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C−S Bond Cleavage in CpRu(PPh$_3$)$_2$SCH$_2$CH=CH$_2$ To Give the Trimer (CpRu)$_3$(μ_3-S)$_2$(μ-SCH$_2$CH=CH$_2$)

Alan Shaver,* Mohammad El-Khateeb, and Anne-Marie Lebuis

Department of Chemistry, McGill University,
801 Sherbrooke Street West,
Montreal, Quebec, Canada H3A 2K6

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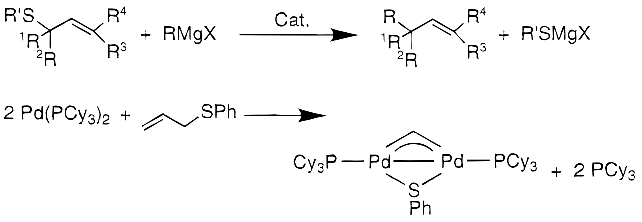
Introduction

Cleavage of the carbon−sulfur bond is important in biological systems[1] 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 reagents[5] catalyzed by Ni, Pd, and Au(I) salts.[7] The π-allyl intermediate (μ-SPh)(μ-C$_3$H$_7$)[PCy$_3$Pd]$_2$ has been isolated from the reaction of Pd(PCy$_3$)$_2$ with allylphenyl sulfide.[5c]

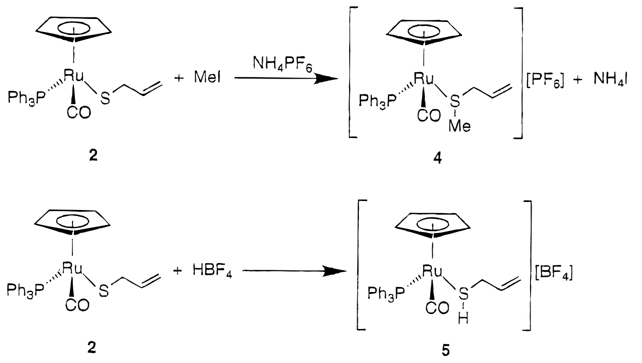


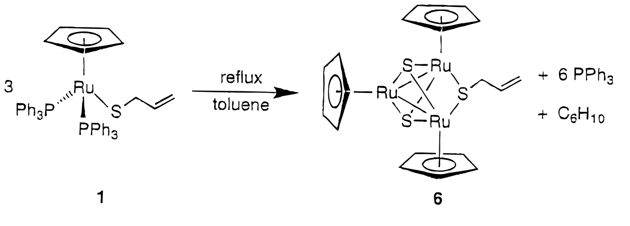
The reactivity of the electron-rich ruthenium thiolates CpRu(PPh$_3$)$_2$SR[8] prompted the preparation of the complex CpRu(PPh$_3$)$_2$SCH$_2$CH=CH$_2$, **1**. When this complex was heated in toluene, carbon−sulfur bond cleavage occurred to give (CpRu)$_3$(μ_3-S)$_2$(μ-SCH$_2$CH=CH$_2$).

Results

When CpRu(PPh$_3$)$_2$Cl was briefly refluxed with excess LiSCH$_2$CH=CH$_2$ in THF, the complex **1** was obtained in 81% yield. When CO gas was bubbled through a THF solution of **1**, the complex CpRu(PPh$_3$)(CO)SCH$_2$CH=CH$_2$, **2**, was produced. Compound **1** reacted easily with CS$_2$ to give the thioxanthate complex CpRu(PPh$_3$)S$_2$CSCH$_2$CH=CH$_2$, **3**, in which a CS$_2$ molecule has inserted into the Ru−S bond. These reactions are analogous to those reported for the simple Ru−thiolate complexes CpRu(PPh$_3$)$_2$SR.[8a]

Complex **2** reacted with MeI in the presence of NH$_4$PF$_6$ to give the salt [CpRu(PPh$_3$)(CO)MeSCH$_2$CH=CH$_2$)]PF$_6$, **4**, in very good yield (81%). Compound **2** also reacted with HBF$_4$ in THF at room temperature to give the thiol complex salt [CpRu(PPh$_3$)(CO)HSCH$_2$CH=CH$_2$)]BF$_4$, **5**. Thus the chemistry of **2** is similar to that of the simple thiolato complexes, CpRu(PPh$_3$)(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 PPh$_3$ ligands in refluxing toluene to give the trimer (CpRu)$_3$(μ_3-S)$_2$(μ-SCH$_2$CH=CH$_2$), **6**, in 42% yield. Complex **6** is air stable and soluble in THF, benzene, and ether. Its ^{1}H 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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* To whom correspondence should be addressed.

