Phenoxyaldimine and Phenoxyketimine Titanium Complexes in Propene Polymerization. A Different Effect of *o*-Phenoxy Halide Substituents

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ABSTRACT: New fluorinated bis(phenoxyaldimine)- and bis(phenoxyketimine)titanium(IV) complexes bearing *o*-halide substituents on the phenolate rings were synthesized and tested as catalysts for propene polymerization. Polymerization of propene at subambient temperature in the presence of bis(*N*-(3,5-dibromosalicylidene)-2,3,4,5,6-pentafluoroaniline)titanium dichloride activated by methylaluminoxane resulted in the unexpected production of a prevailingly isotactic polypropylene. The observed microstructure is that expected for an "enantiomorphic site" mechanism of steric control. End group analysis, also using deuterium labeling techniques, indicated a primary insertion in the initiation step, while a secondary insertion was observed in the termination step. The microstructures of the homopolymer and of a copolymer of propene with trace amounts of ethylene are consistent with the presence of (shorter) highly isotactic primary blocks and (longer) poorly isotactic secondary blocks. Similar results were obtained with the bis(phenoxyaldimine) titanium complexes bearing chlorides or iodides on the ligand phenol rings. The isotacticity of the produced polypropylenes decreases as the size of the halide substituents is reduced. A new phenoxyketimine titanium complex bearing *o*-bromine substituents on the phenolate rings produced, under similar polymerization conditions, truly atactic polypropylene, at variance with the isospecific phenoxyketimine titanium complexes bearing alkyl substituents.

Introduction

Remarkable advances have been made in the last two decades in the design and synthesis of homogeneous olefin polymerization catalysts. The great versatility represented by homogeneous catalysts has been initially expressed by the group 4 metallocene complexes.[1] More recently there has been a growing interest in the development of *non*-cyclopentadienyl group 4 complexes.[2] In particular the phenoxy-based complexes represent an important and versatile class of olefin polymerization catalysts.[3] Group 4 compounds bearing two phenoxyaldimine ligands displayed extremely high activities for ethylene polymerization[4] and a versatile behavior in the polymerization of propene depending on the ligand structure and the metal nature[5] and on the polymerization conditions,[6] especially the type of cocatalyst employed.[7]

In particular, titanium complexes bearing fluorinated *N*-aryl groups and bulky *o*-phenol substituents, despite being C_2-symmetric, promote syndiospecific polymerization of propene in a living manner.[8−10] The mechanism of syndiospecific polymerization has been investigated by both experimental[9b,11,12] and theoretical techniques.[13]

The ^{13}C NMR analysis of the polypropylene microstructure revealed that a chain end mechanism of steric control is responsible for the observed syndiotacticity and that the monomer insertion is prevailingly secondary (2,1).[9b−12] Reasonably, the rather uncommon 2,1-propene insertion during propagation helps in preserving the high syndiospecific control also above room temperature. The mechanism of stereocontrol has been explained by theoretical models hypothesizing the isomerization of fluxional octahedral chiral catalytic sites induced by the insertion of the monomer.[13a]

Experimental studies have evidenced that the stereocontrol mechanism observed for phenoxyaldimine titanium catalysts is significantly affected by the ligand structure and influenced by the steric interactions between the monomer and the ancillary ligands. In particular, the substituents situated on the ortho positions of the phenolic ring[14,15] and on the nitrogen atom of the imine group[5] play a key role in determining the activity and stereoselectivity of the catalytic systems. Reducing the steric bulk of the phenolate substituents leads to a decrease of syndiospecific control, although a prevailingly syndiotactic polypropylene is obtained even with a catalyst bearing a ligand with unsubstituted phenoxy groups. A linear correlation of the size of the ortho substituents with the *rr* triad percentage is also observed.[14]

Recently Coates reported titanium complexes bearing ketimine ligands containing *N*-pentafluorophenyl groups that unexpectedly promote a living isospecific polymerization of propene.[16] The polymer microstructure is consistent with an "enantiomorphic site" stereocontrol mechanism, while a prevailing 2,1-regiochemistry of propagation is supposed. The author proposed that the phenyl group on the carbon atom of the imine moiety, although remote from the catalytic center, is able to inhibit the catalyst isomerization hypothesized for the aldimine catalysts, resulting in the formation of isotactic polypropylene. Also for phenoxyketimine titanium complexes the steric encumbrance of the ortho phenolic substituents seems to have a determinant role on activity and isospecifity of the catalysts, in particular the enantiofacial selectivity is strongly depending on the steric interaction between these substituents and the incoming monomer.

The discussed results highlight that the effects of the structural modification on the ancillary ligands of these catalytic complexes are difficult to predict and induced us to investigate the

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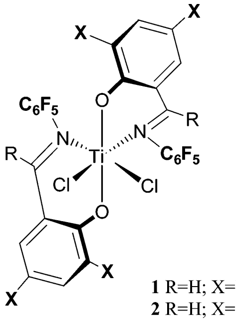
Table 1. Propene Polymerization with Catalysts 1−5: Conditions and Results

run[a]	catalyst	T (°C)	yield (g)	activity[b]	time (min)	[*mm*] (%)	% vicinal CH_3	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	PDI
1	**1**	25	0.300	6	120	46	9	48.8	20.8	2.3
2	**1**	0	0.440	9	120	56	10	44.0	26.1	1.7
3[c]	**1**	−20	0.044	0.9	120	63	10			
4	**2**	25	0.841	17	120	36	10	90.4	37.1	2.4
5	**2**	0	0.600	12	120	37	10	85.0	41.4	2.0
6	**3**	25	0.140	3	120	50	17	56.0	11.4	4.9
7	**3**	0	0.123	2	120	73	14	22.2	13.7	1.6
8	**4**	25	0.305	12	60	25	4	76.8	43.5	2.1
9	**4**	0	0.200	8	60	27	6	49.4	24.8	2.0
10[c]	**4**	−20	0.222	3	180	31	4	78.6	43.5	1.8
11[c]	**5**	−20	0.64	13	120	17	7	106.2	66.4	1.6

[a] General conditions: toluene = 40 mL; precatalyst = 25 μmol; cocatalyst, dried MAO = 3.75 mmol, obtained by distilling off the solvent by the commercial solution; propene pressure = 1 atm. [b] Activity = kg of polymer (mol cat)$^{-1}$ h^{-1}. [c] Propene = 10 mL.



1 R=H; X=Br
2 R=H; X=Cl
3 R=H; X=I
4 R=Ph; X=Br
5 R=H; X=CH_3

Figure 1. Schematic representation of catalysts **1**−**5**.

effects on the polymerization of propene of electron-withdrawing groups on the ortho positions of the phenolate rings of the phenoxyimine titanium complexes.

An evaluation of the role of electron-withdrawing groups on phenolate group 4 metal complexes was recently reported for tridentate diamido[17] and octahedral diamine bis(phenolate) titanium and zirconium complexes.[18,19]

In this work we describe the propene polymerization behavior of three new phenoxyaldimine and one phenoxyketimine titanium complexes bearing ligands with halide substituents on the ortho and para positions of the phenolate rings.

