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Synthesis, characterisation and solid state structures of α-diimine cobalt(II) complexes: Ethylene polymerisation tests

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Abstract

A series of cobalt(II) compounds of the type $[CoX_2(\alpha\text{-diimine})]$ were synthesised by direct reaction of anhydrous $CoCl_2$ or CoI_2 and the corresponding α-diimine ligand, in CH_2Cl_2: $[CoI_2(o,o',p\text{-Me}_3C_6H_2\text{-DAB})]$ (1), $[CoI_2(o,o'\text{-}^iPr_2C_6H_3\text{-DAB})]$ (2), (where Ar-DAB = 1,4-bis(aryl)-2,3-dimethyl-1,4-diaza-1,3-butadiene), and $[CoCl_2(o,o',p\text{-Me}_3C_6H_2\text{-BIAN})]$ (3), $[CoCl_2(o,o'\text{-}^iPr_2C_6H_3\text{-BIAN})]$ (4), and $[CoI_2(o,o'\text{-}^iPr_2C_6H_3\text{-BIAN})]$ (5) (where Ar-BIAN = bis(aryl)acenaphthenequinonediimine). All compounds were characterised by elemental analyses, IR, mass spectrometry, and X-ray diffraction whenever possible. The crystal structures of compounds 2–4 showed, in all cases, distorted tetrahedral geometries about the Co, built by two halogen atoms and two nitrogen atoms of the α-diimine ligand. Compounds 3 and 4, as well as $[CoCl_2(o,o',p\text{-Me}_3C_6H_2\text{-DAB})]$ (1a), and $[CoCl_2(o,o'\text{-}^iPr_2C_6H_3\text{-DAB})]$ (2a), were activated by methylaluminoxane (MAO) and tested as catalysts for ethylene polymerisation, showing low catalytic activities. Selected polyethylene (PE) samples were characterised by ^1H and ^{13}C NMR and FT-IR spectroscopies, and by differential scanning calorimetry (DSC), revealing branching microstructures (2.5–5.5%).
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1. Introduction

The commercial production of polyolefins from ethylene and propylene had an enormous development with the use of Ziegler–Natta type catalysts. This field has been remarkably renewed with the use of catalysts based on early-transition metallocenes [1]. In the mid-1990s, a new type of catalysts have been discovered, based on late transition metals and quite simple ligands, leading to novel polymer microstructures [2,3]. Among these ligands are the sterically demanding α-diimines [4]. These bidentate ligands are very rigid and it is possible to change easily their backbone and *N*-substituents, allowing the control of the steric and electronic effects at the metal centre. A great number of group 10 transition metal complexes bearing α-diimine ligands have been synthesised and characterised since then, and their employ as catalysts for the oligomerisation and polymerisation of α-olefins have been extensively studied [3a]. However, reports on cobalt complexes containing this type of ligands are scarce [5]. Recently, some results in the insertion polymerisation of ethylene have been reported using tetrahedral Co(II) complexes with related ligands [5e,6]. The α-diimine ligands have also been object of

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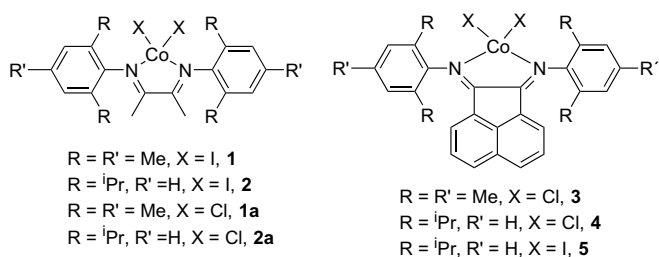
Scheme 1.

different studies regarding the relative binding strengths [7] as well as their reactivity with main group metals [8].

We have been interested in the synthesis and characterisation by X-ray diffraction and EPR spectroscopy of cobalt(II) complexes of the general formula [CoX$_2$(α-diimine)], where X = Cl, or I and α-diimines such as bis(aryl)acenaphthenequinonediimine (Ar-BIAN) and 1,4-bis(aryl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (Ar-DAB) [9]. The present paper reports on the synthesis and characterisation of further α-diimine Co(II) halide complexes (Scheme 1), namely, [CoI$_2$(o,o',p-Me$_3$C$_6$H$_2$-DAB)] (1); [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-DAB)] (2); [CoCl$_2$(o,o',p-Me$_3$C$_6$H$_2$-BIAN)] (3); [CoCl$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-BIAN)] (4); [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-BIAN)] (5). Complexes 3 and 4, and also the previously described BIAN analogues 1a and 2a (similar to 1 and 2, respectively, but with X = Cl instead) [9] were activated by methylaluminoxane and tested as catalysts for ethylene polymerisation.

