

# Synthesis, Structure, and 1-Hexene Polymerization Catalytic Ability of Group 5 Metal Complexes Incorporating an [OSSO]-Type Ligand

Tomoyuki Toda,<sup>†</sup> Norio Nakata,<sup>†</sup> Tsukasa Matsuo,<sup>‡,§</sup> and Akihiko Ishii<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan

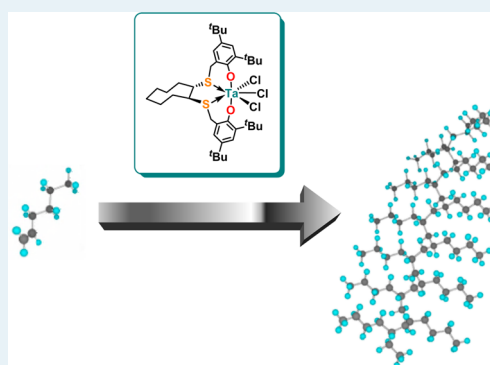
<sup>‡</sup>Functional Elemento-Organic Chemistry Unit, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

<sup>§</sup>Department of Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-osaka, Osaka 577-8502, Japan

## S Supporting Information

**ABSTRACT:** Group 5 metal complexes bearing an [OSSO]-type bis(phenolate) ligand have been successfully prepared by the reaction of a bis(phenol) compound **3** or its dilithio salt **6** with VO(OPr)<sub>3</sub>, NbCl<sub>5</sub>, or TaCl<sub>5</sub>. X-ray crystallographic analyses revealed the monomeric nature of the resulting complexes, [OSSO]VO(OPr) (**5**), [OSSO]NbCl<sub>3</sub> (**7**), and [OSSO]TaCl<sub>3</sub> (**8**), where the metal centers adopted *cis-α* configurations of the [OSSO] tetradentate ligand. The tantalum(V) complex **8** with <sup>t</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as an activator catalyzed the polymerization of 1-hexene to provide completely isotactic poly(1-hexene), with a narrow molecular weight distribution ([*mmmm*] > 95%, *M*<sub>w</sub> = 9100 g mol<sup>-1</sup>, PDI = 1.6); this is the first group 5 metal catalyst for  $\alpha$ -olefin polymerization to afford a highly isospecific polymer.

**KEYWORDS:** vanadium, niobium, tantalum, postmetallocene,  $\alpha$ -olefin polymerization, [OSSO]-type ligand



Since the advent of Ziegler–Natta catalysts,<sup>1–4</sup> group 4 metal complexes with alkyl aluminum reagents have attracted much attention as olefin polymerization catalysts. In both academia and industry, significant efforts have been made in achieving highly active homogeneous catalysts and stereospecific polymerization.<sup>5–9</sup> Accordingly, numerous metallocene and postmetallocene group 4 metal catalysts have shown powerful catalytic activity and complete stereospecificity for  $\alpha$ -olefin polymerization.<sup>10</sup> In contrast, only a few examples of successful  $\alpha$ -olefin polymerization catalyzed by group 5 metal complexes have been published.<sup>11–13</sup> Vanadium-based heterogeneous polymerization systems first appeared in the 1950s and achieved notable success in the production of ethylene–propylene and ethylene–propylene–diene elastomers.<sup>14,15</sup> Vanadium precatalysts bearing chelating aryloxides have been shown by several research groups to be highly active polymerization catalysts for ethylene or ethylene–propylene.<sup>12</sup> Recently, researchers reported tantalum complexes as olefin copolymerization catalysts.<sup>16,17</sup> For example, Fujita and co-workers synthesized tantalum complexes bearing tris(pyrazolyl)borate ligands (Tp) and showed that, when activated with dried methylaluminoxane (dMAO) or <sup>t</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], these complexes were active ethylene polymerization catalysts that produced low- to high-molecular-weight polyethylene with relatively narrow to broad molecular-weight distributions.<sup>16</sup> In particular, a tantalum complex with a sterically demanding mesityl group on the Tp ligand exhibited very high activity (25.7 kg mmol<sup>-1</sup> h<sup>-1</sup>) in

association with <sup>t</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Oda and Mashima presented tantalum complexes supported by silicon-bridged cyclopentadienyl-phenoxy ligands (PHENICS: phenoxy-induced complex of Sumitomo); the complexes showed moderate activity for ethylene/1-hexene copolymerization (1.02 kg mmol<sup>-1</sup> h<sup>-1</sup>) and low activity for 1-hexene polymerization (0.0326 g mmol<sup>-1</sup> h<sup>-1</sup>) upon activation with <sup>t</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].<sup>17</sup> These ancillary ligands are also well-known to play an important role in supporting group 4 metal catalysts that demonstrate higher olefin polymerization activities than group 4 metallocene catalysts.

