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Titanium Complexes Supported by an [OSSO]-Type Bis(phenolato) Ligand Based on a *trans*-Cyclooctanediyl Platform: Synthesis, Structures, and 1-Hexene Polymerization

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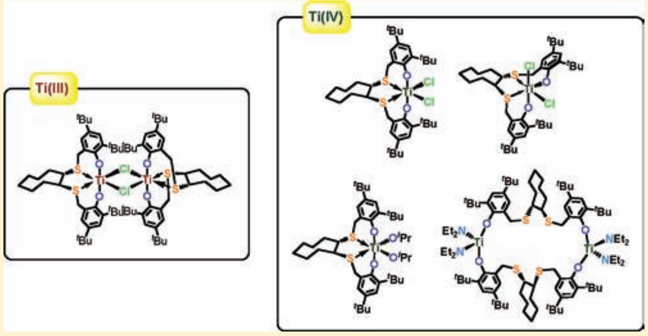
S *Supporting Information*

ABSTRACT: *trans*-Cyclooctanediyl-bridged [OSSO]-type ligand **4** reacts with $TiCl_4(thf)_2$ in toluene to produce the corresponding titanium(IV) dichloro complexes as an inseparable mixture of *cis-α* isomer **6a** and *cis-β* isomer **6b** in a ratio of 2:1, whereas treatment of dilithio salt of **4** with $TiCl_3(thf)_3$ in Et_2O afforded chloride-bridged dimeric titanium(III) complex **8**, which indicated the antiferromagnetic character in a nonpolar solvent solution. Di(isopropoxy) titanium(IV) complex **10** having a C_2-symmetric *cis-α* configuration was synthesized by the reaction of **4** with $Ti(O^iPr)_4$ in toluene as yellow crystals. Moreover, the reaction of **4** with $Ti(NEt_2)_4$ in toluene resulted in the unexpected formation of [OSSO]-type bis(phenolato)-bridged dinuclear diamido titanium(IV) complex **11**, which adopted a distorted tetrahedral geometry on the titanium center. These titanium complexes were characterized on the basis of their NMR spectroscopic data, and the molecular structures of complexes **8**, **10**, and **11** were established by single crystal X-ray diffraction. The titanium(IV) and (III) complexes **6** and **8** upon activation with a cocatalyst in toluene polymerized 1-hexene isospecifically to produce poly(1-hexene) having high molecular weight (M_w = 22,000−52,000 g mol^{-1}) and relatively narrow polydispersity (M_w/M_n = 1.7−1.8), albeit with low activity [0.27−1.0 g $mmol(cat)^{-1}$ h^{-1}].



INTRODUCTION

[OSSO]-type bis(phenolate), in which the two phenoxide frameworks are linked to two donor sulfur atoms in the ortho- or benzyl-positions (Chart 1), has been of great interest as the dianionic ancillary tetradentate ligands for Group 4 metal centers.[1,2] For example, Okuda et al. reported that a methylaluminoxane (MAO)-activated titanium dichloro complex with an 1,4-dithiabutanediyl-linked [OSSO]-type bis(phenolate) ligand (**1**) can be used for the isospecific polymerization of styrene.[3] In addition, they described that optically active copolymers which involve isotactic polystyrene and atactic poly(1-hexene) segments can be generated by titanium catalysts with an enantiopure 1,2-dithiocyclohexanediyl-linked [OSSO]-type bis(phenolate) ligand (**2**).[4] On the other hand, Kol et al. developed a more flexible 1,2-dithioethanediyl-linked [OSSO]-type bis(phenolate) ligand (**3**) featuring a methylene spacer between the sulfur-donor and the phenolate moiety.[5] They and Miyatake et al. independently found that Group 4 metal complexes having this [OSSO]-type ligand **3** served as highly active precatalysts in polymerizations of *α*-olefins such as 1-hexene, propylene, and vinylcyclohexene.[5,6] Recently, we also succeeded in the development of a new [OSSO]-type bis(phenolate) ligand (**4**) based on a *trans*-1,2-cyclooctanediyl platform and syntheses of zirconium dialkyl complexes (R = Me, CH_2Ph, CH_2SiMe_3) (**5**), which have C_2-symmetry in a distorted octahedral framework.[7,8] Upon activation with $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$, dibenzyl zirconium complex **5b** achieved highly active (1610−2500 g $mmol^{-1}$ h^{-1}) and completely isospecific polymerization of 1-hexene (*mmmm* > 95%).[7a] As a part of our investigation of *trans*-cyclooctanediyl-bridged [OSSO]-type ligand **4**, we present here the synthesis and structures of a variety of titanium(IV) and (III) complexes incorporating the ligand **4**. We also describe catalytic behavior in the polymerization of 1-hexene using the titanium complexes.

RESULTS AND DISCUSSION

Syntheses and Structures of a Series of Titanium Complexes. When *trans*-cyclooctanediyl-bridged [OSSO]-type ligand **4** was allowed to react with $TiCl_4(thf)_2$ in toluene at room temperature, the reaction mixture immediately

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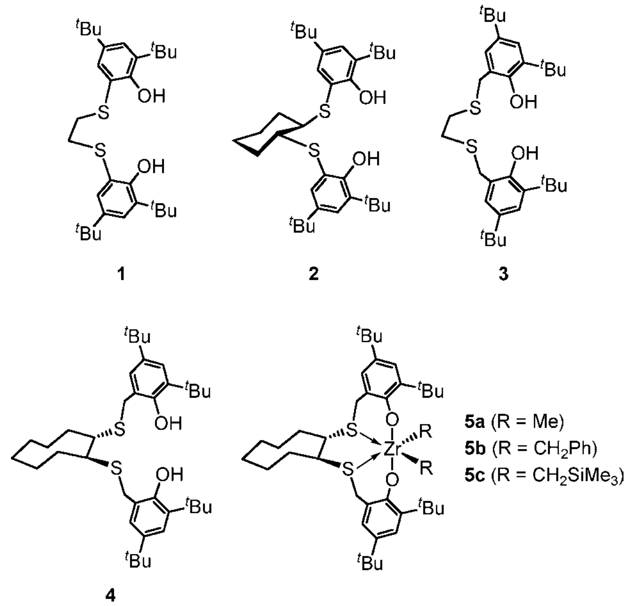
Chart 1



