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Dichlorocobalt(II) Complexes Ligated by Bidentate 8-(Benzoimidazol-2-yl)quinolines: Synthesis, Characterization, and Catalytic Behavior toward Ethylene

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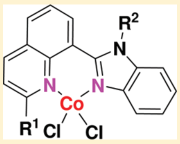
S *Supporting Information*

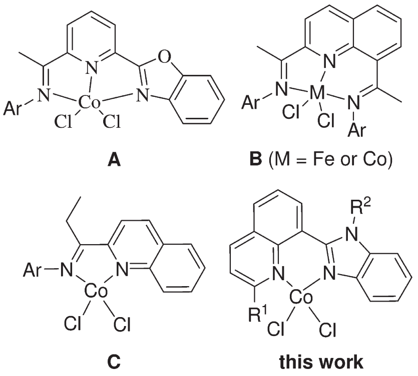
ABSTRACT: A series of (8-(benzoimidazol-2-yl)quinoline)dichlorocobalt(II) complexes was prepared and characterized, and single-crystal X-ray diffraction revealed the distorted-tetrahedral geometry around the cobalt atom. Activated with methylaluminoxane (MAO), these cobaltous complexes showed special properties of ethylene reactivity: ethylene oligomerization with an observed activity up to 3×10^4 g (mol of Co)$^{-1}$ h^{-1} atm^{-1} with reaction temperature lower than 60 °C at ambient or 10 atm ethylene pressure and ethylene polymerization with an observed activity up to 1×10^5 g (mol of Co)$^{-1}$ h^{-1} atm^{-1} with reaction temperature higher than 60 °C at 30 atm ethylene pressure, indicating two potentially active species formed at different reaction parameters. The obtained polyethylenes with high molecular weights and narrow molecular weight distributions, to the best of our knowledge, give the first proof of dichlorocobalt complex precatalysts bearing bidentate ligands acting as single-site catalysts in ethylene polymerization.



1. INTRODUCTION

The utilization of bis(imino)pyridine complexes of iron(II) or cobalt(II) for ethylene oligomerization and polymerization has attracted much interest in both academic and industrial fields over the past dozen years.[1] The extensive investigations have favored the iron derivatives because of better catalytic performances by iron precatalysts than by cobalt precatalysts,[2] and their active species and reaction mechanisms have also been illustrated.[3] The catalytic features rely on the electronic and/or steric influence of the ligands used,[4] and the variations of bis(imino)pyridines and their metal precatalysts have been studied.[5] Meanwhile, some effort has been made to exploit new tridentate N-donating ligands for new model precatalysts,[6] and series of successful precatalysts included novel ligands from our group in Beijing such as 2-benzoimidazolyl-6-iminopyridines,[7] 2-quinoxalinyl-6-iminopyridines,[8] 2-benzoxazolyl-6-iminopyridines,[9] 2-imino-1,10-phenanthrolines,[10] 2-(benzoimidazol-2-yl)-1,10-phenanthrolines,[11] iminoquinoline derivatives,[12] and 2-methyl-2,4-bis-(6-iminopyridin-2-yl)-1*H*-1,5-benzodiazepines.[13] Elevated reaction temperatures commonly resulted in deactivation of the catalytic systems of late-transition-metal procatalysts,[1,5a,14] which has been a critical deficiency because of the highly exothermic reaction of the ethylene polymerization or oligomerization reactions. Therefore, enhancing the stabilities of precatalysts has been targeted through modifying ligands for certain potential precatalysts.[15] Regarding cobalt precatalysts operating at elevated reaction temperatures, two model complexes bearing either 2-(2-benzoxazolyl)-6-iminopyridines (Scheme 1, A)[9a] or 2,8-bis(imino)quinolines (Scheme 1, B)[16] maintained good activities of ethylene polymerization and produced polyethylenes with narrow molecular distributions. The molecular structures of cobalt(II) complexes bearing 2,8-bis(imino)quinoline ligands showed a distorted-pyramidal geometry; therefore, it is worth considering the metal precatalysts bearing bidentate ligands. There were some trials of bidentate cobalt precatalysts showing either ethylene oligomerization[4a,b,17,18] or low polymerization activity at low temperature.[19] The cobalt complexes ligated by *N*-(1-(quinolin-2-yl)propylidene)benzenamines (Scheme 1, C) showed temperature-switch features in ethylene reactivity and favored ethylene polymerization at elevated

