Syndiospecific Living Catalysts for Propylene Polymerization: Effect of Fluorination on Activity, Stereoselectivity, and Termination

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Abstract. The polymerization of propylene using a variety of fluorinated bis(phenoxyimine)titanium complexes is reported. The synthesis of ten complexes containing varying fluorinated *N*-aryl substituents is described. X-ray structural and solution NMR data indicate that these complexes are C_2-symmetric in the solid state, although in some cases C_1-symmetric isomers are observed in solution. When activated with methylalumoxane, all complexes formed syndiotactic polypropylene. Catalysts with *ortho*-fluorine substituents formed polymers with very narrow molecular weight distributions, indicative of a living polymerization. Catalysts with fluorine in at least the ortho and para positions exhibited the highest syndiospecificities. Catalysts with *meta*- or *para*-fluorine-containing substituents were more active for propylene polymerization than the corresponding non-fluorinated catalyst.

INTRODUCTION

The last two decades have witnessed a tremendous amount of research in the area of metallocene-based catalysts for olefin polymerization,[1,2] which led to the development of catalysts with unprecedented control over polymer stereochemistry.[3] In more recent years, non-metallocene catalysts have further expanded the realm of possibilities for polyolefin-based materials.[4,5] Perhaps the most important advance from these new catalysts is the ability to polymerize olefins in a controlled or living fashion.[6] Utilizing a combination of creativity, molecular modeling, and serendipity, judicious combinations of ligand, metal, and activator have produced catalysts capable of forming olefin-based block copolymers previously unavailable by other methods.

Utilizing these principles, researchers at Mitsui Chemical Co. reported a new family of catalysts that displayed remarkable potential for olefin polymerization.[7] These Group IV compounds bearing two phenoxyimine ligands, named *FI* catalysts, displayed extremely high activities for ethylene polymerization upon activation with an appropriate cocatalyst. These results, coupled with the C_2-symmetric nature of these catalyst precursors, prompted us to investigate these compounds as catalysts for stereospecific polymerization of propylene. Utilizing a pooled combinatorial methodology, we quickly identified compound **1** as a promising catalyst for syndiospecific propylene polymerization (Scheme 1).[8] This study revealed the important influence of ligand architecture on polymerization behavior, as only one of the many compounds screened showed promising catalytic behavior. We then employed a more traditional approach to optimize selectivity and activity of this interesting class of catalysts. From this work, the perfluorinated compound **10** was found to give marked improvement over **1**/methylalumoxane (MAO) in activity and gave highly syndiotactic polypropylenes ([rrrr] = 0.96).[9] Furthermore, we found that this catalyst system also polymerized propylene in a living fashion, allowing the synthesis of new polyolefin-based materials. Scientists at Mitsui have independently discovered similar catalysts for living ethylene and syndiospecific propylene polymerization.[10–14] During the work that led to the discovery of **10** for the living, syndiospecific polymerization of propy-

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lene, we screened a variety of bis(phenoxyimine)-based catalysts. Herein we report the effect of these modifications with regard to catalyst activity, selectivity, and living nature of propylene polymerization. These experiments demonstrate the profound effects of ligand substitution patterns on polymerization behavior for this interesting class of catalysts.

RESULTS AND DISCUSSION

Synthesis and Structure of Titanium Complexes

In an effort to better understand the various factors influencing the propylene polymerization behavior of bis(phenoxyimine) titanium catalysts, we decided to investigate the effects of electron-withdrawing substituents on the *N*-aryl ring of the phenoxyimine ligand. Since a wide variety of fluorinated anilines are commercially available, and we have shown that complex **10** is an exceptional catalyst precursor for the formation of living, highly syndiospecific polypropylene,[9] we have synthesized a number of titanium complexes containing fluorinated phenoxyimine ligands. Complexes **1**–**10** (Scheme 1) were formed by deprotonation of the appropriate ligand with *n*-butyllithium, followed by reaction with titanium tetrachloride. The desired products were recrystallized from a mixture of toluene and hexanes, and were isolated in moderate to good yields.

