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Oligomerisation of ethylene to linear α-olefins by tetrahedral cobalt(II) precursors stabilised by benzo[*b*]thiophen-2-yl-substituted (imino)pyridine ligands ☆

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Abstract

On activation by MAO, 2-(imino)pyridine cobalt dichlorides bearing a benzo[*b*]thiophen-2-yl substituent in the 6-position of the pyridine ring oligomerise ethylene to α-olefins with turn-over-frequencies as high as 1.5×10^6 mol of C_2H_4 converted (mol of $Co \times h)^{-1}$ and productivities as high as 3769 kg of oligomers (mol of $Co \times h \times bar)^{-1}$. Aldimine precursors are more active than ketimine analogues, yet ketimines give higher molecular weight oligomers.

Keywords: Oligomerisation; Ethylene; α-Olefins; Cobalt; (Imino)pyridine

1. Introduction

In a recent paper, we reported that tetrahedral bis-chloride Co^{II} complexes stabilised by thiophen-2-yl-substituted (imino)pyridine ligands (N_2^{Th} and N_2^{ThE} in Chart 1) and activated by methylaluminoxane (MAO) catalyse in toluene the oligomerisation of ethylene to short chain α-olefins with turn-over-frequencies (TOF) as high as 10^6 mol of C_2H_4 converted (mol of $Co \times h)^{-1}$ [1]. These results were quite surprising as all previous Co^{II} catalysts with either imino(pyridine) or bis(imino)pyridine ligands provided very low productivities (TOFs $\leqslant 10^4$) [2]. Under analogous conditions to those of the N_2^{Th} and N_2^{ThE} catalysts, Co^{II} precursors with furanyl- and phenyl-substituted ligands (N_2^{Fu}, N_2^{Ph} in Chart 1) were five times less active and also selective for ethylene dimerisation. Steric reasons were considered irrelevant in accounting for the superior activity of the thiophenyl-substituted catalysts, whereas the sulphur atom was suggested to have a role in increasing both the activity and the Schulz–Flory parameter α (mol C_{n+2}/mol C_n) [1,3].

In order to rule out the occurrence of a fortuitous combination of factors enabling the superior activity of the N_2^{Th} and N_2^{ThE} based catalysts and eventually gain insight into this surprising heteroatom effect, we decided to study the ethylene oligomerisation performance of (aldimino)pyridyl and (ketimino)pyridyl Co^{II} bis-chloride precursors featured by the presence of a benzo[*b*]thiophenyl substituent in the 6-position of the pyridine ring (Scheme 1). A Co^{II} precursor with a (ketimino)pyridyl ligand bearing a naphthyl substituent, sterically similar to benzothiophenyl, was also prepared for comparative purposes (Scheme 2). Preliminary results of this study are reported here.

2. Results and discussion

The introduction of a benzo[*b*]thiophenyl group into the 6-position of the iminopyridyl structure was achieved by Stille coupling between benzothiophen-2-yl

