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2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-aryliminoethyl]pyridyl cobalt dichlorides: Synthesis, characterization and ethylene polymerization behavior

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ABSTRACT

A series of 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-aryliminoethyl]pyridyl cobalt(II) dichloride complexes (**Co1**–**Co5**) were prepared and characterized by elemental and spectroscopic analysis. The molecular structures of the representative cobalt complexes **Co1** and **Co4** were determined by single-crystal X-ray diffraction, and revealed a pseudo-square-pyramidal geometry around each cobalt atom. Upon activation with either MMAO or MAO, all cobalt pre-catalysts exhibited high activities toward ethylene polymerization and produced polyethylene products with narrow molecular distributions (1.98–3.61) and molecular weights in the range 72.3–665 kg/mol; the latter is higher than any other molecular weight of polyethylenes obtained by previous cobalt pre-catalysts. Reaction parameters and the nature of the ligands were investigated for their influence on the resultant catalytic activities and properties of the polyethylene products obtained.

1. Introduction

The discovery of bis(imino)pyridyl metal (Fe(II) and Co(II)) dichloride complexes as highly active pre-catalysts in ethylene polymerization and oligomerization was pivotal in initiating the resurrection of late-transition metal based polyolefin science [1,2]. Subsequently, the variation of substituents on the bis(imino)pyridine framework has been extensively explored with a view to improving the catalytic performance of their metal complexes [3–11]. Moreover, a number of studies have targeted the active species and the mechanism of such Fe/Co-catalyzed polymerization reactions [12–27]. Driven by the hypothesis that N^N^N tridentate ligands would provide suitable iron(II) and cobalt(II)-based pre-catalysts [28–35], numerous heterocyclic compounds, which act as tridentate ligands, have been developed in our group. These include 2-imino-1,10-phenanthrolines [36–40], 2-(benzoxazolyl)-1,10-phenanthrolines [41], 2-(2-benzimidazolyl)-1,10-phenanthrolines [42], 2-benzimidazolyl-6-iminopyridines [43–45], 2-benzoxazolyl-6-iminopyridines [46,47], 2-quinoxalinyl-6-iminopyridines [48], *N*-((pyridin-2-yl)methylene)-8-aminoquinolines [49], 8-(*1H*-benzimidazol-2-yl)quinolines [50], as well as the 2-methyl-2,4-bis(6-iminopyridin-2-yl)-*1H*-1,5-benzodiazepines for bimetallic pre-catalysts [51,52]. In addition, several types of iron and cobalt complexes bearing bidentate ligands showed promise in ethylene polymerization or oligomerization [53–55]. The analogous iron pre-catalysts generally performed with higher activities and produced more polyethylene than did their cobalt analogs. However, in the case of pre-catalysts bearing 2-benzoxazolyl-6-iminopyridines, the cobalt pre-catalysts were shown to exhibit an interesting temperature-switch feature for ethylene reactivity, producing 1-butene below 40 °C and favoring ethylene polymerization at elevated temperatures [46]; the iron analogs mainly gave oligomers and small amounts of waxes [47]. Moreover, this finding was contrary to the common thinking that elevated reaction temperatures result in lower activities and produce lower molecular weight polyethylene products. As a consequence, the room temperature inert system comprising the 2,8-bis(1-aryliminoethyl)quinolylmetal halides was reinvestigated and found to exhibit good activity for ethylene polymerization at elevated reaction temperatures without observing any trace of

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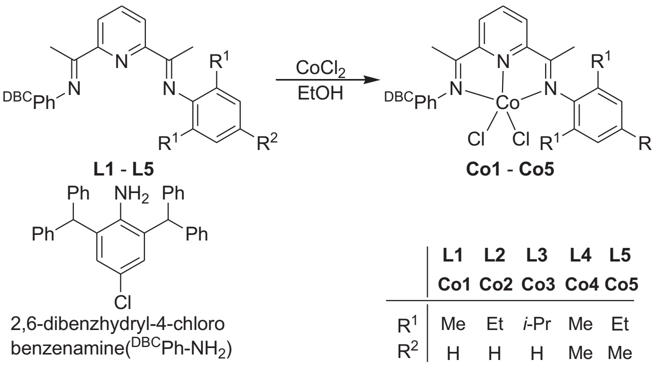

Scheme 1. Synthesis of the complexes **Co1**–**Co5**.

oligomers [56]. Such catalytic behavior was also observed for iron and cobalt complexes bearing 8-benzimidazolyl-quinolines, with the cobalt pre-catalysts exhibiting ethylene oligomerization at relatively low ethylene pressure and low reaction temperature, but ethylene polymerization at high reaction temperature under 30 atm ethylene pressure [54]. Contrastingly, the iron pre-catalysts showed good activity for ethylene polymerization at elevated reaction temperatures only [53]. Inspired by these results, we pondered again over the metal complexes bearing dibenzhydryl-substituted bis(imino)pyridines, which were inert for ethylene reactivity at ambient temperature. Surprisingly, the iron(II) dichlorides complexes ligated by 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino) ethyl]pyridines [57] and 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines [58] showed high activities toward ethylene polymerization at elevated temperatures, producing polyethylene products with tunable polydispersity index (PDI). Moreover, the cobalt pre-catalysts bearing the same ligands were also highly active, producing polyethylenes at the elevated temperature [59,60].

