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Synthesis of Titanium(IV) and Zirconium(IV) Complexes with an [OSSO]-Type Bis(phenolate) Ligand Bearing a *trans*-Cyclohexane-1,2-diyl Ring and 1-Hexene Polymerization

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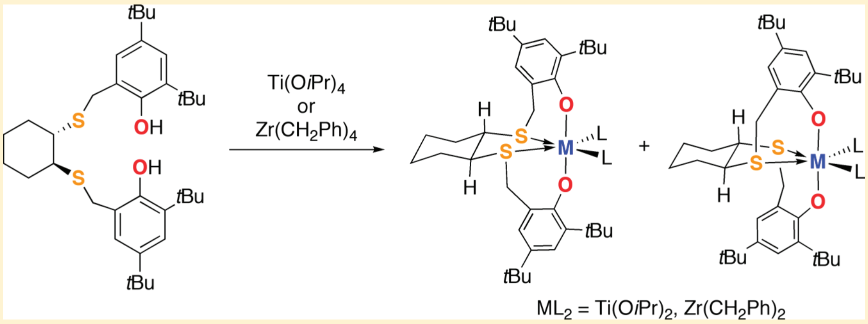
S *Supporting Information*

ABSTRACT:



The Ti(IV) and Zr(IV) complexes **9** and **11** with a new [OSSO]-type bis(phenolate) ligand bearing a *trans*-cyclohexane-1,2-diyl ring (**6**) were synthesized. The reaction of **6** with Ti(O*i*Pr)$_4$ in toluene gave the two C_2-symmetric, diastereomeric Ti complexes (Λ*,*S**,*S**)-**9** and (Δ*,*S**,*S**)-**9**, the latter of which was characterized by X-ray crystallography. The reaction of **6** with Zr(CH$_2$Ph)$_4$ also provided a mixture of the two C_2-symmetric diastereomers (Λ*,*S**,*S**)-**11** and (Δ*,*S**,*S**)-**11**. Polymerization of 1-hexene employing **11** as the precatalyst yielded isotactic poly(1-hexene) with high activity. In relation to the activity, an NMR study was carried out for the cationic zirconium complex $\mathbf{12}^+[\mathrm{B(CH_2Ph)(C_6F_5)_3}]^-$ in comparison with the corresponding complex $\mathbf{13}^+[\mathrm{B(CH_2Ph)(C_6F_5)_3}]^-$, bearing a *trans*-cyclooctane-1,2-diyl ring in the ligand.

INTRODUCTION

Development of homogeneous, single-site metallocene and post-metallocene catalysts for olefin polymerization has been drawing considerable attention[1] since the reports by Sinn and Kaminsky.[2] Recently, group 4 metal complexes having [OSSO]-type bis(phenolate) ligands have been extensively investigated (Chart 1).[3−7] Kol developed complexes **1**, after their study on complexes bearing [ONNO]-type tetradentate ligands,[8] and showed that **1** served as a precatalyst for the polymerization of 1-hexene with moderate activity to give atactic poly(1-hexene).[3a] On the other hand, Okuda and co-workers prepared complexes **2**[4] and **3**.[5] Polymerization of styrene with **2** (R^1, R^2 = *t*Bu; ML_2 = $TiCl_2$, Ti(O*i*Pr)$_2$, Zr(CH$_2$Ph)$_2$, Hf(CH$_2$Ph)$_2$) activated by methylaluminoxane (MAO) gave isotactic polystyrenes,[4a] while that of 1-hexene with **2** (R^1, R^2 = *t*Bu, L = Me, CH$_2$Ph) activated by B(C$_6$F$_5$)$_3$ gave oligo(1-hexene)s.[4b] Polymerization of styrene with 1-hexene as a chain-transfer agent with enantiopure **3** (L = Cl) activated by MAO provided optically active, isotactic polystyrenes with oligo(1-hexene) terminal groups.[5] There is a difference between **1** and **2** in the chelation ring sizes: 6−5−6 for **1** and 5−5−5 for **2**.[3a] These [OSSO]-type bis(phenolate) ligands have also been employed for the synthesis of complexes with transition metals in addition to group 4 elements.[9]

Recently we reported the first syntheses of *trans*-cyclooctane-1,2-dithiol.[10] Stimulated by the earlier studies mentioned above, we prepared Zr complex **4** with a new [OSSO]-type ligand bearing a *trans*-cyclooctane-1,2-diyl ring (**5**) (Chart 2).[7] Complex **4** activated by B(C$_6$F$_5$)$_3$ or (Ph$_3$C)[B(C$_6$F$_5$)$_4$] provided a highly active and highly stereospecific catalytic system for the polymerization of 1-hexene to give isotactic poly(1-hexene)s. We assumed two roles of the fused eight-membered ring: one is the rigidity of the entire molecule to retain a favorable reaction site for the isospecific polymerization, and the other is the partial flexibility to follow fine structure changes of the complex during the course of the polymerization reaction.[7] An aim of the present study is to clarify the influence of the fusion of cycloalkane rings on [OSSO]-type bis(phenolate) tetradentate ligands. We report

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Chart 1. Group 4 Metal Complexes 1−3 with [OSSO]-Type Ligands

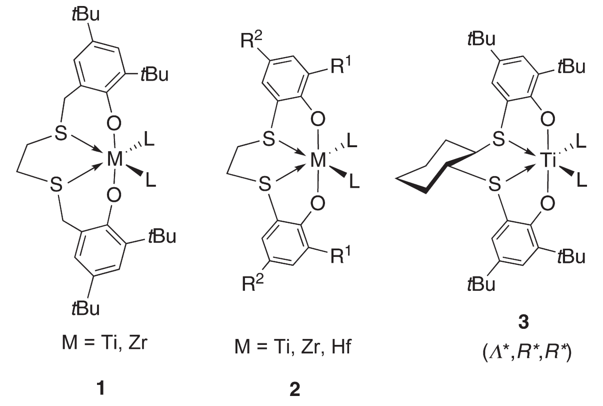
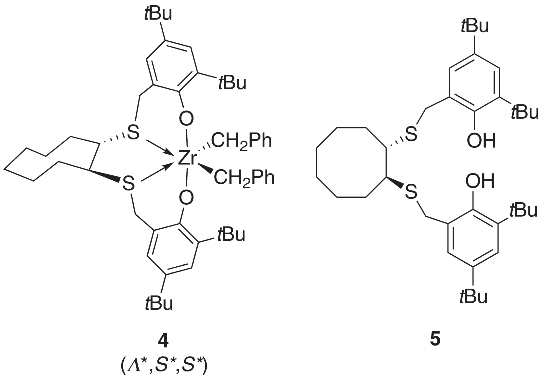


Chart 2. Zirconium Complex 4 and the Ligand 5 with a *trans*-Cyclooctane-1,2-diyl Ring

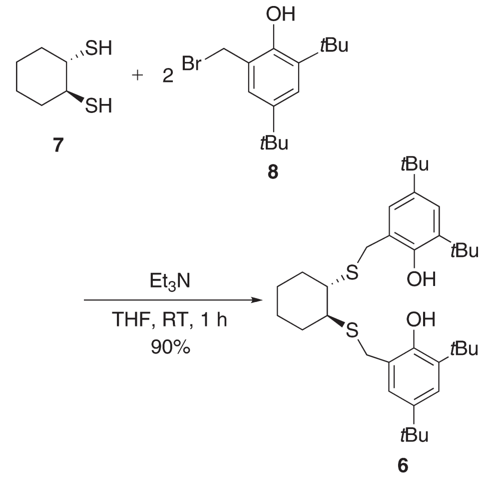


here the preparation of the [OSSO]-type tetradentate ligand **6**, having a *trans-cyclohexane-1,2-diyl* ring, the preparation of titanium and zirconium complexes using **6**, and the catalytic ability of the zirconium complex to polymerize 1-hexene. We also discuss the effect of fusion of a cycloalkane-1,2-diyl ring in ligands **5** and **6**.

