Cyclodextrin-Encapsulated Iron Catalysts for the Polymerization of Ethylene

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The synthesis and characterization of dichloroiron(II) complexes of tridentate nitrogen ligands based on 2,6-bis(imino)pyridine-capped α- and β-cyclodextrin derivatives are described and their propensity to act as ethylene polymerization catalysts reported.

Introduction

Although dominated by the very active Group 4 metallocenes catalysts for a long time,[1] the field of catalytic polymerization has recently been rejuvenated by Brookhart[2] and Gibson's seminal works[3,4] on the use of late transition metal complexes in olefin polymerization. Beside systems containing the α-diimine ligand framework,[5] nitrogen-containing tridentate complexes of iron and cobalt based on the 2,6-bis(iminoaryl)pyridine fragment are amongst the most studied because of their ability to promote the formation of linear polyethylene very efficiently.[6] Steric bulk control around the metal center is a prerequisite not only for forming the neutral trigonal-pyramidal MCl_2 catalyst precursor at the expense of the inactive octahedral cationic $[(N,N,N)_2Fe]^{2+}$ complex,[7] but also for tuning the molecular weight of the polymer produced.[4] So far, the control of the steric environment at the metal has been achieved by changing the size of the aryl (Ar) and imino carbon (R) substituents of the 2,6-bis(iminoaryl)pyridine moiety. An alternative would be to encapsulate the metal fragment in molecular cavities of various sizes. Here we describe the synthesis of methylated α- and β-cyclodextrin (CD) derivatives[8] rigidly capped with a 2,6-bis(imino)pyridyl fragment and the activity of their iron complexes in ethylene polymerization.

Results and Discussion

The ligands **4a** and **4b** used in this study were prepared by condensing 2,6-diformylpyridine with diamines **3a**[9] and **3b**, respectively (Scheme 1). The latter was synthesized in two steps from the known dimesylate **1**[10] according to a procedure adapted from that used for preparing diamine **3a**. The cyclisation of both diamines proceeded smoothly in dilute MeCN solution in the presence of molecular sieves (4 Å) with only small amounts of oligomeric material being produced during the reaction. The latter was removed by simple recrystallisation from $CHCl_3$/pentane so that the pure capped CDs **4a** and **4b** could be obtained in 46 and 64% yields, respectively. As shown by ^1H NMR and ^{13}C NMR spectroscopy, the C_2 symmetry of diamine **3a** is retained upon cyclisation. In addition, it is unlikely that the macrocyclic structures of both **4a** and **4b** are strongly distorted by the presence of the relatively short and rigid capping unit as the signals of the anomeric protons all fall in a narrow chemical shift region ($\Delta\delta < 0.17$ ppm).[9] This observation was confirmed by a single-crystal X-ray diffraction study on ligand **4a** (Figure 1). The structure of the latter reveals an almost perfectly round shape for the C_2-symmetrical CD framework, with all the glucose units in the standard $^4C_1$ conformation. Interestingly, the atoms of the bridging unit lie almost in the same plane, the N(1)−C(27)−C(28)−N(2) torsion angle being 4.5°. This particular feature is a result of the presence of a single water molecule located in the middle of the cavity, which is hydrogen-bonded to two opposing imine nitrogen atoms. A distance of 3.00(2) Å can be calculated between the imine nitrogen N(1)/N(1A) atoms and the encapsulated water oxygen O_w, while the N(1)−O_w−N(1A) angle has a value of 106.5°. In keeping with the C_2 symmetry of the ligand, the plane defined by the water and the 2,6-diformylpyridyl atoms is perpendicular to the average plane defined by the six glucosidic O-4 atoms. Clearly, the three nitrogen atoms are well positioned to coordinate a metal fragment inside the CD cavity. As expected, treatment of ligands **4a/4b** with $FeCl_2$ afforded the desired complexes **5a/5b** in good yields. Both compounds could be univocally identified by mic-

