Synthesis and Ethylene Polymerization Behavior of a New Titanium Complex Having Two Imine–Phenoxy Chelate Ligands

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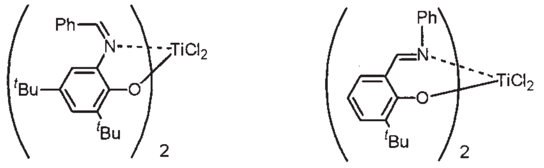
A novel (*N*-benzylidene-2-hydroxy-3,5-di-*t*-butyl-aniline)$_2$TiCl$_2$ complex was synthesized and investigated for its potential as an ethylene polymerization catalyst in the presence of MAO or $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ as a cocatalyst. Upon activation with $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$, the complex displayed higher activities at higher temperatures, and the activity reached a very high value of 5784 kg-PE/mol-Ti·h at 75 °C under atmospheric pressure.

Enormous advances in the chemistry of well-defined group 4 metallocene complex catalysts have made a significant impact in the manufacture of polyolefins. Recently, therefore, the search for new olefin polymerization catalysts based on well-defined transition metal complexes has been a field of major interest involving many academic and industrial research groups.[1,2]

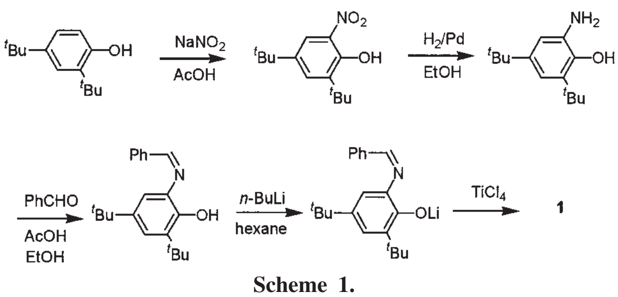
In our own efforts, previously, we have acquired transition metal complexes having non-symmetric [O,N] or [N,N] chelate ligand(s), as catalysts for the polymerization of ethylene and/or α-olefins.[3–6] In this paper, we report on a new titanium complex **1** bearing two non-symmetric imine–phenoxy chelate ligands for ethylene polymerization, which displays different catalytic performance from the previously reported complex **2** having ligands that are structurally different yet contain the same coordination sites (Figure 1).



1 **2**

Figure 1. Structures of new complex **1** and previously reported **2**.[3]

The preparation of the imine–phenoxy ligand, *N*-benzylidene-2-hydroxy-3,5-di-*t*-butylaniline, and its conversion to the desired complex, starting from commercially available 2,4-di-*t*-butylphenol, are shown in Scheme 1.



Scheme 1.

2,4-Di-*t*-butylphenol was transformed in three steps (i: nitration, ii: hydrogenation, iii: condensation with benzaldehyde) to the ligand in 28% yield.[7] Lithiation of the ligand (77%) followed by reaction with 0.5 equiv of $TiCl_4$ in diethyl ether yielded complex **1** (reddish brown powder, 87%).

Complex **1** was characterized by elemental analysis and mass spectrometry.[8] ^{1}H NMR spectroscopy revealed complicated spectra, indicating that the complex **1** exists as an isomeric mixture in solution.[9] Further studies using ^{1}H NMR at varying temperatures suggested the presence of mutually convertible isomers, which may originate from the following; (1) attached/detached state of imine nitrogens, (2) *syn/anti* imine double bonds, and (3) coordination geometry of ligands around the central metal.

Upon activation with methylaluminoxane (MAO) cocatalyst, complex **1** was found to be active towards ethylene polymerization to give solid polyethylenes (Table 1). The activities are moderate in the temperature range of 25–75 °C (101–124 kg-PE/mol-Ti·h) though the molecular weights of the polyethylenes are very high (M_v: 2130000–2320000).[10]

Table 1. Ethylene polymerization results with MAO cocatalyst

Entry	Temp/°C	Yield/mg	Activity[a]	$M_v/10^4$
1	25	321	124	—[b]
2	50	252	101	232
3	75	268	107	213

Conditions: reaction time, 30 min; toluene 250 mL; ethylene gas flow, 100 L/h; pressure, 0.1 MPa; complex, 0.005 mmol; MAO, 1.25 mmol. [a]Activity: kg-PE/mol-Ti·h. [b]Not available due to low yield of polyethylene.

