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Syndiospecific Living Propylene Polymerization Catalyzed by Titanium Complexes Having Fluorine-Containing Phenoxy−Imine Chelate Ligands

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Abstract: The propylene polymerization behavior of a series of Ti complexes featuring fluorine-containing phenoxy−imine chelate ligands is reported. The Ti complexes combined with methylalumoxane (MAO) can be catalysts for living and, at the same time, stereospecific polymerization of propylene at room temperature or above. DFT calculations suggest that the attractive interaction between a fluorine ortho to the imine nitrogen and a β-hydrogen of a growing polymer chain is responsible for the achievement of room-temperature living propylene polymerization. Although the Ti complexes possess C_2 symmetry, they are capable of producing highly syndiotactic polypropylenes. ^{13}C NMR is used to demonstrate that the syndiotacticity is governed by a chain-end control mechanism and that the polymerization is initiated exclusively via 1,2-insertion followed by 2,1-insertion as the principal mode of polymerization. ^{13}C NMR spectroscopy also elucidated that the polypropylenes produced with the Ti complexes possess regio-block structures. Substitutions on the phenoxy−imine ligands have profound effects on catalytic behavior of the Ti complexes. The steric bulk of the substituent ortho to the phenoxy oxygen plays a decisive role in achieving high syndioselectivity for the chain-end controlled polymerization. Over a temperature range of 0−50 °C, Ti complex having a trimethylsilyl group ortho to the phenoxy oxygen forms highly syndiotactic, nearly monodisperse polypropylenes (94−90% *rr*) with extremely high peak melting temperatures (T_m = 156−149 °C). The polymerization behavior of the Ti complexes can be explained well by the recently proposed site-inversion mechanism for the formation of syndiotactic polypropylene by a Ti complex having a pair of fluorine-containing phenoxy−imine ligands.

Introduction

Living olefin polymerization enables consecutive enchainment of monomer units without termination. Therefore, it can be used for the preparation of precisely controlled polymers such as monodisperse polymers, end-functionalized polymers, and block copolymers, all of which are expected to display new or enhanced properties and thus expanded utility. However, living olefin polymerization is normally conducted at very low to subambient temperatures to reduce the rates of chain termination and transfer reactions, and accordingly, low activities and relatively low molecular weights are typically observed. In addition, it is generally difficult to polymerize α-olefins in a living fashion with control of polymer stereochemistry.

Enormous advances in the rational design and synthesis of well-defined transition-metal complexes for olefin polymerization[1] have spurred the development of quite a few high-performance catalysts for the living polymerization of ethylene, propylene, 1-hexene, and others at relatively high temperatures.[2−15] For instance, Brookhart et al. developed Ni and Pd complexes with diimine ligands that initiate living polymerization of

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ethylene, propylene, 1-hexene, etc. and produce α-olefin-based block copolymers.[3,4] Alternatively, McConville,[5] Schrock,[6] and Kim[7] described Ti and Zr complexes featuring diamide-based ligands that form nearly monodisperse atactic poly(1-hexene)s at ambient temperatures. Additionally, Sita et al. reported on Zr complexes containing amidinate donors that are capable of combining living enchainment of 1-hexene and vinylcyclohexane with the control of polymer stereochemistry to create isotactic poly(1-hexene)s and poly(vinylcyclohexane)s.[8] Moreover, Kol and Goldschmidt described Zr complexes containing phenoxy−amine ligands that generate isotactic poly(1-hexene)s with narrow polydispersity.[9] Very recently, Shiono et al. reported that [^{t}BuNSiMe$_2$Flu]TiMe$_2$ combined with dried methylalumoxane (MAO) produced prevailingly syndiotactic polypropylene (sPP; *rr* 63%).[10d] There are, however, a limited number of examples of catalysts that polymerize propylene in a living fashion at elevated temperatures such as above room temperature. Moreover, highly stereospecific living polymerization of propylene has not yet been achieved, despite the fact that nearly perfect stereospecific nonliving propylene polymerization has been performed with appropriately designed group 4 metallocene catalysts.[16] Consequently, there are crucial goals still remaining in the field of the living polymerization of propylene.

Previously, based on ligand-oriented catalyst design research focusing on nonsymmetric [O, N], [N, N], and [O, O] chelate ligands,[13,17,18] we found a new family of group 4 transition-metal complexes featuring phenoxy−imine chelate ligands, named FI Catalysts.[19,20] FI Catalysts on activation with MAO or ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ exhibit unique catalytic properties for polymerization of ethylene and/or α-olefins, including higher α-olefins and dienes. For example, Zr-FI Catalysts are capable of producing vinyl-terminated low molecular weight polyethylenes (PEs)[20j] and ultrahigh molecular weight ethylene/propylene copolymers with high efficiency.[20k] In addition, Ti-FI Catalysts favor 2,1-insertion of 1-hexene and form high molecular weight atactic poly(1-hexene)s with ca. 50 mol % regioirregular units.[20d] Surprisingly, fluorinated Ti-FI Catalysts are capable of mediating highly controlled living ethylene polymerization at a high temperature of 50 °C by the attractive interaction between the ligand and a growing polymer chain.[21] Furthermore, we discovered that these fluorinated Ti-FI Catalysts can be catalysts for the living and, at the same time, highly syndiospecific polymerization of propylene, as introduced in our patent filed in January 2000 and a series of subsequent papers.[19b,22] Thus, fluorinated Ti-FI Catalysts are the first examples of olefin polymerization catalysts capable of initiating the living polymerization of both ethylene and propylene, allowing the synthesis of a variety of block copolymers such as PE-*b*-poly(ethylene-*co*-propylene), PE-*b*-poly(ethylene-*co*-propylene)-*b*-PE, sPP-*b*-poly(ethylene-*co*-propylene), PE-*b*-sPP, and PE-*b*-poly(ethylene-*co*-propylene)-*b*-sPP. Many of these block copolymers are previously unobtainable from conventional

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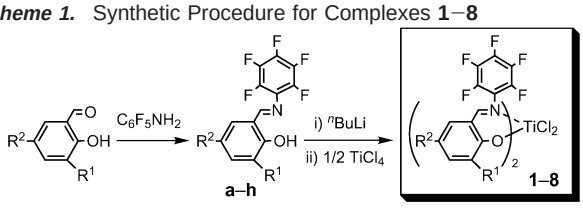
Ziegler−Natta catalysis. Recently, Coates et al. have worked on Ti-FI Catalysts, and based on combinatorial methods, they have independently obtained a modified Ti-FI Catalyst that forms highly syndiotactic polypropylene with narrow MWD and makes sPP-*b*-poly(ethylene-*co*-propylene) and sPP-*b*-poly(methylenecyclopentane-*co*-vinyl tetramethylene).[23] Therefore, FI catalysts and related early-transition-metal complexes have been the subject of active investigation due to their high potential as olefin polymerization catalysts that produce unique polymers.[24]

In this report, we describe the detailed catalytic behavior of Ti complexes with fluorine-containing phenoxy−imine chelate ligands (fluorinated Ti-FI Catalysts) for the polymerization of propylene. These complexes are capable of promoting chain-end controlled, thermally robust, living propylene polymerization via a 2,1-insertion and produce highly syndiotactic nearly monodisperse polypropylenes with very high peak melting temperatures.

Results and Discussion

Syntheses and X-ray Analyses of Titanium Complexes Having Fluorine-Containing Phenoxy−Imine Chelate Ligands. A general preparation route to titanium complexes utilized in this study is shown in Scheme 1. The fluorine-containing phenoxy−imine ligands of structures **a**−**h** were conveniently synthesized in high yields by the Schiff base condensation of the appropriate aniline and salicylaldehyde derivatives. The titanium complexes **1**−**8** were obtained in moderate to good yields by the reaction of $TiCl_4$ with 2 equiv of the lithium salt of the corresponding phenoxy−imine ligands.

Scheme 1. Synthetic Procedure for Complexes **1**−**8**



R^1:	^{t}Bu	^{t}Bu	^{t}Bu	$SiMe_3$	$SiEt_3$	H	Me	^{i}Pr
R^2:	H	^{t}Bu	Me	H	H	H	H	H
ligand	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
complex	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**

Complexes **4** and **6** were analyzed by single-crystal X-ray diffraction. The molecular structures are depicted in Figures 1 and 2; selected bond distances and angles are presented in Table 1, which also includes those for complex **1** as a comparison. Both complexes **4** and **6** possess six-coordinate Ti metal centers in an approximately octahedral structure with a *trans*-O, *cis*-N, and *cis*-Cl disposition, which is the same as that of complex **1**. Thus, complexes **4** and **6**, in addition to complex **1**, are revealed to have structures with approximate C_2 symmetry.

The bond distances of Ti−N (2.268, 2.253 Å) and Ti−O (1.860, 1.854 Å) for complex **4** are slightly longer compared with those for complex **1** (Ti−N, 2.234, 2.217 Å; Ti−O, 1.841, 1.845 Å). These facts suggest that the electron donation from the phenoxy−imine ligand to the Ti center is reduced by the introduction of a trimethylsilyl group in the place of the *tert*-

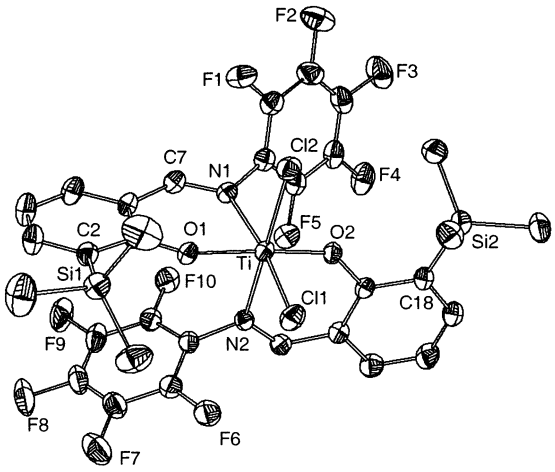


Figure 1. Molecular structure of complex **4** with thermal ellipsoids at 50% probability level.