Results and Discussion

Synthesis and Polymerization Activity of Phenoxyaldimine and Phenoxyketimine Titanium Catalysts. The new titanium complexes **1**−**4** (Figure 1) were prepared, in moderate to high yields, according to literature procedures.[16,20]

For all titanium complexes ^{1}H, ^{13}C and ^{19}F NMR spectra showed the presence of a single chiral C_2-symmetric isomer both in methylene chloride-d_2 solution and tetrahydrofuran-d_8 solution at room temperature. In agreement with the observed structures of previously reported analogous titanium complexes[14] and on the basis of NMR data it is reasonable to assume a C_2 symmetry for these complexes.

When activated with MAO, **1**−**3** are active catalysts in the polymerization of propene. The results are summarized in Table 1.

The ^{13}C NMR spectrum of the polypropylene obtained at 25 °C (run 1) indicates that the sample is poorly stereoregular and regioregular, but an unexpected isotactic enrichment of methyl triads is observed ([*mm*] = 46%, [*mr*] = 38%, and [*rr*] = 16%).[21]Polypropylene samples were then prepared with **1**-MAO at 0 and −20 °C (see runs 2 and 3). The ^{13}C NMR analyses show that the fraction of isotactic triads increases as the temperature decreases. The polypropylene obtained at −20 °C (Figure 2) shows a prevailing isotactic microstructure ([*mm*] ~ 64%).[22]

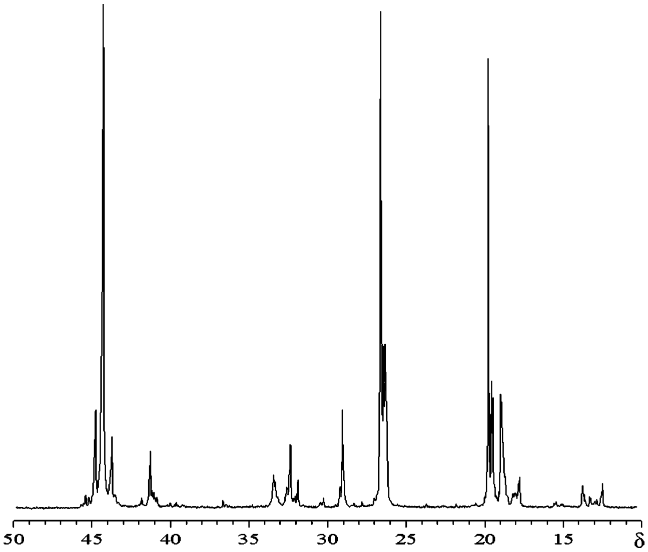


Figure 2. Aliphatic region of the ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of polypropylene (run 3). δ in ppm from hexamethyldisiloxane.

Pentad analysis of the methyl region of the ^{13}C NMR spectrum shows that the most intense resonances detected, in addition to the *mmmm* signal (19.73 ppm), are those due to the *mmmr* (19.50 ppm), *mmrr* (18.94 ppm), *mrrm* (17.75 ppm) pentads, in an approximately 2:2:1 ratio, while the remaining pentad resonances are much less intense. The polymer microstructure therefore mainly consists of blocks of m diads bridged by *rr* triads, i.e., the microstructure expected from the statistical model[23] of the "enantiomorphic sites" mechanism of the stereospecific propagation.[24] Less intense resonances at 12.4−13.7 and 31.8−33.5 ppm, corresponding to the adjacent methyl carbons ($P_{\alpha\beta}$)[25] of tail-to-tail arrangements and the resonances (between 31.8 and 34.3 ppm) of $S_{\alpha\beta}$ carbons[25] of head-to-head junctions indicate that the obtained polypropylene is poorly regioregular, (about 10% of regioirregularly arranged monomer units).

These data show that catalyst **1**-MAO produces, at low temperature, a prevailing isotactic polypropylene via an "enantiomorphic sites" mechanism of steric control and with a microstructure characterized by a considerable amount of regioinversions.

The behavior of the **1**-MAO catalyst is completely different from that of the other phenoxyaldimine catalysts bearing alkyl substituents on the phenol ring (a polymerization run is reported to comparison: run 11, Table 1) which afford prevailingly syndiotactic polypropylene whatever the size of the *o*-phenoxy substituents and also in the absence of substituents.[26]

The unpredicted behavior of catalyst **1** cannot be easily rationalized invocating steric effects deriving from the interactions with the *o*-phenol halide substituents of the ligands, since, for example, the van der Waals radii of the bromide (4.189 Å) and the methyl substituents are quite similar (3.947 Å).[27] Reasonably, electronic effects due to the electron-withdrawing properties of Br substituents could be responsible of the different stereocontrol mechanism. To examine the role played by the *o*-halide substituents on the phenoxyimine ligands on the catalytic performances of the resulting complexes and on the microstructures of the produced polypropylenes we synthesized phenoxyaldimine titanium complexes bearing ligands with chloride and iodide atoms on the ortho positions of the phenol rings (**2** and **3** respectively). Propene polymerizations were carried out under atmospheric monomer pressure under similar polymerization conditions (see Table 1).

The data collected in Table 1 show that the different halide substituents have a considerable effect on the catalytic performances of these complexes and, consequently, on the microstructures of the produced polymers. The reduction of the steric bulk of the halide substituents results in the enhancement of the catalytic activity of the complexes and in an increase of the molecular weights of the polymers. The polypropylenes obtained with **2** and **3** at 0 °C are prevailingly isotactic and in all cases the polymer microstructures are coherent with an "enantiomorphic site" mechanism of stereocontrol, in agreement with the presumable C_2 symmetry of the precatalysts. The microstructural analyses show that the stereoregularities of the polymer chains increase with the increase of the size of the *o*-halides (cf. runs 2, 5, and 7; Table 1) highlighting that the steric bulk of the ortho substituents has an important role in the control of the stereospecificity and the activity of the catalysts **1**−**3**, as previously observed by Fujita about the role of the alkyl ortho substituents for bis(phenoxyaldimine)titanium catalysts.

The hypothesis that the electron-withdrawing properties of the halogens substituents are responsible of the different catalytic behavior observed for the reported catalysts is supported by preliminary studies on polymerization of propene with analogue NO_2 substituted aldimine titanium catalysts. Coherently with that observed for the above catalytic systems the bulkier NO_2 substituents induce a higher isoselectivity sacrificing considerably the activity of the resulting catalytic species. More detailed data will be reported in a future work.

The effect of the temperature on the polymerization behavior was also investigated (Table 1). Both catalyst activities and polymer molecular weights increase while the temperature increases, while the isotacticity of the polypropylene samples decreases.

