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Isospecific Propylene Polymerization with Unbridged Group 4 Metallocenes

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Chiral ansa metallocene complexes have been employed as catalyst precursors for the isospecific and syndiospecific polymerization of propylene.[1] The bridge connecting the two five-membered aromatic ring moieties has been thought to be an essential and integral part of the chelating ligand system. It provides the rigidity and maintains the symmetry prerequisite for stereospecific polymerization reactions.

Partially isotactic polypropylene has been obtained in polymerizations catalyzed with unbridged metallocenes at very low temperatures.[2] The polymer microstructures consisting predominantly of ...mmmmmmmrmmmm... stereosequences were compatible with the chain-end stereoregulation hypothesis.[2a]

In this communication we describe a new type of isotactic-specific propylene polymerization catalyst precursor, the unbridged metallocene complex bis(1-methylfluorenyl)zirconium dichloride (**1**). Complex **1** after activation with methylaluminoxane (MAO), polymerizes propylene to crystalline isotactic polypropylene at conventional polymerization temperatures. The polymer configurational microstructure is consistent with an enantiomorphic site stereochemical control mechanism.[3]

Metallocene. A perspective view of the molecular structure and atom numbering scheme of bis(1-methylfluorenyl)zirconium dichloride is presented in Figure 1. The crystal structure reveals a bent, sandwich complex in which the two nonfluxional, pentahapto-bonded fluorenyl ligands form a helical arrangement around the zirconium metal.[4-6] The molecule as a whole is stereorigid and chiral. It has a C_2 symmetry axis bisecting the Cl–Zr–Cl angle, and both prospective coordination sites are equally shielded by the substituents of the cyclopentadienyl moieties. Thus, identical steric encumbrance of both sites stipulated for an equivalent enantiofacial coordination of prochiral molecules and their isospecific enchainment is perfectly met.

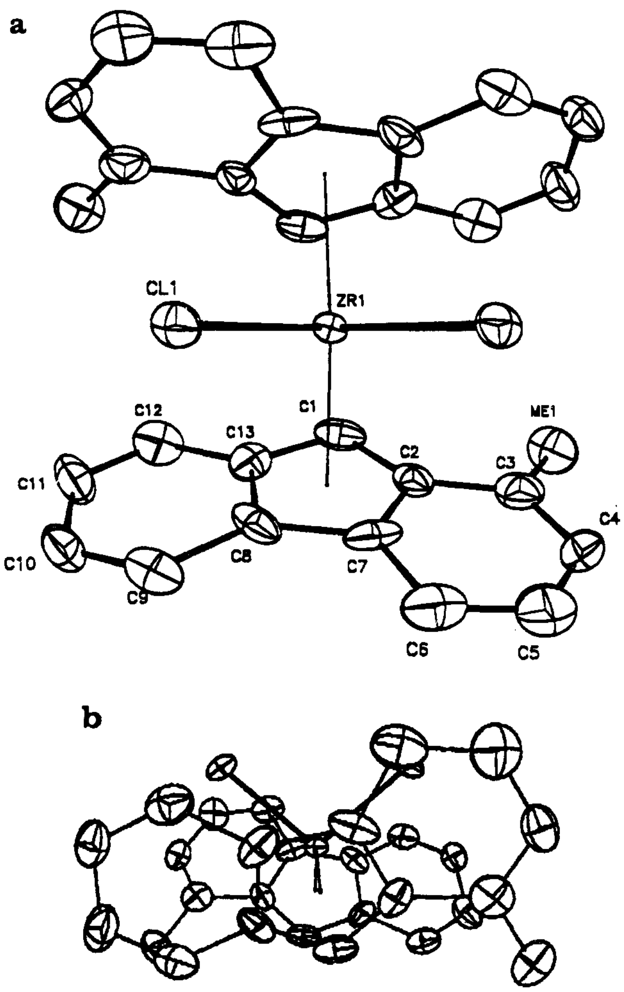

Figure 1. (a) Molecular structure of **1**. The atoms are represented by their 50% probability ellipsoids. Important distances (Å) and bond angles (deg) are as follows: Zr-Cl, 2.408(2); Zr-C(1), 2.415(8); Zr-C(2), 2.579(8); Zr-C(7), 2.669(7); Zr-C(8), 2.655(8); Zr-C(13), 2.530(8); Zr-Cn, 2.271; C(1)-C(2), 1.38(1); C(2)–C(7), 1.40(1); Cl-Zr-Cl′, 95.59(3); Cn-Zr-Cn′, 135.07(6). (Cn denotes the centroid of the five-membered portion of the fluorenyl ring; ′ denotes an atom or centroid related by the crystallographic two-fold axis.) (b) A perspective view of the molecule normal to the plane containing the zirconium and the two chlorine atoms.

