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

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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}

$$2 \operatorname{Pd}(\operatorname{PCy_3})_2 + \operatorname{SPh} \longrightarrow \operatorname{Cy_3P-Pd} \operatorname{Pd-PCy_3} + 2 \operatorname{PCy_3} \operatorname{Ph}$$

The reactivity of the electron-rich ruthenium thiolates $CpRu-(PPh_3)_2SR^8$ prompted the preparation of the complex $CpRu-(PPh_3)_2SR^8$

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(PPh₃)₂SCH₂CH=CH₂, **1**. When this complex was heated in toluene, carbon–sulfur bond cleavage occurred to give (CpRu)₃- $(\mu_3$ -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 NH_4PF_6 to give the salt $[CpRu(PPh_3)(CO)MeSCH_2CH=CH_2)]PF_6$, 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 thiolato 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 $(CpRu)_3(\mu_3-S)_2(\mu-SCH_2CH=CH_2)$, 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 thiolato 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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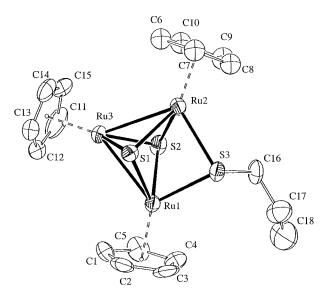


Figure 1. ORTEP drawing (40% probability level) of $(CpRu)_3(\mu_3-S)_2(\mu-SCH_2CH=CH_2)$, **6.** Selected bond lengths (Å) and angles (deg): Ru(1)-S(1), 2.366(3); Ru(1)-S(2), 2.339(3); Ru(1)-S(3), 2.404(3); Ru(2)-S(1), 2.361(3); Ru(2)-S(2), 2.351(3); Ru(2)-S(3), 2.389(3); Ru(3)-S(1), 2.231(3); Ru(3)-S(2), 2.220(3); Ru(1)-Ru(3), 2.800(1); Ru(2)-Ru(3), 2.780(1); Ru(3)-S(1)-Ru(2), 74.47(8); Ru(3)-S(1)-Ru(1), 74.99(8); Ru(2)-S(1)-Ru(1), 85.65(9); Ru(3)-S(2)-Ru(1), 75.74(9); Ru(3)-S(2)-Ru(2), 74.87(9); Ru(1)-S(2)-Ru(2), 86.49(9); Ru(2)-S(3)-Ru(1), 84.20(8); Ru(1)-Ru(3)-Ru(2), 70.30(3).

 μ_2 -SC₃H₇)₃ (average 2.715 Å) and similar to those observed in (CpRu)₃(μ -Cl)(μ_3 -S) (average 2.770 Å). ¹⁰ The Ru–S(allyl) bond lengths of 2.403(4) and 2.388(3) Å are longer than those in (CpRu- μ_2 SC₃H₇)₃ (average 2.296 Å). The Ru–S (triply bridged) bond lengths (average 2.353 Å) are longer than the corresponding lengths in (CpRu)₃(μ_3 -Cl)(μ_3 -S) (average 2.292 Å).

Discussion

The reactions of **1** are similar to those reported for other ruthenium thiolates of the type $CpRu(PPh_3)_2SR$, including the tendency to lose both phosphine ligands^{8b,c} to give trimers of the type $(CpRu-\mu_2-SR)_3$. However the presence of the allyl residue in **1** activates C-S bond cleavage.^{9c} The fate of the C_3 fragment was not determined. It may have dimerized to give hexadienes (C_6H_{10}) which are volatile and may have been lost during the reflux or the removal of the solvent. Warming **1** in toluene- d_8 in a NMR tube gave a NMR spectrum which contained several peaks in the ranges 2.5-3.0, 4.0-5.2, and 5.5-6.1 ppm consistent with the presences of hexadienes.

A possible reaction sequence might involve loss of PPh₃ and C-S bond cleavage to give a coordinatively unsaturated ruthenium sulfide species, CpRu(PPh₃)(=S), which could aggregate to give **6**. Similar species have been reported¹¹ such as Cp*₂Ta(CH₂R)(=S)¹² and Cp*₂Zr(py)(=S).¹³ The formation of the dimer Cp*Ir(PMe₃)(µ₂-S)IrCp*, which is postulated to involve aggregation of the species Cp*Ir(PMe₃)(=S)¹⁴ obtained via dehalogenation of Cp*Ir(PMe₃)(SH)Cl, is particularly relevant to the results reported here.

