

## 2-Ethylcarboxylate-6-iminopyridyl iron and cobalt complexes: synthesis, characterisation and their ethylene oligomerisation

Haiping Wang<sup>a</sup>, Shufen Zhang<sup>a\*</sup>, Jinzong Yang<sup>a</sup>, Yuan Deng<sup>b</sup> and Xiaoming Lu<sup>b</sup>

<sup>a</sup>State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, P.R.China

<sup>b</sup>Department of Chemistry, Capital Normal University, Beijing 100037, P.R.China

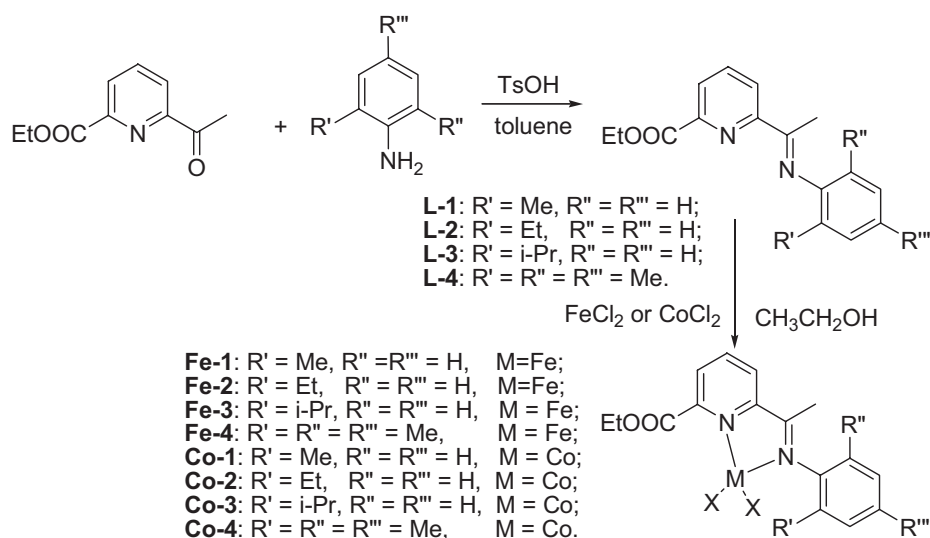
Four 2-carboxylate-6-iminopyridines, prepared by the reaction of 2-ethylcarboxylate-6-actylpyridine with substituted anilines, reacted with FeCl<sub>2</sub> or CoCl<sub>2</sub> to form the title complexes. Both the ligands and complexes were characterised by elemental analysis and IR spectroscopy, and the molecular structures of **Co-3** and **Co-4** were determined by X-ray diffraction analysis. Activated with methylaluminoxane (MAO), these complexes showed good catalytic activity for ethylene oligomerisation with high selectivity of producing linear  $\alpha$ -olefins.

**Keywords:** iron complexes, cobalt complex, ethylene oligomerisation

In the past decade, late-transition metal complex catalysts for ethylene oligomerisation and polymerisation have drawn much attention.<sup>1</sup> The pioneer work with diimine-based cationic catalysts<sup>2</sup> and 2,6-bis(imino)pyridyl-based cationic catalysts<sup>3</sup> were the cause of this research. Driven by the industrial applications, there are many academic and industrial research laboratories engaged in exploring various complexes catalysts containing [O–N],<sup>4</sup> [N–N],<sup>5</sup> [N–P],<sup>6</sup> and [N–N–N]<sup>7</sup> ligands. In addition to metal complexes ligated with 2,6-bis(imino)pyridines, other model iron and cobalt complexes showed lower activity for ethylene oligomerisation and polymerisation.<sup>8</sup> Recently, the complexes containing 2-carboxylate-6-iminopyridine ligands were reported to be active catalysts for ethylene oligomerisation and polymerisation.<sup>9</sup> Regarding the low toxic property of iron, extensive research on iron complexes coordinated with 2-carboxylate-6-iminopyridine derivatives have been carried out by this group. Four 2-carboxylate-6-iminopyridines were prepared as well as their iron and cobalt complexes, in addition, the complexes showed good catalytic activities for ethylene oligomerisation in presence of MAO as co-catalyst. Herein, the synthesis and characterisation of 2-carboxylate-6-iminopyridine-based iron and cobalt complexes are reported with their catalytic behaviours towards ethylene oligomerisation upon activation with MAO.

