

Exceptionally high molecular weight linear polyethylene by using *N,N,N'*-Co catalysts appended with a *N'*-2,6-bis{di(4-fluorophenyl)methyl}-4-nitrophenyl group

Dedicated to Professor Dr. Takeshi Shiono on the occasion of his 60th birthday

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Abstract

The bis(arylimino)pyridines, 2-[CMeN{2,6-{(4-FC₆H₄)₂CH}₂-4-NO₂}]₂-6-(CMeNAr)C₅H₃N (Ar = 2,6-Me₂C₆H₃ **L1**, 2,6-Et₂C₆H₃ **L2**, 2,6-*i*-Pr₂C₆H₃ **L3**, 2,4,6-Me₃C₆H₂ **L4**, 2,6-Et₂-4-MeC₆H₂ **L5**), each containing one *N'*-2,6-bis{di(4-fluorophenyl)methyl}-4-nitrophenyl group, have been synthesized by two successive condensation reactions from 2,6-diacetylpyridine. Their subsequent treatment with anhydrous cobalt(II) chloride gave the corresponding *N,N,N'*-CoCl₂ chelates, **Co1** – **Co5**, in excellent yield. All five complexes have been characterized by ¹H/¹⁹F NMR and IR spectroscopy as well as by elemental analysis. In addition, the molecular structures of **Co1** and **Co3** have been determined and demonstrate the differences in steric properties imposed by the inequivalent *N*-aryl groups; distorted square pyramidal geometries are adopted by each complex. Upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), precatalysts **Co1** – **Co5** collectively exhibited very high activities for ethylene polymerization with 2,6-dimethyl-substituted **Co1** the most active (up to 1.1 × 10⁷ g (PE) mol⁻¹ (Co) h⁻¹); the MAO systems were generally more productive. Linear polyethylenes of exceptionally high molecular weight (*M_w* up to 1.3 × 10⁶ g mol⁻¹) were obtained in all cases with the range in dispersities exhibited using MAO as co-catalyst noticeably narrower than with MMAO [*M_w*/*M_n*: 3.55 – 4.77 (**Co1** – **Co5**/MAO) vs. 2.85 – 12.85 (**Co1** – **Co5**/MMAO)]. Significantly, the molecular weights of the polymers generated using this class of cobalt catalyst are higher than any literature values reported to date using related *N,N,N*-bis(arylimino)pyridine-cobalt catalysts.

Keywords: Ethylene polymerization; cobalt catalyst; high activity; high molecular weight linear polyethylene; electron withdrawing groups.

1. Introduction

The discovery of bis(imino)pyridine-cobalt (and iron) complexes, more than twenty ago, that can efficiently mediate the formation of linear polyethylenes represents a major landmark in late transition metal ethylene polymerization catalysis (**A**, Scheme 1) ^[1-3]. Following this ground breaking work, many synthetic efforts have been dedicated to exploring the full potential of these catalysts which have ^[4-15], in large part, been concerned with modifications to the substituents belonging to bis(arylimino)pyridine or related ligand frameworks ^[16-25]. Of particular note have been the raft of steric and electronic variations made to the *ortho*- and *para*-positions of the *N*-aryl groups of the tridentate ligand ^[25]. Elsewhere, ligand development has seen the emergence of bis(imino)pyridines fused with carbocycles that can be varied in terms of their ring size (**B**, $n = 0 - 3$, Scheme 1) ^[26-37]. Collectively, these structural changes to the chelating ligand have seen important correlations with the activity and temperature stability of the active catalyst as well as the molecular weight of the polyethylene.

< Scheme 1 >

With particular regard to bis(imino)pyridine-cobalt catalysts, we have been interested in unsymmetrical examples that possess one *N*-aryl group appended with “super-bulky” benzhydryl groups (CHPh₂) at both *ortho*-positions (**C**, Scheme 1) ^[38-40]. As a general observation all examples of **C** (X = Me ^[38], Cl ^[39], NO₂ ^[40]) have proved highly active albeit with comparable levels despite the difference in electronic properties displayed by the *para*-X substituents. By contrast, the molecular weights of the corresponding polymers showed some distinct differences with the electron-poor catalysts, **C**_{Cl} and **C**_{NO₂}, forming significantly higher molecular weights than that achievable for electron-rich **C**_{Me}. It is noteworthy that similar enhancements in polymer molecular weight have been seen with *N,N*-nickel ^[41] and *N,N,N*-iron ^[42] catalysts incorporating both *ortho*-benzhydryl and electron-withdrawing *para*-NO₂ groups. On the other hand, the addition of fluoro-substituents to the *ortho*-benzhydryl groups themselves, as in **D** (Scheme 1) ^[43], resulted in higher catalytic activity and thermal stability (optimal temperature up to 60 °C) when compared to **C**. In terms of the polyethylene formed, the molecular weight was slightly higher than for **C**_{Me} but notably less than that generated using **C**_{Cl} and **C**_{NO₂} ^[38-40].

With a view to further balancing high activity with high molecular weight, we report our findings concerning the application of bis(arylimino)pyridine-cobalt catalysts appended with one fixed 2,6-bis{di(4-fluorophenyl)methyl}-4-nitrophenyl unit (**E**, Scheme 1). We reasoned that the

combination of the *para*-nitro and *ortho*-difluorobenzydryl groups would have a beneficial effect on the molecular weight while the presence of the fluoro substituents would additionally influence the catalytic activity and the thermal stability. To this end, we report five examples of unsymmetrical **E** in which the steric and electronic profile of the second aryl group has been modified. An in-depth study of these precatalysts for ethylene polymerization is then undertaken with two types of aluminum co-catalyst, and the effects of temperature, Al:Co molar ratio, run time and pressure on catalytic activity and polymer molecular weight explored. Full synthetic and characterization details are additionally presented for the new ligands and complexes.

2. Experimental

2.1. General considerations

All the experimental manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of nitrogen by the use of standard Schlenk techniques., Freshly distilled toluene was used for polymerization runs that had previously been dried over sodium for approximately 10 h before distillation under a nitrogen atmosphere. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were provided by Albemarle Corp. High purity ethylene was provided by Beijing Yanshan Petrochemical Company and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. The compound 2,6-bis(bis(4-fluorophenyl)methyl)-4-nitroaniline was synthesized using a literature route [44]. The ^1H and ^{13}C NMR spectroscopic measurements for the organic compounds as well as cobalt complexes (^1H NMR and ^{19}F NMR) were performed on Bruker DMX 400 (^1H and ^{13}C NMR) and 500 MHz (^{19}F NMR) instruments at room temperature using TMS as an internal standard. All the chemical shifts and coupling constants are given in ppm and in Hz, respectively. Elemental analyses (C, H, and N) were performed on a Flash EA 1112 microanalyzer. FT-IR spectra were recorded using a PerkinElmer System 2000 FT-IR spectrometer. The molecular weights and molecular weight distributions (M_w/M_n) of the polyethylenes were measured using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the solvent. Data collection and processing were performed using Cirrus GPC Software (Beijing, China) and Multi Detector Software (Beijing, China). The calibrants employed for constructing conventional calibration (Polystyrene Calibration KitS-M-10) were provided by PL Company (Beijing, China). The true average molecular weights of the polyethylenes were attained by inputting the

Mark-Houwink constants of polyethylene; K (0.727) and α (40.6) were provided by PL Company (Beijing, China). The samples were dissolved at a concentration of 1.0 to 2.5 mg mL⁻¹, depending on the molecular weights. The DSC traces and melting points of the polyethylene were obtained from the second scanning run on a PerkinElmer TA-Q2000 DSC analyzer under a nitrogen atmosphere. During the procedure, a sample of about 4.0 – 6.0 mg was heated to 160 °C at a heating rate of 20 °C min⁻¹, followed by 5 min at 150 °C to remove the thermal history and then cooled at a rate of 20 °C min⁻¹ to -20 °C. ¹H and ¹³C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 135 °C in deuterated 1,1,2,2-tetrachloroethane with TMS as an internal standard.

