Electronically variable imino-phenanthrolinyl-cobalt complexes; synthesis, structures and ethylene oligomerisation studies

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Abstract

The 2-imino-1,10-phenanthroline ligands, $1,10\text{-}C_{12}H_7N_2\text{-}2\text{-}CR{=}N(2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}R^1\text{-}C_6H_2)$ [$R = R^1 = H$ (**L1**); $R = H$, $R^1 = Br$ (**L2**); $R = H$, $R^1 = CN$ (**L3**); $R = H$, $R^1 = i\text{-}Pr$ (**L4**); $R = Me$, $R^1 = H$ (**L5**); $R = Me$, $R^1 = i\text{-}Pr$ (**L6**)], have been prepared in high yield from the condensation reaction of $1,10\text{-}C_{12}H_7N_2\text{-}2\text{-}CR{=}O$ ($R = H$, Me) with one equivalent of the corresponding 4-substituted 2,6-diisopropylaniline. The molecular structures of **L2**, **L5** and **L6** reveal the imino nitrogen atoms to adopt a transoid configuration with respect to the phenanthrolinyl nitrogen atoms. Treatment of **Lx** with one equivalent of $CoCl_2$ in *n*-BuOH at 90 °C gives the high spin complexes, (**Lx**)$CoCl_2$ [**Lx** = **L1** (**1a**), **L2** (**1b**), **L3** (**1c**), **L4** (**1d**), **L5** (**1e**), **L6** (**1f**)], in which the metal centres exhibit distorted square pyramidal geometries. Activation of **1a**–**1f** with excess methylaluminoxane (MAO) gives catalysts that are modestly active for the oligomerisation of ethylene affording mainly linear α-olefins along with some degree of internal olefins. While the donor capability of the 4-position of the *N*-aryl group does not appear to affect the activity of the catalyst, it does have an influence on the ratio of α-olefins to internal olefins. Single crystal X-ray diffraction studies have been performed on **L2**, **L5**, **L6**, **1a**, **1c** and **1f**.
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1. Introduction

Since the initial discovery of iron and cobalt catalysts that can deliver very high activities for ethylene polymerisation [1], considerable research activity has been directed towards the modification of the tridentate bis(arylimino)pyridine supporting ligand frame (**A**, Fig. 1). In the main, this has focused on varying the steric [2] and, more recently, the electronic properties [3] of the *N*-aryl groups, the results of which have allowed access to a highly versatile family of catalysts capable of affording high molecular weight polymers through to lower molecular weight oligomers. More drastic modification in **A** such as replacement of the central pyridine [4], one or both exterior imines [5] or all three moieties [6] by alternative donor units, has also

been reported. However, the level of performance exhibited by the resultant catalytic systems has not, on the whole, reached the high levels displayed by the parent bis(arylimino)pyridine-iron or -cobalt prototypes. Nevertheless, by appreciation of the steric and planar characteristics of **A**, neutral tridentate ligands imparting high activities for metal-mediated alkene oligomerisation and polymerisation can be accessed [7,8]. For example, incorporation of a pyridyl group in place of an imino unit in **A** to give aryliminobipyridine ligands (**B**, Fig. 1) has seen the development of a highly active iron ethylene oligomerisation catalyst for the synthesis of short chain α-olefins [8].

During the course of our study, Sun et al. reported the use of unsymmetrical arylimino-phenanthrolinyl ligands (**C**, Fig. 1) as supports for highly active iron catalysts for ethylene oligomerisation [9]. Indeed, the performance of these systems was shown, in a similar fashion to bis(arylimino)pyridine-iron systems, to be related to both the steric
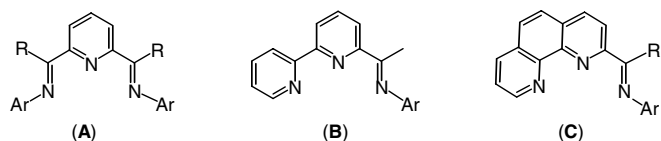

Fig. 1. Bis(imino)pyridine (**A**), imino-bipyridine (**B**) and imino-phenanthroline (**C**); R = H or hydrodrocarbyl, Ar = aryl group.

and electronic properties of **C**. With a view to probing the role of the metal centre in systems bound by **C**, we disclose our results on the synthesis and catalytic evaluation of a series of imino-phenanthrolinyl-cobalt(II) chloride complexes. Specifically, we are concerned with the synthesis and screening of $[1,10\text{-}C_{12}H_7N_2\text{-}2\text{-}CR=N(2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}R^1\text{-}C_6H_2)]CoCl_2$ [R = R^1 = H (**1a**); R = H, R^1 = Br (**1b**); R = H, R^1 = CN (**1c**); R = H, R^1 = i-Pr (**1d**); R = Me, R^1 = H (**1e**); R = Me, R^1 = i-Pr (**1f**)], in which the steric bulk of the *ortho*-aryl substitution pattern has been kept constant and the electronic properties of the *para*-substituent systematically varied for aldimine- and ketimine-based ligand frames.
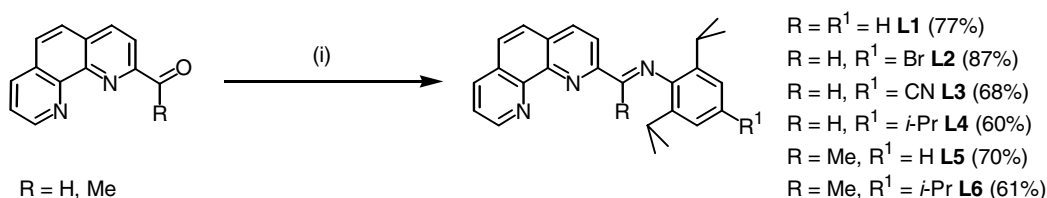
2. Results and discussion

2.1. Ligand synthesis

Treatment of $1,10\text{-}C_{12}H_7N_2\text{-}2\text{-}CR=O$ (R = H, Me) with one equivalent of $2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}{}^1C_6H_2NH_2$ (R^1 = H, Br, CN, i-Pr) in ethanol at elevated temperature, in the presence of a catalytic amount of acetic acid, afforded $1,10\text{-}C_{12}H_7N_2\text{-}2\text{-}$

$CR=N(2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}R^1\text{-}C_6H_2)$ [R = R^1 = H (**L1**); R = H, R^1 = Br (**L2**); R = H, R^1 = CN (**L3**); R = H, R^1 = i-Pr (**L4**); R = Me, R^1 = H (**L5**); R = Me, R^1 = i-Pr (**L6**)] in moderate to good yield (Scheme 1). In general, the aldimine ligands **L1**–**L4** required milder conditions while the ketimine ligands, **L5** and **L6**, higher temperatures and longer reaction times. The carbonyl-containing precursors are not commercially available and were both synthesised from 2-cyano-1,10-phenanthroline [10] in a series of steps (Scheme 2) using slight modifications of the literature procedures (see Section 4). In the case of 2-acetyl-1,10-phenanthroline [9], an improved yield has been obtained by the revised method. **L1**–**L6** have been characterised by ^{1}H NMR, ^{13}C NMR and IR spectroscopy along with Electro-Spray (ES) mass spectrometry (see Section 4). In addition, **L2**, **L5** and **L6** have been the subject of single crystal X-ray diffraction studies.

