Electron-Transfer Reactions of 17-Electron and 19-Electron Organometallic Radicals, $CpW(CO)_3$ and $CpW(CO)_3PPh_3$

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Laser flash photolysis of $[CpW(CO)_3]_2$ was carried out at 490 nm, where the primary photoprocess gives a 17-electron radical, $CpW(CO)_3$. The metal radical acts as both an electron donor and acceptor. The radical reduces ferrocenium ions (k = [1.89(4)] × 10^7 L mol^{-1} s^{-1}) and benzoquinone (k = [2.7(1)] × 10^7 L mol^{-1} s^{-1}) at 23 °C in acetonitrile. Triphenylphosphine accelerates the reaction of the tungsten radical with ferrocenium ions, suggesting the formation of the more strongly reducing 19-electron radical $CpW(CO)_3PPh_3$. It reacts with ferrocenium ions: $k = 3 \times 10^9$ L mol^{-1} s^{-1}. The base-induced disproportionation of $CpW(CO)_3$ was used to evaluate binding constants for $CpW(CO)_3$ and PPh_3 ($K = 6 \pm 1$ L mol^{-1}) and pyridine ($K = 0.16 \pm 0.04$ L mol^{-1}). Also, the $CpW(CO)_3$ radical *oxidizes* decamethylferrocene (2.2 × 10^8 L mol^{-1} s^{-1}) and *N,N,N′,N′*-tetramethylphenylenediamine (2.6 × 10^7 L mol^{-1} s^{-1}). In this system there is a secondary process responsible for the re-reduction of $TMPD^{\bullet+}$. We suggest the rapid formation of the radical anion $[CpW(CO)_3]_2^{\bullet-}$, presumed to be a powerful electron donor, to account for back-electron transfer, but this has not been proved.

Introduction

Organometallic radicals can serve as chain carriers in electron-transfer chain reactions.[1] Also, the interconversion of odd- and even-electron species enhances the rate of ligand substitution at the metal center. For example, the one-electron oxidation of the metal radical catalyzes the exchange of iodide with chloride in the 17-electron complex $CpMoI_2(PMe_3)_2$.[2] Hepp and Wrighton have noted that a 17e radical with a partially filled HOMO will be a better electron donor and a better electron acceptor than its 18e dimetallic parent.[3]

Although several time-resolved studies of *atom-transfer* reactions of 17e radicals have appeared recently,[4-10] few quantitative data have been reported for homogenous outer-sphere *electron-transfer* reactions of 17e radicals. The studies of Brown et al. concerning $Re(CO)_5L$ (L = CO, PR_3, $P(OR)_3$, $AsEt_3$) are a notable exception, in that the independent kinetic processes were observed directly.[11,12] Also, the 17e organometallic radicals $CpW(CO)_3$, $Mn(CO)_5$, and $Re(CO)_5$ undergo oxidation by electron transfer as well as atom transfer. These reactive entities were formed[13] during the photolysis of the stable dimetallic compounds in the presence of both CCl_4 and an outer-sphere oxidant (ferrocenium ions, tropylium ions or methylviologen). The ratio of the chloro complex, formed in the atom-transfer reaction, to the oxidation products gave the relative rate constants for the oxidation step. Also, the rate constants for the oxidation of $Mn(CO)_5$ by substituted pyridinium ions have been reported.[13]

It is equally clear that the 17e species can also be an electron acceptor, at least in principle. The 18e anionic products such as $CpW(CO)_3^-$ and $CpMo(CO)_3^-$ are stable and independently known. Nonetheless, quantitative data on reactions in which $CpW(CO)_3$ and other 17e radicals are reduced are largely lacking. Apart from the well-known disproportionation reactions of organometallic radicals,[14] there appear to be no examples of the outer-sphere reduction of 17e radicals.

In this work, we present the results of a time-resolved study of the electron-transfer reactions of $CpW(CO)_3$ and $CpMo(CO)_3$. These radicals were generated by the laser flash photolysis of the respective dimers $[CpM(CO)_3]_2$ in acetonitrile. For that purpose we used the long-wavelength absorptions at 460–490 nm, so as to minimize the pathway that releases carbon monoxide from the dimer and is more prevalent with higher-energy excitation. The consequences of this concurrent reaction were considered in our earlier work.[10] The absolute reactivities for the oxidation of these 17e radicals by several substrates have been determined in the course of this work.

Photochemical experiments have shown that the addition of ligands that can bind rapidly to the 17e metal radical promotes the formation of electron-transfer products. We show that these exogenous ligands accelerate the electron-transfer reactions and concur with the view that this is because the 19-electron species is a better electron donor both thermodynamically and kinetically. The ligand is also an active catalyst for the disproportionation of the metal radicals. In all of these instances the metal radical acts as an electron donor toward the substrate. It is easy to see, however, that the 17e radical

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should also be capable, at least in principle, of acting as an electron acceptor. We have sought evidence for this type of reaction. Thus, we are able to report the first quantitative study of the reduction of $CpW(CO)_3$ by the substrates decamethylferrocene and tetramethylphenylenediamine.

Experimental Section

Materials. $[CpW(CO)_3]_2$ and $[CpMo(CO)_3]_2$ were prepared as described in the literature.[15] Commercial sources were used for ferrocene, decamethylferrocene, 1,4-benzoquinone, *N,N,N',N'*-tetramethylphenylenediamine (TMPD), triphenylphosphine, and pyridine. 1,4-Benzoquinone and triphenylphosphine were recrystallized before use. Ferrocenium hexafluorophosphate was prepared by the literature method.[16] Solutions of ferrocenium hexafluorophosphate in air-free acetonitrile were standardized spectrophotometrically; ϵ = 410 L mol^{-1} cm^{-1} at 610 nm.[17] Solutions of $[CpW(CO)_3]_2$ in acetonitrile were prepared in the dark and saturated with argon. They were standardized spectrophotometrically (λ 356 nm, ϵ 2.1 × 10^4 L mol^{-1} cm^{-1}; λ 484 nm, ϵ 2.5 × 10^3 L mol^{-1} cm^{-1}).[18] Acetonitrile was not especially dried, since earlier studies showed that the reactions of the tungsten radical are unaffected by traces of moisture.[10]