Using the literature method,<sup>9</sup> the pyridineimine ligands **L-1–L-4** were easily prepared in satisfactory yields through the Schiff-base condensation of 2-carboxylate-6-acetylpyridine with anilines in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in refluxing toluene (Scheme 1). All ligands **L-1–L-4** were fully characterised by IR spectra, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. The ligands reacted with FeCl<sub>2</sub> or CoCl<sub>2</sub> in ethanol to form their corresponding complexes, respectively. These obtained complexes were soluble in ethanol, but did not dissolve in diethyl ether or non-polar solvents. Therefore the complexes could be easily collected and purified as solids by adding petroleum ether into their ethanol solutions. The title complexes were analysed by IR and elemental analysis.

The IR spectra of the ligands show that the C=N stretching frequencies appear in the range from 1641 to 1649 cm<sup>-1</sup>, and the C=N stretching vibrations in iron complexes **Fe-1–Fe-4** shift toward lower frequencies between 1621 and 1626 cm<sup>-1</sup> with weak intensities while the C=N stretching vibrations in cobalt complexes **Co-1–Co-4** shift toward lower frequencies between 1615 and 1626 cm<sup>-1</sup> with weak intensities. This result indicates the coordinating interaction between the imino-nitrogen atom and the metal centre. In addition, the slight wavenumber shift of 10–30 cm<sup>-1</sup> in the C=O stretching vibrations in the IR spectra suggests the presence of a weak bonding interaction between the metal centre and the carbonyl oxygen of the ester group in these complexes.

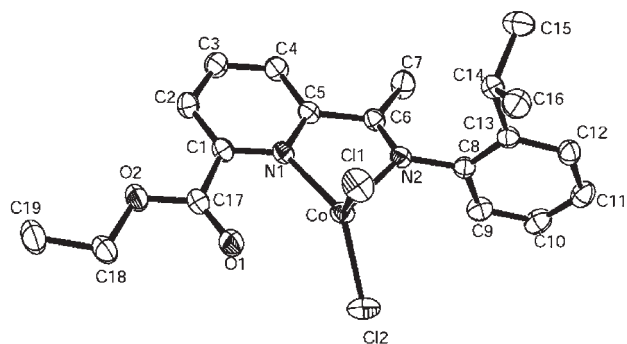


Scheme 1

\* Correspondent. E-mail address: zhangshuf@chem.dlut.edu.cn

Crystals of **Co-3** and **Co-4** suitable for single X-ray diffraction analysis were grown by crystallisation through the slow diffusion of diethyl ether into their dichloromethane solutions, respectively, at room temperature under a dinitrogen atmosphere. Crystal structures of **Co-3** and **Co-4** are shown in Figs 1 and 2, respectively. As shown in Fig. 1, the cobalt atom of **Co-3** is coordinated in a distorted tetrahedral environment. The isopropyl substituted phenyl ring is oriented nearly perpendicular to the coordination plane forming the dihedral angle as 93.0°. Similarly, complex **Co-4** is four-coordinated with the geometry of a distorted tetrahedron around the metal centre. One dichloromethane molecule was observed in the crystal lattice of **Co-4**. The phenyl rings in **Co-4** are also oriented orthogonally to the coordination rings (88.8°). The Co–N (imino) bond lengths in **Co-3** and **Co-4** are 2.1126(10) Å, 2.115(2) Å, respectively. It should be pointed out that the oxygen atom of the carbonyl group orients towards the cobalt centre, and the distances between oxygen and cobalt are 2.523 Å in **Co-3** and 2.532 Å in **Co-4**. Their coordination geometries are greatly distorted from the idealised tetrahedron, and these may be attributable to the effect of the carbonyl oxygen atom on the coordination environment.

