Olefin Polymerization Using Highly Congested *ansa*-Metallocenes under High Pressure: Formation of Superhigh Molecular Weight Polyolefins

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ABSTRACT: Polymerization of 1-hexene or 1-octene under high pressures (100−1000 MPa) was investigated using permethylated *ansa*-metallocenes/methylaluminoxane (MAO) as catalyst systems. Besides the known zirconocene complex (**1**, $Me_2Si(\eta^5\text{-}C_5Me_4)_2ZrCl_2$), dialkylsilylene- and dimethylgermylene-bridged hafnocene dichlorides, $R_2E(\eta^5\text{-}C_5Me_4)_2HfCl_2$ (**2**, R = Me, E = Si; **3**, R = Et, E = Si; **4**, R = vinyl, E = Si; **5**, R = Me, E = Ge), were synthesized and structurally characterized. The catalytic activity of the *ansa*-metallocenes was remarkably enhanced under high pressures despite their very congested structures. Poly(1-hexene) with unprecedented high molecular weight such as $M_w = 1.02 \times 10^7$ ($M_w/M_n = 3.79$, by GPC) was obtained under 750 MPa with **2**. Studies on termination reactions revealed that the bimolecular chain-transfer process (β-hydrogen transfer to olefin) is much accelerated under 500 MPa in **1**, while β-hydrogen elimination to metal is still major termination process in **2**. This indicated that two complexes that have same structure but central metals showed quite different high-pressure effects.

Introduction

Metallocene-catalyzed olefin polymerization under high pressure has recently attracted research interest since a high-pressure polymerization process seems favorable for the industrial utilization of the homogeneous catalyst systems.[1] There have been a number of reports on high-pressure olefin polymerization using group 4 metallocene catalysts.[2] Most of them, however, described investigation under less than 200 MPa. Moreover, the dependence of catalytic activity or molecular weight on various pressures has not been well described. The pressure effect on reactions is governed by activation volumes of the reactions. If two catalysts have very similar structures, it is likely that they show similar high-pressure effects on their catalytic reactivity. To our surprise, however, the present study revealed that two metallocenes of almost identical structures, $Me_2Si(\eta^5\text{-}C_5Me_4)_2ZrCl_2$ (**1**) and $Me_2Si(\eta^5\text{-}C_5Me_4)_2HfCl_2$ (**2**), showed significantly different pressure effects.

Recently we reported remarkable effects of high pressure up to 1500 MPa on metallocene-catalyzed olefin polymerization.[3] The catalytic activities of *non*-bridged group 4 metallocenes were dramatically enhanced by high pressures, and polyhexene of very high molecular weight was given (M_w = 3 380 000 by GPC, $M_w/M_n = 2.70$ by $(\eta^5\text{-}C_5Me_4)_2HfCl_2$/MAO at 250 MPa).[3a] These results prompted us to investigate possibility of preparation of superhigh molecular weight polyolefins under high pressures. Synthesis of linear polyolefins of superhigh molecular weight is one of the important subjects to pursue.

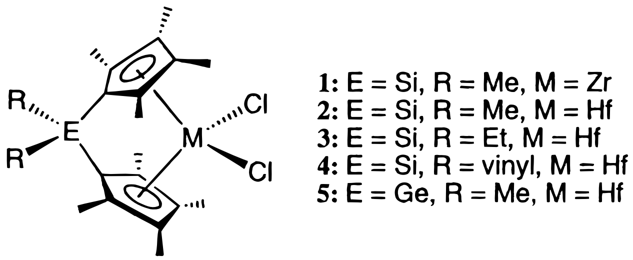

Figure 1. *ansa*-Permethylmetallocene complexes.

Herein we wish to report the remarkable effect of pressure on enhancement of the catalytic activity of sterically congested *ansa*-metallocene complexes and the formation of polyhexene of very high molecular weight ($\geq 1.0 \times 10^7$ by GPC). We also describe the influence of pressure on the termination process in the polymerization reactions examined with the *ansa*-zirconocene **1** and the *ansa*-hafnocene complex **2**, which showed unexpected differences in the catalytic behavior between these two complexes.

