

A Study of Sulfur Ligand Reactivity in Dimeric Dithiolate Complexes of Vanadium and Tungsten

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The reaction of $[\text{CpW}(\text{CO})_3]_2$ ($\text{Cp} = \text{C}_5\text{H}_5$) with ethylene sulfide under certain reaction conditions results in the synthesis of two new tungsten dimers with the formulas $(\text{CpW})_2\text{S}_3(\text{SC}_2\text{H}_4\text{S})$ (I) and $(\text{CpWS})_2(\text{SC}_2\text{H}_4\text{S})$ (II). Structures have been proposed on the basis of spectral data and by analogy to known molybdenum complexes of similar compositions. These data suggest that I contains two μ -sulfido ligands, a terminal sulfido ligand on one tungsten ion, and a bidentate ethanedithiolate ligand coordinated to the second tungsten ion. Complex II is proposed to be a quadruply bridged dimer. The reaction of $[\text{CpWS}(\mu\text{-S})]_2$ with acetylene results in the formation of three new dimeric complexes: $[\text{CpWSC}_2\text{H}_2\text{S}]_2$ (III), $(\text{CpW})_2\text{S}_3(\text{SC}_2\text{H}_2\text{S})$ (IV), and $(\text{CpW})_2\text{S}_2(\text{SC}_2\text{H}_2\text{S})_2$ (V). Complex III is proposed to contain two bridging ethenedithiolate ligands while IV and V contain one and two dithiolate ligands, respectively, each chelated to single tungsten ions. An X-ray diffraction study of V has been completed. The molecule crystallizes in space group $P2_1/c$ with $a = 7.992$ (2) Å, $b = 23.659$ (5) Å, $c = 14.506$ (2) Å, $\beta = 100.62$ (2)°, and $V = 2696$ (1) Å³. The compound crystallizes with $1\frac{1}{2}$ molecules per asymmetric unit. Bond distances and angles of the W_2S_2 cores of the two molecules in the unit cell differ significantly. The reactivity of the sulfur donor ligands in the new tungsten dimers has been studied. The hydrocarbon portions of the dithiolate ligands in I and II undergo exchange reactions with acetylene. The ethanedithiolate ligand in V is hydrogenated under mild homogeneous conditions; the reaction forms IV and ethylene. The reaction of $\text{CpV}(\text{CO})_4$ with alkanedithiols has led to the synthesis of new vanadium dimers with the formulas $[\text{CpVSCHRCH}_2\text{S}]_2$, $\text{R} = \text{H}, \text{CH}_3$ (VIa, VIb). A single crystal of VIa crystallizes in space group $P2_1/c$ with $a = 17.394$ (9) Å, $b = 7.647$ (2) Å, $c = 13.035$ (9) Å, and $\beta = 104.98$ (5)°. The complex is isostructural with the bis(alkanedithiolate)-bridged dimers of molybdenum which have been reported previously. Unlike the molybdenum and tungsten systems, however, the vanadium dimers show no evidence for reactivity at the dithiolate ligands.

Introduction

An extensive reaction chemistry with hydrogen and with unsaturated molecules has been found to occur at the site of the sulfur ligands in tetrasulfur bridged dimers of molybdenum.²⁻⁵ No evidence for the coordination of reactants to the metal ions in these complexes has been observed. Nevertheless, the metal ions are believed to play a critical role in determining the reactivity by regulating both the structural and the electronic characteristics of the M_2S_4 core. The redox characteristics of the metal ions may be particularly relevant since the addition of an unsaturated molecule to the sulfur ligands or its dissociation results in a formal reduction or oxidation, respectively, of the metal complex. We have attempted to probe metal ion influences by synthesizing cyclopentadienyldithiolate complexes which involve other metal ions and by comparing reactivities in these systems.

The organometallic chemistry of tungsten parallels that of molybdenum in many cases.⁶ Several cyclopentadienyl complexes of tungsten with sulfur ligands have been synthesized previously.⁷⁻⁹ We have extended this chemistry

by the synthesis of new dithiolate complexes of W(III) and (IV), which are isostructural with known molybdenum dimers, and by the synthesis of dithiolate sulfido complexes of W(V), which involve new structural types. The redox characteristics of the complexes have been established, and the reactivity of the dimers has been compared with that of the known molybdenum congeners. Although the organometallic chemistry of vanadium is in general less well-developed than that of molybdenum, a number of cyclopentadienyl dimers with thiolate or sulfido ligands have been reported.¹⁰⁻¹⁴ The synthesis of bis(dithiolate)-bridged complexes of vanadium presented the possibility of comparing the reactivity of dimers which are isostructural with the molybdenum systems but which differ in their electronic properties.

Results and Discussion

Tungsten Complexes with Alkanedithiolate Ligands. We have attempted to synthesize tungsten analogues of the known molybdenum complexes by using similar synthetic procedures. Although $[\text{MeCpMo}(\text{S})(\mu\text{-S})]_2$ reacts cleanly with ethylene,¹⁵ the analogous reaction of $[\text{CpW}(\text{S})(\mu\text{-S})]_2$ does not produce characterizable products. Alternate synthetic methods which were used to prepare $[\text{CpMoSC}_2\text{H}_4\text{S}]_2$ ² were also investigated with the tungsten analogues. The reactions of $\text{CpW}(\text{CO})_3\text{H}$ and $[\text{CpW}(\text{CO})_3]_2$ with episulfides were found to be quite

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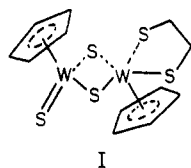
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sensitive to reaction conditions. For example, the reaction of $\text{CpW}(\text{CO})_3\text{H}$ with excess propylene sulfide at 25 °C for 1 h has been reported previously to produce $\text{CpW}(\text{CO})_3\text{SH}$; and at 80 °C in toluene the reported product is $[\text{CpW}(\text{S})(\mu\text{-S})_2]_2$.⁷ When we reacted the carbonyl dimer with excess ethylene sulfide in refluxing THF for much longer time periods, we isolated two new dimeric complexes. A complex of composition $(\text{CpW})_2(\text{S})_3(\text{SC}_2\text{H}_4\text{S})$ (I) was iso-



lated after refluxing for 35–40 h. Its formula is confirmed by mass spectral data and elemental analysis. Crystals suitable for an X-ray diffraction study were not obtained, but the NMR and the IR data provide some structural information. A strong absorption in the IR spectrum at 485 cm^{-1} is characteristic of a terminal sulfido ligand.⁹ In the ^{13}C NMR spectrum a single resonance at 43.19 ppm is assigned to the ethanedithiolate ligand, but the two cyclopentadienyl ligands are inequivalent (98.40 and 102.69 ppm). In the ^1H NMR, the two Cp singlets are separated by 0.5 ppm and the protons of the ethanedithiolate ligands are inequivalent (A_2B_2 pattern at 3.46 ppm). The data are consistent with the structure shown below in which the dithiolate ligand chelates to a single metal ion. A structurally similar molybdenum dimer has been characterized by an X-ray diffraction study.¹⁶ Reactions of this new tungsten(V) dimer are discussed below.

When $[\text{CpW}(\text{CO})_3]_2$ is refluxed with 3.5 equiv of ethylene sulfide in THF for 3 days, a second new complex with the formula $(\text{CpWS})_2(\text{SC}_2\text{H}_4\text{S})$ (II) is isolated. Spectral data indicate that the dimer is quadrupally bridged. We are unable to distinguish definitively between possible coordination modes of the sulfur atoms ($\eta^2\text{-S}_2$, $\eta^2\text{-S}$, or $\eta^1\text{-S}_2$), but the complex appears to be structurally related to the previously characterized Mo(IV) dimer $(\text{CpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2\text{CH}_2)$.⁵ Both complexes are blue; absorptions occur in the visible spectrum at 712 ($\epsilon = 2260\text{ L}/(\text{cm mol})$), 568 (1520), and 408 (sh) nm for the tungsten dimer and at 730 (1950), 588 (1800), and 510 (sh) nm for the molybdenum complex.¹⁷ II undergoes a quasi-reversible one-electron reduction in acetonitrile at -1.46 V vs. SCE and an oxidation at $+0.18\text{ V}$ while the molybdenum dimer is reduced and oxidized at -1.31 and $+0.28\text{ V}$, respectively. Other aspects of the chemical reactivity of II are compared to those of molybdenum(IV) dimers below. Attempts to synthesize II by the abstraction of a sulfido ligand from I were not very successful. When I was heated in the presence of tri-*n*-butylphosphine at 60 °C for 7 days, only a trace of II could be detected by NMR, and most of I was recovered unchanged.

