ELSEVIER

Catalysis Today 66 (2001) 63–73

CATALYSIS TODAY

www.elsevier.com/locate/cattod

FI Catalysts: super active new ethylene polymerization catalysts

Shigekazu Matsui, Terunori Fujita*

Materials Science Laboratory, Mitsui Chemicals, Inc., 530-32 Nagaura, Sodegaura-City, Chiba, Japan

Abstract

Based on "ligand-oriented catalyst design", group 4 transition metal complexes having two phenoxy–imine ligands, FI Catalysts, were synthesized and investigated as olefin polymerization catalysts using ethylene at atmospheric pressure. As a result, these complexes were found to exhibit very high activity using MAO as a cocatalyst. Among them, zirconium complexes displayed the highest activity with moderate (Mv: 0.8×10^4) to very high (Mv: 71.6×10^4) molecular weight ranges. The maximum activity exceeded 4 t-PE/(mmol-cat(superscript:)h) at 25°C even at atmospheric pressure, the activity being two orders of magnitude larger than that exhibited by Cp_2ZrCl_2. Alternatively, by using borate/^{i}Bu$_3$Al as a cocatalyst, a zirconium FI Catalyst produced exceptionally high molecular weight polyethylene (Mv: 505×10^4) displaying considerable activity. As far as we know, this is one of the highest molecular weight values obtained from homogeneous polymerization catalysts. These results indicate that FI Catalysts possess very high potential as olefin polymerization catalysts.

Keywords: FI catalysts; Post-metallocene; Phenoxy–imine ligand; Group 4 transition metal complex; Zirconium; Ethylene polymerization

1. Introduction

Since the discovery of the Ziegler–Natta catalyst in the 1950s, highly active $MgCl_2$-supported Ti catalysts, displaying high catalytic performance, have been developed to simplify the production process in order to save resources and energy as well as to improve properties of produced polymers [1–3]. By using these $MgCl_2$-supported Ti catalysts, many polymers, such as high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and isotactic polypropylene (i-PP), have been industrially produced. However, the catalyst design for tailored polyolefins has not yet been perfected, because of the existence of multiple active sites on these solid catalysts.

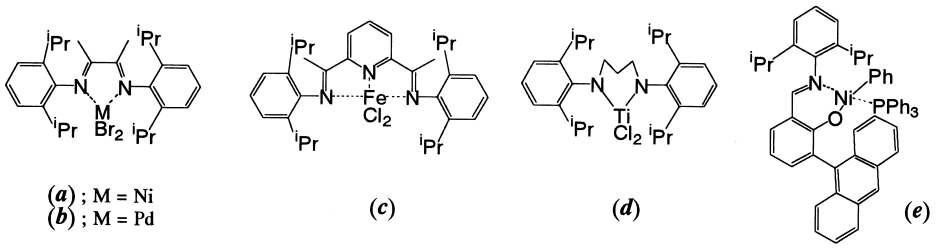
Single-site catalysts possess potential for controlling polymer structure while displaying high polymerization activity by changing the ligand structure and cocatalyst. Thus, research and development of transition metal complexes for olefin polymerization, aiming at high performance single-site catalysts, has made a dramatic impact on the polyolefin industry, as demonstrated by the discovery of highly active group 4 metallocene catalyst systems [4–7]. So far, by employing group 4 metallocenes, the industrial production of LLDPE, isotactic and syndiotactic polypropylene (i-PP, s-PP), etc., has been commercially successful.

Therefore, after the discovery of the group 4 metallocene catalyst systems, transition metal complexes have been intensively investigated as post-metallocene candidates [8–14], and since 1995, some excellent new catalysts have been developed (Scheme 1).

In 1995, Brookhart [15] reported that a nickel complex possessing a di-imine ligand (**a**) produced branched polyethylene in the absence of a

* Corresponding author. Tel.: +81-438-64-2317; fax: +81-438-64-2375.
E-mail addresses: shigekazu.matsui@mitsui-chem.co.jp (S. Matsui), terunori.fujita@mitsui-chem.co.jp (T. Fujita).

0920-5861/01/$ – see front matter
PII: S0920-5861(00)00605-2



Scheme 1.

co-monomer with considerable activity for ethylene polymerization. And, in 1996, Brookhart [16–18] established ethylene/methyl acrylate co-polymerization using the corresponding palladium complex bearing the same ligand (**b**), as the nickel complex. This is the first example of ethylene/methyl acrylate co-polymerization via coordination polymerization.

In 1998, Brookhart and Gibson [19,20] independently discovered a new series of iron complexes possessing imine–pyridine ligands (**c**). These complexes displayed very high ethylene polymerization activity comparable to that of metallocenes. This is fantastic, since they say that metallocenes exhibit the highest polymerization activity and that no catalysts can exceed metallocene activity.

Additionally, a titanium complex with a di-amide ligand displaying excellent properties for higher α-olefin polymerization (**d**) [21–23], and a nickel complex with a phenoxy–imine ligand exhibiting high ethylene polymerization activity and high functional group tolerance (**e**), have also been reported [24,25].

