1-aryliminoethyl)quinolines (L1−L4). According to the procedure of transforming carboxylate groups into acetyl groups,[14] 2,8-diacetylquinoline is prepared in an appropriate yield. The 2,8-bis(1-aryliminoethyl)quinolines are formed through the condensation reaction of 2,8-diacetylquinoline and the corresponding anilines using a catalytic amount of *p*-toluenesulfonic acid (Scheme 1). All compounds are well characterized by elemental, ^{1}H and ^{13}C NMR, and IR spectrometric analyses. In addition, compound **L4** is confirmed by X-ray diffraction analysis.

Scheme 1. Synthesis of L1−L4



	L1	L2	L3	L4
R^1	Me	Me	Et	*i*-Pr
R^2	H	Me	H	H

Scheme 2. Synthesis of Iron and Cobalt Complexes



	Fe1	Fe2	Co1	Co2
M	Fe	Fe	Co	Co
R	H	Me	H	Me

2.2. Synthesis of Iron and Cobalt Complexes. All newly synthesized 2,8-bis(1-aryliminoethyl)quinolines (**L1−L4**) are explored for their coordination with iron(II) and cobalt(II) chlorides. The coordination reaction is limited to the ligands (**L1**, **L2**) having methyl groups at *ortho*-positions of the imino phenyl rings; however, no identifiable complex formed with the ligands **L3** and **L4** though different solvents have been tried for the reactions at various reaction temperatures. The iron(II) complexes **Fe1** and **Fe2** are routinely prepared by mixing the corresponding ligand (**L1** or **L2**) and 1 equiv of $FeCl_2 \cdot 4H_2O$ in THF at room temperature under nitrogen, and the cobalt(II) complexes **Co1** and **Co2** by mixing the corresponding ligand (**L1** or **L2**) and 1 equiv of $CoCl_2$ in ethanol at room temperature (Scheme 2). All metal complexes are characterized by FT-IR spectra and elemental analyses; they are stable in air and decomposed above 280 °C without clear melting points. According to their IR spectra, the stretching vibrations of C=N in these complexes (1615−1623 cm^{-1}) apparently shift to lower wavenumber and their peak intensities are greatly reduced, as compared to the corresponding ligands (1641−1647 cm^{-1}), indicating the effective coordination interaction between the imino-nitrogen and the cationic metal. It is a rare case that the substituents at *ortho*-position of the imino phenyl rings of ligands **L3** and **L4** cause problems in forming tridentate coordination complexes, which is contrary to the coordination behavior of their analogues **L1** and **L2**. The molecular structure of complex **Co1** is confirmed by the X-ray diffraction analysis, which gives an additional explanation for the difficulty of forming tridentate metal complexes containing ligands **L3** and **L4**.

2.3. X-ray Crystallographic Studies. Crystals of **L4** suitable for X-ray structural determination are obtained by the slow evaporation of its ethyl acetate solutions. The molecular structure of **L4** is shown in Figure S1 along with its selected bond lengths and angles in the Supporting Information.

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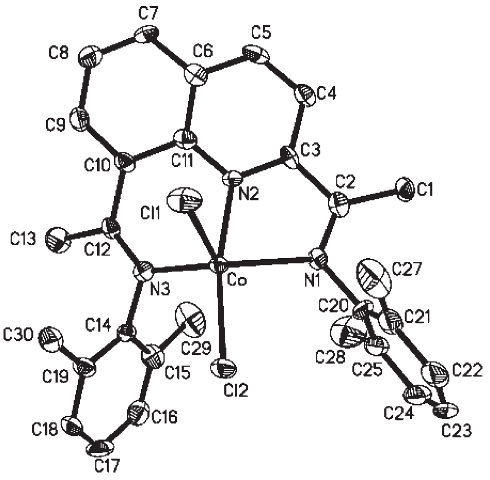

