

required to attempt a correlation between the V=S bond length and its associated IR stretching frequency. Note that it is important to compare structural data with solid (Nujol mull) IR data so that any solid-state effects on these parameters are present in both measurements.

In Figure 3 is presented a plot of bond length vs. IR stretching frequency. As is evident in this figure, a linear dependence is observed. The  $\text{edt}^{2-}$  ligated complex leads to the longest V=S bond length and lowest stretching frequency. Of the several parameters probably influencing the observed data, no doubt the total electron-donating ability of the basal ligands and the overall charge of the complex are of paramount importance. It should be said that we have not observed such a linear dependence on comparing V=O bond lengths in the literature with their associated stretching frequencies. This is probably due to the stronger nature of the V=O<sup>2+</sup> bond vs. the V=S<sup>2+</sup> bond, making the former less responsive to differences in complex charge and the electron-donating abilities of the basal ligands, and possibly to other factors being of equal or even greater importance such as axial-basal ligand-ligand repulsions, which would be attenuated with the longer V=S<sup>2+</sup> bond.

The plot of Figure 3 is somewhat preliminary and must obviously stand the test of time as more data points become available, at which time more general conclusions may be possible. Nevertheless, we present this plot at such an early stage because it can already be put to some interesting use. Poncet et al. have studied the VS(por) (por = octaethylporphyrin) complex by the EXAFS technique and obtained a value of  $2.06 \pm 0.01 \text{ \AA}$  for the V=S bond length.<sup>9</sup> Using their reported value of  $555 \text{ cm}^{-1}$  for  $\nu(\text{V}=\text{S})$  in this complex, we predict from Figure 3 a value of  $2.062 \text{ \AA}$  for the V=S bond length, in excellent agreement with the EXAFS conclusion. This agreement both supports the accuracy of the EXAFS technique for obtaining such bond lengths and

supports the validity of the correlation of Figure 3. This plot may thus have some value in the future should, for instance, on EXAFS study be carried out on thiovanadyl species formed on the surface of HDS catalysts during refining of vanadium-rich, heavier crudes.<sup>10,11</sup> A knowledge of the V=S bond length could allow conclusions to be reached about the identity of other ligands bound to the metal by reference to Figure 3 in its future version containing more data points.

In summary, a direct-synthesis procedure has now been developed for mononuclear vanadium thiolate species containing the V=E<sup>2+</sup> (E = S, Se) moiety and thus avoiding the need for prior synthesis of the V=O<sup>2+</sup> analogue. This development should make future reactivity studies of these species much more convenient to perform. This is particularly true for the E = Se species for which no facile synthetic route has been available to date. Further studies in vanadium/sulfur (selenium) chemistry are in progress.

**Acknowledgment.** This work was supported by NSF Grant CHE07748. We thank the Bloomington Academic Computing Service for a gift of computer time. J.R.N. is a recipient of a U.K. SERC/NATO Fellowship.

**Supplementary Material Available:** Complete listings of atom coordinates, thermal parameters, and bond distances and angles (18 pages); listings of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (Nos. 86022 and 86115 for **1** and **3**, respectively) are available on request from the Indiana University Chemistry Library.

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## Oxidation of Thiolate Ligands in Cyclopentadienyltungsten Carbonyl Complexes

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Received November 13, 1986

The reaction between MCPBA (*m*-chloroperoxybenzoic acid) and a wide variety of CpW(CO)<sub>3</sub>SR compounds [SR = SCH<sub>3</sub>, SC<sub>6</sub>H<sub>5</sub>, S(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), S(*p*-C<sub>6</sub>H<sub>4</sub>Cl), S(*p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>), S(*p*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>), S(*o*-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>), Me<sub>2</sub>dtc, S(2-py), and S(2-btz) where substituent abbreviations are 2-py = 2-pyridyl, 2-btz = 2-benzothiazolyl, Me<sub>2</sub>dtc = dimethyldithiocarbamate; others are substituted phenyl] is a superior synthetic method for preparation of sulfinato-S (-S(O)<sub>2</sub>R) compounds of tungsten. Yields of these compounds are excellent, and preparation of a pure product from the original tricarboxyl thiolate complex generally requires less than 3 h. In addition, the reaction of MCPBA and CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol (Tol = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) is an efficient method for synthesis of the triphenylphosphine-substituted sulfinato-S compound CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SO<sub>2</sub>Tol. Photolyses of CpW(CO)<sub>3</sub>SO<sub>2</sub>R, both by itself (R = Ph) and in the presence of triphenylphosphine (R = Ph, Tol), indicate that carbonyl loss is an important photochemical reaction of these sulfinato-S compounds, although the latter reaction unexpectedly yields CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SR instead of the simple substitution product CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SO<sub>2</sub>R. The results of unsuccessful attempts to prepare tungsten sulfenato-S (-S(O)R) compounds by the reactions of [CpW(CO)<sub>3</sub>]<sup>-</sup> with methanesulfinyl chloride and of CpW(CO)<sub>3</sub>SPh with SeO<sub>2</sub> are also detailed.

Organic peracids such as MCPBA (*m*-chloroperoxybenzoic acid) and peroxyacetic acid have been shown to be useful reagents for the oxidation of elemental sulfur<sup>1</sup> and organic sulfides.<sup>2</sup> Recently, it has been reported that organic peroxyacids will rapidly and selectively oxidize inorganic sulfur, selenium, and tellurium in  $\mu_3\text{-E}$  (E = S, Se, Te) and  $\eta^2\text{-E}_2$  (E = S, Se) ligands.<sup>3</sup> Other

work<sup>4</sup> has demonstrated the oxidation of the bridging sulfide ligand in Pt<sub>2</sub>(dpm)<sub>2</sub>( $\mu\text{-S}$ )Cl<sub>2</sub> [dpm = bis(diphenylphosphino)methane].

The original impetus for our work was to synthesize new examples of compounds containing coordinated sulfur monoxide. The recent findings<sup>3</sup> that MCPBA reacts with [Ir(S)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> to give [Ir(S<sub>2</sub>O)(dppe)<sub>2</sub>]<sup>+</sup> and with Fe<sub>2</sub>Pt(S)<sub>2</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub> to yield Fe<sub>2</sub>Pt(SO)(S)(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub> prompted our further investigation of MCPBA oxidations. Few SO compounds are presently known,

(1) Steudel, R.; Sandow, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 611.

(2) House, H. O. *Modern Synthetic Reactions*; Benjamin: Menlo Park, CA, 1972; pp 334-335.

(3) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130.

(4) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

**Table I.** Carbonyl-Region Infrared Stretching Frequencies for  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  and Corresponding  $\text{CpW}(\text{CO})_3\text{SR}$  Compounds<sup>a</sup>

SR <sup>b</sup>	$\nu_{\text{CO}}, \text{cm}^{-1}$	
	$\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$	$\text{CpW}(\text{CO})_3\text{SR}$
S( <i>p</i> -C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> )	2046, 1956 <sup>c</sup>	2026, 1937 <sup>c</sup>
SMe	2047, 1954 <sup>c</sup>	2025, 1932 <sup>c</sup>
SC <sub>6</sub> H <sub>5</sub>	2048, 1960 <sup>c</sup>	2030, 1939 <sup>c</sup>
S( <i>p</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )	2048, 1958 <sup>c</sup>	2029, 1936 <sup>c</sup>
S( <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl)	2049, 1958 <sup>c</sup>	2031, 1940 <sup>c</sup>
S( <i>o</i> -C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> )	2049, 1960 <sup>c</sup>	2026, 1937 <sup>c</sup>
S( <i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )	2050, 1960 <sup>c</sup>	2037, 1942 <sup>c</sup>
Me <sub>2</sub> dtc	2049, 1973 (sh), 1954	2036, 1958, 1932
S(2-py)	2050, 1960 <sup>c</sup>	2033, 1951, 1930
S(2-btz)	2054, 1979 (sh), 1966	2039, 1959, 1938