Kinetics. A known quantity of the substrate (oxidant or reductant, with Lewis base, if appropriate) was added to the $[CpW(CO)_3]_2$ solution. Then the mixture was subjected to a 0.6-μs flash from a flashlamp-pumped dye laser containing LD 490, LD 473, or Coumarin 460 dye. The use of this wavelength region for excitation was essential in causing the excited state(s) to dissociate homolytically; at shorter wavelengths carbonyl loss predominates.[10] The laser flash photolysis equipment has been described previously.[19] The events following the flash were usually monitored at 356 nm, which is the most intense maximum of the tungsten dimer. The absorbance changes at this wavelength thus correspond to recovery of the dimer, which is only partially complete in experiments with added substrate. Typical initial concentrations of $[CpW(CO)_3]_2$ and $CpW(CO)_3$ were 20–40 and 10–15 μM, respectively.

Another type of design for the kinetics can be considered, where the substrate concentration and its rate constant are high enough that the bimolecular reaction of the metal radical to reconstitute the dimer is unimportant. Even when this could be attained, as would be possible with certain substrates, it would render the kinetic essentially impossible to monitor since the metal radical has too weak an absorption[20] to follow at the typical 10-μM concentration generated in the laser flash. Likewise, none of the reactions studied here has a product that has an absorption sufficient for kinetic monitoring.

That failing, we have resorted to the method used in earlier studies[10] of this radical, wherein the reaction with the substrate and the radical recombination reaction were allowed to occur concurrently. The buildup of the reconstituted dimer was recorded with time. As the following development shows, the absorbance increase includes kinetic contributions from all the reactions of the radical, whether or not they contribute to the absorbance change. The method thus affords to good accuracy the rate constants for the reactions of interest. These are the reactions that take place competitively:

$$2CpW(CO)_3 \xrightarrow{k_c} [CpW(CO)_3]_2 \quad (1)$$

$$CpW(CO)_3 + \text{substrate} \xrightarrow{k_S} CpW(CO)_3^{\pm} + \text{product} \quad (2)$$

In the presence of an electron-transfer substrate, the decrease in the radical concentration follows the rate law in eq 3, where

$$-\frac{d[CpW(CO)_3]}{dt} = 2k_c[CpW(CO)_3]^2 + k_S[\text{substrate}][CpW(CO)_3] \quad (3)$$

k_c is the second-order rate constant for the combination reaction of the organometallic radical and k_S that for the radical–substrate reaction. The experiments were simplified by selecting conditions such that [substrate] ≫ $[CpW(CO)_3]_0$. In that case the product k_S[substrate] = k_ψ.

This is the equation for parallel first-order and second-order kinetics. Integration provides the solution for $[CpW(CO)_3]_t$:

$$[CpW(CO)_3]_t = \frac{k_\psi[CpW(CO)_3]_0 \exp(-k_\psi t)}{k_\psi + 2k_c[CpW(CO)_3]_0\{1 - \exp(-k_\psi t)\}} \quad (4)$$

The mass conservation relation used is

$$[CpW(CO)_3]_0 = [CpW(CO)_3]_t + 2[\{CpW(CO)_3\}_2]_t + [P]_t = 2[\{CpW(CO)_3\}_2]_\infty + [P]_\infty \quad (5)$$

where P is the product of electron transfer. The expression for $[CpW(CO)_3]_t$ is substituted into the equation

$$\frac{d[Cp_2W_2(CO)_6]}{dt} = k_c[CpW(CO)_3]^2 \quad (6)$$

giving a differential equation that can be solved for $[Cp_2W_2(CO)_6]_t$. That equation, expressed in terms of the absorbance of the tungsten dimer, which is the only species that absorbs appreciably at 355 nm, gives the final expression used for curve fitting

$$A_t = A_0 + \frac{\epsilon_D}{2}\left[R_0\frac{\left(\frac{2k_c}{k_\psi}W_0 + 1\right)(1 - e^{-k_\psi t})}{\frac{2k_c}{k_\psi}W_0(1 - e^{-k_\psi t}) + 1} - \frac{k_\psi}{2k_c}\ln\left[\frac{2k_c}{k_\psi}W_0(1 - e^{-k_\psi t}) + 1\right]\right] \quad (7)$$

where W_0 is the initial concentration of the $CpW(CO)_3$ radical, A_0 and A_t are the absorbances due to the dimer at times 0 and t, and ϵ_D is the molar extinction coefficient of the dimer. The dimerization rate constant was measured previously,[10] and its value at 23 °C in acetonitrile (k_c = 6.2 × 10^9 L mol^{-1} s^{-1}) was fixed in these calculations. The pseudo-first-order rate constant, k_ψ = k_S[substrate], is the only unknown kinetic constant. Values of k_ψ were obtained in each experiment by the nonlinear least-squares fitting of the experimental absorbance–time curves to eq 7. Typically, each sample was flashed four times in succession, so that each k_ψ value is the average of four determinations. Values of k_ψ were plotted against [substrate]. In every case the data defined a straight line with an intercept within experimental error of zero. The least-squares slope of this plot provided the value of k_S.

