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Zirconium Complex of an [OSSO]-Type Diphenolate Ligand Bearing *trans*-1,2-Cyclooctanediylbis(thio) Core: Synthesis, Structure, and Isospecific 1-Hexene Polymerization

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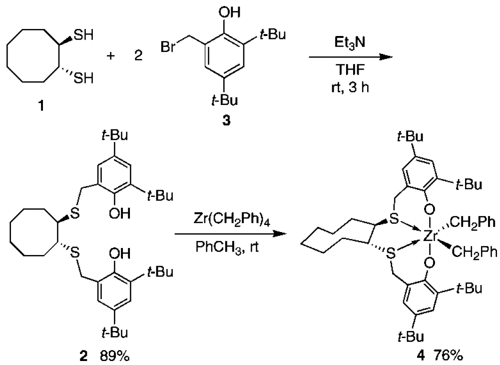
Recently, considerable attention has been paid to the development of postmetallocene single-site transition metal catalysts for alkene polymerization to achieve control of molecular weight and stereochemistry.[1] While most of the catalysts consist of a transition metal and a ligand involving nitrogen and/or oxygen coordination sites,[1] Okuda[2] and Kol[3] developed group 4 metal complexes bearing [OSSO]-type diphenolate ligands. They took a C_2 symmetric octahedral structure as similar as complexes bearing [ONNO]-type tetradentate ligands,[4] which were effective for regioregular oligomerization or polymerization of 1-alkenes. In addition, an optically active complex bearing a cyclohexanediylbis(thio) core was reported to catalyze copolymerization of stylene and 1-hexene giving optically active copolymers which involve isotactic polystylene and atactic poly(1-hexene) segments.[2a,b] Other reactions of similar transition metal or lanthanide complexes were reported.[5−7]

As reported by Okuda,[2a,b] introduction of a 1,2-cycloalkanediylbis(thio) moiety in a ligand is promising with a high tacticity for the polymerization of 1-alkenes owing to configurational stability.[2a,b,e] We recently reported the preparation of *trans*-cyclooctane-1,2-dithiol (**1**).[8] It is well-known that medium rings take a number of conformations,[9] suggesting their flexibility toward the change of R−C−C−R torsion angles (R = substituents). This leads to an expectation that an [OSSO]-type ligand bearing a *trans*-1,2-cyclooctanediylbis(thio) core relieves the strain caused by complexation with a metal and a change of coordination mode of the resulting complex by altering the S−C−C−S torsion angle, which would provide a configuration suitable for further reactions. In this communication, we report the synthesis of a new tetradentate ligand utilizing **1**, complexation of the ligand with zirconium, and the catalytic activity of the resulting zirconium complex for polymerization of 1-hexene.

Ligand **2** was prepared according to the modified Kol's method.[3] The reaction of 1,2-dithiol **1** (racemic) with 2 mol equiv of benzyl bromide **3**[10] in the presence of Et_3N in THF gave **2** in 89% yield (Scheme 1).[11] The reaction of **2** with $Zr(CH_2Ph)_4$ in toluene at room temperature produced dibenzyl Zr complex **4** in 76% yield.[11] In the ^{1}H NMR spectrum for **4**, two doublets at δ 2.16 (J = 10 Hz) and 2.78 (J = 10 Hz) were assigned to the benzyl protons of benzyl ligands and two doublets at δ 3.16 (J = 14 Hz) and 3.50 (J = 14 Hz) were assigned to the benzyl protons from ligand **2**. ^{1}H and ^{13}C NMR data of **4** exhibited the equivalency of the two phenolate moieties as well as the two benzyl ligands, indicating that **4** takes the C_2 symmetry in solution in the NMR time scale. The structure of **4** was unambiguously determined by X-ray crystallography (Figure 1).

Scheme 1. Syntheses of Ligand **2** and Zirconium Complex **4**



In the crystalline state, the central zirconium metal in **4** adopted a distorted octahedral geometry. The O−Zr−O bond is bent to the cyclooctane ring by 21.6° from ideal linearity. The S−C−C−S dihedral angle in **4** changed from 75.3(3)° in **2** to 67.2(2)°. One of the $Zr-C_{benzyl}-C_{ipso}$ bond angles in **4** is characteristically narrower [Zr1−C46−C47 = 94.49(18)°] than the other [Zr1−C39−C40 = 118.29(19)°], and the distance between C47 and Zr1 is 2.820(3) Å, suggesting η^2-coordination of the C46 and C47 to Zr1 in the crystalline state. A similar η^2 coordination of a benzyl group in zirconium complexes was observed by Okuda[2b] and Carpentier.[4c]

Coordinate polymerizations of 1-hexene were examined employing Zr complex **4** and $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ as the activators

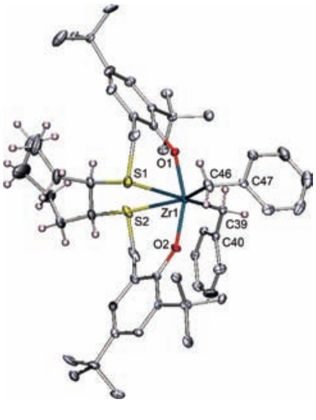


Figure 1. ORTEP drawing of Zr complex **4**. Hydrogen atoms except those of the benzyl methylenes and the cyclooctanediyl group were omitted for clarity. Relevant bond lengths (Å) and angles (deg): Zr1−O1 1.9984(18); Zr1−O2 1.9914(18); Zr1−S1 2.8107(8); Zr1−S2 2.7682(8); Zr1−C39 2.325(3); Zr1−C46 2.298(3); O1−Z1−O2 158.45(8); S1−Zr1−S2 71.25(3); C39−Zr1−C46 114.05(19); Zr1−C39−C40 118.29(19); Zr1−C46−C47 94.49(18).

