

# **Biphenyl-bridged 6-(1-aryliminoethyl)-2-iminopyridyl-cobalt complexes: Synthesis, characterization and ethylene polymerization behavior**

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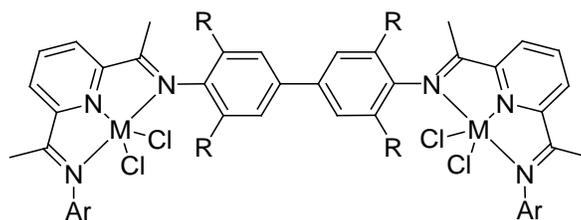
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**Abstract:** A series of biphenyl-bridged 6-(1-aryliminoethyl)-2-iminopyridine derivatives were reacted with cobalt dichloride in dichloromethane/ethanol to afford the corresponding binuclear cobalt complexes. The cobalt complexes were characterized by FT-IR spectroscopy and elemental analysis, and the structure of a representative complex was confirmed by single-crystal X-ray diffraction. Upon activation with either MAO or MMAO, these cobalt complexes performed with high activities of up to  $1.2 \times 10^7$  g·mol<sup>-1</sup>(Co)·h<sup>-1</sup> in ethylene polymerization, which represents one of the most active cobalt-based catalytic systems in ethylene reactivity. These biphenyl-bridged bis(imino)pyridylcobalt pre-catalysts exhibited higher activities than did their mononuclear bis(imino)pyridylcobalt pre-catalyst counterparts, and more importantly, the

binuclear pre-catalysts revealed a better thermo-stability and longer lifetimes. The polyethylenes obtained were characterized by GPC, DSC and high temperature NMR spectroscopy, and mostly possessed unimodal and highly linear features.

## Introduction

2,6-Bis(imino)pyridylmetal (iron or cobalt) complexes were found to act as highly active pre-catalysts in ethylene polymerization back in the 1990s.<sup>1</sup> Subsequently, researchers from both academia and industry have extensively explored various ligand sets through modification of 2,6-bis(imino)pyridine derivatives<sup>2</sup> and designing new heterocyclic compounds,<sup>3</sup> including examples based on nonsymmetrical 2,6-bis(imino)pyridines,<sup>4</sup> 2-benzimidazolyl-6-iminopyridines,<sup>5</sup> 6-(quinoxalin-3-yl)-2-imino-pyridines,<sup>6</sup> 2-imino-1,10-phenanthrolines,<sup>7</sup> 2-(2-benzimidazolyl)-1,10-phenanthrolines,<sup>7</sup> 2-(benzoxazolyl)-1,10-phenanthrolines,<sup>8</sup> *N*-((pyridin-2-yl)methylene)-8-aminoquinolines<sup>9</sup> and 2,8-bis(imino)quinolines.<sup>10</sup> In addition, multinuclear complex pre-catalysts are now attracting attention,<sup>11</sup> and progress in this area has been discussed in a recent review article.<sup>12</sup>



**Scheme 1.** Biphenyl-bridged 2,6-bis(imino)pyridylmetal complex pre-catalysts  
(M = Fe<sup>13</sup> and currently Co).

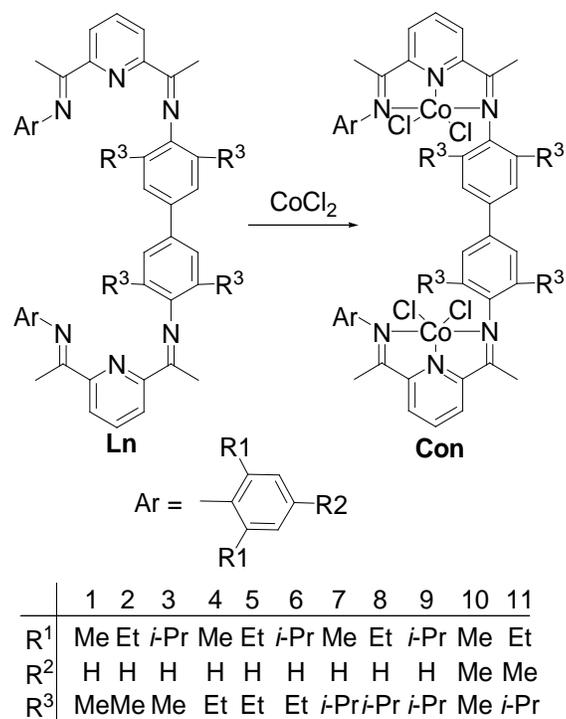
Binuclear complexes and their catalytic behavior in ethylene reactivity have also been an important topic in our research group.<sup>14</sup> Recently, the biphenyl-bridged 2,6-bis(imino)pyridyliron

complexes were revisited and were shown to exhibit high ethylene polymerization activity with enhanced thermo-stability. However, all attempts to elucidate their molecular structures were unsuccessful due to poor quality crystals. Now in subsequent work, the cobalt analogues have been synthesized and single crystals suitable for X-ray diffraction studies have been obtained. Moreover, the cobalt analogues performed with high activity in ethylene polymerization producing linear polyethylene, and this is one of most active cobalt pre-catalysts reported. Herein, the synthesis and characterization of the cobalt complexes are reported, and the ethylene polymerization behavior is discussed.