<sup>a</sup> In methylene chloride solution. <sup>b</sup> Substituent abbreviations: Me = methyl; 2-py = 2-pyridyl; 2-btz = 2-benzothiazolyl; Me<sub>2</sub>dtc = dimethyldithiocarbamate; others are substituted phenyl. <sup>c</sup> Second band is broad and likely due to superposition of two bands. Undefined shoulders are observed on the high-frequency side in most cases.

and these are limited to the metals Ir, Rh, Mn, and Fe.<sup>3,5</sup>

One possible new route to preparing SO ligands coordinated to other metals would be to react 1 equiv of MCPBA with a  $\text{CpW}(\text{CO})_3\text{SR}$  compound to produce  $\text{CpW}(\text{CO})_3\text{S}(\text{O})\text{R}$ . Subsequent irradiation of this sulfenato compound might allow R group migration to yield the desired sulfur monoxide complex. The synthesis of the tungsten-bound sulfenato ( $-\text{S}(\text{O})\text{R}$ ) ligand would be an added benefit of this method since, to our knowledge, coordinated sulfenates are currently limited to complexes of Ir and Co.<sup>6</sup>

We now wish to report that the organic peracid MCPBA is useful for the oxidation of thiolate ligands ( $-\text{SR}$ ); however, the reaction gives sulfinato-S ligands ( $-\text{S}(\text{O})_2\text{R}$ ) instead of the desired sulfenates. We have also investigated some reactions of these sulfinato products, especially in an effort to induce migration of the R group to the metal. Similar reactions are known in iridium and molybdenum chemistry.<sup>7,8</sup> Furthermore, we describe the results of our other unsuccessful attempts to prepare compounds containing a sulfenato ligand ( $-\text{S}(\text{O})\text{R}$ ) bound to tungsten.

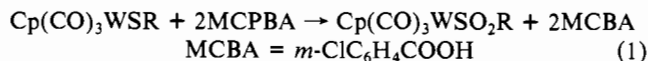
## Results

**Oxidation of Thiolate Complexes.** When  $\text{CpW}(\text{CO})_3\text{SPh}$  and MCPBA are mixed in methylene chloride, infrared monitoring of the solution shows disappearance of the  $\nu_{\text{CO}}$  bands of  $\text{CpW}(\text{CO})_3\text{SPh}$  (Table I) and appearance of two new bands at 2048 and 1960  $\text{cm}^{-1}$ . A preparatory-scale reaction using a 1:1 ratio of the two reactants results in only 50% transformation of  $\text{CpW}(\text{CO})_3\text{SPh}$  to the new carbonyl-containing product, as evidenced by the infrared spectrum. If additional MCPBA is added in this point, complete disappearance of bands due to  $\text{CpW}(\text{CO})_3\text{SPh}$  is achieved.

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- (7) Kubota, M.; Loeffler, B. M. *Inorg. Chem.* **1972**, *11*, 469.
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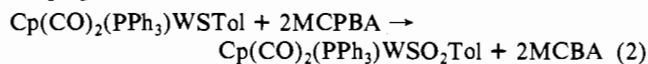
On the basis of the agreement of the IR and <sup>1</sup>H NMR data with those of Pannell and Kapoor,<sup>9</sup> the product must be  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$ . This is further confirmed by the observation of strong infrared bands for the  $\text{SO}_2\text{R}$  unit at 1204, 1053, 594, and 559  $\text{cm}^{-1}$  (KBr) and a satisfactory elemental analysis. In a similar fashion, the analogous *p*-toluene thiolate complex  $\text{Cp}(\text{CO})_3\text{WSTol}$  (Tol = *p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) can be oxidized by 2 mol of MCPBA, forming the corresponding sulfinato complex, with bands for the  $\text{SO}_2\text{R}$  unit falling at 1202, 1044, 637, and 577  $\text{cm}^{-1}$  (KBr).

When other analogous tungsten carbonyl thiolate complexes  $\text{CpW}(\text{CO})_3\text{SR}$  react with MCPBA in  $\text{CH}_2\text{Cl}_2$ , the production of oxidized compounds is evidenced by the shift in carbonyl stretching frequencies to higher energies and a change in the color of the solution from orange to yellow. The  $\nu_{\text{CO}}$  peaks of several tungsten carbonyl thiolate compounds and their oxidized products are given in Table I. The extreme similarity found in all of these cases demonstrates that the reaction



is a general one.

This method is also useful for synthesizing triphenylphosphine-substituted sulfinato-S compounds as demonstrated by the reaction between  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$  and MCPBA in  $\text{CH}_2\text{Cl}_2$ :



When this reaction is monitored by IR spectroscopy, the production of an oxidized compound is evidenced by the shift in carbonyl stretching frequencies to higher energies (from 1950, 1867 to 1970, 1886  $\text{cm}^{-1}$ ) and a change in the color of the solution from brown to orange. The presence of a sulfinato-S ligand is confirmed by the observation of strong infrared bands at 1176, 1035, 637, and 576  $\text{cm}^{-1}$  (KBr).

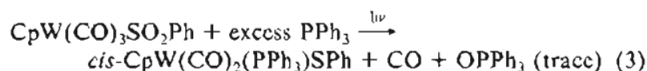
When reaction 2 is monitored by <sup>31</sup>P NMR, a new singlet appears at 31.4 ppm flanked by two satellites (<sup>183</sup>W, *I* = 1/2, 13.9%; *J*<sub>P-W</sub> = 208 Hz). The spectrum also indicates the presence of unbound  $\text{OPPh}_3$  (+29.2 ppm), although its intensity is only 15% when compared to the intensity of the metal-containing product. A <sup>1</sup>H NMR spectrum of the solution confirms the presence of a single cyclopentadienyl-containing product with a doublet resonance at 5.37 ppm (*J*<sub>P-H</sub> = 2 Hz).

Unfortunately, the reaction cannot be further generalized to the related dicarbonyl compounds with bridging or chelating thiolate ligands. For example, when the compounds  $[\text{CpW}(\text{CO})_2\text{SPh}]_2$  and  $\text{CpW}(\text{CO})_2(\text{S}_2\text{CNMe}_2)$  are reacted with MCPBA, the rapid disappearance of the  $\nu_{\text{CO}}$  bands of these compounds without the appearance of new carbonyl stretching bands indicates that the oxidation is giving rise to products that do not contain carbonyl ligands.

**Reactions of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$ .** When a degassed  $\text{CH}_2\text{Cl}_2$  solution of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  is irradiated with broad-band UV light in a sealed infrared cell, the intensity of the  $\nu_{\text{CO}}$  peaks of the benzenesulfinato complex rapidly decreases, and the only carbonyl-containing species formed is a small amount of  $\text{CpW}(\text{CO})_3\text{SPh}$ . If a  $\text{CDCl}_3$  solution is similarly irradiated, <sup>1</sup>H NMR spectra confirm the formation of a small amount of  $\text{CpW}(\text{CO})_3\text{SPh}$ . This is accompanied by a large amount of two precipitates, light tan and blue-gray. An analysis of the mixed precipitates by IR spectroscopy in KBr indicates the complete absence of peaks in the carbonyl region (2200–1700  $\text{cm}^{-1}$ ) and the presence of two distinct peaks at 970 and 815  $\text{cm}^{-1}$ . Analysis of the gases released during the irradiation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  in degassed  $\text{CH}_2\text{Cl}_2$  indicates only the presence of carbon monoxide (and methylene chloride vapor).

