Cite this: Dalton Trans., 2011, 40, 10209



# 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichlorides: Synthesis, characterization and ethylene polymerization behavior<sup>†</sup>

Jiangang Yu,<sup>a</sup> Wei Huang,<sup>a</sup> Lin Wang,<sup>a</sup> Carl Redshaw<sup>\*b</sup> and Wen-Hua Sun<sup>\*a,c</sup>

*Received 7th June 2011, Accepted 2nd August 2011* DOI: 10.1039/c1dt11062d

A series of unsymmetrical 2,6-bis(imino)pyridylcobalt(II) complexes,  $\{2-[2,6-(CH(C_6H_5)_2)_2-4-Me-C_6H_2N=C(CH_3)]-6-(2,6-R_1^2-4-R_2^2-C_6H_2N=CCH_3)-C_5H_3NCoCl_2\}$  where  $R^1 = Me$ , Et or <sup>i</sup>Pr,  $R^2 = H$  or Me, together with the new symmetrical complex 2,6- $[2,6-(CH(C_6H_5)_2)_2-4-Me-C_6H_2N=C(CH_3)]_2-C_5H_3NCoCl_2$ , were synthesized. All of the compounds were fully characterized by <sup>1</sup>H NMR and IR spectroscopy, as well as by elemental analysis. The molecular structures of **Co1** ( $R^1 = Me$ ,  $R^2 = H$ ) and **Co5** ( $R^1 = Et$ ,  $R^2 = Me$ ) were further confirmed by single crystal X-ray diffraction, which indicated that the cobalt centres were *penta*-coordinate with a pseudo square-pyramidal geometry. Upon treatment with MAO or MMAO, these cobalt pre-catalysts exhibited higher activities than any previously reported cobalt pre-catalysts, with values as high as  $4.64 \times 10^6$  g PE mol<sup>-1</sup>(Co) h<sup>-1</sup> for ethylene polymerization at atmospheric pressure. The polyethylenes obtained were of high molecular weight and narrow molecular weight distribution.

# 1. Introduction

The advent of bis(imino)pyridine metal ( $M = Fe^{2+}$  or  $Co^{2+}$ ) complexes possessing high activity toward ethylene polymerization was a milestone for late transition metal complexes as catalysts for ethylene oligomerization and polymerization.<sup>1</sup> Recent review articles have indicated the growth in research papers based on bis(imino)pyridylmetal (Fe<sup>2+</sup> or Co<sup>2+</sup>) chlorides.<sup>2</sup> The literature highlights how the nature of the ligands used can significantly affect the catalytic behavior of these complexes towards ethylene oligomerization/polymerization.<sup>2,3</sup> Facile modifications were achieved through simply changing the substituents at the Nbound aryl groups<sup>2e,4</sup> or the substituents<sup>5</sup> linked to the imino groups of the bis(imino)pyridine framework. This allowed for the control of the steric and electronic influences of the ligands, thereby allowing for the manipulation of the catalytic activities of such metal complexes and indeed the properties of the resulting products formed during the ethylene oligomerization and/or 6-positions have been functionalized to increase the steric demand of the whole ligand set;6a,7 less bulky aryls tend to afford oligomeric materials.4b,4e,f,8 One of the most successful modifications reported by us is the 2-[1-(2.6-dibenzhvdrvl-4-methyl-phenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyliron(II) chlorides,9 which showed high catalytic activity of up to the value of  $2.2 \times 10^7$  g PE mol<sup>-1</sup>(Fe) h<sup>-1</sup> for ethylene polymerization and possessed encouraging thermal behavior with the optimum activity obtained at 80 °C in the presence of MMAO, or at 60 °C in the presence of MAO. However, the ever-present bimodal or multimodal features of the polyethylenes, which are caused by the presence of multi-species of active sites, led to relatively wide molecular weight distributions. On the other hand, cobalt complexes can show differing catalytic behavior during ethylene reactivity. For example, cobalt(II) dichlorides bearing 2,8-bis(imino)quinolines produced higher molecular weight polyethylene than their iron(II) counterparts did, which had almost the same activity.10 2-(1H-2-Benzimidazolyl)-6-(1-(arylimino)ethyl)pyridylcobalt(II) dichloride only gave butenes and hexenes, while the iron counterparts afforded oligomers with a wide molecular weight distribution.11 2-Oxazoline/benzoxazole-1,10-phenanthrolinyl cobalt dichlorides were found to exhibit lower activities, but with higher selectivity for  $\alpha$ -olefins compared to the iron complexes.<sup>12</sup> Inspired by these 'special' properties of cobaltous complexes, we embarked on the investigation of a series of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichloride. Interestingly, these newly synthesized cobalt complexes showed the highest activity of all reported cobalt pre-catalysts for ethylene polymerization

polymerization.<sup>2a,4e,6</sup> Typically, the aryl substituents at the 2- and

<sup>&</sup>lt;sup>a</sup>Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: whsun@iccas.ac.cn; Fax: +86 10 62618239; Tel: +86 10 62557955