Experimental Section

All experiments were performed under nitrogen using vacuum lines and Schlenk techniques. Sa,b The complex CpRu(PPh₃)₂Cl was prepared according to the published procedure. Sallyl mercaptan (Aldrich) was distilled before use. Nuclear magnetic resonance spectra were recorded under nitrogen on a Varian XL-200 spectrometer. Chemical shifts are in ppm relative to TMS at 0 ppm. Infrared spectra were recorded on an Analect AQS-20 Fourier transform infrared (FT-IR) spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

CpRu(PPh₃)₂SCH₂CH=CH₂, 1. A three-neck round-bottom flask equipped with a reflux condenser was charged with THF (100.0 mL) and cooled to -78 °C in an ethanol/dry ice bath. Methyllithium (2.05 mL, 1.4 M in ether, 2.87 mmol) was added followed by allyl mercaptan (0.23 mL, 2.87 mmol). The cooling bath was removed, and the solution was warmed to 0 °C. The flask was immersed in a water bath at 40 °C for 15 min. The complex CpRu(PPh₃)₂Cl (1.00 g, 1.44 mmol) was added, and the resulting slurry was refluxed for 30 min. The volume of the mixture was concentrated under vacuum to about 50 mL, and ethanol (100.0 mL) was added. Further concentration to about 30 mL, followed by standing, gave the product as an orange solid which was collected by decanting the mother liquor. The solid was washed with ethanol and hexanes several times and dried in vacuo overnight (0.90 g, 81%). Mp: 128-130 °C. ¹H NMR (C₆D₆): 3.06 (d, 2H, CH₂CH= CH_2 , J(H-H) = 7.0 Hz), 4.38 (s, 5H, Cp), 5.02 (dd, 1H, $CH_2CH=$ CH_2 , ${}^{1}J(H-H) = 2.4 \text{ Hz}$, ${}^{3}J(H-H) = 9.8 \text{ Hz}$), 5.28 (dd, 1H, $CH_2CH =$ CH_2 , ${}^{1}J(H-H) = 2.4$ Hz, ${}^{3}J(H-H) = 16.9$ Hz), 6.80 (m, 1H, CH₂CH=CH₂), 7.30 (m, 18H, PPh₃), 7.40 (m, 12H, PPh₃). Anal. Calcd for C₄₄H₄₀P₂RuS: C, 69.17; H, 5.28; S, 4.20. Found: C, 69.32; H, 5.21; S, 4.36.

CpRu(PPh₃)(CO)SCH₂CH=CH₂, 2. In a 100-mL Schlenk flask, 1 (0.50 g, 0.65 mmol), was dissolved in THF (50.0 mL). CO gas was bubbled through the solution for 1 h, and the resulting yellow mixture was stirred under CO atmosphere for 5 h. The solution was reduced in volume to 2.0 mL and chromatographed on alumina (20 mm × 30 cm). Elution with hexanes removed PPh3. Elution with THF in hexanes (1:2) gave a yellow fraction which was collected and stripped to dryness. The resulting yellow solid was recrystallized from THF/ hexanes to give yellow crystals (0.30 g, 87%). Mp: 149-150 °C. IR (KBr disk): $\nu_{CO} = 1908$ (s), 1921 (sh) cm⁻¹. ¹H NMR (C₆D₆): 3.24 (d, 2H, $CH_2CH=CH_2$, J(H-H) = 7.7 Hz), 4.70 (s, 5H, Cp), 5.00 (dd, 1H, CH₂CH=C H_2 , 1J (H-H) = 2.3 Hz, 3J (H-H) = 9.8 Hz), 5.21 (dd, 1H, CH₂CH=CH₂, ${}^{1}J$ (H-H) = 2.3 Hz, ${}^{3}J$ (H-H) = 16.9 Hz), 6.21 (m, 1H, CH₂CH=CH₂), 7.09 (m, 9H, PPh₃), 7.69 (m, 6H, PPh₃). Anal. Calcd for C₂₇H₂₅OP₂RuS: C, 61.22; H, 4.76. Found: C, 60.20; H. 4.76.

CpRu(PPh₃)S₂CSCH₂CH=CH₂, 3. A solution of **1** (0.50 g, 0.65 mmol) in toluene (100.0 mL) was treated with CS₂ (40.0 mL) and stirred for 30 min. The solvent was removed under vacuum, the remaining solid was dissolved in THF (3.0 mL), and the solution was chromatographed on alumina (20 mm × 30 cm). Elution with hexanes removed PPh₃. Elution with THF in hexanes (1:2) gave a brown fraction which was collected and stripped to dryness. The resulting brown solid was recrystallized from THF/hexanes to give dark red crystals (0.34 g, 90%). Mp: 132–133 °C. IR (KBr disk): $\nu_{\text{CS of CS3}} = 991$ (s) cm⁻¹, $\nu_{\text{CS of SR}} = 692$ (s) cm⁻¹. ¹H NMR (C₆D₆): 3.43 (d, 2H, CH₂CH=CH₂, ¹/(H−H) = 7.0 Hz), 4.29 (s, 5H, Cp), 4.86 (dd, 1H, CH₂CH=CH₂, ¹/(H−H) = 2.2 Hz, ³/(H−H) = 9.9 Hz), 4.94 (dd, 1H, CH₂CH=CH₂, ¹/(H−H) = 2.2 Hz, ³/(H−H) = 15.9 Hz), 5.61 (m, 1H, CH₂CH=CH₂, 7.03 (m, 9H, PPh₃), 7.60 (m, 6H, PPh₃). Anal. Calcd for C₂₇H₂₅PRuS₃: C, 56.12; H, 4.36. Found: C, 56.53; H, 4.56.