Besides exhibiting slightly lower catalytic activities than their iron analogs, cobalt pre-catalysts often produced oligomers or low-M_w-polyethylenes. Indeed, there are no reports of polyethylene products by cobalt pre-catalysts with molecular weight higher than a half million. To explore the scope and potential application of cobalt pre-catalysts in ethylene polymerization, more cobalt pre-catalysts need to be designed and investigated for their catalytic behavior with a view to obtaining polyethylenes with different molecular weights and distributions. Following the extensive work on iron pre-catalysts bearing 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines, which showed the highest activity within all reported iron pre-catalysts for ethylene polymerization [61], the synthesis, characterization, and catalytic behavior of 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) chloride complexes are investigated and reported herein.

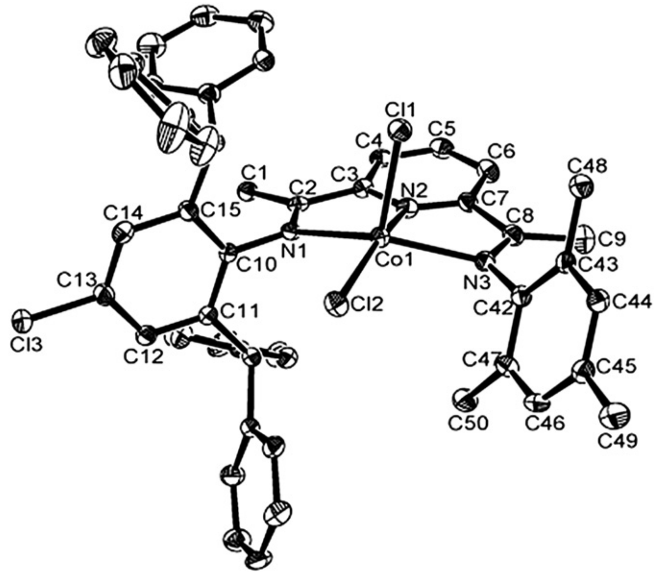

Fig. 2. Molecular structure of **Co4**; thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

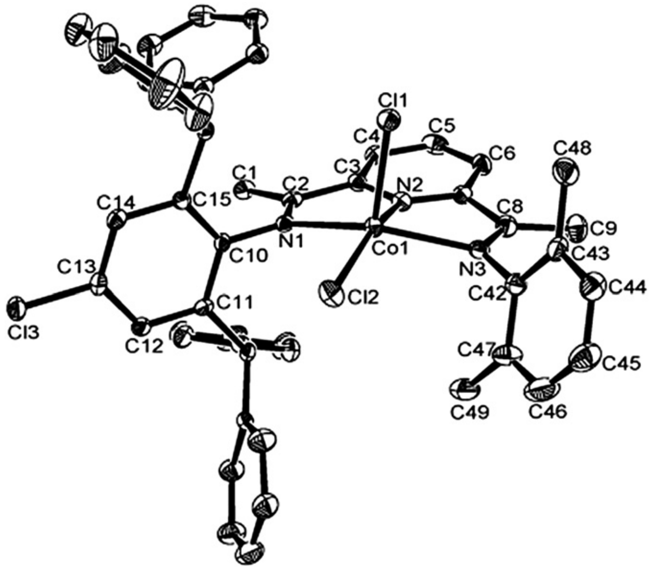

Fig. 1. Molecular structure of **Co1**; thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **Co1** and **Co4**.

	Co1	Co4
Bond lengths (Å)		
Co1–N1	2.234(4)	2.217(4)
Co1–N2	2.067(4)	2.065(4)
Co1–N3	2.190(4)	2.183(4)
Co1–Cl1	2.3054(14)	2.3140(15)
Co1–Cl2	2.2522(17)	2.2596(17)
N1–C2	1.248(7)	1.274(7)
N1–C10	1.425(6)	1.424(6)
N2–C3	1.359(6)	1.335(7)
N2–C7	1.324(6)	1.318(7)
N3–C8	1.266(7)	1.284(7)
N3–C42	1.415(7)	1.425(7)
Bond angles (°)		
N2–Co1–N3	73.97(17)	74.25(18)
N2–Co1–N1	73.24(16)	73.47(18)
N3–Co1–N1	141.50(16)	141.53(16)
N2–Co1–Cl2	157.69(12)	159.59(14)
N3–Co1–Cl2	106.33(13)	107.00(13)
N1–Co1–Cl2	96.66(12)	96.38(12)
N2–Co1–Cl1	92.46(12)	91.31(13)
N3–Co1–Cl1	95.40(12)	93.94(12)
N1–Co1–Cl1	105.60(11)	107.14(11)
Cl2–Co1–Cl1	109.57(6)	108.76(6)

Table 2
Ethylene polymerization with **Co4**/MMAO[a].

