

Fe(II) and Co(II) pyridinebisimine complexes bearing different substituents on *ortho*- and *para*-position of imines: synthesis, characterization and behavior of ethylene polymerization

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Abstract

A series of 2,6-bis(imino)pyridyl iron(II) and cobalt(II) complexes $[2,6-(\text{ArN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}]\text{MCl}_2$ (Ar = 2,6-*i*-Pr₂C₆H₃, M = Fe: **3a**, M = Co: **4a**; Ar = 2,4,6-*i*-Pr₃C₆H₂, M = Fe: **3b**, M = Co: **4b**; Ar = 2,6-*i*-Pr₂-4-BrC₆H₂, M = Fe: **3c**, M = Co: **4c**; Ar = 2,4-*i*-Pr₂-6-BrC₆H₂, M = Fe: **3d**, M = Co: **4d**) has been synthesized, characterized, and investigated as precatalysts for the polymerization of ethylene in the presence of modified methylaluminoxane (MMAO). The substituents of pyridinebisimine ligands and their positions located significantly influence catalyst activity and polymer property. It is found that the catalytic activities of the iron complexes/MMAO systems are mainly dominated by electronical effect, while those of the cobalt complexes/MMAO systems are primarily controlled by hindering effect.

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1. Introduction

The late transition metal catalysts for olefin polymerization have attracted intense interest because of the potential to yield polymers with different microstructures and more tolerant of functionalized monomers [1–3]. Most late transition metal systems often oligomerize olefins due to a strong trend to β -hydride transfer. The key to getting a late transition metal catalyst with high activity and to obtaining high molecular weight polymers is incorporating bulky substituents into the *ortho*-position of coordinating nitrogen atoms of ligands [1]. In 1998, Brookhart's and Gibson's groups [4–9] independently reported that

the iron (II) and cobalt (II) complexes bearing tridentate pyridinebisimine ligands can be activated with methylaluminoxane (MAO) to afford highly active catalysts for the polymerization of ethylene. The catalyst activity and the product property depend on the substitution pattern of the ligands used [10–14].

As well known, two factors can affect catalyst activity and the behavior of olefin polymerization. One is steric effect, the other is electronical factor of ligands. After studying the relationship between ligand structures and catalyst performances, Möhring and Coville [15] concluded that the electronic effect could contribute as much as 80% of the change in the catalytic activities of (CpR)₂ZrCl₂/MAO systems. Yang and coworkers [16–18] reported that electronical effects considerably influence the catalytic activities of metallocene and α -diimine Ni(II) complexes activated with MAO for olefin polymerization. However, there is a little study on the

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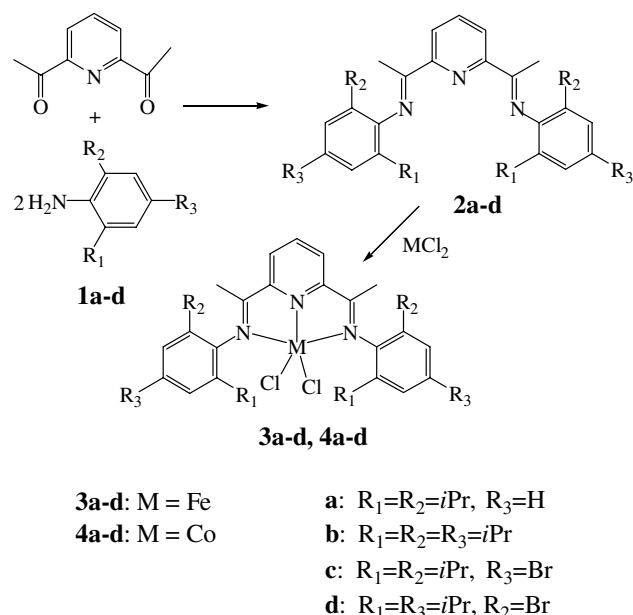
correlation between the activities of iron and cobalt catalyst and the electronic effects of ligands [19].

Here, we wish to report the synthesis and characterization of a series of the iron and cobalt pyridinebisimine complexes, in which the *ortho*- or *para*-position on the imine groups were replaced by the substituents with different electronic effects. We also demonstrate that the both hindering and electronic effects significantly influence the catalytic activities of the pyridinebisimine iron and cobalt catalysts and the properties of the polyethylenes obtained.