## Results and discussion

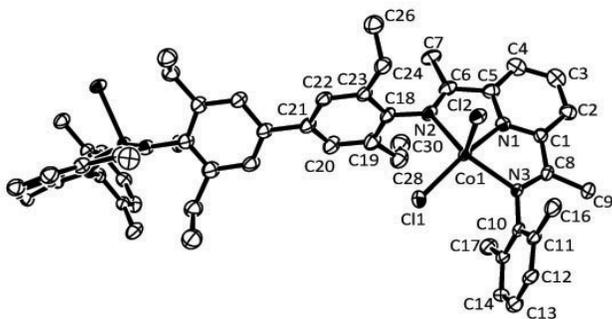
### Synthesis and characterization of the organic compounds and their cobalt complexes

Using the method reported for our previous iron work,<sup>13</sup> the *N,N'*-bis(1-(6-(1-(arylimino)ethyl)pyridin-2-yl)ethylidene)benzidines (**L1** – **L11**) were reacted with cobalt(II) dichloride in the mixture of dichloromethane/ethanol to afford the corresponding binuclear cobalt complexes in good yield (**Co1** – **Co11**, Scheme 2). All cobalt complexes were consistent with their elemental analyses, whilst effective coordination to cobalt was reflected in the FT-IR spectra, where the C=N stretching vibration bands appeared in the range of 1620 – 1632 cm<sup>-1</sup> for cobalt complexes *versus* 1639 – 1650 cm<sup>-1</sup> for the free organic compounds. In addition, the identity of the cobalt complexes was also verified by MALDI-TOF measurements.



**Scheme 2.** Synthetic procedure for the cobalt complexes.

**Single Crystal X-ray diffraction study.** Single crystals of complex **Co4** were grown from a mixture of dichloromethane and methanol (about v/v ratio as 2/1). The molecular structure of **Co4** was confirmed by single crystal X-ray diffraction, and the structure is shown in Figure 1; selected bond lengths and angles are collected in Table 1.



**Fig. 1** ORTEP drawing of **Co4** with thermal ellipsoids at 30 % probability level. Hydrogen atoms have been omitted for clarity.

**Table1** Selected bond lengths (Å) and angles (°) for complex **Co4**

Bond lengths (Å)	
N(2) -C(6)	1.256(10)
N(2)- (18)	1.444(9)
N(3) -C(8)	1.291(8)
N(3) -C(10)	1.448(9)
N(1)- C(1)	1.361(9)
N(1)- C(5)	1.380(9)
Co(1)-N(1)	2.038(6)
Co(1)-N(3)	2.185(5)
Co(1)-N(2)	2.188(6)
Bond angles (°)	
C(1)- N(1)-C(5)	120.6(6)
C(6)-N(2)- (18)	121.4(7)
C(8)-N(3)-C(10)	122.4(5)
N(1)-Co(1)-Cl(1)	155.12(16)
N(3)-Co(1)-Cl(2)	103.87(14)
N(2)-Co(1)-Cl(2)	98.81(16)
Cl(1)-Co(1)-Cl(2)	111.77(8)

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Compared to the previously determined structure of the organic compound **L5** which contains similar C=N bond lengths such as N(2) - C(6) at 1.267(5) Å and N(3) - C(8) at 1.268(6) Å,<sup>13</sup> the corresponding C=N lengths within the complex **Co4** revealed one shorter N(2) - C(6) at 1.256(10) Å and one longer N(3) - C(8) at 1.291(8) Å; meanwhile the single-bond C - N lengths of compound **L5** are N(2) - C(20) at 1.432(5) Å and N(3) - C(10) at 1.427(6) Å, the C - N

lengths of complex **Co4** are N(2) - (18) at 1.444(9) Å and N(3) – C(10) at 1.448(9) Å. These indicate the effective coordination with the cobalt center, meanwhile the electron-donation to cobalt resulted **in** weak bonding between the nitrogen and its nearby carbons and **is** illustrated by longer bond lengths. In addition, there are significant differences in the dihedral angles between nearby aryl planes: the co-planar nature of the two benzene rings within the tetraalkylbenzidine motif in organic **L5**<sup>13</sup> distorted into a dihedral angle of 33.39 ° within complex **Co4**; the pyridyl plane is almost perpendicular to the phenyl plane of the benzidine with a dihedral angle of *ca.* 88.77° in **L5** versus the angle of *ca.* 72.50 ° within complex **Co4**, meanwhile the dihedral angle between the pyridyl and phenyl of the aniline is observed at *ca.* 86.71 ° in **L5** versus *ca.* 72.79 ° for complex **Co4**. Within complex **Co4**, there are no direct bonding interactions between the two cobalt atoms, and there is no conjugated interaction between **the** two phenyl planes within **the** tetraalkylbenzidine motif.

**Catalytic Behavior toward Ethylene Polymerization.** The co-catalysts such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) have been commonly employed to activate cobalt complex pre-catalysts,<sup>5</sup> and this was confirmed to be true in the current work. The complex **Co3** was used to optimize catalytic parameters in the presence of methylaluminoxane (MAO), and results are tabulated in Table 2.

**Table 2** Ethylene polymerization with cobalt complexes <sup>a</sup>

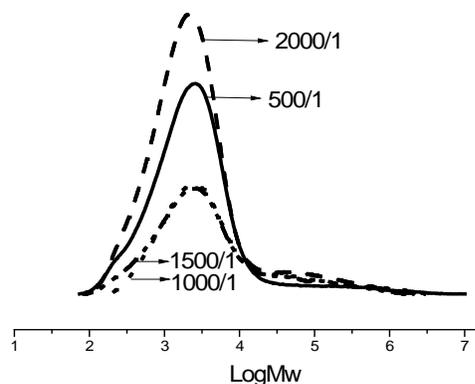
Entry	Pre-cat	Co-cat.	Al/Co	T/°C	t/min	Activity <sup>b</sup>	$M_w^c / 10^3$ g.mol <sup>-1</sup>	$M_w/M_n^c$	$T_m^d / °C$
1	<b>Co3</b>	MAO	500	40	30	5.0	26.2	20.2	125.7
2	<b>Co3</b>	MAO	1000	40	30	6.2	46.8	23.3	130.8
3	<b>Co3</b>	MAO	1500	40	30	5.1	28.0	18.3	128.8

