Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

Controlling molecular weights of polyethylene waxes using the highly active precatalysts of 2-(1-aryliminoethyl)-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt chlorides: Synthesis, characterization, and catalytic behavior

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A series of 2-(1-aryliminoethyl)-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt chlorides was synthesized and characterized by FT-IR and elemental analysis; and the molecular structures of complexes **Co1**, **Co3** and **Co4** were confirmed as the pseudo-square-pyramidal or trigonal-bipyramidal geometry around cobalt center by the single-crystal X-ray diffraction. Upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), all cobalt precatalysts gave high activities up to the level of 10^7 gPE·mol^{-1}(Co)·h^{-1} toward ethylene polymerization, being one of most active cobalt-based precatalysts. In comparison with cobalt analogues, the title precatalysts generally possessed longer lifetime along with the good thermo-stability; moreover, the resultant polyethylenes were highly linear and unimodal in most cases.

Introduction

In the past two decades late-transition metal complex precatalysts have witnessed great progress in ethylene oligo-/polymerization,[1] in which the α-diimino-[2] and 2-imino-pyridylmetal (Ni^{2+} or Pd^{2+}) complexes[3] and bis(imino)pyridyl metal (Fe^{2+} or Co^{2+}) complexes (**A**, Scheme 1)[4] have been extensively studied. Besides the effective modification of 2,6-bis(imino)pyridines[5,6] using bulky substituents[6] for better catalytic performances, the alternative model precatalysts have been developed through designing 2-imino-1,10-phenanthrolines,[7] 2-benzimidazolyl-6-iminopyridines,[8] 8-(pyridylmethylimino)quinolines,[9] 2,8-bis(imino)quinolines,[10] and 1,8-diimino-2,3,4,5,6,7-hexahydroacridines (**B**, Scheme 1).[11] Besides the high activities achieved by the **B**-model metal pre-catalysts, analogues were developed for the metal complex precatalysts;[11] however, both polyethylenes and oligomers were sometime produced as the shortage of such catalytic system. This would be less interesting to the commercial consideration. To obtain the potentially useful product of sole component of either polyethylene or oligomers, the 2-(1-(arylimino)ethyl)-8-arylimino-5,6,7-trihydroquinolyl metal (Fe or Co) complexes (**C**, Scheme 1) were synthesized and only polyethylenes were obtained;[12] moreover, the **C**-model cobalt precatalysts showed the highest activities toward ethylene polymerization.[12b] In order to understand the effects by the ring-sizes appeared in 2-(1-(arylimino)ethyl)-8-arylimino-5,6,7-trihydroquinolines,[12] the alternative models such as 2-(1-(arylimino)ethyl)-7-arylimino-6,6-dimethylcyclopentapyridines (**D**, Scheme 1)[13] and 2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocyclohepta pyridines (**E**, Scheme 1)[14] were developed for their metal pre-catalysts. Though **D**-model iron complexes could not yet be isolated, fortunately, their cobalt complexes were confirmed, but showed lower activities than their analogues.[4-6,12,13] Interestingly, the **E**-model iron complexes showed highest activities toward ethylene polymerization;[14] subsequently, it would be necessary to get the knowledge regarding the **E**-model cobalt analogues. Therefore, the 2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt complexes were prepared; upon activation with either MAO or MMAO, all the title cobalt complexes showed high activities towards ethylene polymerization and good thermal stability. More importantly, the activities of current cobalt precatalysts were almost as high as those of the most active cobalt analogues (**C**-model cobalt complexes);[12b] meanwhile the obtained polyethylene waxes herein match the commercial products regarding molecular weights and polydispersity. The synthesis and characterization of the title complexes are reported in detail, as well as their catalytic behavior in ethylene polymerization.

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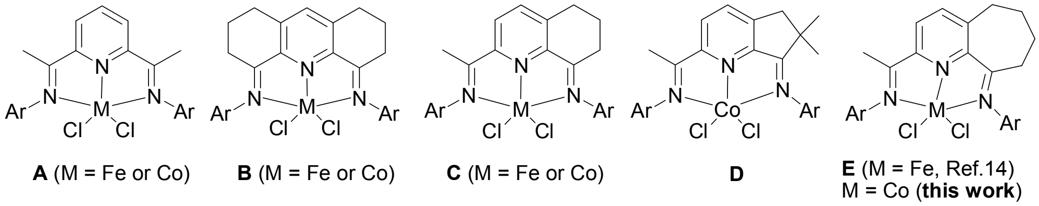
† Appendix A. Supplementary material: CCDC 1426066-1426068 contain the supplementary crystallographic data for Co1, Co3 and Co4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

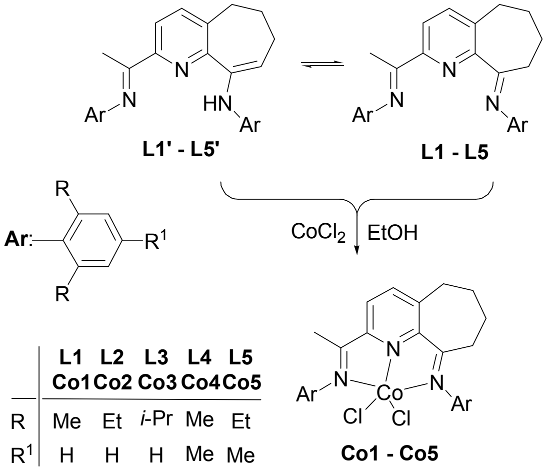


Scheme 1. The derivative precatalysts based on 2,6-bis(imino)pyridylmetal(II) halides

Results and Discussion

1. Synthesis and characterization of organic compounds and cobalt complexes. Using the literature procedure,[14] the 2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocyclohepta-pyridines (**L1**–**L5**) reacted with cobalt(II) dichloride in ethanol to form the corresponding complexes (**Co1**–**Co5**, Scheme 2) in reasonable yields. All the cobalt complexes were consistent with the observed data of their elemental analysis. The effective coordination between cobalt and nitrogen atoms could be reflected by their FT-IR spectra; the $\nu_{C=N}$ stretching vibrations were shifted to the range of 1609–1617 cm^{-1} for the cobalt complexes instead of 1641–1644 cm^{-1} for the free organic compound,[14] meanwhile the complexes showed no signals around 3360 cm^{-1} assigned to the N-H groups of the organic isomers.[14] In addition, the molecular structures of the complexes **Co1**, **Co3** and **Co4** were confirmed by the single-crystal X-ray diffraction study.

