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A Family of Zirconium Complexes Having Two Phenoxy−Imine Chelate Ligands for Olefin Polymerization

Shigekazu Matsui, Makoto Mitani, Junji Saito, Yasushi Tohi, Haruyuki Makio, Naoto Matsukawa, Yukihiro Takagi, Kazutaka Tsuru, Masatoshi Nitabaru, Takashi Nakano, Hidetsugu Tanaka, Norio Kashiwa, and Terunori Fujita*

Contribution from the R & D Center, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba, 299-0265, Japan

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Abstract: A zirconium complex having two phenoxy−imine chelate ligands, bis[*N*-(3-*tert*-butylsalicylidene)-anilinato]zirconium(IV)dichloride (**1**), was found to display a very high ethylene polymerization activity of 550 kg of polymer/mmol of cat•h with a viscosity average molecular weight (M_v) value of 0.9×10^4 at 25 °C at atmospheric pressure using methylalumoxane (MAO) as a cocatalyst. This activity is 1 order of magnitude larger than that exhibited by Cp_2ZrCl_2 under the same polymerization conditions. The use of $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al in place of MAO as a cocatalyst resulted in extremely high molecular weight polyethylene, M_v 505 $\times 10^4$, with an activity of 11 kg of polymer/mmol of cat•h at 50 °C. This M_v value is one of the highest values displayed by homogeneous olefin polymerization catalysts. Complex **1**, using $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as a cocatalyst, provided a high molecular weight ethylene−propylene copolymer, M_v 109 $\times 10^4$, with 8 kg of polymer/mmol of cat•h activity at a propylene content of 20.7 mol %. X-ray analysis revealed that complex **1** adopts a distorted octahedral coordination structure around the zirconium metal and that two oxygen atoms are situated in trans position while two nitrogen atoms and two chlorine atoms are situated in cis position. DFT calculations suggest that the active species derived from complex **1** possesses two available cis-located sites for efficient ethylene polymerization. Changing the *tert*-butyl group in the phenoxy benzene ring enhanced the polymerization activity. Bis[*N*-(3-cumyl-5-methylsalicylidene)cyclohexylaminato]zirconium(IV)dichloride (**7**) with MAO displayed an ethylene polymerization activity of 4315 kg of polymer/mmol of cat•h at 25 °C at atmospheric pressure. This activity corresponds to a catalyst turnover frequency (TOF) value of 42 900/s•atm. This TOF value is one of the largest not only for olefin polymerization but also for any known catalytic reaction. Ligands with additional steric congestion near the polymerization reaction center gave increased M_v values. The maximum M_v value, 220×10^4 using MAO, was obtained with bis[*N*-(3,5-dicumylsalicylidene)-2′-isopropylanilinato]zirconium(IV)dichloride (**15**). Thus, polyethylenes ranging from low to exceptionally high molecular weights can be obtained from these zirconium complexes by changing the ligand structure and the choice of cocatalyst.

Introduction

Research and development of high-performance olefin polymerization catalysts has contributed significantly to the advancement of organometallic chemistry and polymer chemistry and has made a dramatic impact on the polyolefin industry. More than 40 million tons of polyolefins are produced every year using catalytic olefin polymerization. Historically, the discovery of highly active catalysts results in the commercialization of new polyolefins. A recent example is the discovery of group 4 metallocene catalysts, which display very high ethylene polymerization activity.[1−3] These high-performance olefin polymerization catalysts have made possible the industrial production of linear low-density polyethylene, isotactic and syndiotactic polypropylene, syndiotactic polystyrene, etc.

More recently, other classes of metal complexes have been investigated as precursors for a new generation of olefin polymerization catalysts.[4−22] Specifically, olefin polymerization catalysts have been developed from nickel or palladium complexes with diimine ligands,[14] iron or cobalt complexes with diimine−pyridine ligands,[15] nickel complexes with phenoxy−imine ligands,[16] titanium complexes with diamide ligands,[17,18] titanium complexes with two phosphineimide ligands,[20] and tantalum complexes with two amide−pyridine ligands.[21] Many

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Table 1. Ethylene Polymerization with **1** or Cp_2ZrCl_2 Using MAO as a Cocatalyst[a]

entry	complex (μmol)	MAO (mmol)	Al/Zr	yield (g)	acitivety[b]	M_v × 10^{-4}	M_w/M_n	vinyl end groups /1000 carbons
1	**1** (0.2)	1.25	6250	3.29	197[c]	0.8	2.21	2.38
2	**1** (0.02)	1.25	62500	0.92	550	0.9	2.06	2.38
3	**1** (0.02)	2.50	125000	0.89	536	0.7	2.01	2.36
4	**1** (0.02)	6.25	312500	0.82	494	0.7	2.05	2.41
5	**1** (0.01)	1.25	125000	0.42	508	0.6	2.05	2.36
6	Cp_2ZrCl_2 (0.5)	1.25	2500	1.13	27	104	2.61	0.03
7	Cp_2ZrCl_2 (0.2)	1.25	6250	0.46	28	100	2.31	0.03

[a] Conditions: 0.1 MPa ethylene pressure, 25 °C; solvent, toluene 250 mL; polymerization time, 5 min. [b] Activity, kg of polymer/mmol of cat•h. [c] Stirring difficulty was encountered because of excessive polymer production.

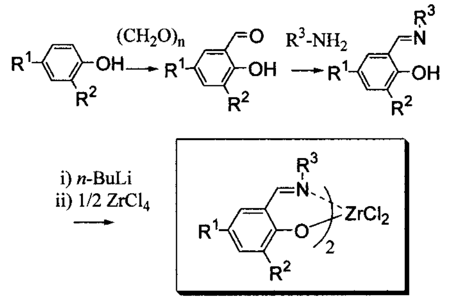
of them display activities comparable to those of the metallocene catalysts[15,16,20] and, in some cases, behave as living polymerization catalysts of α-olefins.[14c,17b,19i] Others are capable of producing functionalized polyolefins via coordination polymerization of ethylene with functionalized olefinic monomers.[14b,16]

Recently, we prepared transition metal complexes that feature unsymmetrical chelating ligands in order to develop highly active new olefin polymerization catalysts. Specifically, we focused on the incorporation of bidentate ligands that afford metal complexes with a pair of cis-located sites, a prerequisite for efficient olefin polymerization. Our efforts have led to a family of group 4 transition metal complexes possessing two phenoxy−imine chelate ligands, named "FI Catalysts", which display high catalytic performance for olefin polymerization including living olefin polymerization.[22] We describe herein the catalytic performance of zirconium FI Catalysts for olefin polymerization.

Results and Discussion

Synthesis of Zirconium Complexes Having Two Phenoxy−Imine Ligands. In this study, we utilized zirconium complexes possessing two phenoxy−imine chelate ligands. A general synthetic route for these complexes is shown in Scheme 1 and consists of three steps; the preparation of an ortho-formylated phenol,[23] its condensation with an appropriate primary amine to provide a phenoxy−imine ligand, and complexation of $ZrCl_4$ with the ligand in a molar ratio of 1:2. Treatment of a phenol derivatives with paraformaldehyde in the presence of a base produced an ortho-formylated phenol in about 60−80% yield. This formylated phenol readily reacted with a primary amine to afford a phenoxy−imine ligand in approximately 80−100% yield. Complex formation was achieved by treatment of 2 equiv of the lithium salt of the phenoxy−imine ligand with $ZrCl_4$. This route utilizes materials that are easily prepared, are relatively stable, and display high reactivity. The overall yield for the three steps is very good.

Scheme 1



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Olefin Polymerization Using Complex 1. A zirconium complex having two 3-*tert*-butylsalicylideneaniline ligands, bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV)dichloride (**1**), was investigated as an ethylene polymerization catalyst using methylalumoxane (MAO) as a cocatalyst at 25 °C under ethylene at atmospheric pressure. The results are summarized in Table 1.

