Photochemical Intramolecular [2+2] Cycloaddition of Bridged Bis-azulenyl Zirconocenes

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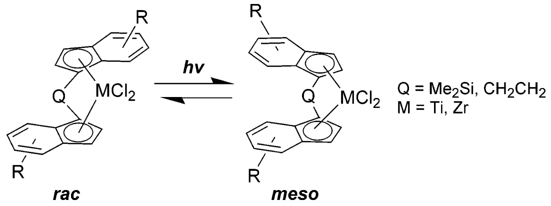
Photochemical reaction of a *rac*/*meso* mixture of bridged bis-azulenyl zirconocenes was investigated. Irradiation of the *rac*/*meso* mixture of dichlorodimethylsilylenebis(2-methyl-4-phenyl-4*H*-azulenyl)zirconium resulted in a rapid conversion of only the *meso* isomer to give a novel bridged metallocene with a bis-azulenyl ligand cross-linked by a cyclobutylene ring, which was produced by intramolecular [2+2] cycloaddition, and the *rac* isomer was stable toward photoirradiation. The structure of the cyclobutylene-bridged metallocene derived from *meso*-dichlorodimethylsilylenebis(2-methyl-4-(2-fluoro-4-biphenylyl)-4*H*-azulenyl)zirconium was determined by X-ray crystallographic analysis. The structure shows a bond formation between two azulenyl rings at the 7- and 8-position, respectively, to form a four-membered ring. The solubility of cyclobutylene-bridged metallocenes in solvent was found to be much higher than those of *rac*/*meso* isomers. After photoirradiation of a *rac*/*meso* mixture, *rac* isomers were easily isolated.

Introduction

Racemic *ansa*-metallocene complexes of group IV transition metals can be activated by methylaluminoxane (MAO) and other cocatalysts to generate catalysts for isotactic propylene polymerization.[1] Since the discovery of *ansa*-zirconocene/MAO catalysts producing isotactic polypropylene,[2] a number of metallocenes have been synthesized and polymerization behavior was examined in terms of activity, melting point, and molecular weight of the polymer. In particular, the bridged bis-indenyl zirconocene system was extensively developed in both academic and industrial fields. In the course of preparation of the metallocene, these bridged metallocenes are obtained as a mixture of *rac* and *meso* isomers in general. To produce isotactic polypropylene, isolation of the *rac* isomer is necessary. However, purification of the mixture by recrystallization and isolation of the *rac* isomer is often difficult because of similar solubility of both isomers. For this problem, some strategies for the control of the diastereoselectivity (i.e., *rac*/*meso* selectivity) in the preparation were investigated.[3−5] Therefore, an efficient method for the diastereoselective synthesis of the *rac*-bridged metallocene and the separation of the *rac*/*meso* mixture would be important. In the bridged bis-indenyl metallocene system, photochemical isomerization of the *rac*/*meso* isomer has been known, as shown in Scheme 1, and it is possible to convert the *rac*/*meso* mixture into pure *rac* isomer in a specific metallocene system.[6]

Scheme 1. Photochemical Interconversion of the Bridged Bis-indenyl System



Recently, we have reported the synthesis and structural analysis of the bridged bis-azulenyl zirconocenes.[7] Here we report the photochemical behavior of the

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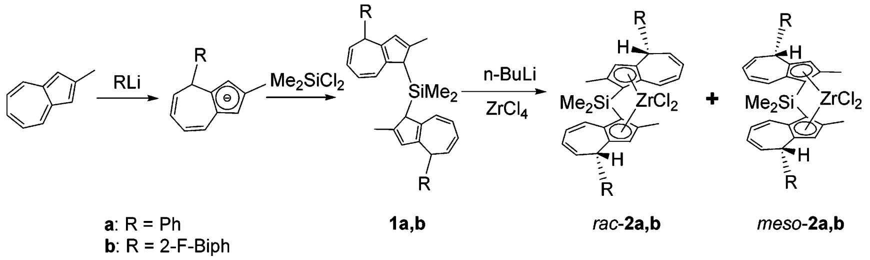
Scheme 2. Synthesis of the Bridged Bis-azulenyl Zirconocenes (2a,b)



