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Photochemical and Thermal Loss of Carbon Monoxide from Tricarbonyl(η^5-cyclopentadienyl)(arenethiolato)tungsten (Arene = Benzene, Toluene)

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Photolysis of the compounds CpW(CO)$_3$SR (Cp = η^5-C$_5$H$_5$; R = phenyl, *p*-tolyl) using broad-band UV light results in formation of the thiolate-bridged dimers [CpW(CO)$_2$SR]$_2$. Thermal reactions of these compounds allow synthesis of the dimers [CpW(CO)SR]$_2$. Higher temperatures and longer reaction times are required for product formation when R = phenyl than when R = tolyl. Careful monitoring of these thermal reactions by IR spectroscopy indicates that the monocarbonyl dimers arise from carbonyl-loss reactions of [CpW(CO)$_2$SR]$_2$. Comparison with previous work shows that carbonyl lability in CpW(CO)$_3$SR complexes increases in the series SCF$_3$ < SCH$_3$ < SPh < STol. Spectroscopic correlations have been developed to assign correct molecular formulas to tungsten carbonyl thiolate-bridged dimers. The dimerization of unsaturated intermediates can be prevented by trapping them with a ligand, e.g. triphenylphosphine. Investigation of the reaction between Ph$_3$P and CpW(CO)$_3$SR shows that the monosubstituted product CpW(CO)$_2$(PPh$_3$)SR is formed stereospecifically as the cis isomer.

Recent work by Grobe[1] and Jaitner[2] has led to an increased understanding of reactivity trends in molybdenum carbonyl thiolate compounds and of the formulation of dimeric and trimeric products arising from CO-loss reactions of these compounds. Our investigation into oxidation reactions of tungsten carbonyl thiolates[3] led us to synthesize the compound [CpW(CO)$_2$SPh]$_2$; however, a discrepancy in the carbonyl stretching frequencies of this compound and the one formulated by Watkins and George[4] to be "[CpW(CO)$_2$STol]$_2$" prompted a closer investigation of tungsten carbonyl thiolate compounds.

A review of the literature indicates that most syntheses of group 6 metal carbonyl thiolate compounds have been conducted under vigorous reaction conditions (high temperatures and long reaction times) and that periodic monitoring of the reactions by spectroscopic methods has not been attempted. This suggests that possible intermediates in these reactions may have been overlooked. Recent data of Brandenburg[5] show that substitution of a range of electron-withdrawing and electron-donating functionalities on the arene group of the thiolate ligand in CpW(CO)$_3$SR compounds shifts the carbonyl stretching frequencies less than 10 cm^{-1}. Significantly larger discrepancies in the ν_{CO} bands of analogous tungsten carbonyl thiolate compounds suggest that the formulation of some dinuclear tungsten compounds may be erroneous.

Separation of thiolate-bridged molybdenum dimers into two types, [CpMo(CO)$_2$SR]$_2$ and [CpMo(CO)SR]$_2$, has been established by the observation of parent molecular ion peaks in the mass spectra[4,6,7] and by a few examples[8,9] of X-ray diffraction studies. However, investigation of the tungsten analogues of these dimers is a vastly less explored area, likely because it is much harder to assign a molecular formula to tungsten thiolate dimers. Reasons for this are that (1) parent molecular ions have not been observed in mass spectra, (2) elemental analyses cannot distinguish unambiguously between mono- and dicarbonyl dimers, and (3) it is difficult to grow suitable crystals for X-ray studies due to their extreme air sensitivity.

We present here our results concerning carbonyl-loss reactions of the tungsten thiolate compounds CpW(CO)$_3$SR (R = phenyl, *p*-tolyl). These results clarify some of the past ambiguities in the formation of tungsten and molybdenum carbonyl thiolate-bridged dimers:

$$2\mathrm{CpM(CO)_3SR} \rightarrow [\mathrm{CpM(CO)_2SR}]_2 + 2\mathrm{CO} \qquad (1)$$

$$[\mathrm{CpM(CO)_2SR}]_2 \rightarrow [\mathrm{CpM(CO)SR}]_2 + 2\mathrm{CO} \qquad (2)$$

We also find that inclusion of a phosphine ligand inhibits this dimer formation reaction. For example, the photochemical reaction between CpW(CO)$_3$SR and PPh$_3$ yields stereospecific formation of *cis*-CpW(CO)$_2$(PPh$_3$)SR. These are believed to be the first reported examples of triphenylphosphine-substituted compounds in these systems.