4	<b>Co3</b>	MAO	2000	40	30	4.4	19.9	15.3	126.0
5	<b>Co3</b>	MAO	1000	50	30	6.7	120.6	27.3	131.4
6	<b>Co3</b>	MAO	1000	60	30	4.3	32.8	10.2	129.6
7	<b>Co3</b>	MAO	1000	70	30	2.8	10.0	4.20	128.6
8	<b>Co1</b>	MAO	1000	50	15	12	1.60	2.10	120.9
9	<b>Co1</b>	MAO	1000	50	30	7.3	1.80	2.20	124.4
10	<b>Co1</b>	MAO	1000	50	45	5.9	2.00	2.50	121.6
11	<b>Co1</b>	MAO	1000	50	60	4.7	1.90	2.60	122.1
12 <sup>e</sup>	<b>Co1</b>	MAO	1000	50	30	0.3	1.30	2.80	104.6
13 <sup>f</sup>	<b>Co1</b>	MAO	1000	50	30	4.1	1.70	2.40	122.6
14	<b>Co1</b>	MMAO	1500	30	30	3.8	1.40	2.00	117.0
15	<b>Co1</b>	MMAO	1500	40	30	4.5	1.10	2.50	116.5
16	<b>Co1</b>	MMAO	1500	50	30	3.6	1.70	2.60	115.8
17	<b>Co1</b>	MMAO	1500	60	30	2.0	1.80	2.60	115.1
18	<b>Co1</b>	MMAO	1500	70	30	0.9	2.00	2.90	112.9
19	<b>Co1</b>	MMAO	500	50	30	1.1	2.30	3.00	121.1
20	<b>Co1</b>	MMAO	1000	50	30	6.0	1.80	2.60	114.6
21	<b>Co1</b>	MMAO	2000	50	30	3.1	1.60	2.30	115.5

<sup>a</sup> General conditions: 1.5  $\mu\text{mol}$  Co; 100 mL of toluene; 10 atm ethylene. <sup>b</sup>  $10^6$  g (PE)  $\text{mol}^{-1}$  (Co)  $\text{h}^{-1}$ . <sup>c</sup> Determined by GPC. <sup>d</sup> Determined by DSC. <sup>e</sup> 1 atm ethylene. <sup>f</sup> 5 atm ethylene.

With the reaction temperature fixed at 40 °C, variation of the molar ratio Al/Co was investigated (entries 1-4, Table 2), and the best activity was obtained with Al/Co ratio at 1000:1 (entry 2, Table 2). The GPC data generally revealed a wider polydispersity for the polyethylene formed (Figure 2); moreover, the polyethylene obtained at the Al/Co ratio 1000:1 showed a higher molecular weight. The higher the Al/Co ratios used (entries 2-4, Table 2), the lower the

molecular weight of the obtained polyethylene; which is ascribed to increased chain-transfer occurring at higher concentrations of co-catalyst.<sup>3,15</sup>

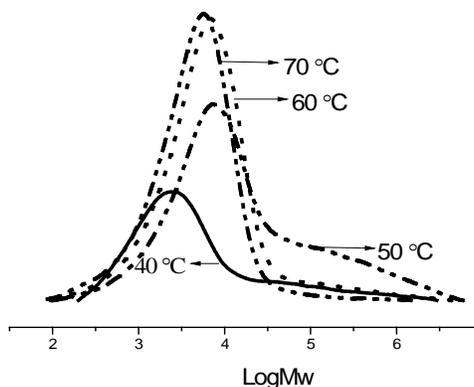


**Fig. 2** GPC curves of polyethylenes obtained with different ratios of Al/Co (entries 1-4, Table 2)

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With the Al/Co molar ratio fixed at 1000, the influence of the reaction temperature was investigated over the range 40 to 70 °C (entry 2, entries 5-7, Table 2), which indicated an optimum temperature of *ca* 50 °C (entry 5, Table 2). The higher the reaction temperature employed (entries 5-7, Table 2), the lower the molecular weights of the polyethylene obtained (Figure 3). This is consistent with **increased** chain-transfer occurring at higher temperature.<sup>3,8,15</sup> **On** comparison with temperature above 50 °C (entries 5-7, Table 2), however, the reaction at 40 °C could not **readily activate the active species thereby** resulting in **the observed** lower activity (entry 2, Table 2). **N**arrower polydispersity of the obtained polyethylene was achieved at higher temperature, indicating single site active species (entries 6 and 7, Table 2) were operating. A common short coming of late-transition metal complex pre-catalysts is to lose activity at elevated reaction temperatures,<sup>3</sup> however the current binuclear cobalt pre-catalysts exhibited better

thermo-stability and higher activities in comparison to their mono-nuclear analogues<sup>1</sup> and other tridentate cobalt complex pre-catalysts.<sup>5,8,9</sup>



**Fig. 3** GPC traces of polyethylenes produced by cobalt complexes at different reaction temperature.

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Employing the optimized parameters, namely an Al/Co molar ratio of 1000:1 at 50 °C, the Co1/MAO system was extensively investigated to understand its life time (entries 8-11, Table 2). Within 15 minutes, the activity was as high as  $10^7 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$ , which is one of highest observed for cobalt complex pre-catalysts. Prolonging the reaction period from 15, 30, 45 and 60 min, resulted in the activities gradually falling, with the activity reaching  $4.7\times 10^6 \text{ g}\cdot\text{mol}^{-1}(\text{Co})\cdot\text{h}^{-1}$  over 60 minutes. This illustrates the favorable stability of the active species in such catalytic systems. Another important parameter is ethylene pressure, and it was found that the catalytic activity increased with increasing ethylene pressure (entries 9, 12, and 13, Table 2). The higher the ethylene pressure used, the better the activity observed with the catalytic reaction. Indeed, when the ethylene pressure was increased to 10 atm, the activity observed was more than twice that observed at 5 atm.

