Synthesis, Structure, and Polymerization Behavior of Novel Azulenyl Metallocenes Producing Propylene-Ethylene Pseudo-Copolymer

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Novel bridged bis-azulenyl metallocenes bearing substituents at the 2-, 4-, and 8-positions, dichlorodimethylsilylenebis(2-methyl-4-phenyl-8-*n*-butyl-8*H*-azulenyl)hafnium and dichlorodimethylsilylenebis(2-methyl-4,8-diphenyl-8*H*-azulenyl)hafnium, were synthesized. The structure of the former compound was determined by X-ray crystallographic analysis to have C_2 symmetry. When activated with methylaluminoxane (MAO), both compounds gave an active propylene polymerization catalyst. In propylene homopolymerization, propylene-ethylene pseudo-copolymer was obtained unexpectedly. Although the metallocene has C_2 symmetry, the obtained polypropylene was elastomeric and showed no melting point on measurement by differential scanning calorimetry (DSC). The ^{13}C NMR analysis of the polymer showed the presence of a large amount of regioinversion.

Introduction

It is well known that *ansa*-metallocenes of group IV transition metals having C_2 symmetry produce isotactic polypropylene, when activated with methylaluminoxane (MAO) and other cocatalysts.[1] Many efforts have been focused on improving the polymerization performance in terms of activity, melting point, and molecular weight of the polymer. During the development of a large number of bridged bis-indenyl and bis-cyclopentadienyl systems, it was found that stereoselectivity (stereodefect) and regioselectivity (regioinversion) of the inserted propylene monomer are influenced by the steric effect of the substituents on the indenyl or cyclopentadienyl moieties.[2−5] In particular, it was elucidated that both the 2- and 4-positions of the bridged bis-indenyl system are important, and for this reason, extensive development and optimization of 2,4-substitutents were examined in order to obtain higher melting point isotactic polypropylene. As previously reported, we have synthesized the bis-azulenyl zirconocenes bearing methyl groups at the 2-position and phenyl groups at the 4-position of the azulenyl rings: $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}4H\text{-}Azu)_2ZrCl_2$.[6] We made a comparison between the bis-azulenyl zirconocene and the bis-indenyl zirconocene, especially the difference of ring size in each system, i.e., six-membered and seven-membered, and the polymerization behavior was compared with that of the bis-indenyl analogue, $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**5**). The biggest difference between the two metallocenes is the carbon atom at the 4-position. The carbon atom at the 4-position to which phenyl groups were attached does not have the same hybridization in both systems, i.e., an sp^3 carbon in bis-azulenyl and an sp^2 carbon in the bis-indenyl system.

We have now synthesized novel bis-azulenyl metallocenes bearing substituents at the 2-, 4-, and 8-positions: $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}8\text{-}n\text{-}Bu\text{-}8H\text{-}Azu)_2HfCl_2$ (**4a**) and $Me_2Si(2\text{-}Me\text{-}4,8\text{-}Ph_2\text{-}8H\text{-}Azu)_2HfCl_2$ (**4b**). As the carbon atoms at the 4-position are sp^2 hybridized in these systems, it would be expected that a more precise

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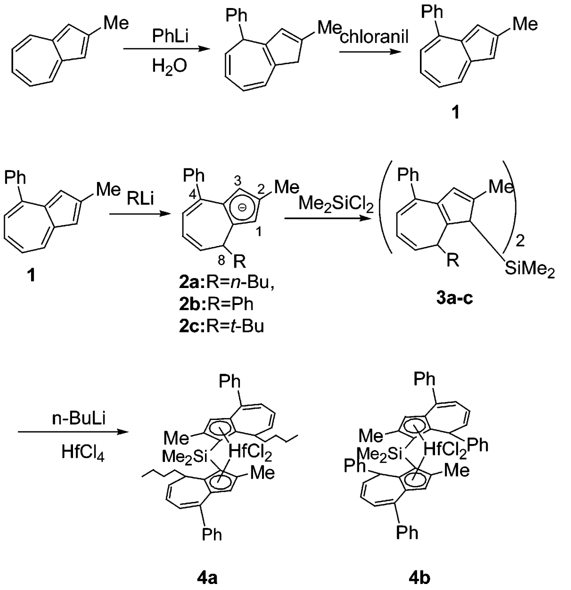
10.1021/om0494418 CCC: $30.25

Scheme 1



comparison of ring size is possible, and it is very interesting to compare the polymerization behavior in the bis-indenyl and these systems.

