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Zr/Zr and Zr/Fe Dinuclear Complexes with Flexible Bridging Ligands. Preparation by Olefin Metathesis Reaction of the Mononuclear Precursors and Properties as Polymerization Catalysts

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Mononuclear Zr complexes $CpZrCl_2\{\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH_2\}$ (n = 1, 2, 3) undergo intermolecular metathesis of the vinyl group catalyzed by a Ru complex to produce dinuclear complexes with bridging ligands, $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH(CH_2)_nC_5H_4\}$. Hydrogenation of the products catalyzed by Pd/C affords complexes with a flexible polymethylene chain that bridges two Cp_2ZrCl_2 groups. A dinuclear complex with a bridging bisfluorenyl ligand, $(CpZrCl_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{13}H_8CH_2CH{=}CHCH_2C_{13}H_8)$, is also obtained from the metathesis of a mononuclear Zr complex with the allylfluorenyl ligand. X-ray crystallography of $(CpZrCl_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_{13}H_8CH_2CH{=}CHCH_2C_{13}H_8)$ revealed the molecular structure with a *trans*-C=C double bond and the two Zr centers situated at different sides of the bridging bisfluorenyl ligand. Cross metathesis reaction of $CpZrCl_2\{\eta^5\text{-}C_5H_4(CH_2)_2CH{=}CH_2\}$ and ferrocenylmethyl acrylate produces the Zr/Fe dinuclear complex $CpZrCl_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_2\text{-}CH{=}CHCOOCH_2C_5H_4\}FeCp$. The dinuclear complexes catalyze polymerization of ethylene and propylene in the presence of MAO (methylaluminoxane). The activity of the Zr/Zr dinuclear complexes for ethylene polymerization is higher than that of the mononuclear precursors. The length and flexibility of the bridging group of the biscyclopentadienyl ligand also influence the catalytic activity.

Introduction

Recent progress in olefin metathesis reactions has enabled intermolecular coupling of the olefinic compounds with polar functional groups because the Ru complexes with carbene ligands catalyze olefin metathesis efficiently and do not decompose even in the presence of a substrate with polar groups.[1] Transition metal complexes having a vinyl group in the ligand are employed for substrates of the metathesis catalyzed by the Ru complexes. $Cl_2Ru({=}CHPh)(PCy_3)_2$ promotes ring-closing metathesis to produce the interlocked molecular assemblies composed of Cu and diimine ligands.[2] Ring-closing metathesis is applied for the preparation of *ansa*-metallocenes from metallocene precursors with two vinyl groups.[3] An intermolecular metathesis reaction of metal complexes with vinyl pendant groups would form dinuclear metal complexes, accompanied by elimination of ethylene.[4] Recently, Erker et al. reported intermolecular metathesis of titanocene and zirconocene chlorides with an olefinic group at the cyclopentadienyl ligand to produce dinuclear complexes and the olefin polymerization catalyzed by these complexes.[5]

Olefin polymerization catalyzed by group 4 metallocenes has been widely investigated.[6] During the past decade, several groups reported preparation of the dinuclear complexes of Ti and Zr and their catalytic ethylene polymerization. Bis(cyclopentadienyl)methane and 1,2-bis(cyclopentadienyl)ethane coordinate to the two metal centers as bridging ligands.[7−12] The dinuclear Zr complexes catalyze ethylene polymerization in the

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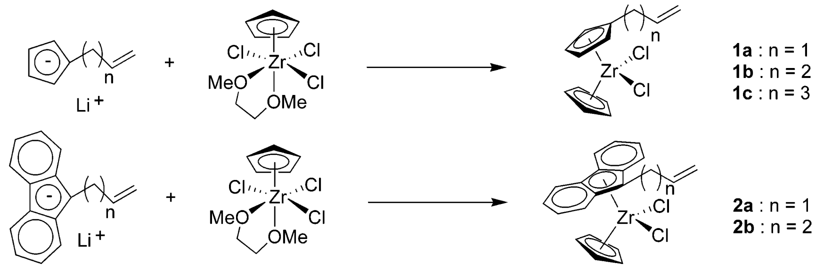
Scheme 1



presence of MAO. Catalytic activities of the dinuclear Zr complexes with a longer bridging chain (C4−C10) were compared.[11,12] Marks et al. designed the ligand for the new dinuclear Ti and Zr complexes, which has two active centers with a structure similar to that of the constrained geometry catalysts (CGC).[13] They discussed unique catalytic properties of the dinuclear complexes in the presence of monovalent and divalent borates as the cocatalyst. Polyethylene obtained from the reaction catalyzed by the dinuclear CGC-Zr complex and MAO has a molecular weight that is 600 times higher than that produced by the mononuclear catalyst.[14] Since catalytic activity of the dinuclear complexes varies depending on the structure and length of the bridging ligand, systematic studies of the polymerization using the catalysts would provide useful information on the cooperative effect of the two metal centers in the catalytic reaction. In this paper, we report the preparation of the new dinuclear Zr complexes and Zr/Fe heterodinuclear complex by the olefin metathesis reaction of the two mononuclear precursors. The catalytic behavior of the dinuclear complexes is compared with that of the mononuclear complexes.

Results and Discussion

Preparation and Characterization of Zr/Zr Dinuclear Complexes. Cyclopentadienyl and fluorenyl ligands with allyl, 3-butenyl, and 4-pentyl substituents are synthesized according to reported methods and employed as their Li salts for the preparation of the Zr complexes.[15] Scheme 1 summarizes the preparation of the Zr complexes with these ligands, $CpZrCl_2\{\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH_2\}$ (**1a**: $n = 1$, **1b**: $n = 2$, **1c**: $n = 3$) and $CpZrCl_2\{\eta^5\text{-}C_{13}H_8(CH_2)_nCH{=}CH_2\}$ (**2a**: $n = 1$, **2b**: $n = 2$). Figures 1 and 2 show the molecular structures of **2a** and **2b** determined by X-ray crystallography. A benzene ring of the fluorenyl ligand of both complexes is on the same side as the Cl ligands.

$Cl_2Ru({=}CHPh)\{CN(Mes)CH_2CH_2N(Mes)\}(PCy_3)$ catalyzes the metathesis reaction of the olefinic group of **1a** to give the dinuclear complex $(CpZrCl_2)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2CH{=}CHCH_2C_5H_4)$ (**3a**) in 76% yield, as shown in eq 1. The ^1H NMR spectrum shows that the product is composed of a mixture of trans and cis isomers (99:1). Erker reported a similar reaction of $CpTiCl_2(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)$ to produce the corresponding dinuclear Ti complex with a trans-vinylene group.[5] They obtained a mixture of the trans and cis complexes in a

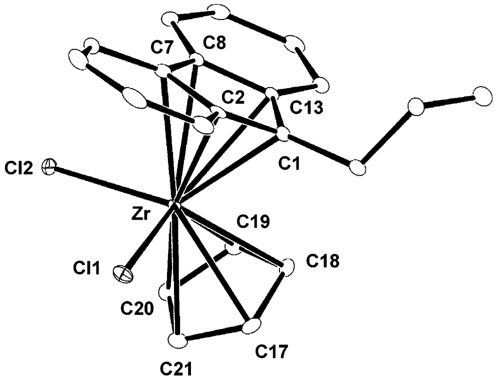


Figure 1. ORTEP drawing of **2a** at 30% ellipsoidal level. Selected bond distances (Å) and angles (deg): Zr−Cl1, 2.4209(6); Zr−Cl2, 2.4597(6); Zr−C1, 2.488(3); Zr−C2, 2.602(3); Zr−C7, 2.580(2); Zr−C8, 2.569(2); Zr−C13, 2.571(2); Zr−C17, 2.503(3); Zr−C18, 2.491(2); Zr−C19, 2.485(3); Zr−C20, 2.527(3); Zr−C21, 2.519(3); Cl1−Zr−Cl2, 96.99(2).

