

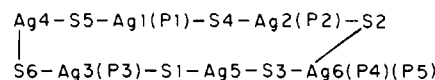
R = Et where a chain structure occurs.²⁰ The structure of **1** is not obviously related to the established $\text{Ag}_4\text{X}_4(\text{PR}_3)_4$ cubane structure,²²⁻²⁴ to heterometallic sulfide-silver-phosphine cages such as $(\text{MoS}_4)_2(\text{AgPPh}_3)_4$,²⁵ or to the distorted $[\text{Ag}_6(\text{SPh})_8]^{2-}$ cage.⁸

The unique component of the structure of **1** is the centered hexagonal $\text{Ag}(\text{SR})_3\text{Ag}_3$ basal section. It is the basal- $\text{Ag}(\text{SR})_3\text{Ag}_3$ plus podal- $(\text{SR})_3\text{Ag}$ idealization of the $\text{Ag}_5(\text{SR})_6$ core, with octahedro- $(\text{SR})_6$, that allows this structure to be related to another known thiolate cage structure, namely the trigonal-bipyramido- M_5 -octahedro- $(\text{SR})_6$ structure, **5**, of $[\text{M}_5(\text{S}-t\text{-Bu})_6]$, M = Cu, Ag.^{16,26} The relationship is shown in Figure 4. The trigonal-bipyramido- M_5 -trigonal-prismo- $(\text{SR})_6$ structure (Figure 4A) is partially twisted about the threefold axis to generate structure **5** (Figure 4B), and then this twisting is continued by the three digonal metal atoms which drop into the lower trigonal plane as shown by the arrows in Figure 4B, thus creating the basal-centered hexagonal unit. The equatorial metal atoms of **5** become the peripheral basal metal atoms, and the upper trigonal plane of Figure 4A becomes the podal trigonal unit. Figure 4C shows

the final structure with new silver-silver approaches marked as broken lines and with the terminal phosphine ligands added to peripheral metal atoms in the basal unit.

This type of interpretation of the structure of **1**, involving symmetrizations of the array of Ag, S, and P core atoms, must be tempered by the observed variability of dimensions. One peripheral Ag-S distance in the basal unit is ca. 0.6 Å longer than the remainder. The geometry of the core must also be subject to the requirements of the bulky phosphine ligands that cover its surface, and it will be pertinent to determine whether the structure **2** recurs with smaller phosphines, by investigations in progress.

In silver-thiolate structures, some Ag-S distances are long and may be relegated to secondary bonding, possibly nonexistent in other conformations of the molecule in solution.^{8,18} This type of structure analysis led to recognition of the monocyclic structure of (cyclohexanethiolato)silver.¹⁸ If only the two shortest Ag-SR bonds at each silver atom in the polycyclic molecule **1** are connected, the following 12-membered monocyclic molecule results:



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Supplementary Material Available: A tabulation of all atomic coordinates and thermal parameters and selected bond lengths and angles and a listing of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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Hexacarbonyl(fulvalene)ditungsten(W-W). A Stretched Tungsten-Tungsten Single Bond

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The title compound, $(\eta^5\text{-C}_5\text{H}_4\text{C}_5\text{H}_4)\text{W}_2(\text{CO})_6$, is found as a byproduct of the synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ via the thermolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_2\text{C}_6\text{H}_5$. The molecule possesses one of the longest W-W distances (3.347 (1) Å) recorded for which a bonding interaction can be established and is accompanied by a bending deformation of the fulvalene ligand toward the metal centers with a 16.1 (5)° dihedral angle. The structure was solved in the triclinic space group $P\bar{1}$ to an *R* factor of 0.049. Unit cell parameters are $a = 6.708$ (2) Å, $b = 9.626$ (2) Å, $c = 12.450$ (2) Å, $\alpha = 76.16$ (1)°, $\beta = 84.37$ (2)°, $\gamma = 74.95$ (2)°, $V = 753$ (4) Å³, and $Z = 2$. The molecule displays noncrystallographic 2-fold symmetry about an axis passing through the W-W bond and through the bridgehead C-C bond of the fulvalene ligand. The compound is more reactive toward iodine than the related unbridged $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ but is substantially less photoreactive than the unbridged dimer.

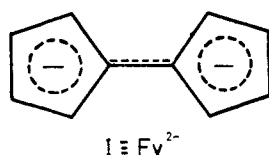
The thermal reactions¹ and photochemical behavior² of metal-metal-bonded compounds are areas of vigorous investigation at present. Many of the most intensively studied compounds are metal carbonyl dimers. A complex like $[\text{CpW}(\text{CO})_3]_2$,³ with a tungsten-tungsten single bond, is useful

because of the relative inertness to thermal substitution of its carbonyl ligands and the reasonable reactivity toward cleavage of the metal-metal bond.^{4,5} Modifications in the reactivity of this compound are to be anticipated if the two fragments are still connected after metal-metal bond cleavage.

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 (2) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Wrighton, M. S.; Graff, J. L.; Luong, J. C.; Reichel, C. L.; Robbins, J. L. Reference 1, Chapter 5, pp 85-110.

- (3) Cp = η^5 -cyclopentadienyl, Fv = $\eta^5\text{-}\eta^5$ -fulvalene, Me₂dte = *N,N*-dimethyldithiocarbamate.
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One way to accomplish this is to link the two cyclopentadienyl ligands to form an $\eta^5:\eta^5$ -fulvalene ligand, I.



