Inorg. Chem. **1994,** *33,* 4327−4333 **4327**

Polysulfanido Ligands:[1] The Preparation and Structures of Complexes of the Type $CpRu(PPh_3)(CO)S_xR$, Possessing Disulfanido ($x = 2$) and Trisulfanido ($x = 3$) Ligands

Alan Shaver* and Pierre-Yves Plouffe[2]

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

Received February 18, 1994⊗

Treatment of $CpRu(PPh_3)(CO)SH$, **1** with the sulfur transfer reagents RSphth gave the complexes $CpRu(PPh_3)(CO)SSR$ (**2a−c**), where phth = phthalimido and R = 4-C_6H_4Me, (**a**), 1-C_3H_7, (**b**), and $CHMe_2$, (**c**), rare examples of complexes containing disulfanido ligands. Crystal data for **1** $P\bar{1}$, $a = 9.408(11)$ Å, $b = 10.6168(9)$ Å, $c = 11.6499(5)$ Å, $\alpha = 76.523(6)°$, $\beta = 78.896(8)°$, $\gamma = 78.562(8)°$, $V = 1314.9$ Å^3, $Z = 2$. Crystal data for **2c**: $P2_1/n$, $a = 9.274(2)$ Å, $b = 11.345(3)$ Å, $c = 25.303(6)$ Å, $\beta = 97.37(2)°$, $V = 2640.2$Å^3, $Z = 4$. Treatment of **1** with the disulfur transfer reagents RSSphth gave the complexes $CpRu(PPh_3)(CO)SSSR$ (**3a−c**) possessing even rarer trisulfanido ligands. Crystal data for **3b**: $P\bar{1}$, $a = 10.643(2)$ Å, $b = 14.040(3)$ Å, $c = 9.205(3)$ Å, $\alpha = 98.11(2)°$, $\beta = 97.26(2)°$, $\gamma = 96.46(2)°$, $V = 1338.9$ Å^3, $Z = 2$. The di- and trisulfanido ligands are resistant to loss of sulfur.

Introduction

The preparation of complexes containing catenated polysulfur ligands (MS_xR, where $x > 1$) is of interest for a number of reasons. First they are relatively rare. While organic sulfides, disulfides, and trisulfides are common, biologically important classes of compounds, only metal thiolates achieve similar status. Only a handful of metal disulfanides (MSSR) have been reported[3−15] and only two examples of metal trisulfanides (MSSSR) are in the literature.[5,6,8] This is somewhat surprising in view of the sulfur's propensity to catenate and in view of the demonstration that catenated polysulfur dianions (S_x^{2-}) are excellent ligands[16] for a large variety of metals. Another reason for interest in catenated polysulfanido ligands is their potential usefulness in understanding sulfur catenation reaction in biology, geology and industry. The Claus process,[17] for example, converts waste H_2S to sulfur via reaction with SO_2 ($2H_2S + SO_2 \rightarrow {}^3/_8S_8$) over an alumina catalyst. Obviously this reaction involves sulfur catenation and oxygen transfer, but the details are poorly understood.[18] We have shown[19] that the thiosulfinato complex $CpRu(PPh_3)(CO)SS(O)$-4-C_6H_4Me undergoes oxygen-disproportionation to give the thiosulfonate $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me and the disulfanido complex $CpRu(PPh_3)(CO)SS$-4-C_6H_4Me. Kubas et al. have also reported[20] interesting models of oxygen transfers involving SO_2 and sulfur−metal complexes.

The goal of the work reported here was to prepare and structurally characterize complexes containing disulfanido and trisulfanido ligands. Complexes of the type $CpW(CO)_3S_{2\text{ or }3}R$[6] and $Cp_2Ti(X)S_2R$[9] readily and spontaneously desulfurize to give the appropriate thiolates while the compounds *cis*-$(PPh_3)_2Pt(phth)S_2R$,[7] where phth = phthalimido, are fairly stable although they are desulfurized by PPh_3. Additional examples of such compounds would provide useful comparisons and possible insights into the factors affecting desulfurization.

---

* Author to whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) The IUPAC convention for linear polysulfur compounds is that they be named polysulfanes: Loening, K. L. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed., Marcel Dekker: New York, 1972; *Vol. 3*, pp 339−354.

(2) Present address: Genpharm, 87 Advance Rd., Etobicoke, Ontario, Canada M8Z 256.

(3) John, E.; Bharadwaj, P. K.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 5015.

(4) Bhattacharyya, S. N.; Senoff, C. V.; Walker, F. S. *Inorg. Chim. Acta* **1980**, *44*, L273.

(5) Shaver, A.; Hartgerink, J., Lai, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938.

(6) Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1986**, *65*, 1190.

(7) Shaver, A.; Lai, R. D. *Inorg. Chem.* **1988**, *27*, 4664.

(8) Shaver, A.; McCall, J. M.; Bird, P. H.; Ansari, N. *Organometallics* **1983**, *2*, 1894.

(9) Shaver, A.; Morris, S. *Inorg. Chem.* **1991**, *30*, 1926.

(10) (a) Noble, M. E.; Williams, D. E. *Inorg. Chem.* **1988**, *27*, 749. (b) Noble, M. E. *Inorg. Chem.* **1987**, *26*, 877. (c) Noble, M. E. *Inorg. Chem.* **1986**, *25*, 3311.

(11) (a) Wu, X.; Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1989**, *8*, 251. (b) Brunner, H.; Grassl, R.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1992**, *427*, 57.

(12) Eremenko, I. L.; Pasynskii, A. A.; Kalinnikov, V. T.; Struchkov, Yu. T.; Aleksandrov, G. G. *Inorg. Chim. Acta* **1981**, *52*, 107.

(13) (a) Legzdins, P.; Rettig, S. J.; Sanchez, L. *Organometallics* **1988**, *7*, 2394. (b) Legzdins, P.; Sanchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (c) Evans, S. V.; Legzdins, P.; Rettig, S. J.; Sanchez, L.; Trotter, J. *Organometallics* **1987**, *6*, 7.

(14) (a) Clark, G. R.; Russell, D. R. *J. Organomet. Chem.* **1979**, *173*, 377. (b) Hoots, J. E.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 2806. (c) Leonard, K.; Plute, K.; Haltiwanger, R. C.; Rakowski-Dubois, M. *Inorg. Chem.* **1979**, *18*, 3246.

(15) For examples of cyclic ligands containing the catenated S_2 unit, see: (a) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476. (b) Giolando, D. W.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 487. (c) Giolando, D. W.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1987**, *6*, 667. (d) Coucouvanis, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1971**, *93*, 307. (e) Fackler, J. D.; Fetchin, J. A.; Fries, D. C. *J. Am. Chem. Soc.* **1972**, *94*, 7323. (f) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301.

(16) (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Muller, A. *Polyhedron* **1986**, *5*, 323. (c) Wachter, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1613. (d) Muller, A.; Deimann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.

(17) (a) Grancher, P. *Hydrocarbon Process.* **1978**, *57*, 155 (b) Grancher, P. *Hydrocarbon Process.* **1978**, *57*, 257.

(18) (a) Datta, A.; Cavell, R. G.; Tower, T. W.; George, Z. M. *J. Phys. Chem.* **1985**, *89*, 443. (b) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 450. (c) Datta, A.; Cavell, R. G. *J. Phys. Chem.* **1985**, *89*, 454. (d) George, Z. M.; Tower, R. W. *Can. J. Chem. Eng.* **1985**, *63*, 618. (e) Karge, H. G.; Dalla Lana, I. G. *J. Phys. Chem.* **1984**, *88*, 1958.

(19) Shaver, A.; Plouffe, P.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 7780.

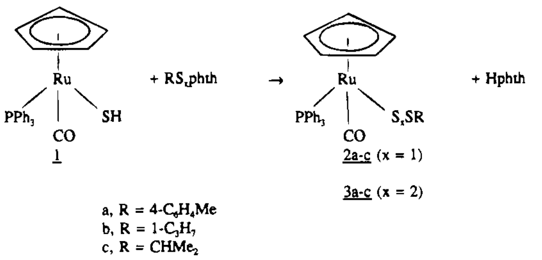
(20) (a) Toupadakis, A.; Kubas, G. J.; Burns, C. J. *Inorg. Chem.* **1992**, *31*, 3810. (b) Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823. (c) Kubat-Martin, K. A.; Kubas, G. J.; Ryan, R. R. *Organometallics* **1989**, *8*, 1910.