We have previously reported the molecular structure of **10**, which was determined using single-crystal X-ray diffraction.[9] Suitable crystals of **1** and **4** have also been obtained; their molecular structures are shown in Figs. 1 and 2, respectively. In the solid state, compounds **1**, **4**, and **10** are C_2-symmetric, with slightly distorted octahedral geometries. The two oxygen atoms are trans to each other, while the nitrogen donors are cis. Selected bond distances and angles are listed in Table 1. Although these complexes appear to be completely C_2-symmetric in the solid state, NMR studies indicate that in some cases there is a mixture of C_1- and C_2-symmetric isomers in solution. Based on integrations of ^{1}H NMR spectra, C_1-symmetric isomers account for 37–39% of the molecules in solution for compounds **1**, **3**, **4**, **6**, and **7**. For compound **8**, the C_1 isomer accounts for only 19%. The presence of a C_1-symmetric isomer cannot be detected for compounds with fluorine in at least one of the ortho positions (**2**, **5**, **9**, and **10**). The factors influencing this C_1/C_2 ratio are still unclear, but it appears that the C_1 isomer can be severely disfavored or eliminated by placing fluorine substituents at the ortho positions of the *N*-aryl ring.

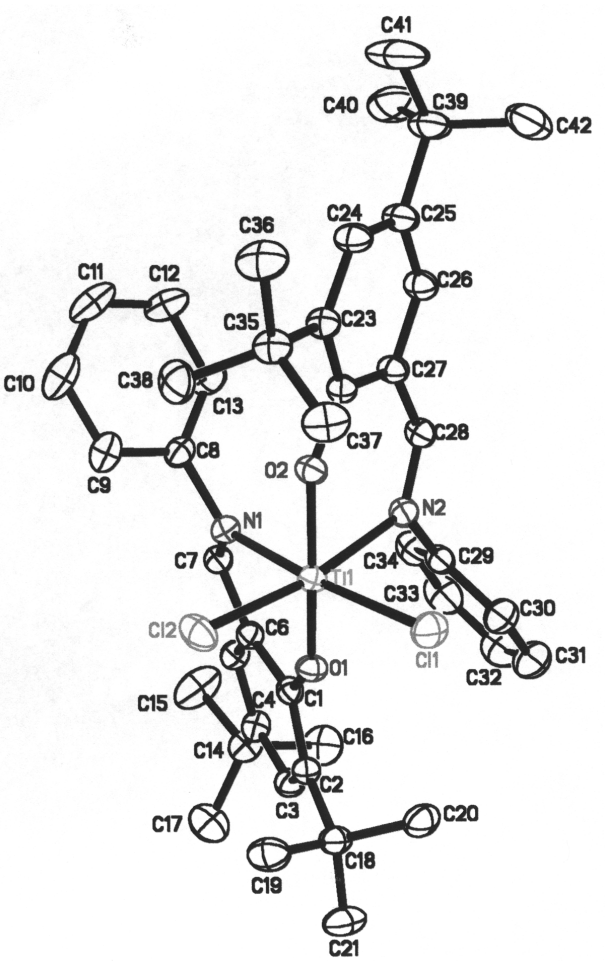
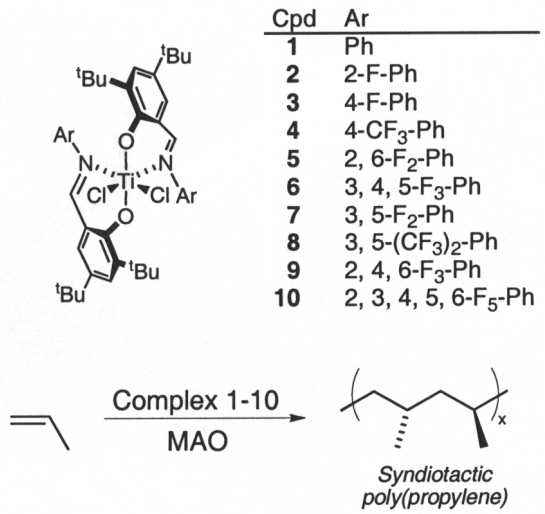


Fig. 1. Molecular structure of **1** (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.