Using the co-catalyst modified methylaluminoxane (MMAO), the catalytic behavior of complex **Co1** was explored with various parameters (entries 14-21, Table 2). Similar catalytic tendencies were observed on variation of the reaction temperature and the Al/Co molar ratio. Moreover, it is worth emphasizing that there were no oligomers detected by GC from the reaction solutions involving all such polymerization procedures. Therefore the current model pre-catalysts showed higher activity and better thermo-stability than did those of the analogous systems, and the application for polyethylene production is promising given the lack of by-products such as oligomers.<sup>16</sup>

In comparison with **Co1**/MAO, the **Co3**/MMAO system generally exhibited relative lower activities, although similar molecular weights and polydispersity were observed for the polyethylene produced in the catalytic systems using either MAO or MMAO. Therefore all cobalt complex pre-catalysts were investigated with the co-catalyst of MAO under the Al/Co molar ratio 1000 at 50 °C with 30 min; their results are tabulated in Table 3.

**Table 3** Ethylene polymerization with complexes **Con**/MAO <sup>a</sup>

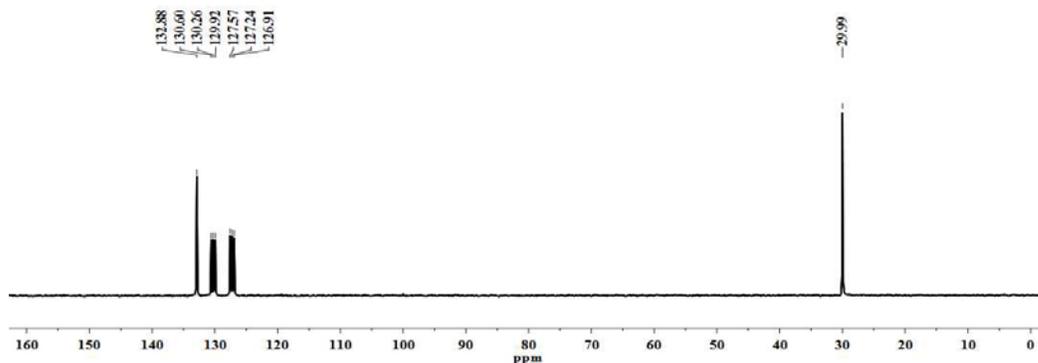
Entry	Pre-catalyst	Yield/g	Activity <sup>b</sup>	$M_w^c / 10^3$ g.mol <sup>-1</sup>	$M_w/M_n^c$	$T_m^d /$ °C
1	<b>Co1</b>	11.0	7.3	1.8	2.0	122.4
2	<b>Co2</b>	10.2	6.8	7.9	5.3	126.9
3	<b>Co3</b>	10.0	6.7	120.6	27.3	131.1
4	<b>Co4</b>	10.5	7.0	4.7	4.0	124.6
5	<b>Co5</b>	5.9	3.9	7.6	3.3	129.0
6	<b>Co6</b>	2.0	1.3	20.9	3.0	131.7

7	<b>Co7</b>	11.6	7.7	10.8	2.3	130.0
8	<b>Co8</b>	6.8	4.5	15.0	1.9	132.4
9	<b>Co9</b>	3.2	2.1	25.5	2.6	133.4
10	<b>Co10</b>	8.3	5.5	4.0	4.1	124.2
11	<b>Co11</b>	1.4	0.9	11.1	1.5	132.9

<sup>a</sup> General conditions: 1.5  $\mu\text{mol}$  Co; 100 mL toluene for 10 atm ethylene and MAO for the co-catalyst at 50 °C with Al/Co ratio at 1000/1; time for 30 min. <sup>b</sup>  $10^6$  g (PE)  $\text{mol}^{-1}$  (Co)  $\text{h}^{-1}$ . <sup>c</sup> Determined by GPC. <sup>d</sup> Determined by DSC.

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According to the Table 3, with the substituent R3 fixed, the activities of the pre-catalysts decreased with a bulkier substituent R1 within the **Co1-Co9** family (entries 1-9, Table 3), illustrating the *ortho*-bulkier substituent hindered coordination of ethylene to the active species.<sup>4</sup> With regard to the additional substituent R2, positive influences were achieved by the pre-catalysts **Co10** and **Co11** in comparison with the analogs **Co1** and **Co6** (entry 1 *versus* entry 10, entry 6 *versus* entry 11, Table 3), which is ascribed to the better solubility of the complexes bearing more alkyl substituents. In general, the obtained polyethylenes have higher molecular weights for complexes bearing bulkier substituents (entries 1-3, entries 4-6, entries 7-9, Table 3), indicating that the active species were protected by such bulkier substituents. In all cases, the binuclear cobalt complexes exhibited higher activity and better thermo-stability than did the mono-nuclear analogs<sup>1</sup> and related binuclear analogs.<sup>16</sup> Compared to their iron analogs,<sup>13</sup> the cobalt complex pre-catalysts exhibited better lifetimes and produced polyethylene of lower molecular weight and narrower polydispersity. The melting points of the resultant polyethylenes were generally higher than 122 °C, consistent with highly linear features for the obtained polyethylene. To verify the linearity, the <sup>13</sup>C NMR spectrum of the polyethylene (entry 3, Table 3) was recorded in dichlorobenzene and revealed a single peak (Figure 4).