0020-1669/94/1333-4327$04.50/0

Organic chemists prepare unsymmetrical di- and trisulfanes ($R'S_{1\text{ or }2}SR$) via reaction of thiols with sulfur transfer reagents[21] of the type $R'S_{1\text{ or }2}$phth. The thiolo complexes $CpRu(PPh_3)(L)SH$, where L = PPh_3 or CO, are well-known;[22] moreover, the CpRu residue forms several complexes containing various catenated polysulfur anions as ligands.[22a,23] We have found the reactions of $CpRu(PPh_3)(CO)SH$ with the sulfur transfer reagents to be a good route to stable ruthenium di- and trisulfanes.

Results

At first the complex $CpRu(PPh_3)_3SH$ was treated with sulfur transfer reagents of the type RSphth, where phth = phthalimido. The NMR spectra of the crude products detected several peaks in the Cp region indicative that several products had been found. Subsequently, treatment of $CpRu(PPh_3)(CO)SH$, (**1**) with RSphth gave the disulfano complexes $CpRu(PPh_3)(CO)SSR$ (**2a**–**c**), as air-stable, yellow compounds in good yield (40–60%) according to eq 1. The NMR sample solutions of **2a**–**c** prepared under N_2 were stable for up to 10 h, but in air, green paramagnetic solutions containing free triphenylphosphine formed within 10 min. The NMR spectra of **2a**–**c** display peaks due to one Cp environment, one PPh_3 group, and the appropriate R group observed in the proper multiplicity and intensity. The IR spectra of **2a**–**c** and the structure of **2c** are discussed below. Similarly the complexes $CpRu(PPh_3)(CO)SSSR$ (**3a**–**c**), were prepared via treatment of **1** with RSSphth. In solution **3a**–**c** are much more stable than **2a**–**c** even when exposed to air for hours. The IR spectra of **3a**–**c** and the structure of **3b** are discussed below.



(1)

Elemental analyses of **3a**–**c** are in agreement with their formulation; however, their NMR spectra clearly reveal the presence of more than one species. There were three peaks in the Cp region of the NMR spectrum of **3a** in the ratio **3a**:**3aA**:**3aB** = 10:2:1. The two minor peaks do not correspond to the disulfano complex **2a** or to the thiolato complex $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$. Complex **3b** gave four peaks in the Cp region in the ratio **3b**:**2b**:**3bA**:**3bB** = 5.4:1:3.1:1. The presence of **2b** was confirmed by TLC analysis of **3b**. The peaks due to **3bA** and **3bB** do not correspond to those of the thiolato complex. Complex **3c** gave three Cp peaks corresponding to **3c**, **2c** and **3cA** in the ratio 11:1:1.4; the presence of **2c** once again being confirmed by TLC. The peaks due to **3cA** do not correspond to the thiolato complex. In every case, for each complex, all the Cp peaks were accompanied by peaks in the spectrum due to the appropriate companion R groups in the expected intensities.

Table 1. Infrared ν(CO) Stretching Frequencies (cm^{-1}) for $CpRu(PPh_3)(CO)S_xR$, Where x = 1, 2, and 3, and $CpRu(PPh_3)(CO)SS(O)_yR$, Where y = 1, 2, in Toluene.

	R		
L[a]	$4\text{-}C_6H_4Me$	$1\text{-}C_3H_7$	$CHMe_2$
SR	1947	1942	1941
SSR	1954	1941	1942
SSSR	1957	1956	1956
SS(O)R	1960	1959	1958
$SS(O)_2R$[24]	1971		

[a] L = S_xR or $SS(O)_yR$.

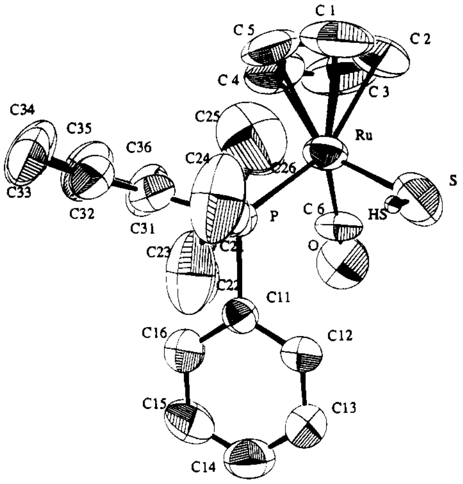


Figure 1. ORTEP drawing of $CpRu(PPh_3)(CO)SH$ (**1**). Selected bond lengths (Å) and bond angles (deg): Ru–S, 2.381(3); Ru–P, 2.306(2); Ru–C(6), 1.896(8); Ru–C(1), 2.228(11); Ru–C(2), 2.207(11); Ru–C(3), 2.228(13); Ru–C(4), 2.227(11); Ru–C(5), 2.268(11); S–Ru–P, 91.44(8); S–Ru–C(6), 90.2(3); P–Ru–C(6), 90.2(3).

Variable temperature NMR spectra of **3b** showed no changes in the relative intensities or in the line widths of the three Cp peaks in the range −60 to +60 °C. NOE experiments did not detect any exchange between the Cp peaks. The pattern of the Cp peaks was invariant with solvent (C_6D_6, $(CD_3)_2CO$, toluene-d_8, CD_2Cl_2) and did not change after further column chromatography and recrystallization. An NMR sample of **3b**, prepared and measured at −78 °C, gave the same spectrum as that taken at room temperature. The presence of added elemental sulfur or triphenylphosphine did not change the spectrum of **3b** after 2 h. Treatment of a C_6D_6 solution of **3b** with excess $P(NEt_2)_3$ slowly (24 h) gave peaks due to **2b** and the thiolato complex. The reaction was monitored over time and the peaks due to **3bA** and **3bB** were consumed before those of **3b**.

The CO stretching frequencies of **2a**–**c**, **3a**–**c**, and other similar complexes are listed in Table 1. In toluene all the complexes show one sharp band with no apparent shoulders or broadening. The IR spectra of **3a**–**c** in CCl_4 showed shoulders consistent with the presence of multiple species as observed in the NMR spectra. The ν(CO) stretching frequencies for complexes of the type $CpRu(PPh_3)(CO)X$ increased with X as follows SR ≤ SSR ≤ SSSR ≤ SS(O)R ≤ $SS(O)_2R$. Thus the disulfano and trisulfano ligands may be slightly less electron donating than the thiolato ligands.

X-ray Structural Analyses

$CpRu(PPh_3)(CO)SH$ (1). The structure of **1** is depicted in Figure 1 and the positional parameters are listed in Table 3. The bond lengths and angles in **1** are unremarkable. There are

---

(21) (a) Harpp, D. N.; Ash, D. K.; Back, T. G.; Gleason, J. G.; Orwig, B. A.; van Horn, W. F.; Snyder, J. P. *Tetrahedron Lett.* **1970**, 3551. (b) Boustany, K. S.; Sullivan, A. B. *Tetrahedron Lett.* **1970**, 3547. (c) Harpp, D. N.; Ash, D. K. *Int. J. Sulfur Chem. A* **1971**, *1*, 211.

(22) (a) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875. (b) Shaver, A.; Plouffe, P.-Y.; Bird, P.; Livingston, E. *Inorg Chem.* **1990**, *9*, *29*, 1826.

(23) (a) Amarasekera, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017. (b) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3308. (c) El-Hinnawi, M. A.; Sumadi, M. L.; Esmadi, F. T.; Jibil, I. *J. Organomet. Chem.* **1989**, *377*, 378.

(24) Plouffe, P.-Y. Ph.D. Thesis, McGill University **1990**.