Results

Dimerization of CpW(CO)$_3$SPh. Photolysis of CpW(CO)$_3$SPh in degassed toluene using broad-band ultraviolet light yields a new compound that we assign as [CpW(CO)$_2$SPh]$_2$ on the basis of its IR and NMR spectra (see Discussion). The carbonyl stretching frequencies (ν_{CO}) of this compound are found in Table I, and the ^{1}H NMR shifts are found in Table II. Although Havlin and Knox[10] discuss the preparation of [CpW(CO)$_2$SPh]$_2$ by photochemical decomposition of CpW(CO)$_3$SPh in solution, the supporting evidence for their assignment of the molecular formula to this product was never reported. Attempted purification of [CpW(CO)$_2$SPh]$_2$ by chromatography on a grade I alumina column results in decomposition to a tan product that cannot be eluted from the column. However, partial separation of brown [CpW(CO)$_2$SPh]$_2$ from orange CpW(CO)$_3$SPh starting material is possible with use of size-exclusion chromatography. Elemental analysis was not attempted because solid [CpW(CO)$_2$SPh]$_2$ decomposes over a 1–2-day period even when stored at 0 °C under nitrogen. In solution, this dicarbonyl dimer decomposes in the course of a few hours time, even under nitrogen.

When CpW(CO)$_3$SPh is thermolyzed in refluxing benzene,[4] the only product formed, as evidenced by both IR and ^{1}H NMR spectroscopy, is the same brown complex obtained from the photochemical reaction, i.e., [CpW(CO)$_2$SPh]$_2$. Longer reaction time fails to yield any additional soluble products but results only in slow decomposition to a tan non-carbonyl-containing product similar to the complex [CpMoTePh]$_x$.[11]

Thermolysis of CpW(CO)$_3$SPh in toluene at 95 °C rapidly yields [CpW(CO)$_2$SPh]$_2$. Continued heating results in the formation of a new compound that, on the basis of its IR and NMR spectra, is assigned the formula [CpW(CO)SPh]$_2$. The IR and ^{1}H NMR spectra of this compound are also found in Tables I and II.

Dimerization of CpW(CO)$_3$STol. Photolysis of CpW(CO)$_3$STol (Tol = *p*-tolyl) in toluene using broad-band UV irradiation results in the partial formation of a new compound that we assign as [CpW(CO)$_2$STol]$_2$ because of its similarity to [CpW(CO)$_2$SPh]$_2$ (see Tables I and II). The reaction can only be driven to about

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Table I. Carbonyl Stretching Frequencies of Group 6 Thiolate Compounds

	$CpM(CO)_3ER$			$[CpM(CO)_2ER]_2$			$[CpM(CO)ER]_2$		
RE	ν(CO), cm^{-1}	soln[a]	ref[b]	ν(CO), cm^{-1}	soln[a]	ref[b]	ν(CO), cm^{-1}	soln[a]	ref[b]
				M = W					
MeS	2030, 1943	C	4	1955 (vs), 1930 (sh), 1861 (s), 1852 (sh)	C	4	...	...	...
PhS	2031, 1938	M	tw	1942, 1854	T	tw	1896, 1847	T	tw
TolS	2031, 1950	C	tw	1948, 1851	T	tw	1892, 1849	B	tw
	2033, 1949	C	4				1893 (m), 1848 (s)[f]	C	4
				M = Mo					
MeS	2032, 1936	H	22	1967, 1948, 1940 (sh), 1879, 1862 (sh), 1852 (sh)	H	4	1875 (sh), 1850	M	7
PhS	*c*		10	*c*,*d*		9	*c*		9
	2033, 1947	T	20	1972 (sh), 1953, 1878 (sh), 1859	M	2			
TolS	2040, 1959	C	4	1964 (sh), 1954, 1873	C	4	...	...	...
t-BuS	...	...	...	*c*		9	1885, 1881[d]	H	9
MeSe	2012, 1947	H	1	1957, 1948, 1933, 1871, 1862, 1850	S	1	...	...	...
PhSe	2026, 1948	S	11	1964, 1952, 1870, 1860	M	2	1874, 1865	S	11
PhSe[e]	...	...	...	*c*		6	1878 (s), 1850 (m)	P	6
PhTe	2016, 1948 (sh), 1937	S	11	1960 (s), 1935 (vs), 1876 (vs), 1860 (s)	S	11	...	...	...
				1935, 1920, 1866, 1848	M	2			
PhTe[e]	...	...	...	*c*		6	1881 (s), 1856 (m)	P	6
				M = Cr					
MeS	*c*		1	1974 (m), 1960 (s), 1942 (m), 1920 (vs), 1884, 1845	H	1	1902, 1884	H	1

[a] Solution codes: H = cyclohexane; M = methylene chloride; C = carbon tetrachloride; T = toluene; B = benzene; S = carbon disulfide; P = *n*-pentane. [b] tw = this work. [c] Author indicated preparation of the compound but no physical data (IR, ^{1}H NMR, MS, elemental analysis) were ever published. [d] Crystal structure determined. [e] η^5-Methylcyclopentadienyl ligand is used instead of Cp. [f] Originally assigned as a dicarbonyl dimer; see text.