Figure 1. Molecular structure of complex **Co1** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Co−N1 = 2.133(7), Co−N2 = 2.151(8), Co−N3 = 2.088(8), Co−Cl1 = 2.309(3), Co−Cl2 = 2.280(3), N1−C2 = 1.298(1), N3−C12 = 1.278(1), N1−Co−N2 = 74.1(3), N2−Co−N3 = 82.6(3), N1−Co−N3 = 131.6(3), N1−Co−Cl1 = 113.1(2), N1−Co−Cl2 = 94.8(2), N2−Co−Cl1 = 86.2(2), N2−Co−Cl2 = 167.9(2), N3−Co−Cl1 = 106.8(2), N3−Co−Cl2 = 102.2(2), Cl1−Co−Cl2 = 102.79(1).

Single crystals of complex **Co1** suitable for X-ray structural determinations were grown by the slow diffusion of diethyl ether into its methanol solution; its molecular structure is shown in Figure 1 along with selected bond lengths and angles. In the solid-state structure, the cobalt of **Co1** adopts a distorted square-based pyramidal coordination environment with Cl1 in the apical position and the cobalt lying about 0.47 Å out of the Cl2−N1−N2−N3 basal plane. The quinoline and N3 planes are slightly inclined (about 9.9°). The cobalt center is coordinated with the nitrogen atom from the ligand, forming one five-membered cobaltacyclic ring and one six-membered cobaltacyclic ring with acute N−Co−N angles of 74.1(3)° and 82.6(3)°. The two rings of chelate cobaltacycles are nonplanar, with a dihedral angle of 15.57°. The cobalt atom deviates from the coordination plane (based on N1−N2−N3) by a large distance (0.860 Å) due to the bulkiness of the ligand. The Co−N3 bond length (2.088(8) Å) is slightly shorter than the other Co−N bonds because of the formation of the six-membered cobaltacyclic ring. The Co−Cl bonds are noticeably asymmetric, with that to the apical chloride being 2.309(3) Å and that to its basal chloride being 2.280(3) Å. Both imino bonds clearly display double-bond character. Compared with the analogue of its ligand, the N1−C2 (1.298(1) Å) imino bond at the *ortho*-position of quinoline becomes longer after coordination; however, no significant difference of the imino bond at the 8-position is observed. Predictably, the phenyl groups linked to the imino groups are oriented to the basal coordination plane N1−N2−N3, with dihedral angles of 106.3° and 107.2°.

2.4. Ethylene Polymerization. The title complexes were investigated for their catalytic behaviors in ethylene reactivity. In the presence of methylaluminoxane, however, the synthesized complexes showed high activities toward ethylene polymerization at higher reaction temperatures.

2.4.1. Ethylene Polymerization by Iron Complexes. The system of **Fe1**/MAO was typically investigated for the optimum catalytic conditions. With various alkylaluminums as cocatalyst, there was no activity observed at ambient temperature, under both ambient pressure and elevated pressure. Inspired by the success of a cobalt catalyst performing ethylene polymerization at elevated temperature, further investigation was carried out with increasing reaction temperature at 10 atm of ethylene pressure. Good activity was observed with temperatures higher than 60 °C by employing MAO as the most effective cocatalyst. Detail results are shown in Table 1 with varying reaction conditions such as the molar ratio of Al/Fe and reaction temperature. As reflected with the data (entries 1−4, Table 1), there was a trace amount of polyethylene produced at 40 °C; more amounts of polyethylenes were obtained with increasing the reaction temperature up to 100 °C. Elevated reaction temperature increase chain transfer and hinder chain propagation, resulting in products (polyethylene waxes or oligomers) with lower molecular weights. In the current system, all polyethylenes obtained have high molecular weights with relatively narrow molecular distributions. The active species are formed and are stable at higher reaction temperature. To the best of our knowledge, this is the first example of an iron catalyst maintaining good activity for ethylene polymerization without oligomerization at a commercial operating temperature (about 80 °C for the Ziegler−Natta catalytic system), although a few iron complexes ligated by modified bis(imino)pyridines were still highly active for ethylene oligomerization along with polymerization.[15]