Run	T/°C	t/min	Al/Co	Yield/g	Activity[b]	M_w[c]/ 10^4 g mol^{-1}	M_w/M_n[c]	T_m[d]/°C
1	20	30	500	4.08	5.44	47.7	3.13	136.1
2	20	30	1000	4.53	6.04	47.7	3.08	135.7
3	20	30	1500	5.11	6.81	46.8	2.79	135.3
4	20	30	2000	4.36	5.81	46.5	2.73	135.4
5	30	30	1500	6.84	9.12	34.0	3.04	135.1
6	40	30	1500	4.13	5.51	17.6	2.87	133.9
7	50	30	1500	1.72	2.29	8.31	2.47	133.6
8	30	5	1500	3.20	25.6	28.9	3.24	134.1
9	30	10	1500	4.79	19.2	32.2	2.93	133.8
10	30	20	1500	5.95	11.9	33.6	3.21	133.9
11	30	45	1500	7.98	7.09	35.8	3.20	133.9
12	30	60	1500	8.82	5.88	37.4	3.11	134.6

[a] General conditions: 1.5 μmol of Co; 10 atm ethylene; 100 mL toluene.
[b] 10^6 g mol^{-1}(Co) h^{-1}.
[c] Determined by GPC.
[d] Determined by DSC.

2. Results and discussion

2.1. Preparation and characterization of the cobalt complexes

A series of 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino) ethyl]-6-[1-(arylimino)ethyl]pyridines (**L1**–**L5**) were prepared following the previously reported procedures [61]. As shown in Scheme 1, the stoichiometric reaction of $CoCl_2$ with **L1**–**L5** in ethanol at room temperature produced brown powders with the general formula $LCoCl_2$ (**Co1**–**Co5**) in good yields. Similar to their iron analogs, all cobalt complexes were characterized by elemental analysis and FT-IR spectra. Compared with the FT-IR spectra of the free ligands (1636–1643 cm^{-1}), the stretching vibrations for $\nu_{C=N}$ in these cobalt complexes (1582–1586 cm^{-1}) shifted to lower wave-numbers and the intensities were decreased due to coordination effects. The molecular structures of the complexes **Co1** and **Co4** were confirmed by single-crystal X-ray diffraction studies.

2.2. X-ray crystallographic studies

Single-crystals of **Co1** and **Co4** were grown by diffusing *n*-hexane into their respective dichloromethane solutions. The molecular structures are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles tabulated in Table 1. With Cl1 occupying the apical position and N1, N2, N3 and Cl2 forming the square plane, both of the complexes are penta-coordinate with a pseudo-square-pyramidal geometry at cobalt, which is similar to that observed for their iron analogs [61] and numerous iron and cobalt analog complexes bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines [57,59] or 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridines [58,60]. The cobalt center is pushed out of the chelate plane due to the associated sterics, namely 0.522 Å out of the chelated plane (N1–N2–N3) in **Co1** and 0.534 Å in **Co4**. For both complexes, the Co1–N2 bond length is drastically shorter than the lengths for Co1–N1 and Co1–N3, revealing the stronger interaction between the Co atom and the pyridyl N atom than that between the Co atom and the imino N atoms, consistent with the double bond character of N1–C2 and N3–C8.

2.3. Catalytic behavior toward ethylene polymerization

Various alkylaluminum reagents were screened to find the most suitable co-catalyst, and both modified methylaluminoxane (MMAO) as well as methylaluminoxane (MAO) were found to be

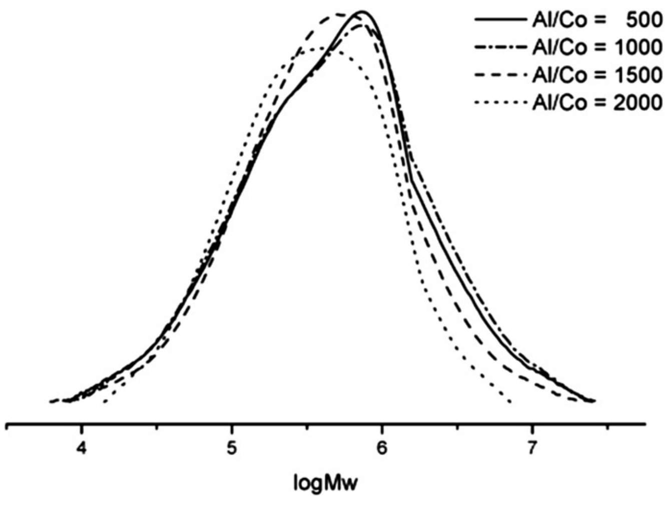

Fig. 3. GPC curves of PEs obtained by **Co4**/MMAO with various Al/Co molar ratios (Runs 1–4 in Table 2).