2. Results and discussion

2.1. Synthesis and characterization of complexes

The ligands **2a–d** were prepared in high yield by the condensation reaction of two equivalents of the appropriate aniline **1a–d** with one equivalent of 2,6-diacetylpyridine (Scheme 1). The iron complexes **3a–d** and cobalt complexes **4a–d** were synthesized in good yield by treating MX_2 ($\text{M} = \text{Fe}, \text{Co}; \text{X} = \text{Cl}$) with the corresponding 2,6-bis(imino)pyridyl ligands in tetrahydrofuran (THF) at room temperature, as shown in Scheme 1. All the iron complexes **3a–d** are blue in color, while the cobalt species **4a–d** are green–brown. The crystal **3c**, grown from a layered CH_2Cl_2 –pentane (1:1) solution, was subject to single-crystal X-ray diffraction study. The molecular structure of the iron complex **3c** is shown in Fig. 1. The data collection and refinement data of the analysis are summarized in Table 1, and



Scheme 1.

the selected bond lengths and angles are presented in Table 2. For the complex **3c**, an orthorhombic crystal system and a $P2_12_12_1$ space group were observed, while a triclinic crystal system and a P space group, for the complex **3a**, were reported by Brookhart's group [4]. Contrast to the pseudo square pyramidal geometry of **3a**, the iron complex **3c** displays C_{2v} molecular symmetry (angles $\text{N}2\text{--Fe--Cl}1$ and $\text{N}2\text{--Fe--Cl}2$ are almost equivalent) and has pseudo trigonal bipyramidal geometry in which $\text{N}1$ and $\text{N}3$ occupy apical positions.

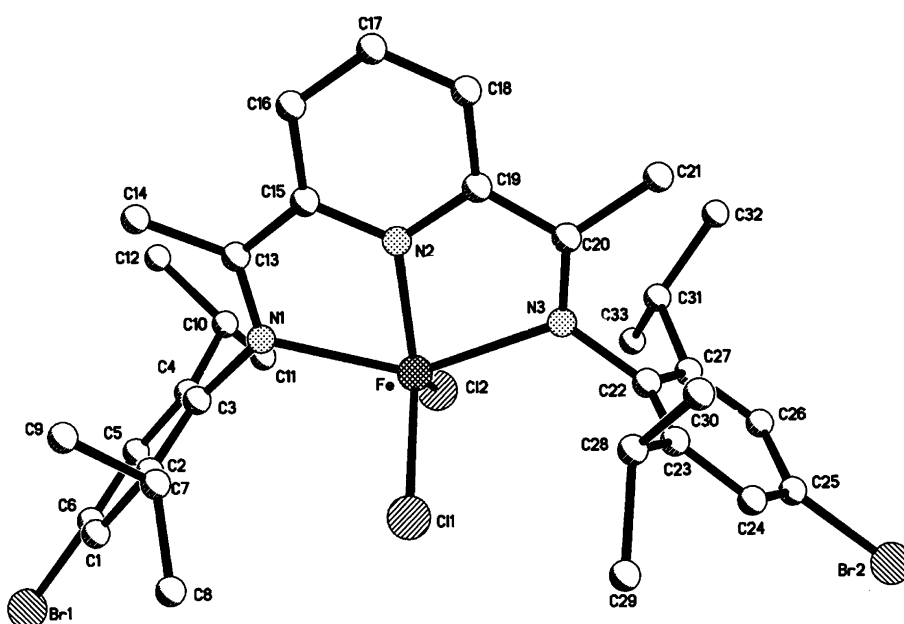


Fig. 1. Molecular structure of the iron complex **3c**. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity.

