Phenoxycycloalkylimine Ligated Zirconium Complexes for Ethylene Polymerization: Formation of Vinyl-Terminated Low Molecular Weight Polyethylenes with High Efficiency

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ABSTRACT: Bis(phenoxyimine)Zr complexes **1**−**8** containing a series of cycloalkyl groups on the imine-N's were synthesized (**1**: cyclopropyl; **2**, **3**: cyclobutyl; **4**: cyclopentyl; **5**, **7**: cyclohexyl; **6**, **8**: 2-methylcyclohexyl). X-ray crystallographic analyses suggested that complexes **3**, **5**, and **8** assume an octahedral coordination geometry with a *trans*-phenoxy-O, *cis*-imine-N, and *cis*-Cl disposition and that the cycloalkyl groups on the imine-N's influence steric environments around the chlorine bound sites (i.e., potential polymerization sites). Upon activation with MAO at 25 °C, these complexes produced low-to-high molecular weight polyethylenes (PEs) (M_w 1900−960000, M_w/M_n 1.6−4.9) with very high efficiency (22−290 kg of PE/(mmol of cat. h)), which is comparable to or exceeds that seen with Cp_2ZrCl_2/MAO (28 kg of PE/(mmol of cat. h)). The cycloalkyl group has a profound effect on both catalytic activity and product molecular weight, indicating the critical importance of the substituent on the imine-N for polymerization catalysis. The catalytic activity increased with an increase in the steric bulk of the cycloalkyl substituent, albeit too much steric bulk reduced the activity. The product molecular weight was also related to the steric bulk of the cycloalkyl group, in that increased steric bulk normally resulted in higher molecular weight PEs. The PEs produced with complexes **1**−**5**/MAO (Al/Zr molar ratio = 1250) possess a high degree of vinyl unsaturation at one of the two polymer chain ends (M_w 2000−14000, vinyl selectivity, 90−96 mol %). Polymerizations performed at a much higher Al/Zr molar ratio of 12500 confirmed the marked preference of these complexes for β-H transfer as the chain termination mechanism (M_w 1900−14000, vinyl selectivity, 90−95 mol %). The vinyl-terminated PEs were readily transformed to the corresponding epoxy- and diol-terminated PEs, which are valuable materials for PE- and polar polymer-based block and graft copolymers. Ethylene pressure studies on complexes **1**, **2**, **4**, and **5** revealed a first-order dependence on ethylene for both the rate of chain propagation and the rate of chain transfer. On the basis of this polymerization behavior together with X-ray analyses and DFT calculation studies, we concluded that β-H transfer to an incoming monomer is responsible for the formation of vinyl-terminated PEs. The calculations revealed that the complexes disfavor β-H transfer to the Zr metal due to the extreme instability of a metal hydride species that is produced in such a chain transfer process. Therefore, the unique polymerization catalysis and distinctive polymer formation with phenoxycycloalkylimine ligated Zr complexes were demonstrated.

Introduction

Discoveries of high-performance molecular catalysts for olefin polymerization have offered exciting opportunities for the synthesis of olefin-based materials with unique microstructures and related properties. Namely, group 4 metallocene catalysts and related catalysts have allowed the preparation of a wide array of new or differentiated polymers, which include high-performance linear low-density polyethylenes (PEs), polyolefinic elastomers, cyclic olefin copolymers, ethylene/styrene copolymers, highly isotactic and syndiotactic polypropylenes (iPPs and sPPs), and highly syndiotactic polystyrenes (sPSs).[1] In addition, recently emerging non-metallocene catalysts have enabled us to synthesize distinctive polymers such as hyperbranched PEs, ethylene/polar monomer copolymers, monodisperse poly(higher α-olefin)s, and polyolefinic block copolymers, which are difficult or virtually impossible to produce using group 4 metallocenes and related catalysts.[2]

Moreover, the above molecular catalysts have provided systematic opportunities to study the mechanisms of the initiation, propagation, and termination steps of coordination polymerization, which has enormously contributed to advances in the rational design of catalysts for the controlled (co)polymerization of olefinic monomers. Altogether, the development of high-performance molecular catalysts has made a dramatic impact on polymer and catalysis chemistry. There is thus great interest in the development of new molecular catalysts for olefin polymerization with a view to achieving unique catalysis and distinctive polymer synthesis.

In our own work, we have developed group 4 transition metal complexes bearing chelating phenoxyimine ligands (now known as FI catalysts) for olefin polymerization,[3,4] as a result of ligand-oriented catalyst design research.[5] FI catalysts combined with appropriate activators can exhibit distinctive polymerization catalysis, which includes highly efficient ethylene polymerization,[6] highly isospecific and syndiospecific propylene polymerizations,[7] regio- and stereoirregular higher α-olefin polymerization,[8] and thermally robust living ethylene[9] and highly syndiospecific living propylene polymerizations.[10] Additionally, FI catalysts display versatility vis-à-vis activator selection, meaning they can be efficiently activated by $MgCl_2/R_mAl(OR')_{3-m}$ and $(Ph_3C)_mH_n[PMo_{12}O_{40}]/Et_3Al$ in addition to MAO and $Ph_3CB(C_6F_5)_4$/*i*-Bu_3Al.[11] Therefore, a wide variety of unique polymers are now available as a consequence of FI catalysis. Recent studies conducted by Bochmann, Busico, Cavallo, Coates, Gibson, Mülhaupt, Pellecchia, Scott, Talsi, and others have made significant contributions to the further development of FI catalysts and relevant complexes.[3,12]

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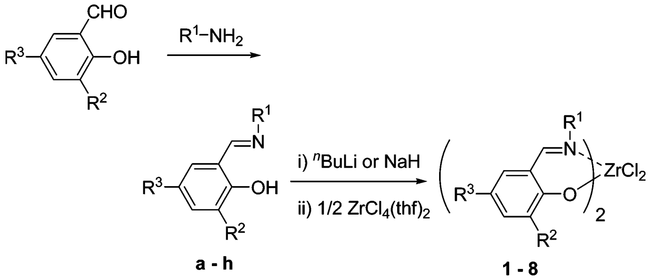
Scheme 1. Synthetic Procedure for Complexes 1−8



Complex	Ligand	R^1	R^2	R^3
1	a	cyclopropyl	^{t}Bu	H
2	b	cyclobutyl	^{t}Bu	H
3	c	cyclobutyl	^{t}Bu	Me
4	d	cyclopentyl	^{t}Bu	H
5	e	cyclohexyl	^{t}Bu	H
6	f	2-methylcyclohexyl	^{t}Bu	H
7	g	cyclohexyl	1-adamantyl	Ph
8	h	2-methylcyclohexyl	1-adamantyl	Ph

In exploring new derivatives of FI catalysts, we have studied FI catalysts having a variety of substituents on the imine-N's. These studies have led to the discovery of a new series of Zr−FI catalysts featuring cycloalkyl groups attached to the imine-N's, which, in association with MAO, form low molecular weight PEs having predominant vinyl chain-ends, with extremely high activities.[13] The selective synthesis of vinyl-terminated PEs has been a challenging subject in the field of polymerization catalysis (precise control of chain transfer) and polymer synthesis (useful materials for chain-end functionalized PEs and long chain branched polymers).[14]

In this article, we describe the structures and ethylene polymerization behavior of a series of bis(phenoxyimine)Zr complexes possessing cycloalkyl groups on the imine-N's. Additionally, we discuss the chain transfer processes of these catalysts on the basis of X-ray analysis and DFT calculations along with experimental results. The phenoxycycloalkylimine ligated Zr complexes are the first examples of group 4 olefin polymerization catalysts capable of yielding vinyl-terminated low molecular weight PEs with high efficiency at ambient temperature.