Higher activities were observed with increasing the Al/Fe molar ratio from 1500 to 3000 (entries 4−7, Table 1). At the Al/Fe molar ratio 3000, its catalytic activity reached 4.14 × 10^5 g·mol^{-1}(Fe)·h^{-1} under 10 atm of ethylene (entry 4, Table 1). Further increasing the Al/Fe molar ratio to 3500 produced a slight decrease of activity (entry 8, Table 2). In addition, the molecular weights and distributions both increased gradually with an increase in Al/Fe molar ratios of the catalytic system. It is assumed that the higher Al/Fe ratio is required to maintain active species, which are not formed at the same time to start ethylene polymerization.

The ethylene polymerization with **Fe1**/MAO catalysts was also conducted under different pressures of ethylene (entries 4, 9, 10, Table 1). The catalytic activities were greatly improved with an increase in ethylene pressure (as shown in Figure 2), attributable to the higher monomer concentration around the active iron centers at higher pressure. Under 30 atm of ethylene, the highest activity reached to 7.61 × 10^6 g·mol^{-1}(Fe)·h^{-1}; however, its molecular weight and PDI value were slightly lower than the data of polyethylene obtained under 10 atm (entry 4 vs 10, Table 1). In general, the resultant polyethylenes possessed high molecular weights with unimodal molecular weight distribution, suggesting uniform active species in the catalytic system.

Using optimum conditions, complex **Fe2** also showed high activity toward ethylene polymerization (entry 11, Table 1), producing polymer with high molecular weight and narrow molecular distribution. In our trial of NMR spectra of

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Table 1. Ethylene Polymerization by Iron Procatalysts/MAO[a]

entry	complex	Al/Fe	P/atm	T/°C	activity/10^5 g·mol^{-1}·h^{-1}	M_w[b]/× 10^{-4}	M_w/M_n[b]
1	**Fe1**	3000	10	40	trace	nd	nd
2	**Fe1**	3000	10	60	1.35	24.1	4.3
3	**Fe1**	3000	10	80	2.00	22.1	3.2
4	**Fe1**	3000	10	100	4.14	11.3	2.9
5	**Fe1**	1500	10	100	0.386	8.0	2.3
6	**Fe1**	2000	10	100	2.49	9.6	2.4
7	**Fe1**	2500	10	100	3.80	10.9	2.5
8	**Fe1**	3500	10	100	3.76	15.7	3.1
9[c]	**Fe1**	3000	20	100	26.3	10.2	2.3
10[c]	**Fe1**	3000	30	100	76.1	9.9	2.8
11[c]	**Fe2**	3000	30	100	65.1	12.5	3.3

[a] General condition: 5 μmol of Fe; 30 min; toluene (100 mL). [b] Determined by GPC. [c] 2 μmol of Fe; 30 min; toluene (40 mL).

Table 2. Ethylene Polymerization of Cobalt Procatalysts/MAO[a]

entry	complex	Al/Fe	P/atm	T/°C	activity/10^5 g·mol^{-1}·h^{-1}	M_w[b]/× 10^{-4}	M_w/M_n[b]
1	**Co1**	3000	10	60	trace	nd	nd
2	**Co1**	3000	10	80	0.509	29.8	3.5
3	**Co1**	3000	10	100	3.41	23.4	5.2
4	**Co1**	2000	10	100	1.22	20.1	4.0
5	**Co1**	2500	10	100	1.74	21.2	4.6
6	**Co1**	3500	10	100	2.40	31.8	6.1
7[c]	**Co1**	3000	20	100	38.2	16.7	3.7
8[c]	**Co1**	3000	30	100	69.3	14.6	3.6
9[c]	**Co2**	3000	30	100	63.1	16.9	3.1

[a] General conditions: 5 μmol of Co; 30 min; toluene (100 mL). [b] Determined by GPC. [c] 2 μmol of Co; 30 min; toluene (40 mL).

