

Novel olefin polymerization catalysts based on iron and cobalt

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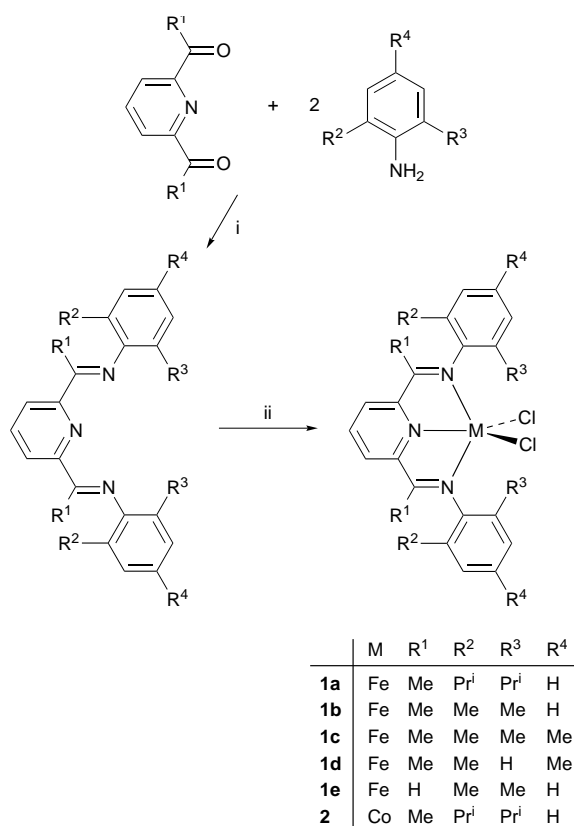
A new family of olefin polymerization catalysts, derived from iron and cobalt complexes bearing 2,6-bis(imino)pyridyl ligands, is described.

Metallocene catalyst technology has made a dramatic impact on the polyolefins industry, providing access to polyolefinic materials with new or improved performance parameters.^{1–7} There is thus great interest in the discovery and development of new families of catalysts for α -olefin polymerisation with a view to obtaining ever greater control over the properties of the resultant polymers and to extending the family of products to new monomer combinations. Late transition metal catalysts are particularly attractive because of their potential for tolerating heteroatom functionalities, which may open up the possibility for copolymerizations of polar comonomers. A significant development in late transition metal polymerization technology was reported by Brookhart and co-workers who showed that catalysts based on nickel and palladium could be used to access a range of linear and branched polyethylenes.^{8–11}

Here we describe a new, strikingly active family of ethylene polymerization catalysts based on iron and cobalt bearing 2,6-bis(imino)pyridyl ligands. To the best of our knowledge

these are the first iron based catalysts to show significant activities for the polymerization of ethylene. The precursor complexes are prepared by treatment of FeCl₂ or CoCl₂ with the 2,6-bis(imino)pyridines in excellent yields according to Scheme 1.[‡] Derivatives containing a variety of bulky aryl substituents are accessible, the iron compounds **1a–d** being blue, while the aldimine complex **1e** and the cobalt compound **2** are green; all are paramagnetic. The magnetic moment of 5.34 μ_B (Evans balance) of complex **1a** indicates a high spin electronic configuration with four unpaired electrons for the d⁶ iron(II) centres in these complexes.

Crystals of **1a** suitable for an X-ray structure determination[§] were grown from a layered CH₂Cl₂–pentane (1 : 1) solution; the molecular structure is shown in Fig. 1. The complex has molecular C_s symmetry about a plane containing the iron, the two chlorides and the pyridyl nitrogen atom. The geometry at the Fe^{II} centre can probably be best described as distorted square pyramidal, with Cl(1) occupying the apical position. The four basal atoms are co-planar to within 0.02 Å, the iron atom lying 0.59 Å out of this plane. The Fe–Cl bonds are noticeably asymmetric, with that to the apical chloride being significantly longer [at 2.311(2) Å] than that to its basal counterpart [2.266(2) Å]. The Fe–N(imino) distances [av. 2.244(4) Å] are noticeably longer than the Fe–N(pyridyl) bond length [2.088(4) Å], probably as a consequence of satisfying the tridentate chelating constraints of the ligand. The bis(imino)pyridine unit is co-planar to within 0.19 Å, the plane extending to include the basal chloride Cl(2) with the 2,6-diisopropylphenyl rings each being inclined by 79° to this plane. There is no apparent delocalisation of the imino double bonds into the pyridyl ring system, the C(7)–N(7) and C(9)–N(9) bond lengths being 1.285(6) and 1.280(6) Å, respectively.