The chemical behavior of II shows significant differences from that of related molybdenum systems with ethanedithiolate ligands. $[\text{CpMo}(\text{CO})_3]_2$ reacts with ethylene sulfide to form the equivalently bridged complex $[\text{CpMoSC}_2\text{H}_4\text{S}]_2$. Although the ethanedithiolate ligands undergo stepwise exchange reactions which involve the

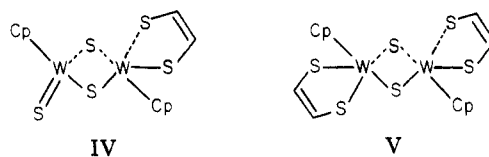
Table I. Electrochemical Data^a for Bis(sulfido)-Bridged Dimers of Tungsten(V)

compd	$E_{p/2}^b$	ΔE_p , mV	$E_{p/2}^b$	ΔE_p , mV
$[\text{CpW}(\text{S})(\mu\text{-S})_2]_2$	-1.35	100	-1.94	170
$(\text{CpW})_2\text{S}_3(\text{SC}_2\text{H}_4\text{S})^c$	-1.30	95	-1.91	
			(irrev)	
$(\text{CpW})_2\text{S}_3(\text{SC}_2\text{H}_4\text{S})^c$	-1.12	70		
$(\text{CpW})_2\text{S}_2(\text{SC}_2\text{H}_4\text{S})_2^c$	-0.65	70	-1.30	80

^a Dimethylformamide solutions with 0.1 M $(n\text{-Bu})_4\text{NBF}_4$ as supporting electrolyte. All waves showed an i_c/i_a ratio of ~ 1 at a scan rate of 100 mV/s. ^b V vs. SCE. ^c Irreversible oxidation observed at $\sim 1.0\text{ V}$ vs. SCE.

dissociation of ethylene,¹⁸ we have not detected the proposed intermediate $(\text{CpMoS})_2(\text{SC}_2\text{H}_4\text{S})$. Attempts to prepare this complex, e.g., by the reaction of $[\text{CpMo}(\text{S})\text{-SH}]_2$ with 1 equiv of $\text{HSC}_2\text{H}_4\text{SH}$ or of $\text{BrC}_2\text{H}_4\text{Br}$, have not been successful. In contrast, the tungsten dimer with a single ethanedithiolate ligand (II) is relatively stable, while attempts to isolate $[\text{CpWSC}_2\text{H}_4\text{S}]_2$ have failed. For example, the addition of ethylene to II results in an irreversible color change from blue to brown, suggesting a reaction with the sulfur bridges, but no discrete complex could be isolated in our hands.

Tungsten Complexes with Alkenedithiolate Ligands. The reaction of $[\text{CpW}(\text{S})(\mu\text{-S})_2]_2$ with acetylene or phenyl acetylene occurs at room temperature to form $[\text{CpWSC}_2\text{H}_2\text{S}]_2$ (III) or the phenyl-substituted analogue. The complexes are readily identified by mass spectral and NMR data. A single crystal of III was determined to be isomorphous with that of the molybdenum analogue with very similar cell dimensions,¹⁹ suggesting that the two complexes are isostructural.²⁰ The yield of III from this reaction is quite low ($\sim 15\%$), and at least two other products are also formed in low yields. These have been isolated by column chromatography and have the formulations $(\text{CpW})_2\text{S}_3(\text{SC}_2\text{H}_2\text{S})$ (IV) and $(\text{CpW})_2\text{S}_2(\text{SC}_2\text{H}_2\text{S})_2$ (V). Spectral data indicate that the structures are related



to that proposed for I. The structure of V has been determined by an X-ray diffraction study which is discussed below. The proton NMR resonances of the vinyl protons in the dithiolate ligands of IV and V occur at ≈ 8 ppm compared to a chemical shift of 6–6.5 ppm for these protons in complexes with $\mu\text{-}\eta^2\text{-alkenedithiolate}$ ligands. Such downfield shifts have been attributed to a contribution from the dithioglyoxal resonance form of the $\text{C}_2\text{H}_2\text{S}_2$ ligand.²¹ The chemical shift appears to be a useful characteristic in distinguishing between terminal and bridging modes for this ligand in both molybdenum¹⁶ and tungsten cyclopentadienyl dimers. The source of the additional sulfur atoms in IV and V (e.g., decomposition of $[\text{CpWS}_2]_2$ or an S_8 impurity) and the mechanism of complex formation have not been established.

(16) $(\text{CpMoS})_2(\text{O})(\text{SCHPhS})$ crystallizes in space group $Pm\bar{m}a$ with cell dimensions $a = 10.284$ (6) Å, $b = 15.175$ (8) Å, $c = 12.018$ (7) Å, and $V = 1875$ (2) Å³; Tanner, L.; Noordik, J.; Rakowski DuBois, M., unpublished results.

(17) Spectral data are reported for 10^{-4} M dichloromethane solutions. An X-ray study of $(\text{MeCpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2\text{CH}_2)$ has been completed recently; McKenna, M.; Noordik, J.; Rakowski DuBois, M., unpublished results.

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Table II. Selected Bond Distances and Angles for $(\text{CpW})_2\text{S}_2(\text{SC}_2\text{H}_2\text{S})_2$

Distances (Å)			
W_1-W_1'	3.021 (2)	W_3-S_5	2.338 (5)
W_1-S_1	2.328 (5)	W_2-S_6	2.392 (5)
W_1-S_2	2.387 (5)	W_2-S_7	2.392 (5)
W_1-S_3	2.412 (5)	W_3-S_8	2.423 (5)
$W_1-C_{\text{Cp(av)}}$	2.367 (22)	W_3-S_9	2.405 (5)
S_2-C_{16}	1.734 (20)	S_6-C_{18}	1.734 (23)
S_3-C_{17}	1.768 (24)	S_7-C_{19}	1.724 (22)
$C_{16}-C_{17}$	1.329 (30)	$C_{18}-C_{19}$	1.352 (29)
W_2-W_3	3.056 (1)	S_8-C_{20}	1.758 (20)
W_2-S_4	2.350 (5)	S_9-C_{21}	1.749 (24)
W_2-S_5	2.359 (5)	$C_{20}-C_{21}$	1.348 (32)
W_3-S_4	2.342 (5)		
Angles (deg)			
$W_1-S_1-W_1'$	80.8 (2)	$S_4-W_2-S_5$	96.7 (2)
$S_1-W_1-S_1'$	99.2 (2)	$S_4-W_3-S_5$	97.5 (2)
$S_1-W_1-S_2$	137.8 (2)	$S_6-W_2-S_7$	78.8 (2)
$S_1-W_1-S_3$	76.6 (2)	$S_4-W_2-S_7$	77.1 (2)
$S_2-W_1-S_3$	78.6 (2)	$S_5-W_2-S_6$	77.0 (2)
$W_1-S_2-C_{16}$	109.9 (8)	$S_3-W_3-S_9$	77.8 (2)
$S_2-C_{16}-C_{17}$	120.2 (1.8)	$S_4-W_3-S_8$	79.2 (2)
$W_2-S_4-W_3$	81.3 (1)	$S_5-W_3-S_8$	78.5 (2)
$W_2-S_5-W_3$	81.2 (1)		

dihedral angle between $S_4W_2S_5$ and $S_4W_3S_5$: 159.2°

Cyclic voltammetric studies have been carried out on the series of tungsten(V) dimers shown in Table I. Each of the complexes shows at least one fairly reversible reduction wave ($\Delta E_p = 70-100$ mV). The stepwise substitution of either alkane- or alkenedithiolate ligands for terminal sulfido groups results in significant anodic shifts in the reduction potentials. Complex V, the most readily reduced dimer in this series, has been found to react with the chemical reducing agent hydrogen under extremely mild conditions as discussed below.

X-ray Diffraction Study of $[\text{CpW}(\mu\text{-S})(\text{SC}_2\text{H}_2\text{S})_2]$. The complex crystallizes in space group $P2_1/c$ with one and one-half molecules per asymmetric unit. Perspective drawings of each of the molecules and the numbering schemes are shown in Figures 1a and 1b. Selected bond distances and angles and positional and thermal parameters are listed in Tables II and III, respectively. Both molecules involve similar bis(μ -sulfido) geometries with a 1,2-ethenedithiolate ligand chelated to each tungsten ion. Each CpW unit is at the apex of an approximate square pyramid in a typical "piano stool" geometry. However significant differences are observed for the two molecules. Since molecule 1 is positioned about a crystallographic inversion center, its W_2S_2 core is required by symmetry to be planar. The core of the second molecule is nonplanar with a dihedral angle of 159.2° between the planes defined by $S_4W_2S_5$ and $S_4W_3S_5$. In addition, the tungsten-tungsten and tungsten-sulfur distances in the core of molecule 2 are consistently longer than those in the planar structure. The reasons for the differences in the solid state are not obvious. Although no particularly short intermolecular distances are noted, it seems likely that packing forces may be causing these structural variations. The metal-metal distances observed for these dimers are similar to the value of 3.045 (2) Å reported previously for a bis(sulfido)-bridged cyclopentadienyl dimer of tungsten.⁸ These values are significantly longer than those reported for other similarly bridged W(V) complexes, which range from 2.791 (1) to 2.95 Å.^{22,23} The somewhat longer average W-S bond

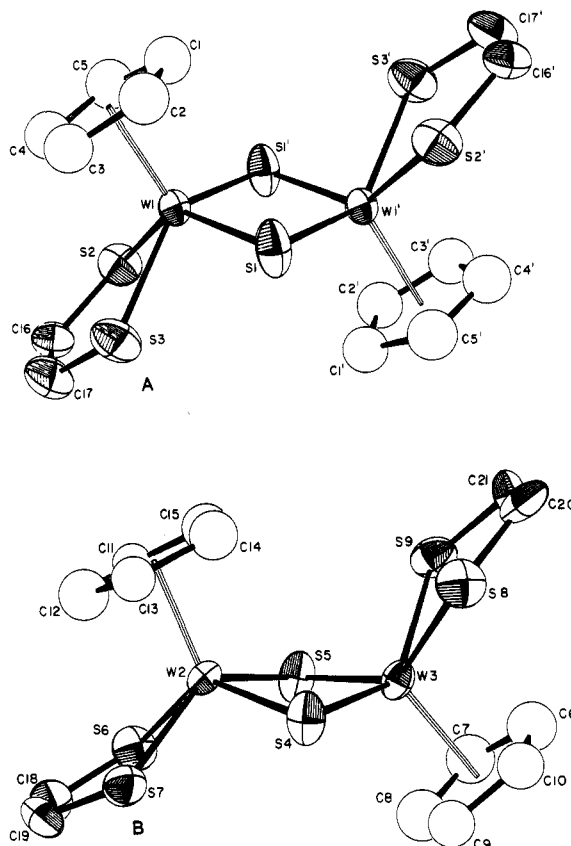
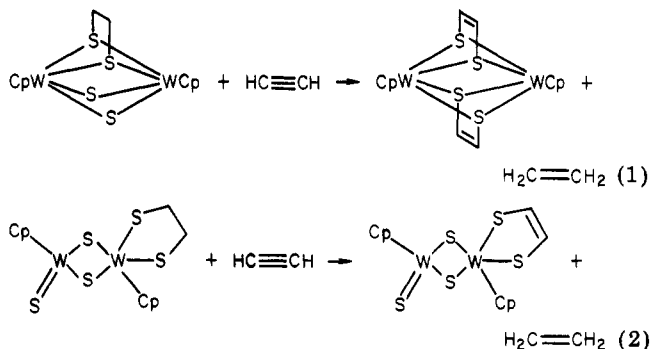


