$(pzHCONH_2\cdot)^{3+}/Cr(pzCONH_2)^{3+}$ couple to be at least 10^3 times greater than the corresponding constant for the $Cr^{3+/2+}$ couple. This difference, coupled with the small transfer coefficient for the oxidation of Cr^{2+},[14] is large enough to account for the observed oxidation of $Cr(pzHCONH_2\cdot)^{3+}$ instead of Cr^{2+} despite the difference in formal potentials that produces a large driving force favoring the oxidation of Cr^{2+} at +0.15 V ($E^f(Cr^{3+/2+})$ = −0.65 V; $E^f(Cr(pzHCONH_2\cdot)^{3+}/Cr(pzCONH_2)^{3+})$ = −0.09 V). If the electrooxidation were carried out in halide-supporting electrolytes where inner-sphere oxidation of Cr^{2+} can proceed[5], it seems likely that the reaction might follow a pathway similar to that described by Gould et al.[2]

Effects of Pyrazine Reduction Potentials. The formation constants for greens derived from substituted pyrazines appear to become greater as the reduction potential for the pyrazine becomes more positive. For example, Gould et al. estimated a formation constant for pyrazinecarboxamide (at pH 0) that is about 10^3 times greater than the corresponding constant for pyrazine,[2] and the reduction of the carboxamide occurs at a potential slightly positive of that for pyrazine.[9] Similarly, chloropyrazine is reduced at much more negative potentials than pyrazine,[9] and no intensely green complex forms when Cr^{2+} is mixed with chloropyrazine at pH 2 with millimolar concentrations (although the formation of a chloropyrazine green was reported[2] in 1.2 M $HClO_4$ with chloropyrazine concentrations exceeding 20 M).

Conclusions

The electrochemistry of pyrazine green can be understood in terms of the known homogeneous redox and coordination chemistry it exhibits. With the carboxylate and carboxamide derivatives, chelated greens are apparently formed, and these undergo reversible, one-electron oxidations to the corresponding chromium(III) complexes of the unreduced ligands. When a chelate is not formed, as with pyrazine and one isomer of the carboxamide, the resulting greens undergo irreversible one-electron oxidations to yield complexes that are reduced directly to the corresponding chromium(III)–dihydropyrazine complexes without the formation of a green.

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Registry No. $Cr(pzH\cdot)^{3+}$, 73090-60-5; $Cr(pzHCOO\cdot)^{2+}$, 77450-44-3; $Cr(pzHCONH_2\cdot)^{3+}$, 77450-21-6; $Cr(pz)^{3+}$, 73090-61-6; $Cr(pzCOO)^{2+}$, 77450-22-7; $Cr(pzCONH_2)^{3+}$, 77450-23-8; $Cr(pzH_2)^{3+}$, 77450-24-9.

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Photochemistry of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ in Solution. Mechanism of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ Formation

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Irradiation (366 nm) of $CpW(CO)_3CH_3$ ($Cp = \eta^5\text{-}C_5H_5$) at room temperature in a variety of solvents produces $Cp_2W_2(CO)_6$ and methane. In CH_2Cl_2 and $CHCl_3$ solutions, $CpW(CO)_3Cl$ and $CpW(CO)_2Cl_3$ are secondary and tertiary photoproducts, respectively. The disappearance quantum yield (366 nm) for $CpW(CO)_3CH_3$ in CH_2Cl_2 solution is 0.08; this value drops to 0.04 when excess CO is present. Irradiation of $CpW(CO)_3CH_3$ in the presence of PPh_3, $AsPh_3$, or Ch_3CN gives the substituted products $CpW(CO)_2(L)CH_3$ ($L = PPh_3, AsPh_3, CH_3CN$). The quantum yield of disappearance for $CpW(CO)_3CH_3$ in these photosubstitution reactions is about 0.4. $CpW(CO)_3CH_3$ reacts photochemically with THF at −78 °C to give $CpW(CO)_2(THF)CH_3$. Solutions of this product are stable at −78 °C, but the complex decomposes to $Cp_2W_2(CO)_6$ and $CpW(CO)_3CH_3$ upon warming to room temperature. Irradiation (366 nm) of $CpW(CO)_2(PPh_3)(COCH_3)$ at room temperature in CH_2Cl_2 or THF solution produces $CpW(CO)_3CH_3$ (and possibly $CpW(CO)_2(PPh_3)CH_3$). The disappearance quantum yield of $CpW(CO)_2(PPh_3)(COCH_3)$ in this reaction is 0.10. The primary photoprocess of the $CpW(CO)_3CH_3$ complex is proposed to be be W–CO bond dissociation, and the following pathway is suggested for the formation of $Cp_2W_2(CO)_6$: $CpW(CO)_3CH_3 \xrightarrow{h\nu} CpW(CO)_2CH_3 + CO$; $CpW(CO)_2CH_3 + CpW(CO)_3CH_3 \rightarrow Cp_2W_2(CO)_5 + 2CH_3$; $Cp_2W_2(CO)_5 + CO \rightarrow Cp_2W_2(CO)_6$. Consistent with this pathway is the observation that the quantum yield of the coupling reaction (0.08) is independent of the light intensity ((2.5–22) × 10^{-8} einstein/min). The source of the extra hydrogen for the methyl radical to form methane is proposed to be the solvent because, in benzene-d_6 and chloroform-d, CH_3D is formed.