**Fig. 4** The <sup>13</sup>C NMR spectrum of the polyethylene produced by **Co3** (entry 3, Table 3).

## Conclusion

Binuclear biphenyl-bridged 6-(1-aryliminoethyl)-2-iminopyridcobalt chloride complexes were synthesized and fully characterized, including by single crystal X-ray diffraction for a representative complex. Upon activation with MAO or MMAO, all the binuclear cobalt complex pre-catalysts exhibited high activities towards ethylene polymerization; MAO was a better initiator than MMAO. The current complex pre-catalysts performed with longer lifetimes and better thermo-stability than did their related mono-metallic complexes<sup>1</sup> and other binuclear analogs.<sup>16</sup> The resultant polyethylene generally revealed high linearity. Under optimized conditions, the polyethylene obtained possessed narrow polydispersity, indicating the single-site feature of the active species. Further explorations for higher activities and finely controlled polyethylenes are still progressed in order to match industrial requirements.

## Experimental Section

**General considerations.** All manipulations involving air- and moisture-sensitive compounds were performed using standard Schlenk techniques under a nitrogen atmosphere. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on 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 a Flash EA 1112 micro-analyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. The melting points of polyethylene were measured from the second scanning run on a Perkin-Elmer TA-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere. In the procedure, a sample of about 4.0 mg was heated to 150 °C with a rate of 20 °C /min and kept for 2 min at 140 °C to remove the thermal history and then cooled at a rate of 20 °C /min to -40 °C. <sup>13</sup>C NMR spectra of the polyethylene were recorded on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. The biphenyl-bridged 6-(1-aryliminoethyl)-2-iminopyridine derivatives were prepared according our previous procedure.<sup>13</sup>

According to the procedure for synthesizing their iron analogs,<sup>13</sup> the binuclear cobalt complexes were prepared; and a typical procedure for complex **Co1** is illustrated as follows: *N,N'*-Bis(1-(3-(1-(2,6-dimethylphenylimino)ethyl)pyridin-2-yl)ethylidene)tetramethyl benzidine

**(L1)** (0.074 g, 0.10 mmol) and  $\text{CoCl}_2$  (0.026 g, 0.20 mmol) were combined in  $\text{CH}_2\text{Cl}_2$  (5 mL) and EtOH (5 mL), and stirred for 8 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3×5 mL), then dried under vacuum to afford **Co1** as a yellow solid (0.090 g, 72.0 % yield). FT-IR ( $\text{cm}^{-1}$ ): 2970 (w), 1626 ( $\nu_{\text{C}=\text{N}}$ , m), 1522 (w), 1457 (s), 1436 (s), 1403 (s), 1269 (m), 1248 (m), 1214 (w), 852 (m), 810 (m), 762 (m), 733 (w). Anal. Calcd. For  $\text{C}_{50}\text{H}_{52}\text{N}_6\text{Co}_2\text{Cl}_4$  (996): N, 8.43; C, 60.25; H, 5.26. Found: N, 8.36; C, 59.92; H, 5.71. MS (MALDI-TOF, m/z): 996.16. Found: m/z 984.1  $[\text{M} - \text{CoCl}_4 + \text{CCA}]^+$ , 735.8  $[\text{M} - \text{Co}_2\text{Cl}_4]^+$ .

**Co2:** In a similar manner, the reaction of 0.10 mmol **L2** (0.079 g) and  $\text{CoCl}_2$  (0.026 g, 0.20 mmol) afforded complex **Co2** as a yellow solid (0.10 g, 95.1 % yield). FT-IR ( $\text{cm}^{-1}$ ): 2960 (m), 1630 ( $\nu_{\text{C}=\text{N}}$ , m), 1587 (s), 1448 (m), 1368 (s), 1321 (w), 1263 (s), 1208 (s), 1097 (m), 870 (m), 818 (s), 791 (w), 742 (m), 695 (m). Anal. Calcd. For  $\text{C}_{56}\text{H}_{60}\text{N}_6\text{Co}_2\text{Cl}_4$  (1052): N, 7.98; C, 61.61; H, 5.74. Found: N, 8.06; C, 61.64; H, 5.72. MS (MALDI-TOF, m/z): 1052.23. Found: m/z 1040.1  $[\text{M} - \text{CoCl}_4 + \text{CCA}]^+$ , 852.0  $[\text{M} - \text{CoCl}_4]^+$ .

**Co3:** Complex **Co3** was collected as a yellow solid (0.120 g, 91.0 % yield) within the reaction of 0.10 mmol **L3** (0.084 g) and 0.20 mmol  $\text{CoCl}_2$ . FT-IR ( $\text{cm}^{-1}$ ): 2958 (m), 2019 (w), 1636 ( $\nu_{\text{C}=\text{N}}$ , m), 1584 (s), 1465 (m), 1367 (s), 1322 (w), 1263 (s), 1211 (s), 1101 (m), 892 (w), 807 (s), 762 (m), 739 (m), 697 (w). Anal. Calcd. For  $\text{C}_{58}\text{H}_{68}\text{N}_6\text{Co}_2\text{Cl}_4$  (1108): N, 7.58; C, 62.82; H, 6.18. Found: N, 7.59; C, 62.89; H, 6.10. MS (MALDI-TOF, m/z): 1108.29. Found: m/z 1096.2  $[\text{M} - \text{CoCl}_4 + \text{CCA}]^+$ , 943.1  $[\text{M} - \text{CoCl}_3]^+$ , 908.1  $[\text{M} - \text{CoCl}_4]^+$ , 850.1  $[\text{M} - \text{Co}_2\text{Cl}_4]^+$ .

**Co4:** The reaction of 0.10 mmol **L4** (0.079 g) and 0.20 mmol  $\text{CoCl}_2$  gave complex **Co4** as a yellow solid (0.091 g, 86.5 % yield). FT-IR ( $\text{cm}^{-1}$ ): 2968 (w), 1621 ( $\nu_{\text{C}=\text{N}}$ , m), 1584 (s), 1464 (m), 1369 (s), 1320 (w), 1259 (s), 1210 (s), 1099 (m), 1056 (w), 865 (m), 806 (s), 765 (m) Anal.