Figure 1. (a) Perspective drawing of and numbering scheme for molecule 1 of $[\text{CpW}(\text{S})\text{SC}_2\text{H}_2\text{S}]_2$. (b) Perspective drawing of and numbering scheme for molecule 2 of $[\text{CpW}(\text{S})\text{SC}_2\text{H}_2\text{S}]_2$. Vibrational ellipsoids are drawn at the 50% probability level.

length of the dithiolate ligands (2.401 (5) Å) compared to the W-S distances observed for the bridging sulfides is suggestive of some dithioglyoxal character in the dithiolate ligands. The C-S and C-C distances in these ligands in V have also been compared to those for the μ - η^2 -ethenedithiolate ligand in $[\text{CpMoSC}_2\text{H}_2\text{S}]_2$.²⁰ Although there is a tendency toward shorter C-S and longer C-C bonds in the former structure, the magnitude of the errors in this study make it difficult to assess the significance of this trend.

Reactivity Studies of Tungsten Complexes. We have observed evidence for sulfur ligand reactivity in several of the tungsten derivatives. Hydrocarbon exchange reactions similar to those characterized for bridging alkanedithiolate ligands in molybdenum dimers² have also been observed for II (eq 1). In addition this type of



exchange has been extended to a terminally coordinated alkanedithiolate ligand in a W(V) dimer (eq 2). Although activated acetylenes have been found to undergo related exchange reactions with nonbridging ethanedithiolate ligands²⁴ and addition reactions with nonbridging disulfides

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Table III. Positional and Thermal Parameters for (CpW)₂S₂(SC₂H₄S)₂

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
W1	-0.1326 (1)	0.46001 (3)	0.44868 (5)	0.0304 (5)	0.0319 (5)	0.0314 (5)	-0.0036 (4)	0.0039 (4)	0.0008 (4)
W2	-0.54291 (9)	0.22021 (3)	0.30338 (5)	0.0245 (5)	0.0363 (5)	0.0262 (4)	-0.0037 (4)	0.0039 (3)	-0.0033 (4)
W3	-0.2576 (1)	0.15670 (4)	0.43121 (5)	0.0250 (5)	0.0436 (6)	0.0291 (4)	0.0035 (4)	0.0048 (3)	-0.0017 (4)
S1	0.1508 (7)	0.4730 (2)	0.4354 (4)	0.037 (3)	0.063 (4)	0.056 (3)	-0.029 (3)	0.010 (3)	-0.008 (3)
S2	-0.4008 (7)	0.5041 (2)	0.3928 (4)	0.051 (4)	0.047 (4)	0.054 (3)	0.003 (3)	0.006 (3)	0.014 (3)
S3	-0.1420 (8)	0.4593 (3)	0.2815 (3)	0.060 (4)	0.075 (4)	0.037 (3)	-0.004 (3)	0.017 (3)	0.007 (4)
S4	-0.2524 (6)	0.2112 (2)	0.2970 (3)	0.035 (3)	0.060 (4)	0.039 (3)	0.015 (2)	0.015 (2)	0.005 (3)
S5	-0.5248 (7)	0.1854 (2)	0.4573 (3)	0.034 (3)	0.072 (4)	0.035 (3)	0.011 (3)	0.014 (2)	0.008 (3)
S6	-0.7115 (7)	0.2860 (2)	0.3718 (4)	0.052 (4)	0.055 (4)	0.058 (3)	-0.009 (3)	0.021 (3)	0.009 (3)
S7	-0.4822 (7)	0.3064 (2)	0.2300 (3)	0.045 (4)	0.046 (4)	0.050 (3)	0.004 (3)	0.004 (3)	-0.009 (3)
S8	-0.1338 (7)	0.0901 (2)	0.3361 (3)	0.049 (4)	0.055 (4)	0.051 (3)	-0.006 (3)	0.021 (3)	0.000 (3)
S9	-0.3775 (7)	0.0684 (2)	0.4695 (3)	0.050 (4)	0.051 (4)	0.050 (3)	0.004 (3)	0.011 (3)	-0.016 (3)
C16	-0.465 (3)	0.4907 (9)	0.274 (1)	0.06 (2)	0.05 (2)	0.04 (1)	0.01 (1)	-0.00 (1)	0.00 (1)
C17	-0.353 (3)	0.473 (1)	0.223 (1)	0.08 (2)	0.07 (2)	0.05 (1)	0.02 (1)	-0.01 (1)	0.00 (2)
C18	-0.744 (3)	0.346 (1)	0.301 (1)	0.08 (2)	0.05 (2)	0.06 (1)	-0.00 (1)	-0.01 (1)	-0.00 (1)
C19	-0.644 (3)	0.3536 (9)	0.236 (2)	0.06 (2)	0.03 (1)	0.07 (2)	0.01 (1)	0.00 (1)	0.00 (1)
C20	-0.148 (3)	0.021 (1)	0.380 (2)	0.04 (2)	0.07 (2)	0.07 (2)	-0.02 (1)	-0.02 (1)	-0.01 (1)
C21	-0.256 (3)	0.012 (1)	0.440 (2)	0.06 (2)	0.04 (1)	0.07 (2)	0.01 (1)	-0.02 (1)	0.02 (1)
atom	x	y	z	U	atom	x	y	z	U
C1	-0.085 (3)	0.3935 (9)	0.574 (1)	0.057 (6)	C9	-0.032 (3)	0.221 (1)	0.492 (1)	0.054 (6)
C2	-0.012 (3)	0.370 (1)	0.503 (1)	0.062 (6)	C10	0.033 (3)	0.1664 (9)	0.500 (1)	0.052 (6)
C3	-0.143 (3)	0.3615 (9)	0.425 (1)	0.061 (6)	C11	-0.806 (2)	0.1773 (8)	0.249 (1)	0.042 (5)
C4	-0.297 (3)	0.378 (1)	0.448 (1)	0.062 (6)	C12	-0.766 (3)	0.214 (1)	0.177 (1)	0.066 (7)
C5	-0.266 (3)	0.400 (1)	0.541 (1)	0.066 (7)	C13	-0.621 (3)	0.1903 (8)	0.149 (1)	0.047 (6)
C6	-0.051 (3)	0.136 (1)	0.566 (1)	0.064 (6)	C14	-0.574 (3)	0.139 (1)	0.205 (1)	0.058 (6)
C7	-0.167 (3)	0.174 (1)	0.592 (1)	0.066 (7)	C15	-0.694 (3)	0.133 (1)	0.264 (1)	0.061 (6)
C8	-0.158 (3)	0.225 (1)	0.547 (2)	0.071 (7)					

Table IV. Selected Bond Distances and Angles for [CpVSC₂H₄S]₂

Distances (Å)	
V ₁ -V ₁ '	2.542 (1)
V ₁ -S ₁	2.416 (1)
V ₁ -S ₂	2.434 (1)
V ₁ -C ^{cp(av)}	2.300 (4)
V ₁ -S ₂ -V ₁ '	63.4 (1)
S ₁ -V ₁ -S ₂	76.0 (1)
S ₁ -V ₁ -S ₁	116.6 (1)
V ₁ -S ₂ -C ₇	107.3 (2)
V ₁ -S ₁ -C ₆	105.5 (2)
S ₁ -C ₆ -C ₇	113.9 (4)

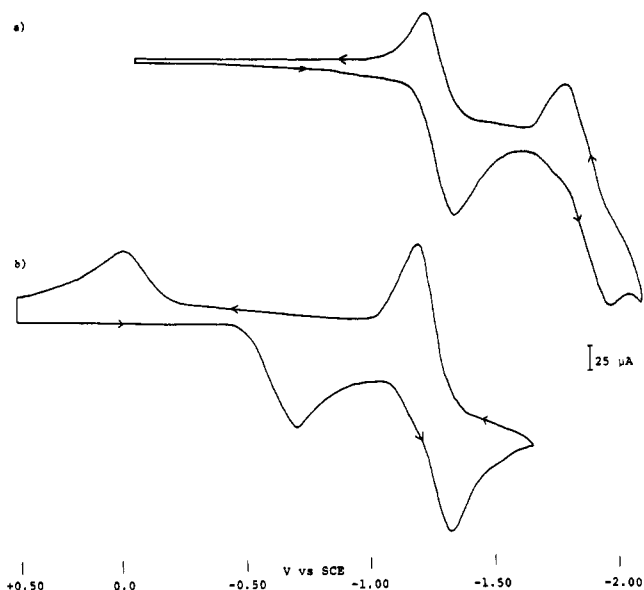
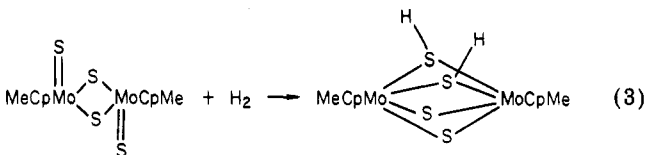


