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Reactivity of a 17e Organometallic Radical in Aqueous Solution

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Laser flash photolysis of $[(C_5H_4CO_2^-)W(CO)_3]_2$ in aqueous solution at 460–532 nm induces homolysis of the metal–metal bond with formation of the 17e radical $(C_5H_4CO_2^-)W(CO)_3$. The rate constant for its dimerization is 3.0×10^9 L mol^{-1} s^{-1} at 23 °C. The radical reacts with haloacetate ions, pseudohalo- and halometal complexes by atom transfer. The reactivity trend is normal (RI > RBr > RCl). The reaction between this radical with *t*-BuOOH in water occurs similarly with a rate constant of 1.37×10^6 L mol^{-1} s^{-1}. For electron-transfer reactions, the radical acts as both reductant and oxidant. It oxidizes tetramethylphenylenediamine to TMPD$^{\bullet+}$ in aqueous solution with a rate constant of 1.49×10^7 mol^{-1} s^{-1}. The radical reduces MV^{2+} and $Fe(CN)_6^{3-}$ to MV$^{\bullet+}$ and $Fe(CN)_6^{4-}$ with rate constants of 2.0×10^6 and 6.06×10^7 L mol^{-1} s^{-1}, respectively. The phosphine Ph_2PPhSO_3Na accelerates the reaction of the radical with MV^{2+} very mildly. This may bear on the question of whether the tungsten–phosphine adduct is a species with 19 valence electrons, a slipped cyclopentadienyl ring, or a phosphoranyl radical.

Introduction

Organometallic catalysis allows for high selectivity and efficiency of processes such as polymerization[1] and hydrogenation.[2,3] Much of the mechanistic effort has been devoted to 18e–16e transformations, although there is now a well-recognized place for single electron and radical chemistry[4] that may be more pervasive than currently realized. The desirability of water as a solvent is more and more appreciated, given the problems of environmentally-permissible waste disposal. It is by no means settled how the change from the more common nonpolar solvents to water will affect certain types of reactions.

The reactions of transition metal radicals, which are currently of much interest,[5] are a case in point, particularly in that both atom-transfer and electron-transfer processes can readily be distinguished and occur by way of transition states that are expected to be quite different in polarity. We have extended some of our previously-reported studies[6–9] of the 17e radicals $CpM(CO)_3$ (M = W, Mo, Cr) to a related, water-soluble one, $(C_5H_4CO_2^-)W(CO)_3$, derived from the dimer $[(C_5H_4CO_2H)W(CO)_3]_2$, as first reported by Tyler and co-workers.[10] They reported the synthesis, crystal structure, and the solubility of $[(C_5H_4CO_2H)W(CO)_3]_2$ in organic solvents and in water. They found that irradiation into the low-energy tail of the lowest energy absorption band results in homolytic cleavage of the W–W bond to form $(C_5H_4CO_2^-)W(CO)_3$ radicals in aqueous solution. These radicals can be trapped with $CCl_3CO_2^-$ in aqueous solution by an atom-transfer reaction. The 19e adduct formed by the reaction between these radicals with phosphine can reduce $Fe(CN)_6^{3-}$, methyl viologen, and cytochrome c. Here we report the results of studies of the radical derived from it by flash photolysis.

Experimental Section

Reagents. The dimeric tungsten complex which serves as the photochemical precursor of the 17e radical was prepared according to the literature procedure.[10] The water-soluble version of triphenylphosphine, $Ph_2P(C_6H_4SO_3Na)$, was prepared as described.[11] The cobalt(III) complexes were available as their perchlorate salts from previous studies.[12] The other reagents were obtained from commercial sources and used as received. Solutions were made up in laboratory distilled and deionized water that had then been passed through a Millipore Q purification system. Buffer solutions were prepared by mixing 50 mL of 0.05 M $NaHCO_3$ and 10.7 mL of 0.1 M NaOH.[13] The uncharged dimer is insoluble in water, but it dissolves in this solution at pH 10, being converted to $[(C_5H_4CO_2^-)W(CO)_3]_2$ as it dissolves.