GPC analyses reveal that the polymer samples produced by **1**−**3** catalysts at 0 °C have narrow molecular weight distributions ($M_w/M_n < 2$) indicating a single site nature of the catalysts. At higher temperature (25 °C) the M_w/M_n ratios increase weakly (runs 1, 4, and 6, Table 1) and the polypropylene samples obtained under these polymerization conditions become fractionable. The crude polypropylenes obtained by **1**−**3** at 25 °C are fractionated by stirring in hexane at room temperature. The insoluble fractions (ca. 10 wt %) consist in highly isotactic and regioregular polypropylenes ([*mm*] >95%). The hexane soluble fractions (ca. 90 wt %) result in less stereo- and regioregular polypropylenes but also in these fractions a considerable enrichment in *mm* methyl triads (~45%) is observed. The presence of polymeric fractions with different microstructures and in some cases similar molecular weights (see PDI of runs 1 and 4, Table 1) suggests the hypothesis that, at room temperature, more active species are produced by the reaction of the precatalysts and MAO. This hypothesis is coherent with previous works describing a multi site nature of the phenoxyimine catalysts strongly depending by the polymerization conditions.[5−7]

The results discussed above show that the phenoxyaldimine titanium complexes **1**−**3** have a catalytic behavior notably different from that of all the previously reported titanium complexes bearing phenoxyaldimine ligands which promote syndiospecific propene polymerization. For the latter catalysts the syndiospecifity derives from a chain-end control mechanism via 2,1-insertion, the stereoselectivity decreases as the size of *o*-phenol alkyl substituents is reduced but it is preserved also in absence of substituents. This stereocontrol mechanism has been explained by theoretical models suggesting the $\Delta-\Lambda$ isomerization of fluxional octahedral chiral catalytic site because of steric repulsion between the ligand framework and the methyl group of the propene coordinated to metal center.[13a] A key aspect for the hypothesized stereocontrol mechanism is the secondary regiochemistry of monomer insertion during propagation. Differently, the unexpected isospecifity of complexes **1**−**3** evidences a deep analogy with the catalytic behavior of phenoxyketimine titanium complexes recently observed by Coates.[16] These catalysts promote, at low temperature (−20 °C), the prevailing isospecific polymerization of propene. The author explained the isospecificity of the catalytic systems hypothesizing an insertion rate faster than the isomerization one determined by the steric encumbrance of the phenyl groups.

Considering the unexpected results obtained with *o*-halide substituted phenoxyaldimine titanium catalysts and the strong analogy in the catalytic behavior with the phenoxyketimine catalysts reported by Coates, we decided to extend our studies to *o*-halides substituted phenoxyketimine titanium catalysts in order to evaluate the combined effect of phenyl groups on the imine carbons and of bromine atoms as phenolate substituents.

The propene polymerization experiments with catalyst **4** were carried out under experimental conditions (runs 8−10, Table 1) analogous to those used for complexes **1**−**3**. Phenoxyketimine catalysts show generally, as previously reported, a lower polymerization activity than phenoxyaldimine ones.[28]

In this case complex **4**, in combination with dried MAO, shows a productivity similar to that of the corresponding aldimine titanium complex **1** (see runs 1 and 8; 2 and 9, Table 1) and twice as large as that of the most active isospecific *o*-alkyl phenoxyketimine titanium complex, previously reported by Coates under analogous experimental conditions.[16] The slight increase in the catalytic activity may be attributed to the increased electrophilicity of the metal center due to the introduction of halides (electron-withdrawing substituents) on the ligand framework.

The ^{13}C NMR analysis revealed that polypropylene obtained with complex **4** is stereoirregular both at room temperature and subambient temperature (runs 8−10). The ^{13}C NMR spectrum of the polypropylene sample obtained at 25 °C is reported in Figure 3.

This disappointing result suggests that the two modifications introduced in the skeleton of the ancillary ligand (the phenyl group on the imine nitrogen and the *o*-halide substituents on the phenol ring) do not operate in a synergic way in influencing the isospecificity of the catalyst.

Regiochemistry and Stereochemistry of Polymerization Promoted by Phenoxyaldimine Catalysts. The unexpected results discussed above induced us to investigate the causes of this different behavior by a more detailed analysis of the microstructure of the polypropylenes produced.

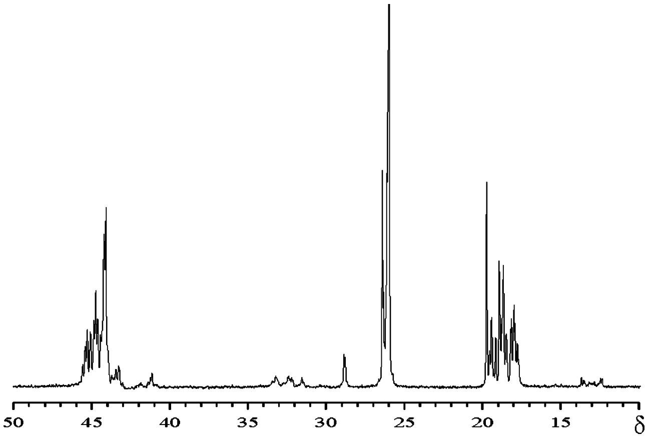


Figure 3. Aliphatic region of the ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of polypropylene obtained with **4**-MAO (run 8). δ in ppm from hexamethyldisiloxane.

Chart 1. Fischer Projections of Vicinal *threo* Methyls of Isolated Regioinverted Unit (a) and of Vicinal *threo* Methyls Bringing Blocks of Different Regiochemistry (b)

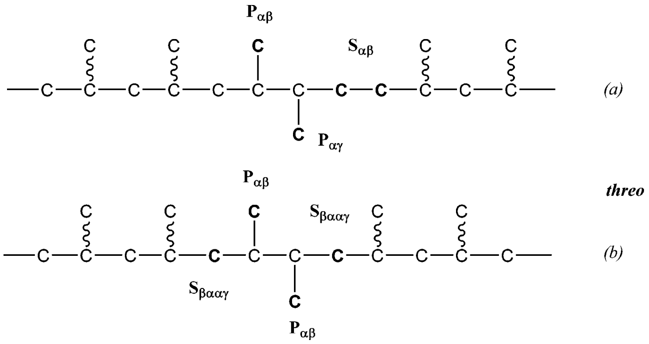


Chart 2. Fischer Projections of Vicinal *erythro* Methyls of Isolated Regioinverted Unit (c) and of Vicinal *erythro* Methyls Bringing Blocks of Different Regiochemistry (d)

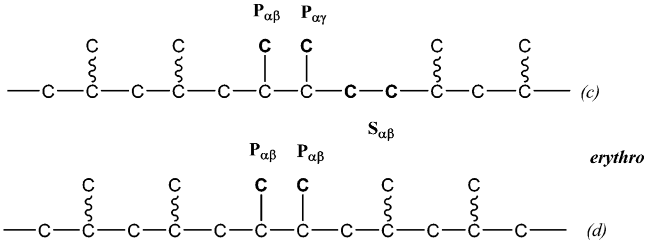


Chart 3. Methylene Units of Head-to-Head Bringing Blocks of Different Regiochemistry

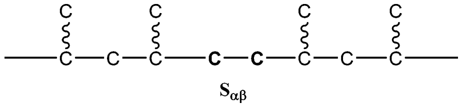
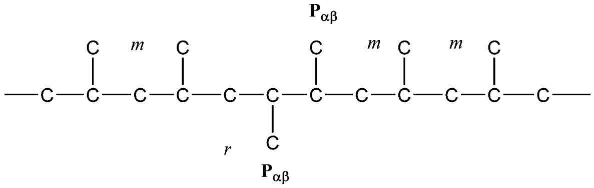


Chart 4. Fischer Projection Describing the Most Frequent Stereochemical Arrangement of the Monomer Units Adjacent to the Vicinal *threo* Methyls



Our attention was turned to the analysis of regiomistakes abundantly present within the polymer chain to establish the prevailing regiochemistry of the monomer insertion during the propagation.

