Enhancing Ethylene Polymerization of NNN-Cobalt(II) Precatalysts Adorned with a Fluoro-substituent

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ABSTRACT: Unsymmetrical 2-(1-(2,4-dibenzhydryl-6-fluorophenylimino)-ethyl)-6-(1-alkylphenyl-imino)pyridine compounds (Ar = 2,6-Me2C6H3 in L1; 2,6-Et2C6H3 in L2; 2,6-Pr2C6H3 in L3; 2,4,6-Me3C6H2 in L4; 2,6-Et2-4-Me−C6H3 in L5) were prepared and characterized. The treatment of CoCl2 with the compounds L1–L5 afforded the corresponding cobalt complexes Co1–Co5 in excellent yields. The molecular structures of Co3 and Co4 were determined by single-crystal X-ray diffraction, revealing the distorted-square-pyramidal geometry with three nitrogen atoms and two chlorine atoms around the cobalt center. Compared with previous bis(imino)pyridylcobalt analogues, all of the cobalt precatalysts displayed exceptionally higher activities toward ethylene polymerization with 1.32 × 10^4 g (PE) mol^−1 h^−1 at 60 °C in the presence of a co-catalyst MAO or MMAO. These cobalt catalysts produced highly linear polyethylene (PE) waxes with vinyl end groups and low molecular weight (Mw up to 8.23 kg mol^−1) along with a relatively lower melting point (all-round Tm5s < 128 °C). The narrow dispersity of resultant polyethylene indicated the single-site active species of the catalytic system.

INTRODUCTION

Bis(imino)pyridine related work with its metal complexes being active research for the last two decades has resulted in a lot of unexpected findings for academic and industrial research,1,2 2,6-Bis(imino)pyridyl cobaltous and ferrous halide precatalysts were discovered in the late 1990s with their rich reactivities for ethylene oligo/polymerization producing α-olefins or/and highly linear polyethylenes.1–5 Subsequent modifications of 2,6-bis(imino)pyridine compounds have been made by finely tuning steric/electronic influences of the substituents, enhancing their catalytic productivities.5–23 Meanwhile, the frameworks of ligands for new catalyst models have been explored through employing cyclolysed pyridine derivatives such as 1,8-diminohexahydroacridines,24 2-(1-arylimino)ethyl-8-aryliminotrihydroquinolines,25,26 2,8-bis-(imino)-7,7-dimethylidihydroquinolines,27 2-(1-arylimino ethyl)-9-aryliminotetrahydrocyclopeptapyridines,28–33 α,α′-bis(arylimino)-2,3,5,6-bis(pentamethylene)pyridines,34–42 α,α′-bis(arylimino)-2,3,5,6-bis(penta-/hexamethylene)-pyridines,43–46 and 2-(arylimino)benzylidine-9-aryliminotetrahydrocyclopeptapyridines,47,48 providing alternative precatalysts in ethylene reactivity. With the most fabricated bis(imino) pyridylmetal precatalysts (A, Chart 1), higher activity and better thermostability have been stepwisely achieved by incorporating bulky groups of benzhydryl,39 anthracenyl, or phenethyl,39 the steric hindrances positively have a major influence in improving the catalytic performance.3,4,13,14,39,40 Therefore, our research group and others investigated the introduction of a range of steric hindrances and controlled the steric and electronic effects on the N-aryl group to improve the catalytic performance, as well as on the polymer properties.6,8,10–12,17 Focusing on the cobalt precatalysts bearing unsymmetrical ligands incorporating double ortho-benzhydryl and a range of para-X groups (X = Me6, Cl9, NO21) (Chart 1B), as well as a single ortho-benzhydryl (Chart 1C),32 the modified precatalysts performed higher activities than prototypical precatalysts (Chart 1A).3,4,50,51 However, the cobalt precatalysts did not have good thermal stability. To enhance their activity and thermostability, a dibenzocycloheptyl substituent was introduced, which had a positive effect (Chart 1D32,42 and E19).

Parallel approaching employed halogen substituents as electron-withdrawing groups, positively enhancing polymerization.52–55 Indeed, performances have been improved by the precatalysts containing ortho-halo-substituted ligands (Chart 1F).56,57 Moreover, the high molecular weight of the resultant polyethylene could be obtained by this kind of cobalt precatalyst.10 Subsequently a series of unsymmetrical 2-(1-(2,4-dibenzhydryl-6-fluorophenylimino))-6-(2,4,6-(alkylphen-
yl-imino)ethyl]pyridyl, Co1–Co5 (Chart 1F), was prepared and characterized. Fortunately, higher catalytic activity and better thermal stability have been observed when using cobalt precatalysts in ethylene polymerization; more importantly, the resultant polyethylenes are improved with quite narrower dispersity being required for the high quality of vinyl-terminated polyethylene waxes (molecular weight, dispersity, and the melting point of polymer). Herein, the details of the synthesis and characterization of all-new tridentate N-ligands and cobalt complexes, as well as their catalytic properties, are documented.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Co1–Co5. Five series of unsymmetrical tridentate NNN-type ligands, 2-[CMeN{2,4-{(C6H5)2CH}2-6-F}]-6-(CMeNAr)C5H3N (Ar = 2,6-Me2C6H3 L1, 2,6-Et2C6H3 L2, 2,6-iPr2C6H3 L3, 2,4,6-Me3C6H2 L4, 2,6-Et2-4-MeC6H2 L5), have been prepared (Scheme 1) by two consecutive Schiff base condensation reactions with reasonable yields, using reaction conditions reported elsewhere.6,7 Then, cobalt (II) complexes, 2-[CMeN-{2,4-{(C6H5)2CH}2-6-F}]-6-(CMeNAr)C5H3N]CoCl2 (Ar = 2,6-Me2C6H3 Co1, 2,6-Et2C6H3 Co2, 2,6-iPr2C6H3 Co3, 2,4,6-Me3C6H2 L4, 2,6-Et2-4-MeC6H2 L5), have been prepared (Scheme 1) in good yield (41–60%) by the reaction of requisite L1–L5 with cobalt dichloride in a mixture of ethanol and dichloromethane at room temperature. All complexes and ligands were characterized by infrared spectroscopy, 1H/13C NMR spectra, and elemental analysis. Complexes Co1–Co5 were also characterized by 1H NMR, which showed a paramagnetic property as observed with broad peaks identifiable in the range of δ +110 to −20 (see Figures S1–S5). In addition, the molecular structures of Co3 and Co4 were determined by single-crystal X-ray diffraction.

Single crystals of Co3 and Co4 were successfully obtained by the slow diffusion of diethyl ether into their dichloromethane solutions at room temperature. The molecular structures of the perspective views of Co3 and Co4 are depicted in Figures 1 and 2; selected bond lengths and angles are tabulated in Table 1. In all cases, bis(aryl)pyridine ligands with imino and pyridine moieties are essentially planar; N-aryl is tilted almost perpendicular to the bis(imino)pyridine plane. The distortion of geometry was quantitatively calculated and compared with the typical five-coordinate geometry index τ5. Typical trigonal-bipyramidal and square-pyramidal geometries have $\tau_5 = 1, 0$, respectively.

