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be observed easily in low-temperature matrices or glasses due to cage effects.

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Supplementary Material Available: Tables of reaction rate constants for **1**, **7**, and **8** at various temperatures and IR data for $Cp_2Fe_2(^{13}CO)_{4-n}(^{12}CO)_n$ (n = 0, 1, 2, 3) in solutions at 25 °C (2 pages). Ordering information is given on any current masthead page.

Reactivity of 17-Electron Organometallic Tungsten and Molybdenum Radicals: A Laser Flash Photolysis Study

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Abstract: Visible (460–490 nm) laser flash photolysis of $[CpW(CO)_3]_2$ or $[CpMo(CO)_3]_2$ induces homolysis of the metal–metal bond with formation of 17-electron radicals, $CpM(CO)_3$. Radical dimerization results in quantitative recovery of the parent dimer and can be followed by the time-resolved increase in dimer absorbance. The reaction follows clean second-order kinetics, $-d[CpM(CO)_3]/dt = 2k_c[CpM(CO)_3]^2$; $k_c(W) = 6.2 \times 10^9$ and $k_c(Mo) = 3.9 \times 10^9$ L mol^{-1} s^{-1} in CH_3CN at 23 °C. The $CpM(CO)_3$ radicals react with organic and inorganic halides and pseudohalides by an atom-transfer mechanism. In the presence of a large excess of the halide-containing substrate, the rate of loss of the radical, $-d[CpM(CO)_3]/dt$, proceeds according to a mixed first- and second-order rate law. The pseudo-first-order rate constants for reactions with organic halides vary linearly with the concentration of the organic halide; bimolecular rate constants for $CpW(CO)_3$ range from 3.9×10^2 L mol^{-1} s^{-1} with CH_2Br_2 to 1.34×10^9 L mol^{-1} s^{-1} for CBr_4. The reactivity trends (RI > RBr > RCl) and (benzyl > allyl > 3° > 2° > 1° > CH_3) are observed. The 7 orders of magnitude variation in bimolecular rate constants is attributed to a highly selective atom abstraction process. The range of rate constants for atom abstraction from halo- and pseudohalopentaamminecobalt(III) and halobis(dimethylglyoximato)cobalt(III) complexes is smaller (2 orders of magnitude, from 1.6×10^7 L mol^{-1} s^{-1} for $NCCo(NH_3)_5^{2+}$ to $>2 \times 10^9$ L mol^{-1} s^{-1} for $BrCo(dmgH)_2py$), because of the upper limit imposed by diffusion. Transfer of the halogen atom from both organic and metal substrates to $CpW(CO)_3$ was confirmed by the IR spectrum of the organometallic product, $CpW(CO)_3X$ (X = Cl, Br, or I). Dioxygen traps $CpW(CO)_3$ with a rate constant $k = 3.3 \times 10^9$ L mol^{-1} s^{-1}. Light-initiated chain reactions were observed at high concentrations of RX, $XCoL_5^{n+}$, or O_2. Hydroperoxides react with $CpW(CO)_3$ by a radical mechanism. The reaction observed between $CpW(CO)_3$ and $(n\text{-}Bu)_3SnH$ is not consistent with either outer-sphere electron transfer or a hydrogen atom abstraction mechanism; oxidative addition to the 17-electron radical is believed to occur in this case. The dimer $[(C_5H_4COOCH_3)W(CO)_3]_2$ shows photoreactivity in organic solvents which is very similar to that of $[CpW(CO)_3]_2$.

Introduction

Mechanisms for organometallic catalysis have been dominated by the 16-/18-electron rule, by which most proposed reactions are formulated with nonradical, even-electron intermediates.[1] However, it is now well-established that some catalytic reactions proceed through organometallic radical intermediates.[2] For example, olefin hydrogenation[3,4] and polymerization[5] are induced by 17-electron radicals. Also, ligand substitution in nonlabile 18-electron complexes can be initiated by formation of 17-electron radicals.[6,7] Although most such radicals are transients, a few 17-electron species are stable toward dimerization. Examples of these are $V(CO)_6$, $Co(CN)_5^{3-}$, $Mn(CO)_3(P(n\text{-}Bu_3))_2$,[8] $Re(CO)_3(PPh_3)_2$,[9,10] and $(C_5Me_5)Cr(CO)_3$.[11]

Formation of 17-electron radicals can be initiated by electron-transfer,[12] electrochemical oxidation[13-17] or reduction[18] and radiolysis[19,20] of metal carbonyl and substituted metal carbonyl monomers and dimers. Also, hydrogen atom abstraction from $HRe(CO)_5$ produces a 17-electron radical.[21] A common initiation step in chain reactions is light-induced metal–metal bond cleavage.[8,22] For $[CpM(CO)_3]_2$ (M = Mo or W), irradiation into either the $d\pi \rightarrow \sigma^*$ or the $\sigma \rightarrow \sigma^*$ transition induces cleavage into 17-electron radicals, $CpM(CO)_3$, as well as CO loss to give $Cp_2M_2(CO)_5$.[23,24] Evidence for the intermediacy of 17-electron radicals includes observation of radical cross-coupling products,[25]

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[1] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; p 138.

[2] Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Vol. 22, pp 67–107.

[3] Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335–8337.

[4] Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886–6898.

[5] Muetterties, E. L.; Sosinsky, B. A.; Zamaraev, K. I. *J. Am. Chem. Soc.* **1975**, *97*, 5299–5300.

[6] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 947–949.

[7] Poli, R.; Owens, B. E.; Linck, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1302–1307.

[8] Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103–4107.

[9] Moelwyn-Hughes, J. T.; Garner, A. W. B.; Gordon, N. *J. Organomet. Chem.* **1970**, *26*, 373–387.

[10] Singleton, E.; Moelwyn-Hughes, J. T.; Garner, A. W. B. *J. Organomet. Chem.* **1970**, *21*, 449–466.

[11] Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907–914.

[12] Krusic, P. J.; Stoklosa, H.; Manzer, L. E.; Meakin, P. *J. Am. Chem. Soc.* **1975**, *97*, 667–669.

[13] Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47–87.

[14] Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Chem. Commun.* **1974**, 660–661.

[15] Treichel, P. M.; Wagner, K. P.; Mueh, H. J. *J. Organomet. Chem.* **1975**, *86*, C13–C16.

[16] Rourke, F.; Gash, R.; Crayston, J. A. *J. Organomet. Chem.* **1992**, *423*, 223–239.

[17] Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062–4068.

[18] Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 749–752.

[19] Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259–7264.

[20] Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842–1846.

[21] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527–2532.

[22] Hallock, S. A.; Wojcicki, A. *J. Organomet. Chem.* **1973**, *54*, C27–C29.

[23] Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246–4251.

[24] Hughey, J. L., IV; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440–4441.

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spin trapping[26,27] and inhibition by the radical scavengers O_2 and hydroquinone.[21] Organometallic radicals react with organic halides in competition with radical combination/disproportionation reactions. The rate of radical combination approaches the diffusion-controlled limit, and it was assumed that reactions with organic halides must also be very fast[23,25] because $CpW(CO)_3X$ is produced quantitatively under continuous photolysis conditions.[2] In previous studies, mechanistic proposals were based on identification of products M–X and M–M′ and quantum yields, i.e., the presence of 17-electron radicals was not directly observed but was inferred.[23,28] In one study, the steady-state concentration of spin-trapped radicals was measured directly by ESR to yield rate constants for the reactions of $CpW(CO)_3$ with three different organic halides.[27]

Despite their widespread application to problems in organometallic photoinduced reactions, long time scale experiments are fundamentally incapable of proving the relationship between primary photoevents and reaction products (which may themselves be photosensitive) or of determining absolute reactivities of transient species.[29] For this reason, time-resolved methods are highly useful for the study of the nature and reactivity of short-lived intermediates. Direct measurement of the rate constants for various reactions of these intermediates is necessary to evaluate their possible roles as chain carriers. Pulse radiolysis[19,20] and laser flash photolysis[30,31] have been used to study the reactions of $Mn(CO)_5$ and $Re(CO)_5$ generated by reduction and photolytic cleavage of $M_2(CO)_{10}$ (M = Mn, Re). The radicals (arene)$W(CO)_3^+$ have been observed directly by rapid electrochemical techniques.[16,17]

Seventeen-electron organometallic radicals are, by virtue of a partially filled molecular orbital, good reducing agents.[32] Reduction of halogen-containing organic substrates proceeds with transfer of the halogen to the organometallic fragment, eq 1.

$$[CpW(CO)_3]_2 \xrightarrow[CCl_4]{h\nu} 2CpW(CO)_3Cl \qquad (1)$$

There are two likely two-electron mechanisms for this reaction: nucleophilic substitution and oxidative addition. The former is a common mechanism for nonradical nucleophiles, both organic and inorganic. The latter was considered for the reactions between radicals $M(CO)_5$ (M = Mn, Re) and H_2, CCl_4, or I_2[21] as well as for the reaction of the even-electron complex $Fe(CO)_4^{2-}$ with RX.[33]

There is also the possibility of a radical mechanism, in which halogen binding to the metal may precede, accompany, or follow the single-electron-transfer event. At one extreme, a preequilibrium involving formation of a precursor complex represents the classic inner-sphere mechanism, as demonstrated by the transfer of chlorine from $(NH_3)_5CoCl^{2+}$ to $Cr^{2+}_{(aq)}$.[34,35] The rates of such reactions depend strongly on the substitutional lability of the reactants and on the ability of the halogen or pseudohalogen to serve as a bridging ligand. The lability requirement is certainly met by organometallic radicals, which exchange ligands many orders of magnitude faster than their even-electron analogs.[36-40] In contrast, if halogen binding occurs after electron transfer, then the reaction is outer-sphere. The rate of such a reaction exhibits a Marcus-type dependence on the driving force ($\Delta G°$), but there is very little dependence on the nature of the halogen. The presence of Lewis bases, such as PPh_3, may accelerate outer-sphere electron transfer by causing the formation of a 19-electron adduct that is more strongly reducing and, therefore, a more reactive outer-sphere reductant than the 17-electron radical itself.[41] Finally, polar transition states have been proposed in which incomplete electron transfer accompanies formation of the halogen-bridged, inner-sphere complex.[42,43] In this case, measured rate constants correlate with both the driving force for the reaction and the bridging ability of the halogen substituent.