Table 1
Crystal data and structure refinements of the complex **3c**

Empirical formula	C ₃₃ H ₄₁ Br ₂ Cl ₂ FeN ₃
Formula mass	766.26
Crystal size (mm ³)	0.31 × 0.18 × 0.06
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	14.648 (6)
<i>b</i> (Å)	16.110 (7)
<i>c</i> (Å)	21.270 (9)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	5019
<i>Z</i>	4
Density (calcd.) (Mg/cm ³)	1.014
Absorption coefficient (mm ⁻¹)	2.017
<i>F</i> (000)	1560
θ range for data collected (°)	1.59 to 24.09
Reflection collected	23,906
Data/restraints/parameters	7916/8/356
Independent reflections	7916
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0997, <i>wR</i> ₂ = 0.2689
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2161, <i>wR</i> ₂ = 0.3504
Absorption correction.	Semi-empirical from equivalents
Goodness-of-fit on <i>F</i> ²	0.961
Max./min. transmission	0.8818 and 0.5700
Largest peak/hole in final diff. map (e/Å ³)	1.067 and -0.670

Table 2
Selected bond lengths (Å) and angles (°) for complex **3c**

Fe–N(2)	2.068(4)	Fe–N(1)	2.260(9)
Fe–N(3)	2.280(8)	C(1)–Br(1)	1.878(6)
C(25)–Br(2)	1.911(13)	Fe–Cl(1)	2.250(7)
Fe–Cl(2)	2.264(7)	C(13)–N(1)	1.268(14)
C(20)–N(3)	1.289(12)		
N(2)–Fe–N(1)	72.7(3)	N(2)–Fe–N(3)	73.2(3)
N(1)–Fe–N(3)	145.8(3)	N(2)–Fe–Cl(1)	124.3(6)
N(1)–Fe–Cl(1)	99.6(5)	N(3)–Fe–Cl(1)	100.2(5)
N(2)–Fe–Cl(2)	124.4(6)	N(1)–Fe–Cl(2)	98.4(5)
N(3)–Fe–Cl(2)	99.9(5)	Cl(1)–Fe–Cl(2)	111.34(17)

2.2. Ethylene polymerization with the iron complexes **3a–d**

On treatment with MMAO, all the iron complexes **3a–d** are active towards ethylene polymerization. The strong temperature dependence of the catalytic activities is their common characteristic. For example, the catalyst activities decrease monotonously with the increase of polymerization temperature, as shown in Fig. 2. In addition, Al/Fe molar ratio can also show a significant influence upon the catalyst activities. Hence, several experiments were carried out to determine the effect of the Al/Fe molar ratio on the catalyst activities. Fig. 3 shows the results of these experiments in a range of Al/Fe from 800 to 2000. The catalyst activities increase with an increase in the Al/Fe molar ratio from 800 to 1600, nevertheless, the Al/Fe molar

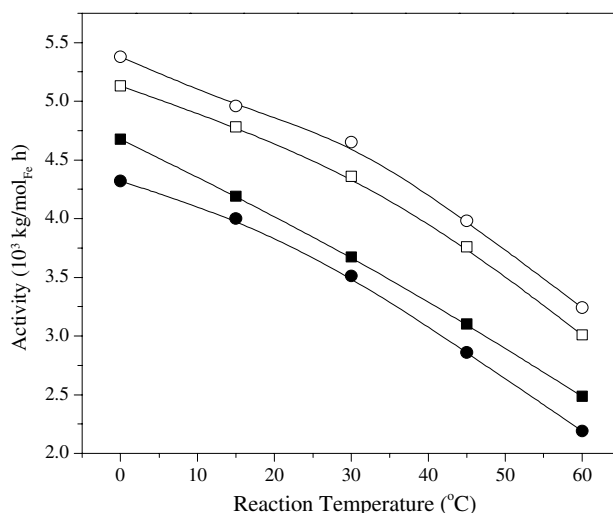


Fig. 2. Plot of reaction temperature versus the catalytic activity of catalyst **3a** (■), **3b** (●), **3c** (□) and **3d** (○). Ethylene pressure, 1 bar; polymerization time, 10 min; Al/Fe = 1200.

