Post-Metallocenes: A New Bis(salicylaldiminato) Zirconium Complex for Ethylene Polymerization

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A new bis(salicylaldiminato) zirconium complex was synthesized and its structure determined by X-ray analysis. This complex displayed an exceptionally high ethylene polymerization activity of 519 kg-PE/mmol-Zr • h using methylaluminoxane (MAO) as a cocatalyst. In contrast, by using $Ph_3C^+B^-(C_6F_5)_4$ / $^iBu_3Al$ as a cocatalyst, the complex furnished polyethylene of exceptionally high molecular weight (*Mv*; 505x10^4).

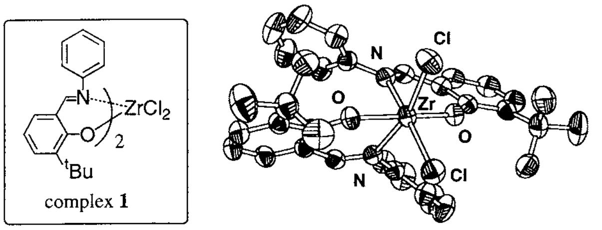
After the discovery of group 4 metallocene catalyst systems, there has been increasing interest in well-defined transition metal complexes.[1] Therefore, not only metallocenes, possessing Cp ligands, but also post-metallocenes, possessing no Cp ligands, have been intensively investigated in an attempt to create high performance polymerization catalysts. Among post-metallocenes, a certain number of complexes were found to exhibit intriguing polymerization properties,[2] but their catalyst performance was not attained the level of group 4 metallocenes. However, recently, some excellent post-metallocenes, displaying comparable catalytic performance in some ways to group 4 metallocenes have been reported.[3] The most notable example concerning polymerization activity was a series of iron complexes, reported by Brookhart et al. [3d] and Gibson et al. [3e] Ethylene polymerization activity of the iron complexes was comparable to that of group 4 metallocenes.

Recently, we reported that new titanium complexes having two bidentate salicylaldimine ligands with MAO as a cocatalyst displayed considerable ethylene polymerization activity.[4] These results boosted us to perform further study on group 4 metal complexes possessing bidentate salicylaldimine ligands.

In this paper, we wish to report on the corresponding zirconium complex bearing two bidentate salicylaldimine ligands. Thus, we here describe a structure of bis[N-(3-t-butylsalicylidene)phenylaminato]zirconium(IV)dichloride (**1**), and its catalytic performance for ethylene polymerization.

The ligand of complex **1** was prepared according to our previous paper.[4] A complexation of $ZrCl_4$•2THF with 2 equiv of N-(3-t-butylsalicylidene)aniline lithium salt in THF furnished complex **1**, in 52% yield. Single crystals of complex **1** were obtained from its dichloromethane / diethyl ether solution. X-Ray crystallographic structure is depicted in Figure 1.[5]

Regarding the configuration of complex **1**, two oxygen atoms were situated in trans-position, (the O-Zr-O angle being 165.5 degrees). Alternatively, two nitrogen atoms were situated in cis-position, (the N-Zr-N angle being 74.0 degrees), and two chlorine atoms were also situated in cis-position, (the Cl-Zr-Cl angle being 100.4 degrees). As a result, complex **1** adopted a distorted octahedral coordination structure around the zirconium metal. This configuration was the same as that of bis[N-(3-t-butylsalicylidene)phenylaminato]titanium(IV)dichloride, as reported in our previous paper.[4] As two chlorine atoms are situated in cis-position in complex **1**, same as the corresponding titanium complex, complex **1** is also expected to possess a convenient stereo-chemical structure for olefin polymerization.



complex **1**

Figure 1. X-Ray structure of complex **1**.
Thermal ellipsoids are shown at 50% probability level. The hydrogen atoms, and a diethyl ether molecule of crystallization are omitted for clarity. Selected bond distances (Å): Zr-O = 1.985(2); Zr-N = 2.355(2); Zr-Cl = 2.4234(9).

Thus, complex **1** was investigated as an ethylene polymerization catalyst using MAO as a cocatalyst.[6] Results are summarized in Table 1.

Table 1. Ethylene polymerization results [Cocatalyst; MAO]

Entry	Cat.	Cat. concentration /μM	Yield /g	Activity *a	*Mv* *b / 10^4
1	**1**	2.0	4.85	116	1
2	**1**	0.08	0.87	519	1
3	Cp_2ZrCl_2	8.0	3.35	20	95
4	Cp_2ZrCl_2	2.0	1.13	27	104

[Conditions: 25 °C, 0.1 MPa pressure, toluene; 250 ml, polymerization time; 5 min, MAO (Al); 1.25 mmol.]
*a / kg-PE · mmol-Zr^{-1} · h^{-1}. *b see ref 8.

Complex **1** displayed a very high activity of 116 kg-PE/mmol-Zr•h in toluene at 25 °C even under atmospheric pressure, (Table 1, Entry 1). This activity value was much higher than that displayed by Cp_2ZrCl_2, (Table 1, Entry 3,4).

Since, for entry 1, stirring difficulty was encountered because of excessive polymer production, we conducted ethylene polymerization under reduced catalyst concentrations in order to obtain the accurate activity of complex **1**, (Table 1, Entry 2). As a result, complex **1** was revealed to display an exceptionally high activity of 519 kg-PE/mmol-Zr•h.[7] To the best of our knowledge, this activity is one of the highest for ethylene polymerization amongst not only post-metallocenes but also olefin polymerization catalysts including group 4 metallocenes.

The molecular weight (*Mv*)[8] of the polymer obtained was 1x10^4. The molecular weight distribution (*Mw*/*Mn*), based on GPC measurement, was 2.06. This *Mw*/*Mn* value suggests that polymer was produced by a single active species. Melting temperature (Tm) of the polymer obtained was 128 °C. ^{13}C-NMR of the polymer indicated a typical linear polyethylene, which was produced by group 4 metallocenes.

