

The chemistry of Group 4 permethylmetallocene complexes with 2-mercaptoethanol: the molecular structure of $\text{Cp}_2^* \text{Zr}(\text{OCH}_2\text{CH}_2\text{SH})_2$

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Abstract

$\text{Cp}_2^* \text{TiCl}_2$ (Cp^* = pentamethylcyclopentadienyl) reacts with 1 molar equivalent of 2-mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$) in the presence of NEt_3 to give the monomeric chelate complex $\text{Cp}_2^* \text{Ti}(\text{OCH}_2\text{CH}_2\text{S})$ (1). However, $\text{Cp}_2^* \text{ZrCl}_2$ reacts with 1 molar equivalent of $\text{HOCH}_2\text{CH}_2\text{SH}$ in the presence of NEt_3 to give the oxygen-bonded monomeric complex $\text{Cp}_2^* \text{ZrCl}(\text{OCH}_2\text{CH}_2\text{SH})$ (2). When $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$ reacts with 1 molar equivalent of $\text{HOCH}_2\text{CH}_2\text{SH}$, the oxygen-bonded complex $\text{Cp}_2^* \text{Zr}(\text{CH}_3)(\text{OCH}_2\text{CH}_2\text{SH})$ (3) is obtained first. Complex 3 gradually loses the methane in the solid state or in solution to give the complex $\text{Cp}_2^* \text{Zr}(\text{OCH}_2\text{CH}_2\text{S})$ (4), which has the monomeric chelate structure like the titanium complex 1. Complexes 3 and 4 can be converted to the monochloro complex 2 by the addition of triethylammonium chloride. When $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$ is in neat $\text{HOCH}_2\text{CH}_2\text{SH}$, the dialkoxy complex $\text{Cp}_2^* \text{Zr}(\text{OCH}_2\text{CH}_2\text{SH})_2$ (5) is obtained. Complex 5 crystallizes in the orthorhombic *Cmca* space group with cell parameters $a = 17.413(3)$ Å, $b = 17.256(3)$ Å, $c = 17.332(3)$ Å, $Z = 8$, $R = 0.041$ and $R_w = 0.053$. The molecule possesses a mirror plane that bisects the Cp^* rings and the O–Zr–O angle. Two Cp^* rings are staggered in conformation and disorders are found for the methylene carbons of the ligand.

Keywords: Zirconium; Titanium; Pentamethylcyclopentadienyl; 2-Mercaptoethanol

1. Introduction

2-Mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$) is an interesting ligand which contains both a hard oxygen donor and a soft sulfur donor. However, the chemistry of $\text{HOCH}_2\text{CH}_2\text{SH}$ with metals has caused little attention and only a few complexes have so far been prepared. Most importantly, this ligand can differentiate the nature of the metal centers and forms complexes of versatile structures with metals. The possible bonding modes of $\text{HOCH}_2\text{CH}_2\text{SH}$ with metals are shown in Fig. 1. Based on the nature of the hard and soft characteristics of the ligand and the properties of the metals, the sulfur-bonded monomeric structure I and the sulfur-bridged dimeric structure II are preferable for complexes prepared from the soft metals. The monomeric chelate structure III, the double-bridged dimeric structure IV, and the sulfur-bridged twisted dimeric structure VI are preferable for complexes prepared from the

borderline metals. The oxygen-bridged dimeric structure VII, the oxygen-bridged twisted dimeric structure VIII, and the oxygen-bonded monomeric structure IX are preferable for complexes prepared from the hard metals. The complexes with the bridged dimeric structure V, in principle, can be prepared from the hard–soft bi-metallic systems. Indeed, $\text{HOCH}_2\text{CH}_2\text{SH}$ reacts with the soft metals to form complexes of predominantly the structures I or II [1–4]. With the hard Group 4 metals, complexes with the structure VIII are obtained [5]. With the Group 14 germanium metal, one complex with the structure IX has been reported [6]. With the borderline metal, the complexes have the structures I, III, IV, or VIII [7–10]. However, complexes with the bridged dimeric structure V, the sulfur-bridged twisted dimeric structure VI, or the oxygen-bridged dimeric structure VII, and Group 4 complexes with the oxygen-bonded monomeric structure IX have not been reported.