Table 2. Crystallographic Data for CpRu(PPh$_3$)(CO)E, where E = SH (**1**), SSCHMe$_2$ (**2c**), and SSS-1-C$_3$H$_7$ (**3b**)

	1	**2c**	**3b**
chem formula	$C_{24}H_{21}OPRuS$	$C_{27}H_{27}OPRuS_2$	$C_{27}H_{27}OPRuS_3$
fw	489.53	556.61	590.69
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.408(11)	9.274(2)	10.643(2)
b (Å)	10.6168(9)	11.345(3)	14.040(3)
c (Å)	11.6499(5)	25.303(6)	9.205(3)
α (deg)	76.523(6)		98.11(2)
β (deg)	78.896(8)	97.37(2)	97.26(2)
γ (deg)	78.562(8)		96.46(2)
V (Å^3)	1314.9(2)	2640.2(1)	1338.9(6)
Z	2	4	2
ϱ_{calcd} (g cm^{-3})	1.483	1.400	1.465
λ (Å)	1.540 56	0.709 30	0.709 30
μ (mm^{-1})	6.69 (Cu Kα)	0.81 (Mo Kα)	0.87 (Mo Kα)
T (°C)	20	20	23
R^a (×100)	4.6	5.6	4.8
$R_w{}^b$ (×100)	6.3	5.8	7.2

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

Table 3. Positional Parameters and Isotropic Thermal Parameters (Å^2) for CpRu(PPh$_3$)(CO)SH (**1**)

	x	y	z	$B_{eq}{}^a$
Ru	0.27250	0.34751	0.83850	5.74(4)
S	0.0225(3)	0.3335(3)	0.84090(23)	8.31(16)
P	0.35076(21)	0.20744(17)	0.70643(16)	3.97(9)
O	0.2612(9)	0.5657(7)	0.6398(8)	8.7(5)
C1	0.277(3)	0.2540(19)	1.0303(12)	11.9(13)
C2	0.2349(23)	0.392(3)	1.0187(16)	14.1(15)
C3	0.351(4)	0.4495(16)	0.9553(19)	13.0(15)
C4	0.4633(17)	0.353(3)	0.9236(12)	10.6(10)
C5	0.4179(25)	0.2324(17)	0.9745(16)	10.8(11)
C6	0.2621(11)	0.4934(9)	0.7089(7)	5.0(5)
C11	0.3136(8)	0.2726(6)	0.5531(6)	3.9(3)
C12	0.1723(9)	0.3242(8)	0.5354(7)	5.6(5)
C13	0.1388(10)	0.3775(9)	0.4229(9)	6.9(5)
C14	0.2477(13)	0.3796(9)	0.3261(8)	7.3(6)
C15	0.3887(12)	0.3273(11)	0.3416(8)	7.8(6)
C16	0.4220(9)	0.2744(8)	0.4550(8)	5.9(5)
C21	0.2792(8)	0.0523(7)	0.7452(7)	4.9(4)
C22	0.2662(9)	−0.0117(7)	0.6586(8)	5.8(4)
C23	0.2092(11)	−0.1301(9)	0.6907(13)	8.2(7)
C24	0.1692(12)	−0.1806(9)	0.8118(15)	9.2(8)
C25	0.1788(15)	−0.1184(11)	0.8953(11)	9.5(7)
C26	0.2323(12)	−0.0018(9)	0.8627(9)	7.5(6)
C31	0.5493(9)	0.1570(7)	0.6857(7)	5.0(4)
C32	0.6150(10)	0.0285(8)	0.6941(7)	5.9(5)
C33	0.7690(11)	−0.0022(10)	0.6803(10)	8.3(6)
C34	0.8519(11)	0.0976(13)	0.6591(12)	9.8(8)
C35	0.7858(13)	0.2251(11)	0.6462(11)	9.2(8)
C36	0.6324(10)	0.2559(9)	0.6603(9)	7.0(6)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

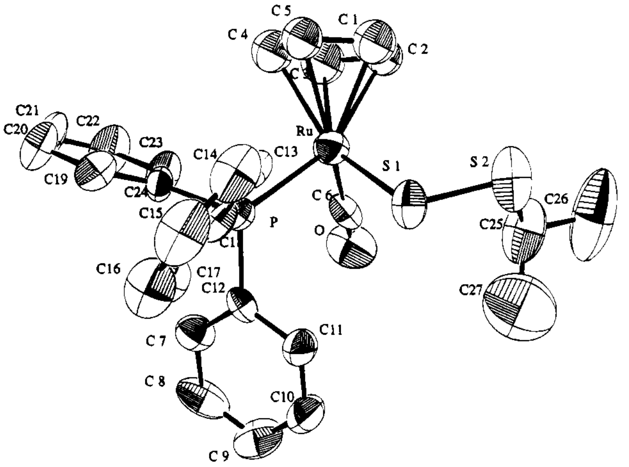


Figure 2. ORTEP drawing of CpRu(PPh$_3$)(CO)SSCHMe$_2$ (**2c**). For simplicity only one Cp ring of partial atoms is shown (see Experimental Section). Selected bond lengths (Å) and angles (deg): Ru—S(1), 2.393(3); S(1)—S(2), 2.047(4); Ru—P, 2.297(3); Ru—C(6), 1.846(10); Ru—C(1), 2.238(14); Ru—C(2), 2.228(15); Ru—C(3), 2.245(16); Ru—C(4), 2.265(13); Ru—C(5), 2.261(14); S(1)—Ru—P, 88.87(9); S—Ru—C(6), 93.7(3); P—Ru—C(6), 89.5(3).

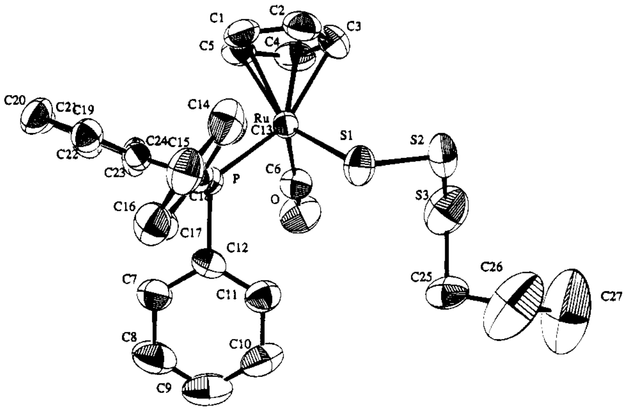


Figure 3. ORTEP drawing of CpRu(PPh$_3$)(CO)SSSC$_3$H$_7$ (**3b**). Selected bond lengths (Å) and angles (deg) are as follows: Ru—S(1), 2.370(2), S(1)—S(2), 2.042(4); S(2)—S(3), 2.005(5); Ru—P, 2.302(2); Ru—C(6), 1.861(10); Ru—C(1), 2.260(9); Ru—C(2), 2.271(9); Ru—C3, 2.236(9); Ru—C4, 2.232(8); Ru—C5, 2.250(9); S1—Ru—P, 89.42(8); S1—Ru—C6, 93.6(3); P—Ru—C(6), 90.3(3).

few structurally characterized complexes containing the SH$^-$ ligand; however, two of these are ruthenium complexes. The terminal Ru—SH distance of 2.381(3) Å in **1** is shorter than those observed in Ru(PPh$_3$)$_2$(CO)$_2$(SH)$_2$[25] (2.470(2) Å, 2.472(2) Å) and (PhMe$_2$P)$_3$Ru(μ-SH)$_3$Ru(PMe$_2$Ph)$_2$SH[26] (2.440(7) Å) but is similar to the Ru—S bonds in **2c** (2.393(3) Å) depicted in Figure 2, **3b** (2.370(2) Å) depicted in Figure 3, the thiosulfinato complexes CpRu(PPh$_3$)(CO)SS(O)CHMe[19] (2.379(2) Å), CpRu(PPh$_3$)(CO)SS(O)CH$_2$Ph[27] (2.377(3)Å), CpRu(PPh$_3$)$_2$SS(O)CH$_2$Ph[28] (average=2.421Å), the thiosulfonato complex CpRu(PPh$_3$)(CO)SS(O)$_2$-4-C$_6$H$_4$Me[19] (2.383(2) Å), and the closely related thiolato complex CpRu(PPh$_3$)(CS)SCHMe$_2$[29] (2.364(2) Å).