Kinetic Procedures. Solutions of the tungsten dimer in water were kept in the dark and saturated with argon before being standardized spectrophotometrically (λ_{max} 365 nm, ϵ 1.9×10^4 L mol^{-1} cm^{-1}; 485 nm, 2.2×10^3 L mol^{-1} cm^{-1}).[10] A known concentration of the desired substrate was added to the solution, along with $Ph_2P(C_6H_4SO_3Na)$ in certain experiments. The solution was then subjected to a single 0.6-μs flash from a flashlamp-pumped dye laser. This eqiupment has been described previously.[14]

In the absence of a substrate the tungsten radicals recombine, the dimer being recovered. Since the radical has an absorption

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that is too weak to be useful, the progress of this reaction can be followed by monitoring the buildup of the dimer at 356 nm. The chemical equation and rate law are

$$2(C_5H_4CO_2^-)W(CO)_3 \xrightarrow{k_c} [(C_5H_4CO_2^-)W(CO)_3]_2 \quad (1)$$

$$-\frac{d[(C_5H_4CO_2^-)W(CO)_3]}{dt} = 2k_c[(C_5H_4CO_2^-)W(CO)_3]^2 \quad (2)$$

The data were fit to the integrated form of eq 2, after conversion of concentrations to absorbance by the incorporation of ϵ_D, the molar absorptivity of the dimer, as follows:

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + \frac{\mathrm{Abs}_0 - \mathrm{Abs}_\infty}{1 + 4\frac{k_c t}{\epsilon_D}(\mathrm{Abs}_0 - \mathrm{Abs}_\infty)} \quad (3)$$

In the presence of a substrate, S, a bimolecular reaction between it and the tungsten radical occurs concurrently. This reaction leads to different products, depending on the substrate, but a single pattern applies to the kinetic treatment. The additional reaction and new rate law are

$$S + (C_5H_4CO_2^-)W(CO)_3 \xrightarrow{k_S} \text{products} \quad (4)$$

$$-\frac{d[(C_5H_4CO_2^-)W(CO)_3]}{dt} = 2k_c[(C_5H_4CO_2^-)W(CO)_3]^2 + k_S[(C_5H_4CO_2^-)W(CO)_3][S] \quad (5)$$

Integration of this equation under the conditions $[S]_0 \gg [(C_5H_4CO_2^-)W(CO)_3]_0$ gives eq 6 for the concentration of the radical. It is then incorporated into eq 2 to yield an expression for the concentration of the dimer and thus for the absorbance, eq 7.

$$[W]_t = \frac{k_S[S][W]_0 e^{-k_S[S]t}}{k_S[S] + 2k_c[W]_0\{1 - e^{-k_S[S]t}\}} \quad (6)$$

$$\mathrm{Abs}_t = \mathrm{Abs}_0 + \frac{\epsilon_D}{2}\left\{[W]_0 \frac{\left(\frac{2k_c[W]_0}{k_\psi} + 1\right)(1 - e^{-k_\psi t})}{\left[\frac{2k_c[W]_0}{k_\psi}(1 - e^{-k_\psi t}) + 1\right]} - \frac{k_\psi}{2k_c}\ln\left[\frac{2k_c[W]_0}{k_\psi}(1 - e^{-k_\psi t}) + 1\right]\right\} \quad (7)$$

where $[W]_0$ represents the initial concentration of the $(C_5H_4CO_2^-)W(CO)_3$ radical and k_ψ represents $k_S[S]$. In the analysis of the data k_c was fixed at the value 3.0×10^9 L mol^{-1} s^{-1} found in experiments lacking a substrate; thus although the mathematical form of the equation used for curve fitting is quite complex, the only unknown is the rate constant k_ψ. The initial concentration of the radical can be estimated from the dimer concentration and the laser parameters from experiments without substrate, but this is only approximate and for that reason both $[W]_0$ and k_ψ were treated as parameters in most of the calculations. Typically, each sample was flashed four times in succession, so the value of k_ψ at a given [S] is the average of four determinations. The programs GraFit and KaleidaGraph were used for nonlinear least squares data fitting.

The procedure just described for the kinetics analysis is clearly inferior to one in which either the tungsten radical or a product of eq 4 could be monitored directly. Neither is possible in the general case (see below, however). These experiments must be designed on the basis of preliminary experiments such that the radical disappears mostly by the reaction of interest, eq 4, in order to optimize the precision of k_ψ, but with enough of reaction 2 remaining to give accurate absorbance readings. This control is exercised by the range of [S] chosen.

