

Photophysics and Photoredox Properties of the Tungsten Carbyne Complex $\text{Cp}\{\text{P}(\text{OPh})_3\}(\text{CO})\text{W}\equiv\text{CPh}$

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Introduction

The long-lived emissive excited states¹ and photochemical reactivity² of metal carbynes have prompted numerous studies of their photophysical properties.^{3,4} Our interest in the photochemistry of these compounds was stimulated by the discovery that photolysis of $\text{Cp}\{\text{P}(\text{OR})_3\}(\text{CO})\text{Mo}\equiv\text{CR}'$ and $\text{Cp}\{\text{P}(\text{OR})_3\}(\text{CO})\text{W}\equiv\text{CR}'$ ($\text{R}' = \text{alkyl}$) in CHCl_3 results in conversion of the carbyne ligands to organic products.⁵ In these reactions, the excited state of the carbyne complex undergoes electron transfer to CHCl_3 to produce a highly reactive 17-electron species. Evidence for the electron transfer process can be found in the radical reactions of the resulting carbyne complexes⁶ and the observation of side reactions from the reduction of chloroform.^{3b,5} The involvement of electron transfer in the photochemistry of metal carbyne complexes has been unequivocally established by recent studies of photoinduced electron transfer between a rhenium carbyne complex and a series of electron donors and acceptors.^{4a}

In an effort to more fully probe the role photochemical electron transfer⁷ plays in the reactions of tungsten carbynes, we have undertaken a study of electron transfer from the excited

state of $\text{Cp}\{\text{P}(\text{OPh})_3\}(\text{CO})\text{W}\equiv\text{CPh}$ (**1**) to a series of electron acceptors. In the course of this study, we examined the quenching of the $d\pi^*$ excited state of **1** by a series of pyridinium and nitroaromatic acceptors of varying reduction potential. Laser flash photolysis reveals that in every case quenching is accompanied by the appearance of radical ion products, thereby demonstrating that quenching occurs via electron transfer. The dependence of the bimolecular quenching rate constant on the reduction potentials of the acceptors establishes that **1** is a potent reducing agent in the $d\pi^*$ excited state. Moreover, a Marcus analysis of the rate data implies that oxidation of **1*** is accompanied by a comparatively low reorganization energy but that electron transfer within the encounter complex may be weakly nonadiabatic.

Results and Discussion

Photophysics of $\text{Cp}\{\text{P}(\text{OPh})_3\}(\text{CO})\text{W}\equiv\text{CPh}$. Previous photophysical studies⁸ of the carbynes $\text{Cp}\{\text{P}(\text{OMe})_3\}(\text{CO})\text{M}\equiv\text{CR}$, where $\text{M} = \text{Mo}$ or W and $\text{R} = \text{aryl}$, allowed the assignment of the lowest lying absorption as arising from a $d\pi^*$ transition.³ This absorption, although spin-allowed, has a low extinction coefficient because the large contribution of d orbitals to the " π^* " LUMO lends the transition a significant degree of dd character. In addition to luminescence in solution, the moderately long-lived $d\pi^*$ excited states feature a strong transient absorption by which the excited state reactivity can be examined.

The absorption spectrum of the carbyne complex $\text{Cp}\{\text{P}(\text{OPh})_3\}(\text{CO})\text{W}\equiv\text{CPh}$ (**1**) in CH_3CN is very similar to that of its $\text{P}(\text{OMe})_3$ analogue in that it displays two UV/visible bands ($\lambda_{\text{max}} = 322 \text{ nm}$, $\epsilon \approx 9000 \text{ M}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max}} = 458 \text{ nm}$, $\epsilon \approx 200 \text{ M}^{-1} \text{ cm}^{-1}$).^{3a} The lower energy band corresponds to the $d\pi^*$ transition while the high-energy band is due to the $\pi\pi^*$ transition of the $\text{W}\equiv\text{CPh}$ chromophore. Complex **1** features red luminescence similar to that of the structurally related Mo and W carbyne complexes that have been previously studied.³ In CH_3CN solution at 298 K, the luminescence appears as a broad, structureless band with $\lambda_{\text{max}} \approx 710 \text{ nm}$ and a lifetime (τ_{em}) of 192 ns. Emission from **1** at 77 K in a 2-MTHF solvent glass is similar in energy and band shape to that observed in solution at 298 K. Franck–Condon band shape analysis of the low-temperature emission affords an estimate of $14\,800 \pm 200 \text{ cm}^{-1}$ (1.85 eV) for E_{00} .¹⁰

