strain in the fulvalene ligand in $Fv[Ru(CO)_2]_2$ (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 $Fv[W(CO)_3]_2$[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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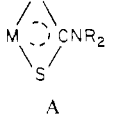
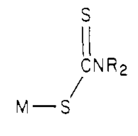
When a mixture of $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ and tetramethylthiuram disulfide in toluene solution is irradiated with visible light, the title complex, $(\eta^5\text{-}C_5H_5)(CO)_3WSC(S)N(CH_3)_2$, is formed in excellent yield. Infrared spectroscopic studies indicate monodentate coordination 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 Kα radiation, 3932 unique reflections with $2\theta \leq 60°$ 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 $W(CO)_5(THF)$ to form a $W(CO)_5$ adduct and with iodine to form oxidized products.

Metal complexes containing dithiocarbamate (alkyl- and dialkylcarbamodithioato, $S_2CNR_2^-$) ligands[1] 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.



A



B

Very few complexes containing monodentate dithiocarbamate ligands, B, are known. In only four cases, $Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$,[7a] $Pt(S_2CNEt_2)_2PPh_3$,[7b] $Ru(S_2CNEt_2)_3(NO)$,[8a] and $Au(S_2CNEt_2)_3$,[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 (C$\overset{\dots}{=}$N) and CS bonds of the molecule.[9] These criteria have been used to establish monodentate coordination in $Mo(S_2CNHR)(\eta^3\text{-}C_3H_5)(CO)_2(bpy)$ (R = Me, Et[10]) and $Cp(CO)_2FeSC(S)NCH_3R$ (R = H,[11] Me[12]). Infrared data in combination with ^{13}C NMR spectra have suggested monodentate coordination in $Ir(S_2CNEt_2)_3$(cyclooctadiene)[13] and

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(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, $[SC(S)N(CH_3)_2]_2$; R_f = perfluoroalkyl.

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have confirmed the monodentate coordination of one dithiocarbamate ligand of $Ru(S_2CNMe_2)(NO)$ in solution.[14] More tenuous ^1H NMR arguments are used in the cases $(\eta^5\text{-}C_5Me_5)Rh(S_2CNR_2)_2$ and $Pt(S_2CNR_2)_2L$ (R = Me, Et; L = PPh_3, $PMePh_2$).[15] With the exception of the molybdenum complexes, all of these examples involve electron-rich group 8 metals. Our synthesis of a tungsten carbonyl complex of type B,[16] the structure of which was inferred from the stoichiometry and infrared spectrum, has now been confirmed by a single-crystal X-ray diffraction structure determination, the details of which are reported herein.

This first example of a monodentate dialkyldithiocarbamate group 6 metal carbonyl complex results from a photochemical reaction. Known syntheses of group 6 metal carbonyl dithiocarbamate complexes by thermal routes lead invariably to bidentate coordination. Three types of reaction have been used; one is the reaction of a metal carbonyl halide with alkali-metal dithiocarbamates:[17]

$$CpW(CO)_3Cl + Na(Me_2dtc) \rightarrow CpW(CO)_2S_2CNMe_2 + NaCl + CO \quad (1)$$

Another is a similar reaction with a main-group dithiocarbamate:[18]

$$CpW(CO)_3Cl + Me_3Sn(Me_2dtc) \rightarrow CpW(CO)_2S_2CNMe_2 + CO + Me_3SnCl \quad (2)$$

Coupling of metal carbonyl dimers and a thiuram disulfide is a third route:[19]

$$[CpMo(CO)_3]_2 + Me_4TDS \rightarrow 2CpMo(CO)_2S_2CNMe_2 + 2CO \quad (3)$$

The lack of monodentate products may be explained by the propensity for carbonyl loss in complexes of this type under the conditions used in thermal reactions (see below).

Our photochemical reaction is related to the photochemical reactions of metal–metal-bonded carbonyl dimers with organic disulfides. A few examples of this type of reactivity are known:

$$[CpM(CO)_2]_2 + S_2R_2 \xrightarrow{h\nu} 2CpM(CO)_2SR \quad (4)$$

M = Fe; R = Me[20] M = Ru; R = Me, Ph, CH_2Ph[21]

In these cases no speculation on possible mechanisms was advanced, apart from implications of the involvement of photochemical disulfide cleavage in the ruthenium chemistry.[21] The perfluoro disulfides $(CF_3S)_2$ and $(C_6F_5S)_2$ are reacted with metal–metal-bonded complexes (e.g., $[CpM(CO)_3]_2$ (M = Mo, W)) under photolysis[22] to produce coupled products (e.g., $CpM(CO)_3SR_f$).[1] The reactivity in these cases was also attributed to disulfide photocleavage since ultraviolet irradiation was used.

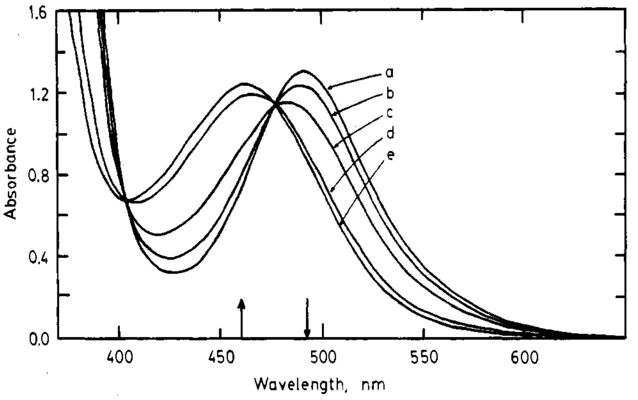

Figure 1. Electronic spectral changes resulting from irradiation of a nitrogen-purged toluene solution containing $[CpW(CO)_3]_2$ and Me_4TDS, each at a concentration of 5.5×10^{-4} M, in a 1-cm path length cell. Photolysis source was a high-intensity desk lamp. Cumulative irradiation times were 0, 90, 225, 315 and 360 s for curves a–e, respectively. Arrows indicate monitoring wavelengths for quantitative analysis.

Table I. Electronic Absorption Spectral Data

complex	solvent	band maxima, nm (ϵ, L mol^{-1} cm^{-1})
$[CpW(CO)_3]_2$	toluene	363 (19 100), 492 (2360)
$Cp(CO)_3W(Me_2dtc)$ (1)	toluene	460 (1230)
	hexane	260 (15 000), 335 (sh), 458 (1300)
$Cp(CO)_2W(Me_2dtc)$ (II)	toluene	345 (2290), 417 (3780)
$Cp(CO)_3W(Me_2dtc)W(CO)_5$ (III)	hexane	226 (62 500), 247 (sh, 48 000), 320 (sh, 8270), 424 (3060), 460 (sh, 2880)
$Cp(CO)WI_2(Me_2dtc)$ (V)	CH_2Cl_2	525 (330)

The results we present here, and in the preliminary communication of this work,[16] clearly show that the production of mononuclear monodentate metal thiolate complexes from the photolysis of metal carbonyl dimers with organic disulfides arises from the photocleavage of metal carbonyl dimers as the primary photoprocess. In the case of the title compound, this provides a route to a complex containing a monodentate dithiocarbamate ligand.

