Novel bridged bis-azulenyl and bis-tetrahydroazulenyl hafnocenes: Synthesis, structure, and propylene polymerization behavior

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Abstract

Novel bridged bis-azulenyl hafnocenes: dichlorodimethylsilylenebis(2-methyl-4-phenyl-4*H*-azulenyl) hafnium (**4a**) and dichlorodimethylsilylenebis[2-ethyl-4-(4-chlorophenyl)-4*H*-azulenyl] hafnium (**4b**) were synthesized from 2-methylazulene and 2-ethylazulene, respectively. Hydrogenation of **4a** and **4b** gave novel bis-tetrahydroazulenyl hafnocenes: dichlorodimethyl-silylenebis(2-methyl-4-phenyl-4*H*-5,6,7,8-tetrahydroazulenyl) hafnium (**5a**) and dichlorodimethylsilylenebis[2-ethyl-4-(4-chloro-phenyl)-4*H*-5,6,7,8-tetrahydroazulenyl] hafnium (**5b**). The structures of **4a** and **5b** were determined by X-ray crystallographic analysis to fold C_2 symmetry. These hafnocenes were found to be active catalysts for propylene polymerization in the presence of methylaluminoxane (MAO), and the preliminary polymerization behavior of these catalysts was evaluated. The melting point and molecular weight of resultant polypropylene were higher than those of the bis-azulenyl zirconocenes. In particular, a high melting point (160 °C for **5a** and 161 °C for **5b**) was observed with the bis-tetrahydroazulenyl system, although the activities by these hafnocenes were lower than those by the corresponding zirconocenes.
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1. Introduction

For more than a decade after the discovery that the *ansa*-zirconocene/MAO catalyst produced isotactic polypropylene [1], various types of metallocenes have been synthesized and the polymerization behavior has been studied. In particular, the bridged bis-indenyl metallocene system has received much attention in propylene polymerization and been extensively investigated [2]. It was elucidated that both the 2- and the 4-position of the bridged bis-indenyl system are important, and extensive development and optimization of the 2,4-substitutents were carried out to obtain higher melting point polypropylene, especially in the industrial field [3–5]. Although several bridged bis-indenyl zirconocenes were synthesized, reports on bridged bis-indenyl

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hafnocenes have been limited to date [6–9]. This can probably be attributed to the lower activity of the catalyst prepared from hafnocene and MAO compared with that obtained from zirconocene. In general, the catalyst prepared from hafnocene gives a higher melting point and molecular weight of the polymer; however, the activity of the catalyst is lower [6a,6b,10]. For example, the $Me_2SiInd_2ZrCl_2$/MAO catalyst exhibits higher activity and gives a lower molecular weight polymer [115 kg-PP/mmol-Zr and 35 kg/mol]; however, the homologous hafnium catalyst shows much lower activity and higher molecular weight [6 kg-PP/mmol-Hf and 260 kg/mol] [6a]. This tendency of the hafnium metallocenes is usually explained as follows: lower activity is attributed to a kinetic reason (i.e., slow monomer coordination and insertion) and higher molecular weight of the polymer results from thermodynamically higher strength of the Hf–C bond compared with the Zr–C bond [2d,2e,11].
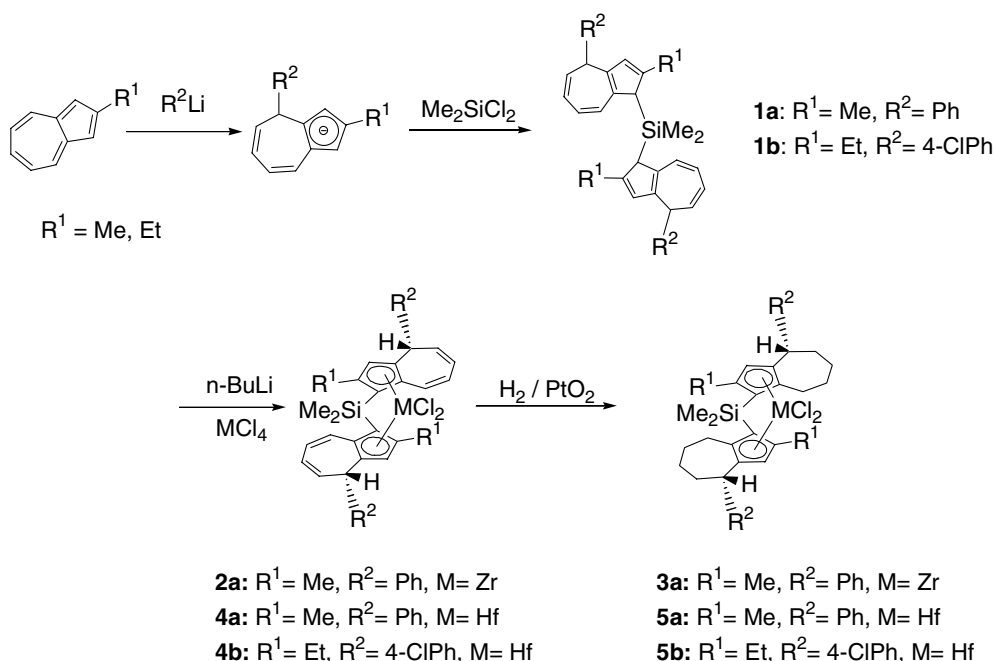
As previously reported, we have developed a novel bis-azulenyl metallocene system containing a seven-membered ring structure [12] and synthesized zirconocenes bearing methyl groups at the 2-positions and phenyl groups at the 4-positions of the azulenyl rings: $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}4H\text{-}Azu)_2ZrCl_2$ (**2a**) and $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}4H\text{-}5,6,7,8\text{-}tetrahydroAzu)_2ZrCl_2$ (**3a**) [12a]. Recently, we synthesized novel bis-azulenyl hafnocenes: $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}4H\text{-}Azu)_2HfCl_2$ (**4a**), $Me_2Si[2\text{-}Et\text{-}4\text{-}(4\text{-}ClPh)\text{-}4H\text{-}Azu]_2HfCl_2$ (**4b**) and bis-tetrahydroazulenyl hafnocenes: $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}4H\text{-}5,6,7,8\text{-}tetrahydroAzu)_2HfCl_2$ (**5a**), $Me_2Si[2\text{-}Et\text{-}4\text{-}(4\text{-}ClPh)\text{-}4H\text{-}5,6,7,8\text{-}tetrahydroAzu]_2HfCl_2$ (**5b**) in our development of the bis-azulenyl metallocene system to improve the

