

Communication

Syntheses and characterization of alkylzirconium complexes containing two silanolato ligands with a bowl-shaped framework

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Abstract

The reaction of a bowl-type silanol with tetrabenzylzirconium yielded a dibenzylbis(silanolato)zirconium complex selectively, which is an intriguing species in connection to the chemistry of silica-supported ZrR_4 olefin polymerization catalysts. Treatment of this neutral complex with $B(C_6F_5)_3$ afforded the corresponding cationic monobenzyl complex, presenting the first example of a cationic zirconium complex containing a silanolato ligand. The structures of both complexes have been characterized by X-ray crystallography.
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Keywords: Bowl-shaped molecule; Silanolato ligand; Alkylzirconium complex; Cationic zirconium complex

1. Introduction

Recently, the use of non-cyclopentadienyl (non-Cp) ligation has been attracting increasing attention in organometallic chemistry [1,2]. In the field of Ziegler–Natta olefin polymerization catalysis, a wide range of non-Cp Group 4 metal complexes of L_2MR_2 type (L = non-Cp ligand, M = Group 4 metal, R = alkyl group) have been developed so far, which contain various ancillary ligands such as phosphinimide [3], diamido [4,5], β -diketimide [6], alkoxide [7], aryloxide [8,9], and imide-aryloxide [10] groups. When activated with Lewis acid cocatalysts such as methylaluminoxane (MAO), boranes, and trityl cation, the resulting complexes can act as olefin polymerization catalysts. Several kinds of cationic monoalkyl complexes, L_2MR^+ , generated in such activation processes have also been synthesized [5,6,9]. Among non-Cp ancillary ligands,

silanolato ligands, R_3SiO- , constitute a major class of electron-donating oxy ligands [11]. They are also intriguing in connection with the chemistry of silica-supported Group 4 metal complexes, which have been utilized as useful heterogeneous catalysts for olefin polymerization [12]. Zirconium complexes bearing two alkyl groups supported on silica surface, $(\equiv SiO)_2ZrR_2$, have been known as olefin polymerization catalysts [13], and the corresponding monoalkyl cations, $[(\equiv SiO)_2ZrR]^+$, are potential candidates for active species. However, there have been only a few examples of homogeneous dialkylbis(silanolato)zirconium complexes, $(R'_3SiO)_2ZrR_2$ [14], and no example of the corresponding cationic complex, $[(R'_3SiO)_2ZrR]^+$. Duchateau et al. reported the synthesis of alkyl(silanolato)zirconium complexes by utilizing various bulky silanols bearing silsesquioxane frameworks, but the synthesis of a dialkylbis(silanolato)zirconium complex was not successful [15]. Alkylzirconium complexes are readily subject to multi-substitution of alkyl groups by silanolato ligands, and it is difficult to control the number of the silanolato ligands with the hitherto known organosilanols. In the course of our study on bowl-type molecules [16–18], we

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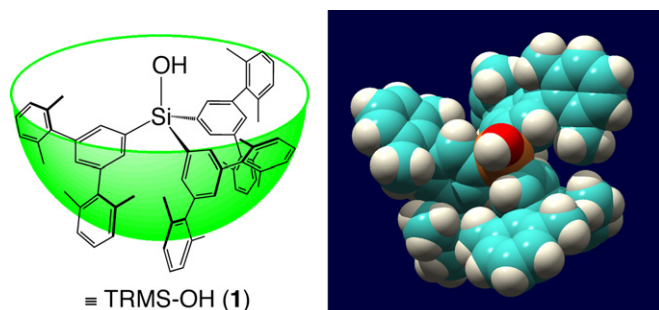
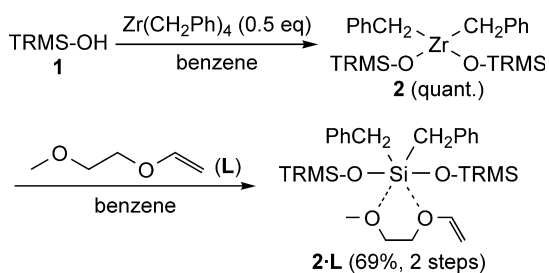


Fig. 1. Bowl-shaped silanol, TRMS-OH (**1**), and the space filling model of the crystal structure of **1**.

have previously developed a novel bowl-type silanol **1** (denoted as TRMS-OH) [17]. This silanol has a shallow bowl-shaped cavity of about 15 Å diameters, and the SiOH group is embedded in its bottom (Fig. 1). When silanol **1** is utilized for the synthesis of alkyl(silanolato)zirconium complex, the number of the ligands introduced to the metal center is expected to be controlled effectively by the steric repulsion between the peripheral moieties of the ligands. In this communication, we describe the selective synthesis of a dialkylbis(silanolato)zirconium complex by utilizing a novel bowl-shaped silanolato ligand and its derivation to a cationic alkylbis(silanolato)zirconium complex. Their crystal structures are also delineated.

