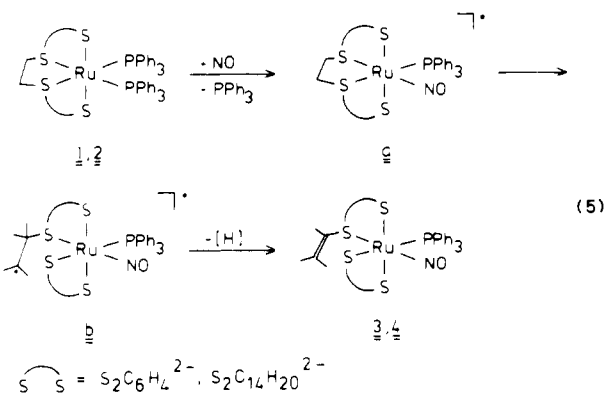

(5)

characterized only in a very few cases;[18] one example is [Fe(NO)('N_HS_4')] ('N_HS_4'$^{2-}$ = dianion of bis(2-((2-mercaptophenyl)thio)ethyl)amine).[7] Its X-ray structure analysis shows that the odd electron causes a bending of the FeNO group and a dramatic lengthening of all core distances in comparison with the analogous 18e$^-$ species.[19] This obviously relieves the electronic strain. The 19e$^-$ species a (eq 5) takes another route: S-C bond cleavage occurs (b) followed by H elimination such that the S-C_2H_4 group becomes a vinyl thioether, leading to **3** and **4**, respectively. S-C bond cleavage in organosulfur ligands[20] and formation of vinyl thioethers from alkyl thioethers[21] has been previously observed in several cases, but here the conversion of *S*-alkyl into *S*-vinyl groups is clearly induced in an unprecedented way by single electron transfer from NO via the Ru center and S atoms.

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Supplementary Material Available: Listings of crystallographic data and data collection parameters, anisotropic thermal parameters, all bond distances and bond angles, and fractional coordinates of hydrogen atoms (8 pages); a listing of F_o and F_c values (22 pages). Ordering information is given on any current masthead page. Further details of the X-ray crystal structure analysis have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, and can be obtained by quoting deposition no. CSD-320096, the authors' names, and the reference.

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Preparation of (η-C_5H_5)Ru(PPh_3)(L)SR (R = 1-C_3H_7, $CHMe_2$, 4-C_6H_4Me; L = PPh_3, CO) and Insertion of CS_2 into the Ru-SR Bond To Give the Thioxanthates (η-C_5H_5)Ru(PPh_3)S_2CSR (R = 1-C_3H_7, $CHMe_2$, 4-C_6H_4Me). Crystal Structure of (η-C_5H_5)Ru(PPh_3)S_2CS-1-C_3H_7

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The reactive thiolato complexes (η-C_5H_5)Ru(PPh_3)$_2$SR, where R = 1-C_3H_7, $CHMe_2$, and 4-C_6H_4Me were prepared by briefly heating (η-C_5H_5)Ru(PPh_3)$_2$Cl and the appropriate alkali-metal thiolate in refluxing tetrahydrofuran. Treatment of the thiolates with CO gave (η-C_5H_5)Ru(PPh_3)(CO)SR. Treatment with CS_2 gave the thioxanthate complexes (η-C_5H_5)Ru(PPh_3)S_2CSR, where R = 1-C_3H_7, $CHMe_2$, and 4-C_6H_4Me, wherein the CS_2 has inserted into the Ru-SR bond. The structure of (η-C_5H_5)Ru(PPh_3)S_2CS-1-C_3H_7 was determined: space group $P\bar{1}$, a = 10.88 (1) Å, b = 10.06 (1) Å, c = 12.82 (2) Å, α = 105.05 (12)°, β = 95.00 (11)°, γ = 101.17 (9)°, V = 1314.9 Å^3, and Z = 2. The rate of CS_2 insertion is accelerated by increasing the CS_2 concentration and depressed by adding free ligand (PPh_3 or CO). The implications with respect to the mechanism of CS_2 insertion are discussed.

Introduction

Organoruthenium-sulfur chemistry is a topic of current interest. Angelici et al.[2] have developed the chemistry of π-bonded CpRu-thiophene cations as a model for hydrodesulfurization. Rauchfuss et al.[3] have reported several CpRu-polysulfide complexes with unusual structures and reactivity. We are interested in preparing complexes containing linear catenated polysulfur ligands[4] of the type RS_x^-, where $x > 1$. Such species are analogues of the ubiquitous organic polysulfanes yet are themselves surprisingly rare. To that end, we investigated the synthesis of complexes of the type $CpRu(PPh_3)_2SR$. The complexes $CpRuL_2SPh$, where L = CO, PMe_3, $P(OMe)_3$, $P(OMe)_2Ph$, and $P(OPr)_3$ and L_2 = $Ph_2PCH_2CH_2PPh_2$ have been reported.[5] A

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Table I. Analytical Data for $CpRu(PPh_3)_2SR$, $CpRu(PPh_3)S_2CSR$, and $CpRu(PPh_3)(CO)SR$[a]

compd	no.	yield, %	mp, °C	% C calcd	% C found	% H calcd	% H found	% S calcd	% S found
$CpRu(PPh_3)_2S$-1-C_3H_7	**1a**	79	167–169	69.00	68.84	5.53	5.45	4.19	4.16
$CpRu(PPh_3)_2SCHMe_2$	**1b**	68	161–163	69.00	68.83	5.53	5.55	4.19	4.23
$CpRu(PPh_3)_2S$-4-C_6H_4Me	**1c**	84	207–210	70.83	70.76	5.20	5.21	3.94	3.90
$CpRu(PPh_3)_2SH$	**1d**	63	171–174	68.04	67.96	5.01	5.08	4.43	4.39
$CpRu(PPh_3)S_2CS$-1-C_3H_7	**2a**	69	120–122	55.94	56.03	4.69	4.69	16.59	16.67
$CpRu(PPh_3)S_2CSCHMe_2$	**2b**	73	162–164	55.94	56.08	4.69	4.73	16.59	16.26
$CpRu(PPh_3)S_2CS$-4-C_6H_4Me	**2c**	83	173–176	59.31	59.42	4.33	4.43	15.31	15.24
$CpRu(PPh_3)(CO)S$-1-C_3H_7	**3a**	41	133–134	61.00	61.13	5.12	5.20	6.03	6.04
$CpRu(PPh_3)(CO)SCHMe_2$	**3b**	48	157–158	61.00	61.18	5.12	5.22	6.03	6.04
$CpRu(PPh_3)(CO)S$-4-C_6H_4Me[b]	**3c**	47	166–168	64.37	64.46	5.07	5.14	5.21	5.29
$CpRu(PPh_3)(CO)SH$	**3d**	67	190[c]	58.89	58.79	4.32	4.22	6.55	6.62

[a] ν(CO), (toluene, Nujol) cm^{-1}: **3a**, 1942, 1934; **3b**, 1941, 1942; **3c**, 1947, 1944; **3d**, 1950, 1935. [b] $CpRu(PPh_3)(CO)S$-4-$C_6H_4Me \cdot {}^1/_2THF$, confirmed by NMR. [c] Decomposed.