2. Results and discussion

2.1. Synthesis and characterisation of compounds

The reaction of equimolar quantities of anhydrous CoX$_2$ (X = Cl or I) and α-diimine ligands, in deoxygenated and dehydrated CH$_2$Cl$_2$, at room temperature, yielded red–brown crystalline solids 1–5, with general formula [CoX$_2$(α-diimine)] (Fig. 1), in ca. 75–94% yields. All synthesised compounds were characterised by elemental anal-

yses, FT-IR and ^{1}H NMR spectroscopies and mass spectrometry (MALDI-TOF-MS) (see Experimental and Table S1 supporting information).

The ^{1}H NMR spectra of compounds 1–5, in CD$_2$Cl$_2$, at room temperature, exhibit paramagnetic contact shifts [10], showing resonances spread from ca. δ 107 to −25. These contact shifts are due to the paramagnetic character of the Co(II) complexes that exhibit high spin S = 3/2 in the solid state [9], although in solution they may be involved in equilibria with their S = 1/2 square planar conformers.

A MALDI-TOF-MS study in dichloromethane was performed for all the synthesised complexes. The samples were dissolved in dichloromethane (1 μg/μL), and no matrix was added to obtain the mass spectra. All the complexes showed peaks attributed to the corresponding species [CoXL]$^+$, and to [L + H$^+$], (where X = Cl or I, and L = diimine ligand). These species were formed by the dissociation of one halide or by protonation of the dissociated neutral α-diimine ligand, to give cationic species in all cases. In compound 4, the peak attributed to the parent ion [CoCl$_2$L4-H$^+$] was detected in the negative ionisation mode (see Experimental and Table S1 supporting information, footnote d). These results agree very well with the proposed structures for the synthesised compounds.

The FT-IR spectra of the cobalt(II) complexes, recorded as Nujol mulls, display medium absorption bands in the range $\bar{v}$ = 1652–1615 cm^{-1}, which is the absorption region for $\bar{v}$(C=N). Bands assigned to the free ligand C=N stretching vibrations were observed in the range $\bar{v}$ = 1674–1637 cm^{-1}. In general, the bands in the complexes are shifted to lower wavenumbers which is a criterion of the coordination of both diimine nitrogen atoms of the α-diimine ligands to the cobalt(II) ion (see Table S2 supporting information).

Crystals were obtained for complexes 2–4 enabling the determination of their crystal structures. Table 1 lists selected bond distances and angles.

The molecular structure of compound 2 shows an asymmetric unit formed by a half molecule of [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-DAB)] (where Ar-DAB = 1,4-bis(aryl)-2,3-dimethyl-1,4-diaza-1,3-butadiene) with the Co atom occupying a special position (0, 0, 0). The corresponding molecular structure is generated by symmetry, giving rise to a distorted tetrahedral geometry around the Co atom, which is built up of two iodine atoms and two nitrogen atoms of the ligand (Fig. 1). In fact, due to the symmetry exhibited, the dihedral angle formed by planes defined by I1–Co1–I2 and N1–Co1–N1_1 is exactly 90°. The I1–Co1–I2 angle is 111.68(3)° which is very close to ideal tetrahedral (109.47°), however the other two bonds to N atoms introduce some distortion since the bite angle N1–Co1–N1_1 is 80.15(16)°. The distances Co–I are 2.5200(7) and 2.5425(8) Å, while the Co–N is 2.045(3) Å. The planes formed by the aryl rings C5–C6–C7–C8–C9–C10 are nearly perpendicular to the plane defined by Co1–N1–C1–C1_1–N1_1 (89.63°). However, the aryl rings themselves are not exactly parallel to each other, making a dihedral angle of 16.79°. These