changed to a red solution to form the corresponding titanium(IV) dichloro complexes in 93% yield as an inseparable mixture of *cis*-α isomer **6a** and *cis*-β isomer **6b** in a ratio of 2:1 (Scheme 1). The structures of dichloro complexes **6** were identified by ^{1}H NMR and elemental analysis. In the ^{1}H NMR spectrum of the mixture, sulfur-bonded methine and benzylic protons for **6a** were observed at δ 2.62 as a broad singlet and at δ 3.16 and 4.57 (J = 15 Hz) as two doublets, respectively (Figure 1). Similar to the NMR observation of the related [OSSO]-type zirconium complexes **5**,[7,8] the ^{1}H NMR spectrum of **6a** exhibited the magnetical equivalency of two phenolate ligands, indicating that **6a** has a C_2-symmetric *cis*-α structure in solution in the NMR time scale. By contrast, in the ^{1}H NMR for **6b** two sulfur-bonded methines appeared at δ 2.66–2.70 and 3.63–3.67 as broad signals and four benzylic protons at δ 3.07 (J = 14 Hz), 3.57 (J = 12 Hz), 4.35 (J = 14 Hz), and 4.88 (J = 12 Hz), indicating an unsymmetrical structure. This upfield-shifted chemical shift of a methine proton (δ 3.63–3.67) is relatively close to the corresponding chemical shift (δ 3.98) for 1,2-dithiocyclohexanediyl-linked [OSNO]-type titanium dichloro complex taking *cis*-β configuration in solution.[9] In contrast to the titanium dichloro complex with the [OSSO]-type ligand **3** containing methylene spacers (*cis*-α:*cis*-β = 1:4),[6] which showed a reversible conversion between *cis*-α and *cis*-β isomers at 60 °C, the *cis*-α and *cis*-β structures of **6** are unchanged in solution up to 100 °C, suggesting no interconversion between the *cis*-α and *cis*-β isomers. The result of elemental analysis of a mixture of **6** is excellently consistent with the calculated values.

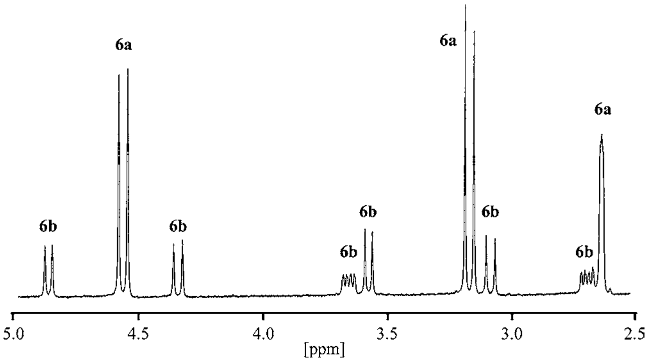
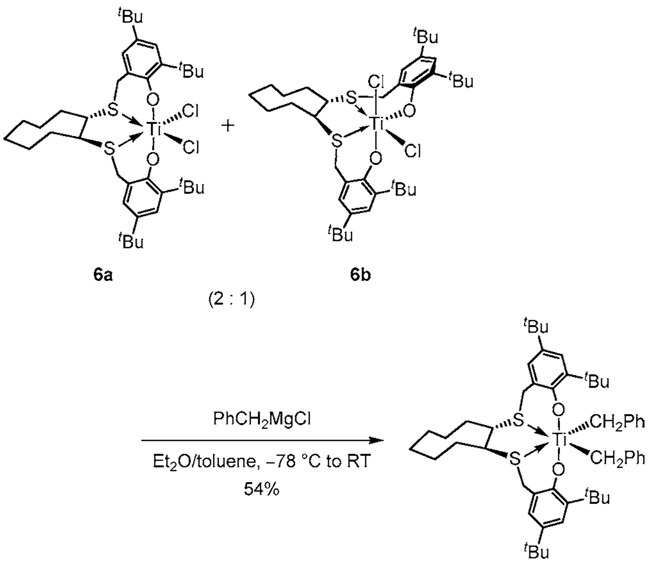


Figure 1. Part of the ^{1}H NMR spectrum (δ 2.5–5.0) of titanium(IV) dichloro complexes **6** as a mixture of *cis*-α and *cis*-β isomers.

A mixture of titanium(IV) dichloro complexes **6** reacted with 2 equiv of PhCH$_2$MgCl in ether/toluene at −78 °C (Scheme 2). The orange color of **6** gradually turned to dark red, suggesting the generation of the corresponding titanium(IV) dibenzyl complex **7**. Accordingly, ^{1}H NMR analysis of the reaction mixture confirmed two Ti-benzyl protons (δ 3.07 and

Scheme 2



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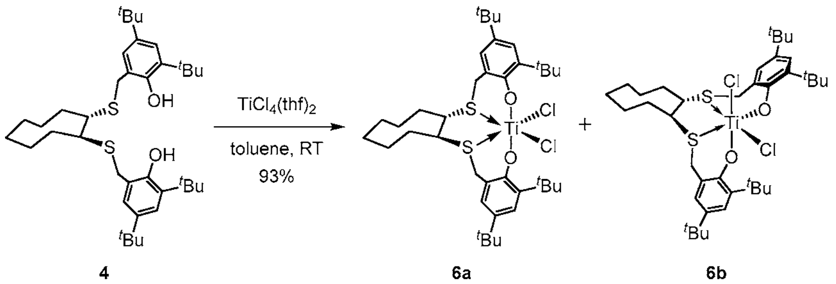
Scheme 1



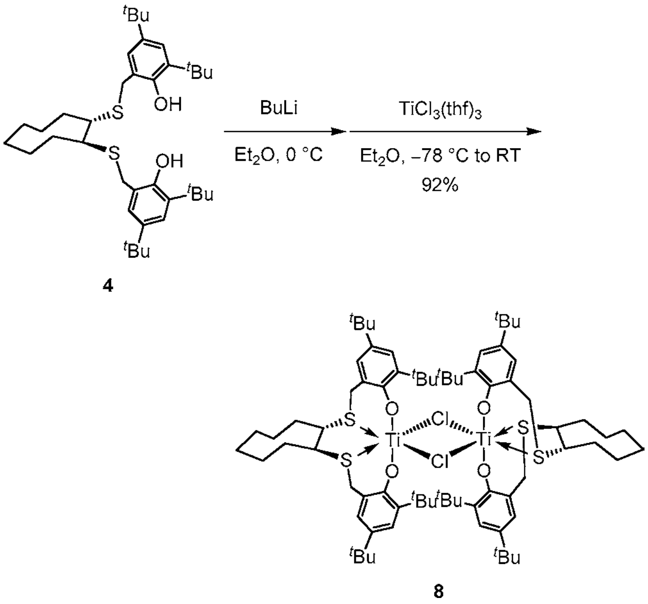
4 6a 6b

(2 : 1)