We have undertaken a complete kinetic and mechanistic analysis of the reactions of the 17-electron radicals $CpW(CO)_3$, $(C_5H_4COOCH_3)W(CO)_3$, and $CpMo(CO)_3$ with various organic halides and halocobalt(III) complexes. The measured bimolecular rate constants are examined for trends in absolute and relative reactivity, steric and electronic properties of the substrate, solvent effects, and effect of Lewis bases. The fate of the reduced substrate is considered. In addition, the rates and mechanisms of the reactions of $CpW(CO)_3$ with O_2, ROOH, and $(n\text{-Bu})_3SnH$ are reported.

Experimental Section

Reagents. $[CpW(CO)_3]_2$, $[CpMo(CO)_3]_2$, and $[(C_5H_4COOCH_3)W(CO)_3]_2$ were prepared as described in the literature.[44,45] Organic halides were purchased (Aldrich) and used as received. Cobalt(III) complexes were available as perchlorate salts from previous studies;[46] most perchlorate salts were not sufficiently soluble in CH_3CN for the kinetics measurements and were therefore converted to triflate salts by stirring in acidic aqueous solution over Dowex 50W-X8 anion-exchange resin that had been converted to the triflate form with aqueous $Li(O_3SCF_3)$. Initial experiments were performed using freshly distilled THF as the solvent. Addition of a small amount of water did not affect the stability of the organometallic dimers or the observed kinetics. Therefore, solvents were not specially dried for subsequent experiments. HPLC-grade CH_3CN was used as the solvent in most experiments.

Reactions of $CpW(CO)_3$. Kinetic Procedures. Solutions of $[CpW(CO)_3]_2$ in CH_3CN, toluene, or THF were kept in the dark and saturated with argon before being 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}).[44] A known quantity of the halide-containing substrate was added to the $[CpW(CO)_3]_2$ solution, and then the solution was subjected to a 0.6-μs pulse from a flashlamp-pumped dye laser containing LD 490, LD 473, or Coumarin 460 dye. The laser flash equipment has been described previously.[47] Events following the flash were monitored at λ 356 nm (CH_3CN) or 365 nm (toluene, THF). Absorbance changes at these wavelengths correspond to recovery of the dimer, which is only partially complete in experiments with added organic or cobalt(III) halides. Typical concentrations of $[CpW(CO)_3]_2$ and $CpW(CO)_3$ were 20–40 μM and 10–15 μM, respectively.

In the absence of added halide-containing substrate, the $CpW(CO)_3$ radicals dimerize according to second-order kinetics:

$$-d[CpW(CO)_3]/dt = 2k_c[CpW(CO)_3]^2 \qquad (2)$$

$$A_t = A_\infty + \frac{(A_0 - A_\infty)}{1 + \frac{4k_ct}{\epsilon_D}(A_0 - A_\infty)} \qquad (3)$$

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(25) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065–2072.

(26) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1974**, 966–967.

(27) Gasanov, R. G.; Sadykhov, E. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* (*Engl.*) **1987**, 913–917.

(28) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388–391.

(29) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187–218.

(30) Stufkens, D. J.; van der Graaf, T.; Stor, G. J.; Oskam, A. *Coord. Chem. Rev.* **1991**, 331–336.

(31) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249–6252.

(32) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1261.

(33) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515–2526.

(34) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 4118–4119.

(35) Taube, H.; Myers, H. *J. Am. Chem. Soc.* **1954**, *76*, 2103–2111.

(36) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613–617.

(37) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007–4008.

(38) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032–4034.

(39) Therien, M. J.; Ni, C.-L.; Anson, F. C.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037–4042.

(40) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703–1706.

(41) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325–331.

(42) Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269–3275.

(43) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881–1886.

(44) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607–3613.

(45) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

(46) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 579–581.

(47) Connolly, P.; Espenson, J.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 2169–2175.

where A_0, A_t, and A_∞ are the absorbances due to the dimer at time 0, t, and ∞, respectively, and ϵ_D is the molar extinction coefficient of the dimer. In the presence of an organic halide (RX), the decrease in radical concentration (still monitored by observing the increase in dimer concentration) is accelerated by an additional bimolecular term:

$$-d[CpW(CO)_3]/dt = 2k_c[CpW(CO)_3]^2 + k_X[RX][CpW(CO)_3] \quad (4)$$

This equation was integrated with the condition $[RX]_0 \gg [CpW(CO)_3]_0$, giving

$$[CpW(CO)_3]_t = \frac{k_X[RX][CpW(CO)_3]_0 \exp(-k_X[RX]t)}{k_X[RX] + 2k_c[A]_0\{1 - \exp(-k_X[RX]t)\}}$$

The mass balance equation in the system is

$$[\{CpW(CO)_3\}_2]_t = [\{CpW(CO)_3\}_2]_0 - \tfrac{1}{2}[CpW(CO)_3]_t - \tfrac{1}{2}[CpW(CO)_3X]_t$$

Thus, the expression for $[CpW(CO)_3]_t$ can be converted into one for $[\{CpW(CO)_3\}_2]_t$, whose concentration is directly proportional to the absorbance. The final expression used for curve-fitting is

$$A_t = A_0 + \frac{\epsilon_D}{2}\left[R_0\frac{[(2k_c/k_\psi)R_0 + 1](1 - e^{-k_\psi t})}{[(2k_c/k_\psi)R_0(1 - e^{-k_\psi t}) + 1]} - \frac{k_\psi}{2k_c}\ln\left[\frac{2k_c}{k_\psi}R_0(1 - e^{-k_\psi t}) + 1\right]\right] \quad (5)$$

where R_0 is the initial concentration of the $CpW(CO)_3$ radical and k_c was fixed at the value measured directly in experiments without added RX. The pseudo-first-order rate constant, designated k_ψ, is equal to $k_X[RX]$. Values of k_ψ were obtained in each experiment by nonlinear least-squares fitting of the experimental absorbance–time curves to eq 5. Typically, each sample was flashed four times in succession, so each k_ψ is the average of four determinations. Values of k_ψ were plotted against [RX]. In every case the data defined a straight line with an intercept close to 0. The least-squares slopes of these plots provided values of k_X. Treatment of kinetic data was identical for experiments with cobalt halides, hydroperoxides, oxygen, and tri-*n*-butyltin hydride.

Reactions of $CpW(CO)_3$. Products. The W-containing products from the reactions with organic and cobalt halides were determined from FTIR spectra of the ν_{CO} region, recorded on a Nicolet 710 FT-IR spectrometer with 4 cm^{-1} resolution. Samples for product analysis were flashed many (20–50) times in order to accumulate enough product to be detected spectroscopically. That is, the solution was stirred intermittently to spread uniformly the products away from the point of laser incidence. It is this large dilution that necessitates so many laser flashes. Peak positions were compared to literature values for identification of $CpW(CO)_3X$ products.[23,29,41,48] Organic products were identified by their GC retention times on an HP 5730A gas chromatograph equipped with a VZ-10 column.

Reactions of $(C_5H_4COOCH_3)W(CO)_3$ and $CpMo(CO)_3$. The procedures described above were also used in the laser flash photolyses of $[(C_5H_4COOCH_3)W(CO)_3]_2$ and $[CpMo(CO)_3]_2$ in CH_3CN. The monochromator was adjusted in order to record the absorbance change at the appropriate spectral maximum, λ 359 nm ($\epsilon = 1.6 \times 10^4$ L mol^{-1} cm^{-1})[44] or λ 384 nm ($\epsilon = 1.69 \times 10^4$ L mol^{-1} cm^{-1})[23], for the substituted-Cp W dimer and the Mo dimer, respectively.

