



# Polymerization of $\alpha$ -olefins promoted by zirconium complexes bearing bis(phenoxy-imine) ligands with *ortho*-phenoxy halogen substituents

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## ABSTRACT

New fluorinated bis(phenoxy-imine)zirconium complexes bearing halogen substituents in the *ortho* and *para* positions of the phenolate rings, bis[N-(3,5-dibromosalicylidene)-2,3,4,5,6-pentafluoroaniline]-Zr(IV) dichloride (**1**) and bis[N-(3,5-dichlorosalicylidene)-2,3,4,5,6-pentafluoroaniline]-Zr(IV) dichloride (**2**) have been synthesized and used as precatalysts in the polymerization of propylene and 1-hexene. Their catalytic behaviour was compared with that of the analogous fluorinated zirconium complexes bearing alkyl groups in the same positions of the phenolate rings to investigate the effects produced by the introduction of additional electron-withdrawing halogen substituents. Complexes **1** and **2** produce stereoirregular, slightly syndiotactic enriched polypropylenes showing enhanced catalytic activities and an improved primary regioselectivity. Both catalysts promote efficiently the oligomerization of 1-hexene to atactic and regioregular oligomers. Interestingly for both the studied monomers it is possible to control the molecular weights and the structures of end groups of the produced polymeric chains by an appropriate choice of the cocatalyst. Functionalization reactions of the unsaturated polymeric chains selectively produced are also reported.

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## 1. Introduction

Remarkable advances have been recently made in the field of *non*-cyclopentadienyl Group 4 complexes as homogeneous olefin polymerization catalysts. [1] The development of “post-metallocene” high-performance single-site catalysts allowed an accurate design of the polymer microstructures through a precise control not only of the stereochemistry of the polymerization, but also of the termination reactions (e.g., living polymerization) [2].

In this context extremely efficient and versatile catalysts are octahedral bis(phenoxy-imine) Group 4 complexes [3]. They displayed high activities for ethylene polymerization [4] and a versatile behaviour in the polymerization of  $\alpha$ -olefins that allowed the synthesis of polymers with distinctive architectural features [3,5].

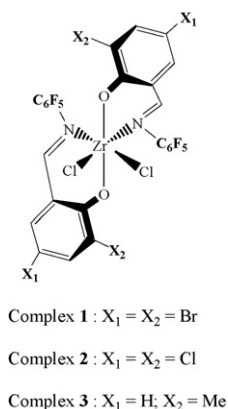
Numerous experimental studies have evidenced that the stereo- and regio-specificity of these catalysts in the polymerization of propylene are significantly affected by the ligand structure, the nature of the metal centre and of the cocatalyst. Titanium complexes bearing fluorinated N-aryl groups and bulky *ortho*-phenol substituents, despite their C<sub>2</sub>-symmetry, promote the syndiospe-

cific and *living* polymerization of propylene [6–8] via a chain end mechanism of steric control [9–11]. The stereoregularity of the polypropylenes turns from syndiotactic (*via* chain end control) to isotactic (*via* enantiomorphic site control) just introducing little structural modifications on the ligand skeleton of titanium complexes, such as phenyl groups on the carbon atoms of the imine moieties [12] or halogen atoms on the phenolate rings [13]. Moreover, zirconium and titanium complexes bearing the same ligands afforded prevalently syndiotactic polypropylenes having very similar structures, but *via* opposite regiochemistries [14].

Several reports revealed that a fundamental role in the catalytic behaviour of the phenoxy-imine complexes is played by the halogen atoms on the phenoxy-imine ligands. For instance, the bis-phenoxy-imine titanium complexes with perfluorophenyl substituent groups on the imine nitrogen mediate living polymerization of both ethylene and propylene allowing the synthesis of a wide array of block copolymers [3,6].

Recently we disclosed that the presence of additional halogen substituents on the phenolate rings of the ligand structure results in an inversion of the stereospecificity of the corresponding titanium catalyst [13]. Herein we report the synthesis of the related fluorinated bis(phenoxy-imine)zirconium complexes (complexes **1** and **2**, Scheme 1) bearing halogen substituents on the phenolate rings. The reactivity of these complexes in the polymerization of propylene and 1-hexene by using different cocatalysts is also

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**Scheme 1.** Schematic representation of catalysts 1–3.

reported and compared with the reactivity of the fluorinated bis(phenoxy-imine)zirconium complex **3**, carrying methyl groups in the *ortho* positions of the phenolate rings. The polymerization data revealed that the introduction of additional halogen substituents in the ligand structure has beneficial effects on the catalytic activity and on the regioselectivity of the catalyst. More interestingly, an appropriate choice of the cocatalyst allowed the control of the termination reactions and consequently of the molecular weights and of the structures of the chain end groups of the produced polymers. A study concerning the functionalization of selectively produced unsaturated polymeric chains is also reported.

## 2. Experimental

### 2.1. General remarks

All manipulations of air- and/or water-sensitive compounds were carried out under a dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. All solvents, purchased from Carlo Erba, were refluxed over sodium-benzophenone and distilled under a nitrogen atmosphere before use. Dichloromethane and dichloromethane- $d_2$  were distilled over calcium hydride and under a nitrogen atmosphere before use. 3,5-Dibromo-2-hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde (Lancaster products), 2,3,4,5,6-pentafluoroaniline,  $\text{ZrCl}_4 \cdot 2\text{THF}$ ,  $\text{Al}(i\text{Bu})_3$  (Aldrich products) and  $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  (Boulder SPA Company product) were used as received. Methylaluminoxane (MAO, Euricen) was purchased as a 10 wt.% solution in toluene. A sample of commercial MAO solution was dried by distilling off the solvent and excess of trimethylaluminum, providing a solid white powder (MAO\*).

Polymerization grade propylene (SON, 99%) was used without further purification.

1-Hexene (Aldrich product) was distilled over calcium hydride under a nitrogen atmosphere before use.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance spectrometer at 400 MHz and 100.6 MHz, respectively. Chemical shift ( $\delta$  in ppm) are referenced vs. tetramethylsilane (TMS).  $^{13}\text{C}$  NMR polymer spectra were recorded in 1,1,2,2-tetrachloroethane- $d_2$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , TCDE at 100 °C) and referenced vs. hexamethyldisiloxane (HMDS).