activity of the catalyst, melting point, and molecular weight of the polymer. In this paper, we compare these novel hafnocenes with the corresponding zirconocene analogues and compare the bis-azulenyl system with the bis-tetrahydroazulenyl system in terms of structure and propylene polymerization behavior.

2. Results and discussion

2.1. Synthesis of the hafnocenes

Novel hafnocenes (**4a**, **4b**, **5a**, and **5b**) were synthesized as shown in Scheme 1. As previously reported, dimethylbis(2-methyl-4-phenyl-4H-dihydroazulenyl)silane (**1a**) was prepared from 2-methylazulene [12a]. Although the yield of **1a** was low and purification was necessary in the previous report, the yield was improved by addition of a catalytic amount of 1-methylimidazole and **1a** was used without further purification [13]. The bis-azulenyl hafnocene (**4a**) was obtained by the subsequent reaction of **1a** with *n*-butyllithium and hafnium tetrachloride as a *rac/meso* mixture (*r/m* = 2/1). After photoirradiation of the *rac/meso* mixture of **4a** using a high-pressure mercury lamp, *meso*-**4a** was not observed. Washing of the resultant mixture with toluene gave pure *rac*-**4a** [14]. The ^1H NMR spectrum of *rac*-**4a** was similar to that of the homologous zirconocene (**2a**), indicating C_2 symmetry. The resonance corresponding to the protons at the 3-position was shifted slightly upfield (5.85 ppm for **4a** and 5.94 ppm for **2a**); on the other hand, the resonances at the 4- and 8-positions and the

2a: R^1= Me, R^2= Ph, M= Zr
4a: R^1= Me, R^2= Ph, M= Hf
4b: R^1= Et, R^2= 4-ClPh, M= Hf

3a: R^1= Me, R^2= Ph, M= Zr
5a: R^1= Me, R^2= Ph, M= Hf
5b: R^1= Et, R^2= 4-ClPh, M= Hf

1a: R^1= Me, R^2= Ph
1b: R^1= Et, R^2= 4-ClPh

R^1 = Me, Et

Scheme 1.

2-methyl groups were shifted slightly downfield (5.02, 6.82, and 2.27 ppm, respectively, for **4a** and 4.93, 6.76, and 2.18 ppm for **2a**, respectively). The bis-tetrahydroazulenyl hafnocene (**5a**) was obtained quantitatively by the reaction of *rac*-**4a** with hydrogen in the presence of platinum(IV) oxide [12a,15]. A similar upfield shift of **5a** in the ^{1}H NMR spectrum was observed in the comparison of **5a** and **3a**.

In addition, we have synthesized the novel hafnocenes (**4b** and **5b**) having 2-ethyl groups for the improvement of the melting point of the polymer. It was discovered that the 2-ethyl substituted metallocene gave a higher melting point for the polymer than that of the 2-methyl substituted catalyst, and several bridged bis-indenyl zirconocenes having 2-ethyl groups have been reported [3a,16]. Furthermore, it would be expected that the melting point of the polymer would be increased by a bulky substituent at the 4-position, so 4-chlorophenyl groups were introduced at the 4-position of the azulenyl ring. The selective synthesis of 2-ethylazulene was developed in our laboratory and it has been previously reported [17]. 4-Chlorophenyllithium was prepared quantitatively from 4-bromochlorobenzene and 2 equiv. of *t*-butyllithium, and the addition of the 4-chlorophenyllithium to 2-ethylazulene proceeded smoothly to give the lithium salt of dihydroazulene. Subsequent treatment of dichlorodimethylsilane in the presence of 1-methylimidazole gave **1b** in good yield. Further reaction with *n*-butyllithium and hafnium tetrachloride gave as a *rac/meso* mixture of **4b** (*r/m* = 6/4). Pure *rac*-**4b** was obtained from the mixture by washing with toluene and hexane without photoirradiation. In the ^{1}H NMR spec-

trum of *rac*-**4b**, the resonances corresponding to the methylene protons of the 2-ethyl groups exhibit one septet, indicating that these two protons are diastereotopic. By a similar procedure to the preparation of **5a**, **5b** was obtained quantitatively.