Scheme 1. Cobalt Precatalysts for Ethylene Polymerization at Elevated Temperature



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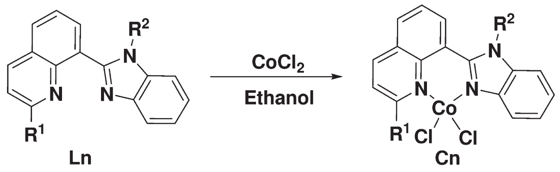
Scheme 2. Synthesis of Cobalt Complexes



Ln	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13	L14
Cn	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14
R^1	Me	Me	Et	Et	Et	Et	Pr	Pr	Pr	Pr	Ph	Ph	Ph	Ph
R^2	H	Me	H	Me	Et	iPr	H	Me	Et	iPr	H	Me	Et	iPr

temperatures,[20] and such a phenomenon was similar to the observation for the 2-(2-benzoxazolyl)-6-iminopyridylcobalt precatalysts.[9a] The achievement by model C,[20] maintaining only an 2-imino group on the quinoline rings from the model B, inspired us to explore the extensive 8-(benzoimidazol-2-yl)-quinolines for cobalt complexes (this work) herein. Iron complexes bearing 8-(benzoimidazol-2-yl)quinolines showed high activities toward ethylene polymerization;[21a] meanwhile, dialkylaluminum compounds ligated by 8-(benzimidazol-2-yl)-quinaldine exhibited high activities in the ring-opening polymerization of ε-caprolactone.[21b] Their cobalt complexes were prepared and characterized, and their catalytic behaviors were investigated under various reaction parameters. Herein the syntheses and characterizations of (8-(benzoimidazol-2-yl)-quinolyl)cobalt dichlorides are reported along with a detailed investigation of their catalytic performance in ethylene reactivity.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of the Cobalt Complexes. The stoichiometric reaction of $CoCl_2$ with one of the ligands **L1**−**L14**[21] in ethanol at room temperature produced a blue powder with the general formula $LCoCl_2$ (**C1**−**C14**) in high yields (Scheme 2). Similar to the case for their iron analogues,[21a] all cobalt complexes were characterized by elemental analyses and FT-IR spectra. In comparison with the FT-IR spectra of the free organic compounds **L1**−**L14**,[21a] the characteristic absorptions of the cobalt complexes shifted to lower frequencies due to coordination effects. These cobalt complexes were stable in the solid state. Their molecular structures were confirmed by single-crystal X-ray diffraction analysis.

2.2. X-ray Crystallographic Studies. Blue crystals were obtained by slow diffusion of diethyl ether into a DMF solution of the complex **C1**, whereas single crystals of complexes **C2**, **C3**, and **C8** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into their methanol solutions. All cobalt complexes **C1**−**C3** and **C8** could be described as featuring a distorted-tetrahedral geometry around the cobalt atom; therefore, complex **C1**, shown in Figure 1, is discussed as an example.

The cobalt atom is bound by two N atoms and two chlorines, assuming a distorted-tetrahedral coordination geometry. The Co−N1 distance of 1.954(3) Å is slightly shorter than that of Co−N2 (2.061(4) Å), and both are within the normal range for this class of four-coordinate cobalt complexes.[22] The Co−Cl1 distance of 2.2476(2) Å is longer than that of Co−Cl2 (2.2354(2) Å). The complex **C1** has a six-membered cobaltacyclic ring with the sum of the internal angles of the ring (712.12°) deviating from the theoretical value of 720°. Unlike other six-membered metallacyclic rings with a boat conformation,[18a] the atoms in the current ring Co−N2−C9−C8−C10−N1 lie nearly in the same plane (mean deviation of 0.0377 Å), with deviations of 0.074 Å at C10 and 0.0542 Å at Co. The dihedral angle between quinoline and benzoimidazole is 17.2°. The other complexes **C2**, **C3**, and **C8** have similar molecular structures and are shown in Figures 2− 4, and selected bond lengths and angles of complexes **C1**−**C3** and **C8** are given in Table 1.