Results and Discussion

Synthesis. Photolysis of metal–metal-bonded metal carbonyl dimers is known[23,24] to produce reactive metal carbonyl radicals. We have recently demonstrated[16] that these radicals will react with organic disulfides to produce metal carbonyl thiolates. We have exploited this reaction to produce the title compound, $CpW(CO)_3(Me_2dtc)$ (I), in excellent chemical yield from the photolysis of the tungsten dimer $[CpW(CO)_3]_2$ in toluene solution in the presence of tetramethylthiuram disulfide, Me_4TDS:[1]

$$[CpW(CO)_3]_2 + Me_2NC({=}S)SSC({=}S)NMe_2 \xrightarrow{h\nu} 2Cp(CO)_3WSC({=}S)NMe_2 \quad (5)$$

Visible irradiation produces changes in the color of the solution from red to orange as the visible absorption maximum changes from that associated with the dimer to that of I, with an isosbestic point at 477 nm (Figure 1). Infrared spectra of solutions irradiated in sealed solution cells show a decrease in the intensity of carbonyl stretching bands of the dimer and growth of bands associated with I, again with maintenance of isosbestic points.[25] (See Table I for electronic spectral data

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(25) See Figure 1, ref 16.

Table II. Infrared Spectral Data

complex	carbonyl region bands[a] solvent	carbonyl region bands[a] energy, cm^{-1}	other bands,[b] cm^{-1}
$CpW(CO)_3(Me_2dtc)$ (I)	toluene	2035, 1957, 1927	3142 (w), 3121 (w), 3104 (w), 2924 (w), 2035 (vs), 1947 (vs), 1929 (vs), 1487 (m), 1422 (m), 1415 (w), 1355 (s), 1241 (s), 1119 (s), 1059 (w), 1045 (w), 1009 (m), 1004 (m), 968 (s), 927 (w), 865 (m), 844 (w), 831 (m), 823 (s), 650 (w, br), 625 (w), 561 (m), 529 (m), 508 (vw), 489 (m), 439 (w)
	CH_2Cl_2	2036, 1958, 1932	
	THF	2033, 1952, 1925	
	hexane	2041, 1966, 1936	
$CpW(CO)_2(Me_2dtc)$ (II)	toluene	1939, 1848	3114 (w), 2922 (w), 2854 (vw), 1918 (vs), 1822 (vs), 1530 (s), 1409 (w), 1393 (s), 1346 (vw), 1249 (w), 1148 (m), 1101 (vw), 1054 (vw), 1002 (vw), 971 (vw), 886 (w), 845 (w), 813 (s), 641 (w), 608 (w), 578 (m), 528 (w), 516 (w), 480 (w), 455 (w)
	CH_2Cl_2	1936, 1839	
$CpW(CO)_3(\mu\text{-}Me_2dtc)W(CO)_5$ (III)	CH_2Cl_2	2066 (w), 2041 (m), 1963 (sh), 1940 (sh), 1926, 1884	3119 (w), 3001 (vw), 2926 (w), 2851 (vw), 2061 (s), 2036 (s), 1970–1860 (vs, br), 1500 (s), 1436 (m), 1423 (m), 1416 (m), 1376 (m), 1233 (s), 1133 (m), 1064 (w), 1056 (w), 1046 (m), 1010 (m), 1002 (w), 943 (s), 914 (w), 879 (w), 834 (s), 595 (s), 578 (s), 521 (m), 465 (m), 455 (w), 390 (s)
	THF	2063 (w), 2037 (m), 1951 (sh), 1928, 1920 (sh), 1889	
	hexane	2066 (w), 2044 (m), 1974, 1952, 1933, 1922, 1910	
$[CpW(CO)_2(Me_2dtc)I]I$ (IV)	CH_3CN	2083, 2043	3110 (w), 3052 (w), 3012 (m), 2073 (vs), 2025 (vs), 1562 (s), 1428 (m), 1419 (m), 1396 (s), 1364 (w), 1250 (w), 1163 (m), 1007 (w), 977 (w), 886 (m), 828 (w), 515 (w), 476 (m), 458 (w), 438 (w), 418 (vw), 395 (vw)
$CpW(CO)(Me_2dtc)I_2$ (V)	CH_2Cl_2	1993	3125 (w), 3095 (m), 3078 (m), 1982 (vs), 1547 (s), 1430 (m), 1418 (w), 1408 (m), 1396 (s), 1250 (m), 1165 (m, br), 1064 (m), 1009 (w), 996 (vw), 862 (s), 515 (m), 499 (m), 467 (vw), 440 (vw), 418 (vw), 395 (w)
$W(CO)_5THF$	THF	2073 (w), 1929, 1890	

[a] Solutions in 0.5-mm NaCl cells (except toluene, 0.1 mm). Spectrometer calibrated with carbon monoxide and water vapor. All bands are strong or very strong, except as noted. [b] KBr pellet.

and Table II for infrared spectral data for all complexes.) The maintenance of isosbestic points and the 2:1 ratio of product I to dimer consumed (see below) indicate that reaction 5 is quantitative; because of losses in chromatography and recrystallization, isolated yields are only 85% (see Experimental Section). Due to the extreme reactivity of the intermediate tungsten radical, dry and oxygen-free conditions are necessary to achieve these yields. Decomposition occurs upon irradiation in the presence of oxygen, in accordance with production of a reactive metal carbonyl intermediate on photolysis.

As in other reactions of the tungsten dimer,[26] both visible and ultraviolet irradiation are effective in inducing reaction 5. Since I is sensitive to ultraviolet light, and secondary photolysis produces the chelated product $Cp(CO)_2WS_2CNMe_2$ (II) (see below), visible irradiation is recommended for preparative reactions. With visible irradiation, secondary photolysis is minimized and production of the chelated dicarbonyl is not seen. This absence of the dicarbonyl as a primary photoproduct indicates that the reactive intermediate cannot be an unsaturated species resulting from carbonyl loss[27] but is more likely to be a radical species produced by the homolysis of the metal–metal bond. If carbonyl-loss intermediates were important, we would expect to see the chelated complex II as a primary photoproduct.