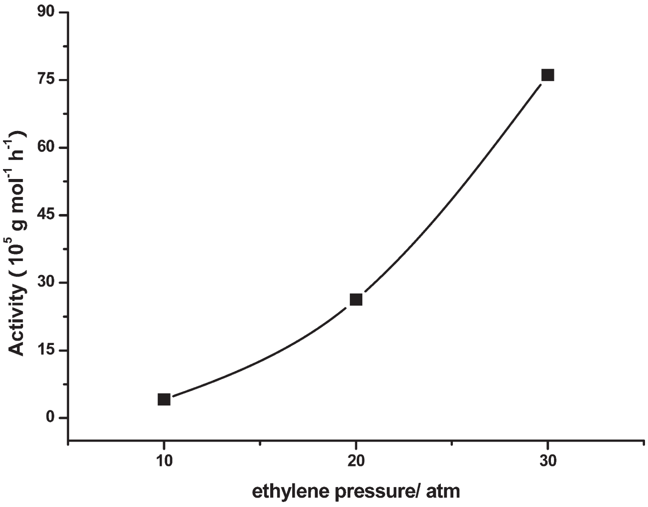

Figure 2. Effect of ethylene pressure on catalytic activity by **Fe1**.

resultant polyethylenes at 110 °C in 1,2-dichlorobenzene-d_4, only one carbon peak confirmed its high molecular weight and high linearity of obtained polyethylenes.

2.4.2. Ethylene Polymerization by Cobalt Complexes. To compare with the catalytic behavior of iron complexes, the catalytic system of **Co1**/MAO was again investigated in detail, and the results are collected in Table 2. The similar tendency of catalytic activities and polyethylenes obtained depends on the molar ratio of Al/Co, reaction temperature, and ethylene pressure. The cobalt complex could be fully activated at higher reaction temperature (entries 1–3, Table 2), and the catalytic activity reached its optimum value at a ratio of 3000 (entries 3–6, Table 2). On increasing the Al/Co molar ratio, the polyethylene obtained has a higher molecular weight and wider molecular distribution. The higher the ethylene pressures used (entries 3, 7, and 8, Table 2), the higher the catalytic activities observed and the lower the molecular weight and the narrower the molecular distribution of polyethylenes obtained. Its analogue **Co2**, activated with MAO, also showed high activity toward ethylene polymerization (entry 9, Table 2).

3. Conclusion

Iron(II) and cobal(II) complexes ligated by 2,8-bis-(1-aryliminoethyl)quinolines have been proved as good procatalysts in ethylene polymerization at higher reaction temperatures (80–100 °C). On increasing the Al/M (M = Fe or Co) molar ratio, the polyethylene obtained has a higher molecular weight and wider molecular distribution. The higher the ethylene pressures used, the higher the catalytic activities observed and the lower the molecular weight and the narrower the molecular distribution of polyethylenes obtained. Compared with other iron and cobalt complexes, these complexes showed better thermostability; therefore such procatalysts could have considerable industrial application.

4. Experimental Section

4.1. General Considerations. All manipulations of air- and moisture-sensitive compounds were performed in a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (a 1.46 M solution in toluene) was purchased from Akzo Nobel Corp. Other reagents were purchased from Aldrich or Acros Chemicals. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 MHz or a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. MALDI-TOF mass spectra were obtained with a Bruker Autoflex III matrix-assisted laser desorption/ionization time of-flight mass spectrometer, with DHB as the matrix. ^{1}H NMR spectra of the iron and cobalt complexes were recorded with a Bruker DMX 600 MHz instrument at 20 °C with the use of TMS as the internal standard. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. ^{1}H and ^{13}C NMR spectra of the PE samples were recorded on a Bruker DMX 300 MHz instrument at 110 °C in 1,2-dichlorobenzene-d_4 using TMS as the internal standard. Molecular weights and polydispersity indices (PDI) of PE were determined by a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the eluant.