In the reaction of silanol **1** with a half equimolar amount of tetrabenzylzirconium in benzene, the selective and quantitative formation of dibenzylbis(silanolato)zirconium complex **2** was revealed by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy, and the complex was isolated as brownish pale yellow solids (Scheme 1) [19]. Reflecting the steric bulkiness of the bowl-shaped ligand, bis(silanolato) complex **2** was selectively obtained even when an excess of **1** was used; neither the tris- nor tetrakis(silanolato) complex was formed. Treatment of **2** with another equimolar amount of tetrabenzylzirconium resulted in no change; the redistribution reaction to give other silanolato complexes was not observed. Although single crystals of **2** suitable for X-ray crystallography were not obtained, recrystallization from benzene/hexane in the presence of an equimolar amount of (2-methoxyethoxy)ethene (**L**) yielded pale yellow crystals of the corresponding adduct **2·L** (Scheme 1) [20]. The structure of **2·L** was determined by X-ray crystallo-



Scheme 1. Synthesis of (silanolato)zirconium complexes by using the bowl-shaped silanol **1**.

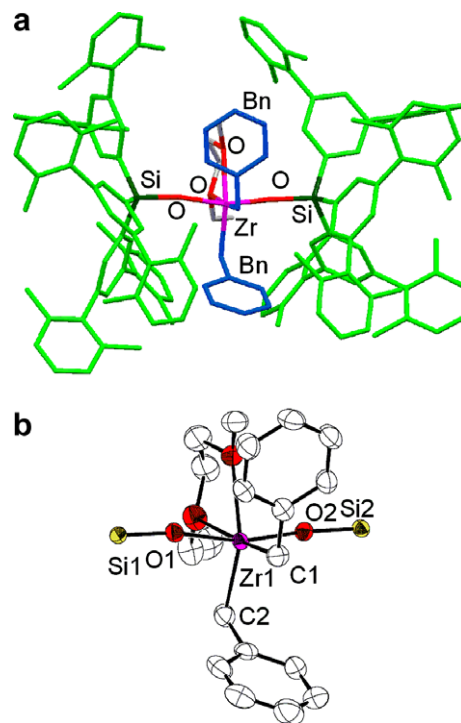
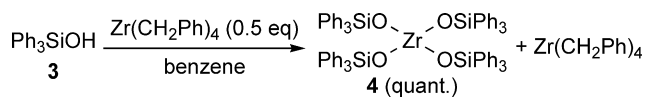
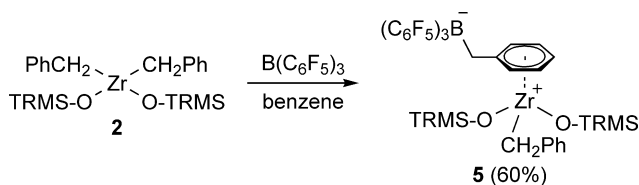


Fig. 2. (a) Crystal structure of **2·L**. (b) ORTEP drawing of the central part of **2·L** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–O(1), 1.972(2); Zr(1)–O(2), 1.977(2); Zr(1)–C(1), 2.306(4); Zr(1)–C(2), 2.283(4); Zr(1)–O(1)–Si(1), 169.73(15); Zr(1)–O(2)–Si(2), 168.75(15).

graphic analysis as shown in Fig. 2 [21]. The zirconium atom is surrounded by six ligands (two silanolato ligands, two benzyl groups, and extra bidentate ether **L**) and adopts octahedral geometry. This extra coordination of **L** to the zirconium is suggestive that the vicinity of the zirconium center of **2** is not so congested. The Zr–O–Si bond angles of **2·L** (168.75(15) and 169.73(15)°) are fairly large, which indicates strong oxygen $p\pi$ – $d\pi$ donation of the silanolato ligands to the zirconium atom [11]. Triphenylsilanol (**3**) is one of the typical bulky silanols utilized for the preparation of various silanolato complexes. In contrast with the reaction of **1**, however, only tetrakis(triphenylsilanolato) complex **4** was obtained when **3** was used as the starting material (Scheme 2). In silanol **1**, six 2,6-dimethylphenyl groups are attached to the 3,5-positions of the phenyl groups of **3** to increase the steric demand in the peripheral moieties whereas the congestion in the close vicinity of the SiOH group remains almost unchanged. The present results indicate that the peripheral steric protection by the bowl-shaped ligand is very effective for control of the ligand number.



