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Resolution of a Diiminopyridine Iron(II) Complex into *rac*- and *meso*-Diasteroisomers Provides Evidence for a Dual Stereoregulation Mechanism in the Polymerization of Propene Including Enantiomorphous Site Control

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Materials, Reagents and Methods. All syntheses and manipulations were carried out under oxygen-free nitrogen or argon conventional Schlenk techniques or in a nitrogen-filled glove-box unless otherwise stated. NMR spectra were recorded on on Bruker DRX 300, (FT 300 ^{1}H; 75 MHz, ^{13}C; 282 MHz), 400 MHz and 500 MHz spectrometers. The ^{1}H and ^{13}C{^{1}H} resonances of the solvent were used as the internal standard but the chemical shifts are reported with respect to TMS. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra and UV were recorded on a Bruker Vector 22 and UV-Vis on a Perkin Elmer Lambda 12 spectrophotomers. Magnetic susceptibility measurements were made on a Sherwood Scientific balance model MSB-Auto. HPLC grade organic solvents were freshly distilled prior to use. THF and diethyl ether were distilled from sodium benzophenone. CH_2Cl_2 was distilled from CaH_2, and hexane, toluene, and benzene from sodium-benzophenone ketyl. Upon collection, all of them were deoxygenated prior used.

Modified methylalumoxane (MMAO) was purchased from Akzo-Nobel as a 7% solution in heptane. The ligands PDI were synthesized from 2,6-diacetylpyridine according to standard procedures. The preparation of $^{iPr/Me}$PDI-4-R (**L2**) (where R = CH_2CMe_2Ph) was carried out following the synthetic method reported in the literature.[1] $FeCl_2·4H_2O$ was purchased from Aldrich and used without further purification and $FeCl_2·DME$ was prepared by us adapting a methodology employed for the synthesis of analogous systems, reported in the literature.[2]

Synthesis and Separation of *rac*- and *meso*- FeCl$_2$($^{iPr/Me}$PDI) (1r and 1m) The synthesis of racemic- and meso- diastereoisomers **1r** and **1m** $FeCl_2$($^{iPr/Me}$PDI) was

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carried out adapting the methodology reported in the literature for this and analogous compounds.[3] Details for the preparation, characterization and separation of the **1r** and **1m** isomers of $FeCl_2(^{iPr/Me}PDI)$ follow.

To a THF suspension of $FeCl_2\cdot 4H_2O$ (0.795 g, 4.0 mmol), 1.1 equiv of $^{iPr/Me}$PDI (1.0 g, 4.4 mmol) was added at room temperature and the mixture was kept under vigorous stirring for 16 h. The resultant yellow mixture changed to deep blue slowly. Then, the suspension was allowed to settle, the liquid fraction was removed by filtration, and the solid was then washed with diethyl ether (2 x 20 mL) and hexane (2 x 20 mL), and dried in vacuum, yielding 1.81 g, 81 % yield. The blue powdery solid was analyzed by ^{1}H-NMR, observing a signal pattern that corresponds with that the isomer **1r**. ^{1}H-NMR of (**1r**) (CD_2Cl_2, 298 K, 400 MHz): δ 81.29($\Delta\nu_{1/2}$= 41 Hz, 2H, *m*-CH_{py}), 60.87 ($\Delta\nu_{1/2}$=44 Hz, 1H, *p*-CH_{py}), 15.96 and 15.10 ($\Delta\nu_{1/2}$= 19 Hz, 4H, *m*-C$H_{(ar)}$), 8.19 ($\Delta\nu_{1/2}$= 99 Hz, 6H, *o*-CH_3), -2.24 ($\Delta\nu_{1/2}$= 54 Hz, 6H, CH(CH_3)$_2$), -4.91 ($\Delta\nu_{1/2}$= 18 Hz, 6H, CH(CH_3)$_2$), -11.03 ($\Delta\nu_{1/2}$= 25 Hz, 2H, *p*-C$H_{(ar)}$), -16.23 ($\Delta\nu_{1/2}$= 280 Hz, 2H, C*H*(CH$_3$)$_2$), -29.87 ($\Delta\nu_{1/2}$= 34 Hz, 12H, CH_3-C=N) Anal. Calcd for $C_{29}H_{35}N_3Cl_2Fe$: C 63.06, H 6.39, N 7.61; found C 62.06, H 5.80, N 7.60, μ_{eff} = 5.7 μ_B (magnetic balance, 25 ºC), UV-vis ($CH_2 Cl_2$): λ_{max} = 696 nm (ε= 3238), IR (Nujol mull): ν(C=N) = 1625, 1587 cm^{-1}.

