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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, $\beta = 65.56$ (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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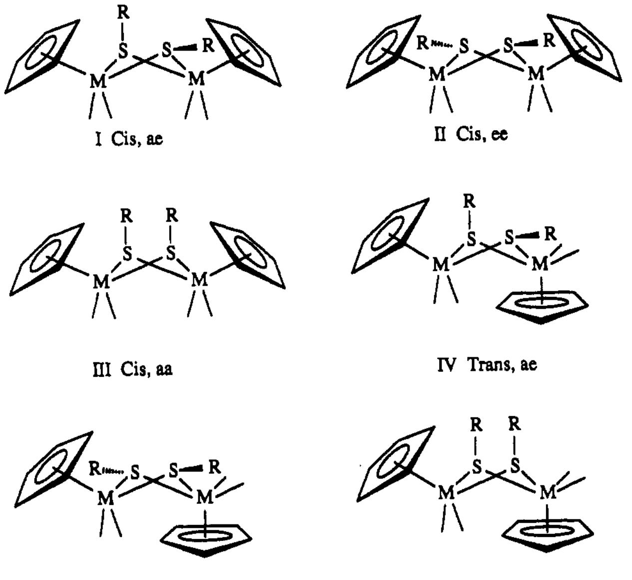

I Cis, ae

II Cis, ee

III Cis, aa

IV Trans, ae

V Trans, ee

VI Trans, aa

Figure 1. Structures I–VI, depicting the possible arrangements of two Cp rings and two R groups about a nonplanar M_2S_2 core.[2f] The descriptions cis and trans refer to the Cp ligands, and the R groups are described[4] by aa (axial–axial), ee (equatorial–equatorial) and ae (axial–equatorial).

$CpW(CO)_3SMe$ but they gave no supporting evidence. Watkins and George reported the preparation of $[CpW(CO)_2SR]_2$ for R = Me and 4-C_6H_4Me by stirring $CpW(CO)_3SR$ in refluxing benzene, and while the dimers were characterized by microanalysis and ^1H NMR and infrared spectroscopy, no X-ray structures were reported.[13] Recently Weinmann and Abrahamson reported that $[CpW(CO)_2SR]_2$, (R = Ph, 4-C_6H_4Me) was the product of photolysis of $CpW(CO)_3SR$ and that an inseparable mixture of both $[CpW(CO)_2SR]_2$ and $[CpW(CO)SR]_2$ was produced from $CpW(CO)_3SR$ in refluxing benzene.[14] The statement by these authors that the tungsten dimers were more difficult to study than the molybdenum dimers kindled our interest since we had in our hands $[CpW(CO)_2SCHMe_2]_2$ (**1**) and $[CpW(CO)SCHMe_2]_2$ (**2**). Therefore, in this report, we describe the preparation and structures of **1** and **2**, the first for any tungsten members of this class. The structures show interesting differences from the known molybdenum analogues.

Results and Discussion

The complex $CpW(CO)_2(PPh_3)SCHMe_2$ exists as a mixture of cis and trans isomers.[15] Gently warming this mixture in THF gave air stable, very dark brown $[CpW(CO)_2SCHMe_2]_2$ (**1**). If the starting complex or **1** is stirred in refluxing THF, air-sensitive, very dark green crystals of $[CpW(CO)SCMe_2]_2$ (**2**) were isolated. When the NMR spectrum of *cis/trans*-$CpW(CO)_2(PPh_3)$-$SCHMe_2$ in warm C_6D_6 was monitored over time the peaks due to **1** appeared at the expense of those due to the cis isomer. The latter had almost disappeared before the peaks due to the trans isomer began to decrease in intensity until both were totally consumed. The addition of free PPh_3 to the NMR sample retarded dimerization. This behavior parallels that observed in the reaction of $CpW(CO)_2(PPh_3)SR$ with CS_2 to give the thioxanthate complexes $CpW(CO)_2S_2CSR$.[15] Loss of PPh_3 from *cis*-$CpW(CO)_2(PPh_3)SCHMe_2$ is probably an important first step in the formation of **1**. Subsequent loss of two CO groups and the formation of a W=W double bond lead to **2**. The conversion of **1** to **2** was not reversed by treating **2** with 1 atm of CO at room temperature in agreement with the observations on analogous molybdenum compounds.[10] Both **1** and **2** are soluble in common organic solvents and in toluene gave bands at 1945 and 1853 cm^{-1} (**1**) and at 1840 cm^{-1} (**2**) in the carbonyl stretching region of their infrared spectra, consistent with their respective formulations. Although **1** and **2** differ by only one CO group per tungsten atom, they were easily distinguishable by their elemental analysis.