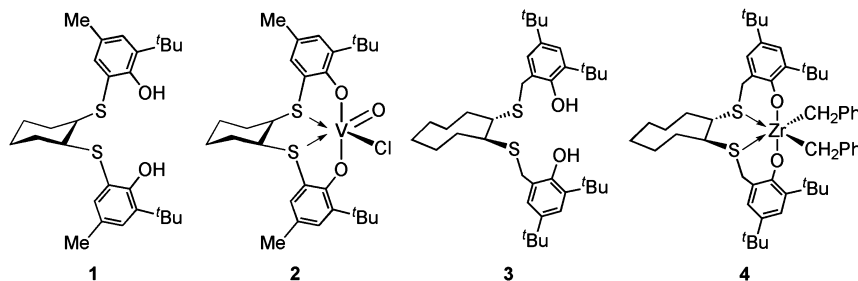
[OSSO]-Type bis(phenolate) ligands, in which two phenoxide frameworks are linked to two donor sulfur atoms at the ortho or benzyl positions, have been of great interest as dianionic ancillary tetradentate ligands for group 4 metal centers (Chart 1).<sup>18</sup> Okuda and co-workers reported that MAO-activated group 4 metal complexes with 1,4-dithiabutanediyl-linked [OSSO]-type bis(phenolate) ligand **1** were effective for the isospecific polymerization of styrene.<sup>19–22</sup> They also showed that vanadium complex **2**, which incorporates **1**, catalyzes the polymerization of ethylene with good activity (0.065–0.774 kg mmol<sup>-1</sup> h<sup>-1</sup>) to provide very high molecular weight polyethylene (*M*<sub>w</sub> = 461–946 kg mol<sup>-1</sup>) upon activation with MAO.<sup>23</sup> However, homogeneous group 5

Received: May 29, 2013

Revised: July 8, 2013

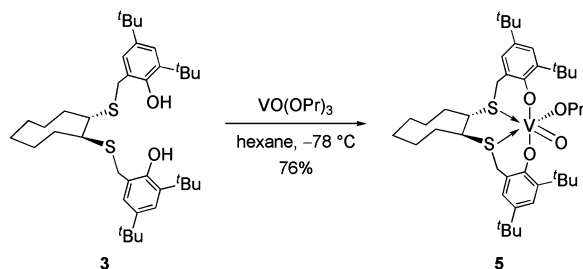
Published: July 8, 2013

Chart 1. [OSSO]-Type Ligands and Their Vanadium and Zirconium Complexes



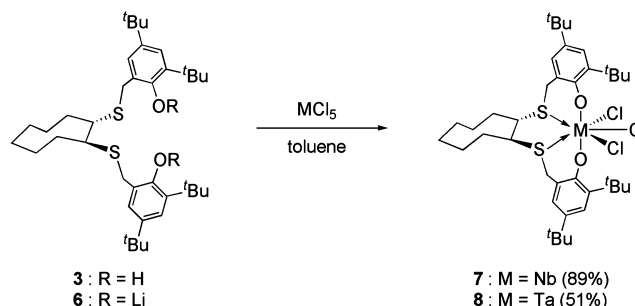
metal postmetallocene catalysts for  $\alpha$ -olefin homopolymerization are still relatively rare. This is a result the easy reduction of the metal center to lower-valence inactive species, which can be overcome by effective ligand design.<sup>24–26</sup> Quite recently, we reported another type of [OSSO]-type ligand (3) bearing a *trans*-1,2-cyclooctanediylbis(thio) core, along with the synthesis of several titanium and zirconium complexes.<sup>27–30</sup> In particular, dibenzyl zirconium complex 4 activated by  $B(C_6F_5)_3$  or  $(Ph_3C)[B(C_6F_5)_4]$  showed high activity toward the polymerization of 1-hexene and provided completely isotactic poly(1-hexene).<sup>27</sup> The success of these [OSSO]-type group 4 metal complexes prompted us to investigate the catalytic potential of the corresponding group 5 metal complexes for  $\alpha$ -olefin polymerization. Herein, we present the synthesis of novel group 5 metal complexes incorporating ligand 3 and a preliminary study of their ability to catalyze 1-hexene polymerization.