Thus, pioneering researchers have been making great strides in the field of post-metallocenes [26–30]. In this paper, we would like to describe our R&D activities within the post-metallocene field, and additionally, introduce our newly discovered olefin polymerization catalysts, named FI Catalysts, which are super active new olefin polymerization catalysts [31–35].

2. Concept behind the catalyst design

The purpose of this project was the development of highly active post-metallocenes based on transition metal complexes. Normally, an olefin polymerization catalyst consists of a transition metal, a ligand, an alkyl group, and a cocatalyst. Among these four catalyst components, we believe ligands play the most important role for polymerization and, subsequently, ligand design is crucial when it comes to catalyst design. Therefore, we carried out "ligand-oriented catalyst design" in order to acquire new and original post-metallocenes.

The general requirements for a highly active polymerization catalyst are:

1. A catalyst must have high olefin-insertion ability.
2. A catalyst must have two available *cis*-located sites for polymerization.
3. A catalyst must be stable enough under usual polymerization conditions.

Having these three general requirements in mind, ligand design was conducted as follows:

With respect to general requirement (1), ligands possessing moderate electron donating properties, ligands having coordination sites such as phenoxy, pyridine and/or a conjugated imine moiety, were considered since surplus electron donation lowers catalyst reactivity and, on the other hand, poor electron donation insufficiently stabilizes the transition state leading to olefin insertion. Regarding general requirements (2) and (3), multidentate ligands capable by chelation of forming a five- or six-membered ring were considered since these ligands are expected to generate catalysts having two available *cis*-located sites needed for polymerization [36,37] and, moreover, these ligands should yield stable catalysts.

Additionally, in this study, we focused on non-symmetric ligands which possess the above mentioned electronic and steric factors because transition metal complexes bearing non-symmetric ligands have been investigated less as olefin polymerization catalysts [38–43].

As for metals, both early transition metals and late transition metals were considered since all transition metals potentially possess olefin-insertion ability [44,45].

Thus, transition metal complexes having multidentate and non-symmetric ligand(s) with moderate electron donating properties were considered to be viable post-metallocenes as a result of "ligand-oriented catalyst design".

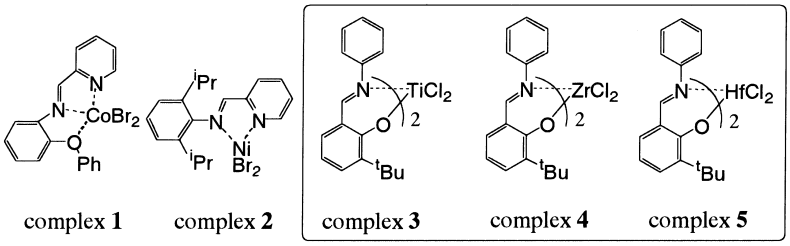
3. Ethylene polymerization using designed transition metal complexes

Five designed transition metal complexes possessing multidentate and non-symmetric ligand(s) were synthesized and investigated as ethylene polymerization catalysts using MAO as a cocatalyst under ethylene at atmospheric pressure at 25°C in toluene. For comparison, the before mentioned Brookhart nickel di-imine complex (**a**) and Cp_2ZrCl_2 were also evaluated. Results are summarized in Table 1.

With respect to late transition metal complexes, cobalt complex **1** bearing a pyridine–imine–ether ligand displayed practically no activity (<0.01 kg PE/(mmol cat h)). Alternatively, nickel complex **2** having an imine–pyridine ligand exhibited an activity of 1.4 kg PE/(mmol cat h) [46]. This activity was relatively high for a nickel complex, however, its activity was inferior to that of the nickel di-imine complex (**a**), displaying 3.0 kg PE/(mmol cat h) of activity.

With regard to early transition metal complexes, titanium complex **3**, and hafnium complex **5**, both possessing two phenoxy–imine ligands, afforded high activities of 3.3 kg PE/(mmol cat h) (Mv: 51×10^4) and 6.5 kg PE/(mmol cat h) (Mv: 3×10^4), respectively. These activity values were comparable to the value obtained from the nickel di-imine complex (**a**). Surprisingly, zirconium complex **4** having the same phenoxy–imine ligands provided an activity of 519 kg PE/(mmol cat h) (Mv: 1×10^4). This activity value was about 20 times larger than the value obtained from Cp_2ZrCl_2. To the best of our knowledge, this activity was one of the highest for ethylene polymerization among not only post-metallocenes but also olefin polymerization catalysts including group 4 metallocenes. This fact has clearly demonstrated that zirconium complex **4** with two phenoxy–imine ligands possesses a very high potential as an olefin

