

# The chemistry of 3-mercapto-1-propanol with Group 4 metallocene derivatives.

## The molecular structure of $\text{Cp}_2^* \text{ZrCl}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH})$

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### Abstract

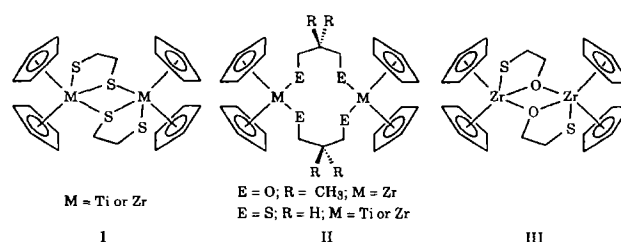
Titanocene or permethylzirconocene dichloride reacts with 1 molar equivalent of 3-mercapto-1-propanol ( $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$ ) in the presence of  $\text{NEt}_3$  to give the monomeric chelate complex  $\text{Cp}_2^* \text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{S})$  (**1**) or the oxygen-bonded monomeric complex  $\text{Cp}_2^* \text{ZrCl}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH})$  (**2**), respectively. When  $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$  reacts with 1 molar equivalent of  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$ , the oxygen-bonded monomeric complex  $\text{Cp}_2^* \text{Zr}(\text{CH}_3)(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH})$  (**3**) is obtained first. The complex **3** loses the methane extremely slowly to give the monomeric chelate complex  $\text{Cp}_2^* \text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{S})$  (**4**). However, the addition of  $\text{HNEt}_3\text{Cl}$  to a solution of **4** in  $\text{C}_6\text{D}_6$  converts **4** to the oxygen-bonded complex **2** in 24 h. The complex **3** can also be converted to **2** by the addition of  $\text{HNEt}_3\text{Cl}$  with a slower rate of 1 week. The dialkoxo complex  $\text{Cp}_2^* \text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH})_2$  (**5**) is obtained from the reaction of  $\text{Cp}_2^* \text{Zr}(\text{CH}_3)_2$  in neat  $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$ . The complex **2** crystallizes in the monoclinic  $P2_1/c$  space group with cell parameters  $a = 9.128(2)$  Å,  $b = 16.276(2)$  Å,  $c = 16.141(3)$  Å,  $\beta = 93.75(2)^\circ$ , and  $z = 4$  with  $R = 0.040$  and  $R_w = 0.049$ . The molecular structure of **2** shows a short Zr–O distance at  $1.930(3)$  Å and a large Zr–O–C(21) angle at  $172.5(3)^\circ$  which are indications of strong Zr–O  $\pi$  bonding.

**Keywords:** Titanium; Zirconium; Metallocene; 3-mercapto-1-propanol

### 1. Introduction

The chemistry of difunctional ligands with metals is interesting owing to the abilities of the difunctional ligands to either bond to a single metal in the bidentate mode or to bridge two metals. The Group 4 transition metal complexes of the diol and dithiol ligands have been studied extensively by Stephan and coworkers [1]. For the metallocene systems, the complexes prepared have the twisted dimeric structure **I** or the macrocyclic structure **II**. For the heterodifunctional 2-mercaptoethanol which possess both the hard oxygen and the soft sulfur donors, the reaction gives the twisted dimeric structure **III** in which two metals are bridged through the hard oxygen donors [2]. For 3-mercapto-1-propanol ( $\text{HO}(\text{CH}_2)_3\text{SH}$ ), it possess differences from the propylene diol or dithiol, the ethylene diol or dithiol, and the 2-mercaptoethanol ligands. First, the propylene linkage of  $\text{HO}(\text{CH}_2)_3\text{SH}$  is similar to  $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$

or to  $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{SH}$ . However, unlike the latter cases containing both hard donors or both soft donors at each end, the  $\text{HO}(\text{CH}_2)_3\text{SH}$  ligand contains both the hard oxygen donor and the soft sulfur donor. Second, unlike the ethylene diol, ethylene dithiol, or 2-mercaptoethanol, the  $\text{HO}(\text{CH}_2)_3\text{SH}$  ligand has one more  $\text{CH}_2$  chain which forms a six-membered chelate ring instead of a five-membered chelate ring if it behaves as a bidentate ligand. It would be interesting to investigate



the behavior of this ligand and its chemistry with transition metals.