Results and Discussion

Synthesis of Zirconium Complexes. A general preparation route to the bis(phenoxycycloalkylimine)Zr complexes used in this study is shown in Scheme 1. Salicylaldehyde derivatives employed for ligand syntheses were prepared according to established procedures.[6d] The phenoxycycloalkylimine ligands of structures **a**−**h** were synthesized in nearly quantitative yields (>99%) by Schiff base condensation of the corresponding cycloalkylamine with the salicylaldehyde derivative. The desired Zr complexes **1**−**8** were obtained in moderate to good yields (23−64%) by the reaction of $ZrCl_4$ with 2 equiv of the lithium or sodium salt of the ligand. All the complexes were characterized by FD-MS, ^{1}H NMR spectroscopy, and microanalysis. Additionally, complexes **3**, **5**, and **8** were subject to single-crystal X-ray diffraction studies.

X-ray Crystallographic Analyses of Complexes 3, 5, and 8. Much interest has been focused on the synthesis and catalytic performance of bis(phenoxyimine) Ti and Zr complexes with aryl groups attached to the imine-N's, and thus little is known about the molecular structures of those having aliphatic alkyl groups on the imine-N's. Crystals of complexes **3**, **5**, and **8** (bearing a cyclobutyl, cyclohexyl, and 2-methylcyclohexyl group on the imine-N, respectively) suitable for X-ray structural determination were grown from a concentrated $Et_2O-CH_2Cl_2$ solution. The molecular structures are displayed in Figures 1−3; selected bond distances and angles are listed in Table 1.[15]

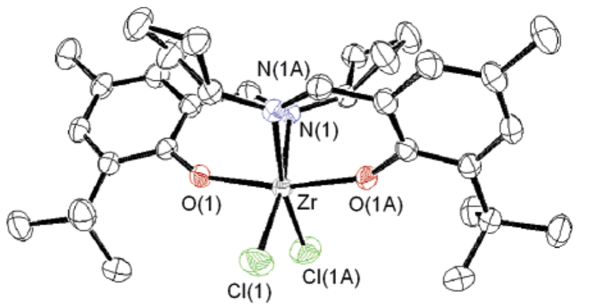


Figure 1. Molecular structure of complex **3** with thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity).

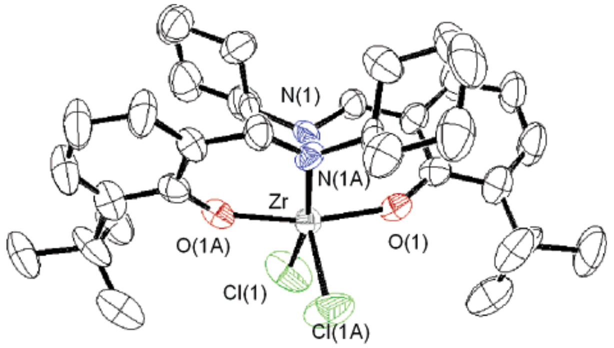


Figure 2. Molecular structure of complex **5** with thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity).

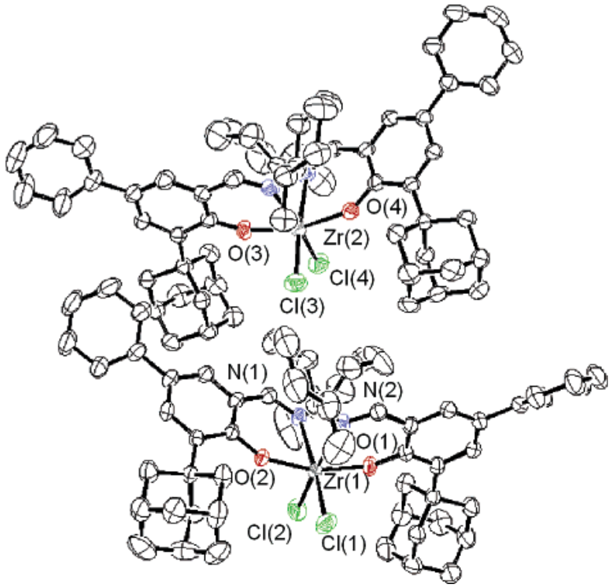


Figure 3. Molecular structure of complex **8** (molecule 1, below; molecule 2, above) with thermal ellipsoids at the 50% probability level (hydrogen atoms and an ether molecule are omitted for clarity).

All structures presented in Figures 1−3 are closely related; i.e., complexes **3**, **5**, and **8** possess approximately octahedrally coordinated metal centers with mutually *cis*-imine-N's, *trans*-phenoxy-O's, and *cis*-Cl's. The spatial arrangements of these complexes are the same as those of the corresponding complexes with phenyl substituents on the imine-N's, demonstrating the general preference of a bis(phenoxyimine)$ZrCl_2$ complex to adopt a *trans*-phenoxy-O, *cis*-imine-N, and *cis*-Cl arrangement. We assume other complexes employed in this study adopt the same configuration.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 3, 5, and 8

	3	5	8
Distances			
Zr(1)−Cl(1)	2.4305(6)	2.419(3)	2.437(2)
Zr(1)−Cl(2)			2.415(1)
Zr(2)−Cl(3)			2.417(1)
Zr(2)−Cl(4)			2.429(2)
Zr(1)−O(1)	1.984(1)	1.966(7)	1.978(3)
Zr(1)−O(2)			1.979(3)
Zr(2)−O(3)			1.986(3)
Zr(2)−O(4)			1.989(3)
Zr(1)−N(1)	2.348(2)	2.309(6)	2.375(3)
Zr(1)−N(2)			2.337(5)
Zr(2)−N(3)			2.369(4)
Zr(2)−N(4)			2.336(5)
Angles			
Cl−Zr−Cl	100.64(3)	99.8(2)	98.00(6)
Cl−Zr(2)−Cl			97.84(6)
O−Zr−O	166.10(8)	166.3(3)	162.6(1)
O−Zr(2)−O			162.7(1)
N−Zr−N	85.90(8)	83.6(4)	85.1(1)
N−Zr(2)−N			84.4(1)

Although complexes **3**, **5**, and **8** generally exhibit key bond distances and angles similar to those for the corresponding phenyl-substituted complexes, they display wider N−Zr−N angles [**3**: 85.90(8)°; **5**: 83.6(4)°; **8**: 85.1(1)° and 84.4(1)°] than the phenyl-substituted congeners [$R^1 = \mathrm{Ph}$, $R^2 = {}^t\mathrm{Bu}$, $R^3 = \mathrm{H}$: 74.0(1)°; $R^1 = \mathrm{Ph}$, $R^2 =$ adamantyl, $R^3 = \mathrm{Me}$: 76.8(1)°].[6d] The wider N−Zr−N angles are probably due to steric repulsion between the two cycloalkyl groups, which are almost perpendicular to the plane formed by the CH═N group, while the phenyl groups of the congeners tend to be coplanar with this plane.

A comparison of the data in Table 1 suggests that there is no clear relationship between the cycloalkyl substituent on the imine-N and the bond distances (Zr−N and Zr−O) and angles (N−Zr−N and O−Zr−O). However, it seems that an increase in the steric bulk of this substituent results in a reduced Cl−Zr−Cl angle, suggesting steric repulsion between the Cl and the substituent on the imine-N. While the complexes possess the same spatial disposition regarding the Zr, O, N, and Cl atoms, an inspection of Figure 4 indicates that steric environments around the Cl-bound sites (i.e., potential polymerization sites) are fairly different among the complexes. Namely, the distances between the Cl and its nearest C atom in the cycloalkyl group attached to the imine-N are 3.64 Å (complex **8**), 4.19 Å (complex **5**), and 4.96 Å (complex **3**). These facts suggest that complex **3** probably has the most sterically open nature vis-à-vis polymerization, followed by complex **5** and complex **8**. It should be noted that, as for complex **8**, the methyl group of the 2-methylcyclohexyl substituent on the imine-N is directed toward the Cl atom, providing the largest steric hindrance to the Cl atom. The evident differences regarding steric environments near the polymerization center presumably affect the catalytic performance, and thus studies of the olefin polymerization behavior of these complexes may provide information on catalyst structure and catalyst performance relationships for this interesting class of catalysts.

