

# Co-catalyst effects on the thermal stability/activity of *N,N,N*-Co ethylene polymerization Catalysts Bearing Fluoro-Substituted *N*-2,6-dibenzhydrylphenyl groups

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## Abstract

The unsymmetrical bis(arylimino)pyridines, 2-[CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]-6-(CMeNAr)C<sub>5</sub>H<sub>3</sub>N (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L1**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L2**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L3**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **L4**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **L5**), each containing one *N*-aryl group bedecked with *ortho*-substituted fluorobenzhydryl groups, have been employed in the preparation of the corresponding five-coordinate cobalt(II) chelates, LCoCl<sub>2</sub> (**Co1** – **Co5**); the symmetrical comparator [2,6-{CMeN(2,6-(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH)<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub> (**Co6**) is also reported. All cobaltous complexes are paramagnetic and have been characterized by <sup>1</sup>H/<sup>19</sup>F NMR spectroscopy, FT-IR spectroscopy and elemental analysis. The molecular structures of **Co3** and **Co6** highlight the different degrees of steric protection given to the metal center by the particular *N*-aryl group combination. Depending on the aluminoxane co-catalyst employed to activate the cobalt precatalyst, distinct variations in thermal stability and activity of the catalyst towards ethylene polymerization were exhibited. In particular with MAO, the resultant catalysts reached their optimal performance at 70 °C delivering high activities of up to 10.1 × 10<sup>6</sup> g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> with **Co1** > **Co4** > **Co2** > **Co5** > **Co3** >> **Co6**. On the other hand, using MMAO, the catalysts operate most effectively at 30 °C but are by comparison less productive. In general, the polyethylenes were highly linear, narrowly disperse and displayed a wide range of molecular weights [*M<sub>w</sub>* range: 18.5 – 58.7 kg mol<sup>-1</sup> (MAO); 206.1 – 352.5 kg mol<sup>-1</sup> (MMAO)].

**Keywords:** Cobalt(II) precatalyst; influence of fluoro-substituent; highly active and thermally stable catalyst; ethylene polymerization; highly linear polyethylene.

## Introduction

The excellent performance characteristics displayed by catalysts derived from bis(imino)pyridine-iron and cobalt dichlorides (**A**, Figure 1) in ethylene polymerization<sup>[1]</sup> and oligomerization,<sup>[2]</sup> has stimulated a prodigious number of research studies since the late 1990s. In the main these have been synthetic-based investigations that have been directed towards structural modifications to the ligand framework with the intent to improve the productivity of the catalyst.<sup>[3,4]</sup> Elsewhere, theoretical calculations concerned with correlating steric and electronic effects with catalytic activities have also been reported.<sup>[5]</sup> Pertaining to electronic factors, the introduction of electron-withdrawing groups (*e.g.*, halides) to the *ortho*- and/or *para*-positions of the N-aryl groups in **A** can influence the catalytic activities and the properties of the polyethylenes, an observation that has been attributed to an increased Lewis acidic character of the cationic metal center in the active species.<sup>[4]</sup> On the other hand, functionalizing the *ortho*-positions of the N-aryl groups with exceptionally bulky substituents such as aryl and more recently benzhydryl (CHPh<sub>2</sub>) has seen some distinctive effects on activity and temperature stability of the catalyst as well as on the polymer properties themselves.<sup>[6,7]</sup> Moreover, the incorporation of bulky substituents that are amenable to electronic variation has emerged as a further means of tuning the performance of cobalt and iron catalysts.<sup>[7,8]</sup>

< Figure 1 >

To provide further insight as to the role of steric and electronic effects on the polymerization process, our group has been exploring the performance of unsymmetrically-chelated bis(arylimino)pyridine-iron and cobalt polymerization catalysts that contain one fixed N-aryl group appended with benzhydryl substituents and the other variable in terms of its substitution pattern. Indeed, several classes of precatalyst are accessible in which the fixed N-aryl group can be 2,6-dibenzhydrylphenyl (**B**, Figure 1),<sup>[7a,8a]</sup> 2,6-dibenzhydryl-4-chlorophenyl (**C**, Figure 1),<sup>[7b,8c]</sup> 2,4-dibenzhydryl-6-methylphenyl (**D**, Figure 1)<sup>[7c,8b]</sup> have been developed. Hitherto, we have observed that the electron withdrawing groups such as the *para*-chloride in **C** exerted a positive effect on the catalytic performance and polymer properties.<sup>[7b,8c]</sup> In a similar vein, the incorporation of fluoride substituents to the *para*-positions of the dibenzhydryl group itself [*i.e.*, CH(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>] can also play an important role in improving the activities and thermal stabilities of the catalyst. For example, the cobalt-containing **E**<sub>Co-mesityl</sub> (Figure 1)<sup>[7f]</sup> was found to display superior thermal

stability ( $0.56 \times 10^7$  g of PE (mol of Co) $^{-1}$  h $^{-1}$  g at 70 °C) when compared to **D**<sub>Co-mesityl</sub><sup>[8b]</sup> ( $0.61 \times 10^7$  g of PE (mol of Co) $^{-1}$  h $^{-1}$  at 40 °C). Perhaps more significantly, these fluoride-containing cobalt catalysts are able to display catalytic activities that can approach levels only achievable by their more productive iron counterparts.

Encouraged by the positive results noted using **E**<sub>Co</sub>, we now disclose our findings using the fluoride-substituted 2-[1-(2,6-bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridine-cobalt(II) chlorides (**F**, Figure 1). Specifically, five examples of **F** are reported in the which the substitution profile for the second aryl group has been varied (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub>). For purposes of comparison, the symmetrical counterpart, [2,6-{CMeN(2,6-(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH)<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub>, is also investigated and the performance of all six cobalt complexes as precatalysts in ethylene polymerization fully discussed in terms of catalytic activity and polymer properties (*e.g.*, molecular weight, dispersity and melt temperature). Furthermore, the synthetic and characterization details for all new *N,N,N*-ligands and cobalt complexes will be documented.

## Experimental section

### General considerations

All manipulations involving air and/or moisture sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The toluene used for the polymerization runs was dried over sodium for 8 h and distilled under nitrogen atmosphere prior to use. The co-catalysts, MAO (1.46 M in toluene) and MMAO (2.00 M in heptane), were provided by Albemarle Corporation. High purity ethylene was purchased from Beijing Yanshan Petrochemical Company. Other reagents were purchased from Aldrich, Acros or Beijing Chemicals. 2,6-Bis(bis(4-fluorophenyl)methyl)-4-*t*-butylaniline was prepared using the literature route.<sup>[9]</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of all organic compounds and cobalt complexes were recorded on a Bruker Avance 400 MHz instrument at room temperature using TMS as an internal standard. By contrast, their <sup>19</sup>F NMR spectra were recorded on an AVANCE III 500WB spectrometer at 470.50 MHz at room temperature with 32 scans. Elemental analyses were carried out using a Flash EA 1112 microanalyzer and FT-IR spectra were recorded on a PerkinElmer System 2000 FT-IR spectrometer. The molecular weight (*M*<sub>w</sub>) and dispersity (*M*<sub>w</sub>/*M*<sub>n</sub>) of the polyethylenes were

measured using a PL-GPC220 instrument operating at 150 °C using 1,2,4-trichlorobenzene as the solvent. The melt temperatures ( $T_m$ ) of the polyethylenes were measured from the second scanning run on a PerkinElmer TA-Q2000 DSC analyzer under a nitrogen atmosphere. The program was set as follows: a sample (4.0 – 6.0 mg) was heated to 150 °C at a rate of 20 °C min<sup>-1</sup> and kept for 5 min at 150 °C to remove the thermal history and cooled to -20 °C at a rate of 20 °C min<sup>-1</sup>. Inverse gated <sup>13</sup>C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 spectrometer at 75.47 MHz in 5 mm standard glass tubes at 100 °C with the number of scans set between 1500 and 2000. Operating conditions used: spectral width 17.9856 kHz; acquisition time 1.8219 s; relaxation delay 2.0 s. The sample preparation for the <sup>13</sup>C NMR studies involved dissolving a weighed amount of polyethylene (80 – 100 mg) in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> (2 mL) by warming with a heat gun.

### Synthesis of 2-{CMeN{2,6-(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}-6-(CMeO)C<sub>5</sub>H<sub>3</sub>N} (1) and 2,6-[CMeN{2,6-((4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH)<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (L6)

To a solution of 2,6-diacetylpyridine (1.60 g, 10.0 mmol) and 2,6-difluorobenzhydryl-4-(*tert*-butyl)aniline (4.40 g, 8.0 mmol) in toluene (100 mL) was added a catalytic amount of *p*-toluenesulfonic acid (1.6 mmol). The reaction mixture was stirred and heated at reflux for 6 h. After cooling to room temperature, the mixture was filtered and all volatiles evaporated under reduced pressure. The residue was purified by column chromatography using basic alumina and an eluent composed of petroleum ether/ethyl acetate (100/1), affording firstly **1** as a light yellow crystalline solid (2.10 g, 30%) followed by **L6** as a pale yellow powder (1.10 g, 22%).

Compound **1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.11 (d,  $J$  = 8.0 Hz, 2H, 2 × Py-H<sub>m</sub>), 7.88 (t,  $J$  = 7.8 Hz, 1H, Py-H<sub>m</sub>), 6.95–6.89 (m, 16H, Ar-H), 7.01 (s, 2H, Ar-H), 5.22 (s, 2H, 2 × CH(*p*-FPh)<sub>2</sub>), 2.70 (s, 3H, O=CCH<sub>3</sub>), 1.24 (m, 3H, N=CCH<sub>3</sub>), 1.13 (m, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 200.3, 169.3, 162.9, 160.5, 160.4, 155.4, 152.7, 145.9, 145.7, 139.4, 138.6, 137.5, 131.6, 131.4, 131.3, 131.0, 130.9, 125.3, 124.6, 122.9, 115.6, 115.4, 115.3, 115.0, 51.2, 34.7, 31.6, 25.8, 17.2. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 116.41, 116.93.