Laser flash photolysis of **1** affords a strongly absorbing transient with $\lambda_{\text{max}} \approx 425 \text{ nm}$ (Figure 1a). The spectrum of this transient is very similar to that assigned to the $d\pi^*$ state in $\text{Cp}\{\text{P}(\text{OMe})_3\}(\text{CO})\text{M}\equiv\text{CR}$ ($\text{M} = \text{W}$ and Mo), and on this basis the transient absorption observed for **1** is also attributed to that state.^{3a} Global analysis of the transient absorption data indicates

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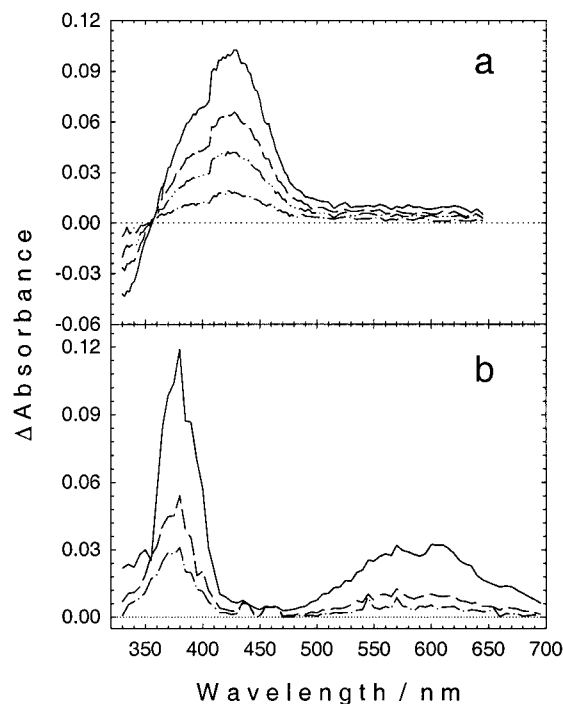
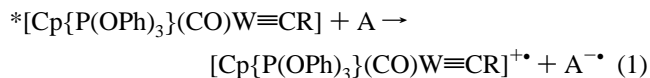


Figure 1. Transient absorption-difference spectra following 355 nm laser excitation (10 mJ/pulse, 10 ns fwhm). (a) Complex **1** ($c = 1 \times 10^{-4}$ M) in CH_3CN , spectra at 40, 80, 120, and 160 ns delay after excitation. (b) Complex **1** ($c = 1 \times 10^{-4}$ M) and N,N' -dimethyl-4,4'-bipyridinium ($c = 0.02$ M) in CH_3CN solution, spectra at 0, 40, and 80 μs delay after excitation.

that the $d\pi^*$ excited state absorption decays with a lifetime of 187 ns, in excellent agreement with the emission lifetime.

Electron Transfer Quenching. The transient absorption assigned to the $d\pi^*$ state of **1** is quenched by the addition of various pyridinium and nitroaromatic electron acceptors to the solutions. For each electron acceptor, $d\pi^*$ quenching is accompanied by the formation of a long-lived transient ($\tau > 20 \mu\text{s}$, vide infra) which can be assigned to the radical ion produced by reduction of the electron acceptor. For example, Figure 1b illustrates the transient absorption spectrum of a solution of **1** with 20 mM dimethylviologen (MV^{2+}). The spectrum is clearly dominated by the viologen radical cation, as evidenced by the characteristic absorptions at 395 and 605 nm.¹¹ On the basis of these laser flash photolysis observations, we attribute the quenching to photoinduced electron transfer in which the excited state carbyne complex reduces the acceptor A to generate $\text{A}^{\cdot-}$ (eq 1).



Transient absorption due to the oxidized carbyne complex $\mathbf{1}^{\cdot+}$ was not observed in these experiments, in spite of many efforts aimed at detecting it. Although the failure to observe $\mathbf{1}^{\cdot+}$ could be attributed to low absorptivity, it is likely that this 17-electron species undergoes rapid secondary reactions owing to its high reactivity. Moreover, several observations support the premise that $\mathbf{1}^{\cdot+}$ reacts very rapidly after being formed. First, in most cases the transient absorption due to $\text{A}^{\cdot-}$ persists out to very long time scales, which suggests that second-order charge recombination (eq 2) does not occur. Second, photochemical