Calcd. For  $C_{54}H_{60}N_6Co_2Cl_4$  (1052): N, 7.58; C, 62.82; H, 6.18. Found: N, 7.46; C, 62.69; H, 6.45. MS (MALDI-TOF, m/z): 1052.23. Found: m/z 1040.2 [M -  $CoCl_4$  + CCA]<sup>+</sup>, 887.0 [M -  $CoCl_3$ ]<sup>+</sup>, 852.0 [M -  $CoCl_4$ ]<sup>+</sup>.

**Co5:** The reaction of 0.10 mmol **L5** (0.084 g) and 2 eq.  $CoCl_2$  afforded complex **Co5** as a yellow solid (0.076 g, 63.0 % yield). FT-IR ( $cm^{-1}$ ): 2963 (m), 2163 (w), 1623 ( $\nu_{C=N}$ , m), 1586 (s), 1447 (s), 1368 (s), 1260 (s), 1207 (m), 1105 (w), 1026 (w), 868 (m), 807 (m), 765 (m). Anal. Calcd for  $C_{58}H_{68}N_6Co_2Cl_4$  (1108): N, 7.58; C, 62.82; H, 6.18. Found: N, 7.26; C, 63.20; H, 6.10. MS (MALDI-TOF, m/z): 1108.29. Found: m/z 1096.2 [M -  $CoCl_4$  + CCA]<sup>+</sup>, 908.2 [M -  $CoCl_4$ ]<sup>+</sup>.

**Co6:** The stoichiometric reaction of 0.10 mmol **L6** with  $CoCl_2$  formed complex **Co6** as a yellow solid (0.072 g, 62.0 % yield). FT-IR ( $cm^{-1}$ ): 2962 (m), 1621 ( $\nu_{C=N}$ , m), 1585 (s), 1449 (s), 1370 (s), 1322 (w), 1248 (s), 1208 (m), 1104 (w), 868 (m), 814 (m), 794 (s), 764 (m). Anal. Calcd. For  $C_{62}H_{76}N_6Co_2Cl_4$  (1164): N, 7.21; C, 63.92; H, 6.58. Found: N, 6.96; C, 64.29; H, 6.51. MS (MALDI-TOF, m/z): 1164.35. Found: m/z 1152.3 [M -  $CoCl_4$  + CCA]<sup>+</sup>, 999.2 [M -  $CoCl_3$ ]<sup>+</sup>, 964.2 [M -  $CoCl_4$ ]<sup>+</sup>, 906.2 [M -  $Co_2Cl_4$ ]<sup>+</sup>.

**Co7:** Complex **Co7** was isolated as a yellow solid in 0.070 g (53.0 % yield) in the reaction of 0.10 mmol **L7** (0.084 g) and 0.20 mmol  $CoCl_2$ . FT-IR ( $cm^{-1}$ ): 2958 (m), 1636 ( $\nu_{C=N}$ , m), 1569 (s), 1460 (s), 1362 (s), 1321 (w), 1244 (s), 1200 (m), 1117 (m), 868 (m), 822 (s), 760 (m). Anal. Calcd. For  $C_{58}H_{68}N_6Co_2Cl_4$  (1108): N, 7.58; C, 62.82; H, 6.18. Found: N, 7.57; C, 62.98; H, 6.05. MS (MALDI-TOF, m/z): 1108.29. Found: m/z 1096.3 [M -  $CoCl_4$  + CCA]<sup>+</sup>, 908.1 [M -  $CoCl_4$ ]<sup>+</sup>.

**Co8:** 0.065 g Complex **Co8** as a yellow solid (56.5 % yield) was obtained from the reaction of 0.10 mmol **L8** (0.090 g) and 0.20 mmol  $CoCl_2$ . FT-IR ( $cm^{-1}$ ): 2962 (s), 2019 (w), 1621 ( $\nu_{C=N}$ ,

m), 1585 (s), 1461 (s), 1368 (s), 1320 (m), 1262 (s), 1206 (m), 1104 (m), 870 (m), 806 (m). Anal. Calcd. For  $C_{62}H_{76}N_6Co_2Cl_4$  (1164): N, 7.21; C, 63.92; H, 6.58. Found: N, 6.99; C, 64.14; H, 6.60. MS (MALDI-TOF, m/z): 1164.35. Found: m/z 1152.3 [M - CoCl<sub>4</sub> + CCA]<sup>+</sup>, 999.2 [M - CoCl<sub>3</sub>]<sup>+</sup>, 964.2 [M - CoCl<sub>4</sub>]<sup>+</sup>, 906.2 [M - Co<sub>2</sub>Cl<sub>4</sub>]<sup>+</sup>.

**Co9:** The complex **Co9** as a yellow solid (0.080 g, 55.0 % yield) was precipitated from the reaction of 0.10 mmol **L9** (0.096 g) and 0.20 mmol CoCl<sub>2</sub>. FT-IR (cm<sup>-1</sup>): 2960 (s), 2160 (w), 2019 (w), 1621 (ν<sub>C=N</sub>, m), 1585 (s), 1462 (s), 1368 (s), 1321 (m), 1262 (s), 1207 (m), 1103 (w), 1024 (w), 940 (w), 869 (m), 802 (s). Anal. Calcd. For  $C_{66}H_{84}N_6Co_2Cl_4$  (1220): N, 6.88; C, 64.92; H, 6.93. Found: N, 6.74; C, 65.26; H, 6.89. MS (MALDI-TOF, m/z): 1220.41. Found: m/z 1208.4 [M - CoCl<sub>3</sub> + CCA]<sup>+</sup>, 1055.2 [M - CoCl<sub>3</sub>]<sup>+</sup>, 1020.3 [M - CoCl<sub>4</sub>]<sup>+</sup>, 962.2 [M - Co<sub>2</sub>Cl<sub>4</sub>]<sup>+</sup>.