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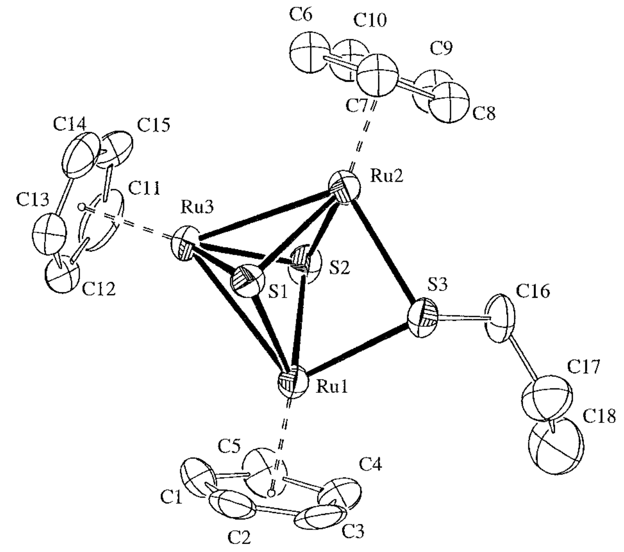

Figure 1. ORTEP drawing (40% probability level) of $(CpRu)_3(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)$, **6**. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1), 2.366(3); Ru(1)−S(2), 2.339(3); Ru(1)−S(3), 2.404(3); Ru(2)−S(1), 2.361(3); Ru(2)−S(2), 2.351(3); Ru(2)−S(3), 2.389(3); Ru(3)−S(1), 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-$SC_3H_7)_3$ (average 2.715 Å) and similar to those observed in $(CpRu)_3(\mu\text{-}Cl)(\mu_3\text{-}S)$ (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 $(CpRu\text{-}\mu_2SC_3H_7)_3$ (average 2.296 Å). The Ru−S (triply bridged) bond lengths (average 2.353 Å) are longer than the corresponding lengths in $(CpRu)_3(\mu_3\text{-}Cl)(\mu_3\text{-}S)$ (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 $(CpRu\text{-}\mu_2\text{-}SR)_3$. 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 PPh_3 and C−S bond cleavage to give a coordinatively unsaturated ruthenium sulfide species, $CpRu(PPh_3)({=}S)$, which could aggregate to give **6**. Similar species have been reported[11] such as $Cp^*_2Ta(CH_2R)({=}S)$[12] and $Cp^*_2Zr(py)({=}S)$.[13] The formation of the dimer $Cp^*Ir(PMe_3)(\mu_2\text{-}S)IrCp^*$, which is postulated to involve aggregation of the species $Cp^*Ir(PMe_3)({=}S)$[14] obtained via dehalogenation of $Cp^*Ir(PMe_3)(SH)Cl$, is particularly relevant to the results reported here.

Experimental Section

All experiments were performed under nitrogen using vacuum lines and Schlenk techniques.[8a,b] The complex $CpRu(PPh_3)_2Cl$ was prepared according to the published procedure.[15] Allyl 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.

$CpRu(PPh_3)_2SCH_2CH{=}CH_2$, 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 $CpRu(PPh_3)_2Cl$ (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 (C_6D_6): 3.06 (d, 2H, $CH_2CH{=}CH_2$, $J(H-H) = 7.0$ Hz), 4.38 (s, 5H, Cp), 5.02 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.4$ Hz, $^3J(H-H) = 9.8$ Hz), 5.28 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.4$ Hz, $^3J(H-H) = 16.9$ Hz), 6.80 (m, 1H, $CH_2CH{=}CH_2$), 7.30 (m, 18H, PPh_3), 7.40 (m, 12H, PPh_3). Anal. Calcd for $C_{44}H_{40}P_2RuS$: C, 69.17; H, 5.28; S, 4.20. Found: C, 69.32; H, 5.21; S, 4.36.

$CpRu(PPh_3)(CO)SCH_2CH{=}CH_2$, 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 PPh_3. 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 (C_6D_6): 3.24 (d, 2H, $CH_2CH{=}CH_2$, $J(H-H) = 7.7$ Hz), 4.70 (s, 5H, Cp), 5.00 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.3$ Hz, $^3J(H-H) = 9.8$ Hz), 5.21 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.3$ Hz, $^3J(H-H) = 16.9$ Hz), 6.21 (m, 1H, $CH_2CH{=}CH_2$), 7.09 (m, 9H, PPh_3), 7.69 (m, 6H, PPh_3). Anal. Calcd for $C_{27}H_{25}OP_2RuS$: C, 61.22; H, 4.76. Found: C, 60.20; H, 4.76.