The iron complexes **Fe-1–Fe-4** were initially studied for their catalytic activities towards ethylene oligomerisation and polymerisation using methylaluminoxane (MAO) as the cocatalyst. The results are summarised in Table 1 (entries 1–4) with 1 atm ethylene at room temperature. Complexes **Fe-1–4** show considerable activities for ethylene oligomerisation under a pressure of 1 atm ethylene, producing butenes and hexenes and small amounts of high oligomers. In addition, the catalytic system **Fe-4** generates a small amount of polyethylene. The cobalt complexes **Co-1–Co-4** were systematically investigated for their ethylene oligomerisation



**Fig. 1** Molecular structure of **Co-3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Co–N1, 2.0558(11); Co–N2, 2.1126(10); Co–Cl1, 2.2373(4); Co–Cl2, 2.2343(4); N2–C6, 1.2774(16); O1–C17, 1.2032(18); N1–Co–N2, 77.70(4); N1–Co–Cl2, 127.49(3); N2–Co–Cl2, 105.15(3); N1–Co–Cl1, 109.75(3); N2–Co–Cl1, 118.919(18).

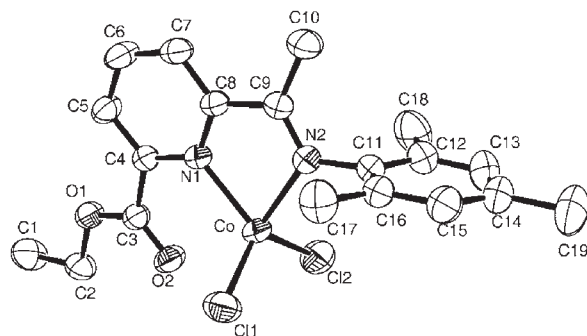
and polymerisation behaviours upon activation with MAO, and the results are summarised in Table 1 (entries 5–8).

The oligomers were formed in the full range as compared to the results obtained by the analogues of the title complexes,<sup>9</sup>  $\alpha$ -olefins were selectively formed and confirmed by both GC–MS and NMR measurements. The effect of the bulky group of the ligand on the catalytic activity is not remarkable and no convincing trend can be concluded. In general, the iron complexes showed higher selectivity for  $\alpha$ -olefins than those of their cobalt analogues, while the activity of the cobalt complexes is higher than that of their iron analogues.

## Experimental

All manipulations of air- and moisture-sensitive compounds were performed under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried by the literature methods. Methylaluminoxane (MAO) was purchased from Albemarle as a 1.4M solution in toluene. Other reagents were purchased from Aldrich or Acros Chemicals. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker DMX-300 MHz instrument at ambient temperature using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. Elemental analysis was carried out using HP-MOD 1106 microanalyser. GC analysis was performed with a Carlo Erba Strumentazione gas chromatograph equipped with a flame ionisation detector and a 30 m (0.25 mm i.d., 0.25  $\mu$ m film thickness) DM-1 silica capillary column. The yield of oligomers was calculated by referencing with the mass of the solvent based on the prerequisite that the mass of each fraction is approximately proportional to its integrated areas in the GC trace.

*Ethyl 6-[1-(2-methylphenylimino)ethyl] pyridine-2-carboxylate (L-1)*: A solution of 2-methylaniline, ethyl 6-acetylpyridine-2-carboxylate and a catalytic amount of *p*-toluenesulfonic acid in toluene were refluxed for 24 h. After solvent evaporation, the crude product was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (15:1) as eluent to afford the product as a yellow powder in 40.5% yield. IR (KBr disc, cm<sup>-1</sup>): 1730(C(O)OCH<sub>3</sub>), 1641(C=N). <sup>1</sup>H NMR(300MHz,CDCl<sub>3</sub>):  $\delta$ : 8.52 (d, 1H, *J* = 7.92,



