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New group 4 half sandwich complexes containing triethanolamine ligand for polyethylene

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Abstract

$(\eta^5\text{-}C_5Me_5)M(TEA)$ (M = Ti, **1**; Zr, **2**; Hf, **3**; TEA = triethanolateamine) was prepared by the reaction of $(\eta^5\text{-}C_5Me_5)MCl_3$ with triethanolamine in the presence of NEt_3. The polyethylene catalytic efficiency in terms of activity decreases in the order **1**/MAO > **2**/MAO ≫ **3**/MAO. In addition, the molecular weight (M_v) and melting temperature (T_m) of all the resulting polyethylene obtained by **2**/MAO show the range of M_v = 91,200–356,200 and T_m = 137.0–141.9 °C, respectively; however, **1**/MAO and **3**/MAO gave polyethylenes with lower molecular weight (M_v = 6800–78,700) and lower melting temperature (T_m = 125.9–136.7 °C). Furthermore, **1**/MAO showed significant decrease in the catalytic activity with increasing polymerization temperature though **2**/MAO and **3**/MAO have no dependence on the polymerization temperature.
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1. Introduction

A wide variety of PE (polyethylene) catalytic systems based on organometallic complexes have been reported in the literature. [1–10] Most studies on PE catalysts has been focused on the use of group 4 metallocene compounds, [1] constrained-geometry catalysts, [2] group 4 compounds with diamide and dialkoxide ligands, [3,4] late transition metal with diimine ligands, [5] and chromium complexes. [6] However, only few reports on half-sandwich group 4 compounds for PE have thus appeared. [7,8] The examples include $Cp'Ti(OAr)X_2$ [7] and $Cp'TiCl_2(NPR_3)$ [8] which are among the most active catalysts.

Recently, we found half-sandwich titanium complexes, i.e., Cp*Ti(TEA) or Cp*Ti(DEA-R)Cl (TEA = triethanolateamine, $N(CH_2CH_2O^-)_3$; DEA-R = *N*-alkyldiethanolateamine, $RN(CH_2CH_2O^-)_2$) could act as very efficient catalytic systems for sPS (syndiotactic polystyrene). [11] The fact that the introduction of multidentate TEA or DEA-R ligand in the catalytic system could electronically modify the catalytic active site for sPS has a room for the application of half-sandwich group 4 catalysts containing TEA ligand into the formation of PE. Only few examples of titanatrane as catalysts for PE are reported; however, examples of zirconium or hafnium complexes containing triethanolamine ligand as catalysts for PE have to our knowledge not been reported [12]. In this regard, reported herein are the synthesis of Cp*M(TEA) (M = Ti, Zr and Hf) as well as their efficient catalytic behavior in the formation of PE in the presence of MAO as cocatalyst.

2. Experimental

2.1. General procedure

All operations were performed under pure argon atmosphere using a Vacuum Atmosphere drybox equipped with a Model HE 493 Dri-Train gas purifier or standard Schlenk techniques. [13] Argon was deoxygenated with activated Cu catalyst and dried with drierite. All solvents were dried under a nitrogen atmosphere and distilled from sodium–potassium alloy/benzophenone ketyl (toluene, THF (tetrahydorfuran), diethylether) or CaH_2 (methylene chloride) and stored over the activated molecular sieves 3A. [14] Deuterated solvents were dried before use by trap-to-trap distillation from the activated molecular sieves 4A. ^1H and $^{13}C\{^1H\}$ FT NMR spectra were recorded on a Bruker AM 300 spectrometer. The chemical shifts are referenced to the residual peaks of the $CDCl_3$ (7.24 ppm in ^1H NMR, 77.0 ppm in $^{13}C\{^1H\}$ NMR). Elemental analyses were obtained by Korea Basic Science Center, Seoul, Korea.

2.2. Synthesis

All chemicals were purchased from Aldrich. Cp*Ti-(TEA) (**1**) [11] and Cp*MCl₃ [15] were synthesized by literature procedure. MAO (Methylalumoxane) was purchased from Akzo (Modified MAO-3A in toluene, Al content = 5.9 wt%, $d = 0.89$ g/mL).