Slow evaporation of ethanol solutions containing **L2**, **L5** and **L6** gave single crystals suitable for the X-ray determinations. Compound **L2** contains three unique molecules in the asymmetric unit, compound **L5** one and **L6** has two with only minor differences evident between unique molecules in each (*e.g.*, the relative inclination of the aryl substituents). The structures are essentially the same and only the structure of **L2** will be discussed in any detail. The molecular structures of **L2** and **L5** are depicted in Fig. 2; selected bonds lengths and angles for **L2**, **L5** and **L6** (including the unique molecules) are shown in Table 1. This structure of **L2** consists of a phenanthroline moiety linked to an arylimino group at the 2-position with the

R = H, Me

R = R^1 = H **L1** (77%)
R = H, R^1 = Br **L2** (87%)
R = H, R^1 = CN **L3** (68%)
R = H, R^1 = i-Pr **L4** (60%)
R = Me, R^1 = H **L5** (70%)
R = Me, R^1 = i-Pr **L6** (61%)

Scheme 1. Reagents and conditions: (i) $2,6\text{-}i\text{-}Pr_2\text{-}4\text{-}R^1\text{-}C_6H_2NH_2$ (R^1 = H, Br, CN, i-Pr), EtOH, cat. H^+, heat.
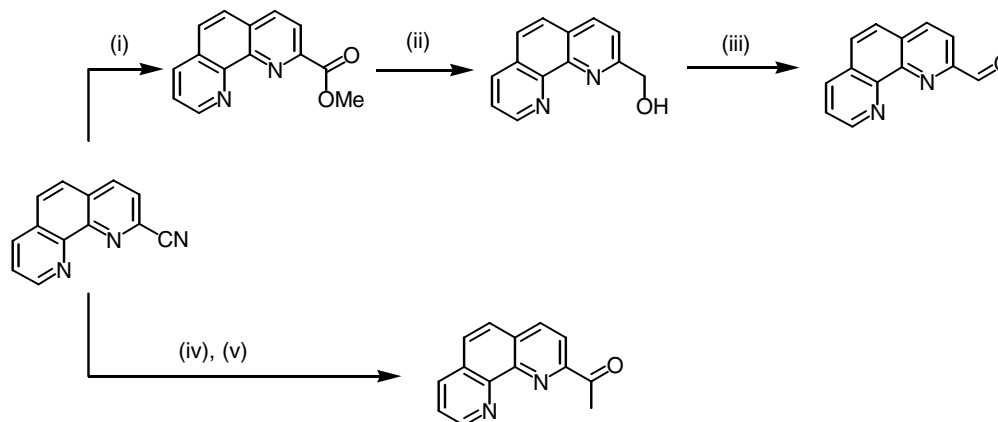
Scheme 2. Reagents and conditions: (i) cat. Na, MeOH, 90 °C; (ii) $NaBH_4$, EtOH, rt; (iii) SeO_2, dioxane, 110 °C; (iv) $2AlMe_3$, toluene, 70 °C; and (v) H_2O, Na_2EDTA.
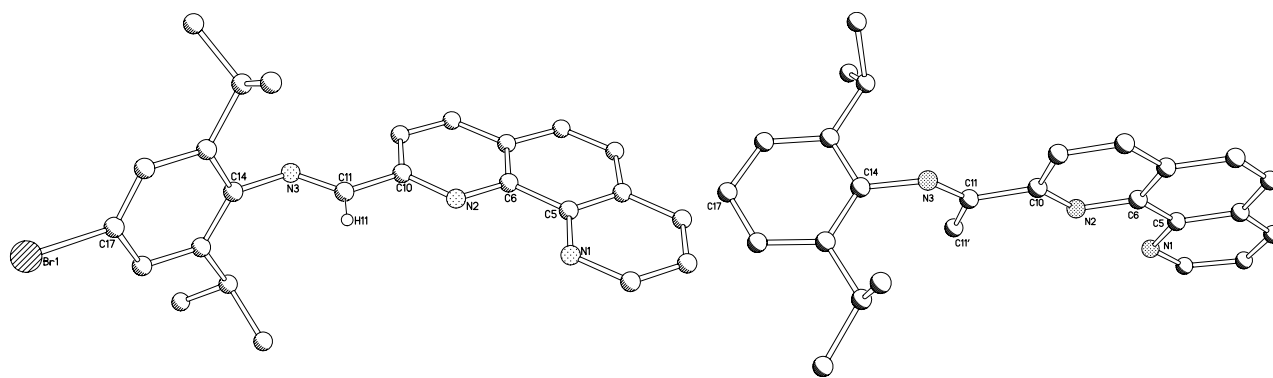
Fig. 2. Molecular structures of **L2** and **L5**. All the hydrogen atoms apart from H11 in **L2** have been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **L2**, **L5** and **L6**

	L2			**L5**	**L6**	
	Molecule A	Molecule B	Molecule C		Molecule A	Molecule B
Bond lengths						
C(10)–C(11)	1.466(5)	1.466(4)	1.475(5)	1.491(2)	1.505(4)	1.496(4)
C(11)–N(3)	1.265(4)	1.255(4)	1.257(4)	1.278(2)	1.292(4)	1.283(4)
C(14)–N(3)	1.433(4)	1.426(4)	1.430(4)	1.423(2)	1.423(4)	1.425(4)
C(17)–Br(1)	1.911(4)	1.913(3)	1.903(4)	–	–	–
C(11)–C(11′)	–	–	–	1.494(2)	1.496(4)	1.513(4)
Bond angles						
C(11)–N(3)–C(14)	118.2(4)	120.5(3)	116.7(3)	121.7(1)	121.5(3)	121.5(3)
C(10)–C(11)–N(3)	121.6(3)	121.4(3)	121.1(3)	116.5(1)	116.1(3)	117.1(3)