Here, we report the reaction of $\text{HOCH}_2\text{CH}_2\text{SH}$ with Group 4 permethylmetallocene derivatives to form complexes of the structures III and IX. In reaction with 2-mercaptoethanol, the permethylmetallocene deriva-

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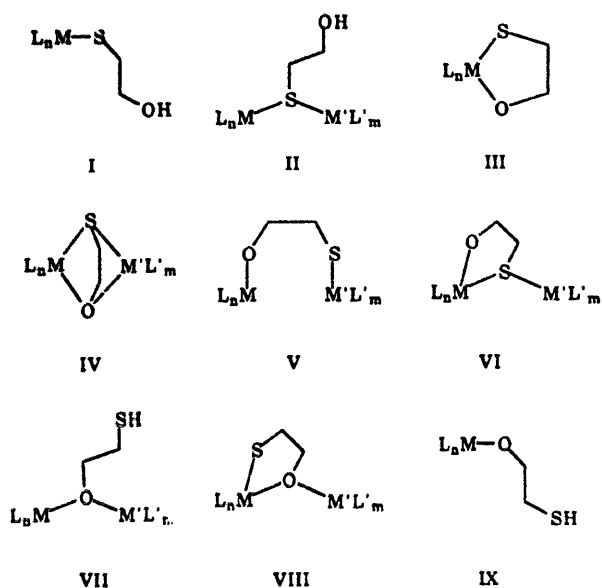


Fig. 1. The possible bonding modes of HOCH₂CH₂SH with metals.

tives show different chemistry from the metallocene derivatives in which the twisted dimeric zirconium complex [Cp₂Zr(OCH₂CH₂S)]₂ [5] is the only zirconocene complex prepared.

2. Experimental section

2.1. Reagents and general techniques

Cp₂^{*}ZrCl₂ [11] and Cp₂^{*}Zr(CH₃)₂ [12] (Cp^{*} = pentamethylcyclopentadienyl) were prepared according to the literature procedures. Cp₂^{*}TiCl₂ (Aldrich) was used without further purification. NEt₃ (Merck) and HOCH₂CH₂SH (Merck) were distilled and stored over molecular sieves. Solvents were dried by refluxing at least 24 h over P₂O₅ (trichloromethane, dichloromethane) or sodium-benzophenone (benzene, *n*-pentane, hexane, diethyl ether) and were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

2.2. Synthesis of bis(pentamethylcyclopentadienyl)(2-thioethoxy)titanium(IV) (1)

NEt₃ (2.2 ml, 15.9 mmol) was added to a solution of Cp₂^{*}TiCl₂ (0.59 g, 1.5 mmol) and HOCH₂CH₂SH (0.12 g, 1.6 mmol) in 40 ml of benzene at room temperature. The mixture was stirred for 8 h and the solution changed color from purple-red to dark green. The solution then was pumped to dryness to give a dark residue which was extracted with 30 ml of *n*-pentane. The extracted solution was slowly evaporated to give dark greenish-red crystals (0.21 g, 35% yield). EI-MS:

$m/z = 394$. ¹H NMR (CDCl₃): δ 4.55 (t, $J_{\text{HH}} = 5.6$ Hz, 2H), 3.41 (t, $J_{\text{HH}} = 5.6$ Hz, 2H), 1.99 (s, 30H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 124.5 (C₅), 82.1 (-CH₂O-), 53.8 (-CH₂S-), 12.4 (CH₃) ppm. Anal. Found: C, 66.98; H, 8.68. C₂₂H₃₄OSTi. Calc.: C, 66.70; H, 8.50%.