Complex **1** displayed an activity of 197 kg of polymer/mmol of cat•h (entry 1), which is much higher than the activity displayed by Cp_2ZrCl_2 (entry 7) at the same catalyst concentration. Difficulty with stirring was encountered for entry 1 because of the large amount of polyethylene produced. Accordingly, screens were run with reduced catalyst concentrations in order to obtain a more accurate activity for complex **1**. As a result, complex **1** was found to display a very high activity of 550 kg of polymer/mmol of cat•h with a viscosity average molecular weight (M_v) value of 0.9×10^4. The activity obtained at reduced catalyst concentration (550 kg of polymer/mmol of cat•h, entry 2) was ~20 times larger than that exhibited by Cp_2ZrCl_2 at 25 °C. The molecular weight distribution (M_w/M_n) of the polymer obtained from complex **1** was 2.06, suggesting that the polymer is produced by a single active species.[2d] Transition melting temperature (T_m) of the polymer was 128 °C. Analysis using ^{13}C NMR spectroscopy indicates that the polymer is a linear polyethylene having virtually no branching (see Supporting Information). Infrared spectroscopy reveals a vinyl end group concentration of ~2.4/1000 carbon atoms, which suggests that β-hydrogen transfer is the main termination pathway. Increasing Al/Zr ratio from 6250/1 to 312 500/1 gave rise to no significant changes in the catalytic performance, except the activity in entry 1 (see Table 1, caption b). This observation confirms that chain transfer to aluminum does not play a dominant role in chain termination.

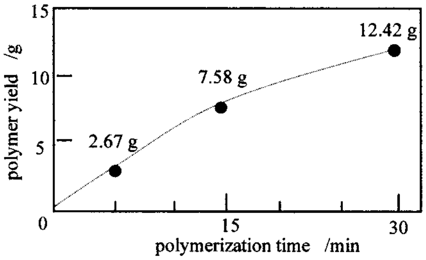

Figure 1. Relationship between the polymerization time and the polymer yield obtained with complex **1**/MAO. Conditions: 25 °C, 0.1 MPa ethylene pressure; solvent, toluene 400 mL; complex **1**, 0.08 μmol; MAO (A1), 1.25 mmol.

To investigate the catalytic lifetime of complex **1**, ethylene polymerizations were conducted for 5, 15, and 30 min. The relationship between the polymerization time and the polymer yield indicates that the **1**/MAO catalyst has a catalytic lifetime of at least 30 min, as shown in Figure 1.

The effects of the polymerization temperature on the catalytic activity of **1**/MAO were studied. The results were compared with those for Cp_2ZrCl_2 (Figure 2). In the case of Cp_2ZrCl_2, the activity was 7 kg of polymer/mmol of cat•h at 0 °C and gradually increased to ~100 kg of polymer/mmol of cat•h at 75 °C. In comparison, **1**/MAO provided 295 kg of polymer/mmol of cat•h activity at 0 °C. Moreover, its activity increased to a maximum of 587 kg of polymer/mmol of cat•h at 40 °C. Above 40 °C, the activity decreased. However, over a temperature range of 0 to 75 °C, the activity remained above 100 kg of polymer/mmol of cat•h.

In addition to MAO, the catalytic performance of complex **1** with $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as the cocatalyst was investigated.[24,25] This catalyst system gave unexpectedly high molecular weight polyethylene. At 25 °C, complex **1** with Ph^3CB-$(C_6F_5)_4$/ *i*-Bu_3Al resulted in an M_v value of 383×10^4 with 4 kg of polymer/mmol of cat•h. Furthermore, at 50 °C, this catalyst system produced exceptionally higher molecular weight polyethylene (M_v 505×10^4) with 11 kg of polymer/mmol of cat•h. In contrast, Cp_2ZrCl_2 with $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al produced

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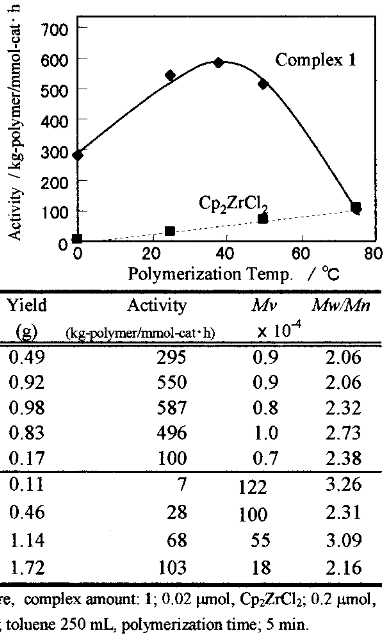
Table 2. Ethylene Polymerization with **1** or Cp_2ZrCl_2 Using $Ph_3CB(C_6F_5)_4$/ *i*-Bu_3Al as a Cocatalyst[a]

entry	complex (μmol)	cocatalyst (μmol) $Ph_3CB(C_6F_5)_4$	cocatalyst (μmol) *i*-Bu_3Al	temp (°C)	yield (g)	activity[b]	M_v $\times 10^{-4}$
1	**1** (2.5)	5.0	100	25	0.84	4	383
2	**1** (2.5)	5.0	100	50	2.31	11	505
3	Cp_2ZrCl_2 (0.5)	1.0	250	25	0.77	18	59
4	Cp_2ZrCl_2 (0.5)	1.0	250	50	0.87	21	36

[a] Conditions: 0.1 MPa ethylene pressure; solvent, toluene 250 mL; polymerization time, 5 min. [b] Activity, kg of polymer/mmol of cat•h.



Entry	Complex	Temp. (℃)	Yield (g)	Activity (kg-polymer/mmol-cat · h)	*Mv* x 10^{-4}	*Mw/Mn*
1	**1**	0	0.49	295	0.9	2.06
2	**1**	25	0.92	550	0.9	2.06
3	**1**	40	0.98	587	0.8	2.32
4	**1**	50	0.83	496	1.0	2.73
5	**1**	75	0.17	100	0.7	2.38
6	Cp_2ZrCl_2	0	0.11	7	122	3.26
7	Cp_2ZrCl_2	25	0.46	28	100	2.31
8	Cp_2ZrCl_2	50	1.14	68	55	3.09
9	Cp_2ZrCl_2	75	1.72	103	18	2.16

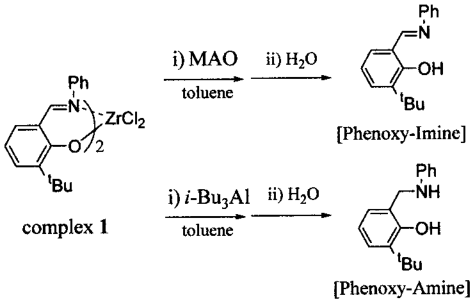
Conditions: 0.1 MPa ethylene pressure, complex amount: **1**; 0.02 μmol, Cp_2ZrCl_2; 0.2 μmol, cocat. MAO (Al) 1.25 mmol, solvent; toluene 250 mL, polymerization time; 5 min.

Figure 2. Relationship between the polymerization temperature and the activity. Conditions: 0.1 MPa ethylene pressure; complex amount, **1** 0.02 μmol, Cp_2ZnCl_2 0.2 μmol, cocatalyst MAO (A1) 1.25 mmol; solvent, toluene 250 mL; polymerization time, 5 min.

polyethylene having an M_v value of 59 × 10^4 and 36 × 10^4 with activity values of 18 and 21 kg of polymer/mmol of cat•h at 25 and 50 °C, respectively. As far as we know, the molecular weight value, 505 × 10^4, displayed by complex **1** with $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al is one of the largest values displayed by homogeneous olefin polymerization catalysts.[5a,26] From these polymerization experiments, it is readily apparent that the choice of cocatalyst can have a dramatic effect on catalyst performance (see Table 2).[24]

Considering the observed difference in catalytic performance as a result of using MAO and $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as cocatalysts, the localized structures of the active species may be modified depending on the aluminum species employed. Treatment of complex **1** with 30 equiv of *i*-Bu_3Al in toluene at 25 °C, followed by treatment with water, exclusively afforded *N*-phenyl-2-hydroxy-3-*tert*-butylbenzylamine [phenoxy−amine] as an organic material (see Scheme 2). Alternatively, the treatment of complex **1** with MAO followed by treatment with water quantitatively gave 3-*tert*-butylsalicylideneaniline [phenoxy−imine]. These facts suggest that, by using $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as a cocatalyst, the active species derived from complex **1** may have a phenoxy−amine ligand, which was produced from the reduction of a phenoxy−imine ligand by *i*-Bu_3Al or aluminum hydride compounds, contaminant in *i*-Bu_3Al, which work as a reducing reagent.[27]

Scheme 2



Complex **1** using MAO or $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as a cocatalyst was also found to exhibit high catalytic performance for ethylene−propylene copolymerization.[28] When MAO was used as a cocatalyst, complex **1** produced a low molecular weight copolymer, M_v 0.5 × 10^4, with 22 kg of polymer/mmol of cat•h activity at 10.1 mol % propylene content. In contrast, using $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al as a cocatalyst, complex **1** produced a high molecular weight copolymer, M_v 109 × 10^4, with 8 kg of polymer/mmol of cat•h activity at 20.7 mol % propylene content (see Table 3).