[CpRu(PPh₃)(CO)CH₃SCH₂CH=CH₂)]PF₆, 4. In a 100-mL Schlenk flask, 2 (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL). Methyl iodide (0.056 g, 0.40 mmol) was added followed by ammonium hexafluorophosphate (0.065 g, 0.40 mmol). The reaction mixture was

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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 \times 5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 73%). Mp: 181–183 °C. IR (KBr disk): $\nu_{\rm CO} = 1991$ (s) cm⁻¹. ¹H NMR (acetone- d_6): 2.36 (s, 3H, C H_3), 3.50 (m, 2H, C H_2 CH=C H_2), 5.29 (m, 1H, C H_2 CH=C H_2), 5.36 (m, 1H, C H_2 CH=C H_2), 5.56 (s, 5H, C H_3), 7.63 (m, 6H, PPh $_3$). Anal. Calcd for C $_{28}H_{28}F_6$ OP $_2$ RuS: C, 48.76; H, 4.09. Found: C, 48.01; H, 4.16.

[CpRu(PPh₃)(CO)HSCH₂CH=CH₂)]BF₄, 5. In a 100-mL Schlenk flask, 2 (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL) and HBF₄•Et₂O (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): $\nu_{CO} = 1991$ (s), 1979 (m) cm⁻¹, $\nu_{SH} = 2508$ (w) cm⁻¹. ¹H NMR (acetone- d_6): 3.40 (tt, 3H, $CH_2CH=CH_2$, SH, J(H-H) = 2.3 Hz, J(P-H) = 6.6 Hz), 5.25 (dd, 1H, $CH_2CH=CH_2$, ${}^1J(H-H) = 1.8 \text{ Hz}$, ${}^3J(H-H) = 8.8 \text{ Hz}$), 5.35 (dd, 1H, CH₂CH=C H_2 , ${}^{1}J$ (H-H) = 1.8 Hz, ${}^{3}J$ (H-H) = 15.6 Hz), 5.50 (s, 5H, Cp), 5.80 (m, 1H, CH₂CH=CH₂), 7.42 (m, 9H, PPh₃), 7.56 (m, 6H, PPh₃). Anal. Calcd for C₂₇H₂₆BF₄OPRuS: C, 52.52; H, 4.24. Found: C, 52.30; H, 4.35.

(CpRu)₃(μ ₃-S)₂(μ -SCH₂CH=CH₂), **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 × 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 (C₆D₆): 2.79 (d, 2H, CH₂CH=CH₂, J(H−H) = 7.3 Hz), 4.46 (s, 10H, Cp), 4.78 (s, 5H, Cp), 4.95 (dd, 1H, CH₂CH=CH₂, 1J (H−H) = 1.9 Hz, 3J (H−H) = 9.9 Hz), 5.01 (dd, 1H, CH₂CH=CH₂, 1J (H−H) = 1.9 Hz, 3J (H−H) = 17.1 Hz), 5.93 (m, 1H, CH₂CH=CH₂). Anal. Calcd for (C₁₈H₂₀Ru₃S₃): C, 33.99; H, 3.17; S, 15.12. Found: C, 34.51; H, 3.28; S, 14.52.

Table 1. Crystallographic Data for $(CpRu)_3(\mu_3-S)_2(\mu-SCH_2CH=CH_2)$

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chem formula: C<sub>18</sub>H<sub>20</sub>S<sub>3</sub>Ru<sub>3</sub>
                                                      Z = 4
fw = 635.75
                                                      d_{\rm calc} = 2.199 \text{ g cm}^{-3}
space group: P_{21}/c (No. 14)
                                                      \lambda = 1.541 \ 78 \ \text{Å}
                                                      \mu(\text{Cu K}\alpha) = 223.57 \text{ cm}^{-1}
a = 12.358(2) \text{ Å}
b = 10.876(2) \text{ Å}
                                                      T = 20 \,^{\circ}\text{C}
c = 15.817(2) \text{ Å}
                                                      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{ Å}
  ^{a} R<sub>1</sub> = \sum |F_{o}| - |F_{c}|/\sum |F_{o}|. ^{b} \omegaR<sub>2</sub> = [\sum \omega (F_{o}^{2} - F_{c}^{2})^{2}/\sum \omega (F_{o}^{2})^{2}]^{1/2}.
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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 Kα 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 Texsan 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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