When activated with $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ cocatalyst, however, complex **1** displayed considerably increased activities at raised polymerization temperatures and produced high molecular weight polyethylenes (M_v: 1170000, 560000, Table 2). Thus, the polymerization behavior of complex **1** is totally different from that of the previously reported complex **2**, which exhibited higher activity with MAO (max. 4150 kg-PE/mol-Ti·h, 50 °C) relative to the activity with $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$

Table 2. Ethylene polymerization results with $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ cocatalyst

Entry	Temp/°C	Yield/mg	Activity[a]	$M_v/10^4$
1	25	34	72	—[b]
2	50	576	1382	117
3	75	2410	5784	56

Conditions: reaction time, 5 min; toluene 250 mL; ethylene gas flow, 100 L/h; pressure, 0.1 MPa; complex, 0.005 mmol; $Ph_3C^+B^-(C_6F_5)_4$, 0.006 mmol; $^iBu_3Al$, 0.25 mmol. [a]Activity: kg-PE/mol-Ti·h. [b]Not available due to low yield of polyethylene.

(max. 670 kg-PE/mol-Ti·h, 75 °C).[3f]

The activity value of 5784 kg-PE/mol-Ti·h exhibited at 75 °C represents one of the highest reported activities to date for ethylene polymerization catalysts based on titanium complexes with no Cp ligands at atmospheric pressure conditions.

Studies on the rate profile of complex **1**/$\mathrm{Ph_3C^+B^-(C_6F_5)_4}$/$^i\mathrm{Bu_3Al}$ catalyst system revealed that there is an induction period for the polymerization (Figure 2).

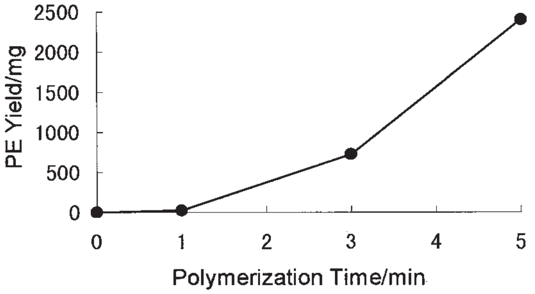


Figure 2. Time dependence of PE yield with **1**/$\mathrm{Ph_3C^+B^-(C_6F_5)_4}$/$^i\mathrm{Bu_3Al}$. Conditions: toluene 250 mL; ethylene gas flow, 100 L/h; pressure, 0.1 MPa; temperature, 75 °C; **1**, 0.005 mmol; $\mathrm{Ph_3C^+B^-(C_6F_5)_4}$, 0.006 mmol; $^i\mathrm{Bu_3Al}$, 0.25 mmol.

An elucidation for the presence of the induction period is given by the structural change of the imine–phenoxy ligand, which is suggested by ^{1}H NMR studies using complex **1**/$^i\mathrm{Bu_3Al}$ mixture (Figure 3). Thus, the treatment of **1** with $^i\mathrm{Bu_3Al}$ resulted in the appearance of AB system peaks at 4.40 ppm and 4.51 ppm, assigned to diastereotopic benzyl protons, as well as a sharp multiplet peak centered at 4.78 ppm, assigned to isobutene protons,[11] indicating that the imine–phenoxy ligand was converted to an amine–phenoxy ligand by the reduction with $^i\mathrm{Bu_3Al}$, which co-produced isobutene during the reaction. This is further confirmed by the fact that the protonolysis of a similar mixture of complex **1** and $^i\mathrm{Bu_3Al}$ (0.25 mmol and 2.80 mmol in 12 mL of toluene, 50 °C, 30 min) gave *N*-benzyl-2-hydroxy-3,5-di-*t*-butylaniline quantitatively.[12] Therefore, a highly active species derived from complex **1**/$\mathrm{Ph_3C^+B^-(C_6F_5)_4}$/$^i\mathrm{Bu_3Al}$ is suggested to have an amine–phenoxy ligand.[13] Although we have reported a similar reduction of an imine-containing ligand,[3b] it is noteworthy that the reduced species exhibits much higher activity in this case.

