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Synthesis, Characterization, and Structures of Group IV Metallocene Complexes of Heterodifunctional Ligands Containing Oxygen and Sulfur Donor Atoms

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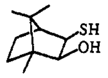
The interaction of the chiral difunctional ligand (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (1) with group IV metallocene complexes affords the product $Cp_2M(OC_{10}H_{16}S)$ (Cp = cyclopentadienyl; M = Ti (2) or Zr (3); $OC_{10}H_{16}S$ = (1*R*,2*S*,3*R*)-3-thio-1,7,7-trimethylbicyclo[2.2.1]heptan-2-olato). In $CDCl_3$ solution, complex 3 exists as a mixture of a monomeric species and an associated dimeric species. Complex 3 readily hydrolyzes to give an air-stable complex, $[Cp_2Zr(\mu\text{-}O)(\mu\text{-}OC_{10}H_{16}S)ZrCp_2)]$ (4). The complex 4 crystallizes in the orthorhombic space group $P2_12_12_1$ with cell parameters a = 10.061 (2) Å, b = 15.476 (4) Å, c = 17.741 (3) Å, V = 2762.4 (10) Å^3, R = 0.044, and R_w = 0.052. The complex 4 is an oxo-bridged zirconocene dimer that is also bridged by a heterodifunctional ligand. The Zr–O–Zr angle is small at 139.9 (2)°, and the Zr···Zr distance is 3.685 Å. Two zirconocene moieties are inequivalent due to the asymmetric difunctional ligand. The related complex $[Cp_2Zr(\mu\text{-}OCH_2CH_2S)]_2$ (5) was also prepared. Complex 5 crystallizes in the monoclinic space group $P2_1/c$ with cell parameters a = 16.730 (3) Å, b = 8.232 (2) Å, c = 17.570 (2) Å, β = 111.21 (2)°, V = 2255.9 (7) Å^3, R = 0.034, and R_w = 0.045. The complex 5 is a zirconocene dimer bridging through the oxygen atoms. The ZrOZrO framework is nearly planar with both sulfur atoms above the plane by ~0.45 Å, and the Zr···Zr distance at 3.719 Å is somewhat longer than that in complex 4.

Introduction

Difunctional ligands containing both oxygen or both sulfur donor atoms are interesting due to their capabilities to form metal complexes of a variety of structures. With group IV metallocenes, possible structures are monomeric structure **A**, open macrocycle dimeric structure **B**, twisted dimeric structure **C**, and associated dimeric structure **D** (Figure 1). The monomeric complexes[1] have been well studied. Recently, Stephan et al.[2] have reported the diol and the dithiol complexes which have the open macrocycle dimeric structure **B** or the twisted dimeric structure **C**.

Here, we report our study of the complexes which are prepared from the interaction of (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (1)[3] with group IV metallocenes. These complexes have the monomeric structure **A**, the weakly associated dimeric structure **D**, or the novel dimeric structure bridged by an oxo and one difunctional ligand. The related zirconocene complex $[Cp_2Zr[(\mu\text{-}OCH_2CH_2S)]_2$ (5) from the reaction of 2-mercaptoethanol with dialkylzirconocene was also prepared, and the molecular structure of 5 is that of a dimeric species of structure **C** with bridging oxygen atoms.



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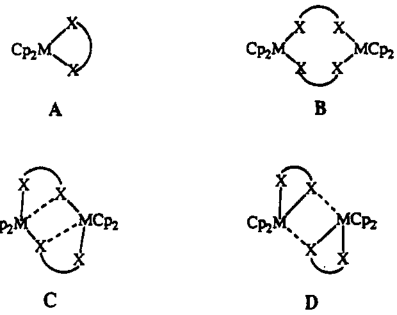

Figure 1. Possible structures for the complexes $[Cp_2M(XX)]_n$ (n = 1 or 2).

Experimental Section

Reagents and General Techniques. The difunctional ligand (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol[3] and $Cp_2Zr(CH_3)_2$[4] were prepared according to the literature procedures. Cp_2TiCl_2 (Aldrich) was used without further purification. NEt_3 (Merck) and $HOCH_2CH_2SH$ (Merck) were distilled and stored over molecular sieves. Solvents were dried by refluxing at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (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.