To test the coordination ability of [OSSO]-type ligand 3 toward group 5 metals, we set out to investigate the reaction of 3 with a vanadium oxytrialkoxide complex. The reaction of 3 with  $VO(OPr)_3$  (Pr is propyl) proceeded smoothly to afford dark purple crystals of a vanadium oxypropoxide complex,

Scheme 1. Reaction of 3 with  $VO(OPr)_3$ 

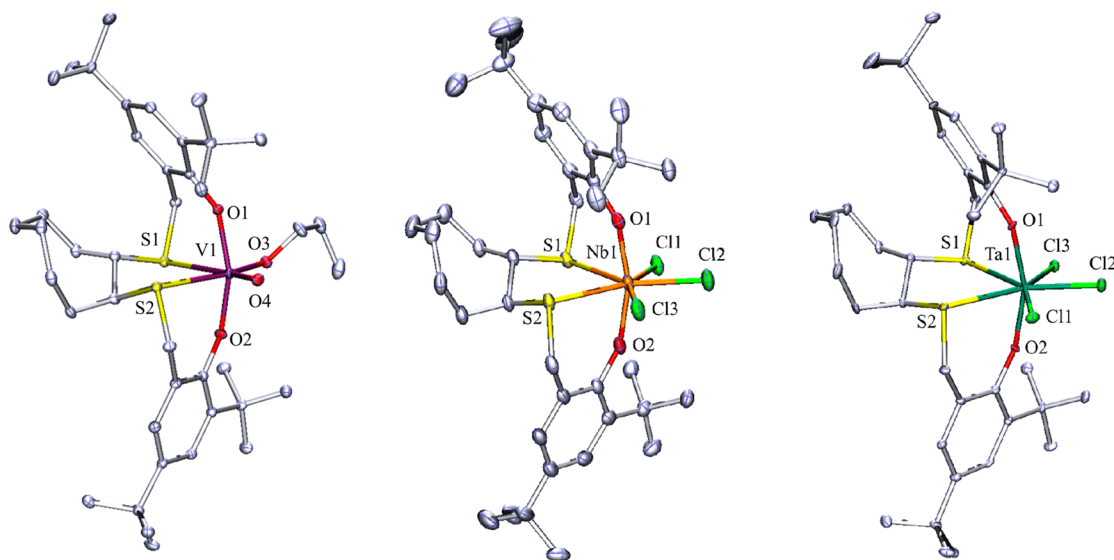
[OSSO]VO(OPr) 5, in 76% yield (Scheme 1). In the  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra of 5, the two phenolate moieties of the [OSSO] ligand were inequivalent as a result of the presence of two different ligands, that is, oxo and propoxy ligands, on the vanadium metal. In the  $^1H$  NMR spectrum, four *tert*-butyl groups were observed at  $\delta$  1.31, 1.33, 1.78, and 1.92, and the protons of the two benzyl groups appeared as doublets at  $\delta$  3.26 and 4.10 ( $J$  = 13 Hz) and  $\delta$  3.35 and 4.52 ( $J$  = 15 Hz); these results indicate that this complex 5 is one of the possible diastereomers.<sup>23</sup>

We then performed the reactions of 3 with  $MCl_5$  ( $M$  = Nb, Ta). The bis(phenol) 3 reacted with  $NbCl_5$  at  $-40$  °C in toluene to give a trichloroniobium complex 7 in a good yield (89% yield) (Scheme 2). In the case of tantalum complex 8, a dilithium salt, 6, which was prepared via the treatment of 3 with

Scheme 2. Reactions of 3 or 6 with  $MCl_5$  ( $M$  = Nb, Ta)