2.2. Synthesis of 2-acetyl-6-[1-(2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrophenylimino)ethyl]pyridine (1). To a round bottomed flask containing toluene (100 mL) was added to a mixture of 2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrobenzenamine (3.79 g, 7.0 mmol), 2,6-diacetylpyridine (1.14 g, 7.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The resulting solution was stirred at reflux for 6 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue purified by alumina column chromatography (300/1 petroleum ether/ethyl acetate), affording **1** as a pale yellow powder (1.31 g, 27%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.15 (d, J = 8.1 Hz, 1H, Py- H_m), 8.10 (d, J = 8.1 Hz, 1H, Py- H_m), 7.92 (t, J = 7.9 Hz, 1H, Py- H_p), 7.76 (s, J = 7.8 Hz, 2H, aryl- H), 6.99-6.93 (m, 16H, aryl- H), 5.24 (s, 2H, $CHPh_2$), 2.68 (s, 3H, O=CCH₃), 1.21 (s, 3H, N=CCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 199.4, 169.4, 163.0, 160.5, 153.8, 153.5, 152.7, 143.9, 137.6, 137.3, 136.5, 133.8, 131.0, 130.9, 130.6, 130.5, 124.5, 123.6, 123.3, 116.0, 115.7, 115.6, 115.4, 50.8, 25.5, 17.7. ¹⁹F NMR (470 MHz, CDCl₃): δ -114.9, -115.4.

2.3. Synthesis of 2-[CMeN{2,6-[(4-FC₆H₄)₂CH]₂-4-NO₂}]₂-6-(CMeNAr)C₅H₃N

2.3.1. Ar = 2,6-Me₂C₆H₃ **L1**. To a round bottomed flask containing toluene (100 mL) was added a mixture of 2,6-dimethylaniline (0.22 g, 1.80 mmol), **1** (1.09 g, 1.60 mmol) and a catalytic amount of *p*-toluenesulfonic acid. The resulting solution was stirred at reflux for 6 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue purified by alumina column chromatography (300/1 petroleum ether/ethyl acetate), affording **L1** as a pale yellow powder (0.31 g, 25%). FT-IR (KBr, cm⁻¹): 2930 (w), 2857 (w), 1650 (ν (C=N), m), 1600 (w), 1505 (vs), 1432 (w), 1338 (s), 1225 (vs), 1120 (m), 1097 (m), 914 (w), 882 (w), 841 (m), 764

(w). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.49 (d, $J = 7.2$ Hz, 1H, Py- H_m), 8.00 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.89 (t, $J = 8.0$ Hz, 1H, Py- H_p), 7.77 (s, 2H, aryl- H), 7.09 (d, $J = 7.6$ Hz, 2H, aryl- H), 7.01-6.91 (m, 17H, aryl- H), 5.27 (s, 2H, CHPh_2), 2.12 (s, 3H, $\text{N}=\text{CCH}_3$), 2.06 (s, 6H, $2 \times \text{CH}_3$), 1.25 (s, 3H, $\text{N}=\text{CCH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 166.8, 163.0, 160.5, 155.5, 153.9, 153.4, 148.5, 143.7, 137.3, 137.1, 136.6, 133.8, 131.1, 131.0, 130.6, 130.6, 128.0, 125.3, 123.6, 123.3, 123.0, 122.3, 115.9, 115.7, 115.6, 115.4, 50.7, 29.8, 29.3, 27.2, 18.0, 17.9, 16.4. ^{19}F NMR (470 MHz, CDCl_3): δ -115.1, -115.5. Anal. calcd for $\text{C}_{49}\text{H}_{38}\text{F}_4\text{N}_4\text{O}_2$ (790.85): C, 74.42; H, 4.84; N, 7.08. Found: C, 74.06; H, 5.00; N, 6.99%.

2.3.2. Ar = 2,6-Et $_2$ C $_6$ H $_3$ **L2**. Using a similar procedure as described for **L1** but with 2,6-diethylaniline as the amine, **L2** was isolated as a pale yellow powder (0.28 g, 23%). FT-IR (KBr, cm^{-1}): 2964 (w), 2880 (w), 1650 ($\nu(\text{C}=\text{N})$, m), 1601 (w), 1506 (vs), 1448 (w), 1338 (s), 1226 (vs), 1121 (w), 1098 (m), 911 (w), 881 (w), 841 (m), 768 (m). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.47 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.99 (d, $J = 8.0$ Hz, 1H, Py- H_m), 7.89 (t, $J = 7.6$ Hz, 1H, Py- H_p), 7.77 (s, 2H, aryl- H), 7.13 (d, $J = 7.6$ Hz, 2H, aryl- H), 7.05 (t, $J = 8.0$ Hz, 1H, aryl- H), 7.01-6.91 (m, 16H, aryl- H), 5.28 (s, 2H, CHPh_2), 2.47-2.31 (m, 4H, $2 \times \text{CH}_2$), 2.13 (s, 3H, $\text{N}=\text{CCH}_3$), 1.26 (s, 3H, $\text{N}=\text{CCH}_3$), 1.16 (t, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 169.9, 166.6, 162.9, 160.5, 155.6, 153.9, 153.4, 147.6, 143.7, 137.3, 137.1, 136.6, 133.8, 131.1, 131.0, 130.6, 130.6, 130.5, 126.0, 123.5, 123.0, 122.3, 115.9, 115.7, 115.6, 115.4, 50.7, 29.3, 27.2, 24.6, 17.9, 16.7, 14.1, 13.8. ^{19}F NMR (470 MHz, CDCl_3): δ -114.9, -115.4. Anal. calcd for $\text{C}_{51}\text{H}_{42}\text{F}_4\text{N}_4\text{O}_2$ (818.90): C, 74.80; H, 5.17; N, 6.84. Found: C, 74.41; H, 5.33; N, 6.84%.

2.3.3. Ar = 2,6-*i*-Pr $_2$ C $_6$ H $_3$ **L3**. Using a similar procedure as described for **L1** but with 2,6-diisopropylaniline as the amine, **L3** was prepared as a pale yellow powder (0.21 g, 21%). FT-IR (KBr, cm^{-1}): 2964 (w), 2876 (w), 1650 ($\nu(\text{C}=\text{N})$, m), 1603 (w), 1505 (vs), 1456 (w), 1338 (s), 1223 (vs), 1122 (w), 1098 (w), 914 (w), 881 (w), 841 (m), 766 (m). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.48 (d, $J = 7.6$ Hz, 1H, Py- H_m), 8.00 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.91 (t, $J = 8.0$ Hz, 1H, Py- H_p), 7.77 (s, 2H, aryl- H), 7.18 (d, $J = 7.6$ Hz, 2H, aryl- H), 7.12 (m, 1H, aryl- H), 7.05-6.90 (m, 16H, aryl- H), 5.28 (s, 2H, CHPh_2), 2.79-2.72 (m, 2H, $2 \times \text{CH}$), 2.14 (s, 3H, $\text{N}=\text{CCH}_3$), 1.27 (s, 3H, $\text{N}=\text{CCH}_3$), 1.19 (t, $J = 7.6$ Hz, 12H, $4 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 168.8, 167.1, 160.5, 155.6, 154.0, 153.9, 143.8, 137.3, 137.1, 136.7, 135.6, 133.8,

131.1, 131.0, 130.6, 130.6, 125.9, 123.8, 123.5, 123.1, 122.2, 120.3, 115.9, 115.7, 115.51, 115.4, 112.3, 53.4, 50.7, 28.4, 23.3, 22.9, 19.2, 18.0, 17.0. ^{19}F NMR (470 MHz, CDCl_3): δ -115.0, -115.5. Anal. calcd for $\text{C}_{53}\text{H}_{46}\text{F}_4\text{N}_4\text{O}_2$ (846.95): C, 75.16; H, 5.47; N, 6.62. Found: C, 75.22; H, 5.75; N, 6.31%.

2.3.4. Ar = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ **L4**. Using a similar procedure as described for **L1** but with 2,4,6-trimethylaniline as the amine, **L4** was prepared as a pale yellow powder (0.09 g, 10%). FT-IR (KBr, cm^{-1}): 2964 (w), 2899 (w), 1646 ($\nu(\text{C}=\text{N})$, m), 1602 (w), 1505 (vs), 1434 (w), 1338 (s), 1222 (vs), 1157 (m), 1119 (w), 1099 (m), 915 (w), 880 (w), 840 (m), 765 (w). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.49 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.99 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.88 (t, 1H, Py- H_p), 7.77 (s, 2H, aryl- H), 7.00-6.91 (m, 18H, aryl- H), 5.27 (s, 2H, CHPh_2), 2.30 (s, 3H, $\text{N}=\text{CCH}_3$), 2.11 (s, 3H, $\text{N}=\text{CCH}_3$), 2.02 (s, 6H, $2 \times \text{CH}_3$), 1.25 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 167.0, 163.0, 160.5, 155.7, 153.9, 153.4, 146.0, 143.7, 137.4, 137.3, 137.0, 136.6, 135.7, 133.8, 132.5, 131.1, 131.0, 130.6, 130.6, 128.7, 125.1, 123.5, 123.0, 122.2, 115.9, 115.7, 115.6, 115.4, 53.4, 50.7, 20.7, 17.9, 16.3. ^{19}F NMR (470 MHz, CDCl_3): δ -115.1, -115.5. Anal. calcd for $\text{C}_{50}\text{H}_{40}\text{F}_4\text{N}_4\text{O}_2$ (804.87): C, 74.61; H, 5.01; N, 6.96. Found: C, 74.98; H, 5.03; N, 6.65%.