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Synthesis of Bis(cyclopentadienyl)[(1*R*,2*S*,3*R*)-1,7,7-trimethyl-3-thiobicyclo[2.2.1]heptan-2-olato-*S*,*O*]titanium(IV) (2). Cp_2TiCl_2 (0.249 g, 1.0 mmol) in a solution of 10 mL of dichloromethane was added dropwise to a solution of NEt_3 (0.35 mL, 2.5 mmol) and (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (0.186 g, 1.0 mmol) in 30 mL of dichloromethane. The solution, which changed color from red to green in 30 min, was stirred at room temperature in a dry dinitrogen atmosphere for 1.5 h. The solvent was removed in vacuo, and the residue was extracted with 30 mL of benzene. The extracted solution was pumped to dryness to give a brownish-green solid which was then dissolved in 5 mL of dichloromethane. The solution was layered with 20 mL of hexane and then cooled to −80 °C to afford a green crystalline material (0.12 g, 33.1%). EI-MS; m/z = 362.1184. ^1H NMR ($CDCl_3$): δ 6.44 (s, 5 H), 6.41 (s, 5 H), 5.04 (d, 1 H), 4.71 (d, 1 H), 1.66 (s, 3 H), 0.72 (s, 3 H), 0.61 (s, 3 H) ppm. (Other ^1H resonances are not assigned.) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 116.3 (Cp), 114.5 (Cp), 103.4 (HCO), 79.2 (HCS), 55.2, 51.8, 47.6, 33.3, 28.6, 22.6, 21.9, 11.3 ppm. Anal. Calcd for $C_{20}H_{26}OSTi$: C, 66.29; H, 7.23. Found: C, 66.13; H, 7.28.

Synthesis of Bis(cyclopentadienyl)[(1*R*,2*S*,3*R*)-1,7,7-trimethyl-3-thiobicyclo[2.2.1]heptan-2-olato-*S*,*O*]zirconium(IV) (3). The reaction apparatus was carefully dried by thoroughly heating in vacuo. A mixture of $Cp_2Zr(CH_3)_2$ (0.251 g, 1.0 mmol) and (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (0.186 g, 1.0 mmol) was placed in a reaction vessel, and 40 mL of diethyl ether was added by vacuum transfer. The reaction mixture was stirred at room temperature under a dry dinitrogen atmosphere for 5 h and then was filtered to give a white powder. This white powder contained major product 3 with a purity of about 90% based on the ^1H NMR and a minor hydrolyzed complex 4. 3 $(C_5H_5)_2Zr(OC_{10}H_{16}S)$. EI-MS: m/z = 404.0751. ^1H NMR ($CDCl_3$, 4.80×10^{-3} M): δ 6.35 (s, Cp), 6.33 (s, Cp), 4.36 (d, CH), 3.84 (d, CH), 1.46 (s, CH_3), 0.75 (s, CH_3), 0.74 (s, CH_3) ppm. ^1H NMR ($CDCl_3$, 2.4×10^{-2} M): 6.29 (s, Cp), 6.28 (s, Cp), 4.23 (d, CH), 3.62 (d, CH), 1.41 (s, CH_3), 0.764 (s, CH_3), 0.757 (s, CH_3) ppm.

Synthesis of (μ-Oxo)[μ-(1*R*,2*S*,3*R*)-1,7,7-trimethyl-3-thiobicyclo[2.2.1]heptan-2-olato-*S*,*O*]bis[bis(cyclopentadienyl)zirconium(IV)] (4). A mixture of $Cp_2Zr(CH_3)_2$ (0.503 g, 2.0 mmol) and (1*R*,2*S*,3*R*)-3-mercapto-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (0.186 g, 1.0 mmol) in 20 mL of diethyl ether was stirred at room temperature for 20 h. The precipitated product was filtered, and the resulting pale yellow powder was washed with 5 mL of diethyl ether to afford a white solid (0.333 g, 52.0% yield). An analytically pure sample was obtained by recrystallization from dichloromethane/hexane solution. ^1H NMR (CD_2Cl_2); δ 6.262 (s, 5 H), 6.202 (s, 5 H), 6.190 (s, 5 H), 6.186 (s, 5 H), 4.004 (d, 1 H), 3.460 (d, 1 H), 1.198 (s, 3 H), 0.817 (s, 3 H), 0.777 (s, 3 H) ppm. (Other ^1H resonances are not assigned.) $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 112.0 (Cp), 111.9 (Cp), 111.6 (Cp), 110.8 (Cp), 93.1, 59.4, 56.9, 51.0, 47.0, 34.1, 29.8, 22.7, 22.1, 13.0 ppm. Anal. Calcd for $C_{30}H_{36}O_2SZr_2$: C, 56.03; H, 5.64. Found: C, 56.10; H, 5.65.