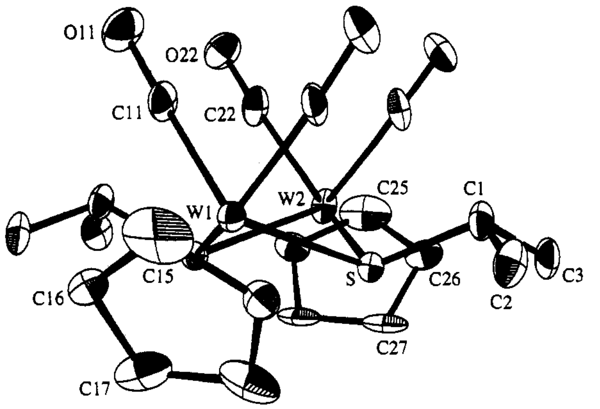

Figure 2. ORTEP view of $[CpW(CO)_2SCHMe_2]_2$ (**1**) showing the numbering scheme.

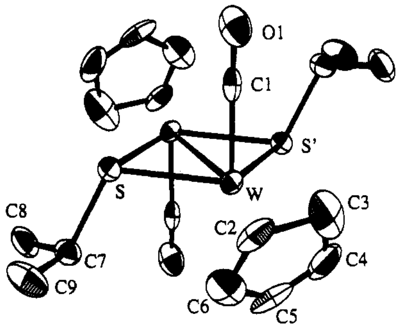

Figure 3. ORTEP view of $[CpW(CO)SCHMe_2]_2$ (**2**) showing the numbering scheme.

Table I. Crystallographic Data for $[CpW(CO)_2SCHMe_2]_2$ (**1**) and $[CpW(CO)SCHMe_2]_2$ (**2**)

	1	2
chem formula	$C_{20}H_{24}O_4S_2W_2$	$C_{18}H_{24}O_2S_2W_2$
fw	760.13	704.11
space group	*Pnnm*	$P2_1/c$
a, Å	12.066 (9)	9.441 (4)
b, Å	12.246 (2)	11.727 (3)
c, Å	15.643 (2)	9.953 (4)
β, deg	90	65.56 (3)
V, $Å^3$	2311.41	1101.94
Z	8	4
T, °C	22	22
λ, Å	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	2.185	2.332
μ(Mo Kα), cm^{-1}	103.56	119.26
transm coeff, %	10–30	23–45
R	0.075	0.054
R_w	0.067	0.074

The NMR spectrum of **1** showed only one environment for the Cp rings, the methine protons, and the methyl groups consistent with structures II and III having cis Cp rings. The NMR spectrum of **2** revealed one environment for the Cp rings and the methine protons but two environments for the methyl groups, which establishes them as being diastereotopic. The complex $[CpMo(CO)SCMe_3]_2$ has a planar Mo_2S_2 ring with a Mo=Mo double bond, and it is reasonable to assume that the structure of **2** would be analogous. The structure of the molybdenum complex corresponds to V/VI, but this is not consistent with the NMR spectrum of **2** since two Cp resonances would be expected. Only structure IV with a planar M_2S_2 ring is consistent with the NMR spectrum (i.e. a trans, trans geometry). The structures of **1** and **2** are depicted in Figures 2 and 3, respectively and the crystal-