**Fig. 2** Molecular structure of **Co-4**. Hydrogen atoms and CH<sub>2</sub>Cl<sub>2</sub> molecule have been omitted for clarity. Selected bond distances (Å) and angles (°): Co–N1, 2.049(2); Co–N2, 2.115(2); Co–Cl2, 2.2221(9); Co–Cl1, 2.2424(8); N2–C9, 1.276(3); O2–C3, 1.205(3); N1–Co–N2, 78.52(8); N1–Co–Cl2, 121.94(7); N2–Co–Cl2, 105.37(7); N1–Co–Cl1, 113.63(7); N2–Co–Cl1, 109.22(7); Cl2–Co–Cl1, 118.64(4).

**Table 1** Ethylene oligomerisations

Entry	Complex	Oligomer distribution/%				Activity/g mol <sup>-1</sup> Fe·h <sup>-1</sup>	
		butene/ $\Sigma$ C	hexenes/ $\Sigma$ C	C <sub>2-8</sub> / $\Sigma$ C	linear $\alpha$ -olefin	Oligomer	Polymer
1	<b>Fe-1</b>	87.3	9.2	3.5	98.2	1.33 $\times$ 10 <sup>5</sup>	Trace
2	<b>Fe-2</b>	86.1	10.0	3.9	97.1	3.78 $\times$ 10 <sup>4</sup>	Trace
3	<b>Fe-3</b>	90.6	9.4	–	98.7	5.07 $\times$ 10 <sup>4</sup>	Trace
4	<b>Fe-4</b>	82.2	10.0	7.8	97.8	5.00 $\times$ 10 <sup>4</sup>	5.2 $\times$ 10 <sup>2</sup>
5	<b>Co-1</b>	75.5	18.3	6.2	86.5	1.57 $\times$ 10 <sup>5</sup>	Trace
6	<b>Co-2</b>	83.5	7.3	9.2	90.4	1.87 $\times$ 10 <sup>5</sup>	Trace
7	<b>Co-3</b>	90.2	5.4	4.4	95.4	9.21 $\times$ 10 <sup>4</sup>	Trace
8	<b>Co-4</b>	88.9	6.2	4.9	94.3	1.47 $\times$ 10 <sup>5</sup>	Trace

Cat: 5 $\mu$ mol; cocat: MAO; Al/M=1000; room temperature; time: 0.5 h; 30 ml toluene.

Py-H);  $\delta$ 8.20 (d, 1H,  $J$  = 6.51, Py-H);  $\delta$ 7.91 (t, 1H,  $J$  = 7.89);  $\delta$ 7.24 (m, 2H,  $J$  = 7.60, Ar-H);  $\delta$ 7.05 (t, 1H,  $J$  = 7.29, Ar-H);  $\delta$ 6.68 (d, 1H,  $J$  = 7.65, Ar-H);  $\delta$ 4.50 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 2.38 (s, 3H, N=CCH<sub>3</sub>);  $\delta$ 2.1 (s, 3H, -CH<sub>3</sub>);  $\delta$ 1.47 (t, 3H,  $J$  = 7.20, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (300MHz, CDCl<sub>3</sub>) : 166.9; 165.5; 157.2; 147.7; 137.7; 130.8; 127.4; 126.8; 126.4; 124.8; 124.2; 118.4; 78.0; 77.6; 77.2; 62.2; 18.1; 16.8; 14.7. Anal.Calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.3; H, 6.4; N, 9.9. Found: C, 72.3; H, 6.4; N, 9.5%.