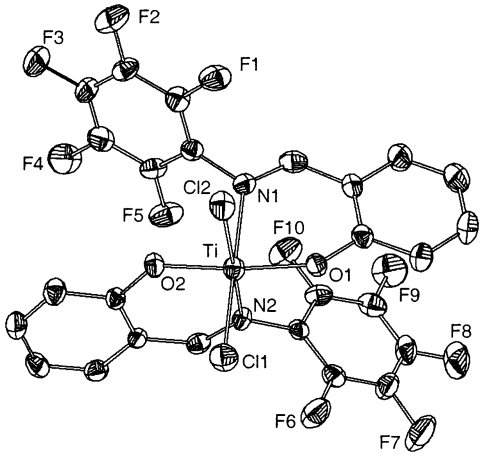


Figure 2. Molecular structure of complex **6** with thermal ellipsoids at 40% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **4**, and **6**

	1	**4**	**6**
	Distances		
Ti−Cl(1)	2.2876(7)	2.245(1)	2.253(2)
Ti−Cl(2)	2.2578(8)	2.284(1)	2.297(2)
Ti−O(1)	1.841(1)	1.860(2)	1.840(3)
Ti−O(2)	1.845(1)	1.854(2)	1.859(3)
Ti−N(1)	2.234(2)	2.268(3)	2.265(4)
Ti−N(2)	2.217(2)	2.253(3)	2.213(4)
Si(1)−C(2)		1.893(4)	
Si(2)−C(18)		1.890(4)	
	Angles		
Cl(1)−Ti−Cl(2)	96.42(3)	99.19(4)	96.49(7)
O(1)−Ti−O(2)	163.61(6)	165.6(1)	162.1(2)
N(1)−Ti−N(2)	86.94(7)	85.30(10)	88.0(1)

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(24) For example: (a) Corden, J. P.; Errington, W.; Moore, P.; Wallbridge, M. G. H. *Chem. Commun.* **1999**, 323−324. (b) Woodman, P. R.; Munslow, I. J.; Hitchcock, P. B.; Scott, P. K. *J. Chem. Soc., Dalton Trans.* **1999**, 4069−4076. (c) Strauch, J.; Warren, T. H.; Erker, G.; Frohlich, R.; Saarenketo, P. *Inorg. Chim. Acta* **2000**, *300*−*302*, 810−821. (d) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2000**, 1969−1972. (e) Emslie, D. J. H.; Piers, W. E.; MacDonald, R. *J. Chem. Soc., Dalton Trans.* **2002**, 293−294. (f) Knight, P. D.; Clarke, A. J.; Kimberley, B. S.; Jackson, R. A.; Scott, P. *Chem. Commun.* **2002**, 352−353. (g) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038−1039.

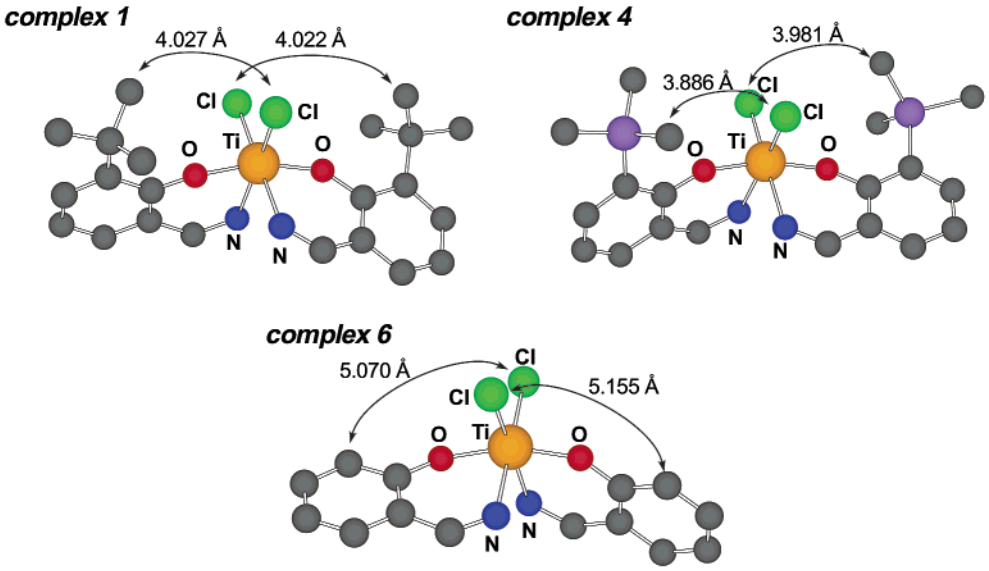

Figure 3. Top views of X-ray structures for complexes **1**, **4**, and **6** and distances between chlorine atoms and nearest carbon atoms in the ligands. The pentafluorophenyl groups are omitted for clarity.

butyl group, probably due to less electron-donating nature of the trimethylsilyl group relative to the *tert*-butyl group.

To compare the steric congestion of complexes **1**, **4**, and **6** in close proximity to the chlorine-bound sites (potential polymerization sites), the top views of the complexes and the distances between a chlorine atom and its nearest carbon atom in the ligand are shown in Figure 3. The distances for complex **6** (5.070, 5.155 Å) are much longer than those for complex **1** (4.027, 4.022 Å) and complex **4** (3.886, 3.981 Å). Therefore, among the complexes complex **6** probably has the most open structure of the catalyst active site, followed by complex **1** and complex **4**. These structural differences among complexes **1**, **4**, and **6** may influence their catalytic behavior for olefin polymerization.

Propylene Polymerization Behavior of Complex 1. As reported, the complex **1**/methylalumoxane (MAO) catalyst system is capable of initiating highly controlled living ethylene polymerization by the unique interaction of a fluorine ortho to the imine nitrogen with a β-hydrogen of a growing polymer chain and produces high molecular weight polyethylenes (M_n > 400 000) with extremely narrow molecular weight distributions (M_w/M_n < 1.2). We reasoned that the interaction may be extended to the living polymerization of propylene because a growing polypropylene chain also possesses a β-hydrogen. Indeed, DFT calculations indicate that the ortho-fluorine of an active species generated from **1**, for propylene polymerization, interacts with a β-hydrogen of a growing polypropylene chain (polymer chain models: *sec*-butyl and isobutyl) derived either from 1,2-insertion or 2,1-insertion[25] (1,2-insertion, ortho F−H_β distance 2.251 Å, electrostatic energy −46.8 kJ/mol; 2,1-insertion, ortho F−H_β distance 2.262 Å, electrostatic energy −30.7 kJ/mol; for ethylene polymerization, ortho F−H_β distance 2.276 Å, electrostatic energy −27.1 kJ/mol), suggesting that **1** may also exhibit living behavior for propylene polymerization. A single-crystal X-ray analysis revealed that complex **1** has a six-coordinate center in a distorted octahedral geometry with a *trans*-O, *cis*-N, and *cis*-Cl arrangement and thus possesses approximate C_2 symmetry. This molecular structure implies that **1** combines living enchainment with isospecific control of polymer stereochemistry.

Table 2. Results of Propylene Polymerization with Complex **1**/MAO[a]

entry	P (MPa)	T (°C)	time (h)	yield (g)	TOF[b] (h^{-1})	M_n[c] ($\times 10^3$)	M_w/M_n[c]	T_m[d] (°C)
1	0.1	25	3	0.096	76	20.5	1.09	137
2	0.1	25	5	0.183	87	28.5	1.11	137
3	0.1	0	5	0.144	68	23.6	1.05	136
4	0.1	50	5	0.148	70	16.4	1.37	130
5	0.6	25	1	0.158	375	30.9	1.07	135
6	0.6	25	2	0.312	371	52.8	1.10	
7	0.6	25	3	0.460	364	73.8	1.10	135
8	0.6	25	5	0.713	339	108.0	1.14	135

[a] Conditions: complex **1** (10 μmol), cocat. MAO (2.5 mmol). [b] Turnover frequency. [c] Determined by GPC using polypropylene calibration. [d] Melting temperature of produced PP determined by DSC.

Propylene polymerization behavior of complex **1** was investigated with MAO cocatalyst in toluene solvent. The results are collected in Table 2. The activities of complex **1** under 0.1 MPa of propylene are moderate (TOF 68−87 h^{-1}) and much lower than those observed with ethylene polymerization. This may be attributed to the stronger binding of propylene to the electrophilic Ti center and the larger molecular size of propylene compared to ethylene, impeding the rate of chain growth relative to that of ethylene polymerization. GPC analyses revealed that the polypropylenes produced under 0.1 MPa of propylene at 25 °C (Table 2, entries 1, 2) possess extremely narrow molecular weight distributions (M_w/M_n 1.09, 1.11), suggesting that complex **1**/MAO catalyst system may have the characteristics of a living propylene polymerization under the given conditions.

To gain further insight into propylene polymerization behavior of the catalyst system, M_n and M_w/M_n values−polymerization time relationships were plotted for the polymerization conducted under 0.6 MPa of propylene at 25 °C (Table 2, entries 5−8).

(25) For detailed results, see the Supporting Information. Significantly, Chan et al. have recently reported the first NMR and X-ray structural evidence for an attractive interaction between a fluorine in the ligand and a hydrogen on a benzyl group attached to the central metal for group 4 transition-metal complexes, potentially indicating the generality of the attractive interaction between the functionalized ligand and the polymer chain. Kui, S. C. F.; Zhu, N.; Chan, M. C. W. *Angew. Chem., Int. Ed.* In press.

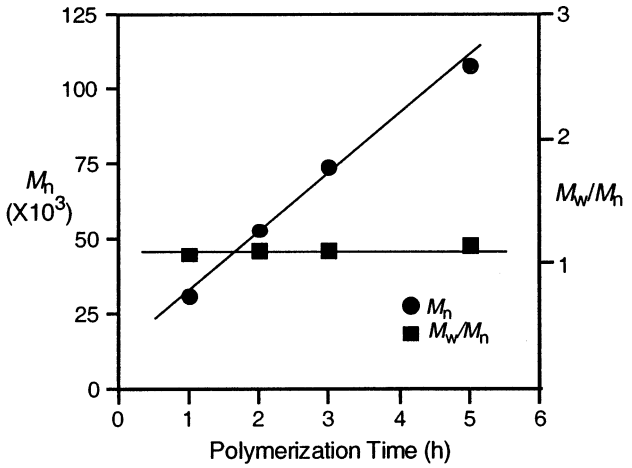

Figure 4. Plots of M_n and M_w/M_n as a function of polymerization time for propylene polymerization with complex **1**/MAO (25 °C, 0.6 MPa).

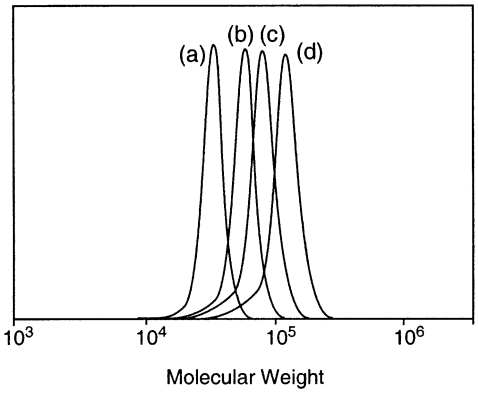

Figure 5. GPC profile of polypropylenes obtained by complex **1**/MAO (25 °C, 0.6 MPa): (a) 1 h, M_n 30 900, M_w/M_n 1.07; (b) 2 h, M_n 52 800, M_w/M_n 1.10; (c) 3 h, M_n 73 800, M_w/M_n 1.10; (d) 5 h, M_n 108 000, M_w/M_n 1.14.