2. X-ray Crystallographic Study. The single crystals of the cobalt(II) complexes **Co1**, **Co3** and **Co4** were grown through the slow diffusion of diethyl ether into the complex solution in a mixture of dichloromethane/methanol (v/v = 2:1) at room temperature, respectively. Their molecular structures are shown in Figures 1 to 3, and the selected bond lengths and angles are tabulated in Table 1. The coordination geometries were generally similar to the observations of their iron analogues,[14] varying from square-pyramidal to trigonal-bipyramidal at the metal center, caused by the steric influences of the substituents within the ligand compounds.



Scheme 2. Synthesis of the cobalt(II) complexes (**Co1**–**Co5**).

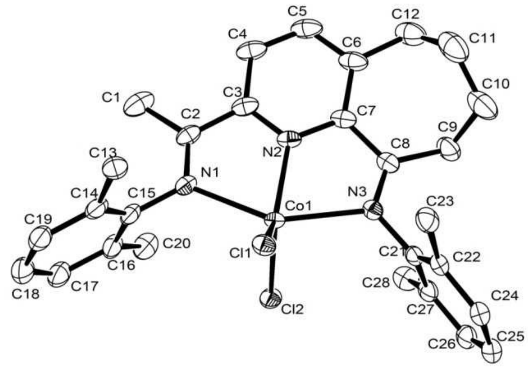


Figure 1. ORTEP drawing of complex **Co1** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

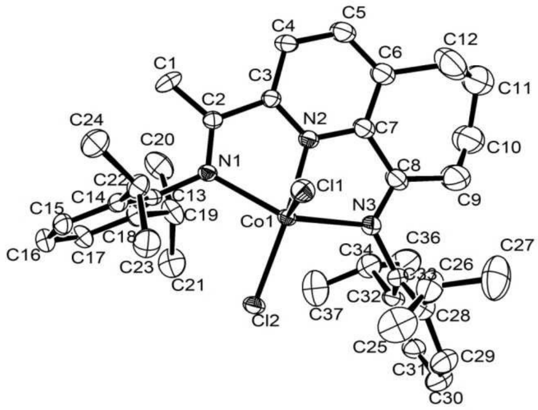


Figure 2. ORTEP drawing of complex **Co3** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

In molecular structure of **Co1** (Figure 1), the coordination environment surrounding the cobalt is a distorted trigonal-bipyramidal geometry; three nitrogen atoms form the fundamental plane and the chlorides occupy the vertex, and the cobalt atom deviates 0.028 Å from the pyridyl plane. Moreover, the two aryl–N_{imino} planes are analogously perpendicular to the N^N^N coordination plane with dihedral angles of 88.34° and 89.14°, respectively. In comparison, as shown in Figure 2 and Figure 3, the coordinating geometries of **Co3** and **Co4** can be approximately square-pyramidal, for which the atoms N1, N2, N3 and Cl2 consist the basal plane, and the Cl1 atom occupies the apical position. In **Co3**, the deviation is 0.170 Å for Cl2 from basic plane whilst the deviation increases to 0.998 Å in **Co4**. Comparing to structure **Co1**, the aryl rings of N_{imine} planes are nearly perpendicular to the basal plane with the dihedral angles in ranges of 78.96° to 84.68°.

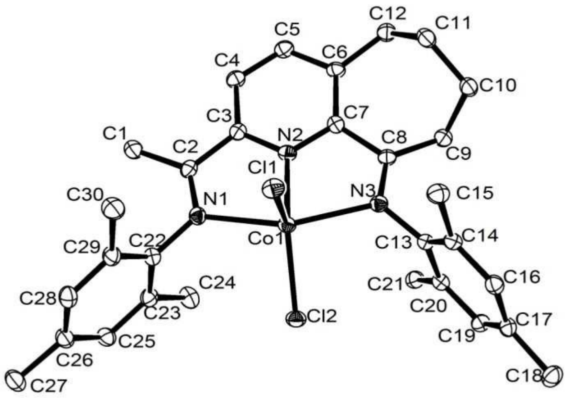


Figure 3. ORTEP drawing of complex **Co4** with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (°) for **Co1**, **Co3** and **Co4**

	Co1	**Co3**	**Co4**
	Bond lengths, Å		
Co(1)–N(1)	2.246(4)	2.197(5)	2.224(4)
Co(1)–N(2)	2.051(4)	2.052(5)	2.036(4)
Co(1)–N(3)	2.271(4)	2.175(6)	2.207(4)
Co(1)–Cl(1)	2.270(16)	2.314(2)	2.299(13)
Co(1)–Cl(2)	2.266(16)	2.256(19)	2.260(13)
N(1)–C(2)	1.280(7)	1.280(8)	1.280(6)
N(3)–C(8)	1.249(7)	1.301(10)	1.289(6)
	Bond angles, °		
N(1)–Co(1)–N(3)	150.42(17)	141.7(2)	149.55(14)
N(1)–Co(1)–N(2)	76.01(19)	74.0(2)	75.69(14)
N(3)–Co(1)–N(2)	74.42(18)	74.6(2)	75.73(14)
N(1)–Co(1)–Cl(1)	99.18(13)	99.11(14)	97.82(10)
N(3)–Co(1)–Cl(1)	98.47(12)	102.88(16)	97.94(10)
N(2)–Co(1)–Cl(1)	124.99(13)	90.88(17)	101.50(10)
N(1)–Co(1)–Cl(2)	98.95(12)	97.62(14)	97.63(10)
N(3)–Co(1)–Cl(2)	96.52(12)	101.31(16)	96.68(10)
N(2)–Co(1)–Cl(2)	123.71(13)	154.59(17)	138.29(11)
Cl(1)–Co(1)–Cl(2)	111.24(6)	114.33(8)	120.21(5)
C(8)–N(3)–Co(1)	113.8(4)	115.7(5)	113.8(3)
C(2)–N(1)–Co(1)	112.1(4)	114.1(4)	113.0(3)