Table II. ^1H NMR Data for $CpRu(PPh_3)_2SR$, $CpRu(PPh_3)S_2CSR$, and $Cp_2Ru_2(PPh_3)_3CS_3$[a,b]

compd	no.	chem shift C_5H_5	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	$CHMe_2$	CH_3
$CpRu(PPh_3)_2S$-1-C_3H_7	**1a**	4.36	2.41[c]	1.98[d]		1.19[e]
$CpRu(PPh_3)_2SCHMe_2$	**1b**	4.37			2.52[f]	1.58
$CpRu(PPh_3)_2S$-4-C_6H_4Me[g]	**1c**	4.14				2.21
$CpRu(PPh_3)_2SH$[h]	**1d**	4.28				
$CpRu(PPh_3)S_2CS$-1-C_3H_7	**2a**	4.31	2.76[i]	1.38[d]		0.67[j]
$CpRu(PPh_3)S_2CSCHMe_2$	**2b**	4.33			3.70[k]	1.08
$CpRu(PPh_3)S_2CS$-4-C_1H_4Me[l]	**2c**	4.28				1.95
$CpRu(PPh_3)(CS)S$-1-C_3H_7	**3a**	4.67[m]	2.61[d]	1.87[d]		1.14[j]
$CpRu(PPh_3)(CO)SCHMe_2$	**3b**	6.67[m]			2.77[d]	1.53[n]
						1.59[n]
$CpRu(PPh_3)(CO)S$-4-C_6H_4Me[o]	**3c**	4.63				2.21
$CpRu(PPh_3)(CO)SH$[p]	**3d**	4.56[q]				
$Cp_2Ru_2(PPh_3)_3CS_3$[r,s]	**4**	4.67				
		4.54				

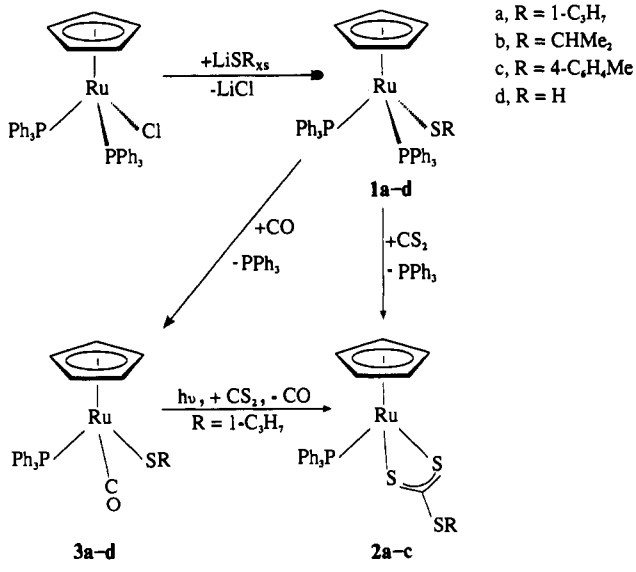
[a] In C_6D_6 solution; reported in ppm. [b] Phenyl resonances of PPh_3 appeared as two multiplets in the ranges 6.90–7.05 ppm and 7.52–7.72 ppm in the ratio 3:2. [c] Triplet, J(H–H) = 7.2 Hz. [d] Multiplet. [e] Triplet, J(H–H) = 6.9 Hz. [f] Septet, J(H–H) = 6.6 Hz. [g] C_6H_4Me, 7.69 ppm, 2 H, doublet, J(H–H) = 8.0 Hz; the other doublet was obscured by PPh_3 resonances. [h] SH, −3.11 ppm, triplet, J(P–H) = 6.15 Hz. [i] Triplet, J(H–H) = 7.3 Hz. [j] Triplet, J(H–H) = 7.4 Hz. [k] Septet, J(H–H) = 6.9 Hz. [l] C_6H_4Me, 6.82 and 7.21 ppm, doublets, J(H–H) = 8.0 Hz. [m] Doublet, J(P–H) = 0.4 Hz. [n] Doublet, J(H–H) = 6.6 Hz. [o] C_6H_4Me, 7.87 ppm, 2 H, doublet, J(H–H) = 8.2 Hz; the other doublet was obscured by PPh_3 resonances. [p] SH, −3.10 ppm, doublet, J(P–H) = 7.4 Hz. [q] Doublet, J(P–H) = 0.6 Hz. [r] The phenyl resonances of the PPh_3 ligands appeared as four multiplets in the ranges 6.86–7.00, 7.06–7.16, 7.30–7.50 and 7.70–7.90 ppm in the ratio 6:3:4:2. [s] ^{31}P NMR (ppm with respect to external H_3PO_4 (intensity)): 41.28 (2), 52.36 (1) ppm.

cationic thiol complex $[CpRu(PPh_3)_2S(H)$-1-$C_3H_7]BF_4$ has been reported.[3a,6,7] Our first attempts to displace the chloro ligand from $CpRu(PPh_3)_2Cl$ with thiolato anions were unsuccessful due to the tendency of the products, $CpRu(PPh_3)_2SR$, to lose PPh_3 easily. However, preparation of the these complexes was achieved via brief reflux of the chloro starting material and thiolato anions in THF. The tendency to lose PPh_3 was exploited[7] by simply treating the complexes with CO to give $CpRu(PPh_3)(CO)SR$. The bis(phosphine) complexes aggregate in solution to form dimers and trimers.[8] The facile insertion of CS_2 into the Ru–SR bond to give the thioxanthates $CpRu(PPh_3)S_2CSR$ is reported, and aspects of the mechanism of this reaction are discussed.

Results

Briefly refluxing $CpRu(PPh_3)_2Cl$ with excess lithium thiolate in THF for 15–20 min gave the thiolate complexes $CpRu(PPh_3)_2SR$ (**1a–d**) in good yields (Table I).[9] The reaction conditions are crucial. Stirring a stoichiometric mixture of the reagents at room temperature always gave a mixture of the chloro complex and **1** regardless of the time of reaction. This suggested that an equilibrium had been established. Prolonged refluxing (1 h) of the chloro complex with excess lithium thiolate gave a mixture of CpRu species as indicated by the complicated Cp region

Scheme I



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(9) Complex **1d** has been reported in ref 7; the preparation reported here gave the same yield but takes less time to perform than that reported.