Kinetic Simulations. The buildup and fall of the concentrations of some intermediates and the buildup of products of later steps follow kinetic equations that are too complex for presentation in closed form. That is particularly so since the rate constants for the different steps differ greatly, meaning that the differential rate equations are "stiff". Numerical methods were used in such cases to generate the concentration–time profiles. This calculation uses the starting concentrations and various rate constants known from this study or from earlier work. These simulations were performed by means of the program KINSIM, which was written and described by Frieden et al.[49]

Results and Discussion

Reactions with Organic Halides. Kinetics. Other organometallic radicals are reported to absorb in the visible and near-IR regions, e.g., $Co(CN)_5^{3-}$, λ 966 nm;[50] $Mn(CO)_5$, λ 830 nm;[20] $Rh(dmgH)_2PPh_3$, λ 580 nm;[51] and $Re(CO)_5$, λ 535 nm.[20] However, molar extinction coefficients are low (typically only a few hundred), making micromolar radical concentrations difficult to detect by our laser flash photolysis system. Consequently, the radicals $CpW(CO)_3$, $(C_5H_4COOCH_3)W(CO)_3$, and $CpMo(CO)_3$ could not be monitored directly in the region of 400–700 nm. Instead, the intense absorbances of the dimers (λ 300–400 nm) were used to probe the kinetics of radical reactions. A typical kinetic trace for the laser flash photolysis of $[CpW(CO)_3]_2$ is shown in Figure 1a. In the absence of added organic halide, quantitative recovery of the absorbance due to $[CpW(CO)_3]_2$ occurs in two successive phases. The faster phase accounts for 80% of the total dimer recovery. The trace follows second-order kinetics, as expected for radical combination, eqs 2 and 3. The measured second-order rate constants are $k_c(CpW(CO)_3) = 6.2 \times 10^9$, $k_c((C_5H_4COOCH_3)W(CO)_3) = 4.9 \times 10^9$, and $k_c(CpMo(CO)_3) = 3.9 \times 10^9$ L mol^{-1} s^{-1} in CH_3CN at 23 °C.

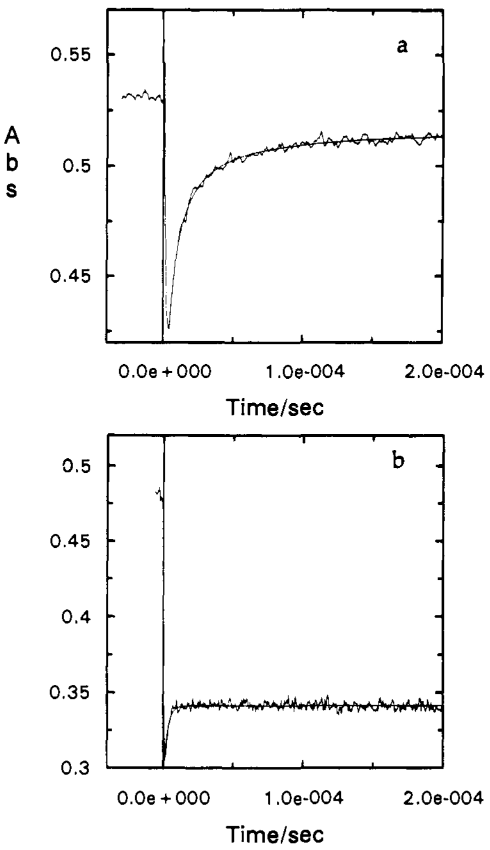

Figure 1. Time-resolved absorbance changes recorded at 356 nm during the 490-nm laser flash photolysis of (a) an argon-saturated solution of 0.025 mM $[CpW(CO)_3]_2$ in CH_3CN, where the smooth curve is the fit to a second-order rate law with $k_c = 6.2 \times 10^9$ L mol^{-1} s^{-1}, and (b) an argon-saturated solution containing 0.023 mM $[CpW(CO)_3]_2$ and 0.45 mM Ph_3CBr in CH_3CN, where the smooth curve is the fit to a mixed first- and second-order rate law with k_c fixed at 6.2×10^9 L mol^{-1} s^{-1} and $k_\psi = 7.0 \times 10^4$ s^{-1}.

The diffusion-controlled rate constant for encounters of molecular species in solution is given by the von Smoluchowski equation,[52] with a diffusion coefficient from a modified[53] version of the Stokes–Einstein relation, $D \approx kT/4\pi\eta r$.[53,54] Thus, $k_{diff} \approx [(4 \times 10^6)RT/\eta]$ m^3 mol^{-1} s^{-1}, and in CH_3CN ($\eta = 0.345$ cP),[55] $k_{diff} = 2.9 \times 10^{10}$ L mol^{-1} s^{-1}. For radical reactions, the diffu-

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(48) Sloan, T. E.; Wojcicki, A. *Inorg. Chem.* **1968**, *7*, 1268–1273.

(49) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134–145. We are grateful to Professor Frieden for a copy of the program KINSIM.

(50) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3356–3357.

(51) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 3147–3151.

(52) Wilkinson, F. *Chemical Kinetics and Reaction Mechanisms*; Van Nostrand: New York, 1980; pp 138–139.

(53) Edward, J. T. *J. Chem. Ed.* **1970**, *47*, 261–270. The modification of the usual form of this equation is to replace the factor of 6 in the denominator by 4. This change is necessary to better account for molecular-sized partners.

(54) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983–4992.

(55) *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983.

Table I. Bimolecular Rate Constants for the Abstraction of Halogen Atoms from Organic Halides by 17-Electron Tungsten and Molybdenum Radicals[a]

	k_X/L mol^{-1} s^{-1}		
organic halide	$CpW(CO)_3$	$(C_5H_4COOCH_3)W(CO)_3$	$CpMo(CO)_3$
$CH_2{=}CHCH_2I$	$(1.22 \pm 0.06) \times 10^8$	$(4.86 \pm 0.04) \times 10^7$	$(3.32 \pm 0.04) \times 10^7$
CH_2I_2	$(9.8 \pm 0.5) \times 10^6$	$(8.19 \pm 0.02) \times 10^6$	$(6.04 \pm 0.03) \times 10^6$
Me_3CI	$(6.0 \pm 0.2) \times 10^6$		
$CH_3(CH_2)_5CH(I)CH_3$		$(1.96 \pm 0.03) \times 10^5$	$(1.37 \pm 0.10) \times 10^5$
$CH_3CH(I)CH_3$	$(3.0 \pm 0.1) \times 10^5$	$(1.63 \pm 0.07) \times 10^5$	$(1.49 \pm 0.04) \times 10^5$
$CH_3(CH_2)_6CH_2I$		$(1.96 \pm 0.06) \times 10^4$	$(1.26 \pm 0.04) \times 10^4$
$CH_3CH_2CH_2I$	$(1.30 \pm 0.07) \times 10^4$	$(1.01 \pm 0.08) \times 10^4$	$(7.05 \pm 0.12) \times 10^3$
Me_3CCH_2I	$(4.0 \pm 0.3) \times 10^3$		
CH_3I	$\leq 6 \times 10^2$		
CBr_4	$(1.34 \pm 0.03) \times 10^9$		
Cl_3CBr	$(5.3 \pm 0.3) \times 10^8$	$(3.20 \pm 0.02) \times 10^7$	$(2.65 \pm 0.04) \times 10^7$
Ph_3CBr	$(1.6 \pm 0.1) \times 10^8$		
$CH_3O_2CCH(Br)CO_2CH_3$	$(4.0 \pm 0.2) \times 10^6$		
$CHBr_3$	$(1.46 \pm 0.03) \times 10^6$	$(1.19 \pm 0.05) \times 10^6$	$(1.16 \pm 0.02) \times 10^6$
$BrCH_2CH{=}CHCO_2CH_3$	$(1.16 \pm 0.05) \times 10^6$		
$BrCH_2CN$	$(4.30 \pm 0.08) \times 10^5$	$(3.0 \pm 0.05) \times 10^5$	$(2.12 \pm 0.04) \times 10^5$
$PhCH(Br)CH_3$	$(3.53 \pm 0.08) \times 10^5$	$(3.04 \pm 0.04) \times 10^5$	$(2.31 \pm 0.05) \times 10^5$
p-$NCC_6H_4CH_2Br$	$(2.47 \pm 0.04) \times 10^5$		
p-$FC_6H_4CH_2Br$	$(1.20 \pm 0.03) \times 10^5$	$(7.89 \pm 0.2) \times 10^4$	$(6.42 \pm 0.04) \times 10^4$
p-$CF_3C_6H_4CH_2Br$	$(1.09 \pm 0.04) \times 10^5$	$(7.04 \pm 0.04) \times 10^4$	$(6.75 \pm 0.03) \times 10^4$
$CH_3CH(Br)CO_2CH_3$	$(1.02 \pm 0.03) \times 10^5$	$(8.98 \pm 0.04) \times 10^4$	$(7.45 \pm 0.05) \times 10^4$
$C_6H_5CH_2Br$	$(9.3 \pm 0.6) \times 10^4$	$(8.9 \pm 0.2) \times 10^4$	$(8.11 \pm 0.4) \times 10^4$
cyclopentyl bromide		$(7.2 \pm 0.4) \times 10^4$	$(6.71 \pm 0.10) \times 10^4$
cyclopropyl bromide	$(8.7 \pm 0.6) \times 10^4$	$(4.7 \pm 0.1) \times 10^4$	$(4.13 \pm 0.8) \times 10^4$
$BrCH_2CH_2CN$	$(6.8 \pm 0.4) \times 10^4$	$(4.45 \pm 0.04) \times 10^4$	$(3.97 \pm 0.05) \times 10^4$
$CH_2{=}CHCH_2Br$	$(5.4 \pm 0.1) \times 10^4$		
$PhCH{=}CH_2Br$	$(2.6 \pm 0.2) \times 10^4$		
$BrCH_2CO_2CH_3$	$(1.63 \pm 0.04) \times 10^4$		
$CH_3CH(Br)CH_3$	$(4.55 \pm 0.13) \times 10^3$		
$BrCH_2CH_2Br$	$(1.7 \pm 0.1) \times 10^3$		
CH_2Br_2	$(3.9 \pm 0.3) \times 10^2$		
$BrCH_2CH_2CH_2Br$	$\leq 2 \times 10^2$		
Ph_3CCl	$(3.8 \pm 0.4) \times 10^6$		
(cyclohexane)C(O)Cl		$(3.37 \pm 0.2) \times 10^6$	$(2.03 \pm 0.1) \times 10^6$
$H_2C{=}CHC(O)Cl$		$(8.18 \pm 0.06) \times 10^4$	$(7.68 \pm 0.2) \times 10^4$
Cl_3CCO_2H	$(3.5 \pm 0.1) \times 10^4$		
CCl_4	$(2.92 \pm 0.09) \times 10^4$		
$ClCH_2CN$	$(7.4 \pm 0.6) \times 10^3$		