Within all three complexes, the bond lengths of Co–$N_{pyridyl}$ are shorter than those of the Co–N_{imino} bonds (Table 1), indicating the stronger bond of Co–$N_{pyridyl}$. The differences of bond lengths between two Co–N_{imino} bonds are mainly attributed to the unsymmetric framework,[6] which are consistent with the previous observation of the Fe–N_{imino} bonds in their iron analogues;[14] in addition, the Co–$N_{pyridyl}$ bonds are shorter than those Fe–$N_{pyridyl}$ bonds,[14] exhibiting more robust coordination within the cobalt complexes. Regarding the distortion of the cycloheptance, the carbon C(11)-atoms are deviated from the pyridyl co-plane with the distances of 1.506 Å for **Co1**, 0.609 Å for **Co3** and 1.393 Å for **Co4**, indicating good flexibility of the fused cycloheptance. In comparison the Co–N bond lengths between 2-(1-aryliminoethyl)-9-arylimino-5,6,7-trihydroquinolylcobalt chlorides[12b] and these title complexes, the Co–N_{imino} bonds bridged through fused cycloheptane (this work) are clearly shorter while the bond lengths of the other Co–N_{imino} bonds and Co–$N_{pyridyl}$ bonds are similar, respectively, which enhancing the coordinative efficiency in the current cobalt complexes due to the fused cycloheptane. On contrary, the 2-(1-aryliminoethyl)-7-arylimino-6,6-dimethylcyclopentapyridyl cobalt chlorides have the very week interaction between cobalt atom and the cyclopentyl-bridged N_{imino} atom (Co–N_{imino} = 2.42 Å, the sum of the corresponding ionic radii 2.43 Å) or none interaction in most cases.[13] The coordinative differences will affect the stabilities and catalytic performances of these complexes.

3. Ethylene Polymerization

According to the results observed for their iron[14] and cobalt analogues[12b], high activities were always obtained on activation with either methylaluminoxane (MAO) or modified methylaluminoxanes (MMAO). Hence, MAO and MMAO were also employed for ethylene polymerization for these title complexes, and the complex **Co4** was principally used to optimize the catalytic parameters.

3.1 Ethylene Polymerization Results by Co1–Co5/MAO systems. Primarily, the system **Co4**/MAO was screened for the optimum parameter at the ambient ethylene pressure (Table 2). With a fixed Al/Co ratio of 1000 (entries 1–5, Table 2), different reaction temperatures were applied to investigate the effect for polymerization from 20 to 60°C. The highest activity of 3.7×10^5 gPE·mol^{-1}(Co)·h^{-1} was observed at 40 °C. However, in consideration of the solubility of ethylene in toluene, the concentration of ethylene was remarkably affected by temperature and ethylene pressures according to the literature;[15] therefore, adjusted activities were obtained through calculating the ethylene concentrations at different temperatures at ambient ethylene pressure (Table 2). Surprisingly, the adjusted activities kept stable from 40 to 60 °C (up to 3.3×10^6 gPE·mol^{-1}(Co)·h^{-1}·$C_{ethylene}{}^{-1}$). The GPC curves of the resultant polyethylenes in Figure 4 clearly showed the polyethylene obtained at lower temperature (20 °C) possessed bimodal character, while polyethylenes obtained at higher temperatures tended to be unimodal. The active species were probably uniformed at higher temperatures and constantly active,[12a,14] meanwhile the initiated active species at lower temperature polymerized ethylene along with exothermal effect and stable active species were gradually formed for the polymerization. Moreover, the lower molecular weights of the obtained polyethylenes were observed at the higher reaction temperatures (entries 1–5, Table 2), being interpreted the fast chain termination at the higher temperature.

Table 2. Polymerization results by **Co1**–**Co5**/MAO at ambient ethylene pressure [a]

Entry	Pre-cat	T (°C)	Al/Co	Polymer(g)	Obs. act. [b]	Adj. act. [c]	T_m (°C) [d]	M_w /Kg.mol^{-1} [e]	M_w/M_n [e]
1	**Co4**	20	1000	0.26	1.8	12.7	128.4	7.1	4.0
2	**Co4**	30	1000	0.36	2.4	19.1	127.9	6.0	3.6
3	**Co4**	40	1000	0.55	3.7	33.6	126.0	3.2	1.8
4	**Co4**	50	1000	0.52	3.5	33.8	124.4	5.9	1.8
5	**Co4**	60	1000	0.42	2.8	33.2	123.5	3.5	1.6
6	**Co4**	40	500	0.34	2.3	20.9	125.9	2.4	1.8
7	**Co4**	40	1500	0.71	4.7	42.7	126.0	6.8	1.8
8	**Co4**	40	2000	0.81	5.4	49.1	124.8	2.9	1.6
9	**Co4**	40	2500	0.76	5.1	46.4	124.0	2.3	1.6
10	**Co1**	40	2000	0.61	4.1	37.3	122.5	3.2	1.7
11	**Co2**	40	2000	0.77	5.1	46.4	127.3	5.2	2.4
12	**Co3**	40	2000	0.54	3.6	32.7	132.5	37	2.8
13	**Co5**	40	2000	0.85	5.6	50.9	127.5	4.6	2.3
14 [f]	**Co4**	40	2000	0.69	4.6	41.8	121.9	4.0	1.9

[a] General conditions: 3 μmol Co, 30 min, 30 mL toluene for 1 atm ethylene. [b] Observing activity, 10^5 gPE·mol^{-1}(Co)·h^{-1}. [c] Adjusted activity, 10^5 gPE·mol^{-1}(Co)·h^{-1}·C$_{ethylene}$$^{-1}$. [d] Determined by differential scanning calorimetry. [e] Determined by gel permeation chromatography. [f] co-catalyst MMAO.

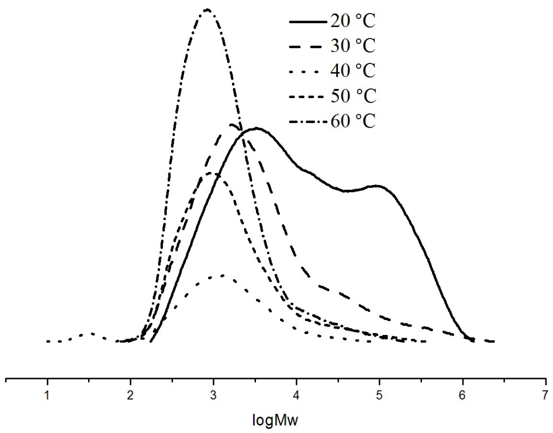


Figure 4. The GPC curves of polyethylene obtained at different temperatures (entries 1–5, Table 2)

On varying the molar ratios of Al/Co from 500 to 2500 at 40 °C (entries 3, 6–9, Table 2), the optimal Al/Co ratio was observed with 2000. Besides molecular weights in thousands, all polyethylenes possessed the narrow polydispersity (lower than 2.0), indicating the single-site active species in all cases.