Synthesis of Bis[bis(cyclopentadienyl)(μ-2-thioethoxo)zirconium(IV)] (5). $Cp_2Zr(CH_3)_2$ (0.84 g, 3.34 mmol) was dissolved in 30 mL of diethyl ether, and then 2-mercaptoethanol (0.26 g, 3.34 mmol) was added. The mixture was stirred at room temperature in a dry dinitrogen atmosphere for 6 h, and the resulted precipitate was filtered to give a white powder of crude product (0.82 g) which contained a trace of impurities. Colorless crystals were obtained by recrystallization of a small portion of the crude product from dichloromethane/hexane solution. ^1H NMR ($CDCl_3$): δ 6.08 (s, Cp), 3.95 (t, J_{HH} = 5.4 Hz, OCH_2), 2.75 (t, J_{HH} = 5.4 Hz, SCH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 111.7 (Cp), 78.9 (OCH_2), 34.1 (SCH_2) ppm.

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 the 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 Joel JMS-SX/SX 102A instrument.

Table I. Crystallographic Data for Complexes 4 and 5

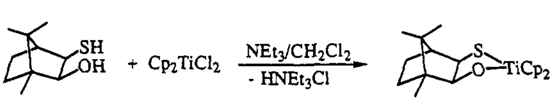
compd	4	5
formula	$C_{30}H_{36}O_2SZr_2$	$C_{24}H_{28}O_2S_2Zr_2$
Fw	643.1	595.0
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a, Å	10.061(2)	16.730(3)
b, Å	15.476(4)	8.232(2)
c, Å	17.741(3)	17.570(2)
β, deg		111.21(2)
V, Å^3	2762.4(10)	2255.9(7)
Z	4	4
D_{calcd}, g·cm^{-3}	1.546	1.752
λ(Mo Kα), Å	0.710 69	0.710 73
μ, cm^{-1}	8.39	11.28
range, deg	4.0–60.0	3.5–60.0
scan type	$\theta/2\theta$	$\theta/2\theta$
no. of reflctns collctd	3906	7054
no. of independt reflctns	3876 (R_{int} = 0.79%)	6421 (R_{int} = 4.07%)
no. of obsd reflctns	3149 ($I > 2.0\sigma(I)$)	4521 ($I > 2.0\sigma(I)$)
no. of refined parameters	316	271
R_f[a] for significant reflctns	0.044	0.034
R_w[b] for sigft reflctns	0.052	0.045
GoF[c]	1.17	1.00

[a] $R_f = [\sum(F_o - F_c)/\sum F_o]$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_0^2]^{1/2}$. [c] $\mathrm{GoF} = [\sum w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

Crystal Structure Determinations. A colorless crystal of 4 of size 0.10 × 0.50 × 0.60 mm and a colorless crystal of 5 of size 0.10 × 0.35 × 0.40 mm were used for X-ray diffraction studies. The diffraction intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation, λ = 0.710 69 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 each 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 were considered as riding atom on the carbon atom 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 of the complexes 4 and 5 are summarized in Table I.

Results and Discussion

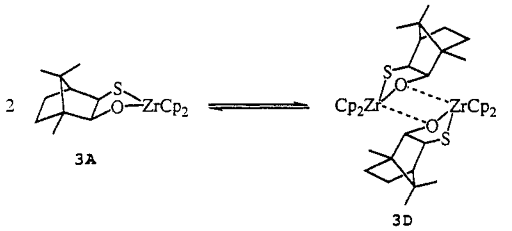
Synthesis and Characterizations. Compound 1 is a chiral difunctional ligand derived from (+)-camphor and contains heterodonor atoms of oxygen and sulfur. Treatment of 1 with 1 molar equiv of titanocene dichloride in the presence of triethylamine affords a green product 2 (eq 1) which is a monomeric complex in the gas phase



