276 *Macromolecules* **2004,** *37,* 276−282

Bis(phenoxyimine)zirconium and -titanium Catalysts Affording Prevailingly Syndiotactic Polypropylenes via Opposite Modes of Monomer Insertion[†]

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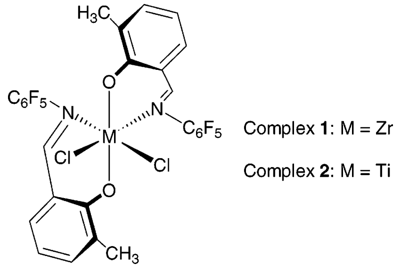
Received August 1, 2003; Revised Manuscript Received October 28, 2003

ABSTRACT: A zirconium(IV) complex bearing two *N*-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroaniline and two Cl ligands has been synthesized (**1**). X-ray analysis indicates that **1** adopts a distorted octahedral structure with a *trans*-O, *cis*-N, and *cis*-Cl arrangement, similarly to previously reported complexes of this class. Polymerization of propene at room temperature in the presence of **1** activated by methylaluminoxane results in the production of poorly stereoregular, prevailingly syndiotactic polypropylene. The polymer microstructure is in agreement with a "chain-end" mechanism of steric control, with $P_r = 0.67$ (where P_r is the probability of a syndiotactic placement). End group analysis, also using deuterium labeling techniques, and NMR analysis of a copolymer of propene with trace amounts of [1-^{13}C]-ethylene, indicate a prevailing primary insertion mode in both initiation and propagation, in contrast to the prevailingly secondary regiochemistry established for related bis(phenoxyimine) titanium catalysts. To discriminate the role played by the nature of the metal from any ligand effect, a titanium complex bearing the same phenoxyimine ligands has been also tested, resulting in the production of a polypropylene having a very similar structure, with $P_r = 0.71$. Investigation of the regiochemistry shows that propagation prevailingly occurs via secondary insertion of propene. Thus, zirconium and titanium complexes bearing the same ligands afford prevailingly syndiotactic polypropylenes having very similar structures, but via opposite regiochemistries.

Introduction

Following the successful design and application of group 4 metallocenes,[1] in the last few years increasing interest has been directed toward the search for new classes of "non-metallocene" catalysts, a rapidly developing area of investigation which has recently comprehensively reviewed.[2] Worthy of mention are highly active late transition metal systems such as Brookhart's Ni and Pd diimine catalysts[3] or the Fe bis(imino)pyridyl catalysts[4] and group 4 metal bis(phenoxyimine) catalysts,[5] all of them showing a number of interesting peculiar features. In particular, bis(phenoxyimine) group 4 metal catalysts, developed by the group of Fujita, are able to produce polyethylene with activities comparable to or exceeding those of metallocene catalysts.[6,7] Titanium complexes of this class can produce syndiotactic polypropylenes[8,9] with stereoregularities ranging from moderate to high depending on the precatalyst structure and the polymerization conditions. Also, titanium complexes bearing fluorinated *N*-aryl groups polymerize ethylene and propene in a living fashion.[8b,9,10] The mechanism of syndiospecific polymerization has been investigated by both experimental[9b,11,12] and theoretical techniques.[13] In particular, the polymer microstructure suggested a "chain end" mechanism of steric control, while end group analysis and other evidence indicated a predominant secondary (2,1) regiochemistry of monomer insertion.

Scheme 1



Less information is available in the literature concerning the polymerization of propene in the presence of bis(phenoxyimine) zirconium catalysts.[6] The production of atactic oligomers was reported for the catalyst bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride/MAO,[6] while activation of the same precatalyst with *i*-Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ resulted in the production of isotactic polypropylene.[14] In the latter case, the true active species was suggested to be a bis(phenoxyamine) zirconium complex produced via in situ reduction of the bis(phenoxyimine) complex by the cocatalyst.[14]

In this paper, we report the synthesis and the catalytic activity in propene polymerization of a new bis(phenoxyimine)zirconium complex (**1**, Scheme 1). Investigation of the polymerization mechanism and comparison with the performances of the corresponding titanium complex (**2**, Scheme 1) showed a rather peculiar feature, i.e., the production of very similar prevailingly syndiotactic polypropylenes in both cases, but via opposite regiochemistries of monomer insertion. Some of the results reported here have been previously communicated.[15]

Results and Discussion

Complex **1** was prepared, according to literature procedures,[16] by reaction of 2 equiv of the ligand lithium

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[†] Dedicated to Prof. Adolfo Zambelli on the occasion of his 70th birthday.