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Table II. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $[CpW(CO)_2SCHMe_2]_2$[a,b]

	x	y	z	B_{iso}
W1	0.35517 (13)	0.27022 (9)	$^1/_2$	3.68 (7)
W2	0.24006 (12)	0.04221 (9)	$^1/_2$	3.21 (6)
S	0.3555 (5)	0.1375 (4)	0.3805 (5)	3.5 (3)
C11	0.2320 (22)	0.3041 (14)	0.3958 (20)	5.2 (14)
O11	0.1664 (15)	0.3272 (11)	0.3420 (16)	7.3 (12)
C22	0.1247 (20)	0.0843 (14)	0.4051 (18)	4.6 (13)
O22	0.0511 (15)	0.1060 (11)	0.3514 (15)	7.1 (12)
C1	0.2965 (19)	0.1549 (15)	0.2427 (19)	4.6 (13)
C2	0.3781 (22)	0.2141 (15)	0.1804 (20	5.5 (15)
C3	0.2928 (21)	0.0665 (15)	0.1840 (20)	5.3 (15)
C15	0.439 (4)	0.3995 (24)	$^1/_2$	9.7 (32)
C16	0.4760 (20)	0.3577 (14)	0.3973 (23)	5.9 (16)
C17	0.0400 (19)	0.2135 (14)	0.0657 (24	6.8 (17)
C25	0.318 (4)	0.4047 (20)	0	9.9 (32)
C26	0.2478 (18)	0.4139 (13)	0.1004 (20)	4.1 (12)
C27	0.1375 (21)	0.4307 (13)	0.064 (3)	7.3 (19)

[a] Esd's given in parentheses refer to the last digit(s) of the preceding number. [b] B_{iso} is the artithemetic mean of the principal axes of the thermal vibration ellipsoid.

Table III. Positional Parameters and Isotropic Thermal Parameters (Å^2) for $[CpW(CO)SCHMe_2]_2$[a,b]

	x	y	z	B_{iso}
W	0.03322 (4)	0.02327 (3)	0.86134 (4)	2.03 (3)
S	−0.1643 (3)	0.12639 (21)	1.0644 (3)	2.33 (11)
C1	0.1770 (11)	0.1355 (8)	0.8822 (10)	2.6 (5)
O1	0.2629 (9)	0.2021 (7)	0.8835 (10)	4.3 (5)
C2	0.0314 (17)	0.1181 (12)	0.6593 (13)	4.1 (7)
C3	−0.0960 (18)	0.0552 (19)	0.7104 (16)	5.7 (10)
C4	−0.0536 (22)	−0.0565 (13	0.6943 (17)	5.0 (10)
C5	0.0856 (22)	−0.0739 (17)	0.6418 (19)	6.3 (12)
C6	0.1638 (24)	0.0371 (23)	0.6076 (18)	9.7 (17)
C7	−0.3660 (13)	0.0858 (9)	1.0905 (13)	3.0 (6)
C8	−0.4229 (15)	0.1866 (15)	1.0265 (17)	5.2 (9)
C9	−0.4679 (13)	0.0626 (15)	1.2503 (16)	4.4 (8)

[a] Esd's given in parentheses refer to the last digit(s) of the preceding number. [b] B_{iso} is the artithemetic mean of the principal axes of the thermal vibration ellipsoid.

lographic data, positional parameters, bond lengths and angles are listed in Tables I–V.