Scheme 1. Catalysts for syndiospecific propylene polymerization.

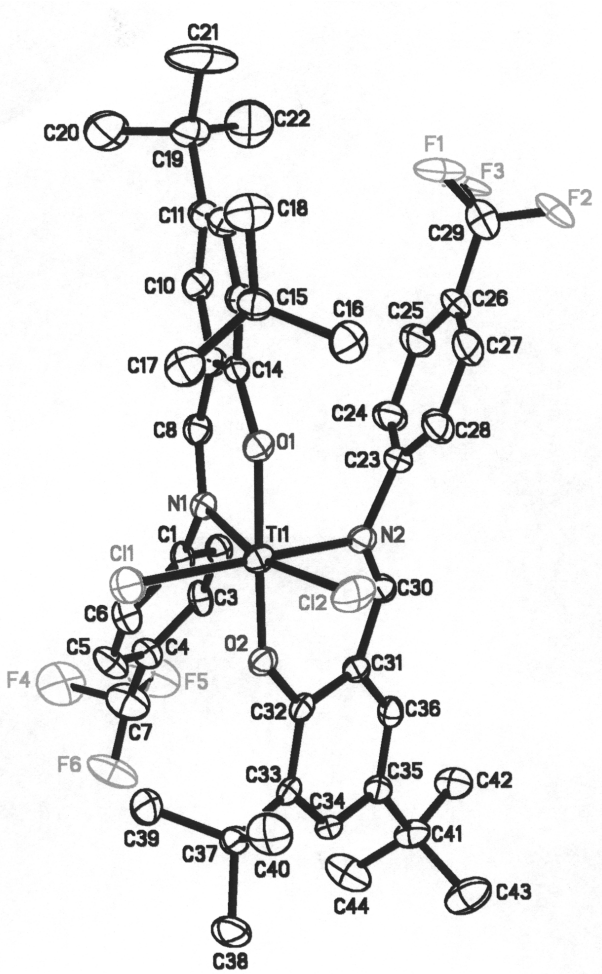


Fig. 2. Molecular structure of **4** (non-hydrogen atoms) with thermal ellipsoids drawn at the 40% probability level.

Table 1. Selected bond distances and angles for complexes **1**, **4**, and **10**

complex	**1**	**4**	**10**
		bond distances (Å)	
Ti-O(1)	1.8478(11)	1.853(4)	1.855(3)
Ti-O(2)	1.8402(11)	1.842(5)	1.844(3)
Ti-N(1)	2.2267(14)	2.245(5)	2.216(4)
Ti-N(2)	2.2536(14)	2.215(6)	2.245(4)
Ti-Cl(1)	2.3040(5)	2.299(2)	2.2744(14)
Ti-Cl(2)	2.3070(5)	2.2936(19)	2.2808(14)
		bond angles (deg)	
O(1)-Ti-O(2)	166.19(5)	171.04(19)	165.29(14)
N(1)-Ti-N(2)	80.01(5)	75.35(18)	88.33(13)
Cl(1)-Ti-Cl(2)	98.63(2)	103.63(8)	97.79(5)

Polymerization Results

Table 2 lists propylene polymerization data for compounds **1**–**10** under a set of standard conditions. When activated with MAO, all complexes were found to be active for the syndiospecific polymerization of propylene. It is interesting to note that complexes **2**, **5**, **9**, and **10** all produce polypropylene with very low molecular weight distributions (M_w/M_n ~ 1.1), which is indicative of a living polymerization. Increasing the number of *N*-aryl fluorine substituents from 2-fluoro (**2**) to 2,6-difluoro (**5**) to 2,4,6-trifluoro (**9**) increases catalyst activity as well as polymer syndiotacticity. These three catalysts all have fluorine groups at the ortho positions, and they all exhibit extremely low activities, especially when compared to catalyst **10**, which is also living, but an order of magnitude more active. Comparison with non-fluorinated **1** indicates that for catalysts **2** and **5**, ortho fluorine groups significantly reduce catalyst activity. Catalyst **9**, containing an additional fluorine group in the para position, is closer in activity to **1**.