Table 1. Rate Constants for the Dimerization of $(C_5H_4R)M(CO)_3$ Radicals

radical	solvent	$10^{-9}k_c$/L mol^{-1} s^{-1}	ref
$(C_5H_5)W(CO)_3$	acetonitrile	6.2	6
$(C_5H_5)W(CO)_3$	toluene	5	20
$(C_5H_4CO_2H)W(CO)_3$	acetonitrile	4.9	6
$(C_5H_5)Mo(CO)_3$	acetonitrile	3.9	6
$(C_5H_5)W(CO)_3$	THF	3.8	21
$(C_5H_4CO_2^-)W(CO)_3$	water	3.0	this work
$(C_5H_5)W(CO)_3$	cyclohexane	1.9	22
$(C_5H_5)Cr(CO)_3$	toluene	0.31	7
$(C_5H_5)Cr(CO)_3$	THF	0.30	7
$(C_5H_5)Cr(CO)_3$	acetonitrile	0.27	7
$(C_5Me_5)Cr(CO)_3$	acetonitrile	0.0070	7

In a few cases, however, a product of reaction 4 absorbs with sufficient intensity to allow its direct monitoring. If a product is monitored at a wavelength where it is the only species that absorbs appreciably, the expression for the absorbance used for curve fitting is

$$\mathrm{Abs}_t = \mathrm{Abs}_0 + \epsilon_P\frac{k_\psi}{2k_c}\ln\left\{1 + \frac{2k_c[W]_0}{k_\psi}(1 - e^{-k_\psi t})\right\} \quad (8)$$

Still other equations apply when the reactions are carried out in the presence of a phosphine, but they will be given in a later section where this chemistry is explained.

Reaction Products. The tungsten-containing products were obtained as follows. A solution of $(C_5H_4CO_2^-)W(CO)_3$ (2 mM) and $Br_3CCO_2^-$ (20 mM) was prepared under argon. Following irradiation with sunlight for 5 h, the components of the solution were separated on QAE Sephadex A25 anion resin, using aqueous NaOH as the eluting agent. The material obtained was examined by HPLC and found to be a single, pure substance. The eluent was recrystallized from THF, dried under vacuum and analyzed. Found (calcd) for $Na[(C_5H_4CO_2)W(CO)_3I]$: C, 21.74 (21.73); H, 1.24 (1.23); Br, 15.93 (16.10). With $I_3CCO_2^-$, the following product analysis was obtained. Found (calcd): C, 20.07 (19.86); H, 1.08 (1.10); I, 23.18 (23.35). Both materials had IR spectra in the ν_{CO} region that were recorded on a Nicolet 710 spectrometer with 4-cm^{-1} resolution. They are 2048 and 1961 cm^{-1} (Br) and 2039 and 1957 cm^{-1} (I). Other samples for the detection of the products were prepared with about 20 laser flashes, with the sample being stirred intermittently, to accumulate sufficient product for detection. Peak positions were compared to the literature values for $C_5H_5W(CO)_3X$.[10,15-19]

Results and Discussion

Radical Dimerization. Experiments in the absence of a substrate were conducted with the laser photodissociation at 490 nm; the buildup of the dimer was monitored at 356 nm. This experiment showed a partial but substantial bleach of the dimer absorption during the flash, following which the dimer buildup occurred, according to second-order kinetics, eq 2. This is depicted in Figure 1a. Analysis of the data according to eq 3 gave the rate constant k_c = 3.0 ± 0.1) × 10^9 L mol^{-1} s^{-1} at 23 °C in aqueous solution at pH 10. This is compared with the values for similar CpM(CO)$_3$ radicals in Table 1.

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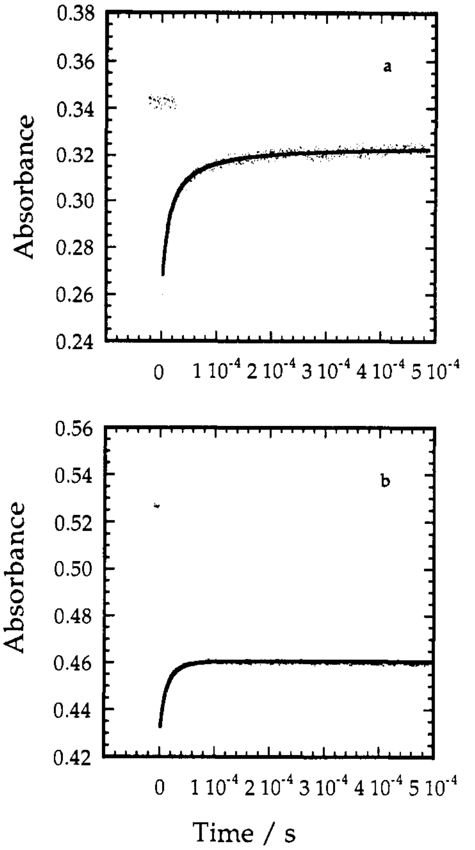

