atom, implies that the precursor(s) of this compound had the capacity to reduce CO.[48] However, the decanuclear cluster is highly stable, and under catalytic reaction conditions it might be expected to remain coordinatively saturated and hence inactive. Therefore, of the compounds observed on the used catalyst, the tetranuclear cluster seems to be a plausible candidate for involvement in a catalytic cycle,[49] and the formation of the carbido osmium cluster may be associated with the deactivation of the catalyst.[50]

Several investigators have reported the formation of small zerovalent metal particles of Fe, Ru, and Os following thermal treatment of the respective surface-bound carbonyl complexes in vacuum or under inert atmospheres.[24,42,51] Experiments with **2** adsorbed on magnesia pretreated at 800 °C indicate that a similar agglomeration to give metallic osmium occurs upon heating the sample to 150 °C under vacuum; a blackening of the sample was observed. Since there was no evidence of metallic osmium on the used magnesia-supported CO hydrogenation catalyst, we infer that the presence of stabilizing CO was critical in preventing destruction of the molecular organometallics that occurs readily on less basic surfaces, especially in the absence of CO.

Conclusions

Adsorption of **1** on the basic surface of magnesia results in the formation of surface-bound **2**, regardless of the degree of hydration of the surface. The major role of surface water or other adsorbed lone-pair donors is to moderate the degree of interaction achieved between a carbonyl ligand of the mononuclear anion and a surface Mg^{2+} ion. Under conditions of catalytic reduction of CO by H_2, the mononuclear anion initially present undergoes condensation, yielding the stable cluster anions **3** and **4**. The formation of these molecular metal clusters on the basic magnesia surface parallels the homogeneous chemistry of osmium cluster synthesis. The tetranuclear cluster may be the precursor of the catalytically active species; the formation of the carbido osmium cluster may be associated with the catalyst deactivation.

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Photochemical Reduction of $CpW(CO)_3CH_3$ ($Cp = \eta^5\text{-}C_5H_5$) to $CpW(CO)_3^-$; An Isolobal Analogy to the Disproportionation of $Cp_2Mo_2(CO)_6$

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Abstract: Irradiation ($\lambda > 380$ nm) of $CpW(CO)_3Me$ in inert solvents in the presence of PPh_3 gives $[PPh_3CH_3^+][CpW(CO)_3^-]$ as well as the substitution product $CpW(CO)_2(PPh_3)Me$ ($\phi_{\text{disappearance } CpW(CO)_3Me} = 0.45 \pm 0.005$, $\phi_{\text{appearance } CpW(CO)_3^-} = 0.04 \pm 0.01$). The mechanism of $CpW(CO)_3^-$ formation was studied. Experiments suggest that $CpW(CO)_2(PPh_3)Me$ may be an intermediate in the reaction but direct reductive elimination of PPh_3Me^+ from this species or from $CpW(CO)(PPh_3)_2Me$ was ruled out. Experiments using $PTol_3$ demonstrated that PAr_3Me^+ (Ar = aryl) is formed from exogenous, not coordinated, phosphine. The mechanism proposed for the reduction of $CpW(CO)_3Me$ involves the intermediate formation of phosphoranyl radicals, $\cdot PPh_3Me$, formed by addition of Me radicals (from W–CH_3 homolysis) to PPh_3. Phosphoranyl reduction of a variety of metal species which are present in solution is shown to lead to $CpW(CO)_3^-$. The proposed mechanism is isolobal with a mechanism we proposed for the photochemical disproportionation of metal–metal bonded dimers (e.g., $Cp_2Mo_2(CO)_6$) involving 19-valence-electron intermediates.

Irradiation of the complex $CpW(CO)_3Me$ ($Cp = \eta^5\text{-}C_5H_5$) in the presence of various ligands, L, is well-known to give the substitution products $CpW(CO)_2(L)Me$.[1-4] Some time ago,

$$CpW(CO)_3Me + L \xrightarrow{h\nu} CpW(CO)_2(L)Me + CO \quad (1)$$

however, we reported[4] that irradiation of $CpW(CO)_3Me$ in the presence of PPh_3 also leads to the formation of $CpW(CO)_3^-$:

$$CpW(CO)_3Me \xrightarrow[PPh_3]{h\nu} CpW(CO)_3^- \quad (2)$$

(The cation formed in reaction 2 was not identified, but it is not a carbonyl-containing species.)

Our interest in reaction 2 was recently reawakened because the $CpW(CO)_3Me$ complex is isolobal[5] with the $Cp_2M_2(CO)_6$ complexes (M = Mo, W) ($Me \underset{\text{O}}{\longleftrightarrow} CpM(CO)_3$). We have been studying[6] the photochemical disproportionation reactions of the