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We report here the chemistry of Group 4 metallocene systems with  $\text{HO}(\text{CH}_2)_3\text{SH}$ .  $\text{HO}(\text{CH}_2)_3\text{SH}$  reacts with Group 4 metallocene or permethylmetallocene derivatives to give  $\text{Cp}_2\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{S})$  (**1**) and  $\text{Cp}_2^*\text{ZrX}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH})$  ( $\text{X} = \text{Cl}$  (**2**),  $\text{CH}_3$  (**3**), or  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH}$  (**5**)). The complex  $\text{Cp}_2^*\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{S})$  (**4**) is obtained by the loss of methane from **3**.

## 2. Experimental details

### 2.1. Reagents and general techniques

$\text{HO}(\text{CH}_2)_3\text{SH}$  was prepared by the reduction of  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SH}$  with an excess of  $\text{LiAlH}_4$ .  $\text{Cp}_2^*\text{ZrCl}_2$  [**3**] and  $\text{Cp}_2^*\text{Zr}(\text{CH}_3)_2$  [**4**] were prepared according to the literature procedures.  $\text{Cp}_2\text{TiCl}_2$  (Aldrich) was used without further purification.  $\text{NEt}_3$  (Merck) was distilled and stored over molecular sieves. Solvents were dried by heating under reflux for at least 24 h over  $\text{P}_2\text{O}_5$  (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 dry dinitrogen.

### 2.2. Synthesis of bis(cyclopentadienyl)(3-thio-1-propoxo)titanium(IV) (**1**)

$\text{Cp}_2\text{TiCl}_2$  (0.286 g, 1.15 mmol) was added to a solution of  $\text{HS}(\text{CH}_2)_3\text{OH}$  (0.106 g, 1.15 mmol) and  $\text{NEt}_3$  (1.00 ml, 7.20 mmol) in 40 ml of benzene at room temperature. The mixture was stirred for 12 h and the precipitate was filtered off. The filtrate was then dried in vacuo to give a red solid (0.262 g, 85.0% yield). EI-MS:  $m/z = 268$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.17 (s, 10H), 4.38 (m, 2H), 2.82 (m, 2H), 1.58 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  113.8 ( $\text{C}_5$ ), 80.1 ( $\text{CH}_2\text{O}$ ), 34.4 ( $\text{CH}_2$ ), 32.0 ( $\text{CH}_2\text{S}$ ) ppm. Anal. Found: C, 58.46; H, 6.18%.  $\text{C}_{13}\text{H}_{16}\text{OSTi}$  Calc.: C, 58.21; H, 6.01%.

### 2.3. Synthesis of bis(pentamethylcyclopentadienyl)-chloro(3-mercapto-1-propoxo)zirconium(IV) (**2**)

To a solution of  $\text{Cp}_2^*\text{ZrCl}_2$  (0.498 g, 1.15 mmol) and  $\text{HO}(\text{CH}_2)_3\text{SH}$  (0.106 g, 1.15 mmol) in 30 ml of benzene,  $\text{NEt}_3$  (0.50 ml, 3.76 mmol) was added at room temperature. The resulting mixture was stirred at room temperature for 4 h and then was taken to dryness to give a pale yellow residue. The residue was extracted with 50 ml of n-pentane and the extracted solution was concentrated to ca. 25 ml. The resulting solution was cooled to  $-15^\circ\text{C}$  to afford yellow crystals (0.263 g, 47.0% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.21 (t,  $J_{\text{HH}} = 6.3$