Results and Discussion

Syntheses and Structure of Permethylated *ansa*-Metallocene Complexes. In this study, we employed dialkylsilylene- (**1**−**3**), divinylsilylene- (**4**), and dimethylgermylene-bridged (**5**) bis(tetramethylcyclopentadienyl)zirconocene and hafnocene compexes shown in Figure 1.[4] All the hafnocenes **2**−**5** are novel complexes. The ligands, dialkylbis(tetramethylcyclopendadienyl)silanes (**6**, **7**) and a -germane (**8**), were prepared by the modified method of Jutzi and co-workers.[5] In 1,2-dimethoxyethane as a solvent, a reaction of 2 equiv of lithiated tetramethylcyclopentadiene and Me_2SiCl_2 readily took place in the presence of 1 equiv of hexamethylphosphoric triamide (HMPA) to give **6** in a good yield in 2 h at 50 °C (eq 1). The divinylsilylene derivative

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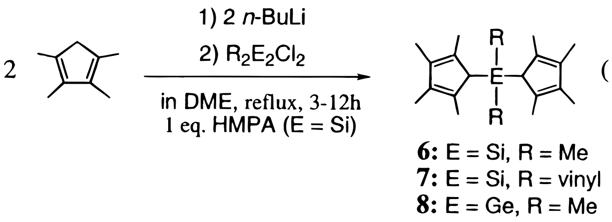
Table 1. Polymerization of 1-Hexene under High Pressures Catalyzed by *ansa*-Metallocene/MAO[a]

						GPC		MALLS
run	catalyst	μmol	pressure/MPa	yield/g	catalytic activity[b]	M_w[c]	M_w/M_n[c]	M_w[d]
1	**1**	0.2	0.1	0.54	1.35	133 000	2.11	
2		0.02	100	1.78	44.3	600 000	2.34	
3		0.02	250	4.43	110.8	2 090 000	2.71	
4		0.01	500	5.27	263.5	2 730 000	3.97	
5		0.01	750	3.43	171.5	1 630 000	3.78	
6	**2**	0.2	0.1	0.42	1.05	385 000	1.64	
7		0.05	100	0.68	1.70	1 25 000	2.33	
8		0.05	250	2.39	23.9	6 990 000	3.45	
9		0.05	500	2.62	26.2	8 460 000	3.90	
10		0.05	750	2.24	22.4	10 200 000	3.79	$(6.0 \pm 0.7) \times 10^6$
11	**3**	0.2	0.1	0.27	0.68	225 000	1.57	
12		0.2	100	0.58	1.46	771 000	2.08	
13		0.05	250	1.65	16.5	3 780 000	2.09	$(3.65 \pm 0.3) \times 10^6$
14		0.03	500	1.96	32.7	7 870 000	2.41	$(5.27 \pm 0.6) \times 10^6$
15		0.05	750	0.38	3.80	1 880 000	2.15	$(1.64 \pm 0.09) \times 10^6$
16	**4**	0.2	0.1	0.42	1.05	478 000	2.22	
17		0.2	100	0.43	1.08	805 000	2.12	
18		0.1	250	0.46	2.30	2 320 000	2.58	
19		0.05	500	1.37	13.7	8 450 000	3.86	
20		0.05	750	0.70	7.00	5 020 000	2.97	
21		0.05	1000	0.84	8.40	4 750 000	4.06	
22	**5**	0.2	0.1	0.24	0.60	132 000	1.79	
23		0.2	100	0.39	0.98	528 000	2.05	
24		0.05	250	3.38	33.8	3 360 00	1.87	
25		0.02	500	3.74	93.5	8 120 000	3.03	
26		0.05	750	4.85	48.5	8 380 000	2.09	
27		0.05	1000	1.20	12.0	4 400 000	3.87	

[a] Al/metal = 10 000, room temperature, 2 h. [b] $\times 10^6$ g of PH/(mol of M h). [c] Determined by GPC. [d] Determined by multiangle laser light scattering analysis.

7 was prepared similarly. Dimethylbis(tetramethylcyclopendadienyl)germane (**8**) could be prepared without HMPA. The diethylsilylene-bridged complex **3** was prepared by palladium-catalyzed hydrogenation of **4**.[6] All the complexes **1**−**5** were structurally characterized by X-ray diffraction analysis (vide infra).



(1)

Polymerization of Higher α-Olefins under High Pressure. In the polymerization reactions, the amount of catalysts was adjusted to keep the monomer conversions ≤20% in most cases so that reaction temperature did not become highly elevated. The results of polymerization of 1-hexene under high pressure using **1**−**5** as catalyst precursors are shown in Table 1.

Catalytic activity of the bridged metallocenes for the polymerization was surprisingly enhanced due to high pressure despite their very congested structure. Even hafnium complexes, which are known to be less effective for olefin polymerization than zirconocenes,[7] exhibited very high activity. It was 200-fold enhanced at 500 MPa in **1** and 150-fold in **5** compared to at atmospheric pressure. It is in a sharp contrast with the results of mono-, di- and trimethyl-substituted *ansa*-metallocenes, $Me_2Si(\eta^5\text{-}C_5H_{4-n}Me_n)_2ZrCl_2$ ($n = 1-3$), in which high pressures made their catalytic activity only twice those observed at atmospheric pressure.[3c]