Molecular weights ( $M_n$  and  $M_w$ ) and polydispersities ( $M_w/M_n$ ) of polypropylenes were determined by high-temperature gel permeation chromatography (GPC) using PL-GPC210 with PL-Gel Mixed A Columns, a RALLS detector (Precision Detector, PD2040 at 800 nm), a H502 viscometer (Viscotek), a refractive detector

and a DM400 data manager. The measurements were recorded at 150 °C using 1,2,4-trichlorobenzene as solvent and narrow molecular weight distribution polystyrene standards as reference. Other high-temperature GPC measurements were performed on Waters GPC-V200 RI detector at 135 °C using 1,2-dichlorobenzene as solvent and Styragel columns (range  $10^7$ – $10^3$ ).

The molecular weights and the molar mass distribution of poly-1-hexene samples were measured by GPC at 30 °C, using chloroform as solvent, flow rate of eluant 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000–1,000,000 Å). Every value was the average of two independent measurements.

Polymer melting points ( $T_m$ ) were measured by differential scanning calorimetry (DSC) using a DSC 2920 TA instrument in nitrogen flow with a heating and cooling rate of 10 °C  $\text{min}^{-1}$ . Melting temperatures were reported for the second heating cycle.

### 2.2. Synthesis

#### 2.2.1. Synthesis of the ligands and of the complexes

Ligands **1** and **2** were synthesized as described in the literature [13].

**Complex 1.** To a stirred solution of *N*-(3,5-dibromosalicylidene)-2,3,4,5,6-pentafluoroaniline (3.3 g, 7.4 mmol) in anhydrous diethyl ether (60 mL) at  $-78$  °C was added a 2.5 M *n*-butyllithium/*n*-hexane solution (3.0 mL, 7.4 mmol) dropwise over a 10-min period. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise to a THF (135 mL) solution of  $\text{ZrCl}_4 \cdot 2\text{THF}$  (1.40 g, 3.7 mmol) at  $-78$  °C. The mixture was allowed to warm to room temperature and stirred for 15 h. Concentration of the reaction mixture under reduced pressure gave a crude yellow product. Anhydrous  $\text{CH}_2\text{Cl}_2$  (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 at 25 mL. Then 35 mL of hexane were slowly added to the solution, yellow brown crystals precipitated at room temperature. The crystals were separated by filtration with a glass filter, washed with hexane and dried in vacuo to give complex **1** (1.214 g) as a yellow solid in 31% yield.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz):  $\delta$  7.57 (d,  $J = 7.0$  Hz, 2H, aromatic-H), 7.98 (d,  $J = 7.0$  Hz, 2H, aromatic-H), 8.29 (s, 2H, N=CH).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100.6 MHz):  $\delta$  175.36 (N=CH), 143.30, 139.73, 137.44, 134.61, 123.06, 112.89.

Anal. found (calcd.) for  $\text{C}_{26}\text{H}_6\text{Br}_4\text{Cl}_2\text{F}_{10}\text{N}_2\text{O}_2\text{Zr}$  (%): C, 29.61 (29.74); H, 0.43 (0.58); N, 2.53 (2.67).

**Complex 2** was synthesized with the same procedure. Yield: 47%.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz):  $\delta$  7.37 (d,  $J = 7.0$  Hz, 2H, aromatic-H), 7.70 (d,  $J = 7.0$  Hz, 2H, aromatic-H), 8.33 (s, 2H, N=CH).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100.6 MHz):  $\delta$  175.10 (N=CH), 137.92 (C–O), 133.51, 126.26, 125.52, 122.84.

Anal. found (calcd.) for  $\text{C}_{26}\text{H}_6\text{Cl}_6\text{F}_{10}\text{N}_2\text{O}_2\text{Zr}$  (%): C, 35.68 (35.80); H, 0.78 (0.69); N, 3.15 (3.21).

#### 2.2.2. Polymerization procedure

Propylene polymerizations were performed in a glass reactor (100 mL) equipped with a mechanical stirrer and a temperature probe. The reaction vessel was charged under nitrogen sequentially with toluene, MAO or the proper cocatalyst mixture. The mixture, thermostated at the required polymerization temperature, was stirred, the propylene gas feed was started and then toluene solution of the precatalyst was added. After the prescribed time the reaction vessel was vented and the polymerization mixture was poured into acidified methanol. The precipitated polymer

was recovered by filtration, dried (80 °C, vacuum oven, overnight) and weighed.

1-Hexene polymerizations were carried out by charging the reaction vessels sequentially with toluene, the opportune volume of 1-hexene, MAO or the proper cocatalyst mixture and a toluene solution of the precatalyst. Then the same procedure used for the propylene was followed.

Ethylene/1-hexene copolymerizations were performed using the same type of equipment as the propylene polymerization described above. A solution of the opportune volume of toluene and MAO was prepared and kept at 25 °C, than the ethylene gas feed was started and 1-hexene was introduced into the reactor and stirred under an ethylene atmosphere for 30 min. Then a 5 mM complex solution in anhydrous toluene (3 mL) was added to the solution. After 5 min, the reaction vessel was vented and the polymerization mixture was poured into acidified methanol. The polymer was collected by filtration, washed with methanol, and then dried *in vacuo* at 80 °C overnight.

### 2.2.3. Functionalization procedure

**Hydroboration of poly(1-hexene).** 3.1 g of polymer (run 9, Table 2) were dissolved in 30 mL of dry toluene in an inert atmosphere. The solution was warmed up at 70 °C, and 9-borabicyclo[3.3.1]nonane (9-BBN) (0.387 g, 2.1 equiv. to the olefinic double bonds) in 20 mL of dry tetrahydrofuran was added. The mixture was stirred at 70 °C for 24 h. The solution was cooled to 40 °C, and NaOH (5.67 g) and a 30% H<sub>2</sub>O<sub>2</sub> aqueous solution (4.3 mL) were slowly added. The resultant mixture was stirred for additional 24 h at 40 °C, then poured into methanol (100 mL). The polymer was collected, washed with methanol (3 × 150 mL), and then dried *in vacuo*. In the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 25 °C), besides the main resonances attributable to the polymer main chain, minor resonances at 3.55 and 3.66 ppm (–CHOH– and –CH<sub>2</sub>OH) were detected, attributable to hydroxyl-functionalized chain ends groups.

