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

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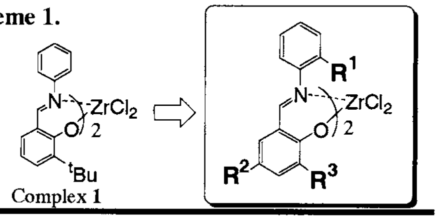
New bis(salicylaldiminato) zirconium complexes were synthesized and investigated as ethylene polymerization catalysts. As a result, we demonstrated that high molecular weight (Mw: 71.6 × 10^4) and super high activity (2096 kg-PE/mmol-Zr·h) were accomplished by changing the ligand structure.

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.



Complex 1

Complex	1	2	3	4	5	6	7
R^1	H	Me	^{i}Pr	H	H	H	H
R^2	H	H	H	Me	H	H	Me
R^3	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Me	^{i}Pr	cumyl

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

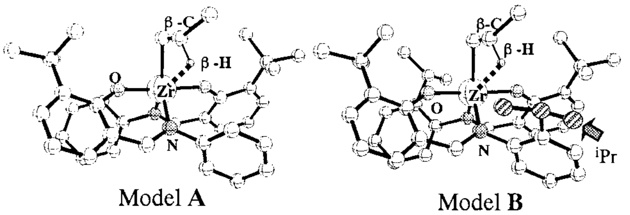
Table 1 summarizes the catalytic performance of bis(salicylaldiminato) zirconium complexes as a result of introducing an alkyl group at the R^1 position.[8] Complex **1** (R^1 = H) furnished an *Mw* value of 0.8 × 10^4, based on GPC measurement. The introduction of a methyl group at the R^1 position (complex **2**) dramatically boosted the *Mw* value to 23.0 × 10^4. Moreover, the introduction of a larger alkyl group further enhanced the molecular weight. Thus, complex **3** (R^1 = ^{i}Pr) provided an *Mw* value of 71.6 × 10^4, an *Mw* value comparable to that of Cp_2ZrCl_2. These results indicate that the molecular weight values depend on the bulkiness of the R^1 substituents.

Table 1. Ethylene polymerization results (Effect of the R^1)

Entry	Complex	Yield / g	Activity^c	Mw^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_2ZrCl_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; ^{a}0.08 μM, ^{b}2.0 μM. ^{c}/ kg-PE· mmol-Zr^{-1}· h^{-1}. ^{d}*Mw* values were determined by usingpolyethylene calibration.

The increase in *Mw* 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 R^1 position energetically destabilized the conformation of the polymer chain leading to β-hydride elimination.



Model **A**
ΔE_β = -43 kJ/mol

Model **B**
ΔE_β = -29 kJ/mol

Figure 1. The stabilization energies (ΔE_β) as a result of β-agostic interaction. Cation complex models **A** and **B** stand for active spices generated from complexes **1** and **3**, respectively. All hydrogens except the β-hydrogen are omitted. ^{n}Pr 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 Cp_2ZrCl_2 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 R^2 position and changing the alkyl substituent at the R^3 position.[10]

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

Table 2. Ethylene polymerization results (Effect of the R^2 and R^3)

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; [a]0.08 μM, [b]20.0 μM, [c]0.04 μM. [d]/ kg-PE· mmol-Zr^{-1}· h^{-1}. [e]*Mw* values weredetermined by using polyethylene calibration.