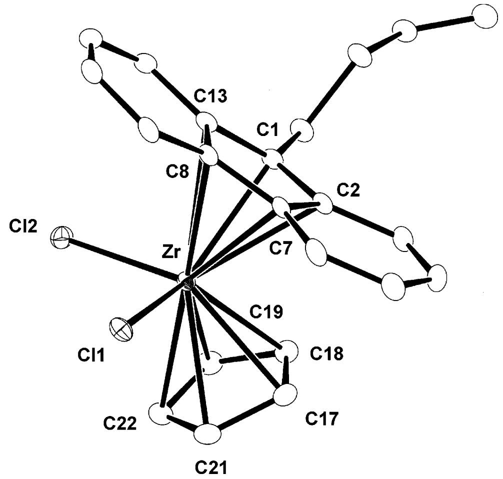


Figure 2. ORTEP drawing of **2b** at 30% ellipsoidal level. Selected bond distances (Å) and angles (deg): Zr−Cl1, 2.4549(7); Zr−Cl2, 2.4130(7); Zr−C1, 2.493(3); Zr−C2, 2.579(2); Zr−C7, 2.550(3); Zr−C8, 2.588(2); Zr−C13, 2.616(3); Zr−C18, 2.526(3); Zr−C19, 2.478(3); Zr−C20, 2.456(3); Zr−C21, 2.514(3); Zr−C22, 2.543(3); Cl1−Zr−Cl2, 97.72(2).

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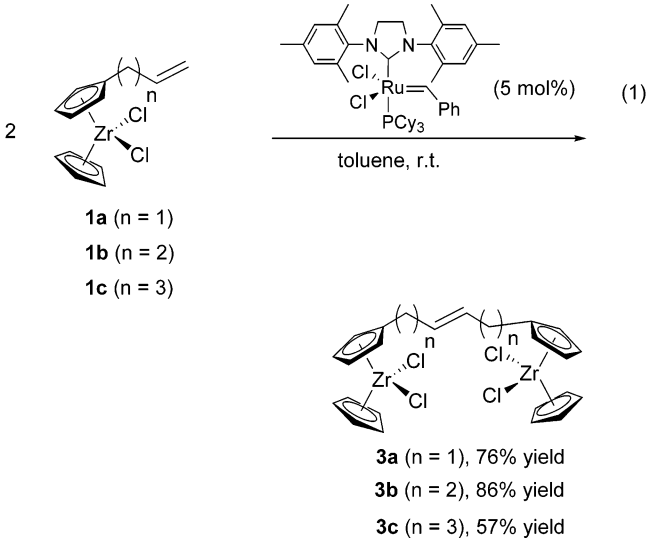
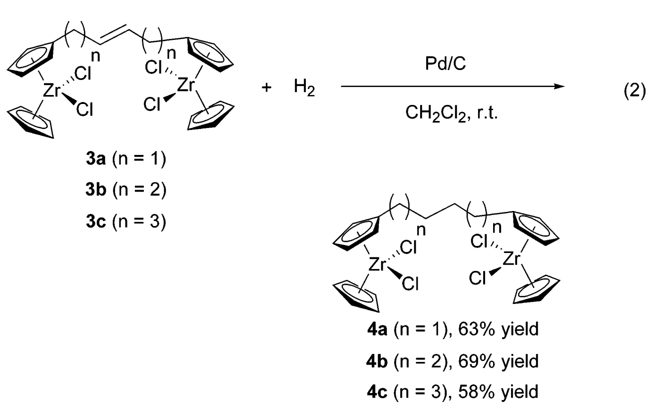
3:1 ratio from the reaction catalyzed by $Cl_2Ru(=CHPh)(PCy_3)_2$ at 80 °C. Metathesis of **1a** catalyzed by the same complex at 40 °C also yields **3a** as a mixture of the trans and cis isomers (6:1). $Cl_2Ru(=CHPh)\{CN(Mes)CH_2CH_2N(Mes)\}(PCy_3)$ catalyzes the metathesis of 3-butenyl and 4-pentenyl groups at the cyclopentadienyl ligand of **1b** and **1c** to afford the dinuclear Zr complexes $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH(CH_2)_nC_5H_4\}$ (**3b**: $n = 2$, **3c**: $n = 3$).



Hydrogenation of **3a**–**c** in the presence of Pd/C catalyst gave $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_nCH_2CH_2(CH_2)_nC_5H_4\}$ (**4a**: $n = 1$, **4b**: $n = 2$, **4c**: $n = 3$) in 58%-69% yields (eq 2). ^1H NMR spectra of **4a**–**c** contain signals due to Cp hydrogens (δ 6.4–6.2) and CH_2 hydrogens (δ 2.6–2.7 and 1.3–1.7) and do not show olefinic signals. The produced dinuclear Zr complexes have a flexible polymethylene group as the bridging chain of the two metallocenes.



Coupling of **2a** by the metathesis reaction of the allyl groups by using $Cl_2Ru(=CHPh)(PCy_3)_2$ at 40 °C gives dinuclear complex **5a** in 82% yield (Scheme 2). The ^1H NMR spectrum of the crude product of the reaction shows minor signals at δ 5.78, 5.41, and 2.61, which are assigned to the Cp, vinylene, and fluorenyl hydrogens of the mononuclear product shown in Scheme 2. The reaction of **2a** using $Cl_2Ru(=CHPh)\{CN(Mes)CH_2CH_2N(Mes)\}(PCy_3)$ catalyst proceeds smoothly at room temperature in toluene and affords **5a** in almost quantitative yield (96%). Low solubility of **5a** in toluene makes separation of it from the solution easy.