Using the optimum condition, all cobalt complexes were investigated toward ethylene polymerization (entries 8, 10–13, Table 2), all precatalysts showed good activities. Generally, the complexes with additional *para*-methyl moiety (**Co4** and **Co5**) performed slightly better activities than the correspondent complexes **Co1** and **Co2** because of the preferable solubility of the complexes containing additional aliphatic group.[5f,6h,12] In parallel, the system **Co4**/MMAO was also investigated and showed the similar activity for ethylene polymerization.

In the commercial process, elevated ethylene pressures are commonly employed such as 10 atm. Therefore further investigation was conducted under the elevated pressure, and their results are collected in Table 3. With a Al/Co ratio fixed at 1000, ~~the~~ reaction temperatures were explored from 30 °C to 70 °C (entries 1–5, Table 3), and the best performance was achieved at 50 °C with the activity of 7.3 × 10^6 gPE·mol^{-1}(Co)·h^{-1} and the adjusted activity was 7.6 × 10^6 gPE·mol^{-1}(Co)·h^{-1}·C$_{ethylene}$$^{-1}$ at the same conditions (entry 3, Table 3) . On rising the reaction temperature from 50 °C to 70 °C (entries 3 – 5, Table 3), the notable decrease of catalytic activity was gradually occurred due to partial deactivation of active species as well as lower concentrations of ethylene at higher temperatures;[15] however, the activity was still maintained high activity with 5.4 × 10^6 gPE·mol^{-1}(Co)·h^{-1} at 70 °C, exhibiting the better thermal stability than the popular bis(imino)pyridylcobalt analogues.[4]

At the optimum temperature of 50 °C, the Al/Co ratio changed in the range from 500 to 2000 (entries 3, 6–8, Table 3), the best catalytic activity was observed at the Al/Co ratio of 1500. When the Al/Co molar ratio increased, the molecular weights were substantially decreased, being probably ascribed to more chain migration and termination occurred at higher concentration of cocatalyst.[16] Regarding the lifetime of active species (entries 7 and 9–11, Table 3), the highest activity was observed as 2.09 ×10^7 gPE·mol^{-1}(Co)·h^{-1} within 5 min (entry 9, Table 3). On prolonging the polymerization time from 5 min to 60 min, there were more polymers obtained to confirm active species well maintained; but the catalytic activities were obviously decreased due to the partial inactivation of the active species.[17] This phenomenon indicated that there was no inducing time for ethylene polymerization in such catalytic system, which was similar to the previous work.[12b] The GPC curves of these obtained polyethylenes were shown in Figure 5, showing unimodal feature and indicating the single-site species of all cases. Along with prolonging reaction time, the resultant polyethylenes possessed relatively lower molecular weights; the regeneration of active species was assumed, meanwhile

Table 3. Polymerization results by **Co1**–**Co5**/MAO at elevated ethylene pressure [a]

Entry	Pre-cat	T (°C)	Al/Co	Polymer(g)	Obv. act. [b]	Adj. act. [c]	T_m (°C) [d]	M_w /Kg.mol^{-1} [e]	M_w/M_n [e]
1	**Co4**	30	1000	6.31	4.2	3.3	126.4	4.1	1.8
2	**Co4**	40	1000	8.40	5.6	5.1	125.4	5.4	2.0
3	**Co4**	50	1000	10.97	7.3	7.6	125.3	5.1	2.0
4	**Co4**	60	1000	9.26	6.2	7.2	124.6	3.4	1.9
5	**Co4**	70	1000	8.13	5.4	7.1	123.8	3.3	1.9
6	**Co4**	50	500	5.31	3.5	3.6	127.8	8.3	1.8
7	**Co4**	50	1500	12.23	8.2	8.5	124.8	3.2	1.8
8	**Co4**	50	2000	10.78	7.2	7.5	124.4	3.2	1.8
9 [f]	**Co4**	50	1500	5.22	20.9	21.6	124.2	3.7	2.0
10 [g]	**Co4**	50	1500	10.65	14.2	14.7	124.1	3.6	1.9
11 [h]	**Co4**	50	1500	14.18	4.7	4.9	123.9	3.0	2.0
12 [i]	**Co4**	50	1500	9.15	6.1	12.6	124.5	3.5	2.0
13	**Co1**	50	1500	11.68	7.8	8.1	123.6	2.6	2.0
14	**Co2**	50	1500	9.10	6.1	6.3	128.8	6.0	2.4
15	**Co3**	50	1500	6.90	4.6	4.8	132.8	27	3.0
16	**Co5**	50	1500	11.06	7.4	7.7	128.9	7.7	1.8

[a] General conditions: 3 μmol Co, 30 min, 100 mL toluene for 10 atm ethylene. [b] Observing activity, 10^6 gPE·mol^{-1}(Co)·h^{-1}. [c] Adjusted activity, 10^6 gPE·mol^{-1}(Co)·h^{-1}·$C_{ethylene}^{-1}$. [d] Determined by differential scanning calorimetry. [e] Determined by gel permeation chromatography. [f] 5min. [g] 15min. [h] 60min., [i] 5atm ethylene.

