Separation of a diiminopyridine iron(II) complex into *rac*- and *meso*- diastereoisomers provides evidence for a dual stereoregulation mechanism in propene polymerization†

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Received (in Cambridge, UK) 18th June 2008, Accepted 13th August 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b810381j

Separation of a diiminopyridine iron(II) complex into its *rac*- and *meso*- diastereoisomers provides for first time the opportunity of observing the enantiomorphic site control competing with the chain-end control mechanism in a non-metallocene catalyst system.

Stereoselectivity control in olefin polymerization through catalyst design is a spectacular success of homogeneous catalysis.[1] Although many catalysts, including heterogeneous Ziegler–Natta systems, exhibit high stereoselectivity, this is often controlled by the chirality centers of the growing polymer molecule (*chain-end control*). Rational design of stereoselective olefin polymerization catalysts only becomes feasible when the stereochemistry of the monomer insertion is imposed by the symmetry of the active center environment (*enantiomorphic site control*).[2] The latter is exemplified by the stereoselective polymerization of propene into isotactic polypropylene by chiral C_2 *ansa*-metallocenes, first developed by Kaminsky and Brintzinger.[3] In spite of the importance of this concept, very few attempts have been made to extend it beyond the family of metallocene catalysts.[4] Catalysts based on imine ligands, such as α-diimines (Ni, Pd) and 2,6-bis(imino)pyridines (Fe, Co) displaying unsymmetrically substituted aryl groups exist as C_2 (*chiral racemic mixture*) and C_s (*meso*) diastereoisomers (Fig. 1) that are formally analogous to those involved in the metallocene family. Several authors have examined the stereochemistry of propene polymerization by such catalysts.[5–8] Pellecchia described the synthesis and isolation of configurationally stable α-diimine ligands, and studied the catalytic performance of the corresponding nickel complexes.[5] Unfortunately, in this case the influence of the isoselective site control by the chiral C_2 configuration of the diimine ligand is blurred by a concurrent syndio-selective chain-end stereocontrol mechanism. A chain-end control mechanism also operates in the propene polymerization by 2,6-diiminopyridine iron complexes, but in contrast with the above mentioned Ni catalysts, it leads to prevailingly isotactic products. In principle, comparison of the different degrees of isotacticity generated by the chiral and achiral diastereoisomers should allow the identification of site control effects, even when they might be minor.[6] However resolution of diiminopyridine iron complexes into stereoisomerically pure *rac* and *meso* forms has never been achieved, and therefore their activities and selectivities have never been compared. Even the mere existence of Ni, Fe or Co catalysts in conformationally stable stereoisomers in solution counts upon little direct evidence, since their paramagnetism hinders their study by NMR techniques. In this communication we identify and resolve the two diastereoisomeric forms of complex **1** (Scheme 1), and we compare their performance as propene polymerization catalysts. We find that, together with the chain-end isotactic stereoselection, an enantiomorphic metal-site mechanism operates for the C_2 diastereoisomer. This demonstrates for the first time that stereoselective olefin polymerization through rational ligand design can be achieved with late transition metal, non-metallocene catalysts.

Complex **1** is readily prepared by the standard procedure that involves the reaction of hydrated iron(II) chloride and the corresponding 2,6-diiminopyridine ligand in THF (Scheme 1). The product precipitates out as an analytically pure blue solid. Although paramagnetic, iron(II) 2,6-diiminopyridine complexes give rise to useful ^{1}H NMR spectra.[9] Samples of complex **1** in CD_2Cl_2 display two sets of signals, which indicate its occurrence in solution as a mixture of isomers. The isomer ratio gradually changes with time, attaining a 1 : 1 equilibrium ratio within 1–2 days at room temperature. Kinetic measurements between 296 and 326 K afford the following activation parameters for relaxation to the equilibrium mixture: $\Delta H^\ddagger = 25.5(8)$ kcal mol^{-1}, $\Delta S^\ddagger = 5(3)$ cal mol^{-1} K^{-1}, and $\Delta G^\ddagger{}_{298} = 24.0(8)$ kcal mol^{-1}.

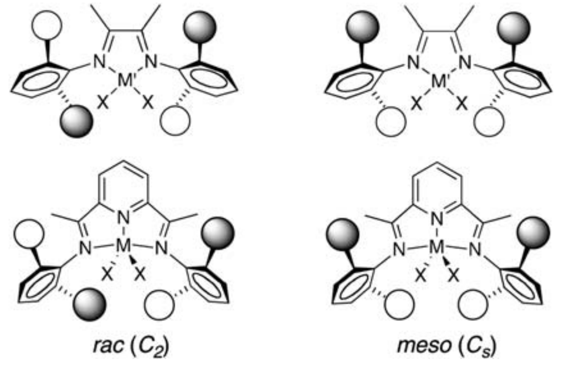

Fig. 1 Racemic and *meso* diastereoisomers of non-metallocene polymerization catalysts (M′ = Ni, Pd; M = Fe, Co).