Table 1
Ethylene polymerization results (1)[a]



complex **1** complex **2** complex **3** complex **4** complex **5**

Entry	Complex	Complex concentration (μM)	Yield (g)	Activity (kg PE/(mmol cat h))	Mv × 10^4[b]
1[c]	**1**	20.0	0.18	<0.01	–
2[c]	**2**	20.0	3.44	1.4	Oil[d]
3[e]	**3**	20.0	1.38	3.3	51
4[e]	**4**	0.08	0.87	519.0	1
5[e]	**5**	20.0	2.69	6.5	3
6[e]	**a**	20.0	1.25	3.0	7
7[e]	Cp_2ZrCl_2	2.0	1.13	27.0	104

[a] Conditions: temperature, 25°C; pressure, 0.1 MPa; solvent, toluene (250 ml); cocatalyst [MAO]; 1.25 mmol (Al).
[b] See point 2 of Appendix A.
[c] Polymerization time: 30 min.
[d] Mv = 280 determined by GPC.
[e] Polymerization time: 5 min.

Table 2
Relative formation energies of complex **4** isomers based on isomer (A)

Isomeric structure	(A)	(B)	(C)	(D)	(E)
Formation energy gap based on isomer (A)	(0.0 kJ/mol)	+ 25.3 kJ/mol	+19.5 kJ/mol	+33.3 kJ/mol	+37.3 kJ/mol

polymerization catalyst. Accordingly, zirconium complex **4** was studied in greater detail in the light of its stereochemical structure and catalytic performance.

4. Detailed study with respect to complex 4

4.1. Stereochemical structure

Since zirconium complex **4** possesses five possible isomeric structures, (A)–(E), we ascertained what was the most stable isomeric structure by means of DFT calculation. Relative formation energies of the five isomers, based on isomer (A), are summarized in Table 2.

Consequently, complex **4** was ascertained to exist best as isomeric structure (A), in vacuo (Fig. 1(a)). Theoretical calculations suggested this stereochemical arrangement: two oxygen atoms were situated in the *trans*-position, while two nitrogen atoms and two chlorine atoms were situated in *cis*-positions.

The molecular structure of complex **4** was depicted by X-ray crystallographic analysis, as shown in Fig. 1(b). In the solid state, complex **4** adopted a distorted octahedral structure around the zirconium center. Two oxygen atoms were situated *trans* to one another (O–Zr–O angle, 165.5°). Alternatively, two nitrogen atoms were located *cis* to one another (N–Zr–N angle, 74.0°), and two chlorine atoms were also located *cis* to one another (Cl–Zr–Cl angle, 100.4°). Subsequently, the calculated isomeric structure (A) for complex **4** was found to be in good accordance with its X-ray crystallographic structure.

An active species of group 4 transition metal complexes for olefin polymerization is known to

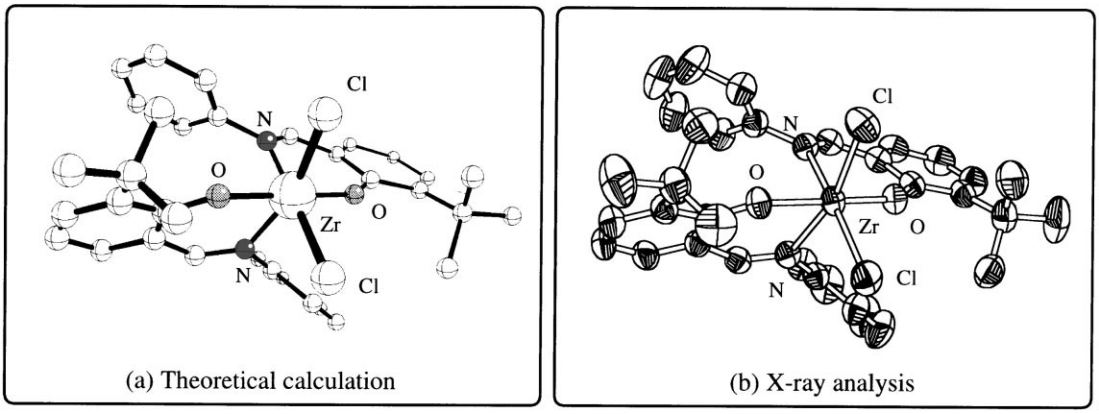


Fig. 1. Structure of complex **4**. (a) DFT calculation: see point 3 of Appendix A. (b) X-ray analysis: thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and a diethyl ether molecule of crystal are omitted for clarity. Selected bond distance (Å): Zr–O = 1.985(2); Zr–N = 2.355(2); Zr–Cl = 2.4234(9).