2.3. Synthesis of Cp*Zr(TEA) (2)

A greenish solution of Cp*ZrCl₃ (1.66 g, 5.0 mmol) in 40 mL CH_2Cl_2 was added dropwise to a solution of triethanolamine (0.75 g, 5.0 mmol) and triethylamine (2.1 mL, 15 mmol) in 40 mL CH_2Cl_2 at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h before filtration. The residue, obtained by removing the solvent under vacuum, was redissolved in toluene and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **2** in 80% yield (1.49 g). ^1H NMR (300.13 MHz, CDCl₃, ppm): $\delta = 4.18$ (t, 6H, $^3J_{HH} = 5.5$ Hz, OCH₂), 2.87 (t, 6H, $^3J_{HH} = 5.54$ Hz, NCH₂), 1.92 (s, 15H, C₅(CH₃)₅). $^{13}C\{^1H\}$ NMR (75.1 MHz, CDCl₃, ppm): $\delta = 118.83$ (C₅(CH₃)₅), 66.79 (OCH₂), 56.04 (NCH₂), 10.29 (C₅(CH₃)₅). Elemental Analysis: Calcd for C₁₆H₂₇O₃NZr: C, 51.57; H, 7.30; N, 3.76. Found: C, 51.98; H, 7.15; N, 3.90%.

### 2.4. Synthesis of Cp*Hf(TEA) (3)

A desired product **3** was prepared in a yield of 78% (1.49 g) by reacting Cp*HfCl₃ (2.10 g, 5.0 mmol) with triethanolamine (0.75 g, 5.0 mmol) and triethylamine (2.1 mL, 15 mmol) in a manner analogous to the procedure for **2**. ^1H NMR (300.13 MHz, CDCl₃, ppm): $\delta = 4.21$ (t, 6H, $^3J_{HH} = 5.5$ Hz, OCH₂), 2.82 (t, 6H, $^3J_{HH} = 5.5$ Hz, NCH₂), 1.94 (s, 15H, C₅(CH₃)₅). $^{13}C\{^1H\}$ NMR (75.1 MHz, CDCl₃, ppm): $\delta = 117.50$ (C₅(CH₃)₅), 65.96 (OCH₂), 55.67 (NCH₂), 10.21 (C₅(CH₃)₅). Elemental Analysis: Calcd for C₁₆H₂₇O₃NHf: C, 41.79; H, 5.92; N, 3.05. Found: C, 41.48; H, 6.33; N, 3.42%.

2.5. Polymerization procedure and polymer characterization

Ethylene polymerizations were carried out in 500 mL-glass reactor with mechanical stirrer. Toluene, the polymerization solvent, was distilled from sodium–potassium (Na–K) alloy under argon atmosphere just before use. Polymerizations were carried out as following: toluene, MAO, and the metal compound were injected into 500 mL-glass reactor with mechanical stirrer in that order at the desired temperatures of 0, 20, 40, and 60 °C. The solution was then saturated with 5 atm. of ethylene and ethylene pressure was kept constant during the polymerization by a Drag-Tescom pressure reducer. The ethylene flow rate was measured by a BRONKHORST mass flow controller (HI-TEC F1CO-FA-22-Z). After the desired reaction time was reached, polymerizations were terminated by venting the ethylene gas and quenching with a small volume of MeOH. The polymer was isolated by filtration, washed with MeOH, a solution of 4 M HCl in MeOH and MeOH in that order, and then dried in vacuo at 80 °C for 12 h. The intrinsic viscosity of the polymer was determined in decalin at 135 °C using Ubbelode viscometer and the value of M_v were calculated from conventional method. [16] The thermal properties of the polymers were investigated by DSC system (Thermal Analyst 200) under nitrogen atmosphere at a heating rate of 10 °C/min. The results of the second scan were recorded to eliminate differences from the sample history.