[a] In CH_3CN at 23 °C.

sion-controlled rate constant for combination of singlet states is $k_s = 0.25k_{diff} = 7.2 \times 10^9$ L mol^{-1} s^{-1}. The latter is close to the measured value for combination of $CpW(CO)_3$ radicals, 6.2×10^9 L mol^{-1} s^{-1}. Previously determined values for this rate constant are $(5 \pm 1) \times 10^9$ L mol^{-1} s^{-1} in toluene,[56] 3.8×10^9 L mol^{-1} s^{-1} in THF,[29] and 1.9×10^9 L mol^{-1} s^{-1} in cyclohexane.[30] The combination of $CpMo(CO)_3$ radicals in CH_3CN is also nearly diffusion-controlled, $k_c = 3.9 \times 10^9$ L mol^{-1} s^{-1}, compared to $(3 \pm 1) \times 10^9$ L mol^{-1} s^{-1} reported previously for the reaction in cyclohexane.[24] The slower stage of $[CpM(CO)_3]_2$ recovery is the capture of CO by $Cp_2M_2(CO)_5$ (a minor photochemical product),[24,56] which occurs on a much longer time scale and therefore does not interfere with the kinetics of the radical reactions reported here.

We noted that, in the absence of RX, 80% of the absorbance of the dimer is recovered in the time needed (some 100–300 μs usually) to attain a stable absorbance. Actually, if one remeasures the absorbance a few seconds later, the full original amount of dimer is seen. We interpret this to mean that there are competing pathways for photodissociation, namely cleavage of the W–W bond (80%) and CO loss (20%). The $CpW(CO)_3$ radicals recombine rapidly, but $Cp_2W_2(CO)_5$ and CO do so only 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 $Cp_2W_2(CO)_5$ was never an issue. The competition between the two photodissociation channels is dependent on the exciting wavelength: higher-energy photons favor CO loss to greater extents.

In the presence of an organic halide such as Ph_3CBr, the extent of dimer recovery is reduced but the rate at which the metal radical disappears is accelerated, Figure 1b. These reactions are represented in eqs 6 and 7. The trityl radical $Ph_3C^\bullet$ was not detected

$$[CpW(CO)_3]_2 \underset{k_c}{\overset{h\nu}{\rightleftharpoons}} 2CpW(CO)_3 \tag{6}$$

$$CpW(CO)_3 + Ph_3CBr \xrightarrow{k_X} CpW(CO)_3X + Ph_3C^\bullet \tag{7}$$

due to its low absorbance (λ 516 nm, ε 6.6×10^2 L mol^{-1} cm^{-1}).[57] However, the postflash recovery of dimer decreases as the concentration of Ph_3CBr increases. That is, reaction 7 is increasingly more important than reaction 6 at higher halide concentrations, although the relationship is not linear because the competing reactions are of different kinetic order. Variation of the pseudo-first-order rate constants k_ψ with the concentration of organic halide is shown for several substrates in Figure 2. The bimolecular rate constants, which are the slopes of the plots in Figure 2, are collected in Table I for a wide variety of organic halides. A small number of rate constants for these reactions have been measured by indirect methods.[27,29,58] The agreement between different methods is shown in Table II.

The measured rate constants k_x for reactions of $CpM(CO)_3$ with RX can be corrected[59-61] for the diffusion effects by the

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(56) van Vlierberge, B. A.; Abrahamson, H. B. *J. Photochem. Photobiol. A* **1990**, *52*, 69–81.

(57) Colle, T. H.; Glaspie, P. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 2722–2725.

(58) Song, J.-S.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 9862–9864.

(59) Jordan, P. C. *Chemical Kinetics and Transport*; Plenum: New York, 1979; p 314.

Table II. Comparison of Bimolecular Rate Constants for the Reactions of $CpM(CO)_3$ (M = W, Mo) with Organic Halides Measured Directly by Laser Flash Photolysis (LFP) and by Indirect Methods

	LFP[a]		quantum yields[b]		competition method[c]		spin trapping[d]	
RX	W	Mo	W	Mo	W	Mo	W	Mo
CH_2I_2	9.8×10^6	6.0×10^6			2.8×10^6	6.4×10^5		
CBr_4	1.3×10^9				3.9×10^8	1.6×10^8		
$PhCH_2Br$	9.3×10^4	8.1×10^4					1.30×10^5	2.0×10^5
$CH_2{=}CHCH_2Br$	5.4×10^4						6.5×10^4	1.0×10^5
CCl_4	2.9×10^4		1.3×10^4		1.2×10^4	8×10^3	2.1×10^4	2.2×10^4
$CHCl_3$			21					
$PhCH_2Cl$			14					
CH_2Cl_2			<0.6					

[a] In CH_3CN, this work. [b] In THF, ref 29. [c] In CD_3CN, ref 58. [d] In benzene, ref 27.

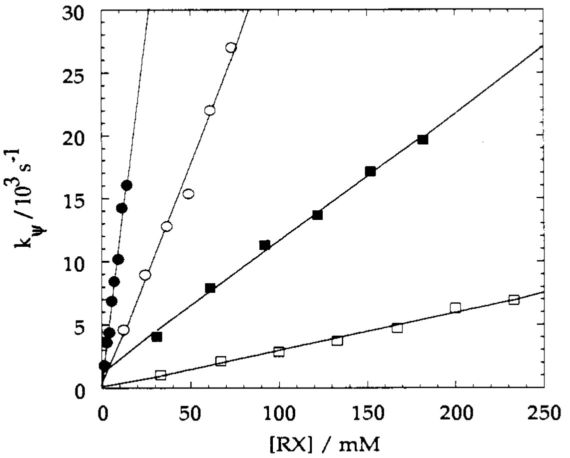

Figure 2. Dependence of the pseudo-first-order rate constants k_ψ on [RX] for the reactions between a variety of organic halides and $CpW(CO)_3$. (●) methyl-4-bromocrotonate; (○) 1-bromo-1-phenylethane; (■) methyl-2-bromopropionate; (□) 2-propyl iodide.

equation $(k_X)^{-1} = (k_{diff})^{-1} + (k_i)^{-1}$, where k_i is the intrinsic bimolecular rate constant for a reaction in a solvent having no viscosity. For the highest rate constant, $k_X = 1.34 \times 10^9$ L mol^{-1} s^{-1} for $CpW(CO)_3 + CBr_4$ in CH_3CN, the calculated value of $k_i = 1.40 \times 10^9$ L mol^{-1} s^{-1} is not significantly different from k_X within the experimental error. Although $k_i \approx k_X$ here, since k_{diff} is so high, that is not always the case. The closely related study[42] of $Re(CO)_4L$ radical reactions required this correction.

General Observations on Reactivity. The three organometallic radicals studied here are very similar in reactivity. Substitution of a hydrogen on the Cp ring by $COOCH_3$ has very little effect on the rate constants for atom transfer. The $CpMo(CO)_3$ radical is slightly less reactive than $CpW(CO)_3$, despite higher self-exchange rates for the $CpMo(CO)_3/CpMo(CO)_3X$ couples.[58,62,63] The slower rates may be due to the lower bond strengths of Mo–X relative to W–X.[62]

The rate constants for reactions of $CpM(CO)_3$ with organic halides show the normal reactivity order, RI > RBr > RCl, for atom-transfer reactions, where reactivity increases as the ability of the halogen atom to serve as an electron-transfer bridge increases. This reactivity order was previously observed for atom abstraction by $Cr^{2+}{}_{(aq)}$ and $Cr(en)_2{}^{2+}$,[64] the tri-*n*-butyltin radical,[13,65] and organic radicals,[66] as well as by the 17-electron organometallic radicals $Rh(dmgH)_2PPh_3$[51] and $Re(CO)_4PR_3$.[43] Linear free energy correlations of log k_x values among organometallic radicals are shown in Figure 3.

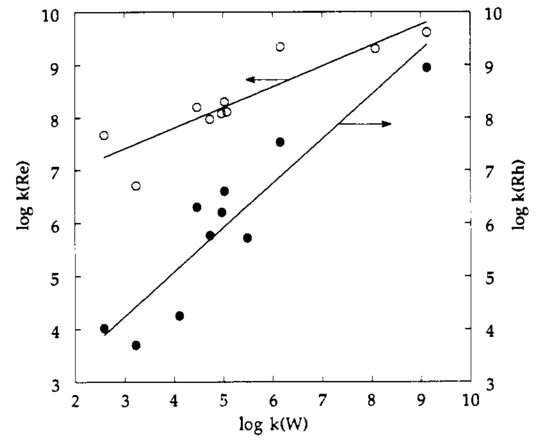

Figure 3. Linear free energy correlations between log *k* values for the abstraction of halogen atoms by different organometallic radicals. "W" is $CpW(CO)_3$ (this work), "Rh" is $Rh(dmgH)_2PPh_3$ (ref 51), and "Re" is $Re(CO)_4(P(OPh)_3)$ (ref 43).