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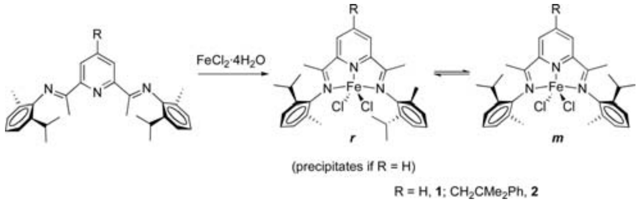
† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for new compounds. See DOI: 10.1039/b810381j



Scheme 1

The initial isomeric ratio of the solutions depends on the origin of the solid sample. Fresh solutions prepared from the precipitated solid are nearly diastereoselectively pure, as they contain more than 90% of a single isomer (**1r**). If this solution is allowed to equilibrate and then rapidly evaporated, the solid residue will contain a mixture of the two isomers.

However, when the equilibrium solutions are allowed to evaporate slowly, the second isomer, **1m**, precipitates selectively. These observations indicate that, while **1r** is formed under kinetic control, the precipitation of **1m** is favored due to its lower solubility. The latter proposal can be readily tested by selective extraction of solid samples containing mixtures of both diastereoisomers with dichloromethane, which leaves a solid residue of **1m**. The different solubility of the two isomers provides an efficient method for the preparation of **1m**. Stirring a suspension of a solid diastereomeric mixture of **1** in hexane–dichloromethane for several days causes **1r** to gradually dissolve and equilibrate with **1m**, which then precipitates until all the sample becomes converted.

A comparison of the NMR spectra of **1r** and **1m** is shown in Fig. 2. As can be seen, although distinctly recognizable, the homologous pairs of signals display very similar chemical shifts and widths, providing no hints at all on the isomers' identity. In spite of our efforts, we were unable to grow X-ray quality crystals of any of them. Brookhart and Small found similar difficulties but reported the crystal structure of a binuclear mixed valence complex probably arising from the oxidation of **1**, which exhibited the *meso* configuration.[6] In order to provide the necessary evidence for positive stereochemical identification, we synthesized complex **2**, bearing the prochiral group 2-methyl-2-phenylpropyl (neophyl) bound to position 4 of the central pyridine ring. We have previously shown that this kind of modification has little impact on either the spectroscopic or catalytic properties of Fe or Co diiminopyridine complexes, and thus they are very well suited for comparative purposes.[10] Although the higher solubility of **2** hampers the selective precipitation of the kinetic isomer, we found that fractional crystallization of this compound affords microcrystalline samples enriched (>80%) in a single isomer, **2m**. On gentle warming in solution, **2m** isomerizes to **2r** until a 1 : 1 equilibrium mixture is attained. While the NMR spectrum of **2m** exhibits a single 6H signal for the C*Me*$_2$ group at δ 2.9 ppm, the two methyls become inequivalent and give rise to two 3H resonances at δ 3.1 and 2.7 ppm in **2r**. This observation proves that **2m** is the achiral *meso* complex; **2r** must be the racemic mixture of chiral diastereoisomers. Brintzinger reported that in some *ansa*-zirconocenes, the *meso* form is the least soluble of the diastereoisomeric pair.[11] Since the *meso* form **2m** displays appreciably lower solubility than **2r**, it becomes very likely that the same relationship would exist in the case of **1**, leading to the conclusion that the kinetic isomer **1r** corresponds to the racemic mixture of diastereoisomers. This conclusion is further supported by the analogous trends observed in the chemical shifts of homologous NMR signals for the two diastereoisomeric pairs. In general, whenever the homologous pairs of signals are well resolved in the spectrum of a mixture of diastereoisomers, the identity of the high/low field signals is the same in the **1r**/**1m** and **2r**/**2m** systems. For example, the signals assigned to the *m*-H atoms of the *N*-aryl groups of **1r** give rise to two very close signals at δ 15.10 and 15.96 ppm. In the spectra of **1r** + **1m** mixtures, these signals of **1r** are flanked by those corresponding to **1m** (δ 16.59, 14.37 ppm), giving rise to a conspicuous feature. The same trend is followed in the **2** system, where the two *m*-H signals of the *rac* diastereoisomer (δ 16.14, 14.86 ppm) also come flanked by the more separated ones of the *meso* (δ 16.29, 14.76 ppm). Similar relationships have been established for the signals corresponding to the imino methyls, the isopropyl CH and Me groups, and the pyridine ring H3 atoms.

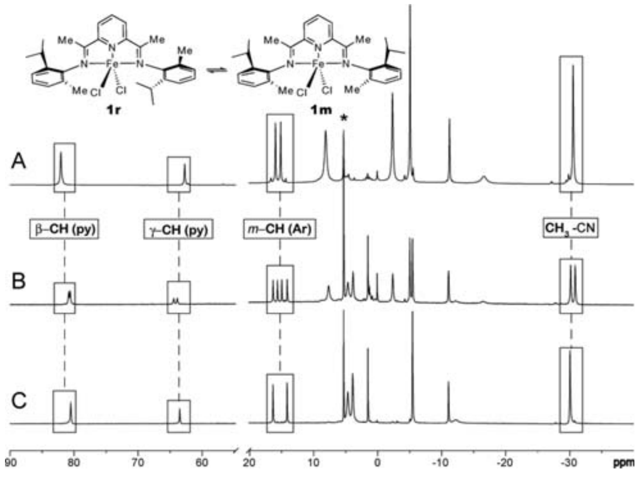


Fig. 2 ^{1}H NMR spectra of complex **1r**, directly precipitated from the reaction mixture (A); **1r** + **1m** equilibrium mixture (B); **1m** (C).

