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Synthesis and Crystal Structures of (Fulvalene)$W_2(SH)_2(CO)_6$, (Fulvalene)$W_2(\mu\text{-}S_2)(CO)_6$, and (Fulvalene)$W_2(\mu\text{-}S)(CO)_6$: Low Valent Tungsten Carbonyl Sulfide and Disulfide Complexes Stabilized by the Bridging Fulvalene Ligand

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Reaction of $FvW_2(H)_2(CO)_6$ with $^2/_8S_8$ in THF results in rapid and quantitative formation of $FvW_2(SH)_2(CO)_6$. The crystal structure of this complex is reported and shows that the two tungsten–hydrosulfide groups are on opposite faces of the fulvalene ligand in an anti configuration. Nevertheless, treatment of $FvW_2(SH)_2(CO)_6$ (**1**) with PhN═NPh produces $FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**) and Ph(H)NN(H)Ph. The crystal structure of the bridging disulfide, which cocrystallizes with **1** in a 2:1 ratio, is also described. Exposure of 2 equiv of •CrCp*$(CO)_3$ to **1** effects similar H atom transfers yielding 2 HCrCp*$(CO)_3$ and **2**. Attempts to obtain crystals of the latter from solutions derived from this reaction mixture furnished a third product, $FvW_2(\mu\text{-}S)(CO)_6$ (**3**), which was analyzed crystallographically. The enthalpy of sulfur atom insertion into $FvW_2(H)_2(CO)_6$, yielding **1**, has been measured by solution calorimetry.

Introduction

The goal of this work was to begin the investigation of the basic sulfur chemistry of fulvalene bridged homobimetallic complexes of group 6. The reactions of analogous cyclopentadienyl (C_5H_5 = Cp, C_5Me_5 = Cp*) systems have generated a number of interesting dimeric structural types, as shown in Chart 1.

Cyclopentadienylchromium carbonyl complexes with one or two bridging sulfur atoms (A−C) have been prepared by the groups of Legzdins,[1] Goh,[2] and Herrmann,[3] whereas cyclopentadienylmolybdenum sulfido complexes of the type D−F have been investigated by the groups of Rakowski DuBois[4] and Wachter.[5] The crystal structure of $[Cp(CO)_3W]_2(\mu\text{-}S)$ has been reported,[6] as well as that of the mixed valence complex $Cp_2W_2(CO)_2(\mu\text{-}S_2)$.[5]

There are no published structures of fulvalene (Fv) complexes analogous to those shown in Chart 1 for the more familiar cyclopentadienyl systems of the group 6 metals. Such compounds could conceivably display quite distinct scaffolds and reactivities due to additional constraints imposed on metal stereochemistry by the bridging fulvalene ligand. In fact, to the authors' knowledge, the only structural data on a fulvalene bridged sulfido complex are for the Zr(IV) dimer $(Fv)(CpZrS)_2$.[7]

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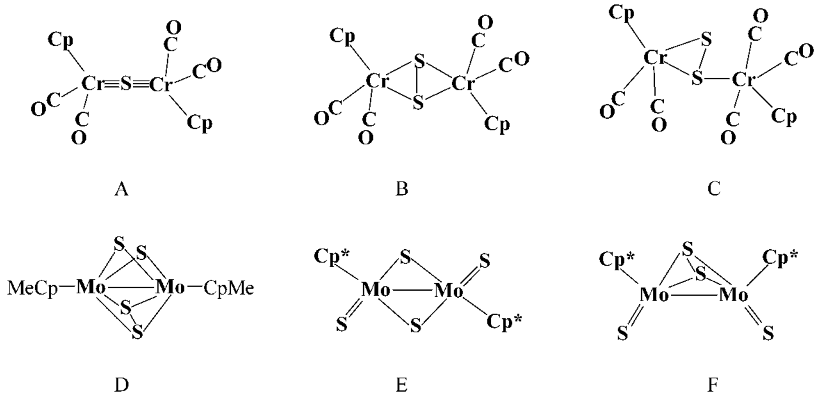
Chart 1. Group 6−Sulfur Compounds Supported by Cyclopentadienyl Ligands



Recently, we described the structural and calorimetric study of sulfur atom insertion[8] into group 6 metal hydrides, as shown in eq 1, as well as physical studies of oxidative addition[9] of H_2 to the fulvalene bridged Cr−Cr bonded dimer, shown in eq 2.