The structure of **1** corresponds to type II with a nonplanar W_2S_2 ring, cis Cp rings, and equatorial $CHMe_2$ groups. The molecule possesses a crystallographically imposed mirror plane containing the Cp carbons C15 and C25 and the two tungsten atoms; the configuration of the Cp rings and the $CHMe_2$ groups is not crystallographically required. The calculated separation of the S–S vector from the W–W vector is 1.63 Å. The W–W distance of 3.835 (4) Å, is consistent with the absence of a W–W bond. The W–S bond lengths are inequivalent, but the difference is not considered statistically significant. The W–S–W angle (99.2 (2)°) and the S–W–S angles (69.5 (2), 70.1 (2)°) are similar to the average values for $[CpMo(CO)_2SPh]_2$ (101.0, 71.7, and 71.5°, respectively).[9,10] However the structure of the latter corresponds to type IV with trans rather than cis Cp rings with the R groups being axial–equatorial rather than equatorial–equatorial. Interestingly, the relative arrangement of the Cp and R groups in **1** is the same as that for the dication[8] $[CpMo(CO)_2SCMe_3]_2^{2+}$.

The structure of **2** confirms the assignment as being of type IV. The molecule has a crystallographically imposed inversion centre with a planar W_2S_2 ring. This requires the Cp rings to be trans with trans $CHMe_2$ groups as well. The tungsten–tungsten distance of 2.602 (5) Å is 1.23 Å shorter than in **1** and is consistent with the presence of a W=W double bond.[10,16] The close proximity of the tungsten atoms is revealed in the changes in the angles in the W_2S_2 ring in going from **1** to **2** (W–S–W, 99.2° for **1**, 65.3° for **2**; S–W–S, 69.5, 70.1° for **1**; 114.7° for **2**). The

Table IV. Bond Lengths (Å) and Angles (deg) for $[CpW(CO)_2SCHMe_2]_2$

W1–W2	3.835 (4)	S–Cl	1.83 (2)
W–S	2.528 (6)	C11–O11	1.09 (3)
W1–C11	2.03 (3)	C22–O22	1.16 (3)
W1–C15	2.27 (4)	C1–C2	1.56 (3)
W1–C16	2.37 (2)	C1–C3	1.55 (3)
W1–C17	2.41 (2)	C15–C16	1.47 (3)
W2–S	2.509 (6)	C16–C17	1.43 (3)
W2–C22	1.93 (2)	C17–C17′	1.58 (6)
W2–C25	2.26 (3)	C25–C26	1.49 (4)
W2–C26	2.35 (2)	C26–C27	1.44 (4)
W2–C27	2.43 (2)	C27–C27′	1.55 (6)
S–W1–S′	69.5 (2)	W1–C11–O11	175.7 (20)
S–W1–C11	82.1 (7)	W–2C22–O22	175.8 (20)
S–W1–C11′	124.6 (7)	S–C1–C2	105.9 (16)
C11–W1–C11′	76.4 (10)	S–Cl–3	107.0 (16)
S–W2–S	70.1 (2)	C2–C1–C3	109.1 (19)
S–W2–C22	82.5 (7)	C16–C15–C16′	115.0 (3)
S–W2–C22′	123.3 (7)	C15–C16–C17	104.5 (25)
C22–W2–C22′	72.6 (10)	C16–C17–C17′	108.2 (21)
W1–S–W2	99.2 (2)	C26–C25–C26′	109.0 (3)
W1–S–C1	113.2 (8)	C25–C26–C27	107.9 (24)
W2–S–C1	112.8 (8)	C26–C27–C27′	107.6 (21)