2.3.5. Ar = 2,6-Et₂-4-MeC₆H₂ **L5**. Using a similar procedure as described for **L1** but with 2,6-diethyl-4-methylaniline as the amine, **L5** was prepared as a pale yellow powder (0.31 g, 25%). FT-IR (KBr, cm^{-1}): 2964 (w), 2885 (w), 1645 ($\nu(\text{C}=\text{N})$, m), 1602 (w), 1505 (vs), 1457 (w), 1338 (s), 1223 (vs), 1157 (m), 1120 (w), 1099 (m), 912 (w), 881 (w), 840 (m), 762 (w). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.47 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.98 (d, $J = 7.6$ Hz, 1H, Py- H_m), 7.88 (t, $J = 8.0$ Hz, 1H, Py- H_p), 7.76 (s, 2H, aryl- H), 7.01-6.90 (m, 18H, aryl- H), 5.27 (s, 2H, CHPh_2), 2.41-2.31 (m, 7H, $2 \times \text{CH}_2$, CH_3), 2.12 (s, 3H, $\text{N}=\text{CCH}_3$), 1.25 (s, 3H, $\text{N}=\text{CCH}_3$), 1.15 (t, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 169.9, 166.7, 163.0, 160.5, 155.7, 153.8, 145.0, 143.7, 137.3, 137.0, 136.6, 135.6, 133.8, 131.0, 130.6, 130.5, 126.8, 123.5, 122.9, 122.2, 115.9, 115.7, 115.6, 115.4, 53.4, 50.7, 31.9, 29.8, 29.3, 27.2, 24.6, 21.0, 17.9, 16.6, 13.9. ^{19}F NMR (470 MHz, CDCl_3): δ -115.1, -115.5. Anal. calcd for $\text{C}_{52}\text{H}_{44}\text{F}_4\text{N}_4\text{O}_2$ (832.92): C, 74.98; H, 5.32; N, 6.73. Found: C, 75.36; H, 5.39; N, 6.52%.

2.4. Synthesis of [2-[CMeN{2,6-{(4-FC₆H₄)₂CH}₂-4-NO₂}]₂-6-(CMeNAr)C₅H₃N]CoCl₂

2.4.1. Ar = 2,6-Me₂C₆H₃ **Co1**. Under a nitrogen atmosphere, a mixture of **L1** (0.27 mmol, 0.21 g), CoCl₂ (0.27 mmol, 0.03 g), dichloromethane (10 mL) and ethanol (5 mL) was stirred at room temperature overnight. All volatiles were then removed under reduced pressure to give a concentrated solution. An excess of diethyl ether was added to induce precipitation and the precipitate collected by filtration and washed with diethyl ether (3 × 10 mL), yielding **Co1** as a brown powder (0.40 g, 81%). FT-IR (KBr, cm⁻¹): 3074 (w), 2972 (w), 2914 (w), 2876 (w), 1628 (ν(C=N), w), 1587 (m), 1508 (vs), 1469 (w), 1434 (w), 1372 (w), 1341 (m), 1224 (s), 1159 (m), 1096 (m), 1022 (w), 915 (w), 881 (w), 837 (s), 781 (m), 737 (w), 664 (w). ¹H NMR (600 MHz, CDCl₃, TMS): δ 117.16 (s, 1H, Py-*H_m*), 108.80 (s, 1H, Py-*H_m*), 43.39 (s, 1H, Py-*H_p*), 10.85 (s, 4H, Ar-*H_m*), 6.82 (s, 6H, aryl-*H*), 3.58 (s, 6H, aryl-*H*), 3.11 (s, 4H, aryl-*H*), 0.88 (s, 2H, 2 × CHPh₂), -4.29 (s, 3H, CH₃), -11.05 (s, 1H, Ar *H_p*), -17.13 (s, 3H, CH₃), -25.53 (s, 6H, 2 × N=CCH₃). ¹⁹F NMR (470 MHz, CDCl₃): δ -115.5, -116.7. Anal. calcd for C₄₉H₃₈Cl₂CoF₄N₄O₂ (920.68): C, 63.92; H, 4.16; N, 6.09. Found: C, 63.60; H, 4.12; N, 6.07%.

2.4.2. Ar = 2,6-Et₂C₆H₃ **Co2**. The synthesis of **Co2** was carried out using a procedure and molar ratios similar to that described for **Co1**, but with **L2** used in place of **L1**. Following work-up, **Co2** was isolated as brown powder (0.11 g, 89%). FT-IR (KBr, cm⁻¹): 3079 (w), 2970 (w), 2878 (w), 1628 (ν(C=N), w), 1605 (w), 1583 (w), 1508 (vs), 1446 (w), 1373 (w), 1342 (s), 1256 (w), 1229 (s), 1159 (m), 1096 (w), 1021 (w), 916 (w), 880 (w), 839 (m), 811 (m), 737 (w), 665 (w). ¹H NMR (600 MHz, CDCl₃, TMS): δ 12.06 (s, 4H, Ar-*H_m*), 6.78 (s, 6H, aryl-*H*), 5.92 (s, 2H, aryl-*H*), 3.73 (s, 6H, aryl-*H*), 2.26 (s, 2H, aryl-*H*), 0.90 (s, 2H, 2 × CHPh₂), -2.97 (s, 4H, 2 × CH₂), -9.48 (s, 1H, Ar-*H_p*). ¹⁹F NMR (470 MHz, CDCl₃): δ -115.4, -116.9. Anal. calcd for C₅₁H₄₂Cl₂CoF₄N₄O₂ (948.74): C, 64.56; H, 4.46; N, 5.91. Found: C, 64.81; H, 4.55; N, 5.92%.

2.4.3. Ar = 2,6-*i*-Pr₂C₆H₃ **Co3**. The synthesis of **Co3** was carried out using a procedure and molar ratios similar to that described for **Co1**, but with **L3** used in place of **L1**. Following work-up, **Co3** was isolated as brown powder (0.07 g, 72%). FT-IR (KBr, cm⁻¹): 3067 (w), 2962 (w), 2921 (w), 2869 (w), 1626 (ν(C=N), w), 1589 (w), 1507 (vs), 1465 (w), 1439 (w), 1373 (w), 1346 (m), 1263 (w), 1231 (s), 1159 (m), 1095 (w), 1021 (w), 915 (w), 882 (w), 837 (m), 796 (w), 722 (w), 665 (w). ¹H NMR (600 MHz, CDCl₃, TMS): δ 119.26 (s, 1H, Py-*H_m*), 111.10 (s, 1H, Py-*H_m*), 47.81 (s, 1H,

Py-*H_p*), 11.93 (s, 4H, Ar-*H_m*), 6.78 (s, 4H, aryl-*H*), 4.70 (s, 4H, aryl-*H*), 3.48 (s, 6H, aryl-*H*), 2.25 (s, 2H, aryl-*H*), 0.87 (s, 2H, 2 × *CHPh*₂), -2.21 (s, 2H, 2 × *CH*), -8.75 (s, 1H, Ar *H_p*), -16.75 (s, 6H, 2 × N=C*CH*₃), -19.35 (s, 12H, 4 × *CH*₃). ¹⁹F NMR (470 MHz, CDCl₃): δ -115.5, -117.0. Anal. calcd for C₅₃H₄₆Cl₂CoF₄N₄O₂ (976.79): C, 65.17; H, 4.75; N, 5.74. Found: C, 64.96; H, 4.84; N, 5.67%.