As shown in Figure 4, a linear relationship between M_n and polymerization time as well as narrow M_w/M_n values for all runs (M_w/M_n 1.07−1.14) was found. Moreover, GPC peaks of the produced polypropylene shifted to higher molecular weight region with an increase in polymerization time, retaining unimodal shape during the course of the polymerization (Figure 5). These results clearly show that the propylene polymerization is indeed living. Considering that MAO used as the cocatalyst is a potential chain transfer agent, the room-temperature living propylene polymerization exhibited by complex **1**/MAO is of great significance. Complex **1** is a unique olefin polymerization catalyst capable of inducing the living polymerization of both ethylene and propylene, resulting in the creation of ethylene-based as well as propylene-based block copolymer.[19b,21,22]

With these polymerization results along with the computational studies, the attractive interaction between a fluorine in the ligand and a β-hydrogen of a growing polymer chain is thought to provide a new strategy for the design of living polymerization catalysts. Catalyst efficiency for the polymerization calculated based on polymer yield, catalyst amount, and the molecular weight of the resulting polymer lies in the range of 51−66%. It is worth noting that at 50 °C the catalyst system is capable of producing polypropylene with a fairly narrow molecular weight distribution (M_w/M_n 1.37), as listed in Table 2, entry 4, though chain termination or transfer and/or catalyst deactivation are not negligible at this temperature. The polypropylenes formed from complex **1**/MAO catalyst system exhibited peak melting temperatures (T_m), indicating the formation of stereoregular polymers.

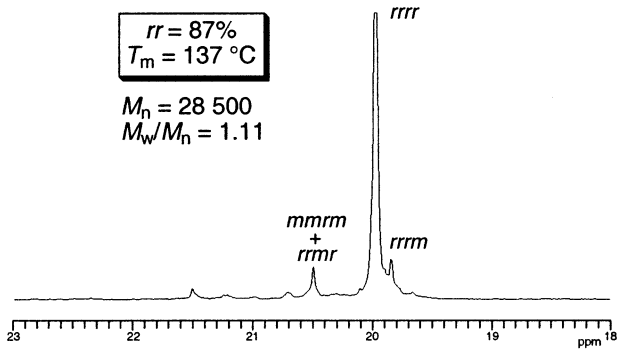

Figure 6. ^{13}C NMR spectra of the highly syndiotactic PP produced by **1**.

Pentad Distribution Analysis and End-Group Analysis of the Polypropylenes Arising from Complex 1/MAO Catalyst System. The nearly monodisperse polypropylene having an M_n value of 28 500 (Table 2, entry 2) displays a peak melting temperature (T_m) of 137 °C, indicative of a high degree of stereocontrol. To our surprise, microstructural analysis using ^{13}C NMR spectroscopy revealed that the polymer is highly syndiotactic polypropylene, which contains 87% *rr* triads. The unexpected formation of syndiotactic polypropylene with complex **1** having C_2 symmetry indicates that the catalyst symmetry is not a rigid requirement for determining polymer stereochemistry. The pentad distribution analysis of the ^{13}C NMR of the syndiotactic polypropylene (Figure 6) shows the presence of single *m* stereodefects, *rrrm* (9.0%) and *rrmr* + *mmrm* (5.6%), as the predominant source of stereoirregularity in the polymer microstructure. These results suggest that the highly syndiospecific polymerization proceeds via a chain-end control mechanism. Complex **1** is unique in its ability to produce a highly stereoregular polymer through a chain-end control mechanism at room temperature since chain-end control operates well at very low to subambient temperatures and rapidly loses its stereoregulating ability at elevated temperatures.[14,26] In fact, the rr triad, 87%, obtained at 25 °C, is exceptionally high for a polypropylene produced by a chain-end control mechanism. On the basis of combinatorial methods, Coates et al. have recently obtained a modified version of complex **1**, which has an additional *tert*-butyl group in the phenoxy−benzene ring[23b] (complex **2**). This complex exhibits a similar catalytic performance compared to complex **1** for living propylene polymerization according to our data.[22d]

Considering that chain-end control is enhanced by 2,1-insertion due to the increased steric influence of the chain-end on enchainment relative to 1,2-insertion[27] and that the complex **1**/^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system is known to prefer 2,1-insertion of 1-hexene, it seems reasonable that the high level of stereoregularity in the polypropylene formed with complex **1** is the result of a 2,1-insertion process.

(26) (a) Pellecchia, C.; Zambelli, A.; Oliva, L.; Pappalardo, D. *Macromolecules* **1996**, *29*, 6990−6993. (b) Pellecchia, C.; Zambelli, A. *Macromol. Rapid Commun.* **1996**, *17*, 333−338. (c) Pellecchia, C.; Zambelli, A.; Mazzeo, M.; Pappalardo, D. *J. Mol. Catal. A* **1998**, *128*, 229−237. (d) Milano, G.; Guerra, G.; Pellecchia, C.; Cavallo, L. *Organometallics* **2000**, *19*, 1343−1349.

(27) Zambelli, A.; Allegra, G. *Macromolecules* **1980**, *13*, 42−49 and references therein.

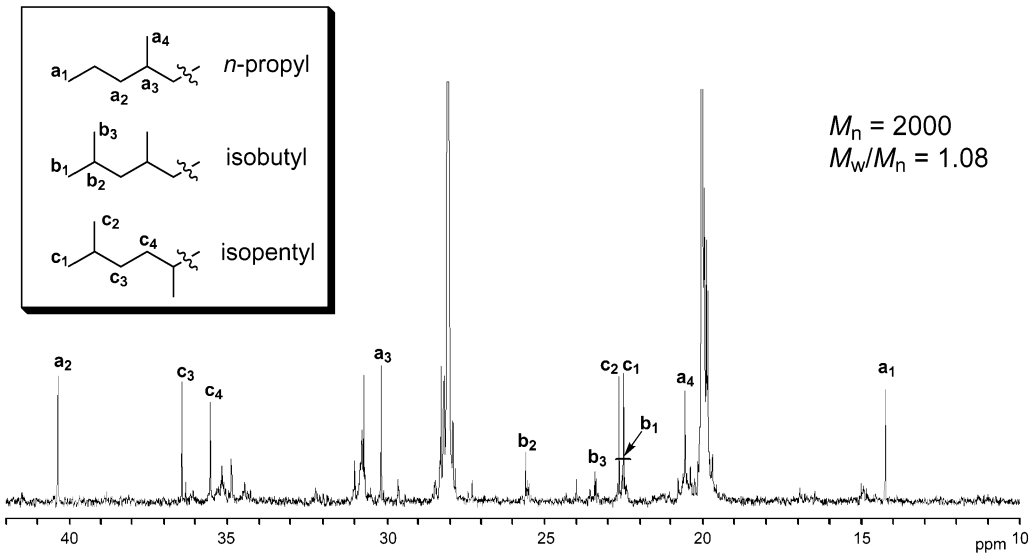

Figure 7. Chain-end analysis of low molecular weight syndiotactic PP produced by **1**.

To obtain information on mechanistic details, ^{13}C NMR analysis of low M_n syndiotactic polypropylene (M_n 2000, M_w/M_n 1.08)[28a] was performed. Figure 7 shows the ^{13}C NMR spectrum of the low M_n polypropylene, which exhibits peaks at 14.2, 20.6, 22.4−22.8, 23.3−23.6, 25.6, 30.2, 35.5, 36.5, and 40.4 ppm relating to chain-end structures in addition to three major sets of peaks derived from the main chain carbons.

The following assignments are based on a comparison with literature data.[29] The peaks at 14.2 and 23.3−23.6 ppm were assigned to the methyl carbons of *n*-propyl and isobutyl chain-end groups, respectively. Additionally, the peaks at 22.4−22.8 ppm were attributed to the methyl carbons of isobutyl and isopentyl chain-end groups. Regarding the CH and CH_2 carbons associated with chain-end groups, the peaks at 35.5 and 36.5 ppm and 25.6 ppm were assigned to the $S_{\alpha\beta}$ CH_2 carbon of isopentyl chain-end group and the CH carbon of isobutyl chain-end group, respectively. These results further confirmed the presence of isopentyl and isobutyl chain-end groups. Thus, the polypropylene contains three kinds of chain-end groups: *n*-propyl, isobutyl, and isopropyl groups. No peaks assignable to other possible chain-end groups, namely ethyl, *n*-butyl, *sec*-butyl, and isopropyl groups, were observed in the NMR spectrum.

The mechanism for the formation of possible chain-end groups is summarized in Scheme 2. On the basis of the peak intensities of the methyl carbons, the amounts of the above-mentioned chain-end groups are suggested to be 1.6 mol % (*n*-propyl group, a termination chain-end, 34.8%), 1.5 mol % (isobutyl group, an initiation or a termination chain-end, 32.6%), and 1.5 mol % (isopentyl group, an initiation chain-end, 32.6%), respectively.

If the first propylene is enchained by a 2,1-insertion, the resulting polymer possesses an ethyl or a *sec*-butyl chain-end group. However, no ethyl or a *sec*-butyl chain-end group is found in the polypropylene. This indicates unambiguously that the first propylene is inserted into the Ti−Me bond of an initial active species derived from complex **1** and MAO in a 1,2-fashion. On the other hand, the ratio of the isopentyl group (an initiation chain-end; 32.6%) and the isobutyl group derived from initiation chain-end (15.2%; estimated based on the amount of the isopentyl group) is 70 to 30. In addition, the amount of the *n*-propyl chain-end group is 34.8%, which is the termination chain-end derived from the termination after two consecutive 2,1-insertions, and the amount of the isobutyl group originating from termination chain-end is 17.4%, which is the termination chain-end derived from the termination after two consecutive 1,2-insertions. These results suggest that 2,1-insertion is predominant for chain propagation (ca. 70%). The absence of *n*-butyl and isopropyl chain-end groups, which originate from the termination after 1,2−2,1- or 2,1−1,2-insertion, may indicate that the polymer has a blocklike structure consisting of consecutive 2,1-insertion and 1,2-insertion segments (regio-block structure). Moreover, the syndiotactic polypropylenes having M_ns of 3300 (M_w/M_n 1.08)[28b] and 9700 (M_w/M_n 1.05)[28c] also possess isopentyl, *n*-propyl, and isobutyl chain-end groups with practically the same content as the living polypropylene described above (M_n 2000), indicating that chain-end structures are independent of polymer molecular weights. These facts further confirm the chain propagation mechanism discussed above. Therefore, the propylene polymerization was demonstrated to be initiated exclusively by a 1,2-insertion, followed by a 2,1-insertion (ca. 70%) as the principal mode of polymerization. To our knowledge, this is the first example of a predominant 2,1-insertion mechanism for chain propagation displayed by a group 4 metal-based catalyst,[22c] though V- and Fe-based catalysts are known to prefer 2,1-insertion of propylene.[29d,30] Predominant 2,1-insertion may be derived from the steric congestion near the polymerization reaction center, which places the methyl of the reacting propylene in the opposite direction from a polymer chain. Recently, the generality of this highly unusual and unprecedented mechanism of insertion in

(28) Polymerization conditions: (a) cat. **1** (100 μmol), MAO (5 mmol), 25 °C, 15 min; (b) cat. **1** (100 μmol), MAO (5 mmol), 25 °C, 30 min; (c) cat. **1** (30 μmol), MAO (5 mmol), 25 °C, 90 min.