The structures of Co3 and Co4 are a similar pseudo-square-pyramidal geometry and are based on a pentacoordinate around cobalt ion, in which N1, N2, N3, and one Cl1 form the square-plane and another Cl2 occupies the apical position (Co3: $\tau_5 = 0.28$; Co4: $\tau_5 = 0.32$). Similar geometries for bis(imino)pyridine iron/cobalt complexes have been reported in previous studies.8,9 The cobalt atom lies 0.643 Å above the basal plane for Co3 and 0.647 Å for Co4. The Co–Npyridine bond length [2.0593(13) Å Co3, 2.045(2) Å Co4] is shorter than the exterior Co–Nimino distances [Co(1)–N(2)
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Co3 and Co4

|       | Co3              | Co4              |
|-------|------------------|------------------|
| Bond Lengths (Å) |                   |                   |
| Co1–N1  | 2.0593(13)       | 2.045(2)         |
| Co1–N2  | 2.2023(12)       | 2.169(2)         |
| Co1–N3  | 2.2203(13)       | 2.143(2)         |
| Co1–C1  | 2.2487(5)        | 2.2466(8)        |
| Co1–C2  | 2.3070(5)        | 2.2885(8)        |
| Bond Angles (°) |                   |                   |
| N1–Co1–N2 | 73.28(5)         | 73.28(5)         |
| N3–Co1–N1 | 73.50(5)         | 74.58(9)         |
| N3–Co1–N2 | 138.30(5)        | 138.55(9)        |
| N3–Co1–C1 | 112.18(4)        | 102.16(7)        |
| N3–Co1–C1 | 99.26(4)         | 101.13(6)        |
| N2–Co1–C1 | 100.60(3)        | 98.16(6)         |
| N2–Co1–C2 | 93.70(3)         | 105.09(6)        |
| N1–Co1–C1 | 155.53(4)        | 157.69(7)        |
| N1–Co1–C2 | 92.44(4)         | 92.22(7)         |
| C12–Co1–C1 | 111.77(2)       | 110.04(3)        |

2.2023(12) Å Co3, 2.169(2) Å Co4; Co1–N(N(3) 2.2203(13) Å Co3, 2.143(2) Å Co4), which is also seen in previous structurally related comparators, and can be attributed to the superior binding properties of pyridine and the constraints imparted by the N,N,N-ligand.6–8,14,21 There are also some differences in the Co–N(amine) distances whereby Co(1)–N(2) is longer than Co(1)–N(3), showing the more sterical demand on the 2,6-bis(di(2,4-diphenyl)methyl)-6-fluorophenyl group linked to N(2). Moderate variation in the N–Co–N angle is observed in the tridentate ligands in Co3 and Co4 [N(1)–Co1–N(2): 73.28(5)° (Co3 and Co4) vs N(2)–Co(1)–N(3): 73.50(5)° Co3, 73.58(9)° Co4], which likely originates from the steric variations of specific N-aryl pairs.

Further support for the structural compositions of Co1–Co5 was provided by the IR data, which reveal C≡N stretching frequencies that fall in the range of 1607–1623 cm⁻¹. By contrast, the corresponding bands in L1–L5 are seen at higher wavenumbers between 1639 and 1643 cm⁻¹, which are consistent with previously reported cobalt and iron analogues.6–9,15

Catalytic Evolution of Co1–Co5/MAO toward Ethylene Polymerization. Precatalysts Co1–Co5 were systematically investigated for ethylene polymerization with activators such as co-catalyst methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), and Co1 was employed as the test precatalyst in optimization of catalytic parameters, which includes the molar ratio of Al/Co, reaction temperature, run time, and ethylene pressure. All of the polymerization results are tabulated in Tables 2 and 3. In the beginning, ethylene polymerization was conducted at various temperatures starting from 30 to 70 °C with ethylene pressure of 10 atm and the Al/Co ratio at 1000 (entries 1–5 in Table 2). The highest activity (8.27 × 10⁶ g of PE (mol of Co)⁻¹ h⁻¹) was achieved at 60 °C, which then gradually decreased. By contrast, structurally related cobalt and chromium precatalysts bearing benzhydryl groups combined with ortho-methyl- and chlorosubstituents such as F (Chart 1) attained their best activity at 40 or 60 °C.10,19 It seems plausible that the positive effect was caused by the ortho-electron-withdrawing substituent of the N-aryl ring, resulting in thermostability. The molecular weight of the resultant PE decreased slowly from 1.81 to 1.27 kg mol⁻¹ (Figure 3), owing to the higher chain transfer rate and the lower concentration of ethylene at a higher temperature.2,5,13,16,56,57 The molecular weight distribution is narrow (M₅/Mₙ: 1.6–1.8) with unimodal characters in GPC curves, suggesting single-site active species.

Second, with the temperature fixed at 60 °C, the Al/Co molar ratios increasing from 1000 to 2500 (entries 4 and 6–10 in Table 2) with the highest activity of 12.70 × 10⁶ g of PE (mol of Co)⁻¹ h⁻¹ was achieved at 2250 molar equivalents. Moreover, the higher amount of MAO gradually reduced the polymerization activity. The molecular weight of polyethylene waxes with fewer differences ranged from 1.27 to 1.30 kg mol⁻¹ (Figure 4), and this clear trend was previously reported.15

Third, to permit a study of the lifetime of the active species at 60 °C, polymerization runs using Co1/MAO were performed at different time intervals between 5 and 60 min. The activity was gradually decreased from 32.96 × 10⁶ g of PE (mol of Co)⁻¹ h⁻¹ to 9.95 × 10⁶ g of PE (mol of Co)⁻¹ h⁻¹ on prolonging the time interval from 5 to 60 min (entries 9 and 13–16 in Table 2), in accordance with deactivation of active species over a prolonged reaction time. The maximum activity of 32.96 × 10⁶ g of PE (mol of Co)⁻¹ h⁻¹ was observed after 5
Remarkably, even after 1 h, the activity still remained at a high level of 12.70 × 10^6 g of PE (mol of Co)^−1 h^−1 (entry 9, Table 2), the obtained product has the lowest molecular weight of 1.10 kg mol^-1 (Figure 5), highlighting the stability of the active species and the slow deactivation of this catalyst. Nevertheless, from the GPC traces, the molecular weight of the PE wax was observed with a lower-difference range from 1.25 to 1.37 kg mol^-1 (Figure 5), which may be because the chain transfer process had occurred.15

Table 2. Ethylene Polymerization Studies Using Co1−Co5 with MAO as a Co-catalyst

| entry | precatalyst | Al/Co | temperature (°C) | time (min) | yield (g) | act. | M_w | M_w/M_n | T_m (°C) |
|-------|-------------|-------|------------------|------------|-----------|------|------|---------|----------|
| 1     | Co1         | 1000  | 30               | 30         | 3.39      | 4.52 | 1.81 | 1.8     | 117.2    |
| 2     | Co1         | 1000  | 40               | 30         | 4.50      | 6.00 | 1.49 | 1.7     | 116.0    |
| 3     | Co1         | 1000  | 50               | 30         | 5.98      | 7.97 | 1.34 | 1.7     | 114.4    |
| 4     | Co1         | 1000  | 60               | 30         | 8.77      | 8.27 | 1.30 | 1.6     | 119.3    |
| 5     | Co1         | 1000  | 70               | 30         | 5.47      | 7.29 | 1.27 | 1.5     | 121.0    |
| 6     | Co1         | 1500  | 60               | 30         | 4.66      | 9.21 | 1.29 | 1.6     | 120.9    |
| 7     | Co1         | 1750  | 60               | 30         | 7.66      | 10.21| 1.28 | 1.6     | 119.5    |
| 8     | Co1         | 2000  | 60               | 30         | 8.54      | 11.39| 1.27 | 1.6     | 119.7    |
| 9     | Co1         | 2250  | 60               | 30         | 9.53      | 12.70| 1.26 | 1.6     | 119.1    |
| 10    | Co1         | 2500  | 60               | 30         | 6.12      | 8.16 | 1.24 | 1.5     | 119.4    |
| 11    | Co1         | 2250  | 60               | 30         | 6.96      | 9.28 | 1.21 | 1.4     | 118.9    |
| 12    | Co1         | 2250  | 60               | 5          | 1.54      | 2.05 | 1.10 | 1.2     | 118.5    |
| 13    | Co1         | 2250  | 60               | 15         | 4.12      | 32.96| 1.25 | 1.6     | 118.7    |
| 14    | Co1         | 2250  | 60               | 45         | 14.00     | 12.44| 1.30 | 1.7     | 118.7    |
| 15    | Co1         | 2250  | 60               | 60         | 14.93     | 9.95 | 1.37 | 1.7     | 119.1    |
| 16    | Co2         | 2250  | 60               | 30         | 7.40      | 9.86 | 2.18 | 1.8     | 122.3    |
| 17    | Co2         | 2250  | 60               | 30         | 3.57      | 4.56 | 1.69 | 2.1     | 128.0    |
| 18    | Co3         | 2250  | 60               | 30         | 9.88      | 13.20| 1.45 | 1.6     | 114.7    |
| 19    | Co4         | 2250  | 60               | 30         | 5.92      | 7.89 | 2.50 | 1.9     | 123.2    |

