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Novel Zirconium–Iron Multinuclear Complex Catalysts for Olefin Polymerizations

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Novel zirconium–iron dinuclear complexes, [FcSiMe$_2$(R^{1}R^{2}Cp)ZrCl$_2$Cp] (Fc; Ferrocenyl, R^1 = R^2 = H; **2a**, R^1 = Me, R^2 = H; **2b**, R^1 = R^2 = Me; **2c**, R^1 = Ph, R^2 = H; **2d**), [FcSiMe$_2$Cp{ZrCl$_2$(Me$_5$Cp)}] (**3a**), hafnium–iron dinuclear complex, [FcSiMe$_2$Cp{HfCl$_2$(Me$_5$Cp)}] (**3b**) and zirconium–iron trinuclear complex, [ZrCl$_2$(FcSiMe$_2$Cp)$_2$] (**4**), were synthesized and complexes **2d** and **4** were characterized by an X-ray diffraction method. Olefin polymerizations were conducted by using these multimetallic zirconocene catalysts with the coexistence of methylaluminoxane or tetrakis(pentafluorophenyl)borates. The maximum catalytic activities of complexes **2**, **3** and **4** were observed at low temperatures (15—45 °C) in ethylene polymerization, contrary to the conventional zirconocene catalyst ([ZrCl$_2$Cp$_2$]), showing the maximum activity at between 70—80 °C. A detailed investigation of ethylene polymerization and NMR measurements of the active species suggested that the interesting behavior of these complexes arose from an electronic cooperative effect between the zirconium and iron atoms. It was also revealed that complexes **2** were highly reactive toward propylene or diene in the copolymerization of ethylene and propylene or terpolymerization of ethylene, propylene and diene.

Homogeneous catalyst systems based on metallocenes containing group-4 elements are currently regarded as being one of the most interesting research fields in Ziegler–Natta olefin polymerization.[1)] It is assumed that the active species of these homogeneous systems are a single metal center with a defined structure. The catalytic activities, stereoregularities, molecular weights, and molecular-weight distributions of the obtained polymer can be controlled by modifying the ligand structure of the complexes. They are also expected to behave as promising catalysts in producing various copolymers due to their high catalytic activities to a wide variety of olefin compounds, such as higher α-olefins, cyclic olefins, and dienes.

It was proposed that multimetallic complexes should serve as reasonable models of the active sites in heterogeneous catalyst systems, and should exhibit novel reactivities not shown by mononuclear complexes.[2)] Also, numerous multimetallic complexes have been prepared to examine their reactivities in various chemical reactions.

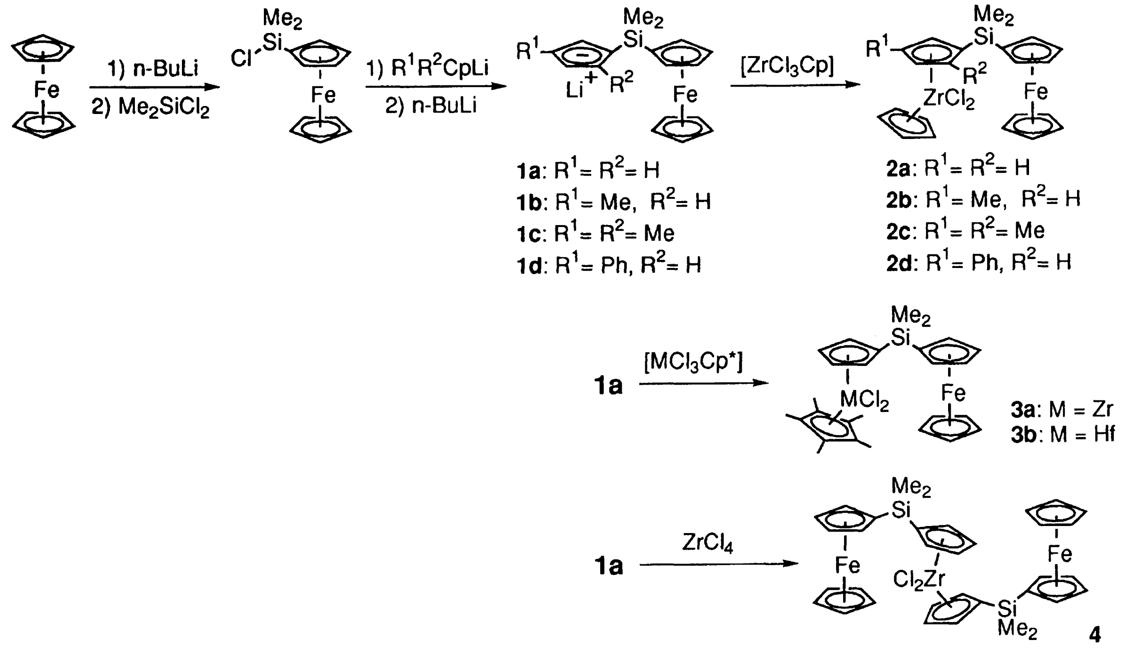
On the basis of these aspects, multinuclear metallocenes containing group-4 elements have possibilities to provide novel and versatile polymerization catalysts by cooperative effects between multimetallic centers. Bridged bis(cyclopentadienyl) ligand systems, for example, offer cooperative effects owing to their resistance to fragmentation of multimetallic sites during polymerization. These homometallic complexes were synthesized[3—7)] as well as studied concerning their catalytic activities in olefin polymerization.[8)] However, the behavior of these complexes in polymerization was almost the same as mononuclear complexes, and the specific properties of multinuclear complexes are as yet unknown. Although several syntheses of heterometallic complexes are known,[9—13)] only a few of them have been employed as polymerization catalysts.[14,15)]

Here, we would like to report on the syntheses and characterization of a new class of multinuclear zirconium–iron complexes; also, a detailed investigation is described with respect to their features as catalysts in olefin polymerizations.[16)]

Results and Discussion

Synthesis and Characterization of Multinuclear Zirconium–Iron Complexes. The syntheses of multinuclear zirconium–iron complexes are shown in Scheme 1. The lithium salt **1a** was prepared by a reaction of chloroferrocenyldimethylsilane with cyclopentadienyllithium and successive lithiation with BuLi. Other lithium salts (**1b**, **1c**, and **1d**) were also prepared from the corresponding cyclopentadienyllithium compounds according to a similar procedure. The dinuclear zirconium–iron complex (**2a** or **2b**) was afforded by treating **1a** or **1b** with an equimolar amount of [ZrCl$_3$Cp] in THF at room temperature. The preparations of complexes **2c**, **2d**, **3a**, and **3b** required a higher reaction temperature because of their bulky structures of lithium salts (**1b**, **1c**) or [MCl$_3$Cp*] (M: Zr, Hf, Cp*: Me$_5$Cp). Trinuclear complex **4** was synthesized by treating **1a** with a 0.5 molar amount of ZrCl$_4$ in THF at 70 °C. The detailed synthetic procedures are described in the experimental section.