Polymerizations. The polymerizations were performed in a 2-L Buchi reactor in liquid propylene and in a temperature range from 40 to 70 °C. In a typical polymerization run, 5 mg of **1** was reacted with 10 mL of 10 wt % aluminoxane solution in toluene at 25 °C for 5 min. The mixture was subsequently injected into a pressure reactor containing 1 L of liquid propylene at a pressure of 18 bar and a temperature of 60 °C. The polymerization was interrupted after 1 h by addition of acidic methanol, and 6 g of polymer was recovered. The polymer was analyzed after being extracted with hexane.

Polymer ^{13}C NMR Analysis. Figure 2 displays the ^{13}C NMR spectrum of the methyl region and polymer analyses of isotactic polymer produced with **1** at 60 °C. The polymer has a ...mmmmmmmrrmmmmm... microstructure. The appearance of a pair of racemic diads in an otherwise long sequence of meso diads in the polymer chain indicates that the stereochemistry of insertion is controlled by the organometallic moiety of the catalyst due to the unique arrangement of the organic ligands framing the central transition metal. In this configuration, the catalyst discriminates between the two enantiofaces of the prochiral

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(1) (a) Kaminsky, W.; Kupler, K.; Brintzinger, H. H.; Wild, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Erker, G.; Nolte, R.; Tasy, Y. H.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628. (c) Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Kruger, C.; Noe, R. *J. Am. Chem. Soc.* **1991**, *113*, 7594. (d) Erker, G.; Temme, B. *J. Am. Chem. Soc.* **1992**, *114*, 4004.

(3) Sheldon, R. A.; Fueno, T.; Tsunesugu, T.; Furukawa, J. *J. Polym. Sci.* **1965**, *3*, 23.

(4) 1-Methylfluorene (5.00 g, 27.0 mmol) was dissolved in 150 mL of THF and aromatized with an equimolar amount of methyllithium. The resulting red solution was stirred for 2 h. After evaporation of the solvent, a red powder was obtained. The residue was suspended in 200 mL of pentane and reacted with 3.15 g (13.5 mmol) of $ZrCl_4$. After 3 h the pentane was discarded, and the red residue was extracted with CH_2Cl_2. Crystallization from methylene chloride yielded 4.5 g (65%) of **1** as red platelets.[7] Anal. Calcd: C, 64.62; H, 4.22; Zr, 17.52; Cl, 13.62. Found: C, 64.01; H, 3.89; Zr, 16.41, Cl, 14.23.

(5) ^{1}H NMR (CD_2Cl_2) shows seven doublets and triplets at δ 8.16 (d, 2H), 8.13 (d, 2H), 8.12 (d, 2H), 7.64 (t, 2H), 7.44 (t, 2H), 7.14 (t, 2H), and 7.01 (d, 2H) for the aromatic six-membered ring protons, a singlet at δ 5.30 (s, 2H) for the five-membered ring protons, and a singlet at δ 1.96 (s, 6H) for the two methyl groups.

(6) The space group for **1** is $C2/c$ with $a = 17.535(5)$, $b = 6.843(3)$, and $c = 18.699(6)$ Å, $\beta = 96.12(3)°$, and $D_c = 1.56$ g cm^{-3} for $Z = 4$. Refinement based on 1822 data ($I > 3\sigma(I)$) resulted in a final R value of 0.073.

(7) The hafnium analog of complex **1** can be prepared with similar yield according to the same procedure used in ref 4. It shows similar catalytic properties. It is, however, less active, and the polymer obtained with it has lower molecular weight and is less stereoregular.

