

C–S Bond Cleavage in CpRu(PPh₃)₂SCH₂CH=CH₂ To Give the Trimer (CpRu)₃(μ₃-S)₂(μ-SCH₂CH=CH₂)

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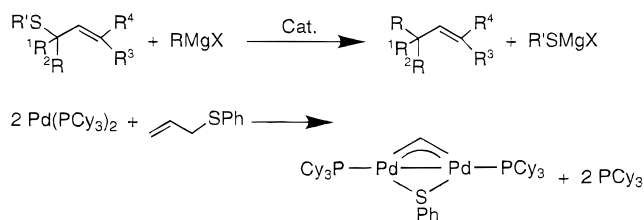
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Introduction

Cleavage of the carbon–sulfur bond is important in biological systems¹ and industrial applications.² Particularly relevant is the removal of sulfur from organosulfur compounds in crude oil via hydrodesulfurization;³ the largest industrial application of transition metal catalysis presently practiced.⁴

Allylic carbon–sulfur bond cleavage reactions,⁵ and those of allylic–oxygen and allylic–halogen bonds,⁶ are useful in synthetic organic chemistry. An important example is the synthesis of alkenes by the reaction of allylic sulfides with Grignard reagents⁵ catalyzed by Ni, Pd, and Au(I) salts.⁷ The π -allyl intermediate (μ -Sph)(μ -C₃H₇)[PCy₃Pd]₂ has been isolated from the reaction of Pd(PCy₃)₂ with allylphenyl sulfide.^{5c}



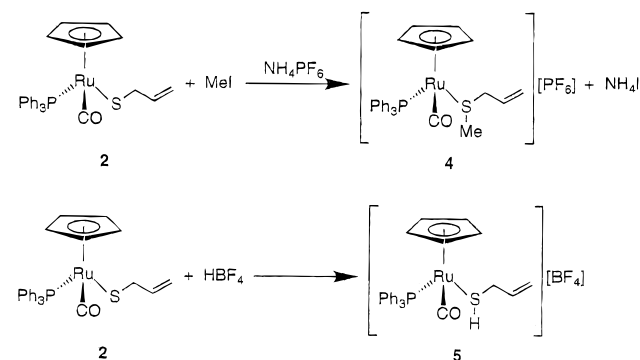
The reactivity of the electron-rich ruthenium thiolates CpRu(PPh₃)₂SR⁸ prompted the preparation of the complex CpRu-

(PPh₃)₂SCH₂CH=CH₂, **1**. When this complex was heated in toluene, carbon–sulfur bond cleavage occurred to give (CpRu)₃(μ₃-S)₂(μ-SCH₂CH=CH₂).

Results

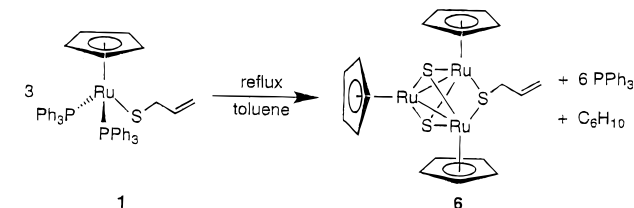
When CpRu(PPh₃)₂Cl was briefly refluxed with excess LiSCH₂CH=CH₂ in THF, the complex **1** was obtained in 81% yield. When CO gas was bubbled through a THF solution of **1**, the complex CpRu(PPh₃)(CO)SCH₂CH=CH₂, **2**, was produced. Compound **1** reacted easily with CS₂ to give the thioxanthate complex CpRu(PPh₃)S₂CSCH₂CH=CH₂, **3**, in which a CS₂ molecule has inserted into the Ru–S bond. These reactions are analogous to those reported for the simple Ru–thiolate complexes CpRu(PPh₃)₂SR.^{8a}

Complex **2** reacted with MeI in the presence of NH₄PF₆ to give the salt [CpRu(PPh₃)(CO)MeSCH₂CH=CH₂][PF₆], **4**, in



very good yield (81%). Compound **2** also reacted with HBF₄ in THF at room temperature to give the thiol complex salt [CpRu(PPh₃)(CO)HSCH₂CH=CH₂][BF₄], **5**. Thus the chemistry of **2** is similar to that of the simple thiolate complexes, CpRu(PPh₃)(CO)SR.⁹ The presence of two chiral centers in **4** and **5** should generate diastereomerism. The NMR spectrum of **4** revealed a broad single peak for the methyl group, and that of **5** gave only one multiplet for the SH proton due to phosphorus proton coupling. This is consistent with relatively rapid inversion at the sulfur atom.

Compound **1** underwent C–S bond cleavage in addition to the loss of both PPh₃ ligands in refluxing toluene to give the trimer (CpRu)₃(μ₃-S)₂(μ-SCH₂CH=CH₂), **6**, in 42% yield.



Complex **6** is air stable and soluble in THF, benzene, and ether. Its ¹H NMR spectrum showed two peaks in the Cp region in the ratio of 2:1. The crystal structure of **6** is presented in Figure 1. The two sulfur atoms triply bridge the ruthenium atoms and the one thiolate group bridges two of the ruthenium atoms. The Ru–Ru bond lengths of 2.800(1) and 2.780(2) Å are longer than the corresponding average length in the trimer^{8b} (CpRu-

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stirred for 3 h. A yellow precipitate was formed during that time which was collected by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3×5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 73%). Mp: 181–183 °C. IR (KBr disk): $\nu_{\text{CO}} = 1991$ (s) cm^{-1} . ^1H NMR (acetone- d_6): 2.36 (s, 3H, CH_3), 3.50 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.29 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.36 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.56 (s, 5H, Cp), 5.70 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.44 (m, 9H, PPh₃), 7.63 (m, 6H, PPh₃). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{F}_6\text{OP}_2\text{RuS}$: C, 48.76; H, 4.09. Found: C, 48.01; H, 4.16.