After purification, analytically pure samples of the com-



Scheme 1.

plexes were obtained. The purity and structures of the complexes were confirmed by ^{1}H NMR. Two virtual triplet and one singlet of the proton peaks were observed at 6—7 ppm on a ^{1}H NMR analysis of complex **2a**, which were assignable to a dimethylsilanediyl bridged Cp ring and a free Cp ring of zirconocene, respectively. The similar peak pattern at 4—4.5 ppm (two virtual triplets and a singlet) was assignable to the ferrocene moiety. Dinuclear complexes having substituents on the Cp ring of zirconocene (**2b**—**2d**) showed unequivalent patterns of the proton peaks because of the unsymmetrical structures of the complexes. The proton signals of the zirconocene moiety in trinuclear complex **4** were only a set of virtual triplets at 6—7 ppm; those of the ferrocene moieties were a set of virtual triplets and a singlet at 4—4.5 ppm. The proton signals of two (ferrocenyldimethylsilyl)-cyclopentadienyl groups bonded to a zirconium atom were observed to be equivalent to each other, indicating that the complex retained a symmetrical structure in solution.

Recrystallization from toluene–hexane or toluene yielded a single crystal of dinuclear complex **2d** or trinuclear complex **4** as an orange plate. The crystal structures of the complexes were determined by an X-ray diffraction method. The crystallographic data and experimental details are summarized in Table 1. Selected distances and angles are given in Table 2, and their structures are represented in Fig. 1 (**2d**) and Fig. 2 (**4**). The coordination environments about the zirconium or iron center in each complex are analogous to the [$ZrCl_2Cp_2$][17] or [$FeCp_2$].[18] The ring centroid-Zr-ring centroid angles of **2d** and **4** are 130.4° and 131.5°, respectively, and fall within the expected ranges of 125—135° as nonbridged types of zirconocene complexes. It has been noted that two ferrocenyl moieties in trinuclear complex **4** are located symmetrically around the central zirconium, and, therefore, the complex molecule has a C_2 symmetry axis bisecting the Cl–Zr–Cl angle. The unit cell in the crystal of complex **4** contained two independent molecules, which were a pair of enantiomers.

Table 1. Crystallographic and Experimental Data for Complexes **2d** and **4**

	2d	**4**
Empirical formula	$C_{28}H_{28}Cl_2FeSiZr$	$C_{34}H_{38}Cl_2Fe_2Si_2Zr$
Formula weight	610.56	776.64
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	11.542(2)	18.321(2)
b/Å	14.773(2)	14.056(3)
c/Å	16.257(2)	27.044(2)
β/deg	108.711(10)	104.409(8)
Vol/Å^3	2625.5(6)	6745(2)
d(calcd)/g cm^{-1}	1.545	1.53
Z	4	8
F(000)	1240	3168
Crystal size/mm^3	0.40 × 0.15 × 0.05	0.50 × 0.20 × 0.06
T/K	298	296
Abs coeff (μ)/mm^{-1}	10.099	1.404
Radiation	Cu $K\alpha$	Mo $K\alpha$
Wavelength/Å	1.54178	0.71073
No. of data collcd	4000	11875
No. of data obsd	4000	9374
No. of data params	300	799
$R/(F)$ ($I > 2\sigma(I)$)	0.0868	0.059
$wR(F^2)$ ($I > 0$)	0.2127	0.117

The structure of complex **2c** from a NOESY measurement was in agreement with that of **2d** determined by the X-ray analysis (Fig. 3). The location of ferrocenyl group against the zirconocene moiety in complex **2c** was assumed to be nearly the same as that of complex **2d**.

Table 2. Selected Distances (Å) and Angles (deg) for Complexes **2d** and **4**

2d		**4**	
Zr–Cl(1)	2.448(3)	Zr–Cl(1)	2.431(2)
Zr–Cl(2)	2.426(3)	Zr–Cl(2)	2.450(2)
Zr–Cp(1)[a)]	2.216	Zr–Cp(1)[a)]	2.197
Zr–Cp(2)[a)]	2.205	Zr–Cp(2)[a)]	2.292
Zr–C	2.475(11)—2.543(11)	Zr–C	2.457(8)—2.534(8)
Fe–C	2.022(11)—2.053(11)	Fe(1)–C	2.017(8)—2.053(10)
Si–C(4)	1.875(10)	Fe(2)–C	2.001(9)—2.060(7)
Si–C(19)	1.856(11)	Si(1)–C(1)	1.881(8)
C(1)–C(11)	1.49(2)	Si(1)–C(8)	1.859(9)
		Si(2)–C(18)	1.886(8)
Cp(1)–Zr–Cp(2)	130.39	Si(2)–C(25)	1.822(8)
Cl(1)–Zr–Cl(2)	96.73(11)		
C(4)–Si–C(19)	109.5(4)	Cp(1)–Zr–Cp(2)	131.51
		Cl(1)–Zr–Cl(2)	98.17(8)
		C(1)–Si(1)–C(8)	111.4(3)
		C(18)–Si(2)–C(25)	107.3(3)

a) Cp(1) and Cp(2) are the centroids of the lower and higher numbered C_5 rings, respectively, bonded to Zr atom.

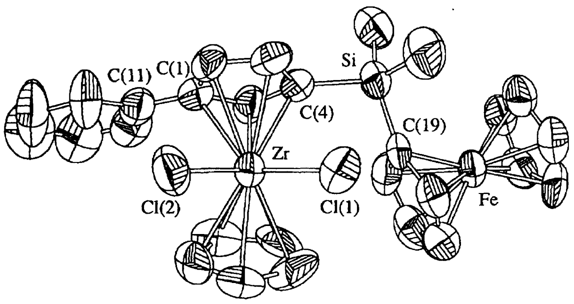


Fig. 1. Molecular structure of dinuclear complex **2d**.

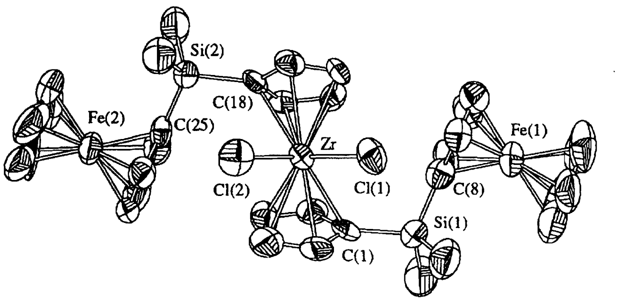


Fig. 2. Molecular structure of trinuclear complex **4**.

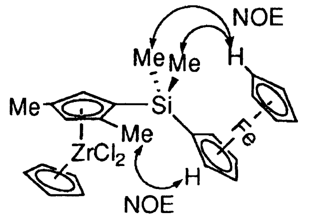


Fig. 3. Structure of complex **2c** from NOESY analysis.