Results and Discussion

Novel metallocenes were synthesized as shown in Scheme 1. As previously reported, reaction of azulene and alkyllithium or aryllithium gave the corresponding lithium salt of dihydroazulene by addition at the 4-position of the azulenyl ring.[7] After quenching with water, treatment of dihydroazulene with tetrachloro-1,4-benzoquinone (chloranil) quantitatively gave the corresponding 4-substituted azulene. Furthermore, addition of alkyllithium or aryllithium to the 4-substituted azulene occurred at the 8-position of the azulenyl ring to give 4,8-substituted azulene. 2-Methyl-4-phenylazulene (**1**) was quantitatively prepared by the reaction of 2-methylazulene and phenyllithium followed by treatment with chloranil. By reaction of **1** with butyllithium or phenyllithium, the lithium salts of dihydroazulenes (**2a**–**c**) were obtained. Subsequent reaction of the lithium salts of dihydroazulenes (**2a**–**c**) and dichlorodimethylsilane in the presence of a catalytic amount of 1-methylimidazole gave bis(dihydroazulenyl)silane (**3a**–**c**). **3a** and **3b** were obtained in good yield and used without further purification. However, **3c** was relatively unstable and the yield was low, probably because of steric repulsion between the bulky 8-*tert*-butyl group and the dimethylsilyl group in **3c**. It is possible that dichlorodimethylsilane could react at the 1-position or the 3-position of **2**; however, it reacts at the 1-position. This shows that the 3-position of **2** is more sterically hindered by the 4-phenyl groups than the 1-position of **2** is hindered by the 8-substituent groups to give **3**. The bis-azulenyl hafnocenes (**4a** and **4b**) were obtained by the subsequent reaction of **3a** or **3b** with *n*-butyllithium and hafnium tetrachloride as *rac*/*meso* mixtures. The mixture of **4a** was purified by recrystallization from toluene to give pure *rac*-**4a**. However, **4b** was recrystallized from toluene/diisopropyl ether to give the *rac*/*meso* mixture (r/m = 5:1) and used for further polymerization.

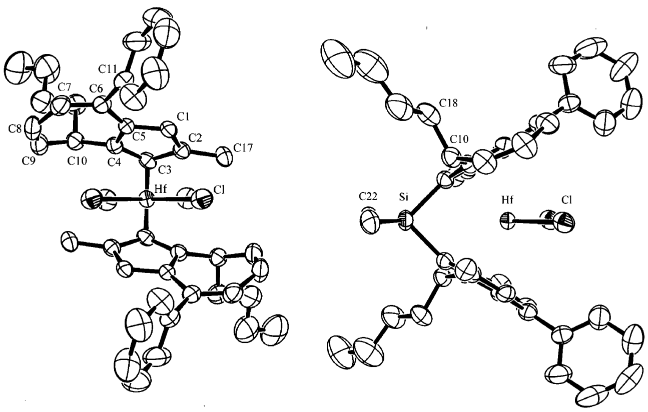


Figure 1. ORTEP drawing of **4a**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf–Cl 2.3999(14), Hf–Cp (centroid) 2.2293, C(5)–C(6) 1.456(7), C(6)–C(11) 1.489(7), Si–C(22) 1.881(7), Si–C(3) 1.896(5), Cl–Hf–Cl 96.16(8), C(22)–Si–C(22) 103.5(5), C(3)–Si–C(3) 93.4(3), C(1)–C(5)–C(6) 124.0(4), C(11)–C(6)–C(5) 117.5(4), C(7)–C(6)–C(11) 117.0(5), C(7)–C(6)–C(5) 125.4(5), Cp–Hf–Cp 126.87.

Table 1. Comparison of Angles for 4a, 5, and 6

	4a	**5**[a]	**6**[b]
ring system	5/7	5/6	5/5
torsion angle[c]	5.4	−7.2	−8.5
θ_1[d]	124.0(4)	131.4	139.3
θ_2[e]	117.5(4)	122.9	126.2

[a] Data from ref 2b. [b] Data from ref 4c. [c] Torsion angle between Cp moiety and 4-Ph group bond. [d] Ligand mouth angles (I, Chart 1). [e] Angles between 4-Ph group bond and fused ring moiety (I, Chart 1).