Figure 3 shows the molecular structure of **5a** determined by X-ray crystallography. Two Zr centers are situated at the opposite sides of the bridging ligand to each other. The vinylene group has a trans configuration with a C=C bond distance of 1.316(7) Å. The ^1H NMR spectrum shows a signal at 5.66 ppm due to =CH hydrogens of the trans-vinylene group. Exclusive forma-

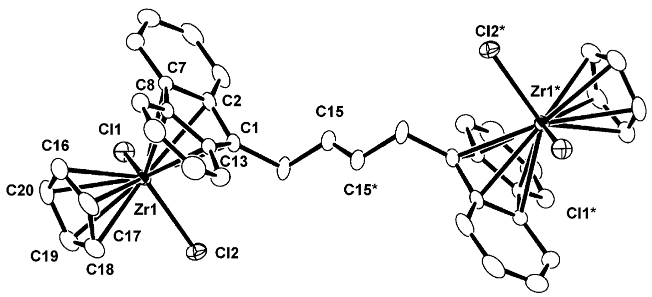
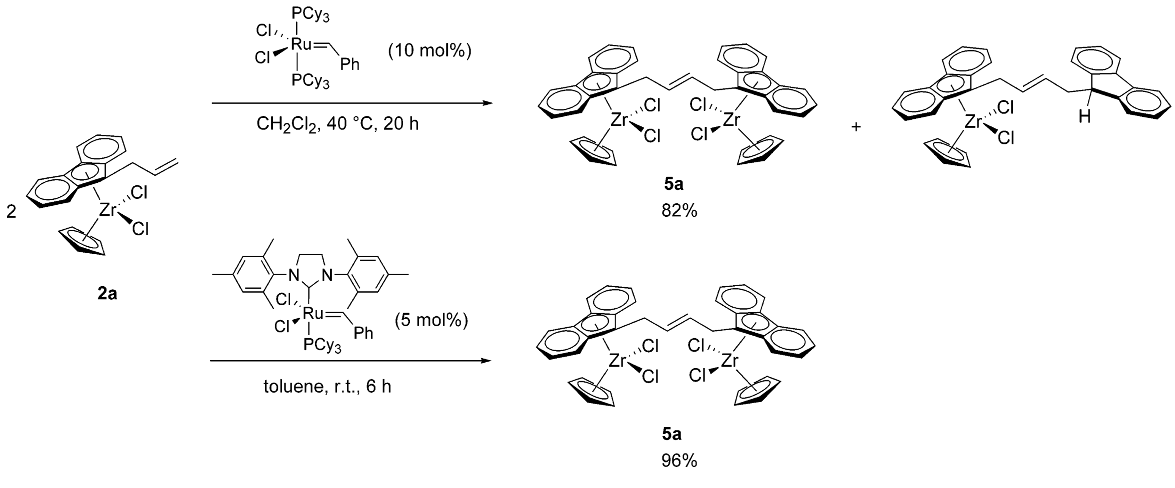


Figure 3. ORTEP drawing of **5a** at 30% ellipsoidal level. The molecule has a crystallographic C_2 symmetry around the midpoint of C15–C15* bond. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisk. Selected bond distances (Å) and angles (deg): Zr–Cl1, 2.427(1); Zr–Cl2, 2.427(1); Zr–C1, 2.524(4); Zr–C2, 2.610(4); Zr–C7, 2.571(4); Zr–C8, 2.600(4); Zr–C13, 2.553(4); Zr–C16, 2.472(6); Zr–C17, 2.462(5); Zr–C18, 2.500(5); Zr–C19, 2.525(6); Zr–C20, 2.536(6); Cl1–Zr–Cl2, 95.58(4).

Scheme 2



tion of the trans-vinylene group by metathesis is ascribed to sterically bulky fluorenyl groups. Coupling of the butenyl-substituted zirconocene **2b** was not successful due to demetalation of the ligand. Weaker coordination of the fluorenyl group than the cyclopentadienyl group[16] and facile change from the η^5- to the η^3-fluorenyl ligand are probably responsible for the decomposition of the complex during the reaction.[17]

Synthesis of a Heterodinuclear Zr/Fe Complex by Cross Metathesis Reaction. Recently, cross metathesis reactions of terminal olefins and α-carbonyl olefins were achieved by using the Ru carbene complexes as the catalyst.[18] This reaction is applied to the preparation of a Zr/Fe heterodinuclear complex whose metal centers are bridged by a biscyclopentadienyl ligand. Ferrocenylmethyl acrylate, which is prepared by the reaction of ferrocenylmethanol with acryloyl chloride in the presence of triethylamine, reacts with **1b** to produce the Zr/Fe dinuclear complex $CpZrCl_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_2CH{=}CHCOOCH_2C_5H_4\}FeCp$ (**6**) in 86% yield (eq 3). The ^1H NMR spectrum of **6** shows the peaks due to =CH hydrogens at δ 6.95 and 5.81, the latter of which is assigned to the α-hydrogen of the carboxyl group. The coupling constant of the signals (16 Hz) indicates a trans configuration of the vinylene group. Analogous cross metathesis of terminal olefins and ethyl acrylate was reported to yield products with a trans-vinylene group in high selectivity.[18b]

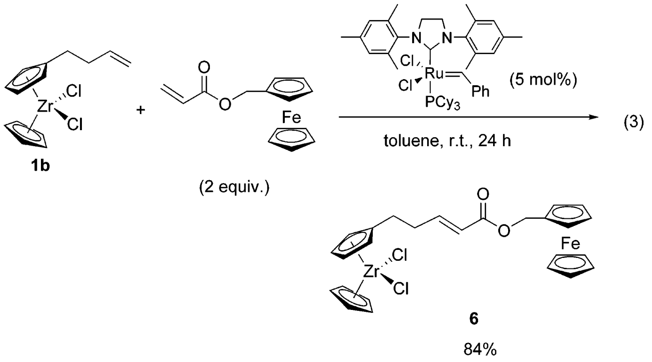


Table 1. Ethylene[a] and Propylene[b] Polymerization

run	catalyst	monomer	activity (g mmol^{-1} h^{-1})	M_n	M_w/M_n
1[c]	**1a**	ethylene	2350	230 000	3.2
2	**1b**	ethylene	1120	49 000	3.2
3	**1c**	ethylene	1560	150 000	4.1
4	**2a**	ethylene	3730	120 000	3.5
5[c]	**3a**	ethylene	3020	130 000	2.2
6	**3b**	ethylene	2750	95 000	3.3
7	**3c**	ethylene	1970	150 000	3.0
8	**4a**	ethylene	3840	210 000	3.2
9	**4b**	ethylene	3270	110 000	3.2
10	**4c**	ethylene	2480	170 000	2.7
11	**5a**	ethylene	3600	87 000	3.8
12	**6**	ethylene	1020	80 000	2.8
13[d]	Cp_2ZrCl_2	ethylene	750	52 000	2.5
14	**1a**	propylene	11	530	3.5
15	**1b**	propylene	42	700	1.4
16	**1c**	propylene	86	920	3.2
17	**2a**	propylene	29	5800	1.7
18	**3a**	propylene	35	940	3.3
19	**3b**	propylene	124	1500	3.0
20	**3c**	propylene	95	1600	3.4
21	**4a**	propylene	151	900	2.8
22	**4b**	propylene	156	1800	2.7
23	**4c**	propylene	121	1900	3.3
24	**5a**	propylene	57	7300	1.9
25	**6**	propylene	44	3400	3.2
26	Cp_2ZrCl_2	propylene	20	1300	2.3

[a] [Zr] = 16.7 μM, ethylene 1 atm, [Al]/[Zr] = 1000, 5 min, 30 mL of toluene, 15 °C. [b] [Zr] = 167 μM, propylene 1 atm, [Al]/[Zr] = 1000, 1 h, 30 mL of toluene, r.t. [c] Reproducibility of activity was checked. [d] Polymerization for 15 min shows lower activity (570 and 610 g mmol^{-1} h^{-1}).