<sup>&</sup>lt;sup>b</sup>School of Chemistry, University of East Anglia, Norwich, UK, NR4 7TJ. E-mail: carl.redshaw@uea.ac.uk

<sup>&</sup>lt;sup>c</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

<sup>&</sup>lt;sup>†</sup>CCDC reference numbers 828331 and 828332 for crystallographic data of complexes **Co1** and **Co5**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11062d

without observing any oligomer in the products, with activities similar to the iron-based pre-catalysts. However, the polyethylenes obtained were of high-density with a narrow molecular weight distribution. Herein, the synthesis and characterization of the 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)-ethyl]pyridyl cobalt(II) dichlorides are reported in detail, as well as their catalytic behavior in the polymerization of ethylene.

# 2. Results and discussion

# 2.1 Synthesis and characterization of the complexes Co1-Co6

All ligands of the type 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine, were prepared according to the literature procedures.<sup>9</sup> The stoichiometric reaction of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine with CoCl<sub>2</sub> in ethanol formed the corresponding N,N,N-tridentate cobalt complexes, 2-[1-(2,6dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichloride, in good yields (Scheme 1).



**Scheme 1** The synthetic procedure for 2-[1-(2,6-dibenzhydryl-4-methyl-phenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichlorides.

Elemental analyses for all of the complexes were consistent with the proposed formulae and, for their IR spectra, a strong band in the range 1580–1590 cm<sup>-1</sup> can be ascribed to the stretching vibration of C==N. The <sup>1</sup>H NMR spectra of **Co1–Co6** were consistent with the paramagnetic nature of these compounds. The molecular structures of **Co1** and **Co5** were further unambiguously confirmed by the single X-ray diffraction.

# 2.2 Molecular structures

Single crystals of **Co1** and **Co5** suitable for X-ray diffraction analysis were obtained by layering *n*-pentane on dichloromethane solution at room temperature. The molecular structures of complexes **Co1** and **Co5** are shown in Figs 1 and 2 and the selected bond lengths and angles are tabulated in Table 1.

Similar to the iron complexes, the coordinating environment for the centre metal (for both **Co1** and **Co5**) is a pseudo squarepyramidal geometry, in which three nitrogen atoms, N(1), N(2), N(3), and one chlorine atom, Cl(1), form the square plane. The cobalt atom lies 0.589 (*ca.*) Å out of the chelated plane (N1–N2– N3) for **Co1** and 0.597 (*ca.*) Å out for **Co5**, indicating that the central metal cobalt is not co-planar with the chelating ligand due to the associated sterics. In the molecular structures of both **Co1** and **Co5**, the interacting force of Co–N(2) is stronger than that of Co–N(1) and Co–N(3), which is reflected by the shorter distance

Table 1	Selected bond	lengths and	angles for	Co1 and	Cos
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	Col	Co5		
Bond lengths (Å)				
Co(1)–N(1)	2.179(3)	2.188(2)		
Co(1)–N(2)	2.047(4)	2.047(2)		
Co(1)–N(3)	2.165(4)	2.163(2)		
Co(1)-Cl(1)	2.2334(14)	2.2451(10)		
Co(1)-Cl(2)	2.3228(13)	2.3004(9)		
N(2)–C(40)	1.337(5)	1.337(3)		
N(2)–C(36)	1.340(6)	1.331(3)		
N(1)-C(35)	1.283(5)	1.288(3)		
N(1)–C(19)	1.446(5)	1.436(3)		
N(3)–C(42)	1.282(6)	1.286(3)		
N(3)–C(43)	1.448(6)	1.436(3)		
Bond angles (°)				
N(2)-Co(1)-N(3)	74.87(14)	74.17(9)		
N(2)-Co(1)-N(1)	73.96(13)	74.03(9)		
N(3)-Co(1)-N(1)	140.68(14)	140.31(8)		
N(2)-Co(1)-Cl(1)	159.90(11)	157.42(7)		
N(3)-Co(1)-Cl(1)	101.60(10)	101.07(7)		
N(1)-Co(1)-Cl(1)	99.50(10)	99.22(7)		
N(2)-Co(1)-Cl(2)	88.00(11)	91.44(7)		
N(3)-Co(1)-Cl(2)	101.68(11)	99.86(7)		
N(1)-Co(1)-Cl(2)	100.57(10)	104.05(7)		
Cl(1)-Co(1)-Cl(2)	112.02(6)	111.14(4)		