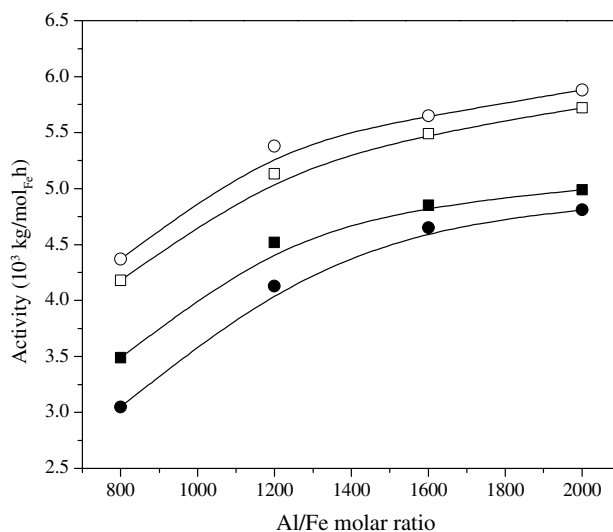


Fig. 3. Plot of Al/Fe molar ratio versus the catalytic activity of catalyst **3a** (■), **3b** (●), **3c** (□) and **3d** (○). Ethylene pressure, 1 bar; polymerization time, 10 min; temperature, 0 °C.

ratio has a little influence on the catalyst activities with further increase.

In order to evaluate the effect of ligand structure on the performances of the iron precatalysts, we polymerize ethylene with the precatalysts **3a–d** under the fixed conditions (atmospheric pressure, 0 °C, and Al/Fe (molar ratio) = 1200). The typical results are summarized in Table 3. The data in Table 3 indicate that the variation of the *ortho*- or *para*-substituents of pyridinebisimine ligands has a pronounced effect not only on the catalyst activity, but also on the molecular weight of the resulting polymer. The replacement of the *para*-aryl proton (**3a**) with an electron-donating isopropyl group (**3b**)

Table 3
Results of ethylene polymerization with the iron and cobalt complexes^a

Entry	Catalyst	Yield (g)	Activity (kg PE/mol _{Fe} h bar)	T_m^b (°C)	\bar{M}_w (kg/mol) ^c	\bar{M}_w/\bar{M}_n^c
1	3a	1.54	4620	129.4	60.4	38.2
2	3b	1.41	4230	128.0	41.6	23.8
3	3c	1.71	5130	132.3	87.1	46.8
4	3d	1.79	5380	127.6	36.9	58.3
5	4a	0.62	1860	128.8	57.8	3.58
6	4b	1.03	3090	131.9	80.3	9.56
7	4c	0.91	2730	131.5	79.1	6.30
8	4d	1.11	3330	126.7	30.1	3.04

^a Polymerization condition: 2 μ mol catalyst, Al/Fe = 1200 (molar ratio), polymerization reaction at 0 °C and under 1 bar for 10 min.

^b Determined by DSC (heating rate: 10 °C/min).

^c Determined by GPC.

results in the decrease of catalyst activity and \bar{M}_w of the polyethylene obtained (the catalyst activity from 4620 to 4230 kg PE/mol_{Fe} h, \bar{M}_w from 60.4 to 41.6 kg/mol). However, an electron-withdrawing Br on the *para*-position of imines (**3c**) increases the catalyst activity to 5130 kg PE/mol_{Fe} h, and \bar{M}_w to 87.1 kg/mol.

It is noteworthy that the precatalysts **3a–c** have the same substituents on the *ortho*-position of the imines in the tridentate ligands, as a result, the rates of β -H eliminations for these systems should be the same. The exclusive difference among these precatalysts is the substituents on the *para*-position of the imines. There are two sides which might explain the differences of the catalyst activities and the polymer mass. One is the bulk of the substituents, the other is the electronic effect of the substituents. According to Cossee [8,20], the mechanism of the homogeneous polymerizations with iron catalysts should involve cationic intermediate species, and the active centers of iron catalysts are generally considered as [LFe–R]⁺. The electrophilic character of the center iron atom is one of the key factors determining the rate of chain propagation. A more electrophilic character of center iron atom favors the insertion of ethylene. In addition, an important feature of iron catalyst is the chain transfer to aluminum. The competition between the chain propagation and the chain-transfer to Al can play a decisive role on the molecular weight of polymer. We consider tentatively that the electronic effect is more important for the precatalysts **3a–c**, although the substituent in the *para*-position can provide a certain extent steric effect. The existence of the electron-donating group on the *para*-position of coordinative nitrogen atom can enhance the electron releasing ability and weaken the electrophilic character of the center iron atom of the precatalyst **3b**, which is unfavorable to chain propagation relative to chain transfer. As a result, the precatalyst **3b** displays a lower activity, and produces lower molecular weight polymers than the precatalyst **3a**. With respect to the precatalyst **3c** containing the electron-withdrawing group, due to the strong electron-withdrawing ability of halogen atom, the electrophilic character on the center iron atom is enhanced remarkably, which makes the cat-

ionic species more unstable. This makes for ethylene insertion. Thus, the precatalyst **3c** presents higher activity and yields higher molecular weight polyethylenes, in comparison with the precatalyst **3a**.