A polypropylene sample was prepared using **1**-MAO at −60 °C (see run 12). The ^{13}C NMR spectrum of the polymer shows a prevailing isotactic microstructure ([*mm*]∼68%) with a large amount of regioinversions (about 10%), analogously to that observed for the polypropylene sample obtained at −20 °C shown in Figure 2 (see run 3, Table 1).

A detailed analysis of the resonances relative to the $P_{\alpha\beta}$ carbons and to the $S_{\alpha\beta}$ carbons allow to identify the nature of the regiomistakes.

The $P_{\alpha\beta}$ carbons, in *threo* or *erythro* configuration, can be due to either isolated regioirregularly arranged monomer units or blocks[29,30] (see Charts 1 and 2): in the first case (structures a, c) the polymer contains some isolated monomer units with inverted orientation randomly distributed along the chain, while the alternative structures (b, d) consist of a polypropylene having blocks of units with head-to-tail orientation and blocks of units with tail-to-head orientation.

Similarly the $S_{\alpha\beta}$ carbons can be due to the regiomistakes produced by either isolated regioinverted units (structures of Charts 1a and 2c) or the head-to-head junctions of blocks of different regiochemistry (Chart 3).[29]

The observed resonances relative to the $S_{\alpha\beta}$ carbons[29,31] (31.8−33.5 ppm) indicate that the polymer chain is formed by segments generated by consecutive 2,1 insertions and 1,2 insertions (Chart 3). Furthermore, in the considered spectrum, the area of the resonances of the $P_{\alpha\beta}$ carbons is approximately one-half of the area of the resonances of the $T_{\alpha\beta}$ and $S_{\alpha\beta}$ carbons (spread between 31.8 and 33.5 ppm) confirming that this polypropylene prevailingly consists of blocks of monomer units having different regiochemical arrangement, as observed for the polypropylenes produced by related phenoxyimine syndiospecific titanium complexes.[15]

Additional information can be deduced from the detailed analysis of the $P_{\alpha\beta}$ region of the ^{13}C NMR spectrum:

(1) The resonances relative to the *threo* $P_{\alpha\beta}$ carbons (between 12.4 and 13.7 ppm) are much more intense of the resonances diagnostic of *erythro* $P_{\alpha\beta}$ carbons (between 14.4 and 15.6 ppm).[31,32] This means that the *threo* type regioinversions are more frequent than the *erythro* ones (*threo*/*erythro* ratio is about 50:1) indicating that the regiodefects occur, prevailingly, with the same enantiofacial selectivity of the precedent monomer insertion. This observation is also confirmed by the analysis of the resonances of the $S_{\beta\alpha\alpha\gamma}$ carbons (between 40.4 an 41.2 ppm) adjacent to the tail-to-tail junctions (Chart 1 a).[33]

(2) The two most intense resonances relative to the *threo* $P_{\alpha\beta}$ carbons, by comparison with literature data,[31,32] allow to identify the diastereoisomeric regioirregular sequences shown in Chart 4. This diasteromer describes the most frequent stereochemical arrangement (meso) of the monomeric units adjacent to the regioirregular junctions of the polypropylene chains. This is in agreement with the prevailing isotacticity of the obtained polypropylene and suggests that both the regiochemical propagation modes are preferentially isospecific.

(3) Less intense resonances referred to the *threo* $P_{\alpha\beta}$ carbons and to the $P_{\alpha\gamma}$ carbons due to isolated regioinverted monomer units (Chart 1a) are also observed.[34] These regiomistakes are formed by the insertion of a single monomeric unit with opposite regiochemistry and with the same enantioface.

These microstructural data reveal that a regiomistake occurs initially with the insertion of the monomeric unit with same enantioface of the previous inserted monomer unit but, if the different propagation mode is preserved, the subsequent insertions occur with the opposite enatioface. This behavior is quite

Table 2. Propene Polymerization and Propene/Ethylene Copolymerization with Catalyst 1: Conditions and Results

run[a]	catalyst	*T* (°C)	yield (g)	time (min)	[*mm*] (%)	% vicinal CH_3
12	**1**	−60	0.230	720	68	10
13[b]	**1**	−20	0.242	15	58	12
14[c]	**1**	−20	0.040	120	55	6

[a] General conditions: toluene = 40 mL; precatalyst = 25 μmol; cocatalyst, dried MAO = 3.75 mmol, obtained by distilling off the solvent by the commercial solution; propene = 10 mL. [b] Toluene = 40 mL; precatalyst = 100 μmol; cocatalyst: dried MAO = 7.50 mmol; propene = 10 mL, terminated by injecting a 1:1 mixture of CF_3CH_2OD and D_2O. [c] Ethylene pressure = 1 atm.

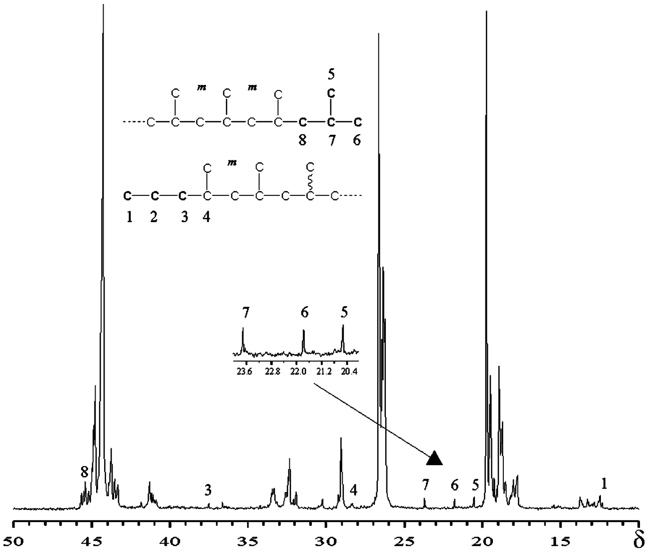


Figure 4. Aliphatic region of the ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of polypropylene (run 13). δ in ppm from hexamethyldisiloxane.

different from that observed for the chiral group 4 metallocene catalysts which produce isotactic polypropylene by enantiomorphic site control. In fact, in the latter case it was clearly established that the infrequent secondary single insertions of propene occur preferably with the opposite enantioface.[35,36]

On the contrary, a behavior similar to **1**, consisting in the production of an isotactic polypropylene having isolated regioirregular units in *threo* configuration, was recently described for some non metallocene group 4 metal catalysts. [34,37,38]

Collecting the above information, we can conclude that the polypropylene obtained at low temperature by **1**-MAO has a prevailing isotactic structure deriving by an "enantiomorphic site" mechanism of stereocontrol and contains blocks of monomer units with head-to-tail orientation and blocks with tail-to-head enchainment.