**Ethyl 6-[1-(2-ethylphenylimino)ethyl]pyridine-2-carboxylate (L-2):** Using the same procedure as for the synthesis of **L-1**, **L-2** was obtained as a yellow powder in 27.2% yield. IR (KBr disc, cm<sup>-1</sup>): 1740 (C=O), 1643 (C=N). <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>):  $\delta$ 8.52 (d, 1H,  $J$  = 7.92, Py-H);  $\delta$ 8.20 (d, 1H,  $J$  = 7.34, Py-H);  $\delta$ 7.95 (t, 1H,  $J$  = 7.77);  $\delta$ 7.28 (d, 1H,  $J$  = 7.60, Ar-H);  $\delta$ 7.22 (t, 1H,  $J$  = 7.36, Ar-H);  $\delta$ 7.13 (t, 1H,  $J$  = 7.32, Ar-H);  $\delta$ 6.66 (d, 1H,  $J$  = 7.84, Ar-H);  $\delta$ 4.50 (dd, 2H, OCH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 2.53 (dd, 2H, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 2.40 (s, 3H, N=CCH<sub>3</sub>);  $\delta$ 1.50 (t, 3H,  $J$  = 7.16, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 1.16 (t, 3H,  $J$  = 7.54, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR: (300MHz, CDCl<sub>3</sub>): 138, 137, 129.1, 128.7, 128.5, 127.2, 126.8, 124.8, 106.0, 111.5, 115.8, 62.4, 62.2, 25.1, 24.4, 14.5, 13.4. Anal.Calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.95; H, 6.8; N, 9.45. Found: C, 72.5; H, 6.8; N, 9.1%.

**Ethyl 6-[1-(2-isopropylphenylimino)ethyl]pyridine-2-carboxylate (L-3):** Using the same procedure as for the synthesis of **L-1**, **L-3** was obtained as a yellow powder in 79.2% yield. IR (KBr disc, cm<sup>-1</sup>): 1739 (C=O), 1649 (C=N). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$ 8.49 (d, 1H,  $J$  = 6.51, Py-H);  $\delta$ 8.17 (d, 1H,  $J$  = 6.51, Py-H);  $\delta$ 7.91 (t, 1H,  $J$  = 7.89);  $\delta$ 7.33 (d, 1H,  $J$  = 7.60, Ar-H);  $\delta$ 7.18 (t, 1H,  $J$  = 7.36, Ar-H);  $\delta$ 7.11 (t, 1H,  $J$  = 7.44, Ar-H);  $\delta$ 6.61 (d, 1H,  $J$  = 7.64, Ar-H);  $\delta$ 4.50 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 2.90 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>);  $\delta$ 2.39 (s, 3H, N=CCH<sub>3</sub>);  $\delta$ 1.47 (t, 3H,  $J$  = 7.16, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 1.17 (d, 6H,  $J$  = 6.88, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR: (300MHz, CDCl<sub>3</sub>): 166.4, 165.2, 157.0, 148.5, 147.4, 138.0, 137.3, 126.1, 125.8, 125.4, 124.4, 124.3, 118.3, 62.0, 28.5, 22.9, 22.3, 16.5, 14.3. Anal.Calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.5; H, 7.1; N, 9.0. Found: C, 73.8; H, 7.2; N, 9.0%.

**Ethyl 6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine-2-carboxylate (L-4):** Using the same procedure as for the synthesis of **L-1**, **L-4** was obtained as a yellow powder in 53.7% yield. IR (KBr disc, cm<sup>-1</sup>): 1725 (C=O), 1643 (C=N). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$ 8.58 (d, 1H,  $J$  = 8.00, Py-H);  $\delta$ 8.19 (d, 1H,  $J$  = 7.63, Py-H);  $\delta$ 7.94 (t, 1H,  $J$  = 7.87);  $\delta$ 6.90 (s, 2H, Ar-H);  $\delta$ 4.50 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>);  $\delta$ 2.30 (s, 3H, N=CCH<sub>3</sub>);  $\delta$ 2.27 (s, 3H, CH<sub>3</sub>);  $\delta$ 2.00 (s, 6H, CH<sub>3</sub>);  $\delta$ 1.47 (t, 3H,  $J$  = 7.12, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR: (300MHz, CDCl<sub>3</sub>): 167.6, 165.5, 157.0, 148.3, 146.5, 138.3, 137.6, 129.0, 129.2, 125.5, 124.7, 62.2, 26.0, 21.0, 18.0, 16.8, 14.7. Anal.Calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.5; H,

7.1; N, 9.0. Found: C, 73.0; H, 7.1; N, 9.0%.

