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Photochemical Disproportionation Reactions of the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ Complexes

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Abstract

Irradiation of the $W_2(CO)_{10}^{2-}$ complex in the presence of phosphines results in disproportionation of the dimer according to the following reaction: $W_2(CO)_{10}^{2-} + PR_3 \xrightarrow{h\nu} W(CO)_5PR_3 + W(CO)_5^{2-}$. The quantum yield for this process is about 0.06. Unlike the analogous reactions of neutral metal–metal bonded dimers, the $W_2(CO)_{10}^{2-}$ complex does not disproportionate with I^-. $Fe_2(CO)_8^{2-}$ disproportionates in a similar fashion: $Fe_2(CO)_8^{2-} + PR_3 \xrightarrow{h\nu} Fe(CO)_4PR_3 + HFe(CO)_4^-$. The $HFe(CO)_4^-$ product forms in these reactions rather than $Fe(CO)_4^{2-}$ unless rigorous precautions are taken to exclude H_2O. The data are consistent with a radical chain mechanism for the disproportionation reactions, analogous to the chain mechanisms proposed for the disproportionation reactions of neutral metal–metal bonded dimers.

Introduction

Irradiation of the $Cp_2Mo_2(CO)_6$ complex ($Cp = \eta^5\text{-}C_5H_5$) with appropriate ligands results in disproportionation [1–3], e.g.

$$Cp_2Mo_2(CO)_6 + PBu_3 \xrightarrow{h\nu} CpMo(CO)_3PBu_3^+ + CpMo(CO)_3^- \quad (1)$$

The disproportionation reaction is general for (neutral) metal–metal bonded complexes, and analogous reactivity is observed for the $Cp_2W_2(CO)_6$, $Cp_2Fe_2(CO)_4$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Co_2(CO)_8$ complexes [3–6], e.g.

$$Cp_2Fe_2(CO)_4 \xrightarrow[P(OEt)_3]{h\nu} CpFe(CO)(P(OEt)_3)_2^+ + CpFe(CO)_2^- \quad (2)$$

$$Mn_2CO)_{10} \xrightarrow[py]{h\nu} Mn(CO)_3(py)_3^+ + Mn(CO)_5^- \quad (3)$$

$$Co_2(CO)_8 \xrightarrow[PEt_3]{h\nu} Co(CO)_3(PEt_3)_2^+ + Co(CO)_4^- \quad (4)$$

The mechanisms of the disproportionation reactions have been studied, and in each case a chain pathway operates [3, 5a]. Scheme 1 illustrates the mechanism for $Cp_2Mo_2(CO)_6$ disproportionation; analogous mechanisms apply for the other dimers.

$$\underset{}{Cp_2Mo_2(CO)_6} \xrightarrow{h\nu} \underset{17}{2CpMo(CO)_3} \quad \text{initiation} \quad (5)$$

$$\underset{17}{CpMo(CO)_3} + L \longrightarrow \underset{19}{CpMo(CO)_3L} \quad \text{propagation} \quad (6)$$

$$CpMo(CO)_3L + Cp_2Mo_2(CO)_6 \longrightarrow CpMo(CO)_3L^+ + Cp_2Mo_2(CO)_6^- \quad (7)$$

$$Cp_2Mo_2(CO)_6^- \longrightarrow CpMo(CO)_3^- + CpMo(CO)_3 \quad (8)$$

$$CpMo(CO)_3L + CpMo(CO)_3 \longrightarrow CpMo(CO)_3L^+ + CpMo(CO)_3^- \quad \text{termination} \quad (9)$$

Scheme 1.

Note that a 19-electron complex* is a key intermediate in the chain process (eqn. (6)).

Photochemical disproportionation reactions have not been reported for the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ dimers**. If these dimers did disproportionate, the mechanistic precedents established with the other dimers suggest that the key intermediates would be the 19-electron $W(CO)_5L^-$ and $Fe(CO)_4L^-$ complexes. We are interested in complexes of this type because we have been using photogenerated 19-electron complexes as reducing agents [4, 9]. The $W(CO)_5L^-$ and $Fe(CO)_4L^-$ complexes would be exceptionally powerful reducing agents and they could be used to reduce substrates that are not reducible with the other 19-electron species. As a

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*The phrase '19-electron' complex is used to describe the adducts that form when 17-electron metal radicals react with 2-electron ligands. A thorough discussion of the electronic structures of these complexes is found in ref. 7.