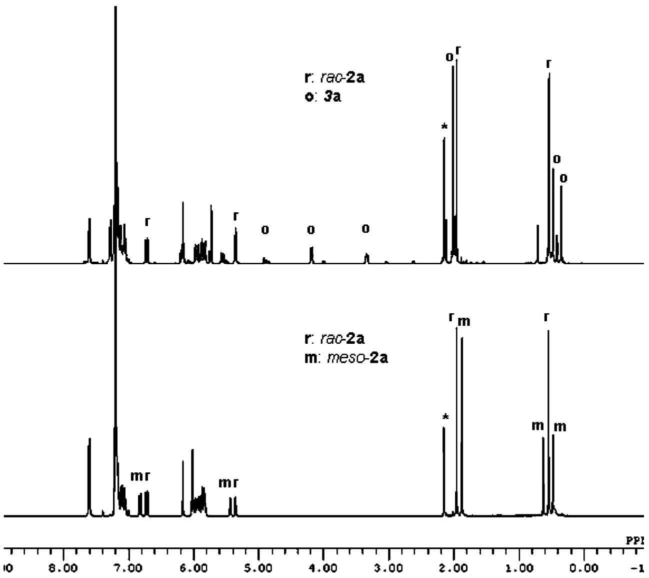


Figure 1. ^{1}H NMR spectra (400 MHz, benzene-d_6) of the mixture of *rac*-**2a** and *meso*-**2a** (bottom) and the mixture of *rac*-**2a** and **3a** (top), which was obtained by photolysis of this sample in the NMR tube. The solvent signal is marked with an asterisk (*).

bridged bis-azulenyl metallocenes and novel bridged metallocene with the bis-azulenyl ligand cross-linked by the cyclobutylene ring produced by intramolecular [2+2] cycloaddition. We have been interested in the difference between the bridged bis-indenyl system and the bridged bis-azulenyl system toward photoirradiation.

Results and Discussion

A mixture of *rac* and *meso* dichlorodimethylsilylenebis(2-methyl-4-phenyl-4*H*-azulenyl)zirconium (**2a**) was prepared by the reported method as shown in Scheme 2.[7] A solution of a *rac*/*meso* mixture of **2a** in C_6D_6 was exposed to sunlight in a NMR tube at room temperature. After irradiation, the ^{1}H NMR spectrum showed complete disappearance of the *meso* isomer and another signal set was observed; however the *rac* isomer remained, as shown in Figure 1. This photochemical reaction proceeded more rapidly in the irradiation by a high-pressure mercury lamp. The structure of **3a** was confirmed by the analysis of the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **3a** in C_6D_6 shows one singlet corresponding to the 2-methyl proton at 2.02 ppm and two singlets corresponding to the dimethylsilyl proton at 0.36 and 0.48 ppm, indicating C_1 symmetry similar to that of *meso*-**2a**. The two signals corresponding to the proton at the 7- and 8-position of the azulenyl rings are largely shifted upfield compared to those of *meso*-**2a**, indicating the protons at the 7- and 8-position are not alkenyl protons. Although photochemical interconversion between the *rac* and *meso* isomer is possible in the specific bridged bis-indenyl metallocene system as shown Scheme 1, photochemical interconversion of *meso*-**2a** into *rac*-**2a** was not observed. This difference was ascribed to the structural difference between the bis-indenyl system and the bis-azulenyl system (**2a**); more specifically, the carbon atoms at the 4-position of the azulenyl rings are sp^3 carbon and have a chiral center in the bis-azulenyl system, as shown in Scheme 3. Interconversion of *meso*-**2a** (4,4′-(*R,R*), (*S,S*)) into a *rac* isomer is expected to be difficult, because steric repulsion of 4-substituents will be increased in the resulting *rac* isomer (4,4′-(*R,S*), (*S,R*)).

Scheme 3. Photochemical Reaction of the Bridged Bis-azulenyl Zirconocenes (2a,b)

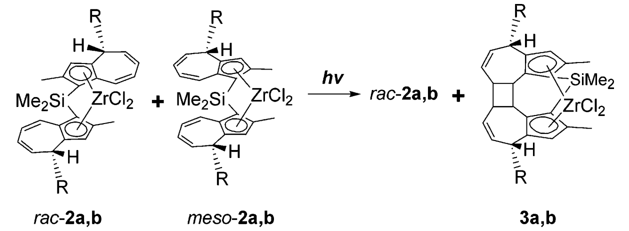
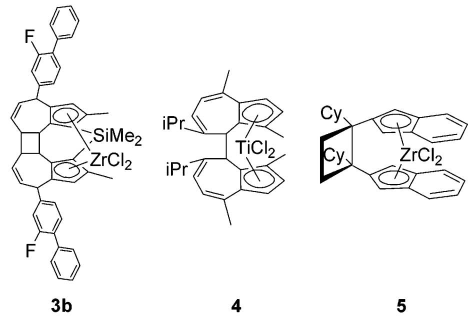