1 2

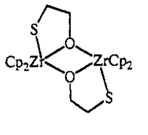
(1)

according to our mass spectrometric study. Complex 2 decomposes either in the solid state or in solution to give a mixture of several unidentified products. The ^1H and ^{13}C NMR of the complex 2 show two resonances for the two magnetically inequivalent Cp's because of the influence of the asymmetric difunctional ligand. The reaction of 1 with 1 molar equiv of dimethylzirconocene under rigorously dry conditions gives a white product 3 of about 90% purity. Complex 3 is extremely moisture sensitive, and thoroughly dried reaction vessels and reagents are essential for the preparation of this compound. The mass spectrum indicates that complex **3** is a monomer in the gas phase. However, in $CDCl_3$ solution this complex exists in the form of a mixture of monomeric species of structure **A** and a weakly associated dimeric species of structure **D** (eq 2).



(2)

These two species are in equilibrium, and the observed ^1H chemical shifts varied with the change of concentration of the material. In a $CDCl_3$ solution at a concentration of 4.80×10^{-3} M, the complex **3** exhibits two Cp resonances at δ 6.35 and 6.33 ppm. However, in a more concentrated solution (2.40×10^{-2} M), the Cp resonances shift upfield to δ 6.29 and 6.28 ppm. This observation indicates more electron donation[5] from the difuntional ligands to the metal, which is consistent with the presence of more dimeric species at higher concentration. Although the sulfur bridging complexes are known for the dithiol complexes **6** and **7**,[2] the association via the oxygen atoms to form **3D** in solution seems more likely since the oxygen donors are better in bonding to group IV transition metals than the sulfur donors. Further support for the proposed dimeric structure **3D** is provided by the X-ray structures of the complexes **5** and **8**[6] which have the same ligand skeleton OCHR′CHR″S as the ligand in complex **3**.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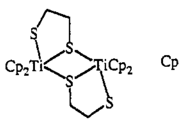
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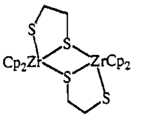
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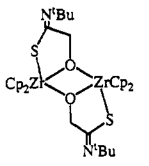
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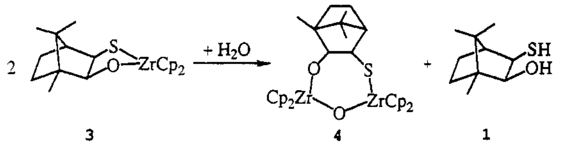
Complex **3** reacts readily with moisture in the air to give the air-stable complex **4** as the major product (eq 3).



(3)

Because of the asymmetry of the ligand, all four Cp ligands in the complex **4** are inequivalent in NMR environments.

The structure of the complex **3** and the formation of the complex **4** are outlined in Scheme I, and the electronic state and the steric factor of these structures are discussed based on the spectral and the structural data of the complexes **3** and **4**. The complex **3A** is an electronically unsaturated 16 e^- species, and the formation of the complex **3C** through oxygen-bridging to achieve 18 e^- around Zr metal centers is expected to be favored. However, the structural rigidity and crowdedness of the asymmetric ligand prevents the formation of **3C**. The formation of the complex **3B** is unfavorable since an unlikely large S–Zr–O angle at ~160° (estimated from the molecular structure of complex **4**) is expected. The complex **3A** does equilibrate in $CDCl_3$ solution with the weakly associated dimeric species **3D**. However, even with the weak association through oxygen atoms, the complex **3D** is still electronically unsatisfied around the Zr metal center. Therefore, the hydrolyzed, air-stable complex **4** is an alternative product when the complexes **3A** and/or **3D** are exposed to air. Apparently, complex **4** is more thermodynamically favorable than the complexes in the forms of **3A**, **3B**, **3C**, or **3D**.