The molecular weight of the polyhexene obtained at high pressure was about 20−60-fold higher compared to at 0.1 MPa in all catalysts. It is noteworthy that all hafnocene complexes **2**−**5** gave polyhexene whose weight-average molecular weight was 8.0×10^6 by GPC. In particular, **2** gave the polymer of $M_w = 1.02 \times 10^7$, which is an unprecedented high molecular weight as linear homopolymers of higher α-olefins. Distribution of molecular weight M_w/M_n was often slightly larger than 2.0 especially when M_w was $>1.0 \times 10^6$. This is probably due to polymerization during elevating and releasing pressures.[8] Since those values were determined by GPC using monodispersed polystyrene as standards, several samples were examined by multiangle light scattering analysis (MALLS) in order to determine accurate values of M_w. These values are shown in Table 1. They are consistent with the data obtained with GPC when M_w was less than 4×10^6, while M_w(MALLS) were smaller than M_w(GPC) when M_w(GPC) were larger than 7.0×10^6. This discrepancy may be due to limitation of ability of the GPC columns to determine the correct values of very high molecular weight. Nevertheless, MALLS analysis supported the formation of very high molecular weight polyhexene ($M_w = 6.0 \times 10^6$, run 10). Kakugo, Miyatake, and co-workers reported that sulfur-bridged bis(phenoxy)titanium chlorides/methylaluminoxane systems catalyzed polymerization of olefins to give atactic polypropylene[9] of $M_w > 8 \times 10^6$ and polyhexene[10] of $M_w > 5 \times 10^6$. Bochmann and co-workers reported formation of atactic polypropylene with M_w values of 4×10^6 catalyzed by $Cp^*TiMe_3/B(C_6F_5)_3$.[11] To the best of our knowledge, these are the examples of polyolefins with the highest molecular weight which have been produced by homogeneous Ziegler−Natta catalysts.

We previously reported that the catalytic activity of $(C_5H_{5-n}Me_n)_2ZrCl_2$ at 250 MPa increased in the order of the number of methyl groups.[3a] Comparison of the results in the present study with those of our previous study on *ansa*-metallocenes leads to the conclusion that a similar trend exists in the bridged metallocene

Table 2. Polymerization of 1-Octene under High Pressures Catalyzed by *ansa*-Hafnocene/MAO[a]

run	catalyst	μmol	pressure/MPa	yield/g	catalytic activity[b]	M_w[c]	M_w/M_n[c]
28	**4**	0.5	0.1	0.58	0.58	262 000	2.71
29		0.2	100	0.46	1.15	1 000 000	2.98
30		0.1	250	0.32	1.60	1 770 000	2.37
31		0.05	500	0.39	3.90	2 730 000	3.59
32		0.1	750	0.35	1.76	1 710 000	2.71
33	**5**	0.1	0.1	0.12	1.20	179 000	1.80
34		0.2	630	0.93	2.33	4 390 000	4.93

[a] Al/metal = 10 000, room temperature, 2 h. [b] $\times 10^6$ g of PH/(mol of M h). [c] Determined by GPC.

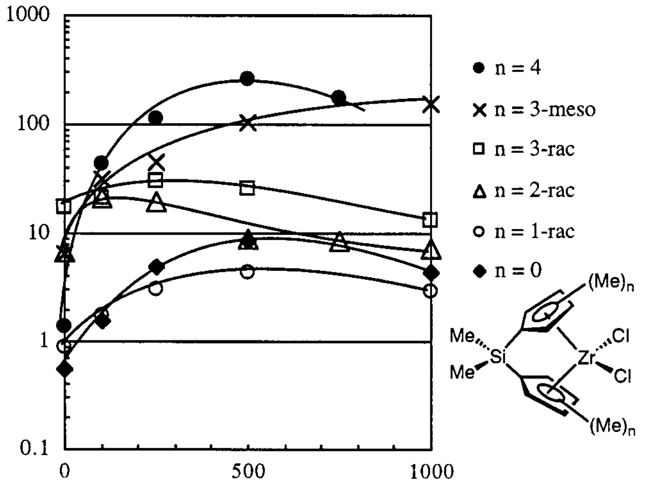


Figure 2. Catalytic activity of methyl-substituted *ansa*-zirconocenes. The values of catalytic activities were obtained with experimental errors of at most ±30%, mostly <±15% (see the Supporting Information).

catalyzed system (Figure 2). The activity of $Me_2Si(\eta^5\text{-}C_5H_{4-n}Me_n)_2ZrCl_2$ ($n = 0-4$) under 250 MPa was in the order *rac*-$Me_1 \approx Me_0 <$ *rac*-$Me_2 <$ *rac*-$Me_3 <$ *meso*-$Me_3 < Me_4$ (Figure 2), although the order at 0.1 MPa was $Me_0 <$ *rac*-$Me_1 < Me_4 <$ *meso*-$Me_3 \approx$ *rac*-$Me_2 <$ *rac*-Me_3. The electronic factor of the substituents might explain the tendency under high pressure. These results imply the possibility that high pressure may overcome some steric hindrance of the complex.