The measurable range of reactivities is 7 orders of magnitude. (Rate constants less than 10^2 L mol^{-1} s^{-1} could not be measured since atom abstraction reactions that are very slow cannot compete effectively with radical dimerization.) The acceleration obtained by substituting Br for Cl is 2–4 orders of magnitude, as in $k(CCl_3Br)/k(CCl_4) = 1.8 \times 10^4$; $k(Ph_3CBr)/k(Ph_3CCl) = 42$; and $k(BrCH_2CN)/k(ClCH_2CN) = 58$ for reactions of $CpW(CO)_3$. Replacing Br by I causes an acceleration of 2–3 orders of magnitude, as in $k(CH_2{=}CHCH_2I)/k(CH_2{=}CHCH_2Br) = 2.3 \times 10^3$ and $k(CH_3CH(I)CH_3)/k(CH_3CH(Br)CH_3) = 66$. The variability in rate ratios may be attributed to differences in C–X bond polarity.[67] Atom abstraction by $Co(CN)_5{}^{3-}$, Co(saloph)B, or $Co(dmgH)_2B$ (B is a Lewis base) exhibits $k_I/k_{Br} \approx k_{Br}/k_{Cl} \approx 10^3$.[68-71] In contrast, outer-sphere reduction of nitrobenzyl halides by $Co(salen)B_2$ is relatively insensitive to the nature of the halogen atom, $k_{Br}/k_{Cl} \approx 2$.[72,73]

Acceleration by geminal halide substitution is very large, as in the series CBr_4, $CHBr_3$, CH_2Br_2 with rate constants 1.34×10^9, 1.46×10^6, and 3.9×10^2 L mol^{-1} s^{-1}, respectively, for the reactions with $CpW(CO)_3$. Therefore, the acceleration achieved upon replacing an α-H by Br is approximately 3 orders of magnitude. The degree of electron transfer accompanying atom abstraction may be larger for geminal polyhalides than for the monohalides because of the greater electronegativity of the in-

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(60) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.
(61) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.
(62) Nolan, S. P.; De La Vega, R. L.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1491.
(63) Schwarz, C. L.; B., R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 1225–1236.
(64) Kochi, J. K.; Powers, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 137–146.
(65) Davies, A. G. *Adv. Chem. Ser.* **1976**, *157*, 26–40.
(66) Evans, F. W.; Fox, R. J.; Szwarc, M. *J. Am. Chem. Soc.* **1960**, *82*, 6414.
(67) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42–45.
(68) Halpern, J.; Maher, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 2311.
(69) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582–588.
(70) Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 1374–1378.
(71) Schneider, P. W.; Phelan, P. F.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 77–81.
(72) Halpern, J. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 2–21.
(73) Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 5752–5753.

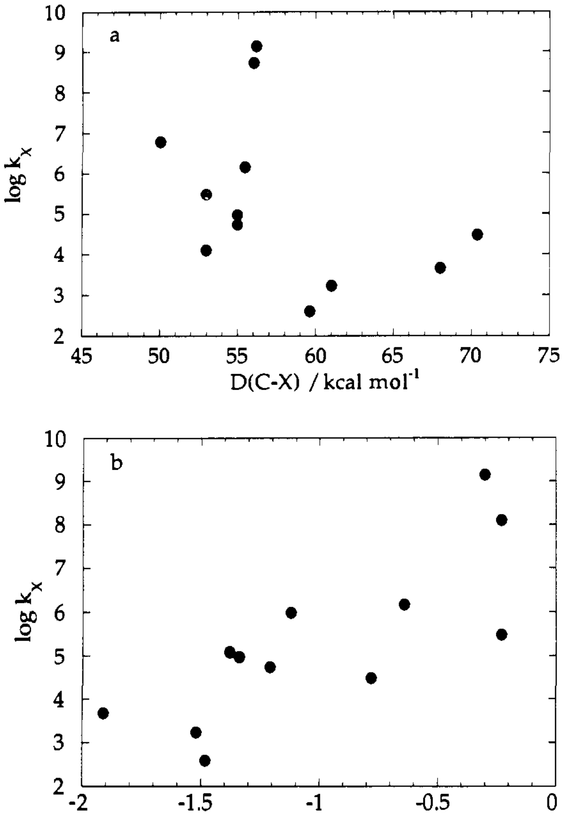

Figure 4. Attempted linear free energy correlations for the reactions between $CpW(CO)_3$ and various organic halides. (a) Correlation between log k_X and C–X bond dissociation energies (*CRC Handbook of Chemistry and Physics*; West, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1985 and refs 43 and 51). (b) Correlation between log k_X and RX half-wave reduction potentials (Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker, Inc.: New York, 1970. Half-wave potentials for reduction of alkyl halides were reported in 75% dioxane/25% water against SCE. $E_{1/2}$ values for the substituted benzyl bromides were reported in DMF against Ag/AgBr and were normalized as in ref 51).

cipient halocarbon radical compared to that of an unsubstituted organic radical.[13] The resulting shift in the position of the transition state along the reaction coordinate may explain why the correlations of log k_X with C–X bond energies and RX half-wave potentials, Figure 4, are poor.

The reactivity of organic halides toward $CpW(CO)_3$ also varies in the order of the stability of the radical product formed in the reaction. That is, rates follow the trend 3° > 2° > 1° > CH_3, as illustrated by the series $(CH_3)_3CI$, $(CH_3)_2CHI$, $CH_3CH_2CH_2I$, CH_3I, with rate constants 6.0×10^6, 3.0×10^5, 1.30×10^4, and $\leq 6 \times 10^2$ L mol^{-1} s^{-1}, respectively. Note that this reactivity order is inconsistent with nonradical mechanisms, such as S_N2 and oxidative addition, which are strongly retarded by steric bulk at the α-carbon atom. Neopentyl iodide is only slightly (3.25 times) slower than 1-propyl iodide, consistent with the minor importance of steric hindrance at the α-carbon.

Allyl iodide reacts 4 orders of magnitude faster with $CpM(CO)_3$ than does 1-propyl iodide, due to allylic stabilization of the primary carbon radical. Cyclopropyl bromide reacts slightly faster than 2-propyl bromide but more slowly than cyclopentyl bromide, since the highly strained cyclopropyl radical is more difficult to form than the cyclopentyl radical. (The unsubstituted cyclopropyl radical does not rearrange to the more stable allyl radical in solution because of a very high activation barrier.)[74] 1,2-Dibromoethane is at least 10 times more reactive than 1,3-dibromopropane. The high reactivity of vicinal dihaloalkanes has been attributed to the ability of a β-halo substituent to stabilize an organic radical by halogen bridging.[75,76] This effect has been observed for atom abstractions by $Co(CN)_5^{3-}$, Cr^{2+}, and Ni(tetramethylcyclam)$^+$,[69,77,78] but it is not a factor in two-electron, S_N2-like mechanisms.[79] Bromo-substituted methyl esters, such as methyl bromoacetate, methyl bromopropionate, and dimethyl bromomalonate, display enhanced reactivity due to radical delocalization onto the carbonyl oxygen. Methyl 4-bromocrotonate, $BrCH_2CH{=}CHCO_2CH_3$, is an especially reactive primary organic halide because extended π-delocalization of the 1° radical is possible.

Electronic Effects. The rate constant for reaction of $CpW(CO)_3$ with benzyl bromide is altered hardly at all by substitution of CN, CF_3, or F for H in the para position (see Table I). Large electronic effects are characteristic of electron-transfer reactions because of the explicit dependence of the rate on driving force. By contrast, the effect of para substituents is negligible in atom-transfer reactions of Cr^{2+}.[1] When a positive Hammett correlation is observed, as in the reactions of $Co(dmgH)_2PPh_3$[43,72] and $Re(CO)_4L$[42] with p-$YC_6H_4CH_2X$, it is attributed to partial electron transfer in the transition state. Correlations of log k with C–X bond dissociation energies and with RX half-wave reduction potentials are shown in Figure 4. Neither correlation is particularly good, implying that neither C–X bond breaking nor electron transfer is particularly advanced in the transition state. Polar effects are not generally thought to be important in radical mechanisms; however, polar transition states may contribute to the reactions with polyhaloalkanes because haloalkyl radicals are more electronegative than unsubstituted organic radicals.[13]

Solvent Effects. Changing the solvent from polar (CH_3CN, THF) to nonpolar (toluene) does not much affect the rates of reaction of $CpW(CO)_3$ with organic halides. Rate constants for the reaction with benzyl bromide in CH_3CN, toluene, and THF are $(9.2 \pm 0.7) \times 10^4$, $(7.3 \pm 0.2) \times 10^4$, and $(4.3 \pm 0.2) \times 10^4$ L mol^{-1} s^{-1}, respectively. This result is typical of atom-transfer reactions,[80] since radical reactants and products are usually not strongly solvated. In contrast, electron-transfer reactions involving organic halides are greatly affected by changes in solvent polarity.[73] The magnitude of the solvent effect has been proposed as a test to discriminate between atom-transfer and electron-transfer reactions.[81] A 5-fold increase in $CpW(CO)_3$ radical yield was observed when the salt $Na[CpW(CO)_3]$ was added to CH_3CN, raising the ionic strength to 0.1 mM. Large solvent effects on quantum yields have previously been noted in these types of systems.[30]

Effect of Lewis Bases. The presence of 5 mM PPh_3 has no effect on the rate of reaction of organic halides with $CpW(CO)_3$. Lewis bases have been demonstrated to bind to 17-electron radicals, forming 19-electron adducts that are stronger reducing agents than their 17-electron precursors.[41] This equilibrium is represented in eq 8. Even though $CpW(CO)_3PPh_3$ is a stronger reductant

$$CpW(CO)_3 + PPh_3 \rightleftarrows CpW(CO)_3PPh_3 \qquad (8)$$

than $CpW(CO)_3$, the lack of rate acceleration by PPh_3 implies that the 17-electron radical is more reactive toward organic halides. This result contrasts with the rate acceleration observed for outer-sphere reactions of $CpW(CO)_3$ (for example with $Fe(C_5H_5)_2^+$) in the presence of PPh_3 and other Lewis bases.[82] Since the equilibrium constant for reaction 8 is quite small, of the order

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(74) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625–1651.