Figure 1. (**a**) Time-resolved absorbance changes recorded at 365 nm during the 490-nm laser flash photolysis of an argon-saturated solution of 18 μM $[(C5H_4CO_2^-)W(CO)_3]_2$ in aqueous solution at pH 10. The smooth curve is a fit to eq 3, which gave k_c = 3.0 × 10^9 L mol^{-1} s^{-1}. (**b**) A similar experiment with 25 μM $[(C_5H_4CO_2^-)W(CO)_3]_2$ and 1.02 mM $ICH_2CO_2^-$. The solid curve is the data fit to eq 7, with k_c fixed at the known value, giving k_ψ = 9124 s^{-1}.

The dimerization rate constant in water is nearly at the diffusion-controlled limit. The von Smoluchowski equation[23] provides an expression for k_{dc} once a modified version[24] of the Stokes–Einstein equation for the diffusion coefficient in terms of the viscosity is incorporated: $k_{dc} \sim [(4 \times 10^6)RT/\eta]$ m^3 mol^{-1} which gives $k_{dc} \sim 1 \times 10^{10}$ L mol^{-1} s^{-1}. Without the modification, $k_{dc} \sim 6 \times 10^9$ L mol^{-1} s^{-1}. The experimental value is about one-fourth of the larger k_{dc}, which may be attributed to quantum mechanical spin restrictions[25] (assuming that they are not removed by spin–orbit coupling).

Like its analogs, the photolysis of the dimer $(C_5H_4CO_2^-)_2W_2(CO)_6$ in aqueous solution results in W–W bond homolysis and W–CO bond dissociation as primary photoprocesses. As figure 1a shows, in the absence of organic halides, 82% of the absorbance of the dimer is recovered in the time needed (about 300 μs usually) to attain a stable absorbance. As we reported[6] for $(C_5H_5)W(CO)_3$, the recombination of $(C_5H_4CO_2^-)_2W_2(CO)_5$ with CO requires a long time (over 1 s or so). In cases where repeat determinations were made on the same solution, at least several seconds elapsed between them, so that buildup of $(C_5H_4CO_2^-)_2W_2(CO)_5$ was never an issue.

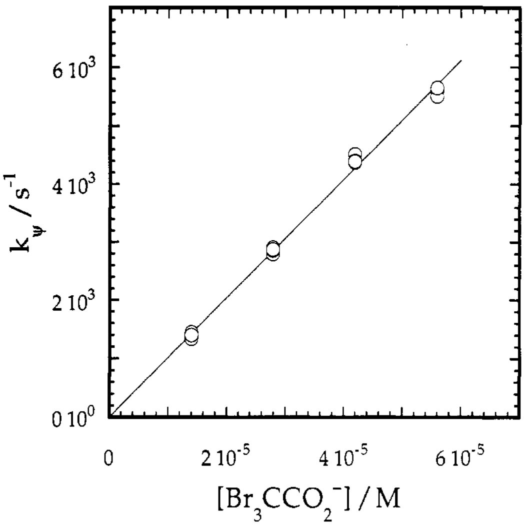

Figure 2. Typical set of kinetic data for $Br_3CCO_2^-$ showing the linear fit of the pseudo-first-order rate constants from eq 7 against concentration, with a slope k = (1.02 ± 0.01) × 10^8 L mol^{-1} s^{-1}.

Table 2. Rate Constants for Halogen Atom Abstraction from Haloacetate Ions by the Tungsten Radical, $(C_5H_4CO_2^-)W(CO)_3$, in Aqueous Solution at 23 °C

halide	k/L mol^{-1} s^{-1}
$Cl_3CCO_2^-$	(1.34 ± 0.05) × 10^4 (3.5 × 10^4)[a]
$Br_2CHCO_2^-$	(7.23 ± 0.06) × 10^5
$Br_3CCO_2^-$	(1.02 ± 0.01) × 10^8
$ICH_2CO_2^-$	(9.05 ± 0.05) × 10^6

[a] For $(C_5H_5)W(CO)_3$ in acetonitrile; from ref 6.

