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

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A series of cobalt(II) dichloride complexes ligated by 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines was synthesized and characterized by FT-IR spectroscopy and elemental analysis. The molecular structure of the representative complex **Co4** (R1 = Me, R2 = Me) was confirmed as pseudo square-pyramidal geometry at cobalt by single-crystal X-ray diffraction. Upon treatment with the co-catalysts MAO or MMAO, all cobalt pre-catalysts exhibited high activities up to 1.81×10^7 g PE mol⁻¹(Co) h⁻¹ in ethylene polymerization, and produced polyethylene products with molecular weights in the tens of thousands and narrow molecular weight distributions. The influence of the reaction parameters and nature of the ligands on the catalytic behavior of the title cobalt complexes was investigated.

Introduction

Polyolefins are important synthesized polymers, providing cheap and easily processable materials, which can be recycled. They are sustainable materials because of their pure hydrocarbon structures from natural oils and are further being useful as resources for energy or hydrocarbon substrates.¹ The recent Asian crisis of the plasticizer (commonly phthalates) within food packages, which can potentially cause harm to the endocrine, reproductive and respiratory systems of humans,² raised some concerns regarding the use of polyolefins produced by Ziegler–Natta catalytic systems possessing phthalate donors.³ In addition, processing lubricates for the engineering of plastics and alloys are comprised of linear polyethylenes, which are required to possess relatively lower molecular weights (usually in the tens of thousands) and narrow molecular weight distributions. These specific polyethylenes could be produced by metallocene⁴ or half-titanocene catalytic systems.⁵ However, late-transition metal complex pre-catalysts,⁶ in which the late-transition metal complex pre-catalysts bearing ligands with finely tuning substituents, could act as single-site catalytic system and

accurately control the properties of resultant polyethylenes are an attractive alternative.

The emergence of bis(imino)pyridine complexes of iron(II) or cobalt(II), exhibiting high activity for ethylene oligomerization and polymerization was a milestone in late transition metal pre-catalysts for polyolefin production.⁷ Based on the bis(imino)pyridyliron(II) chloride pre-catalysts, DuPont and PetroChina had a project for ethylene oligomerization, whilst BP initiated a pilot-process for high density polyethylenes (HDPE). Crucial problems remained in both processing developments for polyethylenes or oligomers (or low molecular polyethylenes).⁶ To explore useful metal (Fe or Co) pre-catalysts, some designed *N*-heterocyclic compounds have been developed and employed as tridentate ligands. Modifications of the ligand frameworks⁷ or substituents on the aryl groups^{8–15} have been accomplished providing metal complex pre-catalysts for ethylene polymerization and oligomerization, including our contributions of tridentate ligands such as 2-imino-1,10-phenanthrolines,^{16,17} 2-benzimidazolyl-6-(1-(arylimino)ethyl)pyridines,^{18–21} 2-quinoxalanyl-6-iminopyridines,²² 2-(Benzimidazol-2-yl)-1,10-phenanthrolines,²³ 2-(benzoxazolyl)-1,10-phenanthrolines²⁴ and 8-(1-aryliminoethylidene)quinaldines,²⁵ as well as a limited number of bidentate ligands such as 2-(2-pyridyl)quinoxaline,²⁶ 2-ethylcarboxylate-6-iminopyridine,²⁷ pyrazolylimino-phosphorane.²⁸ These achievements provided model pre-catalysts for industrial ethylene oligomerization. With regard to ethylene polymerization, recent observations for iron pre-catalysts employing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines confirmed their ability to perform ethylene polymerization at industrial operation

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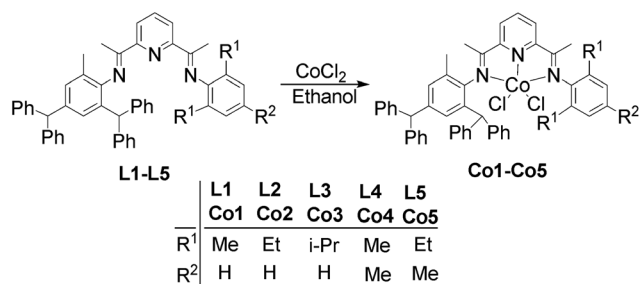
† CCDC reference number 856118. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2py00590e

temperature.²⁹ Importantly, at such high temperatures, polyethylenes with narrow molecular weights were observed; no oligomers were present. The analogous cobalt pre-catalysts bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl] pyridines showed similar polymerization properties.³⁰ Subsequent work showed the successful use of analogous iron pre-catalysts bearing 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-(1-arylimino)ethylpyridines,³¹ and given this, the title cobalt complexes are synthesized and characterized. When activated with co-catalysts, the cobalt complexes showed high activities towards ethylene polymerization, obtaining polyethylenes with narrow molecular weight distributions, and moreover, polyethylenes with molecular weights in the range of tens thousands were obtained, which are in the desired range for good lubricates for processing systems. Herein, the synthesis and characterization of the cobalt(II) complexes containing 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-(1-arylimino)ethyl pyridines are reported, and the impact of the polymerization parameters and the nature of the ligands on the catalytic activities of the cobalt pre-catalysts and on the properties of polyethylene products obtained are investigated.