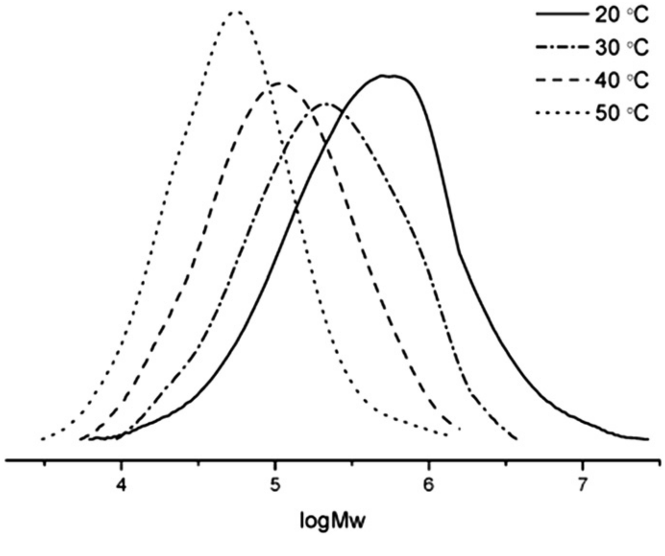

Fig. 4. GPC curves of PEs obtained by **Co4**/MMAO with various temperatures (Runs 3 and 5–7 in Table 2).

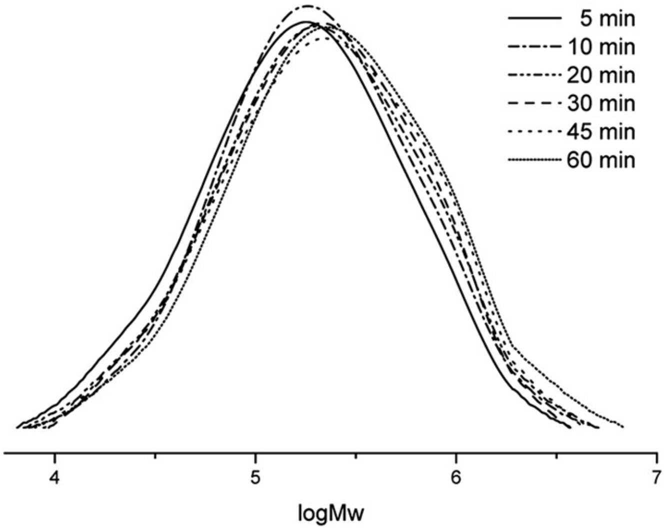

Fig. 5. GPC curves of PEs obtained by **Co4**/MMAO with various times (Runs 5 and 8–12 in Table 2).

effective reagents for generating highly active cobalt complexes for ethylene polymerization.

2.3.1. Ethylene polymerization with Co1–Co5/MMAO

The catalytic system **Co4**/MMAO was typically employed for determining the optimum catalytic conditions by varying the molar ratio of Al/Co, the reaction temperature and the reaction time; results are tabulated in Table 2. By raising the molar ratio of Al/Co from 500 to 2000 (Runs 1–4 in Table 2) under 10 atm pressure of ethylene, this catalytic system exhibited the highest activity at an optimum ratio of 1500, namely, 6.81×10^6 g mol^{-1}(Co) h^{-1} (Run 3 in Table 2). Compared with the polyethylene obtained using the analogous iron pre-catalysts, the PDIs of the polyethylene herein were relatively narrow, with values of about 3.00. The resultant PEs for the lower molar ratios of Al/Co (less than 1500) exhibited bimodal features, whilst those for higher molar ratios approached a more unimodal distribution (Fig. 3). Meanwhile, the molecular weights of the polyethylenes decreased slightly on enhancing the amounts of MMAO used, indicative of chain transfer from cobalt to aluminum as the primary termination process [62]. The precipitation of the polyethylene disturbed the equilibrium between the cobalt and aluminum species, and so the GPC curves at lower molar ratios of Al/Co exhibited two distributions. Such phenomena were observed for their iron analogs [61] as well as for lanthanocene-based systems [63,64]. The influence of the reaction temperature was investigated at the fixed molar ratio Al/Co of 1500 (Runs 3 and 5–7 in Table 2). The catalytic activity initially increased to 9.12×10^6 g mol^{-1}(Co) h^{-1} at 30 °C (Run 5 in Table 2) and then decreased, probably the result of the deactivation of **Co4**/MMAO and lower ethylene solubility in toluene at higher temperature [65]. Furthermore, higher temperatures can also accelerate chain transfer to aluminum, which led to the formation of low-M_w-PEs [66].