Compound **L6**: FT-IR (cm<sup>-1</sup>): 3067 (w), 3039 (w), 2961 (w), 1641 (ν<sub>C=N</sub>, m), 1602 (m), 1506 (s), 1454 (m), 1421 (w), 1367 (w), 1293 (w), 1227 (s), 1158 (m), 1115 (m), 1016 (m), 878 (m), 831 (s), 798 (m), 724 (w). Anal. Calcd for C<sub>81</sub>H<sub>67</sub>F<sub>8</sub>N<sub>3</sub> (1234.44): H, 5.47; N, 3.40; C, 78.81. Found: H, 5.42;

N, 3.12; C, 78.43%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  8.02 (d,  $J = 7.8$  Hz, 2H,  $2 \times \text{Py-H}_m$ ), 7.78 (t,  $J = 7.8$  Hz, 1H,  $\text{Py-H}_p$ ), 6.96–6.93 (m, 24H, Ar-H), 6.88–6.84 (m, 12H, Ar-H), 5.24 (s, 4H,  $4 \times \text{CH}(p\text{-FPh})_2$ ), 1.11 (s, 18H,  $2 \times \text{C}(\text{CH}_3)_3$ ), 1.10 (s, 6H,  $2 \times \text{N}=\text{CCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  169.8, 162.8, 160.4, 160.3, 155.0, 145.8, 145.7, 139.5, 138.6, 138.5, 136.8, 131.6, 131.3, 131.2, 130.9, 130.8, 125.2, 115.5, 115.3, 115.2, 115.0, 51.0, 34.6, 31.5, 17.3.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  116.40, 116.98.

### Syntheses of 2-[CMeN{2,6-[(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}] -6-(CMeNAr)C<sub>5</sub>H<sub>3</sub>N

(a) Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L1**: A toluene (20 mL) solution containing **1** (0.70 g, 1.0 mmol) and a catalytic amount of *p*-toluenesulfonic (*ca.* 0.20 mmol) was stirred and heated until dissolution. 2,6-Dimethylaniline (0.17 g, 1.40 mmol) was then added dropwise and the reaction mixture left to stir at reflux for 6 h. On completion of the reaction (checked by silica TLC), the mixture was cooled to room temperature and then filtered. The filtrate was then concentrated on the rotary evaporator and the residue purified by basic alumina column chromatography using petroleum ether/ethyl acetate as the eluent (70/1 v/v), affording **L1** as a pale yellow powder (0.31 g, 39%). FT-IR ( $\text{cm}^{-1}$ ): 3067 (w), 3039 (w), 2962 (m), 1636 ( $\nu_{\text{C}=\text{N}}$ , m), 1599 (m), 1570 (w), 1504 (s), 1455 (m), 1415 (m), 1365 (m), 1298 (w), 1218 (s), 1156 (m), 1119 (m), 1095 (m), 1015 (m), 878 (m), 817 (s), 756 (m), 732 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  8.44 (d,  $J = 7.6$  Hz, 1H,  $\text{Py-H}_m$ ), 8.00 (d,  $J = 7.6$  Hz, 1H,  $\text{Py-H}_m$ ), 7.84 (t,  $J = 7.6$  Hz, 1H,  $\text{Py-H}_p$ ), 7.09 (d,  $J = 7.6$  Hz, 2H, aryl-H), 6.98–6.87 (m, 17H, aryl-H), 6.84 (s, 2H, aryl-H), 5.25 (s, 2H,  $2 \times \text{CH}(p\text{-FPh})_2$ ), 2.13 (s, 3H,  $\text{N}=\text{CCH}_3$ ), 2.07 (s, 6H,  $2 \times \text{CH}_3$ ), 1.26 (s, 3H,  $\text{N}=\text{CCH}_3$ ), 1.12 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  169.8, 167.3, 162.7, 160.3, 155.3, 154.9, 148.8, 145.7, 145.5, 139.3, 138.6, 136.9, 131.5, 131.3, 131.2, 130.9, 130.8, 128.1, 125.5, 125.1, 123.2, 122.3, 122.2, 51.9, 34.5, 31.5, 18.1, 17.3, 16.5.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  116.59, 117.02. Anal. Calcd for C<sub>53</sub>H<sub>47</sub>F<sub>4</sub>N<sub>3</sub> (801.97): H, 5.91; N, 5.24; C, 79.38. Found: H, 5.98; N, 4.98; C, 79.05%.

(b) Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L2**: Using the same procedure and molar ratios of reactants as that outlined for the synthesis of **L1** but with 2,6-diethylaniline as the amine, **L2** was isolated as a pale yellow powder (0.37 g, 45%). FT-IR ( $\text{cm}^{-1}$ ): 3069 (w), 3039 (w), 2965 (m), 1632 ( $\nu_{\text{C}=\text{N}}$ , m), 1600 (m), 1568 (w), 1505 (s), 1452 (m), 1415 (m), 1365 (m), 1297 (w), 1218 (s), 1194 (m), 1156 (m), 1096 (m), 1015 (m), 876 (m), 816 (s), 763 (m), 730 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  8.41 (d,  $J$

= 7.2 Hz, 1H, Py-H<sub>m</sub>), 8.00 (d,  $J$  = 7.6 Hz, 1H, Py-H<sub>m</sub>), 7.84 (t,  $J$  = 7.8 Hz, 1H, Py-H<sub>p</sub>), 7.12 (d,  $J$  = 7.2 Hz, 2H, Ar-H), 7.04 (t,  $J$  = 7.6 Hz, 1H, Ar-H), 6.97–6.86 (m, 16H, Ar-H), 6.84 (s, 2H, Ar-H), 5.24 (s, 2H, 2 × CH(*p*-FPh)<sub>2</sub>), 2.46–2.33 (m, 4H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 2.14 (s, 3H, N=CCH<sub>3</sub>), 1.25 (s, 3H, N=CCH<sub>3</sub>), 1.16 (t,  $J$  = 7.8 Hz, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 1.11 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 169.6, 166.9, 162.6, 162.5, 160.1, 155.1, 145.8, 147.7, 145.6, 145.3, 139.2, 138.4, 136.7, 131.3, 131.1, 130.9, 130.7, 130.6, 125.9, 124.9, 123.3, 122.1, 50.8, 34.3, 31.3, 24.5, 17.1, 17.0, 13.7. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 116.58, 117.01. Anal. Calcd for C<sub>55</sub>H<sub>51</sub>F<sub>4</sub>N<sub>3</sub> (830.03): H, 6.19; N, 5.06; C, 79.59. Found: H, 6.27; N, 4.85; C, 79.53%.

(c) Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L3**: Using the same procedure and molar ratios of reactants as that outlined for the synthesis of **L1** but with 2,6-diisopropylaniline as the amine, **L3** was isolated as a pale yellow powder (0.51 g, 59%). FT-IR (cm<sup>-1</sup>): 3065 (w), 3039 (w), 2962 (m), 1634 (ν<sub>C=N</sub>, m), 1601 (m), 1571 (w), 1504 (s), 1454 (m), 1416 (m), 1364 (m), 1298 (w), 1223 (s), 1192 (m), 1157 (m), 1098 (m), 1016 (m), 873 (m), 814 (s), 766 (m), 730 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.40 (d,  $J$  = 7.6 Hz, 1H, Py-H<sub>m</sub>), 8.00 (d,  $J$  = 7.6 Hz, 1H, Py-H<sub>m</sub>), 7.84 (t,  $J$  = 7.8 Hz, 1H, Py-H<sub>p</sub>), 7.18 (d,  $J$  = 7.6 Hz, 2H, Ar-H), 7.11 (t,  $J$  = 7.6 Hz, 1H, Ar-H), 6.97–6.86 (m, 16H, Ar-H), 6.84 (s, 2H, Ar-H), 5.25 (s, 2H, 2 × CH(*p*-FPh)<sub>2</sub>), 2.80–2.73 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15 (s, 3H, N=CCH<sub>3</sub>), 1.26 (s, 3H, N=CCH<sub>3</sub>), 1.18 (d,  $J$  = 6.8 Hz, 12H, 2 × CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 169.7, 167.0, 162.6, 162.5, 160.1, 155.1, 154.8, 146.4, 145.6, 145.4, 139.2, 139.1, 138.4, 136.7, 135.7, 131.4, 131.1, 131.0, 130.7, 130.6, 124.9, 123.6, 123.0, 122.2, 53.4, 50.8, 34.3, 31.3, 28.3, 23.2, 22.9, 17.1, 17.0. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 116.57, 117.01. Anal. Calcd for C<sub>57</sub>H<sub>55</sub>F<sub>4</sub>N<sub>3</sub> (858.08): H, 6.46; N, 4.90; C, 79.79. Found: H, 6.29; N, 4.58; C, 79.48%.