When a chloroform solution of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  and triphenylphosphine is irradiated with broad-band UV light, both IR and NMR spectra indicate that substitution of a carbonyl ligand is taking place:

(9) Pannell, K. H.; Kapoor, R. N. *J. Organomet. Chem.* **1984**, *269*, 59.



The reaction is not quantitative, however, apparently due to a sensitivity of the  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SPh}$  to UV light. The  $^1\text{H}$  NMR spectrum indicates stereospecific formation of *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SPh}$ . Prolonged irradiation gives small amounts (<10%) of  $\text{CpW}(\text{CO})_3\text{SPh}$ . Light is necessary for this reaction, because the  $^1\text{H}$  NMR spectrum of a 1:1 solution of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  and  $\text{PPh}_3$  in  $\text{CDCl}_3$  is unchanged after 9 h in the dark.

As another probe of the reaction between  $\text{PPh}_3$  and  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  compounds, a degassed  $\text{CDCl}_3$  solution of excess  $\text{PPh}_3$  and  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Tol}$  was irradiated in a sealed 10-mm NMR tube for 30 min. The color of the solution changes from orange to dark brown, and some gray precipitate is produced. A  $^{31}\text{P}$  NMR spectrum of the solution indicates the presence of unreacted  $\text{PPh}_3$  (-6.0 ppm),  $\text{OPPh}_3$  (+29.2 ppm), and a singlet at 28.5 ppm with two satellites ( $J_{\text{P-W}} = 240$  Hz). Comparison to data for the *cis* and *trans* isomers of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$  (formed by substitution<sup>10</sup> of  $\text{CpW}(\text{CO})_3\text{STol}$ ) confirms that reaction 3 yields the *cis* isomer stereospecifically when  $\text{R} = \text{Tol}$ . The  $\text{OPPh}_3$  peak is much weaker than the singlet at 28.5 ppm, indicating that a nonstoichiometric amount of  $\text{OPPh}_3$  is formed. An IR spectrum of the NMR solution, after removal of unreacted MCPBA, demonstrates the presence of unreacted  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Tol}$ , a small amount of  $\text{CpW}(\text{CO})_3\text{STol}$ ,  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$ , and  $\text{OPPh}_3$ . In addition, infrared spectra of the insoluble precipitates formed in the photolysis again show peaks at 970 and 815  $\text{cm}^{-1}$ .

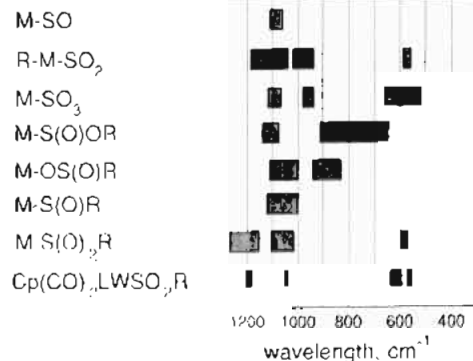
**Reaction of  $\text{CpW}(\text{CO})_3\text{SPh}$  with  $\text{SeO}_2$ .** When  $\text{CpW}(\text{CO})_3\text{SPh}$  is allowed to react with  $\text{SeO}_2$  at room temperature in water-free methanol, periodic monitoring of the solution by IR indicates that there is slow decomposition of the benzenethiolate complex but no concurrent growth of any new carbonyl infrared bands. Visual inspection of the reaction mixture indicates the presence of a significant amount of a tan precipitate.

**Reaction of  $[\text{CpW}(\text{CO})_3]^-$  with Methanesulfonyl Chloride.** When THF solutions of  $[\text{CpW}(\text{CO})_3]^-$  and  $\text{MeS}(\text{O})\text{Cl}$  are allowed to react at -78 °C by slow addition of the tungsten anion solution to the methanesulfonyl chloride solution, the color gradually changes from yellow to dark brown as the solution warms to room temperature. Removal of the solvent by rotary evaporation gives a dark brown-purple solid. Analysis of this solid by IR and  $^1\text{H}$  NMR spectroscopy indicates that the products of this reaction (and their relative amounts) are  $[\text{CpW}(\text{CO})_3]_2$  (50%),  $\text{CpW}(\text{CO})_3\text{SMe}$  (40%),  $\text{CpW}(\text{CO})_3\text{Cl}$  (7%), and  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Me}$  (3%). The percentages are based upon the ratios of the Cp resonance intensities in the  $^1\text{H}$  NMR spectrum.

## Discussion

**Oxidation Reactions.** Earlier work in our group<sup>11</sup> indicates that, of the oxidizing agents  $\text{H}_2\text{O}_2$ ,  $\text{NBu}_4[\text{IO}_4]$ ,  $\text{SOCl}_2$ , and MCPBA, only the peracid MCPBA is successful in selectively oxidizing a sulfide ligand in  $\text{Fe}_2(\text{CO})_9\text{S}_2$ . The other oxidizers either completely decompose the cluster to iron sulfide compounds or oxidize the cluster and yield small amounts of  $\text{Fe}_2(\text{CO})_9\text{S}_2$ . These results, coupled with other uses of this reagent,<sup>3</sup> prompted our further investigation of the oxidizing ability of MCPBA.

The oxidation of  $\text{CpW}(\text{CO})_3\text{SR}$  by MCPBA does form new carbonyl-containing products. The fact that the  $\nu_{\text{CO}}$  bands of the product have a similar pattern but are shifted to higher energies indicates that oxidation of sulfur is occurring without a gross change in the symmetry of the complex. A comparison of the carbonyl stretching frequencies of  $\text{CpW}(\text{CO})_3\text{SMe}$ <sup>12</sup> (2030, 1943  $\text{cm}^{-1}$ ) and  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Me}$ <sup>13</sup> (2050, 1960  $\text{cm}^{-1}$ ) shows a shift similar to those observed here (Table I). These shifts are consistent with a reduction of electron density at the metal center upon



**Figure 1.** Ranges of  $\nu_{\text{SO}}$  for a number of arrangements of M, R, S, and O and their comparison with observed frequencies of  $\text{CpW}(\text{CO})_2(\text{L})\text{SO}_2\text{R}$  ( $\text{R} = \text{Ph, Tol; L} = \text{CO, PPh}_3$ ). For a list of more than 100 compounds surveyed in preparing this figure, see the supplementary material.

oxidation, which is reflected in reduced  $\pi$  back-bonding to the CO ligands and thus a stretching of the C-O bond.

Before the report<sup>9</sup> of the independent preparation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$ , we had hoped that our product was a new example of a sulfenato (-S(O)R) compound. However, the stoichiometry of reaction 1 and the close correspondence between the carbonyl IR and  $^1\text{H}$  NMR data for  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  and our oxidized phenyl compound soon convinced us that the product indeed contained a sulfinato (-SO<sub>2</sub>R) ligand. Additional evidence comes from infrared spectra in KBr of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  ( $\text{R} = \text{Ph, Tol}$ ). The arrangement of bands due to the oxidized thiolate ligand is consistent only with a sulfinato ligand when contrasted with other alternatives (see Figure 1).