Fulvalene complexes of iron (CpFeFvFeCp ,⁶ Fv_2Fe_2^7) were among the first prepared; these do not contain metal-metal bonds. Structures are now known for binuclear fulvalene complexes of Ti,^{8,9} Mo,¹⁰ Ni,¹¹ and Ru.¹² Recently, fulvalene-bridged metal-metal-bonded carbonyl complexes containing Ru,¹² Mo,^{12,13} and W¹⁴ have been prepared. The fulvalene-bridged dinuclear complexes of ruthenium and molybdenum are significantly more reactive than their unbridged counterparts.^{12,13} Unfortunately, published data¹⁴ on the title complex, $\text{Fv}[\text{W}(\text{CO})_3]_2$, do not allow us to make a similar comparison.

We have isolated the title complex from an unexpected source and determined its crystal structure by single-crystal X-ray diffraction. The details of that structure and its relationship to the reactivity of the fulvalene-bridged metal-metal-bonded complexes are presented here.

Experimental Section

Materials and Methods. Hexane and toluene were reagent grade and were purified by acid wash and dried over molecular sieves.¹⁵ The benzyl complex $\text{CpW}(\text{CO})_3\text{CH}_2\text{Ph}$ was prepared via literature procedures.^{16,17} Other materials were reagent grade or better and were used as received. Infrared spectra were taken with a Beckman 4250 spectrometer, Fourier transform 80-MHz ¹H NMR spectra were obtained on an IBM NR-80B instrument, and mass spectra were collected on a Hewlett-Packard 5985B GC/MS/DS in the direct-insertion mode. Electronic spectra were measured on a Hitachi Perkin-Elmer 100-80 spectrophotometer.

Isolation of Hexacarbonyl(fulvalene)ditungsten. The title complex was isolated from a batch of $[\text{CpW}(\text{CO})_3]_2$ prepared by the thermolysis of $\text{CpW}(\text{CO})_3\text{CH}_2\text{Ph}$ following literature procedures,¹⁶ except that the thermolysis was carried out under high vacuum at 180 °C for only 15 min. When the oven was opened to check the reaction, it was noted that the tube stopper had come loose, so the material was exposed to air at the oven temperature for some unknown length of time. (Previous preparations where exclusion of oxygen was complete show no evidence of contamination by $\text{Fv}[\text{W}(\text{CO})_3]_2$.) Purification of the fulvalene dimer was accomplished by chromatography. All operations with the dimers in solution were carried out under conditions of reduced light. About 0.3 g of the tungsten dimer from the above synthesis was dissolved in 40 mL of warm toluene (<40 °C). A 30 × 2.5 cm column of grade II alumina (Sigma) was made with hexane used as solvent. The toluene solution was applied to the column and

Table I. Atomic Positional Parameters for $\text{Fv}[\text{W}(\text{CO})_3]_2$ with Estimated Standard Deviations in Parentheses

atom	x	y	z
W1	0.04546 (7)	0.08507 (5)	0.21475 (4)
W2	0.01456 (8)	0.40158 (5)	0.29004 (4)
C1	0.3500 (19)	0.1159 (14)	0.1149 (10)
C2	0.3369 (20)	-0.0310 (15)	0.1261 (11)
C3	0.3459 (19)	-0.1030 (13)	0.2411 (11)
C4	0.3581 (20)	0.0015 (14)	0.3015 (11)
C5	0.3650 (17)	0.1382 (13)	0.2232 (10)
C6	0.3497 (19)	0.2760 (14)	0.2518 (10)
C7	0.3425 (20)	0.3014 (14)	0.3593 (10)
C8	0.2918 (21)	0.4568 (15)	0.3517 (11)
C9	0.2725 (23)	0.5243 (14)	0.2346 (12)
C10	0.3043 (21)	0.4185 (14)	0.1747 (11)
C11	-0.1448 (20)	0.2204 (14)	0.1007 (11)
O11	-0.2399 (19)	0.2879 (11)	0.0288 (9)
C12	-0.1397 (21)	0.0452 (15)	0.3468 (12)
O12	-0.2344 (17)	0.0031 (12)	0.4243 (8)
C13	-0.0886 (20)	-0.0496 (15)	0.1704 (10)
O13	-0.1632 (16)	-0.1308 (11)	0.1433 (9)
C14	-0.1843 (24)	0.4859 (16)	0.1731 (12)
O14	-0.2972 (18)	0.5575 (12)	0.1029 (8)
C15	-0.1603 (23)	0.5703 (16)	0.3448 (10)
O15	-0.2589 (21)	0.6693 (12)	0.3761 (9)
C16	-0.1363 (22)	0.3045 (15)	0.4201 (11)
O16	-0.2189 (19)	0.2598 (12)	0.4993 (8)