**Fig. 1** An ORTEP drawing of complex **Co1**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.



**Fig. 2** An ORTEP drawing of one of two independent molecules in complex **Co5** (the other molecular is omitted; the C50a and C51a are disordered atoms for C50 and C51). Thermal ellipsoids are shown at 30% probability. Hydrogen atoms are omitted for clarity.

of Co–N(2) then Co–N(1) and Co–N(3). The two imino-phenyl planes are nearly perpendicular to the chelated plane (N1–N2–N3) and the four phenyl substituents of the two benzhydryl groups almost block the axial sites at the metal centre, which is thought to play a critical role in protecting the active site and maintaining the high activity.

 Table 2
 Ethylene polymerization at atmospheric pressure by cobalt pre-catalysts<sup>a</sup>

				Т	t	Yield		$M_{ m w}{}^c$		$T_{\rm m}{}^d$
Entry	Cat.	Co-cat	Al/Co	°C	min	g	Activity <sup>b</sup>	kg mol <sup>-1</sup>	$M_{\rm w}/M_{\rm n}{}^c$	°C
1	Co3	MAO	1000	20	30	0.05	0.7	122	1.9	133.9
2	Co3	MMAO	1000	20	30	0.75	10.0	142	2.1	133.7
3	Co3	MMAO	500	20	30	0.66	8.8	157	2.6	134.0
4	Co3	MMAO	750	20	30	0.83	11.1	153	2.3	133.8
5	Co3	MMAO	750	0	30	0.55	7.3	249	2.4	134.3
6	Co3	MMAO	750	40	30	0.46	6.1	108	2.2	133.5
7	Co1	MMAO	750	20	30	0.90	12.0	130	2.1	133.2
8	Co2	MMAO	750	20	30	1.90	25.3	157	2.8	134.3
9	Co4	MMAO	750	20	30	0.69	9.2	102	1.9	133.1
10	Co5	MMAO	750	20	30	0.94	12.5	264	4.1	134.1
11	Co6	MMAO	750	20	30	trace	trace			
12	CoR	MMAO	750	20	30	0.09	1.2			
13	Co2	MMAO	750	20	5	0.58	46.4	108	1.9	134.1
14	Co2	MMAO	750	20	10	1.13	45.3	146	2.1	133.7
15	Co2	MMAO	750	20	20	1.79	35.8	147	2.5	133.2
16	Co2	MMAO	750	20	40	2.00	20.0	182	3.8	139.8

<sup>*a*</sup> Reaction conditions: 1.5 μmol of Co, 1 atm of ethylene and 30 mL of toluene. <sup>*b*</sup> Activity: 10<sup>5</sup> g PE mol<sup>-1</sup>(Co) h<sup>-1</sup>. <sup>*c*</sup> Determined by GPC. <sup>*d*</sup> Determined by DSC.

### 2.3 Ethylene polymerization

**2.3.1** Ethylene polymerization at atmospheric pressure. Ethylene polymerization catalyzed by these cobalt complexes with different co-catalysts was conducted at atmospheric pressure. MAO and MMAO were initially used to activate complex Co3 for ethylene polymerization at room temperature (Table 1). The type of co-catalyst, molar ratio of Al/Co, reaction temperature, time and nature of the complexes were shown to have an influence on the activities, as well as the  $M_w$  and  $M_w/M_n$  values of the resultant polyethylenes. The activity exhibited by Co3/MMAO (entry 2 in Table 2) is one order of magnitude higher than that exhibited by Co3/MAO (entry 1 in Table 2), though the polyethylene produced had a similar molecular weight and molecular weight distribution. Thus, the co-catalyst MMAO was selected for further investigations.