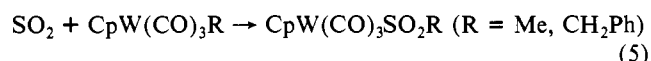
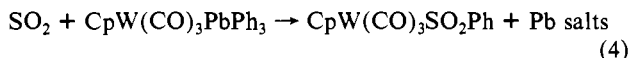
Similarly, the reaction between MCPBA and  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$  results in the formation of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Tol}$ . After removal of  $\text{OPPh}_3$  by methanol washes, the IR spectrum of the product in KBr contains new bands in the region between 1400 and 400  $\text{cm}^{-1}$  that are consistent with the presence of a sulfinato-S ligand. Monitoring this reaction by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy shows that both *cis* and *trans* isomers of the original thiolate compound disappear and that the only organometallic product formed is *trans*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Tol}$ . The doublet Cp resonance in the  $^1\text{H}$  NMR and the lower intensity of the symmetric  $\nu_{\text{CO}}$  stretch compared to the asymmetric  $\nu_{\text{CO}}$  stretch both confirm that the oxidized product exists solely in the *trans* configuration.<sup>14</sup> The  $^{31}\text{P}$  NMR spectrum also confirms the formation of  $\text{OPPh}_3$  during reaction 2. Since the original sample of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$  did not contain free  $\text{PPh}_3$  (by  $^{31}\text{P}$  NMR), the 15%  $\text{OPPh}_3$  must arise from oxidation of  $\text{PPh}_3$  ligands released by  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$ .

Although this  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Tol}$  is apparently the first phosphine-substituted tungsten sulfinato-S compound reported,  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Me}$  has been prepared<sup>8</sup> by  $\text{SO}_2$  insertion into  $\text{CpMo}(\text{CO})_3(\text{PPh}_3)\text{Me}$ . Comparison of the  $\nu_{\text{CO}}$  band positions of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Tol}$  and  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Me}$  indicates a similar two-band pattern. More instructive, however, is a comparison of the shift in  $\nu_{\text{SO}_2}$  frequencies for the pairs  $\text{CpMo}(\text{CO})_3\text{SO}_2\text{Me}$  vs.  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Me}$  with  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Tol}$  vs.  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SO}_2\text{Tol}$ . In the Mo case, the shift in  $\nu_{\text{SO}_2}$  frequencies upon substitution of triphenylphosphine for a carbonyl ligand is 20  $\text{cm}^{-1}$  to lower energy for the asymmetric stretch and 9  $\text{cm}^{-1}$  to lower energy for the symmetric stretch.<sup>8</sup> This is paralleled here in the W compound, where the asymmetric  $\text{SO}_2$  stretch shifts 21  $\text{cm}^{-1}$  to lower energy and the symmetric  $\text{SO}_2$  stretch shifts 6  $\text{cm}^{-1}$  to lower energy.

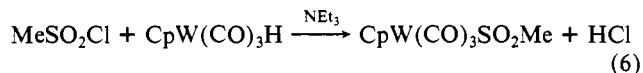
Currently sulfinato complexes of group 6 metals can be synthesized by five different methods. These include sulfur dioxide insertion reactions<sup>9,15</sup>

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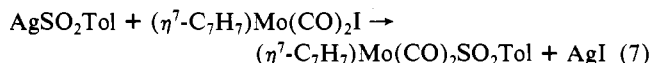
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reaction of an organic sulfonyl halide with a metal hydride<sup>16</sup>



and reaction of a silver sulfinate with a metal halide<sup>17</sup>



and the oxidation method developed here (reaction 1), which holds some distinct advantages over the others. The tricarbonyl thiolate starting material is rapidly prepared<sup>18</sup> by visible-light photolysis of  $[\text{CpW}(\text{CO})_3]_2$  and diphenyl disulfide in degassed toluene. The oxidizing agent MCPBA is an air-stable, easily measured solid that is added directly to a solution of the tungsten tricarbonyl thiolate. Additional amounts of MCPBA can be added as necessary to drive the reaction to completion. Contrast this with the other reactions, some of which require additional steps to synthesize the metal carbonyl starting materials. Sulfur dioxide requires prior distillation before reaction, and methanesulfonyl chloride is moisture sensitive and thus requires rigorous experimental conditions.

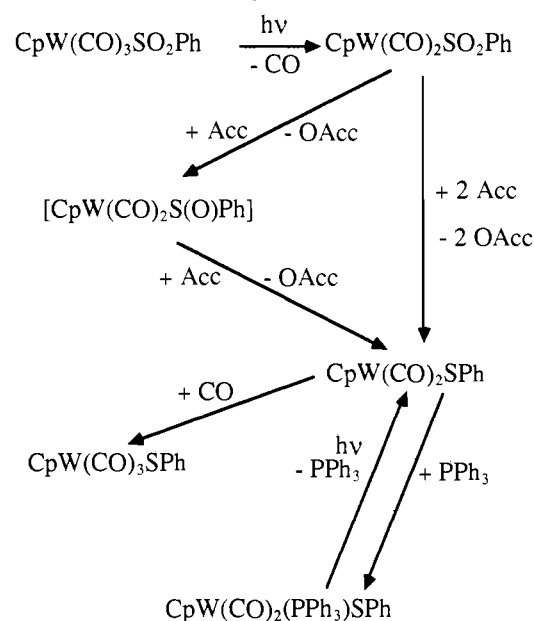
**Reactions of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$ .**  $\text{CpMo}(\text{CO})_3\text{SO}_2\text{CH}_2\text{Ph}$  loses  $\text{SO}_2$  when irradiated in benzene solution<sup>8</sup> to give a 35% yield of  $\text{CpMo}(\text{CO})_3\text{CH}_2\text{Ph}$ . In contrast, we find that irradiation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  in  $\text{CH}_2\text{Cl}_2$  gives no evidence for loss of sulfur dioxide. These findings may indicate that aryl migration is less favorable than alkyl migration when sulfinato compounds are irradiated in solution. However, an alternate explanation may involve differences in the reactivity of molybdenum compared to tungsten.  $\text{CpW}(\text{CO})_3\text{Me}$  does not readily insert sulfur dioxide to form  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Me}$ , but the corresponding molybdenum compound undergoes sulfur dioxide insertion with remarkable ease.<sup>8</sup> If the ability to lose  $\text{SO}_2$  follows the same trend, then tungsten sulfinato complexes would be less likely to lose sulfur dioxide during irradiation than molybdenum sulfinato complexes.

The major products from UV irradiation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  are a tan precipitate and a blue-gray precipitate, neither of which contains carbonyl ligands. Comparison of the IR spectrum of these precipitates (in KBr) to authentic IR spectra (KBr) of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  and of the tan precipitate formed by prolonged photolysis of  $\text{CpW}(\text{CO})_3\text{SPh}$ <sup>10</sup> demonstrates new peaks at 970 and 815  $\text{cm}^{-1}$ , which fall in the correct region for tungsten-oxo complexes.<sup>19</sup> The only soluble product is  $\text{CpW}(\text{CO})_3\text{SPh}$  as indicated by IR and <sup>1</sup>H NMR spectra. One possible mechanism for the formation of  $\text{CpW}(\text{CO})_3\text{SPh}$  and the precipitates that contain oxo ligands involves photoproducted coordinatively unsaturated tungsten intermediates acting as oxygen acceptors in a fashion similar to that described below.

Since these irradiations of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  in  $\text{CH}_2\text{Cl}_2$  imply that carbonyl loss is the major photoprocess, photoreaction with triphenylphosphine might be an efficient method for synthesizing phosphine-substituted sulfinato-S compounds. However, the only metal-sulfur species formed by UV irradiation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  in the presence of  $\text{PPh}_3$  is *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SPh}$  (reaction 2). The small amount of tricarbonyl thiolate formed during prolonged irradiation is most likely due to a secondary photoreaction of  $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SR}$  with free CO liberated by irradiation of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$ . The tricarbonyl is only observed

## Scheme I

(Acc = oxygen acceptor, e.g.  $\text{CpW}(\text{CO})_2\text{SO}_2\text{Ph}$ )



during long irradiations of solutions in capped NMR tubes; the concentration of CO must therefore be fairly large before an observable amount of secondary photoproduct is formed. Photochemical lability of  $\text{PPh}_3$  ligands in phosphine-substituted tungsten carbonyl compounds has been established.<sup>20,21</sup>

Observation of nonoxidized *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SPh}$  as the major product indicates that the sulfinato ligand is transformed into a thiolate ligand in the course of the reaction. Although it is tempting to suggest that the formation of a phosphorus-oxygen bond in  $\text{OPPh}_3$  is the sole driving force for the reaction, the observation of less  $\text{OPPh}_3$  than *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{STol}$  in the <sup>31</sup>P NMR spectrum (based upon the relative intensities of their singlets) indicates that  $\text{PPh}_3$  is not the only species accepting oxygen from the sulfinato ligand. The presence of infrared bands consistent with tungsten-oxo groups in precipitates formed here also suggests the participation of unsaturated tungsten compounds as oxygen acceptors, even in the presence of  $\text{PPh}_3$ .

