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New bis(imino)pyridine-iron(II)- and cobalt(II)-based catalysts: synthesis, characterization and activity towards polymerization of ethylene

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Abstract

The synthesis of a new series of iron(II)- and cobalt(II)-based complexes of the general formula $M(N\cap N\cap N)Cl_2$ (M = Fe; M = Co) bearing 2,6-bis(imin)pyridyl ligands [A–N=C–Py–C=N–A] that carry bulky, alkyl-free aromatic terminals (A = naphthyl, pyrenyl, 2-benzylphenyl, phenyl) or chiral cycloaliphatic auxiliary moieties (A = ((−)-*cis*-myrtanyl) is described. The Fe(II) complexes are exceptionally active (up to 40800 kg PE/(mol M h) towards the polymerization of ethylene in the presence of methylaluminoxane (MAO) as activator. Varying the steric bulkiness of the aromatic groups in the tridentate ligands affects catalytic productivity, molecular weight and for the first time the microstructure of the resulted material. The Fe(II) precatalysts are an order of magnitude more active than the corresponding Co(II) precatalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron(II)- and cobalt(II)-complexes; Diimine ligands; Linear and branched polyethylene; Polymerization catalysts; Methylaluminoxane

1. Introduction

The discovery of methylaluminoxane (MAO) as co-catalyst for olefin polymerization has allowed an explosive development of new homogeneous Ziegler–Natta catalysts. A huge number of Group IV metal complexes have been synthesized and tested as polymerization catalysts after activation with MAO.

Worldwide research activities on Single-site, metallocene-based catalysts [1–3] have led to convincing improvements of poly(1-olefin) materials as well as to understanding of basic reaction mechanisms responsible for the growth of a stereoregular polymer chain at a metal center. However, this catalyst generation allows only the use of a limited number of polar monomers bearing sterically hindered functionalities due to the sensitivity of early transition metal complexes to electron-donating functional groups [4]. Thus, copolymers of technically important polar monomers with ethylene are produced exclusively by radical polymerization routes in high-pressure processes [5]. Therefore, there is still a great interest to discover and develop new families of polymerization catalyst that can allow more control on the polymer material properties.

Late metal complexes are the most attractive candidates because of their tolerance towards polar functionalities. However, until middle of 90s only few reports were introduced utilizing these compounds as catalysts for polymerization of 1-olefins and ethylene [6]. This could be due to the fact that these catalysts generally exhibit reduced activities for olefin insertion and β-hydride elimination, which steadily competes with chain growth resulting in the formation of oligomers [7].

In 1995 Brookhart and coworkers reported new Ni(II)- and Pd(II)-based catalysts bearing bulky diimine ligands for ethylene polymerization [8,9]. These catalysts are highly active and produce high molecular weight polymers. The bulky substituents on the aryl groups of the ligands block an associative olefin exchange, thus effectively retarding chain transfer pro-

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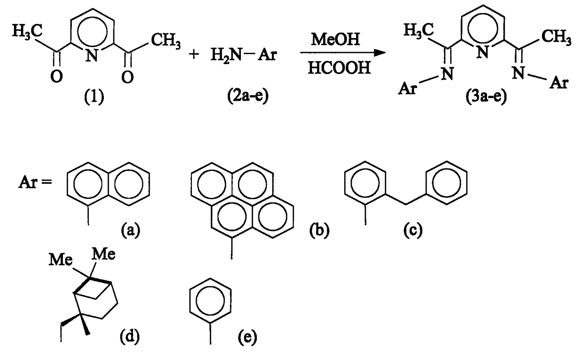
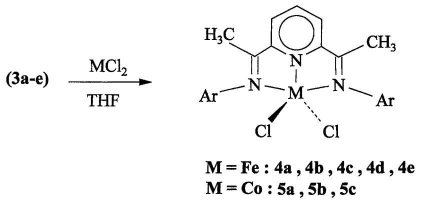
cesses. Furthermore, the microstructure of the polymers produced is a function of temperature, monomer pressure, steric bulkiness of the auxiliary ligands, and transition metal center. Variation of these factors allows access to a range of linear and branched polyethylene.