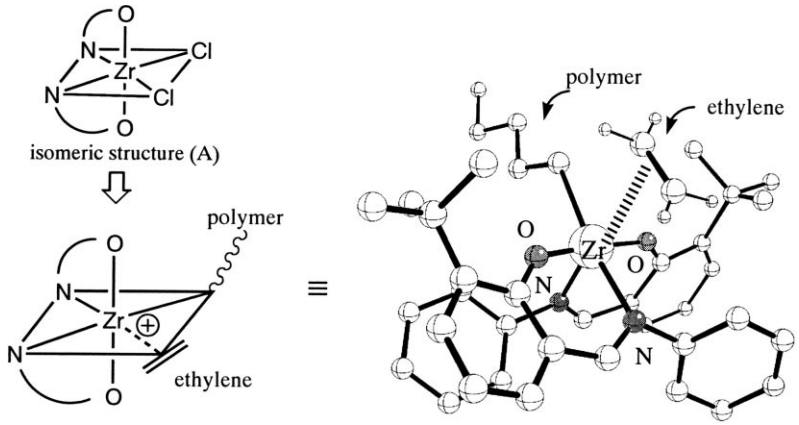


Fig. 2. Calculated structure of ethylene coordinated active species for complex **4**.

be an alkyl cationic complex, having two available *cis*-located sites needed for polymerization, generated by the reaction of catalyst precursors; e.g., a dichloro complex, with MAO. If two chlorine atoms, being situated in *cis*-position in zirconium complex **4**, are to be an alternative for a polymer-bonded site and an ethylene coordinated site vis-à-vis polymerization, the structure of the corresponding alkyl cationic complex should have two available *cis*-located sites needed for polymerization. Theoretical calculations have suggested that an active cationic species generated from zirconium complex **4** has two available *cis*-located sites for polymerization in the presence of ethylene (Fig. 2). We believe that the high activity displayed by zirconium complex **4** originates from the facts that (1) a phenoxy–imine ligand possesses moderate electron donating properties and, at the same time, (2) an active species of complex **4** has two available *cis*-located sites needed for polymerization.

4.2. Catalytic lifetime

In order to investigate the catalytic lifetime of complex **4**, ethylene polymerizations were conducted for 5, 15, and 30 min. By plotting the polymerization time vs. polymer yield, a nearly straight line was found (Fig. 3). This fact indicated that complex **4** retains its catalytic activity for at least 30 min.

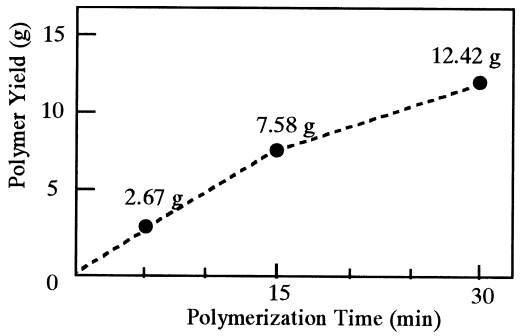


Fig. 3. Relationship between polymerization time and polymer yield. Conditions: temperature, 25°C; pressure, 0.1 MPa; solvent, toluene (400 ml); complex **4**, 0.08 μ mol; cocatalyst [MAO]; 1.25 mmol (Al).

4.3. Polymerization temperature effect

The effect of polymerization temperature on catalytic activity vis-à-vis complex **4** with MAO was studied and the results thus obtained were compared with those for Cp_2ZrCl_2/MAO (Fig. 4).

Cp_2ZrCl_2 exhibited practically low activity at 0°C, and the activity gradually increased as the temperature increased. It reached the maximum value, 103 kg PE/(mmol cat h), at 75°C. Above 75°C, the activity decreased.

Alternatively, complex **4** provided 193 kg PE/(mmol cat h) of activity even at 0°C and this value

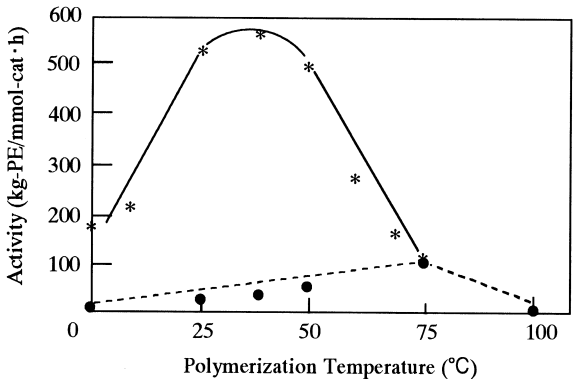


Fig. 4. Relationship between polymerization temperature and activity. Conditions: pressure, 0.1 MPa; polymerization time, 5 min; solvent, toluene (250 ml); complex concentration: complex **4** (∗); 0.08–0.8 μM, Cp_2ZrCl_2 (●); 2.0–8.0 μM, cocatalyst [MAO]; 1.25 mmol (Al).

was far higher than the maximum value for Cp_2ZrCl_2. Moreover, the activity increased as the temperature increased: e.g., 519 kg PE/(mmol cat h) at 25°C, and the maximum value, 587 kg PE/(mmol cat h), at 40°C. Above 40°C, the activity decreased. However, complex **4** was highly active over a temperature range 0–75°C, and provided more than 100 kg PE/(mmol cat h) of activity. Generally speaking, post-metallocenes are apt to rapidly lose their polymerization activity at higher temperatures [47]. Nevertheless, zirconium complex **4** exhibited considerable activity at relatively high temperatures.