2.2. X-ray analysis of the hafnocenes

The structure of *rac*-**4a** and *rac*-**5b** was determined by X-ray crystallographic analysis. ORTEP drawings of **4a** and **5b** are shown in Figs. 1 and 2, respectively, and the crystal data and structure refinement parameters are shown in Table 1. It was found that both hafnocenes have C_2 symmetry and the two 4-phenyl [or 4-(4-chlorophenyl)] groups are located outside the metal center, indicating the carbon atoms at the 4-position have the same configuration, that is, 4, 4′-(*R,R*) or -(*S,S*). The C(18) atoms of the 2-ethyl groups in **5b** were slightly disordered and located outside the metal center to minimize the steric repulsion. The distances and angles of the cyclopentadienyl moiety and the azulenyl moiety are listed in Tables 2 and 3, respectively. The distances between hafnium and carbon atoms of the cyclopentadienyl moiety in **4a** (ranging from 2.452(5) to 2.636(5) Å) are slightly shorter than those in the homologous zirconocene (**2a**, ranging from 2.465(2) to 2.640(2) Å). This tendency is also observed when comparing the zirconocene and the hafnocene having a bridged bis-cyclopentadienyl ligand system [18]. The angles of the cyclopentadienyl moiety in **2a** and **4a** are very close, as shown in Table 2, and the angles of the azulenyl ring are also similar, as shown in Table 3. Therefore, it
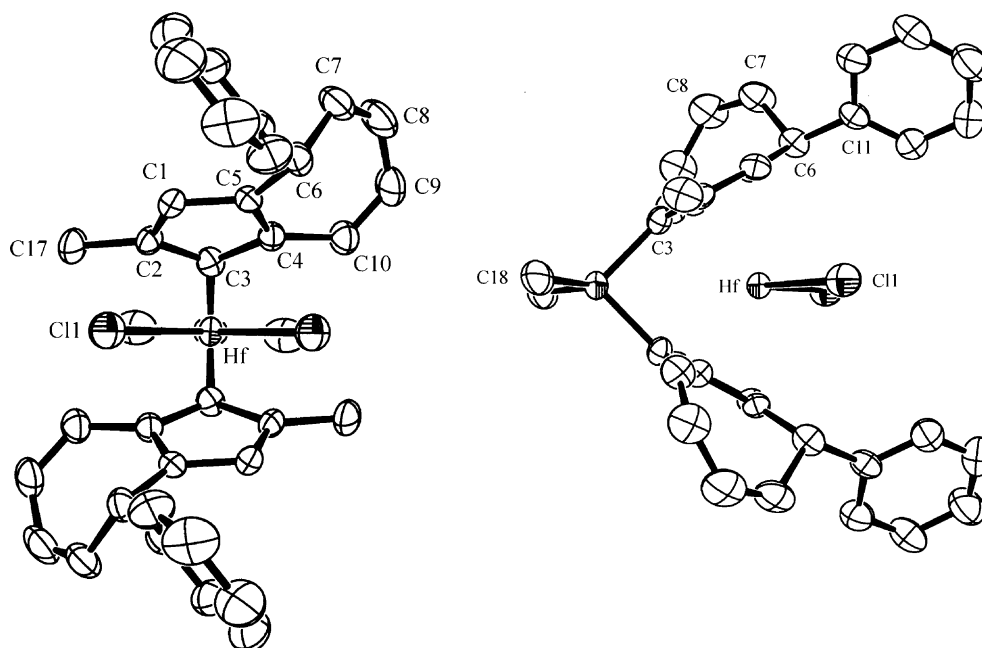