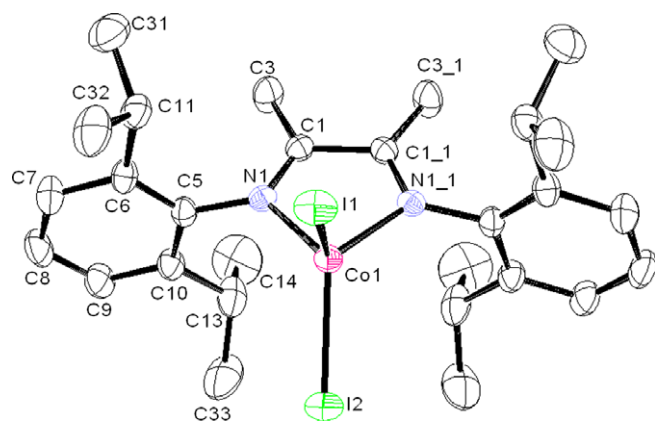

Fig. 1. ORTEP view of the complex 2. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances and angles for complexes **2**–**4**

	2	**3**	**4**	
			Molecule A	Molecule B
Distances (Å)				
Co1–Cl1	–	2.2037(5)	2.192(2)	2.208(2)
Co1–Cl2	–	2.2105(5)	2.227(2)	2.195(2)
Co1–I1	2.5425(8)	–	–	–
Co1–I2	2.5200(7)	–	–	–
Co1–N1	2.045(3)	2.0753(12)	2.084(6)	2.092(5)
Co1–N2	–	2.0678(12)	2.067(6)	2.085(6)
C1–N1	1.279(4)	1.2795(19)	1.232(8)	1.278(8)
C2–N2	–	1.2773(19)	1.283(8)	1.257(8)
C2–C4	–	1.460(2)	1.473(9)	1.489(8)
C1–C3	1.490(5)	1.459(2)	1.464(9)	1.480(9)
C1–C2	–	1.520(2)	1.563(9)	1.504(9)
N1–C5	1.448(5)	1.4345(17)	1.450(9)	1.454(8)
N2–C14	–	1.4436(17)	1.428(9)	1.442(9)
C4–C30	–	1.416(2)	1.419(9)	1.416(9)
C3–C30	–	1.425(2)	1.430(10)	1.407(9)
Angles (°)				
Cl2–Co1–Cl1	–	112.51(2)	115.15(9)	117.27(8)
I2–Co1–I1	111.68(3)	–	–	–
N1–Co1–N2	80.15(16)	82.17(5)	81.5(2)	82.2(2)
N2–C2–C1	–	118.07(12)	117.1(6)	121.1(6)
N1–C1–C2	115.7(2)	118.03(12)	117.0(6)	117.6(6)
C5–N1–C1	121.9(3)	119.38(12)	115.8(6)	117.9(5)
C14–N2–C2	–	119.76(12)	119.1(6)	121.3(6)

features are similar to the ones found in previous α-diimine complexes synthesised by our group, namely **1a** and **2a** [9].

The molecular structure of compound **3** also shows a distorted tetrahedral geometry, just like in the case above, formed by two chloride atoms and two nitrogen atoms of the chelating ligand (Fig. 2). The dihedral angle formed by planes defined by Cl1–Co1–Cl2 and N1–Co1–N2 is 89.25°. The Cl1–Co1–Cl2 angle is 112.51(2)° while the N1–Co1–N2 bite angle is 82.17(5). The distances Co–Cl are 2.2037(5) and 2.2105(5) Å, and the Co–N bond distances are similar to the ones found in complex **2**. The aryl rings C5–C6–C7–C8–C9–C10 and C14–C15–C16–C17–C18–C19 are almost parallel, forming an angle of 7.25°.
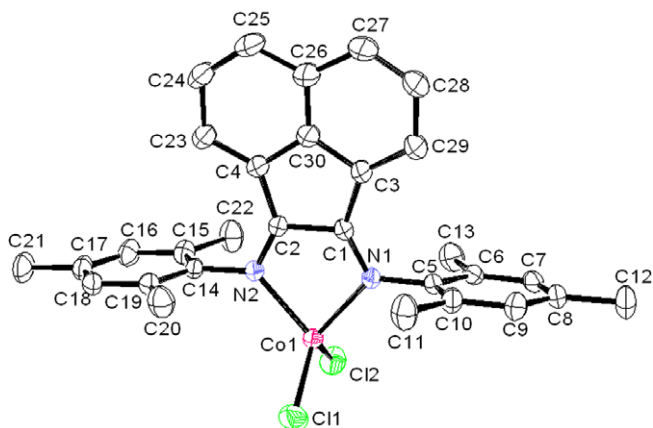
They are nearly perpendicular to the plane defined by Co1–N1–C1–C2–N2 (83.39 and 87.87°).