4.4. Cocatalyst effect

Perfluoroborate is well known as an effective cocatalyst for olefin polymerization, as is MAO. Thus, complex **4** using $PhCB(C_6F_5)_4/^iBu_3Al$ as a cocatalyst was also investigated for ethylene polymerization (Table 3).

In contrast with complex **4**/MAO, complex **4**/$Ph_3CB(C_6F_5)_4/^iBu_3Al$ produced polyethylene having exceptionally high molecular weight, Mv: 505×10^4, with considerable activity, 11 kg PE/(mmol cat h). This Mv value is one of the highest Mv values displayed by homogeneous olefin polymerization catalysts [13,48]. Considering the great difference in catalytic performance as a result of using MAO and $PhCB(C_6F_5)_4/^iBu_3Al$ as cocatalysts, the structures of active species might be different depending on the cocatalyst employed. This is probably the first example of a great difference in catalytic performance as a result of using different cocatalysts.

5. Catalytic performance of bis(salicylaldiminato)zirconium complexes

As demonstrated, bis[*N*–(3-*t*-butylsalicylidene)-anilinato]zirconium(IV)dichloride (**4**) possesses high potential for olefin polymerization. Hence, we investigated the catalytic performance of its derivatives. To study the effect of the ligand structure of derivatives of complex **4**, we changed the substituents, especially changing the substituents R^1 and R^3, both near the polymerization reaction center, and investigated what happened to the catalytic performance (Scheme 2).

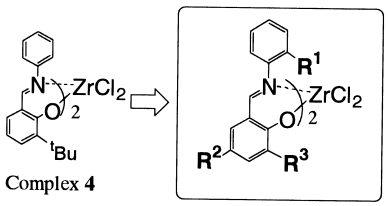
5.1. Increase of molecular weight

Table 4 summarizes the catalytic performance of bis(salicylaldiminato)zirconium complexes as a result

Table 3
Ethylene polymerization results (2)[a]

Entry	Complex	Complex concentration (μM)	Cocatalyst	Yield (g)	Activity (kg PE/(mmol cat h))	Mv × 10^4[b]
1	**4**	0.08	MAO	0.83	496	1
2	**4**	10.0	Borate[c]	2.31	11	505
3	Cp_2ZrCl_2	0.8	MAO	1.13	68	54
4	Cp_2ZrCl_2	2.0	Borate[d]	0.87	21	36

[a] Conditions: temperature, 50°C; pressure, 0.1 MPa; polymerization time, 5 min; solvent, toluene (250 ml); cocatalyst [MAO]; 1.25 mmol (Al), cocatalyst [borate]; complex/$Ph_3CB(C_6F_5)_4 = 1/2$.
[b] See point 2 of Appendix A.
[c] $^iBu_3Al$: 0.25 mmol.
[d] $^iBu_3Al$: 0.10 mmol.



Scheme 2.

of introducing an alkyl group at the R^1 position. Complex **4**, R^1 = H, furnished an Mv value of 0.8×10^4, determined by GPC measurement. The introduction of a methyl group at the R^1 position, complex **6**, dramatically boosted the Mv value to 23.0×10^4. Moreover, the introduction of a larger alkyl group further enhanced molecular weight. Thus, complex **7**, $R^1 = {}^i$Pr, provided an Mv value of 71.6×10^4, an Mv value comparable to that for Cp_2ZrCl_2. These results have indicated that the molecular weight values depend on the bulkiness of the R^1 substituents; therefore, FI Catalysts are capable of producing polyethylene of low molecular weight (Mv: 0.8×10^4) to high molecular weight (Mv: 71.6×10^4) with considerable polymerization activity.

The increase in Mv values is rationalized as follows; namely, introduced alkyl groups diminished chain transfer reaction, or β-hydride elimination. Theoretical calculations supported this rationalization. The stabilization energy (ΔE_β) as a result of β-agostic interaction of the active species generated from complex **7** (model B, Fig. 5 right) was smaller than that for complex **4** (model A, Fig. 5 left), due to the steric repulsion of a β-hydrogen and an isopropyl group. Thus, the introduced isopropyl group at the R^1 position prevented the polymer chain from assuming a conformation leading to β-hydride elimination, which causes low Mv.

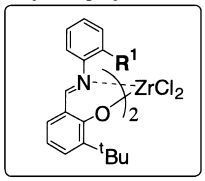
5.2. Increase of polymerization activity

Table 5 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.

Complex **10**, R^2 = Me, afforded 331 kg PE/(mmol cat h) of activity with an Mv value of 0.8×10^4. Thus, introduction of a methyl group at the R^2 position lowered polymerization activity though it resulted in no change vis-à-vis molecular weight.