■ RESULTS AND DISCUSSION

Ligand **6** was prepared by the reaction of *trans*-cyclohexane-1,2-dithiol (**7**)[11] with the 2-hydroxybenzyl bromide **8**[12] in the presence of triethylamine in 90% yield (Scheme 1). The structure of **6** was supported by its spectroscopic data and finally determined by X-ray crystallography (Figure 1). The $C_6H_{10}(SCH_2)_2$ part was disordered, and Figure 1 shows only the major set (occupancy 78%) of the part. Under such circumstances, **6** took a diaxial conformation, which is in contrast with the diequatorial conformation of **5**.[5b]

Scheme 1. Synthesis of Ligand 6 by the Reaction of 7 with 8



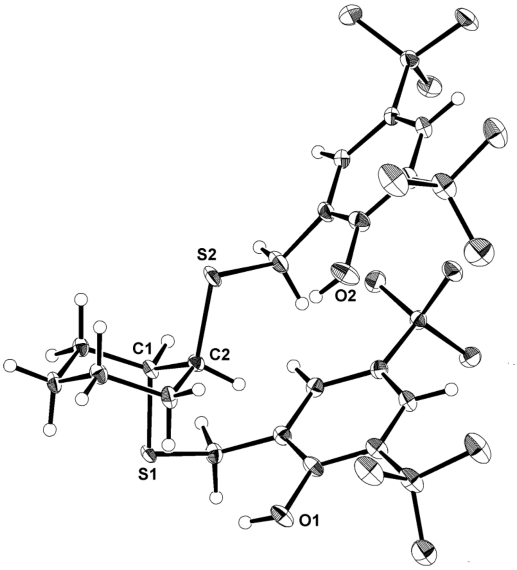
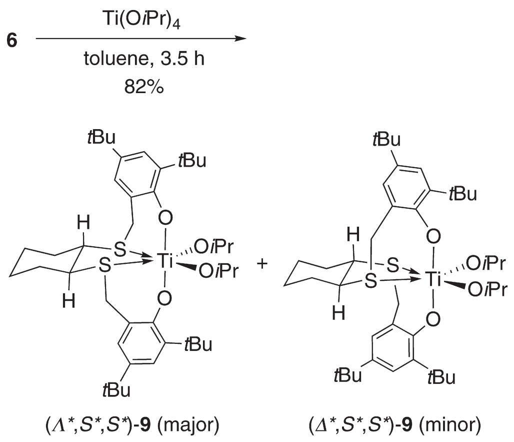


Figure 1. ORTEP drawing of ligand **6** with 30% probability ellipsoids. The $C_6H_{10}(SCH_2)_2$ part was disordered, and only the major set (occupancy 78%) of this part is shown. Hydrogen atoms of *tert*-butyl groups are omitted for clarity. Relevant bond lengths (Å) and a dihedral angle (deg): S1−C1 = 1.841(6), S2−C2 = 1.842(5); S1−C1−C2−S2 = 167.1(2).

Ti Complexes. Ligand **6** was treated with Ti(O*i*Pr)$_4$ in toluene at room temperature for 3.5 h under an argon atmosphere (Scheme 2). Whereas the ^{1}H NMR spectrum measured at 303 K showed only broad signals, that measured at 253 K in C_7D_8 showed two well-resolved sets of signals, indicating C_2 symmetry, in an integral ratio of 3:2. Figure 2 shows the part of the NMR spectrum for benzyl and isopropoxy methine protons. Benzyl protons of the major species appeared at δ 3.39 and 4.01 ppm as doublets (J_{gem} = 14 Hz), and those of the minor species were observed at δ 3.37 and 3.63 ppm as doublets (J_{gem} = 14 Hz). Methine protons of isopropoxy groups in the major and minor species resonated at δ 4.97 and 5.20, respectively, as septets. For aromatic protons, nonequivalent protons of the major species were observed at δ 6.76 and 7.58 ppm as doublets (J = 3 Hz) and those of the minor species appeared at δ 6.69 and 7.50 ppm as doublets (J = 3 Hz). Thus, each species has magnetically equivalent $C_6H_2(t\text{-Bu})_2CH_2$ and isopropoxy groups, indicating that they have C_2-symmetric, cis-α structures in solution. Thus, we assigned the two complexes as diastereomers (Λ*)-**9** and (Δ*)-**9**, having an identical configuration of the cyclohexane-1,2-diyl-fusing moiety. Variable-temperature ^{1}H NMR experiments of **9** in C_7D_8 in the range 273−323 K gave the free energy of activation for the interconversion as $\Delta G^{\ddagger}$ = 65 ± 2 kJ mol^{-1} ($\Delta H^{\ddagger} = 88 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 76 \pm 5$ J K^{-1} mol^{-1}, T_c = 303 K)

Scheme 2. Synthesis of Titanium Complexes 9 by the Reaction of 6 with Ti(O*i*Pr)$_4$



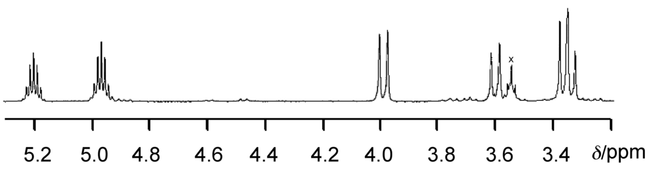


Figure 2. ^{1}H NMR spectrum (δ 3.2−5.3 ppm) of a mixture of (Λ*,*S**,*S**)-**9** and (Δ*,*S**,*S**)-**9** measured at 253 K in C_7D_8.

from the line shape analysis of isopropyl methine protons (Figure 3). This fluxional behavior is similar to that of complex **1** (M = Ti; L = O*i*Pr; $\Delta G^{\ddagger} = 48 \pm 1$ kJ mol^{-1})[3a] having the same 6−5−6 cheleting ring size system, where **9** has a larger $\Delta G^{\ddagger}$ value owing to the fusion of a cyclohexane ring. With regard to complexes having the 5−5−5 cheletion system, their fluxionality is largely dependent on the bulkiness of substituents on the phenolato rings. Complexes **2** (M = Ti; L = O*i*Pr) having H and/or Me groups as the substituents show fluxional behavior (R^1, R^2 = H, $\Delta G^{\ddagger} = 56.5 \pm 1$ kJ mol^{-1}; R^1 = H, R^2 = Me, $\Delta G^{\ddagger} = 56.2 \pm 1$ kJ mol^{-1}; R^1, R^2 = Me, $\Delta G^{\ddagger} = 58.6 \pm 2$ kJ mol^{-1}),[4c] and in contrast, those having bulky CMe_2Ph or *t*Bu groups as the substituents are not fluxional.[4c] Complexes **3** (L = Cl, O*i*Pr),[5] which undergo fusion of a cyclohexane ring, also exist as their respective single stereoisomers in solution. In comparison, among the three diisopropoxy titanium complexes having *t*Bu groups **9**, **2** (M = Ti; L = O*i*Pr, R^1, R^2 = *t*Bu), and **3** (L = O*i*Pr), the 6−5−6 chelation system of **9** is more flexible than the 5−5−5 cheletion system for titanium(IV) complexes, regardless of the presence of a fused cyclohexane ring.

Recrystallization of a mixture of **9** gave yellow crystals, and an X-ray diffraction analysis showed the structure of (Δ*,*S**,*S**)-**9**. There are two independent molecules in the unit cell, and one of them is shown in Figure 4. The structures of the two independent molecules are almost similar, except for the conformation about an O−*i*Pr bond. (Δ*,*S**,*S**)-**9** takes a distorted-octahedral structure: the two sulfur atoms, two oxygen atoms of isopropoxy groups, and Ti atom reside on the same plane. The averaged values of apical O1−Ti1−O2 bond angles and S1−C1−C2−S2