Study of Molecular Stereochemistry for Complex 1. The stereochemical structure of complex **1** was predicted using DFT calculations. Because zirconium complex **1** could exhibit five possible isomeric structures (*cis*-I, -II, -III, *trans*-I, -II), DFT calculations were performed to determine the most plausible one. The relative formation energies of these five isomers are listed in Scheme 3.

Of these, the structure *cis*-I was found to be the most preferred. As shown in Figure 3a, the short Zr−O bonds are trans to each other in the structure *cis*-I.[6e] This arrangement reduces steric congestion of the ligands and maximizes the opportunity for O to Zr π-bonding through the utilization of different Zr d-orbitals.

The calculations suggested that the two oxygen atoms occupy trans positions (O−Zr−O* angle, 168.8°), whereas the two nitrogen atoms and the two chlorine atoms were situated in cis positions (N−Zr−N* angle, 77.0°; Cl−Zr−Cl* angle, 103.2°).

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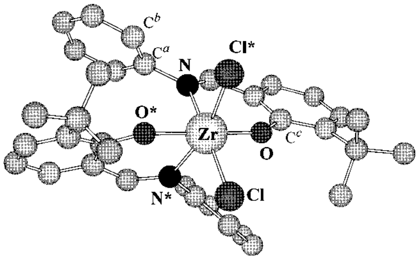
(28) For propylene polymerization at 25 °C at atmospheric pressure, complex **1**/MAO produced an oligomer with an activity of 324 g/mmol of cat•h, whereas complex **1**/$Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al provided isotactic polypropylene (M_w 20.6 × 10^4; T_m 101.6 °C; mm = 73.4%) with an activity of 68 g/mmol of cat•h.

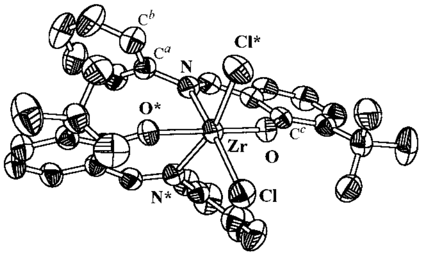
Table 3. Ethylene−Propylene Copolymerization Using **1** or Cp_2ZrCl_2[a]

entry	complex	cocatalyst	yield (g)	activity[b]	propylene content (%)	M_v[c] × 10^{-4}	M_w/M_n
1	**1**	MAO	4.66	22	10.1	0.5	2.45
2	Cp_2ZrCl_2	MAO	4.54	22	25.6	0.8	3.34
3	**1**	$Ph_3CB(C_6F_5)_4$/ i-Bu_3Al	1.63	8	20.7	109	1.83
4	Cp_2ZrCl_2	$Ph_3CB(C_6F_5)_4$/ i-Bu_3Al	1.48	7	11.5	13	1.86

[a] Conditions: 50 °C, 0.1 MPa; solvent, toluene 250 mL; polymerization time, 5 min; complex 2.5 μmol; cocatalyst MAO 1.25 mmol, $Ph_3CB(C_6F_5)_4$ 5 μmol/i-Bu_3Al 0.275 mmol. [b] Activity, kg of polymer/mmol of cat•h. [c] Determined by GPC.



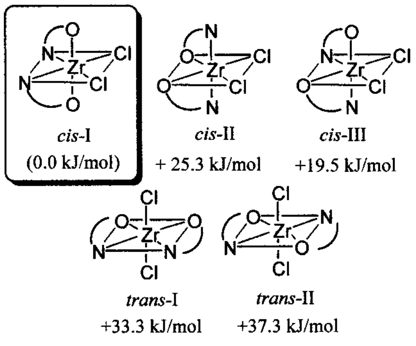
(a) DFT Calculation



(b) X-ray Analysis

Figure 3. Structure of complex **1**. X-ray analysis: Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms and a diethyl ether molecule of crystal are omitted for clarity.

Scheme 3



Calculation relative formation energies of complex 1 isomers: based on isomeric structure *cis*-I

The phenyl unit plane attached to the R^3 position swung out the phenoxy benzene unit, forming a dihedral angle of 60.7°.

The molecular structure of complex **1** was established using single-crystal X-ray diffraction. As shown in Figure 3b, complex **1** adopted a distorted octahedral structure around the zirconium center. Selected bond distances, bond angles, and torsion angles for complex **1** are listed in Table 5. The two oxygen atoms were situated in trans position (O−Zr−O* angle, 165.5(1)°). Alternatively, the two nitrogen atoms were located cis to one another (N−Zr−N* angle, 74.0(1)°), and two chlorine atoms were also located cis to one another (Cl−Zr−Cl* angle, 100.38(5)°). The torsion angle of Zr−N−C^a−C^b was 59.8(4)°. Consequently, the calculated isomeric structure, *cis*-I, for complex **1** was found to be entirely consistent with the results of the X-ray structural analysis, suggesting that DFT calculation is an effective tool for analyzing the structure of a zirconium complex bearing two phenoxy−imine ligands.

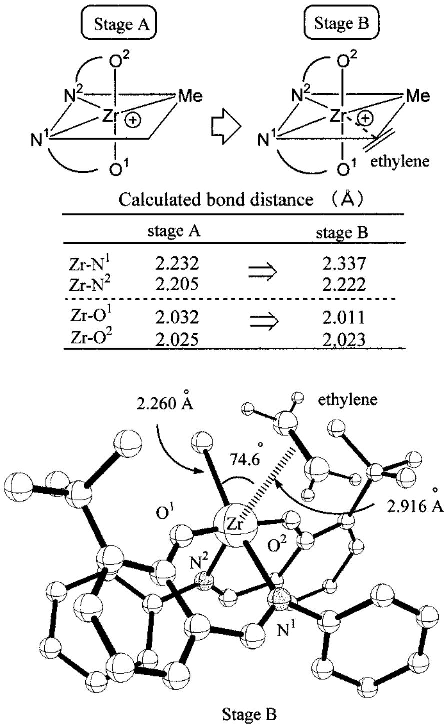
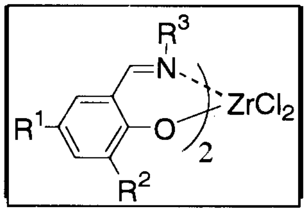


Figure 4. Calculated structure of ethylene coordinated active species derived from complex **1**.

Thus, an active species derived from complex **1** for ethylene polymerization was studied on the basis of DFT calculations to determine why complex **1** displayed exceptionally high ethylene polymerization activity. As indicated by the X-ray analysis as well as the DFT calculations, the two chlorine atoms of complex **1** are in a cis configuration. DFT calculations suggest that a methyl cationic complex derived from complex **1** has two available cis-located sites needed for efficient olefin polymerization (Figure 4). In addition, the calculations indicate that the Zr−N bond distances trans to the alkyl chain lengthen considerably during the polymerization process (stage A, 2.232 Å; stage B, 2.337 Å), whereas the corresponding Zr−O distances remain practically unchanged (stage A, 2.032 and 2.025 Å; stage B, 2.011 and 2.023 Å). Changes in the Zr−N bond distance may result from electronic requirements as well as steric requirements and may play a role for displaying high activity.