**{Ethyl 6-[1-(2-methylphenylimino)ethyl]pyridine-2-carboxylate}FeCl<sub>2</sub> (Fe-1):** The ligand **L-1** (0.141 g, 0.500 mmol) and FeCl<sub>2</sub> (0.064 g, 0.500 mmol) were added to a Schlenk tube, followed by the addition of freshly distilled ethanol (4ml) with rapid stirring at room temperature. The solution turned to deep blue immediately. The reaction mixture was stirred for 10 h, and absolute diethyl ether (10 ml) was added to precipitate the complex. After standing for 30 min, the supernatant was removed. The precipitate was washed with diethyl ether twice and dried in *vacuo* to furnish the pure product as a blue powder in 72.2% yield. Anal. Calcd for C<sub>17</sub>H<sub>18</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 49.9; H, 4.4; N, 6.9. Found: C, 50.1; H, 4.6; N, 6.5. IR (KBr cm<sup>-1</sup>): 1707 (C=O), 1615 (C=N).

**{Ethyl 6-[1-(2-ethylphenylimino)ethyl]pyridine-2-carboxylate}FeCl<sub>2</sub> (Fe-2):** Using the same procedure as for the synthesis of **Fe-1**, **Fe-2** was obtained as a blue powder in 46.9% yield. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 51.1; H, 4.8; N, 6.6. Found: C, 51.0; H, 4.55; N, 6.7. IR (KBr, cm<sup>-1</sup>): 1709 (C=O), 1626 (C=N).

**{Ethyl 6-[1-(2-isopropylphenylimino)ethyl]pyridine-2-carboxylate}FeCl<sub>2</sub> (Fe-3):** Using the same procedure as for the synthesis of **Fe-1**, **Fe-3** was obtained as a blue powder in 20.2% yield. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 52.2; H, 5.1; N, 6.4. Found: C, 52.0; H, 4.9; N, 6.6. IR (KBr cm<sup>-1</sup>): 1705 (C=O), 1626 (C=N).

**{Ethyl 6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine-2-carboxylate}FeCl<sub>2</sub> (Fe-4):** Using the same procedure as for the synthesis of **Fe-1**, **Fe-4** was obtained as a blue powder in 34.8% yield. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>2</sub>FeN<sub>2</sub>O<sub>2</sub>: C, 52.2; H, 5.1; N, 6.4. Found: C, 52.3; H, 5.0; N, 6.4. IR (KBr cm<sup>-1</sup>): 1711 (C=O), 1622 (C=N).

**{Ethyl 6-[1-(2-methylphenylimino)ethyl]pyridine-2-carboxylate}CoCl<sub>2</sub> (Co-1):** To the mixture of ligand **L-1** (0.141 g, 0.500 mmol) and CoCl<sub>2</sub> (0.065 g, 0.500 mmol), was added freshly distilled ethanol (8 ml) at room temperature. The solution turned to green immediately. The reaction mixture was stirred for 5 h, and hexane (20 ml) was added to precipitate the complex. The precipitate was collected by filtration and washed with hexane, followed by drying in *vacuo*. The desired complex was obtained as a green powder in 62.6% yield. Anal.Calcd for C<sub>17</sub>H<sub>18</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub>.0.5H<sub>2</sub>O: C, 48.5; H, 4.55; N, 6.65. Found: C, 48.7; H, 4.4; N, 6.8%. IR (KBr cm<sup>-1</sup>): 1713 (C=O), 1625 (C=N).

**{Ethyl 6-[1-(2-ethylphenylimino)ethyl]pyridine-2-carboxylate}CoCl<sub>2</sub> (Co-2):** Using the same procedure as for the synthesis of **Co-1**, **Co-2** was obtained as a blue powder in 33.9% yield. Anal.Calcd for C<sub>18</sub>H<sub>20</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub>: C, 50.7; H, 4.7; N, 6.6. Found: C, 50.6; H, 4.5; N, 6.8%. IR (KBr cm<sup>-1</sup>): 1715 (C=O), 1626 (C=N).