**Co10:** Complex **Co10** was formed in 0.077 g (75.2 % yield) in the reaction of 0.10 mmol **L10** (0.076 g) and 0.20 mmol CoCl<sub>2</sub>. FT-IR (cm<sup>-1</sup>): 2962 (m), 2030 (w), 1645 (ν<sub>C=N</sub>, w), 1579 (m), 1455 (m), 1366 (s), 1322 (w), 1256 (m), 1208 (s), 1121 (w), 857 (m), 815 (m), 740 (w), 698 (w). Anal. Calcd. For  $C_{52}H_{56}N_6Co_2Cl_4$  (1024): N, 8.20; C, 60.95; H, 5.51. Found: N, 7.81; C, 61.26; H, 5.47. MS (MALDI-TOF, m/z): 1024.20. Found: m/z 1012.3 [M - CoCl<sub>4</sub> + CCA]<sup>+</sup>, 859.1 [M - CoCl<sub>3</sub>]<sup>+</sup>, 824.1 [M - CoCl<sub>4</sub>]<sup>+</sup>, 766.1 [M - Co<sub>2</sub>Cl<sub>4</sub>]<sup>+</sup>.

**Co11:** Compound **L11** (0.092 g, 0.10 mmol) stoichiometrically reacted with CoCl<sub>2</sub> to afford complex **Co11** in 0.097 g as a yellow solid (82.0 % yield). FT-IR (cm<sup>-1</sup>): 2963 (s), 2017 (w), 1624 (ν<sub>C=N</sub>, w), 1584 (m), 1451 (s), 1367 (s), 1323 (w), 1262 (s), 1205 (m), 1104 (w), 868 (m), 798 (m), 764 (m), 739 (w). Anal. Calcd. For  $C_{64}H_{80}N_6Co_2Cl_4$  (1192): N, 7.04; C, 64.43; H, 6.76. Found: N, 6.59; C, 64.26; H, 6.86. MS (MALDI-TOF, m/z): 1192.38. Found: m/z 1180.6 [M - CoCl<sub>4</sub> + CCA]<sup>+</sup>, 1027.4 [M - CoCl<sub>3</sub>]<sup>+</sup>, 992.4 [M - CoCl<sub>4</sub>]<sup>+</sup>, 934.4 [M - Co<sub>2</sub>Cl<sub>4</sub>]<sup>+</sup>.

### **X-ray crystallographic studies**

Complex **Co4** (20 mg) was dissolved in a mixture of dichloromethane and methanol with v/v ratio of about 2/1(3ml/1.5ml), and its solution was kept in a test tube being wrapped by PE membrane. On slow evaporation, brown needlelike crystals suitable for single crystal X-ray diffraction were obtained. The X-ray diffraction study was conducted on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K. 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 structure was solved by direct methods and refined by full-matrix least squares on F2. All hydrogen atoms were placed in calculated positions. Using the SHELXL-97 package,<sup>17</sup> structure solution and refinement was performed. Details of the X-ray structure determinations and refinements are provided in Table 4.

**Table 4** Crystal data and structure refinement for **Co4**

identification code	<b>Co4</b>
Empirical formula	C <sub>54</sub> H <sub>60</sub> N <sub>6</sub> Co <sub>2</sub> Cl <sub>4</sub>
Formula weight	1052.74
Temperature/K	293(2) K
Wavelength/ $\text{\AA}$	0.71073
Crystal system	Monoclinic
Space group	C2/c
$a/\text{\AA}$	38.653(8)
$b/\text{\AA}$	9.879(2)
$c/\text{\AA}$	16.927(3)
Alpha/ $^\circ$	90
Beta/ $^\circ$	110.59(3)

Gamma/°	90
Volume/Å <sup>3</sup>	6051(2)
Z	4
$D_{calcd}/(\text{g}\cdot\text{cm}^{-3})$	1.156
$\mu/\text{mm}^{-1}$	0.761
$F(000)$	2192
Crystal size/mm	0.35 × 0.18 × 0.06
$\theta$ range (°C)	1.13-25.00
Limiting indices	-45 ≤ h ≤ 42 -11 ≤ k ≤ 11 -17 ≤ l ≤ 20
No. of rflns collected	17644
No. unique rflns	5284
R(int)	0.1288
No. of params	335
Completeness to $\theta$	99.1 %
Goodness of fit on $F^2$	1.072
Final R indices [ $I > 2\sum(I)$ ]	R1 = 0.1032 wR2 = 0.2742
R indices (all data)	R1 = 0.1424 wR2 = 0.3057
Largest diff. peak, and hole/(e.Å <sup>-3</sup> )	0.808 and -0.763

### General Procedure for Ethylene Polymerization.

**Ethylene Polymerization at Ambient Pressure.** The pre-catalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ethylene atmosphere (1 atm) with a steam bath for controlling the desired temperature. Finally, the required amount of co-catalyst (MAO) was added by a syringe. After the reaction was carried out for the required period, a small amount of the reaction solution was collected and

terminated by the addition of 10 % aqueous hydrogen chloride immediately. The organic layer was analyzed by gas chromatography (GC) for monitoring the oligomers formed; the precipitated polymer was collected, washed with water and ethanol, and finally dried.

**Ethylene Polymerization at Elevated Pressure (10 atm).** A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the clave which is full of ethylene. When the temperature required was reached, another 30 mL toluene which dissolved the complex (3.0  $\mu$ mol of metal) before, the required amount of co-catalyst (MAO, MMAO), and the residual toluene was added by syringe successively. The reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same procedure as above for ethylene polymerization.

**Supporting Information Available:** Crystal data and processing parameters for complex **Co4** and CIF file giving X-ray crystal structural data. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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### **Notes**

The authors declare no competing financial interest.