Ethylene Polymerization Catalyzed by Multinuclear Zirconium–Iron Complexes. Ethylene polymerization catalyzed by the multinuclear zirconium–iron complexes were examined in the presence of several cocatalysts, as shown in Table 3. The productivity of complex **2a** was found to be 44400 g-PE/mmol cat. h at 45 °C by using methylaluminoxane (MAO) as a cocatalyst (Entry 1). It was reported that the combinations of tetrakis(pentafluorophenyl)-borates, such as $(PhHNMe_2)[B(C_6F_5)_4]$ or $(Ph_3C)[B(C_6F_5)_4]$ and trialkylaluminums, were also effective cocatalysts as well as MAO in olefin polymerization.[19)] These cocatalysts were also applied to the multinuclear complex catalyst in ethylene polymerization. The catalyst system of dinuclear complex **2a** in combination with $(PhHNMe_2)[B(C_6F_5)_4]$ and Me_3Al exhibited a higher productivity rather than by using MAO (Entry 3). When $(Ph_3C)[B(C_6F_5)_4]/(^iBu)_3Al$ was used as a cocatalyst, the productivity of **2a** reached 227000 g-PE/mmol cat. h; this was the highest productivity in the present experiments (Entry 4). Though the trinuclear zirconium-iron complex **4** also afforded a high productivity by using a borate cocatalyst, it was slightly less active than complex **2a** (Entry 6). Conventional zirconocene, $[ZrCl_2Cp_2]$, showed similar variations of productivity by a combination with these cocatalysts (Entries 7—10). The molecular weights of the produced polymers were estimated from their intrinsic viscosity to be nearly equal to that of the polymer obtained by $[ZrCl_2Cp_2]$; also, the molecular-weight distributions of the produced polymer were almost narrow ($M_w/M_n < 3$) in every case.

The catalytic activities of multinuclear zirconium–iron complexes **2a** and **4** were investigated at various temperatures in the presence of MAO or $(PhHNMe_2)[B(C_6F_5)_4]/Me_3Al$. The variations in the productivity versus the polymerization temperature are shown in Figs. 4 and 5. When $[ZrCl_2Cp_2]$ was used as a catalyst, the maximum productivity in ethylene polymerization was observed at about 75 °C; it was almost in agreement with the reported result.[1e)] In contrast, the zirconium–iron dinuclear complex **2a** exhibited the peak of productivity at a low temperature (45 °C) compared with that of $[ZrCl_2Cp_2]$ when each cocatalyst was used. A similar result was observed in polymerization catalyzed by the trinuclear complex **4**. The peak of catalytic

Table 3. Ethylene Polymerization[a] Catalyzed by Multinuclear Zirconium–Iron Complexes with Various Cocatalyst Systems

Entry	Complex catalyst	Cocatalyst	Productivity g-PE(mmol cat. h)$^{-1}$	$[\eta]$[b] cm^3/g^{-1}
1	**2a**	MAO	44400	7.36
2		An[c][$B(C_6F_5)_4$]/$^i Bu_3Al$	54900	7.94
3		An[$B(C_6F_5)_4$]/Me_3Al	86600	7.32
4		Tr[d][$B(C_6F_5)_4$]/$^i Bu_3Al$	227000	6.46
5	**4**	MAO	14300	6.53
6		An[$B(C_6F_5)_4$]/Me_3Al	50800	7.61
7	[$ZrCl_2Cp_2$]	MAO	37700	6.27
8		An[$B(C_6F_5)_4$]/$^i Bu_3Al$	19600	6.09
9		An[$B(C_6F_5)_4$]/Me_3Al	39500	6.35
10		Tr[$B(C_6F_5)_4$]/$^i Bu_3Al$	73300	4.65

a) Polymerization conditions: 45 °C, catalyst 1.0 μmol, [Al]/[cat.] = 750 (Entries 1, 5, and 7), catalyst 0.5 μmol, [B]/[cat.] = 1, [R_3Al] = 1.0 mM, (Entires 2, 6, 8 and 9), catalyst 0.25 μmol, [B]/[cat.] = 1, [R_3Al] = 1.0 mM (Entries 3, 4 and 10), time 0.5 min (Entries 4, 6, 9 and 10), 1.0 min (Entries 2, 3 and 8), 1.5 min (Entries 1, 5 and 7). b) Intrinsic viscosity. c) An: ($PhHNMe_2$). d) Tr: (Ph_3C).

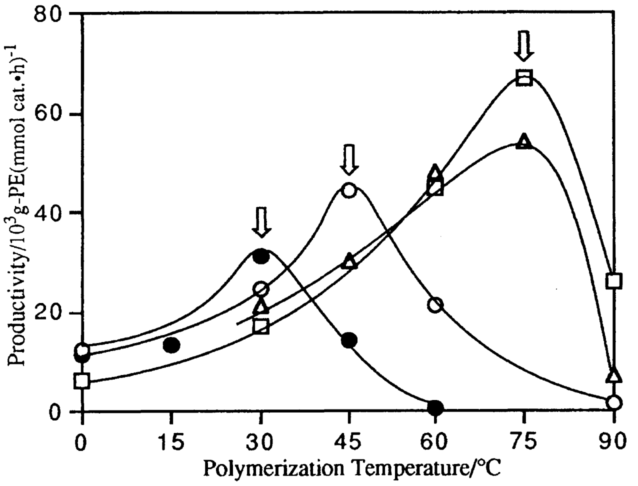
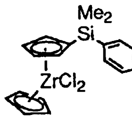


Fig. 4. Plots for the catalyst productivities of **2a**, **4**, [$ZrCl_2Cp_2$], and **5**[a]/MAO at variable polymerization temperature; ○ for **2a**, ● for **4**, □ for [$ZrCl_2Cp_2$], and △ for **5**. Polymerization conditions: [Al]/[cat.] = 750, 1.5—5 min. a) Complex **5**: [$ZrCl_2Cp\{(Me_2PhSi)Cp\}$].



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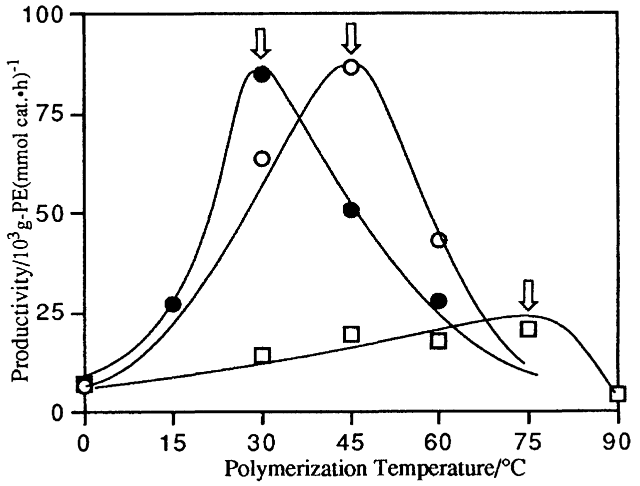


Fig. 5. Plots for the catalyst productivities of **2a**, **4**/An[B(C_6F_5)$_4$][a]/Me_3Al and [$ZrCl_2Cp_2$]/An[$B(C_6F_5)_4$]/(^{i}Bu)$_3$Al at variable polymerization temperature; ○ for **2a**, ● for **4** and □ for [$ZrCl_2Cp_2$]. Polymerization conditions: [B]/[cat.] = 1, [Me_3Al] = 1.0 mM, 0.5—3 min. a) An: ($PhHNMe_2$).