The influence of the molar ratio of Al/Co was investigated by increasing the Al/Co molar ratio from 500 to 1000 (entries 2–4 in Table 2). The activities peaked at an optimum ratio of 750 (entry 4 in Table 2). The molecular weight of the polymers obtained decreased as the Al/Co molar ratio increased, which was probably due to the enhanced chain transfer from cobalt to aluminium, resulting in the short-chain polymers.<sup>13</sup>

With the molar ratio of Al/Co (750) fixed, the influence of the reaction temperature was investigated (entries 4–6 in Table 2). Similar to the observations for their iron counterparts,<sup>9</sup> the highest activity here was observed at 20 °C, however, the polymer obtained was very different, as evidenced by the high molecular weight and narrow molecular weight distribution.

The effects of the nature of the ligands on the catalytic behavior were conducted *via* the catalytic experiments of ethylene polymerization with cobalt pre-catalysts/MMAO (entries 4, 7–11 in Table 2). In contrast to the catalytic system using the iron complexes, the cobalt pre-catalysts, **Co1** and **Co2**, provided slightly higher catalytic activities than the pre-catalysts (**Co4** and **Co5**), which bear an additional *para*-methyl substituent, whilst **Co2** possessing 2,6-diethyl groups on the phenyl ring of the imino

nitrogen showed the highest activity amongst this family. Such phenomena were also observed in the catalytic system utilizing 2-imino-1,10-phenanthrolinyliron complexes.<sup>14</sup> Furthermore, the cobalt complex 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]-pyridylcobalt(II) dichloride (**CoR**),<sup>1</sup> which has the highest reported activity of the bis(imino)pyridylcobalt dichloride family for ethylene polymerization,<sup>2a,e</sup> was selected for evaluation as a comparison. The activity of **CoR** (entry 12 in Table 1) was found to be much lower than those of **Co1–Co5** (entries 7–10 in Table 2).

To determine the lifetime of the active species, trials of **Co2/MMAO** were carried out over different reaction times (entries 8, 13–16 in Table 2) at 20 °C. After examination of the data (and trends), it was evident that the active sites deactivated rapidly in the first 30 min, possibly due to impurities present in the catalytic system and the limitation of mass transfer caused by some insoluble polyethylene formed, and after this period the activity tended to a limiting value of about  $2.0 \times 10^6$  g PE mol<sup>-1</sup>(Co) h<sup>-1</sup>. In addition, the  $M_w$  (107–182 kg mol<sup>-1</sup>) and  $M_w/M_n$  (1.9–3.8) values of the obtained PEs were slightly increased upon extending the reaction time and no induction time was observed during the catalytic process.

**2.3.2** Ethylene polymerization at elevated pressure. Based on previous work, it is anticipated that increases in pressure will significantly increase the activities as well as the molecular weight of the polyethylene obtained.<sup>6a,15</sup> The ethylene polymerization with the **Co3/MMAO** catalyst system was also conducted under different pressures of ethylene (Table 3). Increasing the ethylene pressure, the productivity was enhanced and the resultant PEs showed higher molecular weights, which can probably be attributed to the higher monomer concentration around the active species. Also, similar variations of catalytic activities with regard to the cocatalysts, the reaction temperature, time and Al/Co molar ratio, as well as the nature of the ligand were observed on elevating the ethylene pressure from 1 atm to 5 or 10 atm. The evaluation herein was carried out at elevated ethylene pressures of 5 atm and 10 atm (see Table 3). In general, the co-catalysts significantly impacted