By comparing the molecular structures of the complex **3c** and **3a**, we found that the electron-withdrawing ability of Br atom on the *p*-position of the imines in the complex **3c** increased the bond distances of Fe–N(1) and Fe–N(3) [**3c**, Fe–N(1), 2.260(9) Å; Fe–N(3), 2.280(8) Å. **3a**, Fe–N(1), 2.222(4) Å; Fe–N(3), 2.225(5) Å]. The increase of the bond length of Fe–N(1) and Fe–N(3) indicates that the density of electron cloud of the metallic center decreases, namely, the electron-withdrawing group can indeed enhance the electrophilic character of the center iron atom. The acceleration of chain propagation restrains the chain transfer reaction, resulting in the increase of the catalyst activity and the molecular weight of the polymers obtained. Therefore, the precatalyst **3c** exhibits higher activity and yields higher molecular weight polyethylenes than the precatalyst **3a**.

For the precatalyst **3d**, not only the electronic effect but also the steric effect should be considered. First, the electron-withdrawing ability of halogen atom on the *o*-position of the imines (**3d**) is stronger than that on the *p*-position (**3c**), which enhances the electrophilic character on center iron atom. As a result, the rate of chain propagation increases. Second, the reduction of the steric bulk at the *o*-aryl position causes the increase of the rate of β -H elimination reaction. Thus, the precatalyst **3d** shows the higher activity and produces lower molecular weight polymer than the precatalyst **3c** (Table 3).

2.3. Ethylene polymerization with the cobalt complexes **4a–d**

Since iron is a metal in group 8, and cobalt is a metal in group 9, the electronic environments are different between their pyridinebisimine complexes. It is expected that electronical effect of the pyridinebisimine ligands on the preferences of the two type catalysts might also be different. In comparison with the iron precatalysts, the corresponding cobalt precatalysts show lower

activities and produce lower molecular weight polymers (Table 3). Both the precatalyst **4b** with an electron-donating substituent and the precatalyst **4c** with an electron-withdrawing substituent on the *para*-position of the imines display higher activities and produce higher molecular weight polymers (**4b** (Entry 6 in Table 3): activity, 3090 kg PE/mol_{Fe} h, \bar{M}_w , 80.3 kg/mol; and **4c** (Entry 7 in Table 3): activity, 2730 kg PE/mol_{Fe} h, \bar{M}_w , 79.1 kg/mol) than the corresponding precatalyst **4a** (Entry 5 in Table 3, activity, 1860 kg PE/mol_{Fe} h, 57.8 kg/mol). It is noteworthy that the order of catalyst activities increases (**4a** < **4c** < **4b**) accords with that of the bulk of substituents (H < Br < *i*-Pr). This indicates that the hindering effect of *para*-substituent is the main factor to determine catalyst activities and polymer mass. Similar to the iron precatalysts, due to the reduction of steric bulk on the *ortho*-position of the imines, the precatalyst **4d**, displays higher catalytic activity toward ethylene polymerization and produces lower molecular weight polymers than the precatalyst **4a**.

3. Conclusions

The synthesis and characterization of a series of iron and cobalt precatalysts for ethylene polymerization have been described. For iron precatalysts, not only the steric bulk but also the electronic effect of the substituents on the *ortho*- or *para*-position of the imines in pyridinebisimine ligands plays an important role on the catalyst activities and the properties of the resulting polyethylenes. The electron-withdrawing group can increase the electrophilic character of the center iron atom, which favors the chain propagation. The acceleration of chain propagation results in the increase of catalyst activity. Contrarily, electron-donating group weakens the electrophilic character of the center iron atom, which decreases the rate of chain propagation relative to chain transfer, leading to the decrease in the molecular weight of the polyethylenes obtained. The substituents in pyridinebisimine ligands also affect considerably cobalt catalyst activity and polyethylene property. For the *para*-substituents, hindering effect is more important to determine catalyst activities and polymer mass than electronic effect.