Catalytic Performance of the Derivatives of Complex 1. Complex **1** was demonstrated to have high potential for olefin polymerization. In addition, the steric and electronic environments of the metal center can be adjusted by modifying the ligand structure, because the phenoxy−imine ligand has multiple sites for introducing or changing the substituent(s). Hence, we investigated the catalytic performance of the derivatives of complex **1**.

Table 4. Ethylene Polymerization Using Complexes **1**−**15**/MAO[a]



engry	complex	substituent R1	R2	R3	complex amt (μmol)	yield (g)	activity[b]	M_v $\times 10^{-4}$	M_w/M_n
1	**1**	H	*t*-Bu	Ph	0.02	0.92	550	0.9	2.06
2	**2**	Me	*t*-Bu	Ph	0.02	0.55	331	0.7	2.00
3	**3**	H	Me	Ph	5.00	0.18	0.4	0.3	2.31
4	**4**	H	*i*-Pr	Ph	5.00	0.39	0.9	0.6	2.48
5	**5**	Me	amantyl	Ph	0.02	1.19	714	1.2	2.69
6	**6**	Me	cumyl	Ph	0.01	1.75	2096	1.8	7.20
7	**7**	Me	cumyl	cyclohexyl	0.005	1.80	4315	1.5	1.88
8	**8**	H	*t*-Bu	2-Me-C_6H_4	0.50	1.68	40	32	2.13
9	**9**	H	*t*-Bu	2-*i*-Pr-C_6H_4	0.50	2.41	58	113	2.61
10	**10**	H	*t*-Bu	2-*t*-Bu-C_6H_4	5.00	0.23	0.1	>274[c]	*d*
11	**11**	H	*t*-Bu	3,5-di-*t*-Bu-C_6H-	0.10	2.03	244	2.6	1.79
12	**12**	H	*t*-Bu	4-*t*-Bu-C_6H_4	0.10	2.26	271	0.7	2.03
13	**13**	H	*t*-Bu	2,6-di-*i*-Pr-C_6H_3	5.00	trace			
14	**14**	Me	adamantyl	2-*i*-Pr-C_6H_4	0.10	0.19	23	153	*d*
15	**15**	cumyl	cumyl	2-*i*-Pr-C_6H_4	0.20	0.72	43	220	*d*

[a] Conditions: 25 °C, 0.1 MPa ethylene pressure; MAO (Al), 1.25 mmol; solvent, toluene 250 mL; polymerization time, entries 1−9, 11, 12, 14, and 15 5 min, entries 10 and 13 30 min. [b] Activity, kg of polymer/mmol of cat•h. [c] Obtained from the polyethylene soluble in Decalin under intrinsic viscosity measurement conditions. [d] Polymer did not dissolve wholly in *o*-dichlorobenzene under GPC measurement conditions.

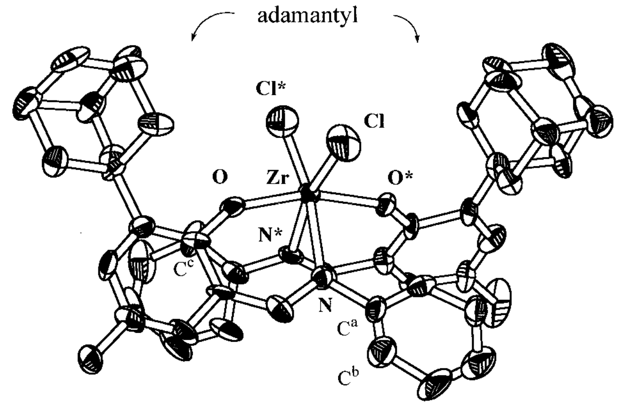


Figure 5. X-ray structure of complex **5**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances, Bond Angles, and Torsion Angles for Complexes **1** and **5**[a]

	1	**5**
Bond Distances (Å)		
Zr−O	1.985(2)	1.97(1)
Zr−N	2.355(2)	2.38(1)
Zr−Cl	2.4234(9)	2.372(4)
Bond Angles (deg)		
O−Zr−O*	165.5(1)	162.4(1)
N−Zr−N*	74.0(1)	76.8(1)
Cl−Zr−Cl*	100.38(5)	98.91(6)
O−Zr−N	91.10(9)	90.2(4)
O−Zr−N*	77.26(8)	78.1(4)
O−Zr−Cl	95.27(7)	96.1(3)
O−Zr−Cl*	93.99(7)	94.8(3)
N−Zr−Cl	93.45(6)	92.0(3)
N−Zr−Cl*	164.30(6)	167.2(3)
Zr−O−C^c	146.5(2)	148.5(8)
Torsion Angles (deg)		
Zr−N−C^a−C^b	59.8(4)	63(1)

[a] Numbers in parentheses are estimated standard deviations of the last significant figure. Atoms are labeled as indicated in Figures 3 and 5.

Table 4 summarizes the catalytic performance of phenoxy−imine zirconium complexes as a result of introducing and/or changing substituent(s) at the R^1−R^3 position.

(a) Polymerization Activity. These data demonstrate that changing the alkyl substituent at the R^2 position significantly affects the polymerization activity. For complex **3** (R^2 = Me) and complex **4** (R^2 = *i*-Pr), activities decreased to 0.4 ($M_v = 0.3 \times 10^4$) and 0.9 kg of polymer/mmol of cat•h ($M_v = 0.6 \times 10^4$), respectively. Alternatively, replacement of the *tert*-butyl group at the R^2 position in complex **2** with a sterically larger adamantyl group or a cumyl group enhanced polymerization activity and slightly increased M_v, compared to complex **2**. Complexes **5** and **6** displayed activities of 714 ($M_v = 1.2 \times 10^4$) and 2096 kg of polymer/mmol of cat•h ($M_v = 1.8 \times 10^4$), respectively.

The X-ray structure of complex **5** is depicted in Figure 5. The molecular structure of complex **5** is practically the same as that of complex **1** (Table 5).

The enhancement in catalytic activity may be ascribed to the effective separation between the cationic active species and the anionic cocatalyst as a result of the introduction of bulkier alkyl substituents in the R^2 position. Separation of cation−anion pair allows more space for ethylene to coordinate to the metal and for its insertion into the carbon−metal bond.[29] Moreover, electronically, the separation increases the degree of unsaturation associated with the cationic active species and thus enhances the reactivity toward ethylene.[25a]

Changing the phenyl group on the imine nitrogen of complex **6** to a cyclohexyl group further enhanced activity, probably due to the electron-donating effects of an aliphatic group at the R^3 position. Complex **7**, featuring a cyclohexyl group on the imine nitrogen, afforded an unprecedented activity of 4315 kg of

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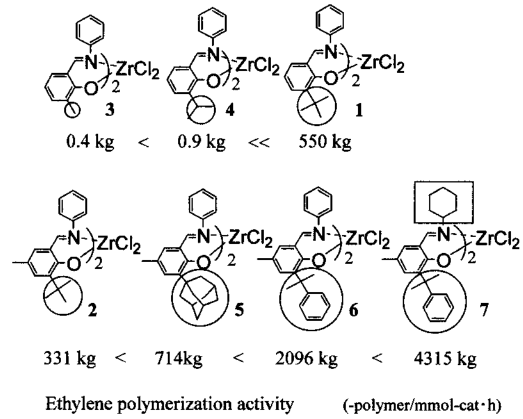
Scheme 4



polymer/mmol of cat·h ($M_v = 1.5 \times 10^4$) at 25 °C at atmospheric pressure. This activity corresponds to a catalyst turnover frequency (TOF) value of 42 900/s·atm. To the best of our knowledge, this TOF value is one of the largest not only for olefin polymerization but for any catalytic reaction at atmospheric pressure conditions (see Scheme 4).[1−4, 30]