Introduction

Irradiation of mononuclear metal carbonyl alkyl and hydride complexes often results in cleavage of the metal–alkyl or metal–hydrogen bond and formation of a metal–metal bonded dimer. Equations 1–4 illustrate several reactions of this type.

$$2HFe(CO)_4^- \xrightarrow{h\nu} Fe_2(CO)_8^{2-} + H_2 \qquad (1)^{1}$$

$$\begin{gathered}2CpM(CO)_3CH_3 \xrightarrow{h\nu} Cp_2M_2(CO)_6 + 2[CH_3] \\ (Cp = \eta^5\text{-}C_5H_5;\ M = Cr, Mo, W)\end{gathered} \qquad (2)^{2-5}$$

$$2CpW(CO)_3H \xrightarrow{h\nu} Cp_2W_2(CO)_6 + H_2 \qquad (3)^{6}$$

$$CpFe(CO)_2(CH_2C_6H_5) \xrightarrow{h\nu} Cp_2Fe_2(CO)_4 + \text{other products} \qquad (4)^{7,8}$$

In general, the mechanisms of these photochemically induced coupling reactions are poorly understood; some mechanistic information is available, however, on the reaction in eq 2.

In the earliest mechanistic study of reaction 2, Rausch and co-workers showed that methane was the major gaseous product formed in the photolysis of $CpMo(CO)_3CH_3$.[2] By

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using deuterium-labeled complexes, they showed that the pathway for methane production was abstraction by the methyl group of a hydrogen atom from the cyclopentadienyl ring. The mechanism of $Cp_2Mo_2(CO)_6$ formation was not specifically studied, but it was suggested that cleavage of the $Mo-CH_3$ bond predominated over Mo–CO bond cleavage; presumably, $Cp_2Mo_2(CO)_6$ is formed by the coupling of two $CpMo(CO)_3$ species.

In another study of the reaction in eq 2, Wojcicki and Severson studied the coupling mechanism of the $CpW(CO)_3CH_3$ complex.[3] They proposed that the primary photoprocess of this complex is W–CO dissociation rather than $W-CH_3$ cleavage. Their mechanism for the coupling reaction is shown in eq 5–8. Consistent with the first step of this

$$CpW(CO)_3CH_3 \xrightarrow{h\nu} CpW(CO)_2CH_3 + CO \quad (5)$$

$$CpW(CO)_2CH_3 \rightarrow CpW(CO)_2 + CH_3 \quad (6)$$

$$CpW(CO)_2 + CO \rightarrow CpW(CO)_3 \quad (7)$$

$$2CpW(CO)_3 \rightarrow Cp_2W_2(CO)_6 \quad (8)$$

pathway is the observation that the coupling reaction is inhibited by excess CO. Also consistent with eq 5 are the numerous photochemical substitution reactions of $CpW(CO)_3CH_3$ (eq 9). In these reactions, W–CO dissociation is clearly favored over $W-CH_3$ bond cleavage.

$$CpW(CO)_3CH_3 + L \xrightarrow{h\nu} CpW(CO)_2(L)CH_3 + CO \quad (9)$$

$$(L = PPh_3,^4\ P(OCH_3)_3,^4\ P(CH_3)_3,^9\ C_2H_4,^{10}\ C_2H_2{}^{11})$$

None of the studies of the mechanism of reaction 2 have probed the reaction steps which occur subsequent to the primary photoprocess. It is a common assumption that $Cp_2M_2(CO)_6$ is formed by the coupling of two $CpM(CO)_3$ species, but there is no experimental evidence for this intermediate in the reaction pathway. Several alternative pathways which yield binuclear products but which do not require the formation of $CpM(CO)_3$ can be proposed.[12] Because of the lack of definitive mechanistic information on reaction 2, it was decided to investigate in detail the mechanism of the photochemical coupling reaction of $CpW(CO)_3CH_3$. Particular emphasis was placed on elucidating the reaction steps which occur subsequent to the primary photoprocess. In addition, the primary photoprocess of the $CpW(CO)_3CH_3$ complex was investigated because it was felt that the inhibition of reaction 2 by excess CO and the photochemical substitution results (eq 9) did not necessarily imply a W–CO dissociation primary photoprocess. This paper reports the results of the investigation.