Quantum yields for the disappearance of the tungsten dimer and for the formation of tricarbonyl product I are calculated from changes in the electronic absorption spectrum caused by irradiation (Figure 1). For 546-nm irradiation, the quantum yield for dimer disappearance is 0.97 ± 0.16 and that for appearance of I is 1.92 ± 0.39, when equimolar concentrations (4×10^{-4} M) of tungsten dimer and thiuram disulfide are used. In the presence of a 4-fold excess of the disulfide, the quantum yields are somewhat smaller ($[Cp_2W_2(CO)_6] = 3 \times 10^{-4}$ M, $[Me_4TDS] = 1.5 \times 10^{-3}$ M: $\phi_d = 0.44 \pm 0.11$, $\phi_a = 0.86 \pm 0.24$). These values are larger than quantum yields reported for halogen abstraction reactions of the tungsten dimer, which proceed by radical mechanisms (e.g., ϕ_d = 0.12–0.31 for CH_nCl_{4-n}, n = 0, 1, 2).[26,28] The ratio of appearance to disappearance quantum yields for reaction 5 falls between 1.9 and 2.1 for individual determinations, as expected from the stoichiometry. Further support for the stoichiometry of reaction 5 comes from the observation that this reaction can be driven nearly to completion, even with only a 1:1 metal dimer:disulfide ratio; this demonstrates that both halves of the

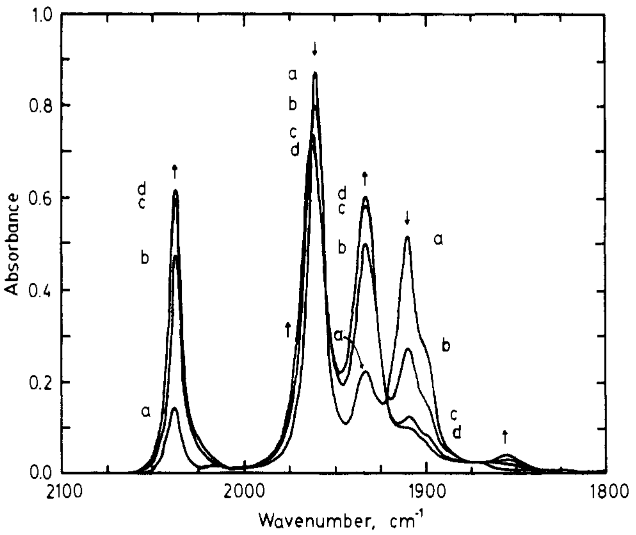

Figure 2. Infrared spectra of $[CpW(CO)_3]_2$ (9.3×10^{-3} M), when photolyzed in the presence of $Fe(Me_2dtc)_3$ (1.9×10^{-2} M) in nitrogen-purged toluene solution. Irradiation times were 0, 5, 10, and 15 s for curves a–d, respectively.

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(28) We obtain $\phi_d = 0.25 \pm 0.01$ and $\phi_a = 0.55 \pm 0.03$ as quantum yields for the reaction of $[CpW(CO)_3]_2$ with CCl_4 to produce $CpW(CO)_3Cl$ under 546-nm irradiation, analyzing by the same methods used here.

disulfide can be used to form product.

The source of the dithiocarbamate ligand in this photoreaction need not be limited to thiuram disulfide. Visible-light photolysis of $[CpW(CO)_3]_2$ in the presence of $Fe(Me_2dtc)_3$ gives infrared changes in the carbonyl stretching region (see Figure 2) nearly identical with those observed when reaction 5 is monitored.[25] A larger scale reaction gives a quantitative yield of I with properties identical with those of material prepared from the thiuram disulfide (reaction 5).

The detailed mechanism for reaction 5 is not known, but some of the more likely steps in it are shown in Scheme I. The evidence above suggests that the primary photoprocess is photocleavage of the metal–metal bond (step a) to form reactive tungsten carbonyl radicals. These radicals either will recombine (step b) or can attack thiuram disulfide (step c) to form product I and a dithiocarbamate radical, whose fate is less clear. It most likely stays in solution until it encounters another radical, either tungsten or sulfur (steps d and e), with which it would combine to form either I or thiuram disulfide.[29] The good chemical yields observed here make it unlikely that either type of radical attacks solvent, which should lead to decomposition. The high quantum yields observed for reaction 5 may be explained by reaction f in Scheme I, which leads to a radical chain and the possible formation of more than 2 mol of product/mol of photons absorbed. Photolyses with disulfides of varying sulfur–sulfur bond strength and electron donating or accepting character in the substituents will help to ascertain the relative importance of steps like these and others that are possible, e.g., those involving electron transfer.[30]

Scheme I

$$Cp_2W_2(CO)_6 \xrightarrow{h\nu} 2CpW(CO)_3\cdot \qquad \text{(a)}$$

$$2CpW(CO)_3\cdot \rightarrow Cp_2W_2(CO)_6 \qquad \text{(b)}$$

$$CpW(CO)_3\cdot + (dtc)_2 \rightarrow CpW(CO)_3(dtc) + dtc\cdot \qquad \text{(c)}$$

$$CpW(CO)_3\cdot + dtc\cdot \rightarrow CpW(CO)_3(dtc) \qquad \text{(d)}$$

$$dtc\cdot + dtc\cdot \rightarrow (dtc)_2 \qquad \text{(e)}$$

$$dtc\cdot + Cp_2W_2(CO)_6 \rightarrow CpW(CO)_3(dtc) + CpW(CO)_3\cdot \qquad \text{(f)}$$

$$dtc = S_2CNMe_2$$

Photochemical Reactivity of $Cp(CO)_3W(Me_2dtc)$. Irradiation of the tricarbonyl complex I with broad-band ultraviolet irradiation leads to loss of one carbon monoxide ligand:

$$Cp(CO)_3WSC({=}S)NMe_2 \xrightarrow{h\nu} Cp(CO)_2WS_2CNMe_2 + CO \qquad (6)$$

to form the known dicarbonyl chelate II.[17,18] Electronic and infrared spectral data for this complex are included in Tables I and II, respectively. Absorbance measurements at 460 and 417 nm can be converted into concentrations for I and II by a standard two-component analysis. The quantitative nature of reaction 6 is reflected in the maintenance of an isosbestic point at 450 nm (Figure 3a) and the constancy of the sum of concentrations of I and II observed as the reaction progresses. On the basis of these concentration changes, the quantum yield for reaction 6 is 0.30 ± 0.10 for disappearance of I and 0.31 ± 0.08 for appearance of II with 366-nm irradiation. Quantum yields for 436-nm irradiation are lower: $\phi_d = 0.10 \pm 0.04$ and $\phi_a = 0.11 \pm 0.02$. Similar values and wavelength dependence are seen in quantum yields for carbonyl substitution in other $CpW(CO)_3X$ complexes (X = Cl, Br, I).[31] Since I absorbs at shorter wavelengths than $[CpW(CO)_3]_2$, reaction 6 does not compete with reaction 5 to a significant extent when visible irradiation is used in the synthesis of I.

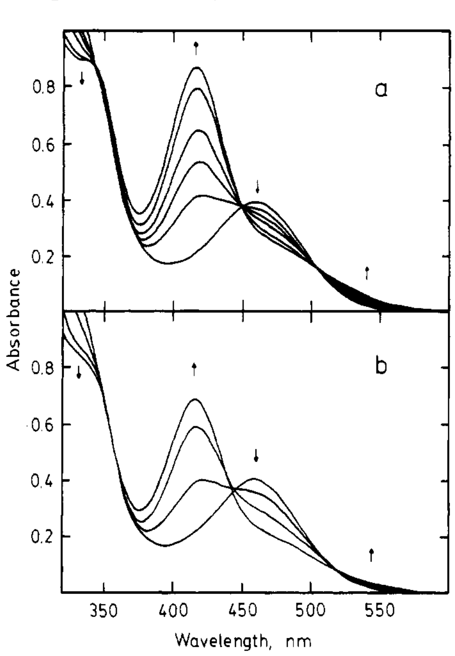

Figure 3. Electronic absorption spectral changes produced by the irradiation of $Cp(CO)_3WSC(S)NMe_2$ in toluene solution. Spectrum a shows the reaction under a dinitrogen atmosphere, and spectrum b shows the reaction done in the presence of air. A broad-band ultraviolet source was used, and irradiation times were 0, 15, 30, 45, 75, and 105 s for spectrum a and 0, 15, 30, and 45 s for spectrum b. Similar changes are seen for the thermolysis of I.