(b) Molecular Weight of the Polymer. The introduction of an alkyl group at the ortho position of the phenyl group at the R^3 position dramatically increased the molecular weight values of polyethylene. Complex **8** (R^3, 2-methylphenyl) displayed an M_v value of 32×10^4. In addition, complex **9** (R^3, 2-isopropylphenyl) provided an M_v value of 113×10^4, which is comparable to that obtained from Cp_2ZrCl_2. Moreover, complex **10** (R^3, 2-*tert*-butylphenyl) produced high molecular weight polyethylene, which did not dissolve completely in Decalin under the intrinsic viscosity measurement conditions. In fact, the M_v value for the soluble part of the polyethylene produced by complex **10** was 274×10^4. In contrast, the introduction of *m*- or *p*-*tert*-butyl(s) on the phenyl group at the R^3 position gave no significant changes in M_v values, as was observed for complexes **11** and **12**. The described increase in the M_v values is probably due to a decrease in the β-hydride elimination rate that is a consequence of the increased steric congestion near the polymerization center.[31] Theoretical calculations support this explanation. Namely, the stabilization energy (ΔE_β) as a result of β-agostic interaction of the active species, derived from complex **9** (model **B**; Figure 6 right), is smaller than that for complex **1** (model **A**; Figure 6 left), due to the steric repulsion of a β-hydrogen and an isopropyl group. Thus, the introduced *o*-isopropyl group sterically blocks access to transition state needed to promote β-hydride elimination.

However, complex **13**, possessing 2,6-diisopropylphenyl group at the R^3 position**,** displayed practically no ethylene polymerization activity, probably due to overwhelming steric congestion derived from two isopropyl groups. The use of the 2,6-diisopropylphenyl substituent in ligands for olefin polymerization catalysts based on late transition metals has been employed to advantage,[14−16] but this is not the case in our system.

Interestingly, changing the R^2 substituent of complex **9** from the *tert*-butyl group to an adamantyl group or a cumyl group further enhanced molecular weight. Thus, complexes **14** and **15**, having a 2-isopropylphenyl group at the R^3 position, and an adamantyl or a cumyl group at the R^2 position, provided polyethylene having higher M_v values of 153×10^4 and 220×10^4, respectively.

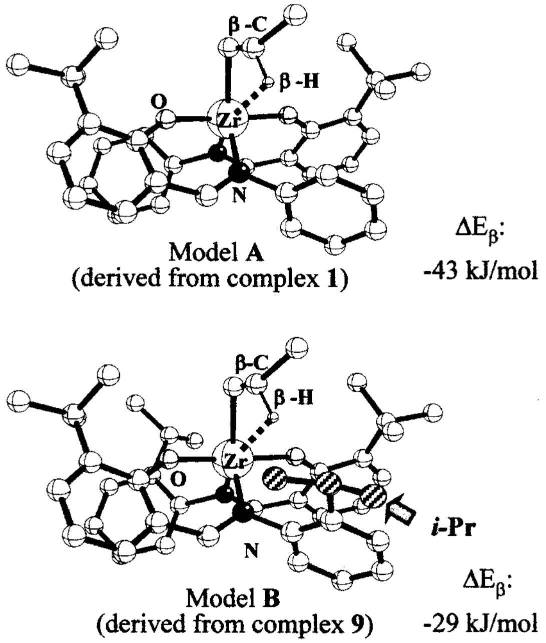


Figure 6. stabilization energies (ΔE_β) as a result of β-agostic interaction. Cationic complex models **A** and **B** stand for active species derived from complexes **1** and **9**, respectively. All hydrogens except the β-hydrogen are omitted. An *n*-propyl group is employed as a model of a polymer chain.

These results suggest that molecular weight of the polymer obtained from these catalysts are strongly dependent on the bulkiness of the substituents placed in the vicinity of active site. Table 4 together with Table 2 shows that zirconium complexes having two phenoxy−imine ligands are capable of controlling the molecular weight of the resulting polymer (M_v 0.3×10^4−505×10^4) by changing the ligand structure and by the choice of the cocatalyst (see Scheme 5).

Experimental Section

General Comments. Materials. Dried solvents (diethyl ether, tetrahydrofuran (THF), dichloromethane, *n*-hexane, *n*-pentane) used for complex synthesis were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Toluene used as a polymerization solvent (Wako Pure Chemical Industries, Ltd.) was dried over Al_2O_3 and degassed by the bubbling of nitrogen gas. Phenol compounds, amine compounds, and paraformaldehyde for ligand synthesis were purchased from Aldrich Chemical Co., Inc., Wako Pure Chemical Industries, Ltd., Acros Organics, or Tokyo Kasei Kogyo Co., Ltd. An ethylmagnesium bromide diethyl ether solution and an *n*-butyllithium hexane solution were purchased from Tokyo Kasei Kogyo Co., Ltd. and Kanto Chemical Co., Inc., respectively. $ZrCl_4$, Cp_2ZrCl_2 (Wako Pure Chemical Industries, Ltd.) and $ZrCl_4(THF)_2$ (Strem Chemicals, Inc.) were used without further purification. Ethylene and propylene were obtained from Sumitomo Seika Co. and Mitsui Chemicals, Inc., respectively. Cocatalysts: Methylalmoxane (MAO) was purchased from Albemarle as a 1.2 M of a toluene solution, and remaining trimethylaluminum was evaporated in vacuo prior to use. $Ph_3CB(C_6F_5)_4$ (Asahi Glass Co., Ltd.) and *i*-Bu_3Al (Tosoh Akzo Corp.) were used as received.

Ligand and Complex Analyses. NMR spectra were recorded on JEOL 270 or NEC-LA500 spectrometers at ambient temperatures. Chemical shifts for ^1H NMR were referenced to internal solvent resonance and reported relative to tetramethylsilane. The melting point (mp) of a ligand was measured by a melting point microapparatus from Yanagimoto Seisakusho. FD-MS spectra were recorded on an SX-102A

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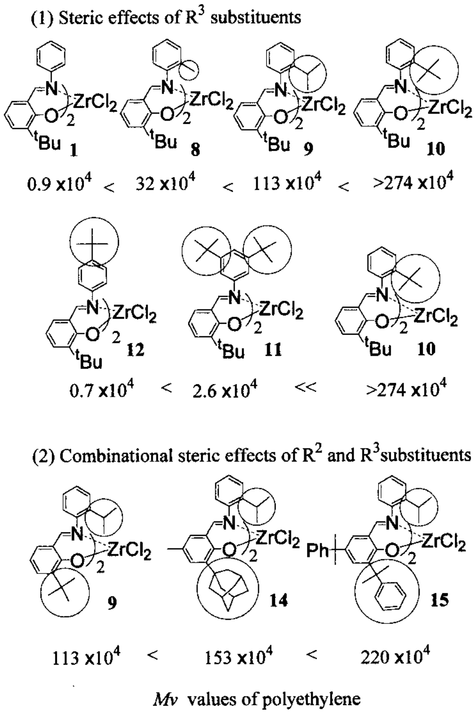
(30) Alt, H. G.; Milius W.; Palackal, S. J. *J. Organomet, Chem.* **1994**, *472*, 113−118.

(31) DFT calculations suggest that β-hydrogen transfer to ethylene is sterically unfavored compared with that to the Zr metal for the Zr complexes used in this study.

Scheme 5



from Japan Electron Optics Laboratory Co., Ltd. Elemental analysis for CHN was carried out by a CHNO type from Helaus Co. Elemental analysis for Zr was done using the ICP method with a Shimadzu ICPS-8000 after dry ashing and dilute nitric acid dissolution.

Polymer Characterization. ^{13}C NMR data for polyethylene were obtained using *o*-dichlorobenzene with 20% benzene-d_6 as a solvent at 120 °C. The intrinsic viscosity [η] was measured in Decalin at 135 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) values of polyethylene were calculated by the following equation:[32] $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$. M_v values of ethylene−propylene copolymers and molecular weight distribution (M_w/M_n) values of polyethylene and ethylene−propylene copolymers were determined using a Waters 150-C gel permeation chromatograph at 145 °C using polyethylene calibration and equipped with three TSKgel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and TSKgelGMH$_6$-HTL). *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min. Transition melting temperatures (T_m) of the polymers were determined by DSC with a Perkin-Elmer DSC-7 differential scanning calorimeter, measured upon reheating the polymer sample to 200 °C at a heating rate of 10 °C/min. Propylene contents of the copolymers were determined by IR analyses.[33]

Syntheses. Ligand syntheses were carried out under nitrogen in oven-dried glassware. All manipulations of complex syntheses were performed with exclusion of oxygen and moisture under argon using standard Schlenk techniques in oven-dried glassware.