Experimental Section

Solutions of the tungsten complexes discussed in this paper decompose when exposed to air. All synthesis and manipulations were carried out on a Schlenk line with use of prepurified nitrogen as an inert gas or on a vacuum line. Solvents were rigorously dried by standard techniques.[13]

$CpW(CO)_3CH_3$ was prepared by the method of Piper and Wilkinson[14] as described in detail by King.[15] A modification suggested by Alt[4] was incorporated into the purification procedure; before $CpW(CO)_3CH_3$ was sublimed, the crude $CpW(CO)_3CH_3$ was extracted with pentane. This extraction separated $CpW(CO)_3CH_3$ from small amounts of unreacted $W(CO)_6$ so that, after sublimation, a product was obtained which was free of $W(CO)_6$. $CpW(CO)_3Cl$,[16] $Cp_2W_2(CO)_6$,[17] and $CpW(CO)_2(PPh_3)(COCH_3)$[18] were prepared by standard literature methods. These complexes were identified and checked for purity by infrared and electronic absorption spectral measurements. $Cp_2Fe_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ were obtained from ROC/RIC Chemical Co. and recrystallized before use. Triphenylphosphine (Aldrich) and triphenylarsine (Strem) were recrystallized before use. Deuterated solvents for use in the mass spectral and NMR experiments were obtained from Aldrich.

Table I. Observed Lowest Energy Electronic Absorption Bands of the Tungsten Complexes

complex	λ_{max}, nm	solvent
$CpW(CO)_3CH_3$	313	CH_2Cl_2
$Cp_2W_2(CO)_6$	493	CCl_4
$CpW(CO)_3Cl$	458	CCl_4
$CpW(CO)_2(PPh_3)(COCH_3)$	363	CH_2Cl_2

Spectroscopic cells containing the solution to be irradiated were prepared in the following way. The solvent was deoxygenated with a nitrogen purge and then transferred with a syringe to a previously deoxygenated septum-capped test tube containing the complex. After the complex had dissolved, the solution was transferred by syringe to the appropriate cell, either an IR or long-stem quartz cell or an NMR tube. These cells and tubes were septum stoppered and deoxygenated with a nitrogen purge prior to introduction of the photolysis solution. When the solutions were added to the cells and tubes, care was taken to avoid letting solvent come in contact with the septum because some solvents leached out a UV-absorbing constituent of the septums. Solutions were irradiated directly in the cell. Photolyses were monitored by electronic absorption, infrared, and NMR spectroscopy. Electronic absorption spectra were recorded on a Cary 17 spectrophotometer; infrared spectra were recorded on a Perkin-Elmer 621 instrument; NMR spectra were recorded on a Varian A-60 instrument.

The wavelengths of the lowest energy electronic absorption bands of the tungsten complexes are listed in Table I. The photochemical reactions were performed by irradiating the complexes at wavelengths corresponding to the lowest energy bands.

A 200-W high-pressure Hg arc lamp was used for the irradiations. The 366-nm Hg line was isolated with use of a Corning CS 7-83 filter. For broad-band irradiations, Pyrex ($\lambda > 320$ nm), Corning CS 3-74 ($\lambda > 405$ nm), and Corning CS 3-69 ($\lambda > 500$ nm) filters were used. So that heating of the sample would be avoided during the photolysis, a water filter was placed between the lamp and the photolysis cell. In addition, the quartz cells and NMR tubes were thermostated in a beaker of room-temperature water during the irradiations.

Ferrioxalate actinometry was used for the quantum yield determinations at 366 nm.[19] The procedure was modified as suggested by Bowman and Demas.[20] A typical photon flux into the photochemical cell was 1×10^{-7} einstein/min at 366 nm. Quantum yields were measured by following the disappearance of isolated infrared absorption bands of the reactant complex (2022 cm^{-1} for the reactions of $CpW(CO)_3CH_3$ and 1599 cm^{-1} for the conversion of $CpW(CO)_2(PPh_3)(COCH_3)$ into $CpW(CO)_3CH_3$). The absorbance mode of the infrared spectrometer was used for these measurements. The procedure was as follows. The initial absorbance of the photolysis solution was measured at the appropriate wavelength. A known volume of the solution was then syringed into a quartz cell and irradiated for a known period of time. (In general, less than 15% of the starting material was allowed to react.) After irradiation, the solution was transferred by syringe back to the IR cell and the new absorbance measured. From the value of $\Delta A/\Delta t$ thus obtained the quantum yield could be calculated. For a reduction in error in the value of $\Delta A/\Delta t$, several trials were run with each trial having a different irradiation time. The average value of $\Delta A/\Delta t$ was used in the calculation. There was no difficulty in reproducing the value of $\Delta A/\Delta t$ for any of the

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quantum yield measurements with this infrared monitoring technique. For experiments requiring quantum yield measurements as a function of light intensity, wire-gauze screens were placed between the source and sample to attenuate the intensity. The path length of the infrared cell used in the quantum yield determinations above was determined precisely by using the interference fringe method.[21]

Photolyses for mass spectral analysis were performed in special two-arm evacuable cells. $CpW(CO)_3CH_3$ was placed in one side arm, and the solvent was pipetted into the other side arm. The solvent was degassed by four freeze–pump–thaw cycles. After degassing, the solvent was mixed with the $CpW(CO)_3CH_3$. Mass spectra of the gases formed in the irradiations were obtained with a JEOL JMS-07 instrument. Thick-walled quartz cells equipped with Kontes quick-release Teflon valves were used for the irradiations done under CO pressure. Pressures up to 6 atm were obtainable in these cells.