Two mechanisms may be postulated, and either Scheme I alone, or both simultaneously, may be operating during the reaction. Scheme I assumes that an oxygen acceptor is able to cleave the sulfur-oxygen bonds of a sulfinato-S ligand. Triphenylphosphine is a very good oxygenophile but shows no reaction without photolysis. Another species that can act as an oxygen acceptor is the unsaturated intermediate that results from carbonyl loss in a photochemically activated  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  molecule. The formation of a tungsten-oxygen bond is thermodynamically favorable, as evidenced by the large number of tungsten-oxo compounds,<sup>22</sup> and the presence of peaks at 970 and 815  $\text{cm}^{-1}$  in infrared spectra of the insoluble precipitates may be evidence of their formation during the reaction. The final product, *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SR}$ , then arises from a ligation reaction of the intermediate  $\text{CpW}(\text{CO})_2\text{SR}$ . Note that UV irradiation of  $\text{CpW}(\text{CO})_3\text{SR}$  ( $\text{R} = \text{Ph}, \text{Tol}$ ) and  $\text{PPh}_3$  in toluene readily produces this substitution with similar stereospecificity.<sup>10</sup> Because  $\text{CpW}(\text{CO})_3\text{SR}$  is not observed at short irradiation times, oxygen loss from intact  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  is unlikely. The details of the abstraction event are obscured by the rapidity of the reaction and may involve either inter- or intramolecular attack of empty tungsten coordination sites on sulfur-bound oxygen atoms. We have little confidence in the stability of an intermediate containing

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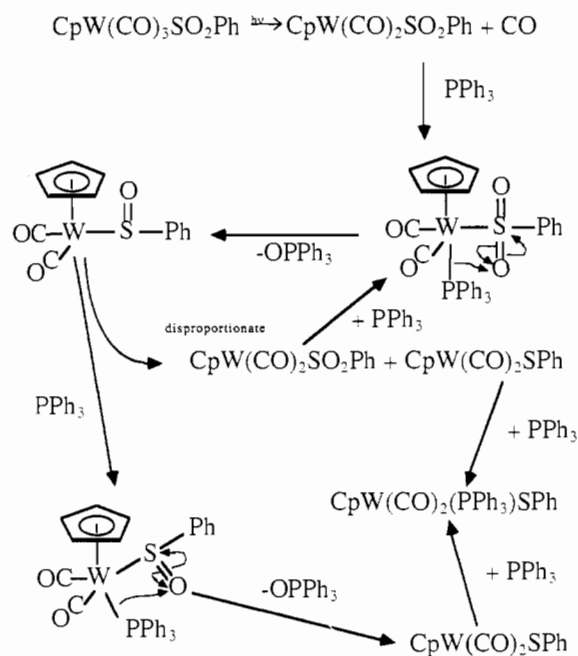
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Scheme II



the S(O)R groups (see below) so the loss of both oxygens may occur in a single step.

The second mechanism (Scheme II) is also based upon the loss of a carbonyl ligand from a photochemically excited  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$  molecule. The unsaturated intermediate then coordinates free  $\text{PPh}_3$ , which abstracts oxygen from the sulfinate ligand in an intramolecular reaction to form a sulfenato intermediate. This can occur again and, having transformed the sulfenato ligand to a thiolate ligand, a third molecule of  $\text{PPh}_3$  can add to yield the final product. An alternative path involves disproportionation of the sulfenato intermediate. However, Scheme II represents at most a minor path, owing to the deficiency of  $\text{OPPh}_3$  produced.

**Other Attempts To Form Sulfenato Ligands.** We have attempted by other means to generate a tungsten-bound S(O)R group. The thiolate-bridged dimers  $[\text{CpW}(\text{CO})_2\text{SR}]_2$  generated by thermolysis or photolysis of the tricarbonyls<sup>10</sup> are potential precursors to a singly oxidized product, since an additional thiolate lone pair is tied up in forming the bridge. Unfortunately, only decomposition is observed when these dimers are oxidized, either because the bridge is disrupted by the MCPBA oxidant or because sulfenato ligands in these complexes are inherently unstable and disproportionate. (Disproportionation products would be coordinatively unsaturated as a consequence of bridge disruption and thus be susceptible to decomposition.)

Another method is to attempt the monooxidation of  $\text{CpW}(\text{CO})_3\text{SPh}$  with  $\text{SeO}_2$ , which is used as a reagent for the oxidation of sulfur in organic compounds.<sup>23</sup> The reaction, however, yields only a precipitate that was similar to the tan precipitate observed when  $\text{CpW}(\text{CO})_3\text{STol}$  is reacted with a large excess of MCPBA (see note in Experimental Section: Reaction of MCPBA...). Due to the inherent difficulties that accompany the use of selenium dioxide as an oxidizing reagent<sup>24</sup> (i.e., the limited solubility in nonprotic solvents, the toxicity of the metallic Se that arises during oxidation reactions, and the complicated reaction scheme required to remove unreacted  $\text{SeO}_2$ ), no further work with this particular reagent was conducted.

The third method attempted for synthesizing sulfenato ligands involves reacting methanesulfinyl chloride with  $[\text{CpW}(\text{CO})_3]^-$ . Reactions between  $[\text{CpW}(\text{CO})_3]^-$  and acyl halides yield  $\text{CpW}(\text{CO})_3\text{C}(\text{O})\text{R}$  compounds.<sup>25,26</sup> If the nucleophilic ability of the

tungsten tricarbonyl anion could be utilized to attack an alkane-sulfinyl chloride in a similar fashion, then this could lead to a general method for the synthesis of sulfenato ( $-\text{S}(\text{O})-\text{R}$ ) compounds. However, the reaction between tungsten tricarbonyl anion and methanesulfinyl chloride does not lead to the desired sulfenato compound but instead to a variety of other products. Since the major product formed was  $[\text{CpW}(\text{CO})_3]_2$ , we conclude that  $\text{MeS}(\text{O})\text{Cl}$  is a strong enough oxidizer to cause rapid single electron oxidation of the anion to the radical  $[\text{CpW}(\text{CO})_3]^\cdot$ . Although altering the reaction by adding the methanesulfinyl chloride to the tungsten tricarbonyl anion solution may have resulted in the desired sulfenato complex via a displacement reaction, any sulfenato compound formed would find itself in a strongly reducing environment (the tungsten anion solution) and most likely be reduced to the thiolate compound.

## Conclusions

In our search for new examples of sulfur monoxide complexes<sup>6</sup> of transition metals we have attempted to synthesize new alkane- and arenesulfenato  $[-\text{S}(\text{O})\text{R}]$  complexes via two routes. The reaction of oxidizing agents with thiolate ( $-\text{SR}$ ) complexes yields only sulfinate  $[-\text{S}(\text{O})_2\text{R}]$  complexes or complete decomposition to non-carbonyl-containing products. The alternate method attempted, reaction of  $[\text{CpW}(\text{CO})_3]^-$  with methanesulfinyl chloride, does not proceed as a nucleophilic substitution reaction; instead, the tungsten anion is transformed into the corresponding radical species, and the desired sulfenato product is not obtained.