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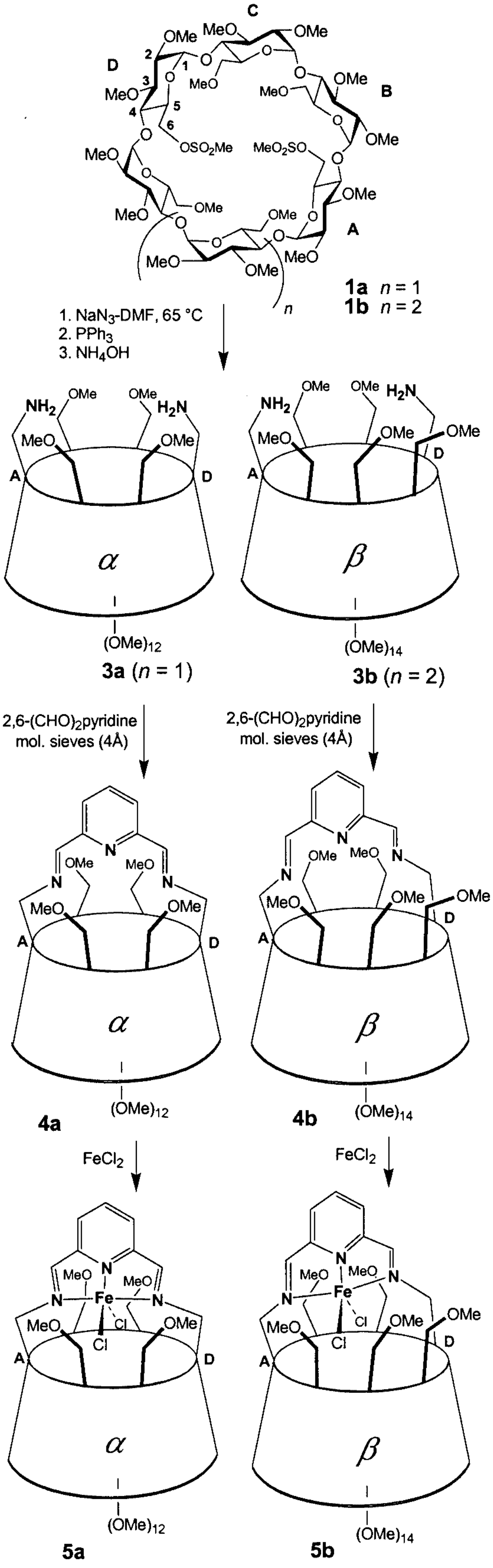


Scheme 1. Synthesis of the iron complexes **5a** and **5b**

roanalysis and FAB-MS measurements, the latter showing an intense peak for the $[M-Cl]^+$ ion in each case. ^1H NMR spectroscopy also proved to be useful even though both complexes are paramagnetic. In particular, the C_2 symmetry of **5a** could be confirmed by the presence of eight signals of equal intensity, corresponding to 16 CD methoxy groups, in its ^1H NMR spectrum. Although similar Fe^{II}-aldimines are reported to be green-brown,[4] **5a/5b** turned out to be deep blue. This difference in color probably results from the fact that the coordinating unit no longer consists of a 2,6-bis(imino*aryl*)pyridine fragment but, for the first time, of a 2,6-bis(imino*alkyl*)pyridine one. We anticipated that the **5a/5b**-promoted ethylene polymerization might be influenced by this modification, which undoubtedly alters the electronic nature of the Fe^{II} complexes.

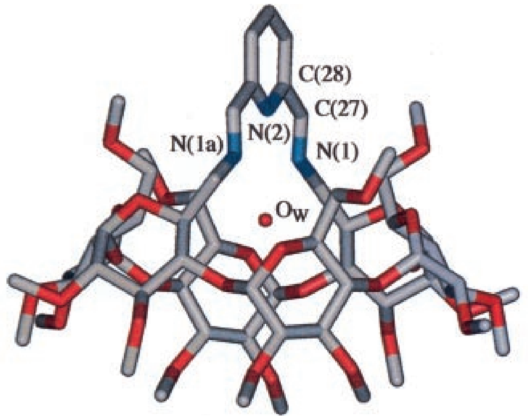


Figure 1. Molecular structure of ligand **5a** (sticks); "O_w" stands for the oxygen atom of the entrapped water molecule

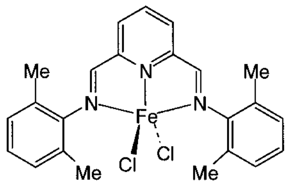
The results of ethylene polymerization are collected in Table 1. Procatalyst **5a**, after activation with a large excess of MAO (methylaluminoxane), proved to be almost inactive. With a maximum TOF value of 125 h^{-1}, **5b**, which possesses a larger cavity, is much more active and produces linear polyethylene, as expected. However, **5b** is still about 1000 times less active than the comparable iron-aldimine system **6**.[3] The presence of a CD cavity tightly wrapped around the metal center may inhibit the chain growing process to the extent that the small α-CD host does not allow any polymerization at all even if **5a** is activated by MAO, as revealed by the change of color from blue to orange. Moreover, **5b** requires larger amounts of MAO than usual to reach the maximum activity (Al/Fe > 2000 equiv.), which means that access to the metal center by MAO may be also hindered to a certain extent. It is also possible that the numerous primary face ether oxygen atoms interact unfavorably with the MAO-generated iron(III) cationic active species,[11] thus reducing the overall rate of polymerization. In terms of molecular weight, melting temperatures and crystallinity, the polyethylene generated by **5b** compares well