3. Results and discussion
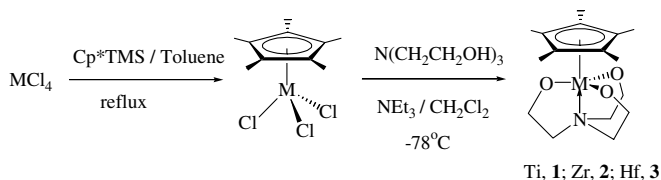
The compounds **1**–**3** were prepared by synthetic routes as outlined above. The reaction of a solution of Cp*MCl₃ in CH_2Cl_2 with triethanolamine in the presence of triethylamine afforded crystalline solids Cp*M(TEA) in a yield of 78–81%. Attempt to synthesize a product using Li₃[(OCH₂CH₂)₃N] instead of triethanolamine in toluene has not been successful and resulted several mixtures of unknown compounds. Yellow crystalline solid **1** is freely soluble in toluene, methylene chloride, ethereal solvent, and hydrocarbon solvents such as hexane. However, pale yellow solid **2** and colorless solid **3** are freely soluble in

toluene and methylene chloride but insoluble in hydrocarbon solvents. In addition, compounds **2** and **3** are fairly air-sensitive and thermally unstable, whereas **1** is air- and thermally stable.

The compounds **2** and **3** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** and **3** show the presence of only one pure compound. In comparison to the free triethanolamine precursors, all signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra are shifted to downfield, which is a consequence of the high Lewis acidity of group 4 metals. In the ^{1}H NMR spectra, the extent of downfield shift in ^{1}H NMR spectra is greater for OCH_2 resonances than those from CH_2N. The OCH_2 resonance in the ^{1}H NMR shifted downfield by approximately 0.8 ppm versus the free ligand. A somewhat smaller downfield shift by 0.4 ppm was observed for the CH_2N resonance. The greater extent of downfield shifts of OCH_2 resonance than those of NCH_2 resonance suggests a strong bond between O atom and the group 4 metal atoms and a weak interaction between the N atom and the group 4 metal atoms upon complexation. In addition, as going from **1** to **3**, the electron density at metal center gradually increased and upfield shift of OCH_2 and Cp* resonances in ^{1}H and ^{13}C{^{1}H} NMR was observed as expected. In the ^{1}H NMR spectra of compounds **1**–**3**, the AA'XX' spin system for the methylene protons for $N(CH_2CH_2O)_3M$ cage (M = Ti, Zr and Hf) manifests itself as two virtual triplets, indicating virtual C_{3v} symmetry in solution at ambient temperature and rapid conformational exchange within structural units. This pattern is a general feature of monomeric atrane and azatrane complexes [11,17]. The NMR signals were sharp and variable-temperature studies showed no evidence of inter- or intramolecular ligand exchange at ambient temperature. In spite of the absence of X-ray structural determination of **2** and **3**, it is possible to clarify that **2** and **3** are monomeric species because the structure for **1** is reported by us [11] and NMR data did not show any dimeric or polymeric characteristics. The same observation has been made for Cp*Ti(TEA) and their derivatives [11]. Furthermore, it is interesting to note that the observed separations of about 5.5 Hz within these triplets in all compounds are independent of kinds of metal ion.

The newly synthesized catalyst precursors **1**–**3** are examined as catalysts for ethylene polymerization in the presence of MAO cocatalyst. The polymerization results are summarized in Tables 1 and 2 in terms of the catalytic activities, T_m, M_v and ΔH_f. To probe the characteristics of catalysts for the polymerization reaction, ethylene polymerizations were carried out at various temperatures under the fixed MAO concentration or at various [Al]/[M] ratio under the same polymerization temperature. Fig. 1 shows the polymerization rate with three different catalysts as a function of time. Unlike **2**/MAO and **3**/MAO, the maximum rate of polymerization for **1**/MAO was obtained within a few minutes and a rapid decrease of the polymerization rate to about one-third of the maximum rate was

Table 1
Ethylene polymerization catalyzed by **1**–**3**/MAO under the same Al/M molar ratio[a]

Run	Catalyst	Al/M	T_p (°C)	A[b]	M_v[c] (×10³)	T_m (°C)	ΔH_f[d] (J/g)
1	**1**	2000	0	1865	78.7	131.2	151.3
2	**1**	2000	20	2207	45.9	127.1	157.3
3	**1**	2000	40	1893	17.3	126.7	143.9
4	**1**	2000	60	1024	6.8	125.9	148.7
5	**2**	2000	0	259	356.2	141.8	129.5
6	**2**	2000	20	372	319.9	140.8	110.2
7	**2**	2000	40	1024	178.6	139.2	156.8
8	**2**	2000	60	866	128.3	137.0	156.1
9	**3**	2000	0	182	41.5	136.7	149.3
10	**3**	2000	20	197	39.3	135.0	153.5
11	**3**	2000	40	142	43.9	133.0	176.0
12	**3**	2000	60	105	15.8	128.5	169.1

[a] Polymerization condition: [M] = 8.61 μmol, T_p = 40 °C, ethylene pressure = 5 atm., time = 30 min, 100 mL toluene.
[b] Activity = kg PE/(mol catalyst h atm).
[c] Viscosity average molecular weight measured by Ubbelode viscometer.
[d] Heat of fusion, which is obtained through DSC.