2.4.4. Ar = 2,4,6-Me₃C₆H₂ **Co4**. The synthesis of **Co4** was carried out using a procedure and molar ratios similar to that described for **Co1**, but with **L4** used in place of **L1**. Following work-up, **Co4** was isolated as brown powder (0.18 g, 71%). FT-IR (KBr, cm⁻¹): 3084 (w), 2917 (w), 2861 (w), 1628 (*ν*(C=N), w), 1589 (w), 1507 (vs), 1437 (w), 1374 (w), 1346 (m), 1261 (w), 1224 (s), 1159 (m), 1097 (w), 1021 (w), 915 (w), 882 (w), 838 (s), 818 (w), 737 (w), 665 (w). ¹H NMR (600 MHz, CDCl₃, TMS): δ 117.22 (s, 1H, Py-*H_m*), 107.99 (s, 1H, Py-*H_m*), 43.44 (s, 1H, Py-*H_p*), 22.40 (s, 3H, *CH*₃), 11.07 (s, 4H, Ar-*H_m*), 6.72 (s, 4H, aryl-*H*), 3.82 (s, 4H, aryl-*H*), 3.66 (s, 6H, aryl-*H*), 2.26 (s, 2H, aryl-*H*), 0.87 (s, 2H, 2 × *CHPh*₂), -4.18 (s, 3H, *CH*₃), -16.89 (s, 3H, *CH*₃), -24.10 (s, 6H, 2 × N=C*CH*₃). ¹⁹F NMR (470 MHz, CDCl₃): δ -115.5, -116.8. Anal. calcd for C₅₀H₄₀Cl₂CoF₄N₄O₂ (934.71): C, 64.25; H, 4.31; N, 5.99. Found: C, 64.04; H, 4.30; N, 5.87%.

2.4.5. Ar = 2,6-Et₂-4-MeC₆H₂ **Co5**. The synthesis of **Co5** was carried out using a procedure and molar ratios similar to that described for **Co1**, but with **L5** used in place of **L1**. Following work-up, **Co5** was isolated as brown powder (0.10 g, 80%). FT-IR (KBr, cm⁻¹): 3079 (w), 2967 (w), 2932 (w), 2878 (w), 1626 (*ν*(C=N), w), 1588 (w), 1507 (vs), 1463 (w), 1373 (w), 1345 (m), 1260 (w), 1224 (s), 1159 (m), 1097 (w), 1021 (w), 913 (w), 838 (s), 737 (w), 665 (w). ¹H NMR (600 MHz, CDCl₃, TMS): δ 118.43 (s, 1H, Py-*H_m*), 108.37 (s, 1H, Py-*H_m*), 45.40 (s, 1H, Py-*H_p*), 23.15 (s, 3H, *CH*₃), 12.11 (s, 4H, Ar-*H_m*), 6.68 (s, 6H, aryl-*H*), 6.00 (s, 2H, aryl-*H*), 3.79 (s, 6H, aryl-*H*), 2.25 (s, 2H, aryl-*H*), 0.87 (s, 2H, 2 × *CHPh*₂), -2.95 (s, 4H, 2 × *CH*₂), -17.32 (s, 3H, *CH*₃), -19.73 (s, 9H, 2 × N=C*CH*₃, *CH*₃). ¹⁹F NMR (470 MHz, CDCl₃): δ -115.3, -117.0. Anal. calcd for C₅₂H₄₄Cl₂CoF₄N₄O₂ (962.76): C, 64.87; H, 4.61; N, 5.82. Found: C, 64.50; H, 4.57; N, 5.94%.

2.5. X-ray crystallographic studies

Single crystals of **Co1** and **Co3** suitable for the X-ray diffraction studies were obtained by layering heptane onto a dichloromethane solution of the corresponding complex at ambient temperature.

With graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. Structure solution was performed by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. Structural solution and refinement were performed by using the SHELXTL-97 package^[45-46]. The free solvent molecules present within the crystal structures were removed by using the SQUEEZE option of the crystallographic program PLATON. Details of the X-ray structure determinations and refinements are provided in Table S1.

2.6. General procedure for ethylene polymerization

2.6.1. Ethylene Polymerization at 1 atm C₂H₄. A pre-weighed amount of **Co1** (2.0 μmol) was placed in a Schlenk vessel, equipped with a magnetic stir bar, followed by freshly distilled toluene (30 mL). The required amount of co-catalyst, MAO or MMAO, was then added via syringe. The reaction mixture was then stirred at 1 atm C₂H₄ at 20 °C. After the required reaction time, the pressure was released and the reaction mixture quenched with 10% hydrochloric acid in ethanol. The resulting polymer was washed with ethanol and then dried under reduced pressure at 60 °C and weighed.

2.6.2. Ethylene Polymerization at 5 or 10 atm C₂H₄. To a 250 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was added via syringe freshly distilled toluene (50 mL) under a blanket of ethylene. The precatalyst (2.0 μmol) in toluene (30 mL), the required amount of co-catalyst (MAO, MMAO) and more toluene (20 mL) were then added successively by syringe. On completion of the addition, the autoclave was heated to the required reaction temperature. The reaction mixture was vigorously stirred for the desired time under the pre-determined pressure of ethylene (5 or 10 atm). Once cooled to room temperature, the ethylene pressure was vented and the reaction mixture quenched with acidified ethanol solution containing 10% hydrochloric acid. The precipitated polymer was collected by filtration, washed with ethanol and water, and the dried under reduced pressure at 60 °C until of constant weight.

3. Results and discussion

3.1. Synthesis and characterization of the ligands and complexes

The unsymmetrical bis(imino)pyridines, 2-[CMeN{2,6-((4-FC₆H₄)₂CH)₂-4-NO₂}]₂-6-(CMeNAr)C₅H₃N (Ar = 2,6-Me₂C₆H₃ **L1**, 2,6-Et₂C₆H₃ **L2**, 2,6-*i*-Pr₂C₆H₃ **L3**, 2,4,6-Me₃C₆H₂ **L4**, 2,6-Et₂-4-MeC₆H₂ **L5**), have been prepared by two consecutive Schiff base condensation reactions, using reaction conditions reported elsewhere [38-40,42-43,47-49]. Firstly, 2,6-diacetylpyridine was reacted with one molar equivalent of 2,6-dibenzhydryl-4-nitrophenylaniline in the presence of a catalytic quantity of *p*-toluenesulfonic acid to give imine-ketone **1** (Scheme 2). Subsequently, reaction of **1** with the corresponding aniline in toluene at reflux gave **L1** – **L5** in reasonable yield.

The cobalt(II) complexes, [2-[CMeN{2,6-((4-FC₆H₄)₂CH)₂-4-NO₂}]₂-6-(CMeNAr)C₅H₃N]CoCl₂ (Ar = 2,6-Me₂C₆H₃ **Co1**, 2,6-Et₂C₆H₃ **Co2**, 2,6-*i*-Pr₂C₆H₃ **Co3**, 2,4,6-Me₃C₆H₂ **Co4**, 2,6-Et₂-4-MeC₆H₂ **Co5**) were then synthesized in high yield (71 - 89%) by the stoichiometric reactions of cobalt dichloride with the requisite **L1** – **L5** in a mixture of ethanol and dichloromethane at room temperature (Scheme 2). As a general observation, **Co1** – **Co5** proved stable in both solution and in the solid state which contrasts with their iron(II) analogues [42]. All organic compounds and complexes have been characterized by FT-IR and NMR spectroscopy as well as by elemental analysis. In addition, the molecular structures of **Co1** and **Co3** have been confirmed by single crystal X-ray diffraction.

< Scheme 2 >

Single crystals of **Co1** and **Co3**, of suitable quality for the X-ray determinations, were grown by the slow diffusion of heptane into a solution of the corresponding complex in a dichloromethane/ethanol mixture at room temperature. Views of **Co1** and **Co3** are depicted in Figures 1 and 2; selected bond distances and angles are presented in Table 1. For **Co1**, two independent molecules (A and B) are present within the unit cell that show only modest differences and mainly relating to the Cl-Co-Cl angle; the following discussion will focus on molecule A. The structures of **Co1** and **Co3** are similar and are based on a penta-coordinate metal center with a geometry that can be best described as pseudo-square pyramidal; related geometries for bis(imino)pyridine-cobalt complexes have been previously reported [38-40,43]. For both complexes, the three nitrogen atoms, N(1), N(2), N(3), and one chlorine atom, Cl(2), form the square base while Cl(1) the apex. The cobalt atom lies 0.564 Å above the basal plane for **Co1** and 0.513 Å for **Co3**. The Co-*N*_{pyridine} bond length [2.068(2) Å **Co1**, 2.036(3) Å **Co3**] is shorter than the exterior Co-*N*_{imino} distances [Co(1)-N(1) 2.143(3) Å **Co1**, 2.141(3) Å **Co3**; Co(1)-N(3)

2.207(2) Å **Co1**, 2.193(3) Å **Co3**], an observation that is common in structurally related comparators and can be accounted for by the superior binding properties of the pyridine and by the constraints imparted by the *N,N,N*-ligand [8-15,38,42-43,47-51]. Some disparity in the Co–*N*_{imino} distances is also evident with the Co(1)–N(3) distance longer than in Co(1)–N(1), which reflects the presence of the more sterically demanding 2,6-bis{di(4-fluorophenyl)methyl}-4-nitrophenyl group linked to N(3). Both the N(1)–C(2) [1.292(4) Å **Co1**, 1.270(4) Å **Co3**] and N(3)–C(8) bond distances [1.270(4) Å **Co1**, 1.282(4) Å **Co3**] are typical of imine functional groups. In addition, the inclination of the 2,6-bis{di(4-fluorophenyl)methyl}-4-nitrophenyl ring with respect to the neighboring imine vector [dihedral angle: 79.0° (**Co1**) and 82.6° (**Co3**)], is inclined closer to perpendicular when compared with the second *N*-aryl group [dihedral angle: 72.0° (**Co1**) and 75.5° (**Co3**)]. Further inspection of the structure reveals the four fluoro-phenyl substituents belonging to the two *ortho*-CH(*p*-FPh)₂ groups provide considerable steric protection to the metal, a feature that is considered to play a crucial role in the polymerization performance [43]. There are no intermolecular contacts of note.