Table V. Bond Lengths (Å) and Angles (deg) for $[CpW(CO)SCHMe_2]_2$

W–W	2.602 (5)	S–C7	1.86 (1)
W–S	2.412 (4)	C1–O1	1.12 (1)
W–S′	2.411 (3)	C2–C3	1.31 (2)
W–C1	1.95 (1)	C2–C6	1.47 (3)
W–C2	2.29 (1)	C3–C4	1.35 (3)
W–C3	2.30 (1)	C4–C5	1.20 (3)
W–C4	2.31 (1)	C5–C6	1.45 (3)
W–C5	2.31 (1)	C7–C8	1.53 (2)
W–C6	2.30 (2)	C7–C9	1.49 (2)
W–W–S	57.3 (1)	C3–C2–C6	106.2 (2)
W–W–S′	57.4 (1)	C2–C3–C4	108.4 (2)
S–W–S	114.7 (1)	C3–C4–C5	115.2 (2)
S–W–C1	84.5 (3)	C4–C5–C6	107.6 (2)
W–S–W	65.3 (1)	C2–C6–C5	102.5 (2)
W–S–C7	112.0 (4)	S–C7–C8	104.8 (8)
W–S–C8	116.0 (4)	S–C7–C9	111.2 (8)
W–S′–C7′	112.9 (4)	C8–C7–C9	113.3 (1)
W–S′–C8′	146.1 (4)		

parameters of the M_2S_2 ring in **2** are quite similar to those in $[CpMo(CO)SCMe_3]_2$[10] and $[W(\mu\text{-}S)(S_2CNEt_2)_2]_2$.[16] In both **1** and **2** the Cp rings are tilted (unsymmetrically bonded); the most distant Cp carbons being transoid to the carbonyl carbons. This is also observed in the structures of the dication[8] $[CpMo(CO)_2SCMe_2]_2^{2+}$ and $[CpMo(CO)_2SPh]_2$.[9]

Despite the number of potential isomers of **1** and **2**, it appears that only one isomer of each is formed and that these are different from analogous molybdenum complexes. No evidence for additional isomers for **1** and **2** was detected in their NMR or infrared spectra. The NMR spectrum of **1** was unchanged down to −100 °C. Pyramidal inversion at bridging sulfur atoms has been well studied,[17] and sulfur inversion in $[CpMo(CO)_2SMe]_2$ was detected at −96 °C by variable-temperature ^1H NMR spectroscopy.[8] Thus it is probable that the barriers to interconversion of the axial and equatorial positions on the sulfur atoms of **1** and **2** are quite small.

As stated in the Introduction, dimers of the type $[CpM(CO)_xSR]_2$ have been fairly well characterized for molybdenum but not for tungsten. It has been implied that the tungsten complexes are inherently less stable than those of molybdenum.[14] Thus, the isolation of **1** and **2** is of interest. However, attempts to dimerize $CpW(CO)_2(PPh_3)SR$ for R = CH_2Ph and 4-C_6H_4Me in warm or refluxing THF gave dark residues, the NMR spectra

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of which revealed the presence of a mixture of Cp- and SR-containing species. It was not possible to identify sets of Cp and SR peaks whose integrated intensities were consistent with a dimeric formulation (i.e. one Cp group to one R group). The mixtures proved intractable, and no single compounds were isolated. While the failure of the method where R = aryl is similar to the results of others,[14] it is not immediately obvious why such complexes should be unstable.

Experimental Section

All reactions were performed in three-necked flasks or Schlenk tubes of the appropriate size and equipped with a nitrogen inlet. Standard inert-atmosphere techniques were used in all manipulations. Flasks charged with solids were twice evacuated and filled with nitrogen. Solvents were transferred by syringe. Filtrations were performed under nitrogen, and filtrates were reduced to dryness under vacuum (oil pump). The packing and elution of chromatography columns was performed in air with solvents used as purchased. Activated alumina (80–200 mesh) was purchased from Anachemia. Recrystallizations were done under nitrogen in Schlenk tubes or three-necked flasks by using distilled solvents. A layering technique was employed for recrystallizations, which consisted of dissolving the crude product in a minimal amount of solvent and then carefully adding a precipitating solvent such that it did not mix with the lower layer. Mixing occurred slowly as the flask was left overnight or longer at −16 °C. The mother liquors were removed via a disposable pipet and the crystals washed with the precipitating solvent and dried overnight under vacuum. Tetrahydrofuran (THF), toluene, and hexanes were refluxed over sodium metal and benzophenone and collected by distillation under nitrogen. Dichloromethane was refluxed over P_2O_5 and distilled just prior to use. Deuterated solvents (Merck, Sharp and Dohme, Montreal, Quebec, Canada) were used as purchased. The tungsten thiolates $CpW(CO)_2(PPh_3)SR$ (R = $CH(CH_3)_2$, $CH_2C_6H_5$, p-C_6H_4Me) were prepared according to published procedures.[15]