The most likely primary photoprocess for reaction 6 is photoejection of a carbonyl ligand to form an unsaturated dicarbonyl intermediate, as in analogous $CpW(CO)_3X$ complexes.[31] This intermediate would be expected to be trapped with high efficiency by the dangling sulfur of the dithiocarbamate ligand. One remarkable aspect of this transformation is that the presence of air does not cause significant decomposition (see Figure 3), as is usually the case with photosubstitutions of metal carbonyl complexes.[23] This can be attributed to the high effective concentration of the entering group, which allows it to compete favorably with dioxygen for the vacant coordination site. This reduced reactivity toward dissolved oxygen also argues against any metal–sulfur cleavage in the primary photoprocess, since the intermediates produced by such a cleavage would likely be very reactive toward oxygen.

Thermal Reactivity of $Cp(CO)_3W(Me_2dtc)$. Carbonyl Loss. The chelation represented in reaction 6 can also be caused by heat as well as light. The first indication of this was the decomposition of I in a melting point capillary at 106–108 °C; an infrared spectrum of the residue dissolved in dichloromethane solution displays bands for both I and II. Similarly, after heating a KBr pellet containing I at 120 °C for 15 min, the infrared spectrum contains only bands of the chelated complex II (although somewhat broadened), at intensities similar to those of the bands for I present before heating.

The time course of this thermal loss of carbon monoxide can be followed in solution by absorption spectroscopy, with spectral changes similar to those in Figure 3. As in the photochemical version of the same transformation, the total tungsten concentration is constant to better than ±2% over the course of the reaction. Plots of log [I] vs. time are linear, with correlation coefficients typically better than 0.998. First-order rate constants and standard deviations calculated

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(29) Cross-coupling of photogenerated thiyl radicals is seen: Gupta, D.; Knight, A. R. *Can. J. Chem.* **1980**, *58*, 1350–1354.

(30) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1260.

(31) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533–1543.

Table III. Rate Constants for Thermal Carbonyl Loss of $Cp(CO)_3WSC(S)NMe_2$[a]

T,[b] °C	[I], mM	10^3k_{obsd},[c] min^{-1}	T,[b] °C	[I], mM	10^3k_{obsd},[c] min^{-1}
41.0	0.52	0.17 ± 0.02	60.0	0.16	2.07 ± 0.49
52.5	0.52	0.82 ± 0.20	60.0	0.05	2.24 ± 0.38
60.0	0.49	1.99 ± 0.28	63.75	0.53	3.39 ± 0.80
60.0	0.27	1.79 ± 0.72	72.0	0.54	8.13 ± 2.25

[a] Calculated from absorbance changes at 460 and 417 nm, see Experimental Section for details. [b] Measured in reference cell, ±0.25 °C. [c] Average of k_{obsd} calculated from disappearance of I and that calculated from appearance of II. Errors are 2 standard deviations (i.e., 95% confidence level). $\Delta H^{\ddagger} = 110 \pm 6$ kJ/mol and $\Delta S^{\ddagger} = 51 \pm 19$ J/(K mol) calculated from linear regression of ln (k) vs. $1/T$ with a correlation coefficient of 0.9998.

from the least-squares analysis of these data are listed in Table III. Note that the rate constants for different concentrations of I at the same temperature are the same, as expected. Weighted least-squares analysis of log (k_{obsd}/T) allows us to calculate $\Delta H^{\ddagger} = 110 \pm 6$ kJ/mol and $\Delta S^{\ddagger} = 51 \pm 19$ J/(K mol). These values are similar to activation parameters in other metal carbonyl complexes.[32] The positive entropy of activation is consistent with carbonyl loss being an important part of the activation process.

Reaction with $W(CO)_5THF$. When solid I is added to a slight excess of $W(CO)_5(THF)$[33] in tetrahydrofuran, infrared changes indicative of displacement of the THF ligand are seen, as the highest ν(CO) changes from 2073 cm^{-1} before the addition to 2063 cm^{-1} afterward; other frequencies indicative of a $W(CO)_5$ fragment are also seen in slightly shifted positions; see Table II. Bands very near the usual positions for I are still seen, indicating that there is not much distortion of the first coordination sphere of that part of the complex. Similar observations are made after the THF solution is evaporated and the complex redissolved in another solvent; see Table II. The $W(CO)_5$ fragment could conceivably bind to two different sites on I, since both sulfur atoms have remaining lone pairs of electrons.[34] The nitrogen is not a likely binding site; its planar geometry (see below) indicates that there is no stereochemically active lone pair.

That there is actual binding of the $W(CO)_5$ fragment to I, and not just cocrystallization of two complexes, can be seen in changes in other portions of the infrared spectrum. Infrared spectra of I and the adduct $Cp(CO)_3W(Me_2dtc)W(CO)_5$ (III) display notable differences in the C–N stretching frequency (1487 and 1500 cm^{-1}, respectively) and in the C–S stretching frequencies (1009, 1004 and 1010, 1002 cm^{-1}, respectively). In addition, there is a slight shift in ^1H NMR resonances for the cyclopentadienyl protons (δ 5.81 and 5.88, respectively) and none for the methyl protons (both δ 3.61). Adduct III has an electronic spectrum that looks like the sum of that for I and that for a $W(CO)_5X$ complex[33] (see Table I), consistent with little interaction between the two chromophores. The data are consistent with complexation of the $W(CO)_5$ fragment to the dangling sulfur of the dithiocarbamate ligand, but the instability of the adduct (the adduct III is fairly stable at 4 °C, but is unstable at room temperature, especially in solution) does not allow a more rigorous assessment of the binding site to be made at this time.

Reaction of I with Iodine. Addition of a stoichiometric (1:1) amount of solid iodine to I produces two major products, tan IV soluble only in polar solvents (CH_3CN, Me_2SO, water) and purple V soluble in less polar solvents (CH_2Cl_2, $CHCl_3$). The high-frequency thioureide stretch in IV at 1562 cm^{-1} is indicative of considerable positive charge delocalization on the dithiocarbamate ligand. On the basis of analytical, spectroscopic, and solubility data, the most likely formula for IV is an ionic one, $[Cp(CO)_2W(S_2CNMe_2)I]I$, with a possible sulfur–iodine interaction.[35]