The molecular structure of compound **4** consists of an asymmetric unit containing two independent molecules, also having distorted tetrahedral geometries (Fig. 3). The planes defined by Cl1–Co1–Cl2 and N1–Co1–N2 form angles of 89.11 and 87.83°, for molecules A and B, respectively. The Cl1–Co1–Cl2 angles are 115.15(9) and 117.27(8)°, while the N1–Co1–N2 bite angles are 81.5(2) and 82.2(2)°, for molecules A and B, respectively. The distances Co–Cl and Co–N are similar to the ones found in complexes **2** and **3**. As for the latter structures, the aryl rings are almost parallel to each other, being nearly perpendicular to the plane defined by Co1–N1–C1–C2–N2.

The coordinated imine C=N bond distances (1.232(8)– 1.283(8) Å), as most of the other structural features of complexes **2**–**4**, are similar to those found for the other [CoX$_2$(α-diimine)] described in the literature [5e,9,11], and are slightly shorter than the C=N bond distances found in the free ligands (e.g. ligand L4: 1.250(6)–1.295(6) Å [12]).

2.2. Ethylene polymerisation tests

Complexes **3** and **4** (BIAN derivatives), were tested as catalysts for ethylene polymerisation in the presence of cocatalyst methylaluminoxane (MAO). In order to compare the influence of the ligand framework (DAB vs. BIAN), studies were also carried out for compounds **1a** and **2a**, described in a previous paper [9], which only differ from **1** and **2** in the halide atom (having Cl instead of I). An experimental matrix encompassing temperature and cocatalyst/catalyst ratio was applied to determine critical factors and characteristics of polymerisation reactions. According to the rating of effectiveness of catalysts, based on its activities, provided by Gibson et al. [3b], the results obtained (Table 2) are characteristic of very low to low activities.

The higher activities were observed at 20 °C, for all catalysts studied. Except for **1a**/MAO system, an increase in the [Al]/[Co] ratio from 500 to 1000 led to improvements in the catalytic activities. Increasing the [Al]/[Co] ratio to

Fig. 2. ORTEP view of the complex **3**. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.
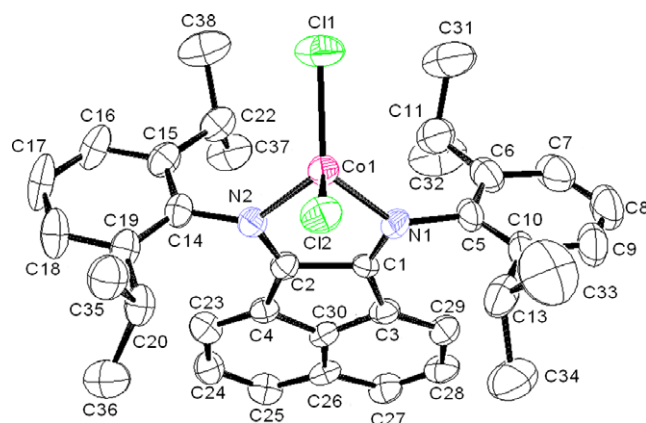

Fig. 3. ORTEP view the complex **4** (molecule A). The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

Table 2
Ethylene polymerisation catalysed by **1a**, **2a**, **3** and **4**/MAO systems[a]

Entries	Complex	[Al]/[Co]	Temp. (°C)	m PE (mg)	Activity (g/(mmol-cat.h.bar))
1	**1a**	500	0	33	0.83
2	**1a**	500	20	43	1.08
3	**1a**	500	40	[b]	
4	**1a**	500	60	0	
5	**1a**	1000	20	32	0.80
6	**1a**	2000	20	1	0.03
7	**2a**	500	0	4	0.10
8	**2a**	500	20	5	0.13
9	**2a**	500	40	[b]	
10	**2a**	500	60	[b]	
11	**2a**	1000	20	9	0.23
12	**2a**	2000	20	4	0.10
13	**3**	500	0	[b]	
14	**3**	500	20	[b]	
15	**3**	500	40	[b]	
16	**3**	500	60	0	
17	**3**	1000	20	4	0.10
18	**3**	2000	20	2	0.05
19	**4**	500	0	16	0.40
20	**4**	500	20	16	0.41
21	**4**	500	40	[b]	
22	**4**	500	60	[b]	
23	**4**	1000	20	26	0.65
26	**4**	2000	20	9	0.23

[a] Conditions: $P_{ethylene} = 2$ bar (relative); $V_{toluene} = 50$ mL; $n_{cat} = 10$ μϖmol; $t = 2$ h.
[b] Traces.