Table II. ^{1}H NMR Cp Resonances of Group 6 Thiolate Compounds

	$CpM(CO)_3ER$			$[CpM(CO)_2ER]_2$			$[CpM(CO)ER]_2$		
RE	δ(Cp)	soln[a]	ref[b]	δ(Cp)	soln[a]	ref[b]	δ(Cp)	soln[a]	ref[b]
				M = W					
MeS	4.77	dB	4	*c*		4	...	...	...
PhS	5.67	dC	tw	5.43	dC	tw	5.30	dC	tw
TolS	5.67	dC	tw	5.40	dC	tw	5.30	dC	tw
				M = Mo					
MeS	4.74	dB	22	5.06, 4.88	dB	6, 4	5.32	dC	14
PhS	*c*		10	5.2	A	2	*c*		9
TolS	4.74	dB	10	4.99	dB	4	...	...	...
t-BuS	...	...	...	*c*		9	5.49, 5.16	dC	9
MeSe	4.69	dB	1	4.98, 4.80	dB	1	...	...	...
PhSe	*c*		11	5.2	A	2	...	...	...
PhSe[d]	...	...	...	*c*		6	*c*		6
PhTe	5.28	S	11	5.12	S	11	...	...	...
				5.2	A	2			
PhTe[d]	...	...	...	*c*		6	*c*		6
				M = Cr					
MeS	...	...	...	5.06, 4.88	dT	1	...	...	...

[a] Solution codes: dB = C_6D_6; dC = $CDCl_3$; A = acetonitrile; S = CS_2; dT = toluene-d_8. [b] tw = this work. [c] Author indicated preparation of the compound but no physical data (IR, ^{1}H, NMR, MS, elemental analysis) were ever published. [d] η^5-Methylcyclopentadienyl ligand is used instead of Cp.

50% completion before decomposition of $[CpW(CO)_2STol]_2$ starts to occur via secondary photolytic reactions. These secondary reactions produce a tan precipitate, similar to the decomposition product seen in the reactions of $CpW(CO)_3SPh$, that does not contain any carbonyl ligands as evidenced by IR spectra in KBr.

Florisil chromatography of the reaction solution after photolysis separates the mixture into two bands. The yellow-orange band is eluted with toluene and is spectroscopically identified as unreacted $CpW(CO)_3STol$. A brown band, which is eluted only as far as the top of the Florisil, partially decomposes to a lighter tan band during the elution of the tricarbonyl complex. A methanol wash of the column yields a small amount of a yellow fraction exhibiting ν_{CO} bands at 2029, 1988, 1959, 1932, 1892, 1863, and 1711 cm^{-1}. This fraction was not fully characterized due to its small amount and likely contains the compounds $CpW(CO)_3STol$ and $[CpW(CO)_2STol]_2$. However, the bridging ν_{CO} band at 1711 cm^{-1} suggests that another compound is present, which may be a trimeric thiolate complex analogous to that found by Petillon.[7]

When $CpW(CO)_3STol$ is refluxed in benzene and monitored as described in the Experimental Section, the first-formed products are $[CpW(CO)_2STol]_2$ and a compound that exhibits ν_{CO} bands that are quite similar to the ν_{CO} positions of $[CpW(CO)SPh]_2$. Continued refluxing (>15 min) results in total conversion to this latter product, which we assign as $[CpW(CO)STol]_2$. The yield is approximately 40%, and significant amounts of a tan precipitate are seen just as in the photochemical dimerization reaction of $CpW(CO)_3STol$.

Substitution of CO in $CpW(CO)_3SR$ by PPh_3. When a solution containing $CpW(CO)_3SR$ (R = Ph, Tol) and PPh_3 is photolyzed in toluene with UV light, the monosubstituted product $CpW(CO)_2(PPh_3)SR$ is formed as evidenced by both IR and NMR spectra. The presence of two distinct Cp resonances in the ^{1}H NMR spectrum indicates that both the cis and trans isomers are synthesized, with the cis isomer predominating.

Additional supporting evidence for assignment of the product is found in the ^{31}P NMR spectrum of the product of the reaction between $CpW(CO)_3STol$ and PPh_3 after chromatography on grade I alumina. Two singlets are observed at +28.5 and +34.7 ppm. Each singlet is flanked by a pair of satellites arising from phosphorus–tungsten coupling (J_{P-W} = 242 and 214 Hz, respectively).

Table III. Infrared and ^1H NMR Spectral Data for η^5-Cyclopentadienyl Tungsten Carbonyl Complexes

compd	solvent[a]	ν_{CO}, cm^{-1}	^1H δ^b Cp	Ph	Me	PPh_3	ref[e]
$CpW(CO)_3SPh$	M	2031, 1938	5.67	7.23 (m)			tw
$CpW(CO)_3STol$	M	2027, 1936	5.67	7.20 (m)	2.26		tw
	T	2027, 1940					
$CpW(CO)_3I$	C	2040, 1960	5.68				13
$CpW(CO)_2(PPh_3)SPh$	M	1950, 1865	5.43 (cis) 5.03 (d) (trans)	7.13 (m)[c,d] 7.33 (m)[c,d]		7.18 (d)[c,d] 7.37 (d)[c,d]	tw
$CpW(CO)_2(PPh_3)STol$	M	1950, 1865	5.40 (cis)	7.36 (m)[c,d]	2.56[c]	7.30 (d)[c,d]	tw
	T	1952, 1871	5.05 (d) (trans)	7.23 (m)[c,d]	2.53[c]	7.16 (d)[c,d]	
$CpW(CO)_2(PPh_3)I$	C	1960, 1860	5.47 (cis) 5.13 (d) (trans)				13

[a] Solvent codes: M = CH_2Cl_2; C = $CHCl_3$; T = toluene. [b] In $CDCl_3$ solution relative to Me_4Si: d = doublet; m = multiplet. [c] These resonances are derived from a cis/trans mixture and *cannot* be accurately assigned as belonging to one or the other isomer. [d] Approximate centroid value. [e] tw = this work.