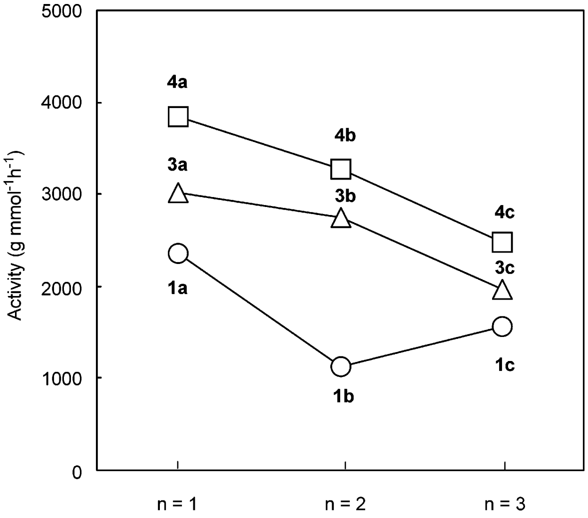


Figure 4. Activity for ethylene polymerization catalyzed by the Zr complexes in the presence of MAO. Reaction conditions are shown in Table 1. n denotes number of CH_2 groups in $CpZrCl_2(\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH_2)$ (**1a**–**c**), $(CpZrCl_2)_2\{\eta^5\text{-}C_5H_4(CH_2)_nCH{=}CH(CH_2)_nC_5H_4\}$ (**3a**–**c**), and $(CpZrCl_2)_2\{\eta^5\text{-}C_5H_4(CH_2)_nCH_2CH_2(CH_2)_nC_5H_4\}$ (**4a**–**c**).

Olefin Polymerization. The dinuclear Zr/Zr and Zr/Fe complexes catalyze the polymerization of ethylene in the presence of MAO ([Zr] = 16.7 μM and [Al]/[Zr] = 1000 in toluene), as summarized in Table 1. Activities of the catalysts are estimated from the polymer yield of the reaction for a short period (5 min) at 15 °C in order to avoid the mass transfer effect.[19] Dinuclear complexes **3a** and **4a** exhibit higher catalytic activity than that of mononuclear precursor **1a** (runs 1, 5, and 8). The activity of **4a**, with a bridging tetramethylene chain, is higher than that of **3a**, whose Zr centers are bridged by a less flexible 2-butenylene group. The same tendency is observed in a series of the mononuclear and dinuclear complexes **1b**, **3b**, and **4b**, as well as in **1c**, **3c**, and, **4c**. The polymers obtained by **1a**, **3a**, and **4a** have similar melting points (134−135 °C) and crystallization temperatures (117 °C). Figure 4 shows the relationship between the catalytic activity and number of carbon atoms in the bridging chain. The catalytic activity of the dinuclear complexes decreases with increasing length of the bridging chain, **3a** (3020 g mmol^{-1} h^{-1}) > **3b** (2750 g mmol^{-1} h^{-1}) > **3c** (1970 g

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mmol^{-1} h^{-1}) and **4a** (3840 g mmol^{-1} h^{-1}) > **4b** (3270 g mmol^{-1} h^{-1}) > **4c** (2480 g mmol^{-1} h^{-1}). No significant difference in the reaction rate is observed between the mononuclear complex **2a** (3600 g mmol^{-1} h^{-1}) and dinuclear complex **5a** (3730 g mmol^{-1} h^{-1}), having a fluorenyl group in the ligand. Heterobimetallic complex **6** exhibits catalytic activity similar to that of mononuclear complex **1b**.

The Zr/Zr dinuclear complexes with C_1 bridged biscyclopentadienyl ligands were reported to show low catalytic activity for ethylene polymerization, which was ascribed to steric hindrance around the metal center caused by close contact of the two metallocene groups.[7] The dinuclear complexes with a polymethylene and oligosiloxane bridge exhibited an increase of the catalytic activity with an increase of the bridging chain lengths.[11,12] This tendency is opposite the results of the polymerization catalyzed by the dinuclear complexes **3a**–**c** and **4a**–**c** shown in Figure 4. Several dinuclear complexes with long polymethylene and oligosiloxane chains showed higher catalytic activity than the mononuclear complexes with similar coordinating groups around the Zr centers.[11b,12a] Substituents on the Cp ligand of the metallocenes lead to diverse effects on the activity of ethylene polymerization. Mononuclear metallocenes with bulky substituents show low catalytic activity for the reaction.[20] This is ascribed to steric hindrance, which suppresses smooth coordination and insertion of the monomer. The Zr/Zr dinuclear complexes having a bulky ligand such as C_5HMe_4 or an indenyl group also showed low catalytic activity.[10,12b] Less bulky substituents at the Cp ligand, however, enhance the polymerization. Mononuclear complexes **1a**–**c** with an alkyl group at the Cp ligand show higher activities than nonsubstituted Cp_2ZrCl_2.

In this study, high catalytic activity is obtained when the complex with a short and flexible bridging chain between zirconocene is employed as the catalyst, as shown in Figure 4. A positive cooperative effect of the two Zr centers probably serves to enhance the ethylene polymerization. Major active species of the polymerization catalyzed by the dinuclear complexes should be the dicationic complexes. Since the two bulky anions formed from MAO have steric or electrostatic repulsion with each other, one of the two anions is separated effectively from the cationic dizirconium complex. The high catalytic activity of the dinuclear complexes can be ascribed to the positive cooperative effect of the two Zr centers induced by effective separation of the Zr complex from the anion. Marks and co-workers discussed interaction of the Zr-containing cation and the anion formed from boron compounds or MAO and the relationship between the interaction and catalytic behavior in olefin polymerization.[21] Some of the molecular weight, molecular weight distribution, and activity data in Table 1 appear to be inconsistent with the general relationship among molecular weight, rate of propagation (activity of polymerization), and rate of chain transfer. This may be ascribed to different numbers of active species depending on the kind of Zr complexes.

Polymerization of propylene catalyzed by the complexes is summarized in Table 1. Dinuclear complexes **3a**–**c** and **4a**–**c** exhibit higher catalytic activity than the mononuclear precursors **1a**–**c**. Molecular weights of the polypropylene formed by the reaction catalyzed by the dinuclear complexes are larger than those from the reactions by the mononuclear complexes. Complexes **2a** and **5a**, having fluorenyl groups in the ligand, form polymers with high molecular weight (M_n = 5800 and 7300, respectively). These results suggest that the dinuclear structure and the fluorenyl groups of the ligand retard chain transfer of the growing polymer and increase the relative rate between chain growth and chain transfer.