Hz, 2H), 2.53 (m, 2H), 1.95 (s, 30H), 1.78 (m, 2H), 1.34 (t,  $J_{\text{HH}} = 8.0$  Hz, 1H) ppm.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.13 (t,  $J_{\text{HH}} = 6.2$  Hz, 2H), 2.44 (m, 2H), 1.85 (s, 30H), 1.73 (m, 2H), 1.20 (t,  $J_{\text{HH}} = 7.9$  Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  121.2 ( $\text{C}_5$ ), 68.8 ( $\text{CH}_2\text{O}$ ), 38.1 ( $\text{CH}_2$ ), 21.3 ( $\text{CH}_2\text{S}$ ), 11.4 ( $\text{CH}_3$ ) ppm. Anal. Found: C, 56.53; H, 7.75%.  $\text{C}_{23}\text{H}_{37}\text{OSClZr}$  Calc.: C, 56.58; H, 7.64%.

### 2.4. Synthesis of bis(pentamethylcyclopentadienyl)(3-mercapto-1-propoxo)methylzirconium(IV) (**3**)

To a solution of  $\text{HO}(\text{CH}_2)_3\text{SH}$  (0.106 g, 1.15 mmol) in 30 ml of diethyl ether,  $\text{Cp}_2^*\text{Zr}(\text{CH}_3)_2$  (0.314 g, 0.80 mmol) was added. The mixture was stirred at room temperature for 12 h and the solvent was removed in vacuo to give a pale yellow residue. The residue was dissolved in 15 ml of n-pentane and the solution was cooled to  $-15^\circ\text{C}$  to afford a pale yellow solid (0.220 g, 48.0% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.02 (t,  $J_{\text{HH}} = 6.3$  Hz, 2H), 2.40 (m, 2H), 1.87 (s, 30H), 1.66 (m, 2H), 1.27 (t,  $J_{\text{HH}} = 7.8$  Hz, 1H),  $-0.49$  (s, 3H) ppm.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.01 (t,  $J_{\text{HH}} = 6.3$  Hz, 2H), 2.34 (m, 2H), 1.81 (s, 30H), 1.66 (m, 2H), 1.18 (t,  $J_{\text{HH}} = 7.8$  Hz, 1H),  $-0.14$  (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  117.3 ( $\text{C}_5$ ), 67.2 ( $\text{CH}_2\text{O}$ ), 38.5 ( $\text{CH}_2$ ), 26.5 ( $\text{CH}_3$ ), 21.3 ( $\text{CH}_2\text{S}$ ), 11.4 ( $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  117.2 ( $\text{C}_5$ ), 67.2 ( $\text{CH}_2\text{O}$ ), 38.9 ( $\text{CH}_2$ ), 27.2 ( $\text{CH}_3$ ), 21.3 ( $\text{CH}_2\text{S}$ ), 11.2 ( $\text{CH}_3$ ) ppm. Anal. Found: C, 61.40; H, 8.42%.  $\text{C}_{24}\text{H}_{39}\text{OSClZr}$  Calc.: C, 61.61; H, 8.62%.

### 2.5. The formation of bis(pentamethylcyclopentadienyl)(3-thio-1-propoxo)zirconium(IV) (**4**)

The complex **3** (4 mg) was dissolved in 0.5 ml of  $\text{C}_6\text{D}_6$  in a Teflon-plug sealed NMR tube. The solution was monitored frequently by the  $^1\text{H}$  spectroscopy at the ambient temperature. The conversion from **3** to bis(pentamethylcyclopentadienyl)(3-thio-1-propoxo)zirconium(IV) (**4**) was completed after 3 weeks. The solution contained traces of impurities.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.20 (t,  $J_{\text{HH}} = 6.0$  Hz, 2H), 2.69 (m, 2H), 1.91 (s, 30H), 1.61 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  119.9 ( $\text{C}_5$ ), 70.2 ( $\text{CH}_2\text{O}$ ), 32.8 ( $\text{CH}_2$ ), 28.6 ( $\text{CH}_2\text{S}$ ), 11.5 ( $\text{CH}_3$ ) ppm. EI-MS:  $m/z = 450$ .