More recently, iron(II)- and cobalt(II)-based/MAO catalysts systems that are capable for polymerizing ethylene were reported by Brookhart et al. [10] and Gibson et al. [11,12] The complexes are pentacoordinate bearing 2,6-bis(imino)pyridyl tridentate ligands with substituted aryl groups as terminals. In contrast to palladium(II)- and nickel(II)-based catalysts that produce linear or branched polyethylene, these iron(II) and cobalt(II) catalysts produce only highly linear polyethylene. Ligand substituents have no influence on the polymer microstructure even at high temperatures and low ethylene pressure. By utilizing catalysts which are lacking the *ortho*-alkyl substituents on the aryl groups of the ligand only oligomers or polymer traces were isolated [13].

In this report we describe the synthesis of new iron(II) and cobalt(II)- based complexes bearing 2,6-bis(imino)pyridyl ligands that contain bulky aromatic terminals such as pyrenyl, 2-benzylphenyl, and naphthyl. The new catalysts are remarkably active towards polymerization of ethylene. Varying the steric bulkiness of the aryl groups in the tridentate ligands can allow the control of both the molecular weight and the microstructure of the resulted polyethylene. In addition, the increase of the steric bulk of the aromatic groups of the ligand parallels the increase of catalyst productivity.



Scheme 1. Synthesis and structures of the tridentate bis(imino)-pyridine ligands (**3a**–**3e**).



Scheme 2. Synthesis of the iron(II) (**4a**–**4e**) and cobalt(II) complexes (**5a**–**5c**) reported in the present study.

2. Results and discussion

2.1. Ligands and complexes

The tridentate 2,6-bis(imino)pyridine ligands (**3a**–**3e**) were prepared in high yields by the condensation reaction of 2,6-diacetylpyridine (**1**) with two equivalent of the desired amine (**2a**–**2e**) in MeOH at 50 °C in the presence of catalytic amount of formic acid (Scheme 1).

Treatment of the metal salts $FeCl_2$, and $CoCl_2$ with the ligands (**3a**–**3e**) in THF for 24 h afford the complexes (**4a**–**4e** and **5a**–**5c**) (Scheme 2) with high to moderate yields.

To confirm the identity of the compounds prepared in the present study, a variety of techniques including elemental analysis, mass spectroscopy (EI), infrared spectroscopy, ^{1}H- and ^{13}C-NMR, and magnetic susceptibility (μ_{eff}, BM) have been used. The isolated complexes are microcrystalline or powder-like and stable at atmospheric conditions.

Magnetic susceptibility (μ_{eff}, BM) of the complexes were determined by a Faraday balance at room temperature. All complexes are paramagnetic. The iron(II) complexes (**4a**–**4c**) and the analogous cobalt(II) complexes (**5a**–**5c**) are high spin species with a magnetic moment (μ_{eff}) of 4.55–5.42 BM [14], but complexes **4d** and **4e** afford a magnetic moment of 1.52 and 2.71 BM, respectively. The electronic environment of the complexes was also influenced by the ligand substituents. In the complexes **4a**–**4c**, a slight difference in the magnetic moment values with varying the bulkiness of the auxiliary aromatic groups was observed, which suggests the presence of some dissimilarity in the geometry among the penta-coordinated complexes.