Fig. 1. ORTEP drawing of **4a**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity.
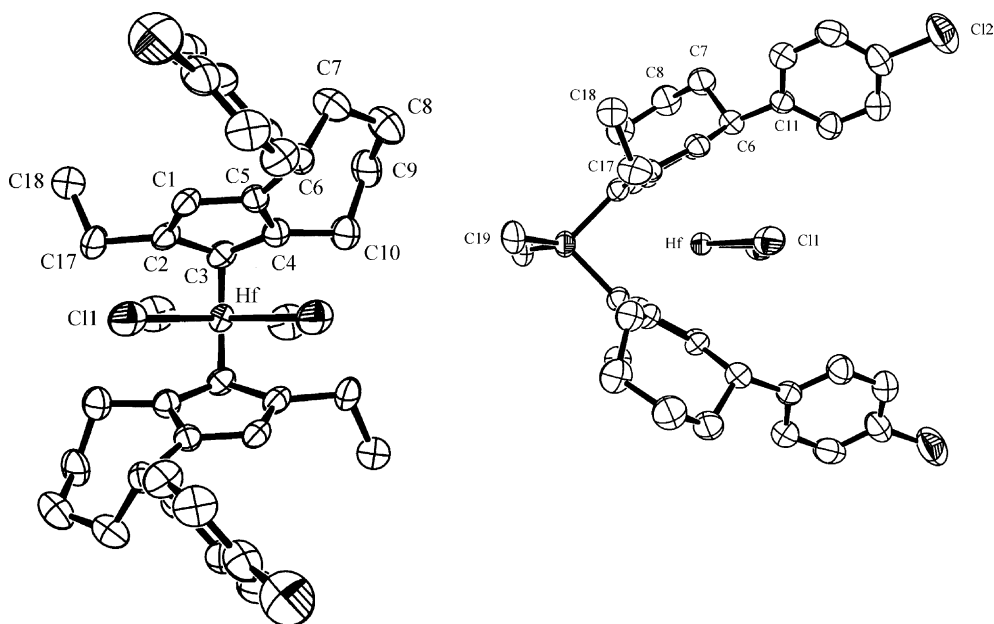
Fig. 2. ORTEP drawing of **5b**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. The C(18) atoms of 2-ethyl groups are disordered.

Table 1
Crystal data and structure refinement parameters for **4a** and **5b**

Empirical formula	$C_{36}H_{34}Cl_2HfSi$	$C_{38}H_{44}Cl_4HfSi$
Formula weight	744.11	849.11
Diffractometer	ENRAF-Nonius CAD4	Bruker SMART1000
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073(40 kV: 40 mA)	0.71073(50 kV: 40 mA)
Crystal system	Monoclinic	Orthorhombic
Space group	$C 2/c$	$Pbcn$
Unit cell dimensions		
a (Å)	14.480(3)	14.711(2)
b (Å)	9.750(3)	9.9280(10)
c (Å)	27.397(3)	24.454(3)
α (°)	90	90
β (°)	106.90(2)	90
γ (°)	90	90
V (Å³)	3700.9(14)	3571.5(7)
Z	4	4
D_c (Mg/m³)	1.336	1.579
Absolute coefficient μ(mm⁻¹)	3.016	3.280
F(0 0 0)	1480	1704
Crystal size (mm)	$0.2 \times 0.2 \times 0.1$	$0.1 \times 0.05 \times 0.05$
2θ Range (°)	1.55 to 25.92	1.67 to 28.40
Index ranges	$0 \leqslant h \leqslant 17, -12 \leqslant k \leqslant 0, -33 \leqslant l \leqslant 32$	$-18 \leqslant h \leqslant 18, -13 \leqslant k \leqslant 12, -32 \leqslant l \leqslant 14$
Number of reflections collected/unique	3583/3444	20370/4045
Completeness to 2θ (%)	–	80.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Number of data/restraints/parameters	3444/6/235	4045 / 22 / 250
Goodness-of-fit on F^2	0.666	0.711
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0380, wR_2 = 0.0997$	$R_1 = 0.0263, wR_2 = 0.0889$
R indices (all data)	$R_1 = 0.0401, wR_2 = 0.1032$	$R_1 = 0.0591, wR_2 = 0.1099$
Largest diff. peak and hole (e/Å³)	2.349 and −2.273	0.524 and −0.621

was found that these homologous hafnocene and zirconocene are nearly isostructural. On the other hand, a structural difference was observed in the comparison of the bis-azulenyl (**4a**) and the bis-tetrahydroazulenyl systems (**5b**). The distances of the Si–C(3) and C(3)–Hf in **5b** are longer than in **4a** and the angles γ and φ are

Table 2
Distances (Å) and angles (°) of the cyclopentadienyl moiety for **2a**, **4a**, and **5b**

Distances	**2a**	**4a**	**5b**
C(1)–M	2.575(2)	2.561(5)	2.542(5)
C(2)–M	2.487(2)	2.466(5)	2.460(5)
C(3)–M	2.465(2)	2.452(5)	2.462(5)
C(4)–M	2.554(2)	2.546(5)	2.521(5)
C(5)–M	2.640(2)	2.636(5)	2.617(5)
Cp(centroid)–M (d)[a]	2.231(2)	2.215(2)	2.209(3)
Cl–M	2.4222(11)	2.4011(13)	2.4096(13)
Si–Me	1.863(3)	1.878(7)	1.869(7)
Si–C(3)	1.889(3)	1.887(5)	1.893(5)
Angles[a]			
α	94.61(14)	94.6(3)	94.1(3)
β	85.2	85.1	85.2
γ[b]	163.3	163.0	156.9
φ[b]	128.4	129.2	141.3
θ	60.69(8)	60.1 (2)	59.7 (2)
Cl–M–Cl′	100.43(5)	99.08(8)	99.24(8)

[a] The figure for the geometrical parameters is shown in Chart 1.
[b] φ is the Cp centroid-metal-Cp centroid angles; γ is the angle between the Si–C(3) vector and Cp centroid–C(3) vector.