2.3. Synthesis of bis(pentamethylcyclopentadienyl)-chloro(2-mercaptoethoxy)zirconium(IV) (2)

To a solution of Cp₂^{*}ZrCl₂ (0.86 g, 2.0 mmol) and HOCH₂CH₂SH (0.17 g, 2.2 mmol) in 40 ml of benzene, NEt₃ (0.41 ml, 3.0 mmol) was added. The resulting mixture was stirred at room temperature for 4 h and then was pumped to dryness to give a pale yellow residue. The solid was extracted with 50 ml of *n*-pentane and the extracted solution was concentrated to about 10 ml. The resulting solution was cooled to -15°C to afford cream colored crystals (0.53 g, 56.0% yield). ¹H NMR (CDCl₃): δ 4.22 (t, $J_{\text{HH}} = 6.8$ Hz, 2H), 2.58 (dt, $J_{\text{HH}} = 8.2, 6.8$ Hz, 2H), 1.95 (s, 30H), 1.68 (t, $J_{\text{HH}} = 8.2$ Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃): δ 121.4 (C₅), 72.5 (-CH₂O-), 27.9 (-CH₂S-), 11.4 (CH₃) ppm. Anal. Found: C, 55.61; H, 7.44. C₂₂H₃₅ClOSZr. Calc.: C, 55.72; H, 7.44.

2.4. Synthesis of bis(pentamethylcyclopentadienyl)-methyl(2-mercaptoethoxy)zirconium(IV) (3)

To a solution of HOCH₂CH₂SH (0.125 g, 1.6 mmol) in 30 ml of diethyl ether, Cp₂^{*}Zr(CH₃)₂ (0.63 g, 1.60 mmol) was added. The mixture was stirred at 0°C for 10 h and was pumped to dryness to give a white residue. The residue was washed with 5 ml of cold hexane to give a white powder (0.31 g) of predominantly complex 3 and some complex 4 and unidentified products. ¹H NMR (CDCl₃): δ 4.02 (t, $J_{\text{HH}} = 7.2$ Hz, 2H), 2.46 (dt, $J_{\text{HH}} = 8.2, 7.2$ Hz, 2H), 1.87 (s, 30H), 1.28 (t, $J_{\text{HH}} = 8.2$ Hz, 1H), -0.46 (s, 3H) ppm. ¹H NMR (C₆D₆): δ 3.98 (t, $J_{\text{HH}} = 7.0$ Hz, 2H), 2.39 (dt, $J_{\text{HH}} = 8.4, 7.0$ Hz, 2H), 1.77 (s, 30H), 1.26 (t, $J_{\text{HH}} = 8.4$ Hz, 1H), -0.13 (s, 3H) ppm.

2.5. Synthesis of bis(pentamethylcyclopentadienyl)(2-thioethoxy)zirconium(IV) (4)

Cp₂^{*}Zr(CH₃)(OCH₂CH₂SH) (impure, 0.31 g) was placed in a reaction flask containing 20 ml of chloroform and the solution was stirred at room temperature for 3 h. The solution then was dried in vacuo to give a white residue which was washed with 20 ml of benzene to give a white product (0.12 g) of predominantly complex 4 and traces of unidentified products. ¹H NMR (CDCl₃): δ 4.38 (t, $J_{\text{HH}} = 5.5$ Hz, 2H), 3.26 (t, $J_{\text{HH}} = 5.5$ Hz, 2H), 2.01 (s, 30H) ppm. ¹³C{¹H} NMR (C₆D₆): δ 121.2 (C₅), 78.4 (-CH₂O-), 48.2 (-CH₂S-), 11.4 (CH₃) ppm.