3.32, J = 15 Hz) and two S-benzyl protons (δ 3.46 and 3.51, J = 10 Hz) as doublet signals, indicating that **7** exists as a single stereoisomer in solution. Dibenzyl complex **7** was isolated in 54% yield as red crystals from recrystallization of hexane at −30 °C. Unfortunately, **7** could not be fully characterized by $^{13}C\{^1H\}$ NMR and elemental analysis because of its thermal and light instability, and decomposition of **7** occurred readily at room temperature in solution to give 1,2-diphenylethane, toluene, and unidentifiable material, which most likely results from the reductive elimination and/or α-hydrogen elimination. In the crystal structure of **7**,[10] it was confirmed that two benzyl ligands adopt η^1-coordination to a titanium center in sharp contrast to the previous zirconium dibenzyl complex **5b**, that has one benzyl ligand displaying η^2-coordination.[7a]

To prove the coordination ability of [OSSO]-type ligand **4** to titanium(III) precursors, we examined the reaction of **4** with $TiCl_3(thf)_3$. The deprotonation of ligand **4** with 2 equiv of BuLi in Et_2O at 0 °C followed by the treatment with $TiCl_3(thf)_3$ at −78 °C cleanly produced chloride-bridged dimeric titanium(III) complex **8** in 92% yield as yellow-green crystals (Scheme 3). The ^1H NMR spectrum of **8** in C_6D_6 showed broad resonances due to an antiferromagnetic coupling of the d^1 electron on the titanium center. Thus, the methine protons in the cyclooctane ring and two benzyl protons appeared at δ 2.38, 3.67, and 4.45, respectively. This magnetic equivalence indicates that dimer **8** has C_2-symmetry in solution. In the ^1H NMR spectrum of **8** in THF-d_8, all signals disappeared completely, thus suggesting the formation of a paramagnetic, monomeric titanium(III) complex. Furthermore, the reaction of **8** with pyridine in benzene for 5 days quantitatively afforded the corresponding paramagnetic, monomeric titanium(III) pyridine-adduct **9** as orange crystals (Scheme 4).[10]

Scheme 3



Single crystals of dimer **8** suitable for X-ray crystallography were grown from a concentrated hexane solution. The molecular structure was illustrated in Figure 2 together with selected bond lengths and angles. The X-ray analysis revealed that each titanium center of **8** has a distorted octahedral environment, and two bridging chlorides linked together the two titanium atoms. The cyclooctane rings in **8** take the boat-chair conformation. Two oxygen atoms are bound to a titanium center at trans positions with an O1−Ti1−O2 bond angle of 167.49(8)°. The central Ti_2Cl_2 fragment exhibits almost planar

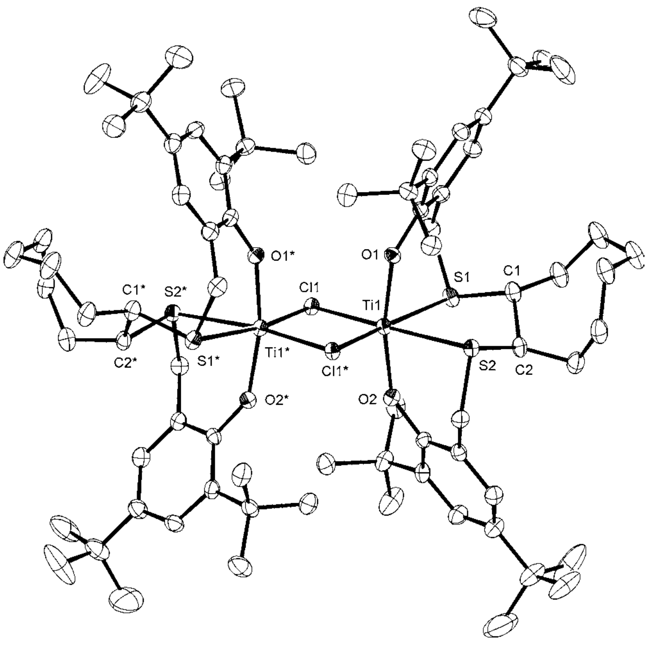
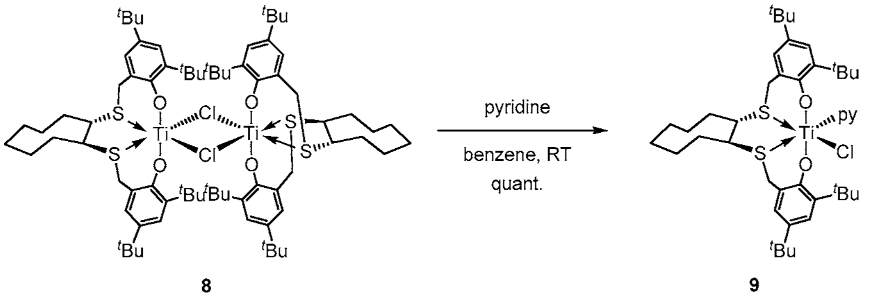


Figure 2. ORTEP drawing of chloride-bridged dimeric titanium(III) complex **8** (50% thermal ellipsoids, hydrogen atoms, and a solvated hexane molecule were omitted for clarity). Selected bond lengths [Å] and bond angles [deg]: Ti1−O1 = 1.8932(18), Ti1−O2 = 1.8888(18), Ti1−S1 = 2.5618(9), Ti1−S2 = 2.5730(8), Ti1−Cl1 = 2.4572(8), Ti1−Cl1* = 2.4504(8), Ti1···Ti1* = 3.1391(10), S1−Ti1−S2 = 80.44(3), O1−Ti1−O2 = 167.49(8)°, Cl1−Ti1−Cl1* = 100.44(3), Ti1−Cl1−Ti1* = 79.53(3), S1−C1−C2−S2 = 75.35(18), Ti1−Cl1−Ti1*−Cl1* = 1.89(4).

