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Oxidative Addition of Thiols, Disulfides, Iodine, and Hydrogen Iodide to $W(CO)_3(P^iPr_3)_2$. Preparation of Stable 17-Electron Tungsten Thiolate Radicals from Complexes with Weak W–H Bonds

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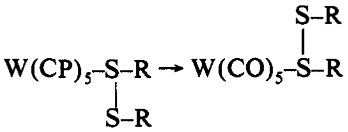
Activation of hydrogen by metals is observed to occur in several types of complexes: "even" systems that form molecular hydrogen and dihydride complexes[1] and "odd" systems involving radicals and H atom transfer,[2] as well as "ligand" based activation such as that shown by Rakowski-Dubois for addition of H_2 to coordinated disulfides.[3] Understanding these different types of reactions from kinetic and thermodynamic points of view may allow their utilization in design of systems that combine their features. In spite of the importance of metal sulfido complexes to industrial[4] and biological[5] catalytic processes, there are few thermochemical data available for metal/sulfur/hydrogen systems.

Disulfides and thiols can react with metal complexes in different ways depending on the metal, ligand environment, and conditions. As part of calorimetric studies of group VI complexes with sulfur-containing ligands, we recently investigated[6] oxidative addition of disulfides to complexes such as that shown in eq 1 below:

$$\mathrm{W(CO)_3(phen)(EtCN) + RSSR \rightarrow W(CO)_2(phen)(SR)_2 + CO + EtCN} \quad (1)$$

This is in contrast to work of Abel and co-workers[7] on a similar system where coordinated disulfide complexes are stable and undergo fluxional rearrangements:



$$\mathrm{W(CP)_5{-}\underset{\substack{|\\ S-R}}{S}{-}R \rightarrow W(CO)_5{-}\overset{\substack{S-R\\ |}}{S}{-}R} \quad (2)$$

The different behavior of the two W(0) fragments, $W(CO)_5$ and $W(CO)_3(phen)$, prompted this investigation. Addition of organic disulfides to a solution of $W(CO)_3(P^iPr_3)_2$ results in rapid and quantitative generation of an unexpected product—intensely colored solutions of stable 17-electron radicals:[8]

$$\mathrm{W(CO)_3(P^iPr_3)_2 + {}^1/_2RSSR \rightarrow {}^\bullet W(CO)_3(P^iPr_3)_2(SR)} \quad (3)$$

Darensbourg, Krusic, and co-workers have reported ESR spectra of electrochemically generated $Cr(CO)_5(SR)$ radicals, but these radicals were unstable at room temperature.[9] The crystal structure of the radical complex $CpMn(CO)_2(SPh)$ has recently been reported.[10]

The enthalpy of reaction 3 was measured for R = Ph [$\Delta H = -18.9 \pm 1.2$ kcal/mol in toluene solution] and allows estimation of the W–SPh bond strength. Using a value of 41 kcal/mol for D(PhS–SPh) leads directly to a value of 39.4 kcal/mol for $D((P^iPr_3)_2(CO)_3W{-}SPh)$.[11] The important implication of this result is that reaction of the sterically crowded W(0) complex to generate the W(I) radical and a free SPh radical as shown in eq 4 should be nearly thermoneutral:

$$\mathrm{W(P^iPr_3)_2(CO)_3 + PhSSPh \rightarrow {}^\bullet W(P^iPr_3)_2(CO)_3(SPh) + {}^\bullet SPh} \quad (4)$$

The rapid nature of this reaction, the thermochemical argument described above, and radical trapping experiments[12] support the conclusion that the first step of the reaction results in generation of the W(I) radical as well as a free thiyl radical. These results show that the nature of the reaction product of PhSSPh with W(0) depends strongly on the ancillary ligands as shown in eq 1–3.