In order to investigate the catalytic lifetime of complex **1**, polymerization was conducted for 5 min, 15 min, and 30 min. By plotting the polymer yields vs polymerization times, a nearly straight line was found, as shown in figure 2. This fact indicated complex **1** had a catalytic lifetime of at least 30 min.

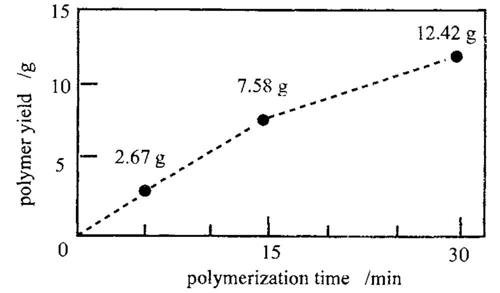


Figure 2. Relationship between polymerization time and polymer yield.
Conditions: 0.1 MPa pressuure, toluene 400 ml, 25 °C, cat.; 0.08 μmol, MAO; 1.25 mmol.

Perfluoroborate is well-known as an effective cocatalyst for olefin polymerization, as well as MAO. Thus, complex **1** using $Ph_3C^+B^-(C_6F_5)_4$ / $^iBu_3Al$ as a cocatalyst was also investigated.[6] Results are shown in Table 2.

Table 2. Ethylene polymerization results
[Cocatlyst; $Ph_3C^+B^-(C_6F_5)_4$ / $^iBu_3Al$]

Entry	Cat.	Cat. concentration /μM	Yield /g	Activity *c	Mv *d / 10^4
1*a	**1**	10.0	2.31	11	505
2*b	Cp_2ZrCl_2	2.0	0.87	21	36

[Conditions: 50 °C, 0.1 MPa pressure, toluene; 250 ml, polymerization time; 5 min., Cat. /$Ph_3C^+B^-(C_6F_5)_4$ = 1 /2, $^iBu_3Al$; *a 0.25 mmol, *b 0.10 mmol.]
*c / kg-PE · mmol-Zr^{-1} · h^{-1}. *d see ref 8.

Complex **1** provided linear (Tm = 135 °C) and exceptionally high molecular weight (Mv; 505×10^4) polyethylene with considerable activity (11 kg-PE/mmol-Zr•h), (Table 2, Entry 1). This molecular weight value was much larger than that displayed by Cp_2ZrCl_2 (Mv; 36×10^4; Table 2, Entry 2) and one of the highest molecular weight values displayed by homogeneous olefin polymerization catalysts.[9] Considering the great difference of catalytic performance as a result of using different cocatalysts, structures of active species are different depending on the cocatalyst employed. Investigation of active species is now in progress.

In summary, a promising novel post-metallocene, bis[N-(3-t-butylsalicylidene)phenylaminato]zirconium(IV)dichloride (**1**), has been introduced. Complex **1** using MAO as a cocatalyst provided exceptionally high ethylene polymerization activity, 519 kg-PE/mmol-Zr•h, which is one of the highest activities amongst that of olefin polymerization catalysts. In contrast, complex **1** using $Ph_3C^+B^-(C_6F_5)_4$ /. $^iBu_3Al$ as a cocatalyst, produced polyethylene having exceptionally high molecular weight, (Mv = 505 × 10^4). This is probably the first example of a great difference as a result of using different cocatalysts.

References and Notes

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5 Complex **1**: $ZrC_{34}H_{36}N_2O_2Cl_2 \cdot 0.5Et_2O$, ^{1}H-NMR (500 MHz, $CDCl_3$); δ 1.33-1.59 (m, 18H, tBu), 6.78-7.42 (m, 16H, aromatic-H), 8.12, (s, 2H, CH=N); Et_2O of crystallization, 1.20 (t, J= 5 Hz, $(C\underline{H}_3CH_2)_2O$), 3.48 (q, J= 5 Hz, $(CH_3C\underline{H}_2)_2O$). (Complex 1 exists as isomeric mixtures in $CDCl_3$ solution.) Anal. Found; C, 60.86; H, 5.36; N, 3.67; Zr, 12.70%. Calcd; C, 61.43; H, 5.87; N, 3.98; Zr, 12.96%. FD-mass, 664 (M+: $ZrC_{34}H_{36}N_2O_2Cl_2$). m.p.; 287 °C (measured by DSC). IR (KBr); 1550, 1590, 1605 cm^{-1}.
Crystal data: F.W. = 703.86, monoclinic system, space group C2/c(#15), a = 25.464(9) Å, b = 8.763(6) Å, c = 17.119(6) Å, V= 3761(3) Å^3, Z =4, D_{calc} = 1.177 g/cm^3, R = 0.039, Rw = 0.041, F_{000} = 1376.00, 4602 unique reflections (R_{int} = 0.030) were collected, λ (Mo-ka) = 4.61 cm^{-1}.

6 Flow of ethylene gas (100 L/h) was charged into 250 ml of toluene at 25 °C. To this solution, a solution of a complex and a cocatalyst (MAO (produced by Albemarle), or $Ph_3C^+B^-(C_6F_5)_4$ / $^iBu_3Al$) was added at 25 °C. After the prescribed time, 25 ml of isobutanol was added to terminate the polymerization. To the resulting mixture, 500 ml of methanol was added. After filteration, the polymer was dried *in vacuo* at 80 °C for 10 h.

7 Complex **1** / MAO displayed an activity of 185 kg-PE/mmol-Zr•h with an Mv of 1 × 10^4 at even 0 °C under 0.1 MPa pressure, (cat. concentration: 0.8 μM).

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