the column was eluted with 1:1 toluene/hexane and pure toluene to remove the unbridged $[\text{CpW}(\text{CO})_3]_2$. During this time a deep purple band moved about halfway down the column. This band was removed by elution with CH_2Cl_2 . Slow evaporation of solvent yielded 20 mg of purple needles. The infrared spectrum we find for $\text{Fv}[\text{W}(\text{CO})_3]_2$ in CH_2Cl_2 solution (2016, 1963, 1921, 1906 (sh) cm^{-1}) is shifted by 5–7 cm^{-1} from that previously reported (2021, 1970, 1929 (br) cm^{-1})¹⁴ but is significantly different from that of the unbridged $[\text{CpW}(\text{CO})_3]_2$ (2010 (w), 1954, 1903, 1893 (sh) cm^{-1} , CH_2Cl_2). The mass spectrum of $\text{Fv}[\text{W}(\text{CO})_3]_2$ displays multiplets with a W_2 isotope pattern for $[\text{M}]^+$, $[\text{M} - n\text{CO}]^+$ ($n = 1-6$), $[\text{M} - 6\text{CO} - \text{H}_2 - n\text{C}_2\text{H}_2]^+$ ($n = 0-3$), and $[\text{M} - 6\text{CO} - 4\text{C}_2\text{H}_2]^+$: 664 (5.8), 636 (2.9), 608 (6.9), 580 (8.7), 552 (46.3), 524 (54.6), 496 (28.5), 494 (31.4), 468 (28.1), 442 (22.0), 416 (18.3), 392 (5.8) and doubly charged ions for each of these except the first and the last; 318 (4.5), 304 (5.6), 290 (8.5), 276 (16.9), 262 (36.5), 248 (83.1), 247 (100), 234 (53.9), 221 (47.2), 208 (15.6). The ¹H NMR spectrum of the title complex in CDCl_3 solution consists of two triplets of equal intensity at δ 5.26 and 4.57, each with $J = 2.5$ Hz (lit.¹⁴ δ 5.60 (t), 5.00 (t), acetone), which again, as expected, is substantially different from what we find for the unbridged dimer (δ 5.38 (s), CDCl_3 ; lit. δ 5.67,¹⁴ acetone; δ 4.79,¹⁸ benzene). The UV-vis spectrum of $\text{Fv}[\text{W}(\text{CO})_3]_2$ in dichloromethane has the following maxima (λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 232 (40000), 278 (sh), 352 (20000), 548 (700). (The extinction coefficients are accurate only to $\pm 15\%$ because of the small amount of sample available.)

X-ray Diffraction Structural Determination of $\text{Fv}[\text{W}(\text{CO})_3]_2$. The title compound typically crystallizes as deep red parallelepipeds. A single crystal of approximate size $0.10 \times 0.12 \times 0.40$ mm was selected and mounted on a CAD-4 automated diffractometer equipped with Mo $\text{K}\alpha$ radiation and a graphite monochromator; 2704 total reflections were collected at ambient temperature in the sphere $3^\circ \leq 2\theta \leq 50^\circ$. After averaging, 2645 unique reflections were obtained; of these, 2306 were observed reflections with $I_o \geq 3\sigma(I)$. Least-squares calculations on 25 high-angle reflections yielded a triclinic unit cell of dimensions $a = 6.708$ (2) Å, $b = 9.626$ (2) Å, $c = 12.450$ (2) Å, $\alpha = 76.16$ (1)°, $\beta = 84.37$ (2)°, $\gamma = 74.95$ (2)°, and $V = 753$ (4) Å³. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable—up to 45 s per scan; scan range, calculated as $(0.80 + 0.20 \tan \theta)^\circ$ with 25% extension on each side for backgrounds. Three intensity monitors were checked every 2 h of X-ray time and fluctuated randomly by 2% over the entire data collection. Three orientation standards were centered after every 200 observations. Absorption corrections were applied with $\mu(\text{Mo K}\alpha) = 161 \text{ cm}^{-1}$; transmission coefficients varied from 0.237 to 0.133. The calculated density was 2.927 g cm^{-3} with $Z = 2$.

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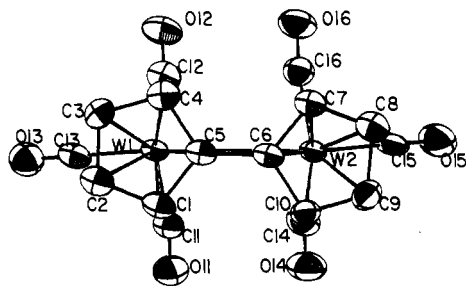


Figure 1. ORTEP plot of $Fv[W(CO)_3]_2$ showing the numbering scheme. View is from above the fulvalene ligand, approximately along the noncrystallographic C_2 axis through the midpoints of C5-C6 and W1-W2. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

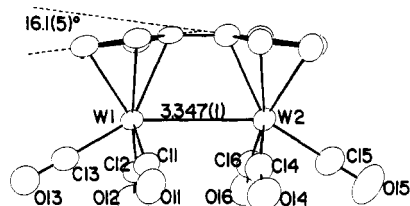


Figure 2. ORTEP plot of $Fv[W(CO)_3]_2$ showing the W-W separation and the deviation of the fulvalene ligand from planarity. The angle shown is that between the least-squares planes in Table V (supplemental material). Thermal ellipsoids are drawn at the 50% probability level.