These equations show that the extent of the recovery of the tungsten dimer after the flash becomes less as the substrate concentration is increased and as the substrate is more reactive. The strategy behind the design of these experiments is to provide a balance between the two reactions, such that enough dimer forms to give an appreciable absorbance change at 356 nm, yet

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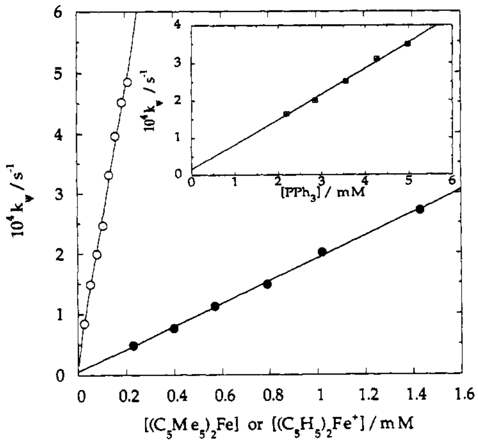

Figure 1. Concentration dependence of the pseudo-first-order rate constants (k_ψ) for the reduction of ferrocenium ions (filled circles) and the oxidation of decamethylferrocene (open circles) by $CpW(CO)_3$ in acetonitrile at 23 °C. The inset shows the effect of PPh_3 on the rate of reduction of 0.36 mM ferrocenium ions by $CPW(CO)_3$.

the substrate reaction predominates so that k_ψ can be determined to good accuracy. That is, the range of concentrations of a given substrate was chosen carefully to match its reactivity. Alternatively, one might use a substrate concentration high enough to divert all of the radical toward electron transfer. This is quite feasible for those substrates which are themselves not too intensely colored at the exciting and monitoring wavelengths, provided the solubilities allow. Nonetheless, it is not suitable for these kinetics determinations, since the tungsten radical does not have a molar absorptivity high enough for reliable UV–visible detection. In a few cases, however, the product of the electron-transfer step can be detected directly, affording a double check on the method used most of the time.

We shall describe the effects on the electron-transfer reactions of Lewis bases such as triphenylphosphine and pyridine. Even in the absence of a substrate, the absorbance of the dimer recovered after the flash to a reduced extent. This is caused by radical disproportionation, which competes with radical combination *but only in the presence of the extraneous ligand.* The relative contribution of the disporportionation path can be calculated as the ratio of the yield of dimer in the presence of added base to the yield in its absence. This comparison requires that the radical concentration be kept constant in the pair of determinations. This was attained by reproducing the concentration of $[CpW(CO)_3]_2$ and the laser flash intensity.

Results and Discussion

Reduction of Ferrocenium Ions. Laser flash photolysis of $[CpW(CO)_3]_2$ with excess ferrocenium ion results in a competition between radical combination and oxidation, (eqs 8 and 9).

$$[CpW(CO)_3]_2 \underset{k_c}{\overset{h\nu}{\rightleftharpoons}} 2CpW(CO)_3 \quad (8)$$

$$CpW(CO)_3 + FeCp_2^+ \rightarrow CpW(CO)_3^+ + FeCp_2 \quad (9)$$

The kinetic traces at 356 nm show partial recovery of the dimer absorbance after the flash, with less dimer formed for higher concentrations of $FeCp_2^+$. Each set of absorbance–time readings was fit to eq 7. The variation of the pseudo-first-order rate constants k_ψ with the concentration of ferrocenium ion is linear (Figure 1). The slope of the line gives the second-order rate constant as $k_9 = (1.89 \pm 0.04) \times 10^7$ L mol^{-1} s^{-1} at 23 °C in acetonitrile.[21]

This value is 1 order of magnitude higher than the rate constant derived for the same reaction by a competition method.[3] We believe that our value from kinetic observation is the more reliable, not only because the observation ties it directly to the tungsten radical concentration but also because the earlier experiments employed photochemical dissociation at 355 nm, where it is now known that carbonyl loss is much more important.[22] The problem with CO loss is that its photoproduct, $Cp_2W_2(CO)_5$, probably reacts with the carbon tetrachloride,[23] which was the reference reaction for the competition.[3] If the total rate of the photochemical transient with carbon tetrachloride is therefore larger than that between $CpW(CO)_3$ and CCl_4, the rate constant for the ferrocenium ion reaction will be artificially low compared to that obtained when the correct[10] rate constant for eq 10 is used to represent the total rate at which phototransients react.

$$CpW(CO)_3 + CCl_4 \rightarrow CpW(CO)_3Cl + {}^{\bullet}CCl_3 \quad (10)$$

The electron-transfer product $CpW(CO)_3^+$ is coordinatively and electronically unsaturated. The solvent may participate in the reaction, either by trapping the 16-electron cationic product of eq 9 to form $CpW(CO)_3(NCCH_3)^+$ or by binding to the 17-electron radical *before* electron transfer (eq 11).

$$CpW(CO)_3 + CH_3CN \rightleftharpoons CpW(CO)_3(NCCH_3) \quad (11)$$

This reaction represents the interconversion of 17e and 19e radicals. Such a process has the thermodynamic and kinetic advantage of yielding a species that more closely resembles the coordinatively and electronically saturated 18e product cation, $CpW(CO)_3(NCCH_3)^+$, after electron transfer occurs. A large solvent effect on the proportion of oxidation relative to atom abstraction was invoked in favor of eq 11.[3] However, the solvent choice generally affects electron-transfer reactions to a much greater extent than atom-transfer reactions.[24] We believe the matter of solvent participation has not yet been resolved but offer these observations.

The role of the solvent is difficult to assess by kinetic methods, since one cannot vary its concentration without changing the reaction medium. However, on the basis of the binding constants of PPh_3 and pyridine to $CpW(CO)_3$ (K = 6 and 0.16 L mol^{-1}, respectively, see below), it seems likely that the equilibrium in eq 11 lies very far to the left. Let us examine the interpretation we might make of these data depending of the degree of inner-sphere solvation of

(21) The standard deviation given here and elsewhere is that from the least-squares fit of k_ψ vs [substrate], without allowance for the systematic errors that may arise in extracting this rate constant from the kinetic curve. The actual error in any of the k_8 values given is estimated to be 10–15%.

(22) Even at 460–490 nm, some 20% of the photodissociation yields $Cp_2W_2(CO)_5$, which recombines with carbon monoxide only over 1 s or so, whereas the radical reactions are complete within *ca.* 100–400 μs. Reactions of this pentacarbonyl species are unimportant in any single experiment because of this difference in time scales. In those experiments where replicates were performed, the interval between flashes was such that the original dimer had already recovered from the carbonyl dissociation process to the maximum extent allowed.

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the radical by acetonitrile. If $CpW(CO)_3(NCCH_3)$ is indeed the predominant form of the metal radical, then it is simply the one whose rate constant has been determined. That is, we would write the rate law in terms of the predominant species, $v = k[CpW(CO)_3(NCCH_3)][FeCp_2^+]$, with the rate constant k now given as $k_9 = 1.8 \times 10^7$ L mol^{-1} s^{-1}.