**Hydroboration of polypropylene.** Reaction was performed as above but using 3.0 g of atactic polypropylene (run 4, Table 1), 99 mg of 9-BBN, 1.45 g of NaOH and 1.1 mL of 30% H<sub>2</sub>O<sub>2</sub> aqueous solution. The polymer was collected, washed with methanol (3 × 150 mL), and then dried *in vacuo*. In the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 25 °C), besides to the main resonances attributable to the polymer main chain, minor resonances at 3.39 and 3.51 ppm (–CH<sub>2</sub>OH) were detected, attributable to hydroxyl-functionalized chain ends groups. In the <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100.6 MHz) the diagnostic signal appears at 65.5 ppm (–CH<sub>2</sub>OH).

## 3. Results and discussion

### 3.1. Synthesis of complexes

Ligands **L1–L3** were synthesized as previously reported [13,14].

Complexes **1–3** (Scheme 1) were prepared, according to literature procedures [15], by reaction of 2 equiv. of the ligand lithium salt with ZrCl<sub>4</sub>·2THF in tetrahydrofuran.

For all complexes <sup>1</sup>H and <sup>13</sup>C NMR spectra showed the presence of a single isomer in dichloromethane-*d*<sub>2</sub> solution at room temperature. In agreement with the observed structures of previously reported analogous zirconium complexes and on the basis of NMR data it is reasonable to assume a C<sub>2</sub>-symmetry for these complexes.

### 3.2. Polymerization of propylene

Catalysts **1–3** were tested in the polymerization of propylene in combination with different cocatalysts. Perusal of the literature data disclosed that the used cocatalyst can have an influence on the polymerization performances of the bis(phenoxyimine)zirconium complexes. For instance, the production of atactic oligomers of propylene is reported for the catalyst bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride/MAO [16], while the same precatalyst with Al(<sup>*t*</sup>Bu)<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> results in the production of isotactic polypropylene [17].

The main polymerization data are summarized in Table 1.

Polymerization of propylene with complex **1** using MAO\* as cocatalyst was carried out under atmospheric pressure at room temperature for 1 h (run 1, Table 1).

The <sup>13</sup>C NMR analysis of the obtained polypropylene showed that it is a stereoirregular, slightly syndiotactic enriched ([mm] = 13%, [mr] = 51%, [rr] = 36%) polymer with a small amount of regioirregularly arranged monomer units (<1%) 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) [18].

In addition to the resonances due to the main chain carbon atoms, the spectrum displayed two peaks in the unsaturated region (at δ 142.9 and 109.3 ppm) and a signal at δ 20.5 ppm attributable, according to the literature data [19] to vinylidene end groups (see Scheme 2). The <sup>1</sup>H NMR analysis of the sample confirmed this attribution [20]. Additional resonances in the <sup>13</sup>C NMR spectrum, approximately of same intensity, attributable to *n*-propyl end groups were also detected (see Scheme 2) [21]. The presence of an equal amount of saturated (*n*-propyl) and unsaturated (vinylidene) chain ends groups is easily explained hypothesizing terminations steps which occur prevalingly by β-hydrogen elimination from primary growing chains and initiation steps by primary insertion of propylene on the Zr–H bonds (Scheme 2).

The high regioregularity of the polypropylene chains suggests, consequently, a primary regiochemistry as main propagation mode.

Similar results were obtained with the catalytic system **2**/MAO\* (run 5, Table 1): the produced polypropylene was a highly regioregular atactic polymer with a pairwise presence of *n*-propyl and vinylidene end groups.

**Table 1**

Propylene polymerization conditions and results

Run <sup>a</sup>	Catalyst	Cocatalyst	Toluene (mL)	Time (h)	Yield (g)	Activity <sup>b</sup>	[rr] (%)	Mw (×10 <sup>3</sup> )	PDI
1	<b>1</b>	MAO*	40	1	7.8	312	36	22.0	1.6
2	<b>1</b>	MAO	40	2	5.0	100	39	14.6	1.7
3 <sup>c</sup>	<b>1</b>	Al( <sup><i>t</i></sup> Bu) <sub>3</sub> /Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	40	1	0.9	36	39	74.8	13
4	<b>1</b>	MAO*	80	0.5	5.1	408	38	21.4	1.7
5	<b>2</b>	MAO*	80	0.5	7.0	466	31	18.1	1.6
6	<b>3</b>	MAO	40	2	4.9	98	45	8.3	2.3
7	<b>3</b>	MAO*	40	2	6.4	128	44	18.2	3.2
8 <sup>c</sup>	<b>3</b>	Al( <sup><i>t</i></sup> Bu) <sub>3</sub> /Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	40	2	0.3	6	28	14.4	3.4

<sup>a</sup> General conditions: precatalyst = 25 μmol; cocatalyst: MAO = 7.25 mmol; [Al]/[Zr] = 150; propylene pressure = 1 atm; T = 18 °C.

<sup>b</sup> Activity = kg-polymer/(mol Zr atm h).

<sup>c</sup> [B]/[Zr] = 2; [Al]/[Zr] = 50.