CpRu(PPh$_3$)(CO)SSCHMe$_2$, 2c. The structure of **2c** is shown in Figure 2 and the positional parameters are listed in Table 4. The most interesting aspect of the structure is the disulfano ligand SSCHMe$_3$. The dihedral angle about the sulfur—sulfur bond is 78.0° which is significantly less than the normal value of 90° observed for organic disulfides.[30] Metal disulfanide complexes, however, exhibit a broad range of values (CpW(CO)$_3$SS-4-C$_6$H$_4$Me,[5] 63.1°; *cis*-(PPh$_3$)$_2$Pt(phth)SSCHMe$_2$,[5] 89.5°; Cu(tet-b)SSCH$_2$CO$_2$,[3] 98.6°). The S—S bond distance in **2c** is 2.047(4) Å which is within the range observed for organic systems (2.03–2.08 Å)[30] and that for the three known terminal disulfano ligands (2.02–2.05 Å).

CpRu(PPh$_3$)(CO)SSSC$_3$H$_7$, 3b. The trisulfano ligand in **3b** (Figure 3, positional parameters in Table 5) displays the transoid

---

(25) Jessop, P. G.; Lee, C.-L.; Rastan, G.; James, B. R.; Lock, C. J. L.; Foggiani, R. *Inorg. Chem.* **1992**, *31*, 4601.

(26) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Inorg. Chem. Acta* **1985**, *105*, L9.

(27) Weigand, W.; Bosl, G.; Robl, C.; Kroner, J. *Z. Naturforsch* **1992**, *48B*, 627.

(28) Weigand, W.; Bosl, G.; Robl, C.; J. *Z. Naturforsch.* **1992**, *47B*, 39.

(29) Shaver, A.; Plouffe, P.-Y.; Boily, H. Manuscript in preparation.

(30) (a) Oae, S. *Organic Chemistry of Sulfur*; Plenum Press: New York, **1977**; pp 304–383. (b) Kice, J. L. In Sulfur in Organic and Inorganic Chemistry; Senning, A. E., Ed.; Marcell Dekker, Inc.: New York, 1971; Vol. 1, pp 153–207.

Table 4. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $CpRu(PPh_3)(CO)SSCHMe_2$ (**2c**)

	x	*y*	*z*	B_{eq}[a]
Ru	0.69087(9)	0.09560(7)	0.13562(3)	4.14(4)
S1	0.9442(3)	0.1053(3)	0.12640(10)	4.86(14)
S2	1.0589(4)	−0.0027(4)	0.18142(14)	8.24(21)
P	0.65233(25)	0.25449(22)	0.07932(9)	2.79(12)
O	0.7095(9)	0.2591(6)	0.2286(3)	7.2(5)
C1	0.6963(13)	−0.0984(12)	0.1200(6)	5.7(5)
C2	0.6512(16)	−0.0803(13)	0.1701(4)	4.6(4)
C3	0.5182(16)	−0.0203(14)	0.1626(6)	6.8(6)
C4	0.4813(14)	−0.0012(13)	0.1079(6)	5.7(5)
C5	0.5913(17)	−0.0496(14)	0.0816(4)	5.1(5)
C1A	0.6663(16)	−0.0839(14)	0.0988(5)	6.3(5)
C2A	0.7016(13)	−0.0954(13)	0.1541(6)	5.9(5)
C3A	0.5882(17)	−0.0465(14)	0.1784(4)	4.9(5)
C4A	0.4827(13)	−0.0047(12)	0.1382(6)	4.8(5)
C5A	0.5310(16)	−0.0279(14)	0.0890(4)	5.4(5)
C6	0.7074(10)	0.1969(8)	0.1932(4)	4.1(5)
C7	0.6247(11)	0.4895(8)	0.1129(4)	4.6(6)
C8	0.6773(13)	0.5928(8)	0.1386(4)	6.3(6)
C9	0.8229(12)	0.6029(10)	0.1586(4)	5.9(6)
C10	0.9117(11)	0.5101(9)	0.1523(4)	5.6(6)
C11	0.8601(10)	0.4078(9)	0.1284(4)	4.8(5)
C12	0.7135(9)	0.3955(8)	0.1076(3)	2.8(4)
C13	0.7832(9)	0.1476(8)	−0.0018(4)	3.9(5)
C14	0.8428(11)	0.1447(10)	−0.0502(4)	5.4(6)
C15	0.8497(11)	0.2440(11)	−0.0789(4)	6.2(7)
C16	0.8033(11)	0.3493(10)	−0.0612(4)	5.9(6)
C17	0.7425(10)	0.3543(9)	−0.0130(4)	4.6(5)
C18	0.7338(8)	0.2517(8)	0.0167(3)	3.3(5)
C19	0.3973(10)	0.2960(9)	0.0063(4)	4.2(5)
C20	0.2459(10)	0.3123(11)	−0.0062(4)	5.4(6)
C21	0.1580(11)	0.3126(11)	0.0346(4)	6.3(6)
C22	0.2206(10)	0.2987(11)	0.0864(4)	6.3(7)
C23	0.3686(10)	0.2819(9)	0.1000(4)	4.7(5)
C24	0.4597(9)	0.2803(8)	0.0589(3)	3.3(4)
C25	1.0667(11)	0.0758(12)	0.2439(4)	8.3(8)
C26	1.1495(15)	0.0003(13)	0.2860(6)	14.9(14)
C27	1.1436(20)	0.1915(12)	0.2408(7)	14.7(14)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid for atoms refined anisotropically. For Cp carbons, $B_{eq} = B_{iso}$. Cp carbons have occupancies of 0.5.

Table 5. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $CpRu(PPh_3)(CO)SSSC_3H_7$ (**3b**)

	x	*y*	*z*	B_{iso}[a]
Ru	0.17027(6)	0.33280(5)	0.27935(7)	3.05(3)
S1	0.19219(23)	0.33716(19)	0.02724(25)	4.69(11)
S2	0.0202(3)	0.34954(24)	−0.0901(3)	6.88(16)
S3	−0.0964(4)	0.2242(3)	−0.1130(4)	8.80(21)
P	0.35725(19)	0.26506(15)	0.30856(21)	2.92(9)
O	0.0147(7)	0.1376(6)	0.2268(9)	6.9(4)
C1	0.2403(10)	0.4636(7)	0.4556(11)	5.0(5)
C2	0.1800(11)	0.4966(7)	0.3336(12)	5.3(5)
C3	0.0510(10)	0.4536(8)	0.3076(12)	5.4(5)
C4	0.0312(10)	0.3954(8)	0.4155(12)	5.6(5)
C5	0.1487(12)	0.4006(7)	0.5098(10)	5.6(5)
C6	0.0763(8)	0.2097(7)	0.2392(10)	4.2(4)
C7	0.4237(9)	0.0756(7)	0.2990(10)	4.7(5)
C8	0.4273(12)	−0.0180(8)	0.2313(14)	6.5(6)
C9	0.3638(13)	−0.0493(8)	0.0909(15)	6.7(6)
C10	0.2938(12)	0.0117(8)	0.0174(12)	6.1(6)
C11	0.2891(9)	0.1057(7)	0.0855(10)	4.6(5)
C12	0.3554(8)	0.1388(6)	0.2264(9)	3.6(4)
C13	0.4953(8)	0.4193(6)	0.2113(9)	3.6(4)
C14	0.5985(9)	0.4646(7)	0.1578(10)	4.7(4)
C15	0.7036(8)	0.4189(8)	0.1371(10)	4.6(5)
C16	0.7052(8)	0.3269(7)	0.1707(10)	4.5(5)
C17	0.6031(8)	0.2809(6)	0.2241(9)	3.8(4)
C18	0.4966(7)	0.3250(6)	0.2436(7)	3.0(4)
C19	0.5286(8)	0.3064(6)	0.5781(9)	4.1(4)
C20	0.5574(10)	0.3047(7)	0.7289(10)	5.2(5)
C21	0.4693(11)	0.2606(7)	0.8061(10)	5.0(5)
C22	0.3536(10)	0.2163(8)	0.7316(10)	5.3(5)
C23	0.3227(9)	0.2181(7)	0.5824(9)	4.6(5)
C24	0.4103(7)	0.2632(6)	0.5046(8)	3.2(3)
C25	−0.0203(10)	0.1293(7)	−0.2377(12)	5.5(5)
C26	−0.0486(20)	0.1524(19)	−0.3986(20)	14.5(15)
C27	−0.1988(18)	0.1231(24)	−0.4860(22)	17.7(22)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