Reactions with Halides. The reactions of the tungsten radical with water-soluble, halogen-containing substances were evaluated. The recovery of the dimer is much lower in this case, since the radical is diverted away; this is depicted in Figure 1b. The kinetic data in each case follow eq 7. This treatment yields values of k_ψ that prove to be linear functions of [S], as expected. A sample for iodoacetic acid is shown in Figure 2. Rate constants for haloacetic acids are summarized in Table 2 and are taken to apply to the halogen atom abstraction reaction:

$$(C_5H_4CO_2^-)W(CO)_3 + RX \rightarrow (C_5H_4CO_2^-)W(CO)_3X + R^\bullet \quad (9)$$

These reactions do indeed form the tungsten halide expected from halogen atom transfer reactions. The products were identified by comparison to $(C_5H_5)M(CO)_3X$ (M = W or Mo), as seen from the IR spectra given in Table 3. The trends in these rate constants show that the reactivity order is RI > RBr > RCl and that additional halogen atoms on a given carbon increase the rate. These trends were elaborated in the more extensive study of organic halides in acetonitrile earlier reported[6] and need not be considered further.

Similar, too, are the reactions with metal halides. These rate constants are given in Table 4, and the IR identifications of products in Table 3. The values obtained here are compared with those previously determined[6] for these

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Table 3. Infrared Spectra of Reaction Products and Comparison Compounds

complex	ν_{CO} (cm^{-1})	ref
	Reaction Products	
$CpCO_2^-W(CO)_3Cl$	2054, 1962	10
$CpCO_2^-W(CO)_3Br$	2047, 1960	this work
$CpCO_2^-W(CO)_3I$	2038, 1957	this work
$CpCO_2^-W(CO)_3OH$	2040, 1966	this work
$CpCO_2^-W(CO)_3NCS$	2057, 1986	this work
$CpCO_2^-W(CO)_3CN$	2079, 2008	this work
$CpCO_2^-W(CO)_3(PPh_2R^-)$	2058, 1990	10
$[CpCO_2^-W(CO)_3]_2$	2011, 1961	10
	Comparison Compounds	
$CpMo(CO)_3Cl$	2063, 1990	26
$CpMo(CO)_3Br$	2055, 1983	26
$CpMo(CO)_3I$	2040, 1968	26
$CpMo(CO)_3NCS$	2068, 1997	26
$CpW(CO)_3Cl$	2052, 1968	26
$CpW(CO)_3Br$	2048, 1966	26
$CpW(CO)_3I$	2040, 1961	26
$CpCO_2^-W(CO)_3Cl$	2054, 1962	10

Table 4. Rate Constants for the Halogen Atom Abstraction Reactions between Cobalt(III) Complexes and Tungsten Radicals

	k/L mol^{-1} s^{-1}	
Co^{III} complex	aqueous solution[a]	acetonitrile[b]
$Co(NH_3)_5CN^{2+}$	$(1.24 \pm 0.40) \times 10^7$	1.6×10^7
$Co(NH_3)_5NCS^{2+}$	$(1.32 \pm 0.10) \times 10^7$	3.0×10^7
$Co(NH_3)_5Cl^{2+}$	$(1.32 \pm 0.23) \times 10^8$	2.1×10^8
$Co(NH_3)_5Br^{2+}$	$(5.83 \pm 0.21) \times 10^8$	7.3×10^8

[a] For $(C_5H_4CO_2^-)W(CO)_3$ in water at pH 10 and 23 °C; this work. [b] For $(C_5H_5)W(CO)_3$ in acetonitrile at 23 °C; from ref 6.

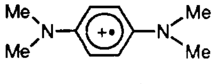
same complexes with the radical $(C_5H_5)W(CO)_3$ in acetonitrile. The difference in rate is quite small. In each case, the reaction in acetonitrile is some 20–30% faster, but it is not only the solvent but also the tungsten radical that changes in this comparison.