4.2. Preparation of the Ligands. Synthesis of 2,8-Diacetylquinoline. A solution of diethyl quinoline-2,8-dicarboxylate (4.10 g, 15 mmol) in 50 mL of freshly distilled ethyl acetate was added dropwise to 8.7 equiv of dried C_2H_5ONa (8.84 g, 130 mmol) with stirring to afford a yellow mixture, which was refluxed for 9 h and allowed to stand overnight. Concentrated HCl (45 mL) was added dropwise with stirring, and the mixture was refluxed for another 6 h to complete the reaction. With addition of 50 mL of water, the aqueous phase was then extracted with CH_2Cl_2 (4 × 30 mL), and the combined extracts were washed with 5% aqueous Na_2CO_3. The organic phase was dried over anhydrous Na_2SO_4 and filtered before the solvent was evaporated at reduced pressure. The desired compound, 2,8-diacetylquinoline, was obtained as a white solid (2.03 g, 9.53 mmol) in 63.5% yield after purification by column chromatography (silica gel, 5:1 (v/v) petroleum ether/ethyl acetate). Mp: 81−82 °C. IR (KBr; cm^{-1}): 3001 (w), 1695 (s), 1668 (s), 1593 (s), 1557 (s), 1428 (m), 1361 (m), 1279 (s), 1259 (s), 1207 (s), 1095 (s), 856 (s), 775 (s), 615 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, $J = 8.5$ Hz, 1H); 8.20 (d, $J = 8.5$ Hz, 1H); 8.07 (d, $J = 7.1$ Hz, 1H); 8.02 (d, $J = 8.2$ Hz, 1H); 7.81 (t, $J = 7.7$ Hz, 1H); 3.04 (s, 3H); 2.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.8, 200.0, 152.9, 144.5, 140.0, 137.7, 131.4, 130.7, 129.6, 128.3, 118.3, 32.9, 26.1. Anal. Calcd for $C_{13}H_{11}NO_4$ (213.23): C, 73.23; H, 5.20; N, 6.57. Found: C, 73.01; H, 5.20; N, 6.57.

Synthesis of 2,8-Bis[1-(2,6-dimethylphenylimino)ethyl]quinoline (L1). A mixture of 2,6-dimethylaniline (0.917 g, 7.6 mmol), 2,8-diacetylquinoline (0.426 g, 2.0 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (40 mL) was refluxed for 24 h. After solvent evaporation, the crude product was purified by an alumina-based column with petroleum ether/ethyl acetate (10:1 v/v) as an eluant to afford the product as a yellow powder (0.652 g, 1.55 mmol) in 78% yield. Mp: 132−134 °C. IR (KBr; cm^{-1}): 2940 (w), 1647 (s), 1593 (m), 1467 (s), 1441 (m), 1360 (m), 1205 (m), 1091 (m), 763 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, $J = 8.7$ Hz, 1H); 8.30 (d, $J = 8.7$ Hz, 1H); 8.03 (d, $J = 7.0$ Hz, 1H); 7.95 (d, $J = 8.2$ Hz, 1H); 7.68 (dd, $J_1 = 7.2$ Hz, $J_2 = 8.0$ Hz, 1H); 7.09 (d, $J = 7.5$ Hz, 4H), 6.95 (m, 2H); 2.36 (s, 3H); 2.26 (s, 3H); 2.24 (s, 3H); 2.17 (s, 3H); 2.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 167.2, 155.4, 148.6, 148.4, 144.9, 141.8, 136.4, 128.7, 128.7, 128.6 127.8, 127.3, 125.7, 125.1, 123.0, 122.8, 118.6, 22.7, 17.8, 16.5. Anal. Calcd for $C_{29}H_{29}N_3$ (419.56): C, 83.02; H, 6.97; N, 10.02. Found: C, 83.22; H, 6.97; N, 9.88.