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Table I

complex	IR, ϵ (M^{-1} cm^{-1})	^1H NMR, δ (J(H,P), Hz)	
		Cp	Me
$CpW(CO)_3Me$	2016 (3300), 1918 (5150)[a]	5.64	0.83
trans-$CpW(CO)_2(PPh_3)Me$	1932, 1848[a,d,e]	4.91 (1.4)	0.46 (2.6)[e,f]
cis-$CpW(CO)_2(PPh_3)Me$	1930, 1849[a,d,e]	5.36	−0.14 (11.8)[f]
trans-$CpW(CO)_2(PTol_3)Me$		4.89 (1.6)	0.43 (2.6)[f]
cis-$CpW(CO)_2(PTol_3)Me$		5.32	−0.19 (11.8)
$PPh_3Me^+CpW(CO)_3^-$	1887 (3200), 1766 (2800)	4.98	3.20 (14.1)
$PTol_3Me^+CpW(CO)_3^-$		4.98	3.07 (14.0)
$PPh_3Me^+I^-$			3.26 (14.2)[c]
$PTol_3Me^+I^-$			3.07 (14.0)[c]
trans-$CpW(CO)(PPh_3)_2Me$	1779 s	4.87 (t, 1.0)	−0.04 (t, 12.6)[h]
$NaCpW(CO)_3$	1894 s, 1790 s, 1740 s[i]		5.07[h]
$NaCpW(CO)_2(PPh_3)$	1787 s, 1688 s[i]		
$CpW(CO)_2(P(OPh)_3)Me$	1949 m, 1874 s[a]		
$CpW(CO)_2(AsPh_3)Me$	1927 s, 1844 m[a]		
$CpW(CO)_2[P(C_6H_{11})_3]Me$	1917 ms, 1831 s[a]		
$CpW(CO)_2(PMe_2Ph)Me$	1927 m, 1848 m[a]		
$CpW(CO)_2(PBu_3)Me$	1922 m, 1835 s[a]	5.06 (1.4)	2.04 (2.8)[c,j]
$PBu_3Me^+I^-$			2.45[c,k]
$[CpW(CO)_2(PBu_3)_2][CpW(CO)_3]$	1942 m, 1886 s, 1860 s, 1766 s[a]		
$CpW(CO)_3H$	2021 s, 1926 vs[a]		
$CpW(CO)_2(PPh_3)H$	1933 s, 1854 s[a]		
$Cp_2W_2(CO)_6$	2012 w, 1952 (6000), 1905 (6000)[a]	5.69	5.53[l]
$Cp_2W_2(CO)_5(PPh_3)$	1960 mw, 1881 m[a]		

[a] C_6H_6. [b] Pentane. [c] Acetone-d_6. [d] Due to overlap of spectra of cis and trans isomers, exact IR frequencies and extinction coefficients were not determined. [e] See ref 11. [f] Acetone-d_6. [g] Cyclohexane. [h] Toluene-d_6. [i] THF. [j] Trans isomer. [k] Multiplet includes P–CH_2 protons. [l] C_6D_6.

latter complexes (eq 3) and wondered if the mechanism for $CpW(CO)_3^-$ formation in reaction 2 was related to that in the disproportionation process. Specifically, we wondered if the

$$Cp_2Mo_2(CO)_6 \xrightarrow[L]{h\nu} CpMo(CO)_3^- + CpMo(CO)_3L^+ \text{ (or } CpMo(CO)_2L_2^+\text{)} \quad (3)$$

mechanisms of reactions 2 and 3 are isolobal. In this paper we present the results of our mechanistic study of reaction 2.

Experimental Section

Materials and Supplies. $CpW(CO)_3Me$,[7] $Cp_2W_2(CO)_6$,[8] $CpW(CO)_3Cl$,[9] $[PPh_3Me]I$, $[PTol_3Me]I$ (Tol = p-$C_6H_4CH_3$), and $[PBu_3Me]I$[10] were prepared by literature methods. $CpW(CO)_2(PPh_3)Me$ was prepared by the method of Barnett and Treichel[1] as modified by Wojcicki and Severson.[3] All solvents used in this study were stored under nitrogen or argon. Benzene was distilled from $LiAlH_4$ and acetone from CaH_2. The following chemicals were obtained commercially and used as received: deuterated solvents (stored over Linde 4A molecular sieves except acetone-d_6 which was removed from the sieves after being stirred for 1 day), tetrahydrofuran (Aldrich "Gold Label"), PPh_3, PBu_3, $P(OEt)_3$, $P(OPh)_3$, NEt_3, 1,2-bis(diphenylphosphino)ethane (diphos), 9,10-dihydroanthracene, 1,4-cyclohexadiene, α-methylstyrene, 1,1-diphenylethylene, 2,3-dimethyl-1-butene, iodomethane, iodobenzene (Aldrich), tricyclohexylphosphine, $AsPh_3$ (Pressure Chemicals), $PTol_3$, PMe_2Ph (Strem Chemicals), and carbon monoxide (99.99%) (Matheson).

Instruments and Techniques. Unless stated otherwise all IR-monitored experiments requiring irradiation of a reaction mixture and no further steps were performed as follows. The reaction solution was prepared and thoroughly degassed with a purge of argon. If required, CO was subsequently bubbled through the solution. An infrared cell was then filled via syringe; the cell was irradiated and spectra were taken at given time intervals in the CO-stretching region, 2200–1500 cm^{-1}, until virtually all of the $CpW(CO)_3Me$ and $CpW(CO)_2(L)Me$ had disappeared. (The width of the spectral domain ensured that any formation of metal acetyls would not be missed; none was ever observed.) The light source was a 200-W Oriel high-pressure mercury arc lamp and a Corning CS 3-75 filter was used ($\lambda > 380$ nm). For irradiation of $Cp_2W_2(CO)_6$ at $\lambda > 560$ nm, a Corning CS 3-66 filter was used. Experiments that were specifically designed as controls were always performed on the same day as the experiments to which they were compared thus minimizing any differences in the irradiation intensity of the lamp as well as solvent impurities, etc. Unless stated otherwise, experiments involving irradiation of $CpW(CO)_3Me$ or $CpW(CO)_2(PAr_3)Me$ (Ar = aryl) in the presence of PAr_3 typically resulted in the complete disappearance of $CpW(CO)_2(PAr_3)Me$ over a period of 10–20 min; times did not greatly vary with conditions or from day to day. Thus, insofar as the disappearance quantum yeild appears relatively constant, the yield of product is a good, albeit crude, indication of the relative quantum yield for product appearance. All infrared spectra were obtained with a Perkin-Elmer PE983 spectrophotometer. Experiments monitored by ^1H NMR involved irradiation either in a screwcap sealed NMR tube (Wilmad) or in a septum covered test tube, with the latter under a positive pressure of argon or CO. Irradiation times varied significantly for such experiments, presumably due to the irreproducibility of focusing the lamp on NMR tubes. NMR spectra were obtained with a Varian XL-200 FT spectrometer.