**Table 2** Crystall data and structure refinement for **Co-3** and **Co-4**

	<b>Co-3</b>	<b>Co-4</b>
Empirical formula	C <sub>19</sub> H <sub>22</sub> Cl <sub>2</sub> Co N <sub>2</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>24</sub> Cl <sub>4</sub> Co N <sub>2</sub> O <sub>2</sub>
Formula weight	440.22	525.14
Crystal colour	Green	Green
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	8.7562(2)	8.1302(2)
<i>b</i> (Å)	11.1793(3)	9.0041(2)
<i>c</i> (Å)	11.2288(3)	16.8188(4)
$\alpha$ (°)	80.712(2)	96.6600(10)
$\beta$ (°)	79.035(2)	94.2990(10)
$\gamma$ (°)	70.7570(10)	95.4150(10)
Volume (Å <sup>3</sup> )	1013.02(4)	1212.85(5)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.443	1.438
$\mu$ (mm <sup>-1</sup> )	1.126	1.166
<i>F</i> (000)	454	538
Crystal size (mm)	0.564 × 0.262 × 0.135	0.30 × 0.20 × 0.20
$\theta$ range (°)	1.86 -31.09	1.22 -28.33
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -16 ≤ <i>k</i> ≤ 15, -16 ≤ <i>l</i> ≤ 16	-9 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 11, -22 ≤ <i>l</i> ≤ 22
Reflections collected	21216	17938
Unique reflections	5752	5957
Completeness to $\theta$ (%)	88.3 ( $\theta$ = 31.09)	98.7 ( $\theta$ = 28.33)
Absorption correction	Empirical	Empirical
Data / restraints / parameters	5752 / 0 / 235	5957 / 0 / 262
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.080	1.002
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0285, <i>wR</i> 2 = 0.0817	<i>R</i> 1 = 0.0440, <i>wR</i> 2 = 0.1344
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0370, <i>wR</i> 2 = 0.0858	<i>R</i> 1 = 0.0802, <i>wR</i> 2 = 0.1538
Largest diff peak and hole (e Å <sup>-3</sup> )	0.443 and -0.318	0.725 and -0.502

{Ethyl 6-[1-(2-isopropylphenylimino)ethyl]pyridine-2-carboxylate}CoCl<sub>2</sub> (**Co-3**): Using the same procedure as for the synthesis of **Co-1**, **Co-3** was obtained as a blue powder in 57.0% yield. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub>: C, 51.8; H, 5.0; N, 6.4. Found: C, 51.2; H, 5.0; N, 6.4%. IR (KBr cm<sup>-1</sup>): 1713 (C=O), 1626 (C=N).

{Ethyl 6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine-2-carboxylate}CoCl<sub>2</sub> (**Co-4**): Using the same procedure as for the synthesis of **Co-1**, **Co-4** was obtained as a blue powder in 57.1% yield. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub>: C, 45.7; H, 4.6; N, 5.3. Found: C, 46.0; H, 4.7; N, 5.5%. IR (KBr cm<sup>-1</sup>): 1706 (C=O), 1621 (C=N).

#### X-ray crystallography

Data sets were collected with a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-K radiation ( $\lambda=0.71073\text{\AA}$ ) using the  $\omega$ -2 $\theta$  scan mode. Unit cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarisation effects and empirical absorption. The structures were solved by direct methods, and refined by full-matrix least-square on  $F^2$ . Each hydrogen atom was placed in a calculated position, and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using SHELXL-97 package.<sup>10</sup> Crystal data and processing parameters are summarised in Table 2.