Table 3. Ethylene Polymerization Studies Using Co1−Co5 with MMAO as a Co-catalyst

| entry | precatalyst | Al/Co | temperature (°C) | time (min) | yield (g) | act. | M_w | M_w/M_n | T_m (°C) |
|-------|-------------|-------|------------------|------------|-----------|------|------|---------|----------|
| 1     | Co1         | 1000  | 30               | 30         | 2.53      | 3.37 | 1.91 | 1.8     | 117.7    |
| 2     | Co1         | 1000  | 40               | 30         | 2.78      | 3.70 | 1.79 | 1.7     | 117.1    |
| 3     | Co1         | 1000  | 50               | 30         | 7.78      | 10.37| 1.53 | 1.7     | 119.4    |
| 4     | Co1         | 1000  | 60               | 30         | 4.22      | 5.62 | 1.32 | 1.5     | 115.3    |
| 5     | Co1         | 1000  | 70               | 30         | 1.73      | 2.30 | 1.31 | 1.6     | 121.2    |
| 6     | Co1         | 1500  | 50               | 30         | 7.86      | 10.48| 1.50 | 1.5     | 119.7    |
| 7     | Co2         | 2000  | 50               | 30         | 7.94      | 10.58| 1.47 | 1.6     | 113.7    |
| 8     | Co2         | 2250  | 50               | 30         | 8.05      | 10.73| 1.34 | 1.6     | 113.7    |
| 9     | Co2         | 2500  | 50               | 30         | 8.19      | 10.92| 1.33 | 1.6     | 113.7    |
| 10    | Co2         | 2750  | 50               | 30         | 6.91      | 9.21 | 1.32 | 1.6     | 113.6    |
| 11    | Co2         | 2500  | 50               | 15         | 4.83      | 6.44 | 1.22 | 1.4     | 114.6    |
| 12    | Co2         | 2500  | 50               | 30         | 1.25      | 1.66 | 1.15 | 1.2     | 114.5    |
| 13    | Co2         | 2500  | 50               | 5          | 3.07      | 24.65| 1.27 | 1.5     | 113.6    |
| 14    | Co2         | 2500  | 50               | 15         | 3.85      | 11.26| 1.32 | 1.5     | 114.4    |
| 15    | Co2         | 2500  | 50               | 45         | 9.09      | 8.08 | 1.39 | 1.6     | 113.9    |
| 16    | Co2         | 2500  | 50               | 60         | 9.52      | 6.34 | 1.55 | 1.7     | 114.1    |
| 17    | Co2         | 2500  | 50               | 30         | 2.96      | 3.94 | 2.49 | 1.9     | 122.6    |
| 18    | Co3         | 2500  | 50               | 30         | 2.04      | 2.72 | 8.23 | 2.4     | 128.2    |
| 19    | Co4         | 2500  | 50               | 30         | 5.07      | 6.76 | 1.80 | 1.7     | 116.3    |
| 20    | Co5         | 2500  | 50               | 30         | 2.73      | 3.64 | 3.04 | 1.9     | 123.0    |

On reducing the ethylene pressure from 10 to 5 atm, the activity dropped from 12.70 to 9.28 × 10^6 g of PE (mol of Co)^−1 h^−1 (entries 9 and 11 in Table 2). On the other hand, the molecular weight of PE fell from 1.21 to 1.26 kg mol^-1, while little variation in the MWD was observed (M_w/M_n: 1.4−1.6). On a further reduction to 1 atm C2H4 with the lowest activity of 2.05 × 10^6 g of PE (mol of Co)^−1 h^−1 (entry 12, Table 2), the obtained product has the lowest molecular weight of 1.10 kg mol^-1 and a narrower MWD 1.2.

To investigate the influence of structural variations of the precatalysts on the catalytic performance and polymer
properties, all five cobalt complexes, Co1−Co5, were systematically investigated (entries 9 and 17−20 in Table 2). First, optimized conditions established for Co1/MAO with a Al/Co ratio of 2250, the temperature of 60 °C, and a run time of 30 min were used. All of the prepared cobalt complexes displayed good activities in the range from 4.56 × 10^6 g of PE (mol of Co)^−1 h^−1 to 13.20 × 10^6 g of PE (mol of Co)^−1 h^−1 in ethylene polymerization with a fall in the order as follows: Co4 (Me2, Me) > Co1 (Me2, H) > Co2 (Et2, H) > Co5 (Et2, Me) > Co3 (Pr2, H). This is because the most sterically hindered substituent precludes ethylene coordination to the metal center in the active catalyst that leads to lower activity. With respect to the molecular weight, values in the range of 1.26−6.90 kg mol^−1 were observed with the bulkiest being Pr containing Co3, affording a polymer at the top, and a similar observation has been reported elsewhere.37

To confirm the linearity of the obtained polymers, a representative sample synthesized using Co1/MAO [Al/Co = 2250, temperature = 60 °C, run time = 30 min] (entry 9, Table 2) was investigated by 1H/13C NMR spectroscopy (Figures 6 and 7). In the 13C NMR spectra, the downfield shift shows two intelligibility signals between δ 139.52 and 114.40 ppm that can be attributed to a vinyl end group in a selected sample. An intense peak at δ 30.0 ppm for −(CH2)n− repeats in linear polymer saturated chain end peaks δ 32.34 (Cn), 22.94 (Cn), and 14.38 (C) ppm for the polymer of Co1/MAO (entry 9, Table 2; Figure 6). The 1H NMR spectra (Figure 7) revealed the coexistence of polyethylene bearing both saturated and unsaturated groups. The vinyl end group (−CH=CH2) was identified as two multiplets, a downfield multiplet signal at 5.90 ppm and an apparent triplet signal at 5.09 ppm, with a relative peak/area ratio of 1:2.06 (Figure 4), implying that both chain termination including β-hydride elimination to produce the vinyl end groups (−CH=CH2) and the chain transfer to AlMe3 to yield n-propyl end groups occur.7,15 The high-intensity peak at 1.37 ppm corresponding to the protons of −(CH2)n− and another signal at 2.13 ppm due to the protons adjacent to the vinyl group (Hg) were observed. The signal of the methyl group (Hf) was observed at 0.98 ppm.37,58 According to these characteristic peak areas in the 1H NMR spectrum, the molar ratio of the two types of end groups, including vinyl/methyl and methyl/methyl, was 81:19, respectively. These linear low-molecular-weight vinyl polyethylene waxes have a huge industrial demand as new co-monomers.