Solution infrared (IR) spectra were recorded by using 0.1 mm path length NaCl cells on a Perkin-Elmer 457 grating infrared spectrophotometer. Spectra were calibrated with the 1601.4-cm^{-1} band of polystyrene film. Band positions are accurate to ±2 cm^{-1}. Spectra in Nujol were recorded on an Analect AQS-20 Fourier transform infrared (FT-IR) spectrophotometer and referenced with 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}. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Varian XL-200 and Varian XL-300 spectrometers and all chemical shifts are in δ (ppm) units relative to an internal standard, tetramethylsilane (TMS). Shift values are accurate to ±0.002 ppm. Low-resolution mass spectra were measured on a Hewlett-Packard 5980A mass spectrometer at the McGill University Biomedical Mass Spectrometry Unit and on a Dupont 21-492B mass spectrometer in the Otto Maass Chemistry Building with ionizing potentials of 10 or 70 eV. All mass spectra were measured with electron-impact (EI) ionization unless otherwise stated. Elemental analyses were carried out by Spang Microanalytical Laboratories, Eagle Harbour, MI. Melting points were determined in grease-sealed capillary tubes under nitrogen on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Bis(cyclopentadienyl)tetracarbonylbis(μ-2-propanethiolato)ditungsten(II), $[CpW(CO)_2(\mu\text{-}SCHMe_2)]_2$ (1). The complex *cis/trans*-$CpW(CO)_2(PPh_3)SCHMe_2$ (2.17 g, 3.38 mmol) in THF (75 mL) was heated with stirring at 40 °C (oil bath) for 6 h. The resulting brown solution was allowed to cool to room temperature and reduced to dryness. The brown residue was dissolved a minimum of CH_2Cl_2 and chromatograhed on an alumina column (5 × 45 cm). Eluting with 1:1 CH_2Cl_2/hexanes gave a brown-red band, which was collected. A orange-yellow band due to a small amount of unreacted starting complex followed but was not collected. A brown residue remained at the top of the column. The brown-red fraction was reduced to dryness and recrystallized (1:4 CH_2Cl_2/hexanes) to give brown-black crystals (0.15 g, 12%; mp > 250 °C). ^{1}H NMR ($CDCl_3$): 5.55 (s, 5 H, Cp); 3.13 (septet, 1 H, $C\mathit{H}(CH_3)_2$, J(H–H) = 6.6 Hz); 1.13 (d, 6 H, $CH(C\mathit{H}_3)_2$, J(H–H) = 6.6 Hz). IR, ν(CO) (toluene): 1945 (s), 1853 (s) cm^{-1}. IR ν(CO), (Nujol): 1934 (s), 1905 (w), 1848 (s), 1818 (w) cm^{-1}. Mass spectrum, m/z (relative intensity, assignment): 704 (0.5, $M^+ - 2CO$); 661 (8.5, $M^+ - 2CO - CH(CH_3)_2$); 594 (100, $M^+ - 2CO - CH(CH_3)_2 - Cp - 2H$); 534 (18.0, $M^+ - 3CO - SCH(CH_3)_2 - Cp - 2H$); 529 (26.2, $M^+ - 2CO - 2S - CH(CH_3)_2 - Cp - 2H$). Anal. Calcd for $C_{20}H_{24}O_4S_2W_2$: C, 31.59; H, 3.18; S, 8.43. Found: C, 31.58; H, 3.29; S, 8.31.