As shown in Table 2 and Fig. 4, the molecular weights of the polyethylenes reduced significantly from 468 kg/mol to 83.1 kg/mol. The influence of the reaction time was studied by quenching the catalytic system **Co4**/MMAO under optimum conditions over different reaction periods (Runs 5, 8–12 in Table 2). On extending the reaction time from 5 to 60 min, the catalytic activity decreased from 2.56×10^7 g mol^{-1}(Co) h^{-1} to 5.88×10^6 g mol^{-1}(Co) h^{-1}, indicative of little or no induction time during the catalytic process [67]. The molecular weights of the polyethylenes increased from 289 to 374 kg/mol on extending the reaction time (Fig. 5) due to the reduction of the available amount of MMAO, which in-turn resulted in a deceleration of chain transfer to aluminum [3].

In order to investigate the influence of the nature of ligands on the catalytic behavior, pre-catalysts with different aryl substituents (**Co1**–**Co5**) were employed for ethylene polymerization under the optimum catalytic conditions found for **Co4**/MMAO (10 atm ethylene, Al/Co = 1500, 30 °C); results are tabulated in Table 3. The observed activity order for these pre-catalysts was found to be **Co1** > **Co2** > **Co3**, which was governed by both the electronic and steric influences of the ligands. The electronic influence has been simulated by computational studies, which indicated that the higher net charge of the metal center enhanced the catalytic activity of the late-transition metal complex [68]. The electron-donating properties of the *ortho*-alkyl substituents (R^1) of the arylimino followed the order Me (**Co1**) < Et (**Co2**) < *i*-Pr (**Co3**), which is consistent with their performance in ethylene polymerization. In addition, for the unsymmetrical ligands, the presence of a bulky benzhydryl substituent on one side, further increasing the steric hindrance (Me (**Co1**) < Et (**Co2**) < *i*-Pr (**Co3**)), which is detrimental in terms of insertion of ethylene and thereby catalytic activity [1–5]. The introduction of a methyl in the *para*-position of the phenyl ring increased the catalytic activities (**Co4** > **Co1** and **Co5** > **Co2**), probably due to enhanced solubility properties. Thus, the highest catalytic activity for these pre-catalysts was obtained for the system **Co4**/MMAO (Run 4 in Table 3), which is higher than that observed for the iron analog (2.46×10^6 g mol^{-1}(Fe) h^{-1}) [61].

Table 3
Ethylene polymerization with **Co1**–**Co5**/MMAO.[a]

Run	Cat.	Yield/g	Activity[b]	M_w[c]/ 10^4 g mol^{-1}	M_w/M_n[c]	T_m[d]/°C
1	**Co1**	5.62	7.47	17.0	2.90	134.4
2	**Co2**	5.31	7.08	22.5	2.30	135.3
3	**Co3**	4.93	6.57	66.5	2.09	135.8
4	**Co4**	6.84	9.12	34.0	3.04	135.1
5	**Co5**	5.96	7.95	27.2	2.15	135.4

[a] General conditions: 1.5 μmol of Co; 10 atm ethylene; 100 mL toluene; Al/Co = 1500; 30 °C; 30 min.
[b] 10^6 g mol^{-1}(Co)·h^{-1}.
[c] Determined by GPC.
[d] Determined by DSC.

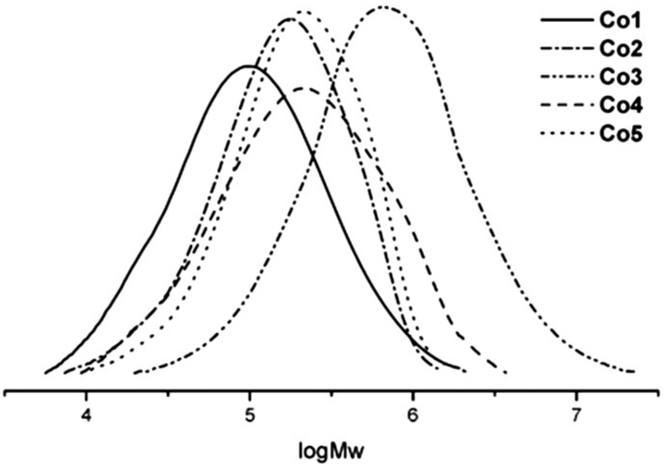

Fig. 6. GPC curves of PEs obtained by **Co1**–**Co5**/MMAO (Runs 1–5 in Table 3).