activity of **4** was located even at 30 °C. Dinuclear complexes having subsutituents on the Cp ring of the zirconocene moiety (**2b**—**2d**, **3a**) and hafnium–iron dinuclear complex **3b** also showed the maximum productivities at low temperatures (15—45 °C). It is assumed that the different behavior from the other zirconocenes in polymerization can be attributed to the peculiar properties of these multinuclear complex catalysts. Although complex **5** ([$ZrCl_2Cp\{(Me_2PhSi)Cp\}$]) was analogous to dinuclear complex **2a** concerning the steric environments around the zirconium center, its maximum productivity was shown to be at about 75 °C (almost equal to [$ZrCl_2Cp_2$]). Therefore, the steric hindrance of the ferrocenyl groups in complex **2a** scarcely contributed to the polymerization behavior observed in the present research.[20]

The decrease in the productivity at a high polymerization temperature could be ascribed to the decomposition of the active species. In order to examine the thermal stability of a multinuclear complex catalyst, another method of polymerization was tried. Complex **2a** was treated with MAO at 90 °C for 10 min. After being cooled to room temperature, polymerization was carried out by this pre-treated catalyst solution at 45 °C (Table 4). No decrease in the activity was observed in this pre-treatment method, which confirmed that the cationic active species did not decompose at the polymerization temperature.

Although 1—100 molar amounts of ferrocene were added

Table 4. Variation of Relative Productivities of **2a**/MAO with Several Polymerization Method in Ethylene Polymerization[a)]

Catalyst	Std. method	Method A[b)]	Method B[c)]
2a	100	106	124

a) Polymerization conditions: 45 °C, 1.5 min, catalyst 1.0 μmol, [Al]/[cat.] = 750. b) Method A; the catalyst solution and MAO were mixed at room temperature before use. c) Method B; the catalyst solution and MAO were mixed and heated at 90 °C for 10 min before use.

to [$ZrCl_2Cp_2$]/MAO system, both the catalytic activity and the variations in the activity versus temperature remained quite unchanged in ethylene polymerization (Table 5). These results suggested that the specific behavior of multinuclear complexes was caused by the effect of intramolecular ferrocenyl groups. It is pointed out here that intramolecular electron-donation from ferrocenyl groups to the cationic zirconium center would influence the characteristic property of the active site during polymerization. The mutual electronic effect of the center metals in multinuclear metallocenes was reported.[21)] A ^{1}H NMR analysis of complex **2c** and a MAO mixture in C_6D_6 provided significant information regarding the electronic effect of the intramolecular ferrocenyl groups (Fig. 6). The peaks of the zirconocene part slightly broadened and shifted to high magnetic fields upon the addition of MAO. A more remarkable influence on the peaks of the ferrocene part in the complex was observed; that is, these peaks considerably broadened and shifted to low magnetic fields. In contrast, no changes in the NMR signal were detected at all in the NMR signal of ferrocene, itself, by the addition of MAO. It is therefore reasonable to consider that the intramolecular electron-donation of the ferrocenyl group to the neighboring cationic zirconium center was generated by MAO.

The variations in the productivity of multinuclear Zr–Fe complexes versus the polymerization temperature could be explained as follows: Since the intramolecular electron-donation of the ferrocenyl group to the zirconium center contributes to the facile generation and stabilization of highly reactive cationic species, the productivities of the complexes increased at low temperature. On the other hand, greater ion separation took place between the cationic zirconium center and the counter anion at high temperature; this ion separation would enhance the intramolecular electron-donation of the ferrocenyl group to the cationic center. This effect reduced the electrophilicity of the metal center and the reactivity to ethylene at the polymerization temperature.[22)]

Table 5. Variation of Relative Productivities of [$ZrCl_2Cp_2$]/MAO by Addition of Ferrocene in Ethylene Polymerization[a)]

[$FeCp_2$][b)]	0	1	10	100	10	10
Relative productivities	100	95	107	92	97[c)]	93[d)]
Temp[e)]/°C	45	45	45	45	30	60

a) Polymerization conditions: 1.5 min, catalyst 1.0 μmol, [Al]/[cat.] = 750. b) /molar amounts for [$ZrCl_2Cp_2$]. c) vs. productivity at 30 °C. d) vs. productivity at 60 °C. e) Polymerization temperature.

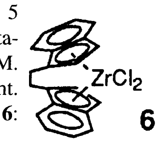
Copolymerization of Ethylene and Propylene Catalyzed by Complexes 2. Complexes **2** were also active in the polymerization of propylene[23)] by the combined use with (Ph_3C)[$B(C_6F_5)_4$]/Me_3Al, and afforded an atactic polypropylene. The catalytic activities and molecular weights of the obtained polymer were higher than those of the other nonbridged metallocenes.[24)] These results led us to examine the copolymerization of ethylene and propylene using complexes **2** (Table 6). When complex **2a** was used as a catalyst, the propylene content of the copolymer was 48 mol% (Entry 1), which is higher than that obtained by [$ZrCl_2Cp_2$] (30 mol%, Entry 5). A similar high incorporation of propylene was observed in the copolymer produced by **2b**—**2d**. In a series of these complexes, complex **2b**, having mono-methyl substituent on the zirconocene part, was most effective concerning the reactivity to propylene (Entry 2). Zirconocene complexes with bridged-Cp ligands, such as [$ZrCl_2\{(\eta^5\text{-}C_9H_6)CH_2\}_2$] (complex **6**), were known to show a high reactivity to propylene and other olefin compounds because of their large bite angles.[1e)] By using complex **6**, the obtained copolymer had a low molecular weight and its propylene content was 52 mol% under the same polymerization conditions (Entry 6). It was found that complexes **2** exhibit a high reactivity toward the propylene monomer, which is almost equal to that of the bridged metallocene complexes; the resulting copolymer had a high molecular weight. The multinuclear Zr–Fe complexes are expected to be a new class of catalysts in the copolymerization of ethylene and other olefin compounds.

Terpolymerization of Ethylene, Propylene, and Diene Catalyzed by Complexes 2. The family of terpolymers comprising ethylene, propylene and diene, referred to as EPDM, possesses several excellent properties not shared by other elastomers. Although EPDM is currently produced

Table 6. Copolymerization[a)] of Ethylene and Propylene Catalyzed by Complexes **2**/(Ph_3C)[$B(C_6F_5)_4$]/Me_3Al

Entry	Complex	Propylene content[b)]	M_w[c)]/10^4	M_w/M_n	Productivity[d)]
1	**2a**	48	20.0	2.46	68600
2	**2b**	55	21.3	2.11	60400
3	**2c**	46	25.0	1.93	21900
4	**2d**	45	21.9	1.95	30400
5	[$ZrCl_2Cp_2$]	30	27.3	2.05	59300
6	**6**[e)]	52	5.6	2.41	86900

a) Polymerization conditions: 30 °C, 5 min, propylene/ethylene feed ratio 60/40, catalyst 0.5 μmol, [B]/[cat.] = 5, [Me_3Al] = 2.0 mM. b) /mol%. c) Weight average molecular weight. d) /g-Polymer(mmol cat. h)$^{-1}$. e) Complex **6**: [$ZrCl_2\{(\eta^5\text{-}C_9H_6)CH_2\}_2$].