< Figure 1 >

< Figure 2 >

< Table 1 >

All the complexes adopt high spin ($S = 3/2$) configurations which manifests itself in paramagnetically shifted ¹H NMR spectra. In their ¹⁹F NMR spectrum, two distinct fluoride resonances are seen which is likely due to the presence of inequivalent CH(4-FC₆H₄)_a(4-FC₆H₄)_b groups [44,52]. A similar pair of fluorine resonances is seen in the ¹⁹F NMR spectra of the free ligands, **L1** – **L5**, but in these cases the signals are more closely spaced. In the FT-IR spectra for **L1** - **L5**, the C=N stretching vibrations are visible as weak intensity peaks between 1645 – 1650 cm⁻¹. By contrast, the corresponding bands in **Co1** - **Co5** are seen at lower wavenumber between 1626 – 1628 cm⁻¹, which is consistent with effective imine coordination to the cobalt center [38-40,43].

3.2. Catalytic evaluation for ethylene polymerization

To explore the potential of precatalysts **Co1** – **Co5** to mediate the polymerization of ethylene, methylaluminoxane (MAO) and modified methylaluminoxane (MMAO) were chosen as co-catalysts; both aluminoxanes have a reputation for being among the most potent in cobalt

polymerization catalysis [26-40,43]. The effect of the Al:Co molar ratio, reaction temperature, run time and ethylene pressure are all parameters to be investigated. The molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the resultant polyethylenes were determined by gel permeation chromatography (GPC), while their melt temperatures (T_m) were determined by differential scanning calorimetry (DSC). In all cases gas chromatography (GC) was used to detect for any oligomeric fractions. In addition, the structural properties of selected samples of polyethylene were investigated using $^1\text{H}/^{13}\text{C}$ NMR spectroscopy.

3.2.1. *Ethylene Polymerization using Co1/MAO*. In the first instance **Co1** was employed as the test precatalyst in combination with MAO as a means to ascertain the optimum set of operating conditions; the results are tabulated in Table 2.

< Table 2 >

As previously reported, cobalt catalysts tend to be quite sensitive towards reaction temperature [10, 38, 50]. Hence this parameter was explored in the initial stage of the investigation. Firstly, with the Al:Co ratio at 2000 and the ethylene pressure at 10 atm, the polymerization runs using **Co1/MAO** were conducted at temperatures ranging from 20 to 60 °C (entries 1 – 5 in Table 2); the best catalytic performance of 11.11×10^6 g (PE) mol⁻¹ (Co) h⁻¹ was obtained at 20 °C. As the temperature was raised, the catalytic activity steadily reduced reaching a minimal value of 2.85×10^6 g (PE) mol⁻¹ (Co) h⁻¹ at 60 °C, which is likely attributable to partial deactivation of the active species and lower solubility of ethylene at elevated temperature [4-15,38,47-49,53-54]. Nevertheless, this activity at 60 °C was relatively high when compared with related cobalt catalysts at a similar operating temperature [10,13,30,32-38], highlighting the appreciable thermal stability of this catalyst. In terms of the polymer molecular weight, it was evident that increasing the temperature gave polyethylene of lower molecular weight (Figure 3), which is in line with more rapid chain transfer/chain termination at the higher temperature compared to chain propagation [55]. Nonetheless, the molecular weight of the polyethylenes was high (up to 8.25×10^5 g mol⁻¹ at 20 °C), and indeed much higher than that obtained with related cobalt catalysts [11,38,43]. With regard to the dispersities, these gradually broadened (M_w/M_n range: 2.85 – 7.72) as the temperature was increased (Figure 3).

< Figure 3 >

Secondly, with the reaction temperature kept at 20 °C, the Al:Co molar ratio in **Co1/MAO**

was varied from 1000 to 3000 (entries 3, 6 – 11, Table 2). The highest activity of 11.11×10^6 g (PE) mol⁻¹ (Co) h⁻¹ was obtained at an Al:Co molar ratio of 2000. Once again, the molecular weights of the polyethylene were high (range: 5.01×10^5 g mol⁻¹ to 10.17×10^5 g mol⁻¹) and decreased as the Al:Co ratio increased (Figure S1). This latter observation can be credited to greater chain transfer from the cobalt to aluminum at higher Al:Co ratios [56-57]. The corresponding polymer samples showed dispersities in the range 2.85 – 7.62 with the narrowest distribution observable with an Al:Co molar ratio of 2000.

Thirdly, to explore the effect of run time on the active species, evaluation of **Co1**/MAO was performed at intervals between 5 and 60 minutes with the temperature kept at 20 °C (entries 1, 12 – 15, Table 2). After 5 minutes the activity reached an exceptionally high value of 24.18×10^6 g (PE) mol⁻¹ (Co) h⁻¹ before rapidly decreasing at the 15 minute mark and then assuming a more steady downward profile; such high initial activity is typical of a catalyst displaying a very fast or possibly no induction period [58]. Nevertheless, this catalyst still maintained a high activity of 6.49×10^6 g (PE) mol⁻¹ (Co) h⁻¹ even after one hour [33,42], underlining the appreciable lifetime of this catalyst. As for the effects of time on the molecular weight of the polyethylene, the value of M_w was found to increase from 6.40×10^5 g mol⁻¹ after 5 minutes to 11.22×10^5 g mol⁻¹ after 60 minutes (Figure S2), in accord with increased propagation of the polymer chain; no clear trends in dispersity could be identified [59].

When the pressure of ethylene was lowered from 10 to 1 atm, the activity also dramatically dropped from 11.11×10^5 g mol⁻¹ to 0.81×10^5 g mol⁻¹ (entries 1 and 17, Table 2) which can be accounted for, in part, to mass transport limitations of the monomer at this low pressure [53]. Likewise, the molecular weights decreased with a decrease in ethylene pressure, in agreement with less facile insertion and lower solubility of the ethylene monomer in the reaction solvent at lower ethylene pressure [42]. As would be expected the 5 atm C₂H₄ run gave an activity and polymer molecular weight intermediate between that seen at 10 or 1 atm (entry 16, Table 2).

3.2.2. *Ethylene Polymerization using **Co1**/MMAO.* In a manner similar to that described with MAO, **Co1** was again evaluated at 10 atm C₂H₄ this time using MMAO as the co-catalyst; the data are collected in Table 3.

< Table 3 >

As with the **Co1**/MAO runs, the highest activity for **Co1**/MMAO was obtained at a

temperature of 20 °C (Figure 4). Initially, this peak level was achieved with an Al:Co molar ratio of 2000 (entry 1, Table 3), but by raising this ratio to 3000 with the temperature maintained at 20 °C (entry 11, Table 3) saw the activity rise to its maximum level of $7.41 \times 10^5 \text{ g mol}^{-1}$ [*c.f.* $11.11 \times 10^5 \text{ g mol}^{-1}$ using **Co1**/MAO]. In general, the molecular weights of the polyethylenes exhibited similar trends to those observed with MAO, with the value of M_w dropping with temperature and with an increase in Al:Co molar ratio (Figures 4 and S3). However, the molecular weights were in most cases lower than that seen with **Co1**/MAO. Likewise, the catalytic activities for **Co1**/MMAO were, in the main, lower than those achievable using **Co1**/MAO.

< Figure 4 >

With the temperature maintained at 20 °C and the Al:Co molar ratio at 3000, **Co1**/MMAO was screened at reaction times between 5 and 60 minutes (entries 10 and 13 – 16, Table 3). A maximum in activity of was found after 5 minutes of $13.38 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}$ which was noticeably lower than that seen with MAO after the corresponding time [$24.18 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}$]. The decline in activity from 5 to 15 minutes was also less dramatic than that seen with MAO (44% drop vs. 26% with MMAO). After 60 minutes the activity had reached a minimum value of $4.78 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}$, which was slightly less than that seen with MAO at the same time period [$6.49 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}$]. Overall, the activity profile for **Co1**/MMAO over the one hour run was generally more stable than that with MAO albeit displaying less maximum activity. As expected the molecular weight of the polyethylene increased on prolonging the run time from $4.24 \times 10^5 \text{ g mol}^{-1}$ after 5 minutes to $5.90 \times 10^5 \text{ g mol}^{-1}$ after 60 minutes as would be anticipated with greater chain propagation (Figure S4) ^[10,38-40,43].