Amines (1-naphthylamine, 1-aminopyrene, 2-benzylaniline, aniline, (−)-(*cis*)-myrtanylamine) that are used as auxiliary ligands were optimized at the B3LYP/SV(P) level of theory by using Gaussian 98 code [15]. Their electronic properties were evaluated by making use of NBO analysis. The results showed that only negligible changes are observed on the electronic properties of the nitrogen upon varying the bulkiness of the aryl groups (C–N bond length $\cong 1.39$ Å; charge at N $\cong -0.83$; purity of lone pair $\cong 91$–92%), while major alterations were observed upon replacing the aryl by the alkyl substituent (−)-(*cis*)-myrtanyl (C–N bond length $\cong 1.46$ Å; charge at N $\cong -0.89$; purity of lone pair $\cong 98$%). [redacted]

Table 1
Polymerization results

Entry no.	Cat. code	Catalyst	Loading (μmol)	Pressure (bar)	Yield (g)	Activity 10^3 kg PE/mol cat. h	M_w [a] $\times 10^3$	T_m [b] (°C)
1	**4a**	(BNaEP)$FeCl_2$	3.0	3.0	28.5	9.50	165.2	115
2	**5a**	(BNaEP)$CoCl_2$	3.0	3.0	2.02	0.673	63.0	129
3	**4b**	(BPyEP)$FeCl_2$	3.0	3.0	33.7	13.48	19.5	110, 121
4	**5b**	(BPyEP)$CoCl_2$	3.0	3.0	0.31	0.103	43.8	128
5	**4c**	(BBzEP)$FeCl_2$	3.0	3.0	44.0	11.00	4.30	125
6	**4c**	(BBzEP)$FeCl_2$	1.0	2.0	20.43	40.86	3.70	n.d. [c]
7	**4c**	(BBzEP)$FeCl_2$	1.1	1.0	3.25	2.96	21.9	109, 122
8	**5c**	(BBzEP)$CoCl_2$	3.0	3.0	0.22	0.073	4.60	123
9	**4d**	(BMyEP)$FeCl_2$	3.0	3.0	0.1	0.033	37.3	90, 126
10	**4e**	(BPhEP)$FeCl_2$	3.0	3.0	0.19	0.063	n.d. [c]	125

Conditions: cat/MAO, 1:1000 (entry 7, 1:300); solvent (toluene, 200 ml); polymerization time 60 min (entry 6, 30 min); temperature, 30 °C.

[a] Molecular weight data reported against polystyrene standards.

[b] Determined by differential scanning calorimetry.

[c] n.d.: not determined.

2.2. Polymerization experiments

The catalysts are generated in situ in toluene by the addition of methylaluminoxane as activator in the presence of ethylene. The polymerization results with the different precatalysts are summarized in Table 1.

Complex **4c** [(BBzEP)$FeCl_2$], where the ligand carries one benzyl substituent on each phenyl group, exhibits extremely high activities that is about 20-fold more compared with the most active iron(II) catalysts reported previously under similar polymerization condition. For example the activity of precatalyst **4c** (entry 6, Table 1) is 40800 kg PE/(mol Fe h), while that for the precatalyst [Fe{(2,6-i-PrPh)$_2$PBIMe$_2$}Cl$_2$] (**I**) (2,6-*i*-PrPh)$_2$PBIMe$_2$: 2,6-bis(1-(2,6-diisopropylphenylimino)-ethyl)pyridine) [10] that contains 2,6-diisopropylphenyl as terminal moieties is 1655 kg PE/(mol Fe h) under the same polymerization conditions ($M_w = 217 \times 10^3$ g mol^{-1}; $M_w/M_n = 47.9$).

For comparison reasons, the ligands 2,6-bis[(1-phenylimino)ethyl]pyridine (**3e**) (carry only phenyl groups as terminals), 2,6-bis[(1-(*cis*)-myrtanylimino)-ethyl]pyridine (**3d**) (carry chiral cycloaliphatic groups) and their iron(II) chloride complexes were prepared and tested for polymerization of ethylene. Both precatalysts showed only low polymerization activities under similar reaction conditions (Table 1). Very low activity was also observed for the catalysts based on the corresponding aldimine ligands [16].