Chart 1



The purification of the resultant photochemical reaction mixture (*rac*-**2a** and **3a**) was attempted by recrystallization; however **3a** could not be isolated due to relatively high solubility in the solvent. Then, an analogous metallocene in which a 2-fluoro-4-biphenylyl group was introduced at the 4-position of the azulenyl ring (**2b**) was synthesized in order to isolate photochemical converted product **3b**, because we believe 2-fluoro-4-biphenylyl groups lower the solubility of the

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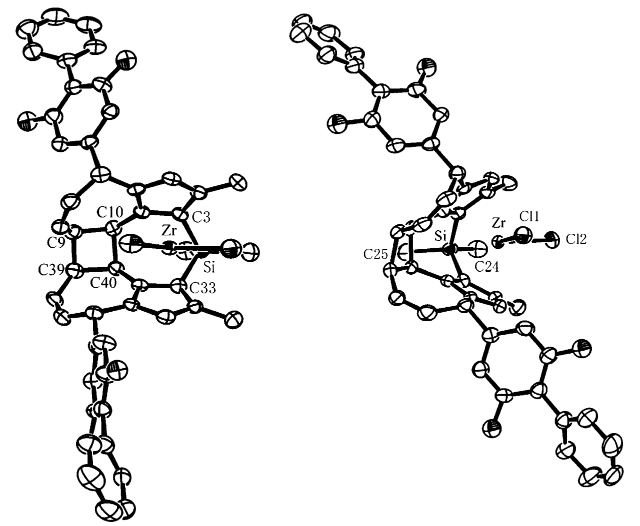

Figure 2. ORTEP drawing of **3b.** Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b

Zr−Cl1	2.4326(17)	Cl1−Zr−Cl2	96.65(7)
Zr−Cl2	2.4327(18)	C3−Si−C33	93.1(2)
Si−C3	1.898(6)	C25−Si−C24	107.8(4)
Si−C33	1.902(6)	C9−C10−C40	89.4(4)
Si−C24	1.861(8)	C39−C40−C10	89.4(4)
Si−C25	1.858(7)	C40−C39−C9	89.3(4)
C9−C10	1.551(9)	C10−C9−C39	88.6(5)
C10−C40	1.561(8)		
C39−C40	1.541(9)		
C9−C39	1.573(8)		

metallocene in solvent. **2b** was synthesized in a good yield by a procedure similar to that of **2a**, as shown in Scheme 2. By the reaction of 2-fluoro-4-bromobiphenyl and 2 equiv of *tert*-butyllithium, 2-fluoro-4-biphenylyllithium was obtained quantitatively. A catalytic amount of 1-methylimidazole was added to improve the yield of **1b** in the reaction of the lithium salt of dihydroazulene and dichlorodimethylsilane.[8] The solubility of **2b** was lower than that of **2a**, as expected. After irradiation to the *rac*/*meso* mixture of **2b**, the pure photoinduced intramolecular [2+2] cycloaddition product (**3b**) was obtained by recrystallization.