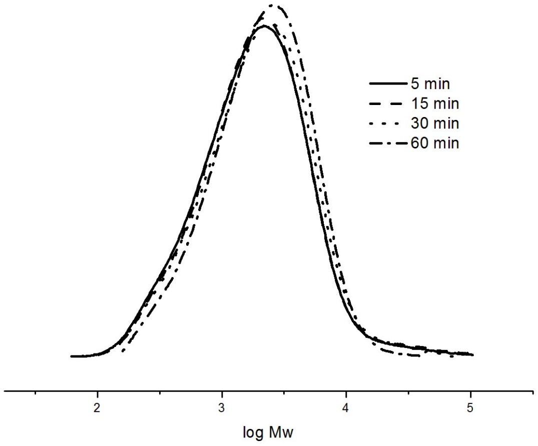


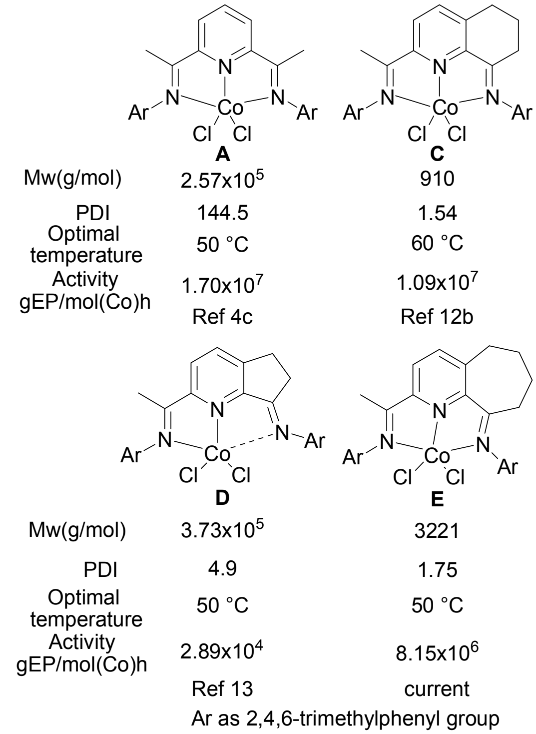
Figure 5. The GPC curves of polyethylene obtained at different times (entries 7, 9–11, Table 3)

the accumulation of polyethylenes in the solution retarded ethylene coordination and insertion for longer polymers.

On the optimum condition, all the cobalt complexes were conducted for ethylene polymerization (entries 7, 13–16, Table 3) and showed high activities in all cases. In comparison with activities obtained at ambient pressure of ethylene (Table 2), the catalytic activities (Table 3) were generally more than ten times of promotion; however, adjusted activities were not significantly affected by higher ethylene pressures. Regarding the tendency of catalytic activities, the complexes bearing smaller *ortho*-substituents, the better activities performed: the activity decreased in the order **Co1** [2,6-di(Me)] > **Co2** [2,6-di(Et)] > **Co3** [2,6-di(*i*-Pr)]; but all showed high catalytic activities. Moreover, the resultant polyethylene by **Co3** possessed apparently higher molecular weight (over 27 Kg.mol^{-1}, entry 15, Table 3) at elevated pressure as well as ambient pressure (37 Kg.mol^{-1}, entry 12, Table 2), indicating that the bulkier substituents protected the active species and prevented chain transfer. Regarding the additional aliphatic *para*-methyl for complexes **Co4** and **Co5** in comparison to their analogues **Co1** and **Co2**, the better activities were achieved which were consistent to those obtained at ambient pressure (Table 2) and literature observations[5f,6h,12] due to the preferable solubility. Generally, all T_m values of the polyethylenes obtained by Co/MAO were over 122 °C. To clearly understand the microstructure of the polyethylenes, the representative polyethylene obtained with **Co4**/MAO at 50 °C was measured for NMR spectra at 100 °C in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$). Its ^{1}H NMR chart clearly showed the quintet at 5.90 ppm and the triplet at 5.01 ppm along with high intensity to the singlet at 0.96 ppm, indicating the highly linear characteristics along with vinyl-group (–CH=CH$_2$). Moreover, single peak observed in the ^{13}C NMR spectra also verified its highly linear feature.

Comparing to the cobalt analogous precatalysts with ligands of typical 2,6-bis(imino)pyridines[4c] and different fused-cycloalkane bridged-imino-2-iminopyridines (Scheme 3, consistent to the Models in Scheme 1),[12b,13] three models of **A** , **C** and **E** performed high activities toward ethylene polymerization, which were all good enough to meet the commercial requirement regarding activities. Beyond their productivities, the commercial value of catalytic system would truly rely on the properties of polyethylenes obtained.

Currently polyethylene waxes obtained are in the range of highly demanded one with molecular weights in thousands and narrow polydispersity. The **E**-model precatalyst would be highly potential for commercial process, approving that the fused-alkyl frame could affect the coordination with cobalt core adapting the catalytic performance of those cobalt complexes. Further investigations are still worthily conducted regarding finely tuning complexes as well as optimizing conditions for ethylene polymerization.



	A	C	D	E
Mw(g/mol)	2.57×10^5	910	3.73×10^5	3221
PDI	144.5	1.54	4.9	1.75
Optimal temperature	50 °C	60 °C	50 °C	50 °C
Activity gEP/mol(Co)h	1.70×10^7	1.09×10^7	2.89×10^4	8.15×10^6
	Ref 4c	Ref 12b	Ref 13	current

Ar as 2,4,6-trimethylphenyl group

Scheme 3. Information of typical **Co**/MAO systems.

3.2 Ethylene Polymerization by Co1–Co5/MMAO Systems. In the presence of MMAO, complex **Co4** was used to optimize the polymerization parameters (entries 1–8, Table 4) according to the procedure reported.[12b] With a molar ratio of Al/Co fixed at 1500 (entries 1–5, Table 4) under 10 atm of ethylene, the reaction temperature was explored to find the optimum as 50 °C with the activity of 5.1×10^6 gPE·mol^{-1}(Co)·h^{-1}, showing better thermal stability than its analogues.[4a,8b,9,14] The activities were gradually increased from 30 to 50 °C, requiring species activated at required temperature; however, the activities were dramatically decreased with further increasing the temperature to 70 °C, indicating the partial decomposition of active species, which underwent a similar trend for adjusted activities. Moreover, it was also considered for minor contribution due to the lower concentration of ethylene in toluene at higher temperature.[17] Importantly, all obtained polyethylenes possessed narrow polydispersity shown in their GPC curves (Figure 6), approving single active species in all cases; more interestingly, the polyethylenes produced at higher temperature showed narrower polydispersity, which could be interpreted that the active species were uniformed at the higher temperature.

With the reaction temperature fixed at 50 °C, the influence of Al/Co molar ratios was investigated in the range of 500 to 2000 (entries 3, 6–8, Table 4), confirming the optimum molar ratio with 1500 (entry 3, Table 4). The higher the molar ratio of MMAO employed, the lower molecular weight of polyethylenes obtained; this was attributed to more chain transfer occurred from the cobalt to aluminum centre for termination.[18] Similarly, the obtained polyethylenes had the narrow polydispersity (2.0 or even lower), revealing the single-site species; which were shown in Figure 7 with their GPC curves.