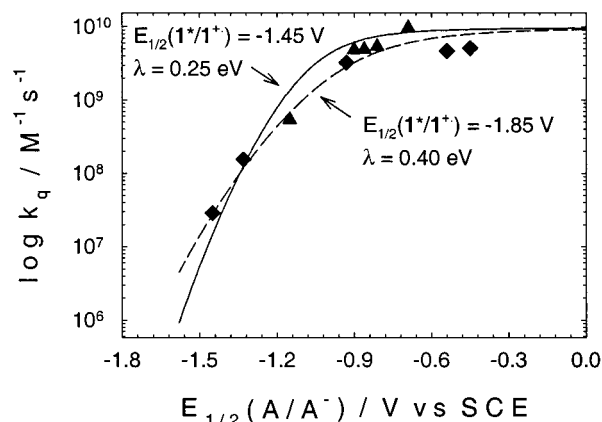
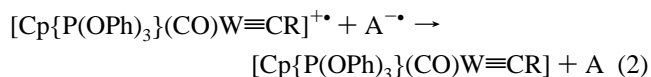


Figure 2. Plots of $\log k_q$ vs $E_{1/2}(\text{A}/\text{A}^{\cdot+})$ for electron acceptors listed in Table 1: \blacktriangle , data for nitroaromatic quenchers; \blacklozenge , data for pyridinium quenchers. Solid lines calculated as described in text.

studies of related tungsten and molybdenum carbyne complexes indicate that the metal center in $17e^-$ radical cations such as $\mathbf{1}^{\cdot+}$ rapidly engages in ligand exchange and atom abstraction reactions.⁵



Stern–Volmer quenching studies were carried out with a series of five pyridinium ion and four nitroaromatic electron acceptors to explore the effect of thermodynamic driving force on the electron transfer quenching kinetics of **1**. The quenching experiments were carried out by measuring the lifetime of **1** as a function of acceptor concentration using laser flash photolysis to monitor the decay kinetics of the excited state absorption of **1**. In every case the Stern–Volmer plots (i.e., τ^0/τ vs $[\text{Q}]$) were linear. The reduction potentials of the electron acceptors¹² and corresponding bimolecular quenching rate constants (k_q) are compiled in a table that is available as Supporting Information. Figure 2 illustrates the correlation between k_q and $E_{1/2}(\text{A}/\text{A}^{\cdot-})$, and as expected for an electron transfer mechanism, k_q increases as $E_{1/2}(\text{A}/\text{A}^{\cdot-})$ becomes less negative.

The cage escape yield (η_{esc}) for quenching of **1** with MV^{2+} was determined to provide information regarding the overall efficiency of photoinduced electron transfer.¹³ This experiment revealed that $\eta_{\text{esc}} = 0.26$, indicating that electron transfer products are produced in comparatively high yield as a result of the quenching process. Interestingly, the cage escape yield for quenching of $\mathbf{1}^*$ by MV^{2+} is very similar to that for oxidative quenching of excited state $\text{Ru}(\text{bpy})_3^{2+}$ by MV^{2+} .^{13,14} Moreover, the cage escape yields for both metal complex systems are considerably larger than observed when singlet excited state donors are quenched by pyridinium acceptors.¹⁵ The relatively high cage escape yield in the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ system has been attributed to arise (in part) because $\text{Ru}(\text{bpy})_3^{2+*}$ has a large degree of triplet spin character.^{13,14,16} By analogy we suggest

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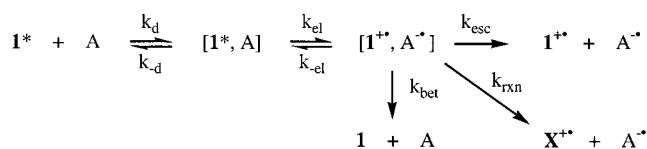
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Scheme 1



that the high cage escape yield in the $\mathbf{1}/\text{MV}^{2+}$ system arises because $\mathbf{1}^*$ also has significant triplet spin character.