Attempts to grow suitable crystals of the sulfur based radicals were unsuccessful. However, analogous products result from iodination:

$$\mathrm{W(CO)_3(P^iPr_3)_2 + {}^1/_2I_2 \rightarrow {}^\bullet W(CO)_3(P^iP_3)_2(I)} \quad (5)$$

ESR studies[12] confirm the radical nature of the products of oxidation by disulfides and iodine. An X-ray crystal structure[13] of the stable W(I) iodo radical is shown in Figure 1. The key points regarding the crystal structure are the nearly octahedral geometry of the bulky radical and the failure to observe any dinuclear interactions in the solid state. To the authors' knowledge, this is the first structural determination of a stable W(I) radical species.

The radical complexes can also be prepared by H atom abstraction from parent hydrido compounds. Thiols undergo rapid oxidative addition to produce thiolate hydrides as shown in eq 6:

$$\mathrm{W(CO)_3(P^iP_3)_2 + RSH \rightarrow W(CO)_3(P^iPr_3)_2(SR)(H)} \quad (6)$$

Yellow solutions of the thiolate hydrides are formed within the time of mixing of the thiols and $W(CO)_3(P^iPr_3)_2$. Spectroscopic data are given in Table 1. For thiophenol, the enthalpy of reaction 6, -17.6 ± 1.8 kcal/mol, can be used in a thermochemical cycle[14] to calculate $D((P^iPr_3)_2(CO)_3(SPh)W{-}H) = 53.2$ kcal/mol. This result indicates that the W–H bond is even weaker than that for the first row complex $H{-}Cr(CO)_2(PPh_3)Cp$, where $D(Cr{-}H) = 59.8$ kcal/mol.[2b] In keeping with this thermochemical prediction, the chromium radical rapidly abstracts a hydrogen atom from

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(1) (a) For an excellent series of review articles, see: *Transition Metal Hydrides*; Dedieu, A., Ed., VCH Publishers: New York, 1992. (b) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (c) Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S. J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Amer. Chem. Soc.* **1991**, *113*, 9170.

(2) (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Amer. Chem. Soc.* **1990**, *112*, 5657.

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(6) Lang, R. F.; Ju, T.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. K., *Inorg. Chem.*, in press.

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(8) A short synthetic description and a table of selected FTIR and NMR data for the complexes $W(CO)_3(P^iPr_3)_2(X)$ and $W(CO)_3(P^iPr_3)_2(H)(X)$ (X = SPh, S-*p*-tolyl, SMe, S-benzyl, I) is available as supplementary material.

(9) Springs, J.; Janzen, C. P.; Darensbourg, M. Y.; Calabrese, J. C.; Krusic, P. J.; Verpeaux, J. N.; Amatore, C. *J. Amer. Chem. Soc.* **1990**, *112*, 5789.

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(11) The value for D(PhS–SPh) of 41 kcal/mol is based on literature data for D(PhS–H) and its enthalpy of hydrogenation [Shaw, R. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974; p 151]. It should be noted that the complex $W[(P^iPr_3)_2(CO)_3W]$ contains a three-center agostic bond (D = 10–15 kcal/mol[1]) and is not truly coordinatively unsaturated. Cleavage of the *W*–SPh bond can be viewed as a two-step process: *W*–SPh → SPh + *W* → *W* (agostic). The value of 39.4 kcal/mol refers to the two-step process which includes exothermic formation of the agostic bond. The first step, cleavage of W–SPh without concomitant formation of the agostic bond, corresponds to the true bond strength; the latter is thus in the range of 50–55 kcal/mol.

(12) Lang, R. F.; Ju, T. D.; Hoff, C. D., work in progress.

(13) Complete structural information is available in the supplementary material. The monoclinic crystals of the complex are in space group $P2_1$. The complex is nearly octahedral, with the all the angles around W ranging from 86 to 93° and a P(1)–W–(P(2) angle of 174.1°. Central bond distances (Å): W–I 2.794(2), W–P(2) 2.556(3), W–P(1) 2.550(3), W–C(1) 2.032(10), W–C(2) 1.958(11), W–C(3) 2.051(10).