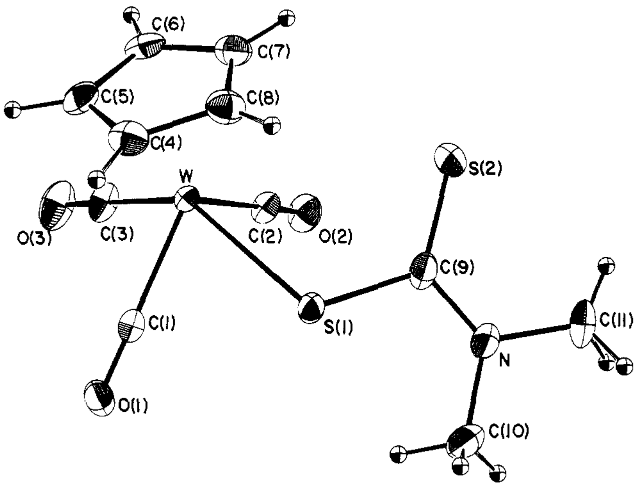

Figure 4. Molecular structure of $CpW(CO)_3(Me_2dtc)$ showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table IV. Bond Distances (Å) in $Cp(CO)_3W(Me_2dtc)$ (with Esd's)

W–S1	2.496 (1)	C1–O1	1.143 (3)
W–C1	1.999 (3)	C2–O2	1.149 (5)
W–C2	2.007 (4)	C3–O3	1.147 (5)
W–C3	1.998 (4)	N–C9	1.341 (3)
W–C4	2.344 (4)	N–C10	1.471 (4)
W–C5	2.297 (3)	N–C11	1.465 (5)
W–C6	2.307 (2)	C4–C5	1.413 (5)
W–C7	2.364 (3)	C5–C6	1.425 (6)
W–C8	2.383 (4)	C6–C7	1.429 (5)
W–Cp[a]	2.004 (3)	C7–C8	1.410 (5)
S1–C9	1.769 (3)	C8–C4	1.416 (5)
S2–C9	1.676 (3)		

[a] Cp represents the centroid of the cyclopentadienyl ring.

Table V. Bond Angles (deg) in $Cp(CO)_3W(Me_2dtc)$ (with Esd's)

C1–W–C2	104.3 (1)	W–S1–C9	114.61 (9)
C1–W–C3	76.7 (1)	W–C1–O1	179.0 (4)
C2–W–C3	76.9 (1)	W–C2–O2	177.0 (3)
S1–W–C1	72.95 (8)	W–C3–O3	178.1 (4)
S1–W–C2	78.38 (8)	S1–C9–S2	123.7 (2)
S1–W–C3	134.25 (8)	S1–C9–N	113.5 (2)
Cp–W–S1[a]	113.9 (1)	S2–C9–N	122.7 (3)
Cp–W–C1	126.8 (1)	C9–N–C10	125.1 (3)
Cp–W–C2	129.0 (1)	C9–N–C11	122.0 (3)
Cp–W–C3	111.6 (1)	C10–N–C11	112.8 (3)

[a] Cp represents the centroid of the cyclopentadienyl ring.

Purple V is most likely $Cp(CO)WI_2(SCNMe_2)$, with the thiocarboxamide ligand formed by reaction of a carbonyl ligand with the iodine-activated dithiocarbamate to form the carbonyl sulfide observed in the gas evolved. Other compounds

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[32] See, e.g.: Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300–306.

[33] (a) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730–737. (b) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105–4109.

[34] Although the lone pair on dangling sulfur S2 is more accessible, binding to S1 is possible; e.g., see $Cp(CO)_3W(\mu\text{-}SMe)W(CO)_5$: Guerchais, J. E.; LeQuere, J. L.; Petillon, F. Y.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1982**, 283–289.

[35] Molecular iodine forms a 1:1 charge-transfer adduct of unknown structure with $Co(S_2CNC_4H_8O)_3$[36a] and reacts with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to yield a stable I^+ adduct.[36b] We thank a reviewer for noting the existence of these compounds.

[36] (a) Crisponi, G.; Deplano, P.; Trogu, E. F., in press (ref 4 in: Bigoli, F.; Leporati, E.; Pellinghelli, M. A.; Crisponi, G.; Deplano, P.; Trogu, E. F. *J. Chem. Soc., Dalton Trans.* **1983**, 1763–1969). (b) Nosco, D. L.; Heeg, M. J.; Glock, M. D.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 7784–7786.

Table VI. Metal-Sulfur (Nonbonding) Distances

compd	dist,[a] Å	ref
$Au(S_2CNEt_2)_3$	3.097,[b] 3.182[b]	8b
$Pt(S_2CN(i\text{-}Bu)_2)_2(PMe_2Ph)_2$	3.392 (3)	7a
$Pt(S_2CNEt_2)_2PPh_3$	3.457 (5)	7b
$Pd(S_2PPh_2)_2PPh_3$	3.485 (11)	7b
$Pt(S_2CC_6H_4C_3H_7)_2PMePh_2$	3.580	49
$Ru(S_2CNMe_2)_3NO$	3.633	8a
$W(S_2CNMe_2)(C_5H_5)(CO)_3$	3.905 (1)	this work
$Pt(S_2P(OEt)_2)_2PPh_3$	3.954 (5)	7b
$Nb(S_2P(OEt)_2)(S_2)(C_5H_5)_2$	4.39[b]	50
$Pt(S_2COEt)_2PPh_3$	4.5	51
$[AsPh_4]Pt(S_2COC_2H_5)_3$	4.85 (3), 4.97 (3)	52
$Ni(S_2P(OMe)_2)_2(phen)$	5.48[b]	53

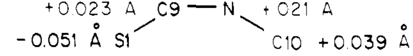
[a] Esd in parentheses, where known. [b] Calculated from given atomic parameters.

are present in smaller amounts than IV and V in the reaction mixtures but have defied separation. The stoichiometry of the reaction is complex, but more than 1 mol of I_2 is consumed for every mole of $Cp(CO)_3W(Me_2dtc)$, since use of an equimolar amount of iodine leaves some of the tungsten complex I unreacted.

Molecular Structure. The structure of $Cp(CO)_3W(Me_2dtc)$ (I) consists of discrete monomeric molecules in the expected four-legged piano-stool conformation (Figure 4) separated by normal van der Waals distances. In general, bond lengths (Table IV) and bond angles (Table V) in the $CpW(CO)_3$ portion of the structure are in agreement with previous determinations of the structures of neutral $Cp(CO)_3WX$ compounds ($X = SMeW(CO)_5$,[34] Cl,[37] Ph,[38] $GaMe_2$,[39a] $AuPPh_3$,[40] $W(CO)_3Cp$,[41] $Ga[W(CO)_3Cp]_2$[39b]) although other accurate structures of $Cp(CO)_3WX$ complexes show slightly ($X = W(CO)_3Cp$)[41] or significantly ($X = Cl$)[37] more distortion in this portion of the structure.