Ethylene Polymerization with Complexes 1−8. Complexes **1**−**8** combined with dried MAO[16] (Al/Zr molar ratio, 1250) were investigated for their potential as ethylene polymerization catalysts under atmospheric pressure at 25 °C. Results are summarized in Table 2.

All the complexes with MAO are highly active catalysts (whose activities surpass or rival that seen with $\mathrm{Cp_2ZrCl_2}$/MAO, 28 kg of PE/(mmol of cat. h)) under the given conditions and formed essentially linear PEs (branching less than 1 per 1000 carbon atoms, IR analysis). The basic trend observed concerning catalytic activity is that an increase in the steric bulk of the cycloalkyl group on the imine-N resulted in enhanced catalytic activity except for complex **1**. Previously, we observed an activity increase effect by a sterically encumbered substituent *ortho* to the phenoxy-O for Zr−FI catalysts.[6d] However, it is shown that for this case, as indicated by the activity exhibited by complex **8**, too much steric congestion provided by the substituent in close proximity to the active site can reduce catalytic activity probably by hindering access of a monomer to the active site and/or growth of the polymer chain. These results suggest that the introduction of steric bulk near the active site can have two competing effects on catalytic activity.

Analysis by GPC revealed that the PEs formed using complexes **1**−**5** and **7** possess narrow molecular weight distributions in the range of 1.7−2.1 (Table 2), which is consistent with the operation of a single active species. As can be seen in Table 2, complexes **6** and **8** incorporating the 2-methylcyclohexyl group on the imine-N afforded PEs with somewhat broadened molecular weight distributions (M_w/M_n: **6**, 4.9; **8**, 4.1). At first, we thought that the presence of *cis*- and *trans*-isomers regarding N/$\mathrm{CH_3}$ of the cyclohexyl moiety was responsible for the production of the broadened molecular weight distribution PEs. However, the pure *trans*-isomer of complex **8** (single crystals obtained from recrystallization) combined with MAO afforded broadened molecular weight distribution PE (M_w/M_n 4.3). In addition, the precatalyst *trans*-isomer exhibited multiple signals that were derived from the imine proton, suggesting that the precatalyst complex exists as a mixture of isomers. We previously reported that Zr−FI catalysts with MAO can produce well-defined multimodal PEs originating from structural isomers that stem from different modes of ligand coordination.[17] Altogether, we rationalized that the formation of the broadened molecular weight distribution PEs with complexes **6** and **8** is probably due to the presence of multiple catalytically active species, which arise from the coordination modes of two phenoxyimine ligands.

An inspection of the GPC data in Table 2 shows that these complexes with MAO are viable tools for the production of low-to-high molecular weight PEs. We have noted that reducing the steric bulk of the substituent *ortho* to the phenoxy-O leads to a reduction in polymer molecular weight and, simultaneously, a considerable reduction in the catalytic activity observed [i.e., M_v 6000: 0.9 kg of PE/(mmol of cat. h) ($R^1 = \mathrm{Ph}$, $R^2 = {}^i\mathrm{Pr}$, $R^3 = \mathrm{H}$); M_v 4000: 0.4 kg of PE/(mmol of cat. h) ($R^1 = \mathrm{Ph}$, $R^2 = \mathrm{Me}$, $R^3 = \mathrm{H}$)].[6d] Therefore, the development of Zr complexes **1**−**5** and **7** provides an opportunity to produce low molecular weight PEs (M_w 2000−24 000) with high productivity.

A striking feature observed is that the substituent attached to the imine-N significantly affects product molecular weight. Complex **5** with the cyclohexyl group on the imine-N produced moderate molecular weight PE (M_w 14 000). Conversely, complexes **1**−**4** possessing sterically less encumbered substituents on the imine-N's (**1**: cyclopropyl; **2**, **3**: cyclobutyl; **4**: cyclopentyl) formed lower molecular weight PEs; in particular, complexes **2** and **3** bearing the cyclobutyl groups furnished very low molecular weight PEs (M_w 2000). In sharp contrast, complex **6** incorporating the 2-methylcyclohexyl group yielded PE with much higher molecular weight (M_w 290 000), which is more than 20 times higher than that of the PE made with complex **5** bearing the cyclohexyl group. A similar but more pronounced

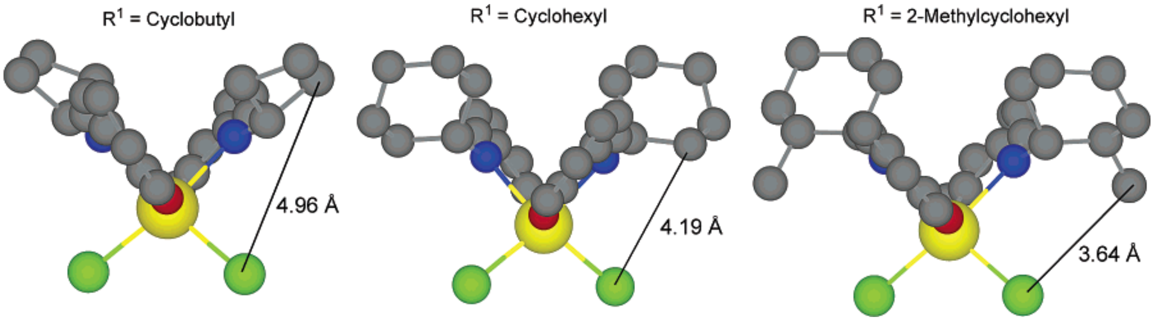


Figure 4. Molecular structures of complexes **3** (left), **5** (middle), and **8** (right) viewed in a perpendicular direction to the N−Zr−Cl plane and distances between Cl atom and C atom of the R^1 group (hydrogen atoms and the R^2 and R^3 groups are omitted for clarity).

Table 2. Polymerization Results for Complexes 1−8[a]

entry	complex	yield (g)	activity[b]	M_w[c]/10^3	M_w/M_n[c]	vinyl end[d] (%)
1	**1**	2.10	50.4	4.4	2.0	91
2	**2**	1.32	31.6	2.0	1.7	95
3	**3**	0.92	22.0	2.0	1.7	94
4	**4**	2.80	67.2	3.6	2.1	96
5	**5**	3.65	87.7	14	1.7	90
6	**6**	3.88	93.0	290	4.9	71[e]
7	**7**	5.93	142.4	24	1.8	84
8	**8**	2.19	52.5	960	4.1	33[e]

[a] Conditions: solvent, toluene (250 mL); polymerization temperature, 25 °C; complex 0.5 μmol, dried MAO (Albemarle) 0.625 mmol, ethylene feed 100 L/h; polymerization time, 5 min. [b] In kg of polymer/(mmol of cat. h). [c] Determined with GPC using polyethylene calibration. [d] Degree of vinyl unsaturation at one of the two polymer chain-ends, determined by ^{1}H NMR. [e] Determined by IR.

Table 3. Polymerization Results for Complexes 1−5 and 7 at a High Al/Zr Molar Ratio[a]

entry	complex	yield (g)	activity[b]	M_w[c]/10^3	M_w/M_n[c]	vinyl end[d] (%)
9	**1**	0.37	43.8	4.0	1.9	90
10	**2**	0.25	30.5	2.1	1.6	93
11	**3**	0.16	19.0	1.9	1.6	94
12	**4**	0.97	116.0	3.4	1.9	95
13	**5**	1.27	152.8	14	1.8	90
14	**7**	3.59	430.6	19	1.8	86

[a] Conditions: solvent, toluene (250 mL); polymerization temperature, 25 °C; complex 0.1 μmol, dried MAO (Albemarle) 1.25 mmol, ethylene feed 100 L/h; polymerization time, 5 min. [b] In kg of polymer/(mmol of cat. h). [c] Determined with GPC using polyethylene calibration. [d] Degree of vinyl unsaturation at one of the two polymer chain ends, determined by ^{1}H NMR.

molecular weight increase effect was observed for complex **8** when compared with **7**.