Generation and Reactions of $CpW(CO)_2PPh_3^-$. $CpW(CO)_2(PPh_3)Cl$ was efficiently generated by 5 h of irradiation ($\lambda > 380$ nm) of $CpW(CO)_3Cl$ (0.147 g, 0.4 mmol) and PPh_3 (0.115 g, 0.44 mmol) in tetrahydrofuran (10 mL); a 90% yield of substitution product was obtained as monitored by IR. Under an argon atmosphere, a 1% Na amalgam was added to the solution (0.23 g, 10 mg-atom Na). Stirring the solution for 1 h resulted in the complete disappearance of $CpW(CO)_2(PPh_3)Cl$ and the unreacted $CpW(CO)_3Cl$, and the appearance of $CpW(CO)_2(PPh_3)^-$, $CpW(CO)_3^-$, and significant amounts of $CpW(CO)_2(PPh_3)H$ (Table I). The latter presumably formed by protonation of the corresponding anion. When CO was bubbled through the reaction solution for 5 min in the dark, conversion of about 5% of $CpW(CO)_2PPh_3^-$ to $CpW(CO)_3^-$ was observed. Photolytic ($\lambda > 380$ nm) substitution of the $CpW(CO)_2PPh_3^-$ complex was highly efficient and at normal light intensities seemed to be limited by the rate of diffusion of CO into solution. Thus, irradiation ($\lambda > 380$ nm) through a neutral density filter (OD = 1.0) for 13 min resulted in about 95% loss of $CpW(CO)_2PPh_3^-$ and concomitant formation of $CpW(CO)_3^-$ and lesser amounts of $CpW(CO)_2(PPh_3)H$. To 10 mL of a 15 mM solution of $CpW(CO)_2PPh_3^-$ prepared as above (also containing small amounts of $CpW(CO)_3^-$ and $CpW(CO)_2(PPh_3)H$), $CpW(CO)_2(PPh_3)Me$ (0.23 g, 40 mM) was added under argon. Irradiation of the solution in an infrared cell for 40 s resulted in about 70% substitution of CO for PPh_3 in the anion and a loss of roughly 10 mM $CpW(CO)_2(PPh_3)Me$ (eq 6). A total of 100 s of irradiation resulted in the reaction going to completion, with no detectable $CpW(CO)_2PPh_3^-$ remaining.

Detection of Methane. 9,10-Dihydroanthracene (5.0 g, 27.7 mmol), PPh_3 (2.62 g, 10 mmol), and $CpW(CO)_3Me$ (.174 g, 0.50 mmol) were dissolved in benzene (20 mL) in a Schlenk flask. The solution was

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(7) See ref 4, Experimental Section.

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Table II. Yields of $PPh_3Me^+CpW(CO)_3^-$ from Reaction 4 as a Function of $[PPh_3]^a$ upon Irradiation ($\lambda > 380$ nm) in Benzene

$[PPh_3]$, M	yield, $\%^b$ (± 0.10 yield)
0.05	15
0.15	30
0.40	44
0.75	59^c
2.00	71^c

[a] $[CpW(CO)_3Me] = 20$ mM in benzene. [b] Yields were determined by IR, monitoring primarily the 1766-cm^{-1} peak of $CpW(CO)_3^-$. [c] To allow for the effect of high $[PPh_3]$ on peak width and extinction coefficient, yields were determined by cut-and-weigh integration of the 1766-cm^{-1} peak.

degassed and then irradiated for 14 h as a closed system. A vacuum was drawn on a gas-phase IR cell (path length, 10 cm; volume, 96 cm^3) that was connected to the flask, and a stopcock was then slowly opened, allowing the gaseous products of the reaction to enter the IR cell. A comparison of the resultant spectrum with one obtained from the addition of 5.0 mL of commerical methane indicated that 5.5 mL (0.225 mmol) of methane had been trapped. IR analysis of the solution revealed $CpW(CO)_2(PPh_3)H$ and small amounts of $CpW(CO)_2(PPh_3)Me$ as the only remaining carbonyl-containing substances.

Results and Discussion

Electronic Spectrum. The electronic spectrum of the yellow $CpW(CO)_3Me$ complex has been previously discussed.[3] The lowest energy absorption band has a maximum at 313 nm and there is a shoulder at 350 nm. All of the photochemistry described in this paper was initiated by irradiating into this shoulder ($\lambda >$ 380 nm).

