Synthesis and Crystal Structure of a Zirconium Complex Containing Germanolato Ligands and Its Catalytic Activity for Ethylene Polymerization

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A dialkylbis(germanolato)zirconium complex was synthesized by taking advantage of a novel bowl-shaped germanol as the ligand source, presenting the first example of a zirconium complex containing germanolato ligands. The bis(germanolato) complex as well as the analogous bis(silanolato) complex was found to exhibit catalytic activity for ethylene polymerization.

The development of early transition-metal complexes containing non-cyclopentadienyl ancillary ligands is a growing area of interest.[1,2] Silanolato ligands (R_3SiO–) constitute a major class of non-cyclopentadienyl ancillary ligands, which have been utilized for the modeling of silica-supported metal complexes.[3] In some reactions of silica-supported early transition-metal complexes such as olefin epoxidation reactions, partial replacement of silicon in silica by germanium was reported to increase their catalytic activity.[4] Zirconium complexes supported on silica surface have been utilized as important heterogeneous catalysts for olefin polymerization.[5] Extensive studies have been carried out to develop their homogeneous model system by using various silanolato ligands.[6] It is intriguing how the replacement of silicon of these silanolato complexes by germanium affects their structure and reactivity. However, no example of a zirconium complex containing a germanolato ligand (R_3GeO–) has been reported to date whereas there is only one example of a germanium(II) compound bearing a Ge–O–Zr linkage.[7,8] Recently, we reported the synthesis of the dialkylzirconium complex **3**[9] containing two silanolato ligands by the reaction of tetrabenzylzirconium with the bowl-shaped silanol **1** (denoted as TRMS-OH)[10] (Chart 1), which would serve as a homogeneous model complex of silica-supported dialkylzirconium complexes, $(\equiv SiO)_2ZrR_2$. In this communication, we report the synthesis of bis(germanolato)zirconium complex **4**, which is a germanium analogue of **3**, by taking advantage of the bowl-shaped germanol **2** (denoted as TRMG-OH) as the ligand source. The catalytic activities of the zirconium complexes containing these bowl-shaped silanolato and germanolato ligands for ethylene polymerization have been evaluated.

We previously reported that germanol **2** is extremely resistant to self-condensation because it has a shallow bowl-shaped structure.[11] When **2** is used as the source of a germanolato ligand, only a limited number of ligands would be introduced to the metal center due to its peripheral steric demands. The reaction of germanol **2** with a half equimolar amount of tetrabenzylziconium in benzene resulted in the quantitative formation of the bis(germanolato) complex **4**, which was indicated by ^{1}H NMR spectroscopy (Scheme 1). During this reaction, the bowl-shaped framework of **2** is considered to prevent the formation of other products such as the tris- or tetrakis(germanolato) complex. Recrystallization of the crude product from benzene/hexane in the presence of DME afforded the corresponding adduct **5** as colorless crystals in 64% yield, presenting the first example of isolation of a zirconium complex containing germanolato ligands.[12]

In the ^{1}H NMR spectrum of **5** in toluene-d_8, the $ZrCH_2Ph$ signal was observed at δ 2.29 as a broad singlet. The structure of **5** was unambiguously established by X-ray crystallographic analysis as shown in Figure 1.[13] The zirconium atom adopts octahedral geometry with two germanolato ligands in the trans-positions. The Zr(1), C(1), C(2), O(3), and O(4) atoms are located on the same plane. The Zr(1)–O(1) and Zr(1)–O(2) bond lengths (1.978(3) and 1.974(3) Å) are almost the same as those of bis(silanolato) complex **6** that we reported recently.[9] The large Zr–O–Ge bond angles of **5** (176.0(2) and 170.1(2)°) indicate that the pπ–dπ donation of the germanolato oxygen to the zirconium center is strong, which is similar to the case of the silanolato complex **6**.

The activities of the zirconium complexes bearing the bowl-shaped germanolato and silanolato ligands as olefin polymerization catalysts were evaluated by using complexes **5** and

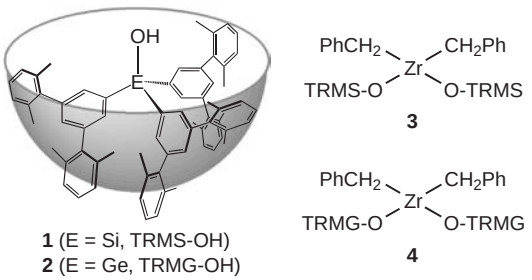
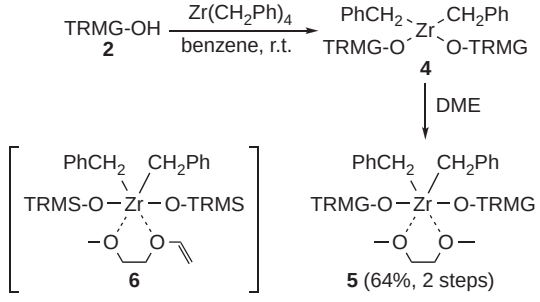


Chart 1.



Scheme 1.