Preparation of Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) Dichloride (1). (a) Ligand Synthesis. A 3.0 M ethylmagnesium bromide diethyl ether solution (18.5 mL, 55.5 mmol) was added dropwise to a stirred solution of 2-*tert*-butylphenol (7.51 g, 50.0 mmol) in THF (40 mL) at room temperature. After the mixture was stirred for 2 h, toluene (100 mL) was added. After the diethyl ether and the THF were removed by distillation, a mixture of triethylamine (7.59 g, 75.0 mmol) and paraformaldehyde (3.95 g (95% purity), 125.0 mmol) in toluene (50 mL) was added, and the mixture was stirred for 2 h at 95 °C. The resulting reaction mixture was poured into 1 N HCl (250 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (200 mL × 3). The combined organic phases were dried over Na_2SO_4 and evaporated in vacuo to give a yellow oil, which was purified by column chromatography on silica gel using hexane as eluent to give 3-*tert*-butylsalicylaldehyde (7.33 g, 41.1 mmol) as a pale yellow oil in 82% yield. ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 9H, *t*-Bu), 6.95 (dd, 1H, J = 7.3, 7.3 Hz, aromatic-H), 7.40 (d, 1H, J = 7.3 Hz, aromatic-H), 7.53 (d, 1H, J = 7.3 Hz, aromatic-H), 9.88 (s, 1H, CH═O), 11.79 (s, 1H, OH). To a stirred mixture of 3-*tert*-butylsalicylaldehyde (2.34 g, 13.4 mmol) and molecular sieves 3A (2 g) in ethanol (20 mL), a solution of aniline (1.41 g, 15.1 mmol) in ethanol (10 mL) was added dropwise over a 1-min period at room temperature. The mixture was stirred for 16 h and filtered. The molecular sieves 3A were washed with ethyl acetate (20 mL). The combined organic filtrates were concentrated in vacuo to afford a crude imine compound. Purification by column chromatography on silica gel using hexane/ethyl acetate (10/1) as eluent gave *N*-(3-*tert*-butylsalicylidene)aniline (3.23 g, 12.8 mmol) as an orange oil in 95% yield. ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 9H, *t*-Bu), 6.82−7.48 (m, 8H, aromatic-H), 8.64 (s, 1H, CH═N), 13.95 (s, 1H, OH).[34]

(b) Complex Synthesis. To a stirred solution of *N*-(3-*tert*-butylsalicylidene)aniline (2.533 g, 10.00 mmol) in THF (100 mL) at −78 °C, a 1.61 M *n*-butyllithium hexane solution (6.52 mL, 10.50 mmol) was added dropwise over a 5-min period. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise over a 30-min period to a stirred solution of $ZrCl_4(THF)_2$ (1.886 g, 5.00 mmol) in THF (100 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. After removal of the solvent, the product was extracted with CH_2Cl_2. Filteration following removal of the volatile gave a yellow solid. The solid was recrystallized from a dichloromethane/diethyl ether (1/4) solution at −40 °C to give complex **1** (1.743 g, 2.61 mmol) as fluorescent yellow single crystals in 52% yield. ^{1}H NMR ($CDCl_3$): δ 1.33−1.59 (m, 18H, *t*-Bu), 6.78−7.42 (m, 16H, aromatic-H), 8.12 (s, 2H, CH═N). Et_2O of crystallization: [1.20 (t, 6H, J = 5.2 Hz, CH_3), 3.48 (q, 4H, J = 5.2 Hz, CH_2)]. Anal. Found: C, 60.86; H, 5.36; N, 3.67; Zr, 12.70. Calcd for $ZrC_{34}H_{36}N_2O_2Cl_2 + Et_2O$: C, 61.60; H, 6.26; N, 3.78; Zr, 12.31. FD-MS, 664 (M^+).

Bis[*N*-(3-*tert*-butyl-5-methylsalicylidene)anilinato]zirconium(IV) Dichloride (2). Ligand *N*-(3-*tert*-Butyl-5-methylsalicylidene)aniline as orange crystals: mp 85 °C. ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9H, *t*-Bu), 2.32 (s, 3H, Me), 7.05−7.38 (m, 7H, aromatic-H), 8.59 (s, 1H, CH═N), 13.50 (s, 1H, OH). (**2**) as fluorescent yellow crystals: ^{1}H NMR ($CDCl_3$) δ 1.22−1.61 (m, 18H, *t*-Bu), 2.21−2.36 (m, 6H, Me), 6.78−7.45 (m, 14H, aromatic-H), 7.90−8.11 (m, 2H, CH═N). Anal. Found: C, 61.87; H, 5.57; N, 3.81. Calcd for $ZrC_{36}H_{40}N_2O_2Cl_2$: C, 62.23; H, 5.80; N, 4.03. FD-MS, 694 (M^+).

Bis[*N*-(3-methylsalicylidene)anilinato]zirconium(IV) Dichloride (3). Ligand *N*-(3-methylsalicylidene)aniline as a pale orange oil: ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H, Me), 6.70−7.49 (m, 8H, aromatic-H), 8.86 (s, 1H, CH═N), 13.59 (s, 1H, OH). (**3**) as a green-yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.50−2.50 (m, 6H, Me), 6.50−7.62 (m, 16H, aromatic-H), 8.00−8.12 (m, 2H, CH═N). Anal. Found: C, 57.90; H, 4.47; N, 4.74. Calcd for $ZrC_{28}H_{24}N_2O_2Cl_2$: C, 57.72; H, 4.15; N, 4.81. FD-MS, 582 (M^+).

Bis[*N*-(3-isopropylsalicylidene)anilinato]zirconium(IV) Dichloride (4). Ligand *N*-(3-isopropylsalicylidene)aniline as a red-brown oil: ^{1}H NMR ($CDCl_3$) δ 1.16−1.52 (m, 6H, Me), 3.10−3.69 (m, 1H, CH), 6.78−7.57 (m, 8H, aromatic-H), 8.65 (s, 1H, CH═N), 13.68 (br s, 1H, OH). (**4**) as a pale green-yellow powder: ^{1}H NMR ($CDCl_3$) δ 0.80−1.43 (m, 12H, Me), 2.74−3.32 (m, 2H, CH), 6.13−7.37 (m, 16H, aromatic-H), 7.89−8.17 (m, 2H, CH═N). Anal. Found: C, 59.86; H, 4.88; N, 4.46. Calcd for $ZrC_{32}H_{32}N_2O_2Cl_2$: C, 60.17; H, 5.05; N, 4.39. FD-MS, 638 (M^+).

Bis[*N*-(3-adamantyl-5-methylsalicylidene)anilinato]zirconium(IV) Dichloride (5). Ligand *N*-(3-adamantyl-5-methylsalicylidene)aniline as an orange powder: mp 53−54 °C. ^{1}H NMR ($CDCl_3$) δ 1.53−2.30 (m, 15H, adamantyl), 2.34 (s, 3H, Me), 7.01−7.42 (m, 7H, aromatic-H), 8.59 (s, 1H, CH═N), 13.72 (br s, 1H, OH). (**5**) as yellow crystals: ^{1}H NMR ($CDCl_3$) δ 1.30−2.41 (m, 30H + 6H, adamantyl, Me), 6.80−7.42 (m, 14H, aromatic-H), 8.09 (s, 2H, CH═N). Anal.

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(33) Tosi, C.; Simonazzi, T. *Angew. Makromol. Chem.* **1973**, *32*, 153.

(34) Single crystals of complexes **1** and **5** displayed ^{1}H NMR spectra having small complicated peaks in addition to the peaks assignable for the structure of type *cis*-I, suggesting that the zirconium complexes investigated in this study exist as isomeric mixtures in solution.