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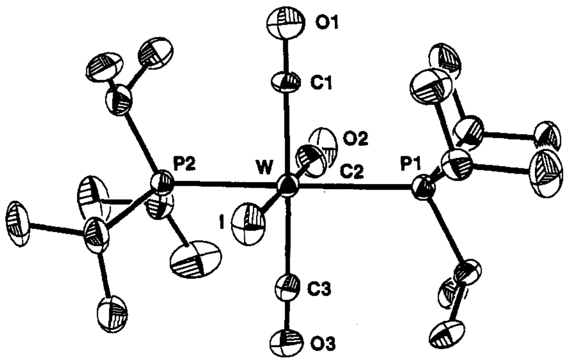


Figure 1. ORTEP drawing of $WI(CO)_3(P^iPr_3)_2$ with 50% probability thermal ellipsoids. For clarity, hydrogen atoms are not shown.

the thiolate hydride, as shown in reaction 7 below:

$$\begin{array}{ccc} W(CO)_3(P^iPr_3)_2(SPh)(H) & & {}^{\bullet}W(CO)_3(P^iPr_3)_2(SPh) \\ + & \rightarrow & + \\ {}^{\bullet}Cr(CO)_2(PPh_3)(Cp) & & HCr(CO)_2(PPh_3)(Cp) \end{array} \quad (7)$$

The color change from yellow to intense blue occurs in the time of mixing of the solutions. The enthalpy of reaction 7, −5.3 ± 1.5 kcal/mol, yields a value of 53.5 kcal/mol for the W–H bond strength in the thiolate hydride complex, in agreement with that measured above by the independent thermochemical cycle described earlier.[14] Reported values of D(W–H) for complexes in solution are typically in the range of 65–80 kcal/mol,[15] so this is the lowest value for a M–H bond reported for any complex in solution to date. It places the thiolate hydride complex below the limit for thermodynamic stability[16] with respect to elimination of hydrogen:

$$2W(CO)_3(P^iPr_3)_2(SPh)(H) \rightarrow H_2 + 2{}^{\bullet}W(CO)_3(P^iPr_3)_2(SPh) \quad (8)$$

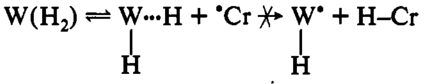
The complexes do not show a tendency toward elimination of hydrogen at an appreciable rate at room temperature, presumably due to kinetic barriers in dinuclear reductive elimination from two 7-coordinate complexes. Reaction of the radical complex with H_2, the reverse of reaction 8, predicted to be thermodynamically disfavored, is not observed to occur even under 100 atm of H_2.

While dinuclear reductive elimination did not occur as shown in eq 8, H atom transfer between the 6-coordinate radical and 7-coordinate thiolate hydride complexes occurred rapidly and quantitatively at room temperature as shown in eq 9:

$$\begin{array}{ccc} {}^{\bullet}W(CO)_3(P^iPr_3)_2(I) & & W(CO)_3(P^iPr_3)_2(I)(H) \\ + & \rightarrow & + \\ W(CO)_3(P^iPr_3)_2(SPh)(H) & & {}^{\bullet}W(CO)_3(P^iPr_3)_2(SPh) \end{array} \quad (9)$$

The fast nature of reaction 9 is surprising in view of the steric hindrance present in the complexes involved. Stopped-flow kinetic studies of reaction 9, as well as calorimetric measurements aimed at understanding the driving forces and mechanisms for these reactions, are in progress.[12] The complex $W(CO)_3(P^iPr_3)_2(I)(H)$ can be independently synthesized by oxidative addition of dry HI to $W(CO)_3(P^iPr_3)_2$ in toluene.

