

Post-Metallocenes: Catalytic Performance of New Bis(salicylaldiminato) Zirconium Complexes for Ethylene Polymerization

Shigekazu Matsui, Makoto Mitani, Junji Saito, Naoto Matsukawa, Hidetsugu Tanaka, Takashi Nakano, and Terunori Fujita*
 Material Science Laboratory, Mitsui Chemicals, Inc., Nagaura, Sodegaura, Chiba 299-0265

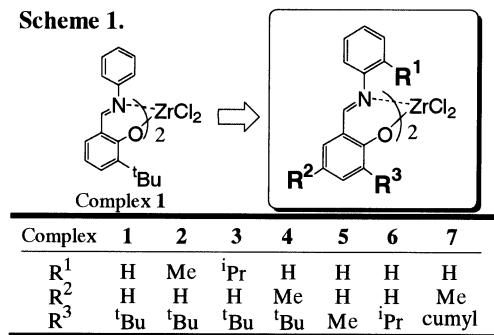
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New bis(salicylaldiminato) zirconium complexes were synthesized and investigated as ethylene polymerization catalysts. As a result, we demonstrated that high molecular weight (M_w : 71.6×10^4) and super high activity (2096 kg-PE/mmol-Zr·h) were accomplished by changing the ligand structure.

In recent years, olefin polymerization catalysts based on well-defined transition metal complexes have been intensively investigated for creating high performance catalysts. These catalysts possess potential for controlling polymer structure while displaying high polymerization activity by changing the ligand structure, as demonstrated by group 4 metallocenes.¹

Recently, a certain number of post-metallocenes, which display intriguing olefin polymerization properties, have been discovered.^{2,3} It has been demonstrated that the catalytic performance of these complexes was controllable by changing the ligand structure.³ We have already reported that post-metallocenes based on group 4 transition metals, having salicylaldimine ligands, exhibit high ethylene polymerization activity.⁴ As a continuation of this work, we synthesized new bis(salicylaldiminato) zirconium complexes and studied their catalytic performance for ethylene polymerization using MAO as a cocatalyst.

Scheme 1.



Concerning the ligand structure of bis[*N*-(3-*t*-butylsalicyl)phenylamino]zirconium(IV) dichloride (**1**),^{4b} we changed the substituent, especially changing the substituents R¹ and R³, both near the polymerization reaction center, and investigated what happened to the catalytic performance (Scheme 1).⁵⁻⁷

Table 1 summarizes the catalytic performance of bis(salicylaldiminato) zirconium complexes as a result of introducing an alkyl group at the R¹ position.⁸ Complex **1** (R¹ = H) furnished an M_w value of 0.8×10^4 , based on GPC measurement. The introduction of a methyl group at the R¹ position (complex **2**) dramatically boosted the M_w value to 23.0×10^4 . Moreover, the introduction of a larger alkyl group further enhanced the molecular weight. Thus, complex **3** (R¹ = ⁱPr) provided an M_w value of 71.6×10^4 , an M_w value comparable to that of Cp₂ZrCl₂. These results indicate that the molecular weight values depend on the

Table 1. Ethylene polymerization results (Effect of the R¹)

Entry	Complex	Yield / g	Activity ^c	$M_w^d / 10^4$
1 ^a	1	0.87	519	0.8
2 ^b	2	1.68	40	23.0
3 ^b	3	2.41	58	71.6
Ref. ^b	Cp ₂ ZrCl ₂	1.13	27	63.6

Conditions: 25 °C, 0.1 MPa pressure, MAO (Al); 1.25 mmol, toluene; 250 ml, polymerization time; 5 min. Complex concentration; ^a0.08 μM, ^b2.0 μM. ^c/ kg-PE · mmol-Zr⁻¹ · h⁻¹. ^d M_w values were determined by using polyethylene calibration.

bulkiness of the R¹ substituents.

The increase in M_w values is rationalized as follows; namely, introduced alkyl groups diminished chain transfer reaction, or β-hydride elimination. Theoretical calculations supported this rationalization.⁹ The stabilization energy (ΔE_β) as a result of β-agostic interaction of the active species generated from complex **3** (model **B**; Figure 1 right) was smaller than that for complex **1** (model **A**; Figure 1 left), due to the steric repulsion of a β-hydrogen and an isopropyl group. Thus, the introduced isopropyl group at the R¹ position energetically destabilized the conformation of the polymer chain leading to β-hydride elimination.