imino nitrogen [N(3)] atom adopting a transoid configuration with respect to the nitrogen donors of the phenanthroline unit [N(2), N(1)]. The imino-phenanthroline unit is almost planar [*tors.* N(3)–C(11)–C(10)–N(2) 2.0°] with the *N*-aryl groups essentially orthogonal to this plane. The short length of the N(3)–C(11) [1.265(4) Å] bond is consistent with double bond character and the C–Br distance [C(17)–Br(1) 1.911(4) Å] is typical of a single bond between these elements.
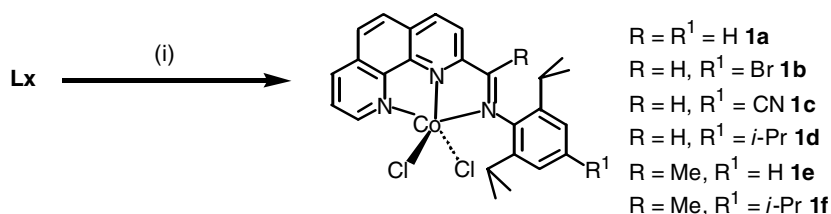
All the compounds (**L1**–**L6**) gave peaks corresponding to their molecular ions in their mass spectra. In their infrared spectra, the absorption bands observed at *ca.* 1629 cm^{-1} were consistent with the presence of a C=N functionality. In the case of **L3** a band at 2224 cm^{-1}, characteristic of a υ(C≡N) stretch, was also evident. The ^{1}H NMR spectra for the aldimines **L1**–**L4** showed singlets at *ca.* δ 8.75 for the C*H*=N proton while the C*H*=N carbon was seen at *ca.* δ 168 in their ^{13}C NMR spectra. For the

ketimine-containing compounds **L5** and **L6**, the *Me*C=N protons were seen as singlets at *ca.* δ 2.5 in their ^{1}H NMR spectra with the *Me*C=N carbon at *ca.* δ 167 in their ^{13}C NMR spectra.

2.2. Synthesis of complexes

Interaction of **L1**–**L6** with one equivalent of cobalt dichloride in *n*-butanol at 90 °C for 1 h gave (**Lx**)CoCl$_2$ [**Lx** = **L1** (**1a**), **L2** (**1b**), **L3** (**1c**), **L4** (**1d**), **L5** (**1e**), **L6** (**1f**)] as green to red–brown solids in good yield (Scheme 3). All the complexes have been characterised by FAB-mass spectrometry, IR spectroscopy and by magnetic susceptibility measurements (Table 2). In addition, **1a**, **1c** and **1f** have been the subject of single crystal X-ray diffraction studies.

Recrystallisation of **1a**, **1c** and **1f** from hot acetonitrile gave single crystals suitable for the X-ray determinations.

R = R^1 = H **1a**
R = H, R^1 = Br **1b**
R = H, R^1 = CN **1c**
R = H, R^1 = *i*-Pr **1d**
R = Me, R^1 = H **1e**
R = Me, R^1 = *i*-Pr **1f**

Scheme 3. Reagents and conditions: (i) CoCl$_2$, *n*-BuOH, heat.

Table 2
Selected characterisation data for the new complexes **1a**–**1f**

Compound	Colour	$\upsilon(C{=}N)\ (cm^{-1})^a$	$\mu_{eff}\ (BM)^b$	FAB mass spectrum	Microanalysis (%)[c]		
					C	H	N
1a	Brown	1609	4.3	461 [M−Cl]$^+$,	60.51	5.21	8.61
				426 [M−2Cl]$^+$	(60.36)	(5.03)	(8.45)
1b	Dark green	1612	3.9	541 [M−Cl]$^+$,	52.41	4.49	7.31
				504 [M−2Cl]$^+$	(52.09)	(4.17)	(7.29)
1c	Olive green	1606	4.1	486 [M−Cl]$^+$,	59.99	4.71	10.81
				451 [M−2Cl]$^+$	(59.78)	(4.60)	(10.73)
1d	Brown	1611	4.0	503 [M−Cl]$^+$,	62.03	5.66	7.65
				468 [M−2Cl]$^+$	(62.34)	(5.75)	(7.79)
1e	Red–brown	1607	4.2	475 [M−Cl]$^+$,	60.95	5.11	8.05
				440 [M−2Cl]$^+$	(61.06)	(5.28)	(8.22)
1f	Red–brown	1615	4.0	517 [M−Cl]$^+$,	62.72	6.05	7.77
				481 [M−2Cl]$^+$	(62.93)	(5.97)	(7.59)

[a] Recorded on a Perkin–Elmer spectrum one FT-IR spectrometer on solid samples.
[b] Recorded on an Evans Balance at room temperature.
[c] Calculated values are shown in parentheses.

The molecular structures of **1a**, **1c** and **1f** are shown in Figs. 3–5, respectively; selected bonds and angles for all structures are listed in Table 3.
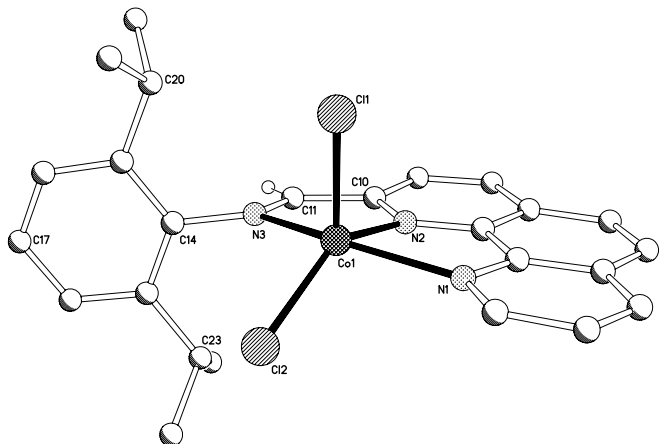
The structures of **1a**, **1c** and **1f** are similar and will be discussed together. In each structure, a single cobalt atom is surrounded by an imino-phenanthroline ligand, **L1** (for **1a**), **L3** (for **1c**) and **L6** (for **1f**), along with two terminally bound chloride ligands. The geometry of the five-coordinate complexes can be best described as distorted square pyramidal as indicated by the low values of their structural index parameters [$\tau = 0.18$ (**1a**), 0.28 (**1c**), 0.03 (**1f**)] [11], with a chloride ligand in each occupying an axial site. The Co–N distances are inequivalent with the central Co(1)–N(2) distance being the shortest [2.0447(18) Å (**1a**), 2.018(6) Å (**1c**), 2.059(3) Å (**1f**)], while the external cobalt nitrogen distances are longer with Co(1)–N(3)$_{imine}$ being the longest [2.2939(18) Å (**1a**), 2.353(6) Å (**1c**), 2.248(6) Å (**1f**)]. The reason for the asymmetry between the external metal nitrogen distances [N(1)$_{imine}$ vs. N(3)$_{phen}$] is likely to be due to the improved donor capability of a pyridine nitrogen over an imine nitrogen [12], with the discrepancy most evident for the aldimine-containing complexes **1a** and **1c**. Moreover in the case of **1c**, the discrepancy is the most significant, probably due to the additional influence of the electron