Table 1. Results of ethylene polymerization runs using precatalysts **5a** and **5b**

Run	Precatalyst (µmol)	Activator[a] (mmol/equiv.)	T (°C)	T (h)	Yield (mg)	TOF[b] (mol/mol·h)	T_f (°C)	χ_c	M_n ($g\cdot mol^{-1}$)	M_w ($g\cdot mol^{-1}$)	IP
1[c]	**5a** (7.0)	MAO (2.8/400)	25	23	Traces	–	–	–	–	–	–
2[c]	**5a** (7.0)	MAO (7.0/1000)	35	30	1	<1	–	–	–	–	–
3[c]	**5b** (6.8)	MAO (6.8/1000)	20	30	70	12	71.4, 105.6, 124.8	0.76	1700	15300	9.0
4[c]	**5b** (6.8)	MAO (6.8/1000)	40	30	210	37	75.3, 105.5, 124.7	0.79	1970	22300	11.3
5[c]	**5b** (6.8)	MAO (13.6/2000)	40	30	710	125	65.8, 104.1, 123.2	0.72	1460	12800	8.7
6[d]	**5b** (3.7)	MAO (7.4/2000)	40	30	140	25	74.0, 108.0, 126.4	0.77	1150	27300	23.8

[a] For runs 1–5, commercial MAO (in toluene); for run 6, solid MAO (see Exp. Sect.). [b] Turnover frequency, mol of converted ethene/mol of catalyst/h. [c] High pressure reactor conditions: toluene solvent (20 mL), P_{Eth} = 6 bar. [d] High pressure reactor conditions: toluene solvent (15 mL), P_{Eth} = 6 bar.

with that obtained with the classical system **6**. Clearly, the β-CD cavity in **5b** provides adequate steric protection of the active site for the polymer chain to reach an appreciable length, although at the expense of activity.



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We have demonstrated that encapsulation of the metal center in molecular cavities like cyclodextrins is a viable alternative to the active site steric protection provided by substituted aryl rings in 2,6-bis(imino)pyridyl-based ethylene polymerization catalysts. The activity and the potential of the latter may be further improved by using large capped calixarenes, which contain only a limited number of oxygen atoms and provide plenty of space for the chain growth to take place. Investigation of these alternative systems is currently underway.

Experimental Section

General: All manipulations were performed under dry nitrogen using purified solvents. Pyridine dicarboxaldehyde,[12] dimesylate **1**,[10] and diamine **3a**[9] were synthesized according to literature procedures. MAO 10-wt% (Aldrich) was used either as received or as a white powder which was obtained after evaporation of the solvent (60 °C, 3 h). This treatment reduces the amount of residual trimethylaluminium to ca. 3%. The synthesis of compound **3b** starts with the preparation of intermediate **2b**.

Diazide 2b: Dry sodium azide (0.550 g, 8.50 mmol) was added to a solution of **1** (0.650 g, 0.42 mmol) in dry DMF (75 mL). The reaction mixture was stirred under N_2 at 65 °C for 18 h, cooled to room temperature, and then poured into ice-water (200 mL). The aqueous solution was extracted with diethyl ether (4 × 100 mL) and the organic extract washed with water (200 mL) before being dried ($MgSO_4$) and the solvents evaporated to dryness to afford **2** (0.610 g, 100%) as a colorless solid. m.p. 188–190 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 3.38 (s, 9 H, CH_3O-6), 3.40 (s, 6 H, CH_3O-6), 3.50 (s, 3 H, OCH_3), 3.51 (s, 9 H, OCH_3), 3.52 (s, 9 H, OCH_3), 3.63 (s, 12 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.15–3.98 (42 H, H-2, H-3, H-4, H-5, H-6), 5.06 (d, ^3J = 3.9 Hz, 1 H, H-1), 5.07 (d, ^3J = 4.1 Hz, 1 H, H-1), 5.12 (d, ^3J = 3.7 Hz, 5 H, H-1) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 51.9 [×2] (CH_2N_3), 58.3 [×3], 58.4, 58.5 [×2], 58.6, 58.8 [×5], 61.1 [×3], 61.2 and 61.4 [×3] (OCH_3), 70.6, 70.7 [×2], and 70.8 [×4] (C-5), 70.9, 71.2, and 71.5 [×3] (C-$6^{B,C,E,F,G}$), 80.0 [×4], 80.1 [×2], 81.3 [×3], 81.5, 81.6 [×5], 81.8 [×4], and 81.9 [×2] (C-2, C-3, C-4), 98.2 [×2], 98.8, 98.9, 99.0, and 99.1 [×2] (C-1) ppm. $C_{61}H_{106}N_6O_{33}$ (1451.54): calcd. C 50.48, H 7.36, N 5.79; found C 50.75, H 7.54, N 5.57.