Products and Stoichiometry. Irradiation ($\lambda > 380$ nm) of a solution of $CpW(CO)_3Me$ and triphenylphosphine in benzene, acetone, or cyclohexane primarily results in substitution of CO to yield $CpW(CO)_2(PPh_3)Me$ as detected by infrared spectroscopy (Table I). ^1H NMR reveals the $CpW(CO)_2(PPh_3)Me$ to be a mixture of cis and trans isomers[2,11] (Table I). Continued irradiation of the reaction mixture results in the disappearance of the $CpW(CO)_2(PPh_3)Me$ and the formation of $CpW(CO)_3^-$ as shown by IR (Table I). When the reaction is carried out in C_6D_6, toluene-d_8, acetone-d_6, or cyclohexane-d_{12}, integrated NMR spectra reveal the presence of 1 mol of PPh_3Me^+ per mol of $CpW(CO)_3^-$ (Table I). Thus, the overall reaction giving ionic products can be expressed by eq 4. The initial quantum yield

$$CpW(CO)_3Me + PPh_3 \xrightarrow{h\nu} CpW(CO)_3^- + PPh_3Me^+ \quad (4)$$

(50 min of irradiation, $\lambda = 405$ nm, 10% disappearance) for the disappearance of $CpW(CO)_3Me$ in a benzene solution of $CpW(CO)_3Me$ (20 mM) and PPh_3 (0.75 M) is $0.45 \pm .05$. The major product is $CpW(CO)_2(PPh_3)Me$. $CpW(CO)_3^-$ forms with a quantum yield of 0.04 ± 0.01. The final yield of $[PPh_3Me][CpW(CO)_3]$ is very dependent upon the initial concentration of PPh_3 (see Table II). Remaining metal-carbonyl products from prolonged irradiation include $[CpW(CO)_3]_2$, $CpW(CO)_3H$, $Cp_2W_2(CO)_5(PPh_3)$, and $CpW(CO)_2(PPh_3)H$ (Table I).

In an attempt to generalize reaction 1, $CpW(CO)_3Me$ (15 mM) was irradiated in the presence of a variety of ligands, L, to see if $CpW(CO)_3^-$ and LMe^+ could form. (Note that irradiation of $CpW(CO)_3Me$ in the absence of ligand is known to afford $Cp_2W_2(CO)_6$;[2-4] an important primary photoprocess of this reaction has been shown to be metal–carbonyl bond dissociation.[3,4]) In the presence of $P(OEt)_3$ (0.15 M) irradiation of $CpW(CO)_3Me$ afforded $CpW(CO)_2(P(OEt)_3)Me$ followed by a much slower second substitution and eventual decomposition. Irradiation with $P(OPh)_3$ (0.15 M) yielded some $CpW(CO)_2(P(OPh)_3)Me$ and rapid decomposition. Tricyclohexylphosphine (0.15 M) and $AsPh_3$ (0.15 M) cleanly substituted to give the respective $CpW(CO)_2LMe$ followed only by slow decomposition. The photoreactivity of $CpW(CO)_3Me$ was not significantly affected by the presence of $N(C_2H_5)_3$ (0.15 M), i.e., $Cp_2W_2(CO)_6$ formed cleanly.[2-4] The reactions of $CpW(CO)_3CH_3$ with other ligands are discussed in the Supplementary Material.

Conclusions Derived from Tests for Alternative Mechanisms. As we discuss below, the mechanism of reaction 4 is indeed isolobal to the mechanism of the dimer disproportionation reactions and the key intermediate is a phosphoranyl radical, PPh_3Me. In order to arrive at this conclusion, it was important to eliminate numerous other reasonable reaction pathways. For the sake of brevity, the complete details of how we eliminated from consideration these alternative pathways and how we established the reactivity of several proposed intermediates are not presented in the discussion below; what follows are simply the conclusions of these studies. Following each conclusion is a brief statement outlining the key experiments that support the conclusion. A complete discussion of each conclusion is found in the Supplementary Material.

(1) Reaction 4 can, but need not necessarily, proceed via the intermediate $CpW(CO)_2PPh_3Me$. Irradiation of this complex yields the ionic products of reaction 4 (although in smaller yields).[12]

(2) $CpW(CO)_2Me$ is not an intermediate in reaction 4. The intermediacy of this species (formed by the photolysis of $CpW(CO)_3Me$ or $CpW(CO)_2(PPh_3)Me$) is not consistent with the increase in efficiency of reaction 4 vs. reaction 5 as the PPh_3 concentration increases (Table II).

$$CpW(CO)_2Me + PPh_3 \rightarrow CpW(CO)_2(PPh_3)Me \quad (5)$$

(3) $CpW(CO)_2PPh_3^-$ may be a primary product in reaction 4. Under a CO atmosphere, $CpW(CO)_2PPh_3^-$ is photochemically converted to $CpW(CO)_3^-$ with remarkable efficiency. It was also established that $CpW(CO)_2(PPh_3)Me$ can act as the CO source in converting $CpW(CO)_2PPh_3^-$ to $CpW(CO)_3^-$.[13]

$$CpW(CO)_2PPh_3^- \xrightarrow[h\nu]{\text{CO or } CpW(CO)_2(PPh_3)Me} CpW(CO)_3^- \quad (6)$$

(4) The phosphonium ion forms from exogenous phosphine. Labeling experiments using $P(Tol)_3$ and PPh_3 showed that eq 4 is more properly written as eq 7.

$$CpW(CO)_2(L)Me + PAr^*_3 \xrightarrow{h\nu} CpW(CO)_3^- + PAr^*_3Me^+ \quad (7)$$

$$(L = PAr_3 \text{ or } CO;\ Ar = \text{aryl})$$

(5) Reductive elimination of PPh_3Me^+ from $CpW(CO)_2(PPh_3)Me$ is not occurring. Irradiation of $CpW(CO)_2(PPh_3)Me$ under an atmosphere of CO in the absence of free PPh_3 did not result in the formation of either PPh_3Me^+ or $CpW(CO)_3^-$. This pathway is also inconsistent with the labeling experiments mentioned above.