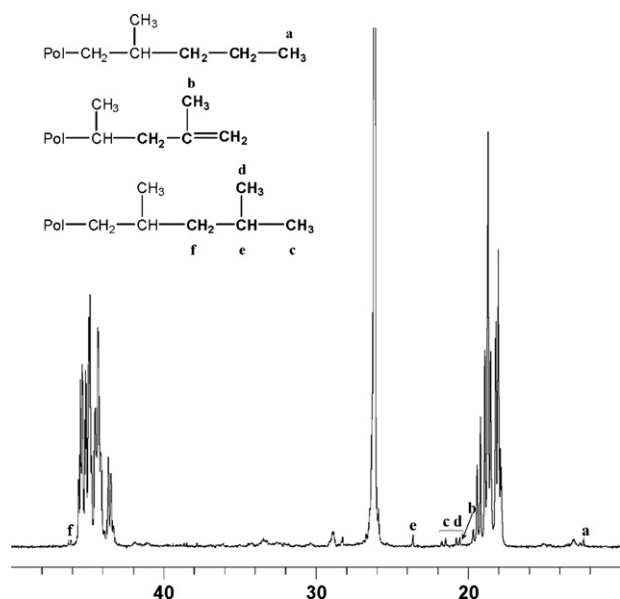


Fig. 1. Aliphatic region of the  $^{13}\text{C}$  NMR spectrum ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100^\circ\text{C}$ ) of polypropylene (run 2, Table 1).  $\delta$  in ppm from hexamethyldisiloxane.

The comparison between the polymerization results obtained with **1** and **2** (see runs 1, 4 and 5, Table 1) and those obtained with an analogous phenoxy-imine catalyst bearing methyl substituents on the phenol rings (complex **3**, run 7, Table 1) provided evidence that the introduction of halogen substituents on the ligand skeleton has beneficial effects on the catalytic activity and on the regioselectivity of the catalytic systems (% of vicinal methyl: <1% run 1 and 3.5% run 7, respectively). In particular, the higher propensity of catalysts **1** and **2** to polymerize propylene with primary regiochemistry has important consequences on the structures of the chain end groups. In fact the polymers produced with bis(phenoxy-imine)zirconium complexes with *ortho*-phenol alkyl substituents show a mixture of different unsaturated end groups formed mostly by a  $\beta$ -H hydrogen transfers following misleading 2,1 insertions (>90%) [16]. Differently, as a consequence of the increased regioselectivity, catalysts **1** and **2** exclusively produce vinyl-terminated low-molecular weight atactic polypropylenes which are interesting precursors for the synthesis of the terminally functionalized polypropylenes.

We also investigated the effect of the use of different cocatalysts on the selective production of unsaturated PPs. Thus, a polymerization run was performed by using complex **1** and a commercial

MAO solution as cocatalyst (run 2, Table 1). The polypropylene obtained under these conditions showed an analogous microstructure (in terms of composition of the methyl triads and percentage of regioinversions) but lower molecular weights (Fig. 1).

The decrease of the molecular weights is imputable to the fact that, in addition to the already discussed termination reactions occurring by  $\beta$ -H transfer (described in Scheme 2), further termination reactions occur by chain transfer to  $\text{Al}(\text{CH}_3)_3$  that is present in the commercial MAO solution.

From the areas of the resonances of the end group carbons (*n*-propyl vs. isobutyl) and considering that the isobutyl end groups are formed both in the initiation and in the termination steps (see Scheme 3) it is possible to conclude that when commercial MAO solution is used as cocatalysts the polymeric chains are terminated preferentially (~70%) by chain transfer to  $\text{Al}(\text{CH}_3)_3$ .

The effects of the use of  $\text{Al}(\textit{i}\text{Bu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  as cocatalyst on the catalytic performances of complexes **1** and **3** have been also investigated (see runs 3 and 8, Table 1).

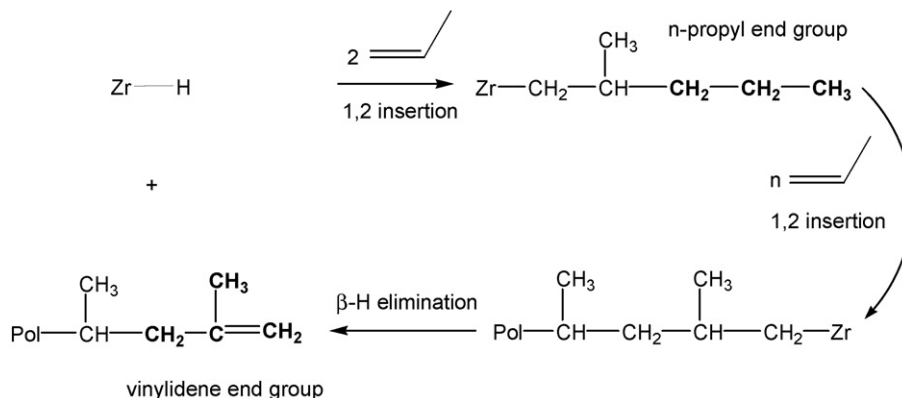
The polypropylene sample obtained with complex **1** activated with  $\text{Al}(\textit{i}\text{Bu})_3$  and  $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  (run 3, Table 1) showed the exclusive formation of vinyl-terminated chains but having substantially the same microstructure of the polymers produced with MAO. In addition GPC analysis showed higher molecular weights than those obtained with MAO\* as cocatalyst, high value of the PDI and a bimodal distribution of the polymers molecular weights, thus suggesting that more than one catalytically active species are formed in the polymerization process. Analogous results were obtained by using complex **3** activated by  $\text{Al}(\textit{i}\text{Bu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  (run 8, Table 1).

In order to verify if a structural modification of the ligand occurred during the polymerization, a mixture of **1** and  $\text{Al}(\textit{i}\text{Bu})_3$  was hydrolyzed. The NMR analysis of the organic extracts revealed that the phenoxy-amine species, deriving by the reduction *in situ* of the imine functionality, was the most abundant component.

Previous literature data showed that when the alkylaluminum reduces the imine moiety of the bis(phenoxy-imine)zirconium dichloride complexes to amine-donor, an inversion of the catalyst stereoselectivity is observed [7,22].