Found: C, 68.04; H, 6.53; N, 3.41. Calcd for $ZrC_{48}H_{52}N_2O_2Cl_2$: C, 67.74; H, 6.16; N, 3.29. FD-MS, 850 (M^+).

Bis[(3-cumyl-5-methylsalicylidene)anilinato]zirconium(IV) Dichloride (6). Ligand *N*-(3-cumyl-5-methylsalicylidene)aniline as an orange oil: ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 6H, cumyl-Me), 2.38 (s, 3H, aromatic-Me), 7.11−7.41 (m, 12H, aromatic-H), 8.51 (s, 1H, CH═N), 13.16 (br s, 1H, OH). (**6**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.35−1.65 (m, 12H, cumyl-Me), 1.70−2.11 (m, 6H, aromatic-Me), 6.25−8.05 (m, 24H + 2H, aromatic-H, CH═N). 0.5Et_2O of crystallization: [1.23 (t, 3H, J = 5.4 Hz, CH_3), 3.49 (q, 2H, J = 5.4 Hz, CH_2)]. Anal. Found: C, 67.61; H, 5.49; N, 3.18. Calcd for $ZrC_{46}H_{44}N_2O_2Cl_2$-($0.5C_4H_{10}O$): C, 67.35; H, 5.77; N, 3.27. FD-MS, 818 (M^+, $ZrC_{46}H_{44}N_2O_2Cl_2$).

Bis[(3-cumyl-5-methylsalicylidene)cyclohexylaminato]zirconium(IV) Dichloride (7). Ligand *N*-(3-cumyl-5-methylsalicylidene)cyclohexylamine as a pale yellow powder: mp 106−107 °C. ^{1}H NMR ($CDCl_3$) δ 1.09−1.68 (m, 10H, cyclohexyl-CH_2), 1.73 (s, 6H, cumyl-Me), 2.33 (s, 3H, aromatic-Me), 3.01−3.22 (m, 1H, cyclohexyl-CH), 6.91−7.30 (m, 7H, aromatic-H), 8.25 (s, 1H, CH═N), 13.40 (br s, 1H, OH). (**7**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 0.84−2.00 (m, 20H, cyclohexyl-CH_2), 1.83 (s, 6H, cumyl-Me), 1.96 (s, 6H, cumyl-Me), 2.27 (s, 3H, aromatic-Me), 2.37(s, 3H, aromatic-H), 3.47 (m, 2H, cyclohexyl-CH), 6.90−7.48 (m, 14H, aromatic-H), 8.09 (s, 2H, CH═N). 0.5Et_2O of crystallization: [1.21 (t, 3H, J = 5.3 Hz, CH_3), 3.49 (q, 2H, J = 5.3 Hz, CH_2)]. Anal. Found: C, 66.89; H, 6.22; N, 3.51. Calcd for $ZrC_{46}H_{56}N_2O_2Cl_2(0.5C_4H_{10}O)$: C, 67.19; H, 5.99; N, 3.26. FD-MS, 830 (M^+, $ZrC_{46}H_{56}N_2O_2Cl_2$).

Bis[*N*-(3-*tert*-butylsalicylidene)-2′-methylanilinato]zirconium(IV) Dichloride (8). Ligand *N*-(3-*tert*-butylsalicylidene)-2′-methylaniline as an orange oil: ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9H, *t*-Bu), 2.49 (s, 3H, Me), 6.81−7.58 (m, 7H, aromatic-H), 8.60 (s, 1H, CH═N), 13.61 (s, 1H, OH). (**8**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.08−1.71 (m, 18H, *t*-Bu), 2.33−2.45 (m, 6H, Me), 6.44−7.70 (m, 14H, aromatic-H), 8.08−8.28 (m, 2H, CH═N). Anal. Found: C, 61.85; H, 5.91; N 3.55. Calcd for $ZrC_{36}H_{40}N_2O_2Cl_2$: C, 62.23; H, 5.80; N, 4.03. FD-MS, 694 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)-2í-isopropylanilinato]zirconium(IV) Dichloride (9). Ligand *N*-(3-*tert*-butylsalicylidene)-2′-isopropylaniline as an orange oil: ^{1}H NMR ($CDCl_3$) δ 1.26 (d, 6H, J = 5.6 Hz, Me), 1.48 (s, 9H, *t*-Bu), 3.46 (q, 1H, J = 5.6 Hz, CH), 6.85−7.50 (m, 7H, aromatic-H), 8.55 (s, 1H, CH═N), 13.79 (s, 1H, OH). (**9**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 0.90−1.35 (m, 12H + 18H, Me, *t*-Bu), 3.10−3.31 (m, 2H, CH), 6.36−7.70 (m, 14H, aromatic-H), 8.08−8.29 (m, 2H, CH═N). Anal. Found: C, 63.57; H, 6.41; N, 3.34. Calcd for $ZrC_{40}H_{48}N_2O_2Cl_2$: C, 63.98; H, 6.44; N, 3.73. FD-MS, 750 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)-2′-*t*-butylanilinato]zirconium(IV) Dichloride (10). Ligand *N*-(3-*tert*-butylsalicylidene)-2′-*tert*-butylaniline as an orabge oil: ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 9H, *t*-Bu), 1.43 (s, 9H, *t*-Bu), 6.60−7.69 (m, 7H, aromatic-H), 8.49 (s, 1H, CH═N), 13.57 (s, 1H, OH). (**10**) as a pale yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 18H, *t*-Bu), 1.47 (s, 18H, *t*-Bu), 6.85−7.60 (m, 12H, aromatic-H), 8.35 (s, 2H, CH═N). Anal. Found: Zr, 12.06; C, 61.89; H, 6.99; N, 3.13.[35] Calcd for $ZrC_{42}H_{52}N_2O_2Cl_2$: Zr, 11.71; C, 64.76; H, 6.73; N, 3.60. FD-MS, 778 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)-3′,5′-di-*tert*-butylanilinato]zirconium(IV) Dichloride (11). Ligand *N*-(3-*tert*-butylsalicylidene)-3′,5′-di-*tert*-butylaniline as yellow crystals: mp 136−137 °C. ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 18H, *t*-Bu), 1.50 (s, 9H), 6.86−7.49 (m, 6H, aromatic-H), 8.64 (s, 1H, CH═N), 14.10 (s, 1H, OH). (**11**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 0.80−1.30 (m, 54H, *t*-Bu), 6.69−7.51 (m, 12H, aromatic-H), 8.35 (s, 2H, CH═N). Anal. Found: C, 67.57; H, 7.41; N, 3.34. Calcd for $ZrC_{50}H_{68}N_2O_2Cl_2$: C, 67.38; H, 7.6; N, 3.14. FD-MS, 890 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)-4′-*tert*-butylanilinato]zirconium(IV) Dichloride (12). Ligand *N*-(3-*tert*-butylsalicylidene)-4′-*tert*-butylaniline as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9H, tBu), 1.49 (s, 9H, *t*-Bu), 6.82−7.54 (m, 7H, aromatic-H), 8.63 (s, 1H, CH═N), 14.00 (s, 1H, OH). (**12**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 18H, *t*-Bu), 1.37 (s, 18H, *t*-Bu), 6.68−7.42 (m, 14H, aromatic-H), 8.10 (s, 2H, CH═N). Anal. Found: C, 64.90; H, 6.70; N, 3.95. Calcd for $ZrC_{42}H_{52}N_2O_2Cl_2$: C, 64.76; H, 6.73; N, 3.60. FD-MS, 778 (M^+).