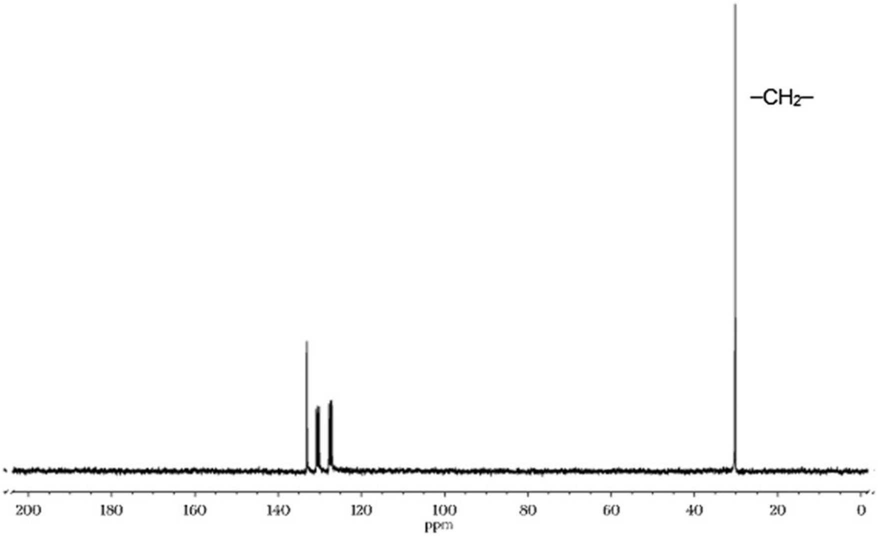

Fig. 7. ^{13}C NMR spectrum of the polyethylene prepared with catalyst **Co4**/MMAO (Run 7 in Table 2).

As shown in Fig. 6, the order of molecular weights (**Co3** > **Co2** > **Co1**) was reversed to that observed for the catalytic activity, suggesting that an increase in the steric bulk at the *ortho*-position could result in a reduction of the rate of β-H transfer and give polyethylene of higher molecular weight. We note that the molecular weight of the polyethylene (eg. 665 kg/mol; Run 3 in Table 3) is the highest obtained to-date using bis(imino)pyridylcobalt(II) dichlorides pre-catalysts (Fig. 7) (Fig. 8).

2.3.2. Ethylene polymerization with Co1–Co5/MAO

Using MAO instead of MMAO as the co-catalyst, the title pre-catalysts performed with relatively lower activities toward the polymerization of ethylene; the results are given in Table 4. Using a similar procedure to that for **Co1**–**Co5/MMAO**, the catalytic system **Co4/**MAO was initially investigated to determine the optimum catalytic conditions with various molar ratios of Al/Co (Runs 1–4 in Table 4) and reaction temperatures (Runs 2, 5 and 6 in Table 4). The highest activity was obtained at 20 °C when a molar ratio of Al/Co of 1000 (Run 2 in Table 4). Subsequently, all pre-catalysts (**Co1**–**Co5**) were employed for ethylene polymerization under these optimum conditions (Runs 2 and 7–10 in Table 4). The variation of catalytic activities and molecular weights exhibited similar trends to those observed when MMAO was employed as the co-catalyst, but the molecular weight of the resultant polyethylene was somewhat higher. Despite variations of the reaction conditions, the PDI values of the polyethylenes were still relatively narrow and were constant in the range between 1.98 and 3.61, consistent with the presence of single-site species. On comparison with the cobalt complexes bearing 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines [60], although the catalytic activities were lower, the two *ortho*-benzhydryls on the imino phenyl ring can further block the axial sites at

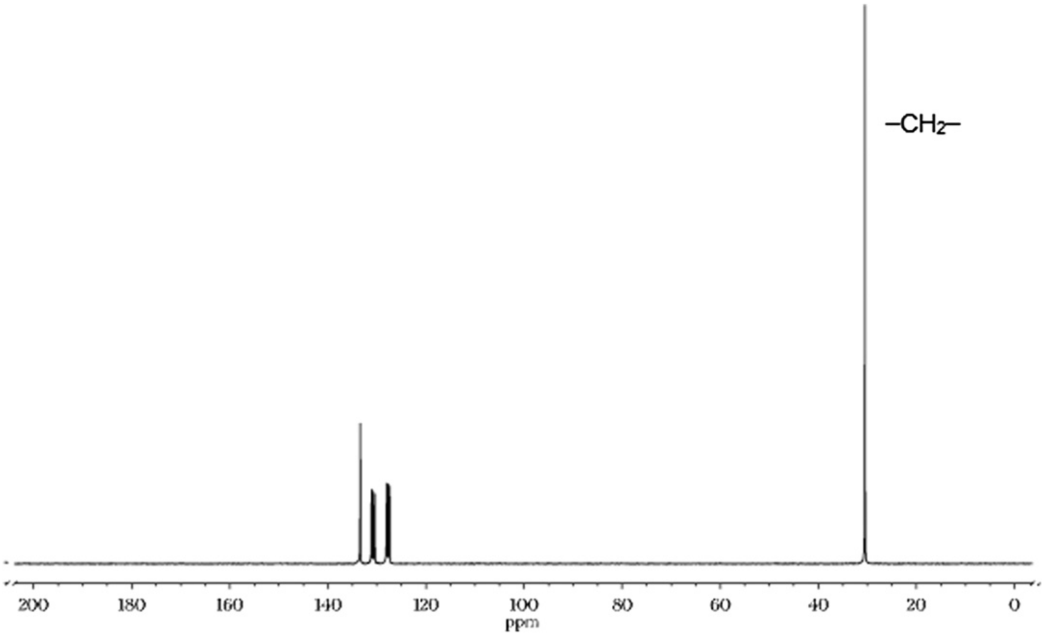

Fig. 8. ^{13}C NMR spectrum of the polyethylene prepared with catalyst **Co4**/MAO (Run 6 in Table 4).