On the other hand, if $CpW(CO)_3(NCCH_3)$ is a minor species (i.e., $K_{11} \ll 1$), and yet the only one that reacts appreciably with $FeCp_2^+$, e.g. at a specific rate designated as k^*_9, then the overall experimental rate constant will be $k^*_9 K_{11} a_{AN}$, where a_{AN} is the activity of the solvent. Since the rate constant for the reduction of ferrocenium ions by $CpW(CO)_3(NCCH_3)$ is necessarily limited by the rate of diffusion, $k^*_9 < 2.8 \times 10^{10}$ L mol^{-1} s^{-1} in acetonitrile. Then, $K_{11}a_{AN}$ must be $<10^{-3}$ L mol^{-1} if solvent binding precedes the rate-controlling electron transfer. This is not implausible: the binding of CH_3CN to (mesitylene)-$W(CO)_3^+$ was estimated to be 3×10^4 times weaker than the binding of $P(OR)_3$.[25] Therefore, it is at least kinetically possible that the reactive but minor species which reduces ferrocenium ions is $CpW(CO)_3(NCCH_3)$, although this seems the less plausible alternative.

Another point argues as well against reaction 11 lying to the right, even when the solvent is acetonitrile. The dimerization of these tungsten radicals[10] occurs essentially as fast as diffusion allows.[26] That is, given the inherent limitation for radical combination that k_c be no larger than one-fourth of k_{dc}, then the experiment shows that $CpW(CO)_3$ attains this limit.[27] Were the 19e species a major one, a thermodynamic barrier, and thus a kinetic one, would hinder its removal prior to combination. Thus, there can be little doubt, given the nature and structure of the kinetically inert dimer, that solvent is not incorporated in it.

This very issue has been commented upon by others. Burke and Brown,[12] in their study of the $Re(CO)_4L$ radical with methylpyridinium ions, comment as follows: "Because acetonitrile is nucleophilic in character, the question arises as to whether the electron transfer occurs from a 19-electron metal carbonyl radical, formed via interaction of the solvent with the 17-electron $Re(CO_4)L^\bullet$ radical. This question has already been addressed [by Rushman and Brown[11]]; it is our view that the evidence argues against a significant role for the solvent in this sense."

Reduction of $(C_5Me_5)_2Fe^+$. No reduction of 0.26 mM decamethylferrocenium ions by $CpW(CO)_3$ was observed. The design of this experiment allows us to set the limit $k < 4 \times 10^6$ L mol^{-1} s^{-1}. It was not possible to use higher concentrations of $(C_5Me_5)_2Fe^+$, and thereby decrease the limit further or determine the value, since the high background absorbance at 356 nm made the probe reaction (formation of $[CpW(CO)_3]_2$) impossible to observe. That is to say, there is a competition between the two reactions shown in eq 12.

At the maximum concentration of $Fe(C_5Me_5)_2^+$, we found that the same amount of $Cp_2W_2(CO)_6$ was recovered in the kinetic step(s) following the laser flash, irrespective of whether or not $Fe(C_5Me_5)_2^+$ was added. Also, the rate of absorbance change followed second-order kinetics with a rate constant that is the same as the value of k_c when $[Fe(C_5Me_5)_2^+] = 0$.

$$CpW(CO)_3 \xrightarrow{CpW(CO)_3} Cp_2W_2(CO)_6$$

$$\xrightarrow{Fe(C_5H_5)_2^+} CpW(CO)_3^- + Fe(C_5H_5)_2^+ \quad (12)$$

The lower reactivity of $Fe(C_5Me_5)_2^+$ compared to that of $FeCp_2^+$ is consistent with the difference in reduction potentials, –0.12 versus +0.37 V (SCE), respectively. Our result is consistent with a report that $Fe(C_5Me_5)_2^+$ reacts many times more slowly with $CpW(CO)_3$ than $FeCp_2^+$ does.[3] From this, we used an extrapolation based on the equation from the Marcus theory for electron transfer to predict that the rate constant for the reduction of decamethylferrocenium ions is then 2.2×10^6 L mol^{-1} s^{-1}, given the value found for k_9 for $Fe(C_5H_5)_2^+$. A rate constant as low as this would not have been detected by the methods we used. Although we found fault with the use of the carbon tetrachloride reference reaction for short-wavelength irradiation, it seems probable that in a relative sense it is correct and that this is at least a provisionally reliable value for $Fe(C_5Me_5)_2^+$.

Reduction of 1,4-Benzoquinone. As with ferrocenium ions, the recovery of the absorbance of $[CpW(CO)_3]_2$ following the laser flash is less when carried out in the presence of 1,4-benzoquinone (Q). The rate constant for the reaction of $CpW(CO)_3$ with 1,4-benzoquinine, evaluated as for ferrocenium ions, is $(2.7 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}. The ultimate product is hydroquinone, observed in the UV spectrum[28] and the HPLC chromatogram of a sample that had been flashed several times. Accompanying the absorbance rise at 356 nm from the buildup of $[CpW(CO)_3]_2$ is an absorbance increase at 458 nm, corresponding[29] to the formation of the semiquinone radical anion $Q^{\bullet-}$. This confirms that the reaction under study is the electron-transfer process. The change at 458 nm is too complex for exact analysis, however, since the tungsten dimer absorbs there (ϵ 2.0×10^3 L mol^{-1} cm^{-1}) as well as the semiquinone radical, and subsequent reactions, not yet fully characterized, then set in. Nonetheless, a comparison between the two kinetic curves, shown in Figure 2, leaves little doubt that they represent the same chemistry in that they occur over the same time period.

The semiquinone radical undergoes disproportionation to form hydroquinone (the proton source being adventitious water) or its anion. A closer look at the kinetic events reveals that: (a) after a fast-rising portion, the absorbance drifts slowly downward at both wavelengths, (2) the downward drift is faster at higher concentrations of the tungsten dimer, and (3) the downward drift is faster at higher concentrations of benzoquinone. These observations show that the tungsten dimer is in some way involved with one pathway by which the semiquinone radical disappears. A possible mechanism for this process is shown in Scheme I.