With the ethylene pressure decreased to 5 atm, a reduced activity of $2.37 \times 10^6 \text{ g (PE) mol}^{-1} \text{ (Co) h}^{-1}$ and a lower molecular weight of $4.41 \times 10^5 \text{ g mol}^{-1}$ were noted (entry 17, Table 3). When the pressure was further decreased to 1 atm, the activity and molecular weight were much lower ($1.75 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}$ and $3.94 \times 10^5 \text{ g mol}^{-1}$, respectively, entry 18, Table 3). Interestingly, **Co1**/MMAO showed higher activity at 1 atm C_2H_4 when compared to **Co1**/MAO and indeed any other cobalt analogues reported to date ^[38,42].

3.2.3. Screening of Co1 - Co5 with either MAO or MMAO. In order to investigate the influence of the ligand structure on the catalytic behavior, **Co2** - **Co5** were additionally screened for ethylene polymerization under the optimum catalytic conditions established independently for **Co1**/MAO

and **Co1**/MMAO; the results are tabulated in Tables 4 and 5.

< Table 4 >

Precatalysts **Co1** – **Co5**, on activation with MAO (optimal conditions: Al:Co ratio = 2000, 10 atm C₂H₄, 20 °C, 30 minutes), collectively displayed good activities [range: 3.32 – 11.1 × 10⁶ g (PE) mol⁻¹ (Co) h⁻¹], falling in the order: **Co1** [2,6-di(Me)] > **Co4** [2,4,6-tri(Me)] > **Co5** [2,6-di(Et)-4Me] ~ **Co2** [2,6-di(Et)] > **Co3** [2,6-di(*i*-Pr)]. In general, the precatalysts containing the least sterically congested 2,6-substitution pattern (**Co1** and **Co4**) gave the highest activity while the most congested (**Co3**) the lowest. Interestingly, **Co4** with an additional methyl group exhibited a lower activity than that displayed with **Co1** which suggests a detrimental effect on catalyst performance by an electron donating group [38,43]. However, this is less clear for the pair, **Co5** and **Co2**, which show comparable levels of activity. Once more, the molecular weight of all the polyethylenes were on the high side with **Co5** giving the highest value of 13.35 × 10⁵ g mol⁻¹. Indeed, this value represents the highest molecular weight polyethylene reported so far using a *N,N,N*-bis(arylimino)pyridine-cobalt catalyst [25]. It was also apparent that the dispersities of the polymers were either reasonably narrow (M_w/M_n 2.9 – 5.3 **Co1** – **Co3**) or broad (M_w/M_n 10.8, 12.9 **Co4**, **Co5**); it is uncertain of the origin of these differences though the *para*-methyl groups in **Co4** and **Co5** may be somehow influential.

< Table 5 >

With MMAO as co-catalyst (optimal conditions: Al:Co ratio = 3000, 10 atm C₂H₄, 20 °C, 30 minutes), **Co1** – **Co5** exhibited noticeably lower activities (range: 1.31 – 5.13 × 10⁶ g (PE) mol⁻¹ (Co) h⁻¹) (entries 1 – 5, Table 5) than that observed with **Co1** – **Co5**/MAO. Likewise, the molecular weights of the resulting polymers were less (3.44 – 5.13 × 10⁵ g mol⁻¹). In terms of the relative order of activity this was found to decrease in the order: **Co1** [2,6-di(Me)] > **Co2** [2,6-di(Et)] > **Co3** [2,6-di(*i*-Pr)] > **Co4** [2,4,6-tri(Me)] > **Co5** [2,6-di(Et)-4Me]. Once again the least bulky **Co1** displays the highest activity and then drops as the steric properties of the *ortho*-positions of the *N*-aryl group progressively increase; this finding can be attributed to the relative ease of ethylene coordination at the active site [10,43]. With regard to electronic effects, the negative influence of a *para*-methyl group on activity is now much clearer to identify with **Co4** and **Co5** undeniably the least active of the series. As with the MAO runs, though not as significant, the dispersities of the polymers were affected by the presence or absence of a *para*-methyl group with **Co4** and **Co5** affording slightly broader values (M_w/M_n : 4.1 – 4.8) than

seen with **Co1** – **Co3** (M_w/M_n : 3.6 – 3.8).

< Figure 5 >

To allow a comparison of the polymer molecular weights with those obtained for previous unsymmetrical bis(imino)pyridine-cobalt catalysts (Scheme 1), the data for mesityl-containing **C** and **D** are presented alongside that for **Co4** (**E**) (Figure 5) [38-40,43]. On inspection of the figure, **Co4** delivers the highest molecular weight polymer of the series (up to 13.35×10^5 g mol⁻¹) while **C_{Me}** the lowest (2.40×10^5 g mol⁻¹). By substituting the *para*-methyl group in **C_{Me}** with firstly a chloride (**C_{Cl}**) and then a nitro group (**C_{NO2}**), a significant increase in molecular weight is observed. Such observations have been ascribed to the electron-withdrawing capacity of these substituents leading to increased electrophilic character of the metal center and in-turn more efficient chain propagation [38,60]. Related arguments can be used to justify the higher molecular weight polymer seen for fluoride-containing **D** when compared to **C_{Me}**. Overall it would seem that the combination of highly electron-withdrawing nitro- and fluoro- groups in **Co4** (**E**) is responsible for the exceptionally high molecular weight of the polyethylene [51].

3.3. Microstructural Properties of the Polyethylenes

All of the polyethylenes obtained with either MAO or MMAO using **Co1** – **Co5** as precatalysts display characteristically high melting temperatures (T_m) of greater than 136 °C, which are typical of highly linear polymeric materials. To gain further information about the structure of these polyethylenes, representative samples obtained using **Co1**/MAO (entry 1, Table 2) and **Co1**/MMAO (entry 1, Table 3) were analyzed by ¹H/¹³C NMR spectroscopy. Typically, the NMR spectra were recorded at 135 °C in deuterated 1,1,2,2-tetrachloroethane. For both samples, the ¹H NMR and ¹³C NMR spectra showed single downfield peaks (¹H *ca.* δ 1.41; ¹³C *ca.* δ 30.0) with chemical shifts that are characteristic of linear polyethylene; Figures 6 and 7 show the corresponding spectra of the polyethylene obtained using **Co1**/MAO (entry 1, Table 2) while those obtained using **Co1**/MMAO are given in Figures S5 and S6 (entry 1, Table 3) [61]. In addition, no evidence for signals corresponding to saturated or unsaturated end groups could be detected which further highlights the high molecular weight of the polymer.

< Figure 6 >

< Figure 7 >

4. Conclusions

Five distinct unsymmetrical bis(arylimino)pyridine-cobalt(II) chloride complexes (**Co1** – **Co5**), each containing one fixed 4-nitro-2,6-difluorobenzhydrylphenyl group and one sterically and electronically variable aryl group, have been prepared and characterized by a broad range of techniques including by single crystal X-ray diffraction (**Co1** and **Co3**). On activation with MAO or MMAO, all the complexes displayed high activities for ethylene polymerization with 2,6-dimethyl-substituted **Co1** exhibiting the highest (1.1×10^7 g (PE) mol⁻¹ (Co) h⁻¹ at 20 °C); a level that is notably higher than that observed for related cobalt precatalysts bearing benzhydryl and benzhydryl-modified substituents. Moreover, these catalysts mediate the formation of strictly linear polyethylenes with very high molecular weights (M_w : as high as 1.33×10^6 g mol⁻¹) and indeed exceeding levels attainable using structurally related cobalt catalysts that have been previously disclosed. This molecular weight enhancement has been accounted for by the joint presence of electron withdrawing nitro and fluoro groups on the ligand manifold and their beneficial effect on chain propagation.