The CD_2Cl_2 solution of **1r** was allowed to stand at room temperature under inert atmosphere for an undetermined time. After one hour, a ^{1}H-NMR spectrum of this solution showed a new set of signals were growth at the expense of those corresponding to **1r**. This new set of signals corresponds to those of the *meso* isomer of complex **1**, **1m**. The mixture reached its equilibrium (for a relative ratio of 1:1) after 24 h at ambient temperature. This equilibrium could also be achieved by heating a dicloromethane solution of the initial **1r** at 40 °C for 3 h. ^{1}H-NMR of **1m** (CD_2Cl_2, 298 K, 400 MHz):δ 81.04 ($\Delta\nu_{1/2}$= 47 Hz, 2H, *m*-CH_{py}), 60.34 ($\Delta\nu_{1/2}$=28 Hz, 1H, *p*-CH_{py}), 16.59 y 14.37 ($\Delta\nu_{1/2}$= 20 Hz, 4H, *m*-C$H_{(ar)}$), 5.03 ($\Delta\nu_{1/2}$= 104 Hz, 6H, *o*-CH_3), 4.58 ($\Delta\nu_{1/2}$= 52 Hz, 6H, CH(CH_3)$_2$), -5.37 ($\Delta\nu_{1/2}$= 18 Hz, 6H, CH(CH_3)$_2$), -10.96 ($\Delta\nu_{1/2}$= 19 Hz, 2H, *p*-C$H_{(ar)}$), -11.61 ($\Delta\nu_{1/2}$= 280 Hz, 2H, C*H*(CH$_3$)$_2$), -29.17 ($\Delta\nu_{1/2}$= 34 Hz, 12H, CH_3-C=N).

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Separation of 1m. 0.1 g (0.18 mmol) of a solid sample of a mixture **1r/1m** (previosly equilibrated) were placed in a Schlenk tube, suspended in hexane/dichloromethane 1:1 (10/10 mL) and stirred at ambient temperature for 3 days. Upon filtration and drying under vacuum, the blue isolated solid was identified by ^{1}H-NMR as essentially pure **1 m**.

Synthesis and Separation of *rac*- and *meso*-$\mathbf{FeCl_2(^{iPr/Me}}$PDI-4-R) (2r and **2m).** A diethylether solution of $FeCl_2$·DME (0.958 g, 0.57 mmol) was treated with 0.386 g (0.63 mmol) of $^{iPr/Me}$PDI-4-R and the mixture was kept under stirring for 16 h. The color of the mixture changed to blue but no precipitate was formed. The solution was evaporated to dryness, extracted with 10 mL of CH_2Cl_2 and traces of unreacted $FeCl_2$·DME were separated by filtration. The residue was again taking to dryness, washed with diethyl ether (2 x 20 mL), hexane (2 x 20 mL) and drying in vacuum, yielding 191 mg, 50 % yield. The solid was analyzed by ^{1}H-NMR, observing two sets of signals which correspond to those of the isomeric mixture (**2r/2m**) in 1:1 ratio. Careful re-crystallization of the mixture with CH_2Cl_2/hexane (1:1) at -20 C afforded after 2 weeks a blue microcrystaline solid, which upon filtration and drying was identified by ^{1}H-NMR as the **2m** isomer.