Table 4
Ethylene polymerization with **Co1**–**Co5**/MAO.[a]

Run	Cat.	T/°C	Al/Co	Yield/g	Activity[b]	M_w[c]/10^4 g mol^{-1}	M_w/M_n[c]	T_m[d]/°C
1	**Co4**	20	500	4.67	6.23	52.3	2.27	135.3
2	**Co4**	20	1000	5.98	7.97	47.9	2.54	135.6
3	**Co4**	20	1500	5.30	7.07	47.2	2.66	134.7
4	**Co4**	20	2000	5.06	6.75	44.5	3.04	134.7
5	**Co4**	30	1000	4.98	6.64	26.5	3.61	134.6
6	**Co4**	40	1000	3.85	5.13	7.23	2.90	134.4
7	**Co1**	20	1000	5.40	7.20	35.7	2.21	134.9
8	**Co2**	20	1000	5.08	6.78	39.5	1.98	134.9
9	**Co3**	20	1000	4.49	5.99	64.4	2.13	134.6
10	**Co5**	20	1000	5.47	7.29	58.8	2.41	135.1

[a] General conditions: 1.5 μmol of Co; 10 atm ethylene; 100 mL toluene; 30 min.
[b] 10^6 g mol^{-1}(Co) h^{-1}.
[c] Determined by GPC.
[d] Determined by DSC.

the cobalt center and restrict the rate of β-H transfer, with the result that polyethylene with higher molecular weight was obtained by using the title cobalt complexes [1–5]. On comparison with the cobalt analog bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines [59], the current complex pre-catalysts showed similar catalytic activities, and the obtained polyethylenes had similar molecular weight polydispersity. However, the polyethylenes obtained in the current system showed much higher molecular weights than those in reference [59], indicating the influence that the substituents of the ligands present had on the produced polymer. Such phenomenon highlights the importance of moderate fine tuning ligands and the influence this can have on catalytic behavior.

In addition, representative polyethylene samples (Figure 7 for Run 7 in Table 2 and Figure 8 for Run 6 in Table 4) were characterized by ^{13}C NMR spectroscopy at 110 °C in deuterated 1,2-dichlorobenzene and were shown to be highly linear in nature.

Table 5
Crystal data and structure refinement for **Co1** and **Co4**.

	Co1	**Co4**
Empirical formula	$C_{49}H_{42}Cl_3CoN_3$	$C_{50}H_{44}Cl_3CoN_3$
Fw	838.14	852.16
T (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	Cc	Cc
a (Å)	23.912(5)	23.972(5)
b (Å)	14.466(3)	14.687(3)
c (Å)	15.958(3)	16.030(3)
α (°)	90	90
β (°)	125.27(3)	126.67(3)
γ (°)	90	90
V (Å^3)	4506.9(16)	4526.9(16)
Z	4	4
*D*calcd. (g cm^{-3})	1.235	1.250
μ (mm^{-1})	0.594	0.592
F(000)	1740	1772
Cryst size (mm)	0.32 × 0.30 × 0.24	0.37 × 0.16 × 0.11
θ range (°)	1.75–27.48	1.74–27.48
Limiting indices	$-21 \le h \le 31$	$-30 \le h \le 31$
	$-18 \le k \le 12$	$-18 \le k \le 19$
	$-20 \le l \le 20$	$-20 \le l \le 18$
No. of rflns collected	10,376	19,043
No. unique rflns [*R*(int)]	6413 (0.0343)	9307 (0.0469)
Completeness to *θ* (%)	99.1	99.3
Abs corr.	None	None
Data/restraints/parameters	6413/2/505	9307/2/514
Goodness of fit on F^2	1.040	1.031
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0578$	$R1 = 0.0727$
	$wR2 = 0.1512$	$wR2 = 0.1786$
R indices (all data)	$R1 = 0.0619$	$R1 = 0.0783$
	$wR2 = 0.1549$	$wR2 = 0.1844$
Largest diff peak and hole (e Å^{-3})	0.609 and −0.404	0.564 and −0.447

3. Conclusions

A series of cobalt(II) complexes (**Co1**–**Co5**) bearing 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridine ligands (**L1**–**L5**) were synthesized and fully characterized. On treatment with MMAO or MAO as the co-catalyst, the pre-catalysts (**Co1**–**Co5**) exhibited high activities and produced highly linear polyethylene with high molecular weights (72.3–665 kg/mol) and narrow PDIs (1.98–3.61). The molecular weights of resultant polyethylenes could be controlled in the range 72.3–665 kg/mol by modifying the nature of ligands or by varying reaction parameters (co-catalyst type, molar ratio of Al/Co, reaction temperature and time).