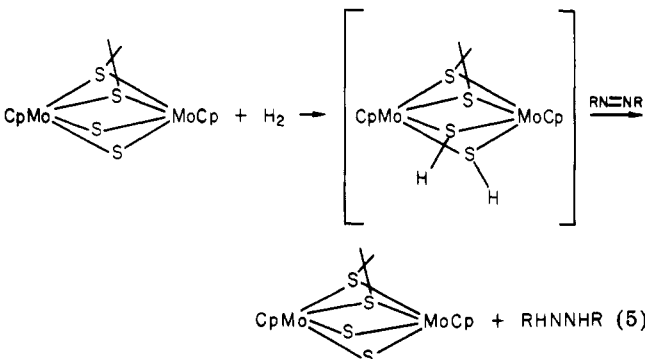
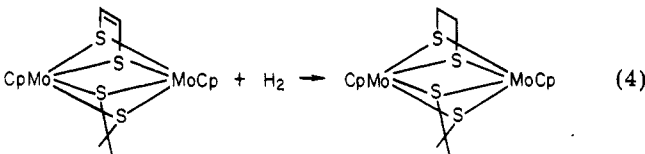
Figure 2. Cyclic voltammograms for (a) $[\text{CpWS}(\mu\text{-S})]_2$ and (b) $[\text{Me}_5\text{C}_5\text{MoS}(\mu\text{-S})]_2$ in DMF, scan rate = 100 mV/s.

and polysulfide ligands,²⁴⁻²⁶ an exchange between unsubstituted acetylene and a hydrocarbon in a nonbridging dithiolate ligand has not been observed previously.

One of the most significant features of the related molybdenum systems is the reactivity of the sulfido ligands with hydrogen. In some cases these reactions have resulted in the formation of stable complexes with bridging mercapto ligands, e.g., eq 3.⁴ In other systems, molybdenum



complexes with SH ligands have been proposed as reactive intermediates in hydrogenation reactions, e.g., eq 4 and 5.^{27,28} We are interested in determining the generality of



(24) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

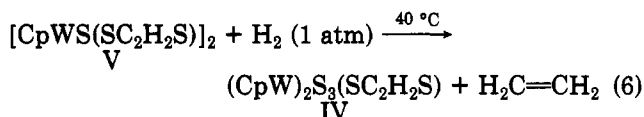
(25) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.

(26) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

(27) Mechanistic studies suggest that mercapto ligands are involved as intermediates in these reactions. McKenna, M.; Casewit, C.; Rakowski DuBois, M., manuscript in preparation.

this reactivity of nonmetals with hydrogen and have investigated similar reactions with the sulfur ligands in the tungsten complexes. Unlike the analogous molybdenum complex, $[\text{CpW}(\text{S})(\mu\text{-S})]_2$ does not react with hydrogen to form an isolable complex with mercapto ligands. Nor have we been successful in generating a mercapto complex by the reaction of $[\text{CpW}(\text{S})(\mu\text{-S})]_2$ with triethylborohydride.²⁹ Since eq 3 involves a two-electron reduction as well as a ligand rearrangement, we have compared the cyclic voltammetry of the related molybdenum and tungsten dimers $[\text{Me}_5\text{C}_5\text{MoS}(\mu\text{-S})]_2$ and $[\text{CpWS}(\mu\text{-S})]_2$ (Figure 2). Both complexes undergo two one-electron reductions. Differences in potentials are a function of the different Cp ligands as well as the metal ions, and a direct comparison of metal ion effects on potentials cannot be made. However the difference in the degree of reversibility in the first reduction process for the two systems may be relevant to observed differences in their reactivity with chemical reducing agents.³⁰ The irreversibility of the first reduction of $[\text{Me}_5\text{C}_5\text{Mo}(\text{S})(\mu\text{-S})]_2$ suggests that the rearrangement to a tetrasulfur-bridged structure occurs with the addition of the first electron. Such a rearrangement appears to be less facile for the tungsten dimer and is not observed on the time scale of the electrochemical experiments.

A comparison of the reactivity of bridging alkenedithiolate ligands with hydrogen also shows significant differences for the molybdenum and tungsten systems. Unlike its molybdenum analogue,² the bis(alkenedithiolate)tungsten dimer (III) does not show any evidence for hydrogenation. However, when the reaction of V with hydrogen was followed by NMR, we observed reduction of a terminal dithiolate ligand as shown in eq 6. No H_2S



is detected; presumably elemental sulfur is formed to balance eq 6, but we have not detected this product in small-scale reactions. NMR data show that two isomers of IV (presumably cis and trans) are produced in a ratio of 4:1.³¹ The formation of both isomers may imply rearrangement to a dithiolate-bridged structure during hydrogenation, but further studies are clearly necessary before a mechanism can be proposed. The hydrogenation of the dithiolate ligand in IV is much less facile; no reduction is observed after heating IV under H_2 at 70 °C for several days.

The catalytic hydrogenation of azo compounds shown in eq 5 appears to proceed in an analogous fashion with the tungsten dimer $(\text{CpWS})_2\text{SC}_2\text{H}_4\text{S}$ (II). Mechanistic studies have not been carried out on the tungsten system, but its apparent electronic and structural similarities to $(\text{CpMoS})_2\text{S}_2\text{CH}_2$ lead us to propose a similar involvement of sulfido ligands. The scope of the catalytic chemistry of II, however, is not as broad as that of $(\text{CpMoS})_2\text{S}_2\text{CH}_2$.⁵ The differences arise from the relative reactivities of the ethanedithiolate vs. the methanedithiolate ligands. For

(28) Miller, W. K.; Wright, L. L.; Rakowski DuBois, M., Manuscript in preparation.

(29) A similar reaction between $[\text{CpMoS}]_2$ and BEt_3H^- has been reported to yield $[\text{CpMo}(\text{S})(\mu\text{-SH})]_2$; Curtis, M. D.; Williams, P. D. *Inorg. Chem.* **1983**, *22*, 2661.

(30) For example, sodium amalgam reduction of $[\text{Me}_5\text{C}_5\text{MoS}(\mu\text{-S})]_2$ in the presence of CH_2Br_2 yields $(\text{Me}_5\text{C}_5\text{MoS})_2\text{S}_2\text{CH}_2$. The analogous reaction with $[\text{C}_5\text{H}_5\text{WS}(\mu\text{-S})]_2$ yields, after work up in air, only the starting tungsten dimer.

(31) Characterization data for the isomers of IV are included in the Experimental Section. The geometry of each has not been assigned.

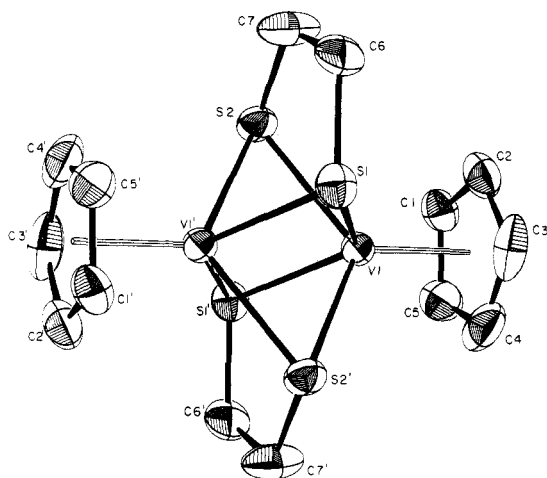
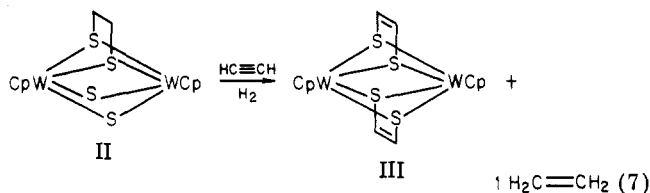


Figure 3. Perspective drawing of and numbering scheme for one molecule of $[\text{CpVSC}_2\text{H}_4\text{S}]_2$. Vibrational ellipsoids are drawn at the 50% probability level.

example, the acetylene adduct of $(\text{CpMoS})_2\text{S}_2\text{CH}_2$ is readily hydrogenated (eq 4) while attempts to hydrogenate acetylene in the presence of II result in the elimination of ethylene and the formation of III (eq 7).³² The latter



complex is inactive with respect to catalytic hydrogenations. It appears that $(\text{CpWS})_2\text{SC}_2\text{H}_4\text{S}$ will remain as an intact catalyst only for substrates such as azo compounds or imines, which form a much less stable adduct with the sulfido ligands than does ethylene.

Syntheses of Vanadium Complexes with Alkanedithiolate Ligands. The reaction of cyclopentadienylvanadium tetracarbonyl with 1,2-ethanedithiol or 1,2-propanedithiol in refluxing toluene produces air-stable complexes with the empirical formula $[\text{CpVSC}_2\text{H}_4\text{S}]_2$ ($\text{R} = \text{H}, \text{CH}_3$) (VIa, VIb). The same products can also be obtained by photolysis of the above reagents. The product formulations are consistent with elemental analyses, and mass spectral data reveal a parent ion for each dimer. Related vanadium dimers with organosulfur ligands, such as $[\text{CpV}(\text{SR})_2]_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) and $[\text{CpVS}(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{S}]_2$, have been prepared previously.¹⁰⁻¹² This series of vanadium dimers, including the bis(dithiolate) derivatives reported here, are paramagnetic (see below) and NMR data are not available for the determination of their structures. No crystallographic data have been reported for these systems. In order to confirm the molecular structure of this class of compounds, an X-ray diffraction study of $[\text{CpVSC}_2\text{H}_4\text{S}]_2$ was carried out.