Table 3
Distances (Å) and angles (°) of the azulenyl ring for **2a**, **4a**, and **5b**

	2a	**4a**	**5b**
Distances[a]			
C(4)–C(5)	1.417(3)	1.427(7)	1.419(7)
C(5)–C(6)	1.520(3)	1.501(7)	1.517(6)
C(6)–C(7)	1.510(4)	1.522(8)	1.546(7)
C(7)–C(8)	1.326(4)	1.327(10)	1.509(8)
C(8)–C(9)	1.440(5)	1.455(11)	1.516(8)
C(9)–C(10)	1.347(4)	1.348(9)	1.528(8)
C(4)–C(10)	1.459(3)	1.467(7)	1.526(7)
Angles[a]			
C(4)–C(5)–C(6)	124.1(2)	124.4(5)	125.0(4)
C(7)–C(6)–C(5)	108.4(2)	108.5(5)	110.3(4)
C(8)–C(7)–C(6)	123.4(3)	123.6(6)	115.6(5)
C(7)–C(8)–C(9)	127.3(3)	126.7(6)	116.6(5)
C(10)–C(9)–C(8)	127.0(3)	126.9(6)	115.0(5)
C(9)–C(10)–C(4)	124.5(3)	124.8(6)	110.8(4)
C(5)–C(4)–C(10)	124.2(2)	123.6(5)	122.0(4)
Dihedral angle[b]	54.3(3)	54.4(7)	1.4(10)
Torsion angle[c]	8.7(4)	8.6(9)	16.2(10)

[a] The selected atom labeling of the azulenyl ring structure is shown in Chart 2.
[b] Dihedral angle between the least-square plane defined by the atoms C(4), C(5), C(6), and C(10) and the least-square plane by the atoms C(7), C(8), and C(9).
[c] Torsion angle between C(1)–C(5) bond of the Cp ring and C(6)–C(11) bond.

also changed. Furthermore, the ring structure of the seven-membered ring is different between **4a** and **5b**. The internal angles of the ring at C(7), C(8), C(9), and C(10) atoms in **5b** are decreased compared with those in **4a**. The dihedral angle between the least-square plane defined by the atoms C(4), C(5), C(6), and C(10) and the plane defined by C(7), C(8), and C(9) is greatly

decreased in **5b** (1.4°) compared with **2a** and **4a** (54.3° and 54.4°, respectively). The conformation of the tetrahydroazulenyl ring in **5b** is similar to the chair conformation that is found in cyclohexane. The direction of the phenyl (or 4-chlorophenyl) groups at the 4-position is also changed due to the conformational change of the seven-membered ring in the comparison of **5b** with **2a** and **4a**. The torsion angles between the cyclopentadienyl moieties and the 4-phenyl group bonds (i.e., C(1)–C(5) and C(6)–C(11)) are compared in Table 3. The angles in the bis-azulenyl system (8.7(4)° for **2a** and 8.6(9)° for **4a**) are the same; on the other hand, a larger angle is observed in the bis-tetrahydroazulenyl (16.2(10)° for **5b**). The X-ray analyses of the unbridged bis-tetrahydroazulenyl and disilyl-bridged bis-tetrahydroazulenyl zirconocenes have been reported previously [19]; however, **5b** is the first X-ray analysis of a dimethylsilyl bridged bis-tetrahydroazulenyl metallocene (see Charts 1 and 2).

2.3. Propylene polymerization

The liquid propylene polymerization of the bis-azulenyl (**4a** and **4b**) and the bis-tetrahydroazulenyl hafnocenes (**5a** and **5b**) has been examined using MAO as cocatalyst. The polymerization data are shown in Table 4 with the reference data obtained for the corresponding homologous zirconocenes (**2a** and **3a**) [20]. The activities of the hafnocene catalysts were much lower than those of the corresponding zirconocene catalysts, which is in agreement with the other metallocene systems. In
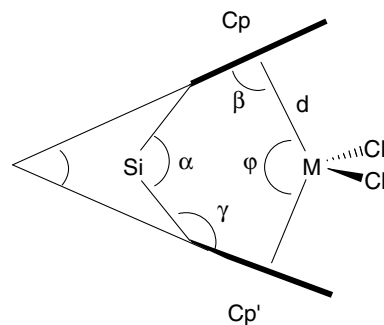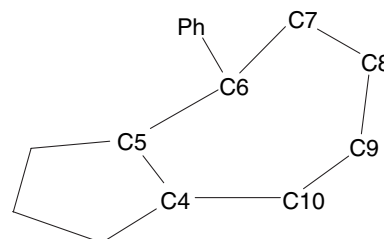

Chart 1. Scheme for the geometrical parameters.

Chart 2. Atom labeling of the azulenyl ring structure.