Fig. 3. Molecular structure of (**L1**)CoCl$_2$ (**1a**). All the hydrogen atoms apart from H11 have been omitted for clarity.
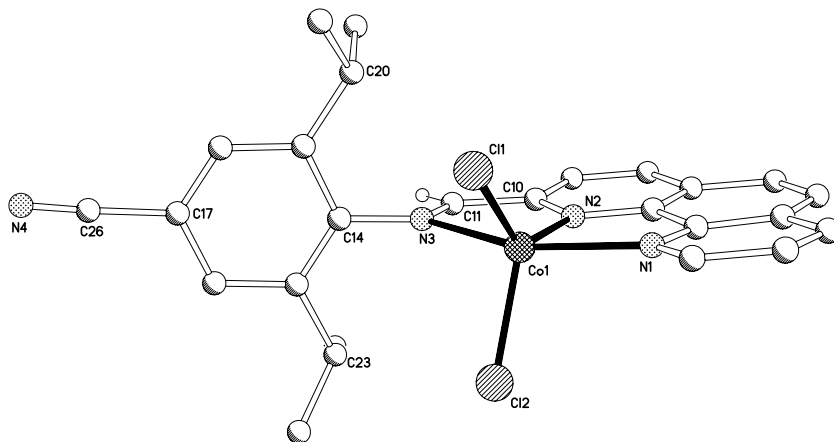

Fig. 4. Molecular structure of (**L3**)CoCl$_2$ (**1c**). All the hydrogen atoms apart from H11 have been omitted for clarity.
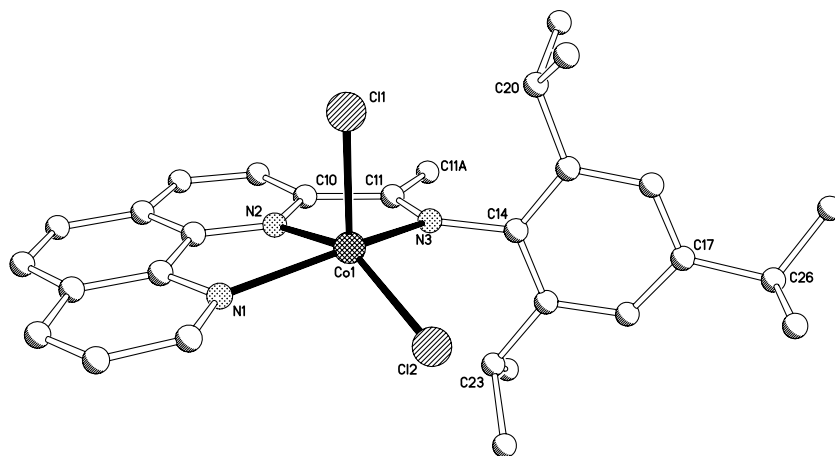
Fig. 5. Molecular structure of (**L6**)CoCl$_2$ (**1f**). All the hydrogen atoms have been omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for **1a**, **1c** and **1f**

	1a	**1c**	**1f**
Bond lengths			
Co(1)–N(1)	2.2138(18)	2.189(6)	2.225(3)
Co(1)–N(2)	2.0447(18)	2.018(6)	2.059(3)
Co(1)–N(3)	2.2939(18)	2.353(6)	2.248(3)
Co(1)–Cl(1)	2.2612(7)	2.251(2)	2.2861(12)
Co(1)–Cl(2)	2.2393(7)	2.247(2)	2.2608(11)
C(17)–C(26)	–	1.485(12)	1.520(5)
C(26)–N(4)	–	1.103(11)	–
C(11)–C(11A)	–	–	1.495(5)
Bond angles			
N(1)–Co(1)–N(2)	75.95(7)	77.7(3)	75.65(11)
N(1)–Co(1)–N(3)	148.23(7)	149.6(2)	145.68(11)
N(1)–Co(1)–Cl(1)	94.64(5)	94.91(18)	99.12(8)
N(1)–Co(1)–Cl(2)	99.29(5)	100.12(18)	97.33(8)
N(2)–Co(1)–N(3)	73.67(7)	72.3(2)	73.14(11)
N(2)–Co(1)–Cl(1)	104.94(5)	132.58(19)	98.76(9)
N(2)–Co(1)–Cl(2)	137.49(5)	122.61(19)	147.44(9)
N(3)–Co(1)–Cl(1)	101.88(5)	101.34(16)	99.39(8)
N(3)–Co(1)–Cl(2)	96.81(5)	96.19(16)	101.25(8)
Cl(2)–Co(1)–Cl(1)	117.57(3)	114.79(9)	113.79(5)

withdrawing cyano group on the donor capability of the imine nitrogen. In **1c** the Co–Cl distances are essentially the same while in **1a** and **1f** the Co–Cl(1) distance is noticeably longer than the Co–Cl(2) distance [2.2612(7) vs. 2.2393(7) Å (**1a**), 2.2861(12) vs. 2.2608(11) Å (**1f**)]. As expected the aryl groups in each structure adopt an orthogonal disposition with respect to the plane formed by the imino-phenanthroline unit. The short length of the N(4)–C(23) [1.103(11) Å] bond is consistent with triple bond character for the nitrile functionality in **1c**. Inspection of the packing diagram for **1a**, **1c** and **1f** shows no evidence for any short intermolecular distances.

The FAB mass spectrometric data for **1a**–**1f** display fragmentation peaks corresponding to the loss of one and two chloride ions. The magnetic moments (measured on an Evans balance at ambient temperature) for all the cobalt(II) complexes exhibit values at *ca.* 4.0 μ$_b$ which are consistent with high spin configurations possessing three unpaired electrons ($S = 3/2$). The IR spectra for **1a**–**1f** show absorption bands between 1606 and 1615 cm^{-1} which correspond to the v(C=N) stretching frequencies for a coordinated imine and are shifted by *ca.* 30 cm^{-1} to lower wavenumber in comparison with the free ligands. In the case of **1c**, the C≡N band is seen at 2215 cm^{-1} and is similar in magnitude to that seen in free **L3**.