10.1021/ma035120g CCC: $27.50

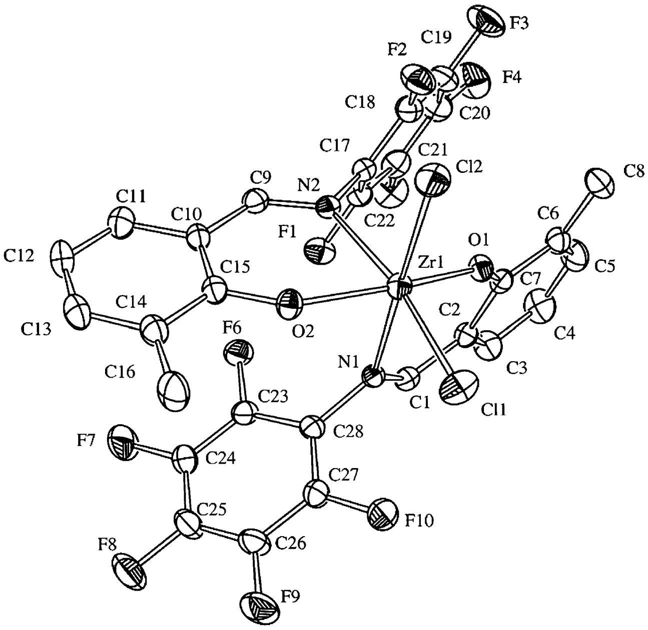


Figure 1. Ortep drawing of the molecular structure of compound **1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level.

Table 1. Selected Bond Distances and Angles for Compound 1

bond distances (Å)		bond angles (deg)	
Zr−Cl1	2.4055(9)	Cl1−Zr−Cl2	93.39(3)
Zr−Cl2	2.4041(9)	N1−Zr−N2	82.39(7)
Zr−N1	2.383(2)	O1−Zr−O2	154.51(7)
Zr−N2	2.402(2)		
Zr−O1	1.9701(18)		
Zr−O2	1.9737(18)		

salt with $ZrCl_4 \cdot 2THF$ in THF. Single crystals of **1** were obtained from its methylene chloride/hexane solution. The molecular structure of **1** is shown in Figure 1; selected bond lengths and angles are given in Table 1.

X-ray analysis indicates that **1** adopts a distorted octahedral structure with a *trans*-O, *cis*-N, and *cis*-Cl arrangement. The molecular structure is similar to those of previously reported complexes of this class.[16] Interestingly the Cl1−Zr−Cl2 bond angle is larger than the corresponding one in analogues compounds,[16] while the N1−Zr−N2 and O1−Zr−O2 bond angles show lower values; this effect can be ascribed to the lower steric hindrance of the methyl substituent in the phenoxy moiety.

^{1}H and ^{13}C NMR spectra show the presence of a single isomer in methylene chloride-d_2 solution.

Polymerization of propene with complex **1** using methylaluminoxane (MAO) as the cocatalyst was carried out under atmospheric pressure at 18 °C for 2 h (run 1, Table 2).

The ^{13}C NMR spectrum of the polypropylene obtained in run 1 (see Figure 2) indicates that the sample is poorly stereoregular, but with a prevailingly syndiotactic structure. Methyl pentad analysis is consistent with the Bernoullian statistical model proposed by Bovey[17] for a "chain-end" mechanism of steric control, with $P_r = 0.67$ and $P_m = 1 - P_r$, where P_r and P_m are the probabilities of syndiotactic (r) and isotactic (m) placements, respectively. A significant amount (∼3,5%) of regioirregularly arranged monomer units is present, as indicated, e.g., by the methyl resonances of the tail-to-tail units observed between 12.6 and 15.0 ppm from hexamethyldisiloxane (HMDS). In addition to the resonances due to the main chain carbon atoms, the spectrum displays peaks at δ 20.5−21.8, 23.7, 46.1, and 46.2 ppm attributable, according to the literature,[18] to isobutyl end groups. No other end group resonances are detected, excepting for resonance in the unsaturated region of the spectrum attributable to vinylidene end groups, whose intensity is only 1/10 than that of the saturated end groups. The almost exclusive presence of isobutyl end groups is indicative of primary (1,2) propene insertion in both the initiation and the termination steps. The plausible polymerization mechanism involves (see Scheme 2) primary propene insertion into $Zr-CH_3$ bonds, followed by prevailingly primary insertion during the propagation, and termination via chain transfer of

Table 2. Polymerization Conditions and Results[a]

run	catalyst	reaction time, min	temp, °C	yield, g	P_r	M_w ($\times 10^3$)	M_w/M_n
1	**1**	120	18	4.95	0.67	8.3	2.3
2	**1**^{b}	30	18	0.90	0.66	4.5	3.6
3	**1**^{c}	120	18	6.40	0.64	18.2	3.2
4	**1**^{d}	120	18	0.32	0.53	14.4	3.4
5	**1**^{e}	120	18	4.73	0.69	21.2	2.8
6	**1**^{f}	120	−60	0.18	0.62	18.2	3.2
7	**1**^{g}	120	−60	2.24	0.66	14.6	2.6
8	**2**	120	18	1.40	0.71	268.9	2.9
9	**2**^{h}	5	18	0.31	0.70	21.5	1.5
10	**2**^{b,i}	5	18	0.27	0.71	19.6	2.1
11	**2**	120	−20	0.64	0.68	66.4	1.6