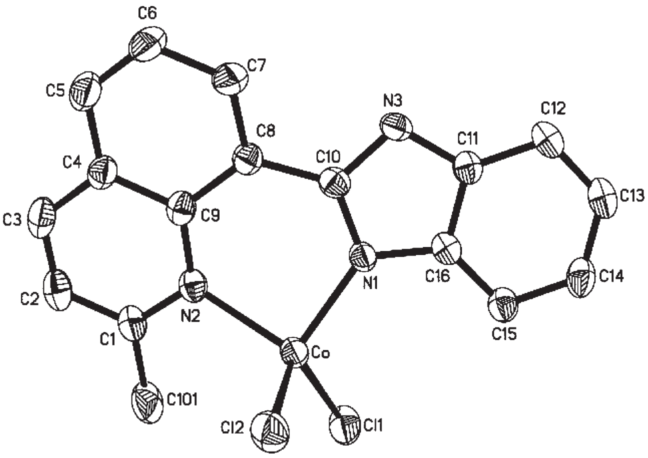


Figure 1. Molecular structure of **C1**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms and solvent (one molecule of DMF) have been omitted for clarity.

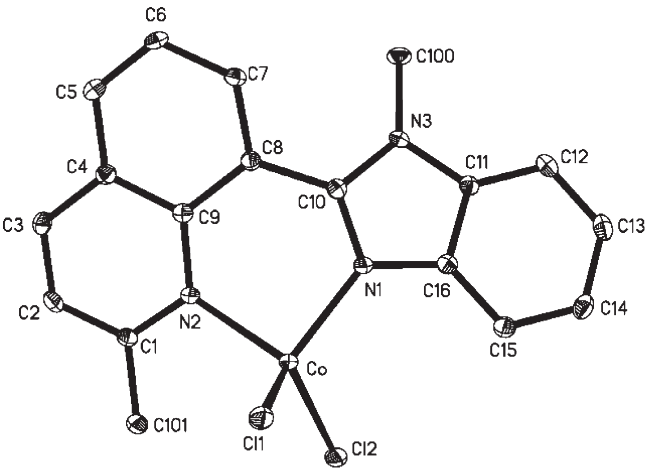


Figure 2. Molecular structure of **C2**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

2.2. Ethylene Oligomerization and Polymerization. At ambient pressure of ethylene, the catalytic behavior of precatalyst **C1** with various cocatalysts of methylaluminoxane (MAO), modified methylaluminoxane (MMAO), and triisobutylaluminium ($i\mathrm{Bu}_3\mathrm{Al}$) were evaluated (runs 1−3, Table 2), but a full-range ethylene oligomerization remained elusive. The obtained oligomers ranged from C_4 to C_{18} with high selectivity for α-olefins (>95%). The distributions of oligomers resembled Schulz−Flory rules, and the chain propagations were represented with the constant K, where K = (rate of propagation)/((rate of propagation) + (rate of chain transfer)) = (moles of C_{n+2})/(moles of C_n); the K values were determined by the molar ratio of C_{12} and C_{14} fractions.[23] Within the **C1**/MAO catalytic system at

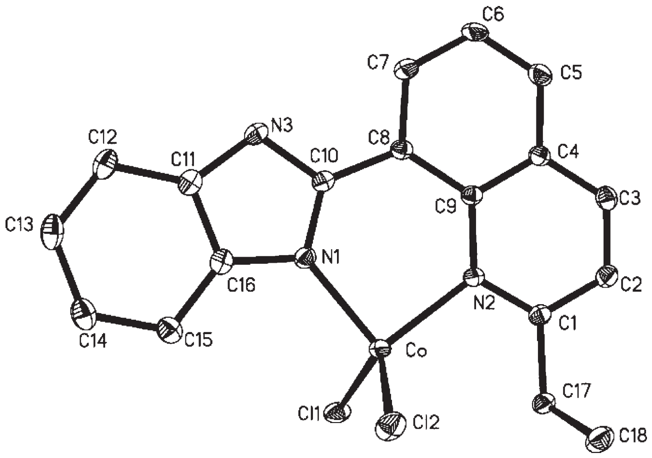


Figure 3. Molecular structure of **C3**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

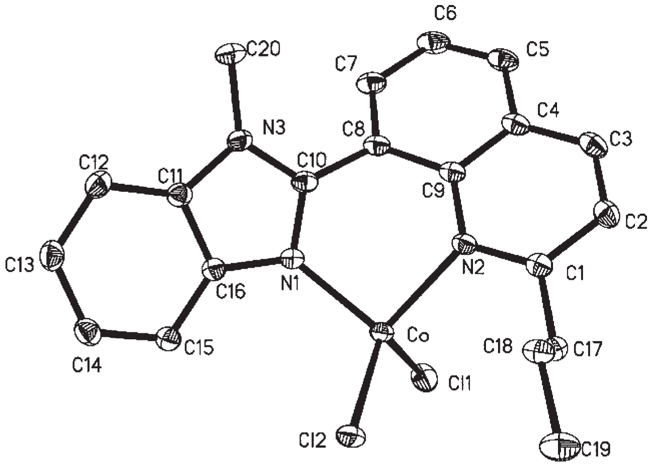


Figure 4. Molecular structure of **C8**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for C1–C3 and C8