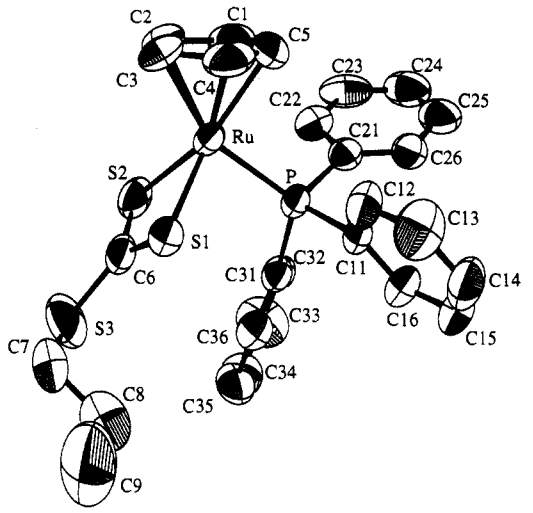

Figure 1. Computer-generated thermal ellipsoid drawing (probability level 50%) of $CpRu(PPh_3)S_2CS\text{-}1\text{-}C_3H_7$.

Table III. Crystallographic Data for $CpRu(PPh_3)S_2CS\text{-}1\text{-}C_3H_7$

chemical formula: $C_{27}H_{27}PRuS_3$	fw = 579.65
a = 10.88 (1) Å	space group: $P\bar{1}$ (No. 2)
b = 10.06 (1) Å	T = 22 °C
c = 12.82 (2) Å	λ = 0.71069 Å
α = 105.05 (12)°	ρ_{calcd} = 1.446 g cm^{-3}
β = 95.00 (11)°	μ(MoKα) = 8.86 cm^{-1}
γ = 101.17 (9)°	transm coeff = 63–76%
V = 1314.9 Å^3	R_1 = 0.065
Z = 2	R_2 = 0.104

Table IV. Positional Parameters for $CpRu(PPh_3)S_2CS\text{-}1\text{-}C_3H_7$

	x	y	z
Ru	0.37437 (6)	0.07406 (7)	0.21193 (6)
P	0.22463 (20)	0.03157 (22)	0.31961 (18)
S(1)	0.28571 (22)	0.85265 (24)	0.08165 (20)
S(2)	0.48064 (22)	0.9050 (3)	0.25083 (24)
S(3)	0.4051 (4)	0.6093 (4)	0.1091 (4)
C(1)	0.4726 (11)	0.2937 (10)	0.2897 (9)
C(2)	0.5435 (10)	0.2279 (11)	0.2058 (11)
C(3)	0.4699 (11)	0.1867 (11)	0.1062 (10)
C(4)	0.3543 (11)	0.2236 (11)	0.1200 (10)
C(5)	0.3557 (10)	0.2877 (10)	0.2280 (9)
C(6)	0.3882 (9)	0.7829 (10)	0.1438 (9)
C(7)	0.3078 (14)	0.5296 (14)	−0.0258 (14)
C(8)	0.1808 (19)	0.4744 (18)	−0.0029 (22)
C(9)	0.118 (3)	0.403 (4)	−0.099 (3)
C(9′)	0.1013 (25)	0.345 (3)	−0.0117 (24)
C(11)	0.0596 (7)	0.0091 (8)	0.2611 (7)
C(12)	0.0349 (9)	0.0603 (11)	0.1721 (8)
C(13)	−0.0892 (11)	0.0515 (14)	0.1286 (9)
C(14)	−0.1859 (9)	−0.0056 (12)	0.1745 (9)
C(15)	−0.1651 (9)	−0.0568 (11)	0.2615 (9)
C(16)	−0.0412 (8)	−0.0495 (10)	0.3046 (8)
C(21)	0.2434 (8)	0.1775 (9)	0.4465 (7)
C(22)	0.3643 (10)	0.2261 (10)	0.5086 (9)
C(23)	0.3848 (12)	0.3352 (11)	0.6042 (10)
C(24)	0.2862 (13)	0.3942 (11)	0.6397 (9)
C(25)	0.1701 (12)	0.3487 (10)	0.5778 (10)
C(26)	0.1475 (9)	0.2373 (9)	0.4814 (8)
C(31)	0.2139 (8)	−0.1254 (9)	0.3682 (7)
C(32)	0.2607 (12)	−0.1175 (12)	0.4756 (10)
C(33)	0.2603 (15)	−0.2385 (15)	0.5053 (11)
C(34)	0.2119 (13)	−0.3686 (13)	0.4331 (12)
C(35)	0.1639 (12)	−0.3801 (11)	0.3280 (10)
C(36)	0.1640 (9)	−0.2563 (10)	0.2950 (8)

in the NMR spectrum of the crude product. Solutions of the complexes **1** are red and they are moderately air-sensitive in solution. They react with methylene chloride, chloroform, and carbon tetrachloride to give the chloro complex. Such sensitivity of metal thiolates to chlorinated hydrocarbon solvents has been

Table V. Selected Bond Lengths (Å) and Angles (deg) for $CpRu(PPh_3)S_2CS\text{-}1\text{-}C_3H_7$

Ru–C(1)	2.184 (4)	Ru–C(5)	2.156 (3)
Ru–C(2)	2.185 (3)	Ru–S(1)	2.374 (4)
Ru–C(3)	2.188 (3)	Ru–S(2)	2.362 (2)
Ru–C(4)	2.168 (3)	Ru–P	2.274 (3)
C(6)–S(1)	1.676 (2)	C(6)–S(3)	1.737 (2)
C(6)–S(2)	1.676 (3)		
C(1)–C(2)	1.471 (2)	C(4)–C(5)	1.363 (3)
C(2)–C(3)	1.365 (3)	C(5)–C(1)	1.420 (2)
C(3)–C(4)	1.392 (1)		
P–C(11)	1.833 (2)	P–C(31)	1.829 (2)
P–C(21)	1.851 (3)		
S(1)–Ru–S(2)	71.47 (11)	S(1)–Ru–C(3)	99.52 (13)
S(1)–Ru–P	90.76 (12)	S(1)–Ru–C(4)	102.88 (12)
S(1)–Ru–C(1)	163.36 (4)	S(1)–Ru–C(5)	134.41 (8)
S(1)–Ru–C(2)	127.01 (10)		
P–Ru–C(1)	103.88 (11)	P–Ru–C(4)	117.38 (8)
P–Ru–C(2)	142.16 (8)	P–Ru–C(5)	93.92 (10)
P–Ru–C(3)	154.17 (4)		
S(2)–Ru–P	93.35 (9)	S(2)–Ru–C(3)	112.35 (8)
S(2)–Ru–C(1)	114.74 (10)	S(2)–Ru–C(4)	149.08 (5)
S(2)–Ru–C(2)	96.55 (9)	S(2)–Ru–C(5)	152.92 (5)
Ru–P–C(11)	116.73 (10)	Ru–P–C(31)	118.00 (8)
Ru–P–C(21)	112.71 (12)		
Ru–S(1)–C(6)	88.45 (12)	S(1)–C(6)–S(2)	111.21 (11)
Ru–S(2)–C(6)	88.86 (11)	S(1)–C(6)–S(3)	127.92 (10)
C(6)–S(3)–C(7)	103.65 (12)	S(2)–C(6)–S(3)	120.87 (10)