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(27) The factor arises from the spin statistical factor of 1/4 to account for the nonreactive encounters of radical pairs in triplet states. A reviewer pointed out, however, that the large spin–orbit coupling of transition-metal radicals may remove this restriction.
(28) Judged by the appearance of a peak at 290 nm, corresponding to the spectral maximum of hydroquinone (Baxendale, J. H.; Hardy, H. R. *Trans Faraday Soc.* **1953**, *49*, 1140).
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Scheme I

$$\{CpW(CO)_3\}_2 \underset{k_c}{\overset{h\nu}{\rightleftarrows}} 2CpW(CO)_3 \qquad (A)$$

$$CpW(CO)_3 + Q \xrightarrow{k} CpW(CO)_3^{+} + Q^{\bullet -} \qquad (B)$$

$$2Q^{\bullet -} \overset{H^+}{\rightleftarrows} Q + Q^{2-}/HQ^{-}/H_2Q \qquad (C)$$

$$\{CpW(CO)_3\}_2 + Q^{\bullet -} \xrightarrow{H^+} \{CpW(CO)_3\}_2^{+} + H_2Q \qquad (D)$$

$$\{CpW(CO)_3\}_2^{+} \rightleftarrows CpW(CO)_3 + CpW(CO)_3^{+} \qquad (E)$$

In this scheme, eq D accounts for the second stage, in which the decreases in [$\{CpW(CO)_3\}_2$] and [$Q^{\bullet -}$] are accelerated by higher [$\{CpW(CO)_3\}_2$] and [Q]. In eq E, the intermediate $\{CpW(CO)_3\}_2^+$ regenerates one tungsten radical which reenters the cycle at step B, since benzoquinone is in excess. However, an efficient catalytic chain reaction is not observed, since the disproportionation reaction C is reasonably efficient, with $k_C = 7.8 \times 10^8$ L mol^{-1} s^{-1}.[30] This aspect of the study leaves some matters unexplored, and further work is planned.

Acceleration by Lewis Bases. The rates of reduction of ferrocenium ions and 1,4-benzoquinone by $CpW(CO)_3$ are accelerated by the addition of Lewis bases. The dependence of the pseudo-first-order rate constants on [PPh_3] is linear, as shown in the inset to Figure 1. The origin of this effect must be an interaction between $CpW(CO)_3$ and PPh_3 prior to the rate-controlling electron-transfer step. We consider two possible explanations for the acceleration. First, rapid substitution of PPh_3 for coordinated CO (eq 13) would yield the $CpW(CO)_2PPh_3$

$$CpW(CO)_3 + PPh_3 \rightarrow CpW(CO)_2PPh_3 + CO \qquad (13)$$

radical. Since PPh_3 is a better electron donor than CO, the PPh_3-substituted radical should be a better reductant than $CpW(CO)_3$ itself. The rate of substitution is known, $k_{13} = 2.5 \times 10^5$ L mol^{-1} s^{-1}.[10,31] Therefore, when [PPh_3] = 5 mM (the maximum used), the pseudo-first-order rate constant for formation of $CpW(CO)_2PPh_3$ is 1.25×10^3 s^{-1}. From the inset to Figure 1, the pseudo-first-order rate constant for the reduction of 0.36 mM ferrocenium in the presence of 5 mM PPh_3 is 3.5×10^4 s^{-1}. Therefore, reaction 13 does not occur to a significant extent before the rate-determining electron transfer *under these conditions*.

The second possibility is that a 19-electron radical formed in the presence of PPh_3 reduces ferrocenium ions (eqs 14 and 15).

$$CpW(CO)_3 + PPh_3 \rightleftarrows CpW(CO)_3PPh_3 \qquad (14)$$

$$CpW(CO)_3PPh_3 + Cp_2Fe^{+} \rightarrow CpW(CO)_3PPh_3^{+} + Cp_2Fe \qquad (15)$$

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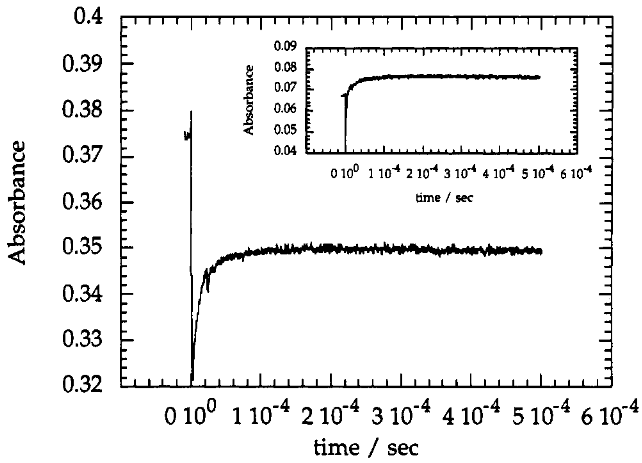

Figure 2. Two kinetic traces for the reduction of 1,4-benzoquinone by $CpW(CO)_3$. The main trace was monitored at 356 nm, where the tungsten dimer is the only absorbing species. The inset shows the same experiment monitored at 458 nm, where both the semiquinone radical and the tungsten dimer absorb. Conditions: [$\{CpW(CO)_3\}_2$] = 16 μM, [quinone] = 0.68 mM; the laser flash produces *ca.* 4 μM $CpW(CO)_3$.