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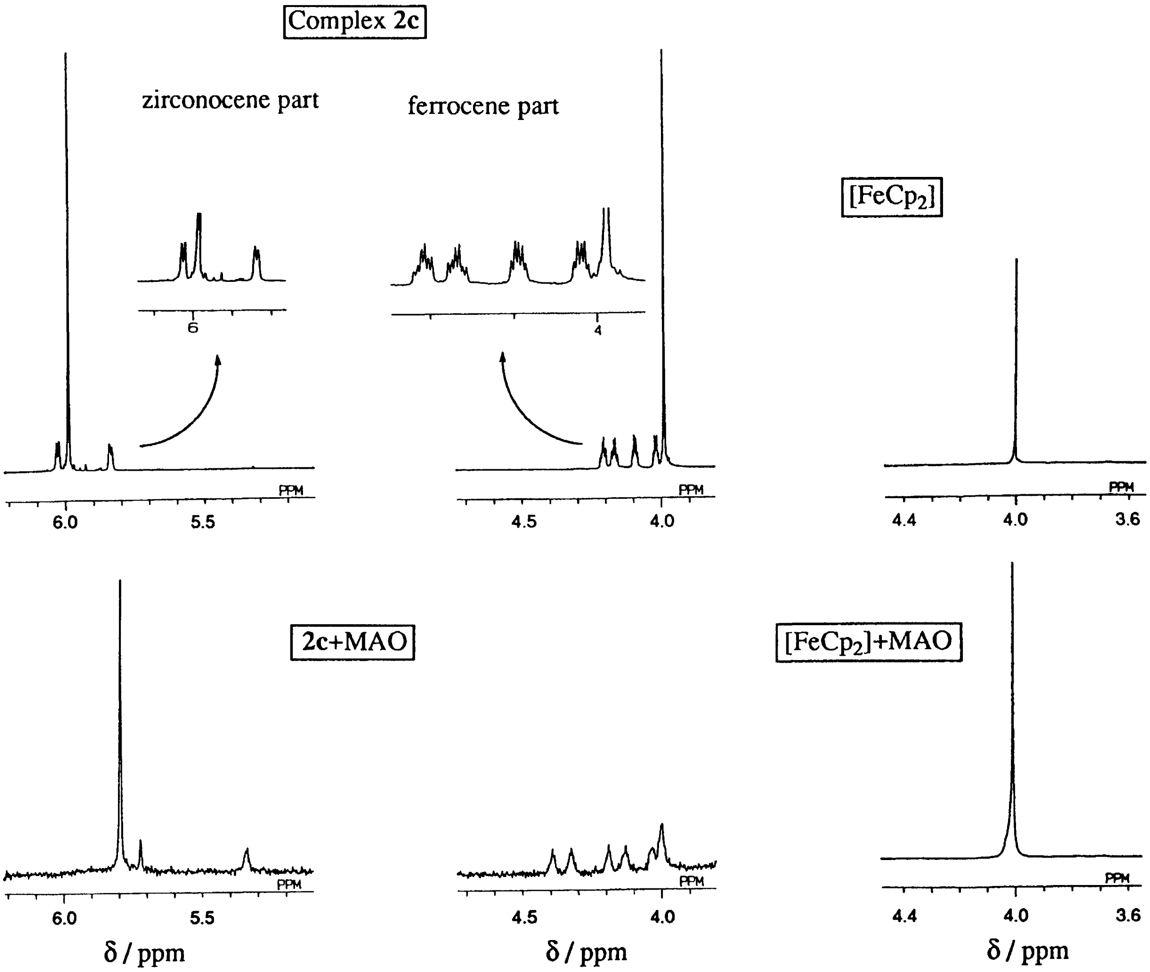

Fig. 6. ^{1}H NMR spectra of complex **2c** and [FeCp$_2$] in C_6D_6 after addition of 100 molar amounts of MAO.

by vanadium-based catalysts, their productivities are not at a satisfactory level. Zirconocene catalysts were tried to produce of these copolymers,[25] however, a sufficient result was not obtained concerning the productivity, molecular weight of the copolymer and reactivity to diene compounds. Since complexes **2** effectively catalyzed ethylene–propylene copolymerizations, the catalyst systems were applied to the terpolymerization of ethylene, propylene, and diene. 5-Ethylidene-2-norbornene (ENB) was employed as a diene compound, which is generally used in EPDM polymerization. The propylene content in the copolymer was adjusted to about 30 mol%, because the highest productivities were usually given at this content in copolymerization of ethylene and propylene.

The results of polymerization are summarized in Table 7. Interestingly, complex **2a** afforded a terpolymer with a high incorporation of diene; the results indicated that the complex was highly reactive toward the diene compound (Entry 1). The methyl or phenyl substituted complex (**2b** or **2d**) was effective to increase the molecular weight of the copolymer retaining high reactivities to diene (Entries 2 and 4). A dimethyl-substituted complex (**2c**) also afforded a copolymer with a high molecular weight, but in low productivity probably because of their steric hindrance (Entry 3). In contrast, low reactivities to diene were observed (Entries 5 and 6) when another nonbridged-type metallocene such as [ZrCl$_2$Cp$_2$] or [ZrCl$_2$(1,3-Me$_2$Cp)$_2$], was used. Although the reactivity of bridged metallocene to diene was nearly equal to that of complexes **2** (Entry 7), only an oily terpolymer with a low molecular weight resulted. It is noted that the highest reactivities toward diene were exhibited by dinuclear complexes **2** in the nonbridged-type of metallocenes, and that the reactivities were comparable to metallocene complexes with bridged-Cp ligands.

Conclusion

The syntheses of novel multinuclear zirconium–iron complexes and characterization by the X-ray diffraction method are described. The multinuclear Zr–Fe complexes exhibited a distinctive behavior in ethylene polymerization, which was caused by cooperative effects between the multimetallic centers. High reactivities toward olefins and diene were also shown in copolymerizations catalyzed by these multinuclear complexes. Because of a wide variety of combinations of center metals, these multinuclear metallocenes containing group-4 elements may provide specific polymerization catalysts with novel reactivities for the production of various useful polymers.