Diamine 3b: Triphenylphosphane (0.610 g, 2.32 mmol) was added to a solution of diazide **2** (0.550 g, 0.39 mmol) in dioxane (6 mL) under N_2. The clear solution was stirred for 1 h at room temperature before adding conc. aqueous NH_4OH solution (1.6 mL) dropwise. After overnight stirring, the reaction mixture was poured into water (200 mL) and the pH of the resulting suspension adjusted to 4 with HCl before being extracted with toluene (5 × 50 mL). The aqueous phase was then made alkaline by adding 2 M NaOH (50 mL) and the compound subsequently extracted with CH_2Cl_2 (5 × 50 mL). The CH_2Cl_2 extract was dried ($MgSO_4$) before being evaporated to dryness. Recrystallisation from heptane afforded **3b** (0.46 g, 84%) as colorless fluffy solid. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.56 (br. s, 4 H, NH_2), 3.37 (s, 9 H, CH_3O-6), 3.38 (s, 6 H, CH_3O-6), 3.49 (s, 6 H, OCH_3), 3.50 (s, 9 H, OCH_3), 3.53 (s, 6 H, OCH_3), 3.58 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.64 (s, 6 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.02–3.90 (42 H, H-2, H-3, H-4, H-5, H-6), 5.04–5.11 (5 H, H-1), 5.19 (d, ^3J = 3.7 Hz, 2 H, H-1) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 42.3 and 42.4 (CH_3N), 57.7, 57.9 [×2], 58.0, 58.2, 58.7 [×3], 58.8 [×2], 58.9 [×2], 60.7 [×2], 61.2 [×2], 61.3 and 61.4 [×2] (OCH_3), 66.7 [×2], 70.9 [×2], and 71.2 (C-$6^{B,C,E,F,G}$), 70.9 [×5] and 71.3 [×2] (C-5), 79.4, 79.5, 80.1, 80.3 [×3], 80.5, 81.4 [×4], 81.5 [×5], 81.6 [×2], 81.7, 82.4 and 82.8 (C-2, C-3, C-4), 98.4 [×2], 98.6, 98.8 [×2], and 99.2 [×2] (C-1) ppm. $C_{61}H_{110}N_2O_{33}\cdot 2H_2O$ (1399.55 + 36.03): calcd. C 51.04, H 8.00, N 1.95; found C 51.16, H 8.03, N 1.85.