Molecular Structure of $[\text{CpVSC}_2\text{H}_4\text{S}]_2$. The complex crystallizes in space group $P2_1/c$ with two identical, but crystallographically independent, molecules positioned about inversion centers in the unit cell. A perspective view of one of the molecules is shown in Figure 3. Final structural parameters and selected bond distances and angles are listed in Tables IV and V, respectively. The gross geometry of the dimer is identical with that observed for bis(dithiolate)-bridged complexes of molybdenum.²

The two dithiolate ligands form a plane which bisects the V-V vector and which is parallel to the planes of the two cyclopentadienyl ligands. The bond distances and angles in the V_2S_4 core are also very similar to those observed in the molybdenum dimers. The metal-metal distances in these types of structures are largely determined by the four bridging sulfur atoms, and relatively little variation has been observed for this parameter as the metal ion or its formal oxidation state is varied. However, the V(III)-V(III) distance of 2.541 (1) Å is shorter than the Mo(III)-Mo(III) distance in $[\text{CpMoSC}_2\text{H}_4\text{S}]_2$ ³³ (2.599 (1) Å) and the Mo(IV)-Mo(IV) distance in $[\text{CpMo}(\text{S})\text{SCH}_3]_2$ ⁴ (2.582 (1) Å). The value is also somewhat smaller than reported single bond lengths in other vanadium dimers multiply bridged by sulfur ligands, e.g., $(\text{MeCp})_2\text{V}_2\text{S}_5$ 2.658 (1) Å,¹³ $(i\text{-PrCp})_2\text{V}_2\text{S}_4$ 2.610 (1) Å,³⁴ and $\text{Cp}_2\text{V}_2\text{S}_4\cdot\text{C}_2(\text{CF}_3)_2$ 2.574 (3) Å.³⁴ The V-S-V angles and V-S distances in VI are similar to these parameters in the Mo_2S_4 cores.²⁰

Redox and Magnetic Properties of Vanadium Dimers. The cyclic voltammograms for the ethanedithiolate- and propanedithiolate-bridged dimers of vanadium are identical. A single one-electron ($n = 1.01$) oxidation at +0.32 V vs. SCE was found to be reversible ($\Delta E_p = 80$ mV) at several different scan rates with a peak current ratio near unity. An irreversible reduction is observed at -1.68 V. The electrochemical behavior is qualitatively similar to that of isoelectronic tetrasulfur-bridged dimers of Mo(IV) (e.g., $[\text{CpMo}(\text{S})\text{SCH}_3]_2$).⁴ The redox processes of the latter systems are shifted to more positive potentials by 0.25-0.30 V as might be expected for metal ions in a higher formal oxidation state. The redox behavior of VI can also be compared with that of the isostructural Mo(III) dimers. Although the molybdenum systems can be oxidized in two one-electron steps to form dicationic species which are isoelectronic with VI,² stable isoelectronic analogues cannot be achieved by a two-electron reduction of the vanadium complexes. Further investigation of the chemistry of the reduced derivatives of VI is discussed below.

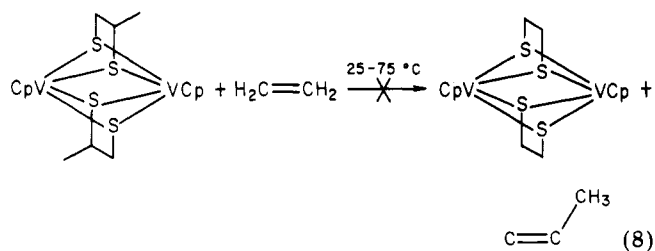
The one-electron oxidation product of VI has been synthesized by the reaction of the dimer with silver tetrafluoroborate. The cyclic voltammetry of the isolated salt confirms that the cation is structurally analogous to the neutral derivative. No NMR resonances were observed for either the neutral or cationic vanadium complexes over a range of several hundred ppm nor were any EPR signals detected at room temperature. The effective magnetic moments for the neutral complexes have been determined at 25 °C and are given in Table VI. Previously reported values for related dimers are included for comparison. The observed moments for the dimers are well below the spin only value of 2.83 μ_B /metal which would be expected for a dimer with completely uncoupled V(III) ions. As discussed elsewhere,¹⁰ the data provide evidence for direct metal-metal interactions and/or antiferromagnetic coupling through the sulfur ligands.

Reactivity of Vanadium Complexes. The dithiolate ligands in both the neutral and cationic vanadium dimers have been found to be inert toward hydrocarbon exchange reactions which have been characterized for the molybdenum and tungsten systems, e.g., eq 8. We therefore investigated the reactivity of reduced derivatives of VI which would be isoelectronic with $[\text{CpMoSC}_2\text{H}_4\text{S}]_2$. Reaction of VIb with excess NaH at 60 °C proceeded over

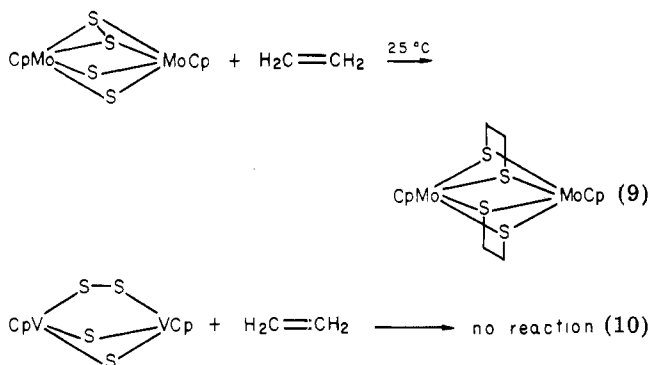
(33) Miller, D. J.; Haltiwanger, R. C.; Rakowski DuBois, M. "Proceedings of the 4th International Conference on the Chemistry and Uses of Molybdenum", Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; p 384.

(34) Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* 1983, 105, 6321.

(32) An analogous elimination reaction has been observed for $[\text{CpMo}(\text{S})(\mu\text{-SH})_2]_2$: $[\text{CpMo}(\text{S})\text{SH}]_2 + \text{HC}\equiv\text{CH} \rightarrow [\text{CpMoSC}_2\text{H}_2\text{S}]_2 + \text{H}_2$.



a period of 2 days as evidenced by a color change from green to orange. Characterization of the volatile products by mass spectrometry established the presence of propene; propane was not detected. Reduced products were not characterized, but after exposure to air, the dimers $[\text{CpVS}_2]_2$,¹⁴ $(\text{CpV})_2\text{S}_5$,¹³ and VIb were observed. Although reduction appears to be effective in activating the hydrocarbon linkages in the dithiolate ligands, hydrocarbon exchange reactions have not been developed via this route because the reoxidized vanadium sulfido dimers have not been found to react with alkenes or unactivated alkynes. The contrasting reactivities observed for $[\text{MeCpMoS}_2]_2$ ³⁵ and $[\text{CpVS}_2]_2$ (e.g., eq 9²⁸ and 10) reflect their significant structural differences^{8,34} and, ultimately, the different electronic requirements of the metal ions.



Summary

The reactivity of dithiolate and sulfido ligands in several new complexes has been investigated and compared to that characterized for molybdenum dimers. The studies have shown that the structural feature of two η^2 -dithiolate ligands bridging redox-active metal ions is not, in itself, sufficient for the observation of reversible hydrocarbon exchange reactions. No evidence for this type of reactivity has been observed for cyclopentadienylvanadium(III) dimers $[\text{CpVSC}_2\text{H}_3\text{RS}]_2$. Nevertheless such a geometry may contribute to the ease of such exchange reactions in other electronic situations. Synthetic studies of cyclopentadienyltungsten dimers with sulfur ligands have led to the identification of new structural types. We have found that terminally chelated dithiolate ligands in certain tungsten V dimers undergo hydrocarbon exchange reactions and hydrogenation under mild conditions. These observations suggest that these unusual modes of reactivity for dithiolate ligands may be observed in a variety of structural and electronic environments, and other examples of dithiolate complexes are under investigation.

Experimental Section

Reagent grade tungsten hexacarbonyl, sodium cyclopentadienide, and cyclopentadienylvanadium tetracarbonyl were purchased from Alfa. $[\text{CpW}(\text{CO})_3]_2$ ³⁶ and $[\text{CpWS}(\mu\text{-S})]_2$ ⁷ were

synthesized as reported previously. 1,2-Ethanedithiol, 1,2-propanedithiol, and ethylene sulfide (technical grade) were purchased from Aldrich. CHCl_3 was distilled from P_2O_5 or passed through neutral alumina. THF was distilled from LiAlH_4 . The acetonitrile used in cyclic voltammetric studies was distilled from P_2O_5 and a second time from CaH_2 . The supporting electrolyte, tetra(*n*-butyl)ammonium fluoborate was purchased from Southwestern Analytical and dried in vacuo.