The germylene-bridged metallocene **5** exhibited much higher catalytic activity than the silylene-bridged complexes **2**−**4** at high pressure, although its activity at atmospheric pressure was lower than **2**−**4**. There have been a few reports on the germylene- and stannylene-bridged zirconocenes.[12] In the present study **5** showed 4 times higher activity than **2** at 500 MPa. It is noteworthy that the difference was observed only under high-pressure conditions. The X-ray diffraction analysis of **2** and **5** revealed that these two complexes are nearly isostructural, and only slight differences were observed around the bridge parts.[13] ^1H and ^{13}C NMR spectroscopy gave very similar spectra for **2** and **5**. The significant differences in their behavior under high pressures might be due to some change of their structural conformation of the active species under high pressures.

The results of the polymerization of 1-octene showed significant differences from 1-hexene (Table 2). The enhanced catalytic activity due to high pressure was only 6.7 times in **4**. The obtained poly(1-octene) had smaller M_w than the polyhexene. Attempt of polymerization of 1-dodecene with **4** at 500 MPa gave only a small amount of viscous polymer (activity: 0.11×10^6 g of polymer/(mol of Hf h), $M_w = 83\ 200$, $M_w/M_n = 1.65$). Although the reasons for these differences are not clear yet, it is probably due to larger steric hindrance of the hexyl and decyl groups in 1-octene, 1-dodecene, and their polymers. A little larger steric factor seems to change drastically the situation of the reactions.

Termination Processes under High Pressure. As discussed above, permethylated *ansa*-hafnocenes gave the polyhexene of very high molecular weight. At 500 MPa, the zirconocene complex **1** showed 200 times higher activity relative to that at 0.1 MPa, while the molecular weights of the polymers obtained at 500 MPa were only 20-fold higher than that at 0.1 MPa. Enhancement of the molecular weight was much smaller (only one-tenth) than the acceleration of the polymerization rate. On the contrary, the hafnocene complex **2** exhibited 25-fold higher activity and produced polyhexene of 22-fold higher molecular weight at 500 MPa. The enhancement of the molecular weight was comparable to the acceleration of the polymerization in **2**. These observations showed that high pressure affected differently the zirconocene and the hafnocene complexes. X-ray diffraction analysis of **1** and **2**, however, indicated that they were almost isostructural.[14] These results led us to investigate termination processes in the olefin polymerization on **1** and **2** according to the method that Brintzinger and co-workers have reported.[15] It is known that two major termination processes in olefin polymerization catalysts are (i) β-hydrogen elimination to the metal that is a unimolecular process and (ii) bimolecular β-hydrogen transfer to the olefin (Scheme 1). Dependence of molecular weight on monomer concentration gave the information about these termination processes. Plotting reciprocal number-average polymerization degree ($1/P_N$) versus reciprocal monomer concentration (1/[M]) gives the ratio k_{TM}/k_P as the slopes and k_{TO}/k_P as the *y*-axis intercepts, where k_{TM}, k_{TO}, and k_P are the rate constant of β-hydrogen elimination to metal, β-hydrogen transfer to olefin, and propagation, respectively. Each complex was studied under 0.1 and 500 MPa (Figure 3). The zirconocene **1** and the hafnocene **2** behave similarly under 0.1 MPa as described in (a). The ratio of the rate constants of β-hydrogen elimination to metal and β-hydrogen transfer to olefin (k_{TM}/k_{TO}) in 1-hexene polymerization by **1** and **2** was 8.8 and 7.0, respectively, indicating that β-hydrogen elimination is a major termination process in both complexes in diluted solutions. On the contrary, their behavior under 500 MPa was significantly different (b). The ratio k_{TM}/k_{TO} drastically changed and was 0.88 in zirconocene **1**. Assuming that β-hydrogen elimination is not very much retarded by high pressure, we may conclude that the β-hydrogen transfer to olefin is accelerated due to high pressure. It is acceptable that the bimolecular termination process is accelerated by high pressure.[16] This result is consistent with the fact that the enhancement of M_w at 500 MPa was much smaller than that of the polymerization rate in **1**. In hafnocene **2**, on the other hand, k_{TM}/k_{TO} was 4.9 at 500 MPa, showing that β-hydrogen transfer