	C1	C2	C3	C8
		Bond Lengths		
Co–N1	1.954(3)	1.979(3)	1.9714(18)	1.990(2)
Co–N2	2.061(4)	2.063(3)	2.0427(18)	2.092(2)
Co–Cl1	2.2476(2)	2.2482(1)	2.2640(7)	2.2304(9)
Co–Cl2	2.2354(2)	2.2566(1)	2.2232(10)	2.2464(11)
N1–C10	1.330(6)	1.331(5)	1.328(3)	1.334(3)
N3–C10	1.350(6)	1.373(4)	1.366(3)	1.358(3)
		Bond Angles		
N1–Co–N2	93.34(2)	93.44(1)	93.94(7)	94.09(9)
N1–Co–Cl1	109.38(1)	114.23(9)	107.74(6)	119.61(7)
N1–Co–Cl2	114.38(1)	109.73(9)	107.63(6)	107.81(7)
N2–Co–Cl1	122.91(1)	109.22(9)	114.14(5)	103.78(6)
N2–Co–Cl2	105.30(1)	119.01(9)	114.93(5)	121.45(7)
Cl1–Co–Cl2	110.74(7)	110.42(4)	115.67(3)	110.10(3)

20 °C, more oligomers were obtained through increasing the ethylene pressure (run 3 vs run 4, Table 2), though the activities likely decreased due to being divided by ethylene pressures. At 10 atm of ethylene pressure, the optimum condition of the Al/Co molar ratio was observed at 1500 (runs 4–7, Table 2), indicating the activity as 1.19×10^4 g mol^{-1} h^{-1} atm^{-1}. When the reaction temperature was varied from 20 to 60 °C (runs 6, 8, and 9), the catalytic activities gradually decreased with production of more low-molecular-weight oligomers. However, there was no ethylene oligomerization at 80 °C; instead, a trace amount of polyethylene was obtained. Therefore, all cobalt precatalysts were investigated with a Al/Co molar ratio of 1500 at 10 atm of ethylene and 20 °C, and the results are given in Table 2 (runs 10–22). Considering the influences of two substituents (R^1 and R^2) on the catalytic performance of cobalt complexes, when the R^2 substituent was fixed, the oligomerization activities were gradually enhanced with bulky R^1 substituents in the order *i*Pr > Et > Ph > Me; for example, when R^2 = H, the catalytic activities were observed in the order **C7** > **C3** > **C11** > **C1**. On the other hand, when the R^1 substituents were fixed, for example R^1 = Et, the catalytic performance was in the order **C3** (R^2 = H) > **C4** (R^2 = Me) > **C5** (R^2 = Et) > **C6** (R^2 = *i*Pr). The influence of R^2 substituents on the catalytic activities agreed with results reported in the literature.[5,7]

Regarding the influence of ethylene solubility in toluene at different temperatures and various ethylene pressures, the adjusted activities (Table 2) were obtained by calculations on the basis of ethylene concentration ($C_{ethylene}$, mol L^{-1} atm^{-1}).[24] Beyond the same tendency of catalytic behavior performed the cobalt precatalysts, the better adjusted activity was observed in the catalytic system **C1**/MAO at 40 °C (run 8, Table 2), indicating favorable activation at a slightly elevated temperature.