Synthesis of 2,8-Bis[1-(2,6-diethylphenylimino)ethyl]quinoline (L2). Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a yellow powder in 67% yield. Mp: 130−131 °C. IR (KBr; cm^{-1}): 3056 (m), 2926 (m), 1636 (s), 1589 (m), 1566 (m), 1453 (s), 1362 (s), 1280 (m), 1257 (m), 1198 (m), 1187 (m), 1095 (s), 876 (m), 856 (m), 767 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, $J = 8.6$ Hz, 1H); 8.30 (d, $J = 8.6$ Hz, 1H);7.99 (d, $J = 6.9$ Hz, 1H); 7.94 (d, $J = 8.2$ Hz, 1H); 7.68 (dd, $J_1 = 7.9$ Hz, $J_2 = 7.2$ Hz, 1H); 7.13 (d, $J = 7.2$ Hz, 4H); 7.07−7.01 (m, 2H), 2.68 (q, $J = 8.4$ Hz, 2H); 2.59 (q, $J = 8.4$ Hz, 2H); 2.45−2.32 (m, 7H); 2.27 (s, 3H); 1.23 (t, $J = 7.5$ Hz, 6H); 1.15 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 166.8, 155.3, 147.4, 147.2, 144.7, 141.8, 136.2, 131.4, 130.7, 128.5, 128.4, 127.1, 125.7, 125.6, 123.1, 123.0, 24.3, 24.1, 22.8, 16.6, 13.6, 13.4. Anal. Calcd for $C_{33}H_{37}N_3$ (475.67): C, 83.33; H, 7.84; N, 8.83. Found: C, 82.90; H, 7.99; N, 8.67.

Synthesis of 2,8-Bis[1-(2,6-diisopropylphenylimino)ethyl]quinoline (L3). Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a yellow powder in 41% yield. Mp: 214−216 °C. IR (KBr; cm^{-1}): 3062 (w), 2962 (s), 1645 (s), 1591 (m), 1565 (m), 1461 (m), 1435 (m), 1363 (m), 1277 (m), 1185 (m), 1095 (m), 856 (m), 765(s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, $J = 8.6$ Hz, 1H); 8.31 (d, $J = 8.9$ Hz, 1H); 8.02 (d, $J = 6.9$ Hz, 1H); 7.96 (d, $J = 7.9$ Hz, 1H); 7.70 (t, $J = 7.5$ Hz, 1H); 7.21−7.09 (m, 6H); 3.17 (q, $J = 6.9$ Hz, 2H); 2.79 (q, $J = 6.9$ Hz, 2H); 2.44 (s, 3H); 2.33 (s, 3H); 1.28−1.16 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2,167.4, 155.8, 146.6, 146.1, 145.2, 142.2, 136.7, 136.6, 135.8, 129.1, 129.0, 127.6, 123.9, 123.8, 123.2, 119.0, 28.5, 28.3, 23.6, 23.4, 23.3, 23.0, 17.4. Anal. Calcd for $C_{37}H_{45}N_3$ (531.36): C, 83.57; H, 8.53; N, 7.90. Found: C, 83.18; H, 8.58; N, 7.75.

Synthesis of 2,8-Bis[1-(2,4,6-trimethylphenylimino)ethyl]quinoline (L4). Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a yellow powder in 57% yield. Mp: 196−197 °C. IR (KBr; cm^{-1}): 2982 (w), 2913 (w), 1641 (s), 1568 (m), 1477 (s), 1361 (m), 1276 (m), 1215 (m), 1147 (m), 1097 (m), 858 (s), 771 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, $J = 8.6$ Hz, 1H); 8.28 (d, $J = 8.6$ Hz, 1H); 8.00 (d, $J = 7.2$ Hz, 1H); 7.93 (d, $J = 8.2$ Hz, 1H); 7.66 (dd, $J_1 = 7.2$ Hz, $J_2 = 8.0$ Hz, 1H); 6.91 (s, 4H), 2.35 (s, 3H); 2.31(s, 3H); 2.30 (s, 3H); 2.24 (s, 3H); 2.20 (s, 6H); 2.02 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 167.6, 155.8, 146.3, 146.2, 145.2, 142.2, 136.5, 132.5, 132.2, 128.9, 127.5, 125.8, 125.2, 118.9, 22.9, 20.9, 18.0, 16.7. Anal. Calcd for $C_{31}H_{33}N_3$ (447.27): C, 83.18; H, 7.43; N, 9.39. Found: C, 82.94; H, 7.67; N, 9.21.