While catalysts with *ortho*-fluorine groups appear to be poor catalysts, fluorine-containing groups in the meta or para positions appear to improve catalyst performance. Compounds **3**, **4**, and **6**–**8** are all more active than non-fluorinated **1** (but less active than perfluorinated **10**). Increasing the number of fluorinated substituents increases catalyst activity (compare **4** with **8** and **6** with **7**). These catalysts form polypropylene with a much broader molecular weight distribution (M_w/M_n = 1.75–2.19) and lower tacticity than **9** and **10**. Catalysts

Table 2. Polymerization of propylene using bis(phenoxyimine) catalysts **1**–**10**

complex	yield (g)	TOF[b]	M_n[c]	M_w/M_n[c]	[rrrr][d]
1	4.20	41.7	9 910	2.14	0.78
2	0.38	3.8	3 220	1.07	0.52
3	7.20	71.4	18 600	1.75	0.78
4	6.40	63.6	19 280	2.19	0.81
5	0.56	5.5	16 410	1.06	0.83
6	14.30	142	9 150	2.03	0.83
7	23.40	232	13 580	1.91	0.81
8	12.10	120	14 090	2.17	0.51
9	2.48	24.5	43 420	1.08	0.95
10	5.34[e]	245	95 900	1.11	0.96
10	16.20	161	216 610	1.26	0.96

[a]General conditions: 0.1 mmol catalyst in toluene (5 mL) added to a propylene-saturated (40 psi) MAO solution (150 mL toluene; [Al]/[Ti] = 150) at 0 ºC for 24 h. [b]Turnover frequency: mol propylene/(mol Ti·h). [c]Determined by GPC in 1,2,4-trichlorobenzene at 140 ºC vs. polystyrene standards. [d]Determined by integration of the methyl region of the ^{13}C NMR spectrum. [e]Reaction time = 5.2 h.

with fluorine in at least the 2, 4, and 6 positions exhibited the highest stereoselectivities. The relationship observed between the living behavior of a catalyst and ortho electron-withdrawing groups is in agreement with work done at Mitsui, where a similar relationship was observed for ethylene polymerizations with similar ligands.[13] It is also interesting to note that the four compounds exhibiting living behavior upon activation (**2**, **5**, **9**, and **10**) do not have any minor C_1-symmetric isomers present in solution.

CONCLUSION

In summary, we report the synthesis of a variety of fluorinated bis(phenoxyimine) titanium complexes that are active for the syndiospecific polymerization of propylene in the presence of MAO cocatalyst. Placement of fluorine groups at the ortho positions of the *N*-aryl ring of the ligand results in living catalysts that produce polymer with narrow molecular weight distributions. Placement of fluorine-containing groups at the meta or para positions greatly increases catalyst activity, but does not impart any living behavior. For these non-living catalyst precursors, there is a significant amount of a C_1-symmetric isomer in solution that may influence their potential for living polymerization behavior. Further mechanistic investigations involving this important class of catalysts are currently underway.[15]

EXPERIMENTAL SECTION

General Methods

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk line techniques. Routine small-molecule ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova (^{1}H, 400 MHz, ^{13}C, 100 MHz) spectrometer and referenced vs. residual non-deuterated solvent shifts. ^{19}F NMR was recorded on a Varian Inova (376 MHz) and referenced vs. internal CCl_3F. ^{13}C NMR spectra of the polymers were recorded on a Varian VXR-400 (100 MHz) spectrometer and referenced vs. residual non-deuterated solvent shifts. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5-mm O.D. tube by heating to 120 ºC in an oil bath. For quantitative analysis, an inverse gated decoupling sequence was employed with a 30º pulse width over a 160-ppm spectral width at a 2.0-s acquisition.

Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) were determined by high-temperature gel-permeation chromatography (GPC). All analyses were performed with a Waters Alliance 2000 liquid chromatograph equipped with a Waters DRI detector and a Jordi styrene–divinylbenzene linear mixed-bed column. The GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.1 wt% Irganox 1010 at 140 ºC at 1.0 mL/min and were calibrated using 23 monodisperse polystyrene standards. X-Ray crystallographic data were collected using a SMART CCD Area Detector System (Mo Kα, λ = 0.71073 Å), and frames were integrated with the Siemens SAINT program.

Materials

Toluene and hexanes were purified over columns of alumina and copper. Methylene chloride was purified over an alumina column and degassed by freeze-pump-thaw cycles prior to use. Diethyl ether and benzene-d_6 were distilled from sodium benzophenone ketyl under nitrogen. Propylene (Matheson, polymer grade) was purified through a mixed-bed column (R & D Separations, BOT-4). Methylalumoxane (PMAO-IP, 12.9 wt% Al in toluene, Akzo Nobel) was concentrated in vacuo to dryness (10^{-3} mmHg) to remove residual trimethylaluminum, providing a solid white powder. (H_5-PHI)$_2$TiCl$_2$ **1** and (F_5-PHI)$_2$TiCl$_2$ **10** were synthesized according to published procedures.[8,9] All other chemicals were used as received from commercial sources.

Ligand Synthesis

General Procedure for Fluorinated Phenoxyimine Ligand Synthesis

A round-bottom flask was charged with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol), the desired aniline (10 mmol), dry phosphorous pentoxide (4.32 g, 30 mmol), and a few crystals of *p*-toluenesulfonic acid. The reaction mixture was heated to 120 ºC and stirred for six h. After cooling, organic materials were extracted into methylene chloride and filtered through Celite. The solvent was removed in vacuo, and the solid residue was recrystallized from methanol at –20 ºC to give the desired product.

N-*(3,5-di*-t-*butylsalicylidene)-2-fluoroaniline (2-F-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.5 g, 6.4 mmol) and 2-fluoroaniline (0.71 g, 6.4 mmol) were reacted to give the desired ligand as orange crystals (1.74 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 7.12–7.27 (m, 5H, Ar), 7.46 (d, 2H, J = 2.4 Hz, Ar), 8.69 (s, 1H, HC = N), 13.55 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –6.11 (s).

N-*(3,5-di*-t-*butylsalicylidene)-4-fluoroaniline (4-F-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.6 g, 6.7 mmol) and 4-fluoroaniline (0.75 g, 6.7 mmol) were reacted to give the desired ligand as orange crystals (1.71 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 1.44 (s, 9H, ^{t}Bu), 7.07 (t, 2H, J = 2.6 Hz, ArF), 7.20–7.30 (m, 3H, Ar), 7.45 (d, 2H, J = 2.4 Hz, Ar), 8.70 (s, 1H, HC = N), 13.57 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –16.21 (s).

N-*(3,5-di*-t-*butylsalicylidene)-4-(trifluoromethyl)aniline (4-CF_3-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.6 g, 6.7 mmol) and 4-trifluoromethylaniline (1.1 g, 6.7 mmol) were dissolved in methanol (20 mL) and heated at reflux for 12 h. Concentration of the solvent and crystallization at –20 ºC produced the desired ligand as orange crystals (2.26 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 7.24 (d, 1H, J = 2.4 Hz, Ar), 7.34 (d, 2H, J = 8.4 Hz, Ar_F), 7.50 (d, 1H,

J = 2.4 Hz, Ar), 7.66 (d, 2H, J = 8.4 Hz, Ar_F), 8.61 (s, 1H, HC = N), 13.34 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –70.28 (s).