**The possibility of $Fe_2(CO)_8^{2-}$ disproportionation has been briefly discussed in ref. 8.

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first step toward investigating the possibility that $W(CO)_5L^-$ and $Fe(CO)_4L^-$ are formed when the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ complexes are irradiated, we studied the disproportionation reactivity of these dimer complexes. In this paper we report the results of our study.

Experimental

All manipulations were done under an inert atmosphere of argon or nitrogen gas using a combination of Schlenk techniques, a Vacuum Atmospheres Company dry box, or a glove bag. Reagent grade solvents were distilled from appropriate drying agents according to literature procedures [10].

$Na_2Fe_2(CO)_8 \cdot 4THF$ was prepared according to a literature procedure [11]. Triphenylphosphine was obtained from Aldrich and recrystallized from an ethanol/benzene solvent mixture. Other phosphines and $Fe(CO)_5$ were obtained from Strem Chemical Company and used as received. Tungsten hexacarbonyl, 2,2′-bipyridine (99 + %), and methanolic 1 M tetrabutylammonium hydroxide were also obtained from Aldrich and used as received.

Preparation of $Na_2W_2(CO)_{10}$ and $(n\text{-}Bu_4N)_2W_2(CO)_{10}$

These complexes were prepared according to the method of Lindner and co-workers [12]. A somewhat modified version is described here. Under a nitrogen atmosphere, a mixture of $W(CO)_6$ (36 g, 0.1 mol), sodium (10 g, 0.4 mol) and 2,2′-bipyridine (0.5 g, 3 mmol) was placed in a 1-l round-bottomed flask equipped with a magnetic stir bar. The flask was stoppered with a rubber septum and then 400 ml of THF were added to the mixture using cannula. The color of the solution was initially yellow but it gradually changed to red. The mixture was stirred (under a positive pressure of nitrogen gas) for about 22 h, after which the infrared spectrum showed that very little reaction had taken place. One more gram (6 mmol) of 2,2′-bipyridine was added to the mixture. The reaction was allowed to continue for another 50 h after which there was virtually no unreacted $W(CO)_6$ left. The mixture was then filtered (under a nitrogen atmosphere) through a frit (medium porosity), the bottom of which was covered with neutral alumina. The layer of alumina (coated with some of the yellow product) was rinsed with dioxane until the eluent was only faintly yellow. Ether was slowly added to the combined filtrate until precipitation of a yellow solid was complete. The yellow solid was collected and transferred to a frit (medium porosity) and washed with more ether (300 ml) and then hexane (150 ml). The solid was then dried under vacuum to give a yield of 8 g (23%). The infrared spectrum (in CH_3CN) confirmed that the substance was the desired product, $Na_2[W_2(CO)_{10}]$.

The tetrabutylammonium salt of $W_2(CO)_{10}^{2-}$ was obtained by adding 2 equiv. of $n\text{-}Bu_4NI$ (in a minimum amount of 2-propanol) to $Na_2W_2(CO)_{10}$ (also in a minimum amount of 2-propanol). The $(n\text{-}Bu_4N)_2[W_2(CO)_{10}]$ salt, which precipitated as an orange product, was then collected, rinsed with 2-propanol, and dried.

Irradiation Procedures

All irradiations were done with an Oriel 200 W high pressure Hg arc lamp fitted with appropriate glass filters (Corning 3-73, $\lambda > 420$ nm; 0-52, $\lambda > 350$ nm). Use of radiation with wavelengths shorter than 400 nm made the reactions more complex (as indicated by IR spectroscopy), probably due to M–CO bond dissociation reactions*. The irradiations were done in CaF_2 infrared solution cells (with a pathlength of 0.5 mm) and the progress of the reactions was monitored by infrared spectroscopy. Essentially identical results were obtained in CH_3CN and THF solvents.

For quantum yield measurements, $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ (24.3 mg, 0.0215 mmol) and PPh_3 (10 mmol) were dissolved in 50 ml dry, oxygen-free CH_3CN. Five milliliters of the solution were irradiated for periods of 1 to 5 min. The disappearance of $W_2(CO)_{10}^{2-}$ was monitored at 400 and/or 436 nm using a Beckman DU-7 spectrophotometer. Lamp intensities were measured using Aberchrome 540 [14].