Varying the bulky aryl terminals on the bis (imino) pyridine ligand produces polymers with different microstructure. According to ^{13}C-NMR analysis (Fig. 1), the Fe(II) catalyst bearing the ligand 2,6-bis[1-(2-benzylphenylimino)ethyl]pyridine (**3c**) can convert ethylene to a linear polymer (Fig. 1A), while precatalysts which contain the ligands 2,6-bis[(1-pyrenyl-imino)ethyl]-pyridine (**3b**) and 2,6-bis[(1-naphthylimino)ethyl] pyridine (**3a**) produce branched polymers (Fig. 1B and C, respectively). The extent of branching is decreased when utilizing complex **4b** that contains the more bulky pyrenyl groups. Analysis of the spectra indicates that both methyl ($\delta = 20.0$ ppm) and ethyl branching ($\delta =$ 11.1 and 39.5 ppm) are taking place [17].

The molecular weights vary with modification of the ligands and metal (Table 1). GPC measurements showed that the resulted materials contain high molar mass polyethylene together with low molecular weight portion. Broad molecular weight distributions (M_w/M_n) were observed, which is typical for these MAO-activated Fe(II) complexes bearing 2,6-bis(imino)pyridyl tridentate ligands with alkyl substituted aryl groups [8,10]. According to differential scanning calorimetry (DSC), the polymer samples exhibit melting temperatures (T_m) ranging from 90 to 129 °C (Table 1).

The mechanism of polymerization using 4c is thought to be similar to that with other systems and involves a cationic alkyl complex as the active species. Coordination of ethylene to the metal center followed by migratory insertion into the M-alkyl bond, leads to chain growth and regeneration of an alkyl species. This can undergo further ethylene insertion, giving long polymer chain [18]. The formation of branched polyethylene upon utilizing the precatalysts **4a** and **4b** could took place according to the mechanism proposed for the branch formation in the presence of Ni(II) and Pd(II) diimine catalysts [19].

In summary, we report on highly active 2,6-bis(arylimino)pyridine iron(II)- and cobalt(II)-based ethylene polymerization catalysts, which lack the ortho alkyl substituents on the aryl groups. [redacted] Successful polymerization of propylene at 30 °C and copolymerization of ethylene with higher olefins will be reported shortly.

3. Experimental

All reactions were carried out under dry argon using standard Schlenk techniques. Elemental analyses were performed at the Pharmacology Department, University of Helsinki (EA 1110 CHNS-O CE instrument). ^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200 MHz. ^{13}C-NMR spectra of the ligands were obtained on a Varian Gemini 200 spectrometer operating at 50.286 MHz and those of polymers on a Varian Gemini 2000 (75 MHz), 10 mm probe in TCB at 100 °C. Infrared spectra were measured on BIO-RAD FTS-7 FT-IR spectrometer using KBr pellet. Mass spectra (EI) were acquired with a JEOL JMS-SX102 mass spectrometer. Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards. Magnetic susceptibility (μ_{eff}, BM) of the complexes was determined by Faraday balance at room temperature (r.t.). The structures of 1-naphthylamine, 1-aminopyrene, 2-benzylaniline, aniline and (−)-(*cis*)-myrtanylamine were optimized at the B3LYP/6-31G level of theory by using Gaussian 98 code, and their electronic properties were evaluated by making use of NBO analyses. The calculated IR spectra at the same level did not show any imaginary frequencies.