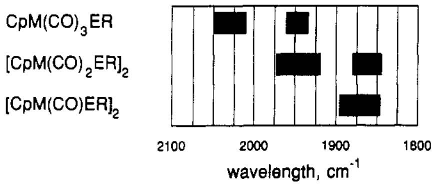


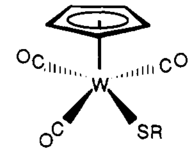
Figure 1. Carbonyl stretching frequencies in cyclopentadienyl carbonyl group 6 metal thiolate compounds: M = Cr, Mo, W; E = S, Se, Te; R = alkyl, aryl. Except for the region above 2000 cm^{-1}, each region may have more than one band (see Table I).

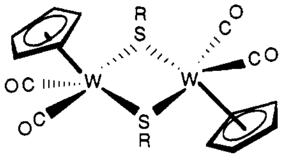
A ^1H NMR experiment in which $CpW(CO)_3SPh$ and Ph_3P are photolyzed in degassed $CDCl_3$ demonstrates that the cis isomer is first formed stereospecifically, but continued irradiation (>20% conversion) produces the trans isomer. The two isomers can be assigned on the basis of well-documented NMR and infrared criteria.[12] The trans isomer has a Cp resonance in the ^1H NMR spectrum at 5.03 ppm (doublet) and exhibits a symmetric carbonyl infrared stretching band (1950 cm^{-1}) that is less intense than that of the asymmetric carbonyl stretching band (1865 cm^{-1}). The cis isomer has a singlet Cp resonance at 5.43 ppm, and the symmetric carbonyl stretch has a larger intensity than the asymmetric carbonyl stretch. Since the cis siomer predominates in the reaction mixture resulting from the photolysis of $CpW(CO)_3SPh$ and Ph_3P, the peak at 1950 cm^{-1} has a greater intensity than the peak at 1865 cm^{-1}; a similar pattern is seen in the tolyl compound. A comparison of the new compounds and $CpW(CO)_2(PPh_3)I$[13] indicates a similar pattern of infrared and ^1H NMR data (see Table III).

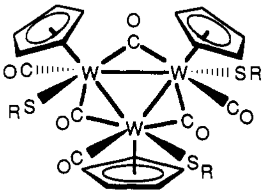
An alternate route leads to more of the trans isomer. When $[CpW(CO)_3]_2$, $[PhS]_2$, and PPh_3 are mixed together in a toluene solution and irradiated with broad-band UV light, periodic monitoring of the reaction by IR indicates that the reaction proceeds first by formation of significant amounts of $CpW(CO)_3SPh$, followed by the appearance of $CpW(CO)_2(PPh_3)SPh$. The ^1H NMR spectrum of the reaction mixture after complete transformation of $CpW(CO)_3SPh$ to the triphenylphosphine-substituted product indicates that $CpW(CO)_3(PPh_3)SPh$ is synthesized as a mixture of cis/trans isomers in which the trans isomer predominates by almost a 2:1 ratio.

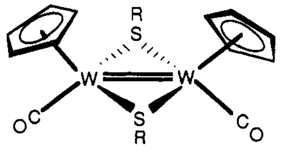
Discussion

Dimerization of $CpW(CO)_3SR$, R = Phenyl, Tolyl. Syntheses of dimers with bridging thiolate groups have been known for years;[14] however, a wide variety of reaction conditions have been employed and, as yet, no study has investigated possible intermediate compounds in these reactions. There are four types of cyclopentadienyl- and carbonyl-containing group 6 metal thiolate compounds that are the common products of reactions between group 6 metal carbonyl dimers and disulfides or subsequent carbonyl-loss reactions of these products. These compounds are $CpM(CO)_3SR$, $[CpM(CO)_2SR]_2$, $[CpM(CO)SR]_2$, and $[CpM(SR)(\mu\text{-}CO)(CO)]_3$:









The type and ratio of the compounds produced during a reaction depends markedly upon the experimental conditions.[7]

Various isomers of both the di- and monocarbonyl dimers are possible on the basis of either cis or trans arrangements of the Cp ligands (with respect to the M_2S_2 ring) and upon mutually syn or anti orientations of the R groups on the sulfur atoms. Benson[9] and Jaitner[2] have noted that IR and NMR spectra of several $[CpM(CO)_2SR]_2$ compounds reveal that such isomers do exist but that they often interconvert rapidly on the NMR time scale as a consequence of pyramidal inversion at sulfur.