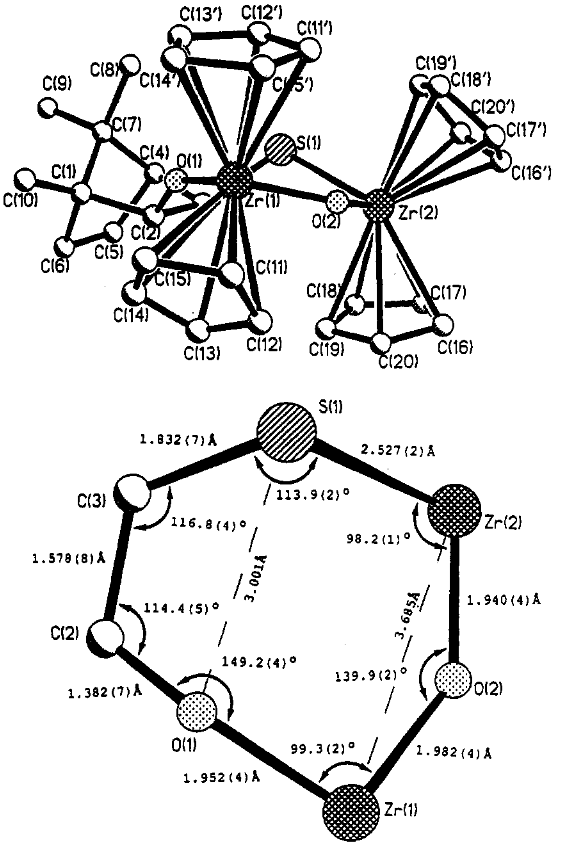


Figure 2. Molecular structure of the complex **4** and the selected bond lengths and bond angles. $(Zr(1)–Cp)_{ave} = 2.273$ Å, $(Zr(2)–Cp)_{avg} = 2.253$ Å, ∠Cp–Zr(1)–Cp = 126.7°, and ∠Cp–Zr(2)–Cp = 127.8°.

Scheme I

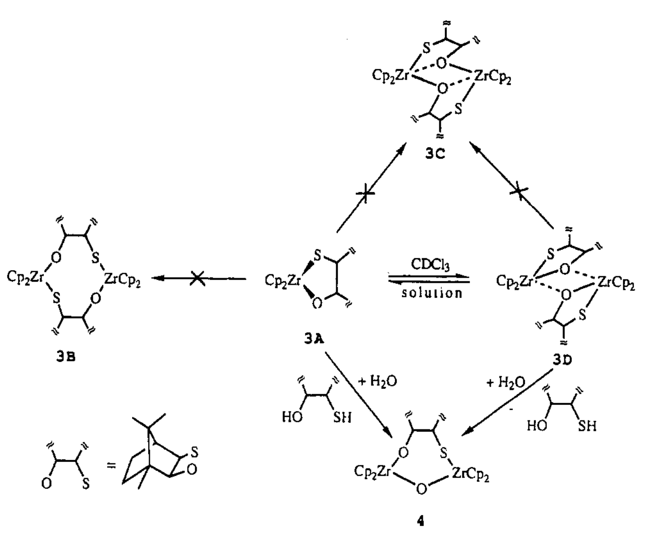


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Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) of Complex 4