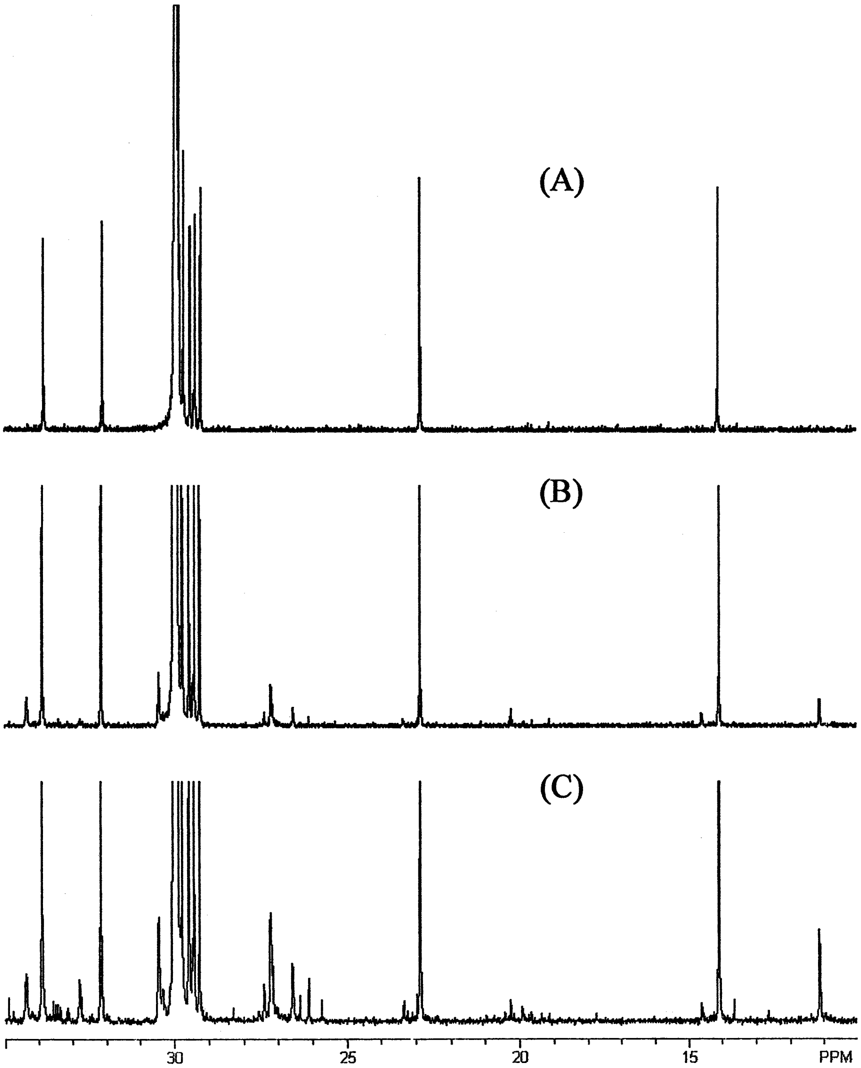


Fig. 1. ^{13}C-NMR spectra of polyethylene produced with different catalysts: (A) (BBzEP)FeCl$_2$ (**4c**, entry 5); (B) (BPyEP)FeCl$_2$ (**4b**); (C) (BNaEP)FeCl$_2$ (**4a**).

3.1. Synthesis of ligands

3.1.1. 2,6-bis[(1-Naphthylimino)ethyl]pyridine (BNaEP) (**3a**)

A solution of 2,6-diacetylpyridine (**1**) (2.0 g, 12.3 mmol) in MeOH (25 ml) was added to a solution of 1-naphthylamine (**2a**) (3.7 g, 25.7 mmol) in the same solvent (25 ml) and three drops of 97% formic acid. After 1 h stirring at r.t., a yellow precipitate was formed which was collected after 5 h, washed with cold methanol (2 × 25 ml) and dried in vacuum.

Yield: 2.75 g (54%), m.p. 172 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 8.68–6.89$ (m, 17H, $H_{arom.}$), 2.47 (s, 6H, $CH_3C{=}N$). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 168.4$ (C=N). IR (KBr, cm^{-1}): 1638 m (C=N). Anal. Calc. for $C_{29}H_{23}N_3$: C, 84.23; H, 5.61; N, 10.16. Found: C, 83.98; H, 5.85; N, 10.32%.