Table I shows a survey of Cp carbonyl group 6 metal compounds with organochalcogen ligands. The dicarbonyl dimers have been prepared by a variety of methods, but in all cases, they arise from experimental conditions that are milder than those used to prepare the monocarbonyl dimers. Additionally, several molybdenum monocarbonyl dimers have been prepared by decarbonylation of the corresponding dicarbonyl dimers via heating crystals of the dicarbonyl compound under a vacuum.

In examination of past work, it can be seen that ER (E = S, Se, Te) compounds exhibit a pervasive pattern of carbonyl stretching frequencies. As Table I indicates, $CpM(CO)_3ER$ complexes exhibit a ν_{CO} pattern consisting of one high-energy peak (>2000 cm^{-1}) and one lower energy peak between 1970 and 1930 cm^{-1}. Although the $[CpM(CO)_2ER]_2$ complexes exhibit a variety of ν_{CO} band patterns, they have at least one peak between 1970 and 1930 cm^{-1} and at least one lower energy peak between 1880 and 1845 cm^{-1}, with more peaks likely if both cis and trans isomers are present. The monocarbonyl dimers are also capable of isomerism, and the presence of two ν_{CO} bands may indicate that the $[CpW(CO)SR]_2$ compounds were synthesized as mixtures of isomers. Results from a group-theoretical analysis of the four possible conformations of Cp monocarbonyl thiolate dimers (cis or trans Cp, syn or anti R) indicate that either one or two IR-active ν_{CO} bands are possible. This pervasive pattern supports using the carbonyl stretching frequencies for assigning molecular formulas to tungsten carbonyl thiolate-bridged dimers. Figure 1 summarizes

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[12] (a) Beach, D. L.; Dattilo, M.; Barnett, K. W. *J. Organomet. Chem.* **1977**, *140*, 47. (b) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

[13] Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533.

[14] Treichel, P. M.; Morris, J. H.; Stone, F. G. A. *J. Chem. Soc.* **1963**, 720.

the regions where ν_{CO} bands are expected to appear in each type of compound.

On the basis of the spectroscopic data, we conclude that the initial product of the UV photolysis of $CpW(CO)_3SR$ (R = Ph, Tol) is $[CpW(CO)_2SR]_2$. Thermal decarbonylation of $CpW(CO)_3SR$ gives both $[CpW(CO)_2SR]_2$ and $[CpW(CO)SR]_2$, with the latter product requiring higher temperatures. In addition, the thermal decarbonylation reactions are easier when R = Tol than when R = Ph. Watkins and George[4] noted the existence of a discrepancy between the ν_{CO} bands of $[CpMo(CO)_2STol]_2$ and "$[CpW(CO)_2STol]_2$" and postulated that either the two complexes exist as different isomers or that the tungsten complex exists as a trimer. On the basis of our investigation, we conclude instead that the compound previously[4] formulated as "$[CpW(CO)_2STol]_2$" is better assigned the formula $[CpW(CO)STol]_2$.

Our results and those of others[1] indicate that ease of carbonyl loss from $CpM(CO)_3SR$ (M = Mo, W) increases in the series SR = SCF_3 < SMe < SPh < STol. This can be interpreted in terms of a σ-inductive effect; i.e., carbonyl lability in group 6 thiolate complexes increases as electron density is pushed onto sulfur.

Triphenylphosphine Substitution of $CpW(CO)_3SR$. Photochemical reactions of $CpW(CO)_3R$ (R = H,[15] Cl,[13] Br,[13] I,[13] CH_3,[16] C_2H_5,[17] benzyl[18]) with various Lewis bases have shown that these compounds undergo clean, efficient substitution reactions arising from loss of carbon monoxide. Our investigation of the photochemical reactions between $CpW(CO)_3SR$ and Ph_3P shows that the photoproducts are remarkably similar to $CpW(CO)_2(Ph_3P)I$[13] as evidenced by both IR and ^{1}H NMR spectra (Table III). On the basis of these similarities, we conclude that these photosubstitution reactions produce the new compound $CpW(CO)_2(Ph_3P)SR$ and believe it to be the first example of a substituted tungsten carbonyl thiolate complex.

Alway and Barnett[13] report that photolysis of $CpM(CO)_3X$ (M = Mo, W; X = halide) in the presence of PPh_3 yields *cis*-$CpM(CO)_2(PPh_3)X$ stereospecifically. They also note that prolonged irradiation of $CpM(CO)_3X$ and PPh_3 in solution (>35% completion) results in formation of traces of the trans isomer. We find that the cis isomer of $CpW(CO)_2(PPh_3)SPh$ is formed stereospecifically upon irradiation of a solution of $CpW(CO)_3SR$ and PPh_3 and that the trans isomer is formed during prolonged irradiations by secondary photolysis of *cis*-$CpW(CO)_2(PPh_3)SR$.