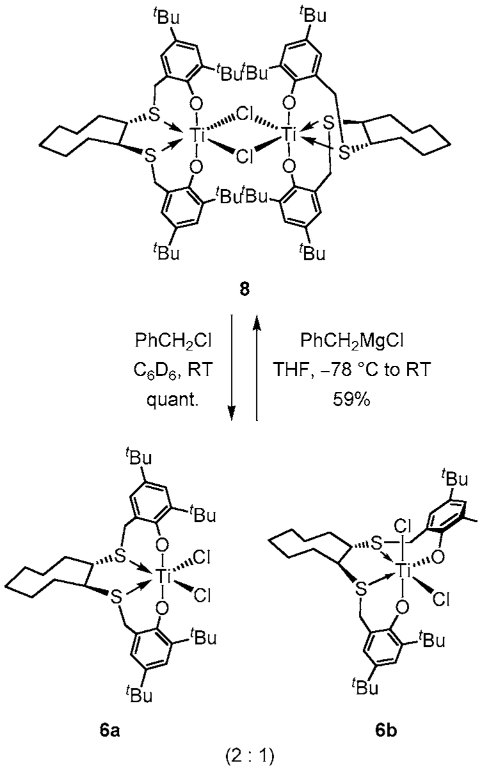
Scheme 4



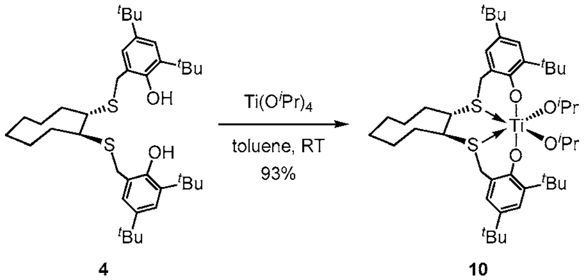
geometry, which has 1.89(4)° of Ti1−Cl1−Ti1*−Cl1* puckered angle. The Ti1···Ti1* distance [3.1391(10) Å] is significantly shorter than those observed in chloro-bridged $\mathrm{Cp_2}$ complexes $[\mathrm{Cp_2Ti}(\mu\text{-Cl})]_2$ [3.943(2) and 3.968(2) Å][11] and $[(\mathrm{C_5H_4Me})\mathrm{Ti}(\mu\text{-Cl})]_2$ [3.926(3) Å],[12] and a chloro-bridged Cp/phenoxide complex $[\mathrm{CpTi(OC_6H_2\text{-}2\text{-}Np\text{-}4,6\text{-}{}^tBu_2)_2}(\mu\text{-Cl})]_2$ [3.336(1) Å],[13] but slightly longer than those in a chloro-bridged bis(phenoxide) complex $[\mathrm{Ti(OC_6H_3\text{-}2,6\text{-}Ph_2)_2}(\mu\text{-Cl})]_2$ [2.9827(7) Å],[14] and bis-octahedral formamidinate complexes $[\mathrm{Ti_2\{RNC(H)CNR\}_2\{RNC(H)CNR\}_2}(\mu\text{-Cl})_2]$ [R = Ph, 2.8890(8), R = Cy, 2.942(2) Å].[15] Both of the Ti−Cl bond lengths [2.4572(8) and 2.4504(8) Å] are similar to those in observed $[\mathrm{Ti_2\{CyNC(H)CNCy\}_2\{CyNC(H)CNCy\}_2}(\mu\text{-Cl}_2)]$ [2.433(3) and 2.457(3) Å].[15b] It is known that dimeric titanium(III) compounds containing a Ti−Ti distance of less than 3 Å imply the existence of a Ti−Ti single bond.[16] In the case of **7**, there is no significant Ti−Ti bond and the observed Ti···Ti distance of **8** would be a consequence by the decrease of Ti−Cl bond lengths within the four-membered $\mathrm{Ti_2Cl_2}$ unit.

Dimeric titanium(III) complex **8** was completely oxidized for 12 days with benzyl chloride as an oxidant in $\mathrm{C_6D_6}$ to give a 2:1 mixture of titanium(IV) dichloro complexes **6** and dibenzyl. The titanium(IV) dichloro complexes **6** also underwent one-electron reduction to form dimeric titanium(III) complex **8** by the reaction with 1 equiv of $\mathrm{PhCH_2MgCl}$ in THF at −78 °C (Scheme 5).

Scheme 5



Scheme 6



In contrast to the formation of dichloro complexes **6** as a mixture, the reaction of **4** with $\mathrm{Ti(O^iPr)_4}$ in toluene at room temperature afforded the corresponding di(isopropoxy) titanium(IV) complex **10** as yellow crystals in 93% yield (Scheme 6). In the ^{1}H NMR spectrum of **10**, the AB pattern due to the benzyl protons appeared at δ 3.41 and 4.10 as doublet signals (J = 14 Hz). The sulfur-bonded methine protons resonated at δ 2.49 as a broad singlet. Methyl and methine protons of isopropyl groups were observed at δ 5.00 as a septet (J = 6 Hz), and at 1.28 and 2.96 as doublets, respectively. Similar to the NMR observation of the related zirconium complexes **5** incorporating the [OSSO]-type ligand **4**,[7,8] ^{1}H and ^{13}C{^{1}H} NMR data of **10** exhibited the equivalency of the two phenolate ligands as well as the two benzyl and isopropoxy moieties, indicating that complex **10** is in agreement with a C_2-symmetric, helical structure in the NMR time scale. In the X-ray crystallographic analysis for complex **10** (Figure 3), the titanium core lay at the center of a distorted octahedral coordination sphere locating cis to sulfur and trans to oxygen dispositions, adopting a *cis-α* (Λ*,*S**,*S**) configuration. The Ti−S bond lengths [2.7022(11) and 2.6958(12) Å] are elongated in comparison with those of the mentioned titanium(III) dimer **8** [2.5618(9) and 2.5730(8) Å], while the Ti−O bond lengths [1.883(2) and 1.892(2) Å] are comparable to those of **7** [1.8932(18) and 1.8888(18) Å]. The O1−Ti1−O2 angle [159.17(11)°] is somewhat larger than that of di(isopropoxo) complex $[\mathrm{Ti(O^iPr)_2(OC_6H_2\text{-}4,6\text{-}di\text{-}CMe_2Ph\text{-}2\text{-}SCH_2)_2}]$ [152.14(11)°] reported by Okuda.[2e] The S1−C1−C2−S2 dihedral angle [63.9(3)°] is slightly deviated from the ideal 60° of the gauche conformation.