### 2.6. Synthesis of bis(pentamethylcyclopentadienyl)-bis(3-mercapto-1-propoxo)zirconium(IV) (**5**)

To a reaction flask containing  $\text{HO}(\text{CH}_2)_3\text{SH}$  (0.820 g, 8.87 mmol),  $\text{Cp}_2^*\text{Zr}(\text{CH}_3)_2$  (0.355 g, 0.91 mmol) was added at room temperature and methane evolved immediately. The solution was stirred for a further 3 h and the solution was taken to dryness to give a yellow oil (0.477 g, 96.8% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.14 (t,  $J_{\text{HH}} = 6.8$  Hz, 4H), 2.57 (m, 4H), 1.93 (s, 30H), 1.83 (m, 4H), 1.38 (t,  $J_{\text{HH}} = 7.7$  Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$

NMR (CDCl<sub>3</sub>): δ 119.3 (C<sub>5</sub>), 60.8 (CH<sub>2</sub>O), 39.7 (CH<sub>2</sub>), 21.4 (CH<sub>2</sub>S), 11.1 (CH<sub>3</sub>) ppm. Anal. Found: C, 55.64; H, 7.93%. C<sub>26</sub>H<sub>44</sub>O<sub>2</sub>S<sub>2</sub>Zr Calc.: C, 57.41; H, 8.15%.

## 2.7. Physical measurements

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

## 2.8. Crystal structure determinations

A colorless crystal of **2** of size 0.20 × 0.40 × 0.80 mm 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 (λ = 0.71073 Å). Absorption correction was not performed on the sample. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a MicroVax 3100-80 computer. The positions of heavy atoms for the structure were determined by direct methods and the remaining nonhydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out using full-matrix least-squares techniques. All nonhydrogen atoms were refined as individual anisotropic atoms. The hydrogen atoms, (except for that attached to the sulfur atom which is not positively defined from the Fourier difference map calculations) were considered as riding on the carbon atoms with a C–H bond length of 0.96 Å and the hydrogen atom temperature factors were fixed at 0.08. The hydrogen atoms were included for refinements in the final cycles. The crystallographic data for the complex **2** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Syntheses and characterizations

The reactions of 3-mercapto-1-propanol (HO(CH<sub>2</sub>)<sub>3</sub>-SH) with Group 4 metallocene or permethylmetallocene derivatives are outlined in Scheme 1. Cp<sub>2</sub>TiCl<sub>2</sub> reacts with 1 molar equivalent of HO(CH<sub>2</sub>)<sub>3</sub>SH in the presence of NEt<sub>3</sub> to give a red product **1**. The mass spectroscopy suggests a monomeric chelate structure for **1**. For the permethylzirconocene derivatives, Cp<sub>2</sub><sup>\*</sup>ZrCl<sub>2</sub> reacts with 1 molar equivalent of HO(CH<sub>2</sub>)<sub>3</sub>SH in the presence of NEt<sub>3</sub> to afford a yellow complex **2** with an oxygen-bonded monomeric structure. In the reaction of

Table 1  
Crystallographic data for Cp<sub>2</sub><sup>\*</sup>ZrCl(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH) (**2**)