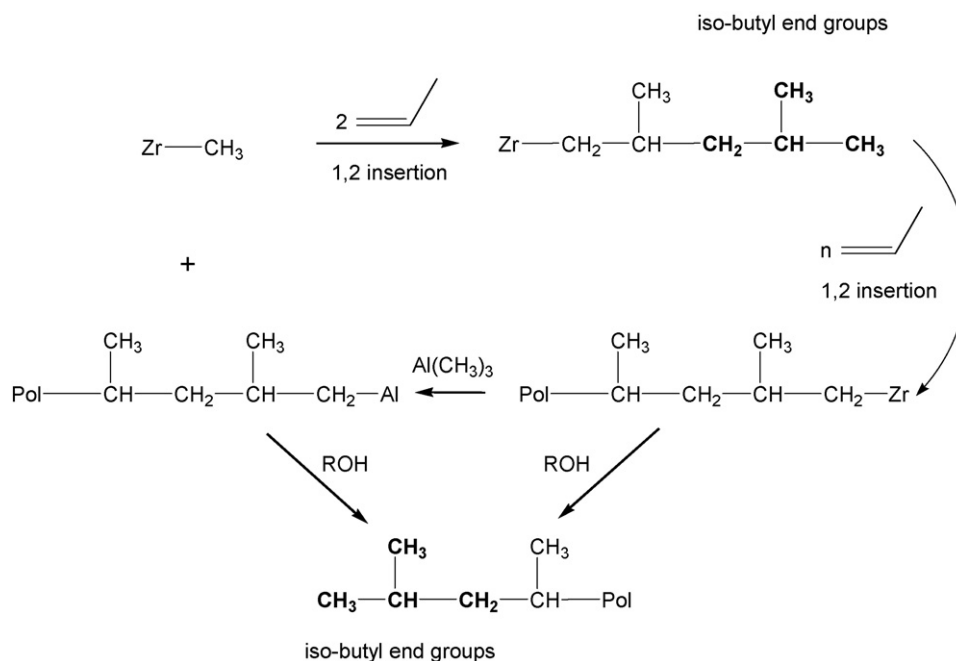
Nevertheless in our case the similarity of the microstructures of the polypropylenes obtained by **1**/MAO\* and **1**/ $\text{Al}(\textit{i}\text{Bu})_3$ / $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ , suggests an analogous behaviour of the phenoxy-amine catalytic specie and of the related imine catalyst.

In conclusion the presence of halogen substituents in different positions of the ligands in bis(phenoxy-imine) zirconium complexes induces an increase of the catalytic activity possibly due to a more electrophilic character of the metal centre, reasonably deriving from the electron-withdrawing properties of halogen atoms, and an improvement of the regioselectivity of the active species.



Scheme 2. Mechanisms for initiation and termination in the polymerization of propylene by the catalytic systems **1**/MAO\* and **1**/ $\text{Al}(\textit{i}\text{Bu})_3$ / $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ .





**Scheme 3.** Mechanisms for initiation and termination in the polymerization of propylene by the catalytic system **1**/MAO.

In addition, by an appropriate choice of the cocatalyst, it is possible to control the termination phenomena producing end groups with defined structures. The interesting aspect is that these complexes, activated by MAO\* or Al(*i*Bu)<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, revealed to be very active catalysts for the selective production, at room temperature, of the vinyl-terminated PPs which are potential precursors for chain-end functionalized PPs [23].

### 3.3. Polymerization of 1-hexene

The high activity observed in the polymerization of propylene induced us to investigate the catalytic behaviour of these complexes in the polymerization of higher olefins. Literature data [24] concerning higher  $\alpha$ -olefin polymerization promoted by phenoxy-imine catalysts are quite scanty. Interesting results were recently reported regarding a fluorinated phenoxy-imine titanium complex which, in combination with Al(*i*Bu)<sub>3</sub>/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, and in *n*-heptane solution, afforded high-molecular weight poly(1-hexene) with highly stereo- and regio-irregular structure [ultra-random poly(1-hexene)] [25]. Differently, when activation of the same pre-catalyst is performed with MAO and when toluene is used as solvent the catalytic system revealed to be inactive.

Herein we report some results regarding polymerization of 1-hexene with **1** and **2** and a detailed analysis of the structure of the chain end groups of the produced polymers.

The <sup>13</sup>C NMR analysis of the poly(1-hexene) obtained by **1**/MAO\* (run 9, Table 2) clearly revealed a stereoirregular polymer with a

very small amount (~2%) of regiomistakes calculated by the resonances of the characteristic signals in the regions 30.3–31.9 and 35.4–36.7 ppm [25] (Fig. 2).

The <sup>1</sup>H NMR analysis (see Fig. 3) of the chain end groups reveals the presence of two different type of unsaturated end groups [26]: vinylidene ( $\delta$  4.68 and 4.76 ppm) and vinylene end groups ( $\delta$  5.3 ppm) in 1/10 ratio deriving, respectively, from termination reactions after 1,2 and 2,1 insertions as shown in Scheme 4.

The <sup>13</sup>C NMR spectrum showed, in addition to the signals of the carbons of the main chains, resonances of minor intensity assigned to the saturated end groups formed in the initiation steps by at least two consecutive 1,2 insertion on the Zr–H bond (type A Scheme 4). Additional resonances of low intensity (1/10 than that of the type A) corresponding to saturated end groups of type B (Scheme 5) were also detected.

The molecular weights (M<sub>n</sub>) calculated from the <sup>13</sup>C NMR spectrum furnished a result (3.8 kDa) which is in good agreement with the value measured by GPC (4.1 kDa). Considering that the end groups of type B (see Scheme 5) are formed both in the initiation steps (from, at least, two consecutive primary insertions on Zr–CH<sub>3</sub> bonds) and in the termination steps (from hydrolysis of Zr- or Al-bound primary growing chain) it is possible to conclude that most polymeric chains (>95%) are terminated by  $\beta$ -hydrogen elimination and that the termination reactions by chain transfer to aluminium are sporadic phenomena.

This whole picture suggests that the following sequence of events occurs: the polymerization of 1-hexene with **1**/MAO is

**Table 2**  
1-Hexene polymerization conditions and results

Run <sup>a</sup>	Catalyst	Cocatalyst	Toluene (mL)	Time (min)	Monomer (mL)	Yield (g)	M <sub>w</sub> ( $\times 10^3$ )	PDI
9	<b>1</b>	MAO*	5	60	5	6.3	6.5	1.6
10	<b>1</b>	MAO	–	60	15	9.1	3.6	1.7
11	<b>1</b>	MAO	2	5	15	7.7	7.0	1.4
12	<b>1</b> <sup>b</sup>	Al( <i>i</i> Bu) <sub>3</sub> /Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	12	60	15	5.3	12.1	1.5
13	<b>2</b>	MAO*	2	5	15	8.0	7.1	1.4

<sup>a</sup> General conditions: precatalyst = 15  $\mu$ mol; cocatalyst: MAO = 7.5 mmol; [Al]/[Zr] = 500; T = 18 °C.