Solution and Refinement of the Structure. The centrosymmetric space group¹⁹ $P\bar{1}$ was assumed and gave a satisfactory refinement. The tungsten atoms were placed by reference to a Patterson²⁰ synthesis which sufficiently phased the data so that the remainder of the molecule was evident on the succeeding Fourier map. Hydrogen atoms on the fulvalene ring were placed on calculated positions (C-H = 1.08 Å, trigonal geometry) and held invariant with $U = 0.06 \text{ \AA}^2$. An empirical systematic secondary extinction correction was applied. The corrected F_c values are of the form

$$F_c(\text{cor}) = F_c(1 - 0.001XF_c^2/(\sin \theta))$$

which is the usual SHELX correction. Full-matrix least-squares calculations on all observed reflections yielded $R = 0.049$ and $R_w = 0.060$.²¹ The final value of X in the above equation was 0.0018. The maximum shift in any parameter in the last cycle was less than 0.03σ , the number of variables was 218, and the number of observations was 2306. In a final difference map the largest five peaks represented 1.5-4.5 electrons and were located within 1 Å of a tungsten atom; otherwise, the map was featureless. Neutral-atom scattering factors and corrections for anomalous dispersion were obtained from ref 22. Final atomic positional parameters are found in Table I; interatomic distances and angles are presented in Tables II and III, respectively. Figures 1 and 2 illustrate the molecular geometry and numbering scheme.

Reaction of Dimers with Iodine. In the dark, 20.2 mg (0.030 mmol) of $[CpW(CO)_3]_2$ and 8.1 mg (0.032 mmol) of iodine were each dissolved in 5 mL of CH_2Cl_2 and the solutions purged with a nitrogen stream for a few minutes. The solutions were mixed, and the progress of the reaction was followed by infrared spectroscopy. Bands for $Cp_2W_2(CO)_6I^+$ (2056, 2045 cm^{-1} ; lit.⁵ 2059, 2049 cm^{-1} , et al.) and $CpW(CO)_3I$ (2037, 1953 (br) cm^{-1} ; lit.⁵ 2037, 1952 (br) cm^{-1}) began to grow in immediately. Conversion to $CpW(CO)_3I$ was nearly complete after 45 min. In a similar fashion, 2 mg (0.003 mmol) of $Fv[W(CO)_3]_2$ and 1 mg of iodine (0.004 mmol) were reacted in a

Table II. Bond Lengths (Å) in $Fv[W(CO)_3]_2$ (Esd's in Parentheses)

W1-W2	3.347 (1)	C11-O11	1.12 (2)
W1-C1	2.33 (1)	C12-O12	1.15 (2)
W1-C2	2.31 (1)	C13-O13	1.16 (2)
W1-C3	2.32 (1)	C14-O14	1.18 (2)
W1-C4	2.32 (1)	C15-O15	1.14 (2)
W1-C5	2.35 (1)	C16-O16	1.13 (2)
W1-C11	1.99 (2)	C1-C2	1.41 (2)
W1-C12	1.98 (2)	C1-C5	1.43 (2)
W1-C13	1.96 (2)	C2-C3	1.43 (3)
W2-C6	2.32 (1)	C3-C4	1.41 (2)
W2-C7	2.32 (1)	C4-C5	1.45 (2)
W2-C8	2.31 (2)	C5-C6	1.43 (2)
W2-C9	2.30 (2)	C6-C7	1.41 (2)
W2-C10	2.32 (2)	C6-C10	1.45 (2)
W2-C14	1.95 (2)	C7-C8	1.43 (2)
W2-C15	1.97 (2)	C8-C9	1.45 (3)
W2-C16	1.99 (2)	C9-C10	1.36 (2)

Table III. Selected Bond Angles (deg) in $Fv[W(CO)_3]_2$ (Esd's in Parentheses)^a

C1-C2-C3	109 (2)	Cp1-W1-C11	127.0 (6)
C2-C3-C4	108 (1)	Cp1-W1-C12	129.1 (6)
C3-C4-C5	108 (2)	Cp1-W1-C13	112.8 (6)
C4-C5-C1	107 (1)	C11-W1-C12	103.7 (6)
C5-C1-C2	108 (1)	C11-W1-C13	77.7 (7)
C1-C5-C6	127 (1)	C12-W1-C13	80.0 (7)
C4-C5-C6	125 (1)	Cp2-W2-C14	126.2 (7)
C5-C6-C7	127 (1)	Cp2-W2-C15	115.0 (6)
C5-C6-C10	125 (1)	Cp2-W2-C16	127.3 (6)
C6-C7-C8	109 (1)	C14-W2-C15	79.1 (7)
C7-C8-C9	106 (2)	C14-W2-C16	106.2 (7)
C8-C9-C10	110 (2)	C15-W2-C16	77.4 (7)
C9-C10-C6	108 (2)	Cp1-W1-W2	96.8 (4)
C10-C6-C7	108 (1)	C11-W1-W2	81.4 (5)
W1-C11-O11	172 (1)	C12-W1-W2	84.5 (5)
W1-C12-O12	171 (1)	C13-W1-W2	150.1 (4)
W1-C13-O13	178 (1)	Cp2-W2-W1	97.3 (4)
W2-C14-O14	169 (2)	C14-W2-W1	84.0 (6)
W2-C15-O15	179 (2)	C15-W2-W1	147.6 (5)
W2-C16-O16	173 (2)	C16-W2-W1	81.1 (5)

^a Cp1 and Cp2 denote the centroids of the component cyclopentadienyl rings of the fulvalene ligand.

total of 1 mL of CH_2Cl_2 . Peaks at 2064 and 2049 cm^{-1} immediately signaled the production of an intermediate, likely $FvW_2(CO)_6I^+$, which decayed in 5 min to form $Fv[W(CO)_3]_2$. (ν_{CO} : 2035, 1958 (br) cm^{-1} ; lit.¹⁴ 2043, 1966 cm^{-1} . ¹H NMR: δ 5.88 (t), 5.56 (t), $CDCl_3$; lit.¹⁴ δ 6.50 (t), 5.97 (t), $(CD_3)_2SO$; the discrepancies in literature values parallel those found in the data for the title complex from the same source (see above).)