We find additional evidence for both cis and trans isomers in the ^{31}P NMR spectrum of pure $CpW(CO)_2(PPh_3)STol$ (from photolysis of $CpW(CO)_3STol$ with PPh_3). The presence of two singlets, each flanked by a pair of satellites (^{183}W, $I = {}^1/_2$, 14.3%), demonstrates that two isomers are present and that phosphorus is directly bonded to tungsten. Comparison of the relative intensities of the two singlets in the ^{31}P NMR spectrum to the relative intensities of the two Cp resonances in the ^{1}H NMR spectrum of the same solution enables the ^{31}P resonances to be assigned: *cis*-$CpW(CO)_2(PPh_3)STol$, +27.1 ppm (J_{P-W} = 242 Hz); *trans*-$CpW(CO)_2(PPh_3)STol$, +34.7 ppm (J_{P-W} = 214 Hz). The magnitude of J_{P-W} is on the same order as the values for the compounds $W(CO)_5PR_3$ (J_{P-W} = 143–485 Hz),[19] where R is a variety of either electron-donating or electron-withdrawing substituents. Our observation that irradiation of a solution of $[CpW(CO)_3]_2$, $[PhS]_2$, and PPh_3 yields a 2:1 ratio of *trans-*/*cis*-$CpW(CO)_2(PPh_3)SPh$ agrees with the finding[13] that $[CpW(CO)_3]_2$ catalyzes the isomerization of *cis*- to *trans*-$CpW(CO)_2(PPh_3)I$.

Conclusions. This study illustrates the importance of carbonyl-loss reactions of the compounds $CpW(CO)_3SR$. In the absence of other ligands, products are $[CpW(CO)_2SR]_2$ and $[CpW(CO)SR]_2$, with yields of each depending upon R and the severity of conditions. If the solution of $CpW(CO)_3SR$ contains a suitable nucleophile such as PPh_3, then the unsaturated intermediates generated by UV photolysis will react with the nucleophile to form the monosubstituted compound $CpW(CO)_2(PPh_3)SR$.

Experimental Section

Materials and Equipment. Hexane was purified by washing with concentrated sulfuric acid, followed by water and aqueous $NaHCO_3$, dried over anhydrous magnesium sulfate, eluted through commercial silica gel, and stored over 4-Å molecular sieves. Toluene was purified in a similar manner; however, the acid wash was done at reduced temperature to prevent sulfonation of the toluene and storage was over 5-Å molecular sieves. Methylene chloride and chloroform were dried by shaking and storing over 3-Å molecular sieves. $[CpW(CO)_3]_2$ was prepared by thermolysis of $CpW(CO)_3CH_2Ph$.[20] Neutral alumina (Sigma) was activated by heating under dynamic vacuum to 250 °C overnight to produce authentic grade I alumina, which was stored under vacuum in the regeneration tube until needed for chromatography. The compounds PPh_3, $[PhS]_2$, $[TolS]_2$, C_6D_6, and $CDCl_3$ were obtained commercially and used without further purification.

Infrared spectra were obtained with a Nicolet MX-5 (FT) spectrometer in a demountable 0.5 mm liquid IR cell with NaCl windows. The proton NMR spectra were recorded on a Varian EM-390 spectrometer in $CDCl_3$. ^{31}P NMR spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.2 MHz. Broad-band irradiation was used to decouple protons. Spectra were recorded in $CDCl_3$ and referenced to 1% H_3PO_4 (0.0 ppm) as an external reference by using the concentric tube method. A high-field-positive convention is used in reporting data. An observed frequency of 59.65 KHz and a spectral width of 10 000 Hz were used. In all cases, the spectra were recorded by using a 10-mm variable-frequency probe. All UV irradiations were performed by using a U-V Products XX-15 broad-band near-UV (black-light) source and an aluminum-foil tent. Visible irradiations were done by using either a 60-W high-intensity desk lamp or a 150-W high-pressure xenon lamp in a PRA ALH-215 condensing housing with an M303X power supply and a Corning UV cutoff filter. Thermostatic control was maintained by a B. Braun Frigomix 1496 circulating bath containing either 1:1 water/isopropyl alcohol for the work at 0 °C or water for the work at 95 °C.

Synthesis of $CpW(CO)_3SPh$. A nitrogen-purged toluene solution containing 0.2498 g (0.375 mmol) of $[CpW(CO)_3]_2$ and 0.0738 g (0.338 mmol) of diphenyl disulfide, $[PhS]_2$, was stirred in a water-jacketed quartz irradiation tube adapted for inert-atmosphere work, having been sealed with a two-hole rubber stopper. The holes of the stopper were then closed with septa-covered glass tubes to allow removal of small aliquots. The solution was cooled by cold-water flow and irradiated with a 60-W high-intensity desk lamp from a distance of 5 cm. Progress of the reaction was monitored periodically by infrared spectroscopy on small aliquots of the reaction solution for the disappearance of the ν_{CO} bands of $[CpW(CO)_3]_2$, 1954 and 1903 cm^{-1}, and for the appearance of the ν_{CO} bands of $CpW(CO)_3SPh$.[21] The irradiation was terminated after 5 h when the intensity of the 1903-cm^{-1} band had been reduced to less than 10% of its original height. The presence of a small amount (1–2%) of the complex $[CpW(CO)_2SPh]_2$ was indicated by the existence of a low-intensity peak at 1848 cm^{-1} (Table I).