Measurements. Elemental analyses were performed by Spang Microanalytical Laboratories. Mass spectra were recorded at 70 eV on a Varian MAT CH-5 spectrometer. Cyclic voltammograms were obtained by using a Princeton Applied Research 174 A polarographic analyzer with platinum wire working and counter electrodes, and a saturated calomel reference electrode. Controlled-potential electrolysis was carried out with a Princeton Applied Research 371 potentiostat-galvanostat and 379 digital coulometer. The working and counter electrodes were platinum gauze, the reference electrode was a Ag/AgCl wire. Magnetic susceptibilities were measured with a Sartorius 4433 Faraday balance. Gaseous products were identified by using a Varian 920 gas chromatograph with a thermal conductivity detector and a 2-m Parapak N column. Proton NMR were recorded at 90 MHz on a Varian 390 spectrometer or on a Bruker WM-250 MHz instrument. The latter instrument was also used for obtaining ¹³C NMR spectra. Chemical shifts are reported relative to tetramethylsilane. Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 337 spectrophotometer.

X-ray Crystallography. Crystals of V and VIa were examined on a Syntex P1 automated diffractometer at room temperature (295–301 K) with graphite monochromated Mo K_α radiation ($\lambda = 0.71069 \text{ \AA}$). On the basis of rotating crystal photographs both crystals were determined to be monoclinic. Examination of the systematic absences showed both to be in the space group $P2_1/c$ (C_{2h}^2 , No. 14).³⁷ Cell dimensions determined on the diffractometer using 15 (V) [24 (VIa)] carefully centered reflections are for V: $a = 7.9922$ (23) \AA , $b = 23.659$ (5) \AA , $c = 14.5062$ (24) \AA , $\beta = 100.62^\circ$, $V = 2696$ (1) \AA^3 , $Z = 6$, $\rho_c = 2.74$, $2.47 < \rho_x < 3.30$; for VIa: $a = 17.394$ (9) \AA , $b = 7.647$ (2) \AA , $c = 13.035$ (8) \AA , $\beta = 104.98$ (5)°, $V = 1675$ (2) \AA^3 , $Z = 4$, $\rho_c = 1.65$. Intensity data of 5542 (V) [6670 (VIa)] reflections in two quadrants with $2\theta < 40.0^\circ$ (V) [$< 52^\circ$ (VIa)] were collected on a crystal of $0.416 \times 0.117 \times 0.028$ mm (V) [$0.30 \times 0.30 \times 0.25$ mm (VIa)] by using θ - 2θ scan techniques with a variable scan rate from 4 to 24 deg/min (V) [fixed scan rate 4.0 deg/min (VIa)]. For both crystals scan ranges were calculated to start 0.7° below 2θ for $K\alpha_1$ ($\lambda = 0.70926$) and end 0.7° below 2θ for $K\alpha_2$ ($\lambda = 0.71354 \text{ \AA}$). Backgrounds were measured at the beginning and end of each scan for a total time equal to the scan time. Check reflections, measured every 100 reflections, showed no significant variation over the course of the data collection. The data were corrected for Lorentz and polarization effects.³⁸ Because of the highly unsymmetrical dimensions of V, the data were corrected for absorption³⁹ ($\mu = 91.56 \text{ cm}^{-1}$, transmission coefficients: average, 0.657; min, 0.329; max, 0.782). No absorption correction was made on VIa because of the low linear absorption coefficient ($\mu = 15.5 \text{ cm}^{-1}$) and the highly symmetrical dimensions of the crystal. Symmetry equivalent reflections were averaged⁴⁰ to 2531 [3316] unique reflections with $R_{av} = 0.039$ (V) [0.034 (VIa)]. The structures were solved with MULTAN⁴¹ and DIRDIF.⁴² The highest four (V) [two (VIa)] peaks

(36) Fischer, E. O. *Inorg. Synth.* 1963, 7, 136.

(37) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(38) The data reduction program was written locally and is based in part on routines supplied by Syntex Analytical Instruments, and in part on routines from J. A. Ibers' Northwestern University Crystallographic Computing Library.

(39) The adequacy of the absorption correction was checked using eight reflections each measured at 37 different values of ψ (transmission coefficients: average, 0.654; min, 0.302; max, 0.778) and averaging the resulting equivalent reflections (R_{av} before correction, 0.30; after correction, 0.07). de Menlaer, J.; Tompa, H. *Acta Crystallogr.* 1965, 19, 1014.

(40) Ibers, J. A. Northwestern University Crystallographic Computing Library.

(41) Main, P.; Hull, S. E.; Lessinger, M.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78. A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York and Louvain, 1978.

(35) $[\text{MeCpMoS}_2]_2$ has been synthesized;²⁸ spectral characteristics are very similar to those reported for $(\text{Me}_6\text{C}_5\text{Mo})_2(\mu\text{-S}_2)(\mu\text{-S})_2$.³

Table V. Positional and Thermal Parameters for $[\text{CpVSC}_2\text{H}_4\text{S}]_2$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V2	-0.06670 (4)	0.4447 (1)	-0.05529 (6)	0.0259 (4)	0.0281 (4)	0.0262 (4)	0.0015 (3)	0.0036 (3)	-0.0012 (3)
V1	-0.43466 (1)	-0.06334 (9)	-0.00960 (6)	0.0268 (4)	0.0253 (4)	0.0268 (4)	0.0014 (3)	0.0066 (3)	-0.0005 (3)
S1	-0.46070 (7)	-0.0241 (2)	0.16225 (9)	0.0385 (7)	0.0407 (7)	0.0255 (6)	0.0049 (5)	0.0055 (5)	0.0025 (5)
S4	-0.04007 (7)	0.4783 (2)	0.13470 (9)	0.0374 (7)	0.0442 (7)	0.0280 (6)	0.0039 (5)	0.0115 (5)	-0.0012 (6)
S3	0.03905 (7)	0.2448 (2)	0.0274 (1)	0.0378 (7)	0.0285 (6)	0.0394 (7)	0.0050 (5)	0.0065 (6)	0.0038 (5)
S2	-0.45493 (7)	0.2503 (1)	0.0013 (1)	0.0388 (7)	0.0262 (6)	0.0419 (7)	0.0012 (5)	0.0119 (6)	-0.0053 (5)
C1	-0.3235 (2)	-0.0323 (4)	-0.0729 (3)	0.028 (3)	0.050 (3)	0.049 (3)	0.001 (3)	0.013 (2)	-0.002 (2)
C2	-0.2984 (2)	-0.0567 (4)	0.0388 (3)	0.028 (3)	0.061 (4)	0.048 (3)	-0.004 (3)	0.007 (2)	0.003 (2)
C3	-0.3230 (2)	-0.2259 (4)	0.0620 (3)	0.055 (4)	0.063 (4)	0.066 (4)	0.030 (3)	0.027 (3)	0.032 (3)
C4	-0.3634 (2)	-0.3060 (4)	-0.0353 (3)	0.049 (4)	0.036 (3)	0.111 (6)	-0.005 (4)	0.037 (4)	0.010 (3)
C5	-0.3636 (2)	-0.1864 (4)	-0.1187 (3)	0.041 (3)	0.058 (3)	0.059 (4)	-0.025 (3)	0.017 (3)	0.002 (3)
C6	-0.4060 (3)	0.1715 (8)	0.2177 (4)	0.048 (3)	0.057 (3)	0.034 (3)	-0.015 (3)	-0.002 (3)	-0.002 (3)
C7	-0.4109 (4)	0.3162 (8)	0.1394 (5)	0.084 (5)	0.044 (3)	0.056 (4)	-0.019 (3)	0.008 (4)	-0.021 (3)
C8	-0.1793 (3)	0.4941 (5)	-0.1879 (4)	0.047 (4)	0.065 (4)	0.067 (4)	0.017 (3)	-0.029 (3)	-0.015 (3)
C9	-0.1423 (3)	0.3424 (5)	-0.2161 (4)	0.047 (4)	0.122 (6)	0.057 (4)	-0.049 (5)	-0.003 (3)	-0.010 (4)
C10	-0.1413 (3)	0.2123 (5)	-0.1381 (4)	0.067 (5)	0.046 (4)	0.114 (7)	-0.012 (4)	-0.033 (5)	-0.015 (3)
C11	-0.1777 (3)	0.2835 (5)	-0.0617 (4)	0.058 (5)	0.124 (7)	0.072 (5)	0.023 (5)	-0.004 (4)	-0.062 (5)
C12	-0.2012 (3)	0.4576 (5)	-0.0924 (4)	0.020 (3)	0.123 (7)	0.090 (6)	-0.060 (5)	0.003 (3)	-0.003 (3)
C13	0.0920 (4)	0.3200 (8)	-0.1524 (5)	0.055 (4)	0.060 (4)	0.049 (3)	-0.012 (3)	0.024 (3)	0.007 (3)

atom	x	y	z	U	atom	x	y	z	U
H1	-0.3138 (2)	0.0832 (4)	-0.1155 (3)	0.06	H8	-0.1890 (3)	0.6158 (5)	-0.2314 (4)	0.07
H2	-0.2662 (2)	0.0369 (4)	0.0960 (3)	0.06	H9	-0.1190 (3)	0.3285 (5)	-0.2849 (4)	0.07
H3	-0.3129 (2)	-0.2835 (4)	0.1401 (3)	0.06	H10	-0.1172 (3)	0.0820 (5)	-0.1371 (4)	0.07
H4	-0.3893 (2)	-0.4353 (4)	-0.0443 (3)	0.06	H11	-0.1861 (3)	0.2169 (5)	0.0077 (4)	0.07
H5	-0.3898 (2)	-0.2087 (4)	-0.2022 (3)	0.06	H12	-0.2305 (3)	0.5468 (5)	-0.0506 (4)	0.07
H61	-0.3443 (3)	0.1387 (8)	0.2524 (4)	0.05	H131	0.1513 (4)	0.3651 (8)	-0.1495 (5)	0.07
H62	-0.4358 (3)	0.1902 (8)	0.2801 (4)	0.05	H132	0.0575 (4)	0.3128 (8)	-0.2341 (5)	0.07
H71	-0.4486 (4)	0.4156 (8)	0.1594 (5)	0.07	H141	0.0402 (4)	0.0814 (7)	-0.1239 (5)	0.07
H72	-0.3534 (4)	0.3717 (8)	0.1415 (5)	0.07	H142	0.1392 (4)	0.1131 (7)	-0.0490 (5)	0.07