To synthesize a bis(diethylamido) titanium(IV) complex supported by [OSSO]-type ligand **4**, we next carried out the reaction of **4** with $\mathrm{Ti(NEt_2)_4}$ in toluene. Surprisingly, the reaction course was completely different from the expected one, and [OSSO]-type bis(phenolato)-bridged dinuclear bis(diethylamido) titanium(IV) complex **11** was produced in 26% isolated yield as pale yellow crystals (Scheme 7). The ^{1}H NMR spectrum of **11** showed four magnetically inequivalent signals for ^{t}Bu groups at δ 1.34, 1.39, 1.67, and 1.68, and multiplet signals for the benzyl protons at δ 4.23−4.43. The protons at diethylamido ligands appeared as multiplet signals at δ 3.69−3.86 and 0.71−086. The molecular structure of **11** was finally determined by X-ray analysis as depicted in Figure 4. Two distorted tetrahedral titanium atoms are held by two bridged [OSSO]-type ligands **4**, which adopts (*R**,*R**) configuration and the other (*S**,*S**) one with respect to *trans*-cyclooctane moieties. The dimeric structure of **11** has a crystallographically imposed C_i symmetry. The Ti−O bond lengths [1.858(3) and 1.827(3) Å] are slightly shorter than those of the mentioned di(isopropoxo) complex **10** [1.883(2) and 1.892(2) Å], because of the increased π-donation from oxygen atoms to titanium center. The Ti−N bond lengths [1.864(4) and 1.909(4) Å] are comparable to those of the related bis(diethylamido) titanium(IV) complex $\{\mathrm{Ti[CH_2(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2](NEt_2)_2}\}$ [1.895(2) and 1.869(2) Å] reported by Harada et al.[17]

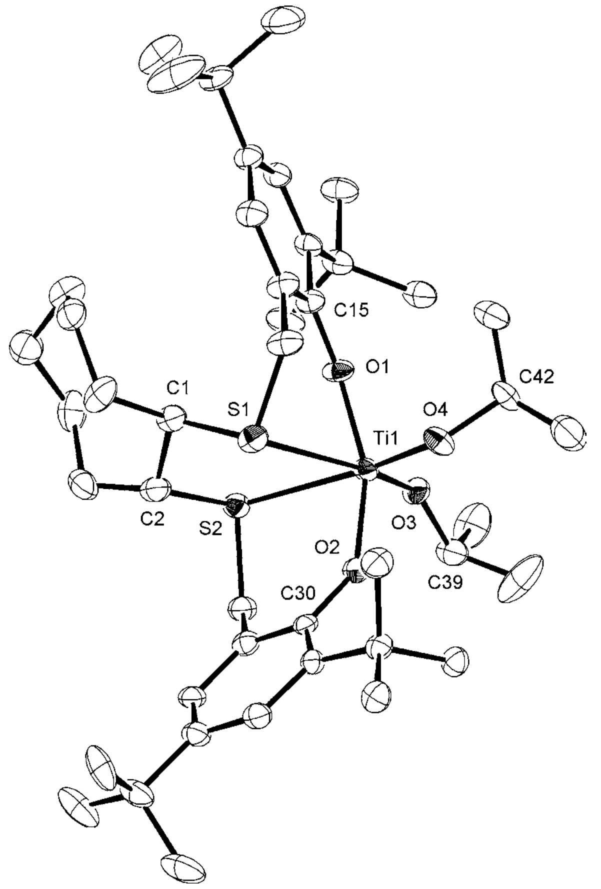
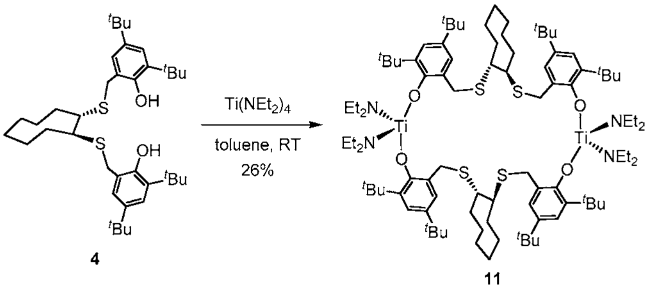


Figure 3. ORTEP drawing of di(isopropoxy) titanium(IV) complex **10** (50% thermal ellipsoids, hydrogen atoms were omitted for clarity). Selected bond lengths [Å] and bond angles [deg]: Ti1−O1 = 1.883(2), Ti1−O2 = 1.892(2), Ti1−O3 = 1.790(3), Ti1−O4 = 1.814(3), Ti1−S1 = 2.7022(11), Ti1−S2 = 2.6958(12), O1−Ti1−O2 = 159.17(11), S1−Ti1−S2 = 74.27(3), O3−Ti1−O4 = 104.94(11), Ti1−O1−C15 = 150.7(2), Ti1−O2−C30 = 144.5(2), Ti1−O3−C39 = 142.0(2), Ti1−O4−C42 = 131.8(2), S1−C1−C2−S2 = 63.9(3).

Scheme 7



Polymerization of 1-Hexene. To evaluate the potential as a polymerization catalyst of α-olefin, we tested 1-hexene polymerization with titanium precatalysts **6** and **8** in toluene at room temperature. The results are compiled in Table 1. Upon activation with dried MAO (DMAO) ([DMAO]/**5** = 250), the polymerization of 1-hexene (3.0 g) with the *cis-α* and *cis-β* mixture of **6** (0.020 mmol) proceeded slowly to yield poly(1-hexene) (0.47 g) (Run 1). The GPC analysis of the resulting polymer revealed a high molecular weight (M_w = 52,000 g mol^{-1}) and a relatively narrow polydispersity (M_w/M_n) of 1.7, indicating a single-site catalyst. The microstructure of the polymer elucidated by $^{13}C\{^1H\}$ NMR spectroscopy, which showed six sharp signals, was excellently isotactic (>95%) (Figure 5). In the case of **6** activated with $(Ph_3C)[B(C_6F_5)_4]$ in the presence of Al^{i}Bu$_3$ (Run 2), the obtained isotactic polymer (*mmmm* > 95%) showed somewhat lower molecular weight (M_w = 22,000 g mol^{-1}). Moreover, the dimeric titanium(III) complex **8** activated by DMAO ([DMAO]/**8** = 250) furnished similar isotactic poly(1-hexene) (*mmmm* > 95%) with M_w = 38,000 g mol^{-1} and M_w/M_n = 1.7 (Run 3). The formation of isotactic poly(1-hexene) with **6** or **8** is in sharp contrast to the polymerization catalyzed by Group 4 metal complexes bearing [OSSO]-type ligands **1−3** leading to oligomers[2h] or stereoirregular (atactic) polymers.[5,6] While a similar high isotacticity in 1-hexene polymerization was observed for the corresponding zirconium homologue **5b**,[7a] titanium complexes **6** and **8** were found to be less active [0.27−1.0 g mmol(cat)$^{-1}$ h^{-1}] by 4 and 5 orders of magnitude, respectively, than **5b** activated by $(Ph_3C)[B(C_6F_5)_4]$ [2,500 g mmol(**5b**)$^{-1}$ h^{-1}].