The toluene was concentrated to 15 mL by rotary evaporation in the absence of light and applied, in minimum-light conditions, to the top of a 2.5 × 20 cm column of grade I neutral alumina wetted with toluene. Toluene elution removed all unreacted diphenyl disulfide and a purple band of unreacted $[CpW(CO)_3]_2$. Elution with CH_2Cl_2 removed an orange band of $CpW(CO)_3SPh$, which was identified by IR and ^{1}H NMR spectra. Unfortunately, any $[CpW(CO)_2SPh]_2$ formed decomposed on the column into a brown band that could not be removed even with a methanol wash of the column. Rotary evaporation of the orange CH_2Cl_2 fractions produced orange crystals of $CpW(CO)_3SPh$. IR: Table I. ^{1}H NMR ($CDCl_3$): δ(Cp) = 5.67; δ(Ph) = 7.23 (m)).

Vastly improved irradiation times, on the order of 30 min, were achieved if a xenon arc lamp was used for irradiation, but the solution had to be cooled to 0 °C and a UV filter used to limit formation of the secondary photoproduct $[CpW(CO)_2SPh]_2$.

Synthesis of $CpW(CO)_3STol$. This was prepared in the manner described above using $[CpW(CO)_3]_2$ and di-*p*-tolyl disulfide. The complex was compared spectroscopically to the experimental data of Watkins and George[4] and found to be satisfactorily identical. IR: Table I. ^{1}H NMR ($CDCl_3$): δ(Cp) = 5.67; *p*-tolyl, δ(Me) = 2.26, δ(aryl) = 7.20 (m)).

Synthesis of $[CpW(CO)_2SPh]_2$ and $[CpW(CO)_2STol]_2$. In a typical reaction, a solution of 0.1325 g (0.2997 mmol) of $CpW(CO)_3SPh$ in degassed benzene was placed in a jacketed quartz irradiation tube and

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cooled to 0 °C. The solution was irradiated with a broad-band UV source from a distance of 2 cm and slowly flushed with nitrogen to remove generated carbon monoxide. After 3 h, the solution had changed from orange to dark brown and an infrared spectrum showed 90% disappearance of the 2031-cm^{-1} peak and the appearance of a ν_{CO} band at 1854 cm^{-1} accompanied by a shoulder at 1950 cm^{-1}. The solution was rotary evaporated in the dark to concentrate the mixture. Attempts at crystallization of the product resulted in crystals that were contaminated by $CpW(CO)_3SPh$. A small amount of pure sample was obtained by using size-exclusion chromatography on S-X12 BioBeads resin eluting with methylene chloride, but all other chromatographic materials (e.g., alumina, Florisil, and silica) resulted in decomposition of the product on the column. The IR and ^1H NMR spectra of $[CpW(CO)_2SPh]_2$ are reported in Tables I and II.

The complex $[CpW(CO)_2STol]_2$ was prepared in exactly the same manner; however, no attempt was made to purify the sample. An infrared spectrum of the benzene reaction solution exhibited ν_{CO} peaks of 2027 (s), 1954 (sh), 1940 (s), and 1849 (m) cm^{-1}. The peaks at 2027 and 1940 cm^{-1} correspond to $CpW(CO)_3STol$, and the remaining peaks at 1954 and 1849 cm^{-1} are assigned to the compound $[CpW(CO)_2STol]_2$ (see Table I).

Removal of the solvent by rotary evaporation, followed by dissolution of the solid in $CDCl_3$, yielded a ^1H NMR spectrum with resonances at 5.67, 5.40, 2.26, 2.23, and 7.15 (broad multiplet) ppm. The peaks at 5.67 and 2.26 ppm have been previously assigned to $CpW(CO)_3STol$ (Table III), and on the basis of its similarity to $[CpW(CO)_2SPh]_2$, the compound $[CpW(CO)_2STol]_2$ is assigned the following ^1H NMR resonances in $CDCl_3$: $\delta(Cp) = 5.40$; *p*-tolyl, $\delta(Me) = 2.23$, $\delta(aryl) = 7.15$.

Synthesis of $[CpW(CO)STol]_2$. When $CpW(CO)_3STol$ was refluxed in benzene in the manner of Watkins and George[4] and monitored every 3 min by cooling the solution to room temperature and removing a small aliquot, a mixture of $[CpW(CO)_2STol]_2$ and $[CpW(CO)STol]_2$ was initially formed as evidenced by both IR and ^1H NMR spectra. Continued refluxing resulted in the formation of $[CpW(CO)STol]_2$ (^1H NMR ($CDCl_3$): $\delta(Cp) = 5.30$; *p*-tolyl, $\delta(Me) = 2.16$, $\delta(aryl) \approx 7.0$) although there was some decomposition to a tan non-carbonyl-containing precipitate. Micropore filtration of the solution removed the precipitate to yield a solution that had spectroscopic parameters similar to those of Watkins and George's[4] "$[CpW(CO)_2STol]_2$"; however, our analysis indicates it should be formulated as $[CpW(CO)STol]_2$.