Table 6. Summary of Crystallographic Data for Complexes **1** and **5**

	1	**5**
	A. Crystal Data	
empirical formula	$ZrC_{34}H_{36}N_2O_2Cl_2/Et_2O$	$ZrC_{48}H_{52}N_2O_2Cl_2$
fw	740.92	851.08
crystal color, habit	colorless, prismatic	colorless, prismatic
crystal demens (mm)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
crystal system	monoclinic	monoclinic
a (Å)	25.464(9)	15.561(2)
b (Å)	8.763(6)	19.636(2)
c (Å)	17.119(6)	13.776(1)
β (deg)	100.00(3)	95.715(9)
V (Å^3)	3761(3)	4188.6(8)
space group	$C2/c$ (No. 15)	Cc (No. 9)
Z	4	4
D_{calcd} (g/cm^3)	1.177	1.350
F_{000}	1376.00	1776.00
μ (Mo Kα) (cm^{-1})	4.61	4.31
	B. Data Collection	
λ (Mo Ka radiation) (Å)	0.710 69	0.710 69
temperature (°C)	23.0	23.0
$2\theta_{max}$	55.0	55.0
no. of total reflns	4707	4983
no. of unique reflns	4602 (R_{int} = 0.030)	4812 (R_{int} = 0.014)
	C. Structure Solution and Refinement	
no. of observns ($I > 3.00\sigma(I)$)	3302	3799
no. of variables	211	497
refln/param ratio	15.65	7.64
residuals: R; Rw	0.039; 0.041	0.033; 0.034
goodness-of-fit indicator	1.87	1.13
max shift/error in fit indicator	6.11	3.19
max peak in final diff map (e$^-$/Å^3)	0.44	0.19
min peak in final diff map (e$^-$/Å^3)	−0.36	−0.21

Bis[*N*-(3-*tert*-butylsalicylidene)-2′6′-diisopropylanilinato]zirconium(IV) Dichloride (13). Ligand *N*-(3-*tert*-butylsalicylidene)-2′6′-diisopropylaniline as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, 12H, J = 5.6 Hz, Me), 1.49 (s, 9H, *t*-Bu), 2.89−3.13 (m, 2H), 6.81−7.52 (m, 6H, aromatic-H), 8.29 (s, 1H, CH═N), 13.59 (s, 1H, OH). (**13**) as a pale yellow powder: ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 24H, J = 5.6 Hz, Me), 1.49 (s, 18H, *t*-Bu), 2.89−3.20 (m, 2H, CH), 6.81−7.60 (m, 12H, aromatic-H), 8.35 (s, 2H, CH═N). Anal. Found: C, 66.44; H, 7.41; N, 3.45. Calcd for $ZrC_{46}H_{60}N_2O_2Cl_2$: C, 66.16; H, 7.24; N, 3.35. FD-MS, 834 (M^+).

Bis[(3-adamantyl-5-methylsalicylidene)-2′-isopropylanilinato]zirconium(IV) Dichloride (14). Ligand *N*-(3-adamantyl-5-methylsalicylidene)-2′-isopropylaniline as a yellow powder: mp 160−162 °C. ^{1}H NMR ($CDCl_3$) δ 1.26 (d, 6H, J = 5.6 Hz, Me), 1.81(s, 6H, adamantyl-CH_2), 2.12 (s, 3H, adamantyl-CH), 2.21 (s, 6H, adamantyl-CH_2), 2.31 (s, 3H, aromatic-CH_3), 3.41−3.68 (m, 1H, CH), 6.95−7.47 (m, 6H, aromatic-H), 8.48 (s, 1H, CH═N), 13.50 (s, 1H, OH). (**14**) as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 0.80−0.95 (m, 12H, isopropyl-Me), 1.05−2.40 (m, 30H, adamantyl), 2.32 (s, 6H, aromatic-Me), 3.65−3.88 (m, 2H, CH), 6.40−7.55 (m, 12H, aromatic-H), 8.02−8.25 (m, 2H, CH═N) Anal. Found: C, 63.57; H, 6.41; N, 3.34. Calcd for $ZrC_{54}H_{64}N_2O_2Cl_2$: C, 63.35; H, 6.90; N, 3.00. FD-MS, 935 (M^+).

Bis[(3,5-dicumylsalicylidene)-2′-isopropylanilinato]zirconium(IV) Dichloride (15). Ligand *N*-(3, 5-dicumylsalicylidene)-2′-isopropylaniline as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 6H, J = 5.7 Hz, Me), 1.71 (s, 6H, cumyl-Me), 1.72 (s, 6H, cumyl-Me), 3.21−3.29 (m, 1H, CH), 6.88−7.39 (m, 16H, aromatic-H), 8.64 (s, 1H, CH═N),

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[35] Reasonable elemental analysis data for CHN were not obtained since complex **10** was unstable and decomposed on standing.

13.16 (br s, 1H, OH). (**15**) as a yellow powder: ^{1}H NMR (CDCl$_3$); δ. 1.14 (d, J = 5 Hz, 12H, isopropyl-Me), 1.71, (s, 12H, cumyl-Me), 1.73 (s, 12H, cumyl-Me), 3.70−3.80 (m, 2H, CH), 6.90−7.41 (m, 32H, aromatic-H), 8.42 (s, 2H, CH═N). Anal. Found: C, 73.57; H, 6.41; N, 2.34. Calcd for $ZrC_{68}H_{72}N_2O_2Cl_2$: C, 73.48; H, 6.53; N, 2.52. FD-MS, 1110 (M$^+$).

X-ray Crystallography. The x-ray structure analyses data were collected using a Rigaku AFC7R diffractometer, and the structure solution and refinement were performed by using the TeXan crystal structure analysis package.[36] Experimental data for the X-ray diffraction analyses of complexes **1** and **5** are summarized in Table 6.

DFT Calculations.[37] All calculations were performed at the gradient-corrected density functional BLYP level by means of the Amsterdam Density Functional (ADF) program. We used the triple ζ STO basis set on the zirconium 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 zirconium and the double ζ plus polarization STO basis set on the other atoms were used and the quasi-relativistic correction was also added.

Ethylene Polymerization. Ethylene polymerization was carried out under atmospheric pressure in toluene in a 500-mL glass reactor equipped with a propeller-like stirrer. Toluene (250 mL) was introduced into the nitrogen-purged reactor and stirred (600 rpm). The toluene was thermostated to a prescribed polymerization temperature, and then the ethylene gas feed (100 L/h) was started. After 15 min, polymerization was initiated by adding a toluene solution of the cocatalyst and then a toluene solution of catalyst into the reactor with vigorous stirring (600 rpm). After a prescribed time, isobutyl alcohol (10 mL) was added to terminate the polymerization, and the ethylene gas feed was terminated. To the resulting mixture, methanol (1000 mL) and concentrated HCl (2 mL) were added. The polymer was collected by filteration, washed with methanol (200 mL), and dried in vacuo at 80 °C for 10 h.

Ethylene−Propylene Copolymerization. Ethylene−propylene copolymerization was performed using a similar procedure for ethylene polymerization, except for using ethylene (100 L/h) and propylene (100 L/h) instead of ethylene as the olefin gas feed. After a prescribed time, isobutyl alcohol (10 mL) was added to terminate the polymerization, and the olefin gas feed was terminated. To a resulting mixture, concentrated HCl (2 mL) was added, and the mixture was washed with water (250 mL × 3) and concentrated in vacuo to give the polymer. The polymer was dried in vacuo at 130 °C for 10 h.

Conclusion

We demonstrated that a new family of zirconium complexes with two phenoxy−imine ligands possesses the very high catalytic performance for ethylene polymerization. Both the maximum activity value, 4315 kg of polymer/mmol of cat•h displayed by bis[*N*-(3-cumyl-5-methylsalicylidene)cyclohexylaminato]zirconium(IV) dichloride/MAO, and the molecular weight value, M_v 505 × 10^4, obtained from bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride/$Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al are some of the highest values exhibited by homogeneous olefin polymerization catalysts including the metallocene catalysts. Moreover, we revealed that the zirconium complexes are capable of controlling the M_v values of polyethylene, M_v 0.3 × 10^4−505 × 10^4. Therefore, the zirconium complexes introduced in this paper have high potential as a new generation of olefin polymerization catalysts.

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Supporting Information Available: Full crystallographic data for complexes **1** and **5**, detailed synthesis data for complexes **2−15,** and ^{13}C NMR spectrum of the polyethylene produced by complex **1**/MAO (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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