The above results suggest that a sterically more encumbered cycloalkyl group is prone to the formation of higher molecular weight PE, though complex **1** with the cyclopropyl group furnished higher molecular weight PE than complex **2** having the cyclobutyl group. While the reason for the production of the higher molecular weight PE with complex **1** is unclear at the present time, it is possible that electronic effects of the cyclopropyl group are related to the unexpected formation of the higher molecular weight PE. It should be emphasized that, though the steric bulk of the substituent on the imine-N has an effect on both the catalytic activity and the product molecular weight, it affects the product molecular weight far more significantly than the catalytic activity, as indicated by the activity and molecular weight data summarized in Table 2. This observation gives useful information on chain transfer processes of the complexes used in this study, which will be discussed later.

End-group analyses using ^{1}H NMR as well as IR spectroscopy revealed that the PEs arising from complexes **1**−**5** have a high degree of vinyl unsaturation at one of the two polymer chain-ends (vinyl selectivity, 90−96 mol %, M_w 2000−14 000), indicating that β-H transfer is the predominant mechanism for chain termination though two major chain transfer processes (i.e., β-H transfer and chain transfer to aluminum) prevail in ethylene polymerization. Thus, complexes **1**−**5**/MAO were demonstrated to produce low molecular weight PEs having predominant vinyl chain ends (90−96 mol %) and narrow molecular weight distributions (M_w/M_n 1.7−2.1). These are the first examples of group 4 olefin polymerization catalysts that yield vinyl-terminated low molecular weight PEs with high efficiency at ambient temperature.[18] The production of vinyl-terminated PEs possessing narrow molecular weight distributions is highly significant since such PEs may serve as well-defined materials for chain-end functionalized PEs and long-chain branched polymers.

Table 3 summarizes the ethylene polymerization results obtained with complexes **1**−**5** and **7** at a higher Al/Zr molar ratio of 12 500. Similar relationships between catalytic performance (i.e., catalytic activity and product molecular weight) and the steric bulk of the cycloalkyl group on the imine-N were observed. Notably, complexes **1**−**5** formed low molecular weight PEs (M_w 1900−14 000, M_w/M_n 1.6−1.9) with predominant vinyl chain ends (vinyl selectivity, 90−95 mol %), suggesting that chain transfer to aluminum (resulting in a fully saturated polymer chain) is only a minor transfer mechanism for these complexes even under such a high Al/Zr ratio (12 500). These results unambiguously indicate the marked preference of these complexes for β-H transfer as the chain termination mechanism.

Vinyl-terminated PEs are potential precursors for chain-end functionalized PEs. We have successfully prepared epoxy- and diol-terminated PEs from the vinyl-terminated PEs (M_w 2000−14 000) arising from the Zr complexes. For example, treatment of the PE formed from complex **2** (M_w 2000, T_m 122 °C) with hydrogen peroxide (30% solution in water) and toluene in the presence of Na_2WO_4 (as a catalyst), methyltri-*n*-octylammonium hydrogen sulfate (as a phase transfer agent), and phosphoric acid (as an additive adjusting pH) at 90 °C for 6 h afforded epoxy-terminated PE (T_m 121 °C) in nearly quantitative yield. Additionally, diol-terminated PE (T_m 121 °C) was obtained by the epoxidation described above followed by hydrolysis using aqueous 2-propanol (in-situ reaction).

Figure 5 displays the ^{1}H NMR spectra of these chain-end functionalized PEs. To the best of our knowledge, these are the first reported examples of epoxy- and diol-terminated PEs having a molecular weight (M_w) as high as 2000.[19] The functional groups should influence the orientation of the polymer chains and thus are expected to provide ways of altering PEs to modify their properties such as dyeability, adhesion, melt,

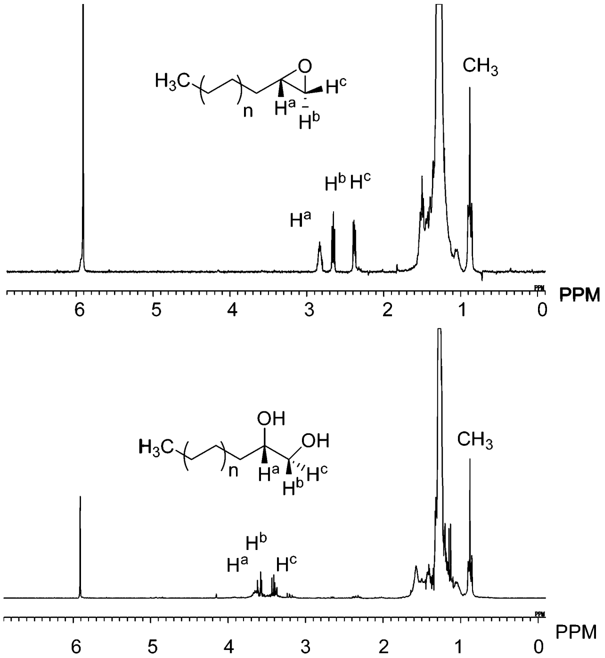


Figure 5. ^{1}H NMR spectra of epoxy- (above) and diol- (below) terminated PEs.

and solution rheology. These unique functionalized PEs are currently being investigated as new materials and as precursors for the production of PE- and-polar-polymer-based block and graft copolymers, which will be discussed elsewhere.[20]

Chain Transfer Mechanism. The molecular weight of PE and the nature of chain-end groups are the product of relative rates of chain propagation and chain transfer (i.e., β-H transfer and chain transfer to aluminum) during the polymerization reaction. The results discussed so far indicate that complexes **1**−**5** favor β-H transfer as the main termination mechanism and form low molecular weight PEs with predominant vinyl chain-ends. β-H transfer vis-à-vis group 4 metal-based catalysts can involve two different pathways: (1) the β-H atom is transferred to the metal, generating a metal hydride species, and (2) the β-H atom is transferred onto the incoming monomer, forming a metal ethyl species. These two pathways are kinetically distinguishable from each other since the former is a unimolecular reaction having a four-centered transition state and the latter a bimolecular reaction with a six-centered transition state. Thus, it is reasonable to think that β-H transfer to the incoming monomer (which proceeds via a sterically bulkier six-centered transition state) is more sensitive to steric environments in close proximity to the active site than β-H transfer to the metal (which involves a four-centered transition state).

As described, the steric bulk exerted by the cycloalkyl substituent attached to the imine-N has significant influence on the product molecular weight relative to the catalytic activity. Considering that olefin insertion proceeds via a four-centered transition state, the observation can be explained as follows: the increase in the steric bulk destabilizes the sterically more encumbered six-centered transition state for β-H transfer to the incoming monomer more significantly than the compact four-centered transition state for ethylene insertion. Therefore, the experimental results described so far are consistent with the proposal that β-H transfer to an incoming monomer is the main termination pathway.

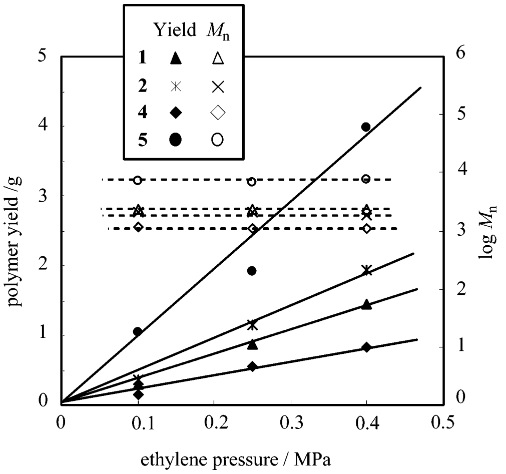


Figure 6. Plots of polymer yield and M_n as a function of ethylene pressure at 25 °C.