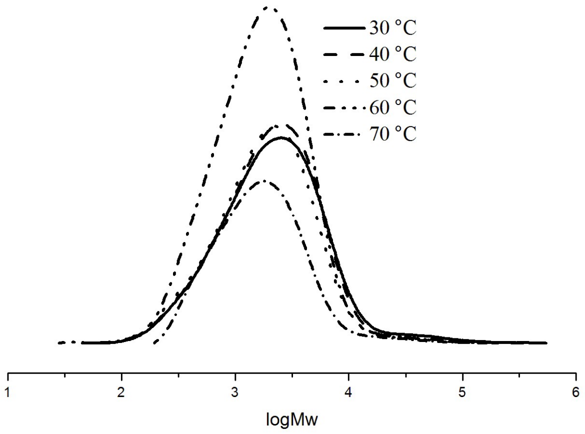


Figure 6. The GPC curves of polyethylene obtained at different temperatures (entries 1–5, Table 4)

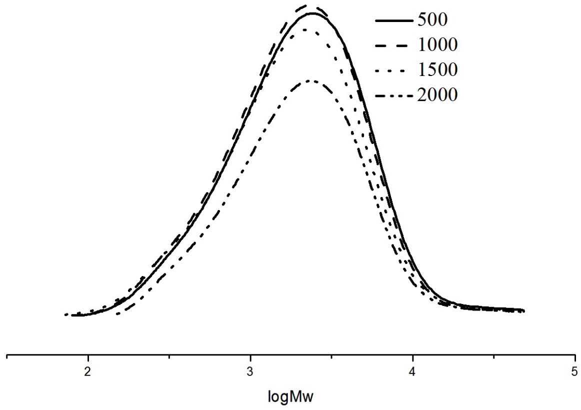


Figure 7. The GPC curves of polyethylene obtained at different Al/Co ratios (entries 3, 6–8, Table 4)

Under the optimal condition, the influences of the ligand nature of the complexes (**Co1**–**Co5**) were extensively investigated (entries 3, 9–12, Table 4); all cobalt precatalysts exhibited high activities toward ethylene polymerization. Different to their iron analogues performing higher activities with bulkier substituents,[14] the less bulky substituents (*ortho*-methyl) were more beneficial to the complex pre-catalysts for the better activities: the activities were in the order as 2,4,6-tri(Me) > 2,6-di(Me) > 2,6-Et-4-Me > 2,6-di(Et) > 2,6-di(*i*-Pr); which was caused by the bulkier substituents which hindered the approaching coordination of ethylene to the active species. However, the bulkier *ortho*-substituents probably protected the active species for the longer lifetime resulting polyethylenes with higher molecular weights; the molecular weights of resultant polyethylenes were observed from 2.5 to 25 Kg.mol^{-1} along with the substituents changed from methyl to isopropyl groups. Moreover, complexes **Co4** and **Co5** with

Table 4. Polymerization results by **Co1**–**Co5**/MMAO at elevated ethylene pressure [a]

Entry	Pre-cat	T (°C)	Al/Co	Polymer(g)	Obs. act. [b]	Adj. act. [c]	T_m (°C) [d]	M_w /Kg.mol^{-1} [e]	M_w/M_n [e]
1	**Co4**	30	1500	4.70	3.1	2.5	125.0	4.6	2.0
2	**Co4**	40	1500	5.69	3.8	3.5	124.8	3.8	2.1
3	**Co4**	50	1500	7.66	5.1	5.3	124.0	3.4	2.0
4	**Co4**	60	1500	3.66	2.4	2.8	124.0	2.9	2.0
5	**Co4**	70	1500	1.58	1.1	1.4	124.2	2.6	1.7
6	**Co4**	50	500	5.76	3.8	3.9	124.4	3.9	2.0
7	**Co4**	50	1000	6.23	4.2	4.3	124.2	3.7	2.0
8	**Co4**	50	2000	3.90	2.6	2.7	124.6	3.3	1.9
9	**Co1**	50	1500	6.93	4.6	4.8	123.1	2.5	1.9
10	**Co2**	50	1500	2.52	1.7	1.8	128.4	7.2	2.2
11	**Co3**	50	1500	2.15	1.4	1.4	132.1	25	2.8
12	**Co5**	50	1500	6.07	4.1	4.2	129.2	8.3	1.8
13 [f]	**Co4**	50	1500	5.97	4.0	8.3	124.2	3.6	2.0

[a] General conditions: 3 μmol Co, 30 min, 100 mL toluene for 10 atm ethylene. [b] Observing activity, 10^6 gPE·mol^{-1}(Co)·h^{-1}. [c] Adjusted activity, 10^6 gPE·mol^{-1}(Co)·h^{-1}·$C_{ethylene}^{-1}$. [d] Determined by differential scanning calorimetry. [e] Determined by gel permeation chromatography. [f] 5atm ethylene.

additional *para*-methyl group achieved higher activities than the corresponding complexes **Co1** and **Co2**, being considered the better solubility of the complexes with the additional aliphatic methyl group.[5f,6h,12] Comparing with their iron analogues,[14] the cobalt complexes exhibited a longer lifetime and obtained polyethylenes with narrower polydispersity but lower molecular weights.

In comparison to their cobalt analogous precatalysts,[12b,13] the 2-(1-aryliminoethyl)-9-arylimino-5,6,7-trihydroquinolylcobalt precatalysts generally showed the highest activity,[12b] and the 2-(1-aryliminoethyl)-7-arylimino-6,6-dimethylcyclopenta-pyridylcobalt precatalysts showed low activity.[13] The title cobalt complexes maintained high activities toward ethylene polymerization, being slightly lower than their analgous system (**C**-model, Co).[12b] In comparison of molecular weights of polyethylenes obtained in current system versus the analogues,[12b] the current system produced polyethylenes in the ranges of several thousand with melting points higher than 123 °C, representing highly linear and useful waxes of Polyethylenes and additives. Therefore the current catalytic systems would be interested to potential commercial consideration, meanwhile further tuning ligands would still be interested in developing complexes for highly active precatalysts.