Ligand 4a: A solution of diamine **3a** (1.000 g, 0.84 mmol) in CH_3CN (50 mL) and a solution of 2,6-diformylpyridine (0.113 g, 0.84 mmol) in CH_3CN (50 mL) were added simultaneously to a vigorously stirred suspension of molecular sieves (4 Å) in CH_3CN (20 mL) in 1 h at room temperature. The reaction mixture was then stirred for 1 h at room temperature before being filtered through Celite. Removal of the solvent in vacuo afforded a colorless solid which was recrystallized from $CHCl_3$/pentane to afford pure **4a** (0.500 g, 46%) as a colorless solid. m.p. 200 °C (dec.). ^1H NMR (200.1 MHz, $CDCl_3$): δ = 3.03 (s, 6 H, CH_3O-6), 3.18 (s, 6 H, CH_3O-6), 3.44 (s, 6 H, OCH_3), 3.48 (s, 6 H, OCH_3), 3.51 (s, 6 H, OCH_3), 3.64 (s, 12 H, OCH_3), 3.71 (s, 6 H, OCH_3), 2.88−4.77 (36 H, H-2, H-3, H-4, H-5, H-6), 4.95 (d, ^3J = 3.4 Hz, 2 H, H-1), 5.00 (d, ^3J = 3.2 Hz, 2 H, H-1), 5.09 (d, ^3J = 3.4 Hz, 2 H, H-1), 7.51 (d, ^3J = 7.3 Hz, 2 H, H_{pyr}-3,5), 7.96 (t, ^3J = 7.6 Hz, 1 H, H_{pyr}-4), 8.41 (br. m, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 57.3, 57.6, 58.0, 58.8, 61.5, 61.8 [×2] and 62.0 (OCH_3), 62.8 (CH_2N), 70.1 and 70.8 (C-$6^{B,C,E,F}$), 70.3, 70.6 and 72.5 (C-5), 80.4, 81.2 [×2], 81.8, 82.0, 82.5 [×2], 82.6 and 85.3 (C-2, C-3, C-4), 99.2, 99.7 and 100.1 (C-1), 125.9 (C_{pyr}-3,5), 137.9 (C_{pyr}-4), 153.2 (C_{pyr}-2,6), 159.8 (C=N) ppm. MS (FAB): *m/z* (%) = 1294.6 (95) [M^+ + H], 1316.6 (25) [M^+ + Na]. $C_{59}H_{95}N_3O_{28}$ (1294.43): calcd. C 54.75, H 7.40, N 3.25; found C 54.71, H 7.69, N 3.14.

Ligand 4b: The previously described procedure was used to prepare **4b** from diamine **3b** (0.450 g, 0.32 mmol) and 2,6-diformylpyridine (0.044 g, 0.32 mmol). Addition of pentane to a solution of crude **4b** in $CHCl_3$ resulted in the precipitation of higher oligomers that were eliminated by filtration. The filtrate was then evaporated to dryness to afford pure **4b** as a colorless amorphous solid (0.300 g, 64%). m.p. 200 °C (dec.). ^1H NMR (200.1 MHz, $CDCl_3$): δ = 3.04 (s, 3 H, OCH_3), 3.10 (s, 3 H, OCH_3), 3.30 (s, 6 H, OCH_3), 3.31 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.47 (s, 9 H, OCH_3), 3.49 (s, 3 H, OCH_3), 3.53 (s, 3 H, OCH_3), 3.58 (s, 3 H, OCH_3), 3.63 (s, 9 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 2.85−4.73 (42 H, H-2, H-3, H-4, H-5, H-6), 4.90 (d, ^3J = 3.7 Hz, 1 H, H-1), 4.97 (d, ^3J = 3.4 Hz, 1 H, H-1), 5.02 (d, ^3J = 3.7 Hz, 1 H, H-1), 5.05 (d, ^3J = 3.7 Hz, 2 H, H-1), 5.17 (d, ^3J = 3.9 Hz, 2 H, H-1), 7.51 (d, ^3J = 6.4 Hz, 1 H, H_{pyr}-3 or H_{pyr}-5), 7.62 (t, ^3J = 7.6 Hz, 1 H, H_{pyr}-4), 7.99 (d, ^3J = 6.6 Hz, 1 H, H_{pyr}-3 or H_{pyr}-5), 8.49 (br. s, 2 H, CH=N) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 57.2, 57.3, 58.0, 58.1 [×3], 58.4 [×2], 58.8 [×3], 59.3, 60.0, 60.6, 60.7, 61.6 [×3], 61.7, 61.9 and 62.0 (OCH_3), 64.9 [×2] (CH_2N), 69.4, 70.1 [×2], and 70.5 [×2] (C-$6^{B,C,E,F,G}$), 70.2, 70.5, 70.7 [×2], 71.0, 71.3 and 73.6 (C-5), 80.9 [×2], 81.0, 81.2 [×2], 81.3, 81.4 [×3], 81.7 [×2], 81.8 [×2], 81.9, 82.0 [×2], 82.2, 82.4, 82.9, 83.0 and 83.1 (C-2, C-3, C-4), 98.4, 98.6, 99.1, 99.3, 99.6, 99.8 and 100.2 (C-1), 121.7 and 125.0 (C_{pyr}-3,5), 136.9 (C_{pyr}-4), 152.7 and 155.3 (C_{pyr}-2,6), 159.4 and 164.5 (C=N) ppm. $C_{68}H_{111}N_3O_{33}$ (1498.64): calcd. C 54.50, H 7.47, N 2.80; found C 54.62, H 7.70, N 2.71.