Photochemical Procedures. In the dark, 0.5 mg of complex ($[CpW(CO)_3]_2$ or $Fv[W(CO)_3]_2$) was dissolved in 1 mL of CH_2Cl_2 . For reactions with methyl iodide, 60 μ L of CH_3I was added at this point. The solution was purged with nitrogen and loaded into a 0.5-mm path length NaCl infrared cell. The cell was irradiated with a broad-band ultraviolet source (Ultraviolet Products XX-15, 300-400 nm) and the progress of the reaction followed by infrared spectroscopy.

Results and Discussion

Isolation and Characterization of the Complex. On one occasion during the preparation of $CpW(CO)_3(Me_2dtc)_3$ from $[CpW(CO)_3]_2$ and $(Me_2NCS)_2$,¹⁵ one of us (H.B.A.) noted the presence of an impurity tricarbonyl tungsten complex. Mass spectral analysis of the 0.5 mg of compound isolated from that synthesis indicated that the likely formula was $C_{10}H_8W_2(CO)_6$. The source of the impurity was traced to a batch of $[CpW(CO)_3]_2$ that had been prepared by the method of Ginley, Bock, and Wrighton,¹⁶ and more was isolated from the preparation. The presence of a contaminant was originally unsuspected, since there is a weak band in spectra of $[CpW(CO)_3]_2$ that occurs at 2010 cm^{-1} that would obscure the stronger 2016 cm^{-1} band of the bridged dimer if it were present only in trace amounts. The mass spectrum of the $Fv[W-$

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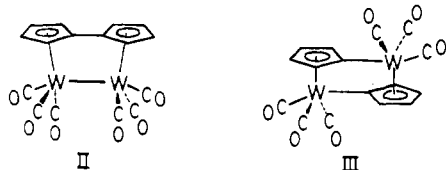
(20) All computations were performed by using local modifications of the programs of SHELX-76; Sheldrick, G. M. "SHELX-76"; University Chemical Laboratory: Cambridge, England, 1976.

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

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(CO)₃]₂ we isolated is very similar to that reported for Fv[W(CO)₃]₂ isolated in the thermolysis of Cp(CO)₃W-(C₅H₄)Mn(CO)₃,¹⁴ but we find differences in NMR and infrared spectral values (see Experimental Section). No evidence for benzyl substitution is seen in either Fv[W(CO)₃]₂ or the unbridged [CpW(CO)₃]₂, in contrast to the thermolysis of CpW(CO)₃CH₂C₆H₅ performed under nitrogen.¹⁷

The electronic spectrum of Fv[W(CO)₃]₂ in dichloromethane (232 nm (ε 40 000), 278 (sh), 352 (20 000), 548 (700)) indicates the presence of a tungsten-tungsten bond, II,



and argues against the alternative C₅H₄-bridged structure III, which should be yellow.²³ In order to assign the structure unambiguously, and to compare it to the unbridged dimer [CpW(CO)₃]₂,²⁴ we have done a single-crystal X-ray diffraction structural determination of the title complex, Fv[W(CO)₃]₂, and find it to exist in conformation II, as expected.

Structure of the Complex. The structure of Fv[W(CO)₃]₂ consists of a fulvalene ligand that is π-bound to two W(CO)₃ moieties in a cis arrangement (see Figures 1 and 2). The asymmetric unit is composed of one binuclear molecule with all atoms occupying general positions. The molecule does, however, exhibit nearly 2-fold symmetry with the noncrystallographic rotation axis passing through the midpoints of the W1-W2 and C5-C6 bonds. The η⁵:η⁵-fulvalene ligand in combination with three carbonyl groups around each tungsten requires a single metal-metal bond to fulfill the 18-electron rule.²⁵ The existence of a W-W bond in this structure is confirmed by the deformation of the optimally planar fulvalene ligand in the direction of a decreasing W1...W2 separation.

The W1-W2 distance of 3.347 (1) Å is one of the longest W-W distances recorded for which a bonding interaction can be established (see Table IV). It thus falls into a class of what can be called "long" W-W single bonds and is one of the longest members of this class. (Normal W-W single-bond distances fall into the range 2.5-2.7 Å;²⁶ nonbonding W-W distances are usually greater than 3.4 Å^{26a,27} but can be shorter in exceptional cases.²⁸) Inspection of Table IV reveals that complexes with "long" W-W single bonds are invariably low-valent-metal carbonyls and that it is complexes with tungsten in higher oxidation states and with more classical