Conclusion. We have demonstrated the coordination chemistry of an [OSSO]-type bis(phenolato) ligand based on *trans*-cyclooctandiyl platform with titanium precursors. In the case of titanium(IV) complexes, while the reaction of **4** with $TiCl_4(thf)_2$ gave the corresponding titanium(IV) dichloro complexes **6** as a mixture of *cis-α* and *cis-β* isomers, treatment of **4** with Ti(O^{i}Pr)$_4$ formed di(isopropoxy) titanium(IV) complex **10** having a C_2-symmetric *cis-α* configuration. In addition, the reaction of **4** with $Ti(NEt_2)_4$ resulted in the unexpected formation of [OSSO]-type bis(phenolato)-bridged dinuclear diamido titanium(IV) complex **11**. On the other hand, the treatment of dilithio salt of **4** with titanium(III) complex $TiCl_3(thf)_3$ afforded chloride-bridged dimeric titanium(III) complex **8**, which exhibited the antiferromagnetic character in nonpolar solvent solution. In the catalytic behavior for 1-hexene polymerization, titanium(IV) and (III) complexes **6** and **8** upon activation with a cocatalyst in toluene produced poly(1-hexene) with high molecular weight (M_w = 22,000−52,000 g mol^{-1}) and relatively narrow polydispersity (M_w/M_n = 1.7−1.8), albeit with low activity [0.27−1.0 g mmol(cat)$^{-1}$ h^{-1}]. Studies of further coordination chemistry and the catalytic potentiality of the [OSSO]-type bis(phenolato) ligands for olefin polymerizations are underway.[18]

■ EXPERIMENTAL SECTION

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in an MBRAUM LABmaster Glovebox under an inert atmosphere of argon. Anhydrous hexane, toluene, and diethyl ether were further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (benzene-d_6) was dried and degassed over a potassium mirror by the freeze−thaw cycle prior to use. Other chemicals and gases were used as received. Melting points were determined on a Mel−Temp capillary tube apparatus and are uncorrected. ^1H (400 MHz) and $^{13}C\{^1H\}$ (100.5 or 125.8 MHz) spectra were obtained with Bruker DRX400, AVANCE500-T or JEOL JNM-ECS400 spectrometers. X-ray crystallography was performed with a Rigaku Saturn724 diffractometer. Elemental analyses were performed by the Chemical Analysis Team of RIKEN Advanced Science Institute. The $^{13}C\{^1H\}$ NMR data of poly(1-hexene) were obtained in $CDCl_3$ at room temperature. The molecular weights and molecular weight distributions of poly(1-hexene) were determined against polystyrene standard by gel permeation chromatography on a HLC-8220 GPC apparatus (Tosoh Corporation) of the laboratory of Dr. Zhaomin Hou (Organometallic Chemistry Laboratory, RIKEN Advanced Science Institute). *trans*-Cyclooctane-1,2-dithiol,[19] [OSSO]-

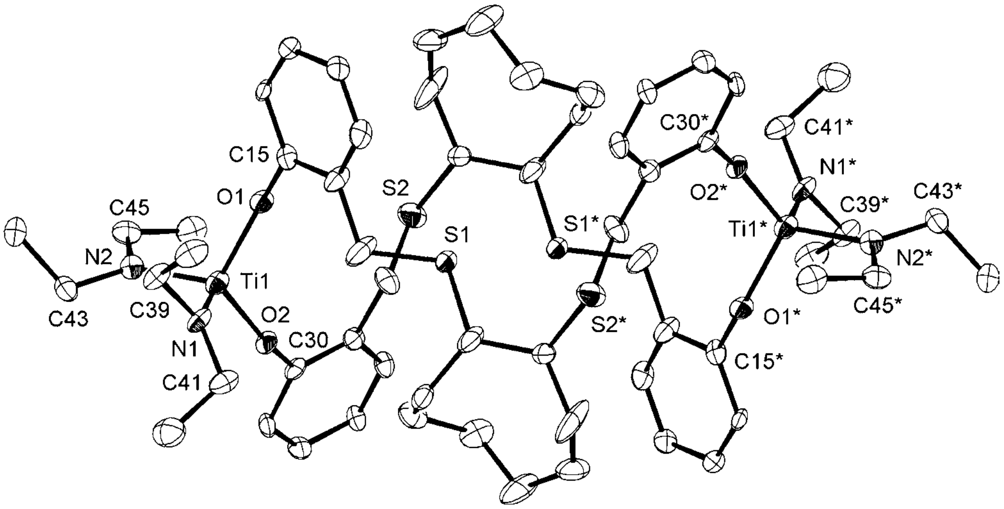


Figure 4. ORTEP drawing of [OSSO]-type bis(phenolato)-bridged dinuclear diamido titanium(IV) complex **11** (50% thermal ellipsoids, hydrogen atoms and ^{t}Bu substituents were omitted for clarity). Selected bond lengths [Å] and bond angles [deg]: Ti1−O1 = 1.858(3), Ti1−O2 = 1.827(3), Ti1−N1 = 1.864(4), Ti1−N2 = 1.909(4), O1−Ti1−O2 = 112.59(15), O1−Ti1−N1 = 108.32(15), O1−Ti1−N2 = 110.17(16), O2−Ti1−N1 = 108.80(16), O2−Ti1−N2 = 110.61(15), N1−Ti1−N2 = 106.10(18), Ti1−O1−C15 = 145.6(3), Ti1−O2−C30 = 156.1(3), Ti1−N1−C39 = 112.9(3), Ti1−N1−C41 = 131.2(3), Ti1−N2−C43 = 127.6(3), Ti1−N2−C45 = 120.9(3), C39−N1−C41 = 115.7(4), C43−N2−C45 = 111.4(4).