Conclusion

In current work, a series of 2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt dichloride complexes were synthesized and characterized by FT-IR and elemental analysis, and the molecular structures of complexes **Co1**, **Co3** and **Co4** were confirmed by single-crystal X-ray diffraction. On activation with MAO or MMAO, all these cobalt pre-catalysts exhibited high activities toward ethylene polymerization, up to 2.09 ×10^7 gPE·mol^{-1}(Co)·h^{-1} in 5 min for **Co4**/MAO system. These precursors performed higher activities, longer lifetimes and better thermal stability. The resultant polyethylenes revealed narrow PDIs and unimodal feature, which would be useful polyethylene waxes. Though the work on 2-(1-(arylimino)ethyl)-7-arylimino-6,6-dimethylcyclopenta-pyridylcobalt complexes was unfavorable for the activity of polymerization, the current 2-(1-arylimino)ethyl-9-arylimino-5,6,7,8-tetrahydrocyclohepta-pyridylcobalt (this work) and their iron analogous systems have been confirmed to conduct beneficial modifications. Undoubtedly, changing the ring size of the fused-cycloalkanes would cause great impact on ethylene polymerization activities, which due to the well-controlled intensity of coordinative bond in the complexes. Further investigation of designing new catalyst for higher activities and well controlled polyethylenes are still the challenge subject.

Experimental Section

General Considerations. All procedures of air- and moisture-sensitive compounds were performed in nitrogen atmosphere with standard Schlenk techniques. Toluene was refluxed over sodium (a small amount of benzophenone) and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in *n*-heptane) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were checked 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 microanalyzer. Molecular weights and molecular weight distribution (MWD) of polyethylenes were determined by a PL-GPC220 GPC/SEC High Temperature System. The Columns are three 300 × 7.5mm PLgel 10μm MIXED-B LS columns connected in series. The testing was undertaken at 150°C with the flow rate of 1.0ml/min. The eluent was 1,2,4-trichlorobenzene (TCB). Data collection and handling were carried out using Cirrus GPC Software and Multi Detector Software. Data were collected at 1 point per second. The calibrants for constructing conventional calibration is Polystyrene Calibration Kit S-M-10 from PL Company. The true average molecular weights of PE are transferred by inputting the M-H constants of PE. K of 0.727 and α of 40.6 are provided by PL Company. Samples were dissolved at a concentration of 0.5 to 2.5 mg/ml, depending on the molecular weights. DSC trace and melting points of polyethylene were obtained from the second scanning run on DSC Q2000 at a heating rate of 10 °C/min from -40 °C to 160 °C. $^1H/^{13}C$ NMR spectra of the polyethylene was recorded on a Bruker DMX 300 MHz instrument at 100 °C in deuterated 1,1,2,2-tetrachloroethane with TMS as an internal standard.

According to the procedures for synthesizing their iron analogues,[14] the cobalt complexes (**Co1**–**Co5**) were prepared in good yield.

Synthesis of 2-(1-(2,6-dimethylphenylimino)ethyl)-9-(2,6-dimethylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridyl cobalt chloride (**Co1**). The ligand L1/L1' (0.16 g, 0.39 mmol) and the metal salt $CoCl_2$ (0.040 g, 0.36 mmol) were added together in a Schlenk tube, 5 ml ethanol was added into the tube, the mixture was rapidly stirred at room temperature for 10 h, then diethyl ether was added to the reaction to precipitate the complex **Co1**, after filtering, the precipitate was washed with diethyl ether (3 × 5 mL) and dried under vacuum to get the product as yellow powder (0.12 g, 63 %). FT-IR (KBr, cm^{-1}): 2947.4(m), 2868.5(w), 1617.3($\nu_{C=N}$, m), 1581.6(m), 1467.4(m), 1373.0(m), 1314.5(w), 1258.8(m), 1201.9(s), 1096.3(m), 1037.5(w), 995.1(w), 923.1(w), 885.9(w), 855.3(w), 772.5(s), 702.8(w). Anal. Calcd. for $C_{28}H_{31}Cl_2CoN_3$: C, 60.87, H, 5.69, N, 7.55; Found: C, 60.95, H, 5.64, N, 7.54.

Synthesis of 2-(1-(2,6-diethylphenylimino)ethyl)-9-(2,6-diethylphenylimino)-5,6,7,8-tetrahydrocycloheptapyridyl cobalt chloride (**Co2**). Similarly, **Co2** was isolated as yellow powder in 78 % yield. FT-IR (KBr, cm^{-1}): 2967.7(m), 2869.5(w), 1609.0($\nu_{C=N}$, w), 1577.1(w), 1563.1(w), 1448.7(s), 1374.1(w), 1258.8(m), 1231.4(w), 1196.4(m), 1120.3(w),1056.4(w), 860.1(w), 840.1(w), 807.2(w), 776.9(s). Anal. Calcd. for $C_{32}H_{39}Cl_2CoN_3$: C, 63.37, H, 5.50, N, 6.89; Found: C, 63.23, H, 6.54, N, 6.94.

Synthesis of 2-(1-(2,6-diisopropylphenylimino)ethyl)-9-(2,6-diisopropylphenylimino)-5,6,7,8-tetrahydrocyclohepta-pyridylcobalt chloride (**Co3**). Similarly, **Co3** was isolated as yellow powder in 80 % yield. FT-IR (KBr, cm^{-1}): 2963.8(m), 2865.5(w), 1611.1($\nu_{C=N}$, w), 1572.1(m), 1462.1(s), 1368.6(m), 1317.4(w), 1254.6(m), 1190.2(m), 1112.0(w), 1052.5(w), 849.7(w), 799.7(m), 771.6(s). Anal. Calcd. for $C_{36}H_{47}Cl_2CoN_3$: C, 65.25, H, 7.17, N, 6.31; Found: C, 65.12, H, 7.18, N, 6.15.

Synthesis of 2-(1-(mesitylimino)ethyl)-9-(mesitylimino)-5,6,7,8-tetrahydrocycloheptapyridylcobalt chloride (**Co4**). Similarly, **Co4** was isolated as yellow powder in 63 % yield. FT-IR (KBr, cm^{-1}): 2920.1(m), 2864.3(w), 1614.7($\nu_{C=N}$, m), 1574.6(m), 1477.9(m), 1373.3(m), 1257.6(m), 1213.2(s), 1158.6(m), 1036.2(w), 855.3(s). Anal. Calcd. for $C_{30}H_{35}Cl_2CoN_3$: C, 62.30, H, 6.12, N, 7.22; Found: C, 62.17, H, 6.13, N, 7.27.