Formula	C <sub>23</sub> H <sub>37</sub> OSCIZr
Formula weight	488.3
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a (Å)	9.128(2)
b (Å)	16.276(2)
c (Å)	16.141(3)
β (°)	93.75(2)
V (Å <sup>3</sup> )	2392.8(7)
z	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.355
λ (Mo K α) (Å)	0.71073
Absorption coefficient (mm <sup>-1</sup> )	0.699
Range (°)	3.0–50
Scan type	θ – 2θ
No. of reflections collected	4708
No. of independent reflections	4529 (R <sub>int</sub> = 1.18%)
No. of observed reflections	2942 (I > 2σI)
No. of refined parameters	244
R <sup>a</sup> for significant reflections	0.040
R <sub>w</sub> <sup>b</sup> for significant reflections	0.049
Goodness of fit <sup>c</sup>	1.07

$$^a R = [\Sigma(F_o - F_c) / \Sigma F_o]$$

$$^b R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$$

$$^c \text{Goodness of fit} = [\Sigma w(F_o - F_c)^2 / (N_{\text{reflms}} - N_{\text{params}})]^{1/2}$$

Cp<sub>2</sub><sup>\*</sup>Zr(CH<sub>3</sub>)<sub>2</sub> with 1 molar equivalent of HO(CH<sub>2</sub>)<sub>3</sub>SH, the pale-yellow oxygen-bonded monomeric complex **3** is obtained. The complex **3** is found to lose the methane slowly to form the complex **4** either in the solid state or in solution. Therefore, the complex **3** in C<sub>6</sub>D<sub>6</sub> solution in a Teflon-plug sealed NMR tube was monitored by <sup>1</sup>H NMR spectroscopy. Loss of methane to form the complex **4** is a rather slow process, taking 3 weeks to complete. Mass spectroscopy indicates a monomeric chelate structure for **4**. With the addition of HNEt<sub>3</sub>Cl, the complex **4** converts to the oxygen-bonded monomeric **2** at a much faster rate (24 h). The complex **2** can also be obtained by the addition of HNEt<sub>3</sub>Cl to **3** but reaction occurs at a slower rate of 1 week. When Cp<sub>2</sub><sup>\*</sup>Zr(CH<sub>3</sub>)<sub>2</sub> is reacted with neat HO(CH<sub>2</sub>)<sub>3</sub>SH, a yellow oil of the dialkoxy complex **5** is obtained.

The above results indicate that the six-membered chelate ring structure is not favorable for the permethylzirconocene systems. When HO(CH<sub>2</sub>)<sub>3</sub>SH reacts with Cp<sub>2</sub><sup>\*</sup>ZrCl<sub>2</sub> or Cp<sub>2</sub><sup>\*</sup>Zr(CH<sub>3</sub>)<sub>2</sub> the reaction stops at the oxygen-bonded product **2** or **3**, respectively. The monomeric chelate complex **4**, though, can be formed by the evolution of methane from **3**, but the process is extremely slow. Conversely, **4** converts to **2** at a relatively fast rate. Besides, the chemistry of Group 4 metallocene with HO(CH<sub>2</sub>)<sub>3</sub>SH is different from that of the dithiol or diol analogues for which the macrocyclic structure **I** is observed. Considering the steric and electronic effects, macrocyclic bonding between Group 4 metallocene and –O(CH<sub>2</sub>)<sub>3</sub>S–, in which the M–O bond