				Т	Р	Yield		$M_{ m w}{}^c$		$T_{\rm m}{}^d$
Entry	Cat.	Co-cat	Al/Co	°C	atm	g	Activity <sup>b</sup>	kg mol <sup>-1</sup>	$M_{\rm w}/M_{\rm n}{}^c$	°C
1	Co3	MAO	1000	20	5	0.67	8.9	109	3.5	133.8
2	Co3	MMAO	750	20	5	2.2	29.3	153	3.1	133.7
3	Co3	MMAO	1000	20	5	3.0	40.0	147	2.8	134.6
4	Co3	MMAO	1250	20	5	2.8	37.3	143	3.2	134.0
5	Co3	MMAO	1000	30	5	3.1	41.3	134	2.9	133.8
6	Co3	MMAO	1000	40	5	2.2	29.3	134	3.6	134.1
7	Co1	MMAO	1000	30	5	3.4	45.3	182	2.3	134.0
8	Co2	MMAO	1000	30	5	3.8	50.7	98	2.5	133.6
9	Co4	MMAO	1000	30	5	2.3	30.7	156	2.2	133.5
10	Co5	MMAO	1000	30	5	3.5	46.7	179	3.1	135.9
11	Co6	MMAO	1000	30	5	trace	trace	_	_	
12	CoR	MMAO	1000	30	5	0.22	2.9	_	_	
13	Co3	MAO	1000	30	10	0.9	12.0	240	3.7	133.8
14	Co3	MMAO	1000	30	10	4.4	58.7	186	2.8	134.3
15	Co3	MMAO	1250	30	10	5.2	69.3	136	2.9	134.0
16	Co3	MMAO	1500	30	10	4.3	57.3	124	2.2	133.6
17	Co3	MMAO	1250	40	10	5.8	77.3	169	3.0	133.9
18	Co3	MMAO	1250	50	10	5.0	66.7	133	2.5	134.1
19	Co1	MMAO	1250	40	10	6.4	85.3	107	2.1	133.3
20	Co2	MMAO	1250	40	10	7.4	98.7	324	3.0	133.4
21	Co4	MMAO	1250	40	10	5.7	76.0	216	4.0	133.0
22	Co5	MMAO	1250	40	10	6.7	89.3	101	2.2	133.2
23	Co6	MMAO	1250	40	10	trace	trace		_	
24	CoR	MMAO	1250	40	10	0.3	4.0		_	_
" Reaction	o conditions:	1.5 $\mu$ mol of Co;	30 min; 100 m	L of toluen	e. <sup><i>b</i></sup> Activity,	10 <sup>5</sup> g PE mol <sup>-1</sup>	$^{1}(\text{Co}) \text{ h}^{-1}$ . <sup><i>c</i></sup> Deter	mined by GPC.	<sup>d</sup> Determined by	DSC.

 Table 3 Ethylene polymerization at elevated pressure by the cobalt pre-catalysts<sup>a</sup>

on the activities both at 5 atm (entries 1 and 2 in Table 3) and 10 atm (entries 13 and 14 in Table 3). The activities exhibited in the presence of MMAO (entries 2 and 14 in Table 3) are always far higher than those in the presence of MAO (entries 1 and 13 in Table 3).

As a consequence, MMAO was used as the activator for further screening and the best performance was obtained with Co3/MMAO at 30 °C with an Al/Co molar ratio of 1000 (entry 5, Table 3) at 5 atm and at 40 °C with an Al/Co molar ratio of 1250 (entry 17, Table 3) for 10 atm, respectively, by varying the Al/Co molar ratio and the reaction temperature (entries 2–6 and 14–18, Table 3). Importantly, the molecular weight and the molecular weight distribution of the polymers obtained remained virtually unaffected, which should be of benefit for producing polymers with a uniform molecular weight and narrow molecular weight distribution. The alkyl substituents ( $\mathbf{R}^1$  and  $\mathbf{R}^2$ ) on the imino-aryl ring proved to be influential to both the catalytic activity and the molecular weight, as well as the molecular weight distribution of the products. The activities decreased in the order Co2 > Co5 > $Co1 > Co3 > Co4 \gg Co6$  at all ethylene pressures used (1, 5 and 10 atm) and the molecular weight of the polyethylenes varied from 97 to 179 kg mol<sup>-1</sup> at 5 atm and from 107 to 323 kg mol<sup>-1</sup> at 10 atm, respectively (entries 5, 7-11, 17 and 19-23, Table 3). However, the molecular weight distribution remained relatively narrow, which is indicative of single-site catalysis. Most interestingly, the catalytic activities observed for Co1-Co5 are much higher than that observed for CoR (entries 12 and 24, Table 3).

# 3. Conclusion

2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyl cobalt complexes were synthesized and fully characterized. Upon treatment with MMAO, the current family of cobalt pre-catalysts was found to exhibit the highest activities reported to date toward ethylene polymerization, with an observed activity of up to  $9.87 \times 10^6$  g PE mol<sup>-1</sup>(Co) h<sup>-1</sup>, producing high- $M_w$  (100–330 kg mol<sup>-1</sup>) and narrow- $M_w/M_n$  (1.9–4.0) polyethylene. The molecular weights and the polydispersity indexes of the resultant polyethylenes could be readily controlled by finely tuning the nature of ligands through varying their substituents and modifying the reaction parameters, such as the molar ratio of Al/Co and reaction temperature.

## 4. Experimental section

## 4.1 General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodiumbenzophenone and distilled under nitrogen before use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) 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 (-40-140 ppm) were recorded on a Bruker DMX 600 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in the range 4000-400 cm<sup>-1</sup>. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights  $(M_w)$  and molecular weight distribution  $(M_w/M_n)$  of the polyethylenes were determined by a PL-GPC220 at 120 °C, with 1,2,4-trichlorobenzene as the solvent. A DSC trace and the melting points of the polyethylenes were obtained from the second scanning run on Perkin-Elmer DSC-7 at a heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup>.