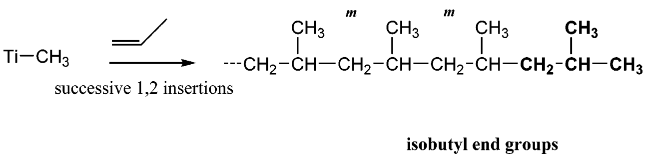
In an effort to elucidate the mechanistic details by which catalyst **1** produces isotactic polypropylene, we prepared a low M_n (~9000)[39] isotactic polypropylene under proper polymerization conditions (run 13 Table 2) to detect the natural abundance end groups formed by initiation and chain termination processes. The ^{13}C NMR spectrum (Figure 4) of the sample is similar to that already discussed ([*mm*] = 59% and 8% of regiomistakes).

In addition to the resonances due to the main chain carbon atoms, the spectrum displays some sharp peaks, at δ 20.5, 21.8, 23.7, and 45.5 ppm attributable, according to the literature,[30,40,41] to a single diastereoisomer of the isobutyl end groups (Scheme 1).

In the ^{13}C NMR spectrum, other weak resonances are observed at δ 12.3, 28.3−28.4 and 37.5−37.6 ppm from HMDS attributable to *n*-propyl end groups (Scheme 2).[30,42] No resonances attributable to other possible end groups, namely ethyl, *n*-butyl and *sec*-butyl or unsaturated end groups are detected. Comparing the peak intensities of the methyl carbons of the above-mentioned chain-end groups the calculated percentage of *n*-propyl is about 46% and that of isobutyl groups is 54%.

Scheme 1

Initiation step



The isobutyl end groups could arise from primary insertion of propene in the titanium−methyl bond of the catalyst (initiation, Scheme 1) and/or from the hydrolysis of the titanium−methylene bonds of the polymer chain growing by primary insertion (termination, see Scheme 2).

The possibility that such isobutyl end groups could arise from the secondary insertion in a metal−hydrogen bond has to be disregarded in view of the absence of unsaturated end groups that should necessarily accompany the formation of the titanium−hydrogen bonds. These data suggest that the polymerization is prevailingly initiated by some consecutive 1,2-insertions of the propene into a Ti−CH_3 bond (generating the isobutyl end groups). The exclusive presence of a single diastereoisomer for the isobutyl end groups (shown in Scheme 1) reveals that (i) the chirality of the titanium center is effective in controlling the stereochemistry of the insertion already in the second propagation step, i.e., during the primary insertion of the third propene unit into the Ti-alkyl bond in which the first chiral carbon of the growing chain was formed, and (ii) the insertions of some of the successive monomer units occur with the same regio- and stereochemistry.

Reasonably the *n*-propyl groups are formed in the termination steps by hydrolysis of titanium-bound secondary growing chains (see Scheme 2). This hypothesis was confirmed by a deuterium labeling experiment (see run 13, Table 2). The ^2H NMR analysis of a sample of polypropylene produced terminating the polymerization by adding a mixture of D_2O and CF_3CH_2OD, clearly shows the presence of a single peak at 1.26 ppm corresponding to CH_3CHDCH_2− end groups, as expected for deuteriolysis of a secondary polymer chain bound to titanium (Scheme 3).

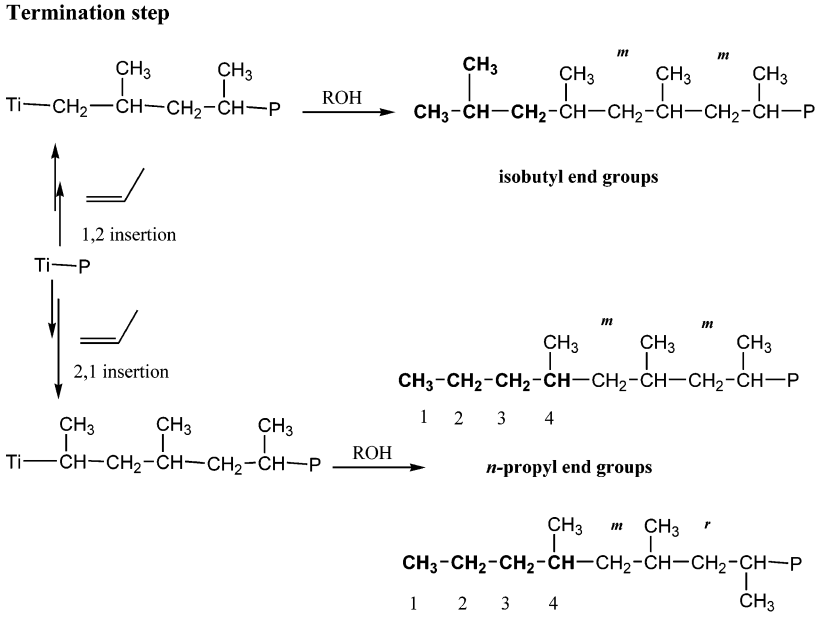
The chemical shifts of methylene carbons[42] of *n*-propyl groups (carbons 3 of the Fischer projections in the Scheme 2) indicate that these ends groups are adjacent, prevailingly, to an isotactic *mm* stereochemical triad, and, with a lower frequency, to a *mr* stereochemical triad. This fact suggests that secondary propene insertion is less isospecific than primary propene insertion.

Since the amount of isobutyl end groups exceeds slightly that of *n*-propyl, some hydrolysis of titanium-bound primary growing chains also occur in the termination steps. The mechanism explaining the formation of the detected end groups is described in Schemes 1 and 2.

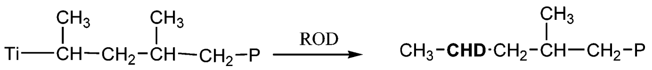
In summary, the whole picture indicates unambiguously that the initiation step proceeds via primary insertion of the monomer into a Ti−CH_3 bond and it is followed by some subsequent stereoregular primary insertions. Differently, the main termination step is the alcoholysis of titanium-bound secondary growing chains.