Table 3
Number of branches per 1000 C and thermal analyses of selected polyethylene samples

Entry	Reaction conditions[a]	No. branches/1000 C[b]	ΔH_m (J g^{-1})[c]	T_{onset}^c (°C)	$T_{max}^{c,d}$ (°C)
2	**1a**/500	25	90.8	84.5	103.7
5	**1a**/1000	25	89.4	85.7	103.6
11	**2a**/1000	55	90.0	85.2	103.5
17	**3**/1000	25	73.0	98.7	109.8
23	**4**/1000	46	47.4	51.0	76.6

[a] Complex/(Al/Co ratio); $T = 20$ °C.
[b] Estimated by ^{1}H NMR [15].
[c] Determined by DSC.
[d] The peak value of the melting endotherm (ideally taken as the temperature at which the largest and most perfect crystals are melting) is frequently assigned as the melting temperature, i.e. $T_m \equiv T_{max}$.

2000 caused a decrease in the activity. Catalyst system **3**/MAO, containing the mesityl-BIAN ligand showed the lowest activity, much lower than its o,o'-^{i}Pr$_2$Ph-BIAN analogue **4**/MAO. On the contrary, the o,o'-^{i}Pr$_2$Ph-DAB based catalyst system **2a**/MAO, containing the bulkier ^{i}Pr substituents on the phenyl groups, showed lower activity in comparison with its mesityl analogue **1a**/MAO, the latter being the most active of all the catalysts studied. All these systems are less active than those reported by Laine et al. [5e], for the similar [CoBr$_2$(α-diimine)]/MAO system, where the α-diimine used was 1,4-(bis-2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene, in which the chelating ligand has a less hindered framework than those used in the present work. However, the activities obtained by these authors were measured at higher ethylene pressures (3–5.5 bar), and the products obtained were mainly oily branched ethylene oligomers.

Selected polyethylene (PE) samples (runs no. 2, 5, 11, 17 and 23) were characterised (Table 3) as white solids with branching degrees typical of low density polyethylene (LDPE), varying from 25–55 branches per 1000 carbon atoms, as determined by ^{1}H NMR spectroscopy. The corresponding FT-IR spectra (see Fig. S1 supporting information) showed in all samples the presence of a band at *ca.* $\bar{v} = 1378$ cm^{-1}, in agreement with the presence of methyl groups associated with branching [13]. Their melting temperatures were determined by DSC (see Fig. S2 supporting information), and lie in the range 77–110 °C. The catalyst systems based on **1a** and **3** (entries 2, 5 and 17), which con-

tain diimine ligands with mesityl substituents, give rise to branching degrees of 25/1000 C, whereas **2a** and **4** (entries 11 and 23), containing the bulkier o,o'-^{i}Pr$_2$Ph substituents, produce PE twice as branched as the others. This effect is also observed in the analogous nickel catalyst systems [14]. The fact that system **2a**/MAO (entry 11) produces PE with thermal features similar to those of **1a**/MAO (entries 2 and 5), but with a higher branching, may be explained by a variation of the PE molecular weight induced by the o,o'-^{i}Pr$_2$Ph diimine substituents of **2a**. On the other hand, comparison of the thermal parameters of the PEs produced by **3** and **4**/MAO shows that the latter catalyst system presents a lower melting temperature and a lower crystallinity in agreement with the higher number of branches shown by this sample.

3. Conclusions

A series of paramagnetic cobalt(II) complexes of general formula [CoX$_2$(α-diimine)]: [CoI$_2$(o,o',p-Me$_3$C$_6$H$_2$-DAB)] (**1**), [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-DAB)] (**2**), [CoCl$_2$(o,o',p-Me$_3$C$_6$H$_2$-BIAN)] (**3**), [CoCl$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-BIAN)] (**4**) and [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-BIAN)] (**5**), were synthesised by direct reaction of equimolar amounts of the corresponding cobalt dihalide and α-diimine ligand, in CH$_2$Cl$_2$, in *c.a.* 75–94% yields. Single crystal X-ray structural data for compounds **2**–**4** show, in all cases, the cobalt atom in a distorted tetrahedral coordination generated by two halide atoms and two nitrogen atoms of the α-diimine ligand. Compounds **3** and **4**, as well as [CoCl$_2$(o,o',p-Me$_3$C$_6$H$_2$-DAB)] (**1a**), and [CoCl$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-DAB)] (**2a**), revealed low activities in ethylene polymerisation when activated with MAO. The resulting branched (2.5–5.5%) low molecular weight polyethylenes are solid samples, with melting points in the range 77–110 °C.