$CpRu(PPh_3)S_2CSCH_2CH{=}CH_2$, 3. A solution of **1** (0.50 g, 0.65 mmol) in toluene (100.0 mL) was treated with CS_2 (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 PPh_3. 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): $\nu_{CS\ of\ CS3} = 991$ (s) cm^{-1}, $\nu_{CS\ of\ SR} = 692$ (s) cm^{-1}. ^1H NMR (C_6D_6): 3.43 (d, 2H, $CH_2CH{=}CH_2$, $J(H-H) = 7.0$ Hz), 4.29 (s, 5H, Cp), 4.86 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.2$ Hz, $^3J(H-H) = 9.9$ Hz), 4.94 (dd, 1H, $CH_2CH{=}CH_2$, $^1J(H-H) = 2.2$ Hz, $^3J(H-H) = 15.9$ Hz), 5.61 (m, 1H, $CH_2CH{=}CH_2$, 7.03 (m, 9H, PPh_3), 7.60 (m, 6H, PPh_3). Anal. Calcd for $C_{27}H_{25}PRuS_3$: C, 56.12; H, 4.36. Found: C, 56.53; H, 4.56.

$[CpRu(PPh_3)(CO)CH_3SCH_2CH{=}CH_2)]PF_6$, 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 × 5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 73%). Mp: 181−183 °C. IR (KBr disk): ν_{CO} = 1991 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.36 (s, 3H, CH_3), 3.50 (m, 2H, CH_2CH═CH$_2$), 5.29 (m, 1H, CH$_2$CH═CH_2), 5.36 (m, 1H, CH$_2$CH═CH_2), 5.56 (s, 5H, Cp), 5.70 (m, 1H, CH$_2$CH═CH$_2$, 7.44 (m, 9H, PPh$_3$), 7.63 (m, 6H, PPh$_3$). Anal. Calcd for $C_{28}H_{28}F_6OP_2RuS$: C, 48.76; H, 4.09. Found: C, 48.01; H, 4.16.

[CpRu(PPh$_3$)(CO)HSCH$_2$CH═CH$_2$)]BF$_4$, 5. In a 100-mL Schlenk flask, **2** (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL) and HBF$_4$•Et$_2$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): ν_{CO} = 1991 (s), 1979 (m) cm^{-1}, ν_{SH} = 2508 (w) cm^{-1}. ^{1}H 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$_2$CH═CH_2, ^1J(H−H) = 1.8 Hz, ^3J(H−H) = 8.8 Hz), 5.35 (dd, 1H, CH$_2$CH═CH_2, ^1J(H−H) = 1.8 Hz, ^3J(H−H) = 15.6 Hz), 5.50 (s, 5H, Cp), 5.80 (m, 1H, CH$_2$CH═CH$_2$), 7.42 (m, 9H, PPh$_3$), 7.56 (m, 6H, PPh$_3$). Anal. Calcd for $C_{27}H_{26}BF_4OPRuS$: C, 52.52; H, 4.24. Found: C, 52.30; H, 4.35.

(CpRu)$_3$(μ_3-S)$_2$(μ-SCH$_2$CH═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 × 30 cm). Elution with hexanes removed PPh$_3$. 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. ^{1}H NMR (C$_6$D$_6$): 2.79 (d, 2H, CH_2CH═CH$_2$, J(H−H) = 7.3 Hz), 4.46 (s, 10H, Cp), 4.78 (s, 5H, Cp), 4.95 (dd, 1H, CH$_2$CH═CH_2, ^1J(H−H) = 1.9 Hz, ^3J(H−H) = 9.9 Hz), 5.01 (dd, 1H, CH$_2$CH═CH_2, ^1J(H−H) = 1.9 Hz, ^3J(H−H) = 17.1 Hz), 5.93 (m, 1H, CH$_2$CH═CH$_2$). Anal. Calcd for ($C_{18}H_{20}Ru_3S_3$): C, 33.99; H, 3.17; S, 15.12. Found: C, 34.51; H, 3.28; S, 14.52.

Table 1. Crystallographic Data for (CpRu)$_3$(μ_3-S)$_2$(μ-SCH$_2$CH═CH$_2$)

chem formula: $C_{18}H_{20}S_3Ru_3$	$Z = 4$
fw = 635.75	$d_{calc} = 2.199$ g cm^{-3}
space group: $P2_1/c$ (No. 14)	$\lambda = 1.541\,78$ Å
$a = 12.358(2)$ Å	μ(Cu Kα) = 223.57 cm^{-1}
$b = 10.876(2)$ Å	$T = 20$ °C
$c = 15.817(2)$ Å	$R_1{}^a = 0.058, 0.086$ ($I > 2\sigma(I)$, all)
$\beta = 116.36(1)°$	$\omega R_2{}^b = 0.168, 0.184$ ($I > 2\sigma(I)$, all)
$V = 1920.3(5)$ Å	

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

X-ray Structure Determination for 6 (Table 1). A dark plate crystal (0.100 × 0.010 × 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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