2.3. Screening for ethylene oligomerisation

All the complexes were screened as precatalysts for oligomerisation of ethylene. Typically, a complex in toluene was treated with 400 equivalents of methylaluminoxane (MAO) at room temperature and ethylene (1 bar) gas introduced over a period of 30 min. In all cases oligomeric material (C$_6$–C$_{26}$) was afforded; the results of the tests are collected in Table 4 (entries 1–6). Catalyst activities were calculated from GC traces, using extrapolated values for C$_4$–C$_{10}$. All the systems screened display only low activities (2.0–5.2 g mmol^{-1} h^{-1} bar^{-1}) for ethylene oligomerisation when compared with their iron counterparts [9] and no dis-

Table 4
Screening for ethylene oligomerisation[a]

Entry	Pre-catalyst	Mass of oligomer[b] (g)	Activity (g mmol^{-1} h^{-1} bar^{-1})	α-Olefin[c] (%)	Internal olefin[c] (%)	α[d]
1	**1a**	0.023	4.5	87	13	0.81
2	**1b**	0.024	4.8	70	30	0.83
3	**1c**	0.013	2.6	61	39	0.67
4	**1d**	0.026	5.2	89	11	0.85
5	**1e**	0.010	2.0	93	7	0.69
6	**1f**	0.016	3.2	60	40	0.82

[a] General conditions: 1 bar (100 kPa) ethylene Schlenk test carried out in toluene (35 ml) at ambient temperature using 4.0 mmol MAO (Al:Co = 400:1), 0.01 mmol precatalyst, over 30 min. Reactions were terminated by addition of dilute HCl.
[b] Mass of oligomer based on GC using a C$_{17}$ standard.
[c] Oligomerisation product percentages calculated via integration of the ^{1}H NMR spectra.
[d] Determined from GC; α = (rate of propagation)/((rate of propagation) + (rate of chain transfer)) = (moles of C$_{n+2}$)/(moles of C$_n$).
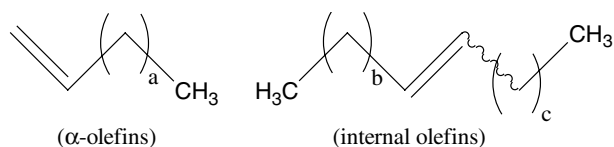
Fig. 6. Oligomeric products accessible using **1a**–**1f**.

cernible trends in activity between aldimine- (**1a**–**1d**) and ketimine-containing (**1e**, **1f**) complexes are apparent. Furthermore, the selectivity of these cobalt systems for linear α-olefins (range: 60–93%) is much reduced in comparison to the imino-phenanthroline-Fe systems with significant levels of internal olefins evident (Fig. 6). No activity for ethylene oligomerisation was reported using MAO alone under these conditions.

For the aldimine-containing species **1a**–**1d** (entries 1–4), the degree of isomerisation seems to be related to the electronic properties of the *para*-aryl substituent with electron withdrawing substituents (Br in **1b** and CN in **1c**) leading to increased levels of internal olefins (entries 2 and 3). On the other hand in the ketimine complexes (**1e** and **1f**), the *para*-isopropyl substituted species (**1f**) gives the highest degree of isomerisation (entry 6). In all cases the catalysts give a Schulz–Flory distribution of oligomers, with the Schulz–Flory parameters α ranging form 0.67 to 0.85 [13].

The observation of solely oligomeric products using **1a**–**1e** is consistent with rapid chain transfer process as a result of there being insufficient steric bulk to prevent associative displacement of the growing oligomeric chain. Indeed, the performance of **1a**–**1e** can be compared to the less bulky members of the bis(arylimino)pyridine-Co family of ethylene oligomerisation catalysts (*e.g.*, aryl = 2-MePh) [2c].

3. Conclusions

Full characterisation of a series of 4-substituted 2,6-isopropylphenylimino-phenanthroline ligands and their resultant cobalt(II) chloride complexes has been achieved. All the systems displayed low activity for ethylene oligomerisation on treatment with excess MAO affording mainly linear α-olefins along with some degree of internal olefins. The nature of the 4-position substitution pattern appears to have little effect on the activity of the catalyst under these conditions but does influence the α-olefin:internal olefin ratio. It is notable that these systems are much less active when compared with the recently reported imino-phenanthrolinyl-iron systems [9], a trend that is also apparent for bis(imino)pyridine-iron over bis(imino)pyridine-cobalt oligomerisation catalysts [2c].

4. Experimental

4.1. General

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques or in a nitrogen purged glove box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use [14]. The infrared spectra were recorded on a Perkin–Elmer spectrum one FT-IR spectrometer on solid samples. The ES and the FAB mass spectra were recorded using a micromass Quattra LC mass spectrometer and a Kratos Concept spectrometer with methanol or NBA as the matrix, respectively. High resolution (HR) FAB mass spectra were recorded on Kratos Concept spectrometer (xenon gas, 7 kV) with NBA as matrix. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX spectrometer (250 or 300 MHz); chemical shifts (ppm) are referred to the residual protic solvent peak and coupling constants are in Hertz (Hz). Magnetic Susceptibility studies were performed using an Evans Balance (Johnson Matthey) at room temperature. The magnetic moments were calculated following standard methods [15] and corrections for underlying diamagnetism were applied to the data [16]. Oligomer products were analysed by GC, using a Perkin–Elmer Autosystem XL chromatograph equipped with a flame ionisation detector and 30 m PE-5 column (0.25 mm thickness), injector temperature 45 °C and the following temperature programme: 45 °C/7 min, 45–195 °C/10 °C min^{-1}, 195 °C/5 min, 195–225 °C/10 °C min^{-1}, 225 °C/5 min, 225–250 °C/10 °C min^{-1}, 250 °C/22 min. Melting points (m.p.) were measured on a Gallenkamp melting point apparatus (model MFB-595) in open capillary tubes and were uncorrected. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The reagents, trimethylaluminium (2.0 M in heptane), MAO (10 wt% in toluene), ethylenediaminetetraacetic acid disodium salt dihydrate, 2,6-diisopropylaniline, *n*-heptadecene and cobalt dichloride were purchased from Aldrich Chemical Co., and used without further purification. The compounds, 2,6-diisopropyl-4-bromo-aniline [17], 2,6-diisopropyl-4-cyano-aniline [17], 2,4,6-triisopropylaniline [18] and 2-cyano-1,10-phenanthroline [10], were prepared according to previously reported procedures. All other chemicals were obtained commercially and used without further purification.

4.2. Preparation of starting materials

4.2.1. Methyl 1,10-phenanthroline-2-carboxylate

The procedure was based on that described by Engbersen et al. [19]. Under an atmosphere of nitrogen 2-cyano-1,10-phenanthroline (3.00 g, 0.014 mol) and a catalytic amount of sodium (50 mg) in dry methanol (130 ml) was stirred and heated to reflux for 0.5 h. The reaction mixture was cooled to 0 °C and made slightly acidic with 2% HCl (*ca.* 100 ml) and stirred for a further 0.5 h. The solution was neutralised with sodium hydrogencarbonate and the methanol removed on the rotary evaporator. The aqueous phase was extracted with chloroform (3 × 75 ml) and the organic extracts combined and dried over magnesium sulphate. Following filtration, the solvent was removed under

reduced pressure to afford methyl 1,10-phenanthroline-2-carboxylate as a dark brown solid (2.14 g, 62%). M.p. 111–113 °C [lit. [19] 110–112 °C].