(29) (a) Corradini, P.; Guerra, G.; Pucciariello, R. *Macromolecules* **1985**, *18*, 2030−2034. (b) Chen, H. N.; Bennett, M. A. *Macromol. Chem.* **1987**, *188*, 135−148. (c) Hagiwara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1997**, *30*, 4783−4785. (d) Zambelli, A.; Sessa, I.; Grisi, F.; Fusco, R.; Accomazzi, P. *Macromol. Rapid Commun.* **2001**, *22*, 297−310.

(30) (a) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120−2130. (b) Pellecchia, C.; Mazzeo, M.; Pappalardo, D. *Macromol. Rapid Commun.* **1998**, *19*, 651−655.

Scheme 2. Mechanism of Initiation and Chain Propagation for Propylene Polymerization Using Complex **1**

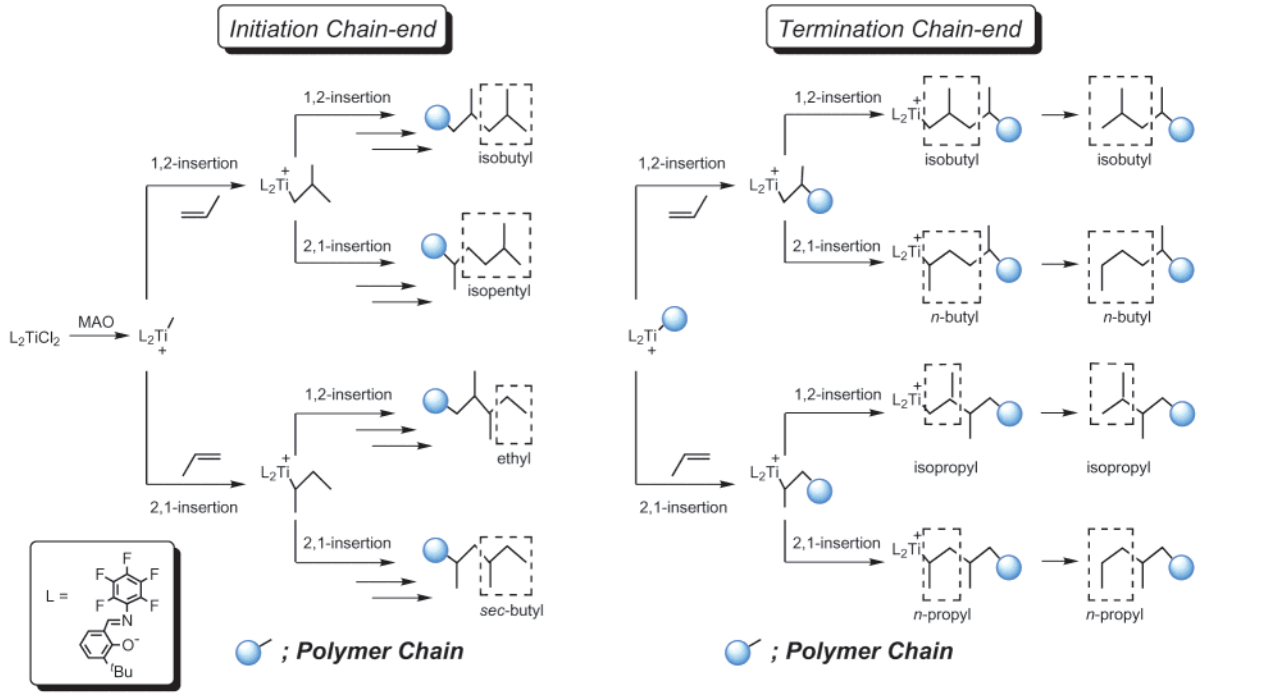

Table 3. Results of Propylene Polymerization with Complexes **2**−**8**/MAO[a]

entry	complex	*T* (°C)	yield (g)	TOF[b] (h^{-1})	M_n[c] ($\times 10^3$)	M_w/M_n[c]	T_m[d] (°C)
1	**2**	0	0.109	52	19.2	1.05	141
2	**2**	25	0.219	104	29.8	1.15	135
3	**2**	50	0.263	125	31.3	3.19	127
4	**3**	0	0.101	48	16.8	1.04	143
5	**3**	25	0.115	55	16.5	1.11	140
6	**3**	50	0.114	54	15.7	1.48	124
7	**4**	0	0.151	72	24.7	1.08	156
8	**4**	25	0.293	139	47.0	1.08	152
9	**4**	50	0.237	113	35.1	1.23	149
10	**5**	0	0.089	42	11.9	1.08	152
11	**5**	25	0.174	83	24.4	1.16	151
12	**5**	50	0.132	63	20.4	1.23	148
13	**6**	25	1.534	729	189.0	1.51	nd[e]
14	**7**	25	3.440	1635	260.2	1.22	nd[e]
15	**8**	25	1.555	739	153.7	1.16	nd[e]

[a] Conditions: complex (10 μmol), cocat. MAO (2.5 mmol), 0.1 MPa, 5 h. [b] Turnover frequency. [c] Determined by GPC using polypropylene calibration. [d] Melting temperature of produced PP determined by DSC. [e] Not detected.

propylene polymerization with Ti-FI Catalysts has been confirmed by Pellecchia[31] and Coates.[23c] More recently, Talarico, Cavallo, and Busico have reported[32] that based on a theoretical approach a 1,2-insertion is slightly favored for a 1,2-inserted polymer chain, whereas a 2,1-insertion is preferred for a 2,1-inserted polymer chain, which is consistent with our experimental data.

The Effects of Ligand Structures on Catalytic Behavior and Polymer Microstructures. To examine the effects of substitutions on the phenoxy−imine ligands on catalytic performance of the resulting complexes and on the microstructures

(31) Lamberti, M.; Pappalardo, D.; Zambelli, A.; Pellecchia, C. *Macromolecules* **2002**, *35*, 658−663.
(32) (a) Cavallo, L.; Talarico, G. *Natl. Meet.-Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng.* **2002**, *87*, 38. (b) Talarico, G.; Busico, V.; Cipullo, R.; Cavallo, L. *Proceedings of the 1st Blue Sky Conference on Catalytic Olefin Polymerization*, Sorrento, Italy, June 20−21, 2002.

Table 4. Microstructural Analysis of PP Obtained by Complexes **1**, **2**, **4**, **6**−**8**/MAO

				microstructural data					
entry	complex	*T* (°C)	T_m[a] (°C)	rr (%)	mr (%)	mm (%)	H–T (%)	H–H (%)	T–T (%)
1	**1**	25	137	87	10	3	92	4	4
2	**2**	25	135	86	10	4	89	4	7
3	**4**	0	156	94	4	2	94	3	3
4	**4**	25	152	93	4	3	94	3	3
5	**4**	50	149	90	7	3	90	6	4
6	**6**	25	nd[b]	43	46	11	81	10	9
7	**7**	25	nd[b]	50	42	8	85	9	7
8	**8**	25	nd[b]	75	22	3	84	8	8

[a] Melting temperature of produced PP determined by DSC. [b] Not detected.

of the produced polymers, the propylene polymerization ability of complexes **2**−**8** having a series of substituents at the R^1 and R^2 positions was investigated. Propylene polymerizations were conducted under atmospheric pressure using MAO as a cocatalyst. The polymerization results are tabulated in Table 3, and the data for ^{13}C NMR microstructural analyses of the produced polypropylenes are summarized in Table 4.

Regarding the R^2 position, the data indicated that the R^2 substituent had no significant effect on the catalytic performance of the complexes, probably because the R^2 position is far from the active site. Thus, complexes **2** (R^2 = *tert*-butyl) and **3** (R^2 = methyl) exhibited similar catalytic properties to complex **1** (R^2 = H) and produced nearly monodisperse syndiotactic polypropylenes with T_ms ranging from 141 to 127 °C (complex **2**) and 143 to 124 °C (complex **3**) over a temperature range of 0−50 °C. At 50 °C, complexes **2** and **3** generated polypropylenes with broadened molecular weight distributions the same as complex **1** (M_w/M_n: **1**, 1.37; **2**, 3.19; **3**, 1.48), suggesting that chain termination or transfer and/or catalyst deactivation are not negligible for these complexes at this temperature.

It was revealed that the R^1 substituent significantly affected the catalytic properties of the complexes. Complex **4** bearing a

trimethylsilyl at the R^1 position yielded (at 25 °C) highly syndiotactic narrow MWD polypropylene (M_w/M_n 1.08, *rr* 93%) with an extremely high T_m of 152 °C. Likewise, complex **5** (R^1 = triethylsilyl) produced highly syndiotactic polypropylene with a very high T_m (151 °C). The pentad distribution analysis revealed that the syndiospecific polymerizations proceed via a chain-end control mechanism. Such an extremely high level of chain-end control at room temperature is unprecedented in a propylene polymerization. The syndiotactic polypropylene produced by complex **4** at 0 °C displayed an exceptionally high T_m of 156 °C (*rr* 94%), which represents one of the highest T_m values among syndiotactic polypropylenes ever known.[33] Remarkably, at 50 °C, complexes **4** and **5** furnished syndiotactic polypropylenes with very high T_ms of 149 and 148 °C, respectively. These are of great significance because generally, as described, chain-end control works well at very low to subambient temperatures and rapidly loses its stereoregulating capability at elevated temperatures.