Table 7. Terpolymerization[a] of Ethylene, Propylene, and Diene Catalyzed by Complexes **2**/(Ph$_3$C)[B(C$_6$F$_5$)$_4$/Me$_3$Al

Entry	Complex	Propylene content[b]	Diene content[c]	$\frac{M_w}{10^4}$[d]	M_w/M_n	Productivity[e]
1	**2a**	28	5.6	17.4	2.15	7180
2	**2b**	28	5.2	29.1	2.17	5590
3	**2c**	30	5.1	25.2	2.11	2700
4	**2d**	37	5.1	24.9	2.46	10400
5	[ZrCl$_2$Cp$_2$]	35	2.7	21.4	2.30	15800
6	[ZrCl$_2$(1,3-Me$_2$Cp)$_2$]	24	1.7	31.2	2.46	8850
7	**6**	32	5.1	7.7	2.42	21700

a) Polymerization conditions: 30 °C, 10 min, propylene/ethylene feed ratio 60/40, catalyst 2.0 μmol (Entries 1—6), propylene/ethylene feed ratio 50/50, catalyst 0.5 μmol (Entry 7), [B]/[cat.] = 5, [Me$_3$Al] = 4.0 mM, [ENB] = 10 mM. b) /mol%. c) /wt%. d) Weight average molecular weight. e) /g-Polymer(mmol cat. h)$^{-1}$.

Experimental

General: All of the manipulations were carried out under dry argon or nitrogen using glove-box or Schlenk techniques. The solvents were dried and purified in the usual manner.

^{1}H and ^{13}C NMR spectra were measured on a JEOL Model FX-270 spectrometer with tetramethylsilane used as an internal standard. Infrared spectra was recorded on a JASCO IR-700 spectrometer. Viscosity measurements were performed in decahydronaphthalene at 135 °C with an Ubbelohde viscometer. The molecular-weight distributions of polyethylene were determined by gel-permeation chromatography (GPC) on a Waters 150-C instrument at 140 °C in 1,2,4-trichlorobenzene. The molecular weights of polypropylene and copolymers were determined by GPC using Waters, μ-Styragel columns 10^3 and 10^4 Å at 75 °C in toluene, and were calibrated with standard polystyrene. The propylene contents of the copolymers were measured by IR and ^{13}C NMR.[26] The incorporations of ENB (wt%) in the copolymer were calculated from the iodine value obtained by titration.[27]

X-Ray Diffraction Analysis: X-Ray measurements of complexes **2d** and **4** were made on a Rigaku AFC-6R and an AFC-7S diffractometer, respectively.[28] The atom coordinates and thermal parameters are listed in Table 8 (**2d**) and Table 9 (**4**).

Material: Trichloro(cyclopentadienyl)zirconium ([ZrCl$_3$Cp]), trichloro(pentamethylcyclopentadienyl)zirconium ([ZrCl$_3$(Me$_5$Cp)]), tetrachlorozirconium (ZrCl$_4$), trichloro(pentamethylcyclopentadienyl)hafnium ([HfCl$_3$(Me$_5$Cp)]) (Strem Chemicals, Inc.), ferrocene ([FeCp$_2$]) (Tokyo Kasei Kogyo Co., Ltd.), *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate ((PhHNMe$_2$)[B(C$_6$F$_5$)$_4$]), triphenylmethyl tetrakis(pentafluorophenyl)borate ((Ph$_3$C)[B(C$_6$F$_5$)$_4$]) (Asahi Glass Co., Ltd.), lithium cyclopentadienide (CpLi) (Aldrich Chemical Company, Inc.), polymerization-grade ethylene and propylene (Sumitomo Seika Co., Ltd.) were employed. Dichlorodimethylsilane (SiCl$_2$Me$_2$), dichlorobis(cyclopentedienyl)zirconium [ZrCl$_2$Cp$_2$], butyllithium in hexane (BuLi), trimethylaluminum in hexane (Me$_3$Al), triisobutylaluminum in hexane ((^{i}Bu)$_3$Al) (Kanto Chemical Co., Inc.) and methylaluminoxane (MAO) (10 wt% in toluene, Schering AG) were used without further purification. 5-Ethylidene-2-norbornene (ENB) (Tokyo Kasei Kogyo Co., Ltd.) was dried over CaH$_2$ and stored under argon. Lithium methylcyclopentadienide,[29] lithium 1,3-dimethylcyclopentadienide,[29] lithium phenylcyclopentadienide,[8b] dichlorobis(1,3-dimethylcyclopentadienyl)zirconium[29] ([ZrCl$_2$(1,3-Me$_2$Cp)$_2$]), dichloro(cyclopentadienyl)[(dimethylphenylsily)cyclopentadienyl]zirconium ([ZrCl$_2$Cp{(Me$_2$PhSi)Cp}]) (complex **5**) and dichloro[1,2-ethanediylbis(1-indenyl)]zirconium[30] ([ZrCl$_2${(η^5-C$_9$H$_6$)CH$_2$}$_2$]) (complex **6**) were prepared by conventional manner.

Table 8. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2d**

Atom	*x*	*y*	*z*	*U*(eq)[a]
Zr(1)	8478(1)	4897(1)	11702(1)	41(1)
Fe(1)	7425(2)	3533(1)	14994(1)	46(1)
Cl(1)	8699(3)	6132(2)	12746(2)	62(1)
Cl(2)	8974(3)	5775(2)	10599(2)	72(1)
Si(1)	6109(3)	4520(2)	12948(2)	54(1)
C(1)	6722(9)	4124(8)	10600(7)	53(3)
C(2)	6403(10)	5056(7)	10537(6)	51(3)
C(3)	6254(9)	5330(8)	11311(6)	52(3)
C(4)	6438(9)	4551(7)	11892(6)	46(2)
C(5)	6700(10)	3821(8)	11424(6)	49(2)
C(6)	10262(11)	4000(9)	11582(8)	66(3)
C(7)	10733(10)	4602(9)	12252(9)	62(3)
C(8)	10294(12)	4357(10)	12923(8)	77(4)
C(9)	9533(12)	3646(10)	12665(9)	73(4)
C(10)	9510(10)	3389(7)	11819(9)	64(3)
C(11)	6934(10)	3544(8)	9912(7)	56(3)
C(12)	7045(15)	3919(11)	9157(8)	87(4)
C(13)	7280(17)	3356(15)	8533(10)	113(6)
C(14)	7327(14)	2463(15)	8611(12)	110(7)
C(15)	7222(13)	2093(11)	9354(10)	89(5)
C(16)	7015(12)	2611(9)	9993(8)	69(3)
C(17)	5900(13)	5708(9)	13294(8)	78(4)
C(18)	4677(12)	3844(11)	12715(9)	84(4)
C(19)	7377(9)	3935(7)	13779(6)	47(2)
C(20)	8401(11)	4338(8)	14445(7)	57(3)
C(21)	9154(11)	3689(9)	14936(8)	64(3)
C(22)	8663(12)	2844(8)	14594(8)	63(3)
C(23)	7564(11)	2980(8)	13887(7)	59(3)
C(24)	5832(11)	3926(8)	15192(7)	59(3)
C(25)	6859(12)	4260(9)	15854(7)	63(3)
C(26)	7586(13)	3544(9)	16288(7)	66(3)
C(27)	7009(11)	2726(9)	15864(8)	65(3)
C(28)	5931(11)	2962(8)	15217(7)	58(3)

a) *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Synthesis of Dichloro(η^5-cyclopentadienyl)[η^5-(ferrocenyldimethylsilyl)cyclopentadienyl]zirconium(IV) (2a). Preparation of Lithium (Ferrocenyldimethylsilyl)cyclopentadienide