conformation expected in organic trisulfides[31] and previously observed in $Cp_2Ti(SPh)SSSPh$, the only other trisulfano complex to have been structurally characterized.[8] The bond lengths S1−S2 and S2−S3 are 2.042(4) and 2.005(5) Å, respectively, with corresponding dihedral angles of 71.5(2) and 65.2(4)°, respectively. The comparative values for the titanium complex are 2.053(3) Å, 2.011(3) Å, 70.4(1)°, and 79.0(1)°, respectively.[8] The S1−S2 bond length in **3b** is comparable to those in organic trisulfides while the S2−S3 distance is abnormally small as are both dihedral angles.[31] It would be unwise, however, to place too much emphasis on these observations for the following reasons.

The NMR spectrum of the crystal of **3b** used in the X-ray analysis indicated the presence of **2b** as described above for the bulk sample. When the crystal structures of **2c** and **3b** are compared, all the common atom relative positions correspond to within 0.2 Å. The atoms S1 and S2 of both compounds are in the same relative positions. Carbon atoms C25 and C27 of **2c** lie in the same positions as S3 and C25 of **3b**, respectively. Thus if **3b** cocrystallized with a small amount of its corresponding disulfane **2b**, one can imagine the atoms of the $SS-C_3H_7$ ligand of the latter fitting nicely into the positions of the $SSS-C_3H_7$ ligand of the former with little or no disruption of the lattice. In such a case the electron densities at the positions of S3 and C27 of **3b** should be less than expected, and consistent with this, the temperature factors of these atoms are somewhat large. Such compositional disorder is not well treated by modern crystallographic computing programs.[32]

Discussion

The complex $CpRu(PPh_3)_2SH$ was not a suitable reactant with sulfur transfer reagents probably due to its tendency to easily lose PPh_3 and, subsequently, to aggregate.[22,33] Replacement of one of the PPh_3 ligands by CO reduces this reactivity,[22] and the complex $CpRu(PPh_3)(CO)SH$ reacted smoothly with the sulfur transfer reagents to give the target complexes in reasonable yield and purity.

The presence of the RuSSR moiety in **2a**−**c** is consistent with their physical and chemical properties, the logic of their syntheses, and the structure of **2b**. Thus they join a small class of complexes containing a disulfanido ligand. Some members of this class such as $CpW(CO)_3SSR$[6] and $Cp_2Ti(X)SSR$[9] easily lose a sulfur atom either spontaneously or promoted by PPh_3 to give the corresponding thiolato complex. Complexes such as *cis*-$(PPh_3)_2Pt(X)SSR$,[7] however, and now **2a**−**c**, are similar to organic disulfides and do not undergo facile desulfurization. The factors that affect the ease of sulfur loss by disulfanido complexes are not well understood.

The complex $CpW(CO)_2SS\text{-}4\text{-}C_6H_4Me$ displays an unusually small dihedral angle about the sulfur−sulfur bond (63.1°) whereas that in *cis*-$(PPh_3)_2Pt(phth)SSCHMe_2$ is normal at 89.5°. This has led to speculation[5,6] that the ease of desulfurization of

---

(31) Laur, P. H. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcell Dekker, Inc.: New York, 1971; Vol. 3.

(32) Gerard, P. *Acc. Chem. Res.* **1992**, *25*, 455.

(33) Shaver, A.; Plouffe, P.-Y.; Liles, D. C.; Singleton, E. *Inorg. Chem.* **1992**, *31*, 997.

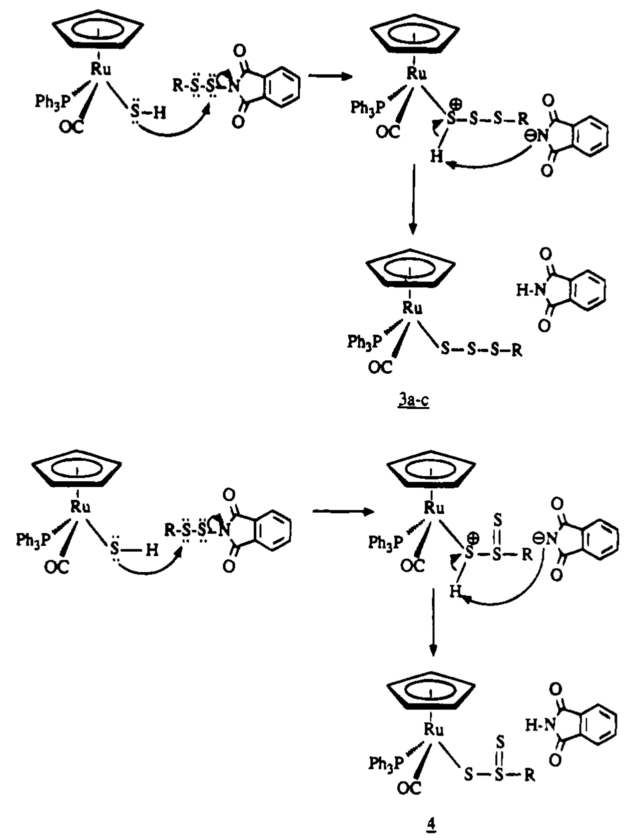
the tungsten complex is related to its small angle and consistent with this the S—S distance (2.053(4) Å) is longer than that in the platinum complex (2.037(4) Å). The dihedral angle in **2b** (78.0°) is between those given above while the S—S distance (2.038(4) Å) is very similar to that of the platinum complex. It is difficult to interpret such data. In organic disulfides the S—S bond lengths vary inversely with the dihedral angle (the Hordvik curve),[34] this being attributed to lone pair—lone pair repulsions between the sulfur atoms which are at their minimum at 90°. It is interesting to note that the shortest S—S distance in a metallodisulfane is 2.017(7) Å, observed for Cu(tet-b)$SSCH_2$-CO_2,[3] which has a dihedral angle of 98.6°. The lone pair—lone pair repulsion should be symmetrical about the 90° dihedral angle, and thus one would have expected the S—S bond distance in the copper complex to be similar to that of the ruthenium complex **2b** (2.047(4) Å; dihedral angle = 78.0°). The copper complex is the product of an unusual chain lengthening reaction that may have involved insertion of sulfur into a copper thiolate bond.

The crystal structure of **3b** confirms the presence of the trisulfano ligand in **3a—c** consistent with the logic of their synthesis. Complexes **3a—c** are only the third examples of metallotrisulfanes, the others being $Cp_2Ti(SPh)(SSSPh)$,[8] whose structure was determined, and $CpW(CO)_3SSSR$,[6] where R = 4-C_6H_4Me, CH_2Ph, and $CH_2CH_2CH_3$. The titanium and tungsten complexes spontaneously lose sulfur in solution to give, in the case of the latter, the disulfanido and thiolato complexes. Complexes **3a—c** by contrast are very stable. As with metallodisulfanes the factors which determine the stability of the trisulfanes with respect to the loss of sulfur are not known. Nevertheless the appearance of extra sets of peaks in the NMR spectra of **3a—c** raises interesting questions. One of these sets correspond to those of the appropriate disulfanes **2a—c** and the others must also be closely related in structure to **3a—c**.