Low-temperature infrared experiments were done with a Specac low-temperature IR apparatus using a cell with NaCl windows. The sample was cooled with use of a dry ice–acetone mixture in the dewar section of the apparatus.

Flash photolysis experiments were performed with use of the 308-nm pulse from an excimer laser (Lambda Physik, Excimer EMG 101) employing XeCl as the lasing medium.

Results

Irradiation of $CpW(CO)_3CH_3$. Room-temperature irradiation ($\lambda = 366$ nm) of $CpW(CO)_3CH_3$ ($\simeq 10^{-2}$ M) in CH_2Cl_2 proceeds according to eq 10. The reaction was monitored by

$$2CpW(CO)_3CH_3 \xrightarrow{366\text{ nm}} Cp_2W_2(CO)_6 + 2CH_4 \qquad (10)$$

infrared spectroscopy which showed the disappearance of the $CpW(CO)_3CH_3$ bands (2022 and 1927 cm^{-1}) and the appearance of bands attributable to $Cp_2W_2(CO)_6$ (1957 and 1908 (sh) cm^{-1}). Reaction 10 also takes place in THF, petroleum ether, chloroform, toluene, benzene, 1,2-dichloroethane, acetone, propanol, isopropyl alcohol, and cyclohexene solutions. Methane was identified as a reaction product by mass spectral analysis of the gaseous products formed in the reaction in benzene, chloroform, and CH_2Cl_2 solutions. When the solvent for reaction 10 is benzene-d_6 or chloroform-d, the only hydrocarbon product is CH_3D. Ethane was not observed as a product of the reaction. The conversion of $CpW(CO)_3CH_3$ to $Cp_2W_2(CO)_6$ described by eq 10 is quantitative within experimental error. The irradiation of a 0.029 M solution of $CpW(CO)_3CH_3$ in cyclohexene was monitored by infrared spectroscopy. The irradiation was stopped when the concentration of $CpW(CO)_3CH_3$ was 0.021 M (corresponding to a change in concentration of 0.008 M or a 28% disappearance of $CpW(CO)_3CH_3$). The concentration of the $Cp_2W_2(CO)_6$ that had formed was 0.0038 M. Thus, $CpW(CO)_3CH_3$ was converted to $Cp_2W_2(CO)_6$ in 95% yield.

Because the product of reaction 10, $Cp_2W_2(CO)_6$, also absorbs at 366 nm (Table I), it is not surprising that secondary photolysis products are observed in some of the solvents. For example, continued irradiation of $CpW(CO)_3CH_3$ in CH_2Cl_2 gives $CpW(CO)_3Cl$; the product was identified by IR measurements ($\nu(C{\equiv}O) = 2052$ and 1960 cm^{-1} in CH_2Cl_2; these values agree closely with those reported earlier[16]). Further irradiation produces a tertiary product, $CpW(CO)_2Cl_3$ (2107 and 2047 cm^{-1}; these values also agree with those reported earlier[23]). In CH_2Cl_2 solution, the final product is $CpW(CO)_2Cl_3$; no other products are formed by further irradiation. In $CHCl_3$ solution, infrared spectral changes occur which are similar to those described above in CH_2Cl_2 solution. However, the photoreaction does not stop with the formation of $CpW(CO)_2Cl_3$. Irradiation of $CpW(CO)_2Cl_3$ in $CHCl_3$ gives a blue solution ($\lambda_{max} = 650$ and 410 (sh) nm). (Irradiation of concentrated solutions of $CpW(CO)_3CH_3$ produces a green solution; note that solutions of $CpW(CO)_3CH_3$ are yellow.) The infrared spectrum of the blue solution has no absorption bands in the region 2200–1700 cm^{-1}. Irradiation ($\lambda = 366$ nm) of $CpW(CO)_3CH_3$ ($\simeq 10^{-2}$ M) in CCl_4 solution immediately produces a blue or green solution. Upon standing for several minutes, a blue product precipitates from the solution. The blue precipitate is only slightly soluble in CCl_4, but it is readily soluble in $CHCl_3$ and CH_3CN. The electronic spectrum of the blue precipitate has a peak at 670 nm in CCl_4, CH_3CN, and $CHCl_3$ solutions. The infrared spectrum of the blue product in CH_3CN has no absorption bands in the region 2200–1700 cm^{-1}. The results of the irradiations of $CpW(CO)_3CH_3$ in chlorocarbon solvents are summarized in Scheme I.