Ultraviolet photolysis of  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Ph}$  in solution demonstrates that aryl migration and loss of sulfur dioxide is not a pathway available for relaxation of the photochemically excited arenesulfinate-S compounds of tungsten, even after dissociation of a carbonyl ligand. Interestingly, the same product *cis*- $\text{CpW}(\text{CO})_2(\text{PPh}_3)\text{SR}$  arises from both the photochemical reaction of  $\text{PPh}_3$  with  $\text{CpW}(\text{CO})_3\text{SR}$ <sup>10</sup> and the photochemical reaction of  $\text{PPh}_3$  with  $\text{CpW}(\text{CO})_3\text{SO}_2\text{R}$ . This similarity arises because of the strong thermodynamic driving force, obtained from the formation of the tungsten-oxygen bond in a tungsten-oxo complex or from the formation of the oxygen-phosphorus bond in  $\text{OPPh}_3$ , that drives the transformation of a sulfinate-S ligand to a thiolate ligand.

## Experimental Section

**Materials and Equipment.** Hexane was purified by washing with concentrated sulfuric acid, followed by water and aqueous  $\text{NaHCO}_3$ , 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. The compounds MCPBA,  $\text{PPh}_3$ ,  $\text{OPPh}_3$ ,  $\text{SeO}_2$ ,  $\text{C}_6\text{D}_6$ ,  $\text{CDCl}_3$ , and anhydrous  $\text{NH}_3$  were obtained commercially and used without further purification.  $\text{CpW}(\text{CO})_3\text{SPh}$  and  $\text{CpW}(\text{CO})_3\text{STol}$  were prepared by photolysis of  $[\text{CpW}(\text{CO})_3]_2$  and the corresponding disulfide,<sup>10</sup> while all other tungsten thiolate compounds were a gift from Dr. K. L. Brandenburg. The  $[\text{CpW}(\text{CO})_3]^-$  was prepared by the method of King.<sup>27</sup>  $[\text{CpW}(\text{CO})_3]_2$  was prepared via  $\text{CpW}(\text{CO})_3\text{CH}_2\text{Ph}$ .<sup>28</sup> The methanesulfinyl chloride was a gift from Richard Vanderpool and purified prior to use by trap-to-trap distillation on a high-vacuum line operating at  $10^{-6}$  Torr. Impure  $\text{MeSOCl}$  was cooled to 0 °C and vacuum distilled into a  $-78$  °C trap, while lower boiling impurities such as  $\text{MeSO}_2\text{Cl}$  were collected in a liquid-nitrogen-cooled trap.

Infrared spectra were obtained by using a Nicolet MX-5 FT instrument. The  $^1\text{H}$  NMR spectra were recorded at 90 MHz on a Varian EM-390 in  $\text{CDCl}_3$ , while  $^{31}\text{P}$  NMR spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.2 MHz. Broad-band irradiation was used to decouple protons. These spectra were recorded in  $\text{CDCl}_3$  and referenced to 1%  $\text{H}_3\text{PO}_4$  (0.0 ppm) as an external reference by using the concentric-tube method. A low field positive convention was used in

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reporting data. An observed frequency of 59.65 kHz and a spectral width of 10000 Hz were used. All UV irradiations were performed using a U-V Products XX-15 broad-band near-UV (black-light) source and an aluminum foil tent.

**Synthesis of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph.** After 0.12 g (0.60 mmol) of MCPBA (85% active/wt) was added to a methylene chloride solution containing 0.13 g (0.30 mmol) of CpW(CO)<sub>3</sub>SPh<sup>10</sup> and the mixture stirred moderately for 1 h, IR analysis of an aliquot of the reaction solution indicated that not all of the CpW(CO)<sub>3</sub>SPh had reacted. Approximately 15–20 mg of MCPBA was added and the solution was allowed to stir for 15 min, by which time the reaction was complete (by IR).

To remove unreacted MCPBA and the reaction byproduct *m*-chlorobenzoic acid, anhydrous ammonia was bubbled into the solution by use of a wide-bore syringe needle until precipitate formation was complete (15–20 min). (Note: Do *not* use a fritted-glass bubbler because the precipitate will clog the bubbler and cause pressure buildup.) The precipitate was filtered through a coarse sintered-glass funnel and then through a fine-porosity frit to remove the precipitate, which was discarded. The filtrate was then vigorously flushed with nitrogen gas until all dissolved ammonia was removed from solution. Recrystallization from methylene chloride/hexane yielded pure microcrystals of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph (0.13 g, 0.27 mmol, 93% yield).<sup>9</sup> IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> 2048, 1960 cm<sup>-1</sup>. IR (KBr): ν<sub>SO</sub> 1204, 1053, 594, 559 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ(Cp) = 5.83, δ(Ph) = 7.70 (m). Mp: 145–148 °C dec. Anal. Calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>S: C, 35.47; H, 2.13; S, 6.76. Found: C, 35.42; H, 2.06; S, 6.68. Electronic spectrum (toluene) [λ, nm (ε)]: 401 (6.68); 297 (9300).

**Synthesis of CpW(CO)<sub>3</sub>SO<sub>2</sub>Tol.** When 66 mg (0.15 mmol) of CpW(CO)<sub>3</sub>STol<sup>10</sup> was reacted with 60 mg (0.30 mmol) of MCPBA in a solution of CH<sub>2</sub>Cl<sub>2</sub>, CpW(CO)<sub>3</sub>SO<sub>2</sub>Tol was produced. After ammonia was bubbled through the solution and the ammonium salts were filtered out, rotary evaporation of the CH<sub>2</sub>Cl<sub>2</sub> solution yielded a yellow powder of CpW(CO)<sub>3</sub>SO<sub>2</sub>Tol (69 mg, 0.14 mmol, 98% yield). IR (CHCl<sub>3</sub>): ν<sub>CO</sub> 2049, 1962 cm<sup>-1</sup>. IR (KBr): ν<sub>SO</sub> 1202, 1044, 637, 577 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ(Cp) = 5.87; *p*-tolyl δ(Me) = 2.36, δ(aryl) ~ 7.37 (m).

**Synthesis of *trans*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SO<sub>2</sub>Tol.** A methylene chloride solution of MCPBA was added dropwise with stirring to a solution of CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol,<sup>10</sup> producing a gradual change in solution color from orange to yellow. (This slow addition is required to minimize the concentration of MCPBA and thus limit the formation of OPPh<sub>3</sub>.) Comparison of an IR spectrum of the product in KBr, after treatment with NH<sub>3</sub>, to an IR spectrum of CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol in KBr demonstrated the presence of new peaks at 1190, 1181, 1119, 1038, 721, 633, and 577 cm<sup>-1</sup>. Comparison of these frequencies to an authentic IR spectrum of OPPh<sub>3</sub> indicated the presence of triphenylphosphine oxide (1190, 1119, and 721 cm<sup>-1</sup>). The remaining product was washed twice with methanol to extract the OPPh<sub>3</sub>, and another IR spectrum in KBr was taken. The spectrum of the purified solid product exhibited new peaks at 1176, 1035, 637, and 576 cm<sup>-1</sup>, confirming the presence of a sulfinate ligand.

When this reaction was repeated in a 10-mm NMR tube, a <sup>31</sup>P NMR spectrum of the reaction solution exhibited a singlet at 31.4 ppm with two satellites (*J*<sub>P-W</sub> = 208 Hz) and a singlet that corresponded to OPPh<sub>3</sub>. <sup>1</sup>H NMR indicated the presence of a single Cp resonance at 5.37 ppm (d), and an IR spectrum of the product in CDCl<sub>3</sub> exhibited two ν<sub>CO</sub> peaks (1971 (s), 1888 (vs) cm<sup>-1</sup>). [IR: see above. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (*trans* isomer only): δ(Cp) = 5.37 (d, *J*<sub>P-H</sub> = 2.0 Hz); δ (Me) = 2.43, δ(aryl) ~ 7.3 (m). <sup>31</sup>P NMR (CDCl<sub>3</sub>): see above.]