Table 1. 1-Hexene Polymerization with Titanium(IV) 6 and Titanium(III) 8 Complexes upon Activation with a Cocatalyst

run	cat [mmol]	cocatalyst[b]	yield [g]	activity [g mmol(cat)$^{-1}$ h^{-1}]	M_w [g mol^{-1}]	PDI[c]	*mmmm*[d] [%]
1[a]	**6**: 0.020	DMAO	0.47	1.0	52,000	1.7	>95
2[a]	**6**: 0.020	Ph_3C^+/AlR_3	0.23	0.49	22,000	1.8	>95
3[a]	**8**: 0.010	DMAO	0.13	0.27	38,000	1.7	>95

[a] Conditions: polymerization time 24 h, toluene (5 mL), room temperature, [Al]/[Ti] = 250; 1-hexene 3.0 g (35.6 mmol) (Run 1), [Al]/[Ti] = 50; 1-hexene 3.0 g (35.6 mmol) (Run 2), [Al]/[Ti] = 250; 1-hexene 3.0 g (35.6 mmol) (Run 3). [b] DMAO 5.0 mmol, Ph_3C^+/AlR_3 = $[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ (0.020 mmol/1.0 mmol). [c] PDI = M_w/M_n. Determined by HT-GPC. [d] Determined by $^{13}C\{^1H\}$ NMR spectroscopy.

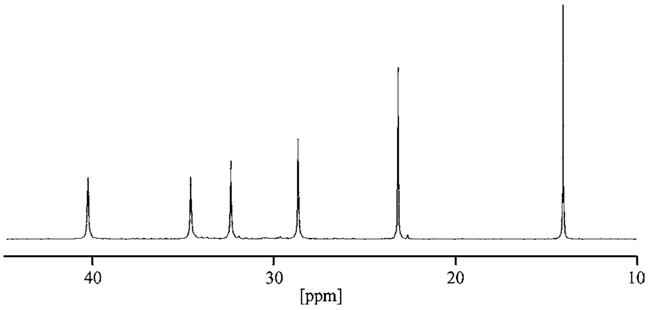


Figure 5. $^{13}C\{^1H\}$ NMR spectrum of poly(1-hexene) obtained by the **6**/DMAO system.

H_2 ligand **4**,[7a] and DMAO[20] were prepared by the literature procedures.

Synthesis of Titanium(IV) Dichloro Complexes 6. A solution of **4** (525 mg, 0.856 mmol) in toluene (20 mL) was added to a solution of $TiCl_4(thf)_2$ (286 mg, 0.856 mmol) in toluene (30 mL) at room temperature. The mixture was stirred for 4 h at room temperature, and the solvent was removed under reduced pressure. The residue was washed with hexane (2 mL) and dried in vacuo to give an inseparable mixture of *cis-α* isomer **6a** and *cis-β* isomer **6b** in an approximate ratio of 2:1 (578.0 mg, 93%) as red crystals. **6**: ^1H NMR (400 MHz, C_6D_6) δ 0.58−1.92 (m, major + minor), 2.62 (br s, major), 2.66−2.70 (m, minor), 3.07 (d, ^2J = 14 Hz, minor), 3.16 (d, ^2J = 15 Hz, major), 3.57 (d, ^2J = 12 Hz, minor), 3.63−3.67 (m, minor), 4.35 (d, ^2J = 14 Hz, minor), 4.57 (d, ^2J = 15 Hz, major), 4.88 (d, ^2J = 12 Hz, minor), 6.59 (d, ^4J = 2 Hz, major), 6.63 (d, ^4J = 2 Hz, minor), 6.94 (d, ^4J = 2 Hz, minor), 7.36 (d, ^4J = 2 Hz, minor), 7.51 (d, ^4J = 2 Hz, minor), 7.54 (d, ^4J = 2 Hz, major). Anal. Calcd. for $C_{38}H_{58}Cl_2O_2S_2Ti$: C, 62.54; H, 8.01. Found: C, 62.38; H, 8.21.

Reaction of 6 with $PhCH_2MgCl$. To a solution of dichloro complexes **6** (163.5 mg, 0.224 mmol) in Et_2O (50 mL) and toluene (50 mL) at −78 °C was added a 1.0 M solution of $PhCH_2MgCl$ in diethyl ether (0.55 mL, 0.55 mmol). The orange colored solution was then gradually allowed to warm to room temperature, and the solvent was removed under reduced pressure. Toluene (40 mL) was added to the residue. The insoluble inorganic materials were removed by decantation. The solvent of the filtration was removed in vacuo, and the residual solid was recrystallized from hexane at −30 °C to give titanium(IV) dibenzyl complex **7** (103.0 mg, 54%) as dark red crystals. **7**: ^1H NMR (400 MHz, C_6D_6) δ 0.65−1.43 (m, 30 H), 1.91 (s, 18 H), 2.30 (br s, 2 H), 3.07 (d, ^2J = 15 Hz, 2 H), 3.32 (d, ^2J = 15 Hz, 2 H), 3.46 (d, ^2J = 10 Hz, 2 H), 3.51 (d, ^2J = 10 Hz, 2 H), 6.68 (d, ^4J = 2 Hz, 2 H), 6.80 (t, ^2J = 7 Hz, 2 Hz), 7.07 (t, ^2J = 7 Hz, 4 H), 7.33 (d, ^2J = 7 Hz, 4 H), 7.61 (d, ^4J = 2 Hz, 2 H).

Synthesis of Chloride-Bridged Dimeric Titanium(III) Complex 8. To a solution of **4** (220.0 mg, 0.359 mmol) in THF (10 mL) at 0 °C was added BuLi (2.6 M in hexane, 0.29 mL, 0.754 mmol). The solution was stirred for 30 min at this temperature. The resulting solution of dilithio salt of **4** was added to a suspension of $TiCl_3(thf)_3$ (137.4 mg, 0.359 mmol) in THF (15 mL) at −78 °C, and the mixture was stirred for 1 h. The solution was then gradually allowed to warm to room temperature, and the solvent was removed under reduced pressure. Toluene (50 mL) was added to the residue, and the insoluble inorganic materials were removed by decantation. The solvent of the filtration was removed in vacuo, and the residual solid was washed with hexane (2 mL) and dried in vacuo to give **8** (230.0 mg, 92%) as yellow green crystals. **8**: Mp 164−166 °C (dec.). ^1H NMR (400 MHz, C_6D_6) δ 0.66 (br s, 8 H), 0.94 (br s, 8 H), 1.25 (s, 36 H), 1.62 (m, 44 H), 2.38 (br s, 4 H), 3.67 (br s, 4 H), 4.45 (br s, 4 H), 6.74 (d, ^4J = 2 Hz, 4 H), 7.40 (d, ^4J = 2 Hz, 4 H). $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6) δ

Table 2. Crystallographic Data and Details of Refinement for **8**, **10**, and **11**