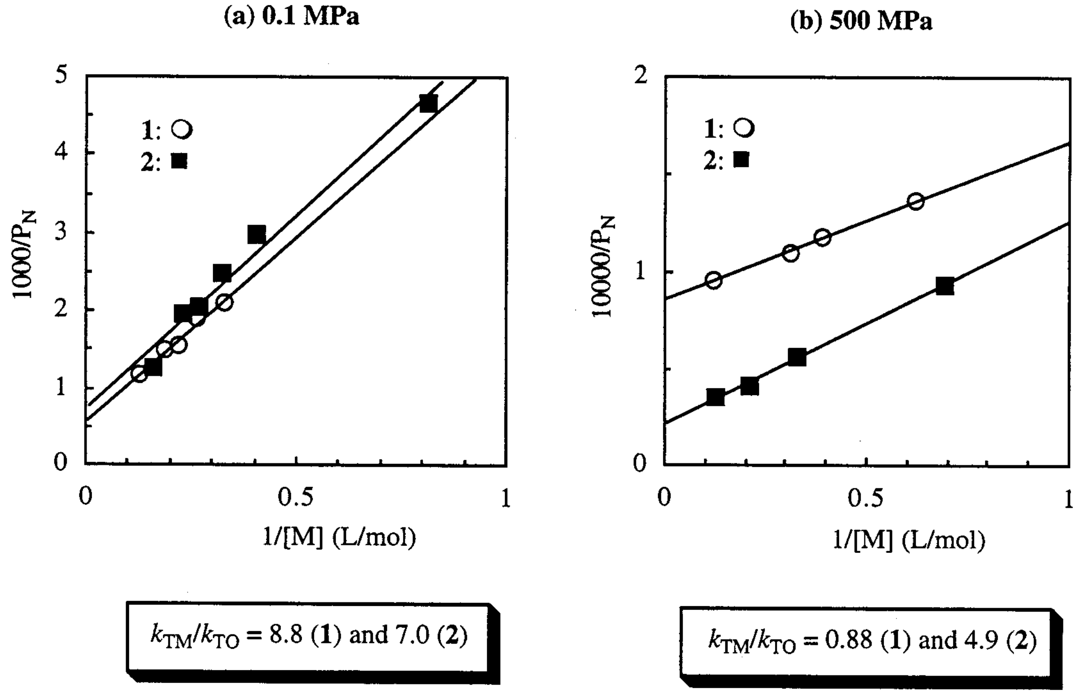
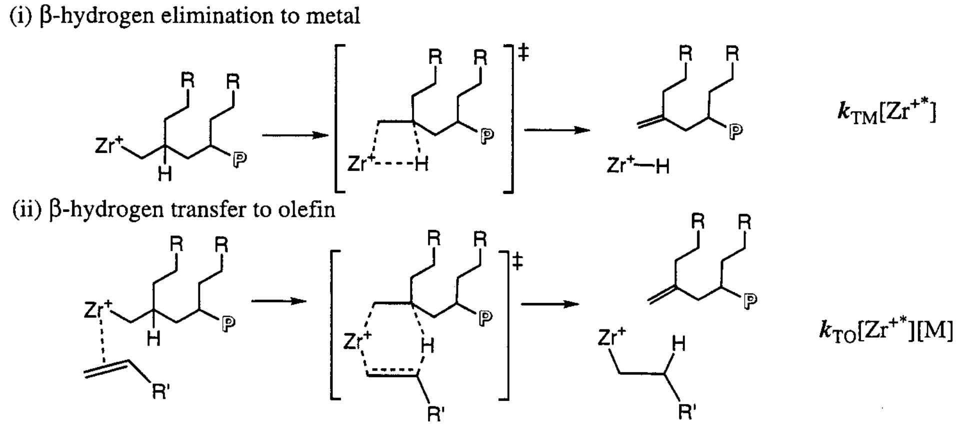


Figure 3. Reciprocal degree of polymerization, 1/P_N, with dependence on reciprocal 1-hexene concentration, 1/[M], for **1** (○) and **2** (■) under 0.1 MPa (a) and 500 MPa (b).

Scheme 1. Termination Processes of Olefin Polymerization



to olefin is not accelerated so much even under high pressure. This is consistent with the formation of the polyhexene with very high molecular weight. It should be noted that the structural difference between **1** and **2** is only the central metals. The present results suggested that the effect of pressure on organometallic reactions seemed to be governed very much by the character of the central metal even though the steric environment of the ligand is very similar.

The results of the polymerization of 1-octene by **5** seem unusual compared to the results of the hexene polymerization (Table 2). The rate of polymerization was accelerated only twice at 500 MPa relative to that at 0.1 MPa, while the molecular weight became higher by 26 times. Complex **4** also showed a similar tendency although the increment of the molecular weight at 500 MPa was smaller (12 times) than **5**. In polymerization of 1-octene, the total rate of termination processes may be retarded due to high pressure. The possibility of decrease of the concentration of active species under high pressure cannot be ruled out.

Conclusions

We studied high-pressure polymerization of α-olefins catalyzed by permethylated *ansa*-zirconocene and hafnocene complexes. It can be summarized that (i) the catalytic activities of the complexes were remarkably enhanced due to high pressure, and polyhexene of extremely high molecular weight (1.0 × 10^7 by GPC) was obtained despite their congested structures; (ii) the germylene-bridged hafnocenes exhibited 4 times higher activity than the silylene-bridged complexes under high pressure; and (iii) investigation on termination processes revealed that bimolecular β-hydrogen transfer to olefin was accelerated due to high pressure in a zirconocene, while unimolecular β-hydrogen elimination to the metal was a major termination process in a hafnocene even under high pressure. Further investigation on the behavior of metallocene species under high pressure is now in progress.