2.2.2. Ethylene Polymerization. Encouraged with observing trace amounts of polyethylene obtained at 80 °C and 10 atm ethylene using **C1** and with regard to the ethylene polymerization by their iron analogues,[21a] we explored in detail the catalytic system of **C1**/MAO under 30 atm of ethylene with varying reaction temperature and Al/Co molar ratios. According to the results (runs 1–4, Table 3), higher activities were achieved at higher temperature. The adjusted activities, on the basis of ethylene concentration at different reaction temperatures, showed a higher value at elevated temperature, giving higher stable active species at 100 °C. The optimum Al/Co molar ratio was found to be 3000 at 100 °C, which was observed through varying the Al/Co ratios (runs 4–8, Table 3). Under the optimum catalytic conditions, the other precatalysts **C2**–**C14** were investigated and also showed high activities in ethylene polymerization (runs 9–21, Table 3). With regard to the influences of R^1 substituents on the catalytic performances of their cobalt complexes, shown with the series of cobalt complexes with R^2 = H, the catalytic activities gave the order R^1 = Me (**C1**) > Ph (**C11**) > Pr (**C7**) > Et (**C3**); meanwhile, the catalytic activities of cobalt precatalysts with R^1 = Et showed the order with R^2 substituent as Me (**C4**) > Et (**C5**) > *i*Pr (**C6**). This is the similar to the trend obtained for their iron analogues.[21a] Moreover, the precatalyst **C3** (R^2 = H) also showed higher catalytic activity, indicating the possible formation of the anionic amide or N–Al species when adding aluminum cocatalyst.[7]

The GPC measurements of the resulting polyethylenes showed high molecular weights ranging from 97 kg/mol to 891 kg/mol and relative narrow molecular distributions from 2.6 to 5.4. Employing a higher reaction temperature (runs 1–4, Table 3) or higher Al/Co molar ratio (runs 4–8, Table 3) gave polyethylenes with lower molecular weights. Such phenomena

Table 2. Ethylene Oligomerization by Cobalt Precatalysts **C1**−**C14**[a]

										oligomer distribn/%[b]				
run	compd	cocat.	P/atm	Al/Co	T/°C	product yield/mg	K	activity[b]	adjusted activity[c]	$C_4/\Sigma C$	$C_6/\Sigma C$	$C_8/\Sigma C$	$C_{10}/\Sigma C$	$C_{\geq 12}/\Sigma C$
1	**C1**	MMAO	1	1000	20	57.3		22.8	16.10	83.2	16.8			
2	**C1**	$i\text{Bu}_3\text{Al}$	1	500	20	78.2		31.3	22.10	95.3	4.7			
3	**C1**	MAO	1	1000	20	72.2	0.62	28.9	20.41	39.2	15.3	12.1	10.1	23.3
4	**C1**	MAO	10	1000	20	121	0.59	4.84	3.42	42.1	22.0	12.7	9.2	14.0
5	**C1**	MAO	10	1250	20	242	0.44	9.68	6.84	36.8	29.3	17.0	9.1	7.8
6	**C1**	MAO	10	1500	20	297	0.53	11.9	8.40	35.8	28.3	15.3	7.6	13.0
7	**C1**	MAO	10	2000	20	49.4	0.54	1.96	1.38	37.1	24.5	15.2	8.8	14.4
8	**C1**	MAO	10	1500	40	244	0.48	9.77	8.88	66.1	16.6	8.8	5.0	3.5
9	**C1**	MAO	10	1500	60	156	0.55	6.25	7.42	68.2	18.7	6.5	4.0	2.6
10	**C2**	MAO	10	1500	20	218	0.58	8.71	6.15	36.0	29.3	17.1	10.9	6.7
11	**C3**	MAO	10	1500	20	597	0.56	23.9	16.88	41.7	23.6	13.0	8.1	13.6
12	**C4**	MAO	10	1500	20	485	0.58	19.4	13.70	42.3	24.8	12.7	7.0	13.2
13	**C5**	MAO	10	1500	20	199	0.51	7.95	5.61	39.1	22.8	10.3	8.6	19.2
14	**C6**	MAO	10	1500	20	50.3	0.48	2.01	1.42	38.3	22.4	11.9	9.1	17.2
15	**C7**	MAO	10	1500	20	747	0.46	29.9	21.12	37.3	25.8	14.2	8.9	13.6
16	**C8**	MAO	10	1500	20	537	0.48	21.5	15.18	32.3	21.2	14.7	9.9	21.9
17	**C9**	MAO	10	1500	20	372	0.53	14.9	10.52	37.3	29.1	16.9	8.1	8.6
18	**C10**	MAO	10	1500	20	82.5	0.55	3.30	2.33	30.3	25.5	18.0	12.4	13.8
19	**C11**	MAO	10	1500	20	425	0.51	17.0	12.01	37.7	27.4	18.8	11.1	5.0
20	**C12**	MAO	10	1500	20	362	0.54	14.5	10.24	38.2	22.4	16.7	10.9	11.8
21	**C13**	MAO	10	1500	20	327	0.51	13.1	9.25	59.6	21.3	9.1	3.9	6.1
22	**C14**	MAO	10	1500	20	26.3	0.52	1.04	0.73	46.9	26.1	11.8	6.1	9.1

[a] General conditions: 5 μmol of Co; 30 min; toluene (30 mL at 1 atm; 100 mL at 10 atm). [b] Activity in units of 10^3 g (mol of Co)$^{-1}$ h^{-1} atm^{-1}, determined by GC; ΣC signifies the total amount of oligomers. [c] Adjusted activity: 10^4 g (mol of Co)$^{-1}$ h^{-1} C^{-1}_{ethylene}.