$$H{-}M(CO)_3(C_5R_5) + {}^1/_8S_8 \rightarrow HS{-}M(CO)_3(C_5R_5) \quad (1)$$

$$FvCr_2(CO)_6 + H_2 \rightarrow FvCr_2(H)_2(CO)_6 \quad (2)$$

This paper details our first investigations of the chemistry of fulvalene group 6 metal−sulfur containing complexes, including synthetic, structural, and calorimetric studies of the complexes $FvW_2(SH)_2(CO)_6$ (**1**), $FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**), and $FvW_2(\mu\text{-}S)(CO)_6$ (**3**). During the course of this work, Shaver and Kovács[10] reported the synthesis of **1**, as shown in reaction 3; other examples of the sulfur chemistry of Fv dimetals are scarce.[11]

$$FvW_2(H)_2(CO)_6 + {}^2/_8S_8 \rightarrow FvW_2(SH)_2(CO)_6\,(\mathbf{1}) \quad (3)$$

Results and Discussion

The fulvalene bridge between two transition metals constitutes a scaffold that is continuing to give rise to unusual dinuclear complex chemistry.[9−13] It is therefore surprising that elemental sulfur has played a very limited role in these investigations,[7,10,11] despite its extensive role as a ligand in complexes ranging in relevance from (potential) catalysts, new materials, and biomimetics, to models for surfaces.[14] This study marks the beginning of a program aiming to fill this void and deals with the FvW_2 nucleus as a representative of the group 6 FvM_2 complexes. Our results have to be viewed within the context of the chemistry of the related $(CpM)_2$ systems depicted in Chart 1. In particular, complex D has been shown to activate H_2 as in eq 4,[4a] and the resulting hydrosulfide, to be capable of reducing azobenzene as in eq 5.[4a,b]

$$Cp^{Me}Mo(\mu\text{-}S)_2(\mu\text{-}S_2)MoCp^{Me} + H_2 \rightarrow Cp^{Me}Mo(\mu\text{-}S)_2(\mu\text{-}SH)_2MoCp^{Me} \quad (4)$$

Reactions 4 and 5 provide a route for the catalytic hydrogenation of azobenzene.[4] In addition, the catalytic reduction of SO_2 by $Cp^*Mo(\mu\text{-}S)_2(\mu\text{-}S_2)MoCp^*$ was discovered by Kubas and co-workers.[15]

$$Cp^{Me}Mo(\mu\text{-}S)_2(\mu\text{-}SH)_2MoCp^{Me} + PhN{=}NPh \rightarrow Cp^{Me}Mo(\mu\text{-}S)_2(\mu\text{-}S_2)MoCp^{Me} + Ph(H)NN(H)Ph \quad (5)$$

Preparation of $FvW_2(SH)_2(CO)_6$ (1), $FvW_2(\mu\text{-}S_2)(CO)_6$ (2), and $FvW_2(\mu\text{-}S)(CO)_6$ (3). The reaction of $FvW_2(H)_2(CO)_6$ with two-eighths of an equivalent of S_8 produced **1** as shown in eq 3. Made by Kovacs and Shaver,[10] using acetone, THF, or benzene as a solvent, the reaction was found by us to proceed rapidly in THF or CH_2Cl_2 in quantitative yield. Monitoring by FTIR showed it to be complete in less than 1 min. Spectroscopic data compiled here are in essential agreement with the literature data. In contrast to the reported

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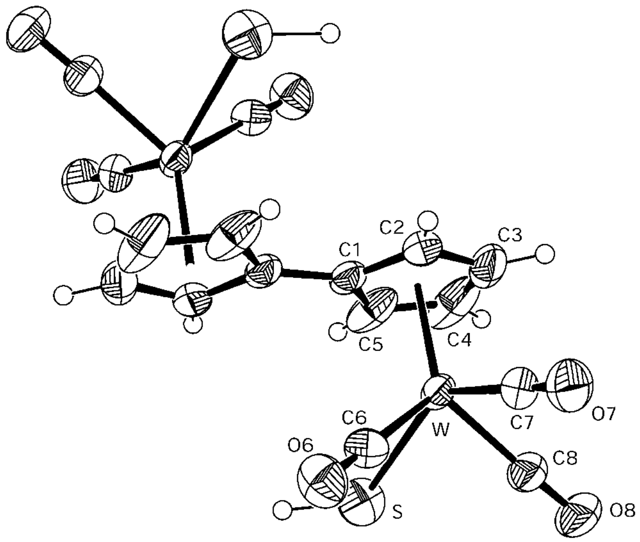

Figure 1. Structure of $FvW_2(SH)_2(CO)_6$ (**1**) in the crystal, showing the 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): W−S, 2.513(2); S−H, 1.39(6); C(1)−C(1A), 1.447(11); C(8)−W−C(7), 77.7(3); C(7)−W−C(6), 77.4(2); C(8)−W−S, 76.67(19); C(6)−W−S, 75.52(17); W−S−H, 109(2); C(1A)−C(1)−C(2)−C(3), −177.9(6).