4.3. Synthesis of Iron Complexes Fe1 and Fe2. Ligand and 1.0 equiv of $FeCl_2 \cdot 4H_2O$ were added together in a Schlenk, which was purged three times with nitrogen and then charged with freshly distilled THF. The reaction mixture was stirred at room temperature for 6 h, and absolute diethyl ether was added to precipitate the complex. The resulting precipitate was filtered, washed with diethyl ether, and dried under vacuum to furnish the product **Fe1** as a green powder in 87% yield. IR (KBr; cm^{-1}): 3010 (w), 1621 (m), 1586 (s), 1560 (m), 1469 (s), 1371 (m), 1284 (m), 1208 (m), 782 (m), 767 (s). Anal. Calcd for $C_{29}H_{29}Cl_2FeN_3$ (546.31): C, 63.76; H, 5.35; N, 7.69. Found: C, 63.47; H, 5.00; N, 7.49. ^{1}H NMR (600 MHz, CD_3OD): δ 8.5 (br, 2H, quino-H), 8.1 (d, 2H, quino-H), 7.7 (br, 1H, quino-H), 7.0 (d, 4H, Ar-*H*m), 6.9 (d, 2H, Ar-*H*p), 2.2 (br, 12H, Ar-CH_3), 1.9 (br, 6H, N═CCH_3). MALDI-TOF: calcd for $C_{29}H_{29}Cl_2FeN_3$ m/z 545, found m/z 510 $(M - Cl)^+$.

Fe2 was prepared in 79% yield by using a similar procedure to that for **Fe1**. IR (KBr; cm^{-1}): 3050 (w), 2912 (m), 1615 (m), 1585 (s), 1479 (s), 1452 (m), 1432 (m), 1370 (m), 1277 (m), 1215 (s), 1150 (m), 853 (s). Anal. Calcd for $C_{31}H_{33}Cl_2FeN_3$ (574.36): C, 64.82; H, 5.79; N, 7.32. Found: C, 64.68; H, 5.69; N, 7.17. ^{1}H NMR (600 MHz, CD_3OD): δ 8.4 (br, 2H, quino-H), 8.0 (br, 1H, quino-H), 7.9 (br, 1H, quino-H), 7.7 (br, 1H, quino-H), 6.8 (d, 4H, Ar-*H*m), 2.2 (3H, Ar-CH_3), 2.2 (6H, Ar-CH_3), 2.1 (3H, Ar-CH_3), 2.1 (6H, Ar-CH_3), 1.9 (br, 6H, N═CCH_3). MALDI-TOF: calcd for $C_{31}H_{33}Cl_2FeN_3$ m/z 573, found m/z 538 $(M - Cl)^+$.