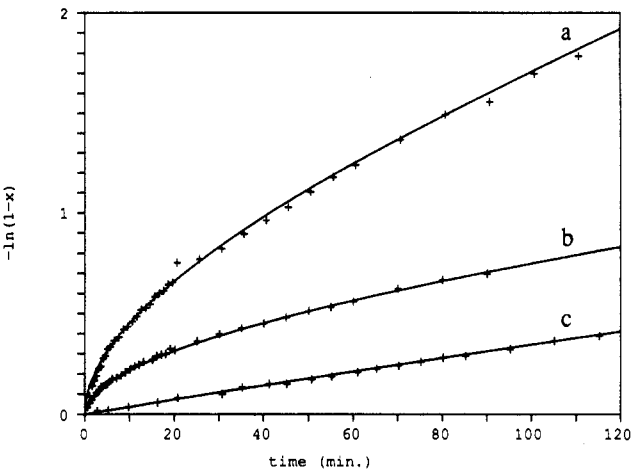

Figure 2. Calculated curves and experimental rate data for the reaction of **1c** with CS_2: (a) reaction with $[\mathbf{1c}]_0$:$[CS_2]$ = 1:385 with no added PPh_3; (b) reaction as in part a with $[\mathbf{1c}]_0$:$[CS_2]$ = 1:96, i.e. a 4-fold reduction; (c) reaction as in part a with $[PPh_3]_0 = 2[\mathbf{1c}]_0$.

observed previously[10] and indicates a high degree of nucleophilicity for the coordinated sulfur atom. Refluxing toluene solutions of **1a,b** led to aggregation with loss of PPh_3.[8] The analytical and selected spectroscopic data for **1a–d** are given in Tables I and II, respectively.

Complexes **1a–c** reacted easily with CS_2 to give the thioxanthates **2a–c** in very good yields (Scheme I). These dark red highly crystalline complexes are much less air-sensitive than **1a–c**. NMR studies of the reaction of **1a–c** with CS_2 indicate that **2a–c** are the only products. Treatment of a C_6D_6 solution of **2a–c** with CO gave no evidence of any reaction in the NMR spectrum. Complexes **1a–c** did not react with CO_2. The X-ray structure of **2a** (Figure 1) confirms the presence of the thioxanthate ligand. The crystal data, atomic coordinates and selected bond lengths and angles are given in Tables III–V, respectively. The structure is consistent with those reported for similar complexes.[11]

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The reaction of **1c** with CS_2 under various conditions was followed by monitoring the NMR spectrum. Increasing the concentration of CS_2 increased the rate of reaction whereas adding free PPh_3 decreased the rate. The results are shown in Figure 2. Purging an NMR sample of **1c** with CO after approximately 50% reaction with CS_2 quenched the reaction and largely converted the remaining **1c** to $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ (**3c**).

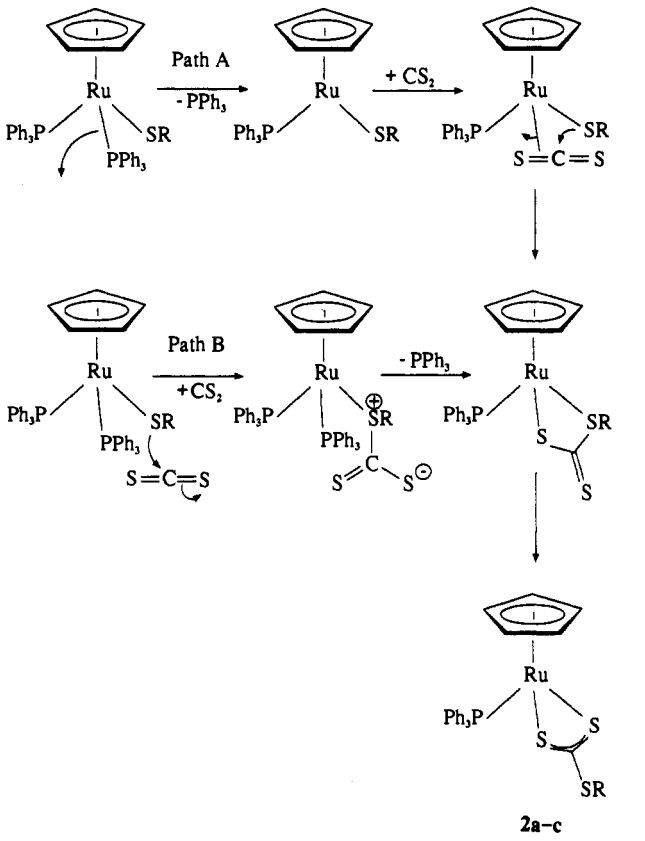
Simply bubbling CO through toluene solutions of **1a–d** gave the carbonyl complexes $CpRu(PPh_3)(CO)SR$ (**3a–d**) in very good yield.[12] These orange to yellow complexes are very stable. They do not react with CS_2 under the same conditions as **1a–c**, but UV irradiation of a C_6D_6 solution of **3a** and CS_2 in an NMR tube gave peaks due to **2a** in the NMR spectrum.

