Ethylene Polymerization Behavior of New Titanium Complexes Having Two Phenoxy–Pyridine Chelate Ligands

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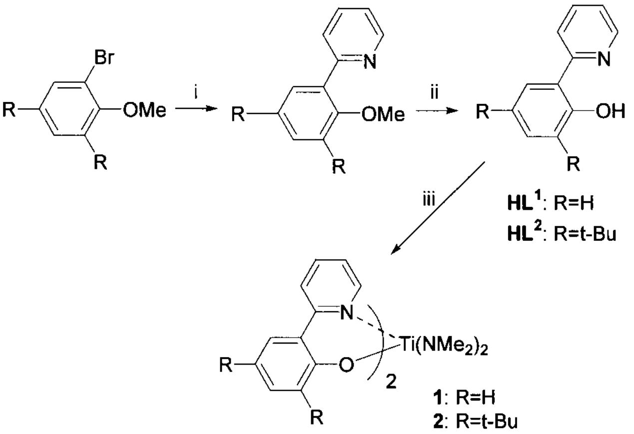
Two new titanium complexes having two phenoxy–pyridine chelate ligands were synthesized and investigated for their potential as ethylene polymerization catalysts. On activation with $Ph_3C^+B^-(C_6F_5)_4$ / i-Bu_3Al, one of the complexes, bis[2-(2'-pyridyl)phenolato] titanium complex, exhibited high activity (227–564 kg-PE/mol-cat·h) and produced high molecular weight polyethylene (M_v; 140000–3230000) at 25–75 °C.

The design and application of group 4 metallocene catalysts have revolutionized not only polyolefin chemistry but also the polyolefin industry to create a variety of high performance polyolefins such as linear low-density polyethylene, isotactic and syndiotactic polypropylene, syndiotactic polystyrene, etc.[1] However, since the discovery of the group 4 metallocene catalysts, the metallocene catalysts have been thoroughly investigated by both academic and industrial research groups. Therefore, in recent years, there has been increasing interest in the development of new olefin polymerization catalysts using transition metal complexes with no Cp ligand. In consequence, quite a few new olefin polymerization catalysts based on both early and late transition metal complexes have been developed.[2]

In our own efforts, we have recently reported that transition metal complexes featuring non-symmetric bidentate ligand(s) (e.g., phenoxy–imine, pyrrolide–imine, indolide–imine, and imine–pyridine ligands) possess high catalytic performance for olefin polymerization including living olefin polymerization.[3] In this communication, we describe the synthesis and ethylene polymerization behavior of two titanium complexes bearing two phenoxy–pyridine chelate ligands. In addition, the ethylene polymerization behavior was compared with that of analogous titanium complexes having two phenoxy–imine chelate ligands (titanium FI Catalysts). The titanium complexes used in this study are bis[2-(2'-pyridyl)phenolato]titanium(IV)-diamide, complex **1**, and bis[4,6-di-*tert*-butyl-2-(2'-pyridyl)phenolato]titanium(IV)diamide, complex **2**. Phenoxy–pyridine chelate ligands, **HL^1** and **HL^2**, were prapared by the coupling reaction of the Grignard reagent derived from the desired bromoanisole with 2-bromopyridine using $Ni(dppe)Cl_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) as a catalyst, followed by the demethylation of the resulting coupling product by pyridinium chloride (**HL^1**; 68%, **HL^2**; 54%, based on bromoanisole).[4] The phenoxy–pyridine ligands reacted smoothly with $Ti(NMe_2)_4$ in toluene to yield the target complexes (**1**; 71%, **2**; 61%)(Scheme 1).[5]

The new complexes are active procatalysts for the polymerization of ethylene (Table 1)[6] and not simply a source of titanium amide.[7] Complex **1**, when activated with MAO, displayed moderate activities (25 °C; 37 kg-PE/mol-cat·h, 75 °C; 110 kg-PE/mol-cat·h) and produced high molecular weight polyethylenes[8] (M_v, 25 °C; 4167000: 75 °C; 580000).[9] On the other hand, upon activation with $Ph_3C^+B^-(C_6F_5)_4$ / i-Bu_3Al, complex **1** exhibited higher activities (25 °C; 227 kg-PE/mol-cat·h, 50 °C; 331 kg-PE/mol-cat·h, 75 °C; 421 kg-PE/mol-cat·h) with somewhat lower, but still high, molecular weight values (M_v, 25 °C; 3231000, 50 °C; 656000, 75 °C; 200000),[9] relative to complex **1**/MAO catalyst system. Increasing the polymerization temperature (entries 2, 4, and 5) gave a corresponding increase in activity. Complex **1** (5 μmol) using $Ph_3C^+B^-(C_6F_5)_4$ (6 μmol)/i-Bu_3Al (0.25 mmol) afforded a reproducible activity of 564 kg-PE/mol-cat·h at 75 °C under