Table 2
Ethylene polymerization catalyzed by **1**–**3**/MAO under the same polymerization temperature[a]

Run	Catalyst	Al/M	T_p (°C)	A[b]	M_v[c] (×10³)	T_m (°C)	ΔH_f[d] (J/g)
1	**1**	1000	40	1429	17.7	127.3	134.4
2	**1**	2000	40	1893	17.3	126.7	143.9
3	**1**	4000	40	3298	10.4	129.8	103.5
4	**1**	6000	40	3699	8.1	127.6	119.8
5	**2**	1000	40	899	91.2	139.1	94.3
6	**2**	2000	40	1024	178.6	139.2	156.8
7	**2**	4000	40	1166	181.1	141.9	119.8
8	**2**	6000	40	1299	180.3	140.2	94.6
9	**3**	1000	40	86	56.3	127.8	148.6
10	**3**	2000	40	142	43.9	133.0	176.0
11	**3**	4000	40	189	37.5	132.9	159.1
12	**3**	6000	40	209	23.4	134.6	177.4

[a] Polymerization condition: [M] = 8.61 μmol, ethylene pressure = 5 atm., time = 30 min, 100 mL toluene.
[b] Activity = kg PE/(mol catalyst h).
[c] Viscosity average molecular weight measured by Ubbelode viscometer.
[d] Heat of fusion, which is obtained through DSC.

observed [18]. This rapid deactivation might be caused by the instability of titanium active center during the propagation step of the polymerization. In addition, Fig. 1 demonstrated that the catalytic activity for **2**/MAO system increased with the polymerization time. It means that much more stable active site from **2**/MAO than that from **1**/MAO was generated and sustained for several hours during the polymerization, in spite of low initial ethylene consumption rate for **2**/MAO. Fig. 1 described that each catalyst might generate the dissimilar active species with different electronic and steric effects on metal center, even though the active species of each catalyst for ethylene polymerization were generated with same polymerization condition.

Table 1 shows the ethylene polymerization data under the condition of various polymerization temperatures at 0, 20, 40 and 60 °C and the fixed MAO contents using **1**–**3**/MAO. The activity in the olefin polymerization using homogeneous catalysts generally increases along with the raised polymerization temperature. However, this generality was broken off and the maximum activities for three different catalyst systems **1**–**3** were observed at 20, 40, and 20 °C, respectively (see the first column of (a) in Fig. 2). In addition, **1**/MAO and **3**/MAO showed the independence of the polymerization temperature with molecular weight (M_v) of PE; however, the remarkable decrease in molecular weight for **2**/MAO was observed at the first column of (b) in Fig. 2. Furthermore, **2**/MAO system is interesting that polyethylenes with high T_m and high molecular weight are consistently made at all polymerization temperature at the first column of (c) in Fig. 2. Additionally, it is natural that all catalyst systems show a lowering T_m value with increasing polymerization temperature. The highest heat of fusion (ΔH_f) of polyethylene obtained by **3**/MAO suggests that they have higher crystallinity than the other polyethylene by **1**/MAO and **2**/MAO through the lower polymerization rate and the slow growth of polymer chain. According to above results, **2**/MAO system can be useful for ethylene polymerization because of its moderate catalytic activity and good polymer properties such as molecular weight and melting temperature.