**Reaction of MCPBA with Other (η<sup>5</sup>-Cyclopentadienyl)tungsten Carbonyl Thiolate Compounds.** In all other cases, a methylene chloride solution of the thiolate (5 mg) was reacted with MCPBA (10 mg) in a small test tube. If the color of the solution did not change to a light yellow after thorough mixing of the solution, a small amount of additional MCPBA was added until the reaction was complete. (Note: Care was exercised to ensure that a large excess of MCPBA was not added to the solution because a reaction monitored by <sup>1</sup>H NMR indicated complete decomposition of the thiolate (CpW(CO)<sub>3</sub>STol) to a tan precipitate, upon addition of large amounts of MCPBA.) After the reaction was complete, an aliquot of the solution was transferred to an IR cell and a carbonyl-region spectrum taken (Table I).

**Photolysis of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph.** When a degassed CH<sub>2</sub>Cl<sub>2</sub> solution of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph was irradiated with broad-band UV light in an amalgam-sealed IR cell, periodic monitoring (1-min intervals) of the solution by IR spectroscopy indicated rapid disappearance of the ν<sub>CO</sub> bands of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph but only a slow growth of ν<sub>CO</sub> bands at 2031 cm<sup>-1</sup> and a small shoulder on the low-energy side of the CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph peak at 1959 cm<sup>-1</sup>. Subtraction of an IR spectrum of an authentic sample of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph from the spectrum of this reaction mixture indicated two new peaks at 2031 and 1935 cm<sup>-1</sup>. These values are similar to the carbonyl stretching frequencies of CpW(CO)<sub>3</sub>SPh.<sup>10</sup>

The gases released during irradiation of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph in degassed CH<sub>2</sub>Cl<sub>2</sub> were vacuum-transferred to a gas IR cell. An IR spectrum of the gases indicated the presence of carbon monoxide and CH<sub>2</sub>Cl<sub>2</sub> vapor.

When 25 mg (0.05 mmol) of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph in degassed CDCl<sub>3</sub> was irradiated by broad-band UV light, periodic monitoring of the solution by <sup>1</sup>H NMR indicated a decrease of the intensity of the cyclopentadienyl resonance of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph and slow increase of a new Cp resonance at δ 5.67 (CpW(CO)<sub>3</sub>SPh).<sup>10</sup> Visual inspection of the NMR tube after irradiation indicated significant amounts of a tan precipitate and a gray-blue precipitate. An IR spectrum of this precipitate mixture in KBr was devoid of bands in the carbonyl region (2200–1700 cm<sup>-1</sup>), but two distinct bands were observed at 970 and 815 cm<sup>-1</sup>. These bands are best attributed to W=O stretching modes as determined by comparison to KBr spectra of several tungsten oxides.<sup>19</sup>

**Reaction of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph and Triphenylphosphine.** When a degassed chloroform solution of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph and PPh<sub>3</sub> was irradiated by broad-band UV light in an amalgam-sealed cell and monitored by IR spectroscopy, disappearance of the ν<sub>CO</sub> bands of CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph was accompanied by the appearance of ν<sub>CO</sub> bands that correspond to CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SPh.<sup>10</sup> Two strong peaks at 1182 and 1122 cm<sup>-1</sup> indicated the presence of OPPh<sub>3</sub>. Monitoring the reaction by <sup>1</sup>H NMR spectroscopy indicated the stereospecific formation of *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SPh<sup>10</sup> (δ(Cp) = 5.43; CDCl<sub>3</sub>); however, prolonged irradiation resulted in trace amounts (10%) of CpW(CO)<sub>3</sub>SPh<sup>10</sup> (δ(Cp) = 5.65, δ(Ph) = 7.23 (m); CDCl<sub>3</sub>).

Repeating this experiment by using a 1:1 ratio of PPh<sub>3</sub> and CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph in the absence of light and monitoring by <sup>1</sup>H NMR spectroscopy over a 9-h period indicated that no reaction was occurring. UV irradiation of this solution directly in the sealed NMR tube over a 45-min period resulted in a series of color changes from the original yellow to orange to dark brown. A <sup>1</sup>H NMR spectrum of the solution after 45 min of irradiation exhibited three strong Cp resonances at 5.83, 5.67, and 5.43 ppm, corresponding to CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph, CpW(CO)<sub>3</sub>SPh, and *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)SPh, respectively. An IR spectrum of this solution contained ν<sub>CO</sub> peaks at 2048, 2033, 1960 (br), and 1867 cm<sup>-1</sup>, verifying the presence of these three compounds. Strong peaks at 1224, 1184, 1120, and 1060 cm<sup>-1</sup> belong to the compounds CpW(CO)<sub>3</sub>SO<sub>2</sub>Ph and OPPh<sub>3</sub>, as determined by comparison to authentic spectra.

In order to determine the amount of OPPh<sub>3</sub> formed during this reaction, a degassed CDCl<sub>3</sub> solution of CpW(CO)<sub>3</sub>SO<sub>2</sub>Tol and excess PPh<sub>3</sub> was irradiated by broad-band UV light for 30 min in a septum-sealed 10-mm NMR tube. After completion of the irradiation, the solution color had changed from yellow-orange to a dark brown. A <sup>31</sup>P NMR spectrum of the solution indicated the presence of unreacted PPh<sub>3</sub> (–5.53 ppm), OPPh<sub>3</sub> (+29.2 ppm), and a singlet for *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol<sup>10</sup> at 28.5 ppm with two satellites (*J*<sub>P-W</sub> = 240 Hz). This corresponds to the previously determined chemical shift of *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol.<sup>10</sup> An IR spectrum of the reaction mixture confirmed the presence of CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol along with unreacted CpW(CO)<sub>3</sub>SO<sub>2</sub>Tol and a trace amount of CpW(CO)<sub>3</sub>STol.

Analysis of the relative intensities of the <sup>31</sup>P NMR peaks for the OPPh<sub>3</sub> and *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol indicated formation of less than a stoichiometric amount of OPPh<sub>3</sub>. Comparison of the peak intensity for the singlet of *cis*-CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)STol to the intensity of the original starting material also indicated that the reaction had not been quantitative. Careful inspection of the dark brown NMR solution indicated that microfine particles of a precipitate had also been produced during the reaction. Analysis of this dark gray precipitate using IR spectroscopy in KBr demonstrated that there were no bands in the carbonyl region and that two strong bands (970, 815 cm<sup>-1</sup>) were in the correct region to be assigned to oxo ligands.<sup>19</sup>

**Reaction of [CpW(CO)<sub>3</sub>]<sup>-</sup> and Methanesulfinyl Chloride.** The compound [CpW(CO)<sub>3</sub>]<sup>-</sup> was prepared<sup>27</sup> from a THF solution of [CpW(CO)<sub>3</sub>]<sub>2</sub> (0.1668 g, 0.25 mmol) and 1% sodium/mercury amalgam (0.5 mL, 2.94 mmol). With assurance that no Hg was removed and still under complete absence of light, addition of the [CpW(CO)<sub>3</sub>]<sup>-</sup> solution by cannula over a 3-h period to 25 mL of a degassed THF solution of MeS(O)Cl (36 μL, 0.5 mmol), which was stirred moderately and maintained at –78 °C, resulted in a dark orange solution. This was allowed to warm to room temperature, and an IR spectrum indicated that the reaction solution contained the following carbonyl-containing products: [CpW(CO)<sub>3</sub>]<sub>2</sub>, CpW(CO)<sub>3</sub>SMe, and a third compound with peaks of 2048 and 1954 cm<sup>-1</sup> (likely CpW(CO)<sub>3</sub>SO<sub>2</sub>Me (Table I) or CpW(CO)<sub>3</sub>Cl<sup>29</sup>). The solid that resulted from rotary evaporation of the THF

(29) An authentic sample was prepared by UV irradiation of [CpW(CO)<sub>3</sub>]<sub>2</sub> in CCl<sub>4</sub><sup>30</sup> and then rotary evaporated. Spectral data of the resulting product: IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>CO</sub> 2049, 1956 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ(Cp) 5.75.