(6) Nucleophilic attack of PR_3 on CH_3 in $CpW(CO)_2(L)CH_3$ ($L = CO, PPh_3$) is not occurring. The inability of phosphines more nucleophilic than PPh_3 to react according to eq 4 rules out this pathway.

The Radical Electron-Transfer Mechanism. In the absence of ligand, irradiation of $CpW(CO)_3Me$ affords $Cp_2W_2(CO)_6$.[2-4] The

$$2CpW(CO)_3Me \rightarrow Cp_2W_2(CO)_6 + 2Me \quad (8)$$

quantum yield for this reaction is significantly lowered by 1 atm of CO and it has therefore been concluded that a primary photoprocess for this reaction is metal–carbonyl photodissociation.[3]

$$CpW(CO)_3Me \xrightarrow{h\nu} CO + CpW(CO)_2Me \quad (9)$$

However, as the quantum yield can only be partially suppressed by CO,[14] another pathway involving a primary photoprocess other

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(11) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860.

(12) The yield of ionic products from $CpW(CO)_2(PPh_3)Me$ is about 50% of that from $CpW(CO)_3Me$.

(13) Leventis and Wagner have also demonstrated that coordinatively unsaturated molecules will abstract CO from coordinatively saturated complexes. They found that $W(CO)_5$ reacts with $W(CO)_5AP$ (AP = 4-acylpyridine) to yield $W(CO)_6$ and $W(CO)_4AP$. Leventis, N.; Wagner, P. J. *J. Am. Chem. Soc.*, submitted for publication.

than metal–carbonyl dissociation must be operative. (Complete details are found in ref 14.) The most straightforward alternative primary photoprocess is homolytic cleavage of the metal–methyl bond. Direct evidence for the formation of methyl radicals formed via this pathway comes from ESR spin trapping experiments. Irradiation of a solution of $CpW(CO)_3Me$ and the spin trap phenyl-*tert*-butylnitrone (PBN) under an atmosphere of CO in the cavity of an ESR spectrometer results in the observation of the ESR spectrum of the adduct of PBN and methyl radical ($a_N = 15$ G, $a_H = 3.5$ G).[15] It might be argued that the methyl radicals thus formed come from the $CpW(CO)_2Me$ species as described in eq 10, but the following results show that this is not the case. Under either Ar or CO in the presence of 50 mM PPh_3,

$$CpW(CO)_2CH_3 \xrightarrow{-CH_3} CpW(CO)_2 \xrightarrow{+CO} CpW(CO)_3 \rightarrow {}^1/_2Cp_2W_2(CO)_6 \quad (10)$$

irradiation of an otherwise identical solution gives an identical ESR signal of essentially the same intensity. The presence of PPh_3 or CO would significantly shorten the lifetime of the unsaturated species $CpW(CO)_2Me$, and if this intermediate were the source of the methyl radicals their concentration would decrease. Because no decrease was observed, we conclude that reactions 9 and 10 cannot be the only photochemical pathway which produces methyl radical. Note that the presence of very high concentrations of PPh_3 does result in a significant decrease in the intensity of the ESR signal. Thus, with $[PPh_3] = 0.75$ M (under either an Ar or CO atmosphere), the intensity of the signal is approximately one fourth of that with $[PPh_3] = 50$ mM. (The rate of growth of the ESR signal is reduced proportionately immediately upon the onset of irradiation; thus this effect is not simply due to photochemical loss of the starting material caused by PPh_3.) The rate of decay of the signal in the dark (on the order of minutes) is unaffected by the presence of the phosphine and thus the diminution of the signal is not due to reaction of PPh_3 with the methyl-PBN adduct. The most reasonable explanation for these observations is that $CpW(CO)_3Me$ undergoes homolytic photodissociation of the metal–methyl bond and that at high concentrations PPh_3 reacts to a significant extent with the resultant methyl radicals. Similar results were obtained when $CpW(CO)_2(PPh_3)Me$ was irradiated in place of $CpW(CO)_3Me$. A more intense signal was obtained with the substituted species. This does not necessarily indicate increased photolability of the metal–methyl bond upon substitution as the substituted complex absorbs light more strongly at the wavelengths used.

Scheme I

$$CpW(CO)_2(L)Me \xrightarrow{h\nu} CpW(CO)_2L + Me\cdot$$

$$Me\cdot + PAr_3^* \rightleftharpoons \cdot PAr_3^*Me$$

$$\cdot PAr_3^*Me + M \rightarrow MePAr_3^{*+} + M^-$$

$$L = (CO \text{ or } PAr_3)$$

(See Scheme II for possible M)

The formation of methyl radicals in a solution of PPh_3 would be expected to lead to formation of the radical $\cdot PPh_3Me$[16] because the addition of methyl radical to PPh_3 should be a facile reaction. For example, the addition of RO· to PPh_3 in methanol has been shown to proceed at close to the diffusion-controlled rate[17] (eq 11). In addition, methyl radicals add to trialkyl phosphites to

$$RO\cdot + PPh_3 \xrightarrow{k} [ROPPh_3] \quad (11)$$

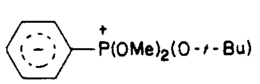
$$R = Me,\ k = 5.1 \times 10^9\ M^{-1}\ s^{-1};\quad R = t\text{-}Bu,\ k = 1.9 \times 10^9\ M^{-1}\ s^{-1}$$

form methyl(trialkoxy)phosphoranyl radicals,[18] eq 12. (In view

$$Me\cdot + (RO)_3P \underset{203\ K}{\overset{K_{eq}}{\rightleftharpoons}} (RO)_3PMe \quad (12)$$