2.6. Synthesis of bis(pentamethylcyclopentadienyl)bis(2-mercaptoethoxy)zirconium(IV) (5)

To a reaction flask containing $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$ (0.39 g, 1.0 mmol), $\text{HOCH}_2\text{CH}_2\text{SH}$ (0.40 g, 5.0 mmol) was added. The methane evolved immediately and the solution was stirred at room temperature for a further 4 h. The solution was pumped to dryness to give a pale-yellow residue which was extracted with 30 ml of *n*-pentane. The extracted solution was concentrated to about 10 ml and then was cooled to -15°C to give colorless crystals (0.19 g, 37.0% yield). ^1H NMR (CDCl_3): δ 4.14 (t, $J_{\text{HH}} = 7.6$ Hz, 4H), 2.61 (dt, $J_{\text{HH}} = 8.2, 7.6$ Hz, 4H), 1.93 (s, 30H), 1.34 (t, $J_{\text{HH}} = 8.2$ Hz, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 119.8 (C_5), 72.0 ($-\text{CH}_2\text{O}-$), 28.4 ($-\text{CH}_2\text{S}-$), 10.9 (CH_3) ppm. Anal. Found: C, 55.85; H, 7.98. $\text{C}_{24}\text{H}_{40}\text{O}_2\text{S}_2\text{Zr}$. Calc.: C, 55.88; H, 7.81%.

2.7. Physical measurements

^1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer and ^{13}C NMR spectra were recorded with a Varian VXR-300 (75.43 MHz) spectrometer. The ^1H and ^{13}C chemical shifts were measured relative to TMS as the internal reference. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument. Mass spectra were obtained using a Jeol JMS-SX/SX 102A instrument.

2.8. Crystal structure determinations

A colorless crystal of **5** of size $0.18 \times 0.42 \times 0.60$ mm³ in a sealed capillary under dry dinitrogen atmosphere was used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVax 3100 computer. The positions of heavy atoms for the structure were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques. All non-hydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms, except the mercapto hydrogen which was also located from successive difference Fourier map calculations, were considered as riding atoms on carbon atoms with a C–H bond length of 0.96 Å; the hydrogen atom temperature factors were fixed at 0.08. The hydrogen atoms were

Table 1
Crystallographic data for complex **5**

Formula	$\text{C}_{24}\text{H}_{40}\text{O}_2\text{S}_2\text{Zr}$
Fw	515.9
Crystal system	orthorhombic
Space group	<i>Cmca</i>
<i>a</i> (Å)	17.413(3)
<i>b</i> (Å)	17.256(3)
<i>c</i> (Å)	17.332(3)
<i>V</i> (Å ³)	5207.9(16)
<i>Z</i>	8
D_{calcd} (g cm ⁻³)	1.316
λ (Mo K α) (Å)	0.71073
Absorption coefficient (mm ⁻¹)	0.599
Range (deg)	3.0–50
Scan type	θ – 2θ
Reflections collected	5165
Independent reflections	1288 ($R_{\text{int}} = 1.87\%$)
Observed reflections	949 ($I > 2\sigma I$)
No. of refined parameters	157
R^a for significant reflections	0.041
R_w^b for significant reflections	0.053
GoF ^c	1.33