<sup>b</sup> [B]/[Zr] = 2; [Al]/[Zr] = 50.

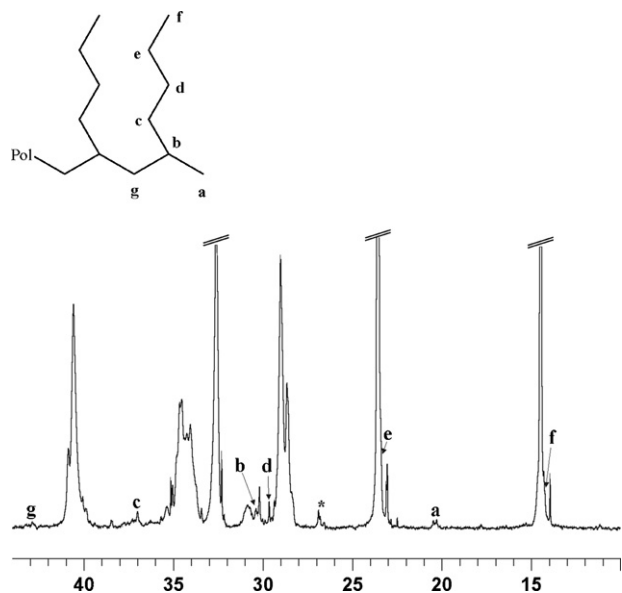


Fig. 2. Aliphatic region of the  $^{13}\text{C}$  NMR spectrum ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100^\circ\text{C}$ ) of poly(1-hexene) (run 9, Table 2).  $\delta$  in ppm from hexamethyldisiloxane.

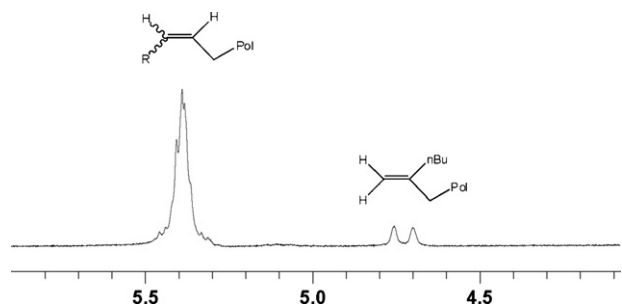


Fig. 3.  $^1\text{H}$  NMR spectrum ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100^\circ\text{C}$ ) of poly(1-hexene) (run 9, Table 2).  $\delta$  in ppm from hexamethyldisiloxane.

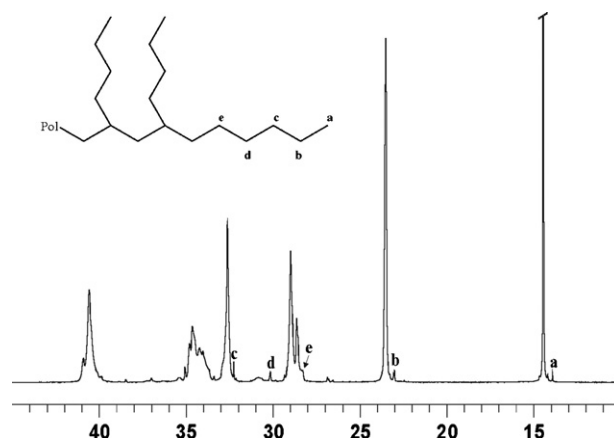


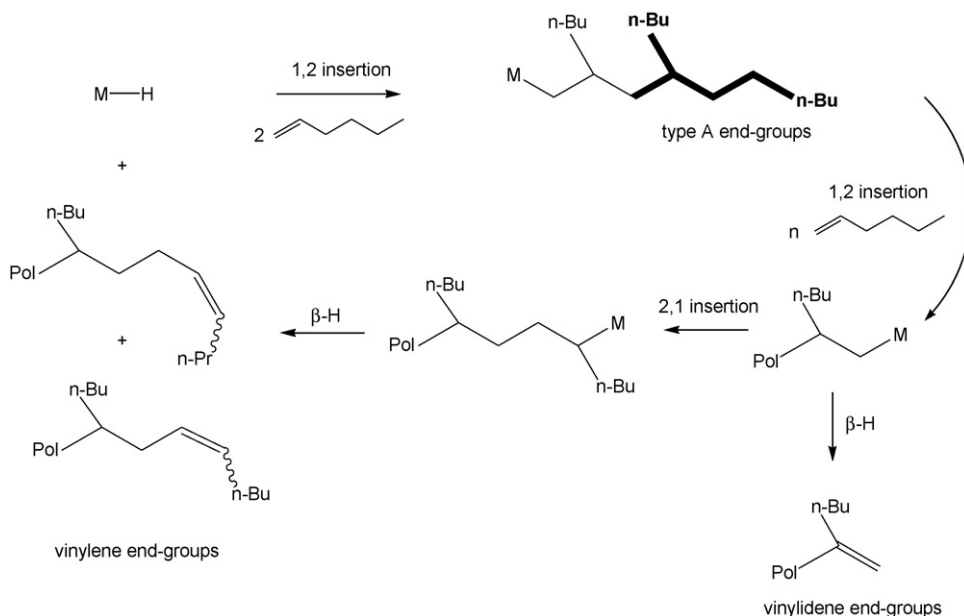
Fig. 4. Aliphatic region of the  $^{13}\text{C}$  NMR spectrum ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100^\circ\text{C}$ ) of poly(1-hexene) (run 12, Table 2).  $\delta$  in ppm from hexamethyldisiloxane.

initiated almost exclusively by 1,2 insertion of the monomer on a Zr–H bond and is terminated by a  $\beta$ -hydrogen transfer mostly following a 2,1 insertion (90%); in fact the predominant formation of vinylene end groups indicates that the chain propagation becomes sluggish after a secondary insertion resulting in a chain release by a  $\beta$ -H transfer (see Scheme 4).