N-*(3,5-di*-t-*butylsalicylidene)-2,6-difluoroaniline (2,6-F_2-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.6 g, 6.7 mmol) and 2,6-difluoroaniline (0.86 g, 6.7 mmol) were reacted to give the desired ligand as yellow crystals (1.78 g, 76%). ^{1}H NMR (400 MHz $CDCl_3$): δ 1.33 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 6.97 (m, 2H, Ar_F), 7.10 (m, 1H, Ar_F), 7.18 (d, 1H, J = 2.4 Hz, Ar), 7.47 (d, 1H, J = 2.4 Hz, Ar), 8.84 (s, 1H, HC = N), 13.40 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 9.14 (t).

N-*(3,5-di*-t-*butylsalicylidene)-3,4,5-trifluoroaniline (3,4,5-F_3-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.6 g, 6.7 mmol) and 3,4,5-trifluoroaniline (0.98 g, 6.7 mmol) were reacted to give the desired ligand as orange crystals (2.25 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 6.92 (m, 2H, Ar_F), 7.21 (d, 1H, J = 2.4 Hz, Ar), 7.48 (d, 1H, J = 2.4 Hz, Ar), 8.54 (s, 1H, HC = N), 13.02 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –30.50 (m), –0.76 (m).

N-*(3,5-di*-t-*butylsalicylidene)-3,5-difluoroaniline (3,5-F_2-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.7 g, 7.2 mmol) and 3,5-difluoroaniline (0.92 g, 7.2 mmol) were reacted to give the desired ligand as yellow-brown crystals (1.99 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 1.46 (s, 9H, ^{t}Bu), 6.71 (m, 1H, Ar_F), 6.80 (m, 2H, Ar_F), 7.22 (d, 1H, J = 2.4 Hz, Ar), 7.48 (d, 1H, J = 2.4 Hz, Ar), 8.60 (s, 1H, HC = N), 13.14 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –23.40 (t).

N-*(3,5-di*-t-*butylsalicylidene)-3,5-bis(trifluoromethyl)aniline (3,5-CF_3-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.6 g, 6.7 mmol) and 3,5-bis(trifluoromethyl)aniline (1.5 g, 6.7 mmol) were dissolved in methanol (20 mL) and heated at reflux for 12 h. Concentration of the solvent and crystallization at –20 ºC produced the desired ligand as orange crystals (1.98 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H, ^{t}Bu), 1.44 (s, 9H, ^{t}Bu), 7.27 (m, 1H, Ar_F), 7.52 (d, 1H, J = 2.4 Hz, Ar), 7.68 (m, 2H, Ar_F), 7.77 (d, 1H, J = 2.4 Hz, Ar), 8.64 (s, 1H, HC = N), 13.28 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –69.50 (s).

N-*(3,5-di*-t-*butylsalicylidene)-2,4,6-trifluoroaniline (2,4,6-F_3-PHI)H*

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.4 g, 5.9 mmol) and 2,4,6-trifluoroaniline (0.87 g, 5.9 mmol) were reacted to give the desired ligand as yellow crystals (1.42 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H, ^{t}Bu), 1.45 (s, 9H, ^{t}Bu), 6.76 (m, 2H, Ar_F), 7.16 (d, 1H, J = 2.4 Hz, Ar), 7.47 (d, 1H, J = 2.4 Hz, Ar), 8.81 (s, 1H, HC = N), 13.17 (s, 1H, ArOH). ^{19}F NMR (376 MHz, $CDCl_3$): δ –12.63 (t), 8.72 (m).