Scheme 1 Reagents and conditions: i, EtOH, AcOH; ii, MCl₂, BuⁿOH, 80 °C, 10 min

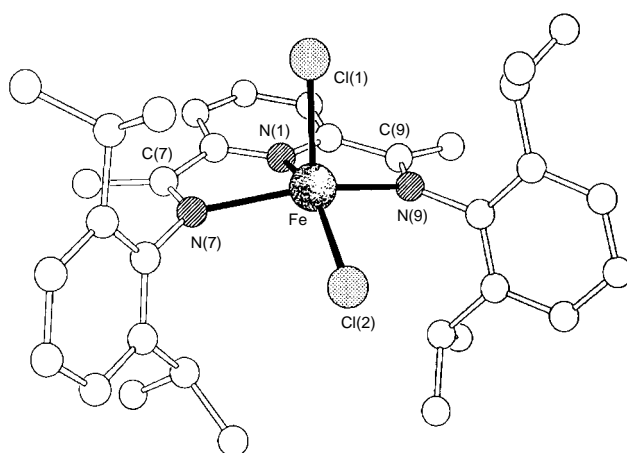


Fig. 1 The molecular structure of **1a**. Selected bond lengths (Å) and angles (°): Fe–Cl(1) 2.311(2), Fe–Cl(2) 2.266(2), Fe–N(1) 2.088(4), Fe–N(7) 2.238(4), Fe–N(9) 2.250(4), C(7)–N(7) 1.285(6), C(9)–N(9) 1.280(6); N(1)–Fe–N(7) 73.2(1), N(1)–Fe–N(9) 72.9(1), N(7)–Fe–Cl(2) 98.6(1), N(9)–Fe–Cl(2) 98.9(1), N(1)–Fe–Cl(2) 147.9(1), N(7)–Fe–N(9) 140.1(1)

Table 1 Results of ethylene polymerisation runs using procatalysts **1** and **2**^a

Run	Procatalyst (μmol)	Activator (mmol/equiv)	$T/^\circ\text{C}$	Solvent	Pressure $\text{C}_2\text{H}_4/\text{bar}$	Yield PE/g	Activity/ $\text{g mmol}^{-1}\text{h}^{-1}\text{bar}^{-1}$	M_w
1	1a (10)	MAO (1.0/100)	25	toluene	1	5.8	1170	203 000
2	1a (0.5)	MAO (0.5/1000)	50	isobutane	10	26.9	5430	611 000
3	1b (20)	MAO (8.0/400)	25	toluene	1	5.7	570	29 000
4	1b (0.6)	MAO (0.6/1000)	50	isobutane	10	56.5	9340	242 000
5	1c (10)	MAO (1.0/100)	25	toluene	1	6.2	1230	52 000
6	1c (0.6)	MAO (0.6/1000)	50	isobutane	10	63.1	11 020	562 000
7	1d (20)	MAO (8.0/400)	25	toluene	1	1.2	120	260
8	1d (0.6)	MAO (0.6/1000)	50	isobutane	10	7.8	1280	470
9	1e (10)	MAO (1.0/100)	25	toluene	1	3.7	740	15 000
10	2 (10)	MAO (1.0/100)	25	toluene	1	2.3	460	26 000
11	2 (0.5)	MAO (0.5/1000)	50	isobutane	10	3.7	450	14 000

^a General conditions: 1 atm Schlenk tests carried out in toluene over 30 min, reaction quenched with dil. HCl and the solid PE washed with MeOH (50 cm^3) and dried in a vacuum oven at 50 $^\circ\text{C}$. 10 atm tests performed in 1 l autoclave, procatalyst dissolved in toluene, isobutane solvent, triisobutylaluminium scavenger, runs carried out over 60 min.

The results of ethylene polymerization tests are collected in Table 1. Several features are noteworthy. In general, the activities of the iron catalysts are exceptionally high, in many cases comparable or even higher than those seen by metallocenes under analogous conditions. All of the catalysts produce essentially linear polyethylene with molecular weights that are dependent upon the aryl substitution pattern. Most notable is a dramatic fall-off in molecular weight to α -olefin oligomers for derivatives with one *o*-methyl substituent (runs 7,8) compared with derivatives that contain methyl substituents in both *ortho* positions. Clearly steric protection of the active site is a crucial factor in controlling molecular weight.

There is also a marked dependence of the polymer molecular weight on ethylene pressure for the iron catalyst system, an effect that is not seen for the cobalt catalyst **2** (runs 10, 11); the cobalt catalyst also displays a considerably lower activity than its iron analogue. ^{13}C NMR end-group analysis of the polymers generated by **1a–c** (runs 2, 4, 6) reveals isopropyl end-groups in addition to low levels of vinyl unsaturation. This is consistent with a termination mechanism involving alkyl group transfer from the AlBu_3 scavenger in addition to β -H transfer. The polymers formed from **1d** and the aldimine catalyst **1e** contain a larger proportion of vinyl end-groups (> 4 per 1000 carbons) indicating that β -H transfer plays a more dominant role in chain termination for these catalysts.

The new catalyst family described herein represents a significant addition to the growing armoury of technologically important olefin polymerization catalysts.

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Notes and References

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‡ Satisfactory elemental analyses have been obtained.

§ *Crystal data for 1a*: $\text{C}_{33}\text{H}_{43}\text{N}_3\text{Cl}_2\text{Fe}\cdot 0.5\text{H}_2\text{O}$, $M = 617.5$, triclinic, $P\bar{1}$ (no. 2), $a = 8.779(1)$, $b = 9.876(1)$, $c = 20.976(1)$ Å, $\alpha = 83.70(1)$, $\beta = 88.18(1)$, $\gamma = 65.67(1)^\circ$, $V = 1646.9(3)$ Å³, $Z = 2$, $D_c = 1.245$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 53.6$ cm⁻¹, $F(000) = 654$. A deep blue platy needle of dimensions $0.40 \times 0.20 \times 0.03$ mm was used. 4878 independent reflections were measured on a Siemens P4/PC diffractometer with Cu-K α radiation using ω -scans. The structure was solved by direct methods and all of the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give $R_1 = 0.061$, $wR_2 = 0.144$ for 3595 independent observed, absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta \leq 120^\circ$] and 362 parameters. CCDC 182/812.

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