4. Experimental

4.1. General

All reactions and manipulations of solutions were performed under nitrogen or argon atmospheres using stan-

dard Schlenk techniques. Reagent grade solvents were deoxygenated and dehydrated before use according to literature methods. $CoCl_2$ and CoI_2 were purchased from Aldrich and the α-diimine ligands were synthesised as described in the literature [16].

Elemental analyses were obtained from REQUIMTE, Chemistry Department, New University of Lisbon Service using a Thermo Finnigan-CE Flash-EA 1112-CHNS Instrument.

Infrared spectra of complexes were recorded as Nujol mulls on NaCl plates using a Mattson Satellite FTIR spectrometer.

MALDI-TOF-MS analysis were obtained from REQUIMTE, MALDI-TOF-MS Service Laboratory, and have been performed in a MALDI-TOF-MS model voyager DE-PRO Biospectrometry Workstation equipped with a nitrogen laser radiating at 337 nm from Applied Biosystems (Foster City, United States). MALDI mass spectra were acquired and treated with Data Explorer software version 4 series. The MALDI-TOF-MS study in dichloromethane was carried out for complexes **1**–**5**. Samples were dissolved in dichloromethane (1 μg/μL), and 1–2 μL of the corresponding solution was spotted on a well of a MALDI-TOF-MS sample plate and allowed to dry. No matrix was added. Measurements were performed in the reflector positive ion mode, with a 20 kV accelerating voltage, 80% grid voltage, 0.005% guide wire, and a delay time of 200 ns, for complexes **1**–**5** and in the negative ion mode for complex **4**. Mass spectral analysis for each sample was based on the average of 500 laser shots.

^{1}H NMR of complexes **1**–**5** were recorded in a Bruker Avance III 400 spectrometer (at 400.13 MHz), in CD_2Cl_2, at room temperature. ^{1}H and ^{13}C NMR spectra of polyethylene samples were recorded in Bruker Avance III 400 (at 400.13 MHz) and Bruker Avance III 300 (at 75.47 MHz) spectrometers, at 110°C. Polymer samples were previously dissolved in a boiling mixture of 3:1 trichlorobenzene:C_6D_6. All spectra taken in both devices were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). Deuterated solvents were dried with molecular sieves and freeze-pump-thaw-degassed prior to use.

Polyethylene thermal analyses were performed with a TA Instruments DSC2920 with MDSC® option, connected to a liquid N_2 cooling system and calibrated with standards. The sample weights were *ca.* 4–10 mg in all the experiments. A temperature range from 0 to 150 °C has been studied and the heating and cooling rates used were 10 °C min⁻¹. The second heating cycle was recorded.

Infrared spectra were collected on polymer films using a Thermo-Nicolet NEXUS FT-IR spectrophotometer. The spectra were normalised in relation to the intensity of the absorption band centred at 720 cm⁻¹ (main polyethylene backbone). Films were prepared in a SpecAc press equipped with heating plates and a SpecAc 20160 temperature controller.

4.2. Synthesis of complexes

4.2.1. Synthesis of [CoI₂(o,o′,p-Me₃C₆H₂-DAB)] (1)

A green suspension of CoI_2 (0.2 g, 0.62 mmol) in CH_2Cl_2 (20 mL) was treated with a yellow solution of $o,o',p\text{-}Me_3C_6H_2\text{-}DAB$, (0.2 g, 0.64 mmol) in CH_2Cl_2 (30 mL). An almost immediate colour change was observed from green to red–brown. The mixture was stirred overnight, at room temperature, until complete dissolution. The solution was filtered, and concentrated by vacuum removal of the solvent. A brown crystalline solid precipitated which was separated by filtration, washed with diethyl ether (2 × 10 mL) and petroleum ether (2 × 10 mL). After recrystallisation from CH_2Cl_2/petroleum ether 0.36 g of **1** were obtained (yield: 94%).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 107.11, 18.44, 15.22, 0.50. IR (nujol mull/NaCl plates), cm⁻¹: 1631 ($\bar{v}_{C=N}$). MS (MALDI-TOF); *m/z*: 506.7 [CoIL]⁺ (54.25%), 321.8 [L + H⁺] (100%) (L = diimine ligand). Anal. Calc. for $C_{22}H_{28}CoI_2N_2$ (MW = 633.21): C, 41.73; H, 4.46; N, 4.42. Found: C, 41.67; H, 4.44; N, 4.71%.