Bis(cyclopentadienyl)dicarbonylbis(μ-2propanethiolato)ditungsten(II), $[CpW(CO)(\mu\text{-}SCHMe_2)]_2$ (2). The complex *cis/trans*-$CpW(CO)_2(PPh_3)SCHMe_2$ (1.59 g, 2.47 mmol) was stirred in refluxing THF (45 mL) for 7 h. During this time, the color changed from orange to black-green. The solution was allowed to cool to room temperature and then reduced to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on alumina (5 × 50 cm). Eluting with 1:2 CH_2Cl_2/hexanes gave a dark green band followed by a brown band and then by an orange band. A brown residue remained at the top of the column. The brown and orange bands were identified by ^{1}H NMR spectroscopy to be **1** and starting material, respectively. The dark green band was reduced to dryness and recrystallized from CH_2Cl_2/hexanes (1:4) to give air-sensitive black-green crystals (0.13 g, 14.6%). ^{1}H NMR ($CDCl_3$): 5.49 (s, 5 H, Cp); 2.14 (septet, 1 H, $C\mathit{H}(CH_3)_2$, J(H–H) = 6.6 Hz); 1.49, 1.31 (dd, 6 H, $CH(C\mathit{H}_3)_2$, J(H–H) = 6.6 Hz). IR, ν(CO) (toluene): 1840 (s) cm^{-1}; IR, ν(CO) (Nujol): 1835 (s), 1832 (s), 1800 (sh, m) cm^{-1}. Mass spectrum, m/z (relative intensity): 705 (2.8, $M^+ + H$); 661 (8.8, $M^+ - CH(CH_3)_2$); 633 (2.1, $M^+ - CH(CH_3)_2 - CO$); 592 (5.7, $M^+ - CH(CH_3)_2 - Cp - 4H$); 590 (5.7, $M^+ - 2CH(CH_3)_2 - CO$); 562 (25.1, $M^+ - 2CH(CH_3)_2 - 2CO$); 534 (6.7, $M^+ - SCH(CH_3)_2 - Cp - CO - 2H$); 43 (100, $CH(CH_3)_2$). Anal. Calcd for $C_{18}H_{24}O_2S_2W_2$: C, 30.70; H, 3.44; S, 9.11. Found: C, 30.49; H, 3.55; S, 9.09.

X-ray Structure Determinations. Table I contains details of the crystal parameters for **1** and **2**.[18] Single crystals of **1** and **2** suitable for crystallograhic studies were each obtained by recrystallization from CH_2Cl_2/hexanes. The crystal of $[CpW(CO)_2SCHMe_2]_2$ was mounted on a lithium borate fiber with 5-min epoxy. The crystal of $[CpW(CO)SCHMe_2]_2$ was placed in a lithium borate capillary and held in place with a trace of silicon grease because the compound decomposes slowly in air. Preliminary Weissenberg and precession photographs were used to identify the possible space groups. 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 structures were solved by conventional heavy-atom methods. The tungsten coordinates were found from Patterson syntheses. Successive rounds of refinement, structure factor calculations, and Fourier syntheses revealed the positions of the sulfur atoms and then the remaining carbon and oxygen atoms. After several cycles of isotropic refinement using the block-diagonal method, a general Gaussian absorption correction was applied and refinement was continued for several more cycles. The structures were then refined anisotropically to convergence: on the last cycle the positional parameter shifts were all less than $^1/_{20}$th of the corresponding standard deviation. Final difference syntheses showed only random noise. Tables II and III list the final coordinates for the molecules, while tables of thermal parameters and structure factors are available as supplementary material.

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Supplementary Material Available: Full-length tables of crystallographic data for **1** (Table 6) and **2** (Table 7) and tables of anisotropic temperature factors for **1** (Table 8) and **2** (Table 9) (4 pages); tables of observed and calculated structure factors for **1** (Table 10) and **2** (Table 11) (23 pages). Ordering information is given on any current masthead page.

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(18) 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, J. R., Van Konigsveld, H., Bassi, J. C., Eds.; Delft University Press: Delft, Holland, 1978; p 81.