Reaction with *tert*-Butyl Hydroperoxide. The same kinetic pattern is followed, and the rate constant is $(1.37 \pm 0.03) \times 10^6$ L mol^{-1} s^{-1}. Compared to this, $(C_5H_5)W(CO)_3$ has $k = 4.5 \times 10^5$ L mol^{-1} s^{-1} in acetonitrile. The organic products by gas chromatography are acetone and ethane. This is consistent with a scheme in which the *tert*-butoxyl radical, the product of absorption of an OH group by the metal radical, undergoes a β-scission reaction:

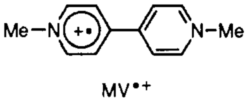
$$(C_5H_4CO_2^-)W(CO)_3 + t\text{-BuOOH} \rightarrow (C_5H_4CO_2^-)W(CO)_3OH + t\text{-BuO}^\bullet$$

$$t\text{-BuO}^\bullet \rightarrow (CH_3)_2CO + {}^\bullet CH_3 \qquad 2{}^\bullet CH_3 \rightarrow C_2H_6 \tag{10}$$

Electron Transfer. Three species that can react with the tungsten radicals by electron transfer were examined. They are the electron donor 1,4-*N,N,N′,N′*-tetramethylphenylenediamine (or TMPD) and the acceptors methyl viologen ions (or MV^{2+}) and ferricyanide ions. The occurrence of the first two reactions (eqs 11 and 12) is easy to recognize because the organic radicals are persistent species with characteristic visible spectra. The reaction with ferricyanide ions, eq 13, is written by analogy to eq 12.



TMPD$^{•+}$



MV$^{•+}$

$$(C_5H_4CO_2^-)W(CO)_3 + TMPD \rightarrow (C_5H_4CO_2^-)W(CO)_3^- + TMPD^{\bullet +} \tag{11}$$

$$(C_5H_4CO_2^-)W(CO)_3 + MV^{2+} \rightarrow (C_5H_4CO_2^-)W(CO)_3^+ + MV^{\bullet +} \tag{12}$$

$$(C_5H_4CO_2^-)W(CO)_3 + Fe(CN)_6^{3-} \rightarrow (C_5H_4CO_2^-)W(CO)_3^+ + Fe(CN)_6^{4-} \tag{13}$$

The rate constant for reaction 11 was evaluated by following the buildup of TMPD$^{•+}$ at 610 nm, which is an absorption maximum, with ϵ 1.2×10^4 L mol^{-1} cm^{-1}. The kinetic curves were analyzed by eq 8, but the data were restricted to $[TMPD]_0 < 10$ mM, because secondary processes[28] occur beyond that. In the useful region, the rate constant k_ψ is a linear function of [TMPD], as expected. The slope of this plot gives $k = (1.4 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}.[27] The same determinations were repeated at 356 nm, by following the tungsten dimer. Equation 7 gives $k = (1.6 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}; we believe that this is less reliable because at 356 nm the absorption of TMPD and of the TMPD$^{•+}$ radical cannot be ignored, which eq 7 does.

In the case of MV^{2+}, kinetic determinations were carried out at three wavelengths. At 606 nm, an absorption maximum,[29] we monitored the buildup of MV$^{•+}$; eq 8 gives $k = (2.13 \pm 0.02) \times 10^6$ L mol^{-1} s^{-1}. The dimer buildup at 356 nm from eq 7 gives $k = (1.91 \pm 0.02) \times 10^6$ L mol^{-1} s^{-1}. We take these as being in essential agreement. At 396 nm, where the tungsten dimer and MV$^{•+}$ (ϵ 4.2×10^3 L mol^{-1} cm^{-1}) both absorb, an apparent rate constant of 2.7×10^6 L mol^{-1} s^{-1} was obtained from eq 8, but it is much less reliable since the equation makes no allowance for the absorbance of two species. The rate constant for the ferricyanide ion reaction is $(6.1 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}, evaluated at 356 nm by use of eq 7.