[a] General conditions: toluene = 40 mL; precatalyst = 25 μmol; cocatalyst: MAO = 3.75 mmol; propene pressure = 1 atm. [b] Terminated by injecting a 1:1 mixture of CF_3CH_2OD and D_2O. [c] Cocatalyst: dried MAO obtained by distilling off the solvent by the commercial solution. [d] Cocatalyst: $Al(^iBu)_3/Ph_3CB(C_6F_5)_4$ = 1.25 mmol/50 μmol. [e] Propene pressure = 6 atm. [f] [propene] = 1.5 mol/L. [g] [propene] = 7.5 mol/L. [h] Precatalyst = 82 μmol; cocatalyst: MAO = 12.3 mmol. [i] Precatalyst = 55 μmol; cocatalyst: MAO = 8.3 mmol.

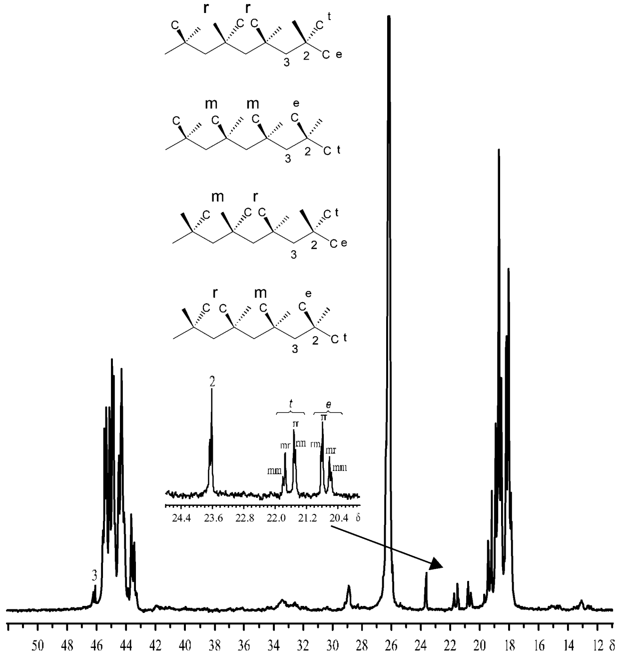
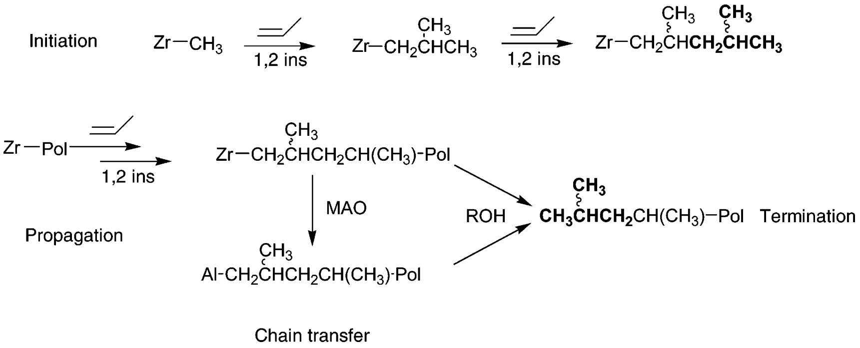


Figure 2. 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a polypropylene sample prepared with **1**/MAO (run 1) and expansion of the 20−24 ppm region, displaying the resonances of the geminal methyls (labeled e and t) of the diastereomeric chain end (labeled *rr*, *mm*, *mr*, and *rm* on the spectrum). δ is given in ppm from hexamethyldisiloxane.

Scheme 2



the primary growing chain to MAO (or rather to $Al(CH_3)_3$ present in the MAO solution, see below) generating a new $Zr-CH_3$ bond for reinitiation. The presence of a few vinylidene end groups would derive from occasional β-hydrogen elimination from a primary growing chain.

The chemical shift of the isobutyl end groups is sensitive to the stereochemistry of the neighboring propene units. The different resonances observed for the diastereotopic methyls of the isobutyl end groups of sample 1 are assigned, by comparison with the spectra of suitable model compounds[18a] and of syndiotactic poly(propylene) obtained in the presence of monoamidinate Ti(IV) complexes,[19] to the diastereomeric end groups shown in Figure 2. The larger amount of the *rr* end groups in comparison with the *mm*, evaluated from the areas of the corresponding resonances, shows that primary propene insertion is predominantly syndiotactic specific. Interestingly the fractions of the *rr*, *mr* + *rm*, and *mm* end groups are close to the fractions of *rr*, *mr* + *rm*, and *mm* stereochemical triads of the polymer chain (end groups *mm* ≈ 12%, *mr* ≈ 25%, *rm* ≈ 23%, and *rr* ≈ 40%; chain *mm* ≈ 9%, *mr* + *rm* ≈ 47%, and *rr* ≈ 44%).