^{1}H-NMR of **2r**: (CD_2Cl_2, 298 K, 400 MHz):δ 83.18 ($\Delta\nu_{1/2}$= 53 Hz, 2H, *m*-CH_{py}), 16.29, 14.86 ($\Delta\nu_{1/2}$= 19 Hz, 4H, *m*-C$H_{(ar)}$), 9.60 ($\Delta\nu_{1/2}$= 93 Hz, 6H, *o*-CH_3), 8.71 ($\Delta\nu_{1/2}$= 15 Hz, 2H, *m*-C$H_{(\mathrm{Neo})}$), 7.37 ($\Delta\nu_{1/2}$= 18 Hz, 2H, *o*-C$H_{(\mathrm{Neo})}$), 7.05 ($\Delta\nu_{1/2}$= 17 Hz, 2H, *p*-C$H_{(\mathrm{Neo})}$), 3.04 and 2.69 ($\Delta\nu_{1/2}$= 8 Hz, 6H, C(Me)$_2$), -1.66 ($\Delta\nu_{1/2}$= 46 Hz, 6H, CH(CH_3)$_2$), -3.77 ($\Delta\nu_{1/2}$= 19 Hz, 6H, CH(CH_3)$_2$), -4.10 ($\Delta\nu_{1/2}$= 23 Hz, 2H, CH_2), -9.43 ($\Delta\nu_{1/2}$= 20 Hz, 2H, *p*-C$H_{(ar)}$), -14.10 ($\Delta\nu_{1/2}$= 267 Hz, 2H, CH(CH_3)$_2$), -18.01 ($\Delta\nu_{1/2}$= 45 Hz, 6H, CH_3-C=N). ^{1}H-NMR of **2m:** (CD_2Cl_2, 298 K, 400 MHz):δ 82.91($\Delta\nu_{1/2}$= 53 Hz, 2H, *m*-CH_{py}), 16.14, 14.76 ($\Delta\nu_{1/2}$= 19 Hz, 4H, *m*-C$H_{(ar)}$), 8.77 ($\Delta\nu_{1/2}$= 15 Hz, 2H, *m*-C$H_{(\mathrm{Neo})}$), 7.41 ($\Delta\nu_{1/2}$= 18 Hz, 2H, *o*-C$H_{(\mathrm{Neo})}$), 7.05 ($\Delta\nu_{1/2}$= 17 Hz, 2H, *p*-C$H_{(\mathrm{Neo})}$), 6.21 ($\Delta\nu_{1/2}$= 93 Hz, 6H, *o*-CH_3), 3.74 ($\Delta\nu_{1/2}$= 46 Hz, 6H, CH(CH_3)$_2$), 2.98 ($\Delta\nu_{1/2}$= 8 Hz, 6H, C(Me)$_2$), -3.77 ($\Delta\nu_{1/2}$= 19 Hz, 6H, CH(CH_3)$_2$), -4.10 ($\Delta\nu_{1/2}$= 23 Hz, 2H, CH_2), -8.26 ($\Delta\nu_{1/2}$= 267 Hz, 2H, CH(CH_3)$_2$), -9.43 ($\Delta\nu_{1/2}$= 20 Hz, 2H, *p*-C$H_{(ar)}$), -17.48 ($\Delta\nu_{1/2}$= 45 Hz, 6H, CH_3-C=N).Anal. Calcd for **2**·DME: $C_{43}H_{57}N_3Cl_2O_2Fe$: C 66.67, H 7.42, N 5.42; found C

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66.31, H 6.99, N 5.85, IR (Nujol mull): ν(C=N) = 1589 cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} = 685 nm (ε= 1421).

General Polymerization Procedures

Propene polymerization reactions were carried out in a Büchi glass reactor POLYCLAVE-BMD 300, thermostatized with a water-ethyleneglycol circulating bath equipped with an internal PT-100 termocouple for temperature monitorization. The reactor was charged with dried and degassed toluene (100 mL) and then connected to a propene polymerization line, equipped with a device for continuous propene consumption monitoring. The circulating bath temperature was set to -10 °C and the internal temperature of the reactor stabilized at the -7 °C. Then the reactor was flushed three times with propene to remove the nitrogen atmosphere for latter pressurization at 2.3 bar and the solvent stirred allowing to absorb propene until the absence of gas consumption, which was indicative of monomer saturation. The polymerization reaction was initiated by consecutive additions of stock solutions containing prestablished amounts of the cocatalyst (MMAO, 4 mL, 1.8 M in heptane) and the precatalyst (4 mL, 1.8 mM in CH_2Cl_2) via syringe, through a septum capped port. Internal temperature and monomer consumption were monitored afterwards. The reaction was terminated by addition of 10 mL of acidified methanol when the specific reaction time was reached. The reactor contents were poured in 500 mL beaker containing 250 mL of methanol, and the resulting suspension was stirred for 12 h. The polymer was separated by filtration, washed several times with ethanol and dried first in vacuum and then in an oven at 100 °C until constant weight.

Polymer Characterizations

Polymer number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) measurements were performed on a high temperature dual-detector size exclusion chromatography (SEC) system. The SEC system was a PL-GPC220 from Waters 150c instrument (Milford, MA) that uses two on-line detectors: a differential viscometer (150R DV) and a differential refractometer (DRI) as concentration detector. The molecular mass values reported are those obtained with the DV detector under universal calibration.

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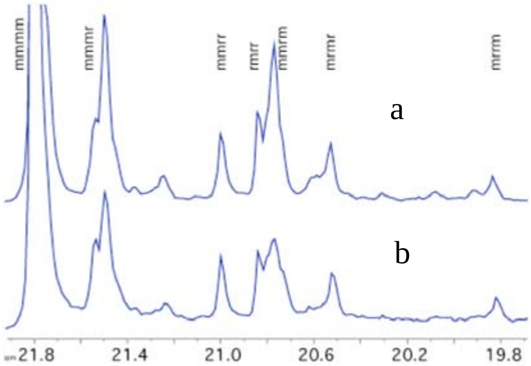
Methyl pentads region (m^4) ^{13}C-NMR spectra of significant samples of prolypropene produced with ***meso*-1** and ***rac*-1** included in the **Table 1** of the original manuscript.



a) Top: Methyl Pentads region of ^{13}C-NMR of polypropene produced with ***meso*-1**.
b) Bottom: Methyl Pentads region of ^{13}C-NMR of polypropene produced with ***rac*-1**.

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