The structure of **3b** was analyzed by X-ray crystallographic analysis. An ORTEP drawing of **3b** is shown in Figure 2, and selected bond lengths and angles are shown in Table 1. The ORTEP drawing shows bond formation between two azulenyl rings at the 7- and 8-position, respectively, to form a four-membered ring. So, two azulenyl rings are triple bridged, and to the best of our knowledge, **3b** is the first example of the triple-bridged *ansa*-metallocene complex of group IV transition metals.[9] In the crystal structure, the two azulenyl moieties are located unsymmetrically; however the ^{1}H NMR spectrum of **3b** shows only one set of signals corresponding to the azulenyl moieties. This indicates that the two azulenyl moieties are equivalent, and **3b** shows C_1 symmetry in solution. Similar intramolecular [2+2] cycloaddition of the unbridged zirconocenes was reported previously.[10] But **3a** and **3b** are the first examples of the intramolecular [2+2] cycloaddition of bridged zirconocene. In the unbridged system, the rotation of the two indenyl moieties or cyclopentadienyl moieties is easy, so that [2+2] cycloaddition would be easily expected. In the bridged system, a conformational change of the framework is relatively difficult due to the structural rigidity. The formation of the [2+2] cycloaddition products (**3a**, **b**) indicates that the conformational change of the seven-membered rings is possible to form the four-membered ring from the *meso* isomers of the bridged bis-azulenyl metallocenes. The bridged bond lengths in **3b** [1.561(8) Å (C10−C40) and 1.573(8) Å (C9−C39)] are similar to that in bis-azulenyl titanocene (1.56 Å in **4**).[11] The bond lengths of the four-membered ring are in the typical range [from 1.541(9) Å (C39−C40) to 1.573(8) Å (C9−C39)] and are slightly larger than those of the cyclobutylene-bridged metallocene of the unbridged zirconocene (from 1.527(5) to 1.556(6) Å in **5**).[10b] The bond angles of the four-membered ring in **3b** are almost the same [from 88.6(5)° to 89.4(4)°]. The sum of the internal bonding angles of the four-membered ring is 356.7°, indicating a slightly puckered structure.

Polymerization of olefin was examined with **3b** and MAO. No activity was found in the propylene polymerization; however, polyethylene was obtained in the ethylene polymerization with relatively low activity. This polymerization behavior indicates that the open space for coordination of the monomer is relatively small and the coordination of propylene monomer and chain propagation are difficult due to the steric hindrance.

In many bridged metallocenes, the solubility of the *rac* and *meso* isomers is similar and purification of the *rac*/*meso* mixture for isolation of the *rac* isomer by recrystallization is often difficult. So far, few efficient purification methods of the *rac*/*meso* mixture were reported.[6c,12] In the bridged bis-azulenyl system, the solubility of the cyclobutylene-bridged metallocenes (**3a**,**b**) was found to be much higher than that of the *rac*/*meso* isomers, in contrast to similar solubility of the *rac* and *meso* isomers. After photoirradiation of the *rac*/*meso* mixture, only the *rac* isomers were easily isolated in high yield. For example, in the reaction of **2a**, the resultant photochemical reaction mixture was washed with toluene to give pure *rac*-**2a** in a high conversion yield. From the toluene-soluble part, only a small

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[8] It was reported previously that the yield of bis-azulenylsilanes and the bis-indenylsilanes was increased by the addition of a catalytic amount of 1-methylimidazole or 4-(dimethylamino)pyridine. Kato, T.; Okano, K.; Sugano, T.; Ohtani, Y.; Kitagawa, H.; Nishimura, S. (Mitsubishi Chemical Corp.) World Patent Application WO98/31690A1, 1998.

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amount of *rac*-**2a** was recovered, indicating the large difference of solubility between *rac*-**2a** and **3a**.[13] The investigation and application of this purification method to other bridged bis-azulenyl metallocenes are currently under way in our laboratory.

Experimental Section

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 prior to use. ^{1}H NMR spectra were recorded on a Varian Gemini-300 and a JEOL GSX-400 spectrometer at 300 and 400 MHz, respectively. Chemical shifts are reported relative to Me_4Si ($CDCl_3$) at 0.00 ppm or residual solvent signals ($CDCl_3$ at 7.26 ppm; C_6D_6 at 7.2 ppm). Mass spectra of zirconocenes were measured on a JEOL JMS-700/MStation using negative desorption chemical ionization (DCI) mode (isobutane) and an Applied Biosystems Voyager Elite-DE using matrix-assisted laser desorption ionization−time-of-flight (MALDI-TOF) mode.

Photochemical Reaction of the *rac/meso* Mixture of Me_2Si(2-Me-4-Ph-4*H*-Azu)$_2$$ZrCl_2$ (2a). The *rac*/*meso* mixture of dichlorodimethylsilylenebis(2-methyl-4-phenyl-4*H*-azulenyl)zirconium (**2a**) was prepared by the reported method.[7] The mixture of **2a** (10.21 g, 15.6 mmol) was suspended in dichloromethane (150 mL) and introduced into a glass reactor equipped with high-pressure mercury lamp (100 W) with the cooling jacket. After irradiation for 4.5 h, complete conversion of *meso*-**2a** to **3a** was observed by ^{1}H NMR. The resulting mixture was concentrated and washed with toluene (50, 30, 20, 10 mL, subsequently) and hexane (20 mL) to give pure *rac*-**2a** (6.06 g, 52%, containing 1 molecule of toluene). The first and second toluene extracts were combined and concentrated under reduced pressure to give a mixture of **3a** and *rac*-**2a** (**3a**/*rac*-**2a** = 40:1, 33%).