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(Table 1).[4c,12] Polymerization of 1-hexene (3.0 g) with **4** (0.056 mol %) and $B(C_6F_5)_3$ (0.056 mol %) without solvent proceeded vigorously and exothermically and completed within 5 min to give poly(1-hexene) (2.7 g) with $M_w = 43\,000$ g mol^{-1} and polydispersity (PDI) = 1.9 (Table 1, entry 1), corresponding to the activity 1610 g·mmol(**4**)$^{-1}$·h^{-1}. Surprisingly, in spite of such an exothermic reaction, the ^{13}C NMR spectrum showed a high isotacticity (*mmmm* > 95%[14]) in addition to the high activity. While the polymerization with **4**/$B(C_6F_5)_3$ or **4**/$(Ph_3C)[B(C_6F_5)_4]$ in benzene−hexane at room temperature gave a similar isotactic polymer (entries 2 and 3), that with **4**/$(Ph_3C)[B(C_6F_5)_4]$ in benzene−hexane at 0 °C furnished a polymer (*mmmm* > 95%) with larger M_w (120 000 g mol^{-1}) and smaller PDI (1.6) values (entry 4). In entries 2−4, the polymerization reaction had been completed before quenching with MeOH, for which the values of appearance of the activity were small (850, 870, and 830 g·mmol(**4**)$^{-1}$·h^{-1}, respectively). In entry 5, the polymerization was carried out using a tenth amount of **4**/$(Ph_3C)[B(C_6F_5)_4]$ in other entries and quenched before completion of the reaction to give a lesser amount of poly(1-hexene) (0.83 g), corresponding to the activity 2500 g·mmol(**4**)$^{-1}$·h^{-1}, which is ~30 times larger than the catalyst reported by Kol.[3]

Table 1. 1-Hexene Polymerization with **4** and an Activator[a]

entry	solvent (mL)	yield (g)	M_w (g mol^{-1})	PDI[d] (M_w/M_n)	*mmmm*[e] (%)
1[b]	none	2.7	43 000	1.9	>95
2[b]	benzene (5) hexane (1)	2.8	43 000	1.9	>95
3[c]	benzene (5) hexane (1)	2.9	41 000	2.1	>95
4[c]	benzene (10) hexane (2)	2.8	120 000	1.6	>95
5[c]	benzene (1)	0.83	59 000	1.7	>95

[a] Conditions: 0.020 mmol of **4** and an activator, and 3.0 g (35.6 mmol) of 1-hexene at rt for 5 min (entry 1) or 10 min (entries 2 and 3) or at 0 °C for 10 min (entry 4). In entry 5, 0.0020 mmol of **4** and $(Ph_3C)[B(C_6F_5)_4]$ were used. [b] Activated by $B(C_6F_5)_3$. [c] Activated by $(Ph_3C)[B(C_6F_5)_4]$. [d] Determined by HT-GPC. [e] Determined by ^{13}C NMR spectroscopy.

The formation of isotactic poly(1-hexene) with **4** and $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ is in contrast to the polymerization using reported [OSSO]-Zr complexes giving oligo(1-hexene) (dimer to octamer)[2d] or an atactic polymer ($M_w = 12\,000$ g mol^{-1}).[3] Kol[4b] and Carpentier[4c] reported the polymerization of 1-hexene with Zr complexes bearing [ONNO]-type tetradentate ligands. Our results achieved by the present system are comparable and superior to those obtained with complexes [Zr(CH$_2$Ph)$_2$(OC$_6$H$_2$-4,6-di-*t*-Bu-2-CH$_2$-NMeCH$_2$)$_2$] ($M_w = 12\,000$ g mol^{-1}, PDI = 1.15, *mmmm* > 95%)[4b] and [Zr(CH$_2$Ph)$_2${*trans*-1,2-*cyclo*-C$_6$H$_{10}$-bis{NMe(CH$_2$)$_2$C(CF$_3$)$_2$O}}]-($M_w = 41\,000$ g mol^{-1}, PDI = 1.76, *mmmm* = 83%).[4c]

In conclusion, we synthesized and characterized six-coordinated Zr complex **4** bearing a novel [OSSO]-type tetradentate ligand. The combination of Zr complex **4** and $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ showed a high activity toward polymerization of 1-hexene and provided highly isotactic poly(1-hexene). These results of **4** are produced by the fusion of the eight-membered ring on the [OSSO]-type ligand, and we are now investigating the polymerization of other 1-alkenes using **4** and the synthesis of analogous ligands bearing smaller rings for comparison with the present results.

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Supporting Information Available: Experimental details and crystallographic data for **2** and **4** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For the experimental procedures and details of spectral and crystallographic data for **2** and **4**, see the Supporting Information.

(12) The generation of zirconium cation by treatment of **4** with $B(C_6F_5)_3$ in C_6D_6 was observed in the ^{19}F NMR of $[B(CH_2Ph)(C_6F_5)_3]^-$: ^{19}F NMR (376 MHz, C_6D_6) δ−166.5 (t, ^2J = 23 Hz, 6 F, *m*-F),−163.8 (t, ^2J = 23 Hz, 3 F, *p*-F),−130.1 (d, ^2J = 23 Hz, 6 F, *o*-F). The Δ(*m*,*p*-F) value was 2.7 ppm, indicating weak coordination between $[B(CH_2Ph)(C_6F_5)_3]^-$ and the zirconium cation.[13]

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(14) The ^{13}C NMR spectra (C3 region) indicated that the polymerization proceeded by 1,2-insertion[2d] (δ 34.6, *mmmm*) accompanying the *mmmr*, *rmmr*, and *mmrr* pentads (δ 34.4) (<5%) without 2,1-regioerror.[4c]

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