Results and discussion

Synthesis and characterization of the cobalt(II) complexes (Co1–Co5)

The series of 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-(1-arylimino)ethylpyridine ligands was prepared according to our previously reported procedures.³¹ The corresponding cobalt(II) complexes (**L1CoCl₂**–**L5CoCl₂**) were synthesized in satisfactory yields (63–81%) by the stoichiometric reactions of cobalt dichloride with the 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-(1-arylimino)ethylpyridine ligands in ethanol at room temperature (Scheme 1). These cobalt complexes exhibited higher stability in both solution and solid state than their corresponding iron(II) analogues. All elemental analyses for these cobalt complexes were consistent with their formulae, and in their FT-IR spectra, the C=N stretching vibration bands appeared in the range of 1580–1584 cm^{−1} (*cf.* 1638–1644 cm^{−1} for the free ligands),³¹ indicating the effective coordination. To confirm the unambiguous molecular structures, a single crystal of complex **Co4** was subjected to single-crystal X-ray diffraction.



Scheme 1 Synthesis of cobalt(II) complexes.

X-ray crystallographic studies

Single crystals of complex **Co4** were grown from a saturated dichloromethane solution layered with *n*-hexane at room temperature. The molecular structure is shown in Fig. 1, and the selected bond lengths and angles are collected in Table 1. As shown in Fig. 1, there is a pseudo square-pyramidal geometry around the cobalt centre with three coordinated nitrogen and two chlorine atoms. The square plane is formed by the three nitrogen atoms, N(1), N(2), N(3), and one chlorine atom Cl(1), and the cobalt atom lies 0.367 Å out of the chelated plane N(1)–N(2)–N(3)–Cl(1). The bond angles are close to right angles, for example N(2)–Co(1)–Cl(1) 95.59(8)°, N(3)–Co(1)–Cl(1) 96.35(8)°, N(3)–Co(1)–Cl(2) 99.99(8)°. In addition, the Co(1)–N(2) (pyridine) bond length (2.048(3) Å) is relatively shorter than the other two Co–N_{imino} bonds listed as Co(1)–N(1) (2.239(3) Å) and Co(1)–N(3) (2.210(3) Å), and the later two Co–N bond are of similar length. The both bonds N(1)–C(6) and N(3)–C(8) at 1.297(4) Å and 1.277(4) Å, are typical of C=N bond character.

Ethylene polymerization

Following screening with various alkylaluminum reagents, high activities for the title cobalt pre-catalysts were obtained with the co-catalyst methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), similar to the catalytic behavior exhibited by the analogous cobalt pre-catalysts bearing 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-(1-arylimino)ethyl pyridines.³⁰ The catalytic behavior for ethylene polymerization were investigated in detail using either MAO or MMAO. Variation of the reaction parameters such as reaction time, temperature, the molar ratio of Al/Co as well as the influence of the ligands, was conducted in order to deduce their effect on catalytic activity and on polymer properties such as the molecular weight and the molecular weight distributions.

Ethylene polymerization in the presence of MAO

Upon activation with MAO, the ethylene polymerization by complex **Co1** was initially evaluated for the optimum conditions under 10 atm ethylene pressure; and the results are tabulated in Table 2. On changing the molar ratio of the Al/Co from 1000 to 3000 (entries 1–4 in Table 2), high activity was observed at Al/Co of 1500, which is the same as observed for the cobalt(II)

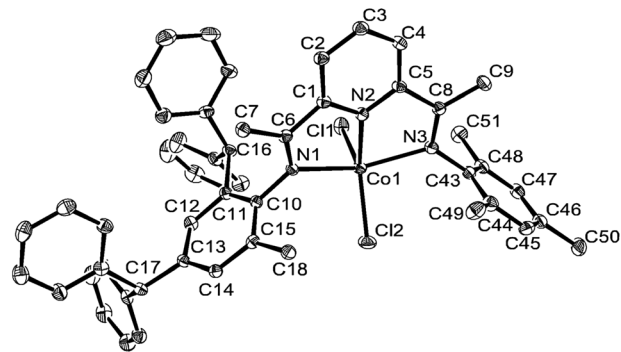


Fig. 1 ORTEP drawing of complex **Co4** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

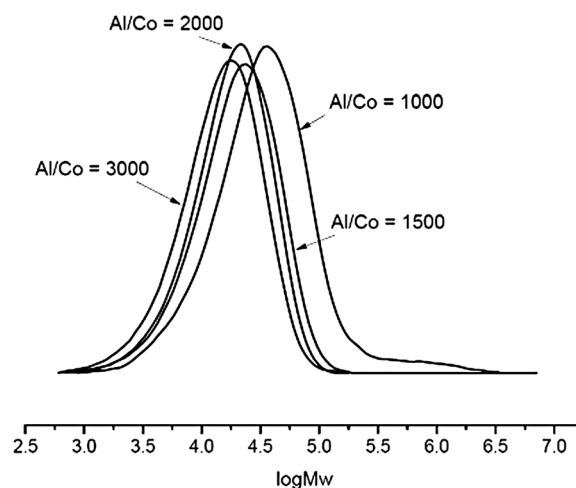
Table 1 Selected bond lengths and angles for complex **Co4**