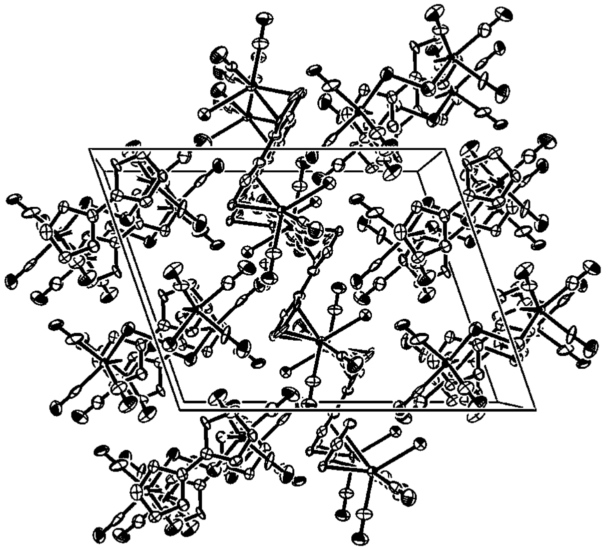

Figure 2. Molecular packing of the cocrystallisate $FvW_2(SH)_2(CO)_6$ (**1**)−$FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**) in the crystal, showing the 50% probability ellipsoids.

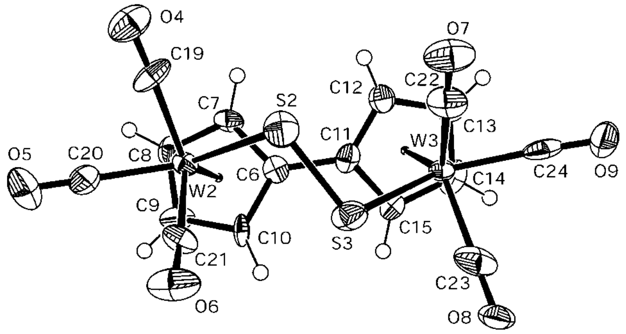

Figure 3. Structure of $FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**) in the crystal of $FvW_2(SH)_2(CO)_6$ (**1**)−$FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**) cocrystallisate, showing the 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): W(2)−S(2), 2.480(5); W(3)−S(3), 2.503(5); S(2)−S(3), 2.065(6); S(2)−W(2)−C(19), 74.8(5); S(2)−W(2)−C(21), 76.7(5); C(19)−W(2)−C(20), 78.0(8); C(20)−W(2)−C(21), 77.6(7); W(2)−S(2)−S(3), 102.5(2); W(3)−S(3)−S(2), 103.4(2); C(6,7,8,9,10)−C(11,12,13,14,15), 150.04.

instability of **1** when prepared in acetone solution,[10] the complex appears sufficiently stable in CH_2Cl_2 or THF to allow the growth of X-ray quality crystals over a period of more than a week. When the compound was kept pure, either in solution or as a solid, there were no signs of decomposition, provided that exposure to light was avoided. The structure of **1** is shown in Figure 1.

Two reactions of **1** were investigated in this work and are shown in eqs 6 and 7.

$$FvW_2(SH)_2(CO)_6\ (\mathbf{1}) + PhN{=}NPh \rightarrow FvW_2(\mu\text{-}S_2)(CO)_6\ (\mathbf{2}) + Ph(H)NN(H)Ph \quad (6)$$

$$FvW_2(SH)_2(CO)_6\ (\mathbf{1}) + 2{\cdot}CrCp^*(CO)_3 \rightarrow FvW_2(\mu\text{-}S_2)(CO)_6\ (\mathbf{2}) + 2HCrCp^*(CO)_3 \quad (7)$$

