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Titanium Catalysts with Ancillary Phenoxyketimine Ligands for Living Ethylene Polymerization

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Summary: New titanium catalysts with ancillary, non-fluorinated phenoxyketimine ligands have been synthesized and found to be active for living ethylene polymerization.

Introduction

A significant amount of recent research has focused on the development of non-metallocene catalysts for olefin polymerization.[1−3] Over the last half decade, impressive advances in living alkene polymerization using such catalysts have been achieved.[4] One system of current interest includes the group IV bis(phenoxyimine) (PHI) ligated catalysts $(PHI)_2MCl_2$ (M = Ti, Zr) reported first by Mitsui in the late 1990s for ethylene polymerization.[5−8] Upon exploring these systems for propylene polymerization, we found a $(PHI)_2Ti$ catalyst that produced moderately syndiotactic polypropylene.[9] We subsequently found that $(PHI)_2Ti$ complexes bearing fluorinated *N*-aryl groups were active for the living and highly syndiospecific polymerization of propylene;[10] scientists at Mitsui have independently discovered related fluorinated complexes for the living polymerization of both ethylene and propylene.[11−15] In fact, living olefin polymerization with $(PHI)_2Ti$ catalysts has only been reported to date with variants containing fluorinated *N*-aryl groups; it has been proposed that *ortho*-fluorine substituents are required for preventing β-H elimination, especially at elevated temperatures.[13]

Since catalyst optimization has been achieved primarily by varying the aniline and phenol moieties of the PHI ligand, we decided to study the influence of substituents on the imine carbon atom on catalyst performance. In addition, we reasoned the ketimine functionality would better resist insertion into a Ti−alkyl bond,[16−21] thereby allowing the synthesis of stable $(PHI)_2$Ti-dialkyl complexes.[22] While PHI ligands are easily accessible from the corresponding and often commercially available salicylaldehydes and anilines, phenoxyketimine (PHI−R) ligands are less common and not as easily synthesized (Scheme 1).[23−25] Scientists at Mitsui have reported group IV complexes bearing phenoxyketimine ligands. The complexes exhibited turnover frequencies between 2000 and 8000 per hour; molecular weight information was not reported.[5] Herein we report the facile synthesis of phenoxyketimine ligands, as well as the synthesis of the corresponding $(PHI{-}R)_2TiCl_2$ complexes. Upon activation with MAO (MAO = methylaluminoxane), these complexes are active for living ethylene polymerization, even though the aniline moiety is not *ortho*-fluorinated. This contrasts the previously reported results for the salicylaldiminato series of complexes.[13]

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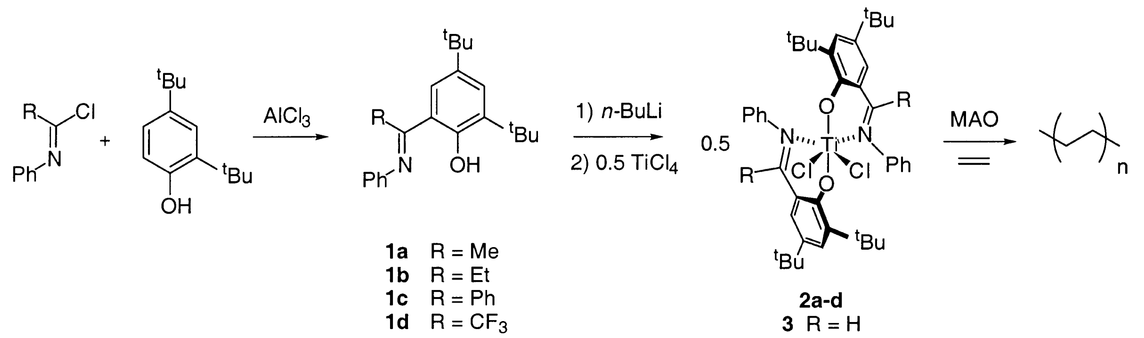
Scheme 1. Synthesis of PHI−R Ligands and (PHI−R)$_2$TiCl$_2$ Complexes