4.2.2. 2-Carbinol-1,10-phenanthroline

To a solution of methyl 1,10-phenanthroline-2-carboxylate (2.50 g, 10.50 mmol) in absolute ethanol (150 ml) was slowly added sodium borohydride (6.0 g, 0.158 mol, 15 equiv.) and the reaction mixture stirred at ambient temperature for 2 days. Water (50 ml) was added carefully and the resultant yellow solution neutralised (pH 7–8) with a solution of dilute hydrochloric acid before being extracted with chloroform (3×75 ml). The organic extracts were combined and dried over magnesium sulphate. Following filtration the solvent was removed under reduced pressure to yield 2-carbinol-1,10-phenanthroline as a brown solid (2.01 g, 91%). The ^{1}H NMR spectrum of the product was consistent with the literature report [20].

4.2.3. 2-Formyl-1,10-phenanthroline

A red suspension of 2-carbinol-1,10-phenanthroline (2.00 g, 9.52 mmol) and selenium dioxide (2.11 g, 19.01 mmol, 2 equiv.) in dioxane (150 ml) were heated to reflux for 2 h. Hot filtration through celite followed by the washing of the celite cake with hot dioxane (100 ml) afforded a red solution. The solvent was removed under reduced pressure yielding 2-formyl-1,10-phenanthroline as a red solid (1.41 g, 71% yield). M.p.: 150–153 °C [lit. [21] 152–153 °C]. IR (cm^{-1}): 1707 υ(C=O). ES mass spectrum, m/z 209 [M+H]$^+$.

4.2.4. 2-Acetyl-1,10-phenanthroline

The procedure was similar to that described by Sun et al. [9] but with some modifications made to the reaction conditions and the work-up. Thus, 2-cyano-1,10-phenanthroline (1.0 g, 4.87 mmol) was suspended in dry toluene (100 ml) under an atmosphere of nitrogen. Trimethylaluminium (5 ml, 10.00 mmol, 2 equiv.) was added dropwise at room temperature and the reaction mixture stirred and heated to 70 °C overnight to give a dark green solution. On cooling to room temperature, all volatiles were removed under reduced pressure and chloroform introduced (30 ml). Water (40 ml) was carefully added to the reaction and the mixture stirred vigorously for 2 h. Following filtration, the organic phase was separated and washed with a saturated solution of the disodium salt of EDTA (2×30 ml) and then with water (2×30 ml). After drying over anhydrous magnesium sulphate the solvent was removed under reduced pressure to give 2-acetyl-1,10-phenanthroline as a pale white solid (80%, 0.87 g). M.p.: 151–153 °C [lit. [9] 152–154 °C]. IR (cm^{-1}) 1694 υ(C=O). ES mass spectrum, m/z 223 [M+H]$^+$.

4.3. Preparation of ligands (L1–L6)

4.3.1. 1,10-C$_{12}$H$_7$N$_2$-CH=N(2,6-i-Pr$_2$-C$_6$H$_3$) (L1)

To a suspension of 2-formyl-1,10-phenanthroline (0.200 g, 0.96 mmol) in absolute ethanol (2 ml) was added

2,6-diisopropylaniline (0.19 ml, 1.01 mmol, 1.05 equiv.). The suspension was allowed to warm to 50 °C and one drop of acetic acid introduced. After stirring at 50 °C overnight the solvent was removed on the rotary evaporator and the residue taken up in chloroform (25 ml) and dried over magnesium sulphate. Following filtration, all volatiles were removed under reduced pressure to give L1 as a pale yellow solid (77%, 0.27 g). M.p.: 194–196 °C [lit. [9] 192–194 °C]. IR (cm^{-1}). ES mass spectrum, m/z 368 [M+H]$^+$.

4.3.2. 1,10-C$_{12}$H$_7$N$_2$-CH=N(2,6-i-Pr$_2$-4-Br-C$_6$H$_2$) (L2)

In a manner similar to that outlined for L1, L2 was prepared as a pale orange solid (87%). Recrystallisation from ethanol gave L2 as pale green plates. M.p.: 198–200 °C. IR (cm^{-1}) 2957, 2865, 1633 υ(C=N$_{imine}$), 1589, 1553, 1492, 1452, 1393, 1318, 1184, 1081, 858, 788, 751. ES mass spectrum, m/z 447 [M+H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.20 (d, $J = 1.8$, 1H, phen-H), 8.69 (s, 1H, CH=N), 8.60 (d, $J = 8.5$, 1H, phen-H), 8.32 (d, $J = 8.2$, 1H, phen-H), 8.24 (dd, $J = 8.2$, 1.5, 1H, phen-H), 7.79 (s, 2H, phen-H), 7.62 (dd, $J = 8.2$, 4.4, 1H, phen-H), 7.20 (s, 2H, Ar-H), 2.93 (sept, $J = 6.7$, 2H, CHMe$_2$), 1.09 (d, $J = 6.7$, 12H, CHMe$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.2, 153.2, 149.6, 148.5, 135.9, 135.5, 133.6, 128.8, 128.0, 127.4, 126.9, 125.4, 125.2, 124.7, 122.1, 120.4, 119.4, 21.2, 19.9. Anal. Calcd. for C$_{25}$H$_{24}$BrN$_3$: C, 67.28; H, 5.38; N, 9.42. Found: C, 67.41; H, 5.70; N, 9.71%.

4.3.3. 1,10-C$_{12}$H$_7$N$_2$-CH=N(2,6-i-Pr$_2$-4-CN-C$_6$H$_2$) (L3)

In a manner similar to that outlined for L1, L3 was prepared as a brick red solid (68%). IR (cm^{-1}) 2963, 2871, 2213 υ(C≡N), 1639 υ(C=N$_{imine}$), 1559, 1492, 1462, 1383, 1165, 1093, 865, 768, 741. ES mass spectrum, m/z 393 [M+H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.20 (d, $J = 1.8$, 1H, phen-H), 8.69 (s, 1H, CH=N), 8.60 (d, $J = 8.5$, 1H, phen-H), 8.40 (d, $J = 8.2$, 1H, phen-H), 8.27 (dd, $J = 8.2$, 1.8, 1H, phen-H), 7.90 (s, 2H, phen-H), 7.66 (dd, $J = 8.2$, 4.4, 1H, phen-H), 7.20 (s, 2H, Ar-H), 2.94 (sept, $J = 7.1$, 2H, CHMe$_2$), 1.12 (d, $J = 6.7$, 12H, CHMe$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.3, 152.7, 151.3, 149.9, 144.8, 135.5, 131.1, 128.8, 128.4, 127.3, 126.4, 125.4, 125.3, 122.5, 121.9, 120.0, 119.3, 99.1, 27.8, 21.8. Anal. Calcd. for C$_{26}$H$_{24}$N$_4$: C, 79.59; H, 5.38; N, 14.29. Found: 79.81; H, 5.74; N, 14.51%.