The reduction in the steric bulk of the R^1 substituent resulted in the enhancement in catalytic activity and, interestingly, marked decrease in polymer stereoregularity, producing amorphous polypropylenes. Complex **8**, bearing an isopropyl group at the R^1 position, formed polypropylene having lower syndiotacticity (*rr* 75%) with a much higher TOF of 739 h^{-1}, which is a factor of ca. 8 higher than that of complex **1**. The effect of the steric bulk of the R^1 substituent was more pronounced for complex **7** having a methyl, which exhibited a far higher TOF of 1635 h^{-1} and produced polypropylene possessing still lower syndiotacticity (*rr* 50%). The enhanced activities probably result from the structurally open nature of the complexes. Complex **6** with a hydrogen at the R^1 position displayed a lower TOF of 729 h^{-1} compared to complex **7** (R^1 = methyl) and formed amorphous polypropylenes (*rr* 43%) with a broadened molecular weight distribution. The lower activity and broadened molecular weight distribution value displayed by complex **6** (R^1 = H) are probably ascribed to the catalyst decay due to the extremely reduced steric bulk of the R^1 substituent, which provides steric protection to the phenoxy oxygen from the attack of aluminum species in the reaction medium.

The decisive role of the R^1 substituent in realizing the highly syndiospecific polymerization indicated that the R^1 substituent is situated in close proximity to the active site, and the R^1 substituent can have steric repulsion against the methyl of the reacting propylene, leading to syndiospecific polymerization. In fact, a correlation exists between the syndioselectivity and the size of the R^1 substituent. The plots of *rr* triad values vs the size of the R^1 substituent[34] are displayed in Figure 8, where a linear relationship was found. These results further confirmed that the steric bulk of the R^1 substituent controls the syndioselectivity of the polymerization. The Ti complexes are unique in their ability to form chain-end-controlled stereoregular polymers whose stereoregularity is governed by their ligand structures, and thus the way of controlling the stereoselectivity is similar to that for a site-control mechanism.

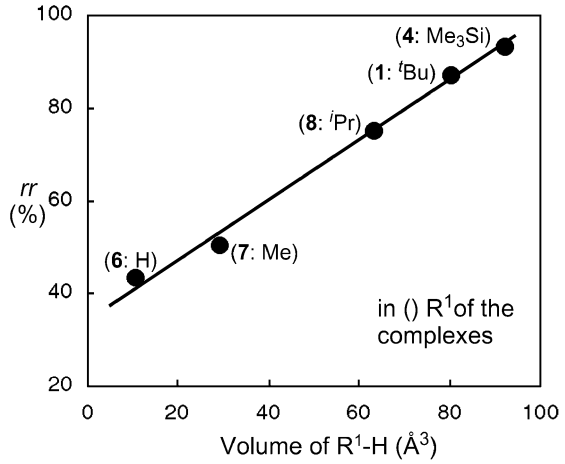

Figure 8. Plots of *rr* triad values as a function of calculated R^1−H volume for propylene polymerization with complexes **1**, **4**, **6**−**8**/MAO (25 °C, 5 h).

Propylene polymerization governed by a chain-end control typically gives low to moderate tacticity polypropylenes, and changing the ligand structure of a catalyst can have influence on tacticity but not significantly. However, the Ti complexes introduced herein are capable of promoting highly syndiospecific propylene polymerizations. Moreover, the ligand structure has a dramatic effect on tacticity, and the sterically bulky substituent ortho to the phenoxy oxygen results in highly stereospecific, thermally robust, chain-end controlled living propylene polymerization. Therefore, we have given the name "ligand-directed chain-end control" to this highly controlled polymerization that enables us to have highly syndiotactic polypropylenes with extremely high T_ms.

The regiochemistry of the polypropylenes produced with these complexes was investigated on the basis of the ^{13}C NMR peaks in the regions of 13−18 and 30−45 ppm, attributable to regioirregular units (Table 4 and Figure 9).[35] The data revealed that the polypropylenes formed with the Ti complexes contain a considerable amount of regioirregularly arranged propylene units (regioinversion: **1**, 8%; **4**, 6%; Table 4, entries 1 and 4) in marked contrast to the syndiotactic polypropylene obtained with the Ewen-type *ansa*-metallocene Ph_2C(Cp, 2,7-di-^{t}Bu-Flu)-$ZrCl_2$ (complex **9**, regioinversion 1%).[36] Although V- and Ni-based catalysts are known to polymerize propylene in a syndiotactic fashion with significant regioinversion, these are rare examples of group 4 metal-based catalysts that produce syndiotactic polypropylenes with considerable regioirregular units.

Further analyses of the spectra indicate that the polypropylenes arising from the Ti complexes possess blocklike structures, which are classified into two types; one involves consecutive regioirregular units (type I, Figure 10) and the other includes isolated regioirregular units (type II, Figure 10). Thus, the syndiotactic polypropylenes, formed from complexes **1** and **4**, with a significant amount of regioirregular units possess a blocklike structure involving long regioregular units and short consecutive-regioirregular units (type I). On the other hand, the

(33) (a) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573. (b) Grisi, F.; Longo, P.; Zambelli, A.; Ewen, J. A. *J. Mol. Catal. A* **1999**, *140*, 225−233.

(34) A volume of substituent was calculated as follows. The geometry of the substituent, which is capped with a hydrogen atom, was optimized using the 6-311G(d, p) basis set at the Hartree−Fock level, and its volume was calculated on the basis of the van der Waals radii of each atom. The geometry and its volume was calculated using the Spartan'02 program (Spartan'02, Wavefunction, Inc. Irvine, CA).

(35) The percentage of regioinversion units (H−H, T−T) is calculated on the basis of NMR peak integrals: H−T, 27.0−29.5 ppm ($T_{\beta\beta}$); H−H, 14.0−18.0 ppm ($P_{\alpha\beta}$); T−T, 30.5−31.5 ppm ($T_{\beta\gamma}$).

(36) The polymer was synthesized under the same conditions (25 °C): M_n, 159.7 × 10^3; M_w/M_n, 1.86; T_m, 148 °C; rr/mr/mm (%), 95/4/1; H−T/H−H/T−T (%), 99/1/0.

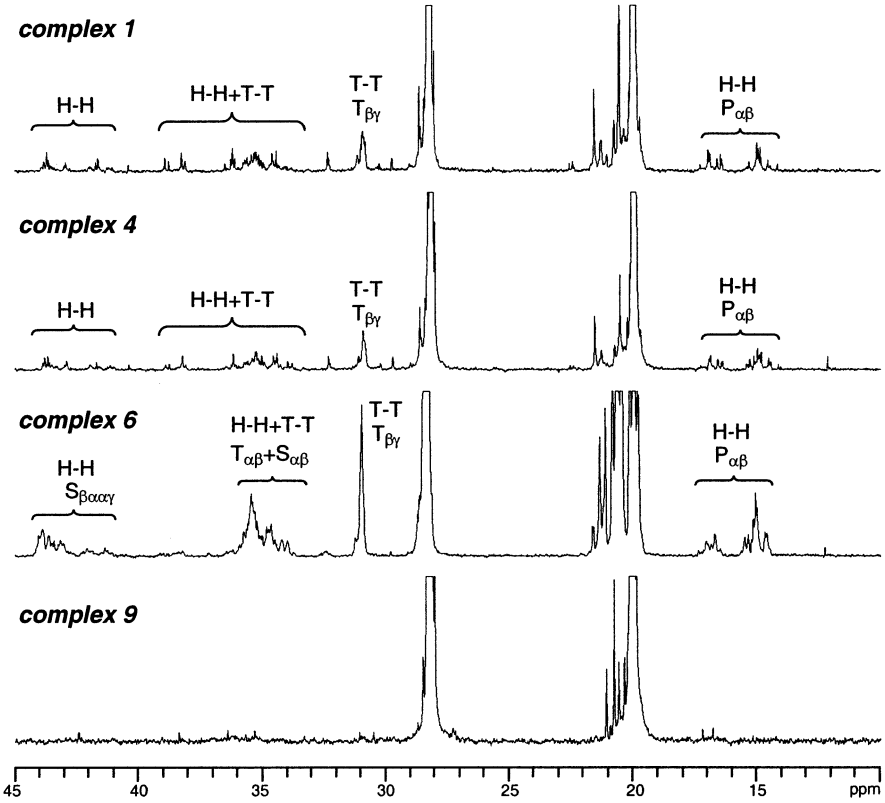

Figure 9. ^{13}C NMR spectrum of PPs obtained by complexes **1**, **4**, **6**, and **9** at 25 °C.

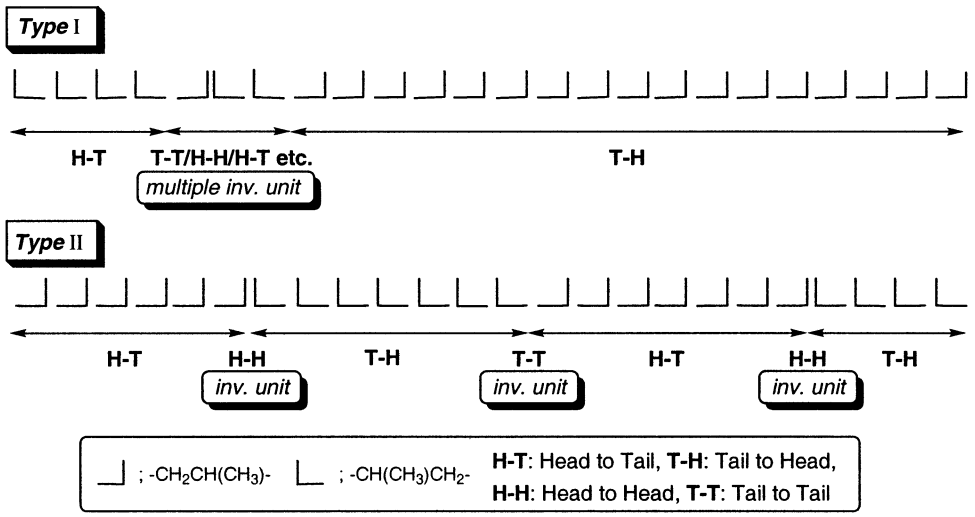

Figure 10. Regiosequence patterns of PPs obtained by fluorinated Ti-FI Catalysts.

syndiotactic-rich polypropylenes, produced with complexes **6**−**8** (see the Supporting Information for the ^{13}C NMR spectra of the polypropylenes formed with complexes **7** and **8**), with a higher amount of regioirregular units, also have a blocklike structure, but it contains relatively short regioregular units and isolated regioirregular units (type II). Therefore, the polypropylenes obtained with the Ti complexes are revealed to possess unique molecular architectures.