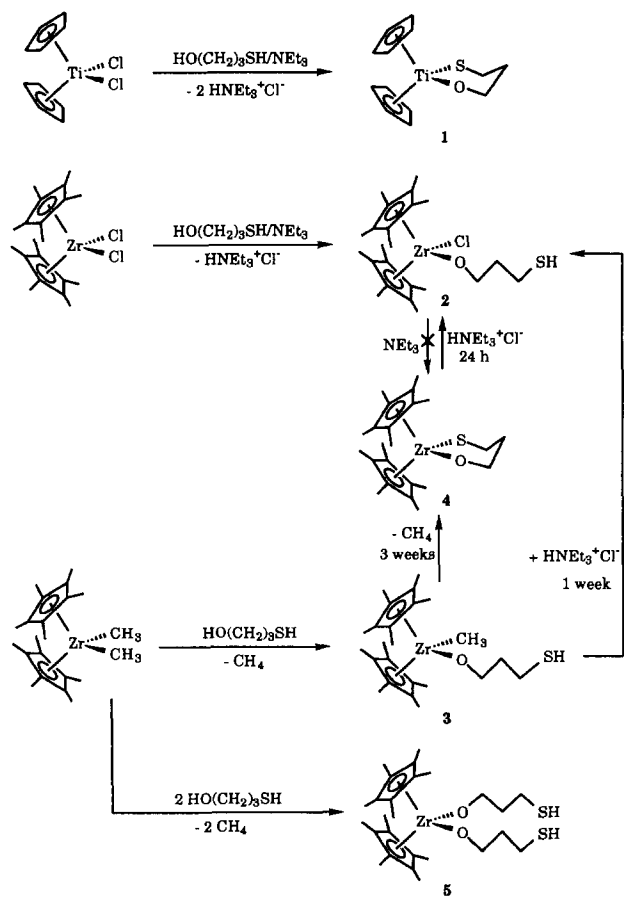
is stronger, is considered to be more favorable than the macrocyclic bonding in  $[\text{Cp}_2\text{M}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{MCp}_2]$  [1]. However, this does not explain why the complexes **1** and **4** adopt the chelate structure instead of the macrocyclic one. Considering the Group 5 metallocene systems with 1,3-propanedithiol, both the monomeric chelate complex  $\text{Cp}_2\text{V}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})$  and the macrocyclic complex  $\text{Cp}_2\text{V}(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{VCp}_2$  exist, but they are prepared by different synthetic approaches [5]. The energy difference between these two structures seems quite small and the structure may vary just owing to a subtle differences in the ligands, the metals, or even the methods of preparation.

Complexes **1–5** have been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The  $^1\text{H}$  chemical shift of the methylene protons attached to the oxygen donor shifts from  $\delta$  3.78 ppm for the free ligand to  $> 4.0$  ppm, indicating bonding of the alkoxy group to the metal. For complex **1**, the proton resonance of the methylene attached to the sulfur donor also shifts downfield to 2.82 ppm from the free ligand value of 2.70 ppm. The downfield shift is not significant compared with the shift of the methylene protons attached to the oxygen donor. For complex **4** in  $\text{C}_6\text{D}_6$ , the  $^1\text{H}$  signal of the methylene attached to the sulfur donor appears at 2.69

Table 2

Atomic coordinates and equivalent isotropic displacement coefficients ( $\text{\AA}^2$ ) of the complex **2**

Atom	x	y	z	$U_{\text{eq}}$
Zr	0.2431(1)	0.1090(1)	0.2084(1)	0.034(1)
Cl	-0.0031(2)	0.0635(1)	0.1543(1)	0.064(1)
O	0.2491(4)	0.2070(2)	0.1415(2)	0.054(1)
S	-0.1822(2)	0.3088(1)	0.0212(1)	0.090(1)
C(1)	0.3568(6)	0.0423(3)	0.0848(3)	0.049(2)
C(2)	0.2948(6)	-0.0241(3)	0.1256(3)	0.048(2)
C(3)	0.3686(6)	-0.0335(3)	0.2042(3)	0.047(2)
C(4)	0.4803(3)	0.0256(3)	0.2124(3)	0.049(2)
C(5)	0.4728(6)	0.0736(3)	0.1381(3)	0.049(2)
C(6)	0.3152(8)	0.0699(4)	-0.0020(3)	0.073(2)
C(7)	0.1794(7)	-0.0823(3)	0.0873(4)	0.069(2)
C(8)	0.3419(7)	-0.1036(3)	0.2632(4)	0.069(2)
C(9)	0.6116(6)	0.0252(4)	0.2745(4)	0.070(2)
C(10)	0.5799(6)	0.1401(4)	0.1179(4)	0.071(2)
C(11)	0.0838(5)	0.1771(3)	0.3146(3)	0.043(2)
C(12)	0.1236(5)	0.0979(3)	0.3478(3)	0.042(2)
C(13)	0.2736(6)	0.0980(3)	0.3692(3)	0.047(2)
C(14)	0.3310(5)	0.1765(3)	0.3468(3)	0.047(2)
C(15)	0.2125(6)	0.2245(3)	0.3162(3)	0.046(2)
C(16)	-0.0686(6)	0.2064(3)	0.2910(3)	0.060(2)
C(17)	0.0163(7)	0.0315(3)	0.3663(3)	0.064(2)
C(18)	0.3537(7)	0.0367(4)	0.4253(3)	0.070(2)
C(19)	0.4829(7)	0.2081(4)	0.3677(4)	0.079(3)
C(20)	0.2203(7)	0.3148(3)	0.2946(3)	0.071(2)
C(21)	0.2598(7)	0.2715(4)	0.0848(3)	0.066(2)
C(22)	0.1117(9)	0.3133(4)	0.0669(4)	0.097(3)
C(23)	0.0005(10)	0.2611(4)	0.0312(5)	0.104(3)