The structure of **4a** was determined by X-ray crystallographic analysis. A suitable crystal of **4a** was obtained by recrystallization from toluene/hexane solution. An ORTEP drawing of **4a** and selected bond lengths and angles are shown in Figure 1. It was found that **4a** is a *rac* isomer and has C_2 symmetry. The two 8-*n*-butyl groups are located outside the metal center, and the 4-phenyl groups are located in front of the metal center. The carbon atoms at the 8-positions are chiral centers and they have the same configuration, i.e., 8,8′-(*R,R*) or -(*S,S*).

The structure of **4a** was compared with the metallocenes containing a smaller ring system, the 5/6 rings in $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ (**5**)[2b] and the 5/5 rings in $Me_2Si(2,5\text{-}Me_2\text{-}3\text{-}Ph\text{-}6\text{-}Cp[b]Tp)_2ZrCl_2$ (**6**),[4c] as shown in Table 1. The structural difference between the 5/6 and 5/5 ring systems has been reported previously.[4c] In these metallocenes (**4a**, **5**, and **6**), the carbon atoms at the 4-position to which the 4-phenyl groups are attached (α position of the cyclopentadienyl moiety) have the same hybridization, i.e., an sp^2 carbon. The torsion angles between the cyclopentadienyl moieties and the 4-phenyl group bonds (i.e., C(1)–C(5) and C(6)–C(11) in **4a**) are almost the same. The two angles depicted in I (Chart 1) (θ_1 and θ_2) decrease due to the ring structure from the 5/5 to the 5/7 ring system. In the larger ring system, these angles become smaller and the directions of the 4-phenyl group are changed as a consequence. The direction of the 4-phenyl groups in **4a** is arranged

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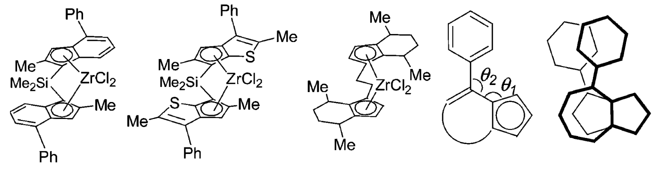
Chart 1



5 **6** **7** **I** **II**

most proximally to the metal center in a comparison of these three metallocenes. A comparison of the different ring structures superimposed on each other is shown in II (Chart 1).

The liquid propylene polymerization of the bis-azulenyl metallocenes (**4a**, **4b**) has been examined using MAO as cocatalyst.[8] The polymerization data are shown in Table 2 with the reference data obtained for the other ring system. In propylene homopolymerization of **4a** and **4b**, propylene-ethylene pseudo-copolymer was unexpectedly obtained instead of isotactic polypropylene. Although **4a** has C_2 symmetry, the obtained polypropylene was elastomeric and showed no melting point on DSC measurement. The ^{13}C NMR analysis showed the presence of a large amount of 3,1-units (12.5 mol %). The reason for the occurrence of a large amount of 3,1-units in **4a** can be explained by the proximity of the 4-phenyl group to the monomer coordination site compared with those in the smaller ring system in **5** and **6**. In the 5/7 ring system (**4a**), greater steric repulsion between the 4-phenyl group and the methyl group of propylene monomer results in favor of 2,1-insertion. Sequentially, 3,1-units arise from the isomerization of the 2,1-units.[9] The increase in the amount of regioinversion (2,1-units and 3,1-units) is consistent with the decrease in the angles (θ_1 and θ_2). In the polymer obtained by **4a**, no 2,1-units were observed and the amount of *mrrm* is larger than that in **4b**. However, a small amount of 2,1-units was observed and the amount of *mrrm* was decreased in **4b**. The difference of the microstructure in the polymers obtained by **4a** and **4b** is possibly attributed to the difference in the electronic effect of the 8-substituents (*n*-butyl groups in **4a** and phenyl groups in **4b**). In a comparison of the chemical shifts of the protons on the Cp moieties (on the 3-position of the azulenyl rings), a difference in the chemical shift (6.32 ppm for **4a** and 6.47 ppm for **4b**) is observed, possibly due to the difference in the electronic effect of the metal center. As the 8-*n*-butyl groups are located outside the metal center, as shown in Figure 1, the steric effect on the insertion of propylene monomer is negligible.