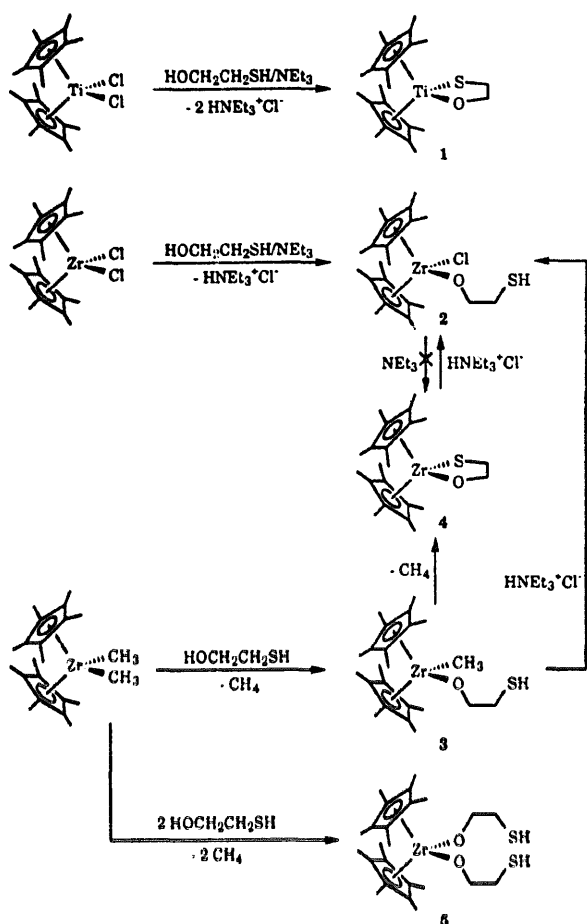
$$^a R = [\sum(F_o - F_c) / \sum F_o], \quad ^b R_w = [\sum w^{1/2}(F_o - F_c) / \sum w^{1/2} F_o], \quad ^c \text{GoF} = [\sum w(F_o - F_c)^2 / (N_{\text{refl}} - N_{\text{params}})]^{1/2}.$$

included for refinements in the final cycles. The crystallographic data of complex **5** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The chemistry of 2-mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$) with Group 4 permethylmetallocene derivatives is outlined in Scheme 1. $\text{Cp}_2^* \text{TiCl}_2$ reacts with 1 molar equivalent of $\text{HOCH}_2\text{CH}_2\text{SH}$ in the presence of NEt_3 to give the monomeric chelate complex **1**. However under the same conditions as the formation of the complex **1** or at higher temperatures, $\text{Cp}_2^* \text{ZrCl}_2$ reacts with 1 molar equivalent of $\text{HOCH}_2\text{CH}_2\text{SH}$ to give the oxygen-bonded monomeric complex **2**. The inertness of the second chloride toward the attack by the sulfur donor is also found in the reaction of $\text{Cp}_2^* \text{ZrCl}_2$ with 3-mercapto-1-propanol [13]. In order to fully understand the chemistry of $\text{HOCH}_2\text{CH}_2\text{SH}$ with Group 4 metals, $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$ was prepared and reacted with 1 molar equivalent of $\text{HOCH}_2\text{CH}_2\text{SH}$. The first methyl group is easily lost to give the oxygen-bonded monomeric complex **3** as a major product, accompanied with complex **4** and unidentified products with a ratio of roughly 8 : 1 : 1 based on the relative intensities of ^1H NMR peaks of Cp^* methyls. The relative ratio of complexes **3** to **4** decreases with increasing time since complex **3** gradually loses the second methyl to form the monomeric chelate complex **4** in either the solid state or solution. In diethyl ether or benzene, the conversion from **3** to **4** is



Scheme 1.

slow and requires more than 24 h. However, the conversion is much faster in chloroform and is completed within 2–3 h. During the process of conversion from **3** to **4**, decomposition also occurs but at a slower rate than the conversion. In addition, the original starting complex **3** was already contaminated with unidentified products which carried over for the conversion, and the purification of **4** was tried unsuccessfully. Complexes **3** and **4** decompose easily to form unidentified products when exposed to air. The reaction of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ in excess $\text{HOCH}_2\text{CH}_2\text{SH}$ affords the dialkoxy complex **5**.

The reactions of Cp_2ZrX_2 with $\text{HOCH}_2\text{CH}_2\text{SH}$ are very similar to the chemistry between permethylmetallocene derivatives and 3-mercapto-1-propanol, except with a much faster rate for the formation of the monomeric chelate complex **4** from the oxygen-bonded monomeric complex **3**. It is well known that the formation of complexes with the monomeric chelate structure of a five-membered ring will expose spaces on the larger Zr metal center and the twisted dimeric species is preferable if the ligands contain donor atoms capable of bridging. Examples are the oxygen- or the sulfur-bridged dimeric complexes $[\text{Cp}_2\text{Zr}(\text{XCH}_2\text{CH}_2\text{Y})_2]$ ($\text{X} = \text{O}$, $\text{Y} = \text{S}$ [5,14] or CH_2 [15]; $\text{X} = \text{S}$, $\text{Y} = \text{S}$ [16]), or in rare