Synthesis of $[CpW(CO)SPh]_2$. A nitrogen-purged toluene solution containing ~30 mg of $CpW(CO)_3SPh$ was maintained at 95 °C for 75 min by the use of a circulating bath of H_2O. A slow flow rate of N_2 *above* the solution was used to remove free CO as it was released from solution. At the end of 75 min, removal of a small aliquot and analysis by IR indicated that the solution contained a mixture of $CpW(CO)_3SPh$, $[CpW(CO)_2SPh]_2$, and a new compound that exhibited ν_{CO} bands at 1896 and 1847 cm^{-1}. Due to the similarity of these ν_{CO} bands to the carbonyl stretching frequencies of $[CpW(CO)STol]_2$, this new compound is assigned as $[CpW(CO)SPh]_2$. Rotary evaporation of the toluene in low-light conditions resulted in the isolation of a brown-black powder. A ^1H NMR spectrum of the powder dissolved in $CDCl_3$ indicated the presence of three distinct Cp resonances at 5.67, 5.43, and 5.30 ppm. The 5.67 and 5.43 ppm peaks correspond with the cyclopentadienyl resonances of $CpW(CO)_3SPh$ and $[CpW(CO)_2SPh]_2$. The third Cp resonance is therefore assigned to the complex $[CpW(CO)SPh]_2$ and is found at the same frequency as the cyclopentadienyl resonance in $[CpW(CO)STol]_2$. Analysis of the Cp intensities reveals that the products of this reaction and their relative amounts were as follows: $CpW(CO)_3SPh$, 30%; $[CpW(CO)_2SPh]_2$, 50%; $[CpW(CO)SPh]_2$, 20%.

Synthesis of $CpW(CO)_2(PPh_3)SPh$. In a manner analogous to the preparation of $[CpW(CO)_2SPh]_2$ above 0.1734 g (0.392 mmol) of $CpW(CO)_3SPh$ and 0.1208 g (0.392 mmol) of triphenylphosphine were dissolved in degassed benzene and cooled with cold-water flow. The solution was irradiated with a broad-band UV source and continuously flushed with nitrogen. After 3 h, an infrared spectrum indicated an appreciable accumulation of a new compound with ν_{CO} peaks of 1950 and 1865 cm^{-1}. After reduction of the volume to 10 mL by rotary evaporation, the solution was applied to the top of a 2.5 × 20 cm grade I neutral alumina column poured under benzene. Benzene elution removed unreacted $CpW(CO)_3SPh$ and PPh_3. A yellow-orange band eluted with a 1:1 mixture of benzene/CH_2Cl_2. Rotary evaporation of the yellow fractions gave orange crystals of $CpW(CO)_2(PPh_3)SPh$ (see Table III for spectral data).

Synthesis of $CpW(CO)_2(PPh_3)STol$. In a manner completely analogous to the method for preparation of $CpW(CO)_2(PPh_3)SPh$, 0.0870 g (0.19 mmol) of $CpW(CO)_3STol$ and 0.0571 g (0.19 mmol) of PPh_3 were dissolved in degassed toluene, cooled, and irradiated with broad-band UV light. After 1 h, an infrared spectrum of an aliquot of the reaction solution indicated that ~95% of the $CpW(CO)_3STol$ had reacted and the irradiation was terminated. The grade I alumina column was filled with toluene, and the concentrated reaction solution was stripped onto the column. Toluene elution removed the unreacted $CpW(CO)_3STol$, and a 1:1 toluene/CH_2Cl_2 mixture eluted an orange solution. Comparison of the IR and ^1H NMR spectra of the chromatographically pure product to the spectra of $CpW(CO)_2(PPh_3)SPh$ demonstrated a high degree of similarity (see Table III). A ^{31}P NMR spectrum of the crystals dissolved in $CDCl_3$ confirmed the presence of two isomers. On the basis of a comparison of the relative intensities of the Cp resonances in the ^1H NMR spectrum to the relative intensities of the ^{31}P resonances, *cis*-$CpW(CO)_2(PPh_3)STol$ is assigned as +27.1 ppm ($J_{P-W} = 242$ Hz) and *trans*-$CpW(CO)_2(PPh_3)STol$ is assigned as +34.7 ppm ($J_{P-W} = 214$ Hz).

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Properties of Triazadienyl Fluoride, N_3F

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A safe preparative method has been developed for the synthesis of the very explosive N_3F in pure form. This allowed the comprehensive characterization of N_3F by means of IR, UV/vis, NMR, and mass spectroscopy as well as a determination of the melting point and vapor pressure. The usefulness of N_3F as a synthetic reagent is demonstrated.

Although the existence of triazadienyl fluoride (fluorine azide, N_3F) has been known since the pioneering work of Haller[1] in 1942, this interesting molecule has rarely been investigated.

Yellow gaseous N_3F is generated by the reaction of HN_3 with F_2 in the gas phase.[1] It decomposes slowly at room temperature to N_2F_2 and N_2. In the liquid and solid states N_3F is extremely explosive, and purification was impossible. Vapor density and boiling and melting points were estimated for the impure compound. Qualitative spectroscopic measurements on N_3F were made in the range 370–450 nm.[2] There are statements about

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