Table 4
Propylene polymerization data with **4a**, **4b**, **5a**, and **5b**/MAO catalysts

Entry	Metallocene	[cat] (μmol)	Al/M	Activity[a]	T_m (°C)	MFR[b] (g/10 min)	M_w (×10^3)	M_w/M_n
1	**4a**	0.4	10,000	80,000	154	0.08	840	3.8
2	**4b**	0.8	5000	23,700	157	0.1	–	–
3	**5a**	0.4	10,000	50,000	160	<0.01	2500	3.8
4	**5b**	0.8	5000	8700	161	0.05	–	–
5	**2a**[c]	0.4	10,000	108,000	151	1.3	350	2.7
6	**3a**[c]	0.2	10,000	450,000	156	0.9	370	2.1

Condition: liquid propylene, 70 °C, 1 h, cocatalyst: MMAO.
[a] g-polymer/mmol-metal.h.
[b] Melt flow rate under standard lading conditions (2.16 kg loaded at 230 °C) [20].
[c] Data from Ref. [12a].

particular, the activities of the bis-tetrahydroazulenyl hafnocenes (entries 3 and 4) were lower than the bis-azulenyl hafnocenes (entries 1 and 2); however, the bis-tetrahydroazulenyl zirconocene exhibited higher activity (entry 5 vs. 6) [21]. On the other hand, the melting point and molecular weight of the polymer obtained by the hafnocene catalysts were much improved, as expected. In the comparison between the corresponding hafnocenes and zirconocenes, both the melting point and the molecular weight were increased (entry 1 vs. 5, and 3 vs. 6). Moreover, introduction of 2-ethyl groups increased the melting point (entry 1 vs. 2, and 3 vs. 4) and a high melting point (160 °C for **5a** and 161 °C for **5b**) was observed with the bis-tetrahydroazulenyl hafnocenes. As mentioned above, the structures of the metallocenes are very similar between hafnocene (**4a**) and zirconocene (**2a**); however, the electronic effect is expected to be changed due to the difference in the metal (i.e., Hf and Zr). In the ^{1}H NMR spectra, a difference in the chemical shifts corresponding to the protons close to the metal was observed, probably indicating a change in the electronic effect. In the comparison between the bis-azulenyl and bis-tetrahydroazulenyl system, the direction of the 4-phenyl (or 4-chlorophenyl) groups is changed due to the conformation of the azulenyl ring, and the interaction of the phenyl groups and the growing polymer chain would be effective in giving the higher melting point and molecular weight in the bis-tetrahydroazulenyl system. It also should be noted that a difference in the chemical shifts corresponding to the protons at the 3-position between the bis-azulenyl and the bis-tetrahydroazulenyl system was also observed (5.85 ppm for **4a** and 5.68 ppm for **5a**). This probably results from a change of the electron density of the hafnium.

3. Experimental section

3.1. General procedures

All manipulations were performed under a nitrogen atmosphere. THF and diethyl ether were distilled from sodium/benzophenone. Dehydrated hexane, toluene, and dichloromethane were purchased from Kanto Chemical Co. and used without further purification. Dichlorodimethylsilane was freshly distilled before use. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JEOL GSX-400 spectrometer at 400 and 100 MHz, respectively. Mass spectra of metallocenes were measured on a Hitachi M-2500 using negative chemical ionization (CI) mode (isobutane) and an Applied Biosystems Voyager Elite-DE using the matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mode.

3.2. Synthesis of Me$_2$Si(2-Me-4-Ph-4H-Azu)$_2$HfCl$_2$ (4a)

2-Methylazulene was prepared by reported method from tropolone [22]. The preparation of dimethylbis(2-methyl-4phenyl-4*H*-dihydroazulenyl)silane (**1a**) from 2-methylazulene was reported previously in a low yield [12a]. The yield of **1a** was improved by the addition of a catalytic amount of 1-methylimidazole (2.5 mol%) and crude product of (**1a**, 5.84 g) was obtained from 2-methylazulene (3.22 g, 22.7 mmol).

To a solution of **1a** (5.84 g) in diethyl ether (30 mL) was added a solution of *n*-butyllithium in hexane (14.2 mL, 22.7 mmol, 1.60 M) at −78 °C and the mixture was stirred at room temperature overnight. To the resulting mixture were added toluene (30 mL) and diethyl ether (0.75 mL), cooled at −78 °C, and hafnium tetrachloride (3.30 g, 10.3 mmol) was added. After warming gradually to room temperature, the mixture was stirred for 4 h. The resulting mixture was concentrated under reduced pressure, filtered and washed with toluene (3 mL × 4), and extracted with dichloromethane (45 mL) to give a *rac/meso* mixture (r/m = 2/1) of **4a** (1.74 g, 20%, containing toluene). The *rac/meso* mixture of **4a** was suspended to dichloromethane (30 mL) and introduced to a glass reactor. After irradiation by high-pressure mercury lamp (100 W) for 40 min, the resulting mixture was concentrated under reduced pressure and washed with toluene (10 mL, 4 mL × 2) and

hexane (2 mL × 2) to give pure *rac*-**4a** as a pale yellow crystalline solid (917 mg, 55%, containing toluene).