2 equiv of BuLi in toluene at 0 °C, was allowed to react with  $TaCl_5$  at  $-78$  °C to produce the corresponding trichlorotantalum complex 8 as a yellow crystals (51% yield) (Scheme 2).<sup>31</sup> In the  $^1H$  NMR spectra of complexes 7 and 8, an AB pattern was evident, and the benzyl protons appeared as doublets at  $\delta$  4.12 and 5.59 ( $J$  = 15 Hz) for 7 and  $\delta$  4.23 and 5.55 ( $J$  = 16 Hz) for 8. The sulfur-bonded methine protons resonated as a broad singlet at  $\delta$  2.99 for 7 and  $\delta$  2.95 for 8. Similarly to the NMR results for the corresponding  $C_2$ -symmetric titanium<sup>30</sup> and zirconium complexes<sup>27,29</sup> with ligand 3, the  $^1H$  NMR data of 7 and 8 demonstrate that the two phenolate ligands are equivalent, which suggests that these complexes have a  $C_2$ -symmetric helical structure on the NMR time scale.

The molecular structures of the complexes 5, 7, and 8 were confirmed by X-ray crystallography, as shown in Figure 1. These complexes feature *cis* sulfur atoms and *trans* oxygen atoms, resulting in a *cis*- $\alpha$  ( $\Lambda^*, S^*, S^*$ ) configuration of the [OSSO]-type tetradentate ligand similar to that of the zirconium complex 4. In the crystalline state of 5, the vanadium(V) center adopts a distorted octahedral geometry similar to that of the vanadium complex 2 with ligand 1.<sup>23</sup> The V–O and V–S bond lengths of 5 [ $V(1)–O(1)$  = 1.869(2),  $V(1)–O(2)$  = 1.841(2),  $V(1)–S(1)$  = 2.7877(11), and  $V(1)–S(2)$  = 2.5956(10) Å] are similar to those in 2 [ $V–O$  = 1.831(7) and 1.855(7), and  $V–S$  = 2.715(3) and 2.530(7) Å],<sup>23</sup> whereas the  $V=O$  bond length in 5 [ $V(1)–O(4)$  = 1.608(2) Å] is slightly shorter than that in 2 [ $V–O$  = 1.662(7) Å]. The  $V(1)–S(1)$  bond length [2.7877(11) Å] is longer than the  $V(1)–S(2)$  bond length [2.5956(10) Å], which indicates that the oxo group exerts a stronger *trans* influence than the propoxide group. The Nb(V) and Ta(V) cores in 7 and 8 lie at the center of slightly distorted pentagonal-bipyramidal coordination spheres. The molecular structures of 7 and 8 are quite similar to each other. Thus, the bond distances of Nb–Cl [2.4528(12), 2.4399(12), and 2.4579(12) Å], Nb–O [1.896(3) and 1.887(3) Å], and Nb–S [2.6765(12) and 2.6889(13) Å] are comparable to those of Ta–Cl [2.4564(9), 2.3975(10), and 2.4566(11) Å], Ta–O [1.894(3) and 1.886(2)



**Figure 1.** ORTEP diagrams of  $(\Lambda^*, S^*, S^*)$ -[OSSO]VO(OPr) (**5**),  $(\Lambda^*, S^*, S^*)$ -[OSSO]NbCl<sub>3</sub> (**7**), and  $(\Lambda, S, S)$ -[OSSO]TaCl<sub>3</sub> (**8**) with 30% thermal ellipsoids. **5**: All hydrogen atoms and a solvated hexane molecule are omitted for clarity. Selected bond lengths (Å): V1–O1, 1.869(2); V1–O2, 1.841(2); V1–O3, 1.799(2); V1–O4, 1.608(2); V1–S1, 2.7877(11); V1–S2, 2.5956(10). Selected bond angles (°): O1–V1–O2, 160.18(9); S1–V1–S2, 74.63(3); O3–V1–O4, 107.12(11). **7**: Three solvated benzene molecules are omitted for clarity. Selected bond lengths (Å): Nb1–O1 = 1.896(3), Nb1–O2 = 1.887(3), Nb1–S1 = 2.6765(12), Nb1–S2 = 2.6889(13), Nb1–Cl1 = 2.4528(12), Nb1–Cl2 = 2.4399(12), Nb1–Cl3 = 2.4579(12). Selected bond angles (°): O1–Nb1–O2 = 162.49(12), S1–Nb1–S2 = 71.00(3), Cl1–Nb1–Cl2 = 75.93(4), Cl2–Nb1–Cl3 = 76.10(4). **8**: A solvated benzene molecule is omitted for clarity. Selected bond lengths (Å): Ta1–O1 = 1.894(3), Ta1–O2 = 1.886(2), Ta1–S1 = 2.6680(10), Ta1–S2 = 2.6813(10), Ta1–Cl1 = 2.4564(9), Ta1–Cl2 = 2.3975(10), Ta1–Cl3 = 2.4566(11). Selected bond angles (°): O1–Ta1–O2 = 161.85(12), S1–Ta1–S2 = 71.64(3), Cl1–Ta1–Cl2 = 76.09(4), Cl2–Ta1–Cl3 = 75.04(4).