## 4.2 Synthesis and characterization of complexes Co1-Co6

All of the cobalt complexes were prepared in the same manner by the reaction of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine with CoCl<sub>2</sub> in ethanol. A typical synthesis of complex Co1, 2-[1-(2,6-dibenzhydryl-4methylphenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridylcobalt(II) dichloride, is described as follows: a mixture of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6dimethylphenylimino)ethyl]pyridine (138 mg, 0.20 mmol), CoCl<sub>2</sub> (26 mg, 0.20 mmol) and ethanol (4 mL) was stirred at room temperature for 3 h and 10 mL of diethyl ether was added to precipitate the cobalt complex. Then, the precipitate was washed with diethyl ether  $(3 \times 5 \text{ mL})$  and dried to give the pure product as a yellow powder in 126 mg (76.9%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  113.92 (s, 1H, Py  $H_m$ ); 109.29 (s, 1H, Py  $H_m$ ); 49.45 (s, 1H, Py  $H_p$ ); 20.95 (s, 3H, C $H_3$ ); 15.15 (s, 2H, Ar (represents the phenyl core with 2,6-dibenzhydryl-4-methylphenylimino)  $H_{\rm m}$ ); 9.03 (s, 2H, Ar  $H_{\rm m}$ ); 4.96 (m, 10H, aryl (represents all phenyl groups beyond the above assigned Ar group) H); 3.61 (s, 4H, aryl *H*); 2.81 (s, 3H, aryl *H*); 2.04 (s, 3H, aryl *H*); 1.23 (s, 2H,  $2 \times CH$ ); -2.11 (s, 3H, CH<sub>3</sub>); -19.09 (s, 3H, CH<sub>3</sub>); -7.59 (s, 1H, Ar H<sub>p</sub>); -23.50 (s, 6H, 2 × N=CCH<sub>3</sub>). FT-IR (KBr; cm<sup>-1</sup>): 3056, 3023, 2912, 1621, 1584 ( $v_{C=N}$ ), 1495, 1446, 1373, 1260, 1217, 1028, 806, 773, 746, 703. Anal. calcd for C<sub>50</sub>H<sub>45</sub>Cl<sub>2</sub>CoN<sub>3</sub> (818): C, 73.44; H, 5.55; N, 5.14%. Found: C, 73.32; H, 5.46; N, 5.51%.

**2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6diethylphenylimino)ethyl]pyridinescobalt(11)** dichloride (Co2). Isolated as a yellow solid, yield: 130 mg (77.1%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  113.53 (s, 1H, Py  $H_m$ ); 112.54 (s, 1H, Py  $H_m$ ); 46.56 (s, 1H, Py  $H_p$ ); 20.85 (s, 3H, CH<sub>3</sub>); 10.94 (s, 2H, Ar  $H_m$ ); 9.04 (s, 2H, Ar  $H_m$ ); 7.20 (s, 6H, aryl H); 5.37 (s, 2H, aryl H); 4.80 (s, 2H, aryl H); 3.59 (s, 6H, aryl H); 2.94 (s, 2H, aryl H); 2.40 (s, 2H, aryl H); 1.29 (s, 2H, 2 × CH); -9.48 (s, 1H, Ar  $H_p$ ); -18.81 (s, 10H, aryl H); -35.30 (s, 3H, N=CC $H_3$ ); -39.06 (s, 3H, N=CC $H_3$ ). FT-IR (KBr, cm<sup>-1</sup>): 3057, 2969, 2918, 1620, 1587 ( $v_{C=N}$ ), 1495, 1444, 1370, 1261, 1216, 1079, 1030, 866, 803, 768, 745, 700. Anal. calcd for C<sub>52</sub>H<sub>49</sub>Cl<sub>2</sub>FeN<sub>3</sub> (846): C, 73.84; H, 5.84; N, 4.97%. Found: C, 73.57; H, 5.77; N, 5.01%.