Co4			
Bond lengths (Å)		Bond angles (°)	
Co(1)–N(1)	2.239(3)	N(2)–Co(1)–N(3)	74.80(11)
Co(1)–N(2)	2.048(3)	N(2)–Co(1)–N(1)	74.45(10)
Co(1)–N(3)	2.210(3)	N(3)–Co(1)–N(1)	146.20(10)
Co(1)–Cl(1)	2.2934(12)	N(2)–Co(1)–Cl(1)	95.59(8)
Co(1)–Cl(2)	2.2558(12)	N(3)–Co(1)–Cl(1)	96.35(8)
N(1)–C(6)	1.297(4)	N(1)–Co(1)–Cl(1)	100.28(8)
N(1)–C(10)	1.444(4)	N(2)–Co(1)–Cl(2)	145.77(8)
N(2)–C(1)	1.336(4)	N(3)–Co(1)–Cl(2)	99.99(8)
N(2)–C(5)	1.345(4)	N(1)–Co(1)–Cl(2)	97.50(8)
N(3)–C(8)	1.277(4)	Cl(1)–Co(1)–Cl(2)	118.64(5)
N(3)–C(43)	1.446(4)	N(2)–Co(1)–N(3)	74.80(11)

dichloride pre-catalysts bearing 2-alkyl-8-(benzimidazol-2-yl) quinolines.³² Notably, the higher the Al/Co molar ratio employed in the reaction, the lower the molecular weight observed for the polyethylene (entries 1–4 in Table 2). The polyethylene products formed at higher Al/Co molar ratio showed narrow molecular weight distribution (Fig. 2), indicating unimodal polyethylenes produced with the Al/Co molar ratio 1500 or higher. As shown in their GPC curves (Fig. 2), the polyethylenes obtained with higher Al/Co molar ratios possessed lower molecular weights, consistent with enhanced chain transfer from the cobalt species to aluminium.³³

At an Al/Co ratio of 1500, the reaction temperatures were varied from 25 to 50 °C (entries 2 and 5–7 in Table 2), and the highest activity was observed up to 9.52×10^6 g PE mol^{−1} (Co) h^{−1} (entry 6 in Table 2) at 40 °C. The obtained polyethylenes were measured by GPC to show the influence on their molecular weights and distributions (Fig. 3). As shown in Fig. 3, the unimodal features of all obtained polyethylenes indicated the presence of the single-site active species (entries 2 and 5–7 in Table 2), which are similar with the properties of the polyethylenes by its cobalt analog pre-catalyst.³⁰

Therefore the optimum conditions were set as an Al/Co ratio of 1500, and the ethylene polymerization with the other cobalt pre-catalysts (**Co2**–**Co5**) was extensively investigated (entries 8–11 in Table 2). Different to the catalytic performances by their iron analogs,³¹ the cobalt pre-catalysts **Co2** and **Co5** with *N*-aryl group having *ortho*-ethyl substituents (entries 8 and 11 in Table 2) showed relatively higher activities, which is similar to

**Fig. 2** GPC curves of the PEs obtained by **Co1**/MAO under 10 atm ethylene with various Al/Co molar ratios (entries 1–4 in Table 2).

the case of catalytic activities observed by pre-catalysts bearing 2-imino-1,10-phenanthrolines.^{16,17,34} Moreover, the catalytic systems of **Co2** and **Co5** produced polyethylenes with higher molecular weights (Fig. 4). As shown in Fig. 4, all PEs obtained by **Co1**–**Co5**/MAO exhibited unimodal features. The system using **Co2** exhibited the highest activity, up to 1.81×10^7 g PE mol^{−1} (Co) h^{−1} (entry 8 in Table 2) and showed the highest molecular weight of the resultant polyethylene produced by using MAO (Fig. 4), up to 1.18×10^5 g mol^{−1} (entry 8 in Table 2).

Ethylene polymerization with **Co1**–**Co5**/MMAO system

In the same manner, the catalytic system of complex **Co1** was explored with the co-catalyst MMAO instead of MAO, and the results are listed in Table 3 (entries 1–7). Under the optimum conditions, an activity of 1.63×10^7 g PE mol^{−1} (Co) h^{−1} was observed using the molar ratio of Al/Co 1500 at 40 °C (entry 6). For molar ratios of Al/Co from 1000 to 3000 at room temperature, the GPC curves for the obtained polyethylenes are shown in Fig. 5. As well as achieving better catalytic activity at the Al/Co ratio of 1500, the obtained polyethylene possessed the highest molecular weight and narrow molecular weight distribution (entry 2, Table 3), indicative of the formation of single-site active