(d) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **L4**: Using the same procedure and molar ratios of reactants as that outlined for the synthesis of **L1** but with 2,4,6-trimethylaniline as the amine, **L4** was isolated as a pale yellow powder (0.41 g, 50%). FT-IR (cm<sup>-1</sup>): 3064 (w), 3039 (w), 2963 (m), 1638 (ν<sub>C=N</sub>, m), 1602 (m), 1570 (w), 1505 (s), 1452 (m), 1415 (m), 1365 (m), 1297 (w), 1260 (m), 1222 (s), 1157 (m), 1092 (m), 1016 (m), 873 (m), 814 (s), 796 (m), 733 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.43 (d,  $J$  = 7.6 Hz, 1H, Py-H<sub>m</sub>), 8.01 (d,  $J$  = 8.0 Hz, 1H, Py-H<sub>m</sub>), 7.83 (t,  $J$  = 7.8 Hz, 1H, Py-H<sub>p</sub>), 6.97–6.87 (m, 18H, Ar-H), 6.84 (s, 2H, Ar-H), 5.25 (s, 2H, 2 × CH(*p*-FPh)<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 2.13 (s, 3H, N=CCH<sub>3</sub>), 2.03 (s, 6H, 2 × CH<sub>3</sub>), 1.26 (s, 3H, N=CCH<sub>3</sub>), 1.12 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  169.5, 167.3, 162.5, 162.4, 160.0, 155.1, 154.6, 146.0, 145.5, 145.2, 139.1, 139.0, 138.3, 136.6, 132.1, 131.3, 131.0, 130.9, 130.6, 130.5, 128.4, 125.1, 124.8, 122.0, 121.9, 50.7, 34.2, 20.6, 17.7, 17.0, 16.2. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  116.59, 117.02. Anal. Calcd for C<sub>54</sub>H<sub>49</sub>F<sub>4</sub>N<sub>3</sub> (816.00): H, 6.05; N, 5.15; C, 79.48. Found: H, 5.96; N, 4.88; C, 79.19%.

(e) Ar = 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **L5**: Using the same procedure and molar ratios of reactants as that outlined for the synthesis of **L1** but with 2,6-diethyl-4-methylaniline as the amine, **L5** was isolated as a pale yellow powder (0.43 g, 51%). FT-IR (cm<sup>-1</sup>): 3066 (w), 3038 (w), 2963 (m), 1639 (ν<sub>C=N</sub>, m), 1603 (m), 1570 (w), 1506 (s), 1457 (m), 1414 (m), 1363 (m), 1296 (w), 1226 (s), 1157 (m), 1099 (m), 1017 (m), 873 (m), 829 (s), 766 (m), 726 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.40 (d, *J* = 8.0 Hz, 1H, Py-H<sub>m</sub>), 8.00 (d, *J* = 8.0 Hz, 1H, Py-H<sub>m</sub>), 7.83 (t, *J* = 8.0 Hz, 1H, Py-H<sub>p</sub>), 6.97–6.87 (m, 18H, Ar-H), 6.84 (s, 2H, Ar-H), 5.25 (s, 2H, 2 × CH(*p*-FPh)<sub>2</sub>), 2.44–2.30 (m, 7H, 2 × CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>), 2.14 (s, 3H, N=CCH<sub>3</sub>), 1.26 (s, 3H, N=CCH<sub>3</sub>), 1.15 (t, *J* = 8.0 Hz, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), 1.12 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  169.7, 167.1, 162.6, 162.5, 160.1, 155.3, 154.7, 145.6, 145.3, 145.2, 139.2, 138.4, 136.7, 132.5, 131.4, 131.1, 131.0, 130.7, 130.6, 126.7, 124.9, 122.1, 121.9, 115.2, 115.0, 114.9, 114.7, 50.8, 34.3, 31.3, 24.5, 21.0, 17.1, 16.7, 13.8. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  116.60, 117.03. Anal. Calcd for C<sub>56</sub>H<sub>53</sub>F<sub>4</sub>N<sub>3</sub> (844.05): H, 6.33; N, 4.98; C, 79.69. Found: H, 6.31; N, 4.68; C, 79.42%.

### Syntheses of [2-[CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}] -6-(CMeNAr)C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub>

(a) Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co1**: **L1** (0.16 g, 0.20 mmol) was dissolved in dichloromethane (5 mL) and then added to a solution of CoCl<sub>2</sub> (0.025 g, 0.19 mmol) in ethanol (10 mL) under a nitrogen atmosphere. Upon stirring, the color of the solution changed from yellow to brown and this reaction mixture was then stirred at room temperature for 12 h. All the solvent was removed under reduced pressure and resulting residue dissolved in dichloromethane (3 mL). Hexane was added to induce precipitation and the precipitate collected and dried under reduced pressure to give **Co1** as a brown powder (0.16 g, 88%). FT-IR (cm<sup>-1</sup>): 3026 (w), 2949 (m), 1601 (ν<sub>C=N</sub>, w), 1584 (m), 1506 (s), 1469 (m), 1426 (m), 1369 (m), 1313 (w), 1258 (m), 1219 (s), 1158 (m), 1096 (m), 1021 (m), 876 (w), 837 (s), 821 (s), 781 (s), 725 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  112.47 (s, 1H, Py-H<sub>m</sub>), 111.80 (s, 1H, Py-H<sub>m</sub>), 44.48 (s, 1H, Py-H<sub>p</sub>), 10.01 (s, 2H, Ar-H<sub>m</sub>), 7.19 (s, 2H, Ar'-H<sub>m</sub> (Ar'

represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 7.11 (s, 3H, N=CCH<sub>3</sub>), 2.98 (s, 3H, N=CCH<sub>3</sub>), 1.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.72 (s, 16H, Ar-H (aryl represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), -10.85 (s, 1H, Ar-H<sub>p</sub>), -18.37 (s, 2H, 2 × CH), -25.73 (s, 6H, 2 × CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.28, 118.35. Anal. Calcd for C<sub>53</sub>H<sub>47</sub>Cl<sub>2</sub>CoF<sub>4</sub>N<sub>3</sub> (931.81): H, 5.08; N, 4.51; C, 68.32. Found: H, 4.90; N, 4.34; C, 67.94%.

(b) Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co2**: **Co2** was prepared using a similar procedure and molar ratios to that described for **Co1** affording a brown solid (0.14 g, 78%). FT-IR (cm<sup>-1</sup>): 3028 (w), 2965 (m), 1605 (ν<sub>C=N</sub>, w), 1581 (m), 1507 (s), 1457 (m), 1428 (m), 1373 (m), 1315 (w), 1260 (m), 1227 (s), 1160 (m), 1102 (m), 1021 (m), 880 (w), 841 (s), 813 (s), 783 (s), 726 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 113.57 (s, 1H, Py-H<sub>m</sub>), 112.14 (s, 1H, Py-H<sub>m</sub>), 45.83 (s, 1H, Py-H<sub>p</sub>), 11.06 (s, 2H, Ar-H<sub>m</sub>), 7.82 (s, 2H, Ar'-H<sub>m</sub> (Ar' represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 7.02 (s, 3H, N=CCH<sub>3</sub>), 3.17 (s, 3H, N=CCH<sub>3</sub>), 2.11 (s, 16H, Ar-H ( represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), 1.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), -9.45 (s, 1H, Ar-H<sub>p</sub>), -18.47 (s, 2H, 2 × CH), -19.36 (s, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), -35.08 (s, 2H, CH<sub>2</sub>CH<sub>3</sub>), -40.54 (s, 2H, CH<sub>2</sub>CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.08, 118.57. Anal. Calcd for C<sub>55</sub>H<sub>51</sub>Cl<sub>2</sub>CoF<sub>4</sub>N<sub>3</sub> (959.86): H, 5.36; N, 4.38; C, 68.82. Found: H, 5.08; N, 4.19; C, 68.45%.

(c) Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co3**: **Co3** was prepared using a similar procedure and molar ratios to that described for **Co1** affording a brown solid (0.16 g, 83%). FT-IR (cm<sup>-1</sup>): 3030 (w), 2961 (m), 1601 (ν<sub>C=N</sub>, w), 1588 (m), 1505 (s), 1463 (m), 1370 (m), 1318 (w), 1260 (m), 1225 (s), 1158 (m), 1099 (m), 1023 (m), 880 (w), 840 (s), 813 (s), 794 (s), 730 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 113.95 (s, 2H, Py-H<sub>m</sub>), 48.32 (s, 1H, Py-H<sub>p</sub>), 10.98 (s, 2H, Ar-H<sub>m</sub>), 8.14 (s, 2H, Ar'-H<sub>m</sub> (Ar' represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 7.08 (s, 3H, N=CCH<sub>3</sub>), 2.95 (s, 3H, N=CCH<sub>3</sub>), 2.15 (s, 16H, Ar-H (aryl represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), 1.23 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.85 (s, 2H, Ar-H), -8.64 (s, 1H, Ar-H<sub>p</sub>), -17.96 (s, 12H, 2 × CH(CH<sub>3</sub>)<sub>2</sub>), -19.87 (s, 2H, 2 × CH), -81.28 (s, 2 × CH(CH<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.26, 118.60. Anal. Calcd for C<sub>57</sub>H<sub>55</sub>Cl<sub>2</sub>CoF<sub>4</sub>N<sub>3</sub> (987.91): H, 5.61; N, 4.25; C, 69.30. Found: H, 5.48; N, 4.36; C, 69.08%.