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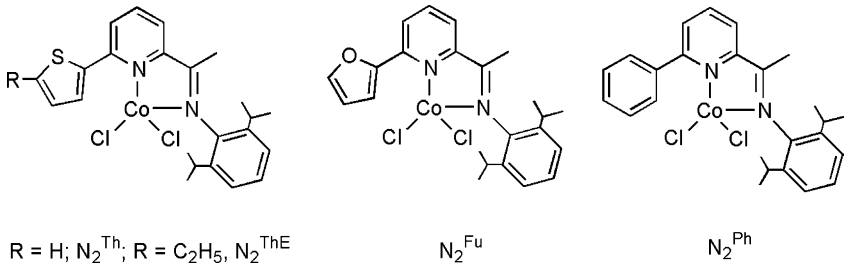
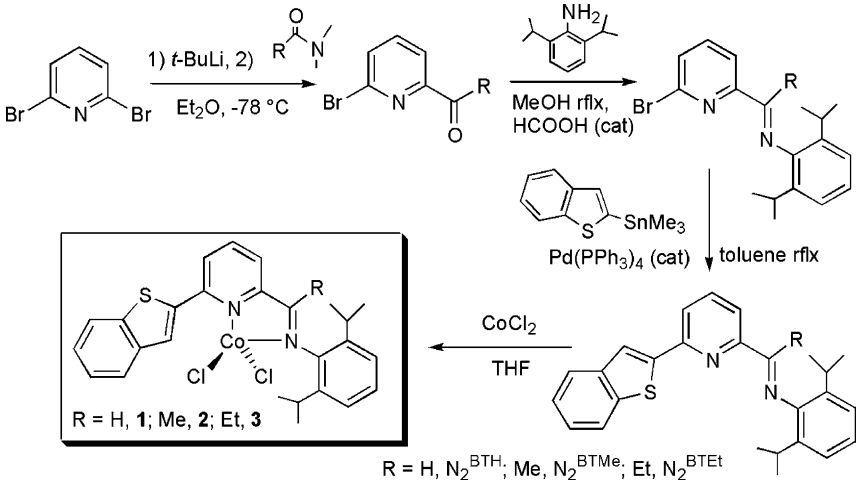
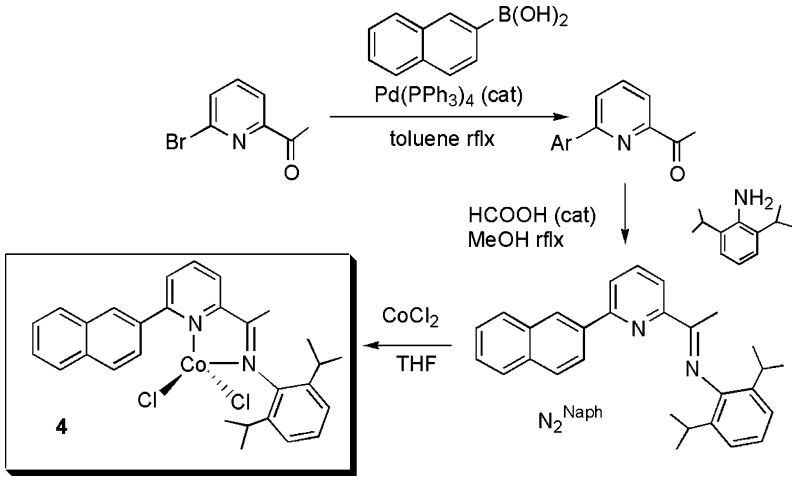


Chart 1.



Scheme 1.



Scheme 2.

stannane and the desired 6-bromo-2-arylimino pyridine. The latter substrates were prepared from 2,6-dibromo pyridine via the two-step process illustrated in Scheme 1.

The 6-naphthyl pyridinimine ligand N_2^{Naph} was prepared by a Suzuki reaction between 6-bromo-2-acetyl ketone and 2-naphthylboronic acid, followed by condensation of the resultant 6-naphthyl-2-acetyl ketone with 2,6-diisopropylaniline.

The Co^{II} complexes $CoCl_2(N_2^{BTH})$ (**1**), $CoCl_2(N_2^{BTMe})$ (**2**), $CoCl_2(N_2^{BTEt})$ (**3**) and $CoCl_2(N_2^{Naph})$ (**4**) were

obtained as green crystals in high yield by reacting one equivalent of the appropriate N_2 ligand with a THF solution of anhydrous $CoCl_2$ at room temperature.

Like the previously reported derivatives with N_2^{Th} and N_2^{Ph} [1], **1–4** are high-spin in the solid state with μ_{eff} at 20 °C ranging from 4.7 to 4.9 BM, which is typical for a d^7 metal ion in a tetrahedral coordination geometry independent of the donor atom set [4]. For all complexes, the electronic spectra in CH_2Cl_2 solution and the reflectance spectra were similar to each other and with the expected bands for a d^7 metal ion in a tetrahedral coordination geometry [1]. None of the present pyridinimine Co^{II} compounds was studied by X-ray diffraction analysis due to the difficulty in getting suitable crystals. However, on the basis of the X-ray structure analysis of the related $CoCl_2(N_2^{ThE})$ derivative [1], a structure can be assigned to **1–3** where the benzothiophenyl sulphur atom does not bind cobalt and is actually oriented away from the cobalt centre which is tetrahedrally coordinated by two nitrogen and two chlorine atoms. Since the spectroscopic characteristics of the naphthyl derivative **4** are fully comparable to those of **1–3**, one may safely conclude that all the cobalt complexes described in this work exhibit a tetrahedral coordination prior to activation with MAO. Due to the presence of three unpaired electrons, all complexes were EPR silent at room temperature in both the solid state and solution [5]. Upon treatment with MAO in toluene, **1–4** became EPR active in X-band showing broad signals with g_{iso} values in the range 2.01(5)–2.04(5). Analogous behaviour had been previously observed for the N_2^{Th}, N_2^{ThE}, N_2^{Fu} and N_2^{Ph} Co^{II} derivatives and attributed to the formation of low-spin square-planar Co^{II} species upon MAO activation [1].