Synthesis of 2-(1-(2,6-diethyl-4-methylphenylimino)ethyl)-9-(2,6-diethyl-4-methylphenylimino)-5,6,7,8-tetrahydrocyclo heptapyridylcobalt chloride (**Co5**). Similarly, **Co5** was isolated as yellow powder in 45 % yield. FT-IR (KBr, cm^{-1}): 2962.1(m), 2932.9(m), 2870.0(w), 1615.0($\nu_{C=N}$, m), 1580.3(w), 1458.6(s), 1369.1(m), 1257.0(m), 1209.5(m), 1183.1(m), 1159.5(m), 1123.2(w), 881.0(w), 857.0(s), 786.1(w). Anal. Calcd. for $C_{34}H_{43}Cl_2CoN_3$: C, 63.26, H, 6.75, N, 6.45; Found: C, 63.25, H, 6.68, N, 6.45.

Procedure for Ethylene Polymerization.

Ethylene polymerization under 10/5 atm ethylene. A 250 mL stainless steel autoclave, equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller, was employed for the reaction. The autoclave was vacuumized and replaced by ethylene for three times. when the desired reaction temperature was reached, toluene, co-catalyst (MAO or MMAO), and a toluene solution of the catalytic precursor (the total volume was 100 mL) were injected into the autoclave by using syringes, then the ethylene pressure was increased to 10/5 atm, maintained at this level with constant feeding of ethylene. After the reaction was carried out for the required period, the reactor was cooled with water bath and the excess ethylene was vented. the reaction solution was quenched with 10% HCl/ethanol. The precipitated polymer was collected by filtration, washed with ethanol and dried in a vacuum at 50 °C until constant weight.

Ethylene polymerization under 1 atm ethylene. The pre-catalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ambient ethylene atmosphere (1 atm) with a water bath for controlling the desired temperature. The required amount of co-catalyst was added by a syringe. After the reaction was carried out for the required period, the reactor was cooled down and the reaction solution was quenched with 10% HCl/ethanol. The precipitated polymer was collected by filtration, washed with ethanol and dried in a vacuum at 50 °C until constant weight.

X-ray Crystallographic Studies. Single crystals of the cobalt(II) complexes **Co1**, **Co3** and **Co4** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into their dichloromethane/methanol (v/v = 2:1) solutions at room temperature, respectively. Data collection for **Co1** and **Co3** were carried out on Rigaku Saturn 724 + CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), whilst that for **Co4** was carried out on Rigaku MM007-HF Saturn 724 + CCD diffractometer with confocal mirror monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using

Table 5. Crystal data and Structure Refinement for **Co1**, **Co3** and **Co4**.

	Co1	**Co3**	**Co4**
Crystal color	brown	red	red
Empirical formula	$C_{56}H_{62}Cl_4Co_2N_6$	$C_{72}H_{94}Cl_4Co_2N_6$	$C_{60}H_{70}Cl_4Co_2N_6$
Formula weight	1078.78	1303.19	1134.88
T (K)	173.15(2)	173.15 (2)	173.15 (2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic
space group	P-1	P-1	C2/c
a (Å)	10.148(2)	9.1872(18)	29.946(6)
b (Å)	13.103(3)	18.382(4)	8.5447(17)
c (Å)	22.379(5)	24.108(5)	26.208(5)
α (°)	94.63(3)	110.60(3)	90
β (°)	92.37(3)	96.73(3)	109.92(3)
γ (°)	102.84(3)	91.19(3)	90
V ($Å^3$)	2886.4(10)	3776.1(13)	6305(2)
Z	2	2	2
Dcalcd. (g cm^{-3})	1.241	1.146	1.196
μ (mm^{-1})	0.799	0.622	0.735
F(000)	1124	1380	2376
cryst size (mm)	0.452×0.264 ×0.141	0.489×0.328 ×0.109	0.146×0.103 ×0.077
θ range (°)	0.91 – 25.00	0.91 – 25.00	1.45 – 25.00
limiting indices	$-11 \leq h \leq 12$ $-15 \leq k \leq 15$ $-26 \leq l \leq 26$	$-10 \leq h \leq 10$ $-21 \leq k \leq 21$ $-28 \leq l \leq 28$	$-35 \leq h \leq 34$ $-9 \leq k \leq 10$ $-31 \leq l \leq 31$
no. of rflns collected	22212	28204	19076
no. unique rflns [R(int)]	10099(0.0463)	13235(0.0673)	5535(0.0507)
completeness to θ (%)	99.4 (θ = 25.00)	99.6 (θ = 25.00)	99.7 (θ = 25.00)
Goodness of fit on F^2	1.047	1.016	1.147
Final R indices [I > 2σ(I)]	R1 = 0.0777 wR2 = 0.2235	R1 = 0.1046 wR2 = 0.2726	R1 = 0.0623 wR2 = 0.1689
R indices (all data)	R1 = 0.0877 wR2 = 0.2341	R1 = 0.1292 wR2 = 0.2935	R1 = 0.0711 wR2 = 0.1748
largest diff peak and hole (e $Å^{-3}$)	1.533 and -0.631	1.883 and -0.658	0.386 and -0.521

the SHELXL-97 package.[19] The SQUEEZE option of the crystallographic program PLATON[20] was applied to remove free solvents from the structures of **Co1**, **Co3** and **Co4**; the geometries of the complexes remained unaffected by employing SQUEEZE. Details of the X-ray structure determinations and refinements are provided in Table 5.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. U1362204, 51473170, 21473160, and 21374123).

Notes and references

‡ Appendix A. Supplementary material: CCDC 1426066, 1426067 and 1426068 contain the supplementary crystallographic data for **Co1**, **Co3** and **Co4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Graphical Abstract

for

Controlling molecular weights of polyethylene waxes using the highly active precatalysts of 2-(1-aryliminoethyl)-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt chlorides: Synthesis, characterization, and catalytic behavior

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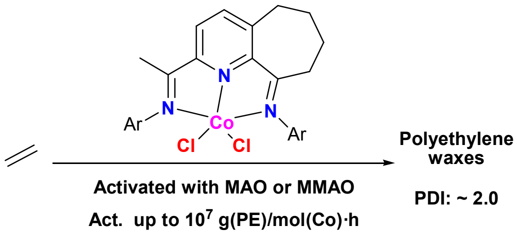

The 2-(1-aryliminoethyl)-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridylcobalt chlorides, upon activation with either MAO) or MMAO, polymerized ethylene in high activities up to the level of 10^7 gPE·mol^{-1}(Co)·h^{-1} and produced potentially useful polyethylene waxes.