$$R = Et,\ K_{eq} = 120;\ R = i\text{-}Pr,\ K_{eq} = 19;\ R = t\text{-}Bu,\ K_{eq} = 0.1$$

of the apparent importance of steric effects it should be noted that Tolman's cone angle[19] for PPh_3, 145°, is between that of $P(O\text{-}i\text{-}Pr)_3$, 130°, and $P(O\text{-}t\text{-}Bu)_3$, 172°.) Because the stability of phosphoranyl radicals toward fragmentation increases with the electronegativity of the ligands,[16a] the $\cdot PAr_3Me$ radical is expected to be less stable than the species formed in eq 11 and 12. For example, the ESR spectrum of $Me_3\dot{P}(O\text{-}t\text{-}Bu)$ is observed when methyl radicals are generated in the presence of $Me_2P(O\text{-}t\text{-}Bu)$ but no spectrum of $\cdot PMe_4$[16a] could be detected in the reaction of methyl radicals with PMe_3. However, even if the rate of addition of the methyl radical to PPh_3 is as much as three orders of magnitude less than that of the methoxy radical, phosphoranyl formation in a 0.1 M solution of PPh_3 will still proceed at a rate approximately 80 times greater than H-atom abstraction in a relatively good H-atom-donor solvent such as toluene. (The rate of H abstraction by Me· from toluene is 6×10^2 M^{-1} s^{-1}.[20]) Additionally, the $\cdot PAr_3Me$ radical should be considerably more stable than a tetraalkylphosphoranyl radical because of electron delocalization over the phenyl rings, e.g., the radical $PhP(OMe)_2(O\text{-}t\text{-}Bu)$ is best considered a "phosphonium substituted benzene radical anion".[21] (This is presumably the reason PAr_3 yields ionic products but PR_3 (R = alkyl) does not.) The point is that methyl radical formation in the system $CpW(CO)_2LMe$ (L = CO, PAr_3) + PAr_3 is expected to result in the formation of phosphoranyl radicals, $\cdot PAr_3Me$.



Whereas the intramolecular chemistry of phosphoranyl radicals (fragmentation, isomerization) has been studied thoroughly,

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[14] If CO dissociation were the only primary photoprocess leading to dimerization, the quantum yield for dimerization

$$CpW(CO)_3Me \underset{k_{-1}[CO]}{\overset{\phi_{dis}}{\rightleftharpoons}} CpW(CO)_2Me + CO \xrightarrow{k_2[CpW(CO)_3Me]} {}^1/_2Cp_2W_2(CO)_5 + 2Me\cdot \xrightarrow{CO} Cp_2W_2(CO)_6$$

would be

$$\Phi_{dim} = \phi_{dis}\frac{k_2[CpW(CO)_3Me]}{k_{-1}[CO] + k_2[CpW(CO)_3Me]};\ \phi_{dis} = 0.4$$

Experimentally, under an argon atmosphere $\Phi = 0.08$. Thus,

$$\frac{k_2[CpW(CO)_3Me]}{k_{-1}[CO] + k_2[CpW(CO)_3Me]} = 0.2 \text{ and } k_{-1}[CO] = 4k_2[CpW(CO)_5Me]$$

Under an atmosphere of CO (ca. 8×10^{-3} M) the concentration of CO should be many times greater than the steady-state concentration resulting from the above reaction, and thus $k_{-1}[CO] \gg k_2[CpW(CO)_3Me]$. Consequently, $\Phi_{dim,CO}$ would be near zero. In fact, it is found to be 0.044 ± 0.005. Under 2 atm of CO, the quantum yield is only reduced to 0.036 ± 0.005. At 5 atm of CO, the absolute quantum yield could not be measured, but the rate of growth of $Cp_2W_2(CO)_6$ was 75% ± 10% that of a solution under 1 atm of CO under otherwise identical irradiation conditions. These results are consistent with and strongly supportive of an alternative pathway involving a primary photoprocess with a quantum yield of 0.033 ± 0.005. The simplest pathway would, of course, be W–Me bond dissociation. It should be noted that the quantum yield of 0.033 is very close to that of the quantum yield for reaction 4 ($[PPh_3] = 0.75$ M), 0.04 ± 0.01.

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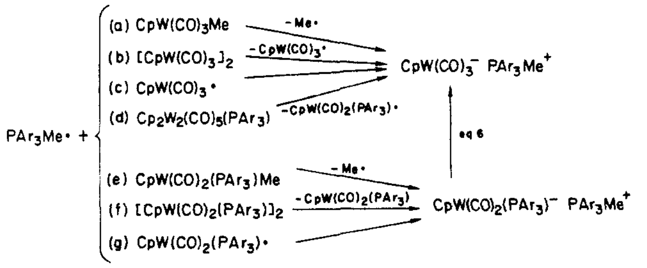
Scheme II



rellatively little is known about their reactivity with other molecules.[16a] Phosphoranyl radicals were first proposed to explain the chain reaction of PPh_3 with bromoform[22] (eq 13a,b).

$$PPh_3 + \cdot CHBr_2 \rightarrow Ph_3\dot{P}CHBr_2 \qquad (13a)$$

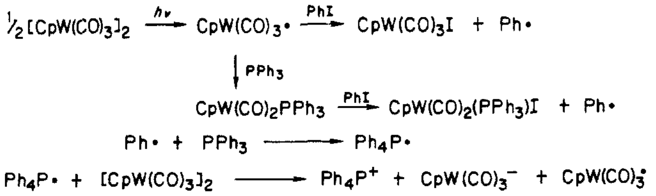
$$Ph_3\dot{P}CHBr_2 + CHBr_3 \rightarrow Ph_3PCHBr_2^+Br^- + \cdot CHBr_2 \qquad (13b)$$

Similar reactions of other phosphines and phosphites with halocarbons and with benzoyl peroxide, involving oxidation of phosphoranyl radicals, have since been reported.[16a] We were thus led to consider the mechanism in Scheme I for reaction 7.