Table 2 Catalyst results of ethylene polymerization with **Co1**–**Co5**/MAO^a

Run	Pro-cat.	Al/Co	<i>T</i> /°C	Yield/g	Activity ^b	<i>M</i> _w ^c /10 ⁴ g mol ^{−1}	<i>M</i> _w / <i>M</i> _n ^c	<i>T</i> _m ^d /°C
1	Co1	1000	25	1.6	2.1	7.39	3.54	131.92
2	Co1	1500	25	5.41	7.21	2.70	1.93	132.28
3	Co1	2000	25	4.23	5.64	2.31	1.82	132.4
4	Co1	3000	25	2.99	3.99	1.95	1.92	132.1
5	Co1	1500	30	6.37	8.49	3.60	2.54	131.91
6	Co1	1500	40	7.14	9.52	5.55	2.76	132.24
7	Co1	1500	50	5.36	7.15	4.14	1.79	131.4
8	Co2	1500	40	13.54	18.05	11.82	2.70	132.22
9	Co3	1500	40	7.36	9.81	9.28	2.52	132.88
10	Co4	1500	40	4.56	6.08	3.54	2.28	131.75
11	Co5	1500	40	13.03	17.4	9.91	1.97	131.99

^a Conditions: 1.5 μmol **Co**; 30 min; 100 mL of toluene; 10 atm ethylene. ^b 10⁶ g PE mol^{−1} (Co) h^{−1}. ^c Determined by GPC. ^d Determined by DSC.

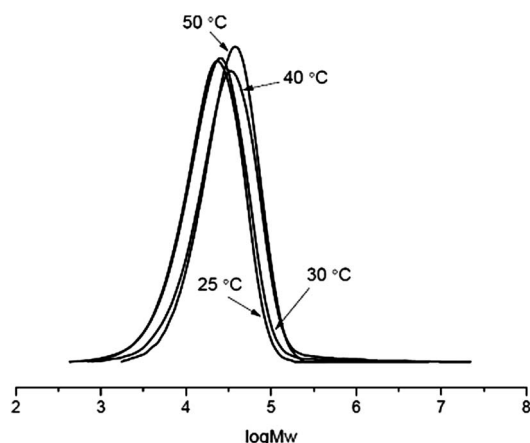


Fig. 3 GPC curves of PEs obtained by **Co1**/MAO under 10 atm ethylene at various temperatures (entries 2 and 5–7 in Table 2).

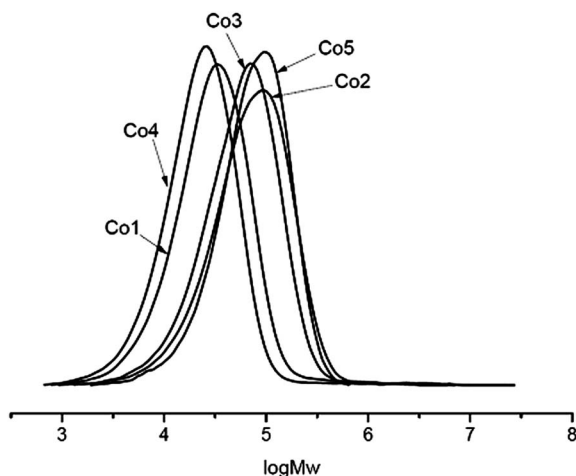


Fig. 4 GPC curves of the PEs obtained by **Co1**–**Co5**/MAO (entries 6 and 8–11 in Table 2).

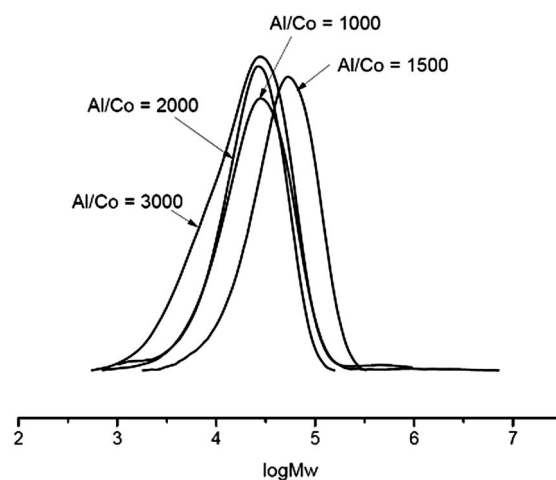


Fig. 5 GPC curves of the PEs obtained by **Co1**/MMAO with various Al/Co molar ratios (entries 1–4 in Table 3).

species. Upon changing the reaction temperatures (entries 2 and 5–7 in Table 3), the highest activity was observed at 40 °C (entry 6). In general, the polyethylene products obtained were of narrow molecular weight distributions (Fig. 6). This information provides an indication that single-site active species are formed in the catalytic system with the Al/Co ratio at 1500. The formed polyethylenes have molecular weights in the tens of thousands, which are in the ball-park area required for new processing lubricants.