Catalytic Evolution of Co1−Co5 with MMAO. With MMAO as a co-catalyst, precatalysts Co1−Co5 were investigated in detail, and the results are collected in Table 3. By fixing the molar ratio of Al/Co at 1000, ethylene polymerization was conducted at different temperatures ranging from 30 to 70 °C, and the highest activity (10.37 × 10^6 g of PE (mol of Co)^−1 h^−1) was found at 50 °C (entries 1−5, Table 3). Further increasing the temperature led to a gradual decrease of activity and molecular weight, similar to the downward trend observed with MAO. With the reaction temperature maintained at 50 °C, the influence of varying the Al/Co molar ratio from 1000 to 2750 was studied (entries 4 and 6−10, Table 3). The peak activity was 10.92 × 10^6 g of PE (mol of Co)^−1 h^−1 at 2000 molar ratio, the activity enhancement was prolonged with less difference on increasing the molar ratio. Unlike MMAO, no anomalous behavior was observed with the molecular weight steadily dropping as the ratio was increased from 1000 to 2750, in agreement with the increased chain transfer rate from the active cobalt species to aluminum.35−37,43

Prolonging the reaction time from 5 to 60 min led to a decrease of the catalytic activity from 24.65 × 10^6 g of PE (mol of Co)^−1 h^−1 to 6.34 × 10^6 g of PE (mol of Co)^−1 h^−1 (entries 9 and 13−16, Table 3), which could be explained by the deactivation becoming more gradual as the run times increased. These observations suggested that the use of MMAO as a co-catalyst allows for the rapid formation of the active species without any significant induction period and then undergoes a rapid deactivation process with a 55% loss in activity during the first 30 min.16,26,34,37,58 The molecular
weight distribution could maintain a narrow steady state \((M_n/M_w \sim 1.7)\).

Under optimized conditions \([\text{Al}/\text{Co} = 2500, \text{temperature} = 50 ^\circ \text{C}, \text{run time} = 30 \text{ min}],\) all cobalt precatalysts \(\text{Co}1 \sim \text{Co}5\) were investigated (entries 9 and 17–20, Table 3), and the polymerization activity decreased in the order \(\text{Co}1(\text{Me}_2, \text{H}) > \text{Co}4(\text{Me}_2, \text{Me}) > \text{Co}2(\text{Et}_2, \text{H}) > \text{Co}5(\text{Et}_2, \text{Me}) > \text{Co}3(\text{iPr}_2, \text{H}),\) with the activity ranging from \(2.72 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}\) to \(10.92 \times 10^6 \text{ g of PE (mol of Co)}^{-1} \text{ h}^{-1}.\) Typically, less steric hindrance is a dominant factor in enhancing the activities. A polymer with the highest molecular weight was produced by \(\text{Co}3(8.23 \text{ kg mol}^{-1});\) however, other cobalt precatalysts generated lower-molecular-weight polyethylene waxes, which could be related to the ortho-position of substituents on the \(N\)-aryl ring reducing the effect on the molecular weight of the polymer and suggesting that chain transfer is suppressed by a bulkier substituent. To understand the microstructure of the obtained polyethylenes, a representative sample of the obtained polyethylene using \(\text{Co}1/\text{MAO}\) (10 atm of ethylene, 30 min, 50 \(^\circ\)C, and 2500 Al/Co ratio) was examined by \(^1\text{H}/\text{C}^13\text{C NMR spectroscopy} (\text{Figure} 8). The \(^1\text{C}^13\text{C NMR} spectrum again revealed a high-intensity peak at around \(\delta 30.00,\) in accord with an intense signal at \(\delta 1.37\) in its \(^1\text{H}^1\text{C NMR} spectrum, supporting the formation of linear polyethylene. Similar to the observation for MAO, both chain termination via \(\beta\)-H elimination along with chain transfer to aluminum occurred for the saturated chain end peaks \((\delta 32.25 (\text{C}_d), 22.94 (\text{C}_c),\) and 14.28 (\(\text{C}_b)) \text{ ppm in } ^1\text{C NMR}; \delta 2.13 (\text{H}_c)\) and 0.98 (\(\text{H}_g) \text{ ppm in } ^1\text{H NMR} and the vinyl end group \((-\text{CH}=\text{CH}_2)\) peaks \((\delta 139.51 (\text{C}_b)\) and 114.40 (\(\text{C}_a)) \text{ ppm in } ^1\text{C NMR}; \delta 5.90 (\text{H}_d)\) and 5.03 (\(\text{H}_e) \text{ ppm in } ^1\text{H NMR})\) and the molar ratio of the two types of end groups was 87:13, respectively, which again indicated an obvious bias toward vinylic chain ends and that \(\beta\)-H

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**Figure 6.** \(^1\text{C}^13\text{C NMR spectrum of the polyethylene obtained using } \text{Co}1/\text{MAO at 60 }^\circ\text{C (entry 9, Table 2) recorded in 1,1,2,2-tetrachloroethane-}d_2 \text{ at 100 }^\circ\text{C.}\)

**Figure 7.** \(^1\text{C}^13\text{C NMR spectrum of the polyethylene obtained using } \text{Co}1/\text{MAO at 60 }^\circ\text{C (entry 9, Table 2) recorded in 1,1,2,2-tetrachloroethane-}d_2 \text{ at 100 }^\circ\text{C; } X \text{ represents the molar ratio of the vinyl-PEs in the polymer mixture.}\)
elimination was the predominant chain transfer pathway (Chart 2).

The catalytic performance of the current precatalyst (Chart 1F) was compared with those of previously reported cobalt catalysts (Chart 1A and C, D, and F). In terms of the catalytic activity, precatalysts D displayed comparable high activity to F, and other optimum activities of the compared cobalt catalysts are lower than that of our designed new cobalt catalyst. Catalyst F maintained its thermal stability compared to the other precatalysts. Orthopositions of the N-aryl groups functionalized with electron-withdrawing and bulky substituents, such as benzhydryl (CHPh$_2$) and fluoro (−F), have some unique effects on the catalytic activity and thermal stability, as well as on polymer properties and the structure. In the case of the molecular weight of the produced polyethylene, the lowest-molecular-weight highly linear polyethylene (PE) waxes with vinyl end groups were produced by F.