The invariability of the NMR spectrum of the mixture of **3b**, **3bA**, and **3bB** with temperature or solvent and the absence of magnetic exchange between the Cp peaks argues against the assignment of **3bA** and **3bB** as conformational isomers due to restricted rotation about the sulfur—sulfur bond(s). Since the peaks due to the Cp groups are still sharp at 60°, one can use this temperature as a minimum value for a coalescence temperature and calculate[35] the minimum value for ΔG^* for exchange to be 16 kcal/mol. It is estimated[30b,36] that lone pair—lone pair interactions between bonded sulfur atoms give rise to barriers to rotation about the bond of 7.0 kcal/mol. Steric interactions in the highly congested molecule bis(2,6-di-*tert*-butylphenyl) disulfide contribute to the barrier raising it to 15.5 kcal/mol. While the $CpRu(PPh_3)(CO)$ residue in **3** is bulky, the organic groups on the other end of the trisulfanes are far removed and not very large. Therefore it seems unlikely that the extra peaks observed in the NMR spectra of **3** are due to conformational isomerism.

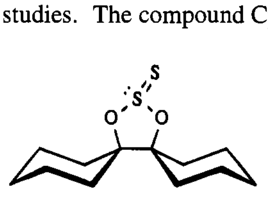
The disulfanes and other species observed account for between 20—40% of the products and thus do not originate from monosulfur transfer reagents (RSphth) or other impurities that might have been present in the disulfur transfer reagents since the NMR spectra of the latter indicated their purity exceeded 95%. The trisulfanes **3a—c** do not lose sulfur spontaneously nor do they react with PPh_3. Therefore, the disulfanes **2b** and **2c** observed in the preparation of **3b** and **3c** must originate in the preparation step. Similarly, the additional species labeled A and B could also be products of side reactions between **1** and the sulfur transfer reagents, RSSphth.

Scheme 1

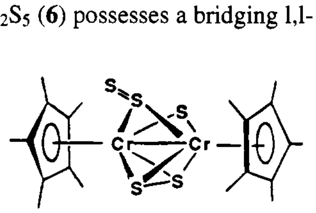


Conventional organic unsymmetrical trisulfanes R′SSSR can be prepared via reaction of the disulfur transfer reagents RSSphth with thiols R′SH. This is thought to involve attack by the thiol on the sulfur atom attached to the phthalinido residue (the α-sulfur). A similar mechanism can be invoked in the preparation of **3a—c** (Scheme 1). If the β-sulfur were attacked, however, displacement of the phth anion could still occur and **4**, a branched trisulfane, would be formed instead. If the thiophalimido anion ($Sphth^-$) were the leaving group, then the disulfanes **2a—c** would be formed. Compounds of type **4** contain two chiral sites: one at the ruthenium atom and one at the β-sulfur atom. Thus diastereomers of **4** are expected giving rise to two sets of peaks in the NMR spectrum.

Branched polysulfanes are not common. The compound F_2S_2 exists as linear and branched isomers in equilibrium.[37] The organic branched disulfane **5**[38] has been characterized by X-ray studies. The compound $Cp^*{}_2Cr_2S_5$ (**6**) possesses a bridging 1,1-disulfur ligand and is easily desulfurized by PPh_3 to give $Cp^*{}_2$-



5



6

---

[34] Hordvik, A. *Acta. Chem. Scand.* **1966**, *20*, 1885.

[35] (a) Sandstrom, J. Dynamic NMR Spectroscopy; Academic Press: New York, 1982. (b) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, England, 1987.

[36] Fraser, R. R.; Boussard, G.; Saunders, J. K.; Lambert, J. B.; Mixam, C. E. *J. Am. Chem. Soc.* **1971**, *93*, 3822.

[37] Tobolsky, A. V. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A. Ed.; Marcel Dekker: New York, 1972; Vol. 3, pp 19—38.

[38] Harpp, D. N.; Steliou, K. *J. Chem. Soc., Chem. Commun.* **1980**, 825.

Cr_2S_4.[39] Branched isomers of organic polysulfanes have been implicated in some reactions.[30a] Calculations suggest that the heat of formation of branched isomers may be only 10 Kcal greater than that of the linear isomer.[40] The oxygen homologues of **4**, namely CpRu(PPh_3)(CO)SS(O)R, have been reported and their structure characterized. The expected diastereomerism was observed.[19,24] Although highly speculative, the postulated existance of branched isomers of **3a**−**c** does account for the observations of their NMR spectra and provides a conceptual basis for further studies.

Experimental Section

All preparations were performed under nitrogen in a Schlenk tube (20 cm × 5 cm) or in a three-necked flask unless otherwise specified. Tetrahydrofuran (THF), hexanes, and toluene were refluxed over sodium/benzophenone and distilled under nitrogen just prior to use. Benzene-d_6 was freeze−thaw degassed prior to use. 2-Propanethiol, 1-propanethiol, and triphenylphoshine (Aldrich) and *p*-toluenethiol (Fairfield) were used as received. Solvents and liquid reagents were transferred by means of a syringe in one rapid injection. Syringes and containers exposed to the toxic thiols were immediately decontaminated by treatment with alcoholic KOH.

The compound $RuCl_3{\cdot}xH_2O$ was kindly supplied by PGM Chemicals Ltd., New Germany, South Africa. The complexes $CpRu(PPh_3)_2Cl$,[41] $CpRu(PPh_3)_2SH$,[22b] and $CpRu(PPh_3)(CO)SH$[22b] were prepared via methods previously reported. The following compounds were prepared as reported:[42] *N*-(4-methylphenyl)thiophthalimide ($4\text{-}MeC_6H_4Sphth$), *N*-(4-methylphenyl)dithiophthalimide ($4\text{-}MeC_6H_4SSphth$), *N*-(1-propyl)thiophthalimide ($1\text{-}C_3H_7Sphth$), *N*-(1-propyl)dithiophthalimide ($1\text{-}C_3H_7SSphth$), *N*-(2-propyl)thiophthalimide ($Me_2HCSphth$), *N*-(2-propyl)dithiophthalimide ($Me_2HCSSphth$).

Nuclear magnetic resonance spectra were recorded on Varian XL-200 and Varian XL-300 spectrometers. Spectra were run on samples in C_6D_6 prepared under nitrogen. Chemical shifts are in ppm units ± 0.01 ppm relative to tetramethylsilane (TMS) present as an internal standard. Infrared spectra were recorded on an Analect AQS-20 Fourier-transform infrared (FT-IR) spectrophotometer and calibrated by using the red line (632.8 nm) of a He/Ne laser. A triglycine sulfate (TGS) detector was used with a standard resolution of 4 cm^{-1}. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI. Melting point determinations were performed in sealed capillary tubes under nitrogen on a Thomas Hoover capillary melting point apparatus.

Cyclopentadienylcarbonyl(triphenylphosphine)((4-methylphenyl)disulfanido)ruthenium(II), $CpRu(PPh_3)(CO)SS\text{-}4\text{-}C_6H_4Me$ (2a). To a solution of $CpRu(PPh_3)(CO)SH$ (0.062 g, 0.13 mmol) in THF (25 mL) was added $4\text{-}MeC_6H_4Sphth$ (0.034 g, 0.13 mmol). The solution was stirred for 1 h, then reduced in volume under vacuum to 2 mL, and placed on a column of alumina (2 cm × 30 cm). Elution with hexanes (150 mL) followed by THF in hexanes (1:4) gave a yellow band which was collected and concentrated under vacuum until a precipitate formed. Yellow clumps of microcrystals were isolated (0.033 g, 42%; mp = 162−163 °C). ^1H NMR (C_6D_6): 7.86 (d, 2H, J(H−H) = 8.3 Hz, $4\text{-}C_6\mathit{H}_4Me$), 7.60 (m, 6H, PPh_3), 7.18 (m, 11H, PPh_3 and $4\text{-}C_6\mathit{H}_4Me$), 4.64 (s, 5H, Cp), 2.12 (s, 3H, $4\text{-}C_6H_4\mathit{Me}$). Anal. Calcd for $C_{31}H_{27}OPRuS_2$: C, 60.87; H, 4.45; S, 10.48. Found: C, 60.74; H, 4.28; S, 10.52.