Under the optimum conditions of molar ratio Al/Co of 1500 at 40 °C, all the other cobalt pre-catalysts (**Co2**–**Co5**) also showed good catalytic activities towards ethylene polymerization (entries 8–11 in Table 3). Again, single-site active species were evident in all the catalytic systems based on these cobalt pre-catalysts and polyethylenes with narrow molecular weight distributions were formed.

In addition, the influence of ethylene pressure on the catalytic activity and on the properties of obtained polyethylenes was investigated.³⁵ Activities were found to increase upon elevating

Table 3 Catalytic results of ethylene polymerization with **Co1**–**Co5**/MMAO^a

Entry	Pro-cat.	Al/Co	P/atm	T/°C	t/min	Yield/g	Activity ^b	$M_w^c/10^4 \text{ g mol}^{-1}$	M_w/M_n^c	$T_m^d/^\circ\text{C}$
1	Co1	1000	10	25	30	4.42	5.89	2.89	2.01	131.85
2	Co1	1500	10	25	30	5.47	7.29	6.02	1.83	131.97
3	Co1	2000	10	25	30	3.63	4.83	4.70	2.77	131.88
4	Co1	3000	10	25	30	1.83	2.44	4.00	3.38	131.60
5	Co1	1500	10	30	30	6.84	9.12	3.68	1.79	131.44
6	Co1	1500	10	40	30	12.20	16.3	6.85	1.69	131.53
7	Co1	1500	10	50	30	6.83	9.1	3.35	1.80	130.64
8	Co2	1500	10	40	30	5.43	7.24	9.37	1.99	131.79
9	Co3	1500	10	40	30	10.37	13.8	10.3	3.23	132.62
10	Co4	1500	10	40	30	10.15	13.5	3.98	1.80	131.46
11	Co5	1500	10	40	30	4.69	6.25	5.42	1.99	132.45
12	Co1	1500	1	40	30	0.97	1.29	2.26	1.94	131.86
13	Co1	1500	5	40	30	5.25	7.01	8.44	4.56	132.81
14	Co1	1500	10	40	15	9.91	26.4	3.34	1.96	130.98
15	Co1	1500	10	40	60	14.11	9.40	29.3	9.44	131.46

^a Conditions: 1.5 μmol Co; 30 mL toluene for 1 atm ethylene and 100 mL toluene for 10 atm ethylene. ^b $10^6 \text{ g PE mol}^{-1} (\text{Co}) \text{ h}^{-1}$. ^c Determined by GPC.

^d Determined by DSC.

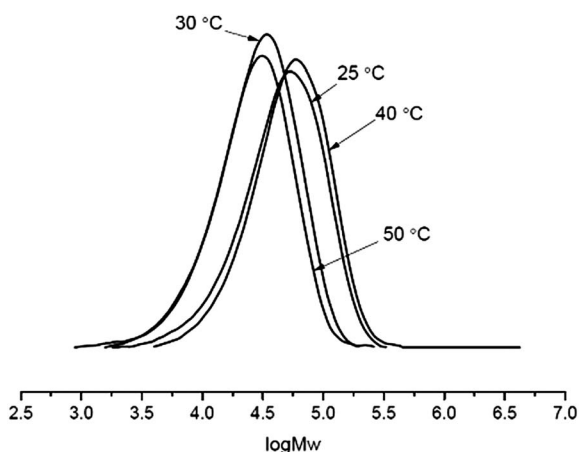


Fig. 6 GPC curves of the PEs obtained by **Co1**/MMAO under 10 atm ethylene at various temperatures (entries 2 and 5–7 in Table 3).

the ethylene pressure. On extending the reaction time (entries 6, 14, 15 in Table 3), the catalytic activities decreased similar to the situation for related catalytic systems.^{29–31} Interestingly, the molecular weights of the obtained polyethylenes also increased along with wide molecular polydispersity (Fig. 7). The wide molecular polydispersity for the obtained polyethylenes could possibly be caused by the termination of polymeric chains happening within the polymerization period; on the contrary, it was also possible to form different active species during the extension of reaction time.³⁶ In general, the termination of polymeric chains at different times were considered to produce polyethylenes with wide molecular polydispersity.

Conclusions

Cobalt(II) chloride pre-catalysts bearing 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridines, activated with either MAO or MMAO, exhibited high activities of the order of 10^7 g PE mol⁻¹ (Co) h⁻¹ for ethylene polymerization. The obtained polyethylenes have narrow molecular weight distributions, and importantly possessed

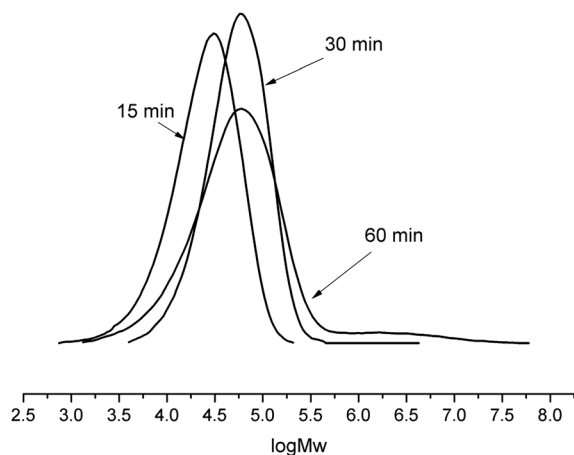


Fig. 7 GPC curves of the PEs obtained by **Co1**/MMAO under 10 atm ethylene within various periods (entries 6 and 14, 15 in Table 3).

molecular weights in the range of tens of thousands, making them of interest for the manufacture of processing lubricants.