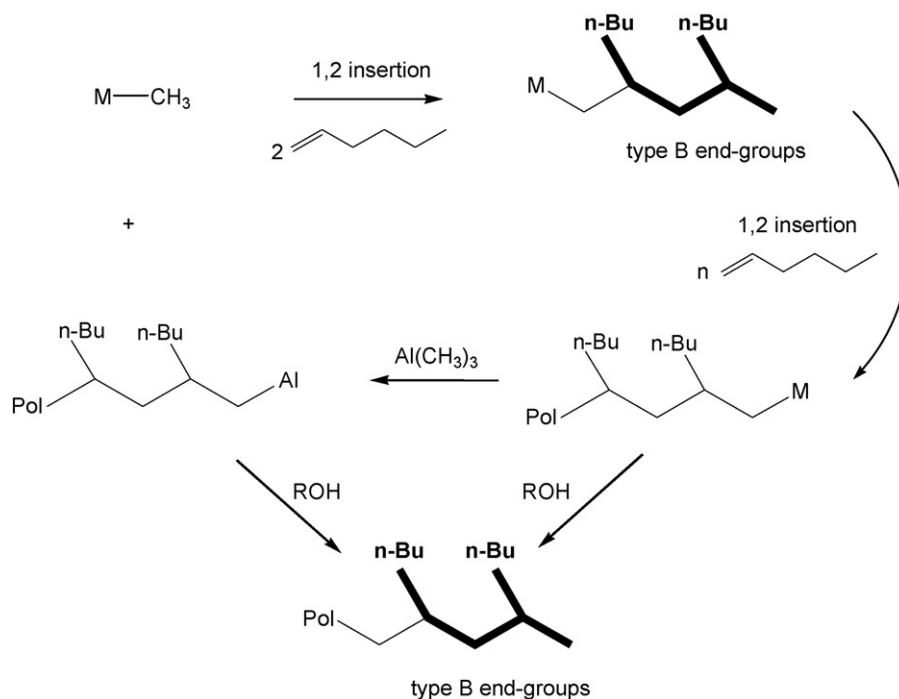
The identification of the structures of the end groups generated in the initiation steps (type A and type B both derived by primary insertion of the monomer) and the regioregularity of the main chain indicate a prevailing primary regiochemistry of monomer insertion during the propagation of the polymeric chain.

To direct the polymerization process toward the production of polymeric chains containing exclusively unsaturated end groups we employed  $\text{Al}(\text{i-Bu})_3$  as alkylating agent.

As already observed in the polymerization of propylene, the poly(1-hexene) produced by complex **1** in combination with  $\text{Al}(\text{i-Bu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  showed the same microstructure but slightly higher molecular weights (see Fig. 4) than the sample obtained using MAO as activator. Since, under the polymerization conditions used, the termination reactions occurred exclusively by  $\beta$ -H transfer, all the polymeric chains had unsaturated end groups,



Scheme 4. Mechanisms for initiation and termination in the polymerization of 1-hexene by the catalytic system **1**/MAO\* and **1**/ $\text{Al}(\text{i-Bu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ .



**Scheme 5.** Mechanisms for initiation and termination in the polymerization of 1-hexene by the catalytic system 1/MAO.

as confirmed by the excellent agreement between the polymer molecular weight calculated by NMR spectra (8400) and the measured value by GPC (8200).

As expected, increasing the amount of Al(CH<sub>3</sub>)<sub>3</sub> in the cocatalytic system, for example using a commercial solution of MAO, a significant reduction of the molecular weights of the polymers was observed (run 11, Table 2). The analysis of the saturated end groups in the <sup>13</sup>C NMR spectrum revealed an inverted ratio between the type A and the type B structures (B/A = 4:1).

### 3.4. Ethylene 1-hexene copolymerization

To gain further insight into the reactivity of phenoxy-imine zirconium complexes bearing halogen substituents on olefin polymerization, the ethylene/1-hexene copolymerization behaviour of complex 2 was investigated. The results of these copolymerizations are reported in Table 3.

Analysis of the copolymers was carried out by <sup>13</sup>C NMR in TCDE at high temperature (100 °C), the microstructure was assessed following previous work reported by Hsieh and Randall [27]. The copolymer compositions and triad distributions [27] are reported in Table 4.

An ethylene/1-hexene copolymerization was performed with a monomer feed ratio  $X_e/X_h = 0.14$  and at 1 atm of ethylene (run 14). The obtained copolymer showed a monomodal molecular

**Table 4**  
<sup>13</sup>C NMR characterization of ethylene/1-hexene copolymers

Run	Triad distributions <sup>a</sup>					
	[HHH]	[EHH] + [HHE]	[EHE]	[HEH]	[EEH] + [HEE]	[EEE]
16	0.006	0.002	0.048	0.012	0.037	0.895
17	0.008	0.023	0.085	0.035	0.121	0.766

<sup>a</sup> Triads do not sum 1.00 for all entries. This reflects the experimental error in the calculation of triads from <sup>13</sup>C{<sup>1</sup>H} NMR.

weight distribution (Mw/Mn = 2.4), but it was compositionally heterogeneous and was separated into fractions containing different amounts of ethylene and 1-hexene by solvent extraction in *n*-hexane at room temperature.