Complex 5a: A solution of **4a** (0.400 g, 0.31 mmol) in degassed *n*-butanol (3 mL) was added dropwise to a solution of anhydrous $FeCl_2$ (0.039 g, 0.31 mmol) in *n*-butanol (5 mL) at 80 °C. The resulting blue solution was stirred at 80 °C for 30 min before being cooled to room temperature. The reaction mixture was evaporated almost to dryness whereupon diisopropyl ether (30 mL) was added to precipitate the product as a blue powder, which was subsequently filtered, washed with diethyl ether (3 × 10 mL), and dried to afford 0.280 g of **4** (64%). ^1H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = −44 to +32 (44 H, H-1, H-2, H-3, H-4, H-5, H-6, C*H*=N), −10.19 (6 H, OCH_3), −7.81 (6 H, OCH_3), 1.36 (6 H, OCH_3), 3.88 (6 H, OCH_3), 4.68 (6 H, OCH_3), 6.23 (6 H, OCH_3), 8.98 (6 H, OCH_3), 9.27 (6 H, OCH_3), 46.87 (1 H, H_{pyr}-4), 66.95 (2 H, H_{pyr}-3,5) ppm. MS (FAB): *m/z* (%) = 1387.7 (100) [M^+ − Cl]. $C_{59}H_{95}Cl_2FeN_3O_{28}$ (1421.17): calcd. C 49.86, H 6.74, N 2.96; found C 49.76, H 6.64, N 2.81.

Complex 5b: The previously described procedure was used to prepare **5b** from ligand **4b** (0.260 g, 0.17 mmol) and anhydrous $FeCl_2$ (0.022 g, 0.17 mmol) in 5 mL of degassed *n*-butanol. Complex **5b** was obtained as a blue microcrystalline solid in 61% yield (0.170 g). ^1H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = −43.4 to +50.7 (51 H, H-1, H-2, H-3, H-4, H-5, H-6, C*H*=N), −15.24 (3 H, OCH_3), −0.98 (3 H, OCH_3), −0.80 (3 H, OCH_3), 0.14 (3 H, OCH_3), 0.24 (3 H, OCH_3), 0.38 (3 H, OCH_3), 0.78 (3 H, OCH_3), 1.24 (3 H, OCH_3), 1.32 (3 H, OCH_3), 1.42 (3 H, OCH_3), 2.37 (3 H, OCH_3), 3.71 (3 H, OCH_3), 4.67 (3 H, OCH_3), 4.85 (3 H, OCH_3), 5.45 (3 H, OCH_3), 6.38 (3 H, OCH_3), 8.56 (3 H, OCH_3), 9.41 (3 H, OCH_3), 13.03 (3 H, OCH_3), 44.96 (1 H, H_{pyr}-4), 54.15 (1 H, H_{pyr}-3 or H_{pyr}-5), 62.33 (1 H, H_{pyr}-3 or H_{pyr}-5) ppm. MS (FAB): *m/z* (%) = 1623.7 (70) [M^+], 1588.7 (100) [M^+ − Cl]. $C_{68}H_{111}Cl_2FeN_3O_{33}$ (1625.39): calcd. C 50.25, H 6.88, N 2.59; found C 50.46, H 7.06, N 2.56.

Crystal Data for 4a: $C_{59}H_{95}N_3O_{28}\cdot H_2O\cdot 5CHCl_3$, M_r = 1909.32, orthorhombic, space group $P2_12_12$, a = 25.3628(2), b = 18.2041(3), c = 9.6156(6) Å, V = 4439.6(3) Å^3, Z = 2 (the ligand has crystallographic C_2 symmetry), ρ = 1.43 g·cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å), μ = 0.321 mm^{-1}. Data were collected on a Kappa CCD Enraf−Nonius system at 173 K. The structure was solved by direct methods and refined on F_0^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. The absolute structure was determined by refining Flack's x parameter. $R1$ = 0.065 and $\omega R2$ = 0.075 for 3478 data with $I > 3\sigma(I)$.
CCDC-192556 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Polymerization Procedure: The polymerization reactions were carried out in a Büchi miniclave (200 mL). In a typical procedure, a Schlenk flask was charged with the complex (7 mmol) and toluene (10 mL). The solution was injected into the autoclave together with additional toluene (10 mL) whereupon MAO was introduced. The autoclave was then pressurized with ethene. After completion of the reaction (see reaction conditions in Table 1), acidified ethanol (30 mL) was added to the reaction mixture. Further precipitation was achieved by adding more ethanol. The white polymer was dried under vacuum at 50 °C for 12 h.

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