A series of experiments in which the pressure of ethylene was increased were undertaken with complexes **1**, **2**, **4**, and **5** to determine the effect of ethylene pressure on catalytic performance (Figure 6), which provided useful information about chain transfer processes. From Figure 6, it can be seen that increasing the ethylene pressure led to a practically linear increase in polymer yield, which corresponds to the catalytic activity. The linear dependence of the polymer yield upon the ethylene pressure shows that the chain propagation process is first order in ethylene concentration. Conversely, it was demonstrated that the product molecular weight remained virtually unchanged when the ethylene pressure increased. Considering that molecular weight is determined by the relative rate of chain propagation and chain transfer, the above result suggests that the chain transfer process is also first order in ethylene, which eliminates the operation of β-H transfer to the metal (which has a zero-order dependence on monomer concentration). Therefore, we conclude on the basis of these results coupled with X-ray studies that β-H transfer to the incoming monomer is the predominant chain transfer process, which accounts for the production of the vinyl-terminated PEs.

To gain further insight into the β-H transfer processes of the bis(phenoxyimine)Zr complexes, DFT calculations were performed on catalytically active cationic species derived from complexes **1**, **2**, **4**, and **5** with respect to two possible β-H transfer pathways (i.e., β-H transfer to an incoming monomer and that to the Zr metal). The results are illustrated in Figure 7 (polymer chain model: *n*-propyl group). A comparison of energy profiles for the two possible pathways (i.e., relative heights of the activation barriers for β-H transfer to the incoming monomer and that to the Zr metal) unambiguously indicates that the phenoxycycloalkylimine ligated complexes favor β-H transfer to the incoming monomer over that to the Zr metal ($\Delta\Delta E$: **1**, 57.9 kJ/mol; **2**, 51.2 kJ/mol; **4**, 51.6 kJ/mol; **5**, 48.0 kJ/mol). Therefore, the calculations support our conclusion based on the polymerization results and X-ray studies that β-H transfer to the incoming monomer is the main termination pathway. An inspection of Figure 7 shows that a correlation exists between the magnitude of steric bulk provided by the cycloalkyl substituent on the imine-N and the activation barrier, and an increase in the steric bulk resulted in an increase in the activation barrier for β-H transfer to the incoming monomer. These results suggest that the cycloalkyl group is located in a strategic position capable of controlling the activation barrier to the β-H transfer.

It should be pointed out that the preference for β-H transfer to the incoming monomer is due to the extreme instability of the metal hydride species generated from these bis(phenoxyimine)Zr complexes. In fact, the formation of the metal hydride species is strongly endothermic (ΔE > 100 kJ/mol). Such

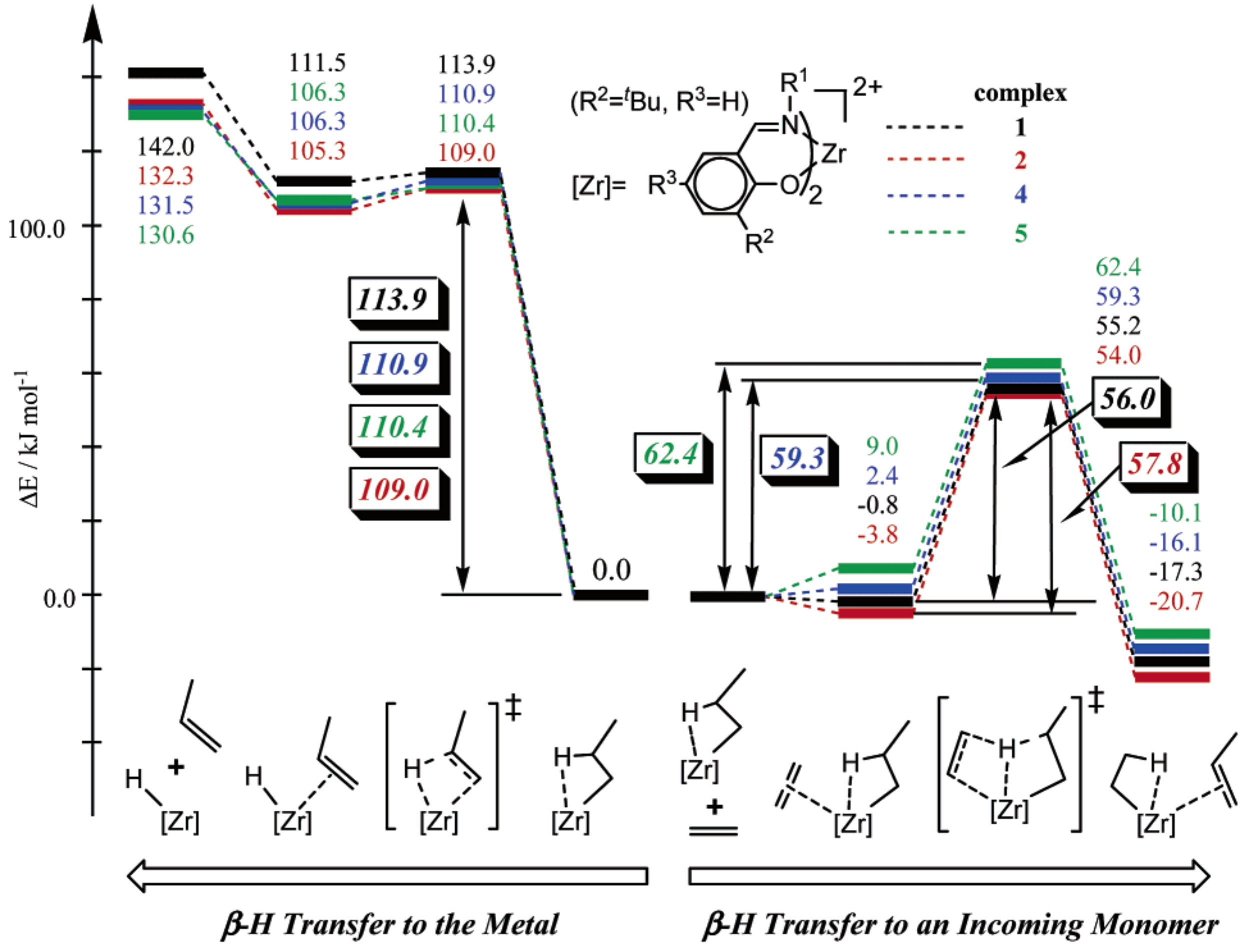


Figure 7. Potential energy profiles for β-H transfer to the metal (left-hand side of figure) and β-H transfer to an incoming monomer (right-hand side of figure) for complex **1** (black), complex **2** (red), complex **4** (blue), and complex **5** (green). Values in this figure are relative energies to a β-agostic ^{n}Pr cation complex (left side) and a β-agostic ^{n}Pr cation complex plus ethylene (right side) in kJ mol^{-1}. All calculations were carried out with B3LYP/LANL2DZ.

excessive instability of a metal hydride species is not seen with common group 4 metallocene catalysts.[21] Indeed, the formation energy for Cp_2ZrH^+ using the same calculation method is 42.4 kJ/mol. We noted that the Zr center of a catalytically active species derived from a phenoxyimine ligated Zr complex possesses high electrophilicity compared with common group 4 metallocene catalysts (e.g., Mulliken charge of a methyl cationic species from **2**; 1.85, that from Cp_2ZrCl_2; 1.63), probably because of the lower HOMO energy level of a phenoxyimine ligand than that of the Cp ligand (HOMO energy level; $(CH_3N{=}CH)PhO^-$ 0.14 eV, Cp^- 1.28 eV). We infer that the high electrophilicity[22] is responsible for the instability of the metal hydride species, which renders β-H transfer to the Zr metal extremely unfavorable.