Direct ESR observation of $\dot{P}Ph_3Me$ was unsuccessful. This is not surprising as there have been no reported successful ESR observations of phosphoranyl radicals with four alkyl or aryl ligands even under conditions much more favorable to observation of such species than the conditions of reaction 7. Furthermore, whereas the formation of $\cdot PPh_3Me$ is virtually certain in the event of methyl radical formation, the observation of such radicals would not constitute strong evidence of their intermediacy in eq 7. Our strategy therefore was to determine whether interception of methyl radicals inhibited reaction 7. Indeed, this proved to be the case. Irradiation of a benzene solution of $CpW(CO)_3Me$ (20 mM), PPh_3 (0.04 M), and the good H-atom-donor 9,10-dihydroanthracene (1.2 M) afforded only an 11% yield of $CpW(CO)_3^-$ as compared with a 44% yield from an otherwise identical control solution to which dihydroanthracene was not added. IR spectroscopy of the gases formed in the reaction revealed CO and methane. The amount of methane trapped for observation was 0.45 mol per mol of $CpW(CO)_3Me$; the actual yield would be somewhat higher taking into account the methane remaining in the reaction vessel in and above the solution (see Experimental Section). Similarly, irradiation of $CpW(CO)_3Me$ (20 mM) in the presence of PPh_3 (0.4 M) and the hydrogen donor 1,4-cyclohexadiene (25% v:v, 2.6 M) in benzene yielded only 7.0% $CpW(CO)_3^-$; a 5.2 M cyclohexadiene solution yielded only 1.7% $CpW(CO)_3^-$. In addition to good H-atom-donors, olefins to which methyl radicals add rapidly[23] were found to inhibit reaction 7. For example, addition of α-methylstyrene (1.0 M) to a benzene reaction solution reduced the yield of $CpW(CO)_3^-$ from the photoreaction of $CpW(CO)_3Me$ (20 mM) with PPh_3 (0.4 M) to 8%. The addition of 1,1-diphenylethylene (1.0 M), an even better methyl trap,[23] resulted in a $CpW(CO)_3^-$ yield of 5%. (Note that the molar effectiveness of each of these reagents in the inhibition of reaction 7 parallels the ordering of their molar reactivity toward methyl radical, i.e., diphenylethylene > α-methylstyrene > dihydroanthracene > cyclohexadiene.[23-25])

To ensure that the olefin functionality was not in some way inhibiting reaction 7 via coordination to an active site on the tungsten center, a control experiment was performed. 2,3-Dimethyl-1-butene is sterically similar to α-methylstyrene and considerably less bulky than diphenylethylene and would be expected to display a similar tendency to coordinate to a metal center; however, it is much less reactive toward methyl radical.[26] Irradiation of $CpW(CO)_3Me$ (20 mM) in the presence of PPh_3 (0.4 M) and 2,3-dimethyl-1-butene (1.0 M) results in smooth substitution by PPh_3 (as was the case with the aryl-substituted olefins) and the formation of $CpW(CO)_3^-$ (46%). The yield of $CpW(CO)_3^-$ is thus unaffected by the presence of the olefin, and it can be safely concluded that the methyl radical is a necessary intermediate in reaction 7. Given this conclusion, the formation and subsequent oxidation of $\dot{P}Ar^*_3Me$ (Scheme I) are plausible steps in the mechanism of reaction 7. Our proposed mechanism is shown in Scheme II.

Scheme III



It should be noted that reduction by the phosphoranyl radical of any of a wide variety of tungsten-containing species (present or possibly present in the reaction mixture of reaction 7) will lead to the observed products either directly or via CO substitution of the anion, $CpW(CO)_2PAr_3^-$ (see Scheme II). The electrochemical reduction potential of PPh_3Et^+ is −2.2 V (Ag/Ag^+);[27] presumably that of PPh_3Me^+ is roughly the same or very slightly more negative. Thus, in solutions containing $CpW(CO)_3Me$ ($E_{1/2}$ = −2.2 V, Ag/Ag^+) step a (Scheme II) may be a significant process. Reduction of $CpW(CO)_3Me$[28,29] would afford $CpW(CO)_3^-$ and methyl radical and could thus lead to the observed products via a chain reaction. However, we have shown that the presence of $CpW(CO)_3Me$, although it may increase the efficiency of reaction 7, is not necessary for the reaction to occur. Alternatively, in the absence of $CpW(CO)_3Me$, reaction 7 could go as a chain via step e. The reduction potential of $CpW(CO)_2(PAr_3)Me$ is probably slightly (<0.2 eV) more negative[30] than that of $CpW(CO)_3Me$; hence, step e may be less likely than step a. The reduction of the 17-electron species $Cp\dot{W}(CO)_3$ and $Cp\dot{W}(CO)_2PAr_3$[28,29] would be energetically much more favorable as would reduction of the corresponding dimers $[CpW(CO)_3]_2$, $Cp_2W_2(CO)_5(PPh_3)$, and possibly $[CpW(CO)_2(PPh_3)]_2$. Because the production of the 17-electron species follows from homolytic cleavage of the tungsten–methyl bond, a proposed pathway involving such reductions (Scheme II, steps b, c, d, f, or g) is also consistent with the data. It should be noted that the similar quantum yields for reaction 8 (CO atmosphere) and for reaction 7 are in agreement with such nonchain pathways.