Table IV. Complexes with Long W-W Single Bonds^a

compd ^b	W-W dist, Å	ref
W ₂ (CO) ₈ (MeCCMeCHCCHMe ₂) ^d	2.90 (2)	36
W ₂ (CO) ₅ Br ₂ (C ₂ Me ₂)(Ph ₂ AsCH ₂ AsPh ₂)	2.937 (1)	37
[Me ₂ N][W ₃ (CO) ₉ (OC ₂ H ₅) ₃]	2.966 (2), 2.939 (2) ^e	38
Cp ₂ W ₂ (CO) ₄ (C ₂ H ₂)	2.987 (1)	33c
Cp ₂ W ₂ (CO) ₄ [C(O)C ₂ (CO ₂ Me) ₂]	3.017 (1)	33i
Cp ₂ W ₂ (CO) ₄ (As ₂)	3.026 (2), 3.013 (2) ^e	33j
W ₂ (CO) ₈ (MeCCMeCHCCHMe ₂)	3.049 (1)	39a
W ₂ (CO) ₈ (PEt ₂) ₂	3.05 (1)	40
W ₂ (CO) ₉ (MeCCMeCHCCHMe ₂)	3.139 (2)	39b
W ₂ (CO) ₉ (CHCHCMe ₂ PMe ₃)	3.140 (1)	41
W ₂ (CO) ₈ I ₂	3.155	42
W ₂ (CO) ₈ (CHCHCMe ₂)	3.157 (1)	43
Cp ₂ W ₂ Os(CO) ₇ [C ₂ (C ₆ H ₄ Me) ₂]	3.159 (2), 3.017 (2) ^e	44
W ₂ (CO) ₈ (HSiEt ₂) ₂	3.183 (1)	45
W ₂ (CO) ₉ (CHCHCMe ₂)	3.189 (1)	46
Cp ₂ W ₂ (CO) ₆	3.222 (1)	24
W ₂ (CO) ₆ (gazl)	3.264 (1)	31
HW ₂ (CO) ₉ (NO)	3.329 (1), 3.328 (3), 3.330 (3) ^{e,f}	47
W ₂ (CO) ₆ (C ₅ H ₄ C ₅ H ₄)	3.347 (1)	this work
W ₂ (CO) ₁₀ (GeBr ₂)	3.370 (1)	29
HW ₂ (CO) ₈ (NO)(P(OMe) ₃)	3.381 (2), 3.393 (4) ^f	48
[(Ph ₃ P) ₂ N][HW ₂ (CO) ₁₀] ^g	3.391 (1)	49

^a Complexes with W-W distances greater than 2.9 Å for which a single W-W bond is postulated or can be inferred. ^b Me = methyl, Et = ethyl, Ph = phenyl, Cp = η⁵-cyclopentadienyl, gazl = guaiazulene. ^c Distances determined by X-ray diffraction, except where noted. ^d End of the last digit in parentheses. ^e No W-W bond is postulated, but a donor-acceptor W→W bond is needed to complete the valence shell. ^f Two crystallographically independent molecules. ^g W-W distance determined by neutron diffraction. ^h This salt is the bent isomer.

ligands that fall into the "normal" category. With the exception of Fv[W(CO)₃]₂ and W₂(CO)₁₀GeBr₂,²⁹ all "superlong" W-W single bonds (W-W greater than 3.3 Å) contain bridging hydride ligands. This attests to the unusual nature of the title complex and the strained nature of the W-W bond it contains.

The strained nature of the W-W bond in Fv[W(CO)₃]₂ is also reflected in other comparisons. The W-W distance in the title complex is 0.125 Å longer than that in the structure of [CpW(CO)₃]₂,²⁴ in which a W-W distance of 3.222 (1) Å is not influenced by bridging ligands. On the other hand, the metal-metal separation reported herein is more than 0.5 Å shorter than the calculated distance between the ring centers for a perfectly planar fulvalene (a nearly planar fulvalene has been noted in Fv₂Fe₂,³⁰ in which the nonbonding Fe...Fe distance is 3.984 (4) Å). Therefore the structure of Fv[W(CO)₃]₂ can be regarded as a compromise between the antagonistic ideal geometries of fulvalene and ditungsten. In Fv[W(CO)₃]₂, a tungsten-tungsten interaction is required to reach an 18-electron configuration, but coordination to the relatively inflexible fulvalene ligand puts a constraint on the closeness the two tungsten atoms can attain.

Another long W-W bond has been described for the closely related (gazl)[W(CO)₃]₂ (gazl = guaiazulene), which is characterized by a folded guaiazulene ligand and a W-W separation of 3.264 (1) Å.³¹ The molybdenum analogue is very similar, with Mo-Mo = 3.267 (6) Å.³² It is interesting

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to note that, in order to accommodate similar M-M distances, the guaiazulene ligand in (gazi)[W(CO)₃]₂ and (gazi)[Mo(CO)₃]₂ is bent away from the metal atoms, while the fulvalene rings bend toward the metal centers in Fv[W(CO)₃]₂, due presumably to the contracted center of electron donation in guaiazulene relative to fulvalene.