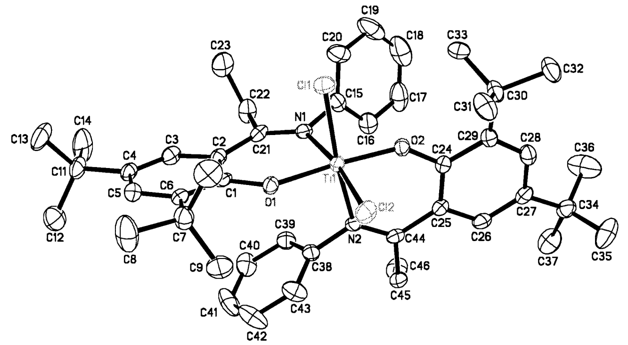


Figure 1. ORTEP diagram of (PHI−Et)$_2$TiCl$_2$ (**2b**). Ellipsoids are drawn at the 50% probability level.

Results and Discussion

PHI−R ligands **1a**−**d** were synthesized in good yields via Friedel−Crafts reaction[26] of 2,4-di-*tert*-butylphenol with the corresponding imidoyl chlorides, which were generally formed in situ from the corresponding amides and PCl$_5$ (Scheme 1).[27,28] This synthetic pathway allows for the incorporation of a variety of substituents, especially electron-withdrawing groups (such as trifluoromethyl; **1d**) into the ligand framework. Ligand deprotonation and reaction with TiCl$_4$ resulted in formation of the (PHI−R)$_2$TiCl$_2$ complexes **2a**−**d** (for details see the Supporting Information). Complexes **2a**−**d** were obtained after recrystallization in good yields as orange to red-brown solids.

NMR data indicated that these octahedral complexes are predominantly C_2-symmetric in solution, as they are in the solid state.[29] Single crystals of (PHI−Et)$_2$TiCl$_2$ (**2b**) were grown from CH$_2$Cl$_2$/pentane at −30 °C and subjected to X-ray structural analysis; the ORTEP diagram is shown in Figure 1.[30] The structure closely resembles the structure of previously reported (PHI−H)$_2$TiCl$_2$ (**3**). All of the bond distances and angles about the titanium center of **2b** are within a percent of the values of **3** except for the O−Ti−O and N−Ti−N angles, which are 171.4° and 83.5°, respectively, for **2b** (166.2° and 80.0° for **3**) (for details see the Supporting Information).

Table 1. Ethylene Polymerization with (PHI−R)$_2$TiCl$_2$ (2a−d, 3)[a]

entry	complex	R	T (°C)	time (min)	yield (mg)	activity mol E/ (mol Ti h)	M_n[c] (g/mol)	$M_{n\ calc}$ (g/mol)	M_w/M_n[c]
1	**3**	H	0	3	730	52 100	78 400	73 000	1.16
2	**3**	H	20	1	420	90 000	48 500	42 000	1.07
3	**3**	H	50	1	370	79 300	44 500	37 000	1.10
4	**2a**	Me	0	10	370	7 900	38 500	37 000	1.07
5[b]	**2a**	Me	20	3	200	14 300	24 000	20 000	1.06
6	**2b**	Et	0	10	360	7700	43 000	36 000	1.07
7	**2b**	Et	20	3	150	10 700	21 300	15 000	1.04
8	**2c**	Ph	0	10	470	10 100	59 600	47 000	1.08
9	**2c**	Ph	20	3	390	27 900	44 500	39 000	1.08
10	**2c**	Ph	50	1	170	36 400	24 000	17 000	1.14
11	**2d**	CF$_3$	0	10	410	8800	57 600	41 000	1.25
12	**2d**	CF$_3$	20	3	180	12 900	28 000	18 000	1.41

[a] 0.01 mmol catalyst; [Al]:[Ti] = 150, 120 mL of toluene, 10 psi ethylene (E). [b] Polyethylene precipitated out of solution. [c] GPC data were obtained relative to polyethylene standards.