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## REFERENCES

- (1) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049; (b) Britovsek, G. P. J.; 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; (c) Britovsek, G. P. J.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
- (2) (a) Gibson, V.C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283; (d) Small, B. L.; Brookhart, M. *Macromolecules*, **1999**, *32*, 2120; (c) Kaul, F.; Puchta, K.; Frey, G.; Herdtweck, E.; Herrmann, W. *Organometallics* **2007**, *26*, 988; (d) Ionkin, A.S.; Marshall, W. J.; Adelman, A. J.; Fones, B. B.; Fish, B. M.; Schiffhauer, M. F. *Organometallics* **2008**, *27*, 1902; (e) Wallenhorst, G.; Kehr, G.; Luftmann, H.; Fröhlich, R.; Erker, G. *Organometallics* **2008**, *27*, 6547; (f) Jin, J.; Wilson, D. R.; Chen, E.Y.-X. *Chem. Commun.* **2002**, 708.
- (3) (a) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745; (b) Gao, R.; Sun, W.-H.; Redshaw, C. *Catal. Sci. Technol.* **2013**, *3*, 1172; (c) Zhang, W.; Sun, W.-H.; Redshaw, C. *Dalton Trans.* **2013**, 42, 8988.
- (4) Yu, J.; Liu, H.; Zhang, W.; Hao, X.; Sun, W.-H. *Chem. Commun.* **2011**, 47, 3257.

- (5) (a) Sun, W.-H.; Hao, P.; Zhang, S.; Shi, Q.; Zuo, W.; Tang, X.; Lu, X. *Organometallics* **2007**, *26*, 2720; (b) Chen, Y.; Hao, P.; Zuo, W.; Gao, K.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 1829; (c) Xiao, L.; Gao, R.; Zhang, M.; Li, Y.; Cao X.; Sun, W.-H. *Organometallics* **2009**, *28*, 2225; (d) Gao, R.; Li, Y.; Wang, F.; Sun, W.-H.; Bochmann, M. *Eur. J. Inorg. Chem.* **2009**, *27*, 4149.
- (6) Wang, K.; Wedeking, K.; Zuo, W.; Zhang D.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 1073.
- (7) (a) Sun, W.-H.; Jie, S.; Zhang, S.; Zhang, W.; Song, Y.; Ma, H.; Chen, J.; Wedeking, K.; Fröhlich, R. *Organometallics*, **2006**, *25*, 666; (b) Jie, S.; Zhang S.; Sun, W.-H. *Eur. J. Inorg. Chem.* **2007**, *35*, 5584; (c) Zhang, M.; Hao, P.; Zuo, W.; Jie, S.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 483.
- (8) Zhang, M.; Gao, R.; Hao, X.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 3867.
- (9) Wang, K.; Wedeking, K.; Zuo, W.; Zhang D.; Sun, W.-H. *J. Organomet. Chem.* **2008**, *693*, 1073.
- (10) Sun, W.-H.; Hao, P.; Li, G.; Zhang, S.; Wang, W.; Yi, J.; Asma, M.; Tang, N. *J. Organomet. Chem.* **2007**, *692*, 4506.
- (11) (a) Guo, N.; Stern, C. L.; Marks, T. J., *J. Am. Chem. Soc.* **2008**, *130*, 2246; (b) Gavrilova, A. L.; Bosnich, B., *Chem. Rev.* **2004**, *104*, 349; (c) Szuromi, E.; Shen, H.; Goodall, B. L.; Jordan, R. F., *Organometallics* **2008**, *27*, 402; (d) Salata, M. R.; Marks, T. J. *Macromolecules* **2009**, *42*, 1920; (e) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am.*

- Chem. Soc.* **2009**, *131*, 5902; (f) Pelletier, J. D. A.; Fawcett, J.; Singh, K.; Solan, G. A. *J. Organomet. Chem.* **2008**, *693*, 2723.
- (12) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450.
- (13) Xing, Q.; Zhao, T.; Qiao, Y.; Wang, L.; Redshaw, C.; Sun, W.-H. *RSC Adv.*, **2013**, DOI:10.1039/C3RA42631A.
- (14) (a) Zhang, S.; Sun, W.-H.; Kuang, X.; Igor, V.; Yi, J. *J. Organomet. Chem.* **2007**, *692*, 5307; (b) Zhang, S.; Igor, V.; Tang, Z.; Sun, W.-H.; *Organometallics* **2007**, *26*, 2456; (c) Sun, W.-H.; Xing, Q.; Yu, J.; Novikova, E.; Zhao, W.; Tang, X.; Liang, T.; Redshaw, C. *Organometallics* **2013**, *32*, 2309; (d) Yang, X.; Wu, B.; Christoph, J.; Sun, W.-H.; Hu, H. Z. *Anorg. Allg. Chem.* **2004**, *630*, 1564; (e) Yang, X.; Wu, B.; Sun, W.-H.; Christoph, J. *Inorganica Chimica Acta.* **2003**, *343*, 366; (f) Jie, S.; Zhang, D.; Zhang, T.; Sun, W.-H.; Chen, J.; Ren, Q.; Liu, D.; Zheng, G.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1739.
- (15) (a) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Rios, I. G.; Meli, A.; Oberhauser, W.; Segarra, A. M.; Sorace, L.; Toti, A. *Organometallics* **2007**, *26*, 4639; (b) Armitage, A. P.; Champouret, Y. D. M.; Grigoli, H.; Pelletier, J. D. A.; Singh, K.; Solan, G. A. *Eur. J. Inorg. Chem.* **2008**, 4597.
- (16) Jie, S.; Zhang, D.; Zhang, T.; Sun, W.-H.; Chen, J.; Ren, Q.; Liu, D.; Zheng, G.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1739.
- (17) Sheldrick, G. M. SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.