Conclusion

In summary, we have described the structures, ethylene polymerization behavior, and chain transfer processes of a series of phenoxycycloalkylimine ligated Zr complexes **1**−**8**. These Zr complexes with MAO activation efficiently transformed ethylene to low-to-high molecular weight PEs with very high productivities. The steric bulk of the cycloalkyl group on the imine-N has a marked influence on the catalytic activity and product molecular weight, showing that the cycloalkyl group is located at a strategic place vis-à-vis polymerization catalysis. It is of great significance that complexes **1**−**5**/MAO polymerized ethylene to afford vinyl-terminated low molecular weight PEs, which can readily be converted to the corresponding epoxy- and diol-terminated PEs, demonstrating the utility of these vinyl-terminated materials. The vinyl-terminated PEs are produced via β-H transfer to the incoming monomer. The results introduced herein have provided a clear picture of the catalyst structure and catalyst performance relationships[23] regarding the substituent on the imine-N, allowing further rational design of FI catalysts for olefin polymerization.

Experimental Section

General Comments. Materials. Dried solvents (diethyl ether (Et_2O), tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and *n*-hexane) used for complex syntheses were purchased from Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd., and used as received, without further purification. The 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 derivatives, amine derivatives, adamantanol, paraformaldehyde, triethylamine, and Amberlyst-15 for ligand syntheses were obtained from Aldrich Chemical Co., Inc., Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co., Ltd., or Organo Co., Ltd. Ethylmagnesium bromide diethyl ether solution and *n*-butyllithium hexane solution were purchased from Tokyo Kasei Kogyo Co., Ltd., and Kanto Chemical Co., Inc., respectively. Cp_2ZrCl_2 (Wako Pure Chemical Industries, Ltd.) and $ZrCl_4(thf)_2$ (Strem Chemicals, Inc.) were used without further purification. Polymerization grade ethylene was obtained from Sumitomo Seika Co. Methylalumoxane (MAO) was purchased from Albemarle as a 1.2 M toluene solution, which was concentrated in vacuo, and stored as a solid white powder (dried MAO, which contains trimethylaluminum of ca.

3.7%). All other chemicals were obtained commercially and used as supplied.

Ligand and Complex Analyses. ^{1}H NMR spectra were recorded on a JEOL 270 spectrometer (270 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard at ambient temperature (25 °C). Chemical shifts are reported in δ units. FD-MS spectra were recorded on an SX-102A from Japan Electron Optics Laboratory Co., Ltd. Elemental analysis for CHN was carried out using a CHNO type from Helaus Co.

Polymer Characterization. ^{1}H NMR spectra for the produced PEs and epoxy- and diol-terminated PEs were recorded on a JEOL 270 spectrometer (270 MHz) using *o*-dichlorobenzene with 20% benzene-d_6 (the produced PEs) or $C_2D_2Cl_4$ (epoxy- and diol-terminated PEs) as a solvent at 120 °C. The epoxy (or diol) content of the end-functionalized PE has been determined by the relative peak intensities between the methyl and the methylene connected to the functional group in ^{1}H NMR. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) were determined using a Waters 150-C gel permeation chromatograph equipped with three TSKgel columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and TSKgelGMH$_6$-HTL) at 145 °C using polyethylene calibration. *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min.

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

Preparation of Bis[*N*-(3-*tert*-butylsalicylidene)cyclopropylaminato]zirconium(IV) Dichloride (1) Ligand a. To a stirred solution of 3-*tert*-butylsalicylaldehyde (2.667 g, 96% purity, 14.37 mmol) in ethanol (10 mL), cyclopentylamine (0.84 g, 14.71 mmol) was added dropwise at room temperature. The resulting mixture was stirred for 20 h at room temperature and then concentrated in vacuo to afford a crude imine compound. Purification by column chromatography on silica gel using *n*-hexane as eluent gave *N*-(3-*tert*-butylsalicylidene)cyclopropylamine (3.12 g, 14.35 mmol) as an orange oil in 99% yield. ^{1}H NMR ($CDCl_3$): δ 0.96 (d, 4H, J = 4.86, cyclopropyl-CH_2), 1.42 (s, 9H, *t*-Bu), 2.90−2.98 (m, 1H, cyclobutyl-CH), 6.79 (t, 1H, J = 7.56 Hz, aromatic-H), 7.07 (dd, 1H, J = 7.56, 1.62 Hz, aromatic-H), 7.28 (dd, 1H, J = 7.56, 1.62 Hz, aromatic-H), 8.47 (s, 1H, CH=N), 13.3 (s, 1H, OH).

Complex. To a stirred solution of *N*-(3-*tert*-butylsalicylidene)-cyclopropylamine (2.09 g, 9.22 mmol) in dried Et_2O (40 mL) at −78 °C, a 1.56 M *n*-butyllithium *n*-hexane solution (6.00 mL, 9.36 mmol) was added dropwise over a 5 min period. The solution was allowed to warm to room temperature and stirred for 3 h. The resulting mixture was added dropwise over a 20 min period to a solution of $ZrCl_4(thf)_2$ (1.74 g, 4.61 mmol) in dried THF (40 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 18 h. Concentration of the reaction mixture in vacuo yielded a crude product. Dried CH_2Cl_2 (60 mL) was added to the crude product, and the mixture was stirred for 15 min and then filtered. The solid residue was washed with dried CH_2Cl_2 (10 mL × 2), and the combined organic filtrates were concentrated in vacuo to afford a yellow solid. Dried Et_2O (15 mL) and dried *n*-hexane (10 mL) were added to the solid, and the mixture was stirred for 20 min and then filtered. The resulting solid was washed with dried *n*-hexane (10 mL × 2) and dried in vacuo to give complex **1** (0.630 g, 1.06 mmol) as a yellow powder in 23% yield. ^{1}H NMR ($CDCl_3$): δ 1.42 (s, 18H, *t*-Bu), 0.50−1.54 (m, 8H, CH_2), 3.22 (br s, 2H, CH), 6.80−7.55 (m, 6H, aromatic-H), 8.48 (s, 2H, CH=N). Anal. Calcd for $ZrC_{28}H_{36}N_2O_2Cl_2$: C, 56.55; H, 6.10; N, 4.71; Zr, 15.34. Found: C, 56.48; H, 5.90; N, 4.43; Zr, 15.06%. FD-MS: 592 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)cyclobutylaminato]zirconium(IV) Dichloride (2) Ligand b. *N*-(3-*tert*-Butylsalicylidene)cyclobutylamine as an orange oil: ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 9H, *t*-Bu), 1.80−1.89 (m, 2H, cyclobutyl-CH_2), 2.17−2.41 (m, 4H, cyclobutyl-CH_2), 4.04−4.16 (m, 1H, cyclobutyl-CH), 7.05 (dd, 1H, J = 8.10, 1.62 Hz, aromatic-H), 7.30 (dd, 1H, J = 8.10, 1.89 Hz, aromatic-H), 8.23 (s, 1H, CH=N), 14.3 (s, 1H, OH). **2** as a yellow powder in 11% yield: ^{1}H NMR ($CDCl_3$): δ 1.21−2.22 (m, 18H; *t*-Bu + 12H; CH_2), 4.55 (br s, 2H, CH), 6.87−7.64 (m, 6H, aromatic-H), 8.27 (s, 2H, CH=N). Anal. Calcd for $ZrC_{30}H_{40}N_2O_2Cl_2$: C, 57.86; H, 6.47; N, 4.50; Zr, 14.60. Found: C, 57.77; H, 6.43; N, 4.24; Zr, 14.40%. FD-MS: 622 (M^+).