Since the end group analysis is not conclusive concerning the main regiochemistry of propagation, especially in the presence of a high content of regioinversions, a copolymerization

Scheme 2



Scheme 3. Deuteriolysis of a Secondary Polymer Chain

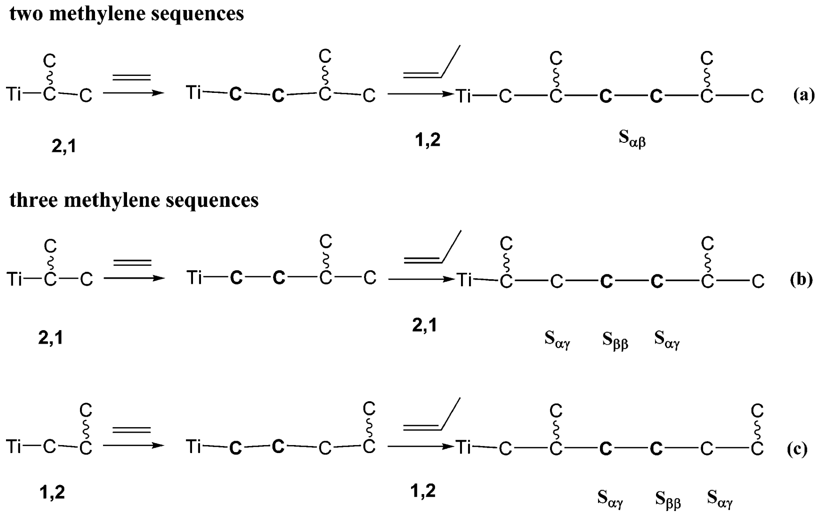


of propene with a low amount of ethylene was carried out at −20 °C (run 14, Table 2). Under the polymerization conditions used all the ethylene units are isolated (the ethylene content is about 9%),[43] i.e., they are located between blocks of polypropylene chains leading to either a two-methylene sequence or a three-methylene sequence (Scheme 4). No resonances attributable to four-methylene sequences are observed in the spectrum. The methylene pairs are formed after the insertion of a single ethylene unit into a metal-secondary carbon followed by a primary insertion of propene; the three methylene sequences are due to the insertion of an ethylene unit between regioregular blocks.

^{13}C NMR analysis of the copolymer shows that in this case methylene pairs outnumber the three methylene sequences (70% vs 30%), as deduced from the area of the resonances of the $S_{\alpha\beta}$ carbons vs the area of the resonances of the $S_{\alpha\gamma}$ carbons (Figure 5). This observation suggests that ethylene insertion occurs preferentially after a propene unit inserted 2,1 and that the 1,2-propene insertion becomes preferred after the insertion of a unit which generates a metal−primary carbon bond (in agreement with the absence of four-methylene sequences in the chain). Thus, ethylene units bridge blocks of propene units with opposite regiochemistry more frequently than blocks of regioregularly arranged propene units (see Scheme 4).

A more detailed analysis of the resonances referred to the carbons of the inserted ethylene units offers some further insight. The resonances relative to $S_{\alpha\gamma}$ carbons of three methylene sequences are influenced by the stereochemistry of the adjacent propene dyads. The *m*-$S_{\alpha\gamma}$ percentage is about 61%, indicating that the ethylene units spanning regioregular blocks of polypropylene are more often bordered by isotactic (*m*) than by syndiotactic (*r*) stereochemical dyads. This observation is in agreement with the prevailing isotacticity of the produced polypropylene. Moreover, considering that the primary propene insertion (1,2) is highly isospecific, as observed by the end groups formed in the initiation steps, we can reasonably exclude that the above three methylene sequences are flanked by regioregular blocks deriving exclusively by primary insertions. More reasonably, these resonances are due either to ethylene units included in less isotactic secondary blocks (Scheme 4b)

Scheme 4. Methylene Sequences Formed by the Insertion of a Single Ethylene Unit between Blocks of Polypropylene Chains



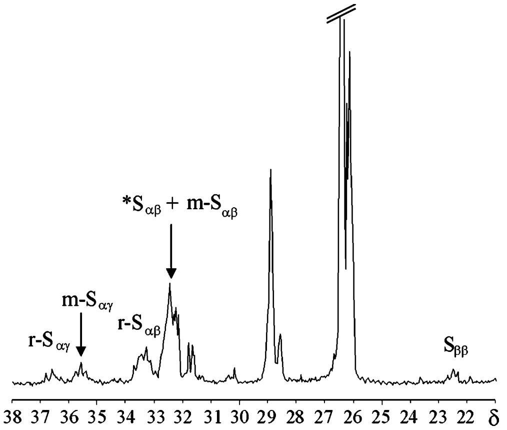
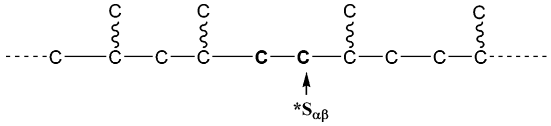


Figure 5. Aliphatic region of the ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of the copolymer (run 14). δ in ppm from hexamethyldisiloxane.

Chart 5. Methylene Units Flanking a Regioirregular Propene Diad



or to ethylene units spanning both primary and secondary blocks (Scheme 4, parts c and b).

The *m*-$S_{\alpha\beta}$ percentage is not quantifiable because in ethylene-propene copolymer, as reported in the literature, the multiplet between 32 and 33 ppm is due to $S_{\alpha\beta}$ carbons flanking either a *m* propene diad or a regioirregular propene diad ($*S_{\alpha\beta}$ carbons in Chart 5).

The data of the ^{13}C NMR spectrum of the copolymer corroborate the hypothesis that the highly isospecific propene primary insertion is not the prevalent mode of propagation, while the moderate isotacticity of the polymer would be due to the presence of a conspicuous fraction of less stereoregular blocks derived from secondary insertions.

In conclusion the catalyst **1**-MAO produces, at low temperature, a prevailing isotactic polypropylene via an "enantiomorphic sites" mechanism of steric control and with a microstructure consisting of shorter primary, highly isotactic blocks and longer, secondary, poorly isotactic blocks.

The polypropylenes obtained under analogue polymerization conditions with **2** and **3** show similar microstructural features.

Conclusions

New fluorinated bis(phenoxyaldimine)- and bis(phenoxyketimine)titanium complexes bearing halide substituents on the ortho positions of the phenolic ring of the ligands have been synthesized and tested as precatalysts for polymerization of propene after MAO activation. The polypropylenes obtained with bis(phenoxyaldimine)titanium complexes are prevailing isotactic and their microstructure is in agreement with an "enantiomorphic site" mechanism of steric control. The regiochemistry of the monomer insertion in the initiation and termination steps has been investigated by end groups analysis and deuterium labeling techniques, indicating an exclusive 1,2-insertion in the initiation step and a prevailing 2,1-regiochemistry of the termination step. The stereochemistry of the end groups suggests that the 1,2-insertion is highly isospecific and the 2,1-insertion is less isospecific. A large amount of regioinversions indicates that the polymers have a regioblock structure consisting of consecutive 2,1- insertion and 1,2-insertion segments. Moreover, considering the low isotacticity of the polypropylene the fraction of secondary regioblocks seems larger than that of the primary ones. This is also in agreement with fine analysis of ^{13}C NMR spectra of the homopolymer and of a copolymer with a low amount of ethylene.