Complex Synthesis

General Procedure for Titanium Complex Synthesis

A gastight syringe was used to dropwise add *n*-butyllithium (1.6 M in hexanes, 2.1 mmol) to a stirred solution of phenoxyimine ligand (2.0 mmol) in diethyl ether (20 mL) at –78 ºC. After warming to room temperature, this solution was stirred for 30 min before being added via cannula to a solution of titanium tetrachloride (1.0 M in toluene, 1.0 mmol) in diethyl ether (20 mL) at –78 ºC. The resulting solution was warmed to room temperature and stirred under nitrogen for 12 h. The solvent was removed in vacuo; residues were taken up in methylene chloride and filtered through Celite to give a clear dark red solution. The solvent was removed in vacuo, and the resulting solid was recrystallized from a toluene/hexane mixture to give the desired complex.

*(2-F-PHI)$_2$TiCl$_2$ (**2**)*

(2-F-PHI)H (0.85 g, 2.6 mmol) was reacted as described above, producing red-brown crystals (0.39 g, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 18H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), 6.90 (m, 4H, Ar_F), 7.08 (d, 2H, J = 2.4 Hz, Ar), 7.30 (m, 4H, Ar_F), 7.43 (d, 2H, J = 2.4 Hz, Ar), 8.10 (s, 2H, HC = N).

*(4-F-PHI)$_2$TiCl$_2$ (**3**)*

(4-F-PHI)H (0.98 g, 3.0 mmol) was reacted as described above, producing red-brown crystals (0.51 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$, isomeric mixture in solution, 63% C_2-symmetric isomer): δ 1.25 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 1.31, 1.33, 1.59 (s, ^{t}Bu, C_1 isomer), 7.05 (d, 2H, J = 2.4 Hz, Ar), 7.08 (d, Ar, C_1isomer), 7.12 (d, 4H, J = 7.6 Hz, Ar_F), 7.27 (d, 4H, J = 8.4 Hz, Ar_F), 7.46, 7.48 (d, Ar_F, C_1 isomer), 7.49 (d, 2H, J = 2.4 Hz, Ar), 7.62, 7.69 (d, Ar, C_1 isomer), 7.92, 8.04 (s, HC = N, C_1 isomer), 8.06 (s, 2H, HC = N).

*(4-CF_3-PHI)$_2$TiCl$_2$ (**4**)*

(4-CF_3-PHI)H (1.16 g, 3.1 mmol) was reacted as described above, producing dark red crystals (0.94 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, isomeric mixture in solution, 63% C_2-symmetric isomer): δ 1.24 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 1.31, 1.32, 1.34, 1.59 (s, ^{t}Bu, C_1 isomer), 6.80 (d, Ar_F, C_1 isomer), 7.06 (d, 2H, J = 2.4 Hz, Ar), 7.08 (d, Ar, C_1 isomer), 7.12 (d, 4H, J = 8.0 Hz, Ar_F), 7.27 (d, 4H, J = 8.0 Hz, Ar_F), 7.45, 7.47 (d, Ar_F, C_1 isomer), 7.49 (d, 2H, J = 2.4 Hz, Ar), 7.63, 7.69 (d, Ar, C_1 isomer), 7.91, 8.04 (s, HC = N, C_1 isomer), 8.07 (s, 2H, HC = N).

*(2,6-F_2-PHI)$_2$TiCl$_2$ (**5**)*

(2,6-F_2-PHI)H (0.96 g, 2.8 mmol) was reacted as described above, producing red-brown crystals (0.72 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 6.43 (m, 2H, Ar_F), 6.87 (m, 2H, Ar_F), 6.95 (m, 2H, Ar_F), 7.15 (d, 2H, J = 2.4 Hz, Ar), 7.51 (d, 2H, J = 2.4 Hz, Ar), 8.19 (s, 2H, HC = N).