Cyclopentadienylcarbonyl(triphenylphosphine)(1-propyldisulfanido)ruthenium(II), $CpRu(PPh_3)(CO)SS\text{-}1\text{-}C_3H_7$ (2b). To a solution of $CpRu(PPh_3)(CO)SH$ (0.194 g, 0.40 mmol) in THF (3 mL) was added $1\text{-}C_3H_7Sphth$ (0.088 g, 0.40 mmol) was added. The resulting solution was stirred overnight, concentrated under vacuum to 3 mL, and chromatographed on elution with hexanes followed by THF in hexanes (1:4) which gave a yellow band which was reduced to 20 mL to give a yellow crystalline product. A second crop was recovered by concentrating the mother liquor to give a combined yield of 0.101 g (45%; mp 155−156 °C). ^1H NMR (C_6D_6): 7.59 (m, 6H, PPh_3), 7.01 (m, 9H, PPh_3), 4.73 (s, 5H, Cp), 2.92 (m, 1H, $C\mathit{H}_2CH_2CH_3$), 2.74 (m, 1H, $C\mathit{H}_2CH_2CH_3$), 1.93 (m, 2H, $CH_2C\mathit{H}_2CH_3$), 1.04 (t, 3H, J(H−H) = 7.34 Hz, $CH_2CH_2C\mathit{H}_3$). Anal. Calcd for $C_{27}H_{27}OPRuS_2$: C, 57.53; H, 4.83; S, 11.38. Found: C, 57.69; H, 4.73; S, 11.41.

Cyclopentadienylcarbonyl(triphenylphosphine)(2-propyldisulfanido)ruthenium(II), $CpRu(PPh_3)(CO)SSCHMe_2$ (2c). To a solution of $CpRu(PPh_3)(CO)SH$ (0.159 g 0.325 mmol) in THF (3 mL) was added $Me_2HCSphth$ (0.072 g, 0.325 mmol). The solution was stirred overnight, reduced in volume under vacuum to 1.5 mL, and chromatographed (alumina). Elution with hexanes followed by THF in hexanes (1:4) gave a yellow band which was collected and concentrated under vacuum until turbid and left overnight. Crystallographic grade crystals were isolated. Concentration of the mother liquors under vacuum gave two more crops of crystallographic grade crystals. The combined weight was 0.120 g (66%; mp 145−147 °C). ^1H NMR (C_6D_6): 7.60 (m, 6H, PPh_3), 7.01 (m, 9H, PPh_3) 4.73 (s, 5H, Cp) 3.20 (septet, 1H, J(H−H) = 6.7 Hz, $C\mathit{H}Me_2$), 1.56 (d, 3H, J(H−H) = 6.7 Hz, $CH\mathit{Me}_2$), 1.41 (d, 3H, J(H−H) = 6.7 Hz, $CH\mathit{Me}_2$). Anal. Calcd for $C_{27}H_{27}OPRuS_2$: C, 57.53; H, 4.83; S, 11.38. Found: C, 57.36; H, 4.79, S, 11.32.

Cyclopentadienylcarbonyl(triphenylphosphine)((4-methylphenyl)trisulfanido)ruthenium(II), $CpRu(PPh_3)(CO)SSS\text{-}4\text{-}C_6H_4Me$ (3a). A sample of $CpRu(PPh_3)(CO)SH$ (0.370 g, 0.756 mmol) was combined with $4\text{-}MeC_6H_4SSphth$ (0.228 g, 0.756 mmol) and then dissolved in toluene (5 mL). The solution was stirred for 1 h and stripped to dryness. The residue was dissolved in THF (3 mL) and chromatographed (alumina). Elution with hexanes (150 mL) followed by THF in hexanes (1:4) gave a yellow band which was collected, concentrated to 40 mL, and cooled overnight at −16 °C. Yellow microcrystals (0.209 g, 43%; mp 141−144 °C) were collected, washed with hexanes (2 × 2 mL) and dried under vacuum. The analytical sample was obtained by recrystallization from CH_2Cl_2/hexanes. ^1H NMR (C_6D_6): 7.82 (d, 2H, J(H−H) = 8.2 Hz, $4\text{-}C_6\mathit{H}_4Me$), 7.5 (m, 6H, PPh_3), 7.0 (m, 9H, PPh_3), 6.88 (d, 2H, J(H−H) = 8.2 Hz, $4\text{-}C_6\mathit{H}_4Me$); 4.71 (s, 5H, Cp), 2.01 (s, 3H, $4\text{-}C_6H_4\mathit{Me}$). The overlapping sets of ^1H NMR signals due to compounds **3a**, **3aA**, and **3aB** in the ratio **3a**:A:B = 10:2:1 were observed. ^1H NMR for **3aA**: 7.5 (m, 6H, PPh_3), 7.0 (m, 9H, PPh_3), 4.68 (s, 5H, Cp), 2.10 (s, 3H, $4\text{-}C_6H_4\mathit{Me}$). ^1H NMR for **3aB**: 7.5 (m, 6H, PPh_3), 7.0 (m, 9H, PPh_3), 4.73 (s, 5H, Cp), 1.96 (s, 3H, $4\text{-}C_6H_4\mathit{Me}$). Anal. Calcd for $C_{31}H_{27}OPRuS_3$: C, 57.84; H, 4.23; S, 14.94. Found: C, 58.45; H, 4.15; S, 14.65.

Cyclopentadienylcarbonyl(triphenylphosphine)(1-propyltrisulfanido)ruthenium(II), $CpRu(PPh_3)(CO)SSS\text{-}1\text{-}C_3H_7$ (3b). A sample of $CpRu(PPh_3)(CO)SH$ (0.560 g, 1.14 mmol) was combined with 1-propyldithiophthalamide (0.290 g, 1.14 mmol) and then dissolved in toluene (5 mL) and stirred for 1 h. The solution was stripped to dryness, the residue dissolved in THF (3 mL) and chromatographed (alumina). Elution with hexanes followed by THF in hexanes (1:4) gave a yellow band which was reduced in volume under vacuum to 40 mL and left in the dark at room temperature overnight. Crystallographic grade yellow crystals were obtained (0.295 g, 44%, mp = 144−147 °C). ^1H NMR (300 MHz) (C_6D_6): 7.54 (m, 6H, PPh_3), 7.05 (m, 9H PPh_3), 4.82 (s, 5H, Cp), 2.89 (t, 2H, J(H−H) = 7.2 Hz, $C\mathit{H}_2CH_2CH_3$), 1.82 (m, 2H, $CH_2C\mathit{H}_2CH_3$), 0.88 (t, 3H, J(H−H) = 7.3 Hz, $CH_2CH_2C\mathit{H}_3$). Four overlapping sets of ^1H NMR signals due to compounds **3b**, **2b**, **3bA**, and **3bB** were observed in the ratio **3b**:**2b**:**3bA**:**3bB** = 5.4:1:3.1:1. ^1H NMR for **3bA**: 7.54 (m, 6H, PPh_3), 7.05 (m, 9H, PPh_3), 4.76 (s, 5H, Cp), 2.78 (t, 2H, J(H−H) = 7.1 Hz, $C\mathit{H}_2CH_2CH_3$, 1.71 (m, 2H, $CH_2C\mathit{H}_2CH_3$), 0.81 (t, 3H, J(H−H) = 7.7 Hz, $CH_2CH_2C\mathit{H}_3$). ^1H

---

(39) (a) Brunner, H.; Wachter, J.; Guggolz, E.; Ziegler, M. L. *J. Am. Chem. Soc.* **1982**, *104*, 1765. (b) Brunner, H.; Kauermann, H.; Meier, W.; Wachter, J. *J. Organomet. Chem.* **1984**, *263*, 183. (c) Brunner, H.; Pfauntsch, J.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1989**, *359*, 179.

(40) (a) Benson, S. *Chem. Rev.* **1978**, *78*, 23. (b) Tebbe, F. N.; Wasserman, E.; Peet, W. F.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971.