**2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diisopropylphenylimino)ethyl]pyridylcobalt(II)** dichloride (Co3). Isolated as a yellow solid, yield: 146 mg (83.3%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  115.41 (s, 1H, Py  $H_m$ ); 113.50 (s, 1H, Py  $H_m$ ); 49.10 (s, 1H, Py  $H_p$ ); 20.91 (s, 3H, CH<sub>3</sub>); 10.40 [s, 2H, Ar  $H_m$ ]; 9.15 (s, 2H, Ar  $H_m$ ); 7.48 (s, 6H, aryl H); 2.54 [s, 2H, aryl H]; 4.87 (s, 2H, aryl H); 3.53 (s, 6H, aryl H); 2.63 (s, 2H, aryl H); 2.02 (s, 2H, aryl H); 1.24 (s, 2H, 2 × CH); -9.00 (s, 1H, Ar  $H_p$ ); -16.83 (s, 2H, 2 × CH); -17.21 (s, 6H, 2 × N=CCH<sub>3</sub>); -17.94 (s, 12H, 4 × CH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 2966, 2918, 1865, 1620, 1583 ( $v_{C=N}$ ), 1494, 1448, 1374, 1263, 1029, 816, 794, 769, 745, 700. Anal. calcd for C<sub>54</sub>H<sub>53</sub>Cl<sub>2</sub>FeN<sub>3</sub> (874): C, 74.22; H, 6.11; N, 4.81%. Found: C, 74.03; H, 5.87; N, 4.97%.

2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridylecobalt(II) dichloride (Co4).

Isolated as a yellow solid, yield: 130 mg (78.3%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  112.30 (s, 1H, Py  $H_m$ ); 111.07 (s, 1H, Py  $H_m$ ); 45.76 (s, 1H, Py  $H_p$ ); 20.06 (s, 6H, 2 × CH<sub>3</sub>); 9.26 (s, 2H, Ar  $H_m$ ); 8.54 (s, 2H, Ar  $H_m$ ); 7.03 (s, 6H, aryl H); 5.54 (s, 2H, aryl H); 4.44 (s, 2H, aryl H); 3.20 (s, 6H, aryl H); 2.48 (s, 2H, aryl H); 1.28 (s, 2H, 2 × CH); 0.994 (s, 2H, aryl H); -19.17 (s, 6H, 2 × CH<sub>3</sub>); -25.10 (s, 6H, 2 × N=CCH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3025, 2917, 1617, 1585 ( $v_{C=N}$ ), 1495, 1448, 1365, 1263, 1222, 1080, 1030, 858, 815, 769, 748, 701. Anal. calcd for C<sub>51</sub>H<sub>47</sub>Cl<sub>2</sub>CoN<sub>3</sub> (831): C, 73.64; H, 5.70; N, 5.05%. Found: C, 73.44; H, 5.51; N, 5.34%.

**2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridylcobalt(II)** dichloride (Co5). Isolated as a yellow solid, yield: 141 mg (82.1%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  115.79 (s, 2H, Py  $H_m$ ); 49.72 (s, 1H, Py  $H_p$ ); 20.68 (s, 3H,  $CH_3$ ); 20.38 (s, 3H,  $CH_3$ ); 10.18 (s, 2H, Ar  $H_m$ ); 8.78 (s, 2H, Ar  $H_m$ ); 6.97 (s, 6H, aryl H); 5.39 (s, 2H, aryl H); 4.70 (s, 2H, aryl H); 3.54 (s, 6H, aryl H); 3.11 (s, 2H, aryl H); 1.76 (s, 2H, aryl H); 1.28 (s, 2H,  $2 \times CH$ ); -18.97 (s, 4H,  $2 \times CH_2$ ); -19.59 (s, 6H,  $2 \times CH_3$ ); -35.17 (s, 3H, N=CCH<sub>3</sub>); -37.07 (s, 3H, N=CCH<sub>3</sub>). FT-IR(KBr, cm<sup>-1</sup>): 3028, 2959, 2917, 2866, 1618, 1583 ( $v_{C=N}$ ), 1495, 1446, 1371, 1264, 1217, 1080, 1030, 865, 830, 767, 746, 702. Anal. calcd for C<sub>53</sub>H<sub>51</sub>Cl<sub>2</sub>CoN<sub>3</sub> (859): C, 74.03; H, 5.98; N, 4.89%. Found: C, 73.99; H, 5.77; N, 4.94%.