The reduction of azobenzene was performed in analogy to the work of DuBois[4] in reaction 5. Complex **2** was characterized by spectroscopic and analytical data, as well as by X-ray crystallography, as discussed later. Exposure of **1** to 2 equiv of chromium radical $\cdot CrCp^*(CO)_3$, as shown in eq 7, also yielded **2**, with spectroscopic properties identical to those observed for the tungsten sulfide from eq 6. In some runs (see later), small amounts of **3** could be detected by ^1H NMR and IR spectroscopy. The other reaction products [Ph(H)-NN(H)Ph and $HCrCp^*(CO)_3$, respectively] were identified spectroscopically to confirm the stoichiometry of the respective transformations. The rate of conversion of **1** in the presence of PhN=NPh was significantly lower than that observed in the presence of $\cdot CrCp^*(CO)_3$. At room temperature, the reaction with azobenzene required days to proceed, but at 30 °C, over several hours, a smooth decrease in the IR bands assigned to **1** (2026 and 1939 cm^{-1}) was noted, with a concomitant increase in bands at 2032, 2016, 1954, and 1928 cm^{-1}, assigned to **2**. Thus, with both reagents in millimolar concentrations, reaction 6 occurred slowly over a period of hours, whereas the H atom transfer of eq 7 was complete within minutes. Additional kinetic studies of these processes are planned. Attempts to prepare **2** from $FvW_2(CO)_6$ dianion[12b] and S_2Cl_2 failed.

As might be expected, the crude mixtures containing compounds **2** and **3** were not very soluble in most solvents, and methylene chloride and acetone were found to be best for their chemical manipulation. Crystallization was very difficult, and we believe that the structures of **2** and **3** presented here were only possible because, in the case of **2**, a cocrystallisate was formed serendipitously from the crude mixture, and in the case of **3**, prolonged standing gave suitable crystals fortuitously.

The crystals obtained from the mixtures in eqs 6 and 7 yielded different structures, despite the similarity of the spectra recorded for the crude product solutions. The crystals grown from reaction 6 were deep purple, and a crystal structure determination showed them to be a cocrystallisate of **1** and **2** in a 2:1 ratio. The molecular packing is shown in Figure 2, and a view of only **2** is shown in Figure 3.

Attempts to crystallize **2** by layering a sample of the reaction mixture obtained in reaction 7 with heptane led to

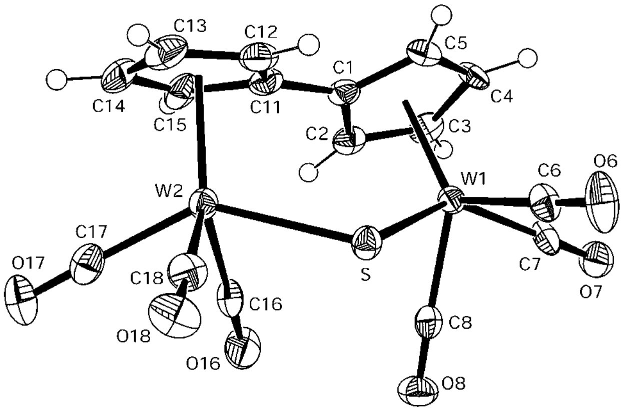

Figure 4. Structure of $FvW_2(\mu\text{-}S)(CO)_6$ (**3**) in the crystal, showing the 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): W(1)−S(2), 2.5446(16); W(2)−S, 2.5299(15); C(1)−C(11), 1.472(9); C(6)−W(1)−C(7), 81.0(3); C(7)−W(1)−C(8), 76.9 (3); C(6)−W(1)−S, 75.35(19); C(8)−W(1)−S, 76.28(19); W(2)−S−W(1), 109.72(6); C(1,2,3,4,5)−C(11,12,13,14,15), 25.4(4).

the formation of well-formed orange crystals of **3** after a period of two weeks. The structure of this complex is shown in Figure 4. It is possible that this compound is the result of a side reaction involving sulfur atom transfer from **2** to $\cdot CrCp^*(CO)_3$. Indeed, a calorimetric study of reaction 7 indicated the occurrence of slow reduction of **2** to **3** when a slight excess of $\cdot CrCp^*(CO)_3$ was present. Following this reaction by ^1H NMR showed only small quantities of **3**, the major product being $FvW_2(CO)_6$. Reaction between **2** and 2 equiv of $\cdot CrCp^*(CO)_3$ revealed clean conversion to $FvW_2(CO)_6$, indicative of the ease of removal of the sulfur ligands. This ready loss of the sulfur ligand is also seen in the mass spectral data, in which the molecular ion was absent, regardless of the technique used. In particular, the mass spectrum of **2** was nearly identical to that of $FvW_2(CO)_6$. It was only through isolation of crystals of **3** that unambiguous identification of this product was accomplished, and the details of the reduction of **2** by $\cdot CrCp^*(CO)_3$ are not known.

Structural Comparison of $FvW_2(SH)_2(CO)_6$ (1), $FvW_2(\mu\text{-}S_2)(CO)_6$ (2), and $FvW_2(\mu\text{-}S)(CO)_6$ (3). The full crystallographic data for the structures of **1**, **2**, and **3** are available as Supporting Information. Table 1 lists the tabulated crystal data and collection parameters.