*(3,4,5-F_3-PHI)$_2$TiCl$_2$ (**6**)*

(3,4,5-F_3-PHI)H (1.13 g, 3.1 mmol) was reacted as described above, producing red-brown crystals (0.54 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$, isomeric mixture in solution, 61% C_2-symmetric isomer): δ 1.27 (s, 18H, ^{t}Bu), 1.30, 1.31 (s, ^{t}Bu, C_1 isomer), 1.38 (s, 18H, ^{t}Bu), 1.58 (s, ^{t}Bu, C_1 isomer), 6.39 (m, Ar_F, C_1 isomer), 6.62 (m, 4H, Ar_F), 6.72 (m, Ar_F, C_1 isomer), 7.11 (d, 2H, J = 2.4 Hz, Ar), 7.22 (d, Ar, C_1 isomer), 7.58 (d, 2H, J = 2.4 Hz, Ar), 7.64, 7.70 (d, Ar, C_1 isomer), 8.00, 8.01 (s, HC = N, C_1 isomer), 8.07 (s, 2H, HC = N).

*(3,5-F_2-PHI)$_2$TiCl$_2$ (**7**)*

(3,5-F_2-PHI)H (1.14 g, 3.3 mmol) was reacted as described above, producing red-brown crystals (0.74 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, isomeric mixture in solution, 63% C_2-symmetric isomer): δ 1.26 (s, 18H, ^{t}Bu), 1.29,1.30 (s, ^{t}Bu, C_1 isomer), 1.36 (s, 18H, ^{t}Bu), 1.59 (s, ^{t}Bu, C_1 isomer), 6.29 (m, 2H, Ar_F), 6.42 (m, 2H, Ar_F), 6.53 (m, 2H, Ar_F), 6.67 (m, Ar_F, C_1 isomer), 6.75 (m, Ar_F, C_1 isomer), 7.11 (d, 2H, J = 2.4 Hz, Ar), 7.15 (d, Ar, C_1 isomer), 7.53 (d, 2H, J = 2.4 Hz, Ar), 7.62, 7.68 (d, Ar, C_1 isomer), 7.99, 8.03 (s, HC = N, C_1 isomer), 8.08 (s, 2H, HC = N).

*(3,5-CF_3-PHI)$_2$TiCl$_2$ (**8**)*

(3,5-CF_3-PHI)H (1.15 g, 2.6 mmol) was reacted as described above, producing dark red crystals (0.76 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, isomeric mixture in solution, 81% C_2-symmetric isomer): δ 1.11 (s, 18H, ^{t}Bu), 1.29 (s, 18H, ^{t}Bu), 1.31, 1.32, 1.33, 1.59 (s, ^{t}Bu, C_1 isomer), 7.16 (m, 2H, Ar_F), 7.22 (m, 2H, Ar_F), 7.26 (d, 2H, J = 2.4 Hz, Ar), 7.30 (d, Ar, C_1 isomer), 7.59 (d, 2H, J = 2.4 Hz, Ar), 7.60 (m, 2H, Ar_F), 7.66 (m, Ar_F, C_1 isomer), 7.71, 7.76 (d, Ar, C_1 isomer), 7.84 (m, Ar_F, C_1 isomer), 8.06, 8.09 (s, HC = N, C_1 isomer), 8.26 (s, 2H, HC = N).

*(2,4,6-F_3-PHI)$_2$TiCl$_2$ (**9**)*

(2,4,6-F_3-PHI)H (0.81 g, 2.2 mmol) was reacted as described above, producing red-brown crystals (0.76 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$,): δ 1.29 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 6.21 (m, 2H, Ar_F), 6.65 (m, 2H, Ar_F), 7.14 (d, 2H, J = 2.4 Hz, Ar), 7.56 (d, 2H, J = 2.4 Hz, Ar), 8.15 (s, 2H, HC = N).

General Procedure for Polypropylene Synthesis

A 6-ounce Lab-Crest pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature and then charged with a desired amount of dry PMAO-IP and toluene. The reactor was then equilibrated at 0 ºC, the atmosphere was exchanged three times with propylene, and the solution was saturated under pressure (40 psi). The titanium catalyst was dissolved in toluene (5 mL) and added to the reactor via gastight syringe to initiate the polymerization. After the desired period of time, the reaction was quenched with methanol (10 mL) and the reactor was vented. The polymer was precipitated in copious methanol/HCl, filtered, washed with methanol, and then dried in vacuo to constant weight.

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