The three Co^{II} complexes **1–3** were all active catalysts on treatment with MAO for the production of Schulz–Flory distributions of low molecular weight α-olefins. Selected data are reported in Table 1.

The aldimine complex **1** gave rise to the most active catalyst, yielding predominantly butenes (entry 1), while the methyl-ketimine precursor **2** (entry 2) was significantly more active than the ethyl-ketimine derivative **3** (entry 3). Both **2** and **3** produced Schulz–Flory distributions of C_4–C_{14} oligomers with prevalence of butenes (82% and 85%, respectively) and hexenes (15% and 12%, respectively). The naphthyl-substituted precursor **4** was much less active than any benzothiophenyl-substituted catalyst and produced almost exclusively butenes (entry 4). Under comparable conditions, the ketimine-thiophenyl precursor $CoCl_2(N_2^{Th})$ was as active as the benzothiophenyl analogue **2**, yet with a lower α value (0.060 vs. 0.179) (entry 8) [1]. It is worth noting that the TOF (1.75×10^6) displayed by precursor **2** at 13 bar of C_2H_4, corresponding to about 3769 kg of oligomers (mol of Co × h × bar)$^{-1}$ (entry 6), is remarkably high for Co^{II} catalysts [2c,6,11].

Experiments with precursor **2** in the C_2H_4 pressure range from 4 to 13 bar (entries 2, 5 and 6) showed a linear dependence of activity with the pressure, while the α factor was independent of the pressure, indicating that the propagation and chain-transfer rates are first order in ethylene [1,2c,6]. In all reactions, the selectivity in α-olefins was ca. 90% in the first 30 min; with time the selectivity decreased due to isomerisation to internal olefins (entry 7), preferentially with *E* conformation (determined by GC–MS), while the α factor increased due to the re-incorporation of α-olefin products into oligomers made later in the reaction. The occurrence of both olefin isomerisation and re-incorporation was confirmed by independent experiments in which the oligomerisation of ethylene with **2** was carried out in the presence of an excess of 1-undecene. Odd carbon oligomers (C_{13}–C_{15}) were formed together with various

Table 1
Ethylene oligomerisation with cobalt(II) catalysts[a]

Entry	Pre-catalyst	Pressure (bar)	TOF[b] ($\times 10^{-5}$)	α[c]	β[c]	Selectivity in α-olefins (%)
1	**1**	4	5.60	0.084	10.9	88
2	**2**	4	4.32	0.179	4.6	91
3	**3**	4	2.30	0.146	5.8	91
4	**4**	4	0.90[d]			
5	**2**	8	8.32	0.174	4.7	93
6	**2**	13	17.5	0.183	4.5	93
7[e]	**2**	4	2.54	0.214	3.7	82
8[f]	$CoCl_2(N_2^{Th})$	4	4.62	0.060	15.6	90

[a] Reaction conditions: pre-catalyst 0.8 μmol, toluene 100 ml, MAO 250 equiv., 30 min., 25 °C.
[b] Mol of C_2H_4 converted (mol of Co × h)$^{-1}$; average value over three runs.
[c] Schulz–Flory parameters, α = mol of C_{n+2} (mol of C_n)$^{-1}$; $\beta = (1-\alpha)/\alpha$.
[d] The amount of butenes was determined as the sum of the product in the liquid and gaseous phases by GC at low temperature. A C_8/C_6 ratio of 0.02 was calculated by GC.
[e] 1 h.
[f] Taken from [1].

undecenes, in fact. No saturated hydrocarbon was produced, which indicates the absence of chain transfer to aluminium [2c,6].

Higher concentrations of Co^{II} precursors (up to 12 μmol) gave the same activity trend, yet with lower productivities as is generally observed for very active oligomerisation catalysts [2c,6a].