Table 9. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **4**

Atom	*x*	*y*	*z*	*U*(eq)[a)]
Zr(1)	7047(1)	6505(1)	2524(1)	32(1)
Fe(1)	5378(1)	8304(1)	3995(1)	49(1)
Fe(2)	9294(1)	7370(1)	1244(1)	54(1)
Cl(1)	6141(1)	5569(2)	2838(1)	52(1)
Cl(2)	7372(1)	5176(2)	2033(1)	56(1)
Si(1)	7028(1)	7142(2)	3933(1)	48(1)
Si(2)	7370(1)	7294(2)	1195(1)	41(1)
C(1)	7598(4)	6876(6)	3459(3)	40(2)
C(2)	7882(5)	7565(6)	3168(3)	45(2)
C(3)	8328(5)	7106(7)	2887(3)	50(2)
C(4)	8363(5)	6159(8)	3020(3)	62(3)
C(5)	7908(5)	6003(7)	3356(3)	55(3)
C(6)	7665(6)	7859(8)	4443(3)	78(3)
C(7)	6771(6)	6002(7)	4190(3)	75(3)
C(8)	6185(5)	7872(6)	3642(3)	43(2)
C(9)	5466(5)	7562(7)	3374(3)	46(2)
C(10)	4997(5)	8337(7)	3223(3)	56(3)
C(11)	5395(5)	9177(8)	3394(4)	62(3)
C(12)	6143(5)	8884(6)	3650(3)	51(2)
C(13)	5665(7)	7930(12)	4746(4)	86(4)
C(14)	5040(9)	7412(10)	4496(5)	86(4)
C(15)	4465(8)	8044(11)	4273(5)	90(4)
C(16)	4730(8)	8958(11)	4401(5)	93(4)
C(17)	5477(10)	8884(10)	4701(5)	99(5)
C(18)	6796(4)	7394(6)	1683(3)	34(2)
C(19)	6121(4)	6929(6)	1697(3)	41(2)
C(20)	5828(5)	7325(7)	2091(3)	48(2)
C(21)	6343(5)	8018(6)	2334(3)	42(2)
C(22)	6916(4)	8069(5)	2076(3)	34(2)
C(23)	7139(5)	6188(7)	813(3)	63(3)
C(24)	7133(6)	8366(7)	777(3)	76(3)
C(25)	8360(5)	7337(6)	1539(3)	37(2)
C(26)	8804(5)	8154(7)	1703(3)	55(3)
C(27)	9539(6)	7874(9)	1959(4)	72(3)
C(28)	9574(5)	6902(10)	1976(3)	67(3)
C(29)	8848(5)	6527(7)	1712(3)	48(2)
C(30)	8947(7)	7421(13)	469(4)	91(4)
C(31)	9377(11)	8211(12)	647(6)	115(5)
C(32)	10097(11)	7913(18)	918(6)	144(9)
C(33)	10094(8)	6901(16)	901(4)	121(7)
C(34)	9372(8)	6599(11)	622(4)	97(4)

a) *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(1a): To a solution of [FeCp$_2$] (7.44 g, 40 mmol) in diethyl ether (150 ml) was added BuLi (35.1 ml, 60 mmol) at room temperature and stirred for 24 h. The reaction mixture was added dropwise to a solution of SiCl$_2$Me$_2$ (15.5 g, 120 mmol) in diethyl ether (60 ml) and stirred for 2 h. After all of the volatiles were removed in vacuo, the residue was extracted with hexane and the insoluble part was removed by filtration. The filtrate was concentrated and the residue was dissolved in THF (100 ml). A THF solution of CpLi (0.48 M, 56.7 ml, 27 mmol, 1 M = 1 mol dm^{-3}) was added to the solution at −78 °C and the mixture was stirred for 3 h at room temperature. After the solvent was removed in vacuo, the residue was extracted with hexane (160 ml). An orange powder was formed upon adding BuLi (15.8 ml, 27 mmol) to the solution at room temperature. The resulting lithium salt **1a** was isolated by filtration over a G4-Schlenk filter, washed with hexane, and dried in vacuo (4.45 g, 36% yield based on [FeCp$_2$]).

Other lithium salts (**1b**, **1c**, **1d**) were prepared from the corresponding cyclopentadienyllithium compounds by a similar procedure to that described above (See Scheme 1).

Lithium 1-Ferrocenyldimethylsilyl-3-methylcyclopentadienide (1b): 40% yield based on [FeCp$_2$].

Lithium 1-Ferrocenyldimethylsilyl-2,4-dimethylcyclopentadienide (1c): 33% yield based on [FeCp$_2$].

Lithium 1-Ferrocenyldimethylsilyl-3-phenylcyclopentadienide (1d): 36% yield based on [FeCp$_2$].

Dichloro(η^5-cyclopentadienyl)[η^5-(ferrocenyldimethylsilyl)cyclopentadienyl]zirconium(IV) (2a). To a solution of **1a** (0.84 g, 2.7 mmol) in THF (15 ml) was added a solution of [ZrCl$_3$Cp] (0.71 g, 2.7 mmol) in THF (23 ml) at room temperature and stirred for 12 h. After the solvent was removed in vacuo, the residue was extracted with toluene and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from toluene afforded complex **2a** (0.69 g, 48% yield).

Found: C, 49.64; H, 4.47%. Calcd for C$_{22}$H$_{24}$Cl$_2$FeSiZr: C, 49.44; H, 4.53%. ^{1}H NMR (CDCl$_3$) $\delta = 6.70$ (2H, t), 6.52 (2H, t), 6.22 (5H, s), 4.44 (2H, t), 4.21 (2H, t), 4.14 (5H, s), 0.57 (6H, s).

Synthesis of Dichloro(η^5-cyclopentadienyl)[η^5-1-(ferrocenyldimethylsilyl)-3-methylcyclopentadienyl]zirconium(IV) (2b). To a solution of **1b** (0.65 g, 2.0 mmol) in THF (5 ml) was added a solution of [ZrCl$_3$Cp] (0.53 g, 2.0 mmol) in THF (18 ml) at room temperature and stirred for 12 h. After the solvent was removed in vacuo, the residue was extracted with refluxing hexane and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from hexane afforded complex **2b** (0.30 g, 27% yield).

Found: C, 50.27; H, 4.53%. Calcd for C$_{23}$H$_{26}$Cl$_2$FeSiZr: C, 50.36; H, 4.78%. ^{1}H NMR (CDCl$_3$) $\delta = 6.61$ (H, t), 6.42 (H, t), 6.16 (5H, s), 6.12 (H, t), 4.46 (2H, t), 4.24 (2H, t), 4.16 (5H, s), 2.23 (3H, s), 0.56 (3H, s), 0.53 (3H, s).

Synthesis of Dichloro(η^5-cyclopentadienyl) [η^5-1-(ferrocenyldimethylsilyl)-2,4-dimethylcyclopentadienyl]zirconium(IV) (2c). To a solution of **1c** (0.59 g, 1.7 mmol) in THF (15 ml) was added a solution of [ZrCl$_3$Cp] (0.44 g, 1.7 mmol) in THF (17 ml) at room temperature and heated under reflux for 6 h. After the solvent was removed in vacuo, the residue was extracted with refluxing hexane and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from hexane afforded complex **2c** (0.47 g, 49% yield).