Scheme 1.



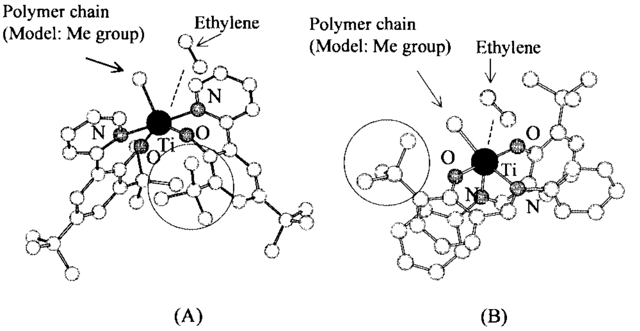
Reagents and isolated yields: (i) (a) Mg, THF, r.t., 2 h, (b) 2-bromopyridine, $Ni(dppe)Cl_2$, THF, r.t., 12h; (ii) Pyridinium chloride, 180 ℃, 3 h, 68% (**HL^1**), 54 %(**HL^2**) (based on bromoanisole); (iii) $Ti(NMe_2)_4$, toluene, r.t., 3 h, 71% (**1**), 61% (**2**).

Table 1. Ethylene polymerization results using complexes **1-2** / co-catalysts systems[a]

Run	Complex	Co-catalyst	Temp. /℃	Activity[b]	M_v /10^4
1	**1**	MAO	25	37	416.7
2	**1**	MAO	75	110	58.0
3	**1**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	25	227	323.1
4	**1**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	50	331	65.6
5	**1**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	75	421	20.0
6[c]	**1**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	75	564	14.2
7	**2**	MAO	25	9	367.9
8	**2**	MAO	75	106	113.0
9	**2**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	25	6	200.0
10	**2**	$Ph_3C^+B^-(C_6F_5)_4$/TIBA	75	206	19.0

[a]Conditions; 0.1 MPa pressure, toluene 250 mL, 30 min. Complex; 5 μmol. Co-catalyst; MAO; 1.25 mmol, $Ph_3C^+B^-(C_6F_5)_4$; 6 μmol, TIBA; 0.25 mmol. [b]kg-PE / mol-cat·h. [c]TIBA; 0.5 mmol.

ethylene at atmospheric pressure,[10] the activity being very high for titanium complexes having no Cp ligand. With the rationale that the introduction of bulky alkyl group ortho to the phenoxy group would provide better steric protection of the titanium center and result in greater separation between the cationic titanium center and anionic cocatalyst,[3b] complex **2** with *tert*-butyl group ortho to the phenoxy group in the ligand was evaluated in the hope of acquiring much higher catalytic activity. As a result, unexpectedly, complex **2** was found to show lower activities using MAO or $Ph_3C^+B^-(C_6F_5)_4$ / *i*-Bu_3Al as the cocatalyst compared with complex **1**,[9] unlike the analogous titanium complexes having two phenoxy–imine chelate ligands whose activity is enhanced by placing bulky alkyl group ortho to the phenoxy group.[3b,3g,11,12] One possible explanation for the difference in polymerization behavior between the complexes having phenoxy–pyridine and those with phenoxy–imine ligands is that the structures of the active species are different between the two.[13] DFT calculations suggest that complexes **1** and **2** possess cis-located active sites trans to the anionic phenoxy-oxygens (Figure 1 (A)) whereas, as already reported, titanium complexes having phenoxy–imine ligands have cis-located active sites trans to the neutral imine-nitrogens (Figure 1 (B)).[3b] It is apparent that, in Figure 1 (A), a substituent ortho to the phenoxy group is not effective for steric protection of the titanium center and for ion separation between the cationic titanium center and anionic cocatalyst, explaining the difference in polymerization behavior between the titanium complexes having phenoxy–pyridine and those with phenoxy–imine ligands. In addition, the lower activities exhibited by the titanium complexes with phenoxy–pyridine ligands relative to those with phenoxy–imine ligands can be explained when the titanium complexes with phenoxy–pyridine ligands possess active sites trans to the anionic phenoxy-oxygens because the neutral imine-nitrogens trans to the active sites are thought to be responsible for high activities displayed by the titanium complexes bearing phenoxy–imine ligands.