Similar propylene-ethylene pseudo-copolymers were reported by using the bridged bis-indenyl system Et-(4,7-Me$_2$-H$_4$-Ind)$_2$ZrCl$_2$ (**7**)[1c,10] and an unbridged bis-indenyl system.[11] In the propylene polymerization with **7** activated using MAO, a large amount of 3,1-units (18.9 mol %) was observed, as shown in Table 2. The reason for the occurrence of a large amount of 3,1-units in **7** was explained by calculation and steric repulsion of the 4-methyl group in **7** and the methyl group of propylene monomer, as discussed previously.[12] Investigation of the relationship between the structure of the metallocene (both steric and electronic effects) and polymerization behavior is currently under way.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere. THF was distilled from sodium/benzophenone. Dehydrated hexane, toluene, diisopropyl ether, and dichloromethane were purchased from Kanto Chemical Co. and used without further purification. Dichlorodimethylsilane was freshly distilled before use. ^{1}H NMR spectra were recorded on a Varian Gemini-300 and a Bruker AVANCE 400 spectrometer at 300 and 400 MHz, respectively. ^{13}C NMR spectra were recorded on a JEOL GSX-400 spectrometer at 100 MHz. Electron impact (EI) mass spectra were measured on a JEOL DX-300. Mass spectra of metallocenes were measured on a JEOL JMS-700/MStation using the negative desorption chemical ionization (DCI) mode (isobutane) and an Applied Biosystems Voyager Elite-DE using the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mode.

Synthesis of 2-Methyl-4-phenylazulene (1). A solution of 2-methylazulene (1.46 g, 10.3 mmol) in hexane (20 mL) was treated with a solution of phenyllithium in cyclohexane/diethyl ether (12.0 mL, 12.3 mmol, 1.03 M) at 0 °C. After stirring for 40 min at room temperature, the violet color of the solution disappeared and the lithium salt of 2-methyl-4-phenyldihydroazulene was precipitated. After quenching with water, the organic phase was separated and dried over MgSO$_4$, and the solvent was removed to give the crude product 2-methyl-4-phenyldihydroazulene. To a solution of the crude product in toluene (30 mL) was added tetrachloro-1,4-benzoquinone (2.77 g, 11.28 mmol) at room temperature. The mixture was stirred for 2 h at room temperature. After the solvent was evaporated, the resulting mixture was purified by column chromatography with silica gel (using hexane as eluent) to give 2-methyl-4-phenylazulene, **1** (2.29 g, quantitative), as a violet viscous oil. **1**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.59 (s, 3 H, 2-Me), 6.91 (s, 1 H), 7.14 (d, 2 H), 7.43−7.60 (m, 7 H), 8.23 (d, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.65 (Me), 119.16, 119.28, 122.02, 126.12, 127.64, 128.05, 129.16, 134.54, 134.80, 138.03, 141.58, 143.95, 147.79, 149.67; EI-MS *m/z* (relative intensity) 218 (M$^+$, 100), 202 (52), 101 (13).

Synthesis of Me$_2$Si(2-Me-4-Ph-8-*n*-Bu-8*H*-Azu)$_2$HfCl$_2$ (4a). A solution of 2-methyl-4-phenylazulene (2.02 g, 9.26 mmol) in a mixture of hexane (50 mL) and diisopropyl ether (5 mL) was treated with a solution of *n*-butyllithium in hexane (5.9 mL, 9.26 mmol, 1.56 M) at 0 °C. After stirring for 30 min at room temperature, THF (1 mL) was added and stirred for another 1 h at the same temperature. The reaction mixture was cooled to 0 °C, and THF (19 mL), 1-methylimidazole (20 μmol), and 0.5 equiv of dichlorodimethylsilane (0.56 mL, 4.63 mmol) were added sequentially. The mixture was warmed to room temperature and stirred at this temperature for 2 h. After quenching with water, the organic phase was separated and dried over MgSO$_4$, and the solvent was removed to give the crude product bis(2-methyl-4-phenyl-8-*n*-butyldihydroazulenyl)dimethylsilane, **3a** (2.8 g), as a diastereomeric mixture.