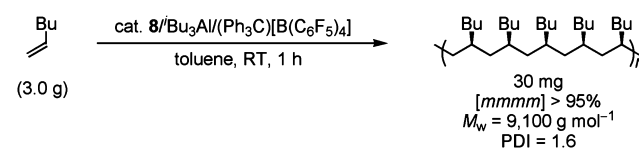
Å], and Ta–S [2.6680(10) and 2.6813(10) Å]. The Ta–Cl bond lengths (av 2.437 Å) in the seven-coordinate Ta(V) complex **8** are slightly longer than those previously found in six-coordinate trichloro-tantalum(V) complexes, for example, [Ta{(OC<sub>6</sub>H<sub>5</sub>Ph)<sub>2</sub>CH<sub>2</sub>}Cl<sub>3</sub>(py)] (av 2.368 Å)<sup>32</sup> and [Ta{(OC<sub>6</sub>H<sub>4</sub>Pr)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>}Cl<sub>3</sub>(thf)] (av 2.374 Å).<sup>33</sup> The bond angles of O–Nb–O [162.53(11)°] and S–Nb–S [70.99(3)°] are also comparable to those of O–Ta–O [161.85(12)°] and S–Ta–S [71.64(3)°], respectively.

We investigated the catalytic ability of complexes **5**, **7**, and **8** toward 1-hexene polymerization. Vanadium complex **5** and niobium complex **7** activated by dMAO or <sup>i</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] did not catalyze any polymerization or oligomerization. Upon activation with <sup>i</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], only tantalum complex **8** acted as an active catalyst for 1-hexene polymerization. Thus, the reaction of 20 μmol of **8** and <sup>i</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] ([Ta]/[Al]/[B] = 1/2/500) with 1-hexene (3.0 g) in toluene (5 mL) at room temperature afforded 30 mg of poly(1-hexene) after 1 h (Table 1, run 1); however, its activity (1.5 g mmol(**8**)<sup>−1</sup> h<sup>−1</sup>) is significantly lower than that of the corresponding zirconium complex **4** (2500 g mmol(**4**)<sup>−1</sup>

h<sup>−1</sup>).<sup>27</sup> In the <sup>1</sup>H NMR spectrum of the resultant polymer, no signals corresponding to terminal olefinic protons were observed.

The microstructure of the polymer was analyzed by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy: Six sharp signals were observed, which indicates excellent isotacticity of the poly(1-hexene) ([*mmmm*] >95%) (Scheme 3). The GPC analysis of the polymer revealed

**Scheme 3. 1-Hexene Polymerization Catalyzed by **8**/ <sup>i</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] System**



a low molecular weight of 9100 g mol<sup>−1</sup> and a relatively narrow polydispersity index (PDI) of 1.6. To the best of our knowledge, tantalum complex **8** (with <sup>i</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) is the first example of group 5 metal complex to catalyze highly isospecific polymerization of  $\alpha$ -olefins. The low activity of the catalytic system might be due to the instability of the active species generated during polymerization. In fact, 1-hexene polymerization experiments carried out for 6 and 12 h yielded almost the same amount of isotactic poly(1-hexene), which indicates that the catalyst was deactivated within 1 h under the present conditions.