Scheme 1.

ppm, a downfield shift from 2.23 ppm for the free ligand in  $\text{C}_6\text{D}_6$ . For complexes **2**, **3** and **5** with oxygen-bonded monomeric structures, the proton resonances of the methylene attached to the mercapto group shift upfield to a range between 2.53 and 2.40 ppm. For all complexes, the proton resonances of the middle methylenes appear upfield relative to those of the methylene attached to the sulfur donor or the mercapto group. However, the 2D-hetcor spectra of **1** and **2** reveal, in contrast, that the  $^{13}\text{C}$  chemical shifts of the middle methylene appear downfield relative to that of the methylene attached to the sulfur donor or the mercapto group. The  $^{13}\text{C}$  resonances for complexes **3–5** are assigned accordingly.

### 3.2. The molecular structure of complex **2**

The final coordinates and the equivalent isotropic displacement coefficients of complex **2** are listed in Table 2 and the molecular structure is shown in Fig. 1. The selected bond lengths and angles are listed in Table 3. The Zr–O distance at 1.930(3)  $\text{\AA}$  is rather short compared with the usual Zr–O distances (1.94–2.00  $\text{\AA}$ ) for the zirconocene alkoxydes such as  $\text{Cp}_2\text{Zr}[\text{OCH}_2\text{-CMe}_2\text{CH}_2\text{O}]_2\text{ZrCp}_2$  (1.945(6)  $\text{\AA}$ ) [1g],  $\text{Cp}_2\text{Zr}[\text{OC}(\text{Me})=\text{C}(\text{Ph})_2]_2$  (1.989(7) and 2.004(6)  $\text{\AA}$ ) [6],  $\text{Cp}_2\text{Zr}(\text{OCH}_2\text{-CH}_2\text{SiMe}_2\text{CH}_2)$  (1.941(2)  $\text{\AA}$ ) [7], and  $\text{Cp}_2\text{Zr}[\text{OC}-$

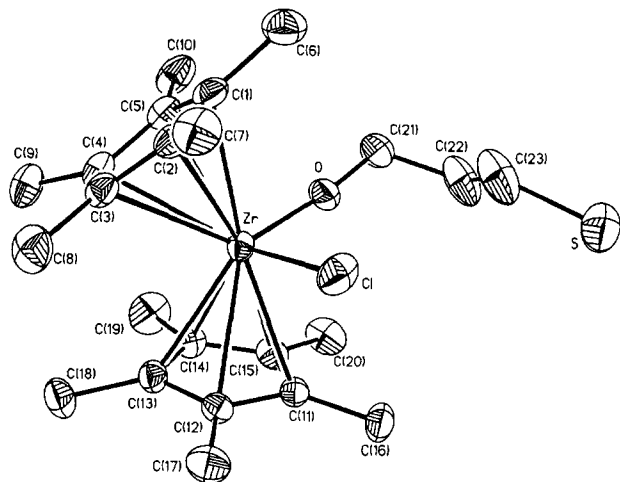


Fig. 1. The molecular structure of **2**. Hydrogen atoms are omitted for clarity.