Compound **1** has a crystallographic center of inversion located at the midpoint of the $C_5H_4-C_5H_4$ bond. The geometry about the tungsten atom is a four-legged piano stool with the three CO and the HS ligands occupying the square base. The picture of **1** in Figure 1 is that expected for a trans-fulvalene system devoid of metal−metal or bridging ligand bonds. The two SH groups are distant in this conformation. However, it is clear that rotation around the C1−C1A bond of the bridging fulvalene ligand allows for intramolecular contact and, hence, reactivity. This structure was also ascertained in the cocrystallisate of **2** and **1** from reaction 6. As shown in Table 2, the data for the two determinations are in reasonable agreement and are similar to those of the related complex $Cp^*W(CO)_3SH$.[8] It is apparent that the microenvironment around the metals is essentially the same for the three compounds.

Table 1. Crystal Data and Collection Parameters

	$FvW_2(SH)_2(CO)_6$ (**1**)	$FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**)	$FvW_2(\mu\text{-}S)(CO)_6$ (**3**)
formula	$C_{16}H_{10}O_6S_2W_2$	$C_{24}H_{15}O_9S_3W_3$	$C_{16}H_8O_6SW_2$
fw	730.06	1095.11	695.28
T (K)	173	157	173
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a	7.5446(3)	16.184(1)	13.257(2)
b	12.4177(5)	13.850(1)	9.7840(5)
c	10.4516(5)	12.608(9)	14.287(1)
α (°)	90	90	90
β (°)	109.333(1)	109.105(1)	116.604(1)
γ (°)	90	90	90
V (Å^3)	923.96(7)	2670.4(6)	1659.2(1)
Z	2	4	4
D_{calc} (g/cm^3)	2.624	2.724	2.786
frame collection time (s)	10	20	10
2Θ range (°)	5.28−55.0	3−52.2	3.48−55.0
μ (mm^{-1})	12.70	13.93	14.01
T_{min}, T_{max}	0.147, 0.449	0.400, 0.716	0.121, 0.540
cryst dimensions (mm^3)	0.06 × 0.19 × 0.19	0.23 × 0.05 × 0.03	0.04 × 0.13 × 0.25
reflns measured	6636	12984	11898
unique reflns	2117	4969	3797
observations ($I > 3\sigma$)	2117	2366	3797
variables	123	371	227
R_{int}	0.024	0.084	0.045
GOF	1.062	0.80	0.973
R, R_w, R_{all}	0.026, 0.065, 0.031	0.032, 0.032, 0.093	0.027, 0.057, 0.041

Table 2. Comparison of Bond Lengths and Angles of $Cp^*W(CO)_3SH$,[a] $FvW_2(SH)_2(CO)_6$ (**1**), and (**1**) Cocrystallized with $FvW_2(S_2)(CO)_6$ (**2**)

$Cp^*W(CO)_3SH$		$FvW_2(SH)_2(CO)_6$		$FvW_2(SH)_2(CO)_6$/ 2 $FvW_2(\mu\text{-}S_2)(CO)_6$	
W−S	2.52	W−S	2.51	W−S	2.50
W−CO_{av}	2.00	W−CO_{av}	2.00	W−CO_{av}	1.98
C2−W−S	75.8	C6−W−S	75.5	S1−W−C16	75.3
C1−W−S	134.5	C7−W−S	134.6	S1−W−C17	131.9
C3−W−S	78.7	C8−W−S	76.7	S1−W−C18	78.0

[a] Ref 8.

In addition to being a 2:1 cocrystallisate with **1**, compound **2** was slightly disordered. The disulfide complex shown in Figure 3 is that which incorporates the two tungsten atoms that were modeled at approximately 90% occupancy. However, the Fourier map showed additional electron density in the proximity of the tungsten disulfide moiety, which was modeled as two tungsten atoms (W4, W5) with an occupancy of approximately 10%. The measured W−W distance in the disulfide complex was 4.99 Å. The W−W distance of the impurity was 4.00 Å, with its tungsten atoms placed 0.67 and 0.43 Å away from those in the disulfide. As in the structure of **1**, the dithiol molecule is oriented in the trans configuration of the fulvalene frame, with a W−S bond distance of 2.504 Å.