Polymerization activity highly depends on the alkyl substituents at the R^3 position. Attachment of a methyl or an isopropyl group, being sterically smaller than a *t*-butyl group, at the R^3 position, dramatically decreased polymerization activity and slightly decreased Mv, based on complex **4**. Complex **8** (R^3 = Me) and complex **9** ($R^3 = {}^i$Pr) displayed activities of 0.4 kg PE/(mmol cat h) (Mv: 0.4×10^4)

Table 4
Ethylene polymerization results (3)[a]



Entry	Complex	R^1	Yield (g)	Activity (kg PE/(mmol cat h))	Mv × 10⁴[b]
1[c]	**4**	H	0.87	519	0.8
2[d]	**6**	Me	1.68	40	23.0
3[d]	**7**	^{i}Pr	2.41	58	71.6
4[d]	Cp_2ZrCl_2	–	1.13	27	63.6

[a] Conditions: temperature, 25°C; pressure, 0.1 MPa; polymerization time, 5 min; solvent, toluene (250 ml); cocatalyst [MAO]; 1.25 mmol (Al).
[b] Mv values were determined by GPC using polyethylene calibration.
[c] Complex concentration: 0.08 μM.
[d] Complex concentration: 2.0 μM.

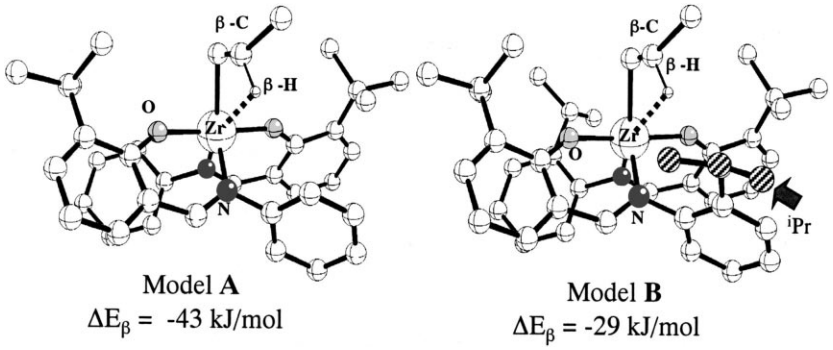
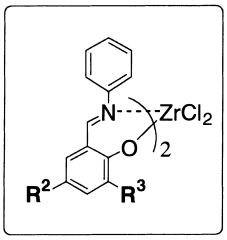


Fig. 5. The stabilization energies (ΔE_β) as a result of β-agostic interaction. Cation complex models A and B stand for active species generated from complexes **4** and **7**, respectively. All hydrogens except the β-hydrogen are omitted. *n*-Pr group is employed as a model of a polymer chain.

Table 5
Ethylene polymerization results (4)[a]

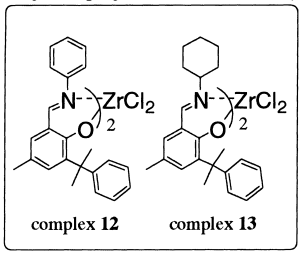


Entry	Complex	R^2	R^3	Yield (g)	Activity (kg PE/(mmol cat h))	Mv × 10^{4}[b]
1[c]	**8**	H	Me	0.18	0.4	0.4
2[c]	**9**	H	^{i}Pr	0.39	0.9	0.5
3[d]	**4**	H	^{t}Bu	0.87	519	0.8
4[d]	**10**	Me	^{t}Bu	0.55	331	0.8
5[d]	**11**	Me	Adamantyl	1.19	714	2.5
6[e]	**12**	Me	Cumyl	1.75	2096	2.6

[a] Conditions: temperature, 25°C; pressure, 0.1 MPa; polymerization time, 5 min; solvent, toluene (250 ml); cocatalyst [MAO]; 1.25 mmol (Al).
[b] Mv values were determined by GPC using polyethylene calibration.
[c] Complex concentration: 20.0 μM.
[d] Complex concentration: 0.08 μM.
[e] 0.04 μM.

and 0.9 kg PE/(mmol cat h) (Mv: 0.5×10^4), respectively. Alternatively, attachment of an adamantyl or a cumyl group, being sterically larger than a *t*-butyl group, at the R^3 position, enhanced polymerization activity and slightly increased molecular weight, based on complex **10**. Complex **11** (R^3 = adamantyl) and complex **12** (R^3 = cumyl) displayed an activity of 714 kg PE/(mmol cat h) (Mv: 2.5×10^4) and 2096 kg PE/(mmol cat h) (Mv: 2.6×10^4), respectively. These results suggested 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, the coordination reducing room for olefin's movement, coordination and insertion, and (2) the large substituent may effectively separate the cationic active species and the anionic cocatalyst, the

Table 6
Ethylene polymerization results (5)[a]



complex **12** complex **13**

Entry	Complex	Yield (g)	Activity (kg PE/(mmol cat h))	Mv × 10^{4}[b]
1[c]	**12**	1.75	2096	2.6
2[d]	**13**	1.80	4315	1.7

[a] Conditions: temperature, 25°C; pressure, 0.1 MPa; polymerization time, 5 min; solvent, toluene (250 ml); cocatalyst [MAO]; 1.25 mmol (Al).
[b] Mv values were determined by GPC using polyethylene calibration.
[c] Complex concentration: 0.04 μM.
[d] Complex concentration: 0.02 μM.

ion separation increasing the unsaturation degree of the active species [49].