When activated with MAO ([Al]/[Ti] = 150), **2a**−**d** are active for the polymerization of ethylene at 0 °C, although the activity is lower than that for the analogous phenoxyaldimine catalyst **3** (Table 1, entries 1−3) under identical conditions. Interestingly, this aldimine complex **3** produces polyethylene of very narrow polydispersity even at 50 °C and short polymerization times (Table 1, entry 3), contrasting the notion that the aniline moiety of the ancillary ligand has to be fluorinated in order to achieve living behavior. All of the catalysts reported here are significantly slower than phenoxyaldimine titanium catalysts with *ortho*-fluorination.[13] The measured polydispersities of the polymers produced by catalysts **2a**−**c** are all very narrow, and the molecular weights correspond to the calculated values, both consistent with living polymerization behavior (Table 1).[31] Polyethylene produced by the CF$_3$-substituted catalyst **2d** has broader molecular weight distributions, and the molecular weight deviates substantially from the theoretical value (Table 1, entries 11, 12), indicating that catalyst **2d** does not fully satisfy the requirements of a living polymerization. Polymerizations at room temperature with catalysts **2a**−**c** do not show significant change in the molecular weight distributions in comparison to the runs at 0 °C, but the activity is enhanced as expected (Table 1, entries 5, 7, 9). In the case of **2c**,

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(30) Crystal data: C$_{46}$H$_{60}$Cl$_2$N$_2$O$_2$Ti, M = 791.76, monoclinic, space group = P2(1)/c, a = 15.1041(6) Å, b = 17.1280(7) Å, c = 18.5498(6) Å, β = 112.279(2)°, V = 4440.6(3) Å^3, Z = 4, m = 0.350 mm^{-1}, T = 173(2) K, F(000) = 1688, 32 359 reflections measured in angle range $3° < 2\theta < 54°$, 8792 independent reflections, 718 parameters, final parameters were wR2 = 0.1294 and R1 = 0.0585 [$I > 2\sigma(I)$].

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Table 2. Ethylene Polymerization with $(PHI-Ph)_2TiCl_2$ (2c) at 0 °C[a]

entry	time (min)	yield (mg)	M_n[b] (g/mol)	$M_{n\ calc}$ (g/mol)	M_w/M_n[b]
1	5	470	29 000	23 500	1.06
2	8	630	39 200	31 500	1.07
3	10	920	55 100	46 000	1.09
4	15	1480	86 400	70 400	1.11

[a] 0.02 mmol catalyst, [Al]:[Ti] = 150, 120 mL of toluene, 10 psi ethylene. [b] GPC data were obtained relative to polyethylene standards.

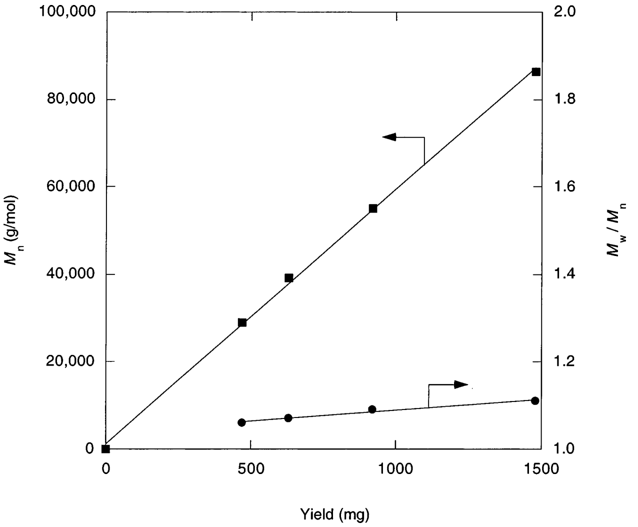

Figure 2. Plot of M_n (■) and M_w/M_n (●) versus polymer yield for polyethylene produced with catalyst **2c** at 0 °C.