The scaffold of **3** (Figure 4) can be compared to that of the analogous [CpW] dimer, previously reported by Kubas and co-workers.[6] In this molecule, the two Cp groups are transoid, and the W−S−W angle is 127°, with an average W−S bond length of 2.53 Å. In **3**, in which the Cp moieties are constrained to be cis, the W−S bonds are surprisingly unaffected (average length 2.54 Å). The W−S−W angle, however, is compressed by nearly 20° to 109.72°. This number might point to the presence of strain, to be confirmed by further thermochemical studies. On a speculative note, it has been reported that the complex $Cp^*(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp^*$ which contains a linear $Cr{\equiv}S{\equiv}Cr$ framework is remarkably inert to carbonylation (and other ligand additions)[1] to yield (presumably angular) $Cp^*(CO)_3Cr{-}S{-}Cr(CO)_3Cp^*$. Conversely, there is no literature describing the generation of $W{\equiv}S{\equiv}W$ complexes by decarbonylation of $[CpW(CO)_3]_2(\mu\text{-}S)$. Thus, it may be that the position of equilibrium shown in eq 8 is shifted to the right for M = Cr and to the left for M = W. The effect of the fulvalene bridge on this equilibrium, as well as related structural and thermochemical questions in these sulfide complexes, is under active investigation.

$$C_5R_5(CO)_3M{-}S{-}M(CO)_3C_5R_5 \rightleftharpoons C_5R_5(CO)_2M{\equiv}S{\equiv}M(CO)_2C_5R_5 + 2CO \tag{8}$$

Similarly, the steric strain of accommodating the (μ-S_2)-(Figure 3) versus (μ-S)-moieties (Figure 4) warrants quantification. The W−W bond distance in **2** (4.99 Å) is much larger than that in $FvW_2(CO)_6$ (3.347 Å)[16] and signals the absence of any W−W bonding interaction. This separation is reduced to 4.14 Å in **3**. The structural parameters of the coordinated disulfide lie in the rather wide range reported for other bridging disulfide complexes.[17] The two component C_5H_4 rings deviate significantly from coplanarity, a further indication of potential strain.

Enthalpy of Sulfur Atom Insertion into $FvW_2(H)_2(CO)_6$. The enthalpy of eq 3 was measured by solution calorimetry. The resulting value of $\Delta H = -19.2 \pm 1.8$ kcal/mol in THF solution is slightly less negative than that measured for sulfurization of two molecules of $C_5H_5W(CO)_3H$, $\Delta H = -22.4 \pm 0.6$ kcal/mol.[8] The difference (1.6 kcal/mol per reacting W−H unit) is near the limits of experimental error, indicating that the W centers in the fulvalene system operate essentially independently and that there is no significant strain associated with their conversion to dithiol.

Enthalpy of Hydrogenation of $FvW_2(\mu\text{-}S_2)(CO)_6$. The enthalpy of reaction 7 was measured by solution calorimetry in toluene and found to have a value of $\Delta H = -8.2 \pm 0.6$ kcal/mol. As reported in the Experimental Section, a slow side reaction occurred to a varying extent, shown in eq 9. It was judged to insignificantly influence the measured enthalpy of reaction, as it manifested itself by only slightly endothermic tailing toward the end of the runs.

$$FvW_2(\mu\text{-}S_2)(CO)_6\ (\mathbf{2}) + 2{\cdot}Cr(CO)_3Cp^* \rightarrow FvW_2(\mu\text{-}S)(CO)_6\ (\mathbf{3}) + 2CO + Cp^*(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp^* \tag{9}$$

Nevertheless, its presence warrants an increase in the estimated experimental error by 1 kcal/mol, suggesting a final $\Delta H = -8.2 \pm 1.6$ kcal/mol.

We have previously measured[18] the enthalpy of hydrogenation of the chromium radical, as shown in eq 11, $\Delta H = -20.4 \pm 2.0$ kcal/mol. Subtraction of eq 7 from eq 10 yields directly the enthalpy of reaction 11, the enthalpy of hydrogenation of the coordinated disulfide bond in **2**, $\Delta H = [-20.4 \pm 2.0\ \text{kcal/mol} - (-8.2 \pm 1.6\ \text{kcal/mol})] = -12.2 \pm 3.6$ kcal/mol.

$$2{\cdot}Cr(CO)_3Cp^* + H_2 \rightarrow 2HCr(CO)_3Cp^* \tag{10}$$

While an unfavorable entropy of reaction on the order of $\Delta S = -25$ cal/mol deg can be estimated,[18] it would not be expected to overcome the favorable enthalpy, implying that eq 11 should proceed, of interest in light of the fact that the molybdenum complex shown in eq 4 readily adds H_2 at atmospheric pressure.

$$FvW_2(\mu\text{-}S_2)(CO)_6\ (\mathbf{2}) + H_2 \rightarrow FvW_2(SH)_2(CO)_6\ (\mathbf{1}) \tag{11}$$

However, attempts to reduce this notion to practice were unsuccessful, even at H_2 pressures up to 68 atm for several days.