The fulvalene ligand of the title structure contains two planar cyclopentadienyl rings (the maximum deviation of an individual atom from its calculated plane is 0.01 Å; see Table V in the supplementary material) canted to form a dihedral angle of 16.1 (5)°. The correlation between metal-metal distance and the dihedral angle of fulvalene has already been summarized by Guggenberger and Tebbe⁸ and Olthof⁹ for a series of binuclear titanium complexes. The structures of binuclear fulvalene complexes are also known for the metals Mo,¹⁰ Fe,³⁰ Ni,¹¹ and Ru.¹² For all of these, the dihedral angle of fulvalene ranges from -2 (1)° in Fv₂Ni₂¹¹ (here a negative sign denotes a bending away from the metal centers), where the metal separation is the largest (Ni...Ni = 4.163 (1) Å), to a value of +28.5° in Fv[Ru(CO)₃]₂,¹² which displays the shortest M...M distance of 2.821 (1) Å. The range of dihedral angles accommodated by the fulvalene ligand demonstrates a certain flexibility in dealing with the electronic and structural requirements of dimeric metal units but also seems to be correlated with the differences in the reactivity of these complexes (see below).

The "twist" angle about C5-C6 of the fulvalene ligand is barely significant as evidenced by the torsion angles C4-C5-C6-C7 = 6 (2)° and C1-C5-C6-C10 = 4 (2)°. The structural parameters of the tungsten-fulvalene interaction are normal and equivalent to tungsten-cyclopentadienyl interactions.^{24,33} The W-C(Fv) distances range from 2.30 (2) to 2.35 (1) Å and average 2.32 (1) Å. The perpendicular distances from W to the centers of the individual rings are 1.983 (1) and 1.973 (1) Å for W1 and W2, respectively. The C-C bonds vary in length from 1.36 (2) to 1.45 (3) Å (mean 1.42 (3) Å) and are equivalent to the bridging C5-C6 distance of 1.43 (2) Å. No systematic variations are apparent in either the W-C(Fv) or C-C distances for this structure.³⁴ The internal C-C-C angles range from 106 (2) to 110 (2)° and average 108 (1)°. The W-C(carbonyl) distances are normal^{24,31,33} and average 1.97 (2) Å, while the C-O distances average 1.15 (2) Å. The W-C-O angles vary from 169 (2) to 179 (2)° but have significant thermal parameters associated with the carbonyl groups.

Reactivity of Fv[W(CO)₃]₂. As has been noted in the case of Fv[Ru(CO)₂]₂,¹² we find that the reactivity of the bridged Fv[W(CO)₃]₂ is both qualitatively and quantitatively different from that of the unbridged analogue Cp₂W₂(CO)₆. As has been reported,¹⁴ we find that the title complex reacts with iodine to form a complex presumably lacking a W-W bond:

$$\text{Fv}[\text{W}(\text{CO})_3]_2 + \text{I}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{I}(\text{CO})_3\text{W}(\text{Fv})\text{W}(\text{CO})_3\text{I} \quad (1)$$

This reaction is complete in about 5 min in the dark, while

under similar conditions the reaction of the unbridged [CpW(CO)₃]₂ to form CpW(CO)₃I is incomplete after 1/2 h. Reaction 1 appears to proceed through an intermediate similar to that observed in the iodination of [CpW(CO)₃]₂.⁵

This increased thermal reactivity of Fv[W(CO)₃]₂ and related molecules, like Fv[Ru(CO)₂]₂,¹² is almost certainly related to the lengthening of the metal-metal bond over that in the unconstrained dimer. This lengthening, and presumably also weakening, of the metal-metal interaction leaves the fulvalene dimers more susceptible to attack by electrophilic reagents like iodine.

In contrast to this marked increase in thermal reactivity relative to that of the unbridged dimer, we observe a decrease in the photochemical reactivity that has come to characterize dinuclear single metal-metal-bonded carbonyl complexes.² Under conditions sufficient to convert 50% of a sample of [CpW(CO)₃]₂ to CpW(CO)₃I (0.8 mM complex, 1 M CH₃I in CH₂Cl₂, 1 mL volume, N₂ purge, 30 s of broad-band UV), the bridged Fv[W(CO)₃]₂ was converted to Fv[W(CO)₃]₂ to the extent of less than 6%. Similarly, when an equimolar mixture of the two dimers is irradiated in CH₂Cl₂ solution under nitrogen, formation of CpW(CO)₃I from the unbridged dimer is relatively rapid, but little of the Fv[W(CO)₃]₂ reacts.

The similarity of the electronic spectrum of Fv[W(CO)₃]₂ (see above) to that of the unbridged [CpW(CO)₃]₂³⁵ leads us to adopt an analogous assignment (352 nm, σ → σ*; 548 nm, πd → σ*) and leads us to expect a similar reactivity. It is obvious from the results above that this expectation is not fulfilled and that Fv[W(CO)₃]₂ undergoes reactions associated with the formation of 17-electron intermediates only slowly. The most obvious explanation for this marked difference in photochemical reactivity is that the joining of the cyclopentadienyl rings to form the fulvalene ligand has inhibited the separation of the radicals presumably formed from the cleavage of the metal-metal bond upon excitation and that fulvalene-enforced radical recombination is the dominant reaction path of the intermediate.

In contrast to Fv[Ru(CO)₂]₂,¹² the irradiation of Fv[W(CO)₃]₂ in tetrahydrofuran solution does not cause any color changes or changes in the infrared spectrum. This implies that formation of the non-metal-metal-bonded isomer III is less favored in this tungsten complex than in the ruthenium analogue. A potential explanation lies in the presence of more

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strain in the fulvalene ligand in $\text{Fv}[\text{Ru}(\text{CO})_2]_2$ (dihedral angle 28.5°)¹² than in this tungsten complex (dihedral angle 16.1°).