[CpRu(PPh₃)(CO)HSC₂H=CH₂)]BF₄, 5. In a 100-mL Schlenk flask, **2** (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL) and $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.069 mL, 0.40 mmol) was added. The reaction mixture was stirred for 30 min. The solution was reduced in volume to 3.0 mL, and 10.0 mL of diethyl ether was added. A yellow precipitate was formed, which was collected by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3×5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 81%). Mp: 162–164 °C. IR (KBr disk): $\nu_{\text{CO}} = 1991$ (s), 1979 (m) cm^{-1} , $\nu_{\text{SH}} = 2508$ (w) cm^{-1} . ^1H NMR (acetone- d_6): 3.40 (tt, 3H, $\text{CH}_2\text{CH}=\text{CH}_2$, SH, $J(\text{H}-\text{H}) = 2.3$ Hz, $J(\text{P}-\text{H}) = 6.6$ Hz), 5.25 (dd, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$, $^1J(\text{H}-\text{H}) = 1.8$ Hz, $^3J(\text{H}-\text{H}) = 8.8$ Hz), 5.35 (dd, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$, $^1J(\text{H}-\text{H}) = 1.8$ Hz, $^3J(\text{H}-\text{H}) = 15.6$ Hz), 5.50 (s, 5H, Cp), 5.80 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.42 (m, 9H, PPh₃), 7.56 (m, 6H, PPh₃). Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{BF}_4\text{OPRuS}$: C, 52.52; H, 4.24. Found: C, 52.30; H, 4.35.

(CpRu)₃($\mu_3\text{-S}$)₂($\mu\text{-SCH}_2\text{CH}=\text{CH}_2$), 6. A solution of **1** (0.50 g, 0.65 mmol) in toluene (50.0 mL) was prepared in a Schlenk flask fitted with a reflux condensor. The solution was refluxed for 3 h and was allowed to cool. The solution was reduced in volume to about 3 mL and was chromatographed on alumina (20 mm \times 30 cm). Elution with hexanes removed PPh₃. Elution with THF in hexanes (1:4) gave a brown fraction which was collected and stripped to dryness. Recrystallization from benzene/hexanes gave brown crystals (0.058 g, 42%). Mp: 177–179 °C. ^1H NMR (C_6D_6): 2.79 (d, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$, $J(\text{H}-\text{H}) = 7.3$ Hz), 4.46 (s, 10H, Cp), 4.78 (s, 5H, Cp), 4.95 (dd, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$, $^1J(\text{H}-\text{H}) = 1.9$ Hz, $^3J(\text{H}-\text{H}) = 9.9$ Hz), 5.01 (dd, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$, $^1J(\text{H}-\text{H}) = 1.9$ Hz, $^3J(\text{H}-\text{H}) = 17.1$ Hz), 5.93 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$). Anal. Calcd for $(\text{C}_{18}\text{H}_{20}\text{Ru}_3\text{S}_3)$: C, 33.99; H, 3.17; S, 15.12. Found: C, 34.51; H, 3.28; S, 14.52.

Table 1. Crystallographic Data for $(\text{CpRu})_3(\mu_3\text{-S})_2(\mu\text{-SCH}_2\text{CH}=\text{CH}_2)$

chem formula: $\text{C}_{18}\text{H}_{20}\text{S}_3\text{Ru}_3$	$Z = 4$
fw = 635.75	$d_{\text{calc}} = 2.199 \text{ g cm}^{-3}$
space group: $P2_1/c$ (No. 14)	$\lambda = 1.54178 \text{ \AA}$
$a = 12.358(2) \text{ \AA}$	$\mu(\text{Cu K}\alpha) = 223.57 \text{ cm}^{-1}$
$b = 10.876(2) \text{ \AA}$	$T = 20 \text{ }^\circ\text{C}$
$c = 15.817(2) \text{ \AA}$	$R_1^a = 0.058, 0.086$ ($I > 2\sigma(I)$, all)
$\beta = 116.36(1)^\circ$	$\omega R_2^b = 0.168, 0.184$ ($I > 2\sigma(I)$, all)
$V = 1920.3(5) \text{ \AA}^3$	

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b \omega R_2 = [\sum \omega(F_o^2 - F_c^2) / \sum \omega(F_o^2)]^{1/2}.$$

X-ray Structure Determination for 6 (Table 1). A dark plate crystal (0.100 \times 0.010 \times 0.500 mm) was mounted on glass fiber. Cell dimensions were obtained from 20 reflections with 2θ in the range 95.0–100.0°. Intensity measurements were made using a Rigaku AFC6S diffractometer with graphite-monochromated Cu K α radiation. A total of 3910 reflections were collected ($h, k, \pm l$) using the $\omega/2\theta$ scan technique to a maximum 2θ value of 140°; of these 3507 were unique (merging $R = 5.0\%$, decay = 1.7%). The data were processed and corrected for absorption (ψ scans, transmission range 0.161–1.000) using the Teksan system of crystallographic computer programs. The structure was solved by the Patterson methods and refined on F^2 using Shelx196. The Cp ring on Ru(2) was found to be disordered over two orientations of related occupancy 0.55 and 0.45. The non-hydrogen atoms were refined anisotropically except for those in the disordered Cp ring. All hydrogen atoms were added in calculated positions. These atoms were kept isotropic. The structure was checked for missed symmetry and solvent-containing areas using Platon. Details of the programs used are given in the Supporting Information.

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Supporting Information Available: : An X-ray crystallographic file in CIF format for complex **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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