Bis[*N*-(3-*tert*-butyl-5-methylsalicylidene)cyclobutylaminato]-zirconium(IV) Dichloride (3) Ligand c. *N*-(3-*tert*-Butyl-5-methylsalicylidene)cyclobutylamine as a yellow solid: ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 9H, *t*-Bu), 1.83−1.88 (m, 2H, cyclobutyl-CH_2), 2.29 (s, 3H, aromatic-Me), 2.14−2.38 (m, 4H, cyclobutyl-CH_2), 4.10 (m, 1H, cyclobutyl-CH), 6.88 (d, 1H, J = 1.89 Hz, aromatic-H), 7.10 (d, 1H, J = 1.89 Hz, aromatic-H), 8.18 (s, 1H, CH=N), 14.00 (br, 1H, OH). **3** as a yellow powder in 53% yield: ^{1}H NMR ($CDCl_3$): δ 1.21−1.48 (m, 18H; *t*-Bu + 12H; CH_2), 2.27 (s, 6H, aromatic-Me), 4.55 (br s, 2H, CH), 7.05 (d, 4H, aromatic-H), 7.35 (d, 4H, aromatic-H), 8.22 (s, 2H, CH=N). FD-MS: 649 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)cyclopentylaminato]zirconium-(IV) Dichloride (4). Ligand d. *N*-(3-*tert*-Butylsalicylidene)cyclopentylamine as a yellow oil: ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 9H, *t*-Bu), 1.65−1.96 (m, 8H, cyclopentyl-CH_2), 2.14−2.38 (m, 4H, cyclobutyl-CH_2), 3.76 (m, 1H, cyclopentyl-CH), 6.79 (t, 1H, J = 7.6 Hz, aromatic-H), 7.07 (d, 1H, J = 1.90 Hz, aromatic-H), 7.30 (d, 1H, J = 1.90 Hz, aromatic-H), 8.33 (s, 1H, CH=N), 14.11 (s, 1H, OH). **4** as a yellow powder in 66% yield: ^{1}H NMR ($CDCl_3$); δ 1.57 (s, 18H, *t*-Bu), 1.18−2.16 (m, 16H, CH_2), 4.30−4.50 (m, 2H, CH), 6.89−7.57 (m, 6H, aromatic-H), 8.28 (s, 2H, CH=N). Anal. Calcd for $ZrC_{32}H_{44}N_2O_2Cl_2$: C, 59.05; H, 6.81; N, 4.30; Zr, 14.02. Found: C, 59.20; H, 6.93; N, 4.37; Zr, 14.23%. FD-MS: 650 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)cyclohexylaminato]zirconium-(IV) Dichloride (5) Ligand e. *N*-(3-*tert*-Butylsalicylidene)cyclohexylamine as a yellow powder: ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 9H, *t*-Bu), 1.20−1.90 (m, 10H, cyclohexyl-CH_2), 3.23 (m, 1H, cyclohexyl-CH), 6.80−7.32 (m, 3H, aromatic-H), 8.35 (s, 1H, CH=N), 14.30 (brs, 1H, OH). **5** as a yellow powder in 53% yield: ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 18H, *t*-Bu), 0.80−2.40 (m, 20H, CH_2), 3.80−4.00 (m, 2H, CH), 6.79−7.64 (m, 6H, aromatic-H), 8.31 (s, 2H, CH=N). Anal. Calcd for $ZrC_{34}H_{48}N_2O_2Cl_2$: C, 60.15; H, 7.13; N, 4.71; Zr, 13.44. Found: C, 60.35; H, 7.07; N, 4.50; Zr, 13.30%. FD-MS: 678 (M^+).

Bis[*N*-(3-*tert*-butylsalicylidene)−(2-Methylcyclohexyl)aminato]zirconium(IV) Dichloride (6) Ligand f. *N*-(3-*tert*-Butylsalicylidene)−(2-methylcyclohexyl)amine as a yellow oil: ^{1}H NMR ($CDCl_3$): δ 0.83 (d, 3H, cyclohexyl-Me), 1.41 (s, 9H, *t*-Bu), 1.20−1.90 (m, 9H, cyclohexyl-CH_2), 2.70, 3.30 (m, 1H, cyclohexyl-CH), 6.79 (m, 1H, aromatic-H), 7.08 (dd, 1H, aromatic-H), 7.28 (dd, 1H, aromatic-H), 8.30, 8.35 (s, 1H, CH=N), 14.20, 14.25 (brs, 1H, OH). **6** as a pale yellow powder in 56% yield: ^{1}H NMR ($CDCl_3$): δ 0.89 (d, 6H, cyclohexyl-Me), 1.59, 1.62 (s, 18H, *t*-Bu), 0.80−2.40 (m, 20H, cyclohexyl-CH_2), 3.80−4.00 (m, 2H, CH), 6.92 (m, 2H, aromatic-H), 7.20 (m, 2H, aromatic-H), 7.59 (m, 2H, aromatic-H), 8.25−8.28 (m, 2H, CH=N). Anal. Found: C, 58.02; H, 7.34; N, 3.68. Calcd for $ZrC_{36}H_{52}N_2O_2Cl_2$ 0.5CH_2Cl_2: C, 58.50; H, 7.13; N, 3.74. FD-MS: 706 (M^+).

Bis[*N*-(3-(1-adamantyl)-5-phenyl-salicylidene)cyclohexylaminato]zirconium(IV) Dichloride (7) Ligand g. *N*-(3-(1-Adamantyl)-5-phenylsalicylidene)cyclohexylamine as a yellow powder: ^{1}H NMR ($CDCl_3$): δ 1.20−1.90 (m, 10H, cyclohexyl-CH_2), 1.77 (s, 6H, adamantyl-CH_2), 2.20 (s, 3H, adamantyl-CH), 2.28 (s, 6H, adamantyl-CH_2), 3.28 (m, 1H, cyclohexyl-NCH), 7.25−7.68 (m, 7H, aromatic-H), 8.45 (s, 1H, CH=N), 14.38 (brs, 1H, OH). **7** as a yellow powder in 70% yield: ^{1}H NMR ($CDCl_3$): δ 1.20−2.00 (m, 9H, cyclohexyl-CH_2), 1.80 (brs, 6H, adamantyl-CH_2), 2.16 (brs, 3H, adamantyl-CH), 2.37 (brs, 6H, adamantyl-CH_2), 3.80−4.00 (m, 2H, CH), 7.30−7.75 (m, 12H, aromatic-H), 8.32 (s, 2H, CH=N). Anal. Found: C, 69.43; H, 6.83; N, 2.80. Calcd for $ZrC_{58}H_{68}N_2O_2Cl_2$: C, 70.56; H, 6.94; N, 2.84. FD-MS: 986 (M^+).

Bis[*N*-(3-(1-adamantyl)-5-phenyl-salicylidene)−(2-methylcyclohexyl)aminato] zirconium(IV) Dichloride (8) Ligand h. *N*-(3-(1-Adamantyl)-5-phenylsalicylidene)−(2-methylcyclohexyl)-amine as a yellow powder: ^{1}H NMR ($CDCl_3$): δ 0.84 (d, 3H,

Table 4. Summary of Crystallographic Data for Complexes 3, 5, and 8

complex	**3**	**5**	**8**
formula	$C_{32}H_{44}N_2O_2ZrCl_2$	$C_{34}H_{48}N_2O_2ZrCl_2$	$C_{124}H_{158}N_4O_5Zr_2Cl_4$
formula weight	650.83	678.89	2108.9
crystal color, habit	yellow, prismatic	pale yellow, prismatic	yellow, prismatic
crystal size/mm	0.45 × 0.40 × 0.30	0.20 × 0.15 × 0.15	0.40 × 0.35 × 0.20
crystal system	monoclinic	tetragonal	triclinic
space group	*C*2/*c* (#15)	*I*4̄2*d* (#122)	*P*1̄ (#2)
a/Å	25.502(3)	23.367(2)	17.131(4)
b/Å	7.851(1)		22.418(5)
c/Å	16.882(3)	14.368(2)	15.140(3)
α/deg			93.28(2)
β/deg	102.40(1)		92.61(2)
γ/deg			72.34(2)
V/Å^3	3301.3(8)	7845(1)	5528(2)
Z	4	8	2
D_{calcd}/g cm^{-3}	1.525	1.150	1.251
F_{000}	1584	2848	2200
μ(Mo Kα)/cm^{-1}	8.24	4.43	3.34
λ (Mo Kα)/Å	0.71069	0.71069	0.71069
T/°C	−50	−40	−50
2θ max	55.0	55.0	55.0
no. of total reflns	4483	3652	30328
no. of unique reflns	3785	2455	25350
no. of observations	3368 ($I > 2.00\sigma(I)$)	2009 ($I > 2.00\sigma(I)$)	13447 ($I > 2.50\sigma(I)$)
no. of variables	243	184	1396
refln/parameter ratio	13.86	10.92	9.94
residuals:R, Rw	0.029, 0.029	0.073, 0.121	0.059, 0.157
goodness of fit indicator	1.90	1.17	1.00
max shift/error in final cycle	0.00	0.00	0.00
max and min peaks in final diff map/e$^-$ Å^{-3}	0.56, −0.28	2.11, −0.81	0.90, −0.63