We conclude that the linking of cyclopentadienyl rings to form fulvalene-bridged dinuclear metal carbonyls results in substantial alterations in spectral and reactivity patterns. These changes can be explained by the existence of the carbon-carbon bond joining the two five-membered rings and by the deformation of the molecule from ideal geometries as evidenced by the substantial lengthening of the W-W bond and the nonplanarity of the fulvalene ligand. Detailed studies of the photochemical reactivity of this compound are in progress.

Note Added in Proof. A rational synthesis of $\text{Fv}[\text{W}(\text{CO})_3]_2$ ^{50a} and its photochemical reaction with alkynes^{50b} have recently been reported.

Supplementary Material Available: Listings of least-squares planes in the fulvalene ligand (Table V), hydrogen atom parameters (Table VI), anisotropic thermal parameters (Table VII), and observed and calculated structure factors (Table VIII) for the title complex (13 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of Tricarbonyl(η^5 -cyclopentadienyl)(η^1 -dimethylcarbamodithioato)tungsten

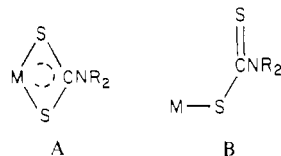
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When a mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2$ and tetramethylthiuram disulfide in toluene solution is irradiated with visible light, the title complex, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WSC}(\text{S})\text{N}(\text{CH}_3)_2$, is formed in excellent yield. Infrared spectroscopic studies indicate monodentate coordination of the dimethyldithiocarbamate ligand; this conclusion is confirmed by X-ray crystallography. The molecule crystallizes in space group $P\bar{1}$, with unit cell parameters $a = 7.616$ (7) Å, $b = 9.962$ (11) Å, $c = 9.931$ (8) Å, $\alpha = 113.38$ (6)°, $\beta = 94.68$ (9)°, $\gamma = 95.83$ (10)°, and $Z = 2$. With the use of Mo $K\alpha$ radiation, 3932 unique reflections with $2\theta \leq 60^\circ$ were collected, and the structure was solved by the heavy-atom technique and refined to a final R factor of 3.2%. The structure clearly shows monodentate coordination of the dithiocarbamate, with a nonbonding W-S2 distance of 3.905 (1) Å. Carbonyl loss from the title complex can be induced either thermally or photochemically, leading to a carbonyl complex with a bidentate dithiocarbamate ligand. Quantum yields are reported for both the formation and decomposition reactions of the title complex. The title complex reacts with $\text{W}(\text{CO})_5(\text{THF})$ to form a $\text{W}(\text{CO})_5$ adduct and with iodine to form oxidized products.

Metal complexes containing dithiocarbamate (alkyl- and dialkylcarbamodithioato, S_2CNR_2^-) ligands¹ have a long and rich history.^{2,3} Due to the flexibility possible in the distribution of electrons in this type of ligand, they can be used to stabilize a wide range of oxidation states.⁴ The uses of both the free ligands and their complexes are widespread and range from accelerators in rubber polymerization to agricultural fungicides.³ In addition, dithiocarbamate complexes are widely used in the study of basic chemical questions,^{3,5} due to their diversity and robustness.

In almost all complexes, dithiocarbamates serve as chelating ligands,^{3,6} binding to the metal through both sulfur atoms, A.



Very few complexes containing monodentate dithiocarbamate ligands, B, are known. In only four cases, $\text{Pt}(\text{S}_2\text{CN}(i\text{-Bu})_2)_2(\text{PMe}_2\text{Ph})_2$,^{7a} $\text{Pt}(\text{S}_2\text{CNET}_2)_2\text{PPh}_3$,^{7b} $\text{Ru}(\text{S}_2\text{CNET}_2)_3(\text{NO})$,^{8a} and $\text{Au}(\text{S}_2\text{CNET}_2)_3$,^{8b} has the monodentate nature of a dithiocarbamate ligand been confirmed by X-ray crystallography.

The usual evidence for monodentate coordination lies in the infrared stretching frequencies of the thioureide ($\text{C}=\text{N}$) and CS bonds of the molecule.⁹ These criteria have been used to establish monodentate coordination in $\text{Mo}(\text{S}_2\text{CNHR})(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{bpy})$ ($\text{R} = \text{Me}, \text{Et}$)¹⁰ and $\text{Cp}(\text{CO})_2\text{FeSC}(\text{S})\text{NCH}_3\text{R}$ ($\text{R} = \text{H}, \text{Me}$)¹². Infrared data in combination with ¹³C NMR spectra have suggested monodentate coordination in $\text{Ir}(\text{S}_2\text{CNET}_2)_3(\text{cyclooctadiene})$ ¹³ and

- (1) Abbreviations used in this paper: R_2dtc = dialkyldithiocarbamate (N,N -dialkylcarbamodithioate), S_2CNR_2 ; Cp = η^5 -cyclopentadienyl; Me_4TDS = tetramethylthiuram disulfide, bis(dimethylthiocarbamyl) disulfide, $[\text{SC}(\text{S})\text{N}(\text{CH}_3)_2]_2$; R_t = perfluoroalkyl.
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