Scheme I

$$\begin{gathered}CpW(CO)_3CH_3 \xrightarrow[CH_2Cl_2,\ CHCl_3,\text{ or }CCl_4]{366\text{ nm}} \\ CH_4 + Cp_2W_2(CO)_6 \xrightarrow{366\text{ nm}} CpW(CO)_3Cl \xrightarrow{366\text{ nm}} \\ CpW(CO)_2Cl_3 \xrightarrow[CHCl_3,\ CCl_4]{366\text{ nm}} \text{blue solution}\end{gathered}$$

The quantum yield for disappearance of $CpW(CO)_3CH_3$ (2.3×10^{-2} M) in reaction 10 at 366 nm in CH_2Cl_2 solution is 0.08. This value is independent of light intensity; over a ninefold range of intensities (2.5×10^{-8}, 1.7×10^{-7}, 2.2×10^{-7} einstein/min) the quantum yield remained 0.08. The quantum yield does change when excess CO is present.

Under 1 atm of CO but with otherwise conditions identical with the measurements under N_2, reaction 10 is inhibited and the disappearance quantum yield drops to 0.04. Triphenylphosphine will also inhibit the coupling reaction. Irradiation of $CpW(CO)_3CH_3$ ($\simeq 10^{-2}$ M) in a CH_2Cl_2 solution containing PPh_3 (5×10^{-2} M) produces $CpW(CO)_2(PPh_3)CH_3$ as a major product (1927 and 1842 cm^{-1}). Only small amounts of $Cp_2W_2(CO)_6$ and $CpW(CO)_3Cl$ formed as indicated by infrared spectroscopy. Prolonged irradiation of the solution caused the $CpW(CO)_2(PPh_3)CH_3$ to disappear, and new bands appeared at 1892 and 1777 cm^{-1}. These latter bands are assigned to $CpW(CO)_3^-$ by comparison to reported values.[25] Similar results are obtained in THF solution.

The substitution reaction of $CpW(CO)_3CH_3$ by PPh_3 in THF was not initiated by the 500-nm photolysis of $Cp_2W_2(CO)_6$. A solution containing $CpW(CO)_3CH_3$ (10^{-2} M), PPh_3 (10^{-2} M) and $Cp_2W_2(CO)_6$ (10^{-4} M) was irradiated with light of wavelengths greater than 500 nm. The reaction was monitored by infrared spectroscopy. The infrared spectrum of the solution remained unchanged even after 10 min of irradiation. Similar experiments using $Cp_2Mo_2(CO)_6$ or $Cp_2Fe_2(CO)_4$ instead of $Cp_2W_2(CO)_6$ also did not initiate substitution of $CpW(CO)_3CH_3$ by PPh_3.

In addition to PPh_3, $CpW(CO)_3CH_3$ also reacts with $AsPh_3$ and CH_3CN to form substitution products according to eq 9. Infrared spectroscopic monitoring of reaction 9 (L = $AsPh_3$, CH_3CN) clearly shows the disappearance of the $CpW(CO)_3CH_3$ bands and the appearance of the product absorption bands (Table II). Regardless of L in reaction 9, prolonged photolysis also produced small amounts of $CpW(CO)_3^-$ (1892 and 1777 cm^{-1} in CH_2Cl_2 and CH_3CN). Although the complexes $CpW(CO)_2(AsPh_3)CH_3$ and $CpW(CO)_2(CH_3CN)CH_3$ have not been reported before, their identity was established by the similarity of their infrared spectra to the infrared spectrum of $CpW(CO)_2(PPh_3)CH_3$ and other known $CpW(CO)_3CH_3$-substituted complexes.[26] In addition to the

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Table II. Observed Infrared Absorption Bands of the Tungsten Complexes in the CO Stretching Region[a,b]

complex	ν(C≡O), cm^{-1}	solvent	ref
$CpW(CO)_3CH_3$	2022 (s) (3200), 1918 (s)	CH_2Cl_2	14
$Cp_2W_2(CO)_6$	1957, 1912	CH_2Cl_2	22
$CpW(CO)_3Cl$	2052 (m), 1960 (s), 1950 (sh)	CH_2Cl_2	
$CpW(CO)_3Cl$	2052 (3000), 1969 (5300), 1950 (2450)	CCl_4	22
$CpW(CO)_2Cl_3$	2107 (m), 2047 (s)	CCl_4	23
$CpW(CO)_2Cl_3$	2107 (900), 2045 (1400)	acetone	
$CpW(CO)_3^-$	1892 (w), 1777 (s)	CH_2Cl_2, CH_3CN	25
$CpW(CO)_2$-$(PPh_3)CH_3$	1927 (s), 1842 (s)	CH_2Cl_2	24
$CpW(CO)_2$-$(AsPh_3)CH_3$	1923 (s), 1839 (s)	CH_2Cl_2	
$CpW(CO)_2$-$(CH_3CN)CH_3$	1917 (s), 1822 (s)	CH_3CN	
$CpW(CO)_2$-$(THF)CH_3$	1912 (s), 1802 (s)	THF (−78 °C)	
$CpW(CO)_2$-$(PPh_3)(COCH_3)$	1932 (920), 1849 (2600), 1599 (550)	CH_2Cl_2	18
$CpW(CO)_2$-$(PPh_3)(COCH_3)$	1932 (m), 1849 (s), 1605 (m)	THF	18