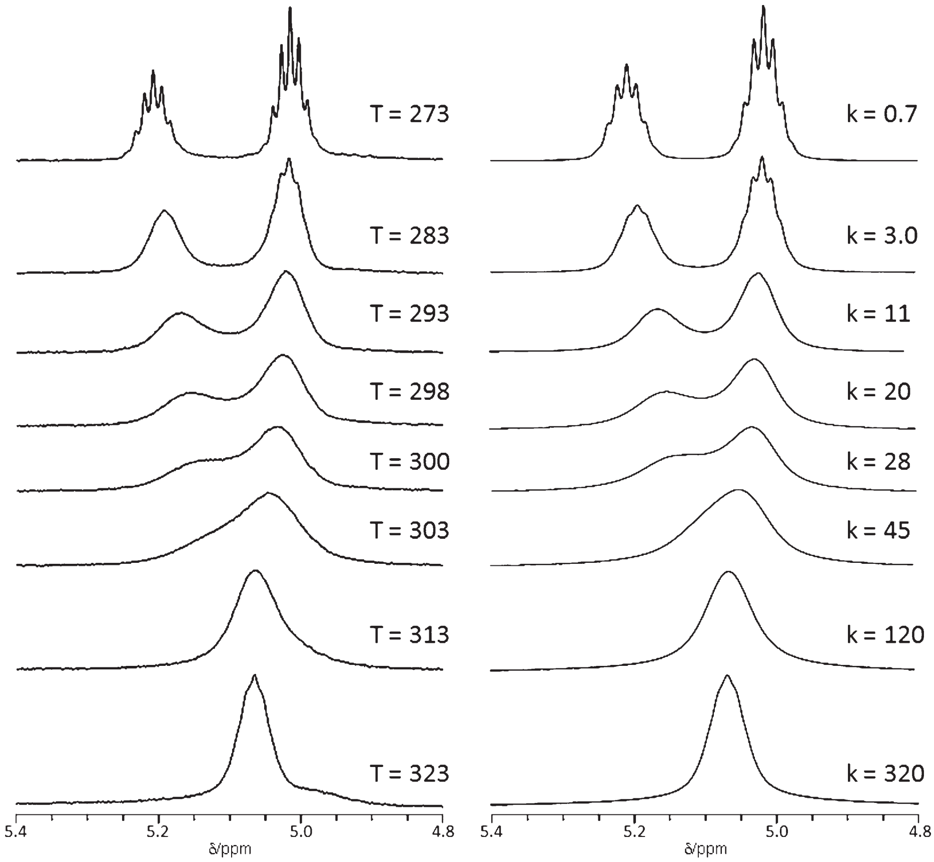


Figure 3. Experimental ^{1}H NMR spectra for isopropoxy methine protons of a mixture of (Λ*,*S**,*S**)-**9** and (Δ*,*S**,*S**)-**9** in the range 273−323 K (T_c = 303 K) in C_7D_8 (left) and simulated spectra computed with the specific rate constant *k* (right).

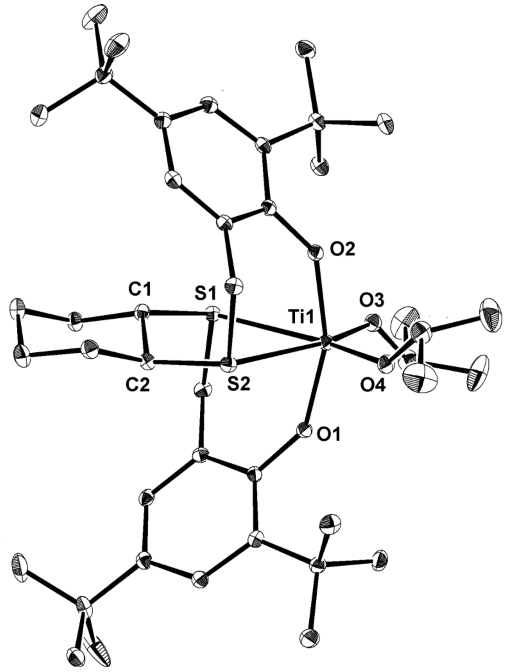


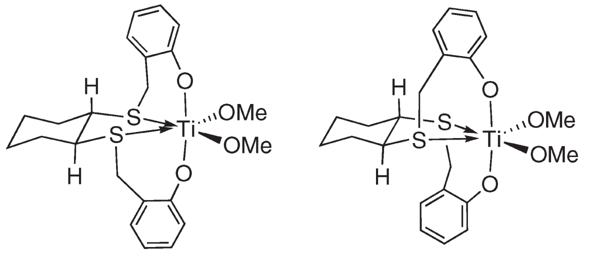
Figure 4. ORTEP drawing of one of two independent molecules of (Δ*,*S**,*S**)-**9** with 30% probability ellipsoids. Hydrogen atoms and a solvated molecule (hexane) are omitted for clarity. Selected bond lengths (Å), angles (deg), and a dihedral angle (deg): Ti1−O3 = 1.8161(14), Ti1−O4 = 1.8081(14), Ti1−O1 = 1.8867(14), Ti1−O2 = 1.9045(14), Ti1−S1 = 2.6941(6), Ti1−S2 = 2.7188(6); O4−Ti1−O3 = 107.08(7), O1−Ti1−O2 = 160.23(6), S1−Ti1−S2 = 76.019(17), S1−Ti1−O3 = 89.04(5), S2−Ti1−O4 = 87.87(5), S2−Ti1−O3 = 165.05(5), S1−Ti1−O4 = 163.82(5), O3−Ti1−O1 = 94.86(6), O2−Ti1−O4 = 94.48(6), O2−Ti1−O3 = 96.50(6), O4−Ti1−O1 = 97.58(6), S1−Ti1−O1 = 82.09(4), S2−Ti1−O2 = 81.92(4), S2−Ti1−O1 = 82.93(4), S1−Ti1−O2 = 81.98(4); S1−C1−C2−S2 =44.68(18).

dihedral angles were 159.4 and 44.8°, respectively. For reference, although the chelation ring sizes and ligands (L) are different, the corresponding values in complexes having the same relative configuration are reportedly 158.50(19) and 53.8(5)° for (Λ,*R*,*R*)-**3** (L = Cl) and 159.6(1) and 48.3(3)° for (Λ*,*R**,*R**)-**3** (L = CH_2Ph, where the *t*Bu group para to phenoxido oxygens is replaced by a Me group).[5] While the apical O−Ti−O bond angles are almost similar, the S−C−C−S dihedral angle in (Δ*, *S**,*S**)-**9** is substantially smaller than those in the reference complexes. Thus, an influence of the difference in chelation ring sizes, 6−5−6 for **9** and 5−5−5 for **3**, was observed in the S−C−C−S dihedral angles.

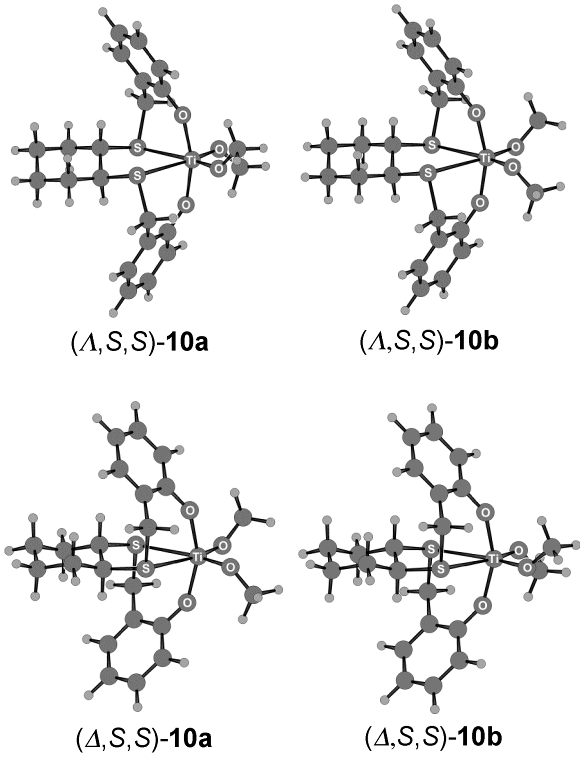
While the structure of the other diastereomer is essentially assigned to be (Λ*,*S**,*S**)-**9**, to obtain some information on the assignment of ^{1}H NMR data of (Δ*,*S**,*S**)-**9** and (Λ*,*S**,*S**)-**9**, DFT calculations were performed for their model compounds (Λ,*S*,*S*)-**10** and (Δ,*S*,*S*)-**10** (Chart 3).[13] Structure optimizations were carried out on two conformers (**10a**,**b**) about Ti−OMe bonds for each and their C_2 symmetry was retained during the calculations. The optimized structures are exhibited in Figure 5. Confomers with suffix **b** have conformations similar to that of (Δ*,*S**,*S**)-**9** in the crystalline state.