Experimental Section

General Comments. All manipulation was carried out under an atmosphere of dry argon by using standard Schlenk techniques. Dimethoxyethane, toluene, and hexane were distilled from sodium benzophenone ketyl prior to use. Hafnium tetrachloride was purchased from Cerac Co., Inc., and sublimed before use. Zirconium tetrachloride, dimethyldichlorogermane, and tetramethylcyclopentadiene were purchased from Aldrich Chemical Co., Inc., and used without further purification. Divinyldichlorosilane was purchased from Shinetsu Corp. *n*-Butyllithium (as hexane solution) was purchased from Kanto Chemical Co., Inc. $Me_2Si(\eta^5\text{-}C_5Me_4)_2ZrCl_2$ (**1**) was prepared according to the literature.[5] 1-Hexene was distilled from sodium and stored over a sodium−potassium alloy. Methylaluminoxane was purchased as a toluene solution (MMAO-3A, 5.6 wt %) from Tosoh-Akzo Corp. The GPC was recorded on Shodex GPC system 11 equipped with two columns (Shodex KF-807L × 2) whose exclusion limit is 2×10^8. THF was eluted at 40 °C, and eight samples of monodispersed polystyrene ($M_{top} = 1.15 \times 10^7$, 3.15×10^6, 1.10×10^6, 5.65×10^5, 1.72×10^5, 6.6×10^4, 1.13×10^4, 1.3×10^3) were used as standards to determine the calibration curve. The multiangle laser light scattering analysis was performed on a Wyatt Technology DAWN DSP at 25 °C. This instrument, equipped with a He−Ne laser, operates at a wavelength of 633 nm using tetrahydrofuran as a solvent. See also the Supporting Information for details of MALLS analysis. NMR was performed on a JEOL AL-300 spectrometer and high-resolution mass spectroscopy on a JEOL JMS-SX102 mass spectrometer.

Preparation of Dimethylbis(2,3,4,5-tetramethylcyclopentadienyl)silane (6).[5] To a DME solution (100 mL) of tetramethylcyclopentadiene (2.65 g, 21.7 mmol) was added *n*-BuLi (1.61 M in hexane, 21.7 mmol) at −78 °C. The mixture was warmed to room temperature and stirred overnight at room temperature. After addition of dichlorodimethylsilane (1.40 g, 10.9 mmol) at −78 °C, the mixture was refluxed for 22 h. The reaction mixture was once cooled to −78 °C, and hexamethylphosphorictriamide (HMPA, 1.94 g, 10.9 mmol) was added dropwise. The reddish solution was then stirred at 50 °C for 2 h. The reaction was quenched by the addition of water at 0 °C, and usual workup gave the title compound as a yellow oil (2.60 g, 80%). Possible isomers were not observed by ^1H and ^{13}C NMR. ^1H NMR (C_6D_6, Me_4Si): $\delta = -0.20$ (s, 6H) 1.83 (s, 12H), 1.97 (s, 12H), 3.14 (s, 2H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = -5.02$, 11.57, 15.22, 53.84, 133.29, 136.24.

Preparation of Divinylbis(2,3,4,5-tetramethylcyclopentadienyl)silane (7). The title compound was prepared similarly to **6**. An isomeric mixture of **7** was obtained as a yellow oil (2.06 g, 6.35 mmol, 48%). The product contains a considerable amount of at least three isomers (total ca. 50%). Major isomer: ^1H NMR (C_6D_6, Me_4Si): $\delta = 1.80$ (s, 12H), 1.99 (s, 12H), 3.13 (s, 2H), 5.57 (dd, $J = 18.4$, 5.6 Hz, 2H), 5.88 (m, 4H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 11.47$, 15.31, 52.07, 132.76, 133.23, 133.44, 136.83. High-resolution mass spectroscopy: calcd for $C_{22}H_{32}Si$: 324.2273; found: 324.2263.

Preparation of Dimethylbis(2,3,4,5-tetramethylcyclopentadienyl)germane (8). To a DME solution (50 mL) of tetramethylcyclopentadiene (2.64 g, 21.6 mmol) was added *n*-BuLi (1.61 M hexane solution, 21.6 mmol) dropwise at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight at room temperature. Dichlorodimethylgermane (1.87 g, 10.8 mmol) was then added at −78 °C. After refluxing for 4 h, the reaction mixture was quenched by the addition of water at 0 °C and extracted into ether. The organic layer was washed with brine and dried over Na_2SO_4. After removal of volatiles, the residue was purified by column chromatography (hexane) to give the title compound as a yellow oil (2.17 g, 58%). The products contained no isomers judging from NMR spectra. ^1H NMR (C_6D_6, Me_4Si): $\delta = -0.06$ (s, 6H) 1.84 (s, 12H), 1.93 (s, 12H), 3.27 (s, 2H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = -5.19$, 11.30, 14.48, 54.38, 132.62, 134.98. High-resolution mass spectroscopy: calcd for $C_{20}H_{32}Ge$: 346.1714; found: 346.1713.