3.1.2. 2,6-bis[(1-Pyrenylimino)ethyl]pyridine (BPyEP) (**3b**)

A solution of (**1**) (0.29 g, 1.78 mmol) in MeOH (25ml) was to added a solution of 1-aminopyrene (**2b**) (0.85 g, 3.92 mmol) in the same solvent (25 ml) and three drops of 97% formic acid. The reaction mixture was stirred at 50 °C for 3 days after which the orange product was filtered, washed with pentane (2 × 50 ml) and dried in vacuum.

Yield: 0.92 g (92%), m.p. 241 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 8.77–7.49$ (m, 21H, $H_{arom.}$), 2.47 (s, 6H, $CH_3C{=}N$). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 168.9$ (C=N), 17.04 ($CH_3C{=}N$). IR (KBr, cm^{-1}): 1633 m (C=N). Anal. Calc. for $C_{42}H_{27}N_3$: 0.5 H_2O: C, 86.29; H, 4.94; N, 7.36. Found: C, 86.38; H, 4.88; N, 7.35%.

3.1.3. 2,6-bis[1-(2-Benzylphenylimino)ethyl]pyridine (BBzEP) (**3c**)

A solution of (**1**) (1.0 g, 6.13 mmol) in MeOH (25 ml) was added to a solution of 2-benzylaniline (**2c**) (2.36 g, 12.87 mmol) in the same solvent (25 ml) and three drops of 97% formic acid. The reaction mixture was stirred at 50 °C for 2 days after which the solvent was evaporated to dryness and the resulted yellow oily product was washed with cold methanol (2 × 5 ml), pentane (2 × 15 ml) and dried in vacuum.

Yield: 2.73 g (90%). ^{1}H-NMR ($CDCl_3$): $\delta = 8.46–6.68$ (m, 21H, $H_{arom.}$), 2.47 (s, 6H, $CH_3C{=}N$). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 167.4$ (C=N), 38.2 ($CH_{2\text{-benzyl}}$), 16.1 ($CH_3C{=}N$). IR (KBr, cm^{-1}): 1638 m (C=N). Anal. Calc. for $C_{35}H_{31}N_3$: C, 85.15; H, 6.32; N, 8.51. Found: C, 84.82; H, 6.41; N, 8.63%.

3.1.4. 2,6-bis[(1-(cis)-Myrtanylimino)ethyl]pyridine (BMyEP) (**3d**)

A solution of (**1**) (0.696 g, 4.26 mmol) in MeOH (25ml) was added a to solution of (−)-(*cis*)-myrtanylamine (**2d**) (1.37 g, 8.94 mmol) in the same solvent (25 ml) and five drops of formic acid. After 1 h of stirring at r.t., a white precipitate was formed which was collected after 14 h, washed with cold methanol (2 × 20 ml) and dried in vacuum.

Yield: 1.2 g (65%), m.p. 106 °C. ^{1}H-NMR ($CDCl_3$): $\delta = 8.07$ (d, *J* (5.0 Hz), $H_{arom.}$), 7.68 (t, *J* (5.0 Hz), $H_{arom.}$), 3.54–3.52 (m, 4H, $CH_{2\text{-Myrtanyl}}$), 2.39 (s, 6H, $CH_3C{=}N$), 1.21, 1.09 (2s, 12H, $CH_{3\text{-myrtanyl}}$). ^{13}C {^{1}H}-NMR ($CDCl_3$): $\delta = 166.2$ (C=N), 13.97 ($CH_3C{=}N$). IR (KBr, cm^{-1}): 1639 m (C=N). Anal. Calc. for $C_{29}H_{43}N_3$: C, 80.32; H, 9.99; N, 9.98. Found: C, 79.99; H, 10.03; N, 9.06%.