Thermodynamics and Kinetics of Photoinduced Electron Transfer. The free energy for photoinduced electron transfer from the $d\pi^*$ state of $\mathbf{1}$ to an electron acceptor can be estimated as shown in eq 3a, where $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet})$ is the oxidation potential

$$\Delta G_{ET} = E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) - E_{1/2}(\text{A}/\text{A}^{\bullet-}) \quad (3a)$$

$$E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) = E_{1/2}(\mathbf{1}/\mathbf{1}^{+\bullet}) - E_{oo} \quad (3b)$$

of the $d\pi^*$ state of $\mathbf{1}$ and $E_{1/2}(\text{A}/\text{A}^{\bullet-})$ is the reduction potential of the acceptor.^{12,17} The excited and ground state oxidation potentials of $\mathbf{1}$ are related by eq 3b, where E_{oo} is the energy of the relaxed $d\pi^*$ excited state.¹² Cyclic voltammetry of $\mathbf{1}$ in $\text{CH}_3\text{-CN}$ solution reveals a single irreversible anodic wave at $E_{pa} = +0.34$ V.¹⁸ This wave arises from one-electron oxidation of the complex to afford the radical cation, $\mathbf{1}^{+\bullet}$, which reacts rapidly on the electrochemical time scale. Although the peak of an irreversible voltammetric wave does not necessarily correspond to the thermodynamic potential for the reversible electrode process (i.e., $E_{1/2}$), typically the peak potential is within several hundred millivolts of $E_{1/2}$.¹⁹ Thus, by assuming $E_{pa} \approx E_{1/2}(\mathbf{1}/\mathbf{1}^{+\bullet}) = +0.34$ V, and using the E_{oo} value obtained from luminescence spectroscopy, eq 3a affords an estimate of $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) \approx -1.5$ V. This estimate suggests that photoinduced electron transfer is exothermic for acceptors with reduction potentials positive of -1.5 V, and therefore $\mathbf{1}^*$ will be quenched efficiently by these acceptors. Inspection of Figure 2 clearly indicates that this qualitative analysis is consistent with the experimental observations in that acceptors with $E_{1/2} > -1.5$ V quench $\mathbf{1}^*$ at rates in excess of $10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The correlation between the kinetics and thermodynamics of photoinduced electron transfer can be placed on a quantitative basis by subjecting the quenching rate data to analysis by using the Marcus semiclassical electron transfer theory.^{20–22} This analysis relies on the mechanism shown in Scheme 1 where k_d and k_{-d} are the rate constants for formation and dissociation of the encounter complex, k_{el} and k_{-el} are the rate constants for the forward and back excited state electron transfer reactions in the encounter complex, k_{esc} is the rate of dissociation of the geminate ion pair, and k_{bet} is the rate of back electron transfer within the geminate pair. The pathway with rate k_{rxn} is added

to include the possibility that $\mathbf{1}^{+\bullet}$ reacts rapidly to form a metal complex cation radical product ($\mathbf{X}^{+\bullet}$) at a rate that is competitive with back electron transfer and cage escape.

Some years ago Balzani and co-workers showed that, for Scheme 1 in the limit where $k_{-d} \approx (k_{esc} + k_{bet} + k_{rxn})$, eq 4 provides the relationship between the observed electron transfer quenching rate constant, k_q , and the parameters ΔG_{ET} and ΔG_{ET}^\ddagger .²⁰ In eq 4, k_q is the experimentally determined quench-

$$k_q = \frac{k_d}{1 + \exp\left\{\frac{\Delta G_{ET}}{RT}\right\} + \frac{k_{-d}}{k_{el}^\circ} \exp\left\{\frac{\Delta G_{ET}^\ddagger}{RT}\right\}} \quad (4)$$

ing rate constant and the other rate constants are as defined above. The parameter k_{el}° is the rate constant for electron transfer within the encounter complex when the reaction is activationless. In the context of Marcus theory, activationless electron transfer occurs when $-\Delta G_{ET} = \lambda$, where λ is the total reorganization energy for electron transfer. Marcus theory defines the relationship between ΔG_{ET}^\ddagger and the reaction driving force and the reorganization energy (ΔG_{ET} and λ , respectively):

$$\Delta G_{ET}^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{ET}}{\lambda}\right)^2 \quad (5)$$

Now, by substituting eq 5 into eq 4, and replacing ΔG_{ET} with $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) - E_{1/2}(\text{A}/\text{A}^{\bullet-})$ (eq 3a) we arrive at eq 6, which defines the dependence of k_q on the rate constants in Scheme 1, as well as on the important parameters k_{el}° , $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet})$, $E_{1/2}(\text{A}/\text{A}^{\bullet-})$, and λ .

$$k_q = k_d \left\{ 1 + \exp\left\{\frac{(E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) - E_{1/2}(\text{A}/\text{A}^{\bullet-}))}{RT}\right\} + \frac{k_{-d}}{k_{el}^\circ} \exp\left\{\frac{\lambda}{4RT} \left[1 + \frac{E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) - E_{1/2}(\text{A}/\text{A}^{\bullet-})}{\lambda}\right]^2\right\} \right\}^{-1} \quad (6)$$

This equation is useful because it allows one to compute the dependence of k_q on $E_{1/2}(\text{A}/\text{A}^{\bullet-})$, by assuming values for k_d , k_{-d} , k_{el}° , λ , and $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet})$.