NMR shielding constants were calculated for (Λ,*S*,*S*)-**10** and (Δ,*S*,*S*)-**10** by the GIAO method,[14] and chemical shifts of benzyl protons (H_{endo} and H_{exo}) and their difference (Δδ) were compared as a common part of model (**10**) and real (**9**) compounds (Table 1). The calculated chemical shifts of benzyl protons with reference to the TMS standard were δ 4.29 and 3.47 ppm (Δδ = 0.82 ppm) for (Λ,*S*,*S*)-**10a** and δ 3.77 and 3.46 ppm (Δδ = 0.31 ppm) for (Δ,*S*,*S*)-**10a**. In the case of conformers **10b**, exo hydrogens (H_{exo}) undergo a high-field shift, δ 3.90 ppm for (Λ,*S*,*S*)-**10b** and δ 3.54 ppm for (Δ,*S*,*S*)-**10b**, leading to smaller Δδ values, 0.41 ppm for (Λ,*S*,*S*)-**10b** and 0.06 ppm for (Δ,*S*,*S*)-**10b**. These trends of chemical shifts and Δδ values for (Λ,*S*,*S*)-**10** and (Δ,*S*,*S*)-**10** are in good agreement with those of two doublets for the major diastereomer of **9** (δ 3.99 and 3.38 ppm, Δδ = 0.61 ppm) and those for the minor species (δ 3.60 and 3.36 ppm, Δδ = 0.24 ppm), respectively (see Figure 2). The remarkable downfield shift of H_{exo} in (Λ,*S*,*S*)-**10a** is considered to be due to its proximity to a Ti−O_e bond. Figure 6 shows the relevant moieties of (Λ,*S*,*S*)-**10a** and (Δ,*S*,*S*)-**10a**. The interatomic

Chart 3. Respective Model Complexes (Λ,*S*,*S*)-10 and (Δ,*S*,*S*)-10 for (Λ,*S*,*S*)-9 and (Δ,*S*,*S*)-9



(Λ,*S*,*S*)-**10** [(Λ)-**10**] (Δ,*S*,*S*)-**10** [(Δ)-**10**]



(Λ,*S*,*S*)-**10a** (Λ,*S*,*S*)-**10b**

(Δ,*S*,*S*)-**10a** (Δ,*S*,*S*)-**10b**

Figure 5. Structures of two conformers for both (Λ,*S*,*S*)-**10** and (Δ,*S*,*S*)-**10** optimized by DFT calculations with the LANL2DZ basis set for Ti and the 6-31+G(d) basis sets for other elements.

Table 1. Calculated Chemical Shifts (δ, ppm) of Benzyl Protons (H_{exo} and H_{endo}) in (Λ,*S*,*S*)-**10** and (Δ,*S*,*S*)-**10** and the Corresponding Values of (Λ*,*S**,*S**)-**9** (Major) and (Δ*,*S**,*S**)-**9** (Minor)

	(Λ,*S*,*S*)-**10a**[a]	(Λ,*S*,*S*)-**10b**[a]	(Δ,*S*,*S*)-**10a**[a]	(Δ,*S*,*S*)-**10b**[a]	(Λ*,*S**,*S**)-**9**[b] (major)	(Δ*,*S**,*S**)-**9**[b] (minor)
$\delta(H_{exo})$	4.29	3.90	3.77	3.54	3.99	3.60
$\delta(H_{endo})$	3.47	3.49	3.46	3.48	3.38	3.36
$\Delta\delta$	0.82	0.41	0.33	0.06	0.61	0.24

[a] Basis sets B3LYP/LANL2DZ (Ti) and 6-31+G(d) (C, H, O, S). [b] In C_6D_6.

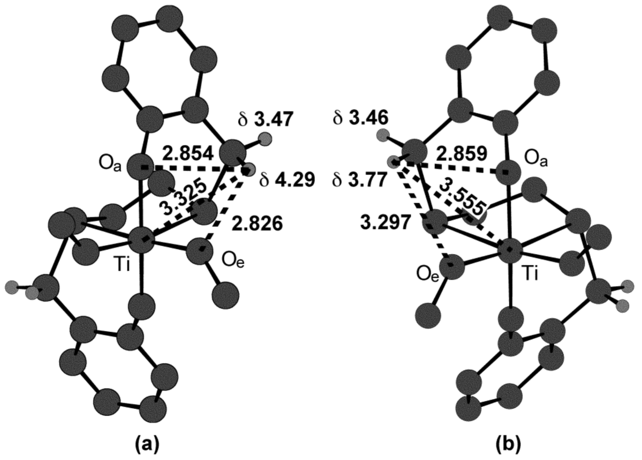
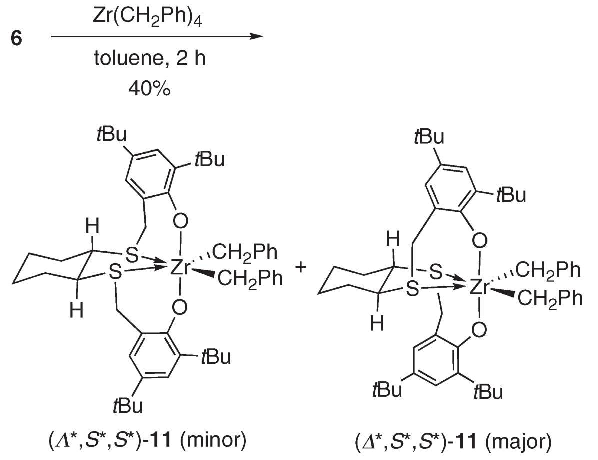


Figure 6. Relevant moieties of (Λ,*S*,*S*)-**10a** (a) and (Δ,*S*,*S*)-**10a** (b) with $H_{exo}\cdots O$ and $H_{exo}\cdots Ti$ distances (Å) and calculated ^1H NMR chemical shifts (ppm) at the B3LYP/LANL2DZ (Ti) and 6-31+G(d) (C, H, O, S) levels.

distances $H_{exo}\cdots O_e$ and $H_{exo}\cdots Ti$ in (Λ,*S*,*S*)-**10a** are 2.826 and 3.325 Å, respectively, which are remarkably smaller than the corresponding distances of 3.297 and 3.555 Å in (Δ,*S*,*S*)-**10a**. Thus, we assigned the major diastereomer of **9** in solution to (Λ*,*S**,*S**)-**9** and the minor one to (Δ*,*S**,*S**)-**9**, the structure of which was determined by X-ray diffraction.

Zr Complexes. Next, ligand **6** was treated with $Zr(CH_2Ph)_4$ in toluene at room temperature to give again a mixture of two diastereomers **11** in 40% combined yield, similarly to the case for titanium complex **9** (Scheme 3). Figure 7 shows the region (δ 1.7−3.7 ppm) of benzyl protons in the ^1H NMR spectrum of the mixture measured at room temperature, which indicates the formation of two C_2-symmetric diastereomers in a ratio of 3:2. On the basis of the similarity of ^1H NMR data for the benzyl protons to those of the zirconium complex (Λ*,*S**,*S**)-**6** (δ 2.16 (d, J = 10 Hz) and 2.78 (d, J = 10 Hz) ppm for $ZrCH_2Ph$ protons and δ 3.16 (d, J = 14 Hz) and 3.50 (d, J = 14 Hz) ppm for SCH_2Ar protons),[7,15] the minor diastereomer was assigned to (Λ*,*S**,*S**)-**11** (denoted with ● in Figure 7: δ 2.17 (d, J = 10 Hz) and 2.79 (d, J = 10 Hz) ppm for $ZrCH_2Ph$ protons and δ 3.23 (d, J = 14 Hz) and 3.52 (d, J = 14 Hz) ppm for SCH_2Ar protons). The other set of signals (denoted ○ in Figure 7) was essentially assigned to those of (Δ*,*S**,*S**)-**11**. Kol reported that **1** (ML_2 = $Zr(OtBu)_2$, $Zr(CH_2Ph)_2$) existed as the respective single isomers and the Δ−Λ interconversion was slow in solution at room temperature, in contrast with the fluxional nature of the corresponding titanium complexes, where these phenomena were explained in terms of the strong soft-S/soft-Zr interaction compared to the soft-S/hard-Ti interaction.[3a] This is also the present case, and broadening of signals was not observed at room temperature, unlike the case for titanium complex **9**, indicating that the Δ−Λ interconversion of **11** is slow enough at room temperature on the NMR time scale.[16] We could not obtain single crystals suitable for X-ray crystallography from the mixture of (Λ*,*S**,*S**)-**11** and (Δ*,*S**,*S**)-**11** and used the mixture for further studies.