Supporting Information

GPC curves of the Molecular weight (M_w) and dispersity (M_w/M_n), ¹³C NMR and ¹H NMR spectra of the polyethylenes and X-ray crystallographic studies data. CCDC 1923242 and 1923243 contain the supplementary crystallographic data for compounds **Co1** and **Co3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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References

- [1] 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**, 0, 849.
- [2] B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.* **1998**, 120, 4049.
- [3] 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.
- [4] G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, S. Mastroianni, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 1639.
- [5] 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.
- [6] G. J. P. Britovsek, V. C. Gibson, O. D. Hoarau, S. K. Spitzmesser, A. J. P. White, D. J. Williams, *Inorg. Chem.* **2003**, 42, 3454.
- [7] T. M. Smit, A. K. Tomov, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, *Catal. Sci. Technol.* **2012**, 2, 643.
- [8] J. Yu, H. Liu, W. Zhang, X. Hao, W.-H. Sun, *Chem. Commun.* **2011**, 47, 3257.
- [9] W. Zhao, J. Yu, S. Song, W. Yang, H. Liu, X. Hao, C. Redshaw, W.-H. Sun, *Polymer* **2012**, 53, 130.
- [10] S. Wang, B. Li, T. Liang, C. Redshaw, Y. Li, W.-H. Sun, *Dalton Trans.* **2013**, 42, 9188.
- [11] W. Zhang, S. Wang, S. Du, C.-Y. Guo, X. Hao, W.-H. Sun, *Macromol. Chem. Phys.* **2014**, 215, 1797.
- [12] N. V. Semikolenova, W.-H. Sun, *ACS Catalysis*. **2017**, 7, 2868.
- [13] L. Guo, M. Zada, W. Zhang, A. Vignesh, D. Zhu, Y. Ma, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, 48, 5604.
- [14] Q. Chen, H. Suo, W. Zhang, R. Zhang, G. A. Solan, T. Liang, W.-H. Sun, *Dalton Trans.* **2019**, 48, 8264.
- [15] M. Zada, L. Guo, Y. Ma, W. Zhang, Z. Flisak, Y. Sun, W.-H. Sun, *Molecules* **2019**, 24, 2007.
- [16] W. Zhang, W.-H. Sun, C. Redshaw, *Dalton Trans.* **2013**, 42, 8988.
- [17] Z. Flisak, W.-H. Sun, *ACS Catal.* **2015**, 5, 4713.
- [18] C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, *Coord. Chem. Rev.* **2010**, 254, 431.
- [19] V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, 107, 1745.
- [20] C. Bianchini, G. Giambastiani, I. G. Rios, G. Mantovani, A. Meli, A. M. Segarra, *Coord. Chem. Rev.* **2006**, 250, 1391.
- [21] S. Jie, W.-H. Sun, T. Xiao, *Chin. J. Polym. Sci.* **2010**, 28, 299.

- [22] S. Gao, *Inorg. Chem. Front.* **2015**, *2*, 7.
- [23] B. L. Small, *Acc Chem Res.* **2015**, *48*, 2599.
- [24] Z. Ma, W. Yang, W.-H. Sun, *Chinese J. Chem.* **2017**, *35*, 531.
- [25] Z. Wang, G. A. Solan, W. Zhang, W.-H. Sun, *Coord. Chem. Rev.* **2018**, *363*, 92.
- [26] J. Ba, S. Du, E. Yue, X. Hu, Z. Flisak, W.-H. Sun, *RSC Adv.* **2015**, *5*, 32720.
- [27] W. Zhang, W. Chai, W.-H. Sun, X. Hu, C. Redshaw, X. Hao, *Organometallics* **2012**, *31*, 5039.
- [28] 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.
- [29] Y. Huang, R. Zhang, T. Liang, X. Hu, G. A. Solan, W.-H. Sun, *Organometallics* **2019**, *38*, 1143.
- [30] F. Huang, W. Zhang, Y. Sun, X. Hu, G. A. Solan, W.-H. Sun, *New J. Chem.* **2016**, *40*, 8012.
- [31] F. Huang, W. Zhang, E. Yue, T. Liang, X. Hu, W.-H. Sun, *Dalton Trans.* **2016**, *45*, 657.
- [32] 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.
- [33] V. K. Appukkuttan, Y. Liu, B. C. Son, C.-S. Ha, H. Suh, I. Kim, *Organometallics* **2011**, *30*, 2285.
- [34] S. Du, W. Zhang, E. Yue, F. Huang, T. Liang, W.-H. Sun, *Eur. J. Inorg. Chem.* **2016**, *2016*, 1748.
- [35] Z. Wang, G. A. Solan, Q. Mahmood, Q. Liu, Y. Ma, X. Hao, W.-H. Sun, *Organometallics* **2018**, *37*, 380.
- [36] Z. Wang, Y. Ma, J. Guo, Q. Liu, G. A. Solan, *Dalton Trans.* **2019**, *48*, 2582.
- [37] C. Bariashir, Z. Wang, H. Suo, M. Zada, G. A. Solan, Y. Ma, T. Liang, W.-H. Sun, *Eur. Polym. J.* **2019** *110*, 240.
- [38] J. Yu, W. Huang, L. Wang, C. Redshaw, W.-H. Sun, *Dalton Trans.* **2011**, *40*, 10209.
- [39] F. He, W. Zhao, X.-P. Cao, T. Liang, C. Redshaw, W.-H. Sun, *J. Organomet. Chem.* **2012**, *713*, 209.
- [40] Q. Mahmood, Y. Ma, X. Hao, W.-H. Sun, *Appl. Organomet. Chem.* **2019**, *33*, e4857.
- [41] Q. Mahmood, Y. Zeng, X. Wang, Y. Sun, W.-H. Sun, *Dalton Trans.* **2017**, *46*, 6934.
- [42] Q. Mahmood, E. Yue, J. Guo, W. Zhang, Y. Ma, X. Hao, W.-H. Sun, *Polymer* **2018**, *159*, 124.
- [43] S. Wang, W. Zhao, X. Hao, B. Li, C. Redshaw, Y. Li, W.-H. Sun, *J. Organomet. Chem.* **2013**, *731*, 78.
- [44] R. Zhang, Z. Wang, Y. Ma, G. A. Solan, Y. Sun, W.-H. Sun, *Dalton Trans.* **2019**, *48*, 1878.
- [45] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3.
- [46] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.
- [47] X. Cao, F. He, W. Zhao, Z. Cai, X. Hao, T. Shiono, C. Redshaw, W.-H. Sun, *Polymer* **2012**, *53*, 1870.
- [48] W.-H. Sun, W. Zhao, J. Yu, W. Zhang, X. Hao, C. Redshaw, *Macromol. Chem. Phys.* **2012**, *213*, 1266.

- [49] W. Zhao, E. Yue, X. Wang, W. Yang, Y. Chen, X. Hao, X. Cao, W.-H. Sun, *J. Polym. Sci, Part A: Polym. Chem.* **2017**, *55*, 988.
- [50] S. Zhang, W.-H. Sun, T. Xiao, X. Hao, *Organometallics* **2010**, *29*, 1168.
- [51] S. McTavish, G. J. P. Britovsek, T. M. Smit, V. C. Gibson, A. J. P. White, D. J. Williams, *J. Mol. Catal. A: Chem.* **2007**, *261*, 293.
- [52] B. R. McGarvey, *Inorg. Chem.* **1995**, *34*, 6000.
- [53] D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules* **2000**, *33*, 2320.
- [54] L. S. Lee, H. J. Ou, H. F. Hsu, *Fluid Phase Equilib.* **2005**, *231*, 221.
- [55] R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764.
- [56] 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.
- [57] A. K. Tomov, V. C. Gibson, G. J. P. Britovsek, R. J. Long, M. van Meurs, D. J. Jones, K. P. Tellmann, J. Chirinos, *Organometallics* **2009**, *28*, 7033.
- [58] A. A. Barabanov, G. D. Bukatov, V. A. Zakharov, N. V. Semikolenova, L. G. Echevskaja, M. A. Matsko, *Macromol. Chem. Phys.* **2008**, *209*, 2510.
- [59] B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143.
- [60] T. Zhang, D. Guo, S. Jie, W.-H. Sun, T. Li, X. Yang, *J. Polym. Sci. Pol. Chem.* **2004**, *42*, 4765.
- [61] C. Huang, S. Du, G. A. Solan, Y. Sun, W.-H. Sun, *Dalton Trans.* **2017**, *46*, 6948.

Captions of Tables, Figures, and Schemes

Table 1 Selected bond lengths (Å) and angles (°) for **Co1** and **Co3**.

Table 2 Ethylene polymerization by **Co1**/MAO.

Table 3 Ethylene polymerization by **Co1**/MMAO.

Table 4 Ethylene polymerization by **Co1** – **Co5**/MAO under optimized conditions.

Table 5 Ethylene polymerization by **Co1** – **Co5**/MMAO under optimized conditions.