In summary, metathesis reaction was applied for coupling of mononuclear transition metal complexes to produce not only symmetrical homodinuclear complexes but also a heterobimetallic complex containing Zr and Fe centers. The Zr/Zr dinuclear complexes with a flexible bridging chain exhibit high catalytic activity. The Zr/Fe heterodinuclear complex is not deactivated by the polar COO group of the ligand and shows a catalytic activity similar to the mononuclear Zr complex. Similar cross metathesis reaction of hydrocarbon olefins and acrylic esters would provide various early-late heterodinuclear complexes with flexible bridging chains.

Experimental Section

General Methods. All manipulations of the air-unstable complexes were carried out under nitrogen or argon using standard Schlenk techniques. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl and stored under nitrogen or argon. CH_2Cl_2 were distilled from CaH_2 and stored under nitrogen or argon. MAO was purchased from TOSOH-FINECHEM and stored under nitrogen or argon. Zirconium tetrachloride and other chemicals were used as received from commercial suppliers. 9-Allylfluorene,[15a] 9-butenylfluorene,[15a] Li{$(C_5H_4)CH_2CH{=}CH_2$},[15b] and $CpZrCl_3$(dme) (dme = 1,2-dimethoxyethane)[22] were prepared according to the literature methods. Li{$(C_5H_4)CH_2CH_2CH{=}CH_2$} and Li{$(C_5H_4)CH_2CH_2CH_2CH{=}CH_2$} were synthesized in a manner similar to the preparation of Li{$(C_5H_4)CH_2CH{=}CH_2$}.[15b] NMR spectra (^{1}H and $^{13}C\{^1H\}$) were recorded on JEOL JNM LA-500 or Varian Mercury 300 spectrometers. Assignment of the NMR signals is shown in Chart 1.

Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. Gel permeation chromatography (GPC) was performed on a TOSOH HPLC-8121GPC/HT using orthodichlorobenzene (152 °C) as eluent for polyethylene and TOSOH HPLC-8220 using THF as eluent for polypropylene. Differential scanning calorimetry (DSC) was performed on a Seiko SSC-5200. Fast atom bombardment mass spectra (FABMS) were obtained from a JEOL JMS-700 (matrix, *m*-nitrobenzyl alcohol).

Preparation of $CpZrCl_2(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)$ (1a), $CpZrCl_2\{\eta^5\text{-}C_5H_4(CH_2)_2CH{=}CH_2\}$ (1b), and $CpZrCl_2\{\eta^5\text{-}C_5H_4(CH_2)_3CH{=}CH_2\}$ (1c). A mixture of Li{$(C_5H_4)CH_2CH{=}CH_2$} (208 mg, 1.9 mmol) and $CpZrCl_3$(dme) (dme = 1,2-dimethoxylehtane) (621 mg, 1.76 mmol) in toluene (20 mL) was stirred for 18 h at room temperature. A solid formed during the reaction was removed by filtration. The obtained colorless solution was evaporated to dryness to give **1a** as a colorless solid, which was washed with hexane (5 mL × 3) and

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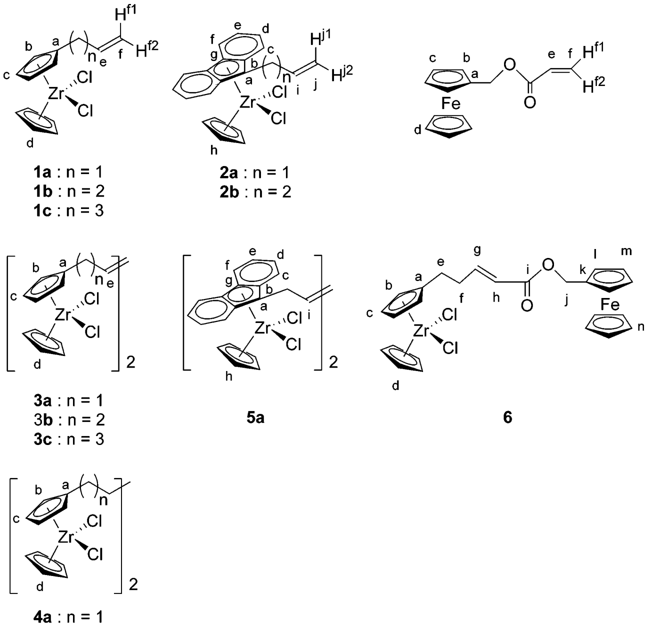
[20] (a) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853. (b) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.

[21] (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 4605.

[22] Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.

Chart 1



1a : n = 1
1b : n = 2
1c : n = 3

2a : n = 1
2b : n = 2

3a : n = 1
3**b** : n = 2
3c : n = 3

5a

6

4a : n = 1
4b : n = 2
4c : n = 3

dried under reduced pressure (322 mg, 55%). Anal. Calcd for $C_{13}H_{14}Cl_2Zr$: C, 46.98; H, 4.25; Cl, 21.33. Found: C, 46.91; H, 4.22; Cl, 21.47. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (s, 5H, H_d), 6.35 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 6.24 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 5.97 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^3J = 7 Hz, H_e), 5.25 (ddt, 1H, ^3J = 17 Hz, $^2J = {}^4J$ = 2 Hz, H_{f1}), 5.08 (ddt, 1H, ^3J = 10 Hz, $^2J = {}^4J$ = 2 Hz, H_{f2}), 3.42 (dt, 2H, ^3J = 7 Hz, ^4J = 2 Hz, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136.1 (s, C_e), 133.3 (s, C_a), 117.2 (s, $C_{b\text{ or }c}$), 117.0 (s, C_f), 115.9 (s, C_d), 113.1 (s, $C_{b\text{ or }c}$), 45.0 (s, CH_2).

1b and **1c** were obtained similarly in the respective yields of 69% and 67%. Data of **1b** are as follows. Anal. Calcd for $C_{14}H_{16}Cl_2Zr$: C, 48.54; H, 4.66; Cl, 20.47. Found: C, 48.95; H, 4.56; Cl, 20.66. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 5H, H_d), 6.32 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 6.24 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 5.81 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^3J = 6 Hz, H_e), 5.03 (dq, 1H, ^3J = 17 Hz, $^2J = {}^4J$ = 2 Hz, H_{f1}), 5.00 (m, 1H, H_{f2}), 2.76 (t, 2H, ^3J = 7 Hz, CH_2), 2.32 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.4 (s, C_e), 135.4 (s, C_a), 117.4 (s, $C_{b\text{ or }c}$), 115.9 (s, C_d), 115.3 (s, C_f), 112.7 (s, $C_{b\text{ or }c}$), 34.5 (s, CH_2), 29.5 (s, CH_2). Data of **1c** are as follows. Anal. Calcd for $C_{15}H_{18}Cl_2Zr$: C, 49.99; H, 5.03; Cl, 19.67. Found: C,49.99; H, 5.23; Cl, 20.05. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 5H, H_d), 6.33 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 6.23 (t, 2H, J = 3 Hz, $H_{b\text{ or }c}$), 5.80 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^3J = 7 Hz, H_e), 5.02 (m, 1H, H_{f1}), 4.97 (m, 1H, H_{f2}), 2.65 (t, 2H, ^3J = 8 Hz, CH_2), 2.08 (q, 2H, ^3J = 8, CH_2), 1.66 (quint, 2H, ^3J = 8, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.4 (s, C_e), 135.4 (s, C_a), 117.4 (s, $C_{b\text{ or }c}$), 115.9 (s, C_d), 115.3 (s, C_f), 112.8 (s, $C_{b\text{ or }c}$), 33.5 (s, CH_2), 30.0 (s, CH_2), 29.8 (s, CH_2).