4.3.4. 1,10-C$_{12}$H$_7$N$_2$-CH=N(2,4,6-i-Pr$_3$-4-C$_6$H$_2$) (L4)

In a manner similar to that outlined for L1, L4 was prepared as an orange solid (60%). M.p.: 191–193 °C. IR (cm^{-1}) 2958, 2867, 1635 υ(C=N$_{imine}$), 1589, 1553, 1490, 1461, 1381, 1319, 1173, 1090, 875, 829, 764. ES mass spectrum, m/z 410 [M+H]$^+$. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.19 (dd, $J = 4.4$, 1.8, 1H, phen-H), 8.76 (s, 1H, CH=N), 8.65 (d, $J = 8.5$, 1H, phen-H), 8.33 (d, $J = 9.0$, 1H, phen-H), 8.25 (dd, $J = 8.2$, 1.8, 1H, phen-H), 7.83 (s, 2H, phen-H), 7.63 (dd, $J = 7.9$, 4.4, 1H, phen-H), 6.84 (s, 2H, Ar-H), 3.0–2.7 (m, 3H, CHMe$_2$), 1.3–1.1 (m, 18H, CHMe$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 163.3, 154.9,

150.6, 146.1, 146.0, 145.8, 144.5, 138.0, 136.8, 136.6, 129.8, 129.0, 127.7, 126.5, 123.2, 120.9, 120.5, 34.1, 28.0, 24.2, 23.4. Anal. Calcd. for $C_{28}H_{31}N_3$: C, 82.21; H, 7.58; N, 10.27. Found: C, 82.11; H, 7.77; N, 10.12%.

4.3.5. *1,10-$C_{12}H_7N_2$-CMe=N(2,6-i-Pr_2-C_6H_3) (L5)*

To a suspension of 2-acetyl-1,10-phenanthroline (0.50 g, 2.25 mmol) in absolute ethanol (2 ml) was added 2,6-diisopropylaniline (0.46 ml, 2.47 mmol, 1.05 equiv.). The suspension was heated to reflux and one drop of acetic acid introduced. After stirring at reflux overnight the solvent was removed on the rotary evaporator and the residue taken up in chloroform (25 ml) and dried over magnesium sulphate. Following filtration, all volatiles were removed under reduce pressure to give **L5** as a pale yellow solid (70%, 0.62 g). Recrystallisation from ethanol gave **L5** as yellow blocks. M.p.: 191–193 °C [lit. [9] 196–198 °C]. ES mass spectrum, m/z 382 $[M+H]^+$.

4.3.6. *1,10-$C_{12}H_7N_2$-CMe=N(2,4,6-i-Pr_3-C_6H_2) (L6)*

In a manner similar to that outlined for **L5**, **L6** was prepared as a brick red solid (92%). Recrystallisation from ethanol gave **L6** as yellow blocks. M.p.: 186–188 °C. IR (cm^{-1}) 3254, 2958, 2067, 1652, 1587, 1552, 1490, 1461, 1362, 1317, 1177, 1116, 874, 834, 785, 751. ES mass spectrum, m/z 424 $[M+H]^+$. ^{1}H NMR (250 MHz, CDCl$_3$): δ 9.21 (d, $J = 3.0$, 1H, phen-H), 8.74 (d, $J = 8.5$, 1H, phen-H), 8.29 (m, 2H, phen-H), 7.80 (s, 2H, phen-H), 7.61 (m, 1H, phen-H), 6.95 (s, 2H, Ar-H), 2.87 (app. sept, $J = 6.8$, 3H, C*H*Me$_2$), 2.53 (s, 3H, CMe=N), 1.19 (m, 18H, CH*Me*$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.8, 156.1, 150.6, 146.7, 146.3, 136.4, 135.7, 129.6, 129.0, 127.5, 126.5, 123.7, 123.4, 123.0, 122.8, 120.4, 118.5, 28.3, 26.1, 23.0, 18.4, 17.6. HRMS (FAB): Anal. Calcd. for $C_{29}H_{33}N_3$ $[M+H]^+$ 424.27527, found 424.27520.

4.4. *Preparation of [1,10-$C_{12}H_7N_2$-CR=N(2,6-i-Pr_2-4-R^1-C_6H_2)]CoCl$_2$ (1)*

4.4.1. *R = R^1 = H (1a)*

An oven dried Schlenk vessel equipped with magnetic stirrer was evacuated and backfilled with nitrogen. The vessel was charged with anhydrous cobalt dichloride (0.048 g, 0.369 mmol) and suspended in *n*-BuOH (5 ml) and the contents stirred at 90 °C until the cobalt salt had completely dissolved. **L1** (0.136 g, 0.369 mmol, 1 equiv.) was added and the mixture heated to 90 °C for 1 h. On cooling to ambient temperature, hexane was added to induce precipitation of the product. Following filtration, washing with hexane and drying under reduced pressure, **1a** (0.120 g, 65%) was isolated as a brown solid. Recrystallisation of **1a** from acetonitrile afforded crystals suitable for a single crystal X-ray diffraction study. IR (cm^{-1}) 2963, 1609, 1573, 1515, 1462, 1436, 1404, 1172, 1118, 856, 811, 736.

4.4.2. *R = H, R^1 = Br (1b)*

Employing the method outlined for **1a** using anhydrous cobalt dichloride (0.112 g, 0.862 mmol), *n*-butanol (5 ml) and **L2** (0.384 g, 0.862 mmol, 1 equiv.) gave **1b** as a dark green solid (0.397 g, 80%). IR (cm^{-1}) 2962, 1612, 1575, 1515, 1494, 1462, 1437, 1404, 1296, 864, 739.

4.4.3. *R = H, R^1 = CN (1c)*

Employing the method outlined for **1a** using anhydrous cobalt dichloride (0.112 g, 0.862 mmol), *n*-butanol (5 ml) and **L3** (0.338 g, 0.862 mmol, 1 equiv.) gave **1c** as an olive green solid (0.293 g, 65%). Recrystallisation of **1c** from acetonitrile afforded crystals suitable for a single crystal X-ray diffraction study. IR (cm^{-1}) 2965, 2215 v(C≡N), 1606, 1517, 1494, 1464, 1442, 1407, 1297, 868, 743.