(d) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **Co4**: **Co4** was prepared using a similar procedure and molar ratios to that described for **Co1** affording a brown solid (0.15 g, 83%). FT-IR (cm<sup>-1</sup>): 3028 (w), 2955 (m), 1600 (ν<sub>C=N</sub>, w), 1583 (m), 1505 (s), 1472 (m), 1426 (m), 1371 (m), 1315 (w), 1258 (m), 1220 (s), 1157 (m), 1098 (m), 1019 (m), 880 (w), 837 (s), 817 (s), 786 (s), 726 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 112.76 (s, 1H, Py-H<sub>m</sub>), 110.50 (s, 1H, Py-H<sub>m</sub>), 44.66 (s, 1H, Py-H<sub>p</sub>), 21.13 (s, 2H, Ar-CH<sub>3</sub>), 10.39 (s, 2H, Ar-H<sub>m</sub>), 7.41 (s, 2H, Ar'-H<sub>m</sub> (Ar' represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 7.01 (s, 3H, N=CCH<sub>3</sub>), 3.14 (s, 3H, N=CCH<sub>3</sub>), 2.12 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.91 (s, 16H, Ar-H (Ar represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), -18.01 (s, 2H, 2 × CH), -24.44 (s, 6H, 2 × CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.23, 118.44. Anal. Calcd for C<sub>54</sub>H<sub>49</sub>Cl<sub>2</sub>CoF<sub>4</sub>N<sub>3</sub> (945.83): H, 5.22; N, 4.44; C, 68.57. Found: H, 5.01; N, 4.29; C, 68.38%.

(e) Ar = 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **Co5**: **Co5** was prepared using a similar procedure and molar ratios to that described for **Co1** affording a brown solid (0.16 g, 86%). FT-IR (cm<sup>-1</sup>): 3033 (w), 2966 (m), 1602 (ν<sub>C=N</sub>, w), 1583 (m), 1505 (s), 1462 (m), 1430 (m), 1372 (m), 1309 (w), 1263 (m), 1223 (s), 1160 (m), 1097 (m), 1022 (m), 882(w), 844 (s), 818 (s), 785 (s), 727 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 113.57 (s, 1H, Py-H<sub>m</sub>), 111.17 (s, 1H, Py-H<sub>m</sub>), 46.39 (s, 1H, Py-H<sub>p</sub>), 21.44 (s, 2H, Ar-CH<sub>3</sub>), 10.83 (s, 2H, Ar-H<sub>m</sub>), 7.76 (s, 2H, Ar'-H<sub>m</sub> (Ar' represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 6.94 (s, 3H, N=CCH<sub>3</sub>), 3.20 (s, 3H, N=CCH<sub>3</sub>), 2.08 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.62 (s, 12H, Ar-H (Ar represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), -18.14 (s, 2H, 2 × CH), -19.31 (s, 6H, 2 × CH<sub>2</sub>CH<sub>3</sub>), -34.66 (s, 2H, CH<sub>2</sub>CH<sub>3</sub>), -37.93 (s, 2H, CH<sub>2</sub>CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.10, 118.63. Anal. Calcd for C<sub>56</sub>H<sub>53</sub>Cl<sub>2</sub>CoF<sub>4</sub>N<sub>3</sub> (973.89): H, 5.49; N, 4.31; C, 69.07. Found: H, 5.42; N, 4.03; C, 68.84%.

#### Syntheses of [2,6-[CMeN{2,6-[(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH]<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub> (**Co6**)

**Co6** was prepared using a similar procedure and molar ratios to that described for **Co1** affording a brown solid (0.24 g, 93%). FT-IR (cm<sup>-1</sup>): 3029 (w), 2955 (m), 1599 (ν<sub>C=N</sub>, w), 1506 (s), 1472 (m), 1418 (m), 1368 (m), 1259 (m), 1226 (s), 1159 (m), 1099 (m), 1019 (m), 838 (s), 728 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 116.48 (s, 2H, Py-H<sub>m</sub>), 49.17 (s, 1H, Py-H<sub>p</sub>), 7.93 (s, 4H, Ar'-H<sub>m</sub> (Ar' represents the phenyl core with bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylimino)), 6.66 (s,

6H, 2 × N=CCH<sub>3</sub>), 2.27 (s, 16H, Ar-H (Ar represents bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl)), 2.09 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), -19.79 (s, 2H, 2 × CH). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ 117.57, 118.45. Anal. Calcd for C<sub>81</sub>H<sub>67</sub>Cl<sub>2</sub>CoF<sub>8</sub>N<sub>3</sub> (1364.27): H, 4.95; N, 3.08; C, 71.31. Found: H, 4.77; N, 3.01; C, 70.98%.

### X-ray crystallographic studies

Single crystals of **Co3** and **Co6** were grown by slowly layering hexane onto their dichloromethane solutions at ambient temperature. The X-ray determinations were carried out on a Rigaku Saturn 724+ CCD with graphite-monochromatic Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 173(2) K and the cell parameters obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. Details of the data collection, refinement and crystal data are listed in [Table 1](#). The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  employed SHELXT (Sheldrick, 2015).<sup>[10]</sup> All hydrogen atoms were placed in calculated positions and all non-hydrogen atoms refined anisotropically.

### Typical procedure for ethylene polymerization

*Ethylene polymerization at 5 or 10 atm C<sub>2</sub>H<sub>4</sub>.* The polymerizations at 5 or 10 atm ethylene were carried out in a stainless steel autoclave (250 mL), equipped with an ethylene pressure control system, a temperature controller and a mechanical stirrer. The autoclave was placed under reduced pressure and backfilled with nitrogen two times and ethylene one time. When the required reaction temperature was reached, the precatalyst (2.0 μmol) pre-dissolved in a toluene solution (25 mL), was injected into the autoclave. More toluene (25 mL) was then added to completely wash any residual precatalyst into the autoclave. The required amount of co-catalyst (*i.e.*, MAO, MMAO) was then introduced by syringe followed by more toluene (40 mL) to complete the addition. The autoclave was immediately pressurized to 10 atm C<sub>2</sub>H<sub>4</sub> and the mechanical stirring commenced. After the required reaction time, the ethylene pressure was released and 10% hydrochloric acid in ethanol was used to quench the reaction. The polymer was collected by filtration and washed with ethanol. Following drying under reduced pressure at 100 °C, the polymer sample was weighed.

*Ethylene polymerization at 1 atm C<sub>2</sub>H<sub>4</sub>.* The precatalyst (2.0 μmol) was added into a 50 mL oven-dried Schlenk flask followed by freshly distilled toluene (30 mL). The required amount of

co-catalyst (i.e., MAO or MMAO) was then introduced by syringe under an ethylene atmosphere (1 atm). The solution was then stirred at the required temperature under 1 atm ethylene. After 30 min, the ethylene pressure was vented and the solution quenched with 10% hydrochloric acid in ethanol. The polymer was collected by filtration, dried under reduced pressure at 100 °C and weighed.

## Results and discussion

### Synthesis and Characterization of Co1 – Co6

Five examples of unsymmetrically substituted bis(arylimino)pyridines, 2-[CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]-6-(CMeNAr)C<sub>5</sub>H<sub>3</sub>N (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L1**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L2**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L3**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **L4**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **L5**), have been prepared by employing two successive Schiff base condensation reactions (Scheme 1). Firstly the mono-ketone, 2-[CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]-6-(CMeO)C<sub>5</sub>H<sub>3</sub>N (**1**), was generated by the acid catalyzed reaction of 2,6-diacetylpyridine with 2,6-bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenylaniline and then **1** was used in combination with the corresponding aniline to furnish **L1** – **L5** in reasonable yields (39 – 59%). It is worthy of note that the symmetrically substituted 2,6-{CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (**L6**) was obtained as a byproduct in the initial condensation reaction in moderate yield (22%). Compounds **L1** – **L6** have been fully characterized by <sup>1</sup>H/<sup>13</sup>C/<sup>19</sup>F NMR and FT-IR spectroscopy as well as by elemental analysis (see experimental).

< Scheme 1 >

Interaction of anhydrous CoCl<sub>2</sub> with **L1** – **L6** in a mixed solvent system composed of ethanol and dichloromethane gave [2-[CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}]-6-(CMeNAr)C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co1**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co2**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Co3**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **Co4**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **Co5**) in high yields (78 – 93%) (Scheme 1). Similarly, [2,6-{CMeN{2,6-{(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH}<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N]CoCl<sub>2</sub> (**Co6**) was readily prepared by treating **L6** with cobalt(II) chloride. All new cobalt complexes have been characterized by elemental analysis as well as by <sup>1</sup>H NMR, <sup>19</sup>F NMR and FT-IR spectroscopy. To confirm the structural identity of the complexes, **Co3** and **Co6** were employed as representative examples for single crystal X-ray diffraction studies.

Crystals of **Co3** and **Co6** of a quality suitable for the X-ray determinations were grown by layering hexane onto their dichloromethane solutions at room temperature. Perspective views of each are shown in Figures 2 and 3; selected bond lengths and angles are listed in Table 2. The structures of **Co3** and **Co6** are closely related and hence are described together. In each case a single cobalt center is bound by two chloride ligands and three nitrogen donors, N1, N2 and N3, to afford a distorted square-pyramidal geometry; structurally related five-coordinate species have been previously reported.<sup>[8]</sup> For **Co3**, the cobalt atom lies 0.477 Å above the square base defined by one chloride and the three nitrogen donors, which compares with 0.499 Å for **Co6**. Modest variations are seen in the N-Co-N angles of the tridentate ligands in **Co3** and **Co6** [N1-Co1-N2: 74.4(3)° (**Co3**), 75.26(11)° (**Co6**) vs. N2-Co1-N3: 74.8(3)° (**Co3**), 74.42(10)° (**Co6**)], which likely derives from the steric variations of the particular N-aryl group pair. In terms of the cobalt-nitrogen bond lengths, the central Co–N bond length [2.030(7) Å **Co3**, 2.046(3) Å **Co6**] is shorter than the exterior ones [2.215(7), 2.203(7) Å **Co3**; 2.209(3), 2.224(3) Å **Co6**] on account of the constraints of this ligand class and the superior donor properties of the pyridine moiety.<sup>[8]</sup> The inclination of the N-aryl groups with respect to their neighbouring imine vectors in **Co3** are similar [tors. C38-N1-C8-C9: 85.80°; tors. C44-N3-C46-C47 86.33°], while in **Co6** there is a discernible difference [tors. C38-N1-C8-C9: 85.72°; tors. C44-N3-C46-C47 89.10°]; the latter variation presumably can be attributed to the presence of the two bulky 2,6-bis(bis(4-fluorophenyl)methyl)-4-(*tert*-butyl)phenyl groups. The imine bond lengths are typical of this functionality [1.289(11), 1.262(12) Å **Co3**; 1.286(4), 1.295(4) Å **Co6**], while the Cl-Co-Cl angle [119.19(12)° **Co3**, 117.59(4)° **Co6**] is comparable with that seen in related structures.<sup>[8a,8b,8c]</sup> There are no intermolecular contacts of note.