The availability of complex **1** in nearly pure *rac* and *meso* diastereoisomeric forms allowed us to compare their catalytic performance in propene polymerization. The experiments were carried out in a Büchi glass reactor with a circulating cooling bath set to −10 °C. Monitoring the internal temperature showed that it never rose above −5 °C. Extrapolation of the kinetic parameters indicates that the **1r**/**1m** interconversion rate is negligible at this temperature, and hence it can be reasonably assumed that the catalyst is stereochemically stable under the reaction conditions. Activity and polymer characterization data are given in Table 1. As can be seen, the experiments have good reproducibility, and thus the averaged data will be discussed.

The diastereoisomeric forms of **1** exhibit significant performance differences. The chiral form is about three times as active as the *meso*, and gives rise to slightly higher molecular weight polypropylene. The two polymers are prevailingly isotactic, with no detectable content of syndiotactic *rrrr* pentads. The relatively high isotactic content (>50%) of the polymer produced by the achiral *meso* diastereoisomer indicates that, in agreement with previous reports,[7] most of the

Table 1 Propene polymerization data for catalysts **1m** and **1r**[a]

Entry	Catalyst[b]	Activity[c]	$M_w \times 10^{-3}$	M_n/M_w	%m^4	%*mmrr*	%*mmrm*	*mmrm*/*mmrr*
1	**1m**	118	10.6	1.6	51.5	4.2	18.6	4.47
2	**1m**	83	4.8	2.0	52.6	4.2	17.9	4.26
3	**1m**	77	8.3	1.4	53.9	4.0	17.0	4.22
4	**1m**	86	7.4	1.9	53.2	4.2	16.3	3.88
Av.	**1m**	***91***	***7.8***	1.6	***52.8***	***4.2***	***17.5***	***4.21***
5	**1r**	355	7.5	1.6	60.8	3.7	10.8	2.93
6	**1r**	367	7.6	1.4	66.7	3.3	9.8	3.01
7	**1r**	357	7.0	1.7	61.6	3.8	9.1	2.39
8	**1r**	251	8.4	1.5	64.3	3.7	9.2	2.49
9	**1r**	354	11.0	1.1	63.0	4.3	10.9	2.51
Av.	**1r**	***337***	***8.3***	***1.5***	***63.3***	***3.8***	***10.0***	***2.65***

[a] Reaction conditions: Solvent, toluene, 100 mL, −6 °C, 2.3 bar, 40–60 min. [b] Catalyst, 7.2 μmol, co-catalyst, MMAO, Al/Fe = 1000. [c] Activity/kg PP (mol Fe)$^{-1}$ h^{-1} bar^{-1}.

stereoselectivity arises from an effective isoselective chain-end control. However, the polypropylene produced by **1r** displays a distinct excess of isotactic pentads, stemming from a concurrent isospecific enantiomorphous site control mechanism. This conclusion is further supported by the analysis of the minor pentad signals in the polymers ^{13}C NMR spectra. Those produced with **1m** display two resonances of similar intensity attributed to the *mmmr* and *mmrm* pentads. This is expected for stereoblock polymers characteristic of the chain-end stereoselection mechanism. The higher isotactic content of the polypropylenes prepared with **1r** is mostly due to the decrease of the frequency of these sequences, while the number of pentads *mmrr* and *mrrm* (approximate intensity ratio 2 : 1), resulting of isolated stereoerrors characteristic of site control, decrease only slightly. For the chiral catalyst **1r**, the relative weight of this second kind of propagation "mistakes", estimated from the *mmrm* to *mmrr* ratio, becomes nearly double than that for the achiral **1m**, as expected for a significant contribution of the site control mechanism. The simultaneous operation of two stereoselection mechanisms has been previously observed with a metallocenic catalyst, and has led to polypropylene products whose NMR spectra match very closely those of our samples.[12]

In summary, we have shown that the same principles used for the design of highly stereoselective metallocene polymerization catalysts can also be applied to other systems, such as the iron(II) polymerization catalysts. The stereoselectivity of this type of catalysts could be improved by suitable ligand design. Our results also suggest that diiminopyridine ligands can be used to impart enantioselectivity to other catalytic reactions where iron(II) complexes have been shown to be active, such as hydrogenation and hydrosilation.[13]

Financial support from the DGI (Project CTQ2006-05527/BQU), European Union (Network of Excellence IDECAT, contract No NMP3-CT-2005-011730) and Junta de Andalucía are gratefully acknowledged. A.R.-D. thanks the Ministerio de Educación y Ciencia for a Ramón y Cajal fellowship, and A.M.N. a predoctoral research grant from CSIC (I3P program).

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