The average degree of polymerization (≈110 monomer units), calculated from the area of the resonances of the main chain carbons and that of the end group carbons, assuming that each macromolecule has two isobutyl end groups, is in reasonable agreement with the molecular weight determined by GPC analysis. The presence of isobutyl end groups deriving from the termination step was confirmed by a deuterium labeling experiment:[20] a polymerization run (Table 2, run 2) was quenched with a mixture of CF_3CH_2OD and D_2O. ^2H NMR analysis of the obtained polypropylene (see the spectrum in Figure 3a) clearly shows the presence of $CH_2DCH(CH_3)CH_2-$ end groups, as expected for deuteriolysis of a primary polymer chain bound to either Zr or Al (Scheme 3a). The ^{13}C NMR spectrum of the same sample contains, in addition to the resonances previously observed for the end groups, a new resonance 0.07 ppm upfield from that of the methine of the nondeuterated isobutyl (see Figure 4). Similar isotopic shifts were observed in the spectra of the model compound 1-deuterio-2,4,6-trimethylheptane,[18a] as well as of deuterated isobutyl end groups of syndiotactic polypropylene produced by α-diimine nickel catalysts,[21] also involving predominant primary regiochemistry.

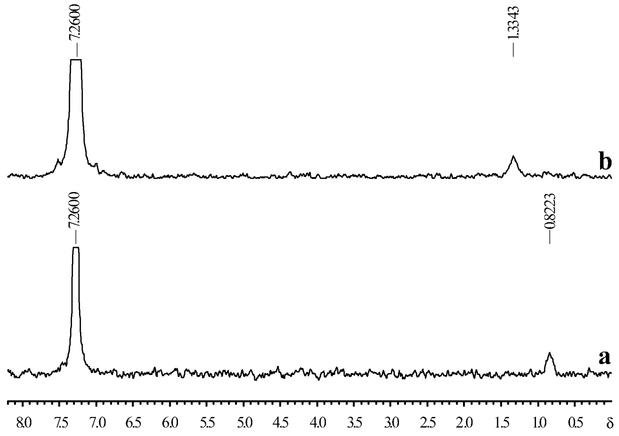


Figure 3. 62.4 MHz ^2H NMR spectra ($CDCl_3$, 25 °C) of two polypropylene samples prepared with (a) **1**/MAO and (b) **2**/MAO (runs 2 and 10 respectively). Polymerization runs 2 and 10 were terminated by injecting a 1:1 mixture of CF_3CH_2OD and D_2O. δ is given in ppm from hexamethyldisiloxane.

Scheme 3

A polymerization run (Table 2, run 3) was also performed by using, as the cocatalyst, solid MAO obtained by distilling off the solvent from the com-

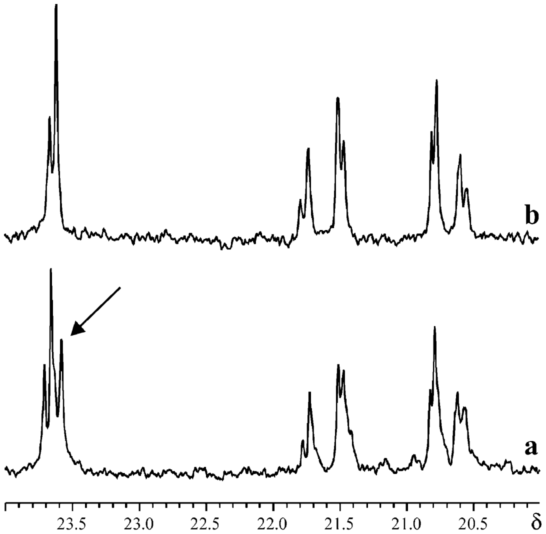


Figure 4. Methyl and methine regions of the 100.6 MHz ^{13}C NMR spectra ($C_2D_2Cl_4$, 100 °C) of two polypropylene samples prepared with **1**/MAO. Polymerization runs were terminated adding (a) acidified ethanol (run 1, Table 2) and (b) a 1:1 mixture of CF_3CH_2OD and D_2O (run 5, Table 2). δ is given in ppm from hexamethyldisiloxane.

Table 3. Copolymerization of Propene with [1-^{13}C]-Ethylene[a]

run	catalyst	reaction time, min	yield, g	P_r
12	**1**	30	3.40	0.67
13	**2**	60	1.20	0.71

[a] General conditions: toluene = 40 mL; precatalyst = 25 μmol; cocatalyst: MAO = 3.75 mmol; T = 18 °C; propene/1-^{13}C-ethylene (99.6/0.4%) pressure = 1 atm.

mercial toluene solution. The ^{13}C NMR spectrum of the obtained polypropylene is very similar to that of sample **1**, excepting for the absence of any detectable end groups, indicating a higher molecular weight, as confirmed by GPC analysis (see Table 2). This finding suggests that $Al(CH_3)_3$ present in the MAO solution is the actual chain transfer agent. To obtain more information about the role of the cocatalyst we carried out a polymerization experiment by using $Al(i\text{Bu})_3/Ph_3CB(C_6F_5)_4$ as the cocatalyst (Table 2, run 4), resulting in the production of a substantially stereoirregular polymer, having a higher molecular weight than that of sample **1** (see Table 2). The cocatalyst has also a significant effect on the polymer yield (cf. runs 1 and 4 of Table 2). In the case of activation by $Al(i\text{Bu})_3/Ph_3CB(C_6F_5)_4$, in situ reduction of the bis(phenoxyimine) complex has been suggested, and so a different active species would be involved.[14]

Further insight in the regiochemical mechanism came from copolymerization of propene with a small amount (≈0.4%) of ethylene, 99% enriched on C1 (run 12, Table 3). Under these conditions, essentially isolated ethylene units flanked on both sides by blocks of propene units are obtained.