Scheme 2. Synthesis of (silanolato)zirconium complexes by using triphenylsilanol (**3**).



Scheme 3. Synthesis of a cationic bis(silanolato)zirconium complex.

The reaction of **2** with an equimolar amount of the neutral borane, $\text{B(C}_6\text{F}_5)_3$, resulted in the immediate abstraction of one benzyl group from **2** and quantitative formation of the cationic complex **5**, which was isolated in 60% yield by recrystallization from benzene/hexane as orange–red crystals (Scheme 3) [23]. In the ^1H NMR spectrum of **5**, two kinds of benzyl methylene protons showed the signals at δ 2.63 (s, ZrCH_2Ph) and 3.45 (brs, BCH_2Ph). Compared with parent complex **2**, the signal of ZrCH_2Ph protons shifted downfield by 0.83 ppm because of the increase of the cationic character of the zirconium center. The resonance of the peripheral methyl groups of the TRMS substituents of **5** was observed non-equivalently as two singlets, while only one signal was observed for the corresponding methyl groups of **2**. The ^{13}C NMR spectra are also consistent with these results observed in the ^1H NMR spectra. The change of the pattern of the methyl signals indicates that there is a strong interaction between cation and anion in **5**. It is probable that **5** exists as a contact ion-pair, where the steric hindrance among the bulky bowl-shaped ligands and the counter anion prevents the free rotation of the Si–C bond of the TRMS substituents. The ^{19}F NMR spectrum of **5** showed the signals at δ -163.96 (*m*-F), -159.79 (*p*-F), and -130.59 (*o*-F) with $\Delta\delta(m,p-F)$ 4.17 ppm, which are typical values for a $[\text{BnB(C}_6\text{F}_5)_3]^-$ anion coordinated to a cation [24]. X-ray crystallographic analysis established the structure of **5** (Fig. 3) [25]. As usually found in such cationic complexes [5,9,26], and as deduced from the spectral features in solution, this complex was found to exist as a contact ion pair involving π -coordination of the aromatic ring of the counter anion to the zirconium center. The zirconium atom is surrounded by four ligands and adopts tetrahedral geometry. The relatively large Zr–O–Si bond angles of **5** ($158.0(2)$ and $160.4(2)^\circ$) are also indicative of oxygen–zirconium $p\pi$ – $d\pi$ donation [11]. While cationic zirconium complexes containing various kind of ligands have been reported so far [5,9,26,27], this is the first isolation of one containing a silanolato ligand.

In summary, we have reported the synthesis of the first cationic zirconium complex containing silanolato ligands by the reaction of the neutral dialkylbis(silanolato) complex with $\text{B(C}_6\text{F}_5)_3$. Their structures were established by NMR spectroscopy and X-ray crystallography. The present results suggest that the bowl-shaped silanolato ligand would be useful for preparation of homogeneous model complexes of various silica-supported heterogeneous catalysts because it can efficiently control the ligand number

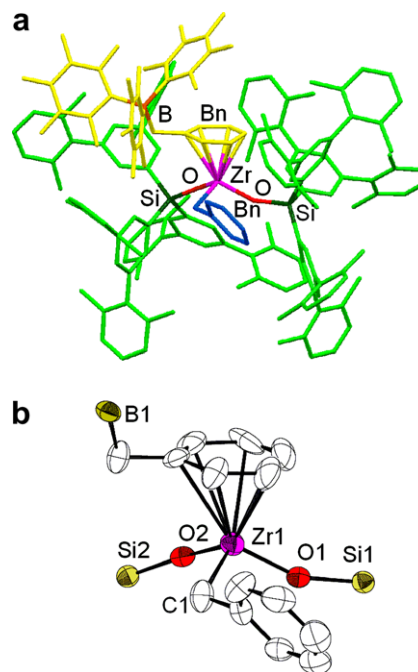


Fig. 3. (a) Crystal structure of **5**. (b) ORTEP drawing of the central part of **5** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Zr(1)–O(1), 1.907(4); Zr(1)–O(2), 1.907(4); Zr(1)–C(1), 2.213(6); Zr(1)–O(1)–Si(1), 158.0(2); Zr(1)–O(2)–Si(2), 160.4(2).

by its peripheral steric bulkiness. Elucidation of the catalytic activities of the complexes obtained here for olefin polymerization is currently in progress.