The study reported in this work confirms that the presence of a sulphur atom in aromatic substituents on the 6-position of the pyridine ring does have a beneficial effect on the catalytic performance of 2-imino-6-(organyl)pyridine Co^{II} bis-chloride/MAO systems.

Notably, the chain length of the oligomers has been found to increase with the size of the sulphur-containing group (entries 2 and 8), which strengthens the importance of steric effects in controlling the ethylene oligomerisation activity of late transition metal catalysts with planar nitrogen ligands such as α-diimines [7,8], (imino)pyridines [7,9,10] and 2-bis(imino)pyridines [2c,6,11]. For these ligands, it is believed that alkyl substituents in the 2,6-positions of the imino phenyl group, in conjunction with a methyl group on the C atom, force the aryl rings to lie perpendicular to the metal coordination plane on the polymerisation timescale [9,12]. As a consequence, the axial positions would become sterically congested, thus disfavouring chain termination by β–H transfer to metal, which does occur in the present systems as shown by the occurrence of olefin isomerisation. NMR spectroscopy shows free rotation about the $N–C_{aryl}$ bond in the aldimine N_2^{BTH} and hindered rotation in the ketimines N_2^{BTMe} and N_2^{BTEt} [1]. Consistently, we have observed that the Schulz–Flory parameter α increases in the order aldimine < ketimine. On the other hand, we have found that the TOF increases in the order ethyl-ketimine < methyl-ketimine < aldimine, which is surprising as the contrary is observed for 2,6-bis(imino)pyridyl iron precursors [2c,6]. It is possible that 2,6-substituted aryl rings perpendicular to the coordination plane may disfavour the coordination/insertion of the monomer in (imino)pyridyl metal complexes, yet no conclusion can be forwarded in the absence of further studies.

3. Experimental

3.1. General

All reactions were carried out under N_2 using standard Schlenck techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker ACP 200 (200.13 and 50.32 MHz, respectively). All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (^1H and ^{13}C). The multiplicity of the $^{13}C\{^1H\}$ NMR spectra were determined with the DEPT 135 technique and quoted as: CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms, respectively. X-band EPR spectra were obtained with a Varian ESR9 spectrometer equipped with a continuous flow ^4He cryostat. Absorption (CH_2Cl_2 solution) and reflectance (powdered sample) spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer 1600 Series FT-IR spectrophotometer using samples mulled in Nujol between KBr plates. Molar susceptibilities were measured on solid samples using a Sherwood Scientific MSB AUTO balance. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyser. The melting points are uncorrected. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionisation detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis.

3.2. Synthesis of the ligands

3.2.1. (6-Benzo[b]thiophen-2-yl-pyridin-2-yl-methylene)-(2,6-diisopropyl-phenyl)-amine (N_2^{BTH})

A deaerated solution of (6-bromo-pyridin-2-yl-methylene)-(2,6-diisopropyl-phenyl)-amine (0.32 g, 0.93 mmol) and benzo[*b*]thiophen-2-yl-trimethyl-stannane (0.30 g, 1.02 mmol) in 10 ml of toluene was treated with $Pd(PPh_3)_4$ (0.055 g, 0.047 mmol) and refluxed for 24 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. Crystallization of the yellow-orange oily residue from the minimum amount of CH_2Cl_2 and MeOH gave the product as yellow crystals (0.32 g, 0.80 mmol, yield 86%). m.p. 212–213 °C. IR ν(C=N) 1640 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.22 (d, $J = 6.9$ Hz, 12H, $CH(CH_3)_2$), 2.80 (sept, $J = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.11–7.24 (m, 3H, CH), 7.34–7.43 (m, 2H, CH), 7.83–7.93 (m, 5H, CH), 8.19–8.28 (m, 1H, CH), 8.40 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.10 (4C, $CH(CH_3)_2$), 28.66 (2C, $CH(CH_3)_2$), 120.44 (1C, CH), 121.74 (1C, CH), 122.35 (1C, CH), 123.25 (1C, CH), 123.70 (2C, CH), 124.89 (1C, CH), 125.14 (1C, CH), 125.25 (1C, CH), 125.85 (1C, CH), 137.87 (1C, C), 138.00 (1C, CH), 141.08 (1C, C), 141.48 (1C, C), 144.91 (1C, C), 149.10 (1C, C), 153.20 (1C, C), 155.09 (1C, C), 167.79 (1C, N=CH). Anal. calc. $C_{26}H_{26}N_2S$ requires: C, 78.35; H, 6.58; N, 7.03%. Found: C, 78.46; H, 6.63; N, 7.11.