Table 3. Ethylene Polymerization by Cobalt Precatalysts **C1**−**C14**/MAO[a]

run	complex	Al/Co	T/°C	PE yield/g	activity[b]	adjusted activity[c]	$10^{-4}M_w$[d]	M_w/M_n[d]
1	**C1**	3000	40	0.533	1.78	1.61	89.1	5.1
2	**C1**	3000	60	1.78	5.93	7.05	59.7	2.7
3	**C1**	3000	80	2.33	7.77	11.5	37.5	3.2
4	**C1**	3000	100	3.04	10.1	18.3	14.3	3.0
5	**C1**	2000	100	1.72	5.73	10.3	35.8	3.8
6	**C1**	2500	100	2.48	8.27	14.9	20.6	3.3
7	**C1**	3500	100	3.07	10.2	18.5	14.2	3.6
8	**C1**	4000	100	3.08	10.3	18.5	9.7	2.6
9	**C2**	3000	100	3.30	11.0	19.9	15.2	3.0
10	**C3**	3000	100	1.38	4.60	8.30	16.5	2.9
11	**C4**	3000	100	2.30	7.66	1.38	18.6	2.9
12	**C5**	3000	100	1.37	4.57	8.24	19.2	3.1
13	**C6**	3000	100	1.01	3.37	6.08	20.3	3.0
14	**C7**	3000	100	1.49	4.97	8.97	20.7	3.0
15	**C8**	3000	100	2.32	7.73	14.0	24.0	3.2
16	**C9**	3000	100	1.39	4.63	8.36	24.9	4.4
17	**C10**	3000	100	1.12	3.73	6.74	26.6	2.7
18	**C11**	3000	100	1.54	5.13	9.27	24.5	5.3
19	**C12**	3000	100	3.09	10.3	18.6	25.5	5.4
20	**C13**	3000	100	1.62	5.40	9.75	25.8	4.8
21	**C14**	3000	100	1.16	3.87	6.98	28.1	4.6

[a] Conditions: 2 μmol of Co; MAO; 30 atm of ethylene; 30 min; toluene (40 mL). [b] Observed activity: 10^4 g (mol of Co)$^{-1}$ h^{-1} atm^{-1}. [c] Adjusted activity: 10^5 g (mol of Co)$^{-1}$ h^{-1} C^{-1}_{ethylene}. [d] Determined by GPC.

were consistent with the suggestion of the extreme sensitivity for chain transfer to aluminum species occurring for the chain termination.[25] In general, the more bulky the substituent used at the 2-position of the quinoline rings, the higher the molecular weight obtained. The precatalysts containing more electron-donating alkyl (R^2) groups produced polyethylenes with higher molecular weights, which is similar to the results reported in the literature.[26] In comparison with polyethylenes obtained by their iron analogues,[21a] the polyethylenes produced by the cobalt precatalysts have narrower molecular distributions. The polyethylenes obtained by complexes **C3**, **C8**, and **C14** (runs 10, 15, and 21, Table 3) were characterized by ^{1}H and ^{13}C NMR at 90 °C in bromobenzene-d_5, and each showed a single peak in the ^{1}H NMR and ^{13}C NMR spectra, indicating the feature of highly linear polyethylene with high molecular weight. Though there is no direct evidence for their active species, two individual species are supposed for ethylene reactivity of either oligomerization or polymerization. Further investigations are still ongoing for the determination of active species and mechanism by experimental and simulation research.