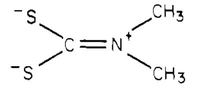
The most striking aspect of the structure is the monodentate nature of the dithiocarbamate ligand. The nonbonding W-S2 distance of 3.905 (1) Å in I is substantially longer than the sum of the covalent radii (2.61 Å) for these two elements,[42] and is also longer than the sum of van der Waals radii.[44] Although there are a number of complexes that likely contain monodentate dithiocarbamate ligands on the basis of spectroscopic data (see above), in only four cases has the structure of the complex been determined by single-crystal X-ray diffraction methods. In all of these, $Pt(i\text{-}Bu_2dtc)_2(PMe_2Ph)_2$,[7a] $Pt(Et_2dtc)_2PPh_3$,[7b] $Ru(NO)(Et_2dtc)_3$,[8a] and $Au(Et_2dtc)_3$,[8b] the metal–dangling-sulfur distance is considerably shorter than in I.[46] However, the W-S2 distance in I is only of intermediate length when compared to corresponding distances in other molecules with monodentate 1,1-disulfur ligands (Table VI).[48]

The dithiocarbamate ligand displays the asymmetry expected of a monodentate group; the S1–C9 distance of 1.769 (3) Å is slightly shorter than a C-S single bond (1.81 Å) and the S2–C9 distance of 1.676 (3) Å is longer than a normal C=S (1.61 Å).[43a] The mean of the two C–S distances in this complex (1.722 Å) is identical with the mean of the C–S distances in $NaS_2CNMe_2{\cdot}2H_2O$,[54] although the deviation from the mean is larger (0.046 vs. 0.013 Å). The C9–N bond also likely retains some residual multiple-bond character since the distance observed here is shorter than a C–N single bond (1.341 (3) vs. 1.48 Å). This is in accordance with infrared spectroscopic evidence, where ν(CN) of 1487 cm^{-1} is on the high-energy end of the range considered normal for monodentate ligands.[9] This residual multiple-bond character is also exhibited in the planarity of the dithiocarbamate skeleton:



It is obvious that deviations from the least-squares plane through the six atoms are relatively small (the rms deviation is 0.039 Å). The dihedral angle between planes defined by S1–C9–S2 and C10–N–C11 is 6.0°. The N–C(methyl) distances are equal as expected, although this is not always the case.[55]

The above data suggest that there is some contribution from the symmetrical thioureide resonance form C, reflected primarily in the shortened C9–N distance, but that this resonance form contributes less in a monodentate dithiocarbamate ligand than in the usual bidentate coordination mode.



C

The W–S1 distance of 2.496 (1) Å is only slightly shorter than W–S distances (2.501–2.569 Å) in the complex $W(CO)_3(Me_2dtc)_2$, which contains two bidentate ligands.[43c] As expected, the W–S1–C9 angle of 114.61 (9)° in I is considerably more open than the angles of 87.4–89.2° found in the bidentate complex. The S–S "bite" distance in I of 3.038 Å is also larger than the values of 2.86 and 2.89 Å found for the bidentate ligands in $W(CO)_3(Me_2dtc)_2$,[43c] but only marginally larger than the 2.997 Å value found for the equivalent distance in $Na(Me_2dtc){\cdot}2H_2O$.[54]

Experimental Section

Materials and Equipment. Hexane was purified by washing with concentrated sulfuric acid, followed by water and aqueous $NaHCO_3$, dried with anhydrous magnesium sulfate, and stored over 4-Å mo-

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(37) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197–2202.

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(39) (a) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Organomet. Chem.* **1977**, *129*, 1–16. (b) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945–1959.

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(41) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090.

(42) Sulfur covalent radius = 1.04 Å;[43a] a tungsten covalent radius of 1.57 Å is inferred from radii for carbon (0.77 Å) and sulfur (1.04 Å)[43a] and W–S and W–C bond distances found in I and other complexes[34,43c] (a value of 1.58 Å is calculated in a similar fashion using data from $Cp(CO)_3WPh$[38]).

(43) (a) Pauling, L. "The Nature of Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) van der Helm, D.; Lessor, A. E., Jr.; Merritt, L. L., Jr. *Acta Crystallogr.* **1962**, *15*, 1227–1232. (c) Templeton, J. L.; Ward, B. C. *Inorg. Chem.* **1980**, *19*, 1753–1759.

(44) The sulfur van der Waals radius is 1.73 Å;[43b] assuming that the van der Waals radius of tungsten is similar to that of platinum (2.07 Å),[45] as the covalent radii are similar,[47] the sum of van der Waals radii is about 3.8 Å.

(45) Stephenson, N. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 791–795.

(46) A direct comparison of these distances is potentially misleading, but the platinum covalent radius is similar to that for tungsten and the radius for ruthenium is only slightly smaller.[47]

(47) Moeller, T. "Inorganic Chemistry"; Wiley-Interscience: New York, 1982; p 71.

(48) Note that those ligands with longer M–S distances usually adopt an anti conformation of the MSXS unit (X = C or P), while in the dithiocarbamate complexes these atoms are in a syn conformation.

(49) Swift, D. R. Ph.D. Thesis, Case Western Reserve University, 1970.

(50) Mercier, R.; Douglade, J.; Viard, B. *Acta Crystallogr., Sect. B* **1981**, *B37*, 949–951.

(51) From ref 7a, Table IX.

(52) Cornock, M. C.; Gould, R. O.; Jones, C. L.; Owen, J. D.; Steele, D. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 496–501.

(53) Shetty, P. S.; Fernando, Q. *J. Am. Chem. Soc.* **1970**, *92*, 3964–3969.

(54) Oskarsson, A.; Ymen, I. *Acta Crystallogr., Sect. C* **1983**, *C39*, 66–68.

(55) For example, N–C(methyl) distances in $W(CO)_3(Me_2dtc)_2$ range from 1.453 to 1.493 Å.[43c]

lecular sieves. Toluene was purified in a similar fashion and stored over 5-Å sieves. The tungsten dimer $[CpW(CO)_3]_2$ was prepared by thermolysis of $CpW(CO)_3CH_2Ph$.[56] Tetramethylthiuram disulfide was a gift from M. C. Palazzotto and was prepared by the iodine oxidation of sodium dimethyldithiocarbamate.[2] Neutral alumina (Sigma) was activated by heating under dynamic vacuum to 250 °C for 6 h to produce authentic grade I alumina. Other grades were generated by shaking grade I alumina with water (grade II, 3%; grade III, 6% (by weight)). All other reagents were commercially available in reagent grade and were used as received.

Infrared spectra were obtained with Beckman 4250 and Perkin-Elmer 283 spectrometers, electronic absorption data were collected on Cary 118 and Hitachi 100-80 ultraviolet–visible absorption spectrophotometers, and ^{1}H NMR spectra were recorded on Varian T-60 and IBM NR-80B instruments. Mass spectra were obtained with a Hewlett-Packard 5985 GC/MS/DS operating in the direct-insertion mode. Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected.