3.2.2. [1-(6-Benzo[b]thiophen-2-yl-pyridin-2-yl)-ethylidene]-(2,6-diisopropyl-phenyl)-amine (N_2^{BTMe})

This ligand was prepared like N_2^{BTH} except for using [1-(6-bromo-pyridin-2-yl)-ethylidene]-(2,6-diisopropyl-phenyl)-amine (0.45 g, 1.06 mmol); yield 86%. m.p.

171–172 °C. IR ν(C=N) 1643 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.19 (d, $J = 6.7$ Hz, 6H, $CH(CH_3)(CH_3)$), 1.20 (d, $J = 7.0$ Hz, 6H, $CH(CH_3)(CH_3)$), 2.35 (s, 3H, $N{=}C(CH_3)$), 2.80 (m, 2H, $CH(CH_3)(CH_3)$), 7.10–7.25 (m, 3H, CH), 7.37–7.41 (m, 2H, CH), 7.83–7.93 (m, 5H, CH), 8.33 (dd, $J = 6.5, 2.4$ Hz, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 17.94 (1C, $N{=}C(CH_3)$), 23.71 (2C, $CH(CH_3)(CH_3)$), 24.02 (2C, $CH(CH_3)(CH_3)$), 29.07 (2C, $CH(CH_3)(CH_3)$), 120.73 (1C, CH), 121.01 (1C, CH), 121.86 (1C, CH), 123.29 (1C, CH), 123.79 (2C, CH), 124.42 (1C, CH), 124.91 (1C, CH), 125.27 (1C, CH), 125.84 (1C, CH), 136.54 (1C, C), 137.85 (1C, CH), 141.30 (1C, C), 141.55 (1C, C), 145.81 (1C, C), 147.25 (1C, C), 152.09 (1C, C), 156.72 (1C, C), 167.64 (1C, $N{=}C(CH_3)$). Anal. calc. $C_{27}H_{28}N_2S$ requires: C, 78.60; H, 6.84; N, 6.79%. Found: C, 78.48; H, 6.77; N, 6.85.

3.2.3. [1-(6-Benzo[b]thiophen-2-yl-pyridin-2-yl)-propylidene]-(2,6-diisopropyl-phenyl)-amine (N_2^{BTEt})

This ligand was prepared like N_2^{BTH} except for using [1-(6-bromo-pyridin-2-yl)-propylidene]-(2,6-diisopropyl-phenyl)-amine (0.24 g, 0.64 mmol); yield 66%. m.p. 167–168 °C. IR ν(C=N) 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.17–1.28 (m, 15H, $CH(CH_3)(CH_3) + CH(CH_3)(CH_3) + CH_2CH_3$), 2.80 (m, 4H, $CH(CH_3)(CH_3) + CH_2CH_3$), 7.10–7.27 (m, 3H, CH), 7.37–7.42 (m, 2H, CH), 7.84–7.92 (m, 5H, CH), 8.26 (dd, 1H, $J = 5.9, 2.9$ Hz, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 11.80 (1C, CH_2CH_3), 23.04 (2C, $CH(CH_3)(CH_3)$), 24.21 (2C, $CH(CH_3)(CH_3)$), 24.52 (1C, CH_2CH_3), 28.96 (2C, $CH(CH_3)(CH_3)$), 120.65 (1C, CH), 121.58 (1C, CH), 121.64 (1C, CH), 123.23 (1C, CH), 123.54 (2C, CH), 124.14 (1C, CH), 124.83 (1C, CH),125.19 (1C, CH), 125.75 (1C, CH), 136.31 (1C, C), 137.88 (1C, CH),141.26 (1C, C), 141.53 (1C, C), 146.00 (1C, C), 146.84 (1C, C), 151.95 (1C, C), 156.10 (1C, C), 171.16 (1C, $N{=}C(CH_2CH_3)$). Anal. calc. $C_{28}H_{30}N_2S$ requires: C, 78.83; H, 7.09; N, 6.57%. Found: C, 78.60; H, 7.01; N, 6.65.