4.2.2. Synthesis of [CoI₂(o,o′-ⁱPr₂C₆H₃-DAB)] (2)

Compound **2** was obtained using the procedure described for **1**. Yield: 77%. Crystals suitable for X-ray diffraction were obtained.

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 95.22, 17.11, 7.59, 0.35, −3.00, −24.59. IR (nujol mull/NaCl plates), cm⁻¹: 1639 ($\bar{v}_{C=N}$). MS (MALDI-TOF); *m/z*: 590.76 [CoIL]⁺ (16.38%), 405.9 [L + H⁺] (67.65%) (L = diimine ligand). Anal. Calc. for $C_{28}H_{40}CoI_2N_2$ (MW = 717.37): C, 46.88; H, 5.62; N, 3.90. Found: C, 46.55; H, 5.47; N, 4.04%.

4.2.3. Synthesis of [CoCl₂(o,o′,p-Me₃C₆H₂-BIAN)] (3)

A blue suspension of $CoCl_2$ (0.16 g, 1.2 mmol) in CH_2Cl_2 (20 mL) was treated with a red solution of o,o',p-$Me_3C_6H_2$-BIAN (0.5 g, 1.2 mmol) in CH_2Cl_2 (30 mL). The mixture turned quickly to dark red, and was further stirred for 2 h, until complete dissolution. After filtration, the solvent was partially removed leaving a red–brown solid, which was separated by filtration, washed with petroleum ether (2 × 10 mL). Recrystallisation from CH_2Cl_2/petroleum ether afforded 0.49 g of **3** (yield: 75%). Crystals suitable for X-ray diffraction were obtained.

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 24.73, 16.13, 7.76, 2.16, 1.29, 0.87, −1.40. IR (nujol mull/NaCl plates), cm⁻¹: 1652, 1628 ($\bar{v}_{C=N}$). MS (MALDI-TOF); *m/z*: [CoCIL]⁺ 510.59 (100%), 417.7 [L + H⁺] (4.49%) (L = diimine ligand). Anal. Calc. for $C_{30}H_{28}CoCl_2N_2 \cdot 1/2\ CH_2Cl_2$ (MW = 588.86): C, 62.21; H, 4.96; N, 4.76. Found: C, 62.86; H, 5.80; N, 4.18%.

4.2.4. Synthesis of [CoCl₂(o,o′-ⁱPr₂C₆H₃-BIAN)] (4)

Compound **4** was obtained using the procedure described for **3**. Yield: 83%. Crystals suitable for X-ray diffraction were obtained.

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 24.89, 7.83, 4.00, 3.49, 3.44, −0.09, −19.94. IR (nujol mull/NaCl plates), cm⁻¹:

1649, 1619 ($\bar{\nu}_{C=N}$). MS (MALDI-TOF); m/z: 594.78 [CoClL]$^+$ (23.73%), 501.9 [L + H$^+$] (38.23%) (L = diimine ligand). MS (MALDI-TOF, negative ionisation mode); m/z: 629.77 [CoCl$_2$L-H$^+$] (68%) (L = diimine ligand). Anal. Calc. for C$_{36}$H$_{40}$CoCl$_2$N$_2$ (MW = 630.56): C, 68.57; H, 6.39; N, 4.44. Found: C, 68.14; H, 6.29; N, 4.40%.

4.2.5. Synthesis of [CoI$_2$(o,o'-^{i}Pr$_2$C$_6$H$_3$-BIAN)] (5)

A green suspension of CoI$_2$ (0.16 g, 0.5 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with a red solution of o,o'-^{i}Pr$_2$-C$_6$H$_3$-BIAN (0.25 g, 0.5 mmol) in CH$_2$Cl$_2$ (20 mL). The mixture turned quickly to dark red and was stirred overnight, until complete dissolution. After filtration, the solvent was removed to 1/4 of the volume, and petroleum ether (40–60 °C) (5 mL) was added. A dark red solid, was formed by storage at −20 °C. After filtration and washing with petroleum ether (2 × 10 mL), it was recrystallised from CH$_2$Cl$_2$/petroleum ether, yielding 0.37 g of complex **5** (yield: 91%).