(75) Kaplan, L. *Bridged Free Radicals*; Marcel Dekker: New York, 1972; pp 302–303.

(76) Kray, W. C., Jr.; Castro, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4603.

(77) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 4231–4235.

(78) Singleton, D. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 6547.

(79) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218.

(80) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852–1856.

(81) Kosower, E.; Mohammed, M. *J. Am. Chem. Soc.* **1968**, *90*, 3271–3272.

(82) Scott, S. L.; Espenson, J. H., manuscript in preparation.

of 6 L mol^{-1},[82] the proportion of the 19-electron complex is very small at [PPh$_3$] ≤ 5 × 10^{-3} M. This is the reason that the rate of dimerization remains invariant with [PPh$_3$] to this level.

Radical Substitution Rates. Substitution of CO by PR$_3$ on the CpW(CO)$_3$ radical, eq 9, was investigated by Turaki and Huggins.[40] Ph$_3$CCl was used to trap CpW(CO)$_3$ and CpW(CO)$_2$PR$_3$,

$$\mathrm{CpW(CO)_3 + PR_3 \xrightarrow{k_a} CpW(CO)_2PR_3 + CO} \tag{9}$$

$$\mathrm{CpW(CO)_3 + Ph_3CCl \xrightarrow{k_X} CpW(CO)_3Cl + Ph_3C^\bullet} \tag{10}$$

and the ratio of the products CpW(CO)$_3$Cl/CpW(CO)$_2$(PR$_3$)Cl was used to derive the ratio of the rate constants k_a/k_X. Since the rate constant k_x for Ph$_3$CCl was not available, these authors used the estimated value[28] of k_X for CCl$_4$ to calculate k_a. However, as this study shows, Ph$_3$CCl is 290 times more reactive than CCl$_4$. Therefore, the calculated value for k_a should be revised upwards by this factor. We calculate k_a = 2.5 × 10^5 L mol^{-1} s^{-1} for PPh$_3$ and 3.8 × 10^6 L mol^{-1} s^{-1} for P(OPh)$_3$. These high substitution rates are consistent with the lability of 17-electron radicals.[36-40]

Products. The expected products of the atom-transfer reaction are CpM(CO)$_3$X and R$^\bullet$ (eqs 6 and 7). CpW(CO)$_3$X was identified qualitatively by FT-IR as a product in the reactions with CCl$_4$, CHBr$_3$, and CH$_2$I$_2$. Small organic products, such as 1,5-hexadiene from the coupling of allyl radicals, proved extremely difficult to determine by gas chromatography because of their low concentration (<10 μM/laser flash) and interference from the organic solvent.

The fate of the organic radical, except in the case of stable radicals such as Ph$_3$C$^\bullet$,[40] has not been previously identified. There are two possible radical coupling reactions, eqs 11 and 12,

$$\mathrm{2R^\bullet \rightarrow R-R} \tag{11}$$

$$\mathrm{CpW(CO)_3 + R^\bullet \rightarrow CpW(CO)_3R} \tag{12}$$

which may consume the organic radicals in addition to reaction with the solvent. The M–R coupling product was not observed in a continuous photolysis study of M$_2$(CO)$_{10}$ (M = Mn, Re).[25] Another study[83] showed that M–X was the *only* primary photoproduct resulting from the flash photolysis of heterodinuclear metal carbonyls in CCl$_4$. Indirect evidence for a reaction between Mn(CO)$_5$ and the 1-hydroxyethyl radical was obtained in a pulse radiolysis study,[19] and the possibility of W–C homolysis has been demonstrated photochemically.[84]

Radical coupling reactions generally have very low activation barriers and rate constants near the diffusion-controlled limit in solution. Values of k_{11} are (2–5) × 10^9 L mol^{-1} s^{-1} for most organic radicals.[85-87] The value of k_{12} is unknown, but it probably also approaches the diffusion-controlled limit. Failure to observe M–R coupling products has been attributed to low light intensity,[25] which results in a small steady-state concentration of organometallic radicals. Trapping of R$^\bullet$ by the organometallic radical was therefore presumed to have low probability.

A different approach to the problem of the fate of the organic radical is an examination of the kinetic requirements of the mechanism. Numerical simulation of the mechanism which consists of reactions 6, 7, 11, and 12, made with the estimate k_{12} = 4 × 10^9 L mol^{-1} s^{-1}, reveals that under no concentration conditions would CpW(CO)$_3$R be a major product. This is a direct result of the breakdown of the steady-state approximation, which requires that

$$-\mathrm{d[CpW(CO)_3]}/\mathrm{d}t = \mathrm{d([R{-}R] + [CpW(CO)_3R])}/\mathrm{d}t$$

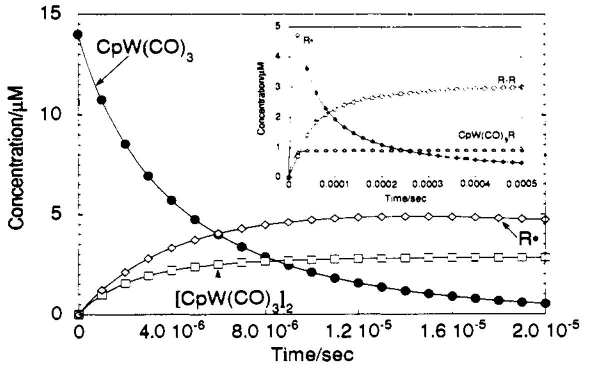

Figure 5. Simulated evolution of organic and organometallic radical concentrations during a laser flash photolysis experiment. Simulation parameters: [CpW(CO)$_3$] = 0.014 mM, [(CH$_3$)$_2$CHI] = 0.33 M, k_c = 6.2 × 10^9, k_x = 3 × 10^5, k_{R-R} = 2 × 10^9, and k_{R-X} = 4 × 10^9 L mol^{-1} s^{-1}. The inset shows later events at longer times.

Table III. Bimolecular Rate Constants for the Abstraction of Halogens and Pseudohalogens from Cobalt(III) Ammine Complexes by CpW(CO)$_3$[a]

cobalt complex	k_X/L mol^{-1} s^{-1}
ClCo(NH$_3$)$_5$$^{2+}$	(2.02 ± × 10^8
BrCo(NH$_3$)$_5$$^{2+}$	(7.3 ± 0.7) × 10^8
NCCo(NH$_3$)$_5$$^{2+}$	(1.6 ± 0.1) × 10^7
SCNCo(NH$_3$)$_5$$^{2+}$	(3.0 ± 0.2) × 10^7
N$_3$Co(NH$_3$)$_5$$^{2+}$	(2.3 ± 0.5) × 10^7
Co(NH$_3$)$_6$$^{3+}$	≤2 × 10^6
ClCo(dmgH)$_2$py	(7.1 ± 0.7) × 10^8
BrCo(dmgH)$_2$py	≥2 × 10^9 s^{-1}[b]

[a] In CH$_3$CN at 23 °C. [b] It was not possible to measure this rate constant accurately because of the onset of a radical chain reaction at low (15 μM) concentrations of BrCo(dmgH)$_2$PPh$_3$ (see discussion in text).

As the simulated evolution of reactants and products in Figure 5 shows, reactions of the organic radicals mostly occur after all of the CpW(CO)$_3$ has been consumed in reactions 6 and 7, thus ruling out reaction 12 despite its (presumed) high rate constant.

Reactions with Halocobalt(III) Complexes. Abstraction of halogens and pseudohalogens bound to Co(III) ammines is believed to proceed by the same mechanism as abstraction from organic halides.[36,37] The organometallic radical CpW(CO)$_3$ also reacts rapidly with XCo(NH$_3$)$_5$$^{2+}$ and XCo(dmgH)$_2$py, with the rate constants listed in Table III. The reactions are very rapid, k = 10^7 – 10^9 L mol^{-1} s^{-1}. The upper limit imposed by diffusion prohibits the observation of as wide a range of reactivity as was seen for the organic halide reactions. Pseudohalides such as azide and isothiocyanate are almost as effective as chloride at forming the bridged inner-sphere complex. The IR spectrum of the product of the reaction between CpW(CO)$_3$ and ClCo(NH$_3$)$_5$$^{2+}$ is identical with that of CpW(CO)$_3$Cl, confirming the transfer of Cl from cobalt to tungsten. The other inorganic product is presumed to be Co(II), which is stable under these conditions. The halocobaloximes are more reactive than the halopentaamminecobalt(III) complexes.