Surprisingly, changing the phenyl group on the imine nitrogen to a cyclohexyl group further enhanced activity (Table 6). Complex **13** having a cyclohexyl group on the imine nitrogen afforded an unprecedented activity, 4315 kg PE/(mmol cat h) (Mv: 1.7×10^4). This activity corresponds to a catalyst turnover frequency (TOF) value of 1.5×10^8/h atm. To the best of our knowledge, this TOF value is the largest of catalytic reactions. Then, naturally, this zirconium complex provided the highest ethylene polymerization activity vis-à-vis other olefin polymerization catalysts [7,50,51].

6. Conclusion

We demonstrated that group 4 transition metal complexes possessing two phenoxy-imine ligands, FI Catalysts, display excellent catalytic performance. Meaning, that exceptionally high activity (more than 4 t-PE/(mmol-cat(superscript:)h)) was obtained using bis[*N*–(3-cumyl-5-methylsalicylidene)cyclohexylaminato]zirconium(IV)dichloride/MAO. Moreover, an exceptionally high molecular weight, (more than 500×10^4) was attained using bis[*N*–(3-*t*-butylsalicylidene)anilinato]zirconium(IV)dichloride/$Ph_3CB(C_6F_5)_4$/$^{i}Bu_3Al$. Having these excellent results, we have given the name FI Catalysts to our newly discovered group 4 transition metal complexes after the Japanese pronunciation of the ligand "Fenokishi-Imin Haiishi", since these complexes were discovered based on "ligand-oriented catalyst design". We believe that FI Catalysts have very high potential as a new generation of olefin polymerization catalysts.

Acknowledgements

We would like to thank M. Mitani, J. Saito, N. Matsukawa, Y. Tohi, H. Makio, K. Tsuru, M. Nitabaru, T. Hayashi, K. Sugimura, S. Matsuura, Y. Inoue, Y. Takagi, Y. Yoshida, Y. Suzuki, T. Matsugi, M. Kamimura, T. Nakano, H. Tanaka, and A. Valentine for their research and technical assistance.

Appendix A. Notes

1. *General procedures for FI catalyst synthesis*. Treatment of an *o*-substituented phenol compound with paraformaldehyde in the presence of a base produced a salicylaldehyde compound. This compound reacted with a primary amine, via Schiff base condensation, to afford a salicylaldimine

ligand. Complexation of a group 4 transition metal salt with 2 equiv. of a lithium salt of the ligand yielded a desired FI catalyst [33–35].

2. *General procedures for ethylene polymerization*. To a well stirred solution of ethylene in toluene (250 ml) with a flow of ethylene gas (100 l/h), a solution of a complex and a cocatalyst (MAO (Albemarle) or $Ph_3CB(C_6F_5)_4$/$^iBu_3Al$) was added at 25°C. After the prescribed time, 10 ml of isobutyl alcohol was added to terminate the polymerization. To the resulting mixture, 1000 ml of methanol and 2 ml of conc. HCl were added. The polymer obtained was collected by filtration and washed with acidic methanol and then methanol. The collected polymer was dried in vacuo at 80°C for 10 h. Mv values were determined by a GPC measurement at 145°C using polyethylene calibration. Intrinsic viscosity [η] was measured in decalin at 135°C using an Ubbelohde viscometer. Mv values were calculated from the following equation $[\eta] = 6.2 \times 10^{-4} Mv^{0.7}$ [52].
3. *Theoretical calculation method* (*DFT calculation*). DFT calculations have been widely used for structural determination of transition metal complexes [53]. All calculations were performed using the gradient corrected density functional method BLYP, by means of the Amsterdam density functional (ADF) program [54]. We used the triple ζ basis set on the metal center, the double ζ basis set on the Cl, N, and O atoms, and the single ζ basis set on the other atoms.