The thiol **1d** reacted with CS_2 quite slowly over 48 h with concomitant evolution of H_2S to give a red product formulated as $Cp_2Ru_2(PPh_3)_3CS_3$ (**4**) on the basis of its spectroscopic properties. The ^1H NMR spectrum (Table II) displayed peaks in the phenyl region consistent with the presence of two different environments for the PPh_3 ligands in the ratio 2:1 and two peaks in the Cp region, each corresponding to one ring in relative intensity, consistent with the formulation. The proton-decoupled ^{31}P NMR spectrum (Table II) also displayed two peaks in the ratio 2:1. In both the ^1H and ^{31}P NMR spectra, additional small peaks due to a contaminant that varied in concentration relative to **4** were observed; it was not possible to obtain a pure sample for elemental analysis. However, the FAB mass spectrum (see Experimental Section) of **4** gave a molecular ion and a fragmentation pattern consistent with its formulation. The infrared spectrum of **4** was compared to those of **1a–c**, **2a–c**, and $CpRu(PPh_3)_2Cl$. One can identify bands due to the C–S stretch of the R–S moiety[13] in **1a–c** and **2a–c** in the range 821–748 cm^{-1}.[14] However, no band was observed in this region for **4**. Strong bands due to the thioxanthate group are reported to appear in the ranges 990–980 and 950–940 cm^{-1}.[13] The ranges observed[14] for **2a–c** were 993–972 and 962–941 cm^{-1} while bands at 964 and 907 cm^{-1} were observed for **4**.

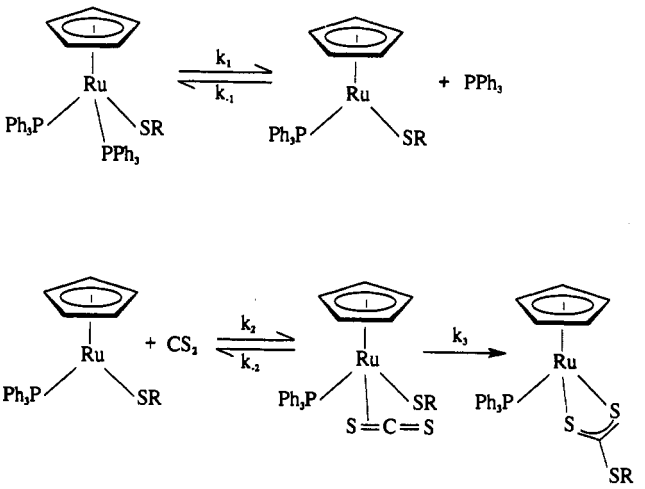
Discussion

The decision to treat **1a–d** with CS_2 was based on an apparent analogy between these complexes and $CpW(CO)_2(PPh_3)SR$. The latter dimerize[15] easily with loss of PPh_3 and also undergo insertion with CS_2 to give $CpW(CO)_2S_2CSR$.[16] The reactions of **1a–d** are remarkably similar. The insertion of CS_2 into the Ru–S bonds of **1a–c** to give thioxanthates is formally analogous to the insertion of CO_2 into metal–alkoxide bonds to give carbonates.[17] Most transition-metal thioxanthate type complexes ($CpRu(PPh_3)S_2COEt$,[18] for example) are prepared via reaction[11a] of the metal halide with $M(S_2CSR)$, where M = alkali-metal ion. Alkali-metal thiolates give thioxanthate salts upon treatment with CS_2,[11a] and insertion of CS_2 into transition-metal thiolates other than the tungsten complexes above has been reported.[11f,19] However, there has been little investigation of the mechanism of the reaction. At least two extremes can be envisioned (Scheme II): (a) attack by precoordinated CS_2 (precoordinated insertion) or (b) attack by free CS_2 on the sulfur atom of the thiolato ligand (free insertion). Although the presence of cis and trans isomers

Scheme II



Scheme III



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(13) Reference 11a, p 183 and references therein.

(14) Infrared spectral data, cm^{-1} (solid state), are as follows: ν(C–S): **1a**, 761; **1b**, 821; **1c**, 748; **2a**, 807; **2b**, 803; **2c**, 805. $\nu(CS_3)$: **2a**, 972, 962; **2b**, 975, 958; **2c**, 993, 941; **4**, 964, 907.

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of $CpW(CO)_2(PPh_3)SR$ complicated the analysis, qualitative observations on the kinetics of the reaction with CS_2 suggested precoordinated insertion in that case.[16]

In the reaction of **1a–c** with CS_2, qualitative observations include (a) rate acceleration with increasing CS_2 concentration, (b) inhibition by added free PPh_3 or CO, (c) formation of **3a–c** in the presence of CS_2 and CO, and (d) failure of **3a–c** to react with CS_2 in the absence of UV irradiation. With respect to the last point, CpRu(dppe)SR, where dppe = $PPh_2CH_2CH_2PPh_2$ and R = 1-C_3H_7, does not react with CS_2. This contrasts sharply with the reactions[20] of both $CpRu(PPh_3)_2H$ and CpRu(dppe)H with CS_2 to give $CpRu(PPh_3)_2SC(S)H$ and CpRu(dppe)SC(S)H, respectively, containing monodentate thioformato ligands. There was no evidence for the presence of intermediates containing monodentate thioxanthato ligands in the NMR spectra taken during the reactions of **1a–c** with CS_2. Nor could monodentate binding be induced by bubbling CO through solutions of **2a–c**.

Assuming a mechanism involving loss of PPh_3 followed by coordination of CS_2 (Scheme III), a rate law

$$\frac{d[\mathbf{2}]}{dt} = \frac{V_s}{K_s[PPh_3]/(K_I[CpRu(PPh_3)_2SR] + 1)}$$

based on inhibited enzyme kinetics[21] was derived, where $V_s = k_3[CS_2]$, $K_I = [CpRu(PPh_3)SR][PPh_3]/[CpRu(PPh_3)_2SR]$, and $K_s = (k_2 + k_3)/k_2$, the Michaelis constant. Integration of this rate equation gave an expression of time as a function of product concentration:

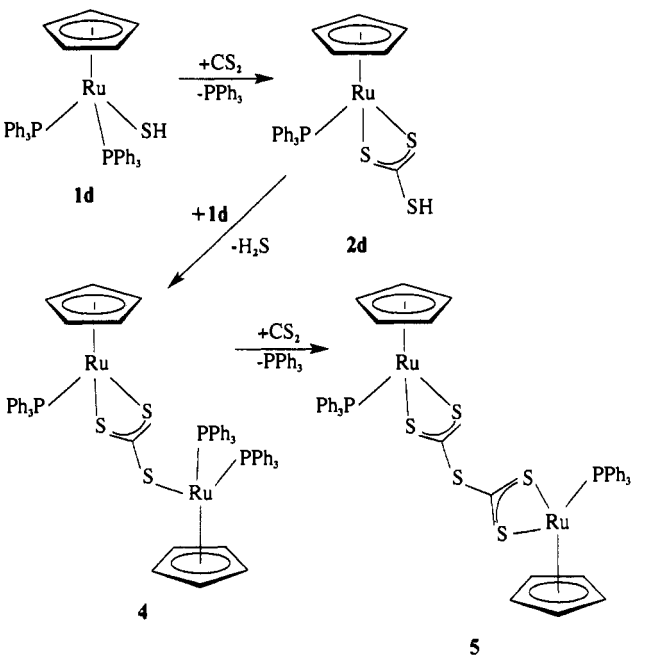
$$t = \frac{K_s}{V_s K_I}\left\{\left(\frac{K_I}{K_s} - 1\right)[CpRu(PPh_2)SR]_0 X - ([CpRu(PPh_3)_2SR]_0 + [PPh_3]_0) - \ln(1 - X)\right\}$$

$$X = \frac{[CpRu(PPh_3)S_2CSR]}{[CpRu(PPh_3)S_2CSR] + [CpRu(PPh_3)_2SR]}$$

The term X, which contains the product concentration, cannot be isolated because it occurs as a ln term and as a linear term. The equation was simplified to $t = C_1\{C_2[CpRu(PPh_3)_2SR]_0 X - C_3 \ln(1 - X)\}$ and with $C_3 = [CpRu(PPh_3)_2SR]_0$, i.e., $[PPh_3]_0 = 0$, the values of C_1 and C_2 were calculated by computer iteration[22] to give curve 2a (Figure 2). If C_1 is multiplied by 4 to simulate a 4-fold decrease in $[CS_2]$, then curve 2b results. Finally changing C_3 to simulate adding 2 equiv of PPh_3 gave curve 2c. These calculated curves agree reasonably well with the experimental data for $C_1 = 1.2 \times 10^4$ and $C_2 = -1$ and one can calculate $K_I/K_s = 2 \times 10^{-4}$ and $k_3 = 1.2 \times 10^{-1}\ s^{-1}$; however, such values are subject to large uncertainties.

The reaction of CO_2 with the W–OR bond of $W(CO)_2OR^-$ was not inhibited by CO which is consistent with free insertion.[17a] However, our results strongly support insertion of precoordinated CS_2 into the Ru-SR bond of **1a–c**. The reactivity of **1a–c** is due to the ease of loss of a PPh_3 ligand. This is probably due to a combination of factors one being the steric congestion in the coordination sphere due to the presence of two bulky PPh_3 groups. Another factor is the ability of the thiolato ligand to both activate the complex toward ligand dissociation[25a] and stabilize the resulting 16-electron coordinatively unsaturated intermediate via $p\pi$–$d\pi$ donation.[25b] Replacing a PPh_3 ligand with a CO group, a smaller and better π-acceptor, as in **3a–c** markedly reduces the reactivity of the system.

Scheme IV



The reaction of $CpRu(PPh_3)_2SH$ (**1d**) with CS_2 gave **4**, which is not a simple analogue of **2a–c**. Nevertheless, it is reasonable to conclude that incorporation of CS_2 has occurred but that further reaction followed. The presence of a CS_3 moiety is consistent with the infrared and mass spectra while the mass of the parent ion and the NMR spectra clearly suggest the presence of two different CpRu moieties. A reasonable reaction sequence wherein CS_2 inserted into the Ru–SH bond to give $CpRu(PPh_3)S_2CSH$ (**2d**) followed by its reaction with **1d** to give **4** is depicted in Scheme IV. The CS_3^{2-} group has been observed as a bidentate ligand bonded to one metal[23] or as a tridentate ligand bridging two metals as postulated in **4**.[24] It is conceivable that **4** could react further with CS_2 via insertion and loss of PPh_3 to give $[CpRu(PPh_3)S_2C]_2S$ (**5**). The reaction of **1d** with CS_2 in C_6D_6 was carefully monitored in the NMR spectrum, and no evidence for the presence of **2d** was detected during the production of **4**. It is possible that the concentration of **2d** never becomes great enough to detect because further reaction with **1d** is rapid. However, it is possible that the impurity that slowly appears concomitantly with **4** is due to **5**. Isolated samples of **4** reacted so slowly even in the presence of high concentrations of CS_2 that it has been difficult to investigate the system further.

Experimental Section

All experiments were performed under nitrogen in a Schlenk tube (20 cm × 5 cm) or in an appropriately sized three-necked flask unless otherwise specified. Tetrahydrofuran (THF), hexanes, and toluene were refluxed over sodium/benzophenone and distilled under nitrogen just prior to use. Absolute ethanol was degassed by repeated evacuation (three times) followed each time by purging with nitrogen. Benzene-d_6 and CS_2 were freeze–thaw degassed prior to use. 2-Propanethiol, 1-propanethiol, and triphenylphosphine (Aldrich) and *p*-toluenethiol (Fairfield) were used as received. Solvents and liquid reagents were transferred by means of an appropriately sized 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 complex $CpRu(PPh_3)_2Cl$ was prepared as reported.[26]

Nuclear magnetic resonance spectra were recorded on Varian XL-200 and Varian XL-300 spectrometers. Spectra were run on samples in C_6D_6

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prepared under nitrogen. Chemical shifts are in ppm units ±0.01 ppm relative to tetramethylsilane (TMS) present as an internal standard. The progress of the reaction of **1c** with CS_2 in C_6D_6 under various conditions was followed by automatically acquiring spectra at appropriate intervals by means of an array of preacquisition delays and comparing the relative integrals of the Cp peaks due to **1c** and **2c**. 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}. The fast atom bombardment (FAB) mass spectrum of **4** was obtained on a ZAB-HS mass spectrometer at the McGill University Biomedical Mass Spectrometry Unit with Xe as the ionizing gas, 8 kV as the ionizing potential, and nitrobenzyl alcohol as the matrix. 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 and are uncorrected.

(Cyclopentadienyl)bis(triphenylphosphine)(1-propanethiolato)ruthenium(II), $CpRu(PPh_3)_2S$-1-C_3H_7 (1a). The preparations of **1a–c** are very similar to that of **1a**, which follows. A Schlenk tube (5-cm diameter) was charged with THF (110 mL) and methyl lithium (2.05 mL, 1.4 M in ether, 2.87 mmol) and cooled to −78 °C (ethanol/dry ice bath). To this was added 1-propanethiol (0.26 mL, 2.87 mmol), the cooling bath was removed, and the stirred solution was allowed to warm to 0 °C and then heated by immersing the Schlenk tube in a water bath at 40 °C. The complex $CpRu(PPh_3)_2Cl$ (1.00 g, 1.44 mmol) was added and the resultant slurry rapidly brought to reflux within 7 min by heating the water bath with a hot plate. A gentle reflux was maintained for a further 15 min, after which the red reaction solution was rapidly concentrated under vacuum to 50 mL and ethanol (100 mL) was added. Further concentration to 50 mL followed by allowing the mixture to stand gave **1a** as red crystals, which were collected by decanting the mother liquors. The crystals were washed successively with ethanol and hexanes and pumped on overnight to give the analytical sample. The compound $CpRu(PPh_3)_2SCHMe_2$ (**1b**) was recrystallized from THF/ethanol to give a beige powder.