**CONCLUSIONS**

In summary, a series of fluoro-functionalized bis( imino)-pyridine-cobaltous chloride complexes (Co1−Co5) were synthesized with good yield and well-characterized using FT-IR and multinuclear NMR techniques. X-ray diffraction...
analysis of complexes Co3 and Co4 revealed the pseudo-square-pyramidal geometry around the metal center. The incorporation of a fluorosubstituent in the NNN-tridentate Co(II) complexes showed the robust catalytic performance toward ethylene polymerization. Upon being activated with MAO or MMAO, all of the titled complexes displayed higher activity and thermal stability during ethylene polymerization with low-molecular-weight polyethylene waxes with narrow molecular weight distributions. In the presence of the MAO co-catalyst, the precatalyst Co4 displayed the highest activity of 13.20 × 10^6 g of PE (mol of Co)^−1 h^−1 as the less steric hindrance is a dominant factor in improving the catalytic activities. Notably, the most sterically hindered precatalyst Co3 has the propensity to generate polyethylene waxes of the highest molecular weight, highlighting the beneficial effect of more bulky substitution on chain propagation. Co1/MAO or Co1/MMAO provided evidence for both β-hydrogen elimination and chain transfer to aluminum being operative during chain termination. Compared to related cobalt systems, the nation and chain transfer to aluminum being operative during more bulky substitution on chain propagation.

acetate (250/1 v/v) as the eluent to obtain further reaction (checked by TLC), the reaction mixture was cooled to

mmol) was stirred (50 mL) and heated to reflux. After 30 min, a catalytic amount of p-toluenesulfonic acid was added and further refluxed in o-xylene for 6 h. Upon completion of the reaction (checked by TLC), the reaction mixture was cooled to room temperature and the volatiles were removed using a rotary evaporator. The residual solids were purified by basic alumina column chromatography using petroleum ether/ethyl acetate (250/1 v/v) as the eluent to obtain L1 as a pale yellow powder (0.4 g, 15%). Mp: 148-150 °C. FT-IR (KBr, cm^−1): 3028 (w), 2937 (w), 1643 (νC=C, s), 1569 (w), 1496 (w), 1453 (s), 1365 (s), 1328 (w), 1299 (w), 1250 (s), 1207 (m), 1121 (s), 1030 (w), 858 (w), 765 (s). 1H NMR, (CDCl3, 400 MHz, TMS): δ 8.43 (d, J = 7.6 Hz, 1H, Py-H1), 8.32 (d, J = 7.6 Hz, 1H, Py-H2), 7.82-6.92 (m, 23H, Ar-H), 6.74 (d, J = 11.2 Hz, 1H, Ar-H), 6.60 (s, 1H, Ar-H), 5.59 (s, 1H, CHPh2), 5.42 (s, 1H, CHPh2), 2.16 (s, 3H, N=C(C2H5)), 2.04 (s, 6H, C-(CH3)2), 1.83 (s, 3H, N=C(CH3)2). 13C NMR (CDCl3): δ 170.93, 167.22, 155.03, 154.88, 151.94, 149.52, 148.74, 143.69, 142.56, 140.03, 139.97, 137.44, 136.72, 135.01, 134.87, 133.85, 128.41, 128.25, 127.89, 126.37, 126.19, 125.44, 123.02, 122.43, 114.86, 114.64, 56.16, 52.10, 17.96, 16.81, 16.79, 16.42. Anal. calcd for C49H42FN3 (748.0): C, 85.04; H, 6.15; N, 6.10.

2-((2,4-Dibenzhydryl-6-fluorophenylimino)ethyl)-6-(1-(2,6-dimethylphenylimino)ethyl)pyridine (L2). L2 was obtained as a pale yellow powder according to the procedure and molar ratios of the synthesis of L1 (0.43 g, 17.5%). Mp: 144-146 °C. FT-IR (KBr, cm^−1): 3024 (w), 2930 (w), 1639 (νC=C, s), 1567 (w), 1493 (w), 1449 (s), 1365 (s), 1326 (w), 1243 (s), 1199 (m), 1119 (s), 1028 (w), 854 (w), 764 (s). 1H NMR, (CDCl3, 400 MHz, TMS): δ 8.42 (d, J = 10.8 Hz, 1H, Ar-H), 8.32 (d, J = 8.0 Hz, 1H, Py-H1), 7.82-6.97 (m, 23H, Ar-H), 6.75 (d, J = 10.8 Hz, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 5.59 (s, 1H, CHPh2), 5.43 (s, 1H, CHPh2), 2.47-2.29 (m, 4H, 2 × CH2), 2.17 (s, 3H, N=C(CH3)2), 1.84 (s, 3H, N=C(CH3)2), 1.15 (t, J = 15.6 Hz, 6H, 2 × -CH3). 13C NMR (CDCl3): δ 169.92, 165.90, 154.00, 153.84, 146.74, 142.64, 141.62, 138.98, 138.91, 136.38, 135.70, 133.97, 130.15, 128.41, 128.25, 127.26, 127.13, 125.33, 125.15, 124.89, 122.27, 131.25, 121.16, 113.81, 55.11, 51.01, 23.55, 15.74, 12.69. Anal. calcd for C53H50FN3 (748.0): C, 85.08; H, 6.14; N, 5.84. Found: C, 85.05; H, 6.39; N, 5.82.

2-((2,4-Dibenzhydryl-6-fluorophenylimino)ethyl)-6-(1-(2,6-diisopropylphenylimino)ethyl)pyridine (L3). L3 was obtained as a pale yellow powder according to the procedure and molar ratios of the synthesis of L1 (0.26 g, 11.0%). Mp: 140-142 °C. FT-IR (KBr, cm^−1): 3024 (w), 2923 (w), 1643 (νC=C, s), 1571 (w), 1493 (w), 1454 (s), 1361 (s), 1322 (w), 1300 (w), 1254 (s), 1205 (m), 1122 (s), 1033 (w), 849 (w), 765 (s). 1H NMR, (CDCl3, 400 MHz, TMS): δ 8.42 (d, J = 8.0 Hz, 1H, Py-H1), 8.32 (d, J = 8.0 Hz, 1H, Py-H2), 7.82-6.78 (m, 23H, Ar-H), 6.75 (d, J = 10.8 Hz, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 5.59 (s, 1H, CHPh2), 5.43 (s, 1H, CHPh2), 2.79-2.72 (m, 2H, 2 × CH(CH3)-), 2.19 (s, 3H, N=C(CH3)2), 1.85 (d, J = 1.2 Hz, 3H, N=C(CH3)2), 1.16 (d, J = 6.8 Hz, 12H, 2 × CH(CH3)-). 13C NMR (CDCl3): δ 169.93, 163.92, 154.01, 153.88, 145.44, 142.65, 141.55, 136.38, 135.69, 134.77, 133.85, 128.41, 128.25, 127.27, 127.13, 125.27, 125.15, 125.53, 121.96, 121.33, 121.20, 113.81, 113.60, 55.12, 51.04, 27.24, 22.19, 21.87, 16.07, 15.79. Anal. calcd for C55H52FN3 (784.0): C, 85.10; H, 6.74; N, 5.62. Found: C, 85.12; H, 6.79; N, 5.62.

2-((2,4-Dibenzhydryl-6-fluorophenylimino)ethyl)-6-(1-(2,4,6-trimethylphenylimino)ethyl)pyridine (L4). L4 was obtained as a pale yellow powder according to the procedure and molar ratios of the synthesis of L1 (0.25 g, 10.0%). Mp: 158-160 °C. FT-IR (KBr, cm^−1): 3022 (w), 2923 (w), 1641 (νC=C, s), 1568 (w), 1493 (w), 1472 (s), 1365 (s), 1327 (w), 1297 (w), 1255 (s), 1216 (m), 1119 (s), 1029 (w), 854 (w), 739 (s). 1H NMR, (CDCl3, 400 MHz, TMS): δ 8.41 (d, J =
7.6 Hz, 1H, Ph-He)), 8.31 (d, J = 7.6 Hz, 1H, Py-H)), 7.86 (t, J = 15.6 Hz, 1H, Py-H)), 7.27-7.65 (m, 22H, Ar-H), 6.73 (d, J = 1.2 Hz, 1H, Ar-H), 6.60 (s, 1H, Ar-H), 5.59 (s, 1H, CPhH)), 5.42 (s, 1H, CPhH)), 2.29 (s, 3H, N=CCH3), 2.15 (s, 3H, N=CCH3), 2.00 (s, 6H, C(CH3)2 (p)), 1.83 (d, J = 0.8 Hz, 3H, C-CH3 (p)). 13C NMR (CDCl3): δ 169.93, 166.36, 154.12, 153.80, 150.90, 148.48, 145.19, 142.65, 141.52, 138.97, 133.96, 134.16, 135.64, 133.98, 133.84, 131.16, 128.40, 128.25, 127.52, 127.26, 127.13, 125.33, 125.14, 124.23, 121.31, 121.18, 113.81, 113.59, 55.11, 51.03, 19.71, 16.84, 15.76, 15.74, 15.32. Anal. calc. for C60H44Cl2Co4N4 (948.9): C, 87.08; H, 5.46; N, 4.94. Found: C, 87.20; H, 5.47; N, 4.90.