It is noted that the T_ms of syndiotactic polypropylenes formed with the Ti complexes are higher than the values expected from the syndiotacticity of the polymers obtained with metallocene catalysts. For example, the syndiotactic polypropylene containing 95% *rr* triads, formed with complex **9**, displays a T_m of 148 °C under the same DSC measurement conditions. The differences in T_m probably originate from the blocklike structures of the polymers arising from the Ti complexes.

The Origin of Syndioselectivity. On the basis of the C_2 symmetric structures of the Ti complexes **1**, **4**, and **6** demonstrated by X-ray analyses, the Ti complexes were initially targeted as living polymerization catalysts capable of forming isotactic polypropylenes via an enantiomorphic site control mechanism, as described. Consequently, the production of the syndiotactic polypropylenes was unexpected and surprising. The unexpected production of the syndiotactic polypropylenes deserves investigation.

The results discussed herein show that the Ti complexes promote chain-end controlled, syndiospecific propylene polymerization via a 2,1-insertion mechanism and that the steric bulk

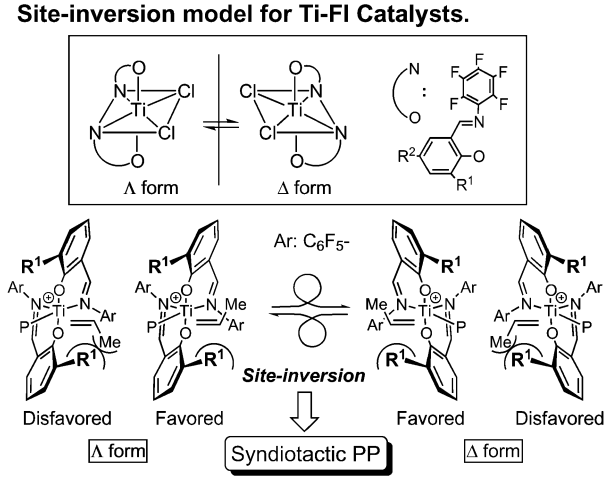

Figure 11. Proposed mechanism for syndiospecific propylene polymerization catalyzed by Ti-FI Catalysts.

of the substituent ortho to the phenoxy oxygen plays a pivotal role in determining the syndioselectivity of the polymerization.

It should be pointed out that the principal behavior of the Ti complexes for propylene polymerization (chain-end controlled syndiospecific polymerization via a 2,1-insertion) is the same as that of V-based catalysts, though the V-based catalysts suffer from low stereoselectivity. There may be a similarity between the polymerization mechanisms displayed by the Ti and V catalysts. In fact, recently, on the basis of a QM/MM theoretical study, Cavallo and Pellecchia have proposed a site-inversion mechanism[37,38] (Figure 11), which was originally introduced for the explanation of syndiospecific propylene polymerization exhibited by V-based catalysts. The bottom line of the proposed mechanism is that a site-inversion between diastereomeric Λ and Δ configurations, which may occur via a five-coordinate Ti cationic species, is much faster than propylene insertion. According to the proposed mechanism, the octahedral active species undergoes fluxional isomerization between Λ and Δ forms governed by the stereochemistry of α-carbon in the last-inserted propylene unit. Thus, propylene insertion to the Ti−alkyl bond of a cationic species with Λ configuration, having a lower energy than that with Δ configuration, leads to a new cationic species with Δ configuration, which undergoes a site-inversion to form a cationic species with Λ configuration prior to propylene insertion.

Assuming that the site-inversion is operating in the propylene polymerization and the catalytically active species possesses an octahedral geometry with a *trans*-O and *cis*-N disposition,[39] the steric bulk of the substituent ortho to the phenoxy oxygen should have profound effects on the syndioselectivity of the polymerization, which is exactly what we observed (Figure 8). In addition, the highly syndiospecific and thermally robust behavior of the catalyst can also be explained by the proposed mechanism, because stereoselectivity is virtually governed by the ligand structure. Thus, the predicted catalytic behavior derived from the site-inversion mechanism and our experimental results (ligand-directed chain-end control) match well. Therefore, the site-inversion mechanism is most probable and reasonable for the unexpected formation of highly syndiotactic polypropylenes at the present time.

The site-inversion mechanism gives the idea that if propylene insertion is faster than the site-inversion, a Ti complex with a sterically hindered substituent ortho to the phenoxy oxygen can be a catalyst for the highly isospecific polymerization of propylene. Reduction in the site-inversion rate may be achieved by ligand modifications such as bridging the ligands and the introduction of steric congestion, which suppresses the site-inversion.[9,20l] Such phenoxy−imine ligated complexes could be catalysts for the isospecific and living polymerization of propylene, resulting in the production of "living isotactic polypropylenes". Detailed mechanistic studies including the elucidation of the structure of catalytically active species are underway, which may provide a new stereoregulating strategy for α-olefin polymerization.

Experimental Section

General Comments. Syntheses. Ligand syntheses were carried out under nitrogen using oven-dried glassware. All manipulations of complex syntheses were performed with the exclusion of oxygen and moisture under argon using standard Schlenk techniques using oven-dried glassware.

Materials. Dried solvents [toluene, tetrahydrofuran (THF), diethyl ether, dichloromethane, and *n*-hexane] used for complex syntheses were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Toluene used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3 and degassed by the bubbling of dried nitrogen gas. Phenol derivatives and aniline derivatives for ligand synthesis were obtained from Aldrich Chemical Co., Inc., Wako Pure Chemical Industries, Ltd., Acros Organics, Kanto Chemicals Co. Inc., or Tokyo Kasei Kogyo Co., Ltd. Trimethylsilyl chloride was purchased from Wako Pure Chemical Industries, Ltd., and 2-triethylsilylphenol was obtained from Shin-Etsu Chemicals Co. A 1.0 M trichloroborane in CH_2Cl_2 solution and a *n*-butyllithium in *n*-hexane solution were purchased from Aldrich Chemical Co., Inc. and Wako Pure Chemical Industries, Ltd., respectively. $TiCl_4$ (Wako Pure Chemical Industries, Ltd.) was used as received. Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**1**) was synthesized according to our previous report.[21b] Complex **9** was synthesized according to the patent.[40] Propylene was obtained from Mitsui Chemicals, Inc.

Cocatalyst. Methylalmoxane (MAO) was purchased from Albemarle as a 1.2 M toluene solution, and the remaining trimethylaluminum was evaporated in vacuo prior to use.

Ligand and Complex Analysis. ^{1}H NMR spectra were recorded on a JEOL270 at ambient temperatures. Chemical shifts for ^{1}H NMR were referenced to the resonance of tetramethylsilane. FD-MS spectra were recorded on an SX-102A from Japan Electron Optics Laboratory Co., Ltd. Elemental analysis for CHN was carried out by a CHNO type from Helaus Co.

Polymer Characterization. ^{13}C NMR data for polypropylenes were obtained using *o*-dichlorobenzene with 20% benzene-d_6 as a solvent at 120 °C using an ECP500 spectrometer from Japan Electron Optics Laboratory Co., Ltd., at 125 MHz. The spectra were referenced vs *r* pentad methyl peak shifts, $\delta = 19.97$ ppm. M_n and M_w/M_n values of

(37) (a) Lamberti, M.; Milano, G.; Cavallo, L.; Guerra, G.; Pellecchia, C. *Natl. Meet.-Am. Chem. Soc., Div. Polym. Mater.: Sci. Eng.* **2002**, *87*, 44−46. (b) Milano, G.; Cavallo, L.; Guerra, G. *J. Am. Chem. Soc.* **2002**, *124*, 13368−13369.

(38) Brookhart et al. have successfully prepared a stereoblock polyketone with a Pd-based catalyst through a ligand exchange. Brookhart, M.; Wagner, M. I. *J. Am. Chem. Soc.* **1996**, *118*, 7219−7220.

(39) Cationic complexes described herein can take more than one configuration as a consequence of the different binding geometries of the phenoxy−imine ligands. Therefore, the possibilities cannot be ruled out that a catalytically active species possesses configurations other than a *trans*-O and *cis*-N arrangement. If a catalytically active species has an octahedral geometry with a *cis*-O and *cis*-N disposition, the mechanism for the production of the syndiotactic polypropylene seems very complicated.

(40) Ewen, J. A.; Reddy, B. R.; Elder, M. J. Europe Patent, EP-0577581.

polypropylenes were determined using a Waters GPC2000 gel permeation chromatograph equipped with four TSKgel columns (two sets of TSKgelGMH_{HR}-H(S)HT and two sets of TSKgelGMH_6-HTL) at 140 °C using polypropylene calibration. *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min. Transition melting temperatures (T_m) of the polypropylenes were determined by DSC with a Shimadzu DSC-60 differential-scanning calorimeter, measured upon reheating the polymer sample to 200 °C at a heating rate of 10 °C/min.

Preparation of Bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride (2).

Ligand Synthesis: 3,5-Di-*tert*-butylsalicylaldehyde. To a stirred solution of 3.0 M ethylmagnesium bromide in dried THF (40 mL) was added a solution of 2,4-di-*tert*-butylphenol (20.63 g, 100 mmol) in dried THF (40 mL) dropwise over a 10-min period at 0 °C and the mixture was stirred for 0.5 h at room temperature. To the resulting mixture, dried toluene (250 mL) was added and then a mixture of triethylamine (19.9 mL, 143 mmol) and paraformaldehyde (7.73 g, 94% purity, 242 mmol) was added. The mixture was heated at 75 °C for 40 min with stirring and cooled to 0 °C. To the resulting mixture was added a mixture of concentrated HCl (20 mL) and H_2O (150 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with *n*-hexane (150 mL × 2). The combined organic phase was washed with saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL) and then dried over $MgSO_4$. Evaporation of the solvent in vacuo gave a yellow oil, which was purified by column chromatography on silica gel using *n*-hexane/AcOEt (100/1) as eluent to give 3,5-di-*tert*-butylsalicylaldehyde (18.61 g, 77.0 mmol) as a pale yellow solid in 77% yield: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H, ^{t}Bu), 1.43 (s, 9H, ^{t}Bu), 7.33 (d, J = 2.7 Hz, 1H, aromatic-H), 7.59 (d, J = 2.7 Hz, 1H, aromatic-H), 9.86 (s, 1H, CHO), 11.64 (s, 1H, OH).