^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 15.17, 11.35, 5.53, 4.99, 3.29, 2.63, −2.44, −22.14. IR (nujol mull/NaCl plates), cm^{-1}: 1640, 1615 ($\bar{\nu}_{C=N}$). MS (MALDI-TOF); m/z: 686.73 [CoIL]$^+$ (100%), 501.9 [L + H$^+$] (71.99%) (L = diimine ligand). Anal. Calc. for C$_{36}$H$_{40}$CoI$_2$N$_2$ (MW = 813.46): C, 53.15; H, 4.96; N, 3.40. Found: C, 53.28; H, 4.96; N, 3.44%.

4.3. Crystallographic details

Crystallographic and experimental details of crystal structure determinations are given in Table 4. Single crystals of complexes **2**, **3**, and **4** were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα λ = 0.71073 Å). The complete conditions of data collection (DENZO software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods (SHELXS-97) and refined against F2 using the SHELXL-97 software [17]. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL-97. Figures were generated using ORTEP3 [18].

4.4. Polymerisation details

Ethylene polymerisation tests were carried out in 200 mL crown capped pressure bottles sealed with neoprene septum and pump filled with nitrogen atmosphere (the bottles were previously dried in the oven at 150 °C for several days and degassed with three cycles of vacuum/nitrogen). Freshly distilled toluene, dried over Na/K alloy, was added (50 mL) to each polymerisation bottle and the resulting solvent was then saturated at an ethylene relative pressure of 2 bar, which was maintained throughout the polymerisation reactions. Then the cocatalyst (MAO) was added in

Table 4
Crystal data and structure refinement for compounds **2–4**

Compound	2	3	4
Formula	C$_{28}$H$_{40}$CoI$_2$N$_2$	C$_{30}$H$_{28}$CoCl$_2$N$_2$	C$_{36}$H$_{40}$CoCl$_2$N$_2$
M	717.3	546.37	630.53
λ (Å)	0.71073	0.71073	0.71073
T (K)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pnma	Pnab	P2$_1$/a
a (Å)	13.6130(2)	16.6540(3)	22.4880(5)
b (Å)	21.1000(2)	17.1900(2)	11.8010(4)
c (Å)	10.4930(5)	22.6670(4)	27.1090(6)
α (°)	90.00	90.00	90.00
β (°)	90.00	90.00	111.450(2)
γ (°)	90.00	90.00	90.00
V (Å^3)	3013.95(15)	6489.16(18)	6695.9(3)
Z	4	8	8
ρ_{calc} (g cm^{-3})	1.581	1.119	1.251
μ (mm^{-1})	2.635	0.711	0.698
θ_{max} (°)	30.034	34.972	30.034
Total data	4826	103035	161895
Unique data	4519	14242	19531
R_{int}	0.0520	0.0000	0.0000
Reflections (R [$I > 3\sigma(I)$])	4519	14242	19531
wR	0.1075	0.1768	0.3434
Goodness-of-fit	1.004	1.015	1.049
ρ_{min}, ρ_{max}	−1.273	−0.551	−0.839
	1.160	0.079	1.387

the proper Al/Co ratio via a glass syringe. Solutions were then brought to the desired temperatures and allowed to equilibrate for 15 min. After this, the corresponding amount of a toluene solution (1 mL) of the desired complex was added to the polymerisation reactors with a glass syringe. The polymerisations were terminated after 2 h by quenching the mixture with 150 mL of an acidic methanol (1% HCl) solution. The absence of ethylene oligomers C$_4$–C$_{24}$ was confirmed by GC chromatography, injecting aliquots of the gas and liquid phases of the polymerisation reaction samples in a Perkin–Elmer Clarus 500 gas chromatograph, equipped with a capillary column Tracer/Teknorma TRB-5MS, 30 m × 0.25 mm ID × 0.25 μm (film), using a temperature program from 60 to 240 °C, and from 240 to 280 °C, at ramp rates of 5 and 10 °C/min, respectively. The obtained polymers were then filtered, washed several times with methanol and dried in a vacuum oven at 60 °C for 3 days. The filtrates were evaporated until all the methanol was removed, and the residual toluene fractions were extracted with distilled water (3 × 50 mL). After separation, the organic phases were evaporated to dryness and no organic materials were observed.

Appendix A. Supplementary material

CCDC 665822, 665823 and 665824 contain the supplementary crystallographic data for **3**, **2** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.007.

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