4. Experimental

4.1. General procedures and materials

All manipulations of water and/or moisture sensitive compounds were performed by means of standard high vacuum Schlenk and cannula techniques under a N₂ atmosphere. Toluene was refluxed and distilled from sodium/benzophenone under dry nitrogen. Modified methylaluminoxane (MMAO) (7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. All other chemicals were commercially available and used without further purification. The iron complexes **3a–d** and the cobalt complexes **4a–d** were prepared according to the procedure reported by Gibson and coworkers [8].

The NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 110 °C with *o*-C₆D₄Cl₂ as the solvent. The NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer at ambient temperature, CDCl₃ as solvent. Mass spectra were obtained using electron impact (EI-MS). Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. The FT-IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin–Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C with a PL-GPC 220 type high temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard Easi-Cal PS-1 (PL Ltd.).

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4.2. Synthesis of aniline derivatives (**1b–d**)

4.2.1. 2,4,6-Triisopropylaniline (**1b**)

The mixture of fuming HNO₃ (16 g, 0.25 mol), CH₃COOH (10 g), Ac₂O (10 g) was dropped into a solution of 1,3,5-triisopropylbenzene 32 g (0.16 mol) and Ac₂O (30 g) at 0 °C in 2 h. The precipitate was filtration and recrystallized in methanol and dried to afford 2,4,6-triisopropyl nitrobenzene as yellow crystal 27 g (68%). ¹H NMR (CDCl₃): δ 6.91 (s, 2H, *Ar–H*), 2.85 (m, 3H, *CHMe*₂), 1.28 (d, 18H, *CHMe*₂).

A 500 ml Schlenk flash containing 200 ml of degassed ethanol was charged with above product (12.5 g, 0.05 mol), 5% Pd/C (12 g) and 150 ml NH₂NH₂·H₂O. The reaction mixture was refluxed for 18 h. After the reaction mixture was cooled to room temperature, the Pd–C catalyst was filtrated and the solvent was removed. The residual was washed with 20% aqueous NaOH, extracted with diethyl ether (100 ml) and dried over Na₂SO₄. The diethyl ether was vaporized to give **1b** as a colorless liquid (11 g, 100%). ¹H NMR (CDCl₃): δ 6.99 (s, 2H, *Ar–H*), 3.60 (s, 2H, NH₂), 2.95 (m, 3H, *CHMe*₂), 1.36 (d, 18H, *CHMe*₂).

4.2.2. 4-Boromo-2,6-diisopropylaniline (**1c**)

Br₂ (15 g, 0.094 mol) was dropped into the solution of 2,6-diisopropylaniline (18 g, 0.102 mol) and Fe (0.056 g, 1 mmol) in 2 h. The precipitate was separated by filtration, recrystallized in ethanol. The white solid was washed with 20% aqueous NaOH, extracted with diethyl ether (100

mL) and dried over Na_2SO_4 . The solvent was removed to give product **1c** as a colorless powder (9.8 g, 41%). ^1H NMR (CDCl_3): δ 7.14 (s, 2H, Ar–H), 3.52 (s, 2H, NH_2), 2.91 (m, 2H, CHMe_2), 1.27 (d, 12H, CH-CH_3).

4.2.3. 2-Bromo-4,6-diisopropylaniline (**1d**)

2-Bromo-4,6-diisopropylbenzene was prepared by nitration of 1,3-diisopropylbenzene using the procedure described in above (4.2.1) as yellow liquid (yield, 90.6%), ^1H NMR (CDCl_3): δ 7.68 (d, 1 H, Ar–H), 7.29 (s, 1 H, Ar–H), 7.14 (d, 1 H, Ar–H), 3.49 (m, 1 H, CHMe_2), 2.98 (m, 1 H, CHMe_2), 1.27 (d, 12H, CH-CH_3) and **1d** as a colorless liquid (11.5 g, 89.8%), ^1H NMR (CDCl_3): δ 7.04 (s, 1H, Ar–H), 7.00 (d, 1H, Ar–H), 6.66 (d, 1H, Ar–H), 3.59 (s, 2H, $\text{NH}_2=\text{C}$), 2.86 (m, 2H, CHMe_2), 1.28 (d, 12H, CHMe_2).