Figure 1 OLEX2 representation of **Co1** (molecule A) with the thermal ellipsoids shown at the 50% probability level; all hydrogen atoms have been omitted for clarity.

Figure 2 OLEX2 representation of **Co3** with the thermal ellipsoids shown at the 50% probability level; all hydrogen atoms have been omitted for clarity.

Figure 3 Molecular weight (M_w) and dispersity (M_w/M_n) versus reaction temperature using **Co1**/MAO.

Figure 4 Molecular weight (M_w) and dispersity (M_w/M_n) versus reaction temperature using **Co1**/MMAO.

Figure 5 Comparison of the molecular weights (M_w) of the polyethylenes obtained using **Co4**/MAO with previously reported cobalt analogues (**C_{Me}**^[38], **C_{Cl}**^[39], **C_{NO₂}**^[40] and **D_{Me}**^[43]); all tests performed at 10 atm C₂H₄ using MAO as co-catalyst.

Figure 6 ¹H NMR spectrum of the polyethylene obtained using **Co1**/MAO at 20 °C; recorded in 1,1,2,2-tetrachloroethane-*d*₂ at 135 °C (entry 1, Table 2).

Figure 7 ¹³C NMR spectrum of the polyethylene obtained using **Co1**/MAO at 20 °C; recorded in 1,1,2,2-tetrachloroethane-*d*₂ at 135 °C (entry 1, Table 2).

Scheme 1 Structural variations in bis(imino)pyridine-cobalt chloride precatalysts (**A** – **E**).

Scheme 2 Synthesis of **L1** – **L5** and their complexes, **Co1** – **Co5**.

Table 1 Selected bond lengths (Å) and angles (°) for **Co1** and **Co3**

	Co1		Co3
	<i>Molecule A</i>	<i>Molecule B</i>	
Bond lengths (Å)			
Co(1)–Cl(1)	2.3022(12)	2.3023(13)	2.2801(10)
Co(1)–Cl(2)	2.2598(13)	2.2427(13)	2.2488(10)
Co(1)–N(1)	2.143(3)	2.151(3)	2.141(3)
Co(1)–N(2)	2.068(2)	2.053(2)	2.036(3)
Co(1)–N(3)	2.207(2)	2.219(2)	2.193(3)
N(1)–C(2)	1.292(4)	1.286(4)	1.270(4)
N(1)–C(42)	1.443(4)	1.423(4)	1.445(4)
N(2)–C(3)	1.332(4)	1.333(4)	1.330(4)
N(2)–C(7)	1.337(4)	1.341(4)	1.336(4)
N(3)–C(8)	1.289(4)	1.289(4)	1.282(4)
N(3)–C(10)	1.430(4)	1.430(4)	1.435(4)
Bond angles (°)			
Cl(1)–Co1–Cl(2)	111.44(5)	114.60(5)	115.05(4)
N(1)–Co1–Cl(1)	101.92(7)	100.29(8)	100.42(8)
N(1)–Co1–Cl(2)	102.45(8)	102.24(8)	103.70(8)
N(1)–Co1–N(2)	74.71(10)	74.78(10)	74.74(11)
N(1)–Co1–N(3)	140.12(9)	140.96(9)	141.31(10)
N(2)–Co1–N(3)	73.18(10)	73.32(10)	73.97(10)
N(2)–Co1–Cl(1)	92.73(8)	91.23(8)	91.21(8)
N(2)–Co1–Cl(2)	155.58(7)	153.95(8)	153.25(8)
N(3)–Co1–Cl(1)	102.62(7)	102.29(7)	102.41(7)
N(3)–Co1–Cl(2)	97.19(7)	96.72(8)	94.33(7)

Table 2 Ethylene polymerization by **Co1**/MAO^a

Entry	Al:Co	t (min)	T (°C)	Mass (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	2000	30	20	11.11	11.11	8.25	2.9	136.2
2	2000	30	30	10.49	10.49	6.04	5.6	136.2
3	2000	30	40	9.73	9.73	4.97	5.8	136.0
4	2000	30	50	3.40	3.40	3.42	7.2	136.0
5	2000	30	60	2.85	2.85	1.50	7.7	134.3
6	1000	30	20	8.07	8.07	10.17	6.8	135.8
7	1500	30	20	8.34	8.34	9.89	4.4	136.0
8	1750	30	20	10.30	10.30	9.72	5.4	136.0
9	2250	30	20	10.98	10.98	7.22	5.1	135.7
10	2500	30	20	8.29	8.29	7.03	5.1	135.9
11	3000	30	20	7.99	7.99	5.01	7.6	136.4
12	2000	5	20	4.03	24.18	6.40	5.2	135.8
13	2000	15	20	6.84	13.68	6.47	6.1	135.9
14	2000	45	20	12.01	8.01	10.18	4.8	135.9
15	2000	60	20	12.98	6.49	11.22	8.6	136.2
16 ^e	2000	30	20	5.83	5.83	4.66	2.9	136.1
17 ^f	2000	30	20	0.81	0.81	3.22	4.4	136.0

^a Conditions: 2.0 μmol of **Co1**, 100 mL of toluene, 10 atm C_2H_4 .

^b Values in units of $10^6 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$.

^c M_w : 10^5 g mol^{-1} ; M_w and M_w/M_n determined by GPC.

^d Determined by DSC.

^e 5 atm C_2H_4 .

^f 1 atm C_2H_4 .

Table 3 Ethylene polymerization by **Co1**/MMAO^a

Entry	Al:Co	t (min)	T (°C)	Mass (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	2000	30	20	4.41	4.41	5.16	4.6	136.2
2	2000	30	30	3.94	3.94	4.97	3.8	135.9
3	2000	30	40	3.07	3.07	2.35	4.2	135.7
4	2000	30	50	2.32	2.32	1.57	4.4	135.4
5	2000	30	60	2.21	2.21	0.75	4.5	134.2
6	1000	30	20	3.25	3.25	9.11	7.7	136.2
7	1500	30	20	3.98	3.98	4.78	4.6	136.2
8	2500	30	20	4.78	4.78	4.77	4.0	136.3
9	2750	30	20	5.02	5.02	3.56	3.3	135.8
10	3000	30	20	7.41	7.41	5.13	3.5	136.3
11	3250	30	20	6.10	6.10	4.61	6.2	136.0
12	3500	30	20	5.25	5.25	1.65	7.7	136.1
13	3000	5	20	2.23	13.38	4.24	4.6	136.1
14	3000	15	20	4.97	9.94	4.95	3.5	135.9
15	3000	45	20	8.83	5.89	5.27	4.5	136.2
16	3000	60	20	9.56	4.78	5.90	6.1	136.4
17 ^e	3000	30	20	2.37	2.37	4.41	2.9	136.2
18 ^f	3000	30	20	1.75	1.75	3.94	4.2	136.2

^a Conditions: 2.0 μmol of **Co1**, 100 mL of toluene, 10 atm C_2H_4 .

^b Values in units of $10^6 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$.

^c M_w : 10^5 g mol^{-1} ; M_w and M_w/M_n determined by GPC.

^d Determined by DSC.

^e 5 atm C_2H_4 .

^f 1 atm C_2H_4 .

Table 4 Ethylene polymerization by **Co1** – **Co5**/MAO under optimized conditions^a

Entry	Precat.	Mass (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	Co1	11.11	11.11	8.25	2.9	136.2
2	Co2	4.58	4.58	9.39	4.6	135.9
3	Co3	3.32	3.32	9.56	5.3	136.2
4	Co4	8.71	8.71	8.43	10.8	135.6
5	Co5	4.68	4.68	13.35	12.9	135.7

^a Conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C_2H_4 , 30 min, 20 °C, Al:Co ratio of 2000.

^b Values in units of 10^6 g (PE) mol^{-1} (Co) h^{-1} .

^c M_w : 10^5 g mol^{-1} ; M_w and M_w/M_n determined by GPC.

^d Determined by DSC.

Table 5 Ethylene polymerization by **Co1** – **Co5**/MMAO under optimized conditions^a

Entry	Precat.	Mass (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	Co1	7.41	7.41	5.13	3.6	136.3
2	Co2	5.76	5.76	3.80	3.8	136.7
3	Co3	4.28	4.28	5.12	3.7	136.5
4	Co4	2.75	2.75	4.11	4.1	136.3
5	Co5	1.31	1.31	3.44	4.8	136.2

^a Conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C_2H_4 , 30 min, 20 °C, Al:Co ratio of 3000.

^b Values in units of 10^6 g (PE) mol^{-1} (Co) h^{-1} .

^c M_w : 10^5 g mol^{-1} ; M_w and M_w/M_n determined by GPC.

^d Determined by DSC.