< Table 2 >

< Figure 2 >

< Figure 3 >

Complexes **Co1** – **Co6** were all paramagnetic as demonstrated by the significant shifts observed in their <sup>1</sup>H NMR spectra with broad peaks identifiable in the range δ +120 to -90 (see Figures S1 – S6). In spite of this paramagnetism, some degree of peak assignment has been achievable through relative integration and closeness to the paramagnetic center as well as by comparison with data recorded for similar cobalt(II) (*S* = 3/2) complexes.<sup>[11,12b]</sup> Using **Co3** as an example, two downfield peaks at δ 48.32 (*F*) and δ 113.95 (*G/G'*) can be assigned to the *para*-pyridyl and *meta*-pyridyl

protons, respectively, which is in line with data reported elsewhere.<sup>[11a,12b]</sup> On the other hand, the inequivalent *meta*-aryl protons can be seen more upfield at  $\delta$  8.14 (*I* for Ar'-*H<sub>m</sub>*) and  $\delta$  10.98 (*E* for Ar-*H<sub>m</sub>*) (Figure 4). As noted in a previous report,<sup>[11a]</sup> the more upfield peaks can be assigned to the isopropyl protons **B** (-17.76, CHMe<sub>2</sub>) and **C** (-81.28, CHMe<sub>2</sub>), while the CH(4-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> protons have been ascribed to the signal at  $\delta$  -19.87.

< Figure 4 >

The <sup>19</sup>F NMR spectra of **Co1** – **Co6** all showed two distinct fluorine resonances that is likely due to the presence of inequivalent CH(4-FC<sub>6</sub>H<sub>4</sub>)<sub>a</sub>(4-FC<sub>6</sub>H<sub>4</sub>)<sub>b</sub> groups (see Figure S7). A similar pair of fluorine resonances is also seen in the <sup>19</sup>F NMR spectra of the free ligands, **L1** – **L6**, but in these cases the signals are found more downfield and are more closely positioned (see Figure S8); representative spectra for **L3**, **Co3**, **L6** and **Co6** are shown Figure 5. In the IR spectra of the complexes, strong  $\nu_{C=N}$  absorption bands are seen in the range 1605 – 1599 cm<sup>-1</sup> which are characteristically around 30 – 40 cm<sup>-1</sup> lower in wavenumber to that seen in the free ligands. Their microanalytical data further supports the LCoCl<sub>2</sub> compositions proposed.

< Figure 5 >

### Catalyst Evaluation for Ethylene Polymerization

To identify a suitable set of conditions that can be used to evaluate all six cobalt precatalysts for the polymerization of ethylene, **Co1** was chosen in the first instance to allow an optimization of various catalytic parameters. Two types of co-catalyst were screened, methylaluminoxane (MAO) and modified methylaluminoxane (MMAO), since both have been shown as among the most effective for the activation of cobalt precatalysts of the type **A** – **E** (Figure 1).<sup>[8,12]</sup> Parameters including run temperature, Al:Co molar ratio, reaction time and ethylene pressure have all been varied using **Co1** and the resulting optimized conditions subsequently applied to **Co2** – **Co6**. All the polymers have been characterized by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC), while the microstructural properties of selected polymer samples have been examined using high temperature <sup>13</sup>C NMR spectroscopy.

(a) *Optimization using Co1/MAO.* To investigate the thermal stability of **Co1**/MAO, the polymerization tests were performed between 40 and 80 °C with the ethylene pressure set at 10 atm and the Al:Co molar ratio at 2000 (entries 1 – 5, Table 3). Inspection of the data reveals that the highest activity of  $7.19 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> was observed at 70 °C (entry 4, Table 3). By way of comparison, structurally related cobalt precatalysts bearing benzhydryl groups devoid of fluoro substituents such as **B** and **C** (Figure 1) attained their best activity at 30 or 40 °C.<sup>[8a,8c]</sup> In terms of the molecular weights of the polyethylenes, these were found to dramatically decrease (from 119.0 to 18.1 kg mol<sup>-1</sup>, Figure 6) with increasing temperature which can attributed to the onset of temperature-induced chain transfer;<sup>[13]</sup> the relatively narrow dispersities ( $M_w/M_n$  range: 2.1 – 4.6) for all the polyethylenes obtained highlight the presence of single site-like active species.

#### < Table 3 >

On reducing the Al:Co molar ratio to 1500 or raising it to 2500, with the temperature maintained at 70 °C, only minor reductions in activity of **Co1**/MAO were seen (entries 4, 7 and 8, Table 3). However, with a ratio of 1000 or 3000 the activity fell by close to half. In terms of the molecular weight of the polymer, higher Al:Co molar ratios caused the unexpected formation of higher molecular weight polyethylene (from 13.8 to 26.6 kg mol<sup>-1</sup>, Figure 7). It is uncertain as to the origin of this unusual behavior but it could plausibly be due to the formation of an increased number of active species at higher molar ratio leading to enhanced chain propagation; a similar observation has been noted elsewhere.<sup>[14a,14b]</sup>

To permit a study of the lifetime of the active species at 70 °C, the polymerization runs using **Co1**/MAO were performed at selected times between 5 and 60 minutes. The highest activity of  $10.1 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> was observed after 5 minutes (entry 10, Table 3) which by the 30 minute mark had dropped by only 19% [ $7.19 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>]. Notably, even after 1 hour the activity had only declined to  $3.94 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>] (entry 13, Table 3), which underlined the remarkable thermal stability of the active species at this temperature.<sup>[15]</sup> The GPC traces showed that longer reactions were accompanied by increases in  $M_w$  from 14.4 to 21.2 kg mol<sup>-1</sup> (Figure 8). Narrow molecular weight distributions ( $M_w/M_n$ : 2.3 – 2.9) again provided an indication that single-site type active species are involved in the catalytic process.

On reducing the pressure from 10 to 1 atm C<sub>2</sub>H<sub>4</sub> the molecular weight of the polymer formed using **Co1**/MAO significantly dropped (entries 4 and 14, Table 3), while at 5 atm C<sub>2</sub>H<sub>4</sub> the

molecular weight was as expected between that observed at the two limiting pressures (entries 4, 14, 15, Table 3).<sup>[16,17]</sup> Likewise the catalytic activity showed a similar downward trend as the ethylene pressure was decreased with value at 5 atm about half that achieved at 10 atm.

< Figure 6 >-

< Figure 7 >

< Figure 8 >

(b) *Optimization using Co1/MMAO*. To compare the effectiveness of the co-catalyst, we also examined the performance of **Co1** using MMAO at 10 atm C<sub>2</sub>H<sub>4</sub>. As before, the first stage of catalyst optimization focused on the effect of temperature by performing polymerization runs over the 20 to 70 °C range (entries 1 – 6, Table 4). The highest activity of  $3.27 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> was observed at 30 °C (entry 2, Table 4) which was almost half that seen with MAO [ $7.19 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> at 70 °C], but of a similar level to that seen with previously reported cobalt analogues studied at the same temperature.<sup>[17]</sup> It is also worthy of note, that the runs performed between 40 and 60 °C saw lower but comparable activity [ $2.47 - 2.07 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>] but then fell more noticeably at 70 °C [ $1.14 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>]. It is unclear as to the origin of the difference in thermal stability observed when using MAO (30 °C) and MMAO (70 °C), but is likely due to the differences in the activation process. With respect to the molecular weight of the polymers formed using **Co1**/MMAO, these were found to progressively drop from 254.3 kg mol<sup>-1</sup> at 20 °C to 34.1 kg mol<sup>-1</sup> at 70 °C on account of increased chain transfer with temperature (Figure S9).

< Table 4 >

With the temperature maintained at 30 °C, the effect of the Al:Co molar ratio (1000 - 3000) on the performance of **Co1**/MMAO was studied (entries 2, 7 – 10, Table 4). A peak in activity of  $3.39 \times 10^6$  g PE mol<sup>-1</sup>(Co) h<sup>-1</sup> was identified with an Al:Co ratio of 2500. As was the case with MAO, the molecular weight was seen to steadily rise as the ratio was increased from 1000 to 3000 which as alluded to earlier may be due to an increased concentration of active species at higher molar ratios (Figure S10).<sup>[14a,14b]</sup>

In terms of run time, the maximum activity of  $9.84 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> was observed after 5 minutes (entry 11, Table 4), which is essentially the same as that observed at 70 °C using

MAO over the same time period (entry 10, Table 3). However, the lifetime of the active species decreased much faster than that seen using **Co1**/MAO with a 65% loss in activity observable after 30 minutes [ $3.39 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>]. On the other hand, after one hour the activity had only reduced to  $2.59 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>] indicating that deactivation become more gradual over more extended run times. These collective findings indicate that the active species was quickly formed using MMAO without any significant induction period and then experienced a rapid deactivation process over the first thirty minutes before assuming a more constant level of performance.<sup>[14,15,18]</sup> Meanwhile, the molecular weight increased from 155.9 kg mol<sup>-1</sup> after 5 minutes to 206.5 kg mol<sup>-1</sup> at the one hour mark in line with increased chain propagation (entries 2, 11 – 14, Table 4).