4.4. Synthesis of Cobalt Complexes Co1 and Co2. To a mixture of **L1** and $CoCl_2$ was added freshly distilled ethanol at room temperature. The reaction mixture was stirred for 6 h, and the precipitate was collected by filtration and washed with diethyl ether, followed by drying under vacuum. The desired complex **Co1** was obtained as a brown powder in 83% yield. IR (KBr; cm^{-1}): 3050 (w), 1623 (m), 1589 (s), 1562 (m), 1468 (s), 1372 (m), 1283 (m), 1208 (m), 782 (m), 767 (s). Anal. Calcs for $C_{29}H_{29}Cl_2CoN_3$ (549.4): C, 63.40; H, 5.32; N, 7.65. Found: C, 63.49; H, 5.44; N, 7.26. ^{1}H NMR (600 MHz, CD_3OD): δ 8.5 (br, 2H, quino-H), 8.1 (br, 1H, quino-H), 8.0 (br, 1H, quino-H), 7.7 (br, 1H, quino-H), 7.1 (br, 4H, Ar-*H*m), 6.9 (br, 2H, Ar-*H*p), 2.3 (s, 3H, Ar-CH_3), 2.2 (s, 9H, Ar-CH_3), 2.0 (s, 6H, N═CCH_3). MALDI-TOF: calcd for $C_{29}H_{29}Cl_2CoN_3$ m/z 548, found m/z 513 $(M - Cl)^+$.

Co2 was prepared in 89% yield by using a similar method to that for **Co1**. IR (KBr; cm^{-1}): 3050 (w), 2912 (w), 1621 (s), 1588 (s), 1560 (s), 1479 (s), 1460 (m), 1436 (m), 1372 (m), 1312 (m), 1282 (m), 1217 (s), 1154 (m), 853 (s), 785 (m). Anal. Calcs for $C_{31}H_{33}Cl_2CoN_3$ (577.45): C, 64.48; H, 5.76; N, 7.28. Found: C, 64.77; H, 5.71; N, 6.97. ^{1}H NMR (600 MHz, CD_3OD): δ 8.4 (br, 2H, quino-H), 8.1 (br, 1H, quino-H), 7.9 (br, 1H, quino-H), 7.7 (br, 1H, quino-H), 6.9 (s, 4H, Ar-*H*m), 2.3 (3H, Ar-CH_3), 2.2 (9H, Ar-CH_3), 2.2 (6H, Ar-CH_3), 2.0 (br, 6H, N=CCH_3). MALDI-TOF: calcd for $C_{31}H_{33}Cl_2CoN_3$ *m*/*z* 576, found *m*/*z* 541 $(M - Cl)^+$.

4.5. Procedure for Ethylene Polymerization. Ethylene polymerization at 10 atm of ethylene pressure was performed in a stainless steel autoclave (250 mL capacity) equipped with a gas ballast through a solenoid clave for continuous feeding of ethylene at constant pressure. A 100 mL amount of toluene containing the catalyst precursor was transferred to the fully dried reactor under a nitrogen atmosphere. The required amount of cocatalyst was then injected into the reactor via a syringe. At the reaction temperature, the reactor was sealed and pressurized to high ethylene pressure, and the ethylene pressure was maintained by feeding of ethylene. After the reaction mixture was stirred for the desired period, the pressure was released and a small amount of the reaction solution was collected, 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 30% hydrochloric acid ethanol. The precipitated polymer was collected by filtration, washed with ethanol and water, and dried in a vacuum until constant weight.

Ethylene polymerization at 30 atm was performed in a stainless steel autoclave (100 mL scale). A typical reaction procedure was as follows. Catalyst (2 μmol), toluene (40 mL), and the required amount of MAO (1.4 mol/L solution in toluene) were added into the autoclave in a drybox. The reactor was sealed and moved out of the drybox. At the reaction temperature, the reaction apparatus was then immediately pressurized to 30 atm. The mixture was magnetically stirred for 30 min, the ethylene remaining was purged after the reaction, and the mixture was cooled to room temperature. Then the residual reaction solution was quenched with 30% hydrochloric acid ethanol. The precipitated polymer was collected by filtration, thoroughly washed with ethanol and water, and then dried in a vacuum until constant weight.

4.6. X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **L4** and **Co1** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[16] Crystal data and processing parameters for **L4** and **Co1** are summarized in Table S1 of the Supporting Information.

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Supporting Information Available: ^{1}H NMR spectra of the iron and cobalt complexes, crystal data, and structure refinement for **L4** and **Co1** with their cif data. This material is available free of charge via the Internet at http://pubs.acs.org.

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