**2,6-Bis**[1-(**2,6**-dibenzhydryl-4-methylphenylimino)ethyl]pyridylcobalt(II) dichloride (Co6). Isolated as a yellow solid, yield: 98.8 mg (43.5%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  115.79 (s, 2H, Py  $H_m$ ); 49.72 (s, 1H, Py  $H_p$ ); 20.54 (s, 6H, 2 × CH<sub>3</sub>); 7.73 (s, 4H, Ar  $H_m$ ); 3.53 (s, 30H, Ar H); 1.27 (s, 4H, 4 × CH); 0.996 (s, 10H, Ar H); -20.15 (s, 6H, 2 × N=CCH<sub>3</sub>). FT-IR (KBr,cm<sup>-1</sup>): 3026, 2920, 2166, 2029, 1978, 1583 ( $v_{C=N}$ ), 1494, 1447, 1264, 1213, 1077, 1031, 916, 859, 809, 768, 747, 700. Anal. calcd for C<sub>75</sub>H<sub>63</sub>Cl<sub>2</sub>CoN<sub>3</sub> (1136): C, 79.28; H, 5.59; N, 3.70%. Found: C, 78.89; H, 5.25; N, 4.05%.

#### 4.3 X-ray crystallographic studies

Single crystals of **Co1** and **Co5** suitable for X-ray diffraction analysis were obtained by layering *n*-pentane on their dichloromethane solutions at room temperature. With graphite-monochromatic Mo-K $\alpha$  radiation (k = 0.71073 Å) at 173(2) K, the 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 hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL– 97 package.<sup>16</sup> Details of the X-ray structure determinations and refinements are provided in Table 4.

## 4.4 General procedure for ethylene polymerization

**Ethylene polymerization under atmospheric ethylene.** Firstly, a 30 mL of toluene solution of the pre-catalyst was added to a glass reactor using a syringe and then the required amount of co-catalyst (MAO, MMAO) was added. The reaction progressed with stirring under an ambient ethylene atmosphere. After the reaction was carried out for the required period, the reaction solution was quenched with 10% hydrochloric acid ethanol. The precipitated

	Co1	2Co5
Empirical formula	$C_{50}H_{45}Cl_2CoN_3$	$C_{106}H_{102}Cl_4Co_2N_6\\$
fw	817.72	1719.60
T/K	173(2)	173(2)
λ/Å	0.71073	0.71073
Cryst. syst.	monoclinic	triclinic
Space group	$P2_1/n$	$P\overline{1}$
a/Å	9.5984(19)	13.237(3)
b/Å	34.200(7)	16.590(3)
c/Å	13.446(3)	25.640(5)
$\alpha$ (°)	90	89.00(3)
$\beta$ (°)	106.94(3)	77.66(3)
$\gamma$ (°)	90	88.11(3)
V (Å3)	4222.4(15)	5497.2(19)
Z	4	2
Dcalcd. (gcm <sup>-3</sup> )	1.286	1.039
$\mu/\text{mm}^{-1}$	0.571	0.441
F(000)	1708	1804
Cryst. size/mm	$0.23 \times 0.20 \times 0.09$	$0.25 \times 0.21 \times 0.17$
$\theta$ range (°)	1.19-27.48	0.81-27.44
Limiting indices	$-12 \le h \le 12$	$-17 \le h \le 17$
-	$-32 \le k \le 44$	$-21 \le k \le 21$
	$-12 \le l \le 17$	$-33 \le l \le 33$
No. of rflns collected	34568	68283
No. unique rflns [R(int)]	9681 (0.0746)	24934 (0.0461)
Completeness to $\theta$ (%)	99.9%	99.4%
Abs corr	none	none
Data/restranints/params	9681/0/505	24934/36/1082
Goodness of fit on $F^2$	1.259	1.037
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0939$	$R_1 = 0.0634$
	$wR_2 = 0.2220$	$wR_2 = 0.1696$
R indices (all data)	$R_1 = 0.1132$	$R_1 = 0.0761$
	$wR_2 = 0.2378$	$wR_2 = 0.1795$
Largest diff. peak and hole/e $Å^{-3}$	0.461 and -0.545	1.388 and -0.480

polymer was collected by filtration, washed with ethanol and water and dried in a vacuum at 60 °C until it was of constant weight.

Ethylene polymerization under 5/10 atm ethylene. 50 mL of toluene was first injected into the autoclave, which is a 300 mL stainless steel vessel equipped with a mechanical stirrer and a temperature controller. When the temperature reached the required value, another 30 mL toluene containing the dissolved complex (1.5 µmol) and the required amount of co-catalyst (MAO, MMAO), plus the residual toluene were successively added using a syringe. The reaction mixture was aggressively stirred for the desired time under the corresponding pressure of ethylene throughout the entire experiment. The reaction was terminated and the polymer was collected using the same method as above for the ethylene polymerization at ambient pressure.

## Acknowledgements

This work is supported by MOST 863 program No. 2009AA034601. The EPSRC are thanked for the awarded travel grant (to C. R.).

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