With the ethylene pressure reduced to 1 atm (entry 15, Table 4), the activity of **Co1**/MMAO at 30 °C was about a quarter of that at 10 atm (entry 9, Table 4) and around two thirds that at 5 atm (entry 16, Table 4). In comparison with the 1 atm pressure polymerization using **Co1**/MAO, that performed with MMAO exhibited marginally better catalytic activity (entry 14, Table 3 vs. entry 14, Table 4).

(c) *Effect of Ligand Structure on Ethylene Polymerization.* To investigate the influence of structural variations to the precatalyst on catalyst performance and polymer properties, **Co2** – **Co6**, were additionally screened (Table 5). Under the optimum polymerization conditions established for **Co1**/MAO [Al:Co = 2000, temperature = 70 °C, run time = 30 min], **Co1** – **Co6**/MAO generally displayed good catalytic activities with values falling in the range  $0.49 - 7.19 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> that varied in the order: **Co1** > **Co4** > **Co2** > **Co5** > **Co3** >> **Co6** (Figure 9). Two key trends can be extracted from this data that derive from steric and electronic effects. With regard to the latter, the *para*-methyl substituted precatalysts, **Co4** and **Co5**, are less active than their *para*-hydrogen counterparts, **Co1** and **Co2**, highlighting a detrimental effect of having an electron donating methyl group on the catalytic activity.<sup>[8a,8b,8f]</sup> In terms of steric properties, the lower the hindrance exerted by the *ortho*-R<sup>1</sup> substituents the higher the activity (*e.g.*, for R<sup>2</sup> = H, **Co1** > **Co2** > **Co3**) which implies that sterically bulky groups hinder coordination and insertion of ethylene at the active species.<sup>[1,17]</sup> Indeed, the most sterically bulky **Co6** was by far the least active [ $0.49 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>] which would suggest that the active site has been severely blocked by the two N-2,6-bis(bis(4-fluorophenyl)methyl)-4-*tert*-butylphenyl groups (entry 6, Table 5).<sup>[1,17,19]</sup> With

regard to the molecular weight, the polyethylenes display values ranging from 58.7 kg mol<sup>-1</sup> to 18.5 kg mol<sup>-1</sup> with **Co3** [2,6-di(*i*-Pr)] exhibiting the highest value (entry 3, Table 5) and **Co1** [2,6-di(Me)] the lowest (entry 1, Table 5). This showed that the particular steric properties in **Co3**/MAO are most suitable to promote chain growth leading to polyethylenes with relatively high molecular weights (entries 1 – 6, Table 5).<sup>[1c,17]</sup>

< Table 5 >

< Figure 9 >

Similarly, **Co1** – **Co6**/MMAO were screened using the optimum polymerization conditions determined for **Co1**/MMAO [Al:Co = 2500, run temperature = 30 °C, run time = 30 min] (Table 6). In this case, **Co1** – **Co6**/MMAO displayed a narrower range in catalytic activities ( $0.77 - 4.22 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>) that fell in the order: **Co3** > **Co1** > **Co4** > **Co2** ~ **Co5** >> **Co6** (Figure S12). The order is essentially the same as that seen with MAO with the exception of **Co3** [2,6-di(*i*-Pr)] which finds itself as most active in this series [ $4.22 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>]. It is uncertain as to the reason behind this apparently anomalous behavior but it may be caused by the better solubility of **Co3** at relatively low temperatures. Aside from this observation, electronic and steric factors once again contributed to the order of activity with increasing hindrance leading to lower activity.<sup>[1,17,18]</sup> In terms of the molecular weight of the polymer, this was found to range from 352.5 kg mol<sup>-1</sup> to 206.1 kg mol<sup>-1</sup> which is appreciably higher than seen with MAO on account of the lower temperature employed for the runs. Nevertheless, the polymer formed using **Co3** [2,6-di(*i*-Pr)] again displayed the highest molecular weight of the series highlighting once more the compatibility of its particular steric properties with chain propagation.

< Table 6 >

To investigate the microstructural properties of the polyethylenes, representative samples synthesized under optimum conditions using **Co1**/MAO at 70 °C (entry 1, Table 5) and **Co1**/MMAO (entry 1, Table 6) at 30 °C were characterized by <sup>13</sup>C NMR spectroscopy. High intensity singlets centered around  $\delta$  30.00 were a feature of both spectra that can be assigned to the -(CH<sub>2</sub>)<sub>n</sub>- repeat unit which confirmed the high linearity of the polyethylenes (Figures S13 and S14).<sup>[10,17b]</sup> no evidence of signals corresponding to the polymer end groups could be detected in either spectra. The linearity of these polymers and others investigated in this work was further confirmed by their characteristically high melt temperatures ( $T_m > 130$  °C). Indeed, only the

polymer samples obtained at lower pressure (*i.e.* 1 atm C<sub>2</sub>H<sub>4</sub>) gave  $T_m$ 's of less than 130 °C (entry 14, Table 3).

To enable a comparison of the performance characteristics of the current precatalyst family (**F**, Figure 1) with previously reported **A – E** (Figure 1),<sup>[7f,8a,8b,8c,12b]</sup> the activity and optimum run temperature for specifically **Co4** are presented alongside the data for the mesityl-containing examples of **A – E** (Figure 10); all runs were performed at 10 atm C<sub>2</sub>H<sub>4</sub> with MAO as activator with the exception of **B** with MMAO. In terms of catalytic activity only **D** and **C** proved significantly more active than **F**. However, **F** maintained its good catalytic activity at a higher temperature (70 °C) when compared to **D** (40 °C), **B** (50 °C) and **C** (20 °C). On the other hand, only **E** appended with 2,4-substituted bis(4-fluorophenyl)methyl substituents, reached its optimal performance at 70 °C and indeed displayed a comparable activity to that seen with mesityl **F** (**Co4**). This latter finding further highlights the positive effect on catalyst stability of placing fluoride substituents on the *para*-positions of the benzhydryl phenyl groups.

< Figure 10 >

## Conclusions

Five types of paramagnetic cobalt(II) chloride complex, **Co1 – Co5**, each chelated by an unsymmetrical bis(arylimino)pyridine incorporating one N-aryl group 2,6-substituted with fluoro-benzhydryl groups, have been successfully prepared; the symmetrically substituted comparator **Co6** is also disclosed. All complexes have been fully characterized by a range of techniques including FT-IR, <sup>1</sup>H NMR and <sup>19</sup>F NMR spectroscopy, elemental analysis and in two cases by single crystal X-ray diffraction. On activation with MAO or MMAO, all the title cobalt complexes showed good to moderate catalytic activities for ethylene polymerization producing strictly linear polyethylene. Notably, in the case of MAO, the catalysts were capable of operating most effectively at 70 °C with activities of up to  $7.19 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup> achievable for **Co1** after half an hour. By contrast, with MMAO the optimal activity of **Co1** was reached at 30 °C and moreover it was less than a half that seen with MAO ( $3.39 \times 10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>) over the same time period. The differences in lifetime of the active species as a consequence of the different activating processes have been identified as contributing factors to the thermal stability. Furthermore, when compared to previous reports, the current MAO-promoted polymerizations operate more effectively at higher temperature which highlights the positive effect of the

introduction of fluoride substituents to the *para*-positions of the dibenzhydryl groups.

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## Notes and references

- [1] a) B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, *120*, 4049–4050. b) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 849–850. c) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728–8740.
- [2] a) B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143–7144. b) G. J. P. Britovsek, S. Mastroianni, G. A. Solan, S. P. D. Baugh, C. Redshaw, V. C. Gibson, A. J. P. White, D. J. Williams, M. R. J. Elsegood, *Chem. Eur. J.* **2000**, *6*, 2221–2231. c) Y. Huang, R. Zhang, T. Liang, X. Hu, G. A. Solan, W.-H. Sun, *Organometallics* **2019**, *38*, 1143–1150. d) Q. Chen, H. Suo, W. Zhang, R. Zhang, G. A. Solan, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, DOI: 10.1039/C9DT01235D.
- [3] a) I. S. Paulino, U. Schuchardt, *J. Mol. Catal. A: Chem.* **2004**, *211*, 55–58. b) Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu, Y. Hu, *J. Mol. Catal. A: Chem.* **2005**, *230*, 1–8. c) J. Liu, Y. Li, J. Liu, Z. Li, *Macromolecules* **2005**, *38*, 2559–2563. d) L.-H. Guo, H.-Y. Gao, L. Zhang, F.-M. Zhu, Q. Wu, *Organometallics* **2010**, *29*, 2118–2125. e) W.-H. Sun, S. Zhang, W. Zuo, *C. R. Chim.* **2008**, *11*, 307–316. f) S. Y. Jie, W.-H. Sun, T. Xiao, *Chin. J. Polym. Sci.* **2010**, *28*, 299–304. g) Z. Wang, G. A. Solan, W. Zhang, W.-H. Sun, *Coord. Chem. Rev.* **2018**, *363*, 92–108.
- [4] a) Y. F. Chen, R. F. Chen, C. T. Qian, X. C. Dong, J. Sun, *Organometallics* **2003**, *22*, 4312–4321. b) C. Görl, H. G. Alt, *J. Organomet. Chem.* **2007**, *692*, 4580–4592.
- [5] a) D. W. Guo, X. Z. Yang, T. Q. Liu, Y. L. Hu, *Macromol. Theory Simulat.* **2001**, *10*, 75–78. b) D. W. Guo, L. Q. Han, T. Z. Zhang, W. H. Sun, T. Li, X. Z. Yang, *Macromol. Theory Simulat.* **2002**, *11*, 1006–1012. c) Y. Chen, W. Yang, R. Sha, R.-D. Fu, W.-H. Sun, *Inorg. Chim. Acta* **2014**, *423*, 450–453. d) W. Yang, Y. Chen, W.-H. Sun, *Macromol. Chem. Phys.* **2014**, *215*, 1810–1817. e) S.