As with the organic halide reactions, the addition of 5 mM PPh$_3$ does not affect the rate of halogen abstraction from Co(NH$_3$)$_5$Cl^{2+}, as expected for an inner-sphere mechanism. The complex Co(NH$_3$)$_6$$^{3+}$, which lacks an effective bridging ligand, reacts immeasurably slowly (k < 2 × 10^6 L mol^{-1} s^{-1}) with CpW(CO)$_3$, ruling out an outer-sphere electron-transfer mechanism.

Reactions with Oxygen and Hydrogen. Organometallic radicals, like most organic radicals, are highly sensitive to traces of O$_2$. In all experiments with halogen-containing substrates, O$_2$ was rigorously excluded from the reaction mixture. In the presence of O$_2$, recombination of the CpW(CO)$_3$ radicals is reduced, Figure 6a. Binding of O$_2$ to CpW(CO)$_3$, eq 13, is a likely first step in

$$\mathrm{CpW(CO)_3 + O_2 \rightarrow CpW(CO)_3O_2} \tag{13}$$

the reduction of O$_2$ by CpW(CO)$_3$ and has precedent with other

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[83] Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 4908–4911.

[84] Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1986**, *108*, 89–94.

[85] Neta, P.; Huie, R. E.; Mosseri, S.; Shastri, L. V.; Mittal, P.; Maruthamuthu, P.; Steenken, S. *J. Phys. Chem.* **1989**, *93*, 4099–4104.

[86] Marchaj, A.; Kelley, D. G.; Bakac, A.; Espenson, J. H. *J. Phys. Chem.* **1991**, *95*, 4440–4441.

[87] Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

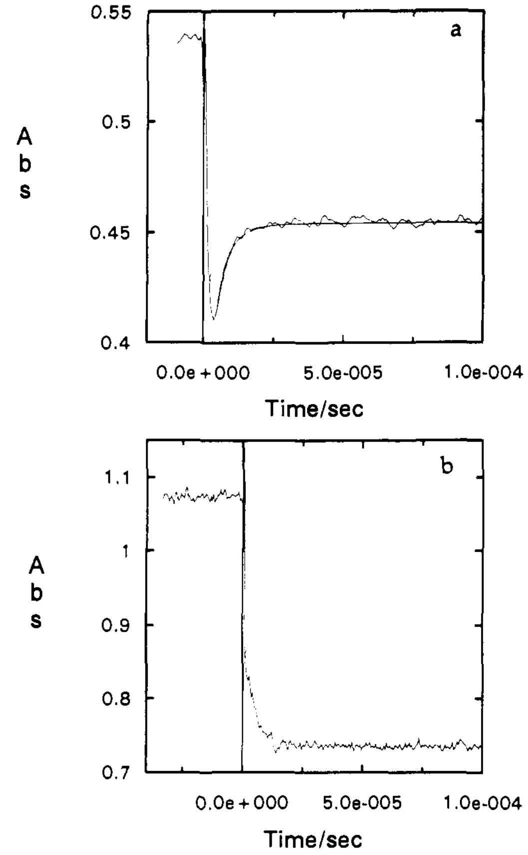

Figure 6. Onset of a chain reaction between $[CpW(CO)_3]_2$ and O_2. Typical kinetic traces at (a) low $[O_2]$ (0.030 mM), showing partial dimer recovery after flash, and (b) high $[O_2]$ (1.7 mM), showing dimer loss after flash.

organometallic radicals.[19,42,51] The 1:1 adducts between O_2 and either $Co(CO)_4$ or $Mn(CO)_5$ have been characterized by EPR spectroscopy.[88] An induction period for the reaction of $HRe(CO)_5$ with PPh_3 in air was attributed to the formation of a 1:1 adduct with O_2.[21]

The rate constant for reaction 13 was determined, as before, from the dependence of k_ψ on $[O_2]$. We obtained $k_{13} = (3.3 \pm 0.4) \times 10^9$ L mol^{-1} s^{-1} at 23 °C in CH_3CN. This value is similar to the rate constants for capture of O_2 by organic radicals, $k = (2\text{-}5) \times 10^9$,[85-87] by $Rh(dmgH)_2PPh_3$, $k = 1.4 \times 10^9$,[51] and by $Mn(CO)_5$, $k = 1.8 \times 10^9$ L mol^{-1} s^{-1}.[19]

The adduct $CpW(CO)_3O_2$ may be formally described as a superoxo complex. Its fate may be dissociation to $CpW(CO)_3^+$ and $O_2^{\cdot -}$ or disproportionation to form a peroxo complex, as in eq 14. In a series of nonradical reactions, the peroxo complex

$$2CpW(CO)_3O_2 \rightarrow CpW(CO)_3^+ + O_2 + CpW(CO)_3O_2^- \quad (14)$$

$W(CO)_4(\eta^2\text{-}O_2)$ (analogous to the last product of eq 14) was identified during photolysis of $W(CO)_6$ in a CH_4 matrix doped with O_2.[89,90] The $W(CO)_4(\eta^2\text{-}O_2)$ has a weak LMCT band at 355 nm and is photosensitive, giving cleavage of the O–O bond to yield *trans*-$W(CO)_4(O)_2$. The ultimate fate of the $CpW(CO)_3O_2$ adduct may be similar but was not determined since its likely photoreactivity precludes generation on a preparative scale.

Saturation of a CH_3CN solution of $[CpW(CO)_3]_2$ with H_2 prior to photolysis had no effect on the kinetics or the yield of radical recombination. Although the anticipated product $CpW(CO)_3H$ can be prepared by other synthetic routes, the solid is known to decompose thermally to $[CpW(CO)_3]_2$ and $Hg_{(g)}$.[91] The reaction between $CpW(CO)_3$ and H_2 is not thermodynamically prohibited, however, because the W–H bond enthalpy, 73 kcal/mol,[92] is higher than the H–H bond enthalpy, 51 kcal/mol per H. A light-initiated reaction has been observed between H_2 and $M(CO)_5$ (M = Mn, Re);[21] also, $Co(CN)_5^{3-}$ reacts thermally with H_2.[93] It is likely that the reaction of $CpW(CO)_3$ with H_2 is simply too slow to compete effectively with radical combination in the laser flash experiment.

Reactions with Hydroperoxides. The $CpW(CO)_3$ radical reacts with H_2O_2 and *t*-BuOOH with rate constants of $(4.0 \pm 0.3) \times 10^5$ and $(4.5 \pm 0.2) \times 10^5$ L mol^{-1} s^{-1}, respectively. The similarity of these values argues against the S_N2 and oxidative addition mechanisms, for which substantial steric effects are expected (i.e., *t*-BuOOH should react more slowly than H_2O_2 in either of these mechanisms). Outer-sphere electron transfer to H_2O_2 is unknown. For example, $Ru(NH_3)_6^{2+}$, a reductant whose primary coordination sphere is inert, reacts extremely slowly (if at all) with H_2O_2.[94] Therefore, the facility of the reactions between $CpW(CO)_3$ and hydroperoxides requires an inner-sphere mechanism. A radical mechanism was also proposed for the reaction between $Co(CN)_5^{3-}$ and H_2O_2.[69] This process is illustrated for $CpW(CO)_3$ in eq 15. The fate of the hydroxyl radical was not determined;

$$CpW(CO)_3 + H_2O_2/t\text{-BuOOH} \rightarrow CpW(CO)_3OH + OH^{\bullet}/t\text{-BuO}^{\bullet} \quad (15)$$

it likely abstracts a H atom from the solvent (CH_3CN). However, the *tert*-butoxyl radical undergoes β-scission,[95] eq 16. Ethane,

$$(CH_3)_3CO^{\bullet} \rightarrow (CH_3)_2O + CH_3^{\bullet} \quad (16)$$

produced by coupling of methyl radicals, was detected by GC in photolyzed reaction mixtures of $[CpW(CO)_3]_2$ and *t*-BuOOH, supporting the proposed reaction mechanism.

Reactions with Tin Compounds. $CpW(CO)_3$ reacts with $(n\text{-}Bu)_3SnX$, where X = Cl, H, or D, with rate constants $(7.4 \pm 0.3) \times 10^4$, $(2.43 \pm 0.08) \times 10^5$, and $(2.29 \pm 0.07) \times 10^5$ L mol^{-1} s^{-1} in toluene. $CpW(CO)_3Cl$ was identified qualitatively by IR as a product of the reaction with $(n\text{-}Bu)_3SnCl$. An efficient light-initiated chain reaction with $(n\text{-}Bu)_3SnI$ precluded measurement of the bimolecular rate constant.