The behavior of these catalysts contrasts that of previously reported syndiospecific bis(phenoxyaldimine)titanium complexes. The substitution of alkyl groups with halides on the ortho positions of the phenol rings causes a substantial change in the catalytic behavior: from syndiospecific polymerization by chain end control mechanism to isospecific polymerization via a site-control mechanism. In a different way, introducing the same modification on the bis(phenoxyketimine)titanium complexes a complete lack of enantioselectivity is observed.

These results confirm that the effects of variation of structural parameters on reactivity and stereoselectivity are difficult to predict also for the members of a single class of catalysts.

Experimental Procedures

General Details. 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 and tetrahydrofuran (THF) were refluxed over sodium-benzophenone and distilled under a nitrogen atmosphere before use. Dichlorometane was distilled over calcium hydride and under a nitrogen atmosphere before use. Dichlorometane-d_2 was distilled over calcium hydride. Commercial reagents were used without further purification. 3,5-Dibromo-2-hydroxybenzaldehyde, 3,5-dichloro-2-hydroxybenzaldehyde and 3,5-diiodio-2-hydroxybenzaldehyde were bought from Lancaster. 2,3,4,5,6-Pentafluoroaniline was bought from Aldrich. Methylaluminoxane (MAO, Euricen) was purchased as a 10 wt % solution in toluene. A sample of MAO solution was distilled under reduced pressure to remove the solvent and residual trimethylaluminum, providing a solid white powder (dried MAO).

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

NMR data were recorded using Bruker AVANCE spectrometers. Chemical shifts are reported in parts per million (δ in ppm) and coupling constants are reported in hertz. The residual protons or ^{13}C carbons of the deuterated solvents were used as internal references. ^{19}F NMR chemical shifts were referenced to the external standard $CFCl_3$.

Synthesis of Ligand 1. To a stirred solution of 2,3,4,5,6-pentafluoroaniline (1.50 g; 8.2 mmol) and 3,5-dibromo-2-hydroxybenzaldehyde (2.00 g; 7.1 mmol) in anhydrous toluene (40 mL) under nitrogen was added *p*-toluensulfonic acid (10 mg) under nitrogen. The resulting mixture was stirred at reflux temperature for 20 h. Removal of solvent under vacuum gave a yellow crystalline solid, which was washed with methanol. Yield: 2.31 g (5.2 mmol; 73%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.10 (1H, O*H*), 8.77 (s, 1H, N=C*H*), 7.80 (d, 1H, *H*−Ar), 7.49 (d, 1H, *H*−Ar).

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 168.35 (*C*=N), 157.34 (*C*−OH), 140.03, 134.59, 120.56, 112.81, 111.21.

^{19}F NMR ($CDCl_3$, 376 MHz): δ −151.17 (d, 2F, ortho), −156.24 (t, 1F, para), −161.86 (t, 2F, meta).

Synthesis of Ligand 2. The synthetic procedure is the same described for ligand **1**. 2,3,4,5,6-pentafluoroaniline (1.83 g; 10.0 mmol) and 3,5-dichloro-2-hydroxybenzaldehyde (1.73 g; 9.1 mmol) in anhydrous toluene (40 mL) with p-toluensulfonic acid (10 mg). Yield: 1.82 g (5.1 mmol; 56%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 12.96 (1H, O*H*), 8.83 (s, 1H, N=C*H*), 7.33 (d, 1H, *H*−Ar), 7.53 (d, 1H, *H*−Ar).

^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 168.32 (*C*=N), 155.78, 134.31, 130.60, 124.12, 123.37, 119.83.

^{19}F NMR ($CDCl_3$, 376 MHz): δ −151.14 (d, 2F, ortho), −156.17 (t, 1F, para), −161.88 (t, 2F, meta).

Synthesis of Ligand 3. The synthetic procedure is the same described for ligand **1**. 2,3,4,5,6-Pentafluoroaniline (3.49 g; 19.0 mmol) and 3,5-diiodio-2-hydroxybenzaldehyde (4.49 g; 12 mmol) in anhydrous toluene (40 mL) were used with *p*-toluensulfonic acid (10 mg). Yield: 5.10 g (9.5 mmol; 79%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.29 (1H, O*H*), 8.72 (s, 1H, $\mathrm{N{=}C}H$), 8.20 (d, 1H, $H{-}\mathrm{Ar}$), 7.70 (d, 1H, $H{-}\mathrm{Ar}$).

^{13}C NMR ($CDCl_3$,100.6 MHz): δ 168.13 ($C{=}\mathrm{N}$), 160.19, 151.06, 141.66, 120.50, 87.66, 80.83.

^{19}F NMR ($CDCl_3$, 376 MHz): δ − 151.28 (d, 2F, ortho), −156.42 (t, 1F, para), −161.95 (t, 2F, meta).

Synthesis of Ligand 4. A 100 mL round-bottom flask with stirrer bar was charged with an aluminum chloride (0.014 mol) in 1,2-dichloroethane solution (36 mL), and then the 1,2-dichloroethane suspension (12 mL) of imidoyl chloride (0.012 mol), prepared as described in the literature,[28] and a solution of 2,4-dibromophenol (0.012 mol) in 1,2-dichloroethane (8 mL) were sequentially added via cannula. Immediately the solution turned from light brown to orange-red. The resulting solution was heated at reflux under nitrogen for ca. 16 h. The suspension was allowed to cool to room temperature and then added to water (60 mL) followed by stirring for 30 min. The organic layer was washed with aqueous sodium carbonate solution and saturated $NaCl_{(aq)}$. The yellow organic fractions were collected together and dried over anhydrous $MgSO_4$, followed by filtration.

Volatiles were removed under reduced pressure to yield a yellow oil which was found to contain ligand **4**. The obtained yellow oil was twice chromatographed on silica (10% ethyl acetate/hexane) to afford the desiderate ligand as light white powder. Yield: 3.3 g (6.3 mmol; 53%).

^{1}H NMR ($CDCl_3$, 400 MHz, −20 °C): δ 7.81 (d, 1H, Ar*H*), 7.59−7.52 (m, 3H, Ph*H*), 7.43 (t, 2H, Ph*H*), 7.26 (m, 1H, Ar*H*).

^{13}C NMR ($CDCl_3$, 400 MHz, −20 °C): δ 163.7 ($C{=}\mathrm{N}$), 149 (Ar*C*-OH), 135.9, 132.3, 131.9, 128.9, 128.8, 128.2, 125.5, 120, 117.5 (Ar*C* or Ph*C*). The three $\mathrm{Ar_FC{-}F}$ and $\mathrm{Ar_FC_{ipso}}$ signals are hidden.