Figure 2 illustrates two plots of the calculated dependence of k_q on $E_{1/2}(\text{A}/\text{A}^{\bullet-})$. Both lines were calculated by using eq 6 with $k_d = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{-d} = 2 \times 10^{10} \text{ s}^{-1}$, and $k_{el}^\circ = 5 \times 10^{11} \text{ s}^{-1}$.^{10a,20} The two differ in that the solid line was computed using $\lambda = 0.25$ eV and $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) = -1.45$ V while the broken line was computed with $\lambda = 0.40$ eV and $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet}) = -1.85$ V. Although both calculations fit the experimental quenching data reasonably well, the broken line provides a better fit. Moreover, the value of $\lambda = 0.25$ eV seems unreasonably small for a charge shift reaction in a polar solvent.²³ We conclude that the parameters used for the broken line fit are better estimates of the "true values" for electron transfer quenching of $\mathbf{1}^*$. An interesting outcome of this analysis is that it implies that $E_{1/2}(\mathbf{1}^*/\mathbf{1}^{+\bullet})$ is approximately 350 mV more negative than the value estimated by using eq 3b assuming that $E_{pa} = E_{1/2}(\mathbf{1}/\mathbf{1}^{+\bullet})$. Thus, we conclude that the ground state oxidation potential of $\mathbf{1}$ must be negative of $E_{pa} = +0.34$ V, and the analysis suggests a value for $E_{1/2}(\mathbf{1}/\mathbf{1}^{+\bullet}) \approx 0$ V.

Photoinduced Electron Transfer and Photochemical Reactivity in Carbyne Complexes. An interesting question concerns the relationship between the well-defined photoinduced electron transfer documented herein and the previously reported

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photochemical reactions of related carbyne complexes in CHCl_3 .^{3b,5} These processes are attributed to initial photoinduced electron transfer to CHCl_3 , followed by reactions of the resulting 17-electron carbyne complexes. Although the reduction potential of CHCl_3 is poorly defined due to the reactivity of the anion radical, polarographic and voltammetric studies suggest that $E_{1/2}$ ($\text{CHCl}_3/\text{CHCl}_3^{\cdot-}$) lies between -1.7 and -2.0 V.²⁴ Given the uncertainty of this estimate for the reduction potential of CHCl_3 and the uncertainty in the excited state oxidation potential of **1** (vide supra), it is possible that photoinduced electron transfer from excited state **1** (and related carbyne complexes) to CHCl_3 could be slightly to moderately endothermic. If so, the process could be comparatively inefficient. This prediction is consistent with a previous study in which we observed that the emission lifetime of $\text{Cp}\{\text{P}(\text{OMe})_3\}(\text{CO})\text{W}\equiv\text{C}-\text{Ph}$ was only slightly shorter in CHCl_3 than in THF (134 ns in CHCl_3 vs 141 ns in THF).^{3a,25} Nonetheless, even if photoinduced electron transfer from the excited state carbyne complex to CHCl_3 is inefficient,

(24) *Encyclopedia of the Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1973.

(25) The emission lifetime of $\text{Cp}(\text{CO})\{\text{P}(\text{OMe}_3)\}\text{W}\equiv\text{C}-\text{Ph}$ in CHCl_3 was not reported previously.

the substantial reactivity of $\text{CHCl}_3^{\cdot-}$ and/or the 17-electron carbyne complexes could render the electron transfer step irreversible and net photochemistry could occur with modest overall quantum efficiency.

Summary. Photoinduced electron transfer from the $d\pi^*$ state of carbyne complex **1** to a series of nitroaromatic and pyridinium electron acceptors with well-defined reduction potentials has been examined. The study confirms that electron transfer occurs; moreover, correlation of k_q with $E_{1/2}(\text{A}/\text{A}^{\cdot-})$ demonstrates that the $d\pi^*$ state of **1** is a potent reducing agent, with $E_{1/2}(\text{1}^*/\text{1}^{\cdot+}) = -1.7 \pm 0.2$ V.

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Supporting Information Available: Absorption and emission spectra for **1**, experimental procedures for the synthesis of **1**, and a table that lists quencher reduction potentials and quenching rate constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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