(41) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

(42) (a) Behforouz, M.; Kerwood, J. E. *J. Org. Chem.* **1969**, *34*, 51. (b) Harpp, D. N.; Back, T. G. *Tetrahedron Lett.* **1972**, *52*, 5313. (c) Kalnins, M. V. *Can. J. Chem.* **1966**, *44*, 2111. (d) Harpp, D. N.; Ash, D. K. *Int. J. Sulfur Chem., Part A* **1971**, *1*, 57. (e) Kawamura, S.; Horii, T.; Nakabayashi, T.; Hamada, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2993. (f) Back, T. G. Ph.D. Thesis, McGill University, 1974. (g) Abe, Y.; Nakabayashi, T.; Tsurugi, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1808. (h) Orwig, B. A. M.S. Thesis, McGill University, 1970.

NMR for **3bB**: 7.54 (m, 6H, PPh_3), 7.05 (m, 9H, PPh_3), 4.73 (d, 5H, *J*(H—P) = 0.6 Hz, Cp), 1.92 (m, 2H, $CH_2C\mathit{H}_2CH_3$), 1.04 (t, 3H, *J*(H—H) = 7.3 Hz, $CH_2CH_2C\mathit{H}_3$). Anal. Calcd for $C_{27}H_{27}OPRuS_3$: C, 54.44; H, 4.57; S, 16.14. Found: C, 54.11; H, 4.57; S, 16.21.

Cyclopentadienylcarbonyl(triphenylphosphine)(2-propyltrisulfanido)ruthenium(II), CpRu(PPh_3)(CO)SSSCHMe$_2$ (3c). A sample of CpRu(PPh_3)(CO)SH (0.314 g, 0.640 mmol) was combined with 2-propyldithiophthalamide (0.162 g, 0.640 mmol) and dissolved in toluene (5 mL) and the solution stirred for 1 h. The solution was stripped to dryness under vacuum; the residue was dissolved in THF (4 mL) and chromatographed (alumina). Elution with hexanes followed by THF in hexanes (1:4) gave a yellow band which was concentrated under vacuum until a small amount of precipitate formed and then left overnight in the dark. Yellow crystals (0.205 g, 54%; mp = 154—156 °C) were isolated, washed with THF in hexanes (10:19, 4 × 2 mL), and dried in a nitrogen stream. ^{1}H NMR (C_6D_6): 7.54 (m, 6H, PPh_3), 7.00 (m, 9H, PPh_3), 4.82 (s, 5H, Cp), 3.35 (septet, 1H, C*H*Me$_2$) 1.41 (d, 3H, *J*(H—H) = 6.1 Hz, CH*Me*$_2$), 1.38 (d, 3H, *J*(H—H) = 6.1 Hz, CH*Me*$_2$). Two additional overlapping sets of ^{1}H NMR signals due to compounds **3cA** and **3cB** were observed in the ratio **3c**:**3cA**:**3cB** = 11:1.4:1. ^{1}H NMR for **3cA**: 7.54 (m, 6H, PPh_3), 7.00 (m, 9H, PPh_3), 4.77 (s, 5H, Cp), 3.20 (m, 1H, C*H*Me$_2$), 1.30 (d, 3H, *J*(H—H) = 2.4 Hz, CH*Me*$_2$), 1.26 (d, 3H, *J*(H—H) = 6.4 Hz, CH*Me*$_2$). ^{1}H NMR for **3cB**: 7.54 (m, 6H, PPh_3), 7.00 (m, 9H, PPh_3), 4.72 (s, 5H, Cp), 3.20 (m, 1H, C*H*Me$_2$), 1.57 (d, 6H, *J*(H—H) = 6.6 Hz, CH*Me*$_2$). Anal. Calcd for $C_{27}H_{27}OPRuS_3$: C, 54.44; H, 4.57; S, 16.14. Found: C, 54.33, H, 4.58; S, 16.25.

Crystallographic Analyses. CpRu(PPh_3)(CO)SH (1). A thin rectangular red crystal (0.25 × 0.29 × 0.05 mm) was mounted on a fiber. Data were collected on an Enraf-Nonius diffractometer run by NRCCAD software. Cell dimensions were obtained from 20 reflections with 2θ in the range 90.00—100.00°. A total of 2816 reflections were collected having 2θ (Cu Kα) $\leq$ 99.8° ($-8 \leq h \leq 8$, $0 \leq k \leq 10$, $-10 \leq l \leq 11$) using the $\theta/2\theta$ scan mode of which 2242 were unique (merging *R* is 2.1%). A ψ correction was made for absorption. Three standards dropped an average of 2.2% in intensity over the course of the data collection. The structure was solved in *P*1, later transformed to $P\bar{1}$, and refined using the NRCVAX system of programs[43] for 1945 reflections having $I > 2.5\sigma(I)$. All non-hydrogen atoms were refined anisotropically. The hydrogen atom bonded to the sulfur atom was located in the difference map but not refined. The hydrogen positions were calculated assuming a C—H distance of 1.08 Å, a S—H distance of 1.23 Å, and a B_{iso} = 1.1 B_{iso} of the bonded atom.

CpRu(PPh_3)(CO)SSCHMe$_2$ (2c). A large yellow crystal (0.45 × 0.55 × 0.70 mm) was mounted on a fiber. Intensity data, supplied by Crystalytics Co., Lincoln, NE, were collected on a Nicolet diffractometer using the Ω scan mode. Cell dimensions were obtained from 15 reflections with 2θ in the range 10.00—25.00°. A total of 2938 reflections were collected having 2θ (Mo Kα) $\leq$ 42.0° ($-9 \leq h \leq 9$, $0 \leq k \leq 11$, $0 \leq l \leq 25$) of which 2851 were unique. Standard intensities (6) were monitored throughout the data collection and showed an average decrease of 1%. Merging *R* for 81 pairs of symmetry related reflections was 3.8%. The structure was solved by direct methods and refined using the NRCVAX system of programs[43] for 2107 reflections having $I > 2.5\sigma(I)$. The Cp ring showed rotational disorder which was modelled as two staggered five membered rings each at 50% occupancy and refined as isotopic rigid groups. The isopropyl group exhibits large thermal motion but could not be modelled as disorder and was refined with constraints on the C—C distances (1.5 Å) and the C—C—C angle (109.5°). All non-hydrogen atoms, except the Cp carbons, were refined anisotropically. The hydrogen atom positions were calculated.

CpRu(PPh_3)(CO)SSSC$_3$H$_7$ (3b). A yellow prism of approximate dimensions 0.10 × 0.10 × 0.35 mm was mounted on a glass fiber. Intensity data were collected on a Rigaku AFC6R diffractometer by the Molecular Structure Co., Woodland, TX, using the $\theta/2\theta$ scan mode. Cell dimensions were calculated from 25 reflections with 2θ in the range 40.63—44.07°. A total of 3767 were collected having 2θ (Mo Kα) $\leq$ 49.9 ($-11 \leq h \leq 11$, $0 \leq k \leq 16$, $-10 \leq l \leq 10$) of which 3540 were unique (merging R = 0.038). A ψ correction was made for absorption. The structure was solved by the Patterson method using the NRCVAX system of programs[43] for 2777 reflections having $I > 3.0\sigma(I)$. Some disorder involving S3, C25, C26, and C27 was indicated by large thermal parameters and residual electron density in the difference map in this area. The disorder could not be modeled accurately. The presence of some **2b** in the crystal of **3b** was tested as a model but this did not improve the *R* factor. The disorder was observed in three independent crystallographic determinations on different instruments using different crystals from the same batch. The non-hydrogen atoms were refined anisotropically, and except for the hydrogen atoms attached to C26 and C27 which were not included, all the other hydrogen atoms were fixed in calculated positions and their B_{iso} values were refined.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Quebec Department of Education for financial support and for scholarships to P.-Y.P. Stephen van Loggerenberg of PGM Chemicals, Ltd., is thanked for a generous gift of $RuCl_3 \cdot xH_2O$. The authors thank Dr. Rosemary Hynes for the structural determination of **1** and also thank Dr. James Britten for the structural determinations of **2c** and **3b**.

Supplementary Material Available: Tables of the methods of X-ray data collection and structure solution, bond lengths and angles, anisotropic temperature parameters and hydrogen atom positions for **1**, **2c**, and **3b** (12 pages). Ordering information is given on any current masthead page.

---

[43] Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.