3.2.4. (2,6-Diisopropyl-phenyl)-[1-(6-naphthalen-2-yl-pyridin-2-yl)-ethylidene]-amine (N_2^{Naph})

1-[6-(2-naphthyl)-pyridin-2-yl]Ethanone (0.25 g, 1.0 mmol) and 2,6-diisopropylaniline (0.89 g, 5.0 mmol) were dissolved in 10 ml of EtOH containing two drops of formic acid and the resulting mixture was refluxed for 24 h. Cooling the resulting yellow-orange solution to room temperature led to the precipitation of the product as yellow microcrystals (0.24 g, 0.62 mmol, yield 64%) within 2 h. From the mother liquor a further 0.080 g (0.20 mmol) was obtained after 24 h. Overall yield 82%. m.p. 170–171 °C. IR ν(C=N) 1651 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.19 (d, $J = 6.8$, 12H, $CH(CH_3)_2$), 2.40 (s, 3H, $N{=}C(CH_3)$), 2.83 (sept, $J = 6.8$ Hz, 2H, $CH(CH_3)_2$), 7.09–7.24 (m, 3H, CH), 7.50–7.59 (m, 2H, CH), 7.87–8.06 (m, 5H, CH), 8.30–8.39 (m, 2H, CH), 8.60 (m, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 18.05 (1C, $N{=}C(CH_3)$), 23.64 (2C, $CH(CH_3)(CH_3)$), 23.93 (2C, $CH(CH_3)(CH_3)$), 28.97 (2C, $CH(CH_3)(CH_3)$), 120.28 (1C, CH), 122.13 (1C, CH), 123.68 (1C, CH), 124.21 (1C, CH), 125.28 (1C, CH), 126.91 (1C, CH), 127.03 (1C, CH), 127.03 (1C, CH), 127.27(1C, CH), 128.41 (1C, CH), 129.18 (1C, CH), 129.40 (1C, CH), 134.18 (1C, C), 134.43 (1C, C), 136.53 (2C, C), 137.11(1C, C), 137.97 (1C, CH), 147.25 (1C, C), 156.54 (1C, C), 156.84 (1C, C), 168.06 (1C, $N{=}C(CH_3)$). Anal. calc. $C_{29}H_{30}N_2$ requires: C, 85.67; H, 7.44; N, 6.89%. Found: C, 85.60; H, 7.36; N, 6.95.

3.3. General procedure for the synthesis of the Co^{II} complexes

To a solution of anhydrous $CoCl_2$ (0.5 mmol) in THF (30 ml) was added the appropriate bidentate ligand (0.5 mmol) under a nitrogen atmosphere and the resulting mixture was stirred for 24 h at room temperature. Removal of the solvent under reduced pressure gave a solid which was filtered on a sintered-glass frit, washed with Et_2O and dried in a stream of nitrogen.

3.3.1. (6-Benzo[b]thiophen-2-yl-pyridin-2-yl-methylene)-(2,6- diisopropyl-phenyl)-amine cobalt(II) dichloride (**1**)

Green microcrystals, yield 89%. IR: ν(C=N) 1590 cm^{-1}. $\mu_{eff} = 4.77$ BM (25 °C). Electronic spectra: diffuse reflectance (40,000–5550 cm^{-1}): 26,000, 22,350 sh, 18,000, 16,400 sh, 14,500, 9600, 7350, 6100; CH_2Cl_2 solution (28,500–6250 cm^{-1}): 26,200 (ε 9000), 17,200 (ε 1100), 14,600 (ε 2000), 9900 (ε 120), 7100 (ε 380). Anal. calc. $C_{26}H_{26}Cl_2CoN_2S$ requires: C, 59.10; H, 4.96; N, 5.30%. Found: C, 58.89; H, 4.85; N, 5.31.