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solution was dissolved in  $\text{CDCl}_3$ . The Cp resonance positions and peak intensities in the  $^1\text{H}$  NMR spectrum showed that the products arising from the reaction of tungsten tricarbonyl anion and methanesulfinyl chloride are  $[\text{CpW}(\text{CO})_3]_2$  (50%),  $\text{CpW}(\text{CO})_3\text{SMe}$  (40%),  $\text{CpW}(\text{CO})_3\text{Cl}$  (7%), and  $\text{CpW}(\text{CO})_3\text{SO}_2\text{Me}$  (3%) (relative amounts from  $^1\text{H}$  NMR analysis in parentheses).

**Acknowledgment.** The support of the donors to the Petroleum Research Fund, administered by the American Chemical Society,

is gratefully acknowledged. Exploratory work, some of which was done by M. L. Freeman, was also supported by the Research Corp. We thank Dr. K. L. Brandenburg for samples of some  $\text{CpW}(\text{CO})_3\text{SR}$  compounds and Dr. R. A. Vanderpool for the  $\text{MeSOCl}$ .

**Supplementary Material Available:** A table of infrared frequencies associated with various sulfur–oxygen ligands in metal complexes used to compile Figure 1 (8 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of Encapsulated Cobalt(III) Hydroxylamine Complexes

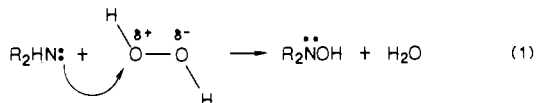
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Received November 21, 1986

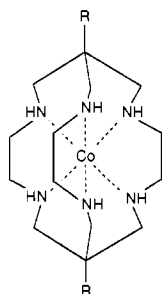
On treatment of two Co(III) cage complexes with  $\text{H}_2\text{O}_2$  in basic solution, up to three coordinated N sites were oxidized to hydroxylamine groups. The complexes isolated and characterized were [(1,8-dinitro-3-hydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dinitro-3,10,16-trihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dinitro-3,13,16-trihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), [(1,8-dichloro-3-hydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+), and [(1,8-dinitro-3,10-dihydroxy-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(III)](3+). For the last of these complexes, the type and sites of oxidation were established by an X-ray structure determination (orthorhombic, space group  $P2_12_12_1$ , with  $a = 16.414$  (5) Å,  $b = 15.122$  (7) Å,  $c = 9.624$  (3) Å,  $Z = 4$ , 1759 reflections,  $R = 0.059$ ). The hydroxylamine groups are rather acidic ( $\text{p}K_a$  2.8–6), and deprotonation leads to a profound change in redox potential ( $\sim -0.5$  V). Reduction back to the secondary amine is not a fast process with one-electron reagents.  $\text{V}^{2+}(\text{aq})$ , however, instantly reduces the hydroxylamine back to the coordinated secondary amine by oxygen atom transfer to  $\text{V}^{2+}(\text{aq})$  generating directly  $\text{VO}^{2+}(\text{aq})$  ion.

### Introduction

Secondary alkylamines are readily oxidized to hydroxylamines by hydrogen peroxide in aqueous solution,<sup>2</sup> but yields of hydroxylamines are usually low due to further oxidation. The mechanism involves attack by the electrophilic peroxidic oxygen on the free amine by direct atom transfer (eq 1). When the amine



is coordinated to Co(III), this mechanism is not feasible unless the amine is deprotonated first. In most cases, coordinated amines are too basic ( $\text{p}K_a > 14$ ) to deprotonate readily in aqueous solution, but for some cage complexes with electronegative substituents on the caps (I) the  $\text{p}K_a$ 's are considerably less ( $\text{p}K_a = 9.87$  for



I.  $\text{R} = \text{NO}_2, \text{Cl}$

$[\text{Co}(\text{dinosar})]^{3+}$ , and  $\text{p}K_a = 10.36$  for  $[\text{Co}(\text{dichlosar})]^{3+}$  at 25 °C and  $\mu = 1.0$  M;<sup>3</sup> dinosar = ligand in I with  $\text{R} = \text{NO}_2$ ; dichlosar

= ligand in I with  $\text{R} = \text{Cl}$ ). This property renders them more susceptible to attack by  $\text{H}_2\text{O}_2$  in basic solutions, and this paper records the results of such reactions.

### Experimental Section

$^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR spectra were obtained with a JEOL JNM-FX-200 spectrometer using  $\text{D}_2\text{SO}_4\text{-D}_2\text{O}$  solutions ( $\text{pD} \sim 1.5$ ) and dioxane as a reference. Electronic spectra were recorded with a Hewlett-Packard 8450A UV/vis spectrophotometer using 0.1 M HCl and a pH 8.2, 0.05 M Tris/ $\text{HClO}_4$  buffer.  $\text{p}K_a$ 's were obtained by potentiometric titrations at  $\mu = 0.1$  and 25 °C with an Action 108 pH meter and an Orion Ross combination electrode. The computer program MINQUAD<sup>4</sup> was used for the calculations. Cyclic voltammetry measurements were performed with a three-electrode  $iR$ -compensated system having a Pt auxiliary electrode and a PAR Model 170 electrochemistry system together with an EG&G Model 303 mercury electrode in the HMDE mode vs. a saturated calomel electrode (SCE) and with a BAS-100 electrochemical analyzer with a glassy-carbon electrode vs. a  $\text{Ag}/\text{AgCl}$ , saturated NaCl electrode.

**Reaction of  $[\text{Co}(\text{dinosar})]^{3+}$  with  $\text{H}_2\text{O}_2$  in Basic Solution.**  $[\text{Co}(\text{dinosar})]\text{Cl}_3$  (25 g,  $4.5 \times 10^{-2}$  mol) was dissolved in water ( $\sim 1$  L). NaOH solution (130 mL of a 1 M solution) was added followed by 30%  $\text{H}_2\text{O}_2$  (40 mL, 0.46 mol). The mixture was left at 20 °C for 1 h and absorbed on a Dowex 50W-X2 cation-exchange column, and the column was washed with  $\text{H}_2\text{O}$  and eluted with 1 M HCl to remove  $\text{Na}^+$ . This was followed by 3 M HCl to elute the complexes. The eluate was taken down to dryness on a vacuum evaporator and the solid dissolved in water and absorbed on a SP Sephadex C-25 cation-exchange column. On elution with 0.3 M  $\text{NaH}_2\text{PO}_4$  three orange bands (A small, B large, C small) separated. Each fraction was collected, and the complexes were isolated from Dowex 50W-X2 columns after elution with 1 M HCl to remove  $\text{Na}^+$  and then with 3 M HCl and evaporation of the solvent. When band B (yield 40%) was resorbed on Dowex 50W-X2 resin and eluted with dilute  $\text{NH}_3$ , a band separated and was isolated via Dowex 50W-X2. On sorption on Dowex 1-X8 anion-exchange resin and elution with dilute  $\text{NH}_3$  the band moved through the column. This suggested a neutral charge of the complex in the basic medium. A similar treatment of band

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