[a] s = strong, m = medium, w = weak, sh = shoulder. [b] Numbers in parentheses are extinction coefficients (cm^{-1} M^{-1}).

characteristic spectrum in the carbonyl region, $CpW(CO)_2(CH_3CN)CH_3$ also has a weak absorption at 2277 cm^{-1}, attributable to coordinated CH_3CN.[27] Attempts to isolate $CpW(CO)_2(CH_3CN)CH_3$ were not successful. In the presence of CO, $CpW(CO)_2(CH_3CN)CH_3$ reacts to form $CpW(CO)_3CH_3$; this back-reaction explains why the quantum yield for substitution by CH_3CN is slightly lower than for substitution by PPh_3 or $AsPh_3$ (see below). The photoreaction of $CpW(CO)_3CH_3$ with CH_3CN-d_3 was also monitored by NMR spectroscopy, and these data are consistent with the formulation of the product as $CpW(CO)_2(CD_3CN)CH_3$. Irradiation caused a decrease in intensity of the $CpW(CO)_3CH_3$ signals (δ 5.47 and 0.40) and two new signals (δ 5.31 and 0.17) appeared and increased in intensity with increasing irradiation time.

The disappearance quantum yields of $CpW(CO)_3CH_3$ in reaction 9 (366 nm, CH_2Cl_2 solution, room temperature) with different ligands are as follows: PPh_3, 0.40; $AsPh_3$, 0.40; CH_3CN (neat), 0.37. The quantum yield for the reaction of $CpW(CO)_3CH_3$ with PPh_3 is independent of the concentration of PPh_3. The value remains 0.40 for 1:1, 3:1, 10:1, and 15:1 molar ratios of PPh_3 to $CpW(CO)_3CH_3$ at a constant concentration of $CpW(CO)_3CH_3$ (2.3×10^{-2} M).

Room-temperature irradiation (366 nm) of $CpW(CO)_3CH_3$ in THF proceeds as in reaction 10. The reaction in THF is inhibited by excess CO. Qualitatively, it was observed that, for equal conversions of $CpW(CO)_3CH_3$ to $Cp_2W_2(CO)_6$, the reaction takes about twice as long under an atmosphere of CO as under an atmosphere of nitrogen. If the irradiation in THF is carried out at −78 °C, then $Cp_2W_2(CO)_6$ does not form. Rather, a new product appears which has infrared absorptions at 1912 and 1802 cm^{-1}. Comparison to the spectra of the $CpW(CO)_2(L)CH_3$ complexes (Table II) suggests that this product is $CpW(CO)_2(THF)CH_3$. This product is stable as long as the solution is kept at −78 °C. Upon warming the solution to room temperature, the absorption bands at 1912 and 1802 cm^{-1} disappear and bands appear at 2017, 1954, and 1920 cm^{-1}; i.e., $CpW(CO)_2(THF)CH_3$ decomposes to $Cp_2W_2(CO)_6$ and $CpW(CO)_3CH_3$ upon warming. Addition of PPh_3 to a solution of $CpW(CO)_2(THF)CH_3$ at −78 °C followed by warming to room temperature in the dark gives $CpW(CO)_2(PPh_3)CH_3$ (1927 and 1849 cm^{-1} in THF) and small amounts of $CpW(CO)_3^-$ (1892 and 1777 cm^{-1} in THF).

In none of the reactions of $CpW(CO)_3CH_3$ with donor ligands were bands attributable to an acetyl complex (1600–1700 cm^{-1})[18,28] observed in the infrared spectrum. Experiments designed to favor the photochemical formation of an acetyl complex also did not produce an acetyl complex. Flash photolysis (308 nm) of a THF solution of $CpW(CO)_3CH_3$ (2.7×10^{-2} M) and PPh_3 (10^{-2} M) in an infrared cell at room temperature gave only $CpW(CO)_2(PPh_3)CH_3$. The infrared spectrum of the flashed solution contained bands attributable to this product and $CpW(CO)_3CH_3$; no bands which could be assigned to an acetyl absorption were observed. In another experiment, irradiation ($\lambda > 320$ nm) for 30 min of a THF solution of $CpW(CO)_3CH_3$ ($\simeq 10^{-2}$ M) containing excess PPh_3 (10^{-1} M) under 6 atm of CO yielded only $CpW(CO)_2(PPh_3)CH_3$ and $Cp_2W_2(CO)_6$. Once again, a careful examination of the CO stretching region revealed no acetyl absorptions.[29]