	x	*y*	*z*	*U*(eq)
Zr(1)	0.6277(1)	–0.0244(1)	0.7430(1)	0.026(1)
Zr(2)	0.8441(1)	0.1160(1)	0.8575(1)	0.032(1)
S(1)	0.7721(2)	0.0044(1)	0.9531(1)	0.034(1)
O(1)	0.5610(4)	–0.0507(3)	0.8437(2)	0.033(1)
O(2)	0.7598(4)	0.0657(3)	0.7694(2)	0.033(1)
C(1)	0.4129(7)	–0.0960(4)	0.9478(3)	0.035(2)
C(2)	0.4972(6)	–0.0237(5)	0.9086(3)	0.031(2)
C(3)	0.5937(6)	0.0060(4)	0.9738(3)	0.031(2)
C(4)	0.5551(6)	–0.0535(5)	1.0391(3)	0.035(2)
C(5)	0.4233(8)	–0.0212(6)	1.0694(4)	0.049(2)
C(6)	0.3246(7)	–0.0480(6)	1.0048(4)	0.053(3)
C(7)	0.5157(7)	–0.1403(5)	1.0008(4)	0.040(2)
C(8)	0.6284(8)	–0.1870(5)	0.9610(4)	0.049(2)
C(9)	0.4548(10)	–0.2054(6)	1.0568(5)	0.066(3)
C(10)	0.3377(8)	–0.1519(5)	0.8923(4)	0.053(2)
C(11)	0.5217(10)	0.0345(9)	0.6241(4)	0.075(4)
C(12)	0.5241(11)	0.1025(7)	0.6737(8)	0.083(4)
C(13)	0.4397(13)	0.0853(8)	0.7312(6)	0.081(4)
C(14)	0.3857(9)	0.0091(10)	0.7168(7)	0.092(5)
C(15)	0.4288(10)	–0.0226(7)	0.6536(7)	0.071(3)
C(11′)	0.8403(7)	–0.0984(4)	0.6958(5)	0.046(4)
C(12′)	0.8066(8)	–0.1405(4)	0.7630(4)	0.046(4)
C(13′)	0.6898(8)	–0.1853(4)	0.7497(5)	0.049(3)
C(14′)	0.6482(8)	–0.1707(5)	0.6760(5)	0.050(3)
C(15′)	0.7440(9)	–0.1160(5)	0.6429(4)	0.050(3)
C(16)	0.8198(12)	0.2783(5)	0.8458(7)	0.078(2)
C(17)	0.8313(11)	0.2634(5)	0.9244(6)	0.072(2)
C(18)	0.7205(12)	0.2188(5)	0.9456(5)	0.064(2)
C(19)	0.6391(9)	0.2065(5)	0.8837(5)	0.059(2)
C(20)	0.7002(10)	0.2443(5)	0.8224(5)	0.056(2)
C(16′)	1.0846(9)	0.1629(7)	0.8591(9)	0.080(4)
C(17′)	1.0687(10)	0.1167(12)	0.7942(7)	0.095(5)
C(18′)	1.0461(9)	0.0350(10)	0.8152(10)	0.096(6)
C(19′)	1.0499(8)	0.0312(8)	0.8920(9)	0.088(5)
C(20′)	1.0730(9)	0.1136(9)	0.9167(6)	0.075(4)

Table III. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) of Complex 5

	x	*y*	*z*	*U*(eq)
Zr(1)	0.1770(1)	–0.0691(1)	–0.1076(1)	0.026(1)
Zr(2)	0.3361(1)	0.0546(1)	0.0938(1)	0.024(1)
S(1)	0.1039(1)	–0.3326(2)	–0.0806(1)	0.065(1)
S(2)	0.4462(1)	0.2454(1)	0.0648(1)	0.040(1)
O(1)	0.2232(2)	–0.0983(3)	0.0255(1)	0.032(1)
O(2)	0.2838(2)	0.0969(3)	–0.0385(1)	0.028(1)
C(1)	0.0666(3)	0.1274(9)	–0.0873(3)	0.085(3)
C(2)	0.0205(3)	0.0066(9)	–0.1426(4)	0.078(2)
C(3)	0.0378(3)	0.0238(7)	–0.2138(3)	0.066(2)
C(4)	0.0953(3)	0.1536(6)	–0.2021(3)	0.065(2)
C(5)	0.1120(3)	0.2169(6)	–0.1244(3)	0.073(2)
C(6)	0.2592(3)	–0.3029(6)	–0.1396(3)	0.055(2)
C(7)	0.1809(3)	–0.2955(6)	–0.2054(3)	0.057(2)
C(8)	0.1793(3)	–0.1547(7)	–0.2473(2)	0.059(2)
C(9)	0.2554(3)	–0.0695(6)	–0.2072(3)	0.056(2)
C(10)	0.3047(3)	–0.1658(6)	–0.1414(3)	0.053(2)
C(11)	0.2382(3)	0.2972(5)	0.0994(3)	0.048(2)
C(12)	0.3207(3)	0.3337(5)	0.1536(3)	0.045(2)
C(13)	0.3441(3)	0.2184(5)	0.2172(2)	0.044(1)
C(14)	0.2745(3)	0.1135(6)	0.2028(3)	0.050(2)
C(15)	0.2090(3)	0.1620(6)	0.1311(3)	0.055(2)
C(16)	0.4578(3)	–0.1355(6)	0.0971(3)	0.049(2)
C(17)	0.4899(3)	–0.0405(5)	0.1700(3)	0.046(1)
C(18)	0.4453(3)	–0.0882(5)	0.2198(2)	0.048(1)
C(19)	0.3842(3)	–0.2037(5)	0.1783(3)	0.048(2)
C(20)	0.3940(3)	–0.2344(5)	0.1026(2)	0.049(2)
C(21)	0.1024(3)	–0.2665(7)	0.0161(3)	0.062(2)
C(22)	0.1024(3)	–0.2665(7)	0.0161(3)	0.062(2)
C(23)	0.3686(3)	0.3417(5)	–0.0224(2)	0.045(1)
C(24)	0.3194(3)	0.2113(5)	–0.0799(2)	0.042(1)