(Cyclopentadienyl)bis(triphenylphosphine)mercaptoruthenium(II), $CpRu(PPh_3)_2SH$ (1d). *Caution*! The preparation involves the use of H_2S, which is toxic and has a bad odor. The reaction was conducted in a well-ventilated fume hood, and the H_2S was handled by means of a gas manifold. The H_2S emanating from an H_2S cylinder (Matheson) via Tygon tubing was dried by means of a calcium chloride column and passed through a Nujol bubbler before entering the reaction vessel: a three-necked round-bottomed flask fitted with a stopcock, a gas inlet bubbler, and a stopper and a magnetic stir bar. After passing through the reagents, unreacted H_2S was passed through three washing towers containing, successively, 5 M NaOH, saturated aqueous lead acetate, and 5 M NaOH. A nitrogen line (Tygon) was connected to the H_2S manifold prior to the calcium chloride drying column by means of a T-connector attached to a stopcock. This permitted the system to be purged before and, importantly, after the reaction, which significantly reduced exposure to residual H_2S during workup.

Sodium (0.10 g, 4.34 mmol) was dissolved in absolute ethanol (20 mL) and H_2S was bubbled through the solution at a steady rate for 30 min. Then the solution was purged with N_2 for 20 min, and THF (50 mL) and $CpRu(PPh_3)_2Cl$ (1.00 g, 1.31 mmol) were added. The resulting slurry was brought rapidly to reflux (heating mantle), which was maintained for 15 min, after which the solution was cooled to room temperature (water bath). The brown solution was stripped to dryness (vacuum pump) and repeatedly extracted with toluene (4 × 15 mL). Each extract was filtered under nitrogen through celite (1 in.). The combined filtrates were stripped to dryness and the resulting dark oil recrystallized from THF/ethanol to give the analytical sample as orange-brown microcrystals. These were washed with ethanol followed by hexanes and pumped on overnight.

(Cyclopentadienyl)(triphenylphosphine)(1-propyl thioxanthato)ruthenium(II), $CpRu(PPh_3)S_2CS$-1-C_3H_7 (2a). The preparations of **2a–c** are similar to that of **2a** which follows except that the chromatography step was omitted in the preparations of **2b** and **2c**. A solution of $CpRu(PPh_3)_2S$-1-C_3H_7 (0.500 g, 0.65 mmol) in toluene (100 mL) was treated with CS_2 (40 mL), and the resulting solution was stirred for 30 min (**2b**, 45 min; **2c**, 60 min). The solution was stripped to dryness under vacuum and the residue dissolved in toluene (5 mL). This solution was chromatographed on a column (2.5 cm × 23 cm) of activated alumina. Elution with hexanes gave a fraction containing free PPh_3. Elution with THF/hexanes (1:4) gave an orange band, which was collected, concentrated to 30 mL, and cooled at −16 °C overnight. The mother liquors were decanted and the red crystals of **2a** were washed with cold (−78 °C) hexanes and pumped on overnight. Another crop of crystals was recovered from the mother liquors.

Complex **2b** was obtained by concentrating the volume of the reaction solution to 10 mL and adding ethanol (15 mL). Further concentration to initiate crystallization followed by cooling at −78 °C gave deep red crystals of **2b**, which were filtered, washed with cold (−78 °C) ethanol followed by hexanes, and then pumped on overnight.

Complex **2c** was isolated by stripping the reaction solution to dryness and recrystallizing the residue from THF/ethanol to give deep red crystals, which were treated as above.

(Cyclopentadienyl)(triphenylphosphine)carbonyl(1-propanethiolato)ruthenium(II), $CpRu(PPh_3)(CO)S$-1-C_3H_7 (3a). The preparations of **3a–d** are slight variations on that of **3a** described as follows. A flask containing **1a** (0.49 g, 0.64 mmol) in THF (70 mL) was evacuated and refilled with 1 atm of carbon monoxide. The reaction solution was stirred overnight and then concentrated to 2 mL in volume. It was transferred to the top of a column of alumina. Elution with hexanes gave a fraction containing PPh_3. Elution with THF/hexanes (2:3) gave a yellow band, which was concentrated to 2 mL in volume and left standing overnight to give orange crystals. These were washed with hexanes and dried under vacuo.

The chromatography step was omitted, and **3c** was precipitated by adding an equal volume of ethanol to the concentrated reaction solution. Recrystallization from THF/hexanes gave bright yellow crystals.

Bis(cyclopentadienyl)tris(triphenylphosphine)(trithiocarbonato)diruthenium(II), $Cp_2Ru_2(PPh_3)_3CS_3$ (4). A brown suspension of **1d** (0.25 g, 0.345 mmol) in toluene (3 mL) was treated with CS_2 (2 mL). The resulting clear red solution was stirred for 48 h, after which it was stripped to dryness. The residue was dissolved in a minimum of THF and chromatographed on alumina. Eluting first with hexanes followed by THF/hexanes (3:7) gave a red band, which was reduced in volume under vacuum and cooled at −20 °C to give a red microcrystalline powder (0.087 g). The mother liquors were further reduced in volume and cooled to form an oil, which slowly crystallized upon standing. The combined yield was 0.16 g (37%); mp 150–154 °C. Repeated attempts to further purify **4** did not succeed in ridding it of a persistent contaminant. Mass spectral data: m/e^+ 1227 ($M^{\bullet+}$ + H), 966 ($M^{\bullet+}$ − PPh_3), 704 ($M^{\bullet+}$ − 2 PPh_3), 691 ($M^{\bullet+}$ − $CpRu(PPh_3)CS_3$), 441 ($M^{\bullet+}$ − 3 PPh_3), 429 ($M^{\bullet+}$ − $CpRu(PPh_3)CS_3$ − PPh_3).