Ligand b. To a stirred mixture of 3,5-di-*tert*-butylsalicylaldehyde (2.42 g, 97% purity, 10.0 mmol) and 2,3,4,5,6-pentafluoroaniline (2.01 g, 11.0 mmol) in toluene (40 mL) was added *p*-toluenesulfonic acid (ca. 10 mg) at room temperature. The mixture was heated at reflux temperature for 6 h. The mixture was allowed to cool to room temperature and concentrated in vacuo to afford a crude imine compound. The crude imine compound was purified by column chromatography on silica gel using *n*-hexane/AcOEt (100/1) as eluent. Evapolation of the solvent gave *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline (**b**) (2.99 g, 7.41 mmol) as a yellow-orange solid in 74% yield: ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 7.19 (d, J = 2.4 Hz, 1H, aromatic-H), 7.53 (d, J = 2.4 Hz, 1H, aromatic-H), 8.81 (s, 1H, CH═N), 12.71 (s, 1H, OH).

Complex Synthesis. To a stirred solution of *N*-(3,5-di-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline (1.21 g, 3.00 mmol) in dried diethyl ether (25 mL) at −78 °C was added a 1.56 M *n*-butyllithium in *n*-hexane solution (1.92 mL, 3.00 mmol) dropwise over a 5-min period. The mixture was allowed to warm to room temperature and stirred for 3 h. The resulting mixture was added dropwise over a 5-min period to a 0.5 M *n*-heptane solution of $TiCl_4$ (3.00 mL, 1.50 mmol) in dried diethyl ether (25 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 19 h. Evapolation of the solvent affords a crude product. To the crude product was added dried CH_2Cl_2 (40 mL), and the mixture was stirred for 15 min. The resulting mixture was filtered, and the residue was washed with CH_2Cl_2 (5 mL × 2). The combined organic filtrates were concentrated in vacuo to give a dark red solid. Diethyl ether (20 mL) and *n*-hexane (40 mL) were added to the solid and the mixture stirred for 30 min. The resulting mixture was filtered, and the solid was washed with *n*-hexane (15 mL × 2) and dried in vacuo to give complex **2** (0.536 g, 0.59 mmol) as brown crystals in 37% yield:

^{1}H NMR ($CDCl_3$) δ 1.32 (s, 18H, ^{t}Bu), 1.36 (s, 18H, ^{t}Bu), 7.20 (d, J = 2.2 Hz, 2H, aromatic-H), 7.67 (d, J = 2.2 Hz, 2H, aromatic-H), 8.21 (s, 2H, CH═N); FD-MS, 914 (M^+).

Ligand c, *N*-(3-*tert*-Butyl-5-methylsalicylidene)-2,3,4,5,6-pentafluoroaniline: orange crystals; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9H, ^{t}Bu), 1.47 (s, 3H, Me), 7.04 (d, J = 1.9 Hz, 1H, aromatic-H), 7.27 (d, J = 1.9 Hz, 1H, aromatic-H), 8.76 (s, 1H, CH═N), 12.71 (s, 1H, OH).

Bis[*N*-(3-*tert*-butyl-5-methylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride, Complex 3: reddish brown crystals; ^{1}H NMR ($CDCl_3$); δ 1.33 (s, 18H, ^{t}Bu), 1.35 (s, 6H, Me), 7.06 (d, J = 1.9 Hz, 2H, aromatic-H), 7.42 (d, J = 1.9 Hz, 2H, aromatic-H), 8.14 (s, 2H, CH═N); FD-MS, 830 (M^+). Anal. Found: C, 51.91; H, 3.51; N, 3.30. Calcd. for $TiC_{36}H_{30}N_2O_2F_{10}Cl_2$: C, 52.01; H, 3.64; N, 3.37.

Preparation of Bis[*N*-(3-trimethylsilylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride (4).

Ligand Synthesis: 2-Trimethylsilylanisole. To a stirred solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5.75 g, 49.5 mmol) in dried diethyl ether (36 mL) at 20 °C was added a 1.6 M *n*-butyllithium in *n*-hexane solution (31 mL, 49.5 mmol) dropwise over a 20-min period. To the mixture was added a solution of anisole (4.87 g, 45.0 mmol) in dried diethyl ether (36 mL) dropwise over a 5-min period and the resulting mixture stirred at 50 °C for 7 h. Chlorotrimethylsilane (6.85 mL, 54.0 mmol) in dried diethyl ether (18 mL) was added dropwise over a 10-min period at 0 °C to the mixture and the resulting mixture stirred for 1.5 h. To the mixture was added H_2O (60 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with *n*-hexane (50 mL × 2). The combined organic solution was washed with aqueous NH_4Cl (50 mL) and brine (100 mL) and dried over $MgSO_4$. Concentration of the organic solution in vacuo gave a crude product as yellow oil, which was purified by column chromatography on silica gel using *n*-hexane as eluent to give 2-trimethylsilylanisole (6.59 g, 36.4 mmol) as colorless oil in 81% yield: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H, $Si(CH_3)_3$), 3.80 (s, 3H, OCH_3), 6.83 (t, J = 7.8 Hz, 1H, aromatic-H), 6.94 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 7.34 (t, J = 7.8 Hz, 1H, aromatic-H), 7.37 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H).

3-Trimethylsilylsalicylaldehyde Methyl Ether. To a stirred solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (21.18 g, 182.3 mmol) in dried diethyl ether (40 mL) at 20 °C was added a 1.6 M *n*-butyllithium in *n*-hexane solution (113.9 mL, 182.3 mmol) dropwise over a 30-min period. To the mixture was added a solution of 2-trimethylsilylanisole (30.18 g, 99% purity, 165.7 mmol) in dried diethyl ether (100 mL) dropwise over a 10-min period. The mixture was stirred at 50 °C for 8 h. *N*,*N*-dimethylformamide (15.4 mL, 198.8 mmol) in dried diethyl ether (70 mL)was added to the mixture at 0 °C over a 25-min period and the mixture was stirred for 1 h at room temperature. To the mixture was added H_2O (200 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (100 mL × 2). The combined organic solution was washed with aqueous NH_4Cl (100 mL) and brine (150 mL) and dried over $MgSO_4$. Concentration of the organic solution in vacuo gave the crude product as an orange oil, which was purified by column chromatography on silica gel using *n*-hexane/AcOEt (20/1) as eluent to give 3-trimethylsilylsalicylardehyde methyl ether (19.95 g, 92.4 mmol) as a yellow oil in 56% yield: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9H, $Si(CH_3)_3$), 3.92 (s, 3H, OCH_3), 7.23 (t, J = 7.3 Hz, 1H, aromatic-H), 7.66 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 7.85 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 10.34 (s, 1H, CHO).

3-Trimethylsilylsalicylaldehyde. To a stirred solution of 3-trimethylsilylsalicylardehyde methyl ether (19.90 g, 97% purity, 92.2 mmol) in CH_2Cl_2 (150 mL) at −78 °C was added a 1.0 M trichloroborane in CH_2Cl_2 solution (200 mL, 200 mmol) dropwise over a 2-h period. The mixture was allowed to warm to room temperature and stirred for 5 h. To the mixture was added H_2O (200 mL) and then the mixture was filtered. The organic phase was separated, and the aqueous phase was extracted with *n*-hexane/AcOEt (9/1, 100 mL × 2). The combined organic solution was washed with brine (200 mL × 2) and dried over $MgSO_4$. Concentration of the organic solution in vacuo gave the crude product as a dark orange oil, which was purified by column chromatography on silica gel using *n*-hexane/AcOEt (100/1) as eluent to give 3-trimethylsilylsalicylaldehyde (16.63 g, 83.9 mmol) as yellow oil in 91% yield: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H, $Si(CH_3)_3$), 7.00 (t, J = 7.3 Hz, 1H, aromatic-H), 7.55 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H),

7.61 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 9.88 (s, 1H, CHO), 11.30 (s, 1H, OH).

Ligand d. To a stirred mixture of 3-trimethylsilylsalicylaldehyde (2.38 g, 98% purity, 12.0 mmol) and 2,3,4,5,6-pentafluoroaniline (3.30 g, 18.0 mmol) in toluene (50 mL) was added *p*-toluenesulfonic acid (ca. 5 mg) at room temperature. The resulting mixture was stirred at reflux temperature for 13 h, and concentration of the reaction mixture in vacuo afforded a crude imine compound. Purification by column chromatography on silica gel using *n*-hexane as eluent and recrystallization from cold methanol gave *N*-(3-trimethylsilylsalicylidene)-2,3,4,5,6-pentafluoroaniline (**d**) (3.28 g, 9.13 mmol) as yellow crystals in 76% yield: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9H, $Si(CH_3)_3$), 6.96 (t, J = 7.3 Hz, 1H, aromatic-H), 7.38 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 7.73 (dd, J = 7.8, 1.8 Hz, 1H, aromatic-H), 8.79 (s, 1H, CH=N), 12.41 (s, 1H, OH).

Complex Synthesis. To a stirred solution of *N*-(3-trimethylsilylsalicylidene)-2,3,4,5,6-pentafluoroaniline (1.44 g, 4.00 mmol) in dried diethyl ether (20 mL) at −78 °C was added a 1.6 M *n*-butyllithium in *n*-hexane solution (2.52 mL, 4.00 mmol) dropwise over a 5-min period. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise over a 5-min period to a 0.5 M *n*-heptane solution of $TiCl_4$ (4.00 mL, 2.00 mmol) in dried diethyl ether (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 19 h. Concentration of the reaction mixture in vacuo gave a crude product. Dried CH_2Cl_2 (50 mL) was added to the crude product, and the mixture was stirred and then filtered. The solid residue was washed with dried CH_2Cl_2 (5 mL × 2), and the combined organic filtrates were concentrated in vacuo to afford a dark red solid. Diethyl ether (10 mL) and *n*-hexane (30 mL) were added to the solid, and the mixture was stirred for 20 min and then filtered. The resulting solid was washed with *n*-hexane (10 mL × 2) and dried in vacuo to give complex **4** (0.764 g, 0.91 mmol) as orange crystals in 46% yield:

^{1}H NMR ($CDCl_3$) δ 0.31 (s, 18H, $Si(CH_3)_3$), 7.06 (t, J = 7.3 Hz, 2H, aromatic-H), 7.40 (dd, J = 7.6, 1.6 Hz, 2H, aromatic-H), 7.73 (dd, J = 7.6, 1.6 Hz, 2H, aromatic-H), 8.19 (s, 2H, CH=N); FD-MS, 834 (M^+). Anal. Found: C, 45.69; H, 2.90; N, 3.22. Calcd. for $TiC_{32}H_{26}N_2O_2F_{10}Si_2Cl_2$: C, 46.00; H, 3.14; N, 3.35.