In an attempt to extend the radical series $W(CO)_3(P^iPr_3)_2(X)$ to include X = H, the interaction of chromium radicals with the molecular hydrogen complex was investigated as shown in reaction 10:



$$W(H_2) \rightleftharpoons \underset{\displaystyle H}{\underset{|}{W}}\cdots H + {}^{\bullet}Cr \not\rightarrow \underset{\displaystyle H}{\underset{|}{W^{\bullet}}} + H{-}Cr \quad (10)$$

$$W = W(CO)_3(P^iPr_3)_2$$
$$Cr = {}^{\bullet}Cr(CO)_2(PPh_3)(Cp)$$

Reaction 10 was studied under 60 atm of H_2 in THF solution. No sign of interaction between the chromium radical and either the molecular hydrogen complex or its dihydride tautomer was observed. We conclude that reaction 10 does not occur since the first bond dissociation energy of $W(CO)_3(P^iPr_3)_2(H)_2$ is much higher than that for $W(CO)_3(P^iPr_3)_2(H)(SPh)$. The low W–H bond strengths in the thiolate derivative may be due in part to stabilization of the 17-electron radical via lone pair donation from sulfur to tungsten.

In spite of the failure of the chromium radical to abstract one H atom from the molecular hydrogen complex as shown in eq 10, phenyl disulfide reacts under hydrogen pressure with net transfer of two hydrogen atoms as shown in eq 11.

$$W(CO)_3(P^iPr_3)_2(H_2) + 1.5PhSSPh \rightarrow W(CO)_3(P^iPr_3)_2(SPh) + 2PhSH \quad (11)$$

Production of up to 2 mol of thiophenol and the tungsten thiolate radical in the approximate stoichiometry shown in eq 11 occurs rapidly on mixing. This represents the first example of a hydrogen transfer reaction (other than H/D exchange[1]) for $W(CO)_3(P^iPr_3)_2(H_2)$. The mechanism of this reaction is unknown, but it could occur via direct attack of disulfide or thiyl radicals generated *in situ* as shown in reaction 4 on either the molecular hydrogen complex or its dihydride tautomer. Thiophenol production occurs only by reaction 11, since, as mentioned earlier, hydrogen does not react with $W(CO)_3(P^iPr_3)_2(SPh)$. Additional kinetic and thermodyanmic studies are in progress aimed at understanding thiol and disulfide reactivity at low-valent metal centers.

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Supplementary Material Available: Synthetic description of preparation of $W(CO)_3(P^iPr_3)_2(I)$ and tables of spectroscopic data (IR and NMR) for the complexes $W(CO)_3(P^iPr_3)_2(X)$ and $W(CO)_3(P^iPr_3)_2(H)(X)$ and atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, and a summary of X-ray diffraction data for $W(P^iPr_3)_2(CO)_3(I)$ (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) This estimate is based on the following thermochemical cycle:

$$\begin{array}{ccc} 2W{-}SPh + H_2 & \xrightarrow{(ii)} & 2H{-}W{-}SPh \\ (i)\uparrow +2W & & (iii)\downarrow -2W \\ PhSSPh + H_2 & \xrightarrow{(iv)} & 2H{-}SPh \end{array}$$

$$W = W(CO)_3(P^iPr_3)_2$$

The enthalpy of step ii is calculated to be −2.4 kcal/mol on the literature data for the enthalpy of step iv [−5.0 kcal/mol],[11] combined with values for step i [−37.8 kcal/mol, twice the enthalpy of reaction 3] and for step iii [+ 35.2 kcal/mol, the opposite of twice the enthalpy of reaction 6]. Using a value of 104 kcal/mol for D(H–H) leads to a value of 53.2 kcal/mol for D(*W*–H). Error limits placed on this estimate are ±3.0 kcal/mol.

(15) Simoes, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(16) The enthalpy of reaction for eq 8 is calculated to be +2.4 kcal/mol (see ref. 14). The favorable entropy of reaction associated with elimination of a mole of $H_2(g)$ (ΔS = 25 cal/mol deg) means that at $T > 100$ K, reductive elimination of H_2 is favored.