X-ray Structure Determination

Table III contains details of the crystal parameters, data collection, and structure refinement.[27] Single crystals suitable for crystallographic studies were obtained by recrystallization from THF/hexanes (1:5) at −16 °C. The sample chosen was mounted on a lithium borate fiber with epoxy glue. Preliminary Weissenberg and precession photographs limited the choice of space group to $P1$ or $P\bar{1}$. The subsequent solution and refinement of the structure was successful in the centrosymmetric space group. Intensity data were collected after the unit cell data and orientation were obtained from 24 automatically aligned reflections. The data were corrected for Lorentz and polarization effects and scaled by using three reference reflections, whose intensities had been remeasured every 50 cycles.

The structure was solved by conventional heavy-atom methods. The ruthenium coordinates were found from a Patterson synthesis. Successive rounds of refinement, structure factor calculations, and Fourier syntheses revealed the positions of the phosphorus and sulfur atoms and then most of the carbon atoms. After eight cycles of isotropic refinement using the block-diagonal method, a Fourier difference synthesis showed some substantial residual electron density around the free end of the propyl group. Two disordered models were tested. The first allowed alternative positions for both C(8) and C(9), but one of the C(8) atoms gave excessively high thermal parameters. The second model allowed an alternative site for C(9) only. This model was well behaved and converged after six cycles of refinement with anisotropic thermal parameters. The occupancies of C(9) and C(9′) were refined in the earlier cycles and then fixed at 0.6 and 0.4, respectively. At this point, all the hydrogen atoms, except those on the propyl group, were placed into calculated positions with the mean isotropic thermal parameters of their carbon atom and refinement was continued for six more cycles for the non-hydrogen atoms. The hydrogens were repositioned every two cycles. A final difference synthesis showed only random noise. Table IV lists the final coordinates for the molecule, and tables of thermal parameters and structure factors are available as supplementary material.

(27) All programs used for the data collection, structure solution, and refinement are part of the X-ray crystallographic system for the PDP-8 minicomputer by Larson and Gabe (Larson, A. C.; Gabe, E. J. In *Computing in Crystallography*; Schlenk, H., Olthof Hazenkamp, R., Van Konigsveld, H., Bassi, J. C., Delft University Press: Delft, Holland, 1978; p 81).

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Supplementary Material Available: A full length table of crystallographic data (Table 6) and a table of anisotropic temperature factors (Table 7) (2 pages); a table of observed and calculated structure factors (Table 8) (19 pages). Ordering information is given on any current masthead page.

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Preparation and Crystal Structure of Bis(cyclopentadienyl)tetracarbonylbis(μ-2-propanethiolato)ditungsten(II), $[CpW(CO)_2(\mu\text{-}SCHMe_2)]_2$, and Bis(cyclopentadienyl)dicarbonylbis(μ-2-propanethiolato)ditungsten(II), $[CpW(CO)(\mu\text{-}SCHMe_2)]_2$

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Warming $CpW(CO)_2(PPh_3)SCHMe_2$ in THF gave the tetracarbonyl dimer $[CpW(CO)_2SCHMe_2]_2$ (**1**) with loss of PPh_3 while further reaction in refluxing THF gave the dicarbonyl dimer $[CpW(CO)SCHMe_2]_2$ (**2**). The structures of **1** and **2** were determined. Crystal data for **1**: *Pnnm*, a = 12.066 (9) Å, b = 12.246 (2) Å, c = 15.643 (2) Å, V = 2311.41 Å^3, Z = 8. Crystal data for **2**: $P2_1/c$, a = 9.441 (4) Å, b = 11.727 (3) Å, c = 9.953 (4) Å, β = 65.56 (3)°, V = 1101.94 Å^3, Z = 4. In both structures, the thiolato groups bridge the two metal atoms, generating a nonplanar W_2S_2 core in **1** and a planar core for **2** that has a W=W bond (2.602 (5) Å). In **1**, a crystallographically required mirror plane bisects the W-W vector and the Cp ligands, which are mutually cis while the $CHMe_2$ groups are both in equatorial positions. A crystallographically required inversion center exists in **2**, and therefore, the Cp groups are mutually trans, as are the $CHMe_2$ groups. The possible geometric isomers of complexes of the type $[CpM(CO)_xSR]_2$ are discussed.

Introduction

Dimeric complexes of the type $[CpM(CO)_xSR]_2$, where Cp = C_5H_5 and x = 0, 1, 2, containing bridging thiolato ligands are an important class of compound.[2] Although conceptually rather simple, the structures of such complexes possess considerable potential for isomerism. In the first instance, there are three possible geometrical arrangements for the R groups about a nonplanar four-membered M_2S_2 ring:[2f,3] axial-axial, axial-equatorial, and equatorial-equatorial.[4] Second, the presence of the Cp rings introduces the opportunity for cis and trans isomerism about the metal-metal vector. Figure 1 depicts the six possible isomers for a nonplanar M_2S_2 ring bearing two Cp rings and two R groups.[2f] The sharing of an edge by the basal planes of the two pyramidal fragments gives rise to the so-called "butterfly" geometry.[4-6] Additional isomers might be imagined wherein the M_2S_2 ring in I-III is inverted, but this would bring the two Cp rings to the interior side of the fold between the two basal planes and hence unacceptably close.[2f] If the M_2S_2 ring is planar, then isomers V and VI become identical and there remain five possible structures.

The relatively few structures reported display several of these isomeric geometries. In the complex $[CpRhSPh]_2$,[6] the Cp rings are mutually cis while the Ph groups are axial and equatorial as in I. In both the cation $[CpFe(CO)(SMe)]_2^+$[7a] and the neutral complex $[CpFe(CO)SPh]_2$[7b] the Cp rings are mutually cis but the R groups are both axial in the former (as in III) and both equatorial in the latter (as in II). The structures of the dications $[CpMo(CO)_2SCMe_3]_2^{2+}$[8a] and $[Cp_2Mo(CO)_3(NCMe)(SPh)_2]^{2+}$[8b] also correspond to type II. The neutral complex $[CpMo(CO)_2SPh]_2$[9,10] has its Cp rings mutually trans with one Ph group axial and the other equatorial as in IV. The complex $[CpMo(CO)SCMe_3]_2$,[9] which has a Mo=Mo double bond and a planar Mo_2S_2 ring, has structure V/VI with trans-oriented Cp rings and cis CMe_3 groups. The factors that determine the geometry of such complexes appear to be finely balanced, and it is difficult to predict a structure.[8c]

While several structural determinations of molybdenum dimers have been conducted, not one structure for a tungsten analogue has been reported. This has not been due to lack of efforts. Attempts to prepare tungsten analogues of the molybdenum complexes above were first reported by Treichel et al.[11] Their formulation of the product as $[CpW(CO)_2SMe]_2$ was disputed by Havlin and Knox,[12] who suggested that it was the monomer

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