3. CONCLUSIONS

Cobalt(II) complexes bearing 8-(benzoimidazol-2-yl)quinolines, activated with MAO, showed unique properties: ethylene oligomerization at relatively low ethylene pressure and low reaction temperature but high ethylene polymerization at 30 atm and high reaction temperature. The resultant polymers possessed high molecular weights with narrow molecular weight distributions. The current bidentate cobalt precatalysts show good thermal stability in ethylene polymerization. The nature of the ligands finely adapted the catalytic behaviors of their cobalt complexes. Two active species could be formed for ethylene oligomerization and polymerization. Further investigations are still ongoing to determine the active species and mechanism by experimental and simulation research.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium benzophenone and distilled under argon prior to use. Methylaluminoxane (MAO, 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. Elemental analysis was carried out using an HPMOD 1106 microanalyzer. GC analysis was performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yield of oligomers was calculated by reference to the mass of the solvent on the basis of the prerequisite that the mass of each fraction was approximately proportional to its integrated area in the GC trace. Selectivity for the linear α-olefin was defined as (amount of linear α-olefin of all fractions)/(total amount of oligomer products) in percent. The activities of ethylene polymerization were calculated on the basis of isolated polyethylenes. A microwave oven, the Midea PJ21B-A (800 W, 21 L), was used for microwave-assisted condensation reactions. ^{1}H and ^{13}C NMR spectra of the PE samples were recorded on a Bruker DMX 200 MHz instrument at 90 °C in bromobenzene-d_5 using TMS as the internal standard.

4.2. Synthesis of Cobalt Complexes C1–C14. The cobalt complexes **C1**–**C14** were synthesized by the reaction of $CoCl_2$ with the corresponding ligand in ethanol. A typical synthetic procedure for **C1** can be described as follows. To a mixture of ligand **L1** (78 mg, 0.3 mmol) and $CoCl_2$ (39 mg, 0.3 mmol) was added ethanol (4 mL) at room temperature. The solution turned blue immediately. The reaction mixture was stirred for 6 h, and absolute diethyl ether was added. The resulting precipitate was filtered, washed with diethyl ether, and dried under vacuum to furnish the pure product as a blue powder (107.1 mg, 0.275 mmol) in 92.1% yield. IR (KBr; cm^{-1}): 3210, 3056, 1604, 1570, 1514, 1432, 1411, 844, 772, 762, 743. Anal. Calcd for $C_{17}H_{13}Cl_2CoN_3$ (389.14): C, 52.47; H, 3.37; N, 10.80. Found: C, 52.57; H, 3.25; N, 10.63.

Complex **C2** was obtained as a blue powder in 90.2% yield. IR (KBr; cm^{-1}): 3055, 1607, 1567, 1512, 1474, 1463, 1432, 1391, 851, 774, 760, 750. Anal. Calcd for $C_{18}H_{15}Cl_2CoN_3$ (403.17): C, 53.62; H, 3.75; N, 10.42. Found: C, 53.24; H, 3.80; N, 10.24.

Complex **C3** was obtained as a blue powder in 92.3% yield. IR (KBr; cm^{-1}): 3180, 2976, 1606, 1515, 1416, 1296, 1151, 1043, 852, 748, 677. Anal. Calcd for $C_{18}H_{15}Cl_2CoN_3$ (403.17): C, 53.62; H, 3.75; N, 10.42. Found: C, 53.66; H, 4.08; N, 10.12.

Complex **C4** was obtained as a blue powder in 90.5% yield. IR (KBr; cm^{-1}): 2986, 1611, 1506, 1466, 1296, 1203, 1051, 856, 786, 746, 678. Anal. Calcd for $C_{19}H_{17}Cl_2CoN_3$ (417.20): C, 54.70; H, 4.11; N, 10.07. Found: C, 54.61; H, 4.09; N, 9.98.

Complex **C5** was obtained as a blue powder in 91.2% yield. IR (KBr; cm^{-1}): 3057, 1606, 1564, 1513, 1432, 967, 845, 759, 721. Anal. Calcd for $C_{20}H_{19}Cl_2CoN_3$ (431.22): C, 55.71; H, 4.44; N, 9.74. Found: C, 55.44; H, 4.07; N, 9.76.

Complex **C6** was obtained as a blue powder in 89.1% yield. IR (KBr; cm^{-1}): 2986, 1602, 1507, 1465, 1206, 1066, 854, 784, 751, 678. Anal. Calcd for $C_{21}H_{21}Cl_2CoN_3$ (445.25): C, 56.65; H, 4.75; N, 9.44. Found: C, 56.46; H, 4.55; N, 9.79.

Complex **C7** was obtained as a blue powder in 92.5% yield. IR (KBr; cm^{-1}): 3214, 2960, 1603, 1511, 1412, 1330, 1146, 839, 750, 677. Anal. Calcd for $C_{19}H_{17}Cl_2CoN_3$ (417.20): C, 54.70; H, 4.11; N, 10.07. Found: C, 54.51; H, 4.14; N, 9.91.