It is well-known that vanadium complexes with high oxidation states are readily reduced to lower divalent states that are inactive for  $\alpha$ -olefin polymerization; this is one of the intrinsic problems associated with vanadium-based catalysts. The use of reactivating agents such as ethyl trichloroacetate (ETA) is an effective method for maintaining the higher

**Table 1. 1-Hexene Polymerization with Group 5 Metal Complexes **5** and **8** and Activators**

run	cat.	time (h)	temp (°C)	activity <sup>c</sup>	<i>M<sub>w</sub></i> (g mol <sup>−1</sup> )	PDI <sup>d</sup>
1 <sup>a</sup>	<b>8</b>	1	25	1.5	9100	1.6
2 <sup>b</sup>	<b>5</b>	24	25	0.77	1560	1.5
3 <sup>b</sup>	<b>5</b>	24	70	0.52	1390	1.4

<sup>a</sup>Conditions: toluene (5 mL), **8** (20 μmol), [dMAO]/[cat.] = 250; (Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (40 μmol); [Al/<sup>i</sup>Bu<sub>3</sub>]/[cat.] = 50; 1-hexene (3.0 g; 35.6 mmol). <sup>b</sup>Conditions: toluene (20 mL), **5** (20 μmol), Et<sub>2</sub>AlCl (10 mmol), ETA (1.0 mL); 1-hexene (3.0 g; 35.6 mmol). <sup>c</sup>g mmol(cat.)<sup>−1</sup> h<sup>−1</sup>. <sup>d</sup>PDI = *M<sub>w</sub>*/*M<sub>n</sub>*. Determined by GPC.



oxidation states of vanadium systems.<sup>24,25,34,35</sup> Thus, we examined the polymerization of 1-hexene with vanadium complex **5** in the presence of ETA: 1-Hexene polymerization using **5**/Et<sub>2</sub>AlCl ([**5**] = 0.020, [Al] = 10 mmol) in the presence of excess ETA (1.0 mL) efficiently produced poly(1-hexene) at room temperature (Table 1, run 2). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra and HMQC experiment of the product exhibited signals corresponding to olefin protons ( $\delta$  5.3–5.4) and carbons ( $\delta$  128–132), which indicates that  $\beta$ -proton or alkyl elimination occurred to introduce vinylene parts to the microstructure from a 2,1-enchained vanadium alkyl complex.<sup>36</sup> GPC analysis revealed a quite low molecular weight of 1560 g mol<sup>-1</sup> and a PDI of 1.5. The polymerization of 1-hexene at 70 °C provided oligo(1-hexene) with a molecular weight of 1390 g mol<sup>-1</sup> and a PDI of 1.4 (Table 1, run 3). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra and HMQC experiment showed no olefinic moieties, which suggests that the active species decomposed via a radical pathway or occurred the transmetalation with alkyl aluminum species at high temperatures.<sup>25</sup>

In this paper, we demonstrated the expansion of [OSSO]-type ligand **3** bearing a *trans*-1,2-cyclooctanediylbis(thio) core to the formation of group 5 metal complexes. Tantalum complex **8** activated with <sup>t</sup>Bu<sub>3</sub>Al/(Ph<sub>3</sub>C)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is active toward 1-hexene polymerization and produces completely isotactic poly(1-hexene) with a molecular weight of  $M_w$  = 9100 g mol<sup>-1</sup> and relatively narrow polydispersity (PDI = 1.6). The polymerization activity was low (1.5 g mmol(**8**)<sup>-1</sup> h<sup>-1</sup>) owing to the instability of the active species generated during polymerization. Further studies on the coordination chemistry of **3** with other transition metals and the catalytic potential of the [OSSO]-type ligands for olefin polymerization are currently underway.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details and crystallographic data for **5**, **7**, and **8** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [ishiiaki@chem.saitama-u.ac.jp](mailto:ishiiaki@chem.saitama-u.ac.jp).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid (No. 23750034) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan. N.N. is thankful for financial support from the Asahi Glass Foundation and JGC-S Scholarship Foundation. T.T. acknowledges a JSPS fellowship for young scientists. The authors thank Dr. Kohei Tamao (RIKEN Advanced Science Institute) for his fruitful discussions.