Experimental section

General considerations

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Before use, toluene was refluxed over sodium-benzophenone and distilled under nitrogen. Methylaluminumoxane (MAO, 1.46 M in toluene) and modified methylaluminumoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Ablemarle Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Company and used as received. FT-IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights (M_w) and molecular weight distribution (MWD) of polyethylenes were determined by a PL-GPC220 at 150 °C with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were measured from the second scanning run on a Perkin–Elmer DSC-Q2000 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere at a heating rate of 20 °C min⁻¹.

Synthesis and characterization of the cobalt complexes **Co1**–**Co5**

2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(2,6-dimethylphenylimino)ethyl]pyridylcobalt dichloride (Co1**)**. All cobalt complexes were prepared by the reaction of CoCl₂ with the corresponding 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine ligands in ethanol.

A typical synthesis of complex **Co1** is described as follows: the ligand **L1** (0.0687 g, 0.10 mmol) and CoCl₂ (0.013 g, 0.10 mmol) were added to a Schlenk tube together with 5 mL of ethanol and then the reaction mixture was stirred for 8 h at room temperature. Most of precipitate was deposited when the reaction was finished. The precipitate was washed with diethyl ether (3 × 5 mL) and dried under vacuum to obtain the pure product as a yellow powder of **Co1** in 62.80% (0.0513 g) yield. FT-IR (KBr; cm⁻¹): 3026, 2167, 2019, 1584 ($\nu_{C=N}$), 1496, 1450, 1368, 1258, 1213, 1102, 1079, 1030, 916, 816, 769, 744, 700. Anal. Calcd. for C₅₀H₄₅Cl₂N₃Co (817.75): C, 73.44; H, 5.55; N, 5.14. Found: C, 73.23; H, 5.44; N, 5.67.

2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(2,6-diethylphenylimino)ethyl]pyridylcobalt dichloride (Co2**)**. Obtained as a yellow powder in 63.08% (0.0533g) yield. FT-IR (KBr; cm⁻¹): 3063, 3024, 2969, 2166, 1976, 1618, 1581 ($\nu_{C=N}$), 1493, 1450, 1369, 1322, 1268, 1205, 1152, 1082, 1027, 904, 869, 842, 811, 780, 748, 729, 698. Anal. Calcd. for C₅₂H₄₉Cl₂N₃Co (845.80): C, 73.84; H, 5.84; N, 4.97. Found: C, 73.79; H, 5.75; N, 5.07.

2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(2,6-diisopropylphenylimino)ethyl]pyridylcobalt dichloride (Co3**)**. Obtained as a yellow powder in 76.58% (0.1337g) yield. FT-IR (KBr; cm⁻¹): 3650, 3480, 2964, 2166, 2026, 1583 ($\nu_{C=N}$), 1494, 1472, 1447, 1371, 1322, 1216, 1080, 1030, 918, 809, 782, 746, 700. Anal.

Calcd. for C₅₄H₅₃Cl₂N₃Co (873.86): C, 74.22; H, 6.11; N, 4.81. Found: C, 74.32; H, 6.05; N, 4.95.

2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridylcobalt dichloride (Co4). Obtained as a yellow powder in 75.49% (0.069g) yield. FT-IR (KBr; cm⁻¹): 2910, 2166, 1977, 1582 ($\nu_{\text{C=N}}$), 1494, 1445, 1367, 1263, 1220, 1153, 1077, 1030, 904, 858, 809, 781, 740, 697. Anal. Calcd. for C₅₁H₄₇Cl₂N₃Co (831.78): C, 73.64; H, 5.70; N, 5.05. Found: C, 73.71; H, 5.82; N, 4.86.

2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridylcobalt dichloride (Co5). Obtained as a yellow powder in 81.14% (0.0697g) yield. FT-IR (KBr; cm⁻¹): 2964, 2166, 1977, 1580 ($\nu_{\text{C=N}}$), 1494, 1469, 1369, 1265, 1217, 1181, 1128, 1076, 1030, 897, 868, 809, 739, 700. Anal. Calcd. for C₅₃H₅₁Cl₂N₃Co (859.83): C, 74.03; H, 5.98; N, 4.89. Found: C, 73.87; H, 6.09; N, 4.77.

X-ray crystallographic study

X-ray diffraction study was conducted using graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) 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 F². All hydrogen atoms were placed in calculated positions. Using the SHELXL-97 package,³⁷ structure solution and refinement were performed. CCDC-856118 (Co4) contains the supplementary crystallographic data for this paper, which is available as supplementary information† or can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Details of the X-ray structure determinations and refinements are provided in Table 4.