3a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (s, 3 H, $SiMe_2$), 0.83 (s, 3 H, $SiMe_2$), 2.05 (s, 6 H, 2-Me), 3.76 (br d, 2 H), 4.50−4.55 (m, 2 H), 5.03 (d, 2 H, 4-*H*), 5.58 (br d, 2 H), 5.61 (s, 2 H, 3-*H*), 5.90−6.00 (m, 2 H), 7.08−7.23 (m, 10 H, arom).

Synthesis of Me_2Si(2-Me-4-(2-F-4-Biphenylyl)-4*H*-Azu)$_2$-$ZrCl_2$ (2b). To a solution of 2-fluoro-4-biphenylyllithium, prepared from 2-fluoro-4-bromobiphenyl (6.08 g, 24.2 mmol) and 2 equiv of a solution of *tert*-butyllithium in pentane (33 mL, 48.4 mmol, 1.45 M) at −40 °C, was added 2-methylazulene (3.2 g, 23 mmol) at −10 °C. After stirring for 1 h at the same temperature, the violet color in solution disappeared and the lithium salt of 2-methyl-4-(2-fluoro-4-biphenylyl)dihydroazulene precipitated. After hexane (50 mL) was added to the suspension, the soluble component was decanted to remove it. The reaction mixture was cooled to 0 °C, and THF (40 mL) and hexane (30 mL) were added to give a homogeneous solution. Dichlorodimethylsilane (1.38 mL, 11.4 mmol) and 1-methylimidazole (50 μL) were added sequentially. The mixture was warmed to room temperature and stirred for 1 h. After quenching with a solution of ammonium chloride, the organic phase was separated and dried over $MgSO_4$, and the solvent was removed to give the crude product bis(2-methyl-4-(2-fluoro-4-biphenylyl)dihydroazulenyl)dimethylsilane (**1b**) (7.72 g) as a diastereomer mixture. **1b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.6 to −0.2 (6 H, Me_2Si), 2.1−2.2 (6 H, 2-Me), 3.6−4.15 (4 H), 5.5−6.05 (4 H), 6.2−6.35 (4 H), 6.7−6.85 (2 H), 7.0−7.6 (16 H, arom).

To a solution of **1b** (7.72 g) in diethyl ether (30 mL) was added a solution of *n*-butyllithium in hexane (14.3 mL, 22.7 mmol, 1.59 M) at −10 °C, and the mixture was stirred at room temperature for 1 h. To the resulting mixture was added toluene (180 mL), the mixture was cooled to −10 °C, and zirconium tetrachloride (2.65 g, 11.37 mmol) was added at the same temperature. After warming gradually to room temperature with stirring, the mixture was stirred for 3 h. The resulting suspension was concentrated under reduced pressure, and the yellow solid was obtained by filtration. Washing with toluene (5 mL × 3), hexane (5 mL × 3), ethanol (10 mL × 2), and hexane (5 mL × 2) subsequently gave the *rac*/*meso* mixture of **2b** (4.48 g, 42%, *rac*/*meso* = 1:1, containing 1 molecule of toluene).

The *rac*/*meso* mixture of **2b** (4.48 g) was suspended in dichloromethane (120 mL) and introduced into a glass reactor. After irradiation by a high-pressure mercury lamp (100 W) for 3.5 h and the volume of the mixture was reduced, the resulting precipitate was filtered and washed with hexane (10 mL) to give pure *rac*-**2b** as a pale yellow crystalline solid (2.24 g, 55%). **2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 6 H, $SiMe_2$), 2.22 (s, 6 H, 2-Me), 4.98 (br d, 2 H, 4-*H*), 5.8−6.2 (m, 8 H), 6.79 (d, *J* = 12 Hz, 2 H), 7.2−7.6 (s, 16 H, arom); negative DCI-MS, parent ion at *m*/*z* 842 ($^{92}Zr^{35}Cl$, M^-) with appropriate isotope ratios. Anal. Found: C, 66.33; H, 5.11. Calcd ($C_{48}H_{40}Cl_2F_2SiZr\cdot 0.25C_2H_4Cl_2$): C, 66.97; H, 4.75.