rac-**4a**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.00 (s, 6H, SiMe$_2$), 2.27 (s, 6H, 2-Me), 5.02 (br d, 2H, 4-H), 5.84–5.92 (m, 6H), 6.05–6.09 (m, 2H), 6.82 (d, J = 12 Hz, 2H), 7.34–7.42 (m, 10H, arom); ^{13}C NMR (100 MHz, CDCl$_3$) δ 3.03 (SiMe$_2$), 18.07 (2-Me), 45.46 (4-C), 99.62, 123.92, 124.94, 126.24, 126.53, 126.83, 127.83, 128.12, 128.60, 128.99, 134.60, 139.61, 142.53; negative CI-MS: parent ion at m/z 744 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Calc. (C$_{36}$H$_{34}$Cl$_2$SiHf · 0.75C$_7$H$_8$): C, 60.92; H, 4.96. Found: C, 60.50; H, 5.26%.

3.3. Synthesis of Me$_2$Si(2-Me-4-Ph-4H-5,6,7,8-tetra-hydroAzu)$_2$HfCl$_2$ (5a)

A dry 0.1-L steel autoclave was charged with nitrogen. A solution of *rac*-**4a** (105 mg, 0.14 mmol) in dichloromethane (10 mL) and a suspension of platinum(IV) oxide (20 mg) in dichloromethane (3 mL) were introduced to the reactor. The mixture was stirred under hydrogen pressure of 1.0 MPa for 30 min. Platinum oxide was removed by decantation, the resulting solution was concentrated to give pure *rac*-**5a** as a colorless crystalline solid (98 mg, 93%).

rac-**5a**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.92 (s, 6H, SiMe$_2$), 1.10–1.30 (m, 4H), 1.60–1.95 (m, 6H), 2.00–2.35 (m, 4H), 2.11 (s, 6H, 2-Me), 2.91 (dd, J = 7 Hz, 2 H), 4.25 (d, J = 10 Hz, 2H, 4-H), 5.68 (s, 2H, 3-H), 7.30–7.39 (s, 10H, arom); ^{13}C NMR (100 MHz, CDCl$_3$) δ 3.29 (SiMe$_2$), 17.20, 29.13, 31.21, 31.72, 35.18, 45.08 (4-C), 99.82, 122.08, 126.24, 127.74, 128.18, 128.35, 131.00, 144.65, 145.36; negative CI-MS: parent ion at m/z 752 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Calc. (C$_{36}$H$_{42}$Cl$_2$SiHf · C$_7$H$_8$): C, 61.17; H, 5.97. Found: C, 60.69; H, 7.13%.

3.4. Synthesis of Me$_2$Si[2-Et-4-(4-ClPh)-4H-Azu]$_2$-HfCl$_2$ (4b)

2-Ethylazulene was prepared by reported method from tropolone [17]. To a solution of 4-chlorophenyllithium in a mixture of hexane (10 mL) and diethyl ether (10 mL), prepared from 4-bromochlorobenzene (1.75 g, 9.14 mmol) and 2 equiv. of a solution of *t*-butyllithium in pentane (11.8 mL, 18.2 mmol, 1.54 M) at −65 °C, was added 2-ethylazulene (1.28 g, 8.21 mmol) at −5 °C. After stirring for 2 h at room temperature, the lithium salt of 2-ethyl-4-(4-chlorophenyl)dihydroazulene was precipitated. To the reaction mixture were added THF (10 mL), 1-methylimidazole (15 μmol), and 0.5 equiv. of dichlorodimethylsilane (0.50 mL, 4.12 mmol) sequentially at 0 °C. The mixture was warmed to room temperature and stirred at this temperature for 45 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 of bis[2-ethyl-4-(4-chlorophenyl)dihydroazulenyl]dimethylsilane **1b** (2.68 g) as a diastereomeric mixture.

1b: ^{1}H NMR (400 MHz, CDCl$_3$) δ −0.55 to −0.30 (m, 6H, Me$_2$Si), 1.05–1.20 (m, 6H, CH_3CH$_2$), 2.30–2.55 (m, 4H, CH$_3$CH_2), 3.65–4.10 (m, 4H), 5.45–5.70 (m, 2H), 5.80–5.95 (m, 2H), 6.15–6.30 (m, 4H), 6.70–6.85 (m, 2H), 7.15–7.35 (m, 8H, arom).