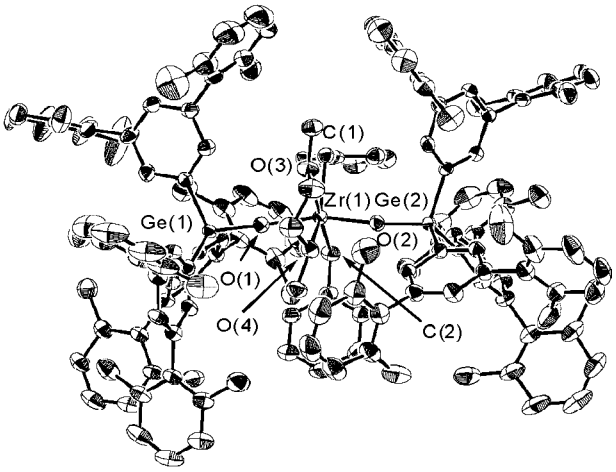


Figure 1. ORTEP drawing of **5** (50% probability). Hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angles (deg): Zr(1)–O(1), 1.978(3); Zr(1)–O(2), 1.974(3); Zr(1)–O(3), 2.589(4); Zr(1)–O(4), 2.389(3); Zr(1)–C(1), 2.293(5); Zr(1)–C(2), 2.283(5); Zr(1)–O(1)–Ge(1), 176.0(2); Zr(1)–O(2)–Ge(2), 170.1(2).

Table 1. Catalytic activity for ethylene polymerization[a]

Catalyst	Activity (g-PE·mmol^{-1}·h^{-1})
$(TRMGO)_2Zr(CH_2Ph)_2$·DME (**5**)	1120
$(TRMSO)_2Zr(CH_2Ph)_2$·L[b] (**6**)	8700

[a]Cocatalyst: modified MAO (Toso Finechem), etheylene: 30 atm, hexane-slurry, 70 °C. [b]L = $CH_3OCH_2CH_2OCH{=}CH_2$.

6, which can be isolated in pure form. The reactions were carried out in hexane-slurry at 70 °C under 30 atm of ethylene with methylaluminoxane (MAO) as the cocatalyst (Table 1). It was revealed that the germanolato complex **5** as well as the silaolato complex **6** generates active ethylene polymerization catalysts. Although the catalytic activity of the germanolato complex **5** is lower than that of the silanolato complex **6**, it was demonstrated for the first time that a zirconium germanolato complex serves as a catalyst for olefin polymerization. In view of the structural similarity between **5** and **6**, the higher activity of the silanolato complex **6** is considered to result from the stronger electron-donating property of silicon than germanium.[14] Concerning the silanolato complex **6**, the catalytic activity observed here is adequate as a model system for silica-supported catalysts.[6c,6d] As expected from the relatively large space around the coordinating site of the bowl-shaped ligand, the reactivity of the metal center does not seem to be significantly reduced by the steric effects of the ligands. These results combined with the structural features which prevent the coordination of more than two ligands indicate that these bowl-shaped silanolato and germanolato ligands are useful in the design of novel homogeneous model systems for silica surface including ones partially modified with germanium. The catalytic activity of Group 4 metal complexes bearing the bowl-shaped germanolato ligand for olefin epoxidation reactions, for which germanolato complexes are expected to show higher activity than their silicon congeners, will be a topic of future research.

This work was partly supported by Grants-in-Aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry (T.K.) and for Scientific Research (K.G. and T.K.) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Japan Polypropylene Corporation for evaluation of ethylene polymerization. We also thank Tosoh Finechem Corporation and Shin-Etsu Chemical Co., Ltd. for the generous gifts of alkyllithiums and silicon compounds, respectively.

This paper is dedicated to late Professor Yoshihiko Ito.

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12 **5**: ^{1}H NMR (500 MHz, toluene-d_8) δ 1.94 (s, 72H), 2.21 (s, 6H), 2.29 (s, 4H), 2.87 (s, 4H), 6.22 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 6.36 (t, $^3J_{HH}$ = 7.6 Hz, 4H), 6.60 (t, $^4J_{HH}$ = 1.6 Hz, 6H), 6.66 (t, $^3J_{HH}$ = 7.4 Hz, 4H), 6.99–7.11 (m, 36H), 7.66 (d, $^4J_{HH}$ = 1.6 Hz, 12H); ^{13}C NMR (126 MHz, toluene-d_8) δ 21.0 (q), 60.7 (q), 63.6 (t), 71.3 (t), 121.0 (d), 127.4 (d), 127.6 (d), 127.7 (d), 128.4 (d), 131.1 (d), 134.0 (d), 136.0 (s), 139.2 (s), 141.8 (s), 142.2 (s), 146.8 (s).

13 Crystallographic data for $\mathbf{5}\cdot 3.5C_6H_6\cdot 3C_7H_8$: fw 2802.88, monoclinic, space group $P2_1/n$, a = 19.004(5), b = 26.653(5), c = 31.257(5) Å, β = 94.255(5)°, U = 15788(6) Å^3, Z = 4, D_{calcd} = 1.179 g cm^{-3}, T = 120 K, R_1 = 0.0862 ($I > 2\sigma(I)$), wR_2 = 0.2183 (all data). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 640169.

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Published on the web (Advance View) May 19, 2007; doi:10.1246/cl.2007.776