References

[1] K. Ziegler, H.G. Gellert, K. Zosel, W. Lehmkuhl, W. Pfohl, Angew. Chem. 67 (1955) 424.
[2] K. Ziegler, E. Holzkamp, H. Breil, H. Martin, Angew. Chem. 67 (1955) 541.
[3] N. Kashiwa, T. Tokumizu, H. Fujimura, USP-3642746 (1968).
[4] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.
[5] H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, Angew. Chem. Int. Ed. Engl. 19 (1980) 390.
[6] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.
[7] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 954.
[8] G.J.P. Biritovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.
[9] W. Kaim, F.H. Kowaldt, R. Goddard, C. Kruger, Angew. Chem. Int. Ed. Engl. 17 (1978) 466.
[10] W. Kaim, R. Appel, A. Storeck, C. Kruger, R. Goddard, Angew. Chem. Int. Ed. Engl. 20 (1981) 116.
[11] V.M. Mohring, G. Fink, Angew. Chem. Int. Ed. Engl. 24 (1985) 1001.
[12] U. Klabunde, S.D. Ittel, J. Mol. Catal. 41 (1987) 123.
[13] T. Miyatake, K. Mizunuma, Y. Saeki, M. Kakugo, Makromol. Chem. Rapid Commun. 10 (1989) 349.
[14] A. Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orphan, J. Am. Chem. Soc. 117 (1995) 3008.
[15] L.K. Johnson, C.M. Killian, M.S. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[16] L.K. Johnson, S. Mecking, M.S. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[17] C.M. Killian, D.J. Temple, L.K. Johnson, M.S. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.
[18] S. Mecking, L.K. Johnson, L. Wang, M.S. Brookhart, J. Am. Chem. Soc. 120 (1998) 888.
[19] B.L. Small, M.S. Brookhart, A.M. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[20] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, J. Maddox, S.J. McTavish, G.A. Solan, A.P. White, D. Williams, Chem. Commun. (1998) 849.
[21] J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vital, Makromolekules 29 (1996) 5241.
[22] J.D. Scollard, D.H. McConville, S.J. Rettig, Organometallics 16 (1997) 1810.
[23] J.D. Scollard, D.H. McConville, J. Vittal, Organometallics 16 (1997) 4415.
[24] C. Wang, S.K. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149.
[25] T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460.
[26] K. Hakala, B. Löfgren, Macromol. Chem. Rapid Commun. 18 (1997) 635.
[27] D. Jones, A. Roberts, K. Cavell, W. Keim, U. Englert, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 255.
[28] D.W. Stephan, F. Guerin, R.E.V.H. Spence, L. Koch, X. Gao, S.J. Brown, J.W. Swabey, Q. Wang, W. Xu, P. Zoricak, D.G. Harrison, Organometallics 18 (1999) 2046.
[29] R. Vollmerhaus, P. Shao, N.J. Nicholas, S. Collins, Organometallics 18 (1999) 2731.
[30] J.C. Flores, J.C.W. Chen, M.D. Ransch, Organometallics 14 (1995) 1827.
[31] T. Fujita, M. Mitani, Y. Tohi, H. Makio, N. Kihara, in: Proceedings of the MetCon'99 on Polymer in Transition.
[32] T. Fujita, Y. Tohi, M. Mitani, S. Matsui, J. Saito, M. Nitabaru, K. Sugi, H. Makio, T. Tsutsui, EP-0874005 (1998).
[33] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, T. Fujita, Chem. Lett. (1999) 1065.
[34] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita, Chem. Lett. (1999) 1163.
[35] S. Matsui, M. Mitani, J. Saito, N. Matsukawa, H. Tanaka, T. Nakano, T. Fujita, Chem. Lett. (2000) 554.
[36] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255.

[37] E.B. Tjaden, D.C. Swenson, R.F. Jordan, Organometallics 14 (1995) 371.
[38] U. Klabunde, S.D. Ittel, J. Mol. Catal. 41 (1987) 123.
[39] L. Matilainen, M. Klinga, M. Leskela, J. Chem. Soc., Dalton Trans. (1996) 219.
[40] X. Bei, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 3282.
[41] T. Tsukahara, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 3303.
[42] I. Kim, Y. Nishihara, R.F. Jordan, R.D. Rogers, A.L. Rheingold, G.P.A. Yap, Organometallics 16 (1997) 3314.
[43] F.J. Schattenmann, R.R. Schrock, W.M. Davis, Organometallics 17 (1998) 989.
[44] K. Saeki, T. Arakawa, JP-7319601 (1973) [Chem. Abstr. 79 (1973) 91559].
[45] K. Saeki, JP-7322682 (1973) [Chem. Abstr. 79 (1973) 145944].
[46] J. Saito, K. Sugimura, T. Fujita, JP-324709A (1998).
[47] P.B. Mackenzie, in: Proceedings of the MetCon'99 on Polymer in Transition.
[48] N. Suzuki, Y. Masubuchi, T. Yamaguchi, T. Kase, T.K. Miyamoto, A. Horiuchi, T. Mise, Macromolecules 33 (2000) 754.
[49] P.A. Deck, C.L. Beswick, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 1772.
[50] Korehasugoi! Kagaku no Sekai Kiroku-shu, KagakuDojin, 1999, p. 111.
[51] H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 472 (1994) 113.
[52] R. Chiang, J. Polym. Sci. 36 (1959) 91.
[53] L. Deng, T. Zieglar, T.K. Woo, P. Margl, L. Fan, Organometallics 17 (1998) 3240.
[54] C. Fonseca Gueerra, J.G. Snijders, G. te Velde, E.J. Baerends, Theor. Chem. Acc. 99 (1998) 391.