2-(1,2,4-Dibenzydryl-6-fluorophenylimino)ethyl)-6-(1,2,6-diaryl-6-phenylpyridyl)imidazol Cobalt Dichloride (Co3). Co3 was prepared using similar procedures and molar ratios as those described for the synthesis of Co1 but using L2 (200 mg, 0.27 mmol) instead of L1. A green powder was obtained (110 mg, 46%). 1H NMR (600 MHz, CDCl3, TMS): δ 111.42 (1H, Py-H)), 108.65 (1H, Py-H)), 41.13 (1H, Py-H)), 18.23 (1H, o-CPhH)), 9.77 (2H, aryl-H), 9.59 (1H, aryl-H)), 9.53 (2H, aryl-H), 8.93 (1H, p-CPhH)), 8.20 (2H, aryl-H), 8.02 (2H, aryl-H), 7.74 (1H, aryl-H), 7.68 (3H, aryl-H), 7.25 (1H, aryl-H), 7.11 (1H, aryl-H), 6.64 (2H, aryl-H), 6.62 (1H, aryl-H), 3.38 (3H, aryl-H), 3.71 (1H, aryl-H), 2.28 (1H, aryl-H), 1.84 (3H, C-CH3)), 1.43 (1H, aryl-H), 1.20 (3H, C-CH3), −0.32 (6H, C(CH3)2), −8.93 (1H, aryl-H), −10.01 (1H, CH3), −16.13 (3H, N=CCH3), −17.28 (1H, CH), −18.34 (3H, N=CCH3). FT-IR (KBr; cm–1): 3026 (w), 2963 (m), 1617 (v(C=N)), 1582 (m), 1494 (w), 1447 (s), 1370 (s), 1261 (s), 1220 (w), 1181 (s), 1079 (m), 1029 (s), 880 (s), 810 (m), 778 (m), 744 (s), 698 (s). Anal. calc. for C60H44Cl2Co4N4 (8877.8): C, 72.52; H, 5.74; N, 4.79. Found: C, 72.54; H, 5.69; N, 4.80.

2-(1,2,4-Dibenzydryl-6-fluorophenylimino)ethyl)-6-(1,2,6-diaryl-6-phenylpyridyl)imidazol Cobalt Dichloride (Co4). Co4 was prepared using similar procedures and molar ratios as those described for the synthesis of Co1 but using L4 (200 mg, 0.28 mmol) instead of L1. A green powder was obtained (137 mg, 41%). 1H NMR (600 MHz, CDCl3, TMS): δ 108.56 (1H, Py-H)), 106.03 (1H, Py-H)), 27.94 (1H, Py-H)), 15.44 (3H, p-CPhH)), 14.13 (1H, o-CPhH)), 8.39 (2H, aryl-H), 7.63 (1H, p-CPhH)), 6.84 (6H, aryl-H), 6.51 (1H, aryl-H), 5.87 (1H, aryl-H), 5.63 (1H, aryl-H), 4.92 (2H, aryl-H), 4.28 (1H, aryl-H), 3.86 (1H, aryl-H), 3.40 (1H, aryl-H), 1.92 (6H, aryl-H), -0.22 (1H, aryl-H), −1.58 (3H, N=CCH3), −5.01 (3H, N=CCH3), −13.01 (1H, p-CPhH)), −14.01 (1H, aryl-H), −23.01 (6H, o-C(CH3)), FT-IR (KBr; cm–1): 3025 (w), 2960 (m), 1620 (v(C=N)), 1587 (m), 1477 (w), 1450 (s), 1371 (s), 1261 (s), 1219 (w), 1184 (s), 1079 (m), 1031 (s), 853 (s), 811 (m), 776 (m), 744 (s), 700 (s). Anal. calc. for C60H44Cl2Co4N4 (8358.8): C, 71.66; H, 5.31; N, 5.03. Found: C, 71.87; H, 5.35; N, 5.01.
The structure was solved by direct methods and the free solvent present in the single crystals was removed using the SQUEEZE option of the crystallization package.59,60 The free solvent present in the single crystals was solved and re

Ethylene Polymerization. Ethylene Polymerization at 5/10 atm of Ethylene Pressure. An autoclave (250 mL) was evacuated and backfilled with ethylene three times. When the required pressure was reached, the precatalysts (2.0 μmol) were dissolved in toluene (30 mL) in a Schlenk tube and injected into the autoclave containing ethylene (ca. 1 atm), followed by the addition of more toluene (30 mL). The required amount of co-catalyst (MAO or MMAO) and additional toluene were added successively using a syringe, taking the total volume of toluene to 100 mL. The autoclave was immediately pressurized with 5/10 atm of ethylene, and stirring was commenced. After the required reaction time, the reactor was cooled with a water bath and the excess ethylene was vented. Following quenching of the reaction with 10% hydrochloric acid in ethanol, the polymer was collected, washed with ethanol, dried under reduced pressure at 50 °C, and weighed. The molecular weight and polydispersity index were characterized by gel permeation chromatography (GPC), and the melting point was characterized by differential scanning calorimetry (DSC), and the microstructure was characterized by high-temperature 13C NMR, which determined the resultant polyethylene from ethylene polymerization.

Ethylene Polymerization at 1 atm of Ethylene Pressure. Polymerization at 1 atm of ethylene pressure was carried out in a Schlenk tube. Under an ethylene atmosphere (1 atm), Co1 (2 μmol) was added, followed by toluene (30 mL), and then the required amount of co-catalyst (MAO and MMAO) was introduced using a syringe. The solution was then stirred at 50 or 60 °C under an ethylene atmosphere (1 atm). After 30 min, the solution was quenched with 10% hydrochloric acid ethanol. The polymer was washed with ethanol, dried under reduced pressure at 40 °C, and then weighed.

X-ray Crystallographic Studies. Single-crystal X-ray crystallography of Co3 and Co4 was carried out on a Rigaku Saturn 724+ CCD diffractometer with graphite-monochromatic Mo Ka radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters were obtained by the global refinement of the positions of all collected reflections. The intensities of the Lorentz and polarization effects and empirical absorption were calibrated. The structure was solved by direct methods and refined by full-matrix least-squares on F2. All nonhydrogen atoms were placed in computational positions. The structure was solved and refined using the SHELXTL-97 software package.59,60 The free solvent present in the single crystals was removed using the SQUEEZE option of the crystallization program PLATON.59,60 Details of the X-ray determination and refinement can be found in Table S1. Deposition Numbers CCDC-2000142 (for Co3) and -2000143 (for Co4) contain the supplementary crystallographic data for this paper. For Co3, there is a B-level alert in the checkCIF reports, which could be attributed to some low-field diffraction points blocked by beamstop during the measurement; therefore, reflections were not detected. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05916.