Conclusions

This paper reports the first structural characterization of fulvalene derivatives of W that incorporate sulfur into the coordination sphere of the metal: $FvW_2(SH)_2(CO)_6$ (**1**), $FvW_2(\mu\text{-}S_2)(CO)_6$ (**2**), and $FvW_2(\mu\text{-}S)(CO)_6$ (**3**). The results, while constituting a modest foray, point to a complex, but rich, chemistry that lies in store in our efforts to extend them.

Although it would be premature to generalize, it appears that the qualitative and quantitative changes often effected by linking the two Cp rings in $(CpM)_2$ complexes to give the FvM_2 framework will also be noticeable in the structure and chemistry of their respective sulfur derivatives. Discovering such will be the essence of future investigations.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk tube and glovebox techniques. Toluene, THF, and C_6D_6 were distilled from Na/benzophenone prior to use. Methylene chloride was distilled from P_2O_5. Analytical reagent grade heptane was degassed prior to use. The complexes $FvW_2(CO)_6$ and $FvW_2(H)_2(CO)_6$ were prepared as described in the literature.[12] Calorimetric measurements were performed using a Setaram C-80 calorimeter. IR samples were prepared as mineral oil mulls between NaCl plates, unless otherwise specified. Crystal structures were determined at the University of California, Berkeley (for **2**), or the University of Florida (for **1** and **3**). All ORTEP figures were created using ORTEP-3 for Windows.[19]

$FvW_2(SH)_2(CO)_6$ (1). A solution of S_8 (0.0527 g, 0.21 mmol) in THF (4 mL) was added to a solution of $FvW_2(H)_2(CO)_6$ (0.503 g, 0.76 mmol) in THF (15 mL) at 0 °C. Upon mixing the reagents, the Schlenk tube was immediately evacuated while still in the ice bath and the volume reduced to 7−8 mL over a 5−10 min period. To this solution was added degassed heptane (20 mL). Storage at 0 °C resulted in the precipitation of an orange crystalline solid that

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was spectroscopically pure. Yield: 0.383 g, 69%. Mp > 250 °C (dec). ^{1}H NMR (C_6D_6): δ 4.74 (m, 4 H, Fv), 4.33 (m, 4 H, Fv), −2.32 (s, 2 H, SH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 227.94, 214.88, 110.91, 93.56, 90.53. IR (cm^{-1}): (toluene) 2026, 1939; (THF) 2024, 1935. EIMS: *m*/*z* (%) 699 (11), 673 (12), 640 (28), 614 (24), 589 (16), 501 (56), 486 (44), 281 (100). Anal. Calcd for $C_{16}H_{10}O_6S_2W_2$: C, 26.32%; H, 1.38. Found: C, 26.24%; H, 1.42.

$FvW_2(\mu\text{-}S_2)(CO)_6$ (2) and $FvW_2(\mu\text{-}S)(CO)_6$ (3). (a) Azobenzene (30 mg, 0.16 mmol) in CH_2Cl_2 (20 mL) was added to a cold solution (−78 °C) of **1** (50 mg, 0.068 mmol) in CH_2Cl_2 (30 mL). The mixture was allowed to warm to room temperature and stirred for an additional 12 h. The brown solution was filtered to remove a very small amount of insoluble material and the total volume reduced to approximately 20 mL. Toluene (10 mL) was then added, the solution cooled to −80 °C, and **2** isolated by filtration as a light brown powder. Yield: 45 mg, 90%. Mp > 250 °C (dec). ^{1}H NMR (toluene-d_8): δ 5.79 (m, 4 H, Fv), 4.04 (m, 4 H, Fv). $^{13}C\{^1H\}$ NMR (toluene-d_8): 216.85, 123.37, 100.73, 90.25 (one CO ligand not observed). IR (toluene, cm^{-1}): 2032, 2016, 1954, 1928. EIMS: *m*/*z* (%) 664 [M − S_2] (10), 636 [−CO] (35), 608 [−CO] (25), 580 [−CO] (20), 552 [−CO] (70), 526 [−CO] (65), 494 [−CO] (35), 77 (100). Anal. Calcd for $C_{16}H_8O_6S_2W_2$: C, 26.40%; H, 1.11. Found: C, 26.79%; H, 1.29. (b) To 15 mL of a 4.6 mM toluene solution of **1** at 11 °C was added 15 mL of a 9.2 mM toluene solution of $\cdot CrCp^*(CO)_3$. IR spectral analysis indicated quantitative conversion of $\cdot CrCp^*(CO)_3$ (1994, 1896 cm^{-1}) to $HCrCp^*(CO)_3$ (1995, 1912 cm^{-1}) and the emergence of peaks at 2032, 2016, 1954, and 1928 cm^{-1} due to **2** (see previous). In an attempted crystallization of the crude product, crystals of **3** were obtained. ^{1}H NMR (C_6D_6): δ 5.78 (m, 4H, Fv), 4.73 (m, 4H, Fv). IR (toluene, cm^{-1}): 2017, 1965, 1927, 1908. This compound could not be obtained pure in the bulk.