cases that the weakly associated dimeric species is obtained due to the presence of bulky ligands [5]. However, the bulky Cp^* ligands prevent the access of two monomeric species of complex **4** for the formation of the twisted dimeric complex; this is probably the reason for the high moisture sensitivity of **4**. Owing to the instability of **4**, it converts to **2** immediately with the addition of HNEt_3Cl . The methyl derivative **3** also converts to **2** with the addition of HNEt_3Cl .

Complexes **1–5** have been characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H chemical shift of methylene protons adjacent to the donor atom shift downfield significantly. However, for complexes **2**, **3**, and **5**, the ^1H chemical shift of the methylene protons adjacent to the uncoordinated thiol group shift upfield from that of the free ligand. The ^{13}C chemical shifts of the difunctional ligand in complexes behave similarly. It is worth noting that the coupling constants between methylene protons of the difunctional dithiol or the heterodifunctional 2-mercaptoethanol ligands in complexes provide information on structures and bonding modes of the difunctional ligands. For example, the $^3J_{\text{HH}}$ values for complexes with structures **X** or **XI** [5,15,16] containing five-membered chelate ring are at 5.5 ± 0.1 Hz. For the macrocyclic dimeric complexes of structure **XII** [16,17] the $^3J_{\text{HH}}$ values are from 6.5 to 6.8 Hz. For the oxygen-bonded monomeric complexes of structure **XIII** reported in this study, the $^3J_{\text{HH}}$ values are larger than 6.8 Hz. Based on the above summary, complex **4** with $^3J_{\text{HH}}$ of 5.5 Hz is likely to have the monomeric structure **X** or the twisted dimeric structure **XI**. However, the structure **XI** may be ruled out because the bulky Cp^* ligands prevent the access of two monomeric species.

3.2. The molecular structure of complex 5

The final coordinates and the equivalent isotropic displacement coefficients of complex **5** are listed in Table 2, and the molecular structure is shown in Fig. 2. The selected bond lengths and bond angles are listed in

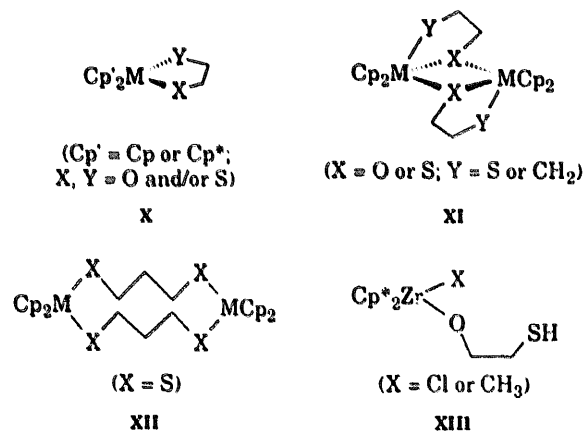


Table 2
Atomic coordinates and equivalent isotropic displacement coefficients (\AA^2) of complex 5