Table 3. Ethylene Polymerization with $(PHI-Et)_2TiCl_2$ (2b) at 50 °C[a]

entry	time (min)	yield (mg)	M_n[b] (g/mol)	$M_{n\ calc}$ (g/mol)	M_w/M_n[b]
1	1	170	10 400	8500	1.07
2	2	290	17 300	14 500	1.09
3	3	350	22 300	17 500	1.12
4	5	440	28 800	22 000	1.15
5	8	570	40 700	28 500	1.20

[a] 0.02 mmol catalyst, [Al]:[Ti] = 150 (dried PMAO), 100 mL of toluene, 10 psi ethylene, 50 °C. [b] GPC data were obtained relative to polyethylene standards.

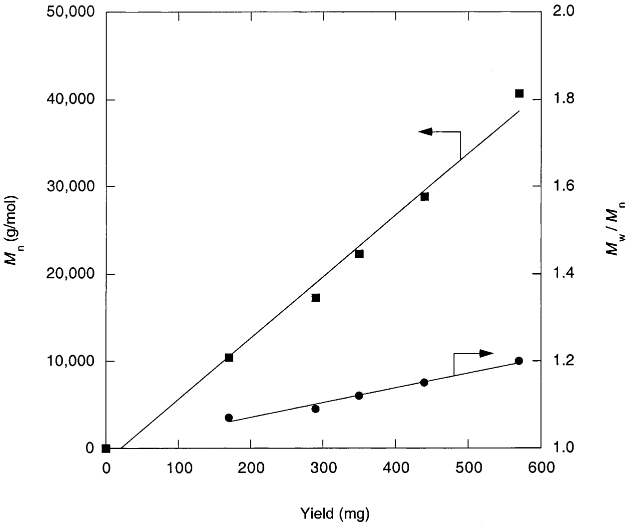

Figure 3. Plot of M_n (■) and M_w/M_n (●) versus polymer yield for polyethylene produced with catalyst **2b** at 50 °C.

polymerization runs were performed at elevated temperatures, and while polyethylene of narrow polydispersity can be obtained for short polymerizations at 50 °C (Table 1, entry 10), **2c** was inactive at 70 °C. This differs from phenoxyaldimine titanium catalysts with *ortho*-fluorination, which are both active and living at 70 °C.[13]

Having shown that catalysts **2a**−**c** produce polyethylene with predictable molecular weight and narrow molecular weight distributions both at 0 °C and at room temperature, we wanted to find additional evidence for the living nature of these polymerizations. Measuring the molecular weight with respect to polymer yield is a convenient way for determining living polymerization behavior, since the molecular weight must increase linearly with conversion. Polymerizations at 0 °C with catalyst **2c** were run for different reaction times (Table 2), and the resultant polymer number average molecular weights were plotted versus polymer yield (Figure 2), indeed revealing a linear relationship indicative of a living polymerization. More importantly, ethylene polymerizations with $(PHI-Et)_2TiCl_2$ (**2b**) are living even at 50 °C, as shown again by the linear molecular weight versus polymer yield plot (Table 3, Figure 3), although the molecular weight distributions begin to broaden at longer reaction times.

On the basis of DFT studies, it has been proposed that an *ortho* fluorine atom of the *N*-aryl group of the PHI ligand interacts with the β-H of the growing polymer chain, thereby preventing β-H elimination by the titanium center and resulting in living behavior at high temperature.[11,13] Interestingly, complexes **2a**−**c** and **3**, which do not contain *ortho* fluorines, are all capable of producing polyethylenes of controlled molecular weights and molecular weight distributions typical of living polymerizations. Although our results presented here do not rule out such a β-H/*o*-F interaction, they do suggest that other factors could be involved in determining the relative rates of propagation and chain transfer.

In summary, we have reported herein a facile synthesis of new titanium catalysts with ancillary phenoxyketimine ligands for living ethylene polymerization. We are currently expanding our array of (PHI−R) ligands and catalysts and testing them with other olefin monomers.

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Supporting Information Available: Complete synthetic and spectroscopic data for ligands **1a**−**d** and complexes **2a**−**d**, and crystallographic data for complexes **2b** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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