Irradiation of $CpW(CO)_2(PPh_3)(COCH_3)$. The room-temperature irradiation (366 nm) of $CpW(CO)_2(PPh_3)(COCH_3)$ in THF solution was monitored by infrared spectroscopy. The infrared spectra showed that short irradiation times produced $CpW(CO)_3CH_3$ (eq 11). Continued irradiation of the solution

$$CpW(CO)_2(PPh_3)(COCH_3) \xrightarrow{366\ \mathrm{nm}} CpW(CO)_3CH_3 + PPh_3 \quad (11)$$

removes all of the $CpW(CO)_2(PPh_3)(COCH_3)$ and $CpW(CO)_2(PPh_3)CH_3$ is formed. Infrared spectral changes similar to those in THF are observed in the irradiation (366 nm) of $CpW(CO)_2(PPh_3)(COCH_3)$ in CH_2Cl_2 solution. The disappearance quantum yield (366 nm) of $CpW(CO)_2(PPh_3)(COCH_3)$ in reaction 11 in CH_2Cl_2 solution is 0.10.

Irradiation of $CpW(CO)_3Cl$. $CpW(CO)_3Cl$ reacts photochemically ($\lambda > 405$ nm) at room temperature in CCl_4 solution to give $CpW(CO)_2Cl_3$ (eq 12). When the reaction is monitored by infrared spectroscopy, the spectra show the disappearance of the $CpW(CO)_3Cl$ bands at 2052, 1969, and 1950 cm^{-1} and the appearance of the $CpW(CO)_2Cl_3$ bands at 2107 and 2047 cm^{-1}. Similar spectral changes are observed for the irradiation ($\lambda > 405$ nm) of $CpW(CO)_3Cl$ in CH_2Cl_2 and $CHCl_3$. Prolonged irradiation of $CpW(CO)_3Cl$ in CCl_4 or $CHCl_3$ yields a green solution, the infrared spectrum of which has no absorptions in the carbonyl region. The disappearance quantum yield (366 nm) of $CpW(CO_3)Cl$ in CCl_4 is 0.62. The rate of reaction 12 in the three chlorocarbon solvents follows the order $CCl_4 >> CHCl_3 >> CH_2Cl_2$. Spectral changes which take place in seconds in CCl_4 require several hours in CH_2Cl_2. The photochemistry of $CpW(CO)_3Cl$ in chlorocarbon solvents is summarized in Scheme I.

$$CpW(CO)_3Cl \xrightarrow[CCl_4]{\lambda > 405\ \mathrm{nm}} CpW(CO)_2Cl_3 \quad (12)$$

Discussion

The results above show that W–CO bond dissociation is the primary photoprocess of the $CpW(CO)_3CH_3$ complex. This conclusion is consistent with Wrighton's results on the low-temperature photochemistry of the related pentyl complex

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[27] For comparison, coordinated CH_3CN in $W(CO)_5(CH_3CN)$ has a C≡N stretch at 2282 cm^{-1}. See Ross, B. L.; Grasselli, J. G.; Ritchey, W. M.; Kaesz, H. D. *Inorg. Chem.* **1963**, *2*, 1023.

[28] (a) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918. (b) Adams, D. M.; Booth, G. *J. Chem. Soc.* **1962**, 1112.

[29] The acetyl complex $CpW(CO)_2(PPh_3)(COCH_3)$ was reported as a minor product from the photoreaction of $CpW(CO)_3CH_3$ with PPh_3.[4] The acetyl complex[18] does form in the thermal reaction of $CpW(CO)_3CH_3$ with PPh_3, and so the observation of this product in ref 4 may be due to improper thermostating of the photochemical reaction vessel.

$CpW(CO)_3(C_5H_{11})$.[30] Direct evidence for the intermediacy of $CpW(CO)_2CH_3$ in the formation of $Cp_2W_2(CO)_6$ comes from the warm-up experiments on $CpW(CO)_2(THF)CH_3$. A solution of this complex in THF at −78 °C is stable, but upon warming the solution to room temperature, the complex disappears and $Cp_2W_2(CO)_6$ forms (as well as some $CpW(CO)_3CH_3$). The obvious interpretation of these observations is that upon warming, the weak W–THF bond is broken thereby generating $CpW(CO)_2CH_2$ which reacts to form the coupled product. (All of the reactants which might be necessary for further reaction of $CpW(CO)_2CH_3$ are still in the cell; unreacted $CpW(CO)_3CH_3$ is present as well as the CO generated during the photolysis. The sealed cell is gastight.)