Preparation of $CpZrCl_2(\eta^5\text{-}C_{13}H_8CH_2CH{=}CH_2)$ (2a) and $CpZrCl_2\{\eta^5\text{-}C_{13}H_8(CH_2)_2CH{=}CH_2\}$ (2b). To a solution of 9-allylfluorene (1.25 g, 6.0 mmol) in Et_2O (30 mL) was added *n*-BuLi in hexane (1.6 M, 4.10 mL, 6.6 mmol) dropwise at −78 °C. The mixture was stirred for 6 h at room temperature. After the solution of allylfluorenide was frozen by cooling with liquid N_2, $CpZrCl_3(dme)$ (2.10 g, 6.0 mmol) was added. The reaction mixture was gently warmed to room temperature and stirred for 36 h. The volatiles were evaporated, and the resulting residue was extracted with toluene. The product was recrystallized from toluene/hexane to give **2a** (1.66 g, 65%). Anal. Calcd for $C_{21}H_{18}Cl_2Zr$: C, 58.32; H, 4.20; Cl, 16.39. Found: C, 58.13; H, 4.35; Cl, 16.55. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (dt, 2H, ^3J = 8 Hz, $^4J = {}^5J$ = 1 Hz, H_c), 7.68 (dt, 2H, ^3J = 8 Hz, $^4J = {}^5J$ = 1 Hz, H_f), 7.68 (ddd, 2H, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, $H_{d\text{ or }e}$), 7.36 (ddd, 2H, ^3J = 17 Hz, ^3J = 10 Hz, ^3J = 6 Hz, $H_{d\text{ or }e}$), 5.95 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^4J = 6 Hz, H_i), 5.83 (s, 5H, H_h), 5.01 (dq, 1H, ^3J = 10 Hz, $^2J = {}^4J$ = 2 Hz, H_{j2}), 4.98 (dq, 1H, ^3J = 17 Hz, $^2J = {}^4J$ = 2 Hz, H_{j1}), 3.92 (dt, 2H, ^3J = 6 Hz, ^4J = 2 Hz, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.6 (s, $C_{b\text{ or }g}$), 130.9 (s, $C_{b\text{ or }g}$), 127.6 (s, $C_{d\text{ or }e}$), 125.1 (s, $C_{c\text{ or }f}$), 124.0 (s, $C_{c\text{ or }f}$), 123.8 (s, $C_{d\text{ or }e}$), 118.0 (s, C_i), 115.8 (s, C_j), 117.2 (s, C_h), 100.7 (s, C_a), 30.6 (s, CH_2).

2b was prepared similarly in 49% yield. Anal. Calcd for $C_{22}H_{20}Cl_2Zr$: C, 59.18; H, 4.52; Cl, 15.88. Found: C, 59.25; H, 4.69; Cl, 16.24. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (dt, 2H, ^3J = 8 Hz, $^4J = {}^5J$ = 1 Hz, $H_{c\text{ or }f}$), 7.69 (dt, 2H, ^3J = 8 Hz, $^4J = {}^5J$ = 1 Hz, $H_{c\text{ or }f}$), 7.47 (ddd, 2H, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, $H_{d\text{ or }e}$), 7.36 (ddd, 2H, ^3J = 8 Hz, ^3J = 7 Hz, ^3J = 1 Hz, $H_{d\text{ or }e}$), 5.86 (ddt, 1H, ^3J = 17 Hz, ^3J = 10 Hz, ^4J = 7 Hz, H_i), 5.83 (s, 5H, H_h), 5.04 (dq, 1H, ^3J = 17 Hz, $^2J = {}^4J$ = 2 Hz, H_{j1}), 4.96 (ddt, 1H, ^3J = 10 Hz, ^2J = 2, ^4J = 1 Hz, H_{j2}), 3.27 (t, 2H, ^3J = 8 Hz, CH_2), 2.38 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.7 (s, $C_{b\text{ or }g}$), 131.4 (s, $C_{b\text{ or }g}$), 128.4 (s, $C_{d\text{ or }e}$), 126.1 (s, $C_{c\text{ or }f}$), 125.0 (s, $C_{d\text{ or }e}$), 124.7 (s, $C_{c\text{ or }f}$), 119.0 (s, C_i), 118.1 (s, C_h), 116.6 (s, C_j), 104.1 (s, C_a), 32.5 (s, CH_2), 23.6 (s, CH_2).

Metathesis Reaction of 1a to Synthesize $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2CH{=}CHCH_2C_5H_4\}$ (3a) and $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_2CH{=}CH(CH_2)_2C_5H_4\}$ (3b). A toluene (4.1 mL) solution of **1a** (81.7 mg, 0.25 mmol) and $Cl_2Ru({=}CHPh)\{\overline{CN(Mes)CH_2CH_2N}(Mes)\}(PCy_3)$ (10.4 mg, 12 μmol) was stirred for 12 h at room temperature. During the reaction, a white solid was separated from the solution. The solid was collected by filtration, washed with toluene (1 mL × 2) and hexane (4 mL × 2), and dried under reduced pressure to give **3a** (60.3 mg, 76%). Anal. Calcd for $C_{24}H_{24}Cl_4Zr_2$: C, 45.27; H, 3.80; Cl, 22.27. Found: C, 44.91; H, 3.73; Cl, 21.83. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 10H, H_d), 6.34 (t, 4H, J = 3, $H_{b\text{ or }c}$), 6.23 (t, 4H, J = 3, $H_{b\text{ or }c}$), 5.62 (m, 2H, H_e), 3.41 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 137.4 (s, C_e), 134.5 (s, C_a), 117.2 (s, $C_{b\text{ or }c}$) 115.6 (s, C_d), 112.4 (s, $C_{b\text{ or }c}$), 34.5 (s, CH_2), 29.5 (s, CH_2).