Changing the alkyl substituent at the R^3 position influenced polymerization activity. Attachment of a methyl or an isopropyl group, which were sterically smaller than a *t*-butyl group, at the R^3 position, dramatically decreased polymerization activity, whereas it slightly decreased *Mw*, compared to complex **1**. Complex **5** (R^3 = Me) and complex **6** (R^3 = ^{i}Pr) displayed activities of 0.4 kg-PE/mmol-Zr·h ($Mw = 0.4 \times 10^4$) and 0.9 kg-PE/mmol-Zr·h ($Mw = 0.5 \times 10^4$), respectively (Table 2, Entry 3, 4). Alternatively, attachment of a cumyl group, being sterically larger than a *t*-butyl group, at the R^3 position, enhanced polymerization activity whereas it slightly increased *Mw*, compared to complex **4**. Thus, complex **7** (R^3 = cumyl) displayed an activity of 2096 kg-PE/mmol-Zr·h ($Mw = 2.6 \times 10^4$), (Table 2, Entry 5). This activity value corresponds to a catalyst turn over frequency (TOF) value of 7.5×10^7 /h/atm. These results suggest that activity values depend on the bulkiness of the substituent at the R^3 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)phenylaminato]zirconium(IV) dichloride (**1**) was feasible by changing the ligand structure. Thus, complex **3** (R^1 = ^{i}Pr, R^2 = H, R^3 = ^{t}Bu) provided a high *Mw* value of 71.6×10^4 with 58 kg-PE/mmol-Zr·h activity. Furthermore, complex **7** (R^1 = H, R^2 = Me, R^3 = cumyl) afforded an unprecedented activity, 2096 kg-PE/mmol-Zr·h with an *Mw* value of 2.6×10^4, even under atmospheric ethylene pressure. To the best of our knowledge, this is the highest olefin polymerization activity to date.[12]

References and Notes

1 Review; H. H. Brinzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34**, 1143 (1995).

2 Review: G. J. P. Biritovsek, V. C. Gibson, and D. F. Wass, *Angew. Chem., Int. Ed. Engl.*, **38**, 428 (1999).

3 For example; a) L. K. Johnson, C. M. Killian, and M. S. Brookhart, *J. Am. Chem. Soc.*, **117**, 6414 (1995). b) C. M. Killian, D. J. Temple, L. K. Johnson, and M. S. Brookhart, *J. Am. Chem. Soc.*, **118**, 11664 (1996). c) C. Wang, A. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, A. Bansleben, and M. W. Day, *Organometallics*, **17**, 3149 (1998). d) B.L. Small, M. S. Brookhart, and A. A. Bennett, *J. Am. Chem. Soc.*, **120**, 4049 (1998). e) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, J. Maddox, S. J. McTavish, G. A. Solan, A. P. White, and D. J. Williams, *Chem. Commun.*, **1998**, 849.

4 a) S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, and T. Fujita, *Chem. Lett.*, **1999**, 1065. b) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, and T. Fujita, *Chem. Lett.*, **1999**, 1263.

5 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 salicylaldimine ligand in approximately 90% yield. Complexation of $ZrC1_4$ with 2 equiv lithium salt of the ligand thus obtained furnished a corresponding zirconium complex in around 70% yield.

6 General polymerization procedure: Flow of ethylene gas (100 L/h) was charged into toluene (250mL). To this solution, a solution of a complex and MAO (produced by Albemarle) was added at 25 °C; see Ref. 4.

7 Spectral data of the complexes: Complex **1**; see Ref. 4b. Complex **2** ($C_{36}H_{40}N_2O_2ZrCl_2$); ^{1}H-NMR ($CDCl_3$); 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** ($C_{40}H_{48}N_2O_2ZrCl_2$); ^{1}H-NMR ($CDCl_3$); 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** ($C_{36}H_{40}N_2O_2ZrCl_2$); ^{1}H-NMR ($CDCl_3$), 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** ($C_{28}H_{24}N_2O_2ZrCl_2$); ^{1}H-NMR ($CDCl_3$); 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** ($C_{32}H_{32}N_2O_2ZrCl_2$); ^{1}H-NMR ($CDCl_3$), 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** ($C_{46}H_{44}N_2O_2ZrCl_2$): ^{1}H-NMR ($CDCl_3$), 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%. Caled for C, 67.46; H, 5.42; N, 3.42; Zr, 11.14%. FD-mass, 818 (M^+).

8 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.

9 DFT calculation has been widely used for theoretical studies of transition metal complexes, cf.; L. Deng, T. Zieglar, 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 ^{n}Pr 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.

10 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.

11 P. A. Deck, C. L. Beswick, and T. J. Marks, *J. Am. Chem. Soc.*, **120**, 1772 (1998).

12 a) H. G. Alt, W. Milius, and S. J. Palackal, *J. Organomet. Chem.*, **472**, 113 (1994). b) W. Spaleck, F. Ktiber, A. Winter, J. Rohrmmann, B. Bachmann, M. Antberg, V. Dolle, and E. F. Paulus, *Organometallics*, **13**, 954 (1994).