Scheme 3. Synthesis of Zirconium Complexes **11** by the Reaction of **6** with $Zr(CH_2Ph)_4$



1-Hexene Polymerization. Polymerization of 1-hexene was examined with zirconium complex **11**, which was used as a mixture of diastereomers, and $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ as the activators (Scheme 4). The results are summarized in Table 2. The polymerization carried out at room temperature for 15 min gave poly(1-hexene) with high isotacticity (*mmmm* = 93%) and an M_w value of 40 500 for $B(C_6F_5)_3$ (run 1) or 44 000 for $(Ph_3C)[B(C_6F_5)_4]$ (run 2). The reaction carried out at 0 °C with $(Ph_3C)[B(C_6F_5)_4]$ yielded poly(1-hexene) with higher isotacticity (*mmmm* = 97%) and a larger M_w value (66 000) (run 3). Thus, the dependence of isotacticity and M_w on the two activators was small, and polydispersity indexes (PDI) were 1.9 in the three runs.

It is worth noting that the activity (370 g $mmol^{-1}$ h^{-1}) of the **11**/$B(C_6F_5)_3$ system is lower by 1 order of magnitude than the **4**/$B(C_6F_5)_3$ system (activity 2500 g $mmol^{-1}$ h^{-1}, M_w = 59 000, PDI = 1.7, *mmmm* >95%)[7] but still 4.5 times higher than the system of **1** (ML_2 = $Zr(CH_2Ph)_2$)/$B(C_6F_5)_3$ reported by Kol (activity 80 g $mmol^{-1}$ h^{-1}, M_w = 7400, PDI = 1.6) that gave regioregular and stereoirregular (*atactic*) poly(1-hexene).[3a] Kol described the possibility that the lack of stereocontrol by **1** (ML_2 = $Zr(CH_2Ph)_2$)/$B(C_6F_5)_3$ could be ascribed to the reduced directing power of the phenolate substituents *rather than* a fluxional catalyst behavior.[3a] The present results show that the *o-tert*-butyl groups in **11** are enough to provide isospecificity.

Observation of Zr Cation. To obtain some insights into the difference in activity between **4**/$B(C_6F_5)_3$[7] and **11**/$B(C_6F_5)_3$ in 1-hexene polymerization, we measured ^1H, ^{13}C, and ^{19}F NMR of the zirconium cation $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ generated from **11**, which is the starting species for the coordination polymerization of 1-olefins,[17] and compared them with those of the corresponding zirconium cation $\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$ (Chart 4)

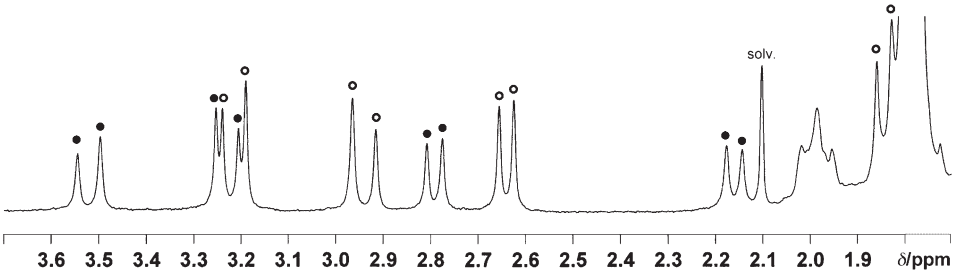
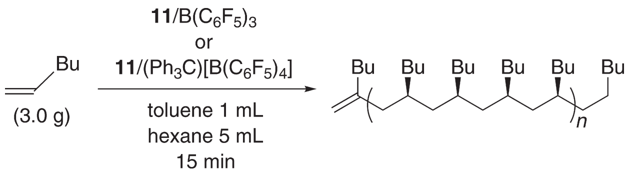


Figure 7. Part of the ^{1}H NMR spectrum (500 MHz, 298 K, C_6D_6) of a mixture of (Λ^*,S^*,S^*)-**11** (●, minor) and (Δ^*,S^*,S^*)-**11** (○, major).

Scheme 4. Polymerization of 1-Hexene with Zirconium Complex 11 as the Precatalyst



from **4**. Thus, a mixture of (Λ^*,S^*,S^*)-**11** and (Δ^*,S^*,S^*)-**11** was treated with $B(C_6F_5)_3$ in C_6D_6 at room temperature. In the $^{19}F\{^1H\}$ NMR, three inequivalent ^{19}F nuclei in the counteranion ($[B(CH_2Ph)(C_6F_5)_3]^-$) were observed at δ −166.5 (m-F), −163.7 (p-F), and −130.2 (o-F) ppm. The $\Delta\delta$ ($|\delta_{m\text{-F}} - \delta_{p\text{-F}}|$) value was 2.8 ppm, which indicates weak coordination between $[B(CH_2Ph)(C_6F_5)_3]^-$ and the zirconium cation center,[18] as observed in $\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$.[7,19] Interestingly, the ^{1}H NMR spectrum indicated a clean formation of a single zirconium cation with C_1 symmetry ($\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$). Thus, four singlets due to t-Bu groups were observed at δ 1.28, 1.32, 1.53, and 1.61 ppm (Figure 8a) and three pairs of two doublets due to three benzyl groups were observed at δ 2.51 (d, J = 9.3 Hz, $ZrCH_2Ph$), 2.83 (d, J = 9.3 Hz, $ZrCH_2Ph$), 3.30 (d, J = 11.5 Hz, SCH_2Ar), 3.40 (d, J = 12.3 Hz, SCH_2Ar), 3.50 (d, 12.3 Hz, SCH_2Ar), and 3.55 (d, J = 11.5 Hz, SCH_2Ar) (Figure 8b). A singlet at δ 3.44 is due to BCH_2Ph protons of the counteranion.[20] We assume that $\mathbf{12}^+$ has a Λ^*,S^*,S^* configuration, as shown in Scheme 5, because the ^{1}H NMR spectrum of $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ bears a close resemblance to that of Zr cation $\mathbf{13}^+$: for instance, for t-Bu groups δ 1.23, 1.31, 1.53, 1.60; for benzyl groups δ 2.55 (d, J = 9.6 Hz, $ZrCH_2Ph$), 2.77 (d, J = 9.6 Hz, $ZrCH_2Ph$), 3.40 (d, J = 12.4 Hz, SCH_2Ar), 3.47 (d, J = 11.4 Hz, SCH_2Ar), 3.54 (d, 11.4 Hz, SCH_2Ar), and 3.59 (d, J = 12.4 Hz, SCH_2Ar) ppm.[19]

In $\mathbf{12}^+$ and $\mathbf{13}^+$, benzyl ligands would have η^2 coordination to the zirconium cation center, similar to that in reported group 4 metal, cationic complexes, on the basis of the $^1J_{C-H}$ value (143 Hz) for the benzyl carbon (δ 72.3) of $\mathbf{12}^+$.[18,20] Okuda and co-workers observed a zirconium cation generated from **3** (L = CH_2Ph) by treatment with $B(C_6F_5)_3$ in C_6D_5Br, albeit not in a clean form, where the ^{1}H NMR spectrum showed an apparent C_2-symmetric species above 10 °C.[5b] Incidentally, they succeeded in the X-ray structure analysis of a cationic zirconium complex prepared from **2** (M = Ti; R^1, R^2 = tBu; L = Me) and $B(C_6F_5)_3$ in the presence of $Me_2PCH_2CH_2PMe_2$ (DMPE), which underwent coordination of two phosphorus atoms of the dmpe and took a pentagonal-bipyramidal structure.[4b]