General procedure for ethylene polymerization

A 250 ml stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was used to conduct the reaction of ethylene oligomerization at 10 atm ethylene pressure. Firstly, when the required temperature was reached, the complex (1.5 μmol) was dissolved in 50 mL toluene in a Schlenk tube then injected into the autoclave, which is full of ethylene. Secondly, the required amount of co-catalyst (MAO and MMAO) and the residual toluene were added continuously by syringe under an ethylene atmosphere (the total volume of toluene was 100 mL). The system was then stirred strongly for the desired time under the corresponding pressure of ethylene. After terminating the reaction at the desired time, the reaction solution was quenched with 10% hydrochloric acid ethanol. The precipitated polyethylene was washed by ethanol, filtrated, collected and dried in a vacuum at 60 °C until constant weight.

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Table 4 Crystal data and structure refinement details for Co4

Co4	
Empirical formula	C ₅₁ H ₄₇ Cl ₂ CoN ₃
fw	831.75
<i>T</i> /K	173(2)
$\lambda/\text{\AA}$	0.71073
Cryst system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> / \AA	9.7130(19)
<i>b</i> / \AA	15.277(3)
<i>c</i> / \AA	16.407(3)
α (°)	81.79(3)
β (°)	84.01(3)
γ (°)	76.97(3)
<i>V</i> / \AA^3	2341.1(8)
<i>Z</i>	2
<i>D</i> calcd. (g cm ⁻³)	1.180
μ/mm^{-1}	0.516
<i>F</i> (000)	870
cryst size/mm	0.20 × 0.18 × 0.15
θ range (°)	1.38–27.48
limiting indices	–12 ≤ <i>h</i> ≤ 12 –19 ≤ <i>k</i> ≤ 19 –21 ≤ <i>l</i> ≤ 21
no. of rflns collected	20967
no. unique rflns [<i>R</i> (int)]	10629 (0.0426)
completeness to θ (%)	99.0%
data/restraints/params	10629/0/514
Goodness of fit on <i>F</i> ²	1.014
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0698 <i>wR</i> ₂ = 0.1791
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0902 <i>wR</i> ₂ = 0.1934
Largest diff peak and hole/e \AA^{-3}	0.572 and –0.512

Notes and references

- 1 C. Vasile, R. B. Seymour, *Handbook of Polyolefins*, Marcel Dekker, 1993.
- 2 J. Meeker, S. Sathyanarayana and S. Swan, *Philos. Trans. R. Soc. London, Ser. B*, 2009, **364**, 2097.
- 3 C. Barbe, G. Cecchin and L. Noristi, *Adv. Polym. Sci.*, 1987, **81**, 1; T. Taniiki and M. Terano, *Macromol. Rapid Commun.*, 2007, **28**, 1918.
- 4 B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849.
- 5 M. Zhang, W. J. Zhang, T. Xiao, J. Xiang, X. Hao and W.-H. Sun, *J. Mol. Catal. A: Chem.*, 2010, **320**, 92; R. Gao, K. F. Wang, Y. Li, F. S. Wang, W.-H. Sun, C. Redshaw and M. Bochmann, *J. Mol. Catal. A: Chem.*, 2009, **309**, 166; R. Gao, T. L. Liang, F. S. Wang and W.-H. Sun, *J. Organomet. Chem.*, 2009, **694**, 3701; D. Zabel, A. Schubert, G. Wolmershaeuser, R. L. Jones and W. R. Thiel, *Eur. J. Inorg. Chem.*, 2008, 3648.
- 6 V. C. Gibson, C. Redshaw and G. A. Solan, *Chem. Rev.*, 2007, **107**, 1745; V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283; S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; C. Bianchini, G. Giambastiani, L. Luconi and A. Meli, *Coord. Chem. Rev.*, 2010, **254**, 431; C. Bianchini, G. Giambastiani, I. G. Rios, G. Mantovani, A. Meli and A. M. Segarra, *Coord. Chem. Rev.*, 2006, **250**, 1391; K. C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420; W.-H. Sun, S. Zhang and W. Zuo, *C. R. Chim.*, 2008, **11**, 307; S. Y. Jie, W.-H. Sun and T. Xiao, *Chin. J. Polym. Sci.*, 2010, **28**, 299; F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem. Res.*, 2005, **38**, 784.
- 7 F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu and Q. Wu, *Macromolecules*, 2009, **42**, 7789.