The question remains: what two species are coupled to form the binuclear product? Because the disappearance quantum yield for reaction 10 is independent of the light intensity, the binuclear product is probably not formed by the coupling of two photochemically generated intermediates.[31] For this reason, the pathway in eq 5–8 is not suggested. The observation that $Cp_2W_2(CO)_6$ forms before $CpW(CO)_3Cl$ in chlorocarbon solvents is also not consistent with this mechanism. A likely pathway for the coupling involves the reaction of $CpW(CO)_2CH_3$ with an unreacted molecule of $CpW(CO)_3CH_3$ (eq 13). Addition of CO to $Cp_2W_2(CO)_5$ would

$$CpW(CO)_2CH_3 + CpW(CO)_3CH_3 \rightarrow Cp_2W_2(CO)_5 + 2CH_3 \qquad (13)$$

give the product (eq 14). This mechanism is consistent with

$$Cp_2W_2(CO)_5 + CO \rightarrow Cp_2W_2(CO)_6 \qquad (14)$$

the intensity-independent quantum yield and with the observation that $CpW(CO)_3$ is not formed. We propose that one of the sources of the extra hydrogen atom for the CH_3 radical to form CH_4 is the solvent. Mass spectral analyses showed that substantial amounts of CH_3D are formed during the photolysis of $CpW(CO)_3CH_3$ in benzene-d_6 and chloroform-d solvents. Control experiments using NMR showed that the hydrogen atoms on the cyclopentadienyl rings do not exchange with the deuterium atoms in the deuterated solvents on the time scale of the photochemical experiments. Hence, the cyclopentadienyl ring is not a major source of the deuterium in CH_3D.

The reaction of a coordinatively unsaturated 16-electron complex with a coordinatively saturated molecule as proposed in eq 13 is not uncommon for metal carbonyl complexes. The photochemical reaction of $Fe(CO)_5$ to form $Fe_2(CO)_9$ occurs by reaction of $Fe(CO)_4$ with an $Fe(CO)_5$ molecule.[32] A similar mechanism was shown for the photochemical formation of $Cp_2Co_2(CO)_3$ from $CpCo(CO)_2$.[33] In addition, Norton has proposed binuclear elimination mechanisms for the thermal decompositions of $H_2Os(CO)_4$[12b] and $HOs(CO)_4CH_3$.[12c] For both complexes, a key step in the decomposition is the reaction of a coordinatively unsaturated complex with a coordinatively saturated one.

Registry No. $CpW(CO)_3CH_3$, 12082-27-8; $Cp_2W_2(CO)_6$, 12091-65-5; $CpW(CO)_3Cl$, 12128-24-4; $CpW(CO)_2(PPh_3)(COCH_3)$, 53079-50-8; $CpW(CO)_2Cl_3$, 12107-08-3; $CpW(CO)_2(AsPh_3)CH_3$, 77462-49-8; $CpW(CO)_2(CH_3CN)CH_3$, 77462-48-7; $CpW(CO)_2(THF)CH_3$, 77462-47-6; $CpW(CO)_2(PPh_3)CH_3$, 12115-41-2.

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Binuclear Copper(I) Complexes Which Reversibly React with CO. 1. Di-μ-halogeno-bis(2,2′-bipyridine)dicopper(I) and Its Derivatives

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Binuclear copper(I) complexes $[CuXL]_2$ and mononuclear copper(I) complexes $[CuL_2]X$ (X = Cl, Br, and I; L = 2,2′-bipyridine and 1,10-phenanthroline) have been synthesized in acetone and ethanol, respectively. The complexes $[CuXL]_2$ react with CO reversibly to give crystalline carbonyl adducts, which are stable at low temperature. The isolated crystalline product exhibits $\nu_{CO} = 2066\ cm^{-1}$, which is consistent with the carbonyl species in acetone solution. The carbonyl adducts are found to be five-coordinate complexes having bridged halogen atoms with the stoichiometry of 1 CO/2 Cu. The affinity of $[CuXL]_2$ for CO is influenced by the bridged halogen and solvent used. The formation constants of the carbonyl adducts increase in the order Cl < Br < I, and solvents with lower dielectric constants favor the formation of the adducts. The mononuclear complexes $[CuL_2]X$ show no affinity for CO. The flexibility of the binuclear complex, associated with the bridged halogen atoms, is a significant factor governing the reactivity toward CO.

Introduction

Carbonyl complexes of copper are confined to the copper(I) oxidation state. Recent activity in this area has been motivated by a desire to elucidate the relationship between structure and reactivity toward carbon monoxide with respect to Cu(I) complexes. Hemocyanin,[1] a copper-containing respiratory protein, also binds CO reversibly.[2] Studies on the carbonyl complex may help to explore the ligand environment in the hemocyanin active site. There are a few stable (i.e., isolable under ambient condition) copper(I) carbonyl complexes in a variety of carbonyl complexes. However, the characterization has not yet been ascertained. Recent synthetic challenges provide us with some thermally stable carbonyl complexes which are characterized by X-ray structural analysis,[3-5,8] in-

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