Four cases are possible, leading to the formation of sequences of two, three, or four methylenes, as shown in Scheme 4.

The ^{13}C NMR spectrum of the copolymer produced in run 12 is displayed in Figure 5a. According to literature assignments,[22] the ethylene units are actually isolated and are located in two different environments, leading to either a two-methylene sequence or a three-methylene sequence. The three methylene sequences outnumber the methylene pairs (79% vs 21%), as deduced from the area of the resonances of the $S_{\alpha\gamma}$ carbons and of the $S_{\beta\beta}$ carbons vs the area of the resonances of the $S_{\alpha\beta}$ carbons (corrected for the contribution of unenriched $S_{\alpha\beta}$ carbons arising from head-to-head propene insertion). This is in agreement with a prevailingly primary regiochemistry: enriched ethylenes mostly span primary propene blocks (Scheme 4b), while insertion of ethylene into a metal−secondary carbon bond leads to metal−primary carbon bonds and is followed by primary insertion of propene (Scheme 4a). In contrast, in a similar experiment performed in the presence of the bis-[N-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanili-

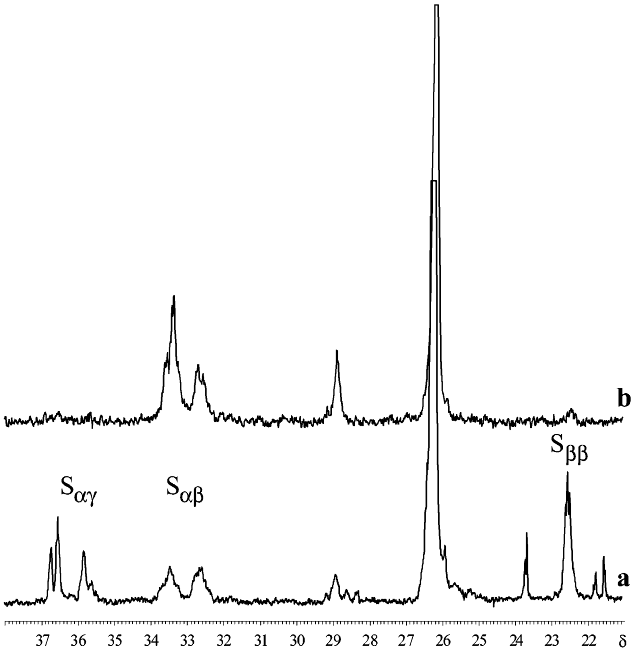
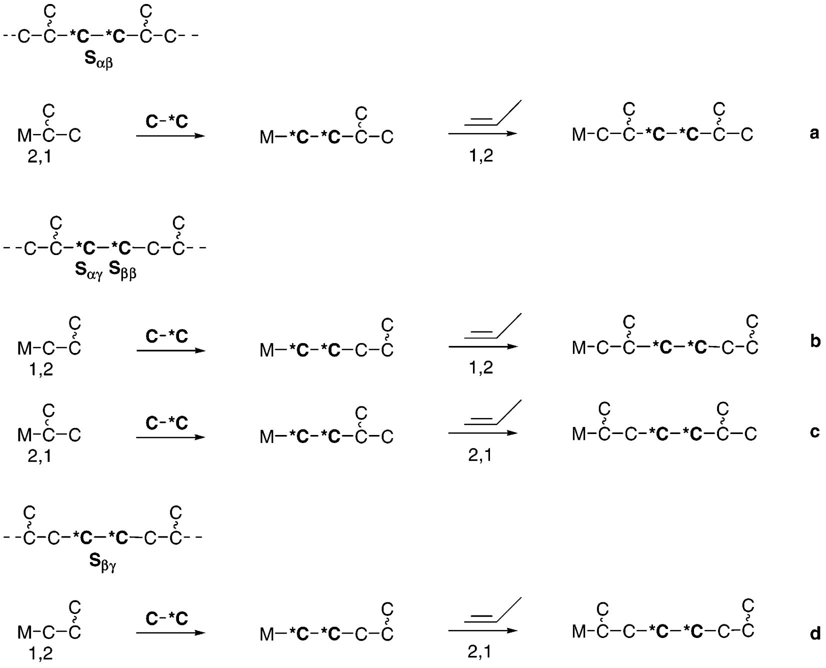
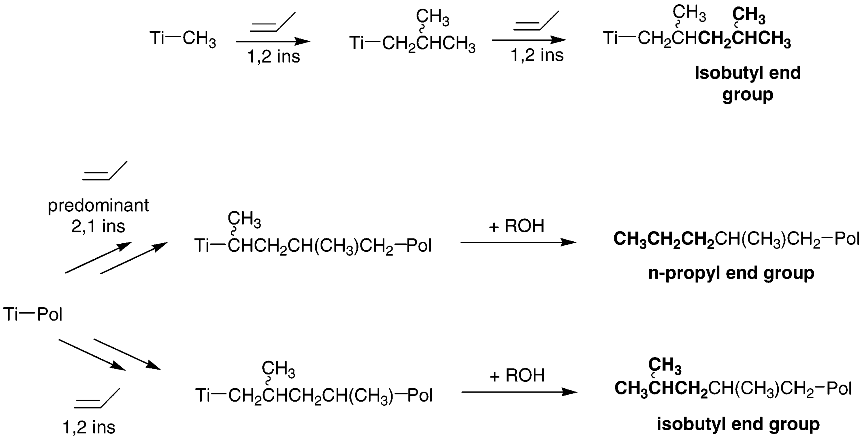