3b was obtained similarly in 86% yield. Aanal. Calcd for $C_{26}H_{28}Cl_4Zr_2$: C, 46.98; H, 4.25; Cl, 21.33. Found: C, 46.86; H, 4.41; Cl, 21.34. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 10H, H_d), 6.32 (t, 4H, J = 3, $H_{b\text{ or }c}$), 6.21 (t, 4H, J = 3, $H_{b\text{ or }c}$), 2.66 (m, 4H, CH_2), 1.60 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.1 (s, C_a), 117.1 (s, $C_{b\text{ or }c}$) 115.6 (s, C_d), 112.4 (s, $C_{b\text{ or }c}$), 30.0 (s, CH_2), 29.8 (s, CH_2).

Preparation of $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\ \eta^5\text{-}C_5H_4(CH_2)_3CH{=}CH(CH_2)_3C_5H_4\}$ (3c). A toluene (6.6 mL) solution of **1c** (142.4 mg, 0.40 mmol) and $Cl_2Ru({=}CHPh)\{\overline{CN(Mes)CH_2CH_2N}(Mes)\}(PCy_3)$ (16.8 mg, 20 μmol) was stirred for 9 h at room temperature. The reaction mixture was evaporated to dryness. The brown residue was washed with Et_2O (5 mL × 3) and with toluene (5 mL × 2). The resultant white solid was dried under reduced pressure to give **3c** (28.2 mg). Additional **3c** (49.3 mg) was obtained from crystallization (toluene/hexane) of the material obtained by evaporation of the toluene filtrate. Total yield: 77.5 mg, 57%. Anal. Calcd for $C_{28}H_{32}Cl_4Zr_2$: C, 48.54; H, 4.66; Cl, 20.47. Found: C, 48.56; H, 4.51; Cl, 20.46. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.64 (s, 10H, H_d), 6.32 (t, 4H, J = 3 Hz, $H_{b\text{ or }c}$), 6.23 (t, 4H, J = 3 Hz, $H_{b\text{ or }c}$), 5.34 (m, 2H, H_e), 2.64 (t, 4H, ^3J = 8 Hz, CH_2), 2.03 (m, 4H, CH_2), 1.62 (quint, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.6 (s, C_a), 130.5 (s, C_e), 117.4 (s, $C_{b\text{ or }c}$), 115.9 (s, C_d), 112.9 (s, $C_{b\text{ or }c}$), 32.3 (s, CH_2), 30.5 (s, CH_2), 29.7 (s, CH_2).

Preparation of $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_4C_5H_4\}$ (4a), $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_6C_5H_4\}$ (4b), and $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_2)_8C_5H_4\}$ (4c). To a solution of **3a** (50.3 mg, 0.079 mmol) in CH_2Cl_2 (15 mL) was added Pd/C (10% palladium, 30 mg). Hydrogen was passed through the mixture at 1 atm with stirring for 3 h. The catalyst was removed by filtration, and the solvent was evaporated to dryness under reduced pressure. The residue was washed with hexane (5 mL × 3) and dried under reduced pressure to give **4a** (31.8 mg, 63%). Anal. Calcd for $C_{24}H_{26}Cl_4Zr_2$: C, 45.13; H, 4.10; Cl, 22.20. Found: C, 44.70; H, 3.93; Cl, 21.83. ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 10H, H_d), 6.32 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 6.21 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 2.66 (m, 4H, CH_2), 1.60 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.1 (s, C_a), 117.1 (s, $C_{b\ or\ c}$) 115.6 (s, C_d), 112.4 (s, $C_{b\ or\ c}$), 30.0 (s, CH_2), 29.8 (s, CH_2).

4b and **4c** were obtained similarly in the respective yields of 69% and 58%. Data of **4b** are as follows. Anal. Calcd for $C_{26}H_{30}Cl_4Zr_2$: C, 46.83; H, 4.53; Cl, 21.27. Found: C, 46.29; H, 4.36; Cl, 21.47. ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 10H, H_d), 6.32 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 6.21 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 2.66 (m, 4H, CH_2), 1.60 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 135.5 (s, C_a), 117.1 (s, $C_{b\ or\ c}$) 115.6 (s, C_f), 112.5 (s, $C_{b\ or\ c}$), 30.3 (s, CH_2), 30.1 (s, CH_2), 28.9 (s, CH_2). Data of **4c** are as follows. Anal. Calcd for $C_{28}H_{34}Cl_4Zr_2$: C, 48.40; H, 4.93; Cl, 20.41. Found: C, 48.19; H, 4.70; Cl, 20.55. ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 10H, H_d), 6.32 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 6.22 (t, 4H, $J = 3$, $H_{b\ or\ c}$), 2.62 (t, 4H, $J = 8$ CH_2), 1.54 (m, 4H, CH_2), 1.28 (m, 8H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 117.3 (s, $C_{b\ or\ c}$) 115.8 (s, C_f), 112.8 (s, $C_{b\ or\ c}$), 30.8 (s, CH_2), 30.3 (s, CH_2), 29.4 (s, CH_2), 29.4 (s, CH_2).

Preparation of $(CpZrCl_2)_2\{\mu\text{-}\eta^5,\eta^5\text{-}C_{13}H_8CH_2CH{=}CHCH_2C_{13}H_8\}$ (5a). A toluene (2.5 mL) solution of **2a** (63.5 mg, 0.15 mmol) and $Cl_2Ru({=}CHPh)\{\overline{CN(Mes)CH_2CH_2N}(Mes)\}(PCy_3)$ (6.4 mg, 7.5 μmol) was stirred for 6 h at room temperature. An orange solid, separated from the solution, was collected by filtration, washed with toluene (1 mL × 2) and hexane (1 mL × 2), and dried under reduced pressure to give **5a** (60.2 mg, 96%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (m, 4H, $H_{c\ or\ f}$), 7.54 (m, 4H, $H_{c\ or\ f}$), 7.33 (m, 8H, $H_{d,\ e}$), 5.75 (s, 10H, H_h), 5.66 (m, 2H, H_i), 3.82 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 130.7 (s, $C_{b\ or\ g}$), 129.1 (s, $C_{b\ or\ g}$) 127.5 (s, $C_{d\ or\ e}$), 125.0 (s, $C_{c\ or\ f}$), 124.0 (s, $C_{c\ or\ f}$), 123.7 (s, $C_{d\ or\ e}$), 118.0 (s, C_a), 117.1 (s, C_h), 101.2 (s, C_i), 29.3 (s, CH_2).