- Ahmed, W. Yang, Z. Ma, W.-H. Sun, *J. Phys. Chem. A* **2018**, *122*, 9637–9644. f) W. Yang, Z. Ma, J. Yi, S. Ahmed, W.-H. Sun, *J. Comput. Chem.* **2019**, *40*, 1374–1386.
- [6] a) J. X. Chen, Y. B. Huang, Z. S. Li, Z. C. Zhang, C. X. Wei, T. Y. Lan, W. J. Zhang, *J. Mol. Catal. A: Chem.* **2006**, *259*, 133–141. b) L.-H. Guo, H.-Y. Gao, L. Zhang, F.-M. Zhu, Q. Wu, *Organometallics* **2010**, *29*, 2118–2125.
- [7] a) J. Yu, H. Liu, W. Zhang, X. Hao, W.-H. Sun, *Chem. Commun.* **2011**, *47*, 3257–3259. b) X. Cao, F. He, W. Zhao, Z. Cai, X. Hao, T. Shiono, C. Redshaw, W.-H. Sun, *Polymer* **2012**, *53*, 1870–1880. c) W. Zhao, J. Yu, S. Song, W. Yang, H. Liu, X. Hao, C. Redshaw, W.-H. Sun, *Polymer* **2012**, *53*, 130–137. d) W.-H. Sun, W. Zhao, J. Yu, W. Zhang, X. Hao, C. Redshaw, *Macromol. Chem. Phys.* **2012**, *213*, 1266–1273. e) S. Wang, B. Li, T. Liang, C. Redshaw, Y. Li, W.-H. Sun, *Dalton Trans.* **2013**, *42*, 9188–9197. f) W. Zhang, S. Wang, S. Du, C.-Y. Guo, X. Hao, W.-H. Sun, *Macromol. Chem. Phys.* **2014**, *215*, 1797–1809. g) Q. Mahmood, J. Guo, W. Zhang, Y. Ma, T. Liang, W.-H. Sun, *Organometallics* **2018**, *37*, 957–970. h) Q. Mahmood, E. Yue, J. Guo, W. Zhang, Y. Ma, X. Hao, W.-H. Sun, *Polymer* **2018**, *159*, 124–137.
- [8] a) J. Yu, W. Huang, L. Wang, C. Redshaw, W.-H. Sun, *Dalton Trans.* **2011**, *40*, 10209–10214. b) J. Lai, W. Zhao, W. Yang, C. Redshaw, T. Liang, Y. Liu, W.-H. Sun, *Polym. Chem.* **2012**, *3*, 787–793. c) F. He, W. Zhao, X. Cao, T. Liang, C. Redshaw, W.-H. Sun, *J. Organomet. Chem.* **2012**, *713*, 209–216. d) Q. Mahmood, Y. Ma, X. Hao, W.-H. Sun, *Appl. Organomet. Chem.* **2019**, *33*, e4857. e) L. Guo, M. Zada, W. Zhang, A. Vignesh, D. Zhu, Y. Ma, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, *48*, 5604–5613. f) J. Guo, Z. Wang, W. Zhang, I. I. Oleynik, A. Vignesh, I. V. Oleynik, X. Hu, Y. Sun, W.-H. Sun, *Molecules* **2019**, *24*, 1176. g) R. Zhang, Y. Huang, G. A. Solan, W. Zhang, X. Hu, X. Hao, W.-H. Sun, *Dalton Trans.* **2019**, DOI: 10.1039/C9DT01345H.
- [9] G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, M. V. Meurs, *J. Am. Chem. Soc.* **2004**, *126*, 10701–10712.
- [10] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3–8. b) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8.
- [11] a) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728–8740. b) G. J. P. Britovsek, V. C. Gibson, S. K. Spitzmesser, K. P. Tellmann, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **2002**, 1159–1171.

- [12] a) Z. Wang, G. A. Solan, Q. Mahmood, Q. Liu, X. Hao, W.-H. Sun, *Organometallics* **2018**, *37*, 380–389. b) Z. Wang, Y. Ma, J. Guo, Q. Liu, G. A. Solan, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, *48*, 2582–2591.
- [13] a) V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745. b) P. Barbaro, C. Bianchini, G. Giambastiani, I. G. Rios, A. Meli, W. Oberhauser, A. M. Segarra, L. Sorace, A. Toti, *Organometallics* **2007**, *26*, 4639. c) A. P. Armitage, Y. D. M. Champouret, H. Grigoli, J. D. A. Pelletier, K. Singh, G. A. Solan, *Eur. J. Inorg. Chem.* **2008**, 4597.
- [14] a) W.-H. Sun, S. Kong, W. Chai, T. Shiono, C. Redshaw, X. Hu, C. Guo, X. Hao, *Appl. Catal. A Gen.* **2012**, *447–448*, 67–73. b) H. Suo, I. I. Oleynik, C. Bariashir, I. V. Oleynik, Z. Wang, G. A. Solan, Y. Ma, T. Liang, W.-H. Sun, *Polymer* **2018**, *149*, 45–54. c) C. Bariashir, Z. Wang, H. Suo, Z. Muhammad, G. A. Solan, Y. Ma, T. Liang, W.-H. Sun, *Eur. Polym. J.* **2019**, *110*, 240–251.
- [15] S. Du, X. Wang, W. Zhang, Z. Flisak, Y. Sun, W.-H. Sun, *Polym. Chem.* **2016**, *7*, 4188–4197.
- [16] D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules* **2000**, *33*, 2320–2334.
- [17] a) T. Xiao, P. Hao, G. Kehr, X. Hao, G. Erker, W.-H. Sun, *Organometallics* **2011**, *30*, 4847–4853. b) S. Du, W. Zhang, E. Yue, F. Huang, T. Liang, W.-H. Sun, *Eur. J. Inorg. Chem.* **2016**, 1748–1755. c) C. Huang, S. Du, G. A. Solan, Y. Sun, W.-H. Sun, *Dalton Trans.* **2017**, *46*, 6948–6957. d) Z. Wang, Y. Ma, J. Guo, Q. Liu, G. A. Solan, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, *48*, 2582–2591.
- [18] D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2005**, *127*, 11037–11046.
- [19] V. K. Appukkuttan, Y. Liu, B. C. Son, C.-S. Ha, H. Suh, I. Kim, *Organometallics* **2011**, *30*, 2285–2294.

### Captions of Tables, Figures, Chart and Scheme

**Table 1** Crystal data and structure refinement for **Co3** and **Co6**.

**Table 2** Selected bond lengths (Å) and angles (°) for **Co3** and **Co6**.

**Table 3** Results of the polymerization screening using **Co1**/MAO<sup>a</sup>.

**Table 4** Results of the polymerization screening using **Co1**/MMAO<sup>a</sup>.

**Table 5** Polymerization results obtained using **Co1** – **Co6**/MAO<sup>a</sup>.

**Table 6** Polymerization results obtained using **Co1** – **Co6**/MMAO<sup>a</sup>.

**Figure 1** Bis(imino)pyridine-containing **A** and its benzhydryl-substituted iron and cobalt derivatives, **B** – **F**.

**Figure 2** ORTEP representation of **Co3** at the 30% probability level. Hydrogen atoms and a molecule of dichloromethane have been omitted for clarity.

**Figure 3** ORTEP representation of **Co6** at the 30% probability level. Hydrogen atoms and one molecule of dichloromethane have been omitted for clarity.

**Figure 4** <sup>1</sup>H NMR spectrum of **Co3** with proton assignments in red; recorded in CDCl<sub>3</sub> at ambient temperature.

**Figure 5** <sup>19</sup>F NMR spectra of **L3**, **Co3**, **L6** and **Co6**; recorded in CDCl<sub>3</sub> at ambient temperature.

**Figure 6** GPC traces of the polyethylenes obtained using **Co1**/MAO at various run temperature (entries 1 – 5, Table 3).

**Figure 7** GPC traces of the polyethylenes obtained using **Co1**/MAO at 70 °C with different molar ratios of MAO (entries 4, 6 – 9, Table 3).

**Figure 8** GPC traces for the polyethylenes produced using **Co1**/MAO at 70 °C over different run times (entries 4, 10 – 13, Table 3).

**Figure 9** Catalytic activities and molecular weights of the polyethylenes obtained using **Co1** – **Co6**/MAO (entries 1 – 6, Table 5).

**Figure 10** Catalytic activity and optimum temperature data for **F** and **A** – **E**; MAO used as activator in all cases and tests conducted under related conditions.