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[8] The homologous zirconocene of **4a** was also prepared. Although polymerization was investigated under the same conditions as that of the polymerization using **4a** and **4b**, unexpectedly no activity was observed.

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Table 2. Propylene Polymerization Results[j]

metallocene	T_p (°C)	Al/M	activity[a]	T_m (°C)	M_w	*mrrm* (%)	2,1-units[b] (mol %)	3,1-units (mol %)
4a	70	5000	55	n.d.[f]	90 000[g]	3.3	0.0	12.5
4b[c]	70	5000	35	n.d.	120 000[h]	1.8	0.2	8.9
5[d]	70	25 000	518	156	1 184 000	0.1	0.4	0.0
6[d]	70	215 000	1953	156	445 000	0.4	0.3	0.0
7[e]	50	2000	5		370 000[i]		0.0	18.9

[a] kg-polymer/mmol metal·h. [b] Erythro 2,1-regioerrors determined by ^{13}C NMR. [c] *Rac*/*meso* mixture (r/m = 5:1). [d] Data from ref 4c. [e] Data from refs 1c and 10b. [f] Not detected. [g] $M_w/M_n = 3.1$. [h] $M_w/M_n = 2.2$. [i] P_n from intrinsic viscosity. [j] Conditions: liquid propylene, 1 h, MMAO.

To a solution of **3a** (2.8 g) in diisopropyl ether (15 mL) was added a solution of *n*-butyllithium in hexane (6.0 mL, 9.26 mmol, 1.56 M) at 0 °C. The mixture was stirred at room temperature overnight. To the resulting mixture was added toluene (75 mL), the mixture was cooled at −10 °C, and hafnium tetrachloride (1.48 g, 4.63 mmol) was added at −10 °C. After warming gradually to room temperature, the mixture was stirred for 4 h and for 1 h at 40 °C. The resulting mixture was concentrated under reduced pressure, washed with hexane (20 mL × 3), and extracted with dichloromethane (20 mL) to give a *rac*/*meso* mixture of **4a** (1.2 g, 30%). Recrystallization of the *rac*/*meso* mixture of **4a** (212 mg) from toluene allowed isolation of the pure *rac*-**4a** (23 mg).

4a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 6 H, Bu), 1.03 (s, 6 H, Me_2Si), 1.1−1.8 (m, 12 H, Bu), 2.22 (s, 6 H, 2-Me), 3.69 (dd, 2 H, 8-H), 5.42 (dd, 2 H), 5.90 (dd, 2 H), 6.15 (d, 2 H), 6.32 (s, 2 H, 3-H), 7.30 (br d, 10 H, arom); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.73 ($SiMe_2$), 14.09, 18.11 (2-Me), 22.74, 29.49, 36.36, 39.77, 101.99, 124.03, 126.97, 128.03, 128.09, 128.58, 129.30, 129.33, 129.80, 134.23, 134.32, 137.94, 143.71; negative MALDI-TOF-MS, parent ion at *m/z* 856 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Found: C, 61.84; H, 6.82. Calcd ($C_{44}H_{50}Cl_2SiHf$): C, 61.71; H, 5.89.

Synthesis of Me_2Si(2-Me-4,8-Ph_2-8*H*-Azu)$_2$$HfCl_2$ (4b). A solution of 2-methyl-4-phenylazulene (2.0 g, 9.3 mmol) in a mixture of hexane (50 mL) and diisopropyl ether (1 mL) was treated with a solution of phenyllithium in cyclohexane/diethyl ether (9.4 mL, 9.3 mmol, 0.99 M) at 0 °C. After stirring for 2 h at room temperature, the lithium salt of 2-methyl-4,8-diphenyldihydroazulene was precipitated and the supernatant liquid was removed by decantation. To the reaction mixture were added THF (25 mL), hexane (20 mL), 1-methylimidazole (20 μmol), and 0.5 equiv of dichlorodimethylsilane (0.53 mL, 4.4 mmol) sequentially. The mixture was warmed to room temperature and stirred at this temperature for 30 min. After quenching with water, the organic phase was separated and dried over $MgSO_4$, and the solvent was removed to give the crude product bis(2-methyl-4,8-diphenyldihydroazulenyl)dimethylsilane, **3b** (3.1 g), as a diastereomeric mixture.