1H NMR spectra of Co1, Co2, Co3, Co4, and Co5 (recorded in CDCl3 at room temperature) (Figures S1–S5) and crystal data and structure refinement for Co3 and Co4 (Table S1) (PDF) (CIF)

Accession Codes
X-ray crystallographic data for Co3 and Co4. CCDC: 2000142 (Co3), 2000143 (Co4). 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, U.K.; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES
(1) Bianchini, C.; Giambastiani, G.; Rios, G. I.; Mantovani, G.; Meli, A.; Segarra, A. M. Ethylene oligomerization, homopolymerization and copolymerization by iron and cobalt catalysts with 2,6-(bis-organylimino)pyridyl ligands. Coord. Chem. Rev. 2006, 250, 1391–1418.
(2) Small, B. L.; Brookhart, M.; Bennett, A.M.A. Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene. J. Am. Chem. Soc. 1998, 120, 4049–4050.
(3) Gibson, V. C.; Redshaw, C.; Solan, G. A. Bis(imino)pyridines: Surprisingly Reactive Ligands and a Gateway to New Families of Catalysts. Chem. Rev. 2007, 107, 1745–1776.
(4) Wang, Z.; Solan, G. A.; Zhang, W.; Sun, W.-H. Carbocyclic-fused N,N,N-pincer ligands as ring-stable supports for iron and cobalt catalysts in ethylene oligo- polymerization. Coord. Chem. Rev. 2018, 363, 92–108.
(5) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McCravish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. Novel olefin polymerization catalysts based on iron and cobalt. Chem. Commun. 1998, 849–850.
(6) Yu, J.; Huang, W.; Wang, L.; Redshaw, C.; Sun, W.-H. 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichlorides: Synthesis, characterization and ethylene polymerization behavior. Dalton Trans. 2011, 40, 10209–10214.
(7) Zhao, W.; Yu, J.; Song, S.; Yang, W.; Liu, H.; Hao, X.; Redshaw, C.; Sun, W.-H. Controlling the ethylene polymerization parameters in iron precatalysts of the type 2-[1-(2,4-dibenzhydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyliron dichloride. Polymer 2012, 53, 130–137.
(8) Cao, X.; He, F.; Zhao, W.; Cai, Z.; Hao, X.; Shiono, T.; Redshaw, C.; Sun, W.-H. 2-[1-(2,6-Dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridyliron(II) dichlorides: Synthesis, characterization and ethylene polymerization behavior. Polymer 2012, 53, 1870–1880.
(9) He, F.; Zhao, W.; Cao, X.-P.; Liang, T.; Redshaw, C.; Sun, W.-H. 2-[1-(2,6-dibenzhydryl-4-chlorophenylimino)ethyl]-6-[1-aryliminoethyl]pyridyl cobalt dichlorides: Synthesis, characterization and ethylene polymerization behavior. J. Organomet. Chem. 2012, 713, 209–216.
(10) Lai, J.; Zhao, W.; Yang, W.; Redshaw, C.; Liang, T.; Liu, Y.; Sun, W.-H. 2-[1-(2,4-Dibenzydryl-6-methylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridylcobalt(II) dichlorides: Synthesis, characterization and ethylene polymerization behavior. Polym. Chem. 2012, 3, 787–793.
(11) Sun, W.-H.; Zhao, W.; Yu, J.; Zhang, W.; Hao, X.; Redshaw, C. Enhancing the Activity and Thermal Stability of Iron Precatalysts Using 2-[1-(2,6-bis[4-fluorophenyl]methyl)-4-methylphenylimino)ethyl]-6-[1-arylimino)ethyl]pyridines. Macromol. Chem. Phys. 2012, 213, 1266–1273.
(12) Wang, S.; Li, B.; Liang, T.; Redshaw, C.; Li, Y.; Sun, W.-H. Synthesis, characterization and catalytic behavior toward ethylene of 2-[1-(4,6-dimethyl-2-benzzydrylphenylimino)ethyl]-6-[1-(arylimino)ethyl]pyridymetal (iron or cobalt) chlorides. Dalton Trans. 2013, 42, 9188–9197.
(13) Chen, Q.; Zhang, W.; Solan, G. A.; Zhang, R.; Guo, L.; Hao, X.; Sun, W.-H. CH(phenol)-Bridged Bis(imino)pyridines as Compart-mental Supports for Diiron Precatalysts for Ethylene Polymerization: Exploring Cooperative Effects on Performance. Organometallics 2018, 37, 4002–4014.
(14) Guo, L.; Zada, M.; Zhang, W.; Vignesh, A.; Zhi, D.; Ma, Y.; Liang, T.; Sun, W.-H. Highly linear polyethylenes tailored by 2,6-bis-[1-(p-dibenzycloheptaryl)imino]ethyl]pyridylcobalt dichlorides. Dalton Trans. 2019, 48, 5604–5613.
(15) Mahmood, Q.; Ma, Y.; Hao, X.; Sun, W.-H. Substantially enhancing the catalytic performance of bis(imino)pyridylcobaltous chloride pre-catalysts adorned with benzylidene and nitro groups for ethylene Polymerization. Appl. Organomet. Chem. 2019, 33, No. e5137.
(16) Zhang, Q.; Ma, Y.; Suo, H.; Solan, G. A.; Liang, T.; Sun, W.-H. Co-catalyst effects on the thermal stability/activity of N,N,N-Co ethylene polymerization Catalysts Bearing Fluoro-Substituted N,2,6-dibenzhydrylphenyl groups. Appl. Organomet. Chem. 2019, 33, No. e5134.
(17) Zhang, R.; Ma, Y.; Han, M.; Solan, G. A.; Pi, Y.; Sun, Y.; Sun, W.-H. 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. Appl. Organomet. Chem. 2019, 33, No. e5157.
(18) Zhang, R.; Han, M.; Ma, Y.; Solan, G. A.; Liang, T.; Sun, W.-H. Steric and electronic modulation of iron catalysts as a route to remarkably high molecular weight linear polyethylenes. Dalton Trans. 2019, 48, 17488–17498.
(19) Gansukh, B.; Zhang, Q.; Flisak, Z.; Liang, T.; Ma, Y.; Sun, W.-H. The chloro-substituent enhances performance of 2,4-bis(imino)pyridylchromium catalysts yielding highly linear polyethylene. Appl. Organomet. Chem. 2020, 34, No. e5471.
(20) Zhang, Q.; Zhang, R.; Han, M.; Yang, W.; Liang, T.; Sun, W.-H. 4,4′-Difluorobenzhydryl-modified bis(imino)pyridyliron(II) chlorides as thermally stable precatalysts for strictly linear polyethylenes with narrow dispersities. Dalton Trans. 2020, 49, 7384–7396.
(21) Zada, M.; Guo, L.; Ma, Y.; Zhang, W.; Flisak, Z.; Sun, Y.; Sun, W.-H. Activity and Thermal Stability of Cobalt(II)-Based Olefin Polymerization Catalysts Adorned with Sterically Hindered Dibenzocy cloheptyl Groups. Molecules 2019, 24, 2007.
(22) Zada, M.; Vignesh, A.; Suo, H.; Ma, Y.; Liu, H.; Sun, W.-H. NNN-type iron(II) complexes consisting sterically hindered dibenzocy cloheptyl group: Synthesis and catalytic activity toward ethylene polymerization. Mol. Catal. 2020, 492, No. 110981.
(23) Appukuttan, V. K.; Liu, Y.; Son, B. C.; Ha, C.-S.; Suh, H.; Kim, I. I. Iron and Cobalt Complexes of 2,3,7,8-Tetrahydroacridine-4,5-(1H,6H)-dimeine Sterically Modulated by Substituted Aryl Rings for the Selective Oligomerization to Polymerization of Ethylene. Organometallics 2011, 30, 2285–2294.
(24) Zhang, W.; Chai, W.; Sun, W.-H.; Hu, X.; Redshaw, C.; Hao, X. 2-(1-Arylimino)ethyl]-8-arylimino]-5,6,7,8-tetrahydroquinoline Iron(II) Chloride Complexes: Synthesis, Characterization, and Ethylene Polymerization Behavior. Organometallics 2012, 31, 5039–5048.
(25) Sun, W.-H.; Kong, S.; Chai, W.; Shiono, T.; Redshaw, C.; Hu, X.; Guo, C.; Hao, X. 2-(1-(Arylimino)ethyl)-8-arylimino]-5,6,7-tri hydroquinolycobalt dichloride: Synthesis and polyethylene wax formation. Appl. Catal., A 2012, 447–448, 67–73.
(26) Zhang, R.; Huang, T.; Solan, G. A.; Zhang, W.; Hu, X.; Hao, X.; Sun, W.-H. gen-Dimethyl-substituted bis(imino)dihydro-quinolines as thermally stable supports for highly active cobalt catalysts that produce linear PE waxes. Dalton Trans. 2019, 48, 8175–8185.
(27) Huang, F.; Xing, Q.; Liang, T.; Flisak, Z.; Ye, B.; Hu, X.; Yang, W.; Sun, W.-H. 2-(1-Arylimino)ethyl]-9-arylimino]-5,6,7,8-tetrahydro- cycloheptapyridyl iron(II) dichloride: synthesis, characterization, and the highly active and tunable active species in ethylene polymerization. Dalton Trans. 2014, 43, 16818–16829.
Ethylene polymerization catalysts.