3.1.5. 2,6-bis[(1-Phenylimino)ethyl]pyridine (BPhEP) (**3e**)

A solution of (**1**) (1.0 g, 6.13 mmol) in MeOH (25 ml) was added to a solution of aniline (**2e**) (1.23 g, 13.21 mmol) in the same solvent (25 ml) and three drops of 97% formic acid. After 1 h of stirring at r.t., a yellow precipitate was formed which was collected after 5 h, washed with cold methanol (2 × 15 ml) and dried in vacuum.

Yield: 1.30 g (68%). Anal. Calc. for $C_{21}H_{19}N_3$: C, 80.48; H, 6.11; N, 13.40. Found: C, 79.93; H, 6.38; N, 14.04%.

3.2. Synthesis of complexes

3.2.1. 2,6-bis[(1-Naphthylimino)ethyl]pyridine iron(II) chloride (**4a**) [20] and 2,6-bis[(1-naphthyl-imino)ethyl]-pyridine cobalt(II) chloride (**5a**)

A filtered solution of the ligand **3a** (0.70 g, 1.69 mmol) in THF (50 ml) was added to $FeCl_2$ or $CoCl_2$ (1.54 mmol) under continuous stirring at r.t. Upon addition a precipitate started to form gradually. After 24 h, the solid was filtered, washed with THF (2 × 25 ml), *n*-pentane (2 × 25 ml) and dried in vacuum.

4a, Yield: 0.46 g (55%), greenish–blue. M.p. (dec) 200 °C. (MS, EI): *m*/*z* (%) 539 (5%), 466 (5%), 413 (100%), 271 (60%). IR: ν [cm^{-1}] = 1593 s (C=N). Anal. Calc. for $C_{29}H_{23}N_3FeCl_2$: C, 64.47; H, 4.29; N, 7.78. Found: C, 63.96; H, 4.51; N, 7.39%. μ_{eff} (Faraday balance): 4.86 BM.

5a, Yield: 0.55 g (65%), brown. M.p. (dec) 240 °C. (MS, EI): *m*/*z* (%): 413 (100%), 271 (60%). IR: ν [cm^{-1}] = 1593 s (C=N). Anal. Calc. for $C_{29}H_{23}N_3$-$CoCl_2$·0.5 H_2O: C, 63.05; H, 4.37; N, 7.60. Found: C, 62.77; H, 4.44; N, 7.19%. μ_{eff}: 4.78 BM.

3.2.2. 2,6-bis[(1-Pyrenylimino)ethyl]pyridine iron(II) chloride (**4b**) and 2,6-bis[(1-pyrenylimino)-ethyl]pyridine cobalt(II) chloride (**5b**)

A filtered solution of the ligand **3b** (0.25 g, 0.445 mmol) in THF (50 ml) was added to $FeCl_2$ or $CoCl_2$ (0.394 mmol) under continuous stirring at r.t. Upon addition a precipitate started to form. After 24 h, the solid was filtered, washed with THF (2 × 25 ml), *n*-pentane (2 × 25 ml) and dried in vacuum.

4b, Yield: 0.17 g (63%), brown. M.p. (dec) 270 °C. IR: ν [cm^{-1}] = 1588 s (C=N). Anal. Calc. for $C_{41}H_{27}N_3FeCl_2$: C, 71.53; H, 3.95; N, 6.10. Found: C, 71.60; H, 4.21; N, 5.93%. μ_{eff}: 4.55 BM.

5b, Yield: 0.20 g (73%), brown. M.p. (dec) 340 °C. IR: ν [cm^{-1}] = 1587 s (C=N). Anal. Calc. for $C_{41}H_{27}N_3CoCl_2$: C, 71.21; H, 3.93; N, 6.07. Found: C, 71.47; H, 4.31; N, 5.78%. μ_{eff}: 4.82 BM.