In a comparison between the ^{1}H NMR spectra of $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ and $\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$,[19] we observe a difference in the chemical shifts of methyne protons (−C*H*S−). Thus, the two inequivalent protons appeared at δ 1.85 and 2.34 ppm for $\mathbf{12}^+$ and δ 2.03 and 2.92 ppm for $\mathbf{13}^+$. One of these protons in $\mathbf{13}^+$ is shifted remarkably downfield, and $\Delta\delta$ values are 0.89 ppm for $\mathbf{13}^+$ and 0.49 ppm for $\mathbf{12}^+$. In addition, the chemical shift differences of the corresponding methine carbons (−CHS−) were 2.8 ppm for $\mathbf{12}^+$ (δ 52.1 and 54.9 ppm) and 6.4 ppm for $\mathbf{13}^+$ (δ 51.6 and 58.0 ppm), where the downfield shift of one of the methine carbons (δ 58.0 ppm) in $\mathbf{13}^+$ is remarkable. These observations suggest that there is some difference in the strength of coordination of sulfur atoms in $\mathbf{12}^+$ and $\mathbf{13}^+$ to the respective cationic Zr centers. We consider that one of the sulfur atoms in $\mathbf{13}^+$ can coordinate the cationic Zr center more strongly than the other, accompanying a structural change provided by the flexible nature of the cyclooctane part, to afford additional stability to $\mathbf{13}^+$. This effect would present a reason for the activity of $\mathbf{4}/B(C_6F_5)_3$ being higher than that of $\mathbf{11}/B(C_6F_5)_3$ in 1-hexene polymerization. Morokuma and co-workers reported a theoretical study on ethylene polymerization reactions catalyzed by zirconium and titanium chelating alkoxide complexes **14a**−**c** (Chart 5)[21] based on the Cossee mechanism.[17] They showed that in the case of **14a** the stabilization effect by the coordination of sulfur to the metal center in the initial complex was initially lost in the formation of the π complex, which resulted in a relatively small energy gain of this step compared with the cases of **14b**,**c**, and then came back in the transition state to the final insertion product. This behavior lowers the activation energy for **14a** to explain well the higher activity of **14a** compared with that of **14b**,**c**. This would be the case for zirconium cations $\mathbf{12}^+$ and $\mathbf{13}^+$, the latter of which undergoes stronger stabilization by a sulfur atom to show a higher reactivity in the polymerization of 1-hexene.

■ CONCLUSION

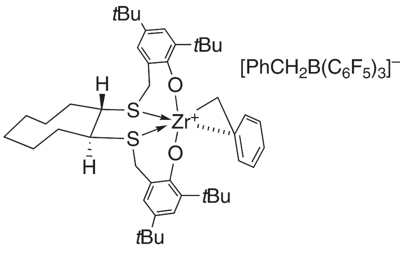
We synthesized hexacoordinated titanium(IV) (**9**) and zirconium(IV) (**11**) complexes with a new [OSSO]-type tetradentate ligand bearing a *trans*-cyclohexane-1,2-diyl ring (**6**). Complexes **9** and **11** were found to be mixtures of Λ^*,S^*,S^* and Δ^*,S^*,S^* diastereomers, and the structures were elucidated by NMR, X-ray diffraction, DFT calculations, and comparison with a corresponding complex having an analogous ligand bearing a *trans*-cyclooctane-1,2-diyl ring (**5**). In 1-hexene polymerization, the catalytic system consisting of dibenzyl zirconium complex **11** and an activator features high isospecificity with high activity, indicating that ligand **6** is rigid enough to retain the C_2 symmetry during polymerization. In comparison between

Table 2. Polymerization of 1-Hexene with Zirconium Complex **11** (0.056 mmol %) and $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ as the Activators

run	amt of **11** (mmol)[a]	activator (amt (mmol))	temp (°C)	yield (g)	activity (g $mmol^{-1}$ h^{-1})	M_w	PDI	amt of *mmmm* (%)
1	0.020	$B(C_6F_5)_3$ (0.020)[a]	room temp	1.8	370	40 500	1.9	93
2	0.020	Ph_3C^{+b} (0.020)[a]	room temp	1.8	370	44 000	1.9	93
3	0.020	Ph_3C^{+b} (0.020)[a]	0	1.0	190	66 000	1.9	97

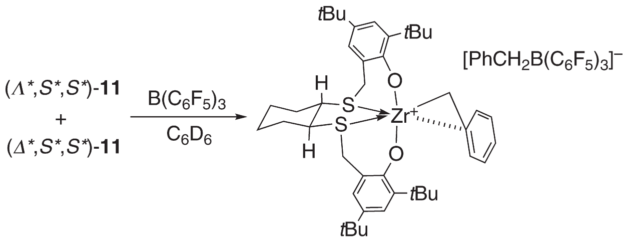
[a] 0.056 mmol % to 1-hexene (3.0 g). [b] $(Ph_3C)[B(C_6F_5)_4]$.

Chart 4. Cationic Zirconium Complex $\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$ Generated from **4** with $B(C_6F_5)_3$.



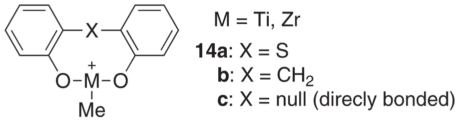
$\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$

Scheme 5. Generation of the Cationic Zirconium Complex $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ from **11** with $B(C_6F_5)_3$



$\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$

Chart 5. Zirconium and Titanium Chelating Alkoxide Complexes **14**



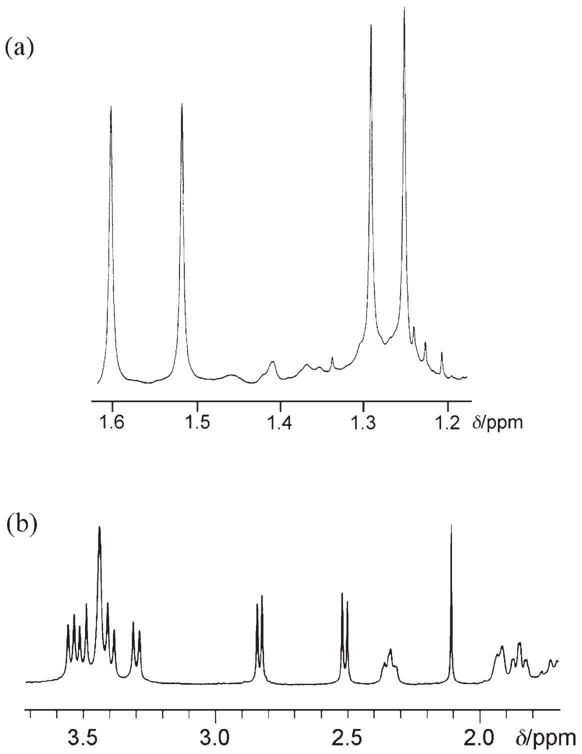


Figure 8. Portions of the ^1H NMR spectrum (500 MHz, 298 K) for *tert*-butyl and cyclohexane-methylene protons (a) and benzyl protons (b) in the cationic complex $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ in C_6D_6.

ligands **6** bearing a *trans*-cyclohexane-1,2-diyl and **5** bearing a *trans*-cyclooctane-1,2-diyl, the catalytic system of complex **11** bearing **6** is less active than the catalytic system of **4** bearing **5**. In the ^1H and ^{13}C NMR observations of the corresponding cationic zirconium complexes $\mathbf{12}^+[B(CH_2Ph)(C_6F_5)_3]^-$ and $\mathbf{13}^+[B(CH_2Ph)(C_6F_5)_3]^-$, we obtained a result suggesting that the difference in reactivity is attributable to the difference in the ability to stabilize zirconium cations between ligands in $\mathbf{12}^+$ and $\mathbf{13}^+$.

■ EXPERIMENTAL SECTION

General Considerations. The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^1H, ^{19}F, and ^{13}C spectra were obtained with Bruker DRX400, AVANCE300, and AVANCE500 spectrometers. In the case of ^{19}F NMR, α,α,α-trifluorotoluene (δ −64) was used as the external standard. X-ray crystallography was performed with Bruker AXS SMART and Rigaku Saturn724 diffractometers. Elemental analyses were performed at the Molecular Analysis and Life Science Center of Saitama University. Molecular weights and molecular weight distributions of poly(1-hexene)s were determined against a polystyrene standard by gel permeation chromatography on a HLC-8220 GPC apparatus (Tosoh Corp.) of the laboratory of Dr. Zhaomin Hou (Organometallic Chemistry Laboratory, RIKEN Advanced Science Institute).

Preparation of *trans*-1,2-bis(3,5-di-*tert*-butyl-2-hydroxybenzylsulfanyl)cyclohexane (6). A mixture of thiol **7** (1.08 g, 7.3 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide (**8**; 4.58 g, 15.3 mmol) was dissolved in THF (90 mL) under argon. To the solution cooled at 0 °C was added triethylamine (2.1 mL, 1.5 mg, 15.3 mmol), and the mixture was stirred for 1 h at 0 °C and overnight at room temperature. The precipitates formed were removed by filtration, and the filtrate was concentrated under reduced pressure. The oily yellow residue was dissolved in ether and aqueous ammonium chloride was added. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane/dichloromethane 1/1) to give **6** (3.86 g, 90%).