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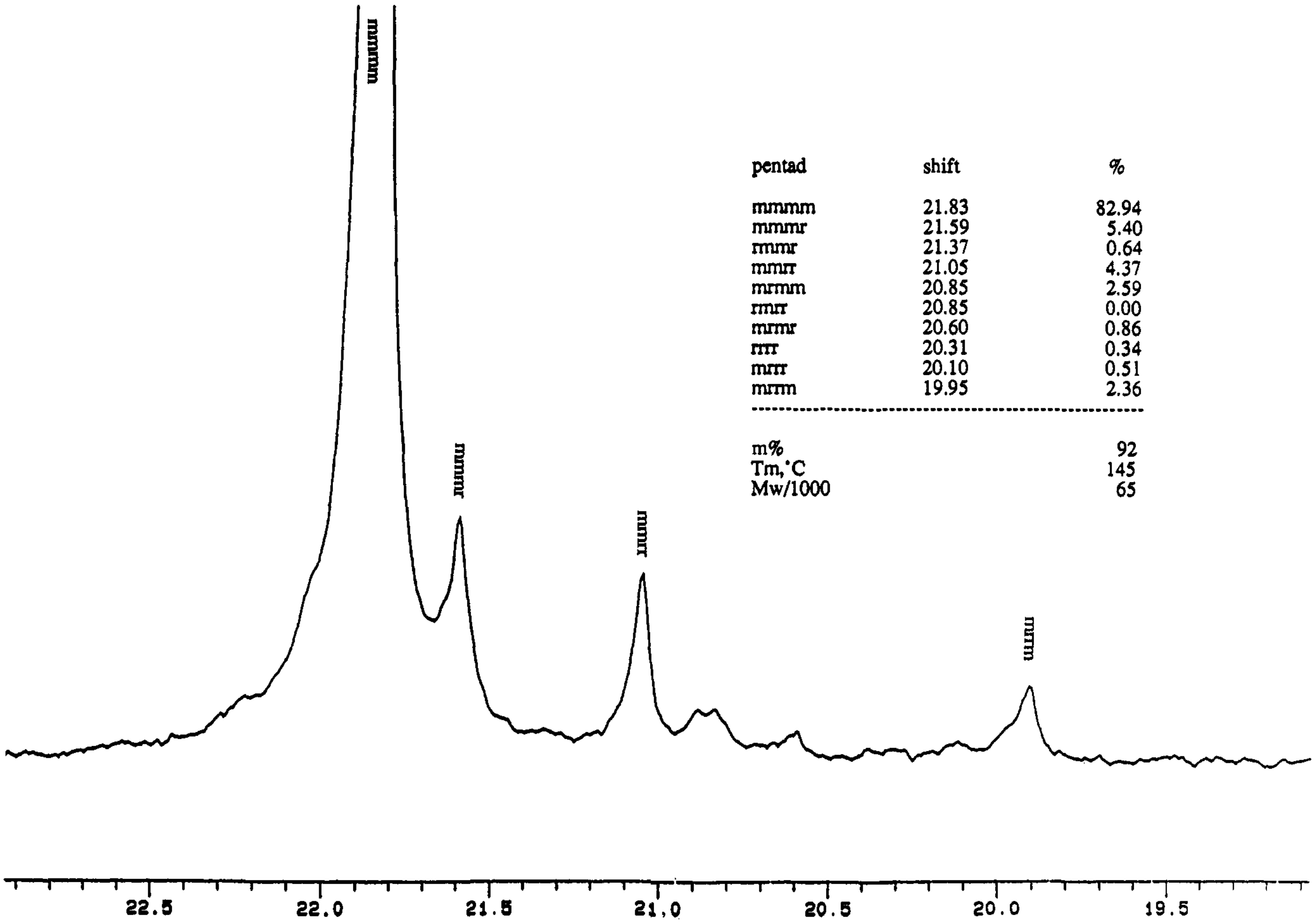

pentad	shift	%
mmmm	21.83	82.94
mmmr	21.59	5.40
rmmr	21.37	0.64
mmrr	21.05	4.37
mrmm	20.85	2.59
rmrr	20.85	0.00
mrmr	20.60	0.86
rrrr	20.31	0.34
mrrr	20.10	0.51
mrrm	19.95	2.36
m%		92
Tm,°C		145
Mw/1000		65

Figure 2. ^{13}C NMR spectrum of the methyl region and polymer analyses of the isotactic polypropylene obtained with **1**.

propylene and complexes one face preferentially. Occasional reversal in enantioface selectivity then results in the formation of a pair of racemic diads as the predominant stereo defect in the polymer chain with an otherwise homosteric microstructure.

Supplementary Material Available: Listings of crystal data, atomic coordinates, bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.