(Ph)<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>2</sub>] (1.946(4) Å) [8]. However, this distance is comparable with the Zr–O distance of 1.927(6) Å in Cp<sub>2</sub>Zr(OC[W(CO)<sub>5</sub>]CH<sub>2</sub>CH=CHCH<sub>2</sub>-C(Me)(CMe<sub>3</sub>)O) [9], in which the complex contains a rather weak Zr–O(carbene) bond with a bond distance of 2.099(5) Å. In view of the short Zr–O distance, complex **2** is considered to have considerable Zr–O π bonding [10]. For the early transition metal alkoxides, M–O π bonding accompanies the enlarging of the M–O–C angle to around 150° [1g, 6–8]. In complex **2**, the Zr–O–C(21) angle at 172.5(3)° is even larger than the Zr–O–C angle of 166.0(5)° in Cp<sub>2</sub>Zr(OC[W(CO)<sub>5</sub>]CH<sub>2</sub>CH=CHCH<sub>2</sub>-C(Me)(CMe<sub>3</sub>)O). The Zr–Cl distance of 2.471(2) Å is somewhat long compared with those in the zirconocene complexes of Cp<sub>2</sub>ZrCl(μ-OC)[Ta(CO)(dmpe)<sub>2</sub>] (2.466(1) Å) [11], R,S-Me<sub>2</sub>Si(3-<sup>t</sup>Bu-5-MeC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl<sub>2</sub> (2.420(1) Å) [12], R,S-en(thind)<sub>2</sub>ZrCl<sub>2</sub> (2.43(1) and 2.45(1) Å) [13]. The Zr–Cp\* (centroid) distances at 2.264 and 2.283 Å are also somewhat long compared with those in many of the permethylzirconocene complexes, such as Cp<sub>2</sub>ZrCl(μ-OC)[Ta(CO)(dmpe)<sub>2</sub>] (2.254 Å) [11], [Cp<sub>2</sub>\*ZrMe(THF)]-[BPh<sub>4</sub>] (2.228(4) and 2.238(4) Å) [14], [Cp<sub>2</sub>\*Zr(CH<sub>2</sub>-

SiMe<sub>3</sub>)(THF)]-[BPh<sub>4</sub>] (2.255(7) and 2.257(7) Å) [15], and [Cp<sub>2</sub>\*Zr(OCPh=CPh)] (2.242(10) and 2.255(10) Å) [16]. The Cp\*–Zr–Cp\* angle at 135.6° is toward the small end of the range 135.2°–139.6° for the permethylzirconocene complexes [11,14–16]. The somewhat long Zr–Cp\* and Zr–Cl distances and the small Cp\*–Zr–Cp\* angle may also be due to the effect of strong Zr–O π bonding.

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Table 3

Selected bond lengths (Å) and bond angles (°) for complex **2**

Zr–O	1.930(3)	Zr–C1	2.471(2)
O–C(21)	1.399(7)	C(21)–C(22)	1.525(10)
C(22)–C(23)	1.417(11)	C(23)–S	1.837(9)
Zr–C(1)	2.551(5)	Zr–C(11)	2.570(5)
Zr–C(2)	2.605(5)	Zr–C(12)	2.571(5)
Zr–C(3)	2.590(5)	Zr–C(13)	2.599(5)
Zr–C(4)	2.552(5)	Zr–C(14)	2.570(5)
Zr–C(5)	2.515(5)	Zr–C(15)	2.589(5)
Zr–Cp* 1 <sup>a</sup>	2.264	Zr–Cp* 2 <sup>a</sup>	2.283
Cp* 1–Zr–Cp* 2	135.6		
C1–Zr–O	96.2(1)	Zr–O–C21	172.5(3)

<sup>a</sup> Cp\* 1 = C(1)–C(5), Cp\* 2 = C(11)–C(15).