**ACS Omega** 2018, 3, 380–389.

- **Wang, Z.; Zhang, R.; Zhang, W.; Solan, G. A.; Liu, Q.; Liang, T.; Sun, W.-H.** Enhancing thermostability of iron ethylene polymerization catalysts through N,N-chelation of double-fused α,α′-bis(arylimino)-2,3,5,6-bis(hexamethylene)pyridines. *Catal. Sci. Technol.* 2019, 9, 1933–1943.

- **Wang, Z.; Ma, Y.; Guo, J.; Liu, Q.; Solan, G. A.; Liang, T.; Sun, W.-H.** Bis(α,α′-pyridyl)pyridines fused with 6- and 7-membered carboxylic rings as N,N,N-scaffolds for cobalt ethylene polymerization catalysts. *Dalton Trans.* 2019, 48, 2582–2591.

- **Wang, Z.; Solan, G. A.; Ma, Y.; Liu, Q.; Liang, T.; Sun, W.-H.** Fusing carbocycles of inequivalent size to a bis(α,α′-pyridyl)iron ethylene polymerization catalyst: distinctive effects on activity, PE molecular weight and dispersity. *Research* 2019, 1–15.

- **Huang, F.; Zhang, W.; Sun, Y.; Hu, X.; Solan, G. A.; Sun, W.-H.** Thermally stable and highly active cobalt precatalysts for vinyl-polystyrenes with narrow polydispersities: integrating fused-ring and imino-carbon protection into ligand design. *New J. Chem.* 2016, 40, 8012–8023.

- **Zhang, Y.; Suo, H.; Huang, F.; Liang, T.; Hu, X.; Sun, W.-H.** Thermo-Stable 2-(Arylimino)benzaldehyde-9-arylimino-5,6,7,8-tetrahydrocyclohepta[k]pyridyliron(II) Precatalysts Toward Ethylene Polymerization and Highly Linear Polymethylenes. *J. Polym. Sci., Part A: Polym. Chem.* 2017, 55, 830–842.

- **Kaul, F.; Puchta, K.; Frey, G.; Herdtweck, E.; Herrmann, W.** Imidopyridinocarbene Complexes of 3d Metals for Ethylene Polymerization: Comparative Structural Studies and Ligand Size Controlled Chain Termination. *Organometallics* 2007, 26, 988–999.

- **Gibson, V. C.; Solan, G. A.** Catalysis Without Precious Metals, 2010: pp 111–141. ISBN: 978-3-527-32354-8.

- **Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P.; White, A. J. P.; Williams, D. J.** Cationic 2,6-bis(α,α′-pyridyl)iron and cobalt complexes: synthesis, structures, ethylene polymerization and ethylene/iron/polar monomer co-polymerisation studies. *J. Chem. Soc., Dalton Trans.* 2002, 1159–1171.

- **Yang, W.; Ma, Z.; Yi, J.; Ahmed, S.; Sun, W.-H.** Catalytic performance of bis(α,α′-pyridyl) Fe/Co complexes toward ethylene polymerization by 2D~/3D-QSAR modeling. *J. Comp. Chem.* 2019, 40, 1374–1386.

- **Yi, J.; Yang, W.; Sun, W.-H.** Quantitative Investigation of the Electronic and Steric Influences on Ethylene Oligo/Polymerization by 2-Azacyclic-6-aryliminopyridylmetal (Fe, Co, and Cr) Complexes. *Macromol. Chem. Phys.* 2016, 217, 757–764.

- **Zhang, T.; Guo, D.; Jie, S.; Sun, W.-H.; Li, T.; Yang, X.** Influence of electronic effect on catalytic activity of salicylaldiminato nickel(II) complexes. *J. Polym. Sci. A: Polym. Chem.* 2004, 42, 4765–4774.

- **Yang, W.; Fidelis, T. T.; Sun, W.-H.** Machine Learning in Catalysis, From Proposal to Practicing. *ACS Omega* 2020, 5, 83–88.

- **Barbaro, P.; Bianchini, C.; Giambastiani, G.; Rios, I. G.; Meli, A.; Oberhauser, W.; Segarra, A. M.; Sorace, L.; Toti, A.** Synthesis of New Polydentate Nitrogen Ligands and Their Use in Ethylene Polymerization in Conjunction with Iron(II) and Cobalt(II) Bis-halides and Methylaluminoxane. *Organometallics* 2007, 26, 4639–4651.

- **Armitage, A. P.; Champsaur, Y. D. M.; Grigoli, H.; Pelletier, J. D. A.; Singh, K.; Solan, G. A.** Probing the Effect of Binding Site and Metal Centre Variation in Pentadentate Oligopyridylimine-Bearing Bimetallic (Fe2, Co2, Ni2) Ethylene Oligomerisation Catalysts. *Eur. J. Inorg. Chem.* 2008, 2008, 4597–4607.

- **Semikolenova, N. V.; Sun, W.-H.; Soshnikov, I. E.; Matsko, M. A.; Kolesova, O. V.; Zakharov, A. V.; Bryluk, K. P.** Origin of “Multisite-like” Ethylene Polymerization Behavior of the Single-Site Nonsymmetrical Bis(α,α′-pyridyl)iron(II) Complex in the Presence of Modified Methylaluminoxane. *ACS Catal.* 2017, 7, 2868–2877.

- **Huang, C.; Zhang, Y.; Solan, G. A.; Ma, Y.; Hu, X.; Sun, Y.; Sun, W.-H.** Vinyl-Polyethylene Waxes with Narrow Dispersity
Obtained by Using a Thermally Robust [Bis(imino)trihydroquinolyl]chromium Catalyst. *Eur. J. Inorg. Chem.* 2017, 2017–4166.

(59) Sheldrick, G. M. SHELXT—Integrated space-group and crystalstructure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.

(60) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.