- 8 D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320.
- 9 R. J. Maldanis, J. S. Wood, A. Chandrasekaran, M. D. Rausch and J. C. W. Chien, *J. Organomet. Chem.*, 2002, **645**, 158.
- 10 H. Zou, F. M. Zhu, Q. Wu, J. Y. Ai and S. A. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1325.
- 11 B. K. Bahuleyan, G. W. Son, D.-W. Park, C.-S. Ha and I. Kim, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 1066.
- 12 M. M. Wegner, A. K. Ott and B. Rieger, *Macromolecules*, 2010, **43**, 3624.
- 13 C.-L. Song, L.-M. Tang, Y.-G. Li, X.-F. Li, J. Chen and Y.-S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1964.
- 14 H.-R. Liu, P. T. Gomes, S. I. Costa, M. T. Duarte, R. Branquinho, A. C. Fernandes, J. C. W. Chien, R. P. Singh and M. M. Marques, *J. Organomet. Chem.*, 2005, **690**, 1314.
- 15 C. S. Popeney and Z. Guan, *Macromolecules*, 2010, **43**, 4091.
- 16 W.-H. Sun, S. Jie, S. Zhang, W. Zhang, Y. Song, H. Ma, J. Chen, K. Wedeking and R. Frohlich, *Organometallics*, 2006, **25**, 666.
- 17 S. Jie, S. Zhang and W.-H. Sun, *Eur. J. Inorg. Chem.*, 2007, 5584.
- 18 W.-H. Sun, P. Hao, S. Zhang, Q. Shi, W. Zuo, X. Tang and X. Lu, *Organometallics*, 2007, **26**, 2720.
- 19 Y. Chen, P. Hao, W. Zuo, K. Gao and W.-H. Sun, *J. Organomet. Chem.*, 2008, **693**, 1829.
- 20 L. Xiao, R. Gao, M. Zhang, Y. Li, X. Cao and W.-H. Sun, *Organometallics*, 2009, **28**, 2225.
- 21 R. Gao, Y. Li, F. Wang, W.-H. Sun and M. Bochmann, *Eur. J. Inorg. Chem.*, 2009, 4149.
- 22 W.-H. Sun, P. Hao, G. Li, S. Zhang, W. Wang, J. Yi, M. Asma and N. Tang, *J. Organomet. Chem.*, 2007, **692**, 4506.
- 23 M. Zhang, P. Hao, W. Zuo, S. Jie and W.-H. Sun, *J. Organomet. Chem.*, 2008, **693**, 483.
- 24 M. Zhang, R. Gao, X. Hao and W.-H. Sun, *J. Organomet. Chem.*, 2008, **693**, 3867.
- 25 S. Song, T. Xiao, T. Liang, F. Wang, C. Redshaw and W.-H. Sun, *Catal. Sci. Technol.*, 2011, **1**, 69.
- 26 C. Shao, W.-H. Sun, Z. Li, Y. Hu and L. Han, *Catal. Commun.*, 2002, **3**, 405.
- 27 X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen and W. Chen, *J. Organomet. Chem.*, 2005, **690**, 1570.
- 28 C. Zhang, W.-H. Sun and Z.-X. Wang, *Eur. J. Inorg. Chem.*, 2006, 4895.
- 29 J. Yu, H. Liu, W. Zhang, X. Hao and W.-H. Sun, *Chem. Commun.*, 2011, **47**, 3257.
- 30 J. Yu, W. Huang, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2011, **40**, 10209.
- 31 W. Zhao, J. Yu, S. Song, W. Yang, H. Liu, X. Hao, C. Redshaw and W.-H. Sun, *Polymer*, 2012, **53**, 130.
- 32 T. Xiao, P. Hao, G. Kehr, X. Hao, G. Erker and W.-H. Sun, *Organometallics*, 2011, **30**, 4847.
- 33 A. K. Tomov, V. C. Gibson, G. J. P. Britovsek, R. J. Long, M. van Meurs, D. J. Jones, K. P. Tellmann and J. J. Chirinos, *Organometallics*, 2009, **28**, 7033.
- 34 L. Guo, H. Gao, L. Zhang, F. Zhu and Q. Wu, *Organometallics*, 2010, **29**, 2118; M. Yang, B. Y. Liu, L. H. Wang, H. G. Ren, W. Y. Hu, L. F. Wen and W. D. Yan, *Catal. Commun.*, 2009, **10**, 1427; M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka and T. Fujita, *J. Am. Chem. Soc.*, 2003, **125**, 4293.
- 35 G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728; G. J. P. Britovsek, S. Mastroianni, G. A. Solan, S. P. D. Baugh, C. Redshaw, V. C. Gibson, A. J. P. White, D. J. Williams and M. R. J. Elsegood, *Chem.-Eur. J.*, 2000, **6**, 2221; Y. Chen, C. Qian and J. Sun, *Organometallics*, 2003, **22**, 1231; I. S. Paulino and U. Schuchardt, *J. Mol. Catal. A: Chem.*, 2004, **211**, 55; Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu and Y. Hu, *J. Mol. Catal. A: Chem.*, 2005, **230**, 1; J.-Y. Liu, Y. Zheng, Y.-G. Li, L. Pan, Y.-S. Li and N.-H. Hu, *J. Organomet. Chem.*, 2005, **690**, 1233.
- 36 A. A. Barabanov, G. D. Bukatov and V. A. Zakharov, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6621; A. A. Barabanov, G. D. Bukatov, V. A. Zakharov, N. V. Semikolenova, L. G. Echevskaja and M. A. Matsko, *Macromol. Chem. Phys.*, 2008, **209**, 2510.
- 37 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.