Complex **C8** was obtained as a blue powder in 92.5% yield. IR (KBr; cm^{-1}): 2970, 1607, 1462, 1394, 1127, 1084, 853, 759, 677. Anal. Calcd for $C_{20}H_{19}Cl_2CoN_3$ (431.22): C, 55.71; H, 4.44; N, 9.74. Found: C, 55.58; H, 4.55; N, 9.40.

Complex **C9** was obtained as a blue powder in 90.1% yield. IR (KBr; cm^{-1}): 2964, 1608, 1572, 1457, 1431, 1335, 1088, 855, 784, 748, 678. Anal. Calcd for $C_{21}H_{21}Cl_2CoN_3$ (445.25): C, 56.65; H, 4.75; N, 9.44. Found: C, 56.37; H, 4.75; N, 9.21.

Complex **C10** was obtained as a blue powder in 93.2% yield. IR (KBr; cm^{-1}): 2974, 1609, 1462, 1395, 1296, 1096, 849, 785, 741, 677. Anal. Calcd for $C_{22}H_{23}Cl_2CoN_3$ (459.28): C, 57.53; H, 5.05; N, 9.15. Found: C, 57.88; H, 5.29; N, 9.11.

Complex **C11** was obtained as a blue powder in 75.8% yield. IR (KBr; cm^{-1}): 3054, 1607, 1566, 1511, 1444, 1408, 1328, 1148, 848, 760, 746, 707, 681. Anal. Calcd for $C_{22}H_{15}Cl_2CoN_3$ (451.21): C, 58.56; H, 3.35; N, 9.31. Found: C, 58.34; H, 3.45; N, 9.26.

Complex **C12** was obtained as a blue powder in 71.6% yield. IR (KBr; cm^{-1}): 3057, 2940, 1598, 1571, 1487, 1474, 1454, 1423, 1288, 845, 770, 750, 696. Anal. Calcd for $C_{23}H_{17}Cl_2CoN_3$ (465.24): C, 59.38; H, 3.68; N, 9.03. Found: C, 59.68; H, 3.99; N, 9.18.

Complex **C13** was obtained as a blue powder in 72.4% yield. IR (KBr; cm^{-1}): 3058, 2875, 1599, 1571, 1487, 1452, 1418, 1279, 1016, 845, 769, 749, 697. Anal. Calcd for $C_{24}H_{19}Cl_2CoN_3$ (479.27): C, 60.15; H, 4.00; N, 8.77. Found: C, 60.46; H, 4.25; N, 8.95.

Complex **C14** was obtained as a blue powder in 69.9% yield. IR (KBr; cm^{-1}): 3053, 2984, 1600, 1571, 1488, 1454, 1429, 1413, 1289, 1158, 1092, 849, 758, 697. Anal. Calcd for $C_{25}H_{21}Cl_2CoN_3$ (493.29): C, 60.87; H, 4.29; N, 8.52. Found: C, 61.14; H, 4.05; N, 8.74.

4.3. Procedure for Ethylene Oligomerization and Polymerization. Ethylene oligomerization at 1 atm of ethylene pressure was carried out as follows: the catalyst precursor was dissolved in toluene in a Schlenk tube, and the reaction solution was stirred with a magnetic stir bar under an ethylene atmosphere (1 atm), with the reaction temperature being controlled by a water bath. Cocatalyst was added by a syringe. After a limited time, the reaction was terminated by acidified water, and the products were analyzed by GC.

Ethylene oligomerization 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 kept with 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) to determine the composition and mass distribution of oligomers obtained.

Ethylene polymerization 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 (1.46 mol/L solution in toluene) were added into the autoclave in the 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 reaction, and the mixture was cooled to room temperature. Then the residual reaction solution was quenched with 5% hydrochloric acid in ethanol. The precipitated polymer was collected by filtration, adequately washed with ethanol and water, and then dried under vacuum to constant weight.

4.4. X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **C1**−**C3** and **C8** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.710\,73$ 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 H atom on the N atom of benzoimidazole in **C1** was calculated from a difference Fourier diagram. Other hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[27] Crystal data collection and refinement details for these compounds are available in the Supporting Information.

■ ASSOCIATED CONTENT

S Supporting Information. A table giving crystal data and processing parameters for complexes **C1**−**C3** and **C8** and CIF files giving X-ray crystal structure data for these complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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