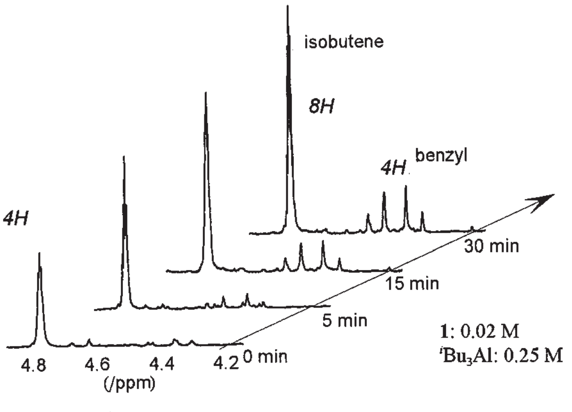


Figure 3. ^{1}H NMR spectra of **1**/$^i\mathrm{Bu_3Al}$ in toluene-d_8 at 50 °C.

In summary, new ethylene polymerization catalyst systems based on Ti complex having two imine–phenoxy chelate ligands have been introduced. The discovery of the **1**/$\mathrm{Ph_3C^+B^-(C_6F_5)_4}$/$^i\mathrm{Bu_3Al}$ catalyst system exhibiting high activities at high polymerization temperatures is of great significance. The results introduced herein demonstrate that a dramatic effect can be obtained on catalytic performance by only changing chelate architecture in the complex. Successful polymerization and copolymerization of olefins and further preparation of derivatives are underway.

References and Notes

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7 ^{1}H NMR data for *N*-benzylidene-2-hydroxy-3,5-di-*t*-butylaniline (δ, ppm, $\mathrm{CDCl_3}$, 25 °C): 8.70 (s, 1H), 7.96–7.92 (m, 2H), 7.73 (s, 1H), 7.48–7.43 (m ,3H), 7.25 (d, 1H, 2 Hz), 7.17 (d, 1H, 2 Hz), 1.46 (s, 9H), 1.35 (s, 9H).

8 Anal. Found: C, 68.72; H, 6.91; N, 3.83%. Calcd for $\mathrm{C_{42}H_{52}Cl_2N_2O_2Ti}$: C, 68.57; H, 7.12; N, 3.81%. FD-MS (*m/z*): 734 ($\mathrm{M^+}$), and the relative intensities of the other peaks are less than 5%.

9 ^{1}H NMR (δ, $\mathrm{C_6D_6}$): At least 10 major singlet peaks attributed to ^{t}Bu groups appeared in the region of 0.8–2.2 ppm at room temperature. The number of the peaks was reduced to 6 when the temperature was raised to 75 °C.

10 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 decalin at 135 °C using an Ubbelohde viscometer.

11 The NMR was identified by comparison with authentic isobutene.

12 ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 7.32 (m, 5H), 6.85 (m, 1H), 6.73 (m, 1H), 5,95 (bs, 1H), 4.12 (s, 2H), 3.20 (bs, 1H), 1.39 (s, 9H), 1.20 (s, 9H). FD-MS (*m/z*): 311 ($\mathrm{M^+}$).

13 This conclusion is confirmed by the fact that the mixture, which gave *N*-benzyl-2-hydroxy-3,5-di-*t*-butylaniline by protonolysis, displayed 7704 kg-PE/mol-Ti·h of activity without any induction period under the conditions given in Table 2.