(A) (B)

Figure 1. Calculated structures of active species generated from (A) Ti complex **2** and (B) Ti-FI complex

In conclusion, two new titanium complexes having phenoxy–pyridine chelate ligands have been introduced. The results described herein show the importance of the active species's structure of complexes, which potentially possess more than one active species, for catalytic performance. These results would contribute to further discovery and development of high performance olefin polymerization catalysts.

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5 Spectral data of the complexes: Complex **1** ($C_{26}H_{28}N_4O_2Ti$); ^1H NMR (270 MHz, $CDCl_3$, TMS): δ 3.11 (s, 12H), 6.66 (m, 2H), 6.76 (m, 2H), 6.99 (dd, 2H), 7.24 (dd, 2H), 7.40 (dd, 2H), 7.54 (m, 4H), 8.23 (m, 2H). Anal. Calcd for $C_{26}H_{28}N_4O_2Ti$: C, 65.55; H, 5.92; N, 11.76%. Found; C, 66.13; H, 5.72; N, 10.72%. Complex **2** ($C_{42}H_{60}N_4O_2Ti$); ^1H NMR (270 MHz, $CDCl_3$, TMS): δ 1.32 (s, 18H), 1.63 (s, 18H), 2.93 (s, 12H), 6.62 (m, 2H), 7.24 (d, 2H), 7.40 (d, 2H), 7.51 (m, 4H), 8.43 (d, 2H). Anal. Calcd for $C_{42}H_{60}N_4O_2Ti$: C, 71.98; H, 8.63; N, 7.99%. Found; C, 71.28; H, 8.84; N, 7.79%. FD-MS; *m/z*; 700 (M^+). The structures of the complexes were supported by ^1H NMR and FD-MS spectra, though reasonable elemental analysis data were not obtained because of impurities.

6 General polymerization procedure: Flow of ethylene gas (100 L/h) was charged into 250 mL of toluene at 25 °C. To this solution, MAO (Albemarle MAO, 1.2 M toluene solution) and a toluene solution of a complex was added at the desired polymerization temperature. After the prescribed time, 25 mL of isobutyl alcohol was added to terminate the polymerization.

7 $Ti(NMe_2)_4$/MAO; 4 kg-PE/mol-cat·h (25 °C), 82 kg-PE/mol-cat·h (75 °C): $Ti(NMe_2)_4/Ph_3C^+B^-(C_6F_5)_4$/*i*-$Bu_3Al$; 78 kg-PE/mol-cat·h (25 °C), 252 kg-PE/mol-cat·h (75 °C).

8 M_v values were calculated from the following equation, $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$; R. Chiang, *J. Polymer Sci.*, **36**, 91 (1959). Intrinsic viscosity $[\eta]$ was measured in decaline at 135 °C using an Ubbelohde viscometer.

9 The polyethylenes formed with complexes **1** and **2** possess relatively broad molecular weight distributions (PDIs 4.45 – 8.67). These will be discussed in more detail in connection with the structures of active species in a future publication.

10 For all runs in Table 1, the polymer yield increased constantly with polymerization time, indicating that complexes **1** and **2** retain their catalytic activities for at least 30 min.

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12 On activation with MAO at 25 °C, bis[*N*-(3-*tert*-butylsalicylidene)-phenylaminato]titanium(IV) dichloride displays about 100 times higher ethylene polymerization activity (3400 kg-PE/mol-cat·h) than the corresponding titanium complex having no *t*-Bu group ortho to the phenoxy group (38 kg-PE/mol-cat·h).

13 The titanium complexes potentially possess more than one active species since the complexes have two non-symmetric bidentate phenoxy–pyridine ligands.