2. Supplementary data

CCDC 629620 and 624112 contain the supplementary crystallographic data for **2**·L and **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- [19] **2**: ^1H NMR (500 MHz, C_6D_6) δ 1.80(s, 4H), 1.94(s, 72H), 6.41–6.44(m, 2H), 6.59(t, $^4J_{\text{HH}} = 1.5$ Hz, 6H), 6.61–6.64(m, 8H), 7.03–7.17(m, 36H), 7.49(d, $^4J_{\text{HH}} = 1.5$ Hz, 12H); ^{13}C NMR (126 MHz, C_6D_6) δ 20.9(q), 60.0(t), 124.3(d), 127.4(d), 127.5(d), 128.5(s), 131.1(d), 131.5(d), 131.7(d), 134.6(d), 135.9(s), 136.8(s), 141.4(s), 141.9(s); ^{29}Si NMR (99 MHz, C_6D_6) δ –15.8.
- [20] **2**·**L**: pale yellow solids; ^1H NMR (500 MHz, C_6D_6) δ 1.99(s, 72H), 2.19(br, 3H), 2.39(s, 4H), 3.07(br, 2H + 1H), 3.27(br, 2H), 3.49(br, 1H), 5.93(br, 1H), 6.43(t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 6.52(m, 4H), 6.67(t, $^4J_{\text{HH}} = 1.6$ Hz, 6H), 6.82(d, $^3J_{\text{HH}} = 7.4$ Hz, 4H), 7.06–7.17(m, 36H), 7.76(d, $^4J_{\text{HH}} = 1.6$ Hz, 12H); ^{13}C NMR (126 MHz, C_6D_6) δ 21.0(q), 62.5(q), 64.8(t), 65.6(t), 72.4(t), 89.5(t), 122.4(d), 127.3(d), 127.5(d), 128.7(d), 128.9(d), 131.0(d), 134.9(d), 135.9(s), 138.6(s), 141.2(s), 142.2(s), 144.1(s), 149.3(s); ^{29}Si NMR (99 MHz, C_6D_6) δ –21.1.
- [21] Single crystals of **2**·**L**·0.5 C_6H_6 were analyzed at 120(2) K using a graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and a Rigaku/MSC Mercury CCD diffractometer. $\text{C}_{154}\text{H}_{153}\text{O}_4\text{Si}_2\text{Zr}$, $M = 2215.16$, monoclinic, space group $P2_1/c$, $a = 20.532(5)$, $b = 24.729(5)$, $c = 27.517(7)$ Å, $\beta = 106.804(4)^\circ$, $V = 13375(5)$ Å 3 , $Z = 4$, $\rho_{\text{calc}} = 1.100$ g·cm $^{-3}$, $\mu = 0.152$ mm $^{-1}$, 84991 reflections collected, of which 23389 were independent [$R_{\text{int}} = 0.0452$] and 18655 observed with $>2\sigma$. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0793$, $wR_2 = 0.2068$. R indices (all data): $R_1 = 0.0966$, $wR_2 = 0.2219$. The structure was solved by the direct method and refined using full-matrix least squares in SHELXL-97 [22]. The asymmetric unit was seen to contain one molecule of **2**·**L** and 0.5 molecule of benzene. The complex was seen to exhibit 9:1 disorder with respect to Zr(1).
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- [23] **5**: orange solids; ^1H NMR (500 MHz, C_6D_6) δ 1.86(s, 36H), 1.88(s, 36H), 2.63(s, 2H, ZrCH $_2$ Ph), 3.45(brs, 2H, BCH $_2$ Ph), 6.29(t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 6.50(t, $^4J_{\text{HH}} = 1.5$ Hz, 6H), 6.78(t, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 6.83(d, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.01(d, $^3J_{\text{HH}} = 7.5$ Hz, 12H), 7.02(d, $^3J_{\text{HH}} = 7.5$ Hz, 12H), 7.13(t, $^3J_{\text{HH}} = 7.6$ Hz, 12H), 7.43(d, $^4J_{\text{HH}} = 1.6$ Hz, 12H); ^{11}B NMR (160 MHz, C_6D_6) δ –12.4; ^{13}C NMR (126 MHz, C_6D_6) δ 20.8(q), 20.9(q), 36.4(t), 75.2(t), 125.7(d), 127.7(d), 127.8(d), 128.3(d), 129.2(d), 133.3(d), 134.2(s), 134.2(d), 135.4(s), 135.5(s), 140.6(s), 141.0(s), 142.2(s); ^{19}F NMR (376 MHz, C_6D_6) δ –163.96(t,

- $^3J_{\text{FF}} = 20.2$ Hz, 6F), -159.79 (t, $^3J_{\text{FF}} = 20.2$ Hz, 3F), -130.59 (d, $^3J_{\text{FF}} = 22.1$ Hz, 6F); ^{29}Si NMR (99 MHz, C_6D_6) $\delta -9.9$. (Assignment of the ^1H and ^{13}C signals of benzyltris(pentafluorophenyl)borate unit was difficult due to the couplings with ^{11}B and ^{19}F nuclei).
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