To a solution of **1b** (2.68 g) in diethyl ether (11 mL) was added a solution of *n*-butyllithium in hexane (5.1 mL, 8.21 mmol, 1.61 M) at −78 °C. The mixture was stirred at room temperature for 2 h. To the resulting mixture was added toluene (90 mL), cooled to −65 °C, and hafnium tetrachloride (1.30 g, 4.06 mmol) was added at −65 °C. After warming gradually to room temperature, the mixture was stirred overnight. The resulting mixture (*r/m* = 6/4) was concentrated under reduced pressure, filtered, washed with toluene (1 mL × 2) and hexane (2 mL), and extracted with dichloromethane (20 mL). After concentrated under reduced pressure, the resulting solid was washed with ethanol (10 mL) and hexane (5 mL × 2) sequentially to give pure *rac*-**4b** (443 mg, 12%).

rac-**4b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.00 (s, 6H, SiMe$_2$), 1.05 (t, J = 8 Hz, 6H, CH_3CH$_2$), 2.49 (sept, J = 8 Hz, 2H, CH$_3$CHH′), 2.67 (sept, J = 8 Hz, 2H, CH$_3$CHH′), 5.00 (br d, 2H, 4-H), 5.78–5.93 (m, 6H), 6.05–6.10 (m, 2H), 6.81 (d, J = 12 Hz, 2H), 7.32 (s, 8H, arom); ^{13}C NMR (100 MHz, CDCl$_3$) δ 3.35 (SiMe$_2$), 17.65, 25.63, 44.79 (4-C), 98.77, 124.30, 125.12, 125.22, 126.34, 126.60, 128.76, 130.32, 132.56, 133.99, 135.63, 139.36, 140.86; negative MALDI-TOF-MS: parent ion at m/z 840 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Calc. (C$_{38}$H$_{36}$Cl$_4$-SiHf · 0.25C$_7$H$_8$): C, 55.25; H, 4.43. Found: C, 55.44; H, 5.07%.

3.5. Synthesis of Me$_2$Si[2-Et-4-(4-ClPh)-4H-5,6,7,8-tetrahydroAzu]$_2$HfCl$_2$ (5b)

A dry 0.1-L steel autoclave was charged with nitrogen. A solution of *rac*-**4b** (223 mg, 0.26 mmol) in dichloromethane (10 mL) and a suspension of platinum(IV) oxide (20 mg) in dichloromethane (4 mL) were introduced to the reactor. The mixture was stirred under hydrogen pressure of 1.0 MPa for 45 min. Platinum oxide was removed by decantation, the resulting solution was concentrated to give pure *rac*-**5b** as a colorless crystalline solid (183 mg, 82%).

rac-**5b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.91 (s, 6H, SiMe$_2$), 1.04 (t, J = 7 Hz, 6H, CH_3CH$_2$), 1.15–1.25 (m, 2H), 1.65–1.90 (m, 6H), 1.95–2.15 (m, 4H), 2.20–2.35 (m, 4H), 2.51 (sept, J = 7 Hz, 2H, CH$_3$CH′H), 2.87–2.93 (m, 2H), 4.21 (d, J = 10 Hz, 2H, 4-H), 5.69 (s, 2H, 3-H), 7.30 (s, 8H, arom); ^{13}C NMR (100 MHz,

CDCl$_3$) δ 3.61 (SiMe$_2$), 18.47, 24.72, 29.02, 31.04, 31.65, 35.19, 44.67 (4-C), 99.09, 128.13, 128.35, 128.61, 129.74, 129.79, 131.83, 143.22, 144.80; negative MALDI-TOF-MS: parent ion at *m/z* 848 (^{180}Hf^{35}Cl, M$^-$) with appropriate isotope ratios. Anal. Calc. (C$_{38}$H$_{44}$Cl$_4$-SiHf $\cdot$ 0.5C$_2$H$_4$Cl$_2$): C, 52.13; H, 5.16. Found: C, 52.26; H, 5.64%.

3.6. Crystallographic studies

The X-ray crystallographic analysis was performed using the crystals of **4a** and **5b**, which were obtained by slow addition of the vapor of hexane to the toluene/dichloromethane solution of **4a** or **5b** at room temperature. The crystal data and structure refinement parameters are shown in Table 1. The structure was solved by direct methods (SHELXS97) [23a] and refined by full matrix least-squares technique (SHELXL97) [23b].

3.7. Propylene polymerization

A dry 2-L steel reactor was charged with nitrogen and liquid propylene (1500 mL) at room temperature. Then a solution of methylaluminoxane in toluene (2.0 mL, 4.0 mmol, Al/Hf = 5000 or 10,000, MMAO purchased from Tosoh Finechem Corp.) and a solution of metallocene in toluene (0.8 mL, 0.8 μmol or 0.4 mL, 0.4 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 weighting.

3.8. Polymer analysis procedures

Molecular weight was 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. Melt flow rate (MFR) was determined under standard conditions [ASTM D 1238: weight of polymer in grams extruded through a standard die under a standard load (2.16 kg) during 10 min at 230 °C]. Molecular weight is reflected inversely in the MFR.

4. Supporting information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 256451 and 256452 for **4a** and **5b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-366-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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[21] The solubility of the bis-tetrahydroazulenyl hafnocenes (**5a** and **5b**) was lower than that of the corresponding bis-azulenyl hafnocenes (**4a** and **4b**). One of the reasons for the lower activities of the bis-tetrahydroazulenyl hafnocenes catalysts may be insufficient activation of the metallocenes with MAO to active species due to the low solubility.

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