Atom	x	y	z	U_{eq}
Zr	0.5000	0.1289(1)	0.7180(1)	0.040(1)
S1	0.2599(2)	0.1210(2)	0.4742(1)	0.111(1)
O1	0.4156(3)	0.1279(3)	0.6437(3)	0.071(2)
C1	0.5000	0.2290(6)	0.8296(6)	0.066(5)
C2	0.5646(5)	0.2456(4)	0.7842(6)	0.070(4)
C(3)	0.5392(5)	0.2737(4)	0.7137(4)	0.074(4)
C4	0.5000	-0.0193(5)	0.7098(6)	0.064(6)
C5	0.5637(6)	-0.0012(5)	0.7534(5)	0.064(4)
C6	0.5401(4)	0.0297(4)	0.8234(4)	0.063(3)
C7	0.3857(9)	0.1180(10)	0.5667(15)	0.085(8)
C7'	0.3465(44)	0.1150(30)	0.6032(23)	0.121(23)
C8	0.3067(10)	0.1355(11)	0.5649(17)	0.104(9)
C8'	0.3388(31)	0.1176(28)	0.5247(19)	0.108(20)
C11	0.5000	0.2192(8)	0.9140(7)	0.158(10)
C12	0.6450(6)	0.2429(6)	0.8074(8)	0.171(8)
C13	0.5887(8)	0.3051(6)	0.6512(6)	0.201(8)
C14	0.5000	-0.0579(7)	0.6328(7)	0.128(8)
C15	0.6462(6)	-0.0169(6)	0.7324(7)	0.152(7)
C16	0.5905(7)	0.0418(6)	0.8921(6)	0.146(6)

Table 3. The solid state structure of **5** possesses a mirror plane which contains the Zr atom, the C(1) and C(11) atoms of one Cp* ligand, and the C(4) and C(14) atoms of another Cp* ligand. This mirror plane bisects the Cp* rings and the O(1)–Zr–O(1a) angle. Two Cp* ligands are staggered in conformation. Disorders are found for the methylene carbon atoms and the disordered pairs are labeled as C7, C7' and C8, C8'. The Zr–O distance at 1.955 (5) Å falls into the range between 1.92 and 2.00 Å for the zirconium alkoxide complexes [18–22]. However, the Zr–Cp*(centroid) distances at 2.299 and 2.300 Å are somewhat longer than the distance in the 18-e⁻ Cp₂Zr(CO)₂ [23] at 2.20 Å and other permethyl zirconocene complexes (2.20–2.26 Å) [24–29]. The Cp*(centroid)–Zr–Cp*(centroid) angle at 134.9° is small compared with many of the

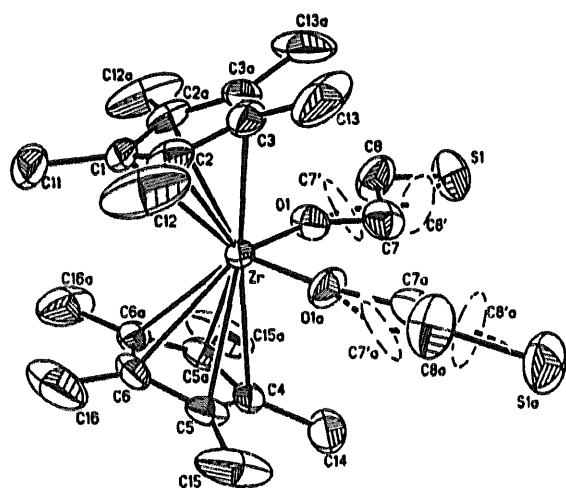


Fig. 2. The molecular structure of complex 5.

Table 3
Selected bond lengths (Å) and bond angles (deg) of complex 5^a

Zr–O1	1.955(5)		
O1–C7	1.442(26)	O1–C7'	1.410(7)
C7–C8	1.410(24)	C7'–C8'	1.368(53)
S1–C8	1.788(27)	S1–C8'	1.630(48)
Zr–Cp* 1	2.300	Zr–Cp* 2	2.299
Cp* 1–Zr–Cp* 2	134.9	O1–Zr–O1a	97.5(3)
Zr–O1–C7	151.9(8)	Zr–O1–C7'	166.1(21)

^a Cp* 1 = (C1, C2, C3, C3a, C2a); Cp* 2 = (C4, C5, C6, C6a, C5a).

permethylzirconocene complexes (135.2–140.7°) [24–29], but it is larger than the 131.5° for the Cp₂⁻Zr[OB(C₆F₅)₃] complex [30].

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