	8	10	11
formula	$C_{82}H_{130}Cl_2O_4S_4Ti_2$	$C_{44}H_{72}O_4S_2Ti$	$C_{92}H_{156}N_4O_4S_4Ti_2$
formula weight	737.40	777.04	803.12
color	yellow green	yellow	yellow
crystal size/mm	0.25 × 0.20 × 0.10	0.25 × 0.10 × 0.10	0.23 × 0.08 × 0.06
temperature	100 K	100 K	100 K
crystal system	monoclinic	orthorhombic	triclinic
space group	$C2/c$	$Pna2_1$	$P\bar{1}$
a/Å	27.067(4)	24.476(5)	9.670(4)
b/Å	18.036(3)	9.954(2)	14.572(7)
c/Å	17.145(3)	18.156(4)	17.708(9)
α/deg.	90	90	108.357(4)
β/deg.	93.440(2)	90	102.910(9)
γ/deg.	90	90	93.858(5)
V/Å^3	8355(2)	4423.4(15)	2282.7(18)
Z	4	4	1
D_{calcd}/g cm^{-3}	1.172	1.167	1.168
no. of unique data	7760	7589	8307
no. of parameters	438	501	504
no. of restraints	0	1	0
R_1 ($I > 2\sigma(I)$)	0.0569	0.0500	0.0728
wR_2 (all data)	0.1224	0.1241	0.1378
GOF	1.094	1.068	1.067

24.9, 26.3, 28.6, 30.6, 31.6, 31.7, 34.1, 35.4, 37.2, 121.4, 124.2, 124.9, 137.0, 139.8, 160.3. Anal. Calcd. for $C_{76}H_{116}Cl_2O_4S_4Ti_2$: C, 65.73; H, 8.42. Found: C, 65.66; H, 8.49.

Reaction of 8 with Pyridine. To a solution of **8** (347.2 mg, 0.250 mmol) in benzene (10 mL) at room temperature was added an excess amount of pyridine (1 mL, 0.983 g, 10.2 mmol). The solution was stirred for 7 days at this temperature, and the solvent was removed under reduced pressure. The residue was washed with hexane (2 mL) and dried in vacuo to give the corresponding titanium(III) pyridine adduct **9** (383.1 mg, 99%) as orange crystals. In the ^{1}H NMR spectrum of **9**, no signals were observed.

Synthesis of Di(isopropoxy) Titanium(IV) Complex 10. A solution of **4** (91.2 mg, 0.149 mmol) in toluene (10 mL) was added to a solution of Ti(O^{i}Pr)$_4$ (42.3 mg, 0.149 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 recrystallized from hexane (2 mL) at room temperature. The yellow crystals were collected by filtration and dried in vacuo to give **10** (107.3 mg, 76%) as yellow crystals. **10**: Mp 107−108 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.20−1.52 (m, 42 H), 1.88 (s, 18 H), 2.48 (m, 2 H), 3.41 (d, ^2J = 14 Hz, 2 H), 4.09 (d, ^2J = 14 Hz, 2 H), 4.99 (sep, ^2J = 6 Hz, 2 H), 6.77 (d, ^4J = 3 Hz, 2 H), 7.56 (d, ^4J = 2 Hz, 2 H). ^{13}C{^{1}H} NMR (100.4 MHz, C_6D_6) δ 25.3, 26.2, 26.5 (2C), 28.9, 30.6, 32.0, 34.3, 34.8, 35.7, 47.1, 78.9, 121.0, 124.0, 125.7, 138.2, 139.7, 160.5. Anal. Calcd. for $C_{44}H_{72}O_4S_2Ti$: C, 68.01 ; H, 9.34, Found: C, 67.94 ; H, 9.34.

Reaction of 4 with Ti(NEt$_2$)$_4$. A solution of **4** (805.0 mg, 1.31 mmol) in toluene (20 mL) was added to a solution of Ti(NEt$_2$)$_4$ (286 mg, 0.856 mmol) in toluene (30 mL) at room temperature. The mixture was stirred for 1 day at room temperature, and the solvent was removed under reduced pressure. The residue was washed with pentane (2 mL) and dried in vacuo to give [OSSO]-type bis(phenolato)-bridged dinuclear diamido titanium(IV) complex **11** (278.0 mg, 26%) as yellow crystals. **11**: Mp 111−112 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 0.73−2.09 (m, 120 H), 3.26−3.30 (m, 4 H), 3.69−3.86 (m, 16 H), 4.23−4.43 (m, 8 H), 7.42 (s, 4 H), 7.81 (s, 4 H). We were unable to obtain ^{13}C{^{1}H} NMR spectra because of the poor solubility of this complex **11** in C_6D_6 or C_7D_8. Anal. Calcd. for $C_{92}H_{156}N_4O_4S_4Ti_2$: C, 68.79; H, 9.79; N, 3.49. Found: C, 68.36; H, 9.78; N, 3.20.

General Procedure for 1-Hexene Polymerization. A 50 mL Schlenk flask was charged sequentially with catalyst precursor **6** (0.020 mmol) or **8** (0.010 mmol), cocatalyst (DMAO or [Ph$_3$C][B(C$_6$F$_5$)$_4$]/Al^{i}Bu$_3$), and toluene at room temperature. After stirring for 1 min at room temperature, 1-hexene (3.0 g, 35.6 mmol) was added to the reaction mixture. The mixture was stirred for 24 h at room temperature. The reaction was quenched by addition of 2-propanol and water. The mixture was extracted with toluene, and the organic layer was washed with water and dried over MgSO$_4$. The solvent was removed in vacuo at 70 °C overnight to leave poly(1-hexene).

X-ray Crystallographic Analyses. Yellow green single crystals of **8** were grown by slow evaporation of its saturated hexane solution at room temperature, yellow single crystals of **10** were grown by slow evaporation of its saturated toluene and hexane solution at room temperature, and yellow single crystals of **11** were grown by slow evaporation of its saturated hexane solution at −30 °C, respectively. The intensity data were collected at 100 K for **8**, **10**, and **11** on a Rigaku AFC10 diffractometer equipped with a Saturn724+ CCD detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[21] Hydrogen atoms of **8**, **10**, and **11** were located by assuming ideal geometry and were included in the structure calculations without further refinement of the parameters. The structures of **10** and **11** involved disorders in a ^{t}Bu group for **10** and a sulfur atom for **11**. The occupancies of each fragment were refined with constraints where their sum is 1 (0.653(7): 0.347(7) for the ^{t}Bu group and 0.724(3): 0.276(3) for the sulfur atom). Crystallographic data and details of refinement for **8**, **10**, and **11** are summarized in Table 2.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **8**, **10**, and **11** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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