Figure 5. Aliphatic region of the 100.6 MHz ^{13}C NMR spectra ($C_2D_2Cl_4$, 100 °C) of two copolymers of propene with a little amount of [1-^{13}C]-ethylene prepared with (a) **1**/MAO and (b) **2**/MAO (runs 11 and 13, respectively). δ is given in ppm from hexamethyldisiloxane.

Scheme 4



Scheme 5



nato]titanium(IV) dichloride catalyst, for which a prevailingly secondary regiochemistry was established, a larger amount of two-methylene sequences than three-methylene sequences was observed.[11]

The resonances of the enriched methylenes are mainly sensitive to the stereochemical arrangement of the adjacent propene dyad. Since the propene insertion is prevailingly 1,2, the $S_{\alpha\gamma}$ carbon resonance is diagnostic of the stereochemistry of the two propene units entered into the chain after the enriched ethylene (Scheme 4b).[22] Thus, one can evaluate P'_r (and $P'_m = 1 - P'_r$), the probability of having an *r* (*m*) dyad immediately following an ethylene unit: from the areas of the resonances of the *r*-$S_{\alpha\gamma}$ and *m*-$S_{\alpha\gamma}$ enriched carbons, $P'_r = 0.58$, which is less than P_r in the main chain (0.67), as expected considering that the chiral carbon of the last unit of the growing chain bears substituents of less different ranks in comparison with propene homopolymerization.

Some polymerization runs were also carried out by changing the monomer concentration and the polymerization temperature in order to evaluate the effect of these reaction conditions on the polymer microstructure. The syndiotacticity of the polymers resulted poorly affected by either the monomer concentration (as expected for a chain-end mechanism of steric control) or the polymerization temperature (cf. runs 1, 5, 6 and 7, Table 2). The molecular weight increases with the increase of the monomer concentration (cf. runs 1 and 5), in agreement with chain termination occurring prevailingly via transfer to Al.

In conclusion, primary insertion is the prevailing mode of monomer insertion in the polymerization of propene promoted by this bis(phenoxyimine) zirconium catalyst. This result is unexpected, in view of the opposite regiochemistry observed for related bis(phenoxyimine) titanium catalysts. To discriminate the role played by the nature of the metal in determining the regiochemistry of propene insertion from any ligand effect, we synthesized the analogous titanium complex (**2**, Scheme 1). While this work was in progress, the synthesis of **2** and the living polymerization of propene to a prevailingly syndiotactic polymer by **2**/MAO has been reported.[23] Accordingly, a polymerization run under conditions similar to those of run 1 (Table 2, run 8) resulted in the production of a polypropylene sample having a ^{13}C NMR spectrum very similar to that of sample **1** (P_r = 0,71; 9.1% of regioerrors), but with no detectable end group resonances. To detect the natural abundance end groups, a propene polymerization was carried out at 18 °C under 1 atm of monomer pressure for 5 min (Table 2, run 9). In addition to the three major sets of peaks due to the main-chain carbon atoms, the spectrum displays peaks attributable to carbon atoms of *n*-propyl and isobutyl end groups (see Experimental Section). These data suggest that the polymerization is prevailingly initiated by at least two consecutive 1,2-insertions into a Ti−CH_3 bond (generating the isobutyl end groups), while the main termination step is the alcoholysis of titanium-bound secondary growing chains (generating *n*-propyl end groups; see Scheme 5). Since the amount of isobutyl end groups exceeds that of *n*-propyl, some alcoholysis of titanium-bound primary growing chains also occurs in the termination step. The nature of end groups deriving from the termination step was confirmed by the same deuterium labeling technique used for catalyst **1** (see Table 2, run 10). In the case of catalyst **2**, ^{2}H NMR analysis of the obtained polypropylene (see the spectrum in Figure 3b) clearly shows the presence of CH_3CHDCH_2− end groups, as expected for deuteriolysis of a secondary polymer chain bound to Ti (Scheme 3b).