Isolation of Dichloro[(1,2,3,3a,12d-η:9a,10,11,12,12a-η)-4,9-bis(2-fluoro-4-biphenylyl)-2,11-dimethyl-4,6a,6b,9,-12b,12c-hexahydro-1,12-epidimethylsilanocyclobuta[1,2-e:4,3-e′]diazulenyl]zirconium (3b). The dichloromethane extraction from the mixture after irradiation of the *rac*/*meso* mixture of **2b** was concentrated, washed with toluene (15 mL, 10 mL × 2) and dichloromethane (50 mL × 3), and recrystallized with 1,2-dichloroethane to give pure **3b** as a white-yellow crystalline solid.

3b: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.67 (s, 3 H, $SiMe_2$), 0.92 (s, 3 H, $SiMe_2$), 2.16 (s, 6 H, 2-Me), 3.87 (br d, 2 H), 4.61 (br d, 2 H), 5.12 (d, *J* = 6 Hz, 2 H, 4-*H*), 5.70 (br d, 2 H, 6-*H*), 5.75 (s, 2 H, 3-*H*), 6.06 (dd, *J* = 12 Hz, *J* = 6 Hz, 2 H, 5-*H*), 6.94 (d, *J* = 15 Hz, 2 H, arom), 7.07 (d, *J* = 6 Hz, 2 H, arom), 7.35−7.55 (m, 12 H, arom); negative MALDI-TOF-MS, parent ion at *m*/*z* 842 ($^{92}Zr^{35}Cl$, M^-) with appropriate isotope ratios. Anal. Found: C, 67.32; H, 5.14. Calcd ($C_{48}H_{40}Cl_2F_2SiZr\cdot 0.2C_2H_4Cl_2$): C, 67.22; H, 4.76.

Crystallographic Studies. The X-ray crystallographic analysis was performed using a crystal with the size 0.2 × 0.1 × 0.03 mm, obtained by recrystallization from hexane/1,2-dichloroethane 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)[14a] and refined by full matrix least-squares technique (SHELXL97).[14b] A total of 9215 reflections were measured, of which 5677 unique reflections were used in the structure refinement. The final *R* factor was 0.0532 for 5677 reflections.

Crystal data: fw = $C_{48}H_{40}Cl_2F_2SiZr$, triclinic system, space group $P\bar{1}$, $a = 12.394(2)$ Å, $b = 14.075(2)$ Å, $c = 11.552(2)$ Å, $\alpha = 91.296(2)°$, $\beta = 99.691(2)°$, $\gamma = 71.317(2)°$, $V = 1880.7(5)$ Å^3, $Z = 2$, $D_{calc} = 1.492$ g/cm^3, $R = 0.0532$ for 4217 reflections ($F_o > 2\sigma(F_o)$).

Ethylene Polymerization. A dry 1 L steel reactor was charged with nitrogen and dry toluene (500 mL, dried over 4 Å molecular sieves) at room temperature. Then a solution of methylaluminoxane in toluene (2.0 mL, 4.0 mmol, Al/Zr = 10 000, MMAO purchased from Tosoh Finechem Corp.) and a solution of **3b** (1.68 mg, 2 μmol) in toluene (2.0 mL) were added

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[13] In contrast, recrystallization of the *rac*/*meso* mixture (*rac*-**2a**/*meso*-**2a** = 60/40) from toluene gave the mixture (*rac*/*meso* = 65/35), indicating the small difference of solubility between them. Fractional recrystallization of the mixture gave pure *rac*-**2a** in a low yield (12%).

[14] (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL97*, Program for Crystal Structure Refinement; University of Gottingen: Germany, 1997.

to the reactor at room temperature. The reactor was heated to 70 °C within 10 min, pressurized with 2 MPa of ethylene, and kept at 70 °C for 1 h with stirring. The reaction was stopped by adding ethanol. The polymer obtained was filtered and dried. The activity of polymerization was 27 000 g PE/g complex, and the melting point of the polymer was 137 °C measured by DSC (Dupont TA2000).

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Supporting Information Available: Crystallographic details, including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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