The complex $[Cp_2Zr(\mu\text{-}OCH_2CH_2S)]_2$ (**5**) was prepared as a white precipitate by the reaction of dimethylzirconocene with 1 molar equiv of 2-mercaptoethanol in diethyl ether. The crude product contained traces of unidentified impurities and was sparingly soluble in organic solvents. The insolubility of the complex indicated that an oligomeric species was obtained.

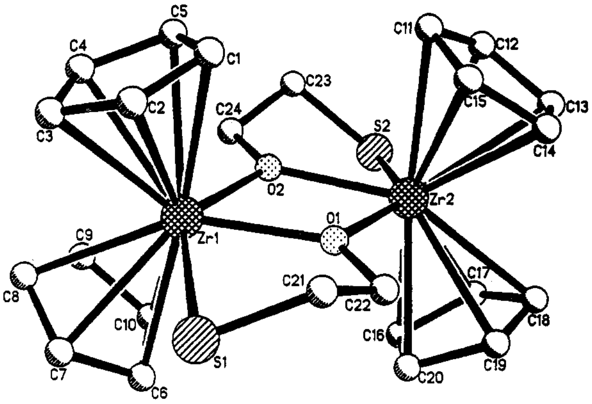

Figure 3. Molecular structure of complex **5**.

The ^1H and ^{13}C NMR of the methylene group attached to the oxygen donor atom in $[Cp_2Zr[\mu\text{-}OCH_2CH_2S)]_2$ shift downfield by 0.21 and 14.95 ppm, respectively, relative to the chemical shifts of the free ligand. The chemical shifts of the methylene attached to the sulfur atom also shift downfield but with less extent, by 0.02 and 6.5 ppm, respectively. This result is an indication of the coordination of oxygen and sulfur atoms to zirconium.

Molecular Structure of Complex 4. The complex **4** was crystallized from dichloromethane/hexane solution as colorless crystals, and the structure of the complex was determined by X-ray diffraction. The molecular structure of **4** with selected bond distances and bond angles is shown in Figure 2, and the final atomic coordinates and the isotropic displacement coefficients are listed in Table II. The Zr(1)–O(1) bond distance at 1.951 (4) Å and the Zr(2)–S(1) bond distance at 2.527 (2) Å appears to be normal compared to those of the zirconocene complexes of alkoxide[7,8] and dithiolate.[2] The two zirconocene moieties are structurally different owing to their bonding to different donor atoms. The less electron donation from the S(1) atom to the Zr(2) metal is compensated by shortening the Zr(2)–Cp and the Zr(2)–O(2) bonds by a value of 0.02 and 0.04 Å relative to the Zr(1)–Cp and Zr(1)–O(2) bonds, respectively. The O(1)–Zr(1)–O(2) plane and the S(1)–Zr(2)–O(2) plane are not coplanar with a dihedral angle of 20.7°. The Zr(1)–O(2)–Zr(2) angle at 139.9° in the complex **4** is rather small. The only complex with smaller angle at 119.2 (2)° is $Cp'_2Zr(\mu\text{-}Te)(\mu\text{-}O)ZrCp'_2$[9] ($Cp' = C_5H_4{}^tBu$). This small angle is caused mostly by the short O(1)···S(1) distance (at 3.001 Å) of the rigid ligand. Besides the small Zr–O–Zr angle, the effects of the short O(1)···S(1) distance have also been revealed on several observations: (1) the enlarging of the O(1)–C(2)–C(3) and the S(1)–C(3)–C(2) angles of the difunctional ligand in the molecular structure of **4** by ~4 and ~7° relative to the value of 110° found for the related camphor-derived compound,[10] (2) the slight elongation by ~0.03 Å of the C(2)–C(3) bond that bridges the oxygen and sulfur donors, and (3) the relatively short nonbonded Zr(1)···Zr(2) distance at 3.685 Å. The μ-oxometallocene complexes $(Cp_2MX)_2O$ usually exhibit a nearly linear