Since the end group analysis is not conclusive concerning the main regiochemistry of propagation, a copolymerization of propene with a low amount of [1-^{13}C]-ethylene was carried out as discussed above (run 13, Table 3). ^{13}C NMR analysis of the copolymer (see the spectrum in Figure 5b) showed that in this case methylene pairs outnumber the three methylene sequences (90% vs 10%). Thus, ethylene units bridge blocks of propene units with opposite regiochemistry more often than blocks of regioregularly arranged propene units (see Scheme 4), suggesting that 2,1-insertion of propene is the “normal” mode of propagation, and that 1,2-insertion becomes preferred after the insertion of an ethylene unit, which generates a metal−primary carbon bond. A similar behavior was established for closely related titanium catalysts bearing more hindered phenoxyimine ligands.

Conclusions

A new perfluorinated bis(phenoxyimine)zirconium complex has been synthesized, characterized also through X-ray diffraction analysis, and tested as precatalyst for the polymerization of propene after MAO activation, resulting in the production of prevailingly syndiotactic, low molecular weight polypropylene with high activity. The polymer microstructure is in agreement with a “chain-end” mechanism of steric control. The regiochemistry of monomer insertion in the initiation, termination and propagation steps has been investigated by end group analysis, deuterium labeling techniques and NMR analysis of a copolymer of propene with trace amounts of [1-^{13}C]-ethylene, indicating a prevailing primary insertion mode in both initiation and propagation. A titanium complex bearing the same phenoxyimine ligands has been also synthesized and tested, resulting in the production of a polypropylene having a very similar structure, according to recent literature data.[23] However, a similar investigation of the regiochemistry has shown that propagation prevailingly occurs via secondary insertion of propene, as previously observed for related bis(phenoxyimine) titanium catalysts.[9b,11,12]

In conclusion, zirconium and titanium complexes bearing the same ligands afford prevailingly syndiotactic polypropylenes having very similar structures, but via opposite regiochemistries, implicating that the nature of the metal plays a significant role in determining the preferred regiochemistry, independent of the ligand environment. This rather unusual finding is in qualitative agreement with a recent theoretical study[13b] on the regiochemistry involved in propene polymerization promoted by octahedral catalysts of this class. In fact, calculations indicated that, independently of the nature of the growing chain, primary propene insertion with Zr-based systems is more favored (or less disfavored in the case of insertion on a secondary growing chain) by roughly 1 kcal/mol relative to the analogous Ti-based system. The different regiochemistry of propagation could also account for the lower molecular weights of polymers obtained by zirconium catalysts with respect to titanium analogues, if one consider that chain transfer to Al is easier for a metal−primary growing chain. As to the mechanism of steric control, the model proposed by Guerra and Cavallo for highly syndiospecific bis(phenoxyimine) titanium catalysts, involving inversion of the chirality of the octahedral catalytic site at each insertion step, driven by the configuration of the last unit of the growing chain, implicates a 2,1-regiochemistry.[13a] The same authors proposed a different "unified mechanism of chain-end stereocontrol" for polymerization of propene occurring via primary insertion.[24] Accordingly, one could hypothesize that the mechanism of the (weak) syndiospecific steric control observed for the zirconium catalyst reported here is of the type involved in the latter case.

Experimental Section

General Information. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. Toluene was refluxed over sodium−benzophenone and distilled under a nitrogen atmosphere before use. Methylaluminoxane (MAO, Aldrich) was purchased as a 10 wt % solution in toluene and used as received. Polymerization grade propylene (SON, 99%) was used without further purification.

Synthesis of the Ligand and of the Complexes. To a stirred solution of 2,3,4,5,6-pentafluoroaniline (3.36 g; 18 mmol) and 3-methyl-2-hydroxybenzaldeyde (2.23 mL; 18 mmol) in anhydrous toluene (40 mL) under nitrogen was added *p*-toluenesulfonic acid (7.2 mg). The resulting mixture was stirred at reflux temperature for 12 h. Removal of solvent under vacuum gave a yellow crystalline solid which was crystallized in methanol, the resulting crystals were washed with the same solvent. (3.3 g; yield 60%). To a stirred solution of *N*-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroaniline (3.3 g, 10.9 mmol) in dried diethyl ether (90 mL) at −78 °C was added a 2.5 M *n*-butyllithium/*n*-hexane solution (4.4 mL, 10.9 mmol) dropwise over a 10-min period. The solution was allowed to warm to room temperature and was stirred for 2 h. The resulting solution was added dropwise to a THF (200 mL) solution of $ZrCl_4 \cdot 2THF$ (2.06 g, 5.45 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. Concentration of the reaction mixture in vacuo gave a crude yellow product. Dried CH_2Cl_2 (80 mL) was added to the crude product, and the mixture was stirred for 15 min and then filtered on Celite to remove insolubles. The filtrate was concentrated under reduced pressure, and the solid precipitated was separated from the solution and dissolved in 10 mL of methylene chloride. To the solution was then slowly added 40 mL of heptane. The solution was allowed to stand at room temperature to precipitate yellow brown crystals. The crystals were separated by filtration with a glass filter and dried in vacuo to give complex **1** (0.61 g) as a pale yellow solid in 30% yield. Single crystals of **1**, suitable for X-ray crystallography, were grown by a solvent/nonsolvent crystallization (methylene chloride/hexane solution of complex).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.03 (s, 6H, Me), 7.00 (t, J = 7.0 Hz, 2H, aromatic-H), 7.32 (d, J = 7.0, 2H, aromatic-H), 7.52 (d, J = 7.0, 2H, aromatic-H), 8.32 (s, 2H, CH═N). ^{13}C NMR (CD_2Cl_2, 100.6 MHz): δ 176.79, 171.73, 159.95, 140.39, 134.66, 128.64, 121.76, 15.09.