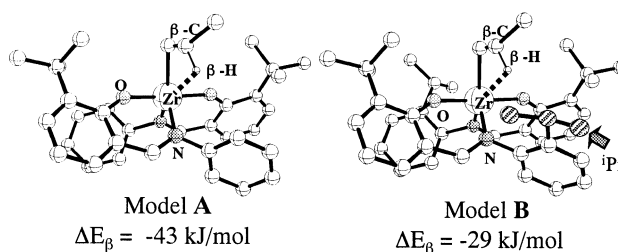


Figure 1. The stabilization energies (ΔE_β) as a result of β-agostic interaction. Cation complex models **A** and **B** stand for active species generated from complexes **1** and **3**, respectively. All hydrogens except the β-hydrogen are omitted. ⁿPr group is employed as a model of a polymer chain.

Regarding polymerization activity, complex **3** displayed 58 kg-PE/mmol-Zr·h, which was higher than that of Cp₂ZrCl₂ under the same polymerization conditions.

Table 2 summarizes the catalytic performance of bis(salicylaldiminato) zirconium complexes as a result of introducing an alkyl group at the R² position and changing the alkyl substituent at the R³ position.¹⁰

Introduction of a methyl group at the R² position resulted in no significant change with respect to catalytic performance though it somewhat lowered polymerization activity. Complex **4**, R² = Me, afforded 331 kg-PE/mmol-Zr·h of activity with an M_w value of 0.8×10^4 (Table 2, Entry 1, 2).

Table 2. Ethylene polymerization results (Effect of the R² and R³)

Entry	Complex	Yield / g	Activity ^d	Mw ^e / 10 ⁴
1 ^a	1	0.87	519	0.8
2 ^a	4	0.55	331	0.8
3 ^b	5	0.18	0.4	0.4
4 ^b	6	0.39	0.9	0.5
5 ^c	7	1.75	2096	2.6

Conditions: 25 °C, 0.1 MPa pressure, MAO (Al); 1.25 mmol, toluene; 250 ml, polymerization time; 5 min., Complex concentration; ^a0.08 μM, ^b20.0 μM, ^c0.04 μM. ^d/ kg-PE · mmol-Zr⁻¹ · h⁻¹. ^eMw values were determined by using polyethylene calibration.

Changing the alkyl substituent at the R³ position influenced polymerization activity. Attachment of a methyl or an isopropyl group, which were sterically smaller than a *t*-butyl group, at the R³ position, dramatically decreased polymerization activity, whereas it slightly decreased Mw, compared to complex **1**. Complex **5** (R³ = Me) and complex **6** (R³ = ⁱPr) displayed activities of 0.4 kg-PE/mmol-Zr·h (*Mw* = 0.4 × 10⁴) and 0.9 kg-PE/mmol-Zr·h (*Mw* = 0.5 × 10⁴), respectively (Table 2, Entry 3, 4). Alternatively, attachment of a cumyl group, being sterically larger than a *t*-butyl group, at the R³ position, enhanced polymerization activity whereas it slightly increased *Mw*, compared to complex **4**. Thus, complex **7** (R³ = cumyl) displayed an activity of 2096 kg-PE/mmol-Zr·h (*Mw* = 2.6 × 10⁴), (Table 2, Entry 5). This activity value corresponds to a catalyst turn over frequency (TOF) value of 7.5 × 10⁷ /h/atm. These results suggest that activity values depend on the bulkiness of the substituent at the R³ position. Regarding this activity enhancement, our speculation is as follows; (1) the sterically large substituent protected phenoxy oxygen from the coordination of the cocatalyst, which will reduce space for incoming ethylene to coordinate to the metal center and insertion of the ethylene into the carbon metal bond, and (2) the large substituent may effectively separate the cationic species and the anionic cocatalyst, and the ion separation will increase unsaturation degree of the active species.¹¹

In summary, we have demonstrated that enhancing the catalytic performance of bis [*N*-(3-*t*-butylsalicylidene)phenylamino]zirconium(IV) dichloride (**1**) was feasible by changing the ligand structure. Thus, complex **3** (R¹ = ⁱPr, R² = H, R³ = ^tBu) provided a high *Mw* value of 71.6 × 10⁴ with 58 kg-PE/mmol-Zr·h activity. Furthermore, complex **7** (R¹ = H, R² = Me, R³ = cumyl) afforded an unprecedented activity, 2096 kg-PE/mmol-Zr·h with an *Mw* value of 2.6 × 10⁴, even under atmospheric ethylene pressure. To the best of our knowledge, this is the highest olefin polymerization activity to date.¹²