The fraction of polymer insoluble in hexane (HI) accounted for 10 wt.% of the entire sample and contained ~93% of ethylene. The (HI) fraction showed a <sup>13</sup>C NMR spectrum with signals at 38.1 and 34.5 ppm attributed to the methine and methylene ( $S_{\alpha\delta^+}$ ) of the main-chain carbons, respectively, and signals at 34.1, 29.3, 23.4, and 14.3 ppm attributed to the carbon atoms in the butyl branch. In addition, the lack of any peaks at 40 ppm (indicating the absence of poly-1-hexene blocks within the copolymer) and at 24 ppm (indicative of alternating sequences of monomers) supports the idea of isolated incorporations of 1-hexene monomer unit into polyethylene chains (% *n*-butyl branches = 6.9). The hexane soluble

**Table 3**  
Ethylene/1-hexene copolymerization conditions and results

Run <sup>a</sup>	Toluene (mL)	1-Hexene (mL)	$X_e/X_h^b$	Yield (g)	Productivity <sup>c</sup>	$H_{\text{copolymer}}$ (%mol)	$T_m$	Mw ( $\times 10^3$ )	PDI
14	20.0	5.0	0.14	3.2	2560	–	–	7.4	2.4
15	24.3	0.7	1.00	1.1	960	16	107	65	2.1
16 <sup>d</sup>	24.7	0.35	2.04	0.2	320	8	114	85	2.4
17 <sup>d</sup>	20.6	1.4	0.49	0.3	480	15	94	74	2.3

<sup>a</sup> General conditions: precatalyst 2 = 15 μmol; cocatalyst: MAO\* = 7.5 mmol; [Al]/[Zr] = 500; T = 18 °C,  $P_{\text{ethylene}}$  = 1 atm, reaction time = 5 min.

<sup>b</sup> Initial monomer feed ratio:  $X_e$  = mol fraction of ethylene,  $X_h$  = mol fraction of 1-hexene.

<sup>c</sup> Productivity = kg-polymer/(mol Zr h).

<sup>d</sup> Precatalyst 2 = 7.5 μmol, MAO = 3.7 mmol; [Al]/[Zr] = 500.

(HS) fraction is a mixture formed prevalingly by poly-1-hexene and polyethylene with *n*-butyl branches.

An ethylene/1-hexene copolymerization was performed with a higher initial monomer feed ratio  $X_e/X_h = 1$  (run 15) and at 1 atm pressure of ethylene. Under these reaction conditions a homogeneous polymeric sample was obtained and the incorporation of 1-hexene into the copolymer was almost quantitative (97%). The  $^{13}\text{C}$  NMR analysis of the copolymer revealed that it appears to be formed exclusively by long chains of polyethylene with isolated units of hexene (% *n*-butyl branches = 16). No peaks indicating the presence of poly(1-hexene) blocks within the polymer and of alternating sequences of monomers were detected.

In runs 16 and 17 the ethylene/1-hexene copolymerization reactions were performed with different initial monomer feed ratios ( $X_e/X_h = 2.04$  and  $0.49$ , respectively) and started by disconnecting the ethylene feed. In both cases polyethylenes containing prevalingly *n*-butyl branches were obtained. The different concentrations of 1-hexene in the initial compositions of the reaction systems were coherently reflected in the triads distributions observed for the two copolymers.

This initial screening for the ethylene/1-hexene copolymerization shows that complex **2** exhibited high propensity for 1-hexene insertion during copolymerization. An analogous ability was observed for ethylene/propylene polymerization behaviour of bis(phenoxy-imine)Zr and Hf complexes possessing perfluorophenyl substituents [28].

### 3.5. Polymer end-groups functionalization

The inert nature of polyolefins while constitutes the strength point of these materials, at the same time represents a significant limit for their uses, particularly those in which interaction with different materials is necessary. As matter of fact, polyolefins often lack in adhesion, dyeability, paintability, printability, or compatibility with other functional polymers. Therefore functionalization of polyolefins has been a research subject for many decades. Various synthetic strategies have been reported, including the direct copolymerization of ethylene or propylene with functionalized protected monomers [29] or the postpolymerization functionalization of unsaturated polymers [30].

The presence of unsaturated chain ends of the obtained polypropylene and polyhexene samples allowed their functionalization. In order to obtain hydroxyl-terminated polymer chains, we performed a hydroboration followed by oxidative work up. In the  $^1\text{H}$  NMR spectrum of the treated polypropylene besides to the polymer chain main resonances, minor resonances at 3.39 and 3.51 ppm attributable to the hydrogen atoms of a primary alcohol ( $-\text{CH}_2\text{OH}$ ) were detected. The corresponding carbon appeared at 65.5 ppm ( $-\text{CH}_2\text{OH}$ ) in the  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 298 K). The same hydroboration reaction was performed on a poly(1-hexene) sample, which was analyzed by  $^1\text{H}$  NMR. The disappearance of the unsaturated end groups signals and the detection of minor resonances at 3.55 and 3.66 ppm attributable to secondary and primary alcohol functionalities ( $-\text{RCHOH}$  and  $-\text{CH}_2\text{OH}$ ) indicated that, also on these substrates, the reaction was successfully performed.

## 4. Conclusions

New bis(phenoxy-imine) zirconium complexes bearing halogen substituents in the *ortho* and *para* positions of the phenolate rings have been synthesized and tested as precatalysts for the polymerization of propylene and 1-hexene.

Both complexes, in combination with different cocatalytic systems ( $\text{Al}(\text{i-Bu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  or MAO), resulted in the production

of stereoirregular, slightly syndiotactic enriched, highly regioregular and low-molecular weight polypropylenes. The presence of the halogen substituents has beneficial effect on the catalytic activity of the complexes if compared with the one observed with the analogous compound **3** having alkyl substituents. This behaviour is imputable to the more electrophilic character of the metal centre derived by the electron-withdrawing properties of the halogen atoms.

End groups NMR analysis of the polypropylene samples suggests that the regiochemistry of monomer insertion in the initiation, termination and propagation steps is 1,2.

Interestingly, in combination with appropriate cocatalysts these complexes are able to produce exclusively vinyl-terminated low-molecular weights PPs with high efficiency at room temperature. Analogous results have been observed in the polymerization of 1-hexene. In this case, a detailed NMR analysis of the oligomers of 1-hexene obtained promoting specific termination reactions allowed an accurate attribution of the  $^{13}\text{C}$  NMR resonances corresponding to the carbons of the different formed end groups. In addition in the ethylene/1-hexene copolymerization the described complexes exhibited an enhanced incorporation ability for the higher olefin, offering the possibility to produce copolymers in a very large range of compositions.

The vinyl-terminated, vinylene and vinylidene-terminated polymers were successfully functionalized, demonstrating thus a further potentiality of this family of catalysts.

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