A photolyzed reaction mixture of $[CpW(CO)_3]_2$ and $(n\text{-}Bu_3)_3SnH$ showed IR bands at 1985, 1907, 1884, and 1707 cm^{-1}. The ν_{CO} bands at 2024 and 1927 cm^{-1} which are characteristic of $Cp(CO)_3WH$ were not present.[91] Despite the thermodynamic feasibility of a hydrogen-atom-transfer mechanism (based on the bond strengths of W–H, 73 kcal/mol,[92] and Sn–H, 70 kcal/mol,[96] respectively) and evidence for this mechanism in the reaction of $(n\text{-}Bu)_3SnH$ with other organometallic radicals (e.g., $Re(CO)_4PR_3$),[80] the absence of the $CpW(CO)_3H$ product and the lack of a deuterium kinetic isotope effect makes hydrogen atom transfer to $CpW(CO)_3$ unlikely. At the same time, addition of PPh_3 has no effect on the rate, which suggests that the mechanism is not outer-sphere electron transfer either.[82] Oxidative addition to a 15-electron radical ($CpM(CO)_2$) was suggested for the photochemical reaction between $(n\text{-}Bu)_3SnH$ and $[Co(CO)_3PR_3]_2$ or $[CpM(CO)_3]_2$ (M = Mo, W).[97] The observed products were H_2 and $(n\text{-}Bu)_3SnCo(CO)_3(PR_3)$ or $CpM(CO)_3Sn(n\text{-}Bu)_3$, respectively. The nonlinear transition state for oxidative addition is not required to show a primary kinetic isotope effect, consistent with our results.

No kinetic inhibition of the reaction was observed when the solution of $[CpW(CO)_3]_2$ and $(n\text{-}Bu)_3SnH$ in toluene was presaturated with CO. Therefore, the reaction cannot involve prior dissociation of CO to form the 15-electron $CpW(CO)_2$ radical.

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(88) Fieldhouse, S. A.; Fullam, B. W.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1974**, 567–569.

(89) Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 19–25.

(90) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051–3056.

(91) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124.

(92) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717.

(93) Halpern, J.; Pribanic, M. *Inorg. Chem.* **1970**, *9*, 2616–2618.

(94) Pladziewicz, J. R.; Meyer, T. J.; Broomhead, J. A.; Taube, H. *Inorg. Chem.* **1973**, *12*, 639–643.

(95) Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. 2, p 665.

(96) Jackson, R. *J. Organomet. Chem.* **1979**, *166*, 17–19.

(97) Wegman, R. W.; Brown, T. L. *Organometallics* **1982**, *1*, 47–52.

We propose that oxidative addition to the 17-electron radical occurs to form, transiently, a 19-electron product which rapidly loses CO, eq 17. The product $CpW(CO)_2(Sn(n\text{-}Bu_3)(H)$ is also

$$CpW(CO)_3 + (n\text{-}Bu)_3SnH \xrightarrow{rds} CpW(CO)_3(Sn(n\text{-}Bu)_3)(H) \xrightarrow{fast} CpW(CO)_2(Sn(n\text{-}Bu)_3)(H) + CO \quad (17)$$

a 17-electron radical and may abstract H from $(n\text{-}Bu)_3SnH$.[97] This reaction occurs after the rate-determining step; therefore, no information about it can be obtained from the kinetic data.

Chain Reactions. For some organic halides, such as CHI_3, Ph_3CBr, and $BrCH_2CH_2CN$, as well as for $BrCo(dmgH)_2PPh_3$, $(n\text{-}Bu)_3SnI$, and O_2, high concentrations gave postflash loss of dimer absorbance, shown for O_2 in Figure 6b. The concentration of oxidant required to observe dimer loss rather than radical recombination (dimer recovery) was $[ox] > 10^5/k_X$. Our observations are consistent with the onset of a chain reaction in which organic and organometallic radicals are chain carriers. A possible mechanism is shown in Scheme I. When the rate of reaction 18

Scheme I

$$CpW(CO)_3 + RX \rightarrow CpW(CO)_3X + R^\bullet \quad (18)$$

$$R^\bullet + [CpW(CO)_3]_2 \rightarrow R^+ + CpW(CO)_3^- + CpW(CO)_3 \quad (19)$$

is large (high [RX]), a high concentration of $[R^\bullet]$ is produced. Consequently, enough $R^\bullet$ proceeds by reaction 19 (even though radical coupling is simultaneously enhanced) to make loss of the dimer $[CpW(CO)_3]_2$ significant. A similar scheme can be written with superoxide (free or coordinated to $CpW(CO)_3^+$) or $Co(II)(dmgH)_2PPh_3$ as the species which reduces $[CpW(CO)_3]_2$. Further studies of the mechanisms of these photoinitiated chain reactions are in progress.

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Ligand Conformational Changes Affecting $^5T_2 \rightarrow {}^1A_1$ Intersystem Crossing in a Ferrous Complex

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Abstract: Results are presented from a variable-temperature solution-phase laser photolysis study of the $^5T_2 \rightarrow {}^1A_1$ intersystem crossing in $[Fe(t\text{-tpchxn})](ClO_4)_2$, where the hexadentate ligand *t*-tpchxn is *trans*-1,2-bis(bis(2-pyridylmethyl)amino)cyclohexane. The complex $[Fe(t\text{-tpchxn})](ClO_4)_2{\cdot}H_2O{\cdot}CH_3OH$ crystallizes in the space group $P2_12_12_1$, which at 299 K has a unit cell with $a = 9.565(4)$ Å, $b = 13.178(5)$ Å, $c = 27.276(23)$ Å, and $Z = 4$. Refinement with 1905 observed $[F > 3.0\sigma(F)]$ reflections gave $R = 0.0924$ and $R_w = 0.1147$. The structure indicates that the complex has spontaneously resolved into optically pure crystals. After excitation into a $^1MLCT \leftarrow {}^1A_1$ band ($\lambda_{pump} = 440$ nm), relaxation profiles were determined at 420 nm for a CH_3OH solution of $[Fe(t\text{-tpchxn})](ClO_4)_2$ in the range 191–280 K. In the range 190–250 K, the compound exhibits biphasic relaxation kinetics, whereas a single-exponential model was adequate from 260 to 280 K. From plots of $\ln(k)$ versus $1/T$ for each of the two relaxation processes in the 190–250 K range, activation parameters and frequency factors were found to be 964 ± 23 cm^{-1} and $(3.7 \pm 0.5) \times 10^9$ s^{-1}, respectively, for the τ_1 process and 2370 ± 60 cm^{-1} and $(5 \pm 2) \times 10^{12}$ s^{-1}, respectively, for the τ_2 process ($\tau_1 < \tau_2$). The observation of *two* relaxation processes for $[Fe(t\text{-tpchxn})](ClO_4)_2$ in CH_3OH stands in contrast to the data reported previously for the same complex in either DMF or CH_3CN, where in both solvents only a single-exponential relaxation profile is seen. Both of the relaxation processes observed for the methanol solution are assigned as $^5T_2 \rightarrow {}^1A_1$ intersystem crossing processes. It is suggested that $[Fe(t\text{-tpchxn})]^{2+}$ undergoes a solvent-induced conformational change of the cyclohexyl ring, giving rise to two different high-spin forms of the complex having different spin-state interconversion dynamics.

Introduction

A spin-crossover complex has a low-energy excited electronic state which can be thermally populated.[4] The factors which affect the rate of intersystem crossing between the low-spin ($^1A_1$) and high-spin ($^5T_2$) states of ferrous spin-crossover complexes are being studied for a variety of reasons.[5] Apart from fundamental interest in the dynamics of intersystem crossing processes, transition metal sites in metalloenzymes catalyze the reaction of paramagnetic O_2 with diamagnetic organic substrates. In fact, spin-state changes occurring at metal sites in proteins can be rate controlling in the functioning of certain metalloenzymes, e.g., mammalian P450.[6] Finally, intersystem crossing rates in Fe^{II} complexes are being studied in order to understand the LIESST (light-induced excited-spin-state trapping) effect discovered by Gütlich et al.[7] In

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(4) (a) Toftlund, H. *Coord. Chem. Rev.* **1989**, *94*, 67. (b) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527–622. (c) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (d) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. (e) Scheidt, W. R.; Reed, C. A. *Chem.* Rev. **1981**, *81*, 543. (f) König, E.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219. (g) Bacci, M. *Coord. Chem. Rev.* **1988**, *86*, 245. (h) Gütlich, P. In *Chemical Mössbauer Spectroscopy*; Herber, R. H., Ed.; Plenum Press: New York, 1984. (i) Maeda, Y.; Takashima, Y. *Comments Inorg. Chem.* **1988**, *7*, 41. (j) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1–22.

(5) Beattie, J. K. *Adv. Inorg. Chem.* **1988**, *32*, 1–53.

(6) Fisher, M. T.; Sligar, S. G. *Biochemistry* **1987**, *26*, 4797–4803. (b) Backes, W. L.; Sligar, S. G.; Schenkman, J. B. *Biochemistry* **1982**, *21*, 1324–13330. (c) Tamburini, P. P.; Gibson, G. G.; Backes, W. L.; Sligar, S. G.; Schenkman, J. B. *Biochemistry* **1984**, *23*, 4526–4533.

(7) (a) Decurtins, S.; Gütlich, P.; Kohler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1. (b) Decurtins, S.; Gütlich, P.; Kohler, C. P.; Spiering, H. *J. Chem. Soc., Chem. Commun.* **1985**, 430. (c) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. *Inorg. Chem.* **1985**, *24*, 2174. (d) Poganuich, P.; Decurtins, S.; Gütlich, P. *J. Am. Chem. Soc.* **1990**, *112*, 3270–3278. (e) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140–151.

0002-7863/93/1515-1797$04.00/0