References and Notes

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- General synthesis procedure: Treatment of an *o*-substituted phenol derivative with paraformaldehyde in the presence of a base produced a salicylaldehyde derivative in about 80% yield. This compound reacted with aniline, via Schiff base condensation, to afford a salicylaldehyde ligand in approximately 90% yield. Complexation of ZrCl₄ with 2 equiv lithium salt of the ligand thus obtained furnished a corresponding zirconium complex in around 70% yield.
- General polymerization procedure: Flow of ethylene gas (100 L/h) was charged into toluene (250 mL). To this solution, a solution of a complex and MAO (produced by Albemarle) was added at 25 °C; see Ref. 4.
- Spectral data of the complexes: Complex **1**; see Ref. 4b. Complex **2** (C₃₆H₄₀N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 1.08–1.71 (m, 18H), 2.33–2.45 (m, 6H), 6.44–7.70 (m, 14H), 8.08–8.28 (m, 2H). Reasonable elemental analysis data was not obtained since complex **2** was unstable and decomposed on standing. FD-mass, 694 (M⁺). Complex **3** (C₄₀H₄₈N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 0.90–1.35 (m, 18H + 12H), 3.10–3.31 (m, 2H), 6.36–7.70 (m, 14H), 8.08–8.29 (m, 2H). Anal. Found; C, 63.57; H, 6.41; N, 3.34; Zr, 11.89%. Calcd for C, 63.98; H, 6.44; N, 3.73; Zr, 12.15%. FD-mass, 750 (M⁺). Complex **4** (C₃₆H₄₀N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 1.22–1.61 (m, 18H), 2.21–2.36 (m, 6H), 6.78–7.45 (m, 14H), 7.90–8.11 (m, 2H). Anal. Found; C, 61.87; H, 5.57; N, 3.81; Zr, 13.06%. Calcd for C, 62.23; H, 5.80; N, 4.03; Zr, 13.13%. FD-mass, 694 (M⁺). Complex **5** (C₂₈H₂₄N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 1.50–2.50 (m, 6H), 6.50–7.62 (m, 16H), 8.00–8.12 (m, 2H). Anal. Found; C, 58.90; H, 4.47; N, 4.74; Zr, 15.37%. Calcd for C, 57.72; H, 4.15; N, 4.81; Zr, 15.66%. FD-mass, 580 (M⁺). Complex **6** (C₃₂H₃₂N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 0.80–1.43 (m, 12H), 2.74–3.32 (m, 2H), 6.13–7.37 (m, 16H), 7.89–8.17 (m, 2H). Anal. Found; C, 59.86; H, 4.88; N, 4.46; Zr, 14.12%. Calcd for C, 60.17; H, 5.05; N, 4.39; Zr, 14.28%. FD-mass, 638 (M⁺). Complex **7** (C₄₆H₄₄N₂O₂ZrCl₂); ¹H-NMR (CDCl₃); δ 1.35–1.65 (m, 12H), 1.70–2.11 (m, 6H), 6.25–8.05 (m, 24H + 2H). Anal. Found; C, 67.61; H, 5.49; N, 3.18; Zr, 10.79%. Calcd for C, 67.46; H, 5.42; N, 3.42; Zr, 11.14%. FD-mass, 818 (M⁺).
- The molecular weight distribution (*Mw/Mn*) for complexes **1–3** were as follows; complex **1**; 2.06, complex **2**; 2.13, complex **3**; 2.61.
- DFT calculation has been widely used for theoretical studies of transition metal complexes, cf.; L. Deng, T. Ziegler, T. K. Woo, P. Margl, and L. Fan, *Organometallics*, **17**, 3240 (1998). All calculation were performed at the gradient corrected density functional BLYP level by Amsterdam Density Functional (ADF) program; C. Fonseca Guerra, J. G. Snijders, G. te Velde, and E. J. Baerends, *Theor. Chem. Acc.*, **99**, 391 (1998). We used the triple ζ STO basis set on the Zr and the double ζ STO basis set on the N, O and ⁱPr as a model of a polymer chain, and the single ζ STO basis set on the other atoms to calculate the optimized geometries. For energy calculations, the triple ζ STO basis set on the Zr and the double ζ plus polarization STO basis set on the other atoms are used and the quasi-relativistic correction is also added.
- The molecular weight distribution (*Mw/Mn*) for complexes **4–7** were as follows; complex **4**; 2.00, complex **5**; 2.31, complex **6**; 2.48, complex **7**; 7.20.
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