## ■ REFERENCES

- (1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 426.
- (2) Ziegler, K.; Gellert, H. G.; Zosel, K.; Lehmkühl, W.; Pfohl, W. *Angew. Chem.* **1955**, *67*, 424.
- (3) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710.
- (4) Kashiwa, N.; Tokumizu, T.; Fujita, H. U.S. Patent 3642746, 1968.
- (5) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447.
- (6) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1493–1517.
- (7) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–316.
- (8) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745–1776.
- (9) Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. *Chem. Rev.* **2011**, *111*, 2363–2449.
- (10) *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L. S., Canich, J.-A. M., Eds.; CRC Press: Boca Raton, FL, 2008.
- (11) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229–243.
- (12) Redshaw, C. *Dalton Trans.* **2010**, *39*, 5595–5604.
- (13) Nomura, K.; Zhang, S. *Chem. Rev.* **2011**, *111*, 2342–2362.
- (14) Noordermeer, J. W. M. Ethylene–Propylene–Diene Rubber. In *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, J. M., Eds.; Wiley & Sons: New York, 1993; Vol. 8, p 978.
- (15) See, for example: Christman, D. L.; Keim, G. I. *Macromolecules* **1968**, *1*, 358–363.
- (16) Michiue, K.; Oshiki, T.; Takai, K.; Mitani, M.; Fujita, T. *Organometallics* **2009**, *28*, 6450–6457.
- (17) Senda, T.; Hanaoka, H.; Oda, Y.; Tsurugi, H.; Mashima, K. *Organometallics* **2010**, *29*, 2080–2084.
- (18) For a recent review on group 4 metal complexes featured [OSSO]-type ligands, see: Nakata, N.; Toda, T.; Ishii, A. *Polym. Chem.* **2011**, *2*, 1597–1610.
- (19) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965.
- (20) Beckerle, K.; Capacchione, C.; Ebeling, H.; Manivannan, R.; Mülhaupt, R.; Proto, A.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2004**, *689*, 4636–4641.
- (21) Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 2971–2982.
- (22) Beckerle, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 3019–3026.
- (23) Meppelder, G.-J. M.; Halbach, T. S.; Spaniol, T. P.; Mülhaupt, R.; Okuda, J. *J. Organomet. Chem.* **2009**, *694*, 1235–1237.
- (24) Gumboldt, V. A.; Helberg, J.; Schleitzer, G. *Makromol. Chem.* **1967**, *101*, 229–245.
- (25) Christman, D. L. *J. Polym. Sci., Part A-1* **1972**, *10*, 471–487.
- (26) Pritchard, H. M.; Etienne, M.; Vender, L.; McCrady, G. S. *Organometallics* **2004**, *23*, 1203–1206.
- (27) Ishii, A.; Toda, T.; Nakata, N.; Matsuo, T. *J. Am. Chem. Soc.* **2009**, *131*, 13566–13567.
- (28) Ishii, A.; Toda, T.; Nakata, N.; Matsuo, T. *Phosphorus Sulfur Silicon Relat. Elem.* **2011**, *186*, 1169–1174.
- (29) Toda, T.; Nakata, N.; Matsuo, T.; Ishii, A. *J. Organomet. Chem.* **2011**, *696*, 1258–1261.
- (30) Nakata, N.; Toda, T.; Ishii, A.; Matsuo, T. *Inorg. Chem.* **2012**, *51*, 274–281.
- (31) Due to lower Lewis acidity of TaCl<sub>5</sub> than that of NbCl<sub>5</sub>, we chose a synthetic method for the tantalum complex using the dilithium salt **6** instead of free [OSSO]-type ligand **3**.
- (32) Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **2000**, *19*, 35–42.
- (33) Anthiis, J. W.; Filippov, I.; Wigley, D. E. *Inorg. Chem.* **2004**, *43*, 716–724.
- (34) Addison, E.; Deffieux, A.; Fontanille, M.; Bujadoux, K. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1033–1041.
- (35) Reardon, D.; Guan, J.; Gambarotta, S.; Yap, G. P. A.; Wilson, D. R. *Organometallics* **2002**, *21*, 4390–4397.
- (36) Lian, B.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8507–8510.