Preparation of (η^5-C_5H_5)(CO)$_3$WSC(S)NMe$_2$ (I): Method A. Using Tetramethylthiuram Disulfide. Under a nitrogen atmosphere, 0.641 g (0.96 mmol) of $[CpW(CO)_3]_2$ and 0.249 g (1.03 mmol) of Me_4TDS ($Me_2NC(S)SSC(S)NMe_2$) were stirred in 125 mL of deaerated toluene, and the solution was cooled to 0 °C. Not all of the tungsten dimer dissolved. The solution was irradiated with a 40-W high-intensity desk lamp from a distance of 5 cm. Progress of the reaction was monitored periodically by infrared spectroscopy. After 2 h of irradiation, nearly all of the tungsten dimer had been dissolved and consumed, so irradiation was terminated. The toluene was removed by rotary evaporation in the dark. The resulting residue was redissolved in 15 mL of toluene and the solution applied to the top of a 2.5 × 26 cm column of grade III neutral alumina poured under hexane. The column was eluted with hexane and 1:1 hexane/touene to remove unreacted tungsten dimer. Elution with dichloromethane served to remove the orange band remaining on the column. The orange fractions were combined and rotary evaporated to yield 0.732 g (1.62 mmol) of I. Infrared spectroscopy indicated a trace amount of a tricarbonyl impurity,[57] so the crude product was recrystallized from dichloromethane/hexane to yield 0.688 g (1.52 mmol) of pure I, a yield of 85% after accounting for recovered tungsten dimer (0.044 g). The recrystallized sample of I had a satisfactory elemental analysis (Schwarzkopf). Anal. Found (calcd for $C_{11}H_{11}NO_3S_2W$): C, 29.15 (29.15); H, 2.60 (2.45); N, 3.35 (3.09); S, 14.62 (14.15); W, 40.03 (40.57); O (by difference), 10.25 (10.59). The 60-MHz ^{1}H NMR spectrum (in $CDCl_3$) consists of two singlets, one at δ 3.61 (6 H, methyl) and another at δ 5.81 (5 H, cyclopentadienyl).

Method B. Using Tris(dimethyldithiocarbamato)iron. Under a nitrogen atmosphere, 0.0683 g (0.103 mmol) of $[CpW(CO)_3]_2$ and 0.0917 g (0.220 mmol) of $Fe(Me_2dtc)_3$ were dissolved in 50 mL of nitrogen-purged toluene in the dark. The solution was irradiated with the 40-W high-intensity desk lamp from a distance of 2 cm for 2 h. The irradiated solution was mixed with 50 mL of hexane and the mixture applied to the top of a grade II alumina column under reduced light. Elution with 1:1 hexane/toluene removed the unreacted tungsten dimer (20.4 mg after evaporation of solvent) and moved the orange band due to I only slightly. Elution with CH_2Cl_2 served to remove the orange band, which was evaporated to yield 65.7 mg (0.145 mmol) of I with properties identical with those of the compound prepared by method A. Remaining at the top of the column was a dark gray band, which did not move appreciably during the above elution. Elution with methanol did finally move the band but only spread it out on the column, moving it about halfway down the 20-cm length of the column.

Preparation of (η^5-C_5H_5)(CO)$_2$WS$_2$CNMe$_2$ (II). A solution of 0.0948 g (0.209 mmol) of $Cp(CO)_3W(Me_2dtc)$ in 30 mL of dichloromethane was equipped with a gentle nitrogen purge and irradiated with the broad-band ultraviolet source (see below) from a distance of 2 cm. Solvent was added periodically to maintain a reasonable level in the flask. After 2 h of irradiation, an infrared spectrum showed that there was an appreciable accumulation of product and that its rate of formation had slowed. At this point the nitrogen purge was removed and the solution filtered through diatomaceous earth to remove a small amount of solid decomposition product. To the filtrate was added 30 mL of hexane and the mixture rotary evaporated until the CH_2Cl_2 was removed to yield 0.0470 g (0.111 mmol) of brown II. From the filtrate was recovered 0.0349 g of unreacted I by evaporation; the yield of II is 84%, based on the amount of I consumed. The recrystallized carbonyl displays an infrared spectrum identical with that previously reported (Table II, this work): 1952 (10), 1867 (7.3) cm^{-1} (cyclohexane);[18] 1943, 1854 cm^{-1} (carbon disulfide).[17] The ^{1}H NMR spectrum of II in $CDCl_3$ shows two singlets: cyclopentadienyl at δ 5.62 (5 H) and methyl at δ 3.11 (6 H) (lit.:[17] δ 5.67, 3.14).

Photochemistry. Qualitative irradiation sources used were a 40-W high-intensity desk lamp (visible) and a fixture with two GE broad-band UV lamps (ultraviolet). Quantum yields for the production of I were measured on 3 mL of solution containing the reactants in a 1-cm quartz cuvette capped with a rubber septum (deoxygenated by nitrogen purge) or in a special 1-cm cuvette with attached tube (Figure 6, supplemental material) (deoxygenated by freeze–pump–thaw cycles). The sample was irradiated with a filtered medium-pressure mercury arc source, the intensity of which was determined by Reineckate[60] (546 nm) or ferrioxalate[61] (436, 336 nm) actinometry.

Quantum Yield Calculations. For reaction 5, the concentrations of tungsten dimer and product I as a function of time were calculated from changes in absorbance at 492 and 460 nm, by using a standard two-component analysis with extinction coefficients determined from standard solutions. For reaction 6, the wavelengths monitored were 460 and 417 nm. Quantum yields were determined for each irradiation time, by using changes in reactant concentration to calculate disappearance yields and changes in product concentration for corresponding appearance yields. Corrections were made for incomplete absorption of the starting material and the inner-filter effect where appropriate.[62] Calculations were performed in a differential manner,[63] and the corrected values for each time interval were averaged over the course of the photolysis. The values quoted in the text are weighted means of at least two determinations, and the error quoted is 2 standard deviations (i.e., 95% confidence level) calculated from the standard deviations of the averages for each experiment.[63]

Thermal Transformation of I to II. Four milliliters of a 4 × 10^{-4} M solution of $Cp(CO)_3WSC(S)NMe_2$ in toluene in the sidearm of a special cell (Figure 6, supplemental material) was degassed by four freeze–pump–thaw cycles (10^{-4} torr) in the dark. The solution was warmed to room temperature and transferred to the cell side and the Teflon valve closed. The cell was placed in the thermostated cell holder of the Hitachi spectrometer; temperature control was provided by a Haake FK2 circulating temperature bath. A capped cuvette of pure toluene was used for a reference. The temperature was measured in the reference cell at the end of each run. Absorbance data were collected periodically (every 5–30 min) at 460 and 417 nm until a 50–75% conversion to dicarbonyl II had taken place. Data were subjected to a standard two-component analysis to calculate the concentrations of I and II from the absorbance data; extinction coefficients were adjusted for the change in concentration of the solution due to expansion of solvent.[64]

Reaction of I with W(CO)$_5$THF. A nitrogen gas purge was used to deoxygenate 50 mL of tetrahydrofuran, to which was added 71.8 mg (0.204 mmol) of $W(CO)_6$. The solution was irradiated with the broad-band UV source to produce $W(CO)_5THF$,[33] and the progress of the photoreaction was monitored by infrared spectra. After 2 h, conversion to $W(CO)_5THF$ was complete and 83.3 mg (0.184 mmol) of $Cp(CO)_3WSC(S)NMe_2$ was added. An infrared spectrum of the mixture indicated that substantial displacement of the THF ligand had occurred, so the solution was added to an equal volume of hexane

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(57) The impurity is also present in our sample of the tungsten dimer. We have identified it as $[(\eta^{10}\text{-}C_5H_4C_5H_4)W_2(CO)_6]$ on the basis of infrared and mass spectra[58] and confirmed by an X-ray crystal structure.[59]