To a solution of **3b** (3.1 g) in diisopropyl ether (20 mL) was added a solution of *n*-butyllithium in hexane (5.6 mL, 8.7 mmol, 1.59 M) at 0 °C. The mixture was stirred at room temperature overnight. To the resulting mixture was added toluene (70 mL), the mixture was cooled to −10 °C, and hafnium tetrachloride (1.4 g, 4.4 mmol) was added at −10 °C. After warming gradually to room temperature, the mixture was stirred for 1 h and for 2 h at 40 °C. The resulting mixture was concentrated under reduced pressure, washed with hexane (25 mL), and extracted with toluene (15 mL) and diisopropyl ether (40 mL) to give a *rac*/*meso* mixture of **4b** (1.2 g, 31%). Recrystallization of the *rac*/*meso* mixture of **4b** (1.05 g) from a mixture of toluene (10 mL) and diisopropyl ether (10 mL) gave the *rac*/*meso* mixture of **4b** (80 mg, r/m = 5:1).

4b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 6 H, Me_2Si), 2.38 (s, 6 H, 2-Me), 5.18 (d, 2 H), 5.7−6.1 (m, 6 H), 6.47 (s, 2 H, 3-H), 7.2−7.4 (m, 20 H, arom); negative DCI-MS, parent ion at *m/z* 896 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Found: C, 63.46; H, 5.57. Calcd ($C_{48}H_{42}Cl_2SiHf$): C, 64.32; H, 4.72.

Crystallographic Studies. The X-ray crystallographic analysis was performed using the crystal with the size 0.2 × 0.15 × 0.07 mm, obtained by recrystallization from toluene/hexane solution at room temperature. The X-ray diffraction data were collected on a κ-axis diffractometer with a Bruker SMART 1000 CCD detector with the ω scan mode (0.3°) using Mo Kα radiation (50 kV, 40 mA). The structure was solved by direct methods (SHELXS97)[13a] and refined by full matrix least-squares technique (SHELXL97).[13b] A total of 12 478 reflections were measured, of which 4756 unique reflections were used in the structure refinement. The final *R* factor was 0.0315 for 4756 reflections.

Crystal data: fw = $C_{44}H_{50}Cl_2HfSi$, orthorombic, space group *Fdd*2, a = 15.2911(14) Å, b = 51.965(5) Å, c = 9.8662(9) Å, β = 90°, V = 7839.7(13) Å^3, Z = 8, D_{calc} = 1.451 g/cm^3, R = 0.0315 for 4756 reflections ($F_o > 2\sigma(F_o)$).

Propene Polymerization. A dry 2 L steel reactor was charged with nitrogen and liquid propene (1500 mL) at room temperature. Then a solution of methylaluminoxane in toluene (2.0 mL, 4.0 mmol, Al/Hf = 5000, MMAO purchased from Tosoh Finechem Corp.) and a solution of metallocene in toluene (0.8 mL, 0.8 μmol) were added to the reactor at room temperature. The reactor was heated to 70 °C within 10 min and kept at this temperature for 1 h. The reaction was stopped by venting the unreacted monomer and cooling. The yield of polymer was determined by weighing.

Polymer Analysis Procedures. Molecular masses were determined on a Waters 150C at 135 °C in 1,2-dichlorobenzene. The melting point of the polymer (T_m) was determined on a Dupont TA2000 at a heating rate of 10 °C/min. The result of the second scan is reported. The ^{13}C NMR analysis of the polymer was performed on a JEOL EX-270 (67.8 MHz) at 130 °C. The sample was obtained with the polymer (200 mg) dissolved in 1,2-dichlorobenzene (2.0 mL) and C_6D_6 (0.5 mL). The 2,1-units and 3,1-units were evaluated as described previously.[14] The amount of *mrrm* was evaluated from the peak of *mrrm* (20.0 ppm) and the peaks corresponding to the methyl carbons (19.8−22.0 ppm). The methyl peak of the 3,1-units (20.9 ppm) was corrected; it was overlapped by the peaks of the methyl carbons.

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Supporting Information Available: Crystallographic details, including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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