Received 9 October 2005; accepted 12 December 2005

Paper 05/3537

#### References

- (a) G.J.P. Britovsek, V.C. Gibson and D.F. Wass, *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 428; (b) S.D. Ittel, L.K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (c) V.C. Gibson and S.K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283; (d) W. Zhang, W.J. Zhang and W.-H. Sun, *Prog. Chem.*, 2005, **17**, 310; (e) L. Chen, H. Yang, W.-H. Sun, *Prog. Chem.*, 2003, **15**, 401.
- (a) L.K. Johnson, C.M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (b) L.K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267; (c) S. Mecking, L.K. Johnson, L. Wang and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 888; (d) C.M. Killian, D.J. Tempel, L.K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664; (e) J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese and S.D. Arthur, *Organometallics*, 1997, **16**, 1514.
- (a) B.L. Small, M. Brookhart and A.M.A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049; (b) G.P.J. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White and D.J. Williams, *Chem. Commun.*, 1998, 849.
- (a) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs and D.A. Bansleben, *Science* 2000, **287**, 460; (b) F.M. Bauers and S. Mecking, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 3020; (c) W.-H. Sun, H. Yang, Z. Li and Y. Li, *Organometallics*, 2003, **22**, 3678; (d) L. Wang, W.-H. Sun, L. Han, Z. Li, Y. Hu, C. He and C. Yan, *J. Organomet. Chem.*, 2002, **650**, 59; (e) W.-H. Sun, W. Zhang, T. Gao, X. Tang, L. Chen, Y. Li and X. Jin, *J. Organomet. Chem.*, 2004, **689**, 917; (f) L. Chen, J. Hou and W.-H. Sun, *Appl. Cat. A*, 2003, **246**, 11.
- (a) B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon and X. Bu, *J. Am. Chem. Soc.*, 2001, **123**, 5352; (b) J. Li, T. Gao, W. Zhang and W.-H. Sun, *Inorg. Chem. Commun.*, 2003, **6**, 1372; (c) W.-H. Sun, C. Shao, Y. Chen, H. Hu, R.A. Sheldon, H. Wang, X. Leng and X. Jin, *Organometallics*, 2002, **21**, 4350; (d) E.V. Salo and Z. Guan, *Organometallics*, 2003, **22**, 5033.
- (a) F. Speiser, P. Braunstein, L. Saussine and R. Welter, *Inorg. Chem.*, 2004, **43**, 1649; (b) W.-H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng and H. Wang, *New J. Chem.*, 2002, **26**, 1474; (c) O. Daugulis, M. Brookhart and P.S. White, *Organometallics*, 2002, **21**, 5935.
- (a) K. Michiue and R.F. Jordan, *Organometallics*, 2004, **23**, 460; (b) L. Wang, W.-H. Sun, L. Han, H. Yang, Y. Hu and X. Jin, *J. Organomet. Chem.*, 2002, **658**, 62.
- (a) L. LePichon, D.W. Stephan, X. Gao and Q. Wang, *Organometallics*, 2002, **21**, 1362; (b) M. Qian, M. Wang and R. He, *J. Mol. Cat. A.*, 2000, **160**, 243; (c) M. Qian, M. Wang, B. Zhou and R. He, *Appl. Cat. A.*, 2001, **209**, 11; (d) C. Bianchini, G. Mantovani, A. Meli, F. Migliacci and F. Laschi, *Organometallics*, 2003, **22**, 2545; (e) M.-S. Zhou, S.-P. Huang, L.-H. Weng, W.-H. Sun and D.-S. Liu, *J. Organomet. Chem.*, 2003, **665**, 237; (f) G.J.P. Britovsek, V.C. Gibson, O.D. Hoarau, S.K. Spitzmesser, A.J.P. White and D.J. Williams, *Inorg. Chem.*, 2003, **42**, 3454.
- (a) W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang and H. Ma, *Organometallics*, 2004, **23**, 5037; (b) X. Tang, W.-H. Sun, T. Gao, J. Hou, J. Chen and W. Chen, *J. Organomet. Chem.*, 2005, **690**, 1570.
- G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal Structures, University of Gottingen: Germany, 1997.