**Scheme 1** Stepwise route to **L1** – **L6** and their corresponding complexes **Co1** – **Co6**.

**Table 1** Crystal data and structure refinement for **Co3** and **Co6**.

Identification code	<b>Co3</b>	<b>Co6</b>
Empirical formula	C <sub>57</sub> H <sub>55</sub> Cl <sub>2</sub> CoF <sub>4</sub> N <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>81</sub> H <sub>67</sub> Cl <sub>2</sub> CoF <sub>8</sub> N <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	1072.79	1449.13
Temperature/K	173.15	173(2)
Crystal system	monoclinic	monoclinic
Space group	Cc	P2 <sub>1</sub> /n
a/Å	28.5404(11)	19.4437(5)
b/Å	13.7331(5)	16.6187(4)
c/Å	19.1143(7)	22.9632(5)
$\alpha$ /°	90	90
$\beta$ /°	131.134(4)	96.757(2)
$\gamma$ /°	90	90
Volume/Å <sup>3</sup>	5642.6(4)	7368.5(3)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.263	1.306
$\mu/\text{mm}^{-1}$	0.545	0.444
F(000)	2228.0	2996.0
Crystal size/mm <sup>3</sup>	0.254 × 0.101 × 0.070	0.581 × 0.295 × 0.094
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection/°	3.52 to 54.966	3.032 to 54.968
Index ranges	-37 ≤ h ≤ 37, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24	-25 ≤ h ≤ 25, -21 ≤ k ≤ 21, -29 ≤ l ≤ 29
Reflections collected	32700	86559
Independent reflections	12398 [R <sub>int</sub> = 0.0887, R <sub>sigma</sub> = 0.1187]	16906 [R <sub>int</sub> = 0.0748, R <sub>sigma</sub> = 0.0579]
Data/restraints/parameters	12398/2/640	16906/0/887
Goodness-of-fit on F <sup>2</sup>	1.010	1.041
Final R indexes [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0824, wR <sub>2</sub> = 0.1903	R <sub>1</sub> = 0.0777, wR <sub>2</sub> = 0.1961
Final R indexes [all data]	R <sub>1</sub> = 0.1489, wR <sub>2</sub> = 0.2317	R <sub>1</sub> = 0.1099, wR <sub>2</sub> = 0.2178
Largest diff. peak/hole / e Å <sup>-3</sup>	0.91/-0.44	0.66/-0.73

**Table 2** Selected bond lengths (Å) and angles (°) for **Co3** and **Co6**

	<b>Co3</b>	<b>Co6</b>
Bond lengths (Å)		
Co(1)–Cl(1)	2.256(3)	2.2974(9)
Co(1)–Cl(2)	2.308(3)	2.2441(10)
Co(1)–N(1)	2.215(7)	2.209(3)
Co(1)–N(2)	2.030(7)	2.046(3)
Co(1)–N(3)	2.203(8)	2.224(3)
N(1)–C(8)	1.446(11)	1.448(4)
N(1)–C(38)	1.289(11)	1.286(4)
N(2)–C(39)	1.358(12)	1.350(4)
N(2)–C(43)	1.333(12)	1.340(4)
N(3)–C(44)	1.272(12)	1.295(4)
N(3)–C(46)	1.430(12)	1.439(4)
Bond angles (°)		
Cl(1)–Co(1)–Cl(2)	119.19(12)	117.59(4)
N(1)–Co(1)–N(3)	144.0(3)	144.98(10)
N(1)–Co(1)–Cl(1)	97.27(19)	98.80(7)
N(1)–Co(1)–Cl(2)	99.52(19)	100.16(8)
N(2)–Co(1)–Cl(1)	149.5(2)	93.07(8)
N(2)–Co(1)–Cl(2)	91.3(2)	149.29(8)
N(2)–Co(1)–N(3)	74.8(3)	74.42(10)
N(2)–Co(1)–N(1)	74.4(3)	75.26(11)
N(3)–Co(1)–Cl(1)	99.8(2)	99.91(7)
N(3)–Co(1)–Cl(2)	99.4(2)	97.00(7)

**Table 3** Results of the polymerization screening using **Co1**/MAO<sup>a</sup>

Entry	T (°C)	t (min)	Al:Co	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m^d$ (°C)
1	40	30	2000	2.73	2.73	119.0	3.3	136.0
2	50	30	2000	3.23	3.23	41.9	4.6	132.4
3	60	30	2000	6.43	6.43	18.7	2.4	130.9
4	70	30	2000	7.19	7.19	18.5	2.4	131.9
5	80	30	2000	3.91	3.91	18.1	2.1	131.4
6	70	30	1000	3.39	3.39	13.8	2.9	134.9
7	70	30	1500	6.68	6.68	18.4	2.2	131.5
8	70	30	2500	6.90	6.90	20.8	2.0	132.7
9	70	30	3000	3.68	3.68	26.6	2.4	132.7
10	70	05	2000	1.68	10.1	14.4	2.4	133.0
11	70	15	2000	4.46	8.92	15.0	2.6	132.1
12	70	45	2000	7.59	5.06	20.9	2.3	133.2
13	70	60	2000	7.87	3.94	21.2	2.9	131.2
14 <sup>e</sup>	70	30	2000	0.20	0.20	6.3	2.4	129.7
15 <sup>f</sup>	70	30	2000	2.73	2.73	16.1	2.3	131.8

<sup>a</sup> General conditions: 2.0  $\mu$ mol of **Co1**, 100 mL of toluene, 10 atm of ethylene.<sup>b</sup> In units of  $10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>.<sup>c</sup>  $M_w$  in units of kg mol<sup>-1</sup>.  $M_w$  and  $M_w/M_n$  were determined by GPC.<sup>d</sup> Determined by DSC.<sup>e</sup> 1 atm of ethylene.<sup>f</sup> 5 atm of ethylene.

**Table 4** Results of the polymerization screening using **Co1**/MMAO<sup>a</sup>

entry	T (°C)	t (min)	Al:Co	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m^d$ (°C)
1	20	30	2000	2.92	2.92	254.3	2.8	137.2
2	30	30	2000	3.27	3.27	197.8	2.9	135.9
3	40	30	2000	2.47	2.47	121.7	2.9	135.2
4	50	30	2000	2.25	2.25	64.0	3.1	132.8
5	60	30	2000	2.07	2.07	45.6	2.3	133.3
6	70	30	2000	1.14	1.14	34.1	1.9	133.4
7	30	30	1000	3.13	3.13	188.4	2.2	137.4
8	30	30	1500	3.22	3.22	192.0	2.3	136.4
9	30	30	2500	3.39	3.39	203.7	2.2	136.2
10	30	30	3000	3.11	3.11	217.6	2.0	136.0
11	30	05	2500	1.64	9.84	155.9	3.1	137.0
12	30	15	2500	2.45	4.90	187.0	2.3	136.5
13	30	45	2500	4.44	2.96	204.3	1.9	136.5
14	30	60	2500	5.19	2.59	206.5	2.9	136.8
15 <sup>e</sup>	30	30	2500	0.87	0.87	86.3	3.3	136.2
16 <sup>f</sup>	30	30	2500	2.05	2.05	169.4	2.6	136.5

<sup>a</sup> General conditions: 2.0  $\mu$ mol of **Co1**, 100 mL of toluene, 10 atm of ethylene.<sup>b</sup> In units of  $10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>.<sup>c</sup>  $M_w$  in units of kg mol<sup>-1</sup>.  $M_w$  and  $M_w/M_n$  were determined by GPC.<sup>d</sup> Determined by DSC.<sup>e</sup> 1 atm of ethylene.<sup>f</sup> 5 atm of ethylene.

**Table 5** Polymerization results obtained using **Co1 – Co6**/MAO<sup>a</sup>

Entry	Precat.	Mass of PE (g)	Activity <sup>b</sup>	$M_w$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	$T_m$ <sup>d</sup> (°C)
1	<b>Co1</b>	7.19	7.19	18.5	2.4	131.9
2	<b>Co2</b>	4.72	4.72	31.8	2.6	132.4
3	<b>Co3</b>	2.94	2.94	58.7	2.2	133.8
4	<b>Co4</b>	5.35	5.35	23.5	2.4	132.0
5	<b>Co5</b>	4.59	4.59	39.1	2.1	132.6
6	<b>Co6</b>	0.49	0.49	35.9	2.7	133.4

<sup>a</sup> General conditions: 2.0  $\mu$ mol of Co complex, 100 mL of toluene, 10 atm of ethylene, 30 min, 70 °C, Al:Co molar ratio = 2000.

<sup>b</sup> In units of  $10^6$  g PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup>  $M_w$  in units of kg mol<sup>-1</sup>.  $M_w$  and  $M_w/M_n$  were determined by GPC.

<sup>d</sup> Determined by DSC.

**Table 6** Polymerization results obtained using **Co1 – Co6**/MMAO<sup>a</sup>

Entry	Precat.	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m^d$ (°C)
1	<b>Co1</b>	3.39	3.39	209.4	2.2	135.9
2	<b>Co2</b>	2.25	2.25	270.1	3.5	136.0
3	<b>Co3</b>	4.22	4.22	352.5	3.3	136.5
4	<b>Co4</b>	3.19	3.19	206.1	3.1	136.9
5	<b>Co5</b>	2.24	2.24	223.3	3.5	136.7
6	<b>Co6</b>	0.77	0.77	280.3	2.3	136.3

<sup>a</sup> General conditions: 2.0  $\mu$ mol of cobalt precatalyst, 100 mL of toluene, 10 atm of ethylene, 30 min, 30 °C, Al:Co molar ratio = 2500.

<sup>b</sup> In units of  $10^6$  g of PE (mol of Co)<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup>  $M_w$  in units of kg mol<sup>-1</sup>.  $M_w$  and  $M_w/M_n$  were determined by GPC.

<sup>d</sup> Determined by DSC.