Data for **6**: colorless crystals, mp 104−106 °C dec (EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19−1.43 (m, 44 H), 2.09−2.15 (m, 2 H), 2.58−2.61 (m, 2 H), 3.79 (s, 4 H), 6.75 (s, 2 H), 6.93 (d, *J* = 2 Hz, 2 H), 7.25 (d, *J* = 2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 29.7, 31.6, 32.6, 33.9, 34.2, 35.0, 48.1, 121.6, 123.7, 125.2, 137.3, 142.2, 152.0. Anal. Calcd for $C_{36}H_{54}O_2S_2$: C, 73.92; H, 9.34. Found: C, 74.17; H, 9.31.

Preparation of [OSSO]Ti(O*i*Pr)$_2$ (9). A solution of **6** (206.6 mg, 0.336 mmol) in toluene (10 mL) was added to a solution of Ti(O*i*Pr)$_4$ (153.2 mg, 0.336 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 5 h at room temperature, and the solvent was removed under reduced pressure. The residue was washed with hexane (2 mL) and dried to give **9** (215.7 mg, 76%).

Data for **9** (a mixture of (Λ*,*S**,*S**)-**9** (major) and (Δ*,*S**,*S**)-**11** (minor)): yellow crystals; mp 110 °C dec; ^{1}H NMR (500 MHz, C_7D_8, 253 K) δ 0.50−1.12 (m, 8 H, major, minor), 1.27 (d, ^3J = 6 Hz, 6 H, major), 1.33 (s, 18 H, major, minor), 1.38 (d, *J* = 6 Hz, 6 H, minor), 1.50 (d, *J* = 6 Hz, 6 H, major), 1.59−1.67 (m, 2 H, major), 1.63 (d, *J* = 6 Hz, 6 H, minor), 1.92 (s, 18 H, major, minor), 2.01−2.07 (m, 2 H, minor), 3.37 (d, *J* = 13 Hz, 2 H, minor), 3.39 (d, *J* = 14 Hz, 2 H, major), 3.63 (d, *J* = 14 Hz, 2 H, minor), 4.01 (d, *J* = 14 Hz, 2 H, major), 4.97 (sep, *J* = 6 Hz, 2 H, major), 5.20 (sep, *J* = 6 Hz, 2 H, minor), 6.69 (d, *J* = 2 Hz, 2 H, minor), 6.76 (d, *J* = 3 Hz, 2 H, major), 7.50 (d, *J* = 3 Hz, 2 H, minor), 7.58 (d, ^4J = 3 Hz, 2 H, major). Anal. Calcd for $C_{42}H_{68}O_4S_2Ti$: C, 67.35; H, 9.15. Found: C, 67.51; H, 9.37.

Preparation of [OSSO]Zr(CH$_2$Ph)$_2$ (11). In the glovebox, a solution of **6** (300 mg, 0.513 mmol) in toluene (5 mL) was added to a solution of Zr(CH$_2$Ph)$_4$ (234 mg, 0.513 mmol) in toluene (5 mL) at room temperature. The mixture was stirred for 2 h at room temperature, and the solvent was removed under reduced pressure. The residue was washed with pentane (2 mL) and dried to give **11** (176 mg, 40%). **11** was extremely unstable to air and moisture, so that we could not carry out elemental analysis and HRMS measurements.

Data for **11** (a mixture of (Λ*,*S**,*S**)-**11** (minor) and (Δ*,*S**,*S**)-**11** (major)): ^{1}H NMR (500.0 MHz, C_6D_6) δ 0.42−1.08 (m, 8 H, major, minor), 1.22 (s, 18 H, major), 1.24 (s, 18 H, minor), 1.57−1.61 (m, 2 H, major), 1.77 (s, 18 H, major), 1.80 (s, 18 H, minor), 1.84 (d, *J* = 9 Hz, 2 H, major), 1.96−2.02 (m, 2 H, minor), 2.16 (d, *J* = 10 Hz, 2 H, minor), 2.64 (d, *J* = 9 Hz, 2 H, major), 2.79 (d, *J* = 10 Hz, 2 H, minor), 2.94 (d, *J* = 12 Hz, 2 H, major), 3.22 (d, *J* = 15 Hz, 2 H, major), 3.23 (d, *J* = 15 Hz, 2 H, minor), 3.52 (d, *J* = 15 Hz, 2 H, minor), 6.57 (d, *J* = 2 Hz, 2 H, major), 6.63 (d, *J* = 2 Hz, 2 H, minor), 6.90−7.27 (m, 10 H, major, minor), 7.42 (d, *J* = 2 Hz, 2 H, major), 7.52 (d, *J* = 2 Hz, 2 H, minor); ^{13}C{^{1}H} NMR (100.7 MHz, C_6D_6) δ 24.9 (CH$_2$, minor), 26.4 (CH$_2$, major), 30.6 (CH$_3$, C*Me*$_3$, minor), 31.0 (CH$_3$, C*Me*$_3$, major), 31.5 (CH$_2$, ZrCH$_2$Ph, major), 31.7 (CH$_3$, C*Me*$_3$, minor), 31.8 (CH$_3$, C, major), 31.8 (CH$_2$, major or minor). 33.9 (CH$_2$, major or minor), 34.1 (C, CMe$_3$, major), 34.2 (C, CMe$_3$, minor), 34.66 (CH$_2$, ZrCH$_2$Ph, minor), 35.6 (C, CMe$_3$, major), 35.6 (C, CMe$_3$, minor), 47.5 (CH, CHS, minor), 52.9 (CH, CHS, major), 59.3 (CH$_2$, SCH$_2$Ar, major), 63.2 (CH$_2$, SCH$_2$Ar, minor), 122.2 (C, *ipso*-C of ZrCH$_2$*Ph*, minor), 123.2 (CH, ZrCH$_2$*Ph*, major or minor), 123.4 (CH, ZrCH$_2$*Ph*, major or minor), 123.7 (CH, Ar, major), 124.3 (CH, Ar, minor), 124.8 (C, *ipso*-C of ZrCH$_2$*Ph*, major), 125.5 (CH, Ar, major), 125.6 (CH, Ar, minor), 129.6 (CH, ZrCH$_2$*Ph*, minor), 130.1 (CH, ZrCH$_2$*Ph*, major), 137.96 (C, Ar, minor), 137.99 (C, Ar, major), 140.8 (C, Ar, major), 140.9 (C, Ar, minor), 145.4 (C, Ar, major), 145.7 (C, Ar, minor), 158.0 (C, Ar, minor), 158.7 (C, Ar, major). The assignment of "major" and "minor" in ^{13}C NMR is based on peak height and C−H COSY experiments. Not all of the CH carbons of ZrCH$_2$*Ph* in the major and minor diastereomers could be assigned).

Polymerization of 1-Hexene with 11/(Ph$_3$C)[B(C$_6$F$_5$)$_4$] (Table 2, Run 2). In a glovebox, (Ph$_3$C)[B(C$_6$F$_5$)$_4$] (18.4 mg, 0.020 mmol) was added to a solution of **11** (17.1 mg, 0.020 mmol) in toluene (1 mL) and hexane (5 mL) at room temperature. After the mixtue was stirred for 5 min at room temperature, a solution of 1-hexene (3.0 g) was added. This mixture was stirred for 15 min at this temperature. The reaction was quenched by addition of methanol, and volatile materials were removed in vacuo at 70 °C overnight to leave poly(1-hexene) (1.8 g).