3.3.2. [1-(6-Benzo[b]thiophen-2-yl-pyridin-2-yl)-ethylidene]-(2,6-diisopropyl-phenyl)-amine cobalt(II) dichloride (**2**)

Green powder, yield 71%. IR: ν(C=N) 1592 cm^{-1}. $\mu_{eff} = 4.80$ BM (25°C). Electronic spectra: diffuse reflectance (40,000–5550 cm^{-1}): 26,000, 22,350 sh, 18,100, 16,000 sh, 14,700, 9700, 7400, 6100; CH_2Cl_2 solution (28,500–6250 cm^{-1}): 26,000 (ε 9000), 17,400 (ε 1100), 14,700 (ε 2100), 9900 (ε 125), 7200 (ε 380). Anal. calc. $C_{27}H_{28}Cl_2CoN_2S$ requires: C, 59.78; H, 5.20; N, 5.16%. Found: C, 59.75; H, 5.33; N, 5.21.

3.3.3. [1-(6-Benzo[b]thiophen-2-yl-pyridin-2-yl)-propylidene]-(2,6-diisopropyl-phenyl)-amine cobalt(II) dichloride (**3**)

Green microcrystals, yield 91%. IR: ν(C=N) 1595 cm^{-1}. $\mu_{eff} = 4.75$ BM (25 °C). Electronic spectra: diffuse reflectance (40,000–5550 cm^{-1}): 26,000, 22,250 sh, 18,100, 15,900 sh, 14,500, 9600, 7200, 6100; CH_2Cl_2 solution (28,500–6250 cm^{-1}): 2450 (ε 8500), 17,200 (ε 1000), 14,350 (ε 2000), 9700 (ε 120), 7100 (ε 350). Anal.

calc. $C_{28}H_{30}Cl_2CoN_2S$ requires: C, 60.44; H, 5.43; N, 5.03%. Found: C, 60.29; H, 5.31; N, 5.10.

*3.3.4. (2,6-Diisopropyl-phenyl)-[1-(6-naphthalen-2-yl-pyridin-2-yl)-ethylidene]-amine cobalt(II) dichloride (**4**)*

Pale green powder, yield 85%. IR: ν(C=N) 1594 cm^{-1}. $\mu_{eff} = 4.84$ BM (25 °C). Electronic spectra: diffuse reflectance (40,000–5550 cm^{-1}): 25,900 sh, 16,500, 15,100, 9450, 7100, 5600; CH_2Cl_2 solution (28,500–6250 cm^{-1}): 25,000 sh, 16,900 (ε 1220), 15,100 sh, 14,850 (ε 2780), 9500 (ε 130), 7000 (ε 390). Anal. calc. $C_{29}H_{30}Cl_2CoN_2$ requires: C, 64.93; H, 5.64; N, 5.22%. Found: C, 64.79; H, 5.50; N, 4.98.

3.4. Oligomerisation procedure

A 500 ml stainless-steel reactor was heated at 60 °C under vacuum for 16 h, then back-filled four times with N_2 and subjected to vacuum again, at room temperature. The pre-catalyst (12 μmol) was suspended in 75 ml of deaerated toluene and 250 μmol of MAO in toluene was added. A 5 ml portion of the resulting solution was introduced into a flask containing 95 ml of toluene and 200 μmol of MAO, and the mixture was transferred through a cannula sinto the autoclave. The reactor was then pressurized with ethylene at the desired pressure and stirred (1500 rpm). In all cases, the addition of ethylene to the catalyst/co-catalyst mixture resulted in a rapid exotherm, indicative of no induction period. The pressure was kept constant during the reaction. At the end of each experiment, the autoclave was rapidly cooled to 5 °C, depressurised and the reaction was quenched by addition of 2 ml of MeOH acidified with dilute HCl. *n*-Heptane (200 μl) was finally introduced as internal standard for GC measurements.

In a separate experiment, a 5 ml portion of the activated pre-catalyst was introduced into a flask containing 95 ml of toluene, 5 ml (24.3 mmol) of 1-undecene and 200 μmol of MAO. The resulting mixture was transferred by means of a cannula into the autoclave. The reactor was then pressurised with ethylene (4 bar) and stirred (1500 rpm) for 30 min. Work-up as above, followed by GC analysis gave a TOF of 3.9×10^5 ($\alpha = 0.174$) and showed the formation of odd oligomers C_{13}–$C_{15} \approx 2$ mmol (8% of the added 1-undecene).

4. Supplementary material

Text giving the synthesis and characterization of the pyridinimine ligand intermediates.

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