Calorimetric Measurements of the Enthalpy of Reaction of $FvW_2(H)_2(CO)_6$ with $^2/_8S_8$ and of $FvW_2(SH)_2(CO)_6$ (1) with $2\cdot CrCp^*(CO)_3$. In a typical procedure, a solution mixing cell of a Setaram calorimeter was taken into a glovebox and loaded with 2.0 mL of a 73 mM THF solution of $FvW_2(H_2)(CO)_6$ and 2.0 mL of a 9.9 mM THF solution of S_8. The cell was sealed, taken from the glovebox, and placed in the calorimeter. Following thermal equilibration, the reaction was initiated.

After completion of the measurement (1−2 h, 30 °C), the cell was returned to the glovebox. Analysis of the reaction mixture by FTIR spectroscopy confirmed quantitative conversion to $FvW_2(SH)_2(CO)_6$; $\Delta H = -9.6 \pm 0.9$ kcal/mol.

The calorimetry of the reaction of the $FvW_2(SH)_2(CO)_6$ (**1**) with $\cdot CrCp^*(CO)_3$ was measured in a similar manner. Varying, but small, amounts of $FvW_2(\mu\text{-}S)(CO)_6$ (**3**) and $Cp^*(CO)_2Cr{\equiv}S{\equiv}Cr(CO)_2Cp^*$ were detected by IR spectroscopy in some of the runs, particularly during prolonged measurements or in the presence of excess $\cdot CrCp^*(CO)_3$. Examination of the thermograms indicated that this side reaction did not significantly alter the measured enthalpy of the primary process, as it appeared to be nearly thermoneutral (slightly endothermic) and thus of minor consequence to the integrated heat of reaction. Nevertheless, because of its occurrence, the experimental error in this measurement is increased by 1 kcal/mol to yield $\Delta H = -8.2 \pm 1.6$ kcal/mol.

Attempted Reaction of $FvW_2(\mu\text{-}S_2)(CO)_6$ (2) with H_2. In a glovebox, 20 mL of an approximately 4 mM toluene solution of **2** was filtered into a high-pressure FTIR cell (Harrick Scientific) and fitted with a 40 mL Hoke bomb autoclave and quartz pressure transducer (Omega Scientific). The apparatus was removed from the glovebox and taken to a manifold where it was filled with 1000 psi pressure of research grade (99.995%) H_2 (Matheson Gas). There was no measurable change over a period of 2 days at rt. After 1 month, some $FvW_2(\mu\text{-}S)(CO)_6$ (**3**) was detected, but no $FvW_2(SH)_2(CO)_6$ (**1**).

General X-ray Crystallography Procedures. Data were collected at low temperature on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structures were solved by the direct methods and refined using full-matrix least squares. The non-hydrogen atoms were treated anisotropically, whereas the hydrogens were calculated in idealized positions attached to their respective carbon atoms. Refinement employed F^2.

Determination of the Structure of 1. Single crystals suitable for structural analysis were grown by slow diffusion of heptane into a CH_2Cl_2 solution of **1**. The structure was solved by the direct methods in *SHELXTL5*.[20] The mercapto proton was obtained from a difference Fourier map and refined without constraints.

Determination of the Structure of 2. Deep purple crystals of **2** (4 molecules) cocrystallizing with **1** (2 molecules) were obtained by layering the crude solution from the experiments described previously with heptane. The structure was solved by the direct methods in SIR92.[21] The locations of the hydrogens bonded to sulfur in the dithiol were neither included nor refined during least squares calculations.

Determination of the Structure of 3. The crude product mixture from the reaction of **1** with $\cdot CrCp^*(CO)_3$ (see previous) was filtered into a small diameter tube and layered with heptane. Over a period of a week, orange crystals of **3** were obtained. The structure was solved by the direct methods in *SHELXTL5*.[20]

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Supporting Information Available: Complete information on data collection, atomic coordinates, thermal parameters, and structural tables for $FvW_2(SH)_2(CO)_6$ (**1**), $FvW_2(\mu\text{-}S_2)(CO)_6$(**2**), and $FvW_2(\mu\text{-}S)(CO)_6$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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