cyclohexyl-Me), 1.20−2.00 (m, 9H, cyclohexyl-CH_2), 1.80 (s, 6H, adamantyl-CH_2), 2.24 (s, 3H, adamantyl-CH), 2.36 (s, 6H, adamantyl-CH_2), 2.81, 3.33 (m, 1H, cyclohexyl-CH), 7.25−7.31 (m, 3H, aromatic-H), 7.38−7.44 (m, 2H, aromatic-H), 7.49−7.56 (m, 3H, aromatic-H), 8.38, 8.40 (s, 1H, CH═N), 14.26 (brs, 1H, OH). **8** as a yellow powder in 57% yield: ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 6H, cyclohexyl-Me), 1.0−1.8 (m, 18H, cyclohexyl-CH_2), 1.90 (brs, 12H, adamantyl-CH_2), 2.18 (brs, 6H, adamantyl-CH), 2.46 (brs, 12H, adamantyl-CH_2), 3.87 (m, 2H, cyclohexyl-CH), 7.25−7.55 (m, 8H, aromatic-H), 7.56−7.59 (m, 4H, aromatic-H), 7.76−7.78 (m, 2H, aromatic-H), 8.15−8.40 (s, 2H, CH═N). FD-MS: 1014 (M^+).

X-ray Crystallography. Single crystals of complexes **3**, **5**, and **8** suitable for X-ray structural determination were grown from a saturated $Et_2O-CH_2Cl_2$ solution. The X-ray structure analyses data were collected using a Rigaku AFC7R diffractometer. The structure was solved by direct method (SIR92)[24] and expanded using Fourier techniques.[25] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan (**3**,**5**) or the CrystalStructure (**8**) crystallographic software package of the Rigaku/MSC and Rigaku Corp.[26] Crystallographic data and the experimental details are summarized in Table 4.

Ethylene Polymerization under Atmospheric Pressure. Ethylene polymerization was carried out under atmospheric pressure in toluene using a 500 mL glass reactor equipped with a propeller-like stirrer and a condenser. Toluene (250 mL) was introduced to a nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at 25 °C, and then the ethylene gas feed (100 L/h) was started. After 10 min, polymerization was initiated by adding a 1.25 M MAO solution in toluene and then a 0.002 M complex solution in toluene into the reactor with vigorous stirring (600 rpm). The temperature control (25 °C) during the polymerization was performed by using an ice−water bath. After 5 min, the polymerization was quenched by the injection of isobutyl alcohol (3 mL), and the ethylene gas feed was stopped. The resulting mixture was added to acidified methanol (1 L containing 2 mL of concentrated HCl). The polyethylene was collected by filtration, washed with methanol (200 mL × 2), and dried in vacuo at 80 °C for 10 h.

Pressurized Ethylene Polymerization. Toluene (500 mL) was introduced into a 1000 mL stainless steel reactor equipped with two propeller-like stirrers under nitrogen at atmospheric pressure at 25 °C. A 1.25 M MAO solution in toluene (0.4 mL, 0.5 mmol) was added, and then ethylene was pumped into the reactor up to a prescribed pressure with stirring (350 rpm). Polymerization was initiated by adding a 0.000 25 M complex solution in toluene (0.4 mL, 0.0001 mol) into the reactor. The temperature control (25 °C) during the polymerization was performed by using an ice−water bath. After 5 min, the polymerization was quenched by injection of methanol (5 mL). The reactor was vented, and the resulting mixture was added to acidified methanol (1.5 L containing 5 mL of concentrated HCl). The polyethylene was collected by filtration, washed with methanol (200 mL × 2), and dried in vacuo at 80 °C for 10 h.

Preparation of Epoxy-Terminated Polyethylene (α-Epoxypolyethylene) A mixture of vinyl-terminated polyethylene (100 g, M_w 2000, M_w/M_n 2.35, T_m 122 °C), $Na_2WO_4{\cdot}2H_2O$ (1.79 g, 5.4 mmol), $CH_3(n\text{-}C_8H_{17})_3NHSO_4$ (1.27 g, 2.7 mmol), phosphoric acid (0.31 g, 2.7 mmol), and toluene (300 g) was stirred at reflux temperature for 30 min and then cooled to 90 °C under N_2. To the resulting mixture, aqueous H_2O_2 (30 wt %, 37 g, 326 mmol) was added dropwise over a 3 h period and stirred at 90 °C for 3 h with vigorous stirring under N_2. Aqueous sodium thiosulfate (40 wt %, 21.5 g, 54.4 mmol) was added to the reaction mixture at 90 °C in order to decompose the remaining H_2O_2. To the mixture, CH_3CN (300 g) was added at 80 °C, and the resulting mixture was cooled to room temperature. The epoxy-terminated polyethylene was collected by filtration, washed with CH_3CN, aqueous CH_3OH (50 wt %), and CH_3OH, and then dried in vacuo at 80 °C for 10 h (96 g, epoxy content 96 mol %, M_w 2000, M_w/M_n 1.84, T_m 121 °C). ^{1}H NMR ($C_2D_2Cl_4$): δ 0.88 (t, 3H, J = 6.92 Hz), 1.18−1.66 (m), 2.38 (dd, 1H, J = 2.64, 5.28 Hz), 2.66 (dd, 1H, J = 4.29, 5.28 Hz), 2.80−2.87 (m, 1H).

Preparation of Diol-Terminated Polyethylene (α,*β*-Dihydroxypolyethylene). Epoxy-terminated polyethylene was prepared from vinyl-terminated polyethylene (100 g, M_w 2000, M_w/M_n 2.35) using the same procedures described above. After the completion of decomposing the remaining H_2O_2, *i*-PrOH (150 g) was added slowly to the mixture at 80 °C, and the resulting mixture was stirred for 1 h at 65 °C. The mixture was cooled to room temperature, and the diol-terminated polyethylene was collected by filtration, washed with *i*-PrOH, aqueous CH_3OH (50 wt %) and CH_3OH, and then dried in vacuo at 80 °C for 10 h (95 g, diol content 95 mol %, M_w 2000, M_w/M_n 1.84, T_m 121 °C). ^1H NMR ($C_2D_2Cl_4$): δ 0.89 (t, 3H, $J = 6.9$ Hz), 1.05−1.84 (m), 3.41 (dd, 1H, $J = 5.9$, 9.9 Hz), 3.57−3.63 (m, 2H).

Calculations. Geometries and energies of the reactant, intermediates, transition states, and products for complexes **1**, **2**, **4**, and **5** were calculated using Becke's three-parameter hybrid functionals, B3LYP method[27] as implemented in the Gaussian 98 and Gaussian 03 programs.[28] The standard valence-double-ζ LANL2DZ basis set[29] with the corresponding effective core potential (for Zr atom) was used, and the polarization functions were augmented on the C atoms of reaction center for all calculations. The transition states were verified by means of the normal-mode analysis.

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Supporting Information Available: Crystallographic information files (CIF) for complexes **3**, **5**, and **8** and complete refs 28a and 28b. This material is available free of charge via the Internet at http://pubs.acs.org.

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