To further test our hypothesis of the intermediacy of a phosphoranyl reductant, we irradiated $CpW(CO)_3Me$ in the presence of nitrobenzene.[31] When a solution of $CpW(CO)_3Me$ (20 mM), PPh_3 (0.4 M), and nitrobenzene 0.1 M) was irradiated, no detectable $CpW(CO)_3^-$ was formed, as monitored by infrared spectroscopy, but ^1H NMR showed the formation of PPh_3Me^+ (7 mM). The reduction potential of nitrobenzene, −1.15 V (Ag/Ag^+), is less negative than that of any of the organometallic species discussed above as potential electron acceptors; the production of phosphonium cation without concomitant $CpW(CO)_3^-$ formation thus occurs because the photogenerated PPh_3Me radical preferentially reduces nitrobenzene. The fate of the reduced

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nitrobenzene was not determined. The disappearance of ca. 25 mM nitrobenzene was observed by IR; the disappearance of greater than stoichiometric amounts is to be expected because $Cp_2W_2(CO)_6$ and $Cp_2W_2(CO)_5PPh_3$, the expected organometallic products from this reaction, react with nitrobenzene to give non-carbonyl-containing products.[32] Significantly, control experiments showed that $CpW(CO)_3^-$ does not react with nitrobenzene under the conditions of our experiment.

In order to explore the scope of and provide confirmatory evidence for phosphoranyl radicals as reducing intermediates in organometallic reactions, we carried out, in the presence of PPh_3, a reaction known to produce radicals, namely, the photolysis of $Cp_2W_2(CO)_6$ in the presence of organohalide (see Scheme III). Phenyl iodide was chosen as the organic radical precursor because of its lack of susceptibility toward nucleophilic substitution by either PPh_3 or $CpW(CO)_3^-$[33] and because the phenyl radical would be expected to form a stable phosphoranyl adduct. Results consistent with formation and subsequent oxidation of $\cdot PPh_4$ were obtained: irradiation under a CO atmosphere ($\lambda > 500$ nm) of a phenyl iodide solution of $[CpW(CO)_3]_2$ (10 mM) and PPh_3 (0.4 M) afforded $CpW(CO)_3^-$ (5 mM, 50% based on Scheme III), $CpW(CO)_2(PPh_3)I$, small amounts of $CpW(CO)_3I$, and no organometallic cation as monitored by IR. PPh_4^+ was identified by adding cyclohexane to the reaction solution and then dissolving the resulting precipitate in acetone-d_6. The resulting ^1H NMR spectrum showed the characteristic multiplet of the PPh_4^+ species (7.83–7.90 ppm), which was identical with that of an authentic sample of PPh_4I. Scheme III explains these results and products.

Conclusion

At a first glance, Schemes I and II seem unrelated to a mechanism we have recently reported for disproportionation of metal–metal bonded dimers (see Scheme I, ref 6). However, the Me radical is isolobal to the $CpMo(CO)_3$ and $CpMo(CO)_2L$ fragments and thus the reactants and products of eq 4 and the dimer disproportionation reactions are "isolobal" (more specifically they are comprised of isolobal fragments). But what is most important, the key intermediate in Schemes I and II, PPh_3Me, is isolobal to the 19-electron intermediate, $CpMo(CO)_2L_2$, formed in the disproportionation reactions. Schemes I and II are thus *mechanistically isolobal* to the disproportionation pathway. In drawing this comparison between apparently unrelated reactions, we seek not only to point out the utility of the isolobal concept in mechanistic chemistry but also to alert mechanistic chemists to what we believe may be a far more general phenomenon, namely, the intermediacy of electronically "super-saturated" species as reductants.

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Supplementary Material Available: Elaboration of the conclusions presented in the section entitled Conclusions Derived from Tests for Alternative Mechanisms (9 pages). Ordering information is given on any current masthead page.

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Vibrational Circular Dichroism of Phenylcarbinols. A Configurational Correlation

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Abstract: The vibrational circular dichroism (VCD) spectra of enantiomers of phenylcarbinols were studied in the 1600–800 cm^{-1} region. In these molecules, the PhC(OH)H group is a common structural feature, and the chirality of this probe group correlates with the sign of a VCD band at about 1200 cm^{-1}. Viewing the probe group with the fourth ligand behind it, a clockwise arrangement of the probe group substituents (with the usual sequence rule priority, OH > Ph > H), designated as a clockwise probe group chirality, results in a negative sign for the VCD band at about 1200 cm^{-1}. For a counterclockwise probe group chirality, the VCD band is positive. On the basis of infrared and Raman spectral observations with deuterated analogues, this band is assigned to a *C–H deformation mode of the phenylcarbinols.

Vibrational circular dichroism (VCD) and Raman optical activity (ROA) are two types of vibrational optical activity (VOA) that have emerged in the past decade.[1-3] In order to realize the full potential of VOA in elucidating the configurations and conformations of chiral molecules, correlations relating VOA spectral features to known structural and stereochemical details need to be found. The antisymmetric stretching and deformation modes of the methyl group were predicted[4-6] to have bisignate VOA features with the respective signs reflecting the configuration at the chiral center to which the methyl group is attached. In this context, the VOA studies of enantiomers of α-phenylethylamine, α-phenylethyl alcohol, and deuterated α-phenylethanes have attracted much attention.[7-10] As a continuation of our previous

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