Table VI. Magnetic Moments for Quadrupally Bridged Dimers of Vanadium

dimer	μ^{eff} per V ion, μB	T, °C	ref
$[(\text{C}_5\text{H}_5)\text{VSCH}_2\text{CH}_2\text{S}]_2$	1.04	27	this work
$[(\text{C}_5\text{H}_5)\text{VSCH}_2\text{CH}(\text{CH}_3)\text{S}]_2$	1.15	24	this work
$[(\text{C}_5\text{H}_5)\text{V}(\text{SCH}_3)_2]_2$	1.84	25	10
$[(\text{C}_5\text{H}_5)\text{VS}(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{S}]_2$	1.2	25	11
$[(\text{C}_5\text{H}_5)\text{V}(\text{SPh})_2]_2$	2.30	27	12

in the most probable MULTAN solution used as input to DIRDIF gave the remaining eight sulfur atoms (V) [all remaining 18 atoms (VIa)] as the highest peaks. Upon isotropic refinement, the parameters converged with $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.052$ (V) [0.073 (VIa)].⁴³ Final refinement of V treated W and S atoms anisotropically, cyclopentadiene carbons isotropically. Hydrogen atoms were not seen in difference maps and were not included. Final refinement on VIa treated all non-hydrogen atoms anisotropically and included hydrogen atoms in calculated positions in the constrained idealized cyclopentadiene rings. Refinement converged with $R = 0.031$ (V) [0.041 (VIa)] and $wR = \{\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2\}^{1/2} = 0.037$ (V) [0.047 (VIa)] for 223 (V) [175 (VIa)] parameters and 1821 (V) [2382 (VIa)] observations. For all refinement a reflection was considered observed if $F_o^2 > 3.0 \sigma(F_o^2)$, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/(\sigma^2(F_o))$ where $\sigma^2(F_o) = \sigma_o^2 + \rho F_o^2$ with σ_o^2 calculated from counting statistics and $\rho = 0.0005$ (V) [0.0001 (VIa)]. The scattering factors used were those for neutral atoms.⁴⁴

Syntheses. Reactions were carried out under a nitrogen atmosphere with Schlenk ware. Products were isolated in air unless otherwise noted.

(CpW)₂S₃(SC₂H₄S) (I). [CpW(CO)₃]₂ (1.3 g, 2 mmol) was dissolved in 50 mL of THF, and ethylene sulfide (16 mmol) was added. The solution was heated at reflux for ~35 h. After cooling to room temperature, the solution was filtered to remove the brown complex [CpW(μ-S)]₂ (yield 25%). The filtrate was evaporated to yield the crude product which was chromatographed on an alumina column with CH₂Cl₂. The third, red-brown fraction was collected and the solvent evaporated. The product was recrystallized from a CHCl₃-hexane mixture. Yield, 18%. ¹H NMR (CDCl₃): 3.48 (m, 4, SC₂H₄S), 5.55, 6.08 (2 s, 10, Cp) ppm. ¹³C NMR (CDCl₃): 43.19 (SC₂H₄S), 98.40, 102.69 (Cp) ppm. MS: *m/e* 686 (P), 658 (P - C₂H₄), 626 (Cp₂W₂S₄). IR (Nujol): 485 (s), 430 (m) cm⁻¹. Anal. Calcd for C₁₂H₁₄W₂S₆: C, 20.99; H, 2.04; S, 23.36. Found: C, 21.04; H, 2.05; S, 23.38.

(CpWS)₂SC₂H₄S (II). [CpW(CO)₃]₂ (2.6 g, 4 mmol) was dissolved in 60 mL of THF, and ethylene sulfide (0.85 mL, 14 mmol) was added by syringe. The solution was heated at reflux for 72 h. The greenish-brown solution was filtered, and the filtrate was flash evaporated. The resulting dark solid was eluted through an alumina column with CH₂Cl₂. The last fraction was collected and on flash evaporation of the solvent gave the desired violet-blue product. Note: The product is slightly air sensitive, so the elution and flash evaporation should be done as quickly as possible. Yield 10%. ¹H NMR (CDCl₃): 2.04 (s, 4, SC₂H₄S), 6.59 (s, 10, Cp) ppm. ¹³C NMR (CDCl₃): 43.71 (SC₂H₄S), 96.37 (Cp) ppm. MS: 626 (Cp₂W₂S₄) and fragmentation products. Anal. Calcd for C₁₂H₁₄W₂S₄: C, 22.01; H, 2.14; S, 19.57. Found: C, 21.89; H, 2.11; S, 19.46.

[CpWSC₂H₂S]₂ (III). Acetylene (1 atm) was added to a degassed solution of [CpW(μ-S)]₂ (0.5 g, 0.8 mmol) in 100 mL of CH₂Cl₂ at 25 °C. The solution was stirred at 25 °C for 3 days. The purple-brown solution was filtered and the filtrate evaporated. The resulting residue was eluted through an alumina column with CH₂Cl₂/hexane (4:1). The first fraction was collected and on evaporation of the solvent gave a dark green crystalline product. Yield 12%. ¹H NMR (CDCl₃): 5.82 (s, 10, Cp), 6.24 (s, 4, HC=CH) ppm. MS: 678 (P), 652 (P - C₂H₂), 626 (Cp₂W₂S₄).

[(CpW)₂S₃(SC₂H₂S)] (IV). (a) The procedure given for the synthesis of [CpWSC₂H₂S]₂ was followed except that the solution was stirred at 25 °C for 6 days. Chromatography as described above produced a green band ([CpWSC₂H₂S]₂), a blue band ((CpW)₂S₃(SC₂H₂S)), and one or two purple bands. The major purple fraction was collected and, on evaporation of the solvent, gave the dark purple crystalline product. Yield, 14%. ¹H NMR

(CDCl₃): 6.28 (s, 5, Cp), 5.18 (s, 5, Cp), 8.11 (s, 2, CH=CH). MS: 684 (P), 626 (P - SC₂H₂). In some cases a second red-purple fraction could be isolated; this was presumed to be a second isomer of IV. Yield <5%. ¹H NMR (CDCl₃): 6.11 (s, 5, Cp), 5.41 (s, 5, Cp), 8.10 (s, 2, CH=CH) ppm. MS: 684 (P), 626 (P - SC₂H₂), 594 (P - SC₂H₂S). (b) From (CpW)₂S₃(SC₂H₄S): In a pressure flask, acetylene (1 atm) was added to a degassed solution of (CpW)₂S₃(SC₂H₄S) (0.060 g, 0.087 mmol) in 9 mL of CHCl₃ at 25 °C. The solution was stirred at room temperature for 18 h. It was then filtered and the filtrate evaporated. The resulting residue was eluted through an alumina column with CH₂Cl₂/hexane (4:1). The purple fraction was collected and on evaporation gave the product. Yield 70%.

(CpW)₂S₃(SC₂H₂S)₂ (V). Procedure a given for the synthesis of (CpW)₂S₃(SC₂H₂S) was followed. The second blue fraction on the chromatographic column was collected and on evaporation of the solvent gave the dark blue microcrystalline product. It was recrystallized from a CH₂Cl₂-hexane mixture. Yield, 11%. An increased yield could be obtained by letting the reaction go for 10 days. ¹H NMR (CDCl₃): 5.44 (s, 10, Cp), 7.85 (s, 4, CH=CH) ppm. MS: 742 (P), 710 (P - S), 684 (P - SC₂H₂), 652 (P - SC₂H₂S), 626 (Cp₂W₂S₄).

[CpVSCH₂CHRS]₂ (VIa, R = H; VIb, R = CH₃). (a) CpV(CO)₄ (0.23 g, 1 mmol) was dissolved in toluene (75 mL) and 1,2-ethanedithiol or 1,2-propanedithiol (1.1 mmol) was pipetted into the solution. The mixture was refluxed for 48 h. Rotoevaporation of the solvent and chromatography of the recovered solid (1:4 pentane/CH₂Cl₂ on Al₂O₃) produced an olive green product. VIa: Yield 80%. MS: 416 (P, 100%), 388 (P - C₂H₄, <2%), 360 (Cp₂V₂S₄, 93%). Anal. Calcd for C₁₄H₁₈S₄V₂: C, 40.38; H, 4.36; S, 30.80. Found: C, 40.36; H, 4.27; S, 30.78. VIb: Yield 68%. MS: 444 (P, 100%), 402 (P - C₃H₆, 2%), 360 (Cp₂V₂S₄, 96%). Anal. Calcd for C₁₆H₂₂S₄V₂: C, 43.24; H, 4.99; S, 28.85. Found: C, 43.44; H, 5.07; S, 28.89. (b) CpV(CO)₄ (0.23 g, 1 mmol) and the dithiol (1.5 mmol) in THF or CH₃CN was irradiated with a commercial sunlamp for ca. 16 h under a N₂ atmosphere. The product was purified by chromatography as described above. VIa: Yield 80%. VIb: Yield 60%.

[CpVSCH₂CHRS]₂BF₄ (VIIa, R = H; VIIb, R = CH₃). The neutral dimer VIa or VIb (0.3 mmol) was dissolved in distilled CH₂Cl₂ (75 mL); AgBF₄ (0.375 mmol) was dissolved in absolute EtOH (75 mL). The two solutions were mixed and stirred in air for ca. 1 h. The solution was filtered and evaporated. The purple salt was recrystallized from CH₂Cl₂/toluene. Yield 30-70%. Similar results were obtained with NOBF₄ or I₂.