The observed rate constant for this mechanism, if reaction 14 is equilibrated rapidly compared to the electron transfer, is given by

$$k_\psi = \frac{k_9 + K_{14}k_{15}[PPh_3]}{1 + K_{14}[PPh_3]}[Cp_2Fe^+] \qquad (16)$$

This model predicts a linear dependencer of k_ψ on [PPh_3] if $K_{14}[PPh_3] \ll 1$. That is, we require that $K_{14} \ll 20$ L mol^{-1}, allowing that a deviation from linearity of up to 10% might go undetected. From the slope of the line shown in the inset to Figure 1, $K_{14}k_{15} = 1.9 \times 10^{10}$ L^2 mol^{-2} s^{-1}. At the same time, the bimolecular rate contant may not exceed the diffusion-controlled limit, or $k_{15} < 2.8 \times 10^{10}$ L mol^{-1} s^{-1}. The combination of the two arguments defines a range for k_{15} of 10^9–$10^{10.3}$ L mol^{-1} s^{-1}. This is equivalent to setting $0.8 < K_{14} < 20$ L mol^{-1}, an estimate we shall subsequently improve upon.

It is most interesting that the effect of Lewis base found here is absent in a system that seems to be quite similar. The reaction of $Re(CO)_4P(CH_3)_3^\bullet$ with 1-methyl-4-cyanopyridinium ions is unaffected by the addition of PPh_3 in acetonitrile.[11] In this case, therefore, either the 19e adduct does not form to a significant extent or it is kinetically ineffective relative to the original 17e radical. A reviewer has suggested that the ability of the cyclopentadienyl ligand to adopt variable hapticities allows the $CpW(CO)_3PPh_3$ complex to retain the reactive 17e structure of its parent.

Estimation of the Binding Constant for Lewis Bases to $CpW(CO)_3$. In order to evaluate k_{15}, it is necessary to obtain independently a value for K_{14}. In the presence of very high concentrations of PPh_3, less dimer absorbance is restored owing to radical disproportionation (eq 17).

$$CpW(CO)_3PPh_3 + CpW(CO)_3 \rightarrow CpW(CO)_3PPh_3^{+} + CpW(CO)_3^{-} \qquad (17)$$

It is assumed that the disproportionation is *not* a chain process. The reaction is again monitored by the buildup of the parent tungsten dimer, which competes with reaction 17. As in the reactions with other substrates, the absorbance-time curve is governed by a combination of all of the pertinent rate constants. In this case both processes are second order with respect to the concentration of radical. The pertinent concentration variable is now the sum of the equilibrated 17e and 19e radicals, written as $[CpW(CO)_3]_T$. Thus, the absorbance–time traces were fit to second-order kinetics, giving good agreement with this model. In terms of the reactions already written, the expression for the reaction rate is

$$-\frac{d[CpW(CO)_3]}{dt} = 2k_c[CpW(CO)_3]^2 + 2k_{17}[CpW(CO)_3][CpW(CO)_3PPh_3] \quad (18)$$

The mass balance expression is $[CpW(CO)_3]_T = [CpW(CO)_3] + [CpW(CO)_3PPh_3]$. The assumption (previously made and justified) that reaction 14 is much faster than any of the further steps (which allows the influence of reaction 14 to be expressed in terms of its equilibrium constant) provides the forms

$$[CpW(CO)_3] = [CpW(CO)_3]_T \frac{1}{1 + K_{14}[PPh_3]}$$

$$[CoW(CO)_3PPh_3] = [CpW(CO)_3]_T \frac{K_{14}[PPh_3]}{1 + K_{14}[PPh_3]} \quad (19)$$

Thus, the expression for the reaction rate becomes

$$-\frac{d[CpW(CO)_3]_T}{dt} = 2\frac{k_c + k_{17}K_{14}[PPh_3]}{1 + K_{14}[PPh_3]}[CpW(CO)_3]_T^2 \quad (20)$$

The yield of radical disproportionation products was calculated from the difference in the yield of dimer after consumption of the photochemical transients (other than $Cp_2W_2(CO)_5$, of course) in an experiment with a given concentration of phosphine, as compared to one without phosphine. The ratio of disproportionation products so calculated to the yield of dimer is related to the equilibrium constant K_{14} by

$$\frac{\dfrac{d[CpW(CO)_3PPh_3^+]}{dt}}{\dfrac{d[Cp_2W_2(CO)_6]}{dt}} = \frac{k_{17}[CpW(CO)_3][CpW(CO)_3PPh_3]}{k_c[CpW(CO)_3]^2} \quad (21)$$

With the usual substitution from the equilibrium constant expression and from eq 19, this becomes

$$\frac{2[W]_T - [D]_\infty}{[D]_\infty} = \frac{k_{17}K_{14}}{k_c}[PPh_3] \quad (22)$$

where $[W]_T$ is the total concentration of radicals formed in the flash and $[D]_\infty$ is the yield of dimer. A plot of the yield ratio versus $[PPh_3]$, shown in Figure 3, has a slope of $k_{17}K_{14}/k_c = 6 \pm 1$ L mol^{-1}.

If we choose to assume a particular value of k_{17}, an estimate of K_{14} can then be made. We shall take the disproportionation reaction as being very rapid. At most,

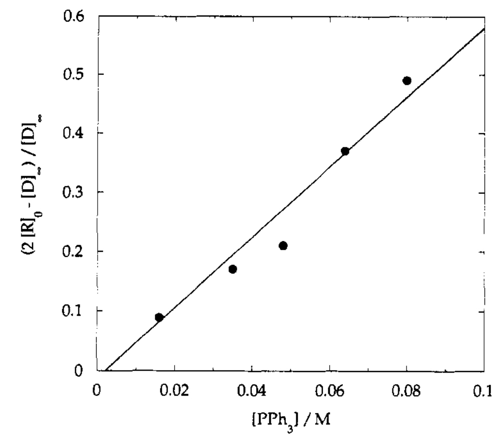

Figure 3. Dependence of the product ratio (radical disproportionation products)/(radical combination product) on the concentration of PPh_3, which is used to define the binding constant of phosphine to the tungsten radical.

it can have a rate constant of $k_{17} = k_c$ that is 6×10^9 L mol^{-1} s^{-1} in acetonitrile. This is, moreover, a reasonable result in that the radical disproportionation and dimerization reactions are usually close to one another. In that event, K_{14} would be 6 ± 1 L mol^{-1}. A similar treatment for pyridine gives an estimated binding constant of 0.16 ± 0.04 L mol^{-1} between $CpW(CO)_3$ and pyridine. Both equilibrium constant values depend on the assumed values of the rate constants for disproportionation being at the diffusion limit, which thus could be some 100 times larger, were the rate constants correspondingly less.