3.2.3. 2,6-bis[(1-(2-Benzylphenylimino)ethyl]pyridine iron(II) chloride (**4c**) and 2,6-bis[(1-(2-benzylphenylimino)ethyl]pyridine cobalt(II) chloride (**5c**)

A filtered solution of the ligand **3c** (0.50 g, 1.01 mmol) in THF (50 ml) was added to $FeCl_2$ or $CoCl_2$ (0.78 mmol) under continuous stirring at r.t. Upon addition a precipitate started to form. After 24 h, the solid was filtered, washed with THF (2 × 25 ml), *n*-pentane (2 × 25 ml) and dried in vacuum.

4c, Yield: 0.27 g (56%), blue. M.p. (dec) 232 °C. IR: ν [cm^{-1}] = 1590 s (C=N). Anal. Calc. for $C_{35}H_{31}N_3FeCl_2$: C, 67.76; H, 5.03; N, 6.77. Found: C, 67.90; H, 5.12; N, 6.48%. μ_{eff}: 5.42 BM.

5c, Yield: 0.38 g (78%), light green. M.p. (dec) 317 °C. IR: ν [cm^{-1}] = 1591 s (C=N). Anal. Calc. for $C_{35}H_{31}N_3CoCl_2$: C, 67.42; H, 5.01; N, 6.74. Found: C, 67.63; H, 5.33; N, 6.55%. μ_{eff}: 4.73 BM.

3.2.4. 2,6-bis[(1-(cis-Myrtanylimino)ethyl]pyridine iron(II) chloride (**4d**)

A filtered solution of the ligand **3d** (0.40 g, 0.922 mmol) in THF (50 ml) was added to $FeCl_2$ (0.106 g, 0.836 mmol) under continuous stirring at r.t. Upon addition a dark blue precipitate started to form. After 24 h, the solid was filtered, washed with THF (2 × 25 ml), *n*-pentane (2 × 25 ml) and dried in vacuum.

Yield: 0.43 g (91%), blue powder. M.p. (dec) 205 °C. (MS, EI): *m*/*z* (%): 560 (5%), 435 (60%), 364 (50%), 310 (100%)$^+$. IR: ν [cm^{-1}] = 1530 m (C=N). Anal. Calc. for $C_{29}H_{43}N_3FeCl_2 \cdot 2H_2O$: C, 58.39; H, 7.94; N, 7.04. Found: C, 58.08; H, 7.79; N, 6.20%. μ_{eff}: 1.52 BM.

3.2.5. 2,6-bis[(1-Phenylimino)ethyl]pyridine iron (II) chloride (**4e**)

A filtered solution of the ligand **3e** (0.50 g, 1.59 mmol) in THF (50 ml) was added to $FeCl_2$ (0.18 g, 1.42 mmol) under continuous stirring at r.t. Upon addition a dark blue precipitate started to form. After 24 h, the solid was filtered, washed with THF (2 × 25 ml), *n*-pentane (2 × 25 ml) and dried in vacuum.

Yield: 0.47 g (75%), blue. M.p. (dec) 206 °C. IR: ν [cm^{-1}] = 1590 m (C=N). Anal. Calc. for $C_{21}H_{19}N_3FeCl_2$: C, 57.30; H, 4.35; N, 9.54. Found: C, 57.12; H, 4.49; N, 9.17%. μ_{eff}: 2.71 BM.

3.3. Polymerization experiments

All polymerization reactions were performed in a 1-l Büchi glass reactor. In a typical polymerization experiment, the autoclave was charged with 200 ml toluene and the system was charged with ethylene up to the desired concentration and the appropriate amount of the complex and MAO (mixed previously together). Pressure, inside temperature and the consumption of ethylene as a function of time were recorded online with Advantech GENIE® runtime software. The mechanical stirrer was run with 1800 rpm for all experiments to avoid diffusion controlled polymerization reactions. After the desired polymerization time, the polymerization were stopped by quenching with methanol containing 2% HCl. Polymers were washed with methanol and dried overnight at 70 °C.

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