Preparation of $CpFe(\eta^5\text{-}C_5H_4CH_2OOCCH{=}CH_2)$. To a solution of $CpFe(\eta^5\text{-}C_5H_4CH_2OH)$ (1.08 g, 5.0 mmol) in CH_2Cl_2 (16 mL) and NEt_3 (1.4 mL) was added acryloyl chloride (0.480 mL, 6.0 mmol) at 0 °C. After stirring the mixture for 15 min at 0 °C, an aqueous solution of $NaHCO_3$ was added. The mixture was extracted with ethyl acetate and dried over $MgSO_4$. The product was purified by chromatography on silica gel with hexane/ethyl acetate (10:1) as an eluent. The solvent was removed at reduced pressure to give ferrocenylmethyl acrylate as an orange solid (581 mg, 43%). FABMS *m/z* calcled for $C_{14}H_{14}O_2Fe$: 270.0343. Found: 270.0325. ^1H NMR (300 MHz, $CDCl_3$): δ 6.41 (dd, 1H, $^3J = 17$ Hz, $^2J = 2$ Hz, H_{f1}), 6.11 (dd, 1H, $^3J = 17$ Hz, $^3J = 10$ Hz, H_e), 5.81 (dd, 1H, $^3J = 11$ Hz, $^2J = 2$ Hz, H_{f2}), 4.98 (s, 5H, H_d), 4.30 (t, 2H, $J = 3$ Hz, $H_{b\ or\ c}$), 4.19 (t, 2H, $J = 3$ Hz, $H_{b\ or\ c}$), 4.17 (s, 5H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.9 (s, CO), 130.7 (s, $C_{e\ or\ f}$) 128.4 (s, $C_{e\ or\ f}$), 81.2 (s, C_a), 69.5 (s, $C_{b\ or\ c}$), 68.7 (s, $C_{b\ or\ c}$), 62.8 (s, CH_2), 117.1 (s, C_h), 101.2 (s, C_i), 29.3 (s, CH_2).

Preparation of $CpZrCl_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2CH_2CH{=}CHCOOCH_2C_5H_4)FeCp$ (6). A toluene (2.0 mL) solution of **1b** (41.3 mg, 0.12 mmol), ferrocenylmethyl acrylate (64.9 mg, 0.24 mmol), and $Cl_2Ru({=}CHPh)\{\overline{CN(Mes)CH_2CH_2N}(Mes)\}(PCy_3)$ (5.1 mg, 6.0 μmol) was stirred for 24 h at room temperature. The orange solution was evaporated and the residue was washed with hexane (1 mL × 3). Crystallization of the toluene extracts from toluene/hexane gave **6** (58.9 g, 84%). Anal. Calcd for $C_{26}H_{26}Cl_2FeO_2Zr$: C, 53.07; H, 4.45; Cl, 12.05. Found: C, 52.83; H, 4.48; Cl, 11.89. ^1H NMR (300 MHz, $CDCl_3$): δ 6.95 (dt, 1H, $J_3 = 16$ Hz, $J_3 = 7$ Hz, H_g), 6.46 (s, 5H, H_d), 6.31 (t, 2H, $J = 3$ Hz, $H_{b\ or\ c}$), 6.20 (t, 2H, $J = 3$ Hz, $H_{b\ or\ c}$), 5.81 (dt, 1H, $J_3 = 16$ Hz, $J_4 = 2$ Hz, H_h), 4.94 (s, 2H, $J_3 = 2$ Hz, H_j), 4.28 (s, 2H, $J_3 = 2$ Hz, H_j), 4.17 (s, 2H, $J_3 = 2$ Hz, H_j), 4.16 (s, 5H, H_n), 2.82 (t, 2H, $^3J = 8$ Hz, H_e), 2.24 (m, 2H, H_f). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.1 (s, C_i)147.7 (s, C_g), 133.5 (s, C_a), 122.3 (s, C_h), 117.3 (s, $C_{b\ or\ c}$), 115.7 (s, C_d), 112.1 (s, $C_{b\ or\ c}$), 69.5 (s, $C_{l\ or\ m}$), 68.7 (s, $C_{l\ or\ m}$), 68.5 (s, C_n), 62.6 (s, C_j),32.6 (s, C_f), 30.2 (s, C_e).

Table 2. Crystallographic Data and Details of Refinement of 2a, 2b, and 5a

	2a	**2b**	**5a**
empirical formula	$C_{21}H_{18}Cl_2Zr$	$C_{22}H_{20}Cl_2Zr$	$C_{40}H_{32}Cl_4Zr_2$
fw	432.50	446.53	836.94
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/a$ (No. 14)
a, Å	8.605(2)	10.383(2)	9.221(4)
b, Å	11.369(3)	11.417(2)	12.772(6)
c, Å	18.087(5)	15.731(3)	14.443(6)
β, deg	96.885(4)		91.413(7)
V, Å^3	1756.9(8)	1864.7(7)	1700(1)
Z	4	4	2
μ, cm^{-1}	9.28	8.77	9.56
F(000)	872	904	840
D_{calcd}, g cm^{-1}	1.635	1.590	1.634
cryst size, mm	0.5 × 0.5 × 0.2	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.2
exposure rate, s/deg	90.0	20.0	120.0
no. of data	12 891	13 669	25 730
no. of unique data	3980	2379	3790
no. of obsd data ($I > 3\sigma(I)$)	3090	2294	2608
no. of variables	235	306	272
$R(F_o)$	0.025	0.023	0.041
$R_w(F_o)$	0.039	0.032	0.048
GOF	1.014	0.886	0.780

Crystal Structure Determination. Crystals were mounted in glass capillary tubes under Ar. The data were collected at a temperature of −160 ± 1 °C to a maximum 2θ value of 55.0° on Rigaku Saturn CCD area detector. Calculations were carried out by using the program package CrystalStructure for Windows. The structure was solved by direct methods and expanded using Fourier techniques. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotoropic thermal parameters. Atomic scattering factors were obtained from the literature.[23] Crystallographic data and details of refinement of the complexes are summarized in Table 2.

Polymerization of Ethylene. A typical experimental procedure is as follows. To a solution of **2a** (4.3 mg, 0.01 mmol) in toluene (6.4 mL) was added a toluene solution of MAO (2.79 M Al, 3.6 mL, 10 mmol Al). The catalyst solution (1.0 mM Zr) was stirred at room temperature for 15 min for the preactivation. To a toluene (30 mL) solution saturated with ethylene (1 atm) was added the solution of the catalyst (0.50 mL, 0.50 μmol). The solution was stirred for 5 min under atmospheric ethylene at 15 °C. The reaction was quenched with MeOH and 5 M HCl/MeOH. The separated polyethylene solid was filtrated, washed with MeOH, H_2O, and hexane, and dried in vacuo. In the case of Zr dinuclear catalyst, 0.25 μmol of catalyst was used.

Polymerization of Propylene. A typical experimental procedure is as follows. To a solution of **2a** (4.3 mg, 0.01 mmol) in toluene (6.4 mL) was added a toluene solution of MAO (2.79 M Al, 3.6 mL, 10 mmol Al). The catalyst solution (1.0 mM Zr) was stirred at room temperature for 15 min for the preactivation. To a toluene (25 mL) solution saturated with propylene (1 atm) was added the solution of the catalyst (5.0 mL, 5.0 μmol). The solution was stirred for 1 h under atmospheric propylene at room temperature. The reaction was quenched with MeOH and 5 M HCl/MeOH. The organic phase was separated and washed with H_2O and brine and dried over

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(23) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

$MgSO_4$. The volatile was removed and dried under reduced pressure over 6 h. In the case of Zr dinuclear catalyst, 2.5 μmol of catalyst was used.

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Supporting Information Available: Crystallographic data of **2a**, **2b**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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