Found: C, 51.39; H, 4.90%. Calcd for C$_{24}$H$_{28}$Cl$_2$FeSiZr: C, 51.24; H, 5.02%. ^{1}H NMR (C$_6$D$_6$) $\delta = 6.03$ (H, d), 5.99 (5H, s), 5.84 (H, d), 4.21 (H, m), 4.16 (H, m), 4.09 (H, m), 4.02 (H, m), 3.99 (5H, s), 2.23 (3H, s), 1.84 (3H, s), 0.54 (3H, s), 0.48 (3H, s).

Synthesis of Dichloro(η^5-cyclopentadienyl)[η^5-1-(ferrocenyldimethylsilyl)-3-phenylcyclopentadienyl]zirconium(IV) (2d). To a solution of **1d** (0.60 g, 1.5 mmol) in THF (10 ml) was added a solution of [ZrCl$_3$Cp] (0.40 g, 1.5 mmol) in THF (15 ml) at room temperature and heated under reflux for 4 h. After the solvent was removed in vacuo, the residue was extracted with refluxing hexane and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from toluene–hexane afforded complex **2d** (0.34 g, 37% yield).

Found: C, 55.33; H, 4.38%. Calcd for C$_{28}$H$_{28}$Cl$_2$FeSiZr: C, 55.08; H, 4.62%. ^{1}H NMR (CDCl$_3$) $\delta = 7.59$—7.32 (5H, m), 7.06 (H, dd), 6.91 (H, t), 6.77 (H, dd), 5.97 (5H, s), 4.45 (2H, m), 4.27 (H, m), 4.24 (2H, m), 4.16 (5H, s), 0.66 (3H, s), 0.57 (3H, s).

Synthesis of Dichloro[η^5-(ferrocenyldimethylsilyl)cyclo-

pentadienyl](η^5-pentamethylcyclopentadienyl)zirconium(IV) (3a). To a solution of **1a** (0.21 g, 0.69 mmol) in toluene (8 ml) was added [$ZrCl_3Cp^*$] (0.24 g, 0.71 mmol) at room temperature and heated under reflux for 10 h. After the solvent was removed in vacuo, the residue was extracted with refluxing hexane and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from hexane afforded complex **3a** (0.20 g, 48% yield).

Found: C, 53.75; H, 5.76%. Calcd for $C_{27}H_{34}Cl_2FeSiZr$: C, 53.64; H, 5.76%. ^1H NMR ($CDCl_3$) $\delta = 6.47$ (2H, t), 6.10 (2H, t), 4.31 (2H, t), 4.09 (2H, t), 4.08 (5H, s), 1.99 (15H, s), 0.59 (6H, s).

Synthesis of Dichloro[η^5-(ferrocenyldimethylsilyl)cyclopentadienyl](η^5-pentamethylcyclopentadienyl)hafnium(IV) (3b). To a solution of **1a** (0.12 g, 0.38 mmol) in THF (3.8 ml) was added a solution of [$HfCl_3Cp^*$] (0.16 g, 0.38 mmol) in THF (2 ml) at room temperature and heated under reflux for 6 h. After the solvent was removed in vacuo, the residue was extracted with hexane and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from hexane afforded complex **3b** (0.16 g, 60% yield).

Found: C, 46.59; H, 4.75%. Calcd for $C_{27}H_{34}Cl_2FeSiHf$: C, 46.87; H, 4.96%. ^1H NMR ($CDCl_3$) $\delta = 6.39$ (2H, t), 6.06 (2H, t), 4.31 (2H, t), 4.09 (2H, t), 4.08 (5H, s), 2.04 (15H, s), 0.59 (6H, s).

Synthesis of Dichlorobis[η^5-(ferrocenyldimethylsilyl)cyclopentadienyl]zirconium(IV) (4). To a solution of **1a** (1.39 g, 4.4 mmol) in THF (44 ml) was added a THF solution of $ZrCl_4$ (0.10 M, 17.4 ml, 1.7 mmol) at room temperature and heated under reflux for 9 h. After the solvent was removed in vacuo, the residue was extracted with toluene and filtered over a G4-Schlenk filter. The concentration of the filtrate and recrystallization from toluene afforded complex **4** (0.35 g, 27% yield).

Found: C, 52.48; H, 4.85%. Calcd for $C_{34}H_{38}Cl_2Fe_2Si_2Zr$: C, 52.58; H, 4.93%. ^1H NMR ($CDCl_3$) $\delta = 6.51$ (4H, t), 6.19 (4H, t), 4.39 (4H, t), 4.14 (4H, t), 4.11 (10H, s), 0.53 (12H, s).

Polymerization of Ethylene with MAO or Borate-Based Cocatalysts: A five-necked flask (500 ml) equipped with a thermometer, gas inlet and outlet tubes and an agitator was flushed with dry nitrogen. Dry toluene (200 ml) was placed in the flask and ethylene was introduced into the flask at the temperature given in Table 3, Figs. 4 and 5. In the cases of using MAO as a cocatalyst, the polymerization was initiated by the successive addition of a prescribed amount of MAO and a toluene solution of the catalyst. In the case of borate-based cocatalysts, polymerization was initiated by the successive addition of the prescribed amount of trialkylaluminum, the toluene solution of the catalyst and $(PhHNMe_2)[B(C_6F_5)_4]$ or $(Ph_3C)[B(C_6F_5)_4]$. During the polymerization, ethylene was continuously fed at atmospheric pressure and the polymerization temperature was kept constant. The polymerization was quenched by the addition of methanol, and the polymer solution was poured into a large amount of methanol/HCl aq. The resulting polymer was isolated by filtration, washed with methanol, acetone and dried in vacuo.

Polymerization of Propylene, Copolymerization of Ethylene and Propylene or Terpolymerization of Ethylene, Propylene, and Diene: By using the same reactor as that for ethylene polymerization, dry toluene (200 ml) was placed in the flask and monomer gases (propylene or ethylene/propylene mixed gas) were introduced into the flask at 0 °C (propylene polymerization) or 30 °C (other copolymerization). In the case of propylene polymerization or copolymerization of ethylene and propylene, the polymerization was initiated by the successive addition of trialkylaluminum, toluene solutions of the catalyst and $(Ph_3C)[B(C_6F_5)_4]$. In the case of the terpolymerization of ethylene, propylene, and diene, after the addition of trialkylaluminum and a toluene solution of the catalyst, the diene monomer (ENB) was added into the flask and the polymerization was initiated by the addition of a toluene solution of $(Ph_3C)[B(C_6F_5)_4]$. During the polymerization, monomer gases were continuously fed at atmospheric pressure and the polymerization temperature was kept constant. The polymerization was quenched by the addition of methanol, and the polymer solution was poured into a large amount of methanol/HCl aq. The resulting polymer was isolated by filtration, washed with methanol, acetone and dried in vacuo.

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