Complex **2** was synthesized as reported in the literature.[23]

X-ray Analysis. A suitable crystal of **1** ($0.5 \times 0.4 \times 0.2$ mm) was selected and mounted in Lindemann capillaries under inert atmosphere. Diffraction data were measured at room temperature with a Rigaku AFC7S diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Data reduction was performed with the crystallographic package TEXSAN.[25]

An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.30 to 1.00. No decay correction was applied.

The structures were solved by direct methods using the program SIR97[26] and refined by means of full-matrix least-squares based on F^2 using the program SHELXL97.[27]

All non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically and their positions refined using a riding model.

A total of 406 refinable parameters were finally considered. Maximum and minimum residual density were respectively +0.42 and −0.44 e Å^{-3}, final disagreement indices: $R = 0.039$ for 4166 reflections with $F > 4\sigma_F$, $_wR_2$ = 0.0734 for 8532 reflections.

The program ORTEP32 has been used for crystal structure drawing.[28]

Crystallographic Data. Formula: $ZrCl_2F_{10}N_2O_2C_{28}H_{14}$. FW = 762.53. system: monoclinic, space group $P2_1/c$, $Z = 4$, a = 13.1003(3) Å, b = 16.2060(3) Å, c = 14.7373 (2) Å, β = 110.65(15)°, V = 2927.7(9) Å^3, D_x = 1.73 g cm^{-3}, μ_{calcd} = 0.65 mm^{-1}.

Polymerization Procedure. Polymerizations were performed in a glass reactor (100 cm^3) equipped with a mechanical stirrer and a temperature probe. The reaction vessel was first conditioned under dynamic vacuum at the desired temperature and then charged by adding sequentially toluene solutions of the cocatalyst and the precatalyst. The mixture, thermostated to the required polymerization temperature, was stirred, and then the propene gas feed was started. After the prescribed time the reaction vessel was vented and the polymerization mixture was poured into acidified ethanol. The precipitated polymer was recovered by filtration, dried (80 °C, vacuum oven, overnight) and weighed.

Copolymerization Procedure. Copolymerizations of propene with [1-^{13}C]-ethylene were performed by introducing anhydrous toluene and MAO into a stirred reactor, which was thermostated at the desired polymerization temperature and saturated with propene. The precatalyst was dissolved in 10 mL of toluene and introduced into the reactor using a syringe. During the polymerization, the pressure was kept constant by continuously feeding the reactor with a gas mixture of propene

(99.6 mol %) and ethylene-[1-^{13}C] (0.4 mol %). The polymerization was stopped by the addition of methanol acidified with HCl and the copolymer isolated according to the usual procedure.

Characterization. ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$, TCDE) and referenced vs hexamethyldisiloxane (HMDS) at 100 °C. The polymer samples were dissolved in TCDE in a 5 mm o.d. tube.

^{13}C NMR spectrum of sample 7 displays peaks at δ 20.5−21.8, 23.7, 46.1, and 46.2 ppm attributable to the methyl, methine, and methylene carbons, respectively, of the isobutyl end groups and peaks at δ 12.4, 28.4, and 38.5 ppm attributable to the methyl, methine and methylene carbons, respectively, of the *n*-propyl end groups, according to the literature data.[17b,29] (end group: *n*-propyl $\approx$ 33%; isobutyl $\approx$ 67%).

The molecular weight distributions of the polymers were analyzed with a PSS SDV gel permeation chromatograph (GPC) containing three divinylbenzene gel columns (100, 10^4, and 10^6 Å pore size), a WGE refraction index detector using $CHCl_3$ as eluent at 25 °C, a flow rate of 1 mL/min, and standard polystyrene samples for calibration.

Acknowledgment. We thank Professors Adolfo Zambelli, Gaetano Guerra, and Luigi Cavallo for valuable discussions. We also thank Ennio Comunale (Dipartimento di Ingegneria Chimica e Alimentare) for the GPC measurements. This work was supported by the Italian Ministry of Education (MIUR), PRIN 2002.

Supporting Information Available: Diffraction data in cif format of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035120G