Synthesis of Complex 1. To a stirred solution of *N*-(3,5 dibromosalicylidene)-2,3,4,5,6-pentafluoroaniline (2.38 g, 5.48 mmol) in anhydrous toluene (40 mL) at 0 °C was added a $TiCl_4$ toluene solution (0.30 mL of $TiCl_4$, 2.74 mmol in 10 mL of toluene) dropwise over a 10-min period. The mixture was allowed to warm to room temperature and stirred for 15 h. The toluene was removed from the red solution in vacuo and a crude red-brown product was obtained. The residue was extracted with 80 mL of dried CH_2Cl_2, the obtained solution was filtered on Celite to remove insoluble impurities. The filtrate was concentrated under reduced pressure and stored at −20 °C for 16 h. The solid precipitated was separated from the solution by filtration with a glass filter and dried in vacuo to give complex **1** (2.05 g) as a deep red solid in 75% yield.

^{1}H NMR (THF-d_8, 400 MHz): δ 8.70 (s, 2H, $\mathrm{N{=}C}H$), 8.18 (d, 2H, $H{-}\mathrm{Ar}$), 7.84 (d, 2H, $H{-}\mathrm{Ar}$).

^{13}C NMR (THF-d_8, 100.6 MHz): δ 174.85 ($C{=}\mathrm{N}$), 143.57, 138.42, 125.47, 125.75, 114.34, 113.12.

^{19}F NMR (CD_2Cl_2, 376 MHz): δ −146.17, −147.72, −156.39, −160.03, −164.05 ($\mathrm{Ar_F{-}}F$). Anal. Calcd for $C_{26}H_6Br_4N_2O_2F_{10}$-$TiCl_2$: C, 31.02; N, 2.78; H, 0.6. Found: C, 29.88; N, 2.505; H, 1.40.

Synthesis of Complex 2. To a stirred solution of *N*-(3,5-dichlorosalicylidene)-2,3,4,5,6-pentafluoroaniline, 1.43 g (4,0 mmol) in anhydrous toluene (40 mL) at 0 °C, was added a $TiCl_4$−toluene solution (0.22 mL of $TiCl_4$, 2.0 mmol, in 10 mL of toluene) dropwise over a 10-min period. The synthetic procedure is the same described for complex **1**. Complex **2** (1.13 g) was obtained as a red solid in 80% yield.

^{1}H NMR (THF-d_8, 400 MHz): δ 8.83 (s, 2H, $\mathrm{N{=}C}H$), δ 7.97 (d, 2H, $H{-}\mathrm{Ar}$), δ 7.59 (d, 2H, $H{-}\mathrm{Ar}$)

^{13}C NMR (THF-d_8, 100.6 MHz): δ 174.66 ($C{=}\mathrm{N}$), 137.92, 134.49, 125.47, 127.27, 125.34, 123,67.

^{19}F NMR (CD_2Cl_2, 376 MHz): δ −146.06, −147.88, −156.36, −160.22, −164.12 ($\mathrm{Ar_F{-}}F$). Anal. Calcd for $C_{26}H_6Cl_6N_2O_2F_{10}Ti$: C, 37.67; N, 3.38; H, 0.73. Found: C, 35.84; N, 3.03; H, 1.45.

Synthesis of Complex 3. To a stirred solution of *N*-(3,5-diiodiosalicylidene)-2,3,4,5,6-pentafluoroaniline, 1.5 g (2.70 mmol) in anhydrous toluene (40 mL) at 0 °C, was added a $TiCl_4$ toluene solution (0.15 mL of $TiCl_4$, 1.35 mmol in 10 mL of toluene) dropwise over a 10-min period. The synthetic procedure is the same described for complex **1**. Complex **3** (1.20 g) was obtained as a red solid (yield 74%).

^{1}H NMR (THF d_8, 400 MHz): δ 8.83 (s, 2H, $\mathrm{N{=}C}H$), 7.97 (d, 2H, $H{-}\mathrm{Ar}$), 7.59 (d, 2H, $H{-}\mathrm{Ar}$)

^{13}C NMR (THF d_8, 100.6 MHz): δ 174.88 ($C{=}\mathrm{N}$), 162.69, 154.74, 151.92, 127.27, 145.45, 125,27.

^{19} F NMR (CD_2Cl_2, 376 MHz): δ −146.24, −147.41, −156.41, −159.76, −163.95.

$C_{26}H_6I_4N_2O_2F_{10}TiCl_2$: C, 26.14; N, 2.34; H, 0.51. Found: C, 27.01; N, 3.03; H, 0.83.

Synthesis of Complex 4. A 100 mL round-bottomed flask was charged with 2,4-Dibromo-6-[phenyl(pentafluorophenylimino)-methyl]phenol (3.3 g, 6.3 mmol), and by addition of diethyl ether (70 mL), a bright yellow solution was formed. As the reaction mixture was cooled to −78 °C, *n*-BuLi was added (2.5 M in hexane, 1 equiv) drop by drop via siringe, resulting in a color change to bright neon yellow. After ca. 30 min, the ligand lithium salt was slowly added via cannula to a stirred diethyl ether solution (70 mL) of $TiCl_4$ (3.0 mmol) at −78 °C, so that the color of solution intensified to deep red. The reaction mixture was allowed to cool to room temperature, and it was stirred overnight.

A red solid was isolated by distilling off diethyl ether, the recovered solid was dissolved in toluene (50 mL), and the solution was concentrated down (25 mL) and kept at −20 °C for one night. A crystalline powder was then isolated by filtration and it was found to be complex **4** (1.05 g) as a red solid in 30% yield.

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.61 (dd, 1H, Ar*H*), 7.45−7.35 (m, 3H, Ph*H*), 7.23 (m, 2H, Ph*H*), 7.04 (d, 1H, Ar*H*).

^{13}C NMR (CD_2Cl_2, 400 MHz): δ 181.1 ($C{=}\mathrm{N}$), 162.7 (Ar*C*-O), 140.5, 138, 135, 131.4, 129.4, 129.3, 126.6, 126.3, 126.2, 118, 114.3 (Ar*C* or Ph*C*). The three $\mathrm{Ar_F}C{-}\mathrm{F}$ and $\mathrm{Ar_F}C_{\mathrm{ipso}}$ signals are hidden.

^{19}F NMR (CD_2Cl_2, 376 MHz): δ −139.6, −145.1, −157.5, −162.4, −164.9($\mathrm{Ar_F{-}}F$).

Anal. Calcd for $C_{38}H_{14}N_2O_2F_{10}Br_4TiCl_2$: C, 39.38; H, 1.22; N, 2.42. Found: C, 40.0; H, 1.5; N, 2.6.

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.

Characterization. ^{13}C NMR polymer spectra were recorded on a Bruker Advance 300 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. Molecular weight and molar mass distribution of polymers were measured by gel permeation chromatography (GPC). GPC measurements were carried out at 140 °C, using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standards as reference. The measurements were performed on PL-GPC210 with PL-Gel Mixed A Columns, RALLS detector (Precision detector, PD2040 at 800 nm), H502 viscometer (Viscotek), refractive detector and DM400 datamanger (Viscotek). Every value is the average of the two independent measurements.

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