With this value of K_{14}, we calculate $k_{15} = 3 \times 10^9$ L mol^{-1} s^{-1}. Therefore, the 19-electron radical $CpW(CO)_3PPh_3$ is *more reactive* than $CpW(CO)_3$ toward ferrocenium ions by a factor of 1.6×10^2. This calculation is a lower limit since k_{15} is close to the diffusion-controlled rate. Also, it assumes that the reactive species in the absence of PPh_3 is $CpW(CO)_3$, and not $CpW(CO)_3(NCCH_3)$, for the reasons given above.

Oxidation of $(C_5Me_5)_2Fe$. Others have reported that decamethylferrocenium ions do oxidize the tungsten radicals,[3] but our results have shown that the reaction occurs more slowly than the present technique can measure. That result, and the closeness of the standard reduction potentials of the partners, led us to try a related reaction, the reduction of $CpW(CO)_3$ by decamethylferrocene:

$$Fe(C_5Me_5)_2 + CpW(CO)_3 \rightarrow Fe(C_5Me_5)_2^+ + CpW(CO)_3^- \quad (23)$$

An efficient electron-transfer reaction does indeed occur as shown, as evidenced by a lesser buildup of the tungsten dimer when decamethylferrocene is present and by the shorter time required for it to reach completion.

The treatment of the kinetic data proceeds as in eqs 3–7. The second-order rate constant is $k_{23} = (2.23 \pm 0.07) \times 10^8$ L mol^{-1} s^{-1} (Figure 1). The analogous reaction occurs with $CpMo(CO)_3$, with a second-order rate constant of $(9.7 \pm 0.4) \times 10^7$ L mol^{-1} s^{-1}. Assuming that the electron exchange rates for the partners $CpW(CO)_3/CpW(CO)_3^-$ and $CpMo(CO)_3/CpMo(CO)_3^-$ are similar, the lower reactivity of $CpMo(CO)_3$ can be rationalized on the basis of its reduction potential, −0.078 V (SCE) compared to −0.022

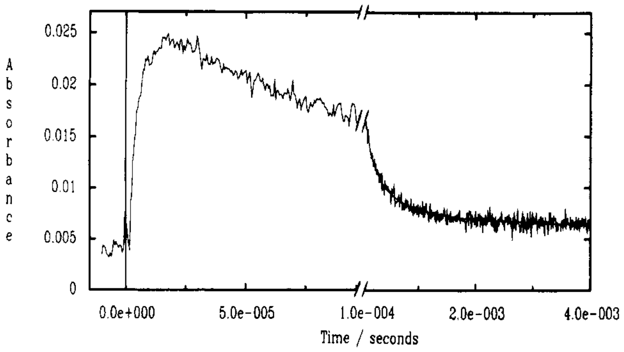

Figure 4. Kinetic trace recorded at 612 nm during the laser flash photolysis of $[CpW(CO)_3]_2$ in the presence of TMPD. Note the change in time scale on the abscissa. The solid line is the fit to a second-order rate law.

V (SCE) for $CpW(CO)_3$.[32] Detection of the presumed product, $Fe(C_5Me_5)_2^+$, during the flash photolysis experiment was not feasible owing to the small concentration (10–15 μM) formed in the flash and its low extinction coefficient (394 L mol^{-1} cm^{-1} at 778 nm).[17] We looked for the accumulated product after several flashes but were unsuccessful because of other reactions that later set in (see below).

Oxidation of TMPD. To confirm that $CpW(CO)_3$ can indeed oxidize a substrate such as decamethylferrocene, we sought another reaction where the electron-transfer product could be detected directly. We thus turned to tetramethylphenylenediamine, since its oxidation product is $TMPD^{\bullet+}$, an intensely absorbing radical cation (ϵ 1.2 × 10^4 L mol^{-1} cm^{-1} at 612 nm).[33] The tungsten radical does indeed oxidize TMPD. Its rate constant was evaluated as before: $k_{24} = (2.6 \pm 0.3) \times 10^7$ L mol^{-1} s^{-1}.

$$CpW(CO)_3 + TMPD \rightarrow CpW(CO)_3^- + TMPD^{\bullet+} \quad (24)$$

In addition the formation of $TMPD^{\bullet+}$ was directly observed immediately following the laser flash (Figure 4). The rate of its buildup agrees with that derived from the recovery of the tungsten dimer, confirming that they represent the same reaction.

When $TMPD^{\bullet+}$ is made by independent methods, it persists in this medium for a long time. In particular, this radical is stable in the dark with $\{CpW(CO)_3\}_2$ and also on addition to the mixed system after all the reactivity of the photochemical transients had ceased. In this system, however, the absorbance of the $TMPD^{\bullet+}$ product is not stable but decreases slowly over several milliseconds following the laser flash. The absorbance decrease follows second-order kinetics. At 356 nm, the dimer absorbance is also not stable, and an additional quantity of $Cp_2W_2(CO)_6$ forms in a second phase. On a short time scale (several microseconds), the formation of $[CpW(CO)_3]_2$ is due, as usual, to recombination of the $CpW(CO)_3$ radicals in competition with their oxidation of TMPD. On a longer time scale (several milliseconds), the absorbance increases concurrently with the loss of the $TMPD^{\bullet+}$ spectrum.

There is thus no *net* photochemical reaction of $[CpM(CO)_3]_2$ with TMPD, even though reduction of the $CpM(CO)_3$ radical is clearly observed on a short time scale. Scheme II presents a mechanism—admittedly with certain speculative features, not yet verified—proposed to account for these results.