4.4.4. *R = H, R^1 = i-Pr (1d)*

Employing the method outlined for **1a** using anhydrous cobalt dichloride (0.078 g, 0.60 mmol), *n*-butanol (10 ml) and **L4** (0.245 g, 0.60 mmol, 1 equiv.) gave **1d** as a brown solid (0.193 g, 60%). IR (cm^{-1}) 3061, 2960, 2868, 1611, 1579, 1513, 1493, 1458, 1402, 1381, 1318, 1170, 1119, 1071, 865, 796, 742.

4.4.5. *R = Me, R^1 = H (1e)*

Employing the method outlined for **1a** using anhydrous cobalt dichloride (0.102 g, 0.79 mmol), *n*-butanol (10 ml) and **L5** (0.300 g, 0.79 mmol, 1 equiv.) gave **1e** as a red–brown solid (0.280 g, 70%). IR (cm^{-1}) 2969, 1607, 1582, 1511, 1466, 1407, 1373, 1287, 1206, 1192, 1146, 1088, 873, 833, 784, 741, 657.

4.4.6. *R = Me, R^1 = i-Pr (1f)*

Employing the method outlined for **1a** using anhydrous cobalt dichloride (0.100 g, 0.77 mmol), *n*-butanol (9 ml) and **L6** (0.326 g, 0.77 mmol, 1 equiv.) gave **1f** as a red–brown solid (0.26 g, 61%). Recrystallisation of **1f** from hot acetonitrile afforded crystals suitable for a single crystal X-ray diffraction study. IR (cm^{-1}) 2960, 1615, 1582, 1511, 1469, 1407, 1371, 1285, 1211, 1180, 1151, 869, 835, 788, 741, 658.

4.5. *General screening for ethylene oligomerisation*

An oven dried 200 ml Schlenk vessel equipped with magnetic stir bar was evacuated and backfilled with nitrogen. The vessel was charged with the precatalyst (0.01 mmol) and dissolved or suspended in toluene (35 ml). MAO (2.10 ml, 4.0 mmol) was introduced and the reaction mixture left to stir for 5 min. The vessel was purged with ethylene and the contents magnetically stirred under 1 bar ethylene pressure at room temperature for the duration of the test. After 0.5 h, the test was terminated by the addition of dilute aqueous hydrogen chloride (5 ml). The organic phase was separated and dried over magnesium sulphate and filtered. Quantitative GC analysis was performed by taking an aliquot of the solution containing a weighted amount of a standard (*n*-heptadecene). For

Table 5
Crystallographic and data processing parameters for **L2**, **L5**, **L6**, **1a**, **1c** and **1f**

Complex	L2	L5	L6	1a	1c	1f
Formula	$C_{25}H_{24}BrN_3$	$C_{26}H_{28}N_3 \cdot CH_3CH_2OH$	$C_{29}H_{33}N_3$	$C_{25}H_{25}Cl_2CoN_3$	$C_{26}H_{24}Cl_2CoN_4$	$C_{29}H_{33}Cl_2CoN_3$
M	446.38	427.57	423.58	497.31	522.32	553.41
Crystal size (mm^3)	$0.24 \times 0.18 \times 0.08$	$0.29 \times 0.21 \times 0.16$	$0.22 \times 0.14 \times 0.11$	$0.28 \times 0.19 \times 0.15$	$0.33 \times 0.21 \times 0.09$	$0.20 \times 0.18 \times 0.07$
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclimic	Triclinic
Space group	C2/c	P-1	P2(1)/c	Pbca	P2(1)	P-1
a (Å)	34.646(5)	8.2035(15)	17.966(6)	14.863(2)	9.457(3)	8.200(2)
b (Å)	9.5442(15)	11.747(2)	20.715(7)	15.957(2)	13.843(4)	9.399(3)
c (Å)	43.782(7)	13.004(2)	13.640(5)	19.182(3)	9.736(3)	19.369(5)
α (°)	90	82.296(3)	90	90	90	87.602(5)
β (°)	108.448(3)	73.587(3)	105.130(7)	90	94.597(5)	78.408(5)
γ (°)	90	85.972(3)	90	90	90	71.459(5)
U ($Å^3$)	13 733(4)	1190.5(4)	4900(3)	4549.4(11)	1270.4(6)	1385.9(6)
Z	24	2	8	8	2	2
D_c ($Mg\,m^{-3}$)	1.295	1.193	1.148	1.452	1.365	1.326
$F(000)$	5220	460	1824	2056	538	578
μ (Mo Kα) (mm^{-1})	1.811	0.073	0.067	1.007	0.907	0.834
Reflections collected	51960	8698	35320	31159	9179	10941
Independent reflections	13489	4171	8640	4009	4450	5372
R_{int}	0.0584	0.0380	0.1536	0.0455	0.0720	0.0711
Restraints/parameters	0/796	0/267	0/591	0/284	1/302	0/323
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0500$ $wR_2 = 0.0974$	$R_1 = 0.0468$ $wR_2 = 0.1166$	$R_1 = 0.0610$ $wR_2 = 0.0869$	$R_1 = 0.0326$ $wR_2 = 0.0742$	$R_1 = 0.0700$ $wR_2 = 0.01392$	$R_1 = 0.0624$ $wR_2 = 0.1235$
All data	$R_1 = 0.1112$ $wR_2 = 0.1067$	$R_1 = 0.0645$ $wR_2 = 0.1229$	$R_1 = 0.1710$ $wR_2 = 0.1122$	$R_1 = 0.0456$ $wR_2 = 0.0781$	$R_1 = 0.1046$ $wR_2 = 0.1517$	$R_1 = 0.0880$ $wR_2 = 0.1329$
Goodness-of-fit on F^2 (all data)	0.793	1.006	0.812	0.968	0.901	0.986

Data in common: graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å; $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness-of-fit $= [\sum(F_o^2 - F_c^2)2/(n-p)]^{1/2}$ where n is the number of reflections and p is the number of parameters.

analysis of the oligomers by ^{1}H NMR spectroscopy, the solvent was removed on the rotary evaporator and the residue dissolved in CDCl$_3$.

4.6. Crystallography

Data for **L2**, **L5**, **L6**, **1a**, **1c** and **1f** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 5. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement on F^2 employed SHELXTL version 6.10 [22]. Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Disordered solvent was omitted using the SQUEEZE option in platon for **L2** and **L5**.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 608572–608577 for compounds **L2**, **L5**, **L6**, **1a**, **1c** and **1f**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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