Preparation of [$Me_2Si(\eta^5\text{-}C_5Me_4)_2HfCl_2$] (2). To a THF solution (60 mL) of dimethylbis(tetramethylcyclopentadienyl)silane (**6**) (1.58 g, 5.26 mmol) was added *n*-BuLi (3.04 M in hexane, 3.45 mL, 10.5 mmol) dropwise at −78 °C. The mixture was allowed to warm to room temperature and was kept stirring for 1 h at 50 °C. The reaction mixture was added dropwise to the DME solution (15 mL) of $HfCl_4$ (1.75 g, 5.46 mmol) at −78 °C. Then the mixture was warmed to room temperature, and the resulting solution was kept stirring for 60 h. After the solvent was removed in vacuo, the solid residue was extracted with toluene. The solvent was removed in vacuo from the extract to leave a yellow solid. Recrystallization from toluene afforded colorless crystals of the title compound (0.38 g, 13% yield). Anal. Calcd for $C_{20}H_{30}Cl_2SiHf$: C, 43.84%; H, 5.52%. Found: C, 43.65%; H, 5.61%. ^1H NMR (C_6D_6, Me_4Si): $\delta = 0.61$ (s, 6H) 1.86 (s, 12H), 2.08 (s, 12H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 3.30$, 12.46, 14.93, 95.89, 121.99, 134.41.

Preparation of [$(CH_2{=}CH)_2Si(\eta^5\text{-}C_5Me_4)_2HfCl_2$] (3). The title compound was prepared in a manner similar to **2** from divinylbis(tetramethylcyclopentadienyl)silane (**7**) (2.06 g, 6.35 mmol) and $HfCl_4$ (2.01 g, 3.51 mmol). Recrystallization from toluene afforded colorless crystals of **3** (0.26 g, 14% yield). Anal. Calcd for $C_{22}H_{30}Cl_2SiHf$: C, 46.20%; H, 5.29%. Found: C, 46.32%; H, 5.29%. ^1H NMR ($CDCl_3$, Me_4Si): $\delta = 2.00$ (s, 12H), 2.08 (s, 12H), 6.19 (dd, $J = 3.0$, 20.3 Hz, 2H), 6.39 (dd, $J = 3.0$, 14.7 Hz, 2H), 6.83 (dd, $J = 14.7$, 20.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 12.30$, 15.37, 93.64, 122.31, 134.76, 135.03, 136.65. Crystallographic data were deposited in Cambridge Crystallographic Database (CCDC-121719).

Preparation of [$Et_2Si(\eta^5\text{-}C_5Me_4)_2HfCl_2$] (4). A solution of **3** (14.2 mg, 24.8 mmol) in THF was exposed to atmospheric pressure of hydrogen in the presence of 5% of Pd/C. The mixture was stirred for 5 h at room temperature. After the solvent was removed in vacuo, extraction with hexane and recrystallization gave the title compound (6.4 mg, 45% yield). Anal. Calcd for $C_{22}H_{34}Cl_2SiHf$: C, 45.87%; H, 5.95%. Found: C, 45.83%; H, 5.85%. ^1H NMR (C_6D_6, Me_4Si): $\delta = 1.08$ (t, $J = 7.7$ Hz, 6H), 1.28 (q, $J = 7.7$ Hz, 4H), 1.86 (s, 12H), 2.07 (s, 12H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 6.01$, 6.60, 12.56, 14.87, 95.15, 122.47, 134.71. Crystallographic data were deposited in Cambridge Crystallographic Database (CCDC-121720).

Preparation of [$Me_2Ge(\eta^5\text{-}C_5Me_4)_2HfCl_2$] (5). To a DME solution (40 mL) of $Me_2Ge(C_5HMe_4)_2$ (**8**) (2.17 g, 6.29 mmol) was added dropwise *n*-BuLi (1.61 M in hexane, 12.6 mmol) at −78 °C. The mixture was allowed to warm to room temperature and was kept stirring 1 h at 50 °C. This reaction mixture was added dropwise to the DME solution (60 mL) of $HfCl_4$ (2.05 g, 6.4 mmol) at −78 °C. Then the mixture was warmed to room temperature, and the resulting solution was refluxed for 24 h. After the solvent was removed in vacuo, the solid residue was extracted with hexane. The hexane solution was dried in vacuo to leave yellow solid. Recrystallization from toluene gave colorless crystals of the title compound (0.63 g, 17% yield). Anal. Calcd for $C_{20}H_{30}Cl_2GeHf$: C, 40.55%; H, 5.10%. Found: C, 40.33%; H, 5.13%. ^1H NMR (C_6D_6, Me_4Si): $\delta = 0.70$ (s, 6H), 1.85 (s, 12H), 2.11 (s, 12H). ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 3.34$, 12.56, 14.70, 97.35, 120.90, 133.50.