4.3. Synthesis of ligands (**2b–d**)

4.3.1. 2,6-Diacetylpyridinebis(2,4,6-triisopropylanil) (**2b**)

A solution of 2,6-diacetylpyridine (0.6 g, 4 mmol), **1b** (1.97 g, 9 mmol), and *p*-toluenesulfonic acid (0.02 g) in toluene (100 mL) was refluxed for 3 days, with azeotropic removal of water using a Dean-Stark trap. Upon cooling to room temperature, the product was precipitated from ethanol. After filtration the yellow solid was washed with cold ethanol and dried in a vacuum oven (50 °C) over night. The ligand **2b** as a yellow powder was obtained in 79% yield. The other ligands **2c** and **2d** were prepared by the same procedure with similar yields. ^1H NMR (CDCl_3): δ 8.47 (d, 2H, Py–Hm), 7.91 (t, 1H, Py–Hp), 7.02 (s, 4H, Ar–H), 2.85 (m, 6H, CHMe_2), 2.28 (s, 6H, $\text{N}=\text{CCH}_3$), 1.20 (d, 36H, CH-CH_3).

4.3.2. 2,6-Diacetylpyridinebis(4-bromo-2,6-diisopropylanil) (**2c**)

Yield: 91.3%. ^1H NMR (CDCl_3): δ 8.49 (d, 2 H, Py–Hm), 7.96 (t, 1 H, Py–Hp), 7.30 (s, 4H, Ar–H), 2.91 (m, 4H, CHMe_2), 2.28 (s, 6H, $\text{N}=\text{CCH}_3$), 1.18 (d, 24H, CH-CH_3).

4.3.3. 2,6-Diacetylpyridinebis(2-bromo-4,6-diisopropylanil) (**2d**)

Yield: 90.1%. ^1H NMR (CDCl_3): δ 8.43 (d, 2 H, Py–Hm), 7.86 (t, 1H, Py–Hp), 7.25 (s, 2 H, Ar–H), 7.04 (s, 2 H, Ar–H), 2.81 (m, 4 H, CHMe_2), 2.26 (s, 6H, $\text{N}=\text{CCH}_3$), 1.19 (d, 24 H, CH-CH_3).

4.4. Synthesis of iron and cobalt complexes (**3a–d**, **4a–d**)

4.4.1. [2,6-Diacetylpyridinebis(2,4,6-triisopropylanil)] FeCl_2 (**3b**)

To a suspension of ligand **2b** (0.283 g, 0.5 mmol) were added to a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.099 g, 0.5 mmol)

in tetrahydrofuran (THF) (20 mL). The mixture was stirred at room temperature for 5 h under nitrogen atmosphere, and then a blue solid was isolated by filtration and washed several times by cold THF to yield iron complex **3b** as a blue powder 0.292 g (84.4%). EI-MS (70 eV): $m/z = 691$ [M^+]. Anal. Calcd. for $\text{C}_{39}\text{H}_{55}\text{Cl}_2\text{FeN}_3$: C, 67.63; H, 8.00; N, 6.07. Found: C, 67.32; H, 7.91; N, 6.00%.

4.4.2. [2,6-Diacetylpyridinebis(2,6-diisopropylanil)] FeCl_2 (**3a**)

The procedure as above using ligand **2a** (0.241 g, 0.5 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.099 g, 0.5 mmol) gave iron complex **3a** as a blue powder 0.266 g (87.6%). EI-MS (70 eV): $m/z = 607$ [M^+]. Anal. Calcd. for $\text{C}_{33}\text{H}_{43}\text{Cl}_2\text{FeN}_3$: C, 65.14; H, 7.12; N, 6.91. Found: C, 65.32; H, 7.04; N, 6.82%.

4.4.3. [2,6-Diacetylpyridinebis(4-bromo-2,6-diisopropylanil)] FeCl_2 (**3c**)

The procedure as above using ligand **2c** (0.320 g, 0.5 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.099 g, 0.5 mmol) gave iron complex **3c** as a blue powder 0.332g (86.8%). EI-MS (70 eV): $m/z = 763$ [M^+]. Anal. Calcd. for $\text{C}_{33}\text{H}_{41}\text{Br}_2\text{Cl}_2\text{FeN}_3$: C, 51.73; H, 5.39; N, 5.48. Found: C, 51.86; H, 5.27; N, 5.37%.