Scheme II

$$[CpW(CO)_3]_2 \underset{k_c}{\overset{h\nu}{\rightleftarrows}} 2CpW(CO)_3 \quad (8)$$

$$CpW(CO)_3 + TMPD \rightarrow CpW(CO)_3^- + TMPD^{\bullet+} \quad (24)$$

$$CpW(CO)_3 + CpW(CO)_3^- \rightleftarrows [CpW(CO)_3]_2^{\bullet-} \quad (25)$$

$$[CpW(CO)_3]_2^{\bullet-} + TMPD^{\bullet+} \rightarrow [CpW(CO)_3]_2 + TMPD \quad (26)$$

The intermediate $[CpM(CO)_3]_2^{\bullet-}$ is a radical anion and is expected to be a stronger reductant than $CpM(CO)_3$ itself. It is exactly analogous to the well-recognized species $CpW(CO)_3L$ with, for example, L = PPh_3 and C_5H_5N, characterized in this work and from earlier research. One can argue that such acid–base adducts form to an extent depending on the Lewis basicity of the donor, other things (*e.g.*, steric factors) being equal. Since the tungsten anion is an excellent nucleophile, we assume it to be a good base. Given that, the formation of the dimer radical anion appears reasonable. To be kinetically competent in this scheme, $Cp_2W_2(CO)_6^{\bullet-}$ need form only to a minor extent, provided it is sufficiently reactive. That it would be a much better electron donor than the monomeric radical in both kinetic and thermodynamic senses has been justified in comments made in this work and by Tyler and other authors in reference to 19e radicals in general. These points of stability and reactivity are just the ones we made earlier about $CpW(CO)_3PPh_3$, the extent of formation of which was minor at the phosphine concentrations used. To account for the nearly quantitative regeneration of the $[CpM(CO)_3]_2$ absorbance observed, however we find it necessary to assume that equilibrium in eq 25 is achieved very rapidly and lies to the right. This is so because the low concentration of the tungsten anion generated in this reaction suffices to drive it such that the original concentration of the tungsten dimer is completely restored. This electron chain remains under active investigation, to prove its validity and to detect more of the component steps directly.

Earlier work has provided an analog. Evidence for a long-lived one-electron-reduced metal dimer was obtained in pulse radiolysis studies of $Re_2(CO)_{10}$.[34] Other species such as $Cp_2W_2(CO)_6^{\bullet-}$ may be formed to a small extent at equilibrium. This is not necessarily a deterrent to its being an intermediate, however, if it is sufficiently reactive. We must carefully note, though, that the $M_2^{\bullet-}$ species are generally thought to lie on a dissociative coordinate. If this is the case here, the role suggested is not feasible.

The second stage of dimer formation is also observed in the reactions of $CpW(CO)_3$ and $CpMo(CO)_3$ with $(C_5Me_5)_2Fe$. The complete recovery of the dimer explains why no product accumulates even after several laser flashes. Without that, the accumulation of decamethylferrocenium ion should have been observable. This can be explained also by Scheme II, with the substitution of $(C_5Me_5)_2Fe^+$ for $TMPD^{\bullet+}$ and $(C_5Me_5)_2Fe$ for TMPD. Again, however, the unprecedented reaction 25 must be

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invoked for this to be valid. Further studies of the electron-transfer reactions of $CpM(CO)_3$ are planned in order to obtain direct evidence for $[CpM(CO)_3]_2^{\bullet-}$ and to define its reactivity.

Electron-Exchange Rates for 17-Electron Radicals. Mechanistic Implications. The electron-transfer rate constants for the reactions described above can be used to estimate the electron exchange rates of the $CpW(CO)_3/CpW(CO)_3^-$ and $CpW(CO)_3^+/CpW(CO)$ couples by applying the Marcus equation. The driving force for the oxidation of decamethylferrocene by $CpW(CO)_3$ is 0.10 V, and the electron exchange rate constant[17] is 3.8×10^7 L mol^{-1} s^{-1} for $Fe(C_5Me_5)_2Fe^+/Fe(C_5Me_5)_2$. These values combined to give an electron exchange rate for the $CpW(CO)_3/CpW(CO)_3^-$ couple of 3×10^7 L mol^{-1} s^{-1}. This high value indicates that very little nuclear reorganization is required to add an electron to the half-filled HOMO of the 17-electron radical.

Similarly, we consider the oxidation of TMPD, given that the electron exchange rate constant[35] for $TMPD/TMPD^{\bullet+}$ is 1.0×10^9 L mol^{-1} s^{-1}. The driving force for the reaction is −0.05 V, and thus the calculated electron exchange rate for $CpW(CO)_3/CpW(CO)_3^-$ is 5×10^6 L mol^{-1} s^{-1}. The two values agree within 1 order of magnitude, perhaps as well as one can expect from such calculations.

The driving force for reduction of ferroceniumions by $CpW(CO)_3$ is 1.13 V, based on $E°\{CpW(CO)_3(NCCH_3)^+/CpW(CO)_3\} = -0.76$ V versus SCE.[36] Even though this is much larger than the driving force for oxidation of decamethylferrocene (0.10 V), the former reaction is actually slower. Using 5.7×10^6 L mol^{-1} s^{-1} for the electron exchange rate of $FeCp_2^+/FeCp_2$,[16] we calculate an electron exchange rate for $CpW(CO)_3^+/CpW(CO)_3$ of 5×10^{-12} L mol^{-1} s^{-1}. This low value may arise because of the reorganization barrier caused by the coordination unsaturation of the 16-electron cation, which must bind a solvent molecule after it is formed. Of course, since this calculation combines a reduction potential of the 18e cation to which acetonitrile is coordinated, with the reaction of the metal radical which presumably (see above) lacks the solvent, the result is of dubious value. Alternately, one might be tempted to argue that CH_3CN is bound to the metal radical before electron transfer with a very low binding constant ($5 \times 10^{-5} < K_{11} < 0.1$ L mol^{-1}). That would lead to an observed electron-transfer rate that incorporates K_{11}. The true electron-transfer rate constant for the reaction of $CpW(CO)_3(NCCH_3)$ might then be 10^{10} L mol^{-1} s^{-1}, and the electron exchange rate for the $CpW(CO)_3(NCCH_3)^+/CpW(CO)_3(NCCH_3)$ couple could not be estimated from the Marcus equation since the reaction would be diffusion-controlled. We conclude that the value of the electron exchange rate of the tungsten cation/radical pair remains undefined.

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