4. Experimental

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 nitrogen prior to use. Methylaluminoxane (MAO, a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, a 1.93 M solution in heptane, 3A) were purchased from Akzo Nobel Corp. 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines were prepared following the previously reported procedures [61]. Other reagents were purchased from Acros Chemicals or local suppliers. ^{1}H and ^{13}C NMR spectra of compounds were recorded on 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 polydispersity index of polyethylenes were determined by a PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. DSC trace and melting points of polyethylenes were obtained from the second scanning run on Perkin–Elmer DSC-7 at a heating rate of 10 °C/min. ^{13}C NMR spectra of PE samples were recorded on a Bruker DMX-300 MHz instrument at 110 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

4.2. Synthesis and characterization of cobalt complexes (Co1–Co5)

General procedure: to a solution of the ligand in ethanol (10 mL), the equivalent $CoCl_2$ was added and a brown suspension was observed. The reaction mixture was stirred at room temperature for 8 h. Then the precipitate was filtered and washed with diethyl ether (3 × 5 mL). The pure complex was obtained as a brown powder after dried *in-vacuo* overnight. All of the complexes were prepared in high yield following this procedure.

2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridylcobalt(II) dichloride (**Co1**) was prepared in 86% yield. FT-IR (KBr, cm^{-1}): 3059, 2966, 2169, 2030, 1584 ($\nu_{C=N}$), 1495, 1431, 1261, 1192, 1078, 1027, 808, 772, 744, 698. Anal. Calcd for $C_{49}H_{42}Cl_3CoN_3$ (838.17): C, 69.90; H, 5.40; N, 4.93. Found: C, 70.22; H, 5.05; N, 5.01.

2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(2,6-diethylphenylimino)ethyl]pyridylcobalt(II) dichloride (**Co2**) was prepared in 90% yield. FT-IR (KBr, cm^{-1}): 3061, 2965, 2166, 2032, 1582 ($\nu_{C=N}$), 1495, 1443, 1262, 1190, 1079, 1028, 809, 768, 741, 700. Anal. Calcd for $C_{51}H_{46}Cl_3CoN_3$ (866.22): C, 70.48; H, 5.73; N, 4.72. Found: C, 70.71; H, 5.35; N, 4.85.

2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(2,6-diisopropylphenylimino)ethyl]pyridylcobalt(II) dichloride (**Co3**) was prepared in 80% yield. FT-IR (KBr, cm^{-1}): 3060, 2959, 2164, 2030, 1584 ($\nu_{C=N}$), 1494, 1439, 1263, 1194, 1110, 1027, 806, 767, 744, 699. Anal. Calcd for $C_{53}H_{50}Cl_3CoN_3$ (894.28): C, 70.87; H, 5.79; N, 4.49. Found: C, 71.18; H, 5.64; N, 4.70.

2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridylcobalt(II) dichloride (**Co4**) was prepared in 81% yield. FT-IR (KBr, cm^{-1}): 3033, 2958, 2167, 2031, 1586 ($\nu_{C=N}$), 1495, 1434, 1265, 1198, 1080, 1028, 813, 767, 733, 701. Anal. Calcd for $C_{50}H_{44}Cl_3CoN_3$ (852.20): C, 70.14; H, 5.59; N, 4.80. Found: C, 70.47; H, 5.20; N, 4.93.

2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridylcobalt(II) dichloride (**Co5**) was prepared in 86% yield. FT-IR (KBr, cm^{-1}): 3059, 2962, 2166, 2031, 1582 ($\nu_{C=N}$), 1495, 1433, 1262, 1195, 1077, 1028, 809, 768, 744, 700. Anal. Calcd for $C_{52}H_{48}Cl_3CoN_3$ (880.25): C, 70.66; H, 5.87; N, 4.53. Found: C, 70.95; H, 5.50; 4.77.

4.3. X-ray crystallographic studies

Single-crystal X-ray diffraction studies for **Co1** and **Co4** were carried out on a Rigaku Saturn724 + CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173(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 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 [69]. Crystal data and processing parameters for **Co1** and **Co4** are summarized in Table 5.

4.4. General procedure for ethylene polymerization

A 250 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 into the autoclave which was full of ethylene. Then 30 mL toluene solution of the complex (1.5 μmol), the required amount of co-catalyst (MAO, MMAO) and 20 mL toluene were added by syringe successively after the autoclave was heated to the required reaction temperature. The reaction mixture was intensively stirred for the desired time under 10 atm pressure of ethylene through the entire experiment and then quenched with acidified ethanol solution containing 10% hydrochloric acid. The precipitated polymer was collected by filtration, washed with ethanol and water, and dried in a vacuum at 60 °C until of constant weight.

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Appendix A. Supplementary material

CCDC 855922 and 855923 contain the supplementary crystallographic data for the complexes **Co1** and **Co4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version.

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