4.4.4. [2,6-Diacetylpyridinebis(2-bromo-4,6-diisopropylanil)] FeCl_2 (**3d**)

The procedure as above using ligand **2d** (0.320 g, 0.5 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.099 g, 0.5 mmol) gave iron complex **3d** as a blue powder 0.335 g (87.4%). EI-MS (70 eV): $m/z = 763$ [M^+]. Anal. Calcd. for $\text{C}_{33}\text{H}_{41}\text{Br}_2\text{Cl}_2\text{FeN}_3$: C, 51.73; H, 5.39; N, 5.48. Found: C, 51.62; H, 5.28; N, 5.45%.

4.4.5. [2,6-Diacetylpyridinebis(2,4,6-triisopropylanil)] CoCl_2 (**4b**)

To a suspension of ligand **2b** (0.226 g, 0.4 mmol) were added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.095 g, 0.4 mmol) in THF (20 mL). The mixture was stirred at room temperature for 5 h under nitrogen atmosphere, and then a brown powder was isolated by filtration and washed several times by cold THF to yield cobalt complex **4b** 0.224 g (80.4%). EI-MS (70 eV): $m/z = 694$ [M^+]. Anal. Calcd. for $\text{C}_{39}\text{H}_{55}\text{Cl}_2\text{CoN}_3$: C, 67.33; H, 7.97; N, 6.04. Found: C, 67.17; H, 7.89; N, 5.93%.

4.4.6. [2,6-Diacetylpyridinebis(2,6-diisopropylanil)] CoCl_2 (**4a**)

The procedure as above using ligand **2a** (0.192 g, 0.4 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.095 g, 0.4 mmol) gave cobalt complex **4a** as a brown powder 0.207 g (84.6%). EI-MS (70 eV): $m/z = 610$ [M^+]. Anal. Calcd. for $\text{C}_{33}\text{H}_{43}\text{Cl}_2\text{CoN}_3$: C, 64.81; H, 7.09; N, 6.87. Found: C, 65.01; H, 7.00; N, 6.80%.

4.4.7. [2,6-Diacetylpyridinebis(4-bromo-2,6-diisopropylanil)]CoCl₂ (**4c**)

The procedure as above using ligand **2c** (0.256 g, 0.4 mmol) and CoCl₂·6H₂O (0.095 g, 0.4 mmol) gave cobalt complex **4c** as a brown powder 0.261 g (84.7%). EI-MS (70 eV): *m/z* = 766 [M⁺]. Anal. Calcd. for C₃₃H₄₁Br₂Cl₂CoN₃: C, 51.52; H, 5.37; N, 5.46. Found: C, 51.37; H, 5.23; N, 5.59%.

4.4.8. [2,6-Diacetylpyridinebis(2-bromo-4,6-diisopropylanil)]CoCl₂ (**4d**)

The procedure as above ligand **2d** (0.256 g, 0.4 mmol) and CoCl₂·6H₂O (0.095 g, 0.4 mmol) gave cobalt complex **4d** as a brown powder 0.271 g (88.2%). EI-MS (70 eV): *m/z* = 766 [M⁺]. Anal. Calcd. for C₃₃H₄₁Br₂Cl₂CoN₃: C, 51.52; H, 5.37; N, 5.46. Found: C, 51.39; H, 5.25; N, 5.37%.

4.5. Polymerization procedure

The polymerization was carried out in a 200 mL Schlenk flask equipped with a magnetic stirrer. The flask was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene gas (ambient pressure) from an Schlenk line. MMAO and toluene were added via a gastight syringe. The catalyst was dissolved in toluene under a dry nitrogen atmosphere. The solution was transferred into the Schlenk flask to initiate the polymerization. After 10 min at given temperature, all the polymerization experiments were stopped by a large excess of methanol containing a small amount of hydrochloric acid. The coagulated polymer was washed with methanol, filtered and dried under vacuum.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 245654 for the iron complexes **3c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033;

e-mail: deposit@ccdc.cam.ac.uk or WWW: <http://ccdc.cam.ac.uk>).

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