High-Pressure Polymerization. A 25 mL Teflon sample holder was charged in a Schlenk tube with argon, ca. 0.2 mL of the metallocene catalyst in toluene, and a solution of MAO in toluene (Al = 5.98 wt %; 10 000-fold excess). After 10 min, 1-hexene (ca. 25 mL) was added via cannula, and the sample holder was firmly closed by a screw cap and immediately cooled to −78 °C. High pressure was applied by a direct piston−cylinder apparatus, during warming to room temperature (Figure 4). After 2 h the pressure was released, the reaction mixture was transferred to a flask, and MeOH (10 mL) and 1 N HCl (10 mL) were added to quench the reaction. The polymer was extracted with hexane in order to separate the decomposed aluminum compounds and catalysts. Solvents were evaporated to dryness, and the residue was dried in vacuo at 70 °C overnight. The polymer was yielded as a colorless viscous oil or rubberlike solid. The molecular weight was determined by GPC and multiangle laser light scattering analysis. Since the values of the polymerization rates were obtained with some experimental variance, the reactions were repeatedly examined to confirm their activity (see the Supporting Information).

Investigation of Termination Processes. The polymerization reactions under 500 MPa were carried out similarly

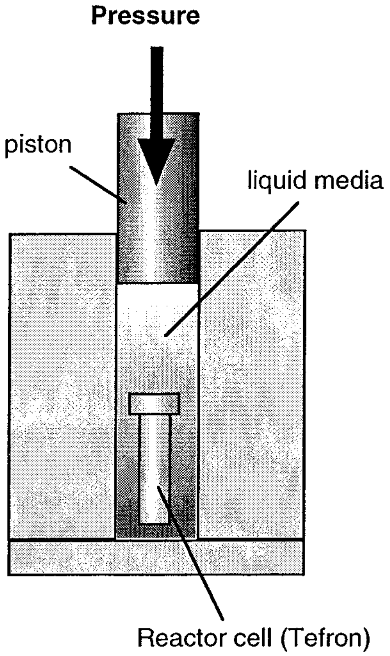


Figure 4. High-pressure reaction apparatus.

to that described above. The polymerization under atmospheric pressure was run in a Schlenk tube with stirring at room temperature for 2 h. Hexane was used as solvent. The concentration of 1-hexene, yields of the polymer, number-averaged polymerization degree, and calculated parameters by the least-squares method are described in the Supporting Information.

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Supporting Information Available: Experimental details of polymerization reactions, data of multiangle laser light scattering analysis, crystallographic data for **1**−**5**, and spectroscopic data for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) This is the first example of comparison between germylene- and silylene-bridged group 4 metallocenes in concern with their molecular structures and catalytic activities. Crystallographic data for **2**: monoclinic, colorless cubic crystal, space group $C2/c$ (#15), $a = 15.461(2)$, $b = 12.2617(8)$, $c = 11.1308(9)$ Å, $\beta = 104.855(8)°$, $V = 2039.7(3)$ Å^3, $Z = 4$, $d_{calc} = 1.784$ g/cm^3, $R = 0.033$, $R_w = 0.043$. Goodness of fit of 0.98. The data were deposited in Cambridge Crystallographic Database Center (CCDC-121718). **5:** monoclinic, colorless cubic crystal, space group $C2/c$ (#15), $a = 15.5014(9)$, $b = 12.3600(7)$, $c = 11.1326(7)$ Å, $\beta = 104.647(5)°$, $V = 2063.7(2)$ Å3, $Z = 4$, $d_{calc} = 1.907$ g/cm^3, $R = 0.040$, $R_w = 0.049$. Goodness of fit = 0.91. The data were deposited in Cambridge Crystallographic Database Center (CCDC-121721). See the Supporting Information for details.

(14) Crystallographic data for **1**: monoclinic, colorless cubic crystal, space group $C2/c$ (#15), $a = 15.4775(9)$, $b = 12.2708(6)$, $c = 11.188(1)$ Å, $\beta = 104.882(6)°$, $V = 2053.6(2)$ Å^3, $Z = 4$, $d_{calc} = 1.490$ g/cm^3, $R = 0.034$, $R_w = 0.044$. Goodness of fit = 1.09. The data were deposited in Cambridge Crystallographic Database Center (CCDC-121717). See the Supporting Information.

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