It is interesting to compare these rate constants in aqueous solution to those of $(C_5H_5)W(CO)_3$ in acetonitrile. These are the pertinent comparisons:

		$(C_5H_4CO_2^-)W(CO)_3$	$(C_5H_5)W(CO)_3$
reagent	reacn type	water	acetonitrile
TMPD	reduction	1.4×10^7	2.6×10^7
MV^{2+}	oxidation	2.0×10^6	3.7×10^6

We assert that these minimal changes are not likely to arise from canceling the effect of the ring substitution of the cyclopentadienyl ligand by the solvent effect. With that assumption, it is noteworthy that there is hardly any change in the rate of either reaction in the more polar solvent. Nonetheless, the transition state must be quite polar, since two ions are being formed; indeed, the small rate effect for TMPD is in the direction opposite than expected on the basis of solvent polarity. It must be noted, on the other hand, that water is a sufficiently strong Lewis base that at 55 M concentration it may convert the 17e radical $(C_5H_4CO_2^-)W(CO)_3$ to an adduct that some would describe (see later) as a 19e adduct. This species would be a less powerful electron acceptor, both thermodynami-

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cally and kinetically, since one cannot transfer an electron to it from TMPD without dissociation of the solvent molecule, so as to realize the 18e product, $(C_5H_4CO_2^-)W(CO)_3^-$. This would impose an appreciable kinetic barrier that could more than offset the effect of solvent polarity.

Addition of Phosphine. The addition of triphenylphosphine or pyridine to the reaction mixtures in acetonitrile showed a strong accelerating effect on reactions in which the tungsten radical acts as an electron donor.[9,30,31] We have now explored whether similar effects would be seen in aqueous solution with added $Ph_2PC_6H_4SO_3^-$, employing the reaction of the tungsten radical with MV^{2+} as the trial reaction. As before,[9] the simultaneous effects of adding the phosphine are these: more $MV^{\bullet+}$ is formed, more rapidly, and the final yield of the tungsten dimer is reduced.

The reaction scheme consists of a very rapid equilibrium involving a 1:1 adduct of the tungsten radical and the phosphine, eq 14. This adduct may react with the tungsten

$$(C_5H_4CO_2^-)W(CO)_3 + Ph_2PC_6H_4SO_3^- \overset{K_{14}}{\rightleftarrows} \text{Adduct} \quad (14)$$

$$(C_5H_4CO_2^-)W(CO)_3 + \text{Adduct} \xrightarrow{k_{15}} (C_5H_4CO_2^-)W(CO)_3^- + (C_5H_4CO_2^-)W(CO)_3(PR_3)^+ \quad (15)$$

$$MV^{2+} + \text{Adduct} \xrightarrow{k_{16}} MV^{\bullet+} + (C_5H_4CO_2^-)W(CO)_3(PR_3)^+ \quad (16)$$

radical, but not combine to the dimer, instead leading to disproportionation, eq 15. The adduct may also undergo electron transfer to MV^{2+}, eq 16. These are in addition to the usual dimerization and electron-transfer reactions of the phosphine-free radical.

The reactions were carried out so as to monitor in separate but otherwise identical experiments the buildup of the tungsten dimer at 356 nm and of the methylviologen radical at 606 nm. These calculations (see the Appendix) were carried out with the rate constants k_c and $k(MV^{2+} + (C_5H_4CO_2^-)W(CO)_3)$ fixed at their previously-determined values. They were first applied to experiments in which MV^{2+} was absent. This gives these parameters: $K_{14} = 300 \pm 16$ L mol^{-1} and $k_{15} = (2.5 \pm 0.2) \times 10^9$ L mol^{-1} s^{-1}. Then, with added MV^{2+}, the analysis gave the value $k_{16} = (8.0 \pm 0.3) \times 10^6$ L mol^{-1} s^{-1}.

The acceleration seen in k_{16} over the analogous reaction of the radical lacking the phosphine is extraordinarily modest, but a factor of 4. Another comparison was provided by a pair of reactions of $Fe(C_5H_5)_2^+$ in acetonitrile, where the acceleration factor is 160. And, there, it was thought to be leveled in part by the diffusion-controlled limit, which clearly does not apply to the reactions of MV^{2+}. We suggest two reasons for this seeming anomaly: (1) In water, unlike acetonitrile, both of the tungsten radicals may be the formally 19e adducts, $(C_5H_4CO_2^-)W(CO)_3(OH_2)$ and $(C_5H_4CO_2^-)W(CO)_3(Ph_2PC_6H_4SO_3^-)$. In that case a large reactivity ratio in favor of the phosphine is not to be expected. (2) The description of the adducts as genuine 19e species has not been fully verified.[9] Alternative formulations are as phosphorus-centered radicals (in which case the reactivity ratio is not easily predicted) or as 17e species with a slipped or η^3-Cp ring; all of these possibilities, when the authentic one is unknown, are customarily called 19e adducts.[32]