Reaction of [OSSO]Zr(CH$_2$Ph)$_2$ (11) with B(C$_6$F$_5$)$_3$. To an NMR tube equipped with a PTFE valve (J. Young Ltd.) were added **11** (17.1 mg, 0.020 mmol), benzene-*d*$_6$ (0.5 mL), and B(C$_6$F$_5$)$_3$ (10.2 mg, 0.020 mmol) in that order. The mixture immediately turned yellow and separated into two phases: ^{19}F NMR (470.6 MHz, C_6D_6) δ −166.5 (t, ^2J = 20 Hz, 6 F, *m*-F), −163.7 (pseudo t, ^2J = 21 Hz, 3 F, *p*-F), −130.2 (d, ^2J = 22 Hz, 6 F, *o*-F); ^{1}H NMR (500 MHz, C_6D_6) δ 0.85−1.0 (m, 6H), 1.2−1.7 [m, 38 H {1.27 (s, *t*-Bu), 1.32 (s, *t*-Bu), 1.53 (s, *t*-Bu), 1.61 (s, *t*-Bu)}], 1.81−1.89 (m, 1 H, C*H*S), 1.89−1.96 (m, 1 H), 2.31−2.38 (m, 1 H, C*H*S), 2.51 (d, *J* = 9.3 Hz, ZrC*H*$_2$Ph), 2.83 (d, *J* = 9.3 Hz, ZrC*H*$_2$Ph), 3.30 (d, *J* = 11.5 Hz, SC*H*$_2$Ar), 3.40 (d, *J* = 12.3 Hz, SC*H*$_2$Ar), 3.44 (br s, 2 H, BC*H*$_2$Ph), 3.50 (d, 12.3 Hz, SC*H*$_2$Ar), and 3.55 (d, *J* = 11.5 Hz, SC*H*$_2$Ar), 6.20 (br s, 2 H, *o*-H of BCH$_2$*Ph*), 6.7−6.82 [m, 3 H {1H of *p*-H of ZrCH$_2$*Ph* (δ 6.78, t, *J* = 7 Hz) and 2 H of *m*-H of BCH$_2$*Ph*}], 6.85 (t, *J* = 7 Hz, 1 H, *p*-H of BCH$_2$*Ph*), 6.92 (t, *J* = 8 Hz, 2 H, *m*-H of ZrCH$_2$*Ph*), 7.15 (Ar-*H*, overlapped with signals due to residual protons of the solvent and detemined by the H−H COSY experiment), 7.18 (d, *J* = 7.5 Hz, 2 H, *o*-H of ZrCH$_2$*Ph*), 7.34 (d, *J* = 2 Hz, Ar-*H*), 7.51 (d, *J* = 2 Hz, Ar-*H*), 7.60 (d, *J* = 2 Hz, Ar-*H*); ^{13}C{^{1}H} NMR (100.7 MHz, C_6D_6) δ 24.6 (CH$_2$, *c*-C$_6$H$_{10}$S$_2$), 25.5 (CH$_2$, *c*-C$_6$H$_{10}$S$_2$), 30.4 (CH$_3$, C*Me*$_3$), 30.5 (CH$_3$, C*Me*$_3$), 31.2 (CH$_2$, ArCH$_2$), 31.34 (CH$_3$, C*Me*$_3$), 31.37 (CH$_3$, C*Me*$_3$), 31.5 (CH$_2$, *c*-C$_6$H$_{10}$S$_2$), 32.6 (CH$_2$, br s, BCH$_2$Ph), 34.6 (C, CMe$_3$), 34.7 (C, CMe$_3$), 35.4 (CH$_2$ and C, *c*-C$_6$H$_{10}$S$_2$ and CMe$_3$, respectively), 35.5 (C, CMe$_3$), 38.4 (CH$_2$, ArCH$_2$), 52.1 (CH, CHS), 54.9 (CH, CHS), 72.3 (CH$_2$, ZrCH$_2$Ph), 120.2 (C, *ipso*-C of BCH$_2$*Ph* or ZrCH$_2$*Ph*), 121.1 (C, *ipso*-C of BCH$_2$*Ph* or ZrCH$_2$*Ph*), 123.2 (CH, *p*-C of ZrCH$_2$*Ph*), 125.7 (2CH, Ar), 126.0 (CH, Ar), 126.2 (CH, Ar), 127.5 (CH, *m*-C of ZrCH$_2$*Ph*), 129.3 (2CH, *o*-C and *p*-C of BCH$_2$*Ph*), 129.4 (CH, *o*-C of ZrCH$_2$*Ph*), 133.1 (C, Ar), 136.7 (C, Ar), 136.9 (C, Ar), 137.1 (dm, $^1J_{C-F}$ = 249 Hz, *o*- or *m*-C of BC$_6$F$_5$), 137.7 (dm, $^1J_{C-F}$ = 249 Hz, *p*-C of BC$_6$F$_5$), 139.4 (m, *ipso*-C of BC$_6$F$_5$), 145.7 (C, Ar), 145.9 (C, Ar), 149.0 (C, Ar), 149.1 (dm, $^1J_{C-F}$ = 237 Hz, *o*- or *m*-C of BC$_6$F$_5$), 157.3 (C, Ar), 157.9 (C, Ar) (*m*-C of BCH$_2$*Ph* was observed as a broad singlet centered at δ 128.0 ppm in the C−H COSY spectrum).

^{13}C NMR data for **13**$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$ (125.7 MHz, C_6D_6): δ 22.2 (CH$_2$), 24.3 (CH$_2$), 26.2 (CH$_2$), 27.1 (CH$_2$), 28.9 (CH$_2$), 30.4 (CH$_3$), 30.5 (CH$_3$), 31.2 (CH$_2$), 31.3 (CH$_3$), 31.4 (CH$_3$), 31.7 (CH$_2$), 32.5 (CH$_2$, br s, BCH$_2$Ph), 34.6 (C), 34.7 (C), 35.4 (C), 35.5 (C), 38.8 (CH$_2$), 51.6 (CH, CHS), 58.0 (CH, CHS), 72.0 (CH$_2$, ZrCH$_2$Ph, J_{C-H} = 143 Hz), 120.5 (C), 121.4 (C), 123.2 (CH, *p*-C of ZrCH$_2$*Ph*), 125.7 (2CH, Ar), 126.0 (CH, Ar), 126.1 (CH, Ar), 127.5 (CH, *m*-C of ZrCH$_2$*Ph*), 129.1 (CH, *p*-C of BCH$_2$*Ph*), 129.2 (CH, *o*-C of ZrCH$_2$*Ph*), 132.9 (C, Ar), 136.9 (C, Ar), 137.2 (dm, J_{C-F} = 251 Hz), 138.2 (dm, J_{C-F} = 242 Hz), 145.8 (C, Ar), 146.0 (C, Ar), 149.0 (C, Ar), 149.1 (dm, J_{C-F} = 240 Hz), 157.4 (C, Ar), 157.8 (C, Ar). One of the quaternary sp^2 carbons (Ar) and *o*- and *m*-C of BCH$_2$*Ph* were not assigned because of overlapping and broadening, respectively.

X-ray Crystallographic Analysis of 6 and (Δ*,*S,*S**)-9.** Colorless single crystals of **6** were obtained by recrystallization from ethanol, and yellow single crystals of (Δ*,*S**,*S**)-**9** were obtained by recrystallization from pentane. The intensity data were collected at 103 K for **6** on a Bruker AXS SMART diffractometer and at 100 K for (Δ*,*S**,*S**)-**9** on a Rigaku AFC10 diffractometer equipped with a Saturn724+ CCD detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[22]

Crystallographic data and details of refinement for **6**: $C_{36}H_{56}O_2S_2$, MW = 584.93, monoclinic, space group $P2_1/n$, *a* = 9.9252(7) Å,

b = 33.704(2) Å, c = 11.0361(7) Å, β = 109.3670(10)°, V = 3482.9(4) Å^3, Z = 4, D_{calcd} = 1.116 g cm^{-3}, R1 ($I > 2\sigma(I)$) = 0.0661 and wR2 (all data) = 0.1864 for 6478 reflections and 446 parameters, GOF = 1.094.

Crystallographic data and details of refinement for (Δ^*,S^*,S^*)-**9**: $C_{87}H_{143}O_8S_4Ti_2$ (($C_{42}H_{68}O_4S_2Ti)_2 \cdot 0.5C_6H_{14}$), MW = 1541.05, monoclinic, space group $P2_1/n$, a = 19.3273(17) Å, b = 13.9791(11) Å, c = 34.816(3) Å, β = 104.7800(10)°, V = 9095.3(13) Å^3, Z = 4, D_{calcd} = 1.125 g cm^{-3}, R1 ($I > 2\sigma(I)$) = 0.0452 and wR2 (all data) = 0.1073 for 16 868 reflections and 943 parameters, GOF = 1.094.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for **6** and (Δ^*,S^*,S^*)-**9** and figures and tables giving NMR spectra of **9**, **11**, and **12**$^+$[B(CH$_2$Ph)(C$_6$F$_5$)$_3$]$^-$, line-shape analysis of VT-^{1}H NMR of **9**, optimized coordinates of **10**, and ^{13}C NMR spectra of poly(1-hexene)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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