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Table VII. Atomic Parameters ($\times 10^4$) with Esd's in Parentheses

atom	*x*	*y*	*z*
W	2200.7 (2)	8439.8 (1)	2330.8 (1)
S1	3037 (1)	7487 (1)	4234 (1)
S2	2468 (2)	4373 (1)	1814 (1)
O1	2040 (4)	10976 (3)	5440 (3)
O2	−1199 (4)	6132 (3)	1861 (4)
O3	−968 (5)	10005 (4)	1725 (5)
N	2511 (6)	5077 (4)	4690 (4)
C1	2082 (5)	10051 (4)	4307 (4)
C2	66 (5)	6941 (4)	2020 (4)
C3	170 (5)	9410 (5)	1931 (5)
C4	5035 (5)	9337 (5)	2016 (5)
C5	3727 (6)	9570 (5)	1070 (5)
C6	2855 (6)	8164 (5)	17 (4)
C7	3652 (6)	7059 (5)	320 (4)
C8	4987 (6)	7791 (5)	1545 (5)
C9	2621 (5)	5541 (4)	3598 (5)
C10	2608 (8)	6048 (6)	6269 (5)
C11	2354 (8)	3508 (5)	4411 (7)

and placed in a −25 °C freezer. An infrared analysis of the resulting crystals showed a mixture of the $W(CO)_5$ adduct III, along with some dicarbonyl II. Attempts at column chromatography invariably led to the decomposition of the adduct on the column so that only I and II were obtained. Recrystallization from CH_2Cl_2/hexane yields first II and then, as more CH_2Cl_2 is removed by rotary evaporation, the adduct III. We were able to recover only 50 mg of relatively pure III (30% yield) by this process. Uncomplexed I seems to be a ubiquitous contaminant. The infrared and electronic spectra are listed in Tables I and II, respectively. The ^1H NMR spectrum consists of two singlets at δ 5.88 (5 H, Cp) and 3.61 (6 H, Me).

Reaction of I with Iodine. In a typical preparation, 0.0589 g (0.232 mmol) iodine in 5 mL of CH_2Cl_2 was added via cannula, under reduced light, to 0.1031 g (0.227 mmol) of $Cp(CO)_3WSC(S)NMe_2$ in 7 mL of dichloromethane. Infrared spectra of the gas evolved were dominated by bands for CH_2Cl_2 and carbon monoxide, along with smaller bands due to carbonyl sulfide, OCS. The gas evolution halted after about 5 min, at which point a fine tan solid had settled to the bottom of the tube; filtration served to isolate 50.5 mg of solid IV. After $^1/_2$-h additional reaction time, an additional 8.8 mg of IV was recovered by filtration. To the red-orange filtrate was added 20 mL of hexane, and the CH_2Cl_2 was removed by rotary evaporation to yield 55.2 mg of a purple-brown precipitate and an orange filtrate which was evaporated to yield 17.3 mg of unreacted $Cp(CO)_3WSC(S)NMe_2$. The purple-brown precipitate was partially purified by dissolving it in CH_2Cl_2 and rapidly passing it through a 1-cm column of grade II alumina. An orange-brown band remained at the top of the column, and elution with CH_2Cl_2 removed a purple band consisting of mainly V, with at least 10% contamination by some other unidentified CpW compounds (by ^1H NMR: δ 5.77, 5.30).

Elemental analysis (Schwarzkopf) of IV is consistent with the formula $C_{10}H_{11}I_2NO_2S_2W$. Anal. Found (calcd): C, 17.31 (17.69); H, 1.60 (1.63); N, 2.19 (2.06); S, 9.97 (9.44). The ^1H NMR spectrum of a solution of IV in Me_2SO-d_6 shows one major peak at δ 3.41, with minor peaks that indicate the presence of a small amount of contaminating I. Infrared spectral data are listed in Table II.

Purple V is slightly soluble in $CHCl_3$ and CH_2Cl_2. The ^1H NMR spectrum in $CDCl_3$ has major peaks at δ 5.47, 3.23, and 3.29 in a 5:3:3 ratio. The mass spectrum is dominated by a peak for I_2^+ at 254 (100%). In addition, weak multiplets with the tungsten isotope pattern can be found for ions with formulas $C_8H_{11}I_2NSW$ (591), $C_8H_{11}INSW$ (464), C_7H_8INSW (449), C_5H_5ISW (408), and C_5H_5IW (376). Along with the NMR and mass spectral data, the thioureide stretch at 1547 cm^{-1} and additional bands are also consistent with a thiocarboxamido ligand.[65]

X-ray Crystal and Molecular Structure Determination of $Cp(CO)_3WSC(S)NMe_2$. A prismatic crystal of dimensions 0.21 × 0.14 × 0.09 mm, obtained by recrystallization from dichloromethane/hexane, was used for all X-ray measurements. Preliminary investigations indicated that the crystal was triclinic, and space group $P\bar{1}$ was confirmed by the structure determination and subsequent refinement.

The cell parameters were determined by least-squares fit to $\pm 2\theta$ of 48 reflections measured at 138 K with use of Mo Kα_1 radiation. The crystal data for $C_{11}H_{11}NO_3S_2W$ are $M_r = 453.2$, $a = 7.616$ (7) Å, $b = 9.962$ (11) Å, $c = 9.931$ (8) Å, $\alpha = 113.38$ (6)°, $\beta = 94.68$ (9)°, $\gamma = 95.83$ (10)°, $V = 681.87$ Å^3, $Z = 2$, and d (calcd) = 2.207 g/cm^3.[66]

Intensities of 3932 unique reflections with $2\theta \leq 60°$ were collected at 138 ± 2 K with use of Mo Kα radiation (graphite monochromator) on an Enraf-Nonius CAD-4 automatic diffractometer fitted with a liquid-N_2 low-temperature device. A θ–2θ scan technique was employed, using variable scan width and variable scan speed. The maximum scan time for a reflection was 50 s. Of the total scan time, two-thirds was spent scanning the peak and one-sixth was spent scanning each of the left and right backgrounds. The intensities of three standard reflections, monitored after every 7200 s of X-ray exposure, showed a maximum variation of about 7%. The orientation of the crystal was checked after every 200 measurements. Intensities were corrected for Lorentz and polarization factors and also for absorption.[67] The maximum and minimum transmission factors are 0.480 and 0.290, respectively ($\mu = 83.9$ cm^{-1}).

Solution and Refinement of the Structure. The structure was determined by the heavy-atom technique and was refined by a full-matrix least-squares routine[67] using anisotropic thermal parameters for the non-hydrogen atoms. All of the hydrogen atoms were located from a different Fourier map and were refined isotropically. The refinement converged to a final R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.025 for 3714 observed reflections ($I > 2\sigma(I)$) and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2})$ of 0.031, while the standard deviation of an observation of unit weight was 1.3. The R factor for all 3932 reflections was 0.032. The final atomic parameters are listed in Table VII. The bond distances and bond angles are given in Tables IV and V, respectively. The atom numbering scheme is shown in Figure 4.

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Supplementary Material Available: Listings of structure factor amplitudes (observed and calculated) (Table VIII), anisotropic thermal parameters (Table IX), and hydrogen atom parameters (Table X), a packing drawing (Figure 5) for $Cp(CO)_3WSC(S)NMe_2$, and a drawing of the special irradiation cell (Figure 6) (21 pages). Ordering information is given on any current masthead page.

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