Ligand e, *N*-(3-Trimethylsilylsalicylidene)-2,3,4,5,6-pentafluoroaniline: a yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.85−1.02 (m, 15H, $Si(C_2H_5)_3$), 6.96 (t, J = 7.4 Hz, 1H, aromatic-H), 7.38 (dd, J = 7.6, 1.6 Hz, 1H, aromatic-H), 7.53 (dd, J = 7.3, 1.6 Hz, 1H, aromatic-H), 8.77 (s, 1H, CH=N), 12.39 (s, 1H, OH).

Bis[*N*-(3-triethylsilylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]-titanium(IV) Dichloride, Complex 5: reddish brown crystals; ^{1}H NMR ($CDCl_3$) δ 0.61−1.14 (s, 30H, $Si(C_2H_5)_3$), 7.05 (t, J = 7.4 Hz, 2H, aromatic-H), 7.39 (dd, J = 7.6, 1.6 Hz, 2H, aromatic-H), 7.70 (dd, J = 7.8, 1.6 Hz, 2H, aromatic-H), 8.16 (s, 2H, CH=N); FD-MS, 918 (M^+). Anal. Found: C, 49.88; H, 3.87; N, 3.03. Calcd. for $TiC_{38}H_{38}N_2O_2F_{10}Si_2Cl_2$: C, 49.63; H, 4.16; N, 3.05.

Ligand f, *N*-(Salicylidene)-2,3,4,5,6-pentafluoroaniline: pale yellow crystals; ^{1}H NMR ($CDCl_3$) δ 6.98 (dt, J = 1.1, 7.6 Hz, 1H, aromatic-H), 7.05 (dd, J = 8.6, 1.1 Hz, 1H, aromatic-H), 7.40 (dd, J = 7.6, 1.6 Hz, 1H, aromatic-H), 7.46 (dt, J = 8.6, 1.6 Hz, 1H, aromatic-H), 8.82 (s, 1H, CH=N), 12.22 (s, 1H, OH).

Bis[*N*-(salicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride, Complex 6: reddish brown crystals; ^{1}H NMR ($CDCl_3$) δ 6.63 (d, J = 8.1 Hz, 2H, aromatic-H), 7.09 (dt, J = 1.1, 7.6 Hz, 2H, aromatic-H), 7.46 (d, J = 8.1 Hz, 2H, aromatic-H), 7.60 (dt, J = 1.6, 7.6 Hz, 2H, aromatic-H), 8.28 (s, 2H, CH=N); FD-MS, 690 (M^+). Anal. Found: C, 45.31; H, 1.53; N, 4.02. Calcd. for $TiC_{26}H_{10}N_2O_2F_{10}Cl_2$: C, 45.18; H, 1.46; N, 4.05.

Ligand g, *N*-(3-Methylsalicylidene)-2,3,4,5,6-pentafluoroaniline: yellow crystals; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, Me), 6.89 (t, J = 7.6 Hz, 1H, aromatic-H), 7.25 (dd, J = 7.3, 1.5 Hz, 1H, aromatic-H), 7.33 (dd, J = 7.3, 1.5 Hz, 1H, aromatic-H), 8.81 (s, 1H, CH=N), 12.49 (s, 1H, OH).

Bis[*N*-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride, Complex 7: reddish brown crystals; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 6H, Me), 6.99 (t, J = 7.6 Hz, 2H, aromatic-H), 7.27 (dd, J = 7.3, 1.5 Hz, 2H, aromatic-H), 7.48 (dd, J = 7.3, 1.5 Hz, 2H, aromatic-H), 8.24 (s, 2H, CH=N); FD-MS, 718 (M^+). Anal. Found; C, 46.59; H, 1.79; N, 3.58. Calcd. for $TiC_{28}H_{14}N_2O_2F_{10}Cl_2$: C, 46.76; H, 1.96; N, 3.90.

Ligand h, *N*-(3-Isopropylsalicylidene)-2,3,4,5,6-pentafluoroaniline: yellow crystals, 2.96 g, 8.98 mmol; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 7.0 Hz, 6H, CH_3), 3.44 (sp, J = 6.9 Hz, 1H, CH), 6.95 (t, J = 7.6 Hz, 1H, aromatic-H), 7.24 (dd, J = 8.2, 1.5 Hz, 1H, aromatic-H), 7.46 (dd, J = 7.6, 1.6 Hz, 1H, aromatic-H), 8.81 (s, 1H, CH=N), 12.55 (s, 1H, OH).

Bis[*N*-(3-isopropylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) Dichloride, Complex 8: reddish brown crystals; ^{1}H NMR ($CDCl_3$) δ 1.19 (d, J = 7.0 Hz, 6H, CH_3), 1.23 (d, J = 6.8 Hz, 6H, CH_3), 2.90 (sp, J = 6.8 Hz, 2H, CH), 7.05 (t, J = 7.7 Hz, 2H, aromatic-H), 7.29 (dd, J = 7.8, 1.6 Hz, 2H, aromatic-H), 7.52 (dd, J = 7.6, 1.4 Hz, 2H, aromatic-H), 8.26 (s, 2H, CH=N); FD-MS, 774 (M^+). Anal. Found: C, 49.36; H, 2.42; N, 3.58. Calcd. for $TiC_{32}H_{22}N_2O_2F_{10}Cl_2$: C, 49.57; H, 2.86; N, 3.61.

X-ray Crystallography. Single crystals of complexes **4** and **6** suitable for an X-ray analysis were grown from a saturated pentane/CH_2Cl_2 solution (complex **4**) or Et_2O/CH_2Cl_2 solution (complex **6**). The X-ray structural analysis data were collected using a Rigaku AFC7R diffractometer. The structure was solved by direct method[41] (complex **4**) or heavy-atom Patterson methods[42] (complex **6**) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXan crystallographic software package of Molecular Structure Corp.[43] Experimental data for the X-ray diffraction analyses of complexes **4** and **6** are summarized in Table 5.

Table 5. Summary of Crystallographic Data for Complexes **4** and **6**

complex	**4**	**6**
formula	$C_{32}H_{26}N_2O_2F_{10}Si_2TiCl_2$	$C_{27}H_{12}N_2O_2F_{10}TiCl_4$
formula weight	835.53	776.10
crystal color, habit	red, block	red, needle
crystal size (mm)	0.20 × 0.20 × 0.20	0.60 × 0.10 × 0.10
crystal system	monoclinic	orthorhombic
space group	*C*2/*c* (no. 15)	*Pbca* (no. 61)
a (Å)	29.963(4)	16.450(4)
b (Å)	16.29(1)	24.882(5)
c (Å)	17.264(4)	14.521(2)
β (deg)	115.82(1)	
V (Å^3)	7582(5)	5943(2)
Z	8	8
D_{calcd} (g cm^{-3})	1.464	1.735
*F*000	3376.00	3072.00
μ (MoKα) (cm^{-1})	5.10	7.41
λ (MoKα) (Å)	0.710 69	0.710 69
T (°C)	−15	−50
2θ max	55.0	55.0
no. of total reflns	10380	9807
no. of unique reflns	8698	6829
no. of observations	4618 ($I > 3.00\sigma(I)$)	3042 ($I > 3.00\sigma(I)$)
no. of variables	460	415
refln/parameter ratio	10.04	7.33
residuals: *R*, R_w	0.055, 0.098	0.056, 0.065
R^1	0.040	0.048
GOF indicator	1.30	1.88
max shift/error in final cycle	0.00	0.00
max and min peaks in final diff map (e Å^3)	0.58, −0.41	0.64, −0.83

Propylene Polymerization under Atmospheric Pressure. Propylene polymerization under atmospheric pressure was carried out in a

500-mL glass reactor equipped with a propeller-like stirrer. Toluene (250 mL) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The toluene was kept at a prescribed polymerization temperature, and then propylene gas feed (100 L/h) was started. After 15 min, the propylene gas feed was changed to 30 L/h. Polymerization was initiated by adding a 1.25 M MAO solution in toluene (2 mL, 2.5 mmol) and then a 0.002 M complex solution in toluene (5.0 mL, 10 μmol) was added into the reactor. After a prescribed time, *sec*-butyl alcohol (10 mL) was added to terminate the polymerization. To the resulting mixture were added methanol (1000 mL) and concentrated HCl (2 mL). The polymer was collected by filtration, washed with methanol (200 mL $\times$ 2), and dried in vacuo at 80 °C for 10 h.

Propylene Polymerization under Pressurized Conditions. Pressurized polymerization was carried out at 25 °C under 0.6 MPa propylene pressure in a 1000 mL stainless steel reactor equipped with a propeller-like stirrer. Toluene (380 mL) was introduced into the reactor under propylene at atmospheric pressure. Propylene was pumped into the reactor up to 0.6 MPa pressure with stirring (350 rpm) at 25 °C. Polymerization was initiated by adding a 1.25 M MAO solution in toluene (2 mL, 2.5 mmol) and then a 0.002 M complex solution in toluene (5.0 mL, 10 μmol) into the reactor. After a prescribed time, the polymerization was quenched by injection of methanol (5 mL). The reactor was vented and the resulting mixture was added to acidified methanol (1500 mL containing 5 mL of concentrated HCl). The polymer was collected by filtration, washed with methanol (200 mL $\times$ 2), and dried in vacuo at 80 °C for 10 h.

Conclusions

The catalytic properties of Ti complexes having fluorine-containing phenoxy−imine chelate ligands (Ti-FI Catalysts) for the polymerization of propylene have been described. These Ti complexes (with MAO activation) initiate the living polymerization of propylene at room temperature or above by the attractive interaction between a fluorine in the ligand and a β-hydrogen of a growing polymer chain. The attractive interaction provides a conceptually new strategy for the achievement of highly controlled living olefin polymerization.

These complexes can also promote chain-end controlled, highly syndiospecific propylene polymerization via a 2,1-insertion mechanism. Although chain-end control mechanism is responsible for the stereoselectivity on the basis of the pentad distribution analysis, the polymerization behavior is similar to that directed by a site-control mechanism, and the steric bulk of the substituent ortho to the phenoxy oxygen plays a crucial role in determining the stereoselectivity of the catalyst. Thus, we have given the name "ligand-directed chain-end control" to this unique stereospecific polymerization behavior. "Ligand-directed chain-end control" behavior can be explained well by the recently proposed site-inversion mechanism.

The Ti complexes reported herein (fluorinated Ti-FI Catalysts) represent a new class of living propylene polymerization catalysts capable of mediating highly stereospecific, thermally robust propylene polymerization.

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Supporting Information Available: Detailed synthesis data for complexes **3** and **5**−**8**, full crystallographic data for complexes **4** and **6**, DFT calculation results, and polymer analysis data (NMR, DSC). See any current masthead page for ordering information and Web access instructions.

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