In conclusion, we find that the tungsten radicals react in water very nearly the same as they do in nonpolar solvents (*e.g.*, toluene) and in polar, aprotic solvents (*e.g.*, acetonitrile). This is easily rationalized for the halogen atom abstraction processes, where the transition state appears to be nonpolar. The lack of appreciable solvent kinetic effects on the tungsten radical both as an electron donor and as an electron acceptor is more surprising, but well documented by the kinetic data obtained in this study. Coordination of a water molecule (so-called 19e adduct formation) may be in part responsible, as discussed in the text.

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Appendix

The rate of disappearance of the tungsten radical when reactions, 2, 14, and 15 take place concurrently is

$$-\frac{d[W]}{dt} = 2\left\{\frac{k_c + k_{15}K_{14}[PR_3]}{(1 + K_{14}[PR_3])^2}\right\}[W]_T^2 \quad (A\text{-}1)$$

where $[W]_T = [(C_5H_4CO_2^-)W(CO)_3(Ph_2PC_6H_4SO_3^-)] + [(C_5H_4CO_2^-)W(CO)_3]$ at each point in time. The mass balance in these systems is

$$[W_2]_T = \frac{1}{2}\{[W]_0 - [W]_t - [WPR_3^+]_t - [W^-]_t\} \quad (A\text{-}2)$$

The solution of this equation gives the expression for the absorbance of the dimer (molar absorptivity ϵ_D), which is the only species absorbing appreciably.

$$\text{Abs}_t = \text{Abs}_0 + \epsilon_D \frac{k_c[W]_0^2 t}{(1 + K_{14}[PR_3])^2 + 2(k_c + k_{15}K_{14}[PR_3])[W]_0 t} \quad (A\text{-}3)$$

The application of this equation to find K_{14} and k_{15} was carried out at four different phosphine concentrations, with four separate determinations of each solution. The values of K_{14} and k_{15} were the average of 16 independently-known values.

In the presence of a substrate that can oxidize (or reduce) the metal radical, the rate law becomes

$$-\frac{d[W]}{dt} = 2k_c[W]^2 + 2k_{15}[W][WPR_3] + k[W][S] + k_{16}[WPR_3][S] \quad (A\text{-}4)$$

Integration of this equation, as describe for the derivation of eq 7, gives the expression for the absorbance of the tungsten dimer, assuming that it is the only species that

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[32] Tyler, D. T. In *Organometallics Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Vol. 22, pp 339–340.

absorbs appreciably:

$$\mathrm{Abs}_t = \mathrm{Abs}_0 + \epsilon_{\mathrm{D}}\left[\frac{k_{15}K_{14}[\mathrm{PR}_3]}{2(k_c + k_{15}K_{14}[\mathrm{PR}_3])}\right]\left\{[\mathrm{W}]_0 - \frac{k'[\mathrm{W}]_0\exp(-k't)}{k' + 2k''[\mathrm{W}]_0\{1 - \exp(-k't)\}} - \frac{k'}{2k''}\ln\left(1 + \frac{2k''[\mathrm{W}]_0}{k'}\{1 - \exp(-k't)\}\right)\right\} \quad (\text{A-5})$$

where $k' = (k_{12}[\mathrm{S}] + k_{16}[\mathrm{S}]K_{14}[\mathrm{PR}_3])/(1 + K_{14}[\mathrm{PR}_3])$ and $k'' = (k_c + k_{16}K_{14}[\mathrm{PR}_3])/(1 + K_{14}[\mathrm{PR}_3])^2$. All of the quantities in this equation except k_{16} are known from the determinations in the absence of substrate, leaving it as the only parameter to be adjusted in the computer fit.

When the reaction product has an absorption band of sufficient intensity, the kinetic analysis can be conducted at this wavlength as well. Provided the product is the only species that absorbs appreciably, the equation is

$$\mathrm{Abs}_t = \mathrm{Abs}_0 + \epsilon_{\mathrm{D}}\left\{\frac{k'}{2k''}\ln\left(1 + \frac{2k''[\mathrm{W}]_0}{k'}\{1 - \exp(-k't)\}\right)\right\} \quad (\text{A-6})$$

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