Attempted Reaction of I with P(*n*-Bu)₃. The phosphine (18 μL, 0.06 mmol) and I (0.04 mmol) were dissolved in CDCl₃, and the solution was degassed and sealed in an NMR tube in vacuo. The reaction was heated at 70 °C for 5 days. A new resonance at 6.59 ppm, which corresponds to the Cp resonance of II, was observed (relative intensity 5%).

Reaction of I with Acetylene. To a degassed solution of I (0.035 g, 0.05 mmol) in 2 mL of CHCl₃ was added acetylene (1 atm) at 25 °C. The solution was stirred at 30 °C for 18 h. Gases were sampled, and ethylene was detected by GC. The brownish-purple solution was filtered and the filtrate evaporated. The resulting residue was eluted through an alumina column with CH₂Cl₂/hexane (3:1) and the third purple band was collected. Yield 75%. The NMR and MS data are identical with that of IV. The other two minor products were not characterized.

Reaction of II with Acetylene. To a degassed solution of II (0.035 g, 0.05 mmol) in CH₂Cl₂ was added acetylene (1 atm) at 25 °C. The solution was stirred at 25 °C for 17 h. Gases were sampled, and ethylene was detected by GC. The purple-red solution was filtered and evaporated. The NMR of the crude product in CDCl₃ showed that the major product was III; resonances of IV were also observed. Pure III could be obtained by eluting through an alumina column with CH₂Cl₂/hexane (3:1) and collecting the first light green fraction. Yield 65-70%.

Attempted Reaction of [CpWS(μ-S)]₂ with Hydrogen. To a degassed slurry of [CpWS(μ-S)]₂ (0.2 g, 0.3 mmol) in 30 mL of CHCl₃ was added H₂ (1 atm) at -196 °C. The solution was heated at 70 °C for 20 days. Almost all of the material remained undissolved. After cooling, the solution was filtered and the filtrate evaporated to yield 30 mg of material. Several resonances were observed in the Cp region of the NMR spectrum, and further

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characterization was not attempted.

Attempted Reaction of $[\text{CpWS}(\mu\text{-S})_2]$ with $\text{LiB}(\text{Et})_3\text{H}$. $[\text{CpWS}(\mu\text{-S})_2]$ (0.5 g, 0.8 mmol) was slurried in 70 mL of THF in a 500-mL round-bottomed flask which was then degassed two times on the Schlenk line. To this, under N_2 , was added LiEt_2BH (9 equiv). The initial brown color changed to a light green. The solution was stirred at 25 °C for 18 h and was then quenched with deaerated distilled water. The THF was removed by flash evaporation. Attempts to extract the resulting brown product into CH_2Cl_2 or CHCl_3 were unsuccessful.

Attempted Reaction of III with H_2 . One atmosphere of hydrogen was added to a degassed CDCl_3 solution of III, and the NMR tube was sealed. The solution was heated at 60 °C for 7 days. The color of the solution changed to purple, and new NMR resonances were observed which corresponded to those of complex IV. Neither ethylene nor other molybdenum products were identified. A similar transformation of III was found to occur under a nitrogen atmosphere.

Reaction of V with H_2 . In an NMR tube H_2 (1 atm) was added at -196 °C to a degassed solution of V (0.025 g, 0.03 mmol) in CDCl_3 . The NMR tube was then sealed and kept at 38 °C. After 2 days new resonances in the spectrum could be assigned to IV and free ethylene. Conversion was >90% after 8 days. No intermediates were detected.

Catalytic Hydrogenations. The tungsten dimer II was dissolved in CHCl_3 and one of the following substrates was added: *cis*-azobenzene (3 equiv), diethyl azodicarboxylate, (5 equiv), *N*-benzylideneaniline (2.5 equiv). Each solution was degassed, and H_2 (1 atm) was added at -196 °C. The reaction tubes were sealed and stirred at 55 °C. The following turnover frequencies were determined by NMR analysis of products (mol/(mol of catalyst)h): diphenylhydrazine (0.12), *N*-benzylaniline (0.08), diethyl hydrazodicarboxylate (1.3).

Attempted Reactions of $[\text{CpVSC}_2\text{CHRS}]_2$ with Alkynes or Alkenes. The neutral dimer VIa or VIb (0.1 mmol) was dissolved in CHCl_3 (15 mL) in a 50-mL flask and the solution was twice freeze-thaw degassed. The alkyne or alkene was introduced

in the following amounts: acetylene (1 atm), 2-butyne (25 mmol), ethylene (3 atm), propene (3.2 atm), *cis*-2-butene (4.2 atm). The reaction mixture was stirred at 55-85 °C for 3-6 days. The gases were analyzed by gas chromatography, and the recovered solids were analyzed by mass spectrometry. No evidence for reaction was observed.

$[\text{CpVSC}_2\text{CH}(\text{CH}_3)\text{S}]_2 + \text{NaH}$. VIb (0.08 g, 0.18 mmol) was dissolved in THF (25 mL) in a reaction vessel (100 mL) fitted with a Kontes Teflon high-vacuum stopcock. The solution was twice freeze-thaw degassed; NaH (0.06 g, 2.7 mmol) was added under N_2 . After 48 h at 60 °C the solution was orange in color. Propene was detected in the gases by mass spectrometry. TLC of the solution on alumina showed two products in addition to the starting dimer. The solution was evaporated and redissolved in CDCl_3 . $(\text{CpV})_2\text{S}_5$ and $[\text{CpVS}]_2$ were identified by comparison of the NMR spectrum with those of authentic samples.

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Registry No. I, 89397-48-8; II, 89397-49-9; III, 89397-50-2; *trans*-IV, 89397-51-3; *cis*-IV, 89460-79-7; V, 89397-52-4; VIa, 89397-53-5; VIb, 89397-54-6; VIIa, 89397-56-8; VIIb, 89397-58-0; $[\text{CpW}(\text{CO})_3]_2$, 12091-65-5; $[\text{CpW}(\mu\text{-S})_2]$, 78356-89-5; $\text{CpV}(\text{CO})_4$, 12108-04-2; $\text{P}(n\text{-Bu})_3$, 998-40-3; $\text{HC}\equiv\text{CH}$, 74-86-2; *cis*-azobenzene, 1080-16-6; diethyl azodicarboxylate, 1972-28-7; *N*-benzylideneaniline, 538-51-2; diphenylhydrazine, 38622-18-3; *N*-benzylaniline, 103-32-2; diethyl hydrazodicarboxylate, 4114-28-7; ethylene sulfide, 420-12-2; 1,2-ethanedithiol, 540-63-6; 1,2-propanedithiol, 814-67-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes for both structures and the perspective drawing and numbering scheme for the second molecule of $[\text{CpVSC}_2\text{H}_4\text{S}]_2$ (19 pages). Ordering information is given on any current masthead page.

Iron Carbonyl Complexes of Dimethyl Cyclooctatetraene-1,8-dicarboxylate

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Reaction of dimethyl cyclooctatetraene-1,8-dicarboxylate with iron carbonyls yields, in addition to the known $3-6-\eta^4\text{-Fe}(\text{CO})_3$ complex, two new $\text{Fe}_2(\text{CO})_6$ complexes. One is a yellow $1-4-\eta^4,5-8-\eta^4\text{-bis}[\text{Fe}(\text{CO})_3]$ complex, with the iron tricarbonyl groups probably *trans*. The other is a red compound with a $1,5,6-\eta^3,2-4-\eta^3\text{-Fe}_2(\text{CO})_6(\text{Fe}-\text{Fe})$ structure. The X-ray crystallographic structure of the latter compound shows an iron-iron distance of 2.771 Å and indicates a strong interaction of the Cl-bound ester group with the C-Fe σ -bond. The red $\text{Fe}_2(\text{CO})_6(\text{Fe}-\text{Fe})$ complex is the most stable, probably as a consequence of that interaction. None of the compounds exhibits haptotropy at room temperature, in contrast to the parent hydrocarbon complexes.

Study of metal complexes of cyclooctatetraene and its derivatives has contributed immeasurably to our understanding of organometallic structure and reactivity. In the case of iron carbonyl derivatives of cyclooctatetraene, Scheme I summarizes the known compounds and their interconversions.¹ The variety of bonding modes observed

and the fluxional character of several of the products make derivatives of these compounds excellent choices for assessment of substituent effects on organometallic structure and reactivity. We report here the results of studies of the

(1) This scheme summarizes information from extensive reviews of (cyclooctatetraene)iron complexes, which appear in: (a) Kerber, R. C. "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F. W., Fischer, I., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 1. (b) Deganello, G. "Transition Metal Complexes of Cyclic Polyenes"; Academic Press: New York, 1979.

(2) Compound 4 was originally assigned a bis(allyl), $1-3-\eta^3,4-6-\eta^3(\text{Fe}-\text{Fe})$ structure (Keller, C. E.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* 1965, 87, 1388). Subsequent studies¹ of numerous cyclooctatriene and -tetraene complexes have shown the unsymmetrical $1,5,6-\eta^3,2-4-\eta^3(\text{Fe}-\text{Fe})$ structure to be preferred in eight-membered rings, and the latter structure is assigned here. The analogous diruthenium compound, with similar IR and NMR spectra (Cotton, F. A.; Musco, A. *J. Am. Chem. Soc.* 1968, 90, 1444), has the unsymmetrical structure (Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* 1968, 90, 5412).