Table 2 shows the ethylene polymerization data under the condition of various mole ratio of Al/M in the range of 1000–6000 and the fixed polymerization temperature of 40 °C using **1**–**3**/MAO. The tremendous enhancement of the catalytic activity with an increase of MAO concentration for **1**/MAO is as expected; however, **2**/MAO and **3**/MAO abnormally showed only slight increment in catalytic activity under various range of Al/Zr ratio at the second column of (a) in Fig. 2. In addition, the molecular weight of polyethylene by **1**/MAO and **3**/MAO decreased slightly with increase of MAO content, but molecular weight for **2**/MAO increased slightly with
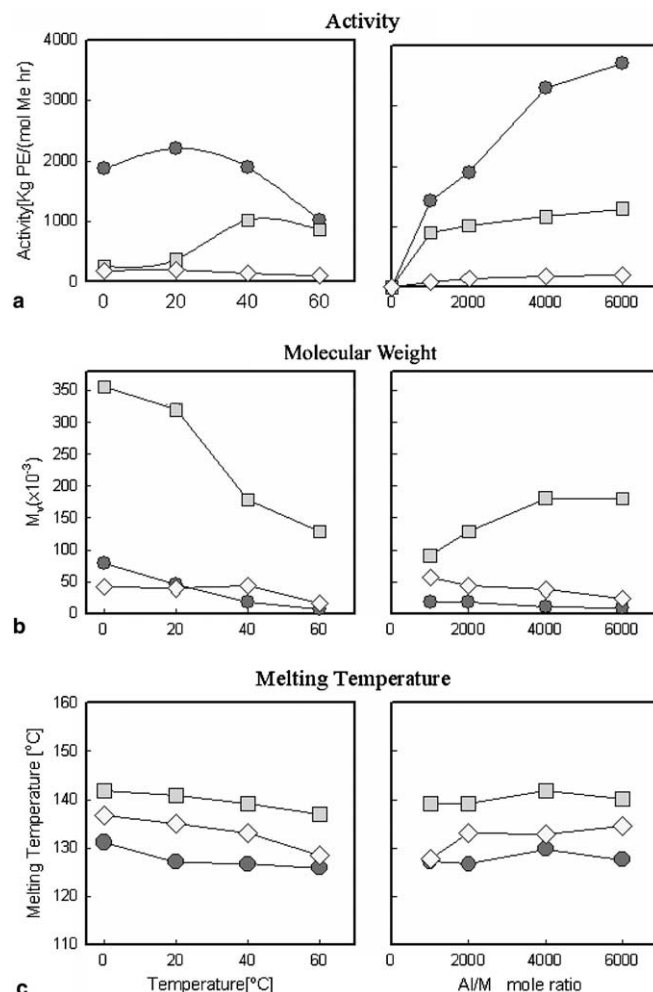

Fig. 2. The properties of PE as function of polymerization temperature and Al/M mole ratio: ●, **1**/MAO; □, **2**/MAO and ◇, **3**/MAO.

amount of MAO at the second column of (b) in Fig. 2. The dependence of T_m on Al/M ratio for **1**–**3**/MAO is not clear. (See the second column of (c) in Fig. 2.)

In Summary, the polymerization data in Tables 1 and 2 reveal that **1**/MAO is the most efficient system in producing polyethylene in terms of activity and conversion at all polymerization temperatures; however, **2**/MAO is the most effective in terms of T_m and molecular weight at all polymerization temperatures.

Acknowledgement

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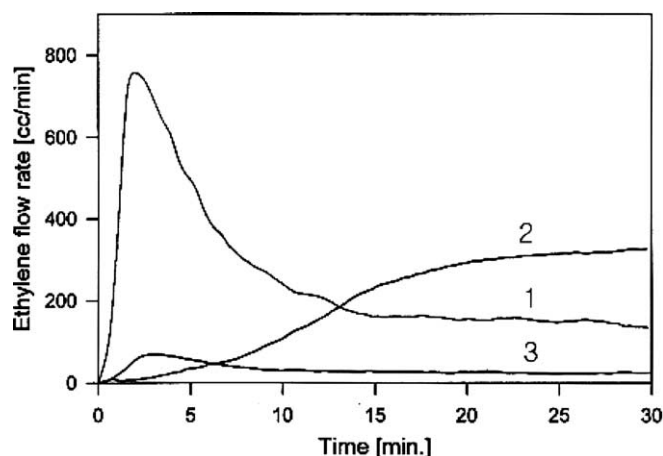K. Soga, T. Shiono, Prog. Polym. Sci. 22 (1997) 1503;

Fig. 1. Kinetic profile of ethylene polymerization using **1**–**3**/MAO.

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