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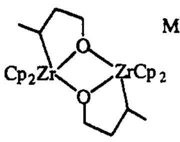
Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) of $[Cp_2Zr(\mu\text{-}OCH_2CH_2S)]_2$ (5)[a]

Zr(1)–O(1)	2.195(2)	Zr(2)–O(1)	2.225(2)
Zr(1)–O(2)	2.229(2)	Zr(2)–O(2)	2.195(2)
Zr(1)–S(1)	2.617(2)	Zr(2)–S(2)	2.606(1)
O(1)–C(22)	1.439(6)	O(2)–C(24)	1.442(5)
S(1)–C(21)	1.792(5)	S(2)–C(23)	1.795(4)
C(21)–C(22)	1.477(6)	C(23)–C(24)	1.500(5)
Zr(1)–Cp(1)	2.253	Zr(2)–Cp(3)	2.271
Zr(1)–Cp(2)	2.259	Zr(2)–Cp(4)	2.265
S(1)–Zr(1)–O(1)	73.9(1)	S(2)–Zr(2)–O(2)	74.7(1)
O(1)–Zr(1)–O(2)	65.3(1)	O(1)–Zr(2)–O(2)	65.4(1)
Zr(1)–O(1)–Zr(2)	114.6(1)	Zr(1)–O(2)–Zr(2)	114.4(1)
Cp(1)–Zr(1)–Cp(2)	123.0	Cp(3)–Zr(2)–Cp(4)	123.1

[a] Cp(1) = C(1–5), Cp(2) = C(6–10), Cp(3) = C(11–15), Cp(4) = C(16–20).

M–O–M angle for better π interaction.[11] It might be expected that the small M–O–M angle would decrease the π interaction between the metals and the bridging oxo. However, the average Zr–O(bridging) distance at 1.962 Å in 4 is in the range of 1.94–1.968 Å typically for the $(Cp_2ZrX)_2O$ complexes.[12-15] In $Cp'_2Zr(\mu\text{-}Te)(\mu\text{-}O)ZrCp'_2$ the average Zr–O distance is 1.967 (7) Å and the Zr–O–Zr angle is 119.2 (2)°. It seems that the M–O–M angle is rather flexible in terms of the M–O π-bonding capability.

Molecular Structure of Complex 5. The final coordinates and the equivalent isotropic displacement coefficients of complex 5 are listed in Table III, and the molecular structure is shown in Figure 3. The selected bond lengths and bond angles are listed in Table IV. The molecular structure of 5 shows a dimeric species bridged by the oxygen atoms and this structure is similar to the structure of the dimeric complexes 8 and 9.[16] The average Zr–S distance at 2.612 Å is similar to those in 7 (2.609 Å) and 8 (2.633 Å) but longer than the values in 4 by ~0.1 Å. The average Zr–O(bridging) distance is 2.221 Å, and the elongation of Zr–O distances by 0.3 Å relative to the Zr–O(terminal) bond length is a usual feature for the bridging alkoxide complexes of similar structure like complex 8 (2.196 Å) and complex 9 (2.212 Å). The similar Zr–O distances are also found in complex 10[17] (2.185 Å) and complex 11[18] (2.165 Å). The Zr_2O_2 framework is nearly in a plane with both sulfur atoms above the plane by ~0.45 Å. The O–Zr–O angles at 65.3 (1) and 65.4 (1)° and the Zr–O–Zr angles at 114.6 (1) and 114.4 (1)° are comparable to the values found in the related compounds.[6,16,17] The Zr···Zr distance at 3.719 Å is somewhat longer by 0.03 Å than that in complex 4.



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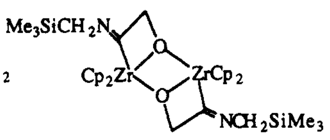

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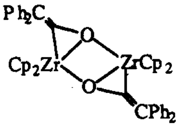

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Supplementary Material Available: Tables of crystallographic data, final coordinates, bond lengths, bond angles, and anisotropic displacement coefficients of complexes 4 and 5 (19 pages). Ordering information is given on any current masthead page.

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