Results

The Electronic Spectra of $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$

The $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ complex exhibits absorption features at 347 nm ($\epsilon = 7210$) and 390 nm (shoulder, $\epsilon = 4840$). This two-peak pattern is typical for metal–metal bonded carbonyl dimers, and Harris and Gray therefore assigned these bands to the $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions, respectively [15]. Similarly, the $Na_2Fe_2(CO)_8$ complex has absorption bands at 352 nm ($\epsilon = 8900$ nm) and 537 nm ($\epsilon = 500$) in CH_3CN. Assignment to the $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions is again proposed [16].

Irradiation of $W_2(CO)_{10}^{2-}$ in CH_3CN or THF

Irradiation ($\lambda > 420$ nm) of $W_2(CO)_{10}^{2-}$ (3 mM) in CH_3CN or THF led to a very slow decrease in the intensity of the CO stretching bands of the starting material. Accompanying the slow disappearance of $W_2(CO)_{10}^{2-}$ was the slow formation of $W(CO)_6$, as indicated by the appearance and gradual increase in

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*Under these conditions, *trans*-$W(CO)_4(PPh_3)_2$ and free CO were the major products (see ref. 13).

TABLE I. Infrared Spectral Data

Complex	Solvent	$\nu(C\equiv O)$ (cm^{-1})	Reference
$Na_2W_2(CO)_{10}$	CH_3CN	1941m, 1891vs, 1790s,	12
	THF	2024vs, 1945m, 1903vs, 1881m,sh 1834vw, 1811vw, 1753m	12
$(n\text{-}Bu_4N)_2W_2(CO)_{10}$	CH_3CN	1941m, 1891vs, 1790s	12
	THF	1941m, 1890vs, 1789s	this work
$W(CO)_6$	CH_3CN	1978	24
	THF	1983	
$W(CO)_5PPh_3$	CH_3CN	2074w, 1981w, 1940vs	this work
	cyclohexane	2073w, 1944s	25
$W(CO)_5PBu_3$	cyclohexane	2068w, 1943w, 1936s	25
$W(CO)_5I^-$	$CHCl_3$	2058w, 1915s, 1840m	26
$W(CO)_5(4\text{-cypy})^a$	THF	2075w, 1933s, 1913sh	20
$W(CO)_5(4\text{-cypy})^-$	THF	2058w, 1914s	this work
$Na_2W(CO)_5$	DME	1827s, 1757s,br	27
	HMPA	1775s, 1731s	28
	THF	1827s, 1757s,br	28
	THF	1829vs, 1772s,br	29
$(n\text{-}Bu_4N)_2W(CO)_5$	CH_3CN	1780s, 1740s	this work
$[AsPh_4]_2Fe_2(CO)_8$	CH_3CN	1922s, 1873s, 1827m	8
$Na_2Fe_2(CO)_8$	CH_3CN	1915s, 1862s, 1837sh	this work
$Fe(CO)_4{}^{2-}$	DMF	1730	17a, p. 100; 23
	CH_3CN	1750	this work
$KHFe(CO)_4$	DMF	2008w, 1914m, 1880s	23
$NaHFe(CO)_4$		1910m, 1880s	this work
$Fe(CO)_4PPh_3{}^b$	$CHCl_3$	2059m, 1978m, 1938vs	30
	CH_3CN	2046m, 1976m, 1938s	this work
$Fe(CO)_3(PPh_3)_2{}^c$	$CHCl_3$	1887	30
	CH_3CN	1883	this work

[a] $\nu(C\equiv N)$ = 2235 cm^{-1}. [b] This complex was chosen as typical of the $Fe(CO)_4L$ products. Similar spectra were observed for the other $Fe(CO)_4L$ products. [c] This complex was chosen as typical of the $Fe(CO)_3L_2$ products. Similar spectra were observed for the other $Fe(CO)_3L_2$ products.

intensity of a band at 1978 cm^{-1} (Table I). No other spectral changes were observed. The quantum yield (in CH_3CN) for the disappearance of $W_2(CO)_{10}{}^{2-}$ in this reaction is 0.01. Thus, CH_3CN and THF are essentially inert solvents for the disproportionation reactions described below. In the reactions which follow, identical results were obtained in CH_3CN and THF.

Irradiation of $W_2(CO)_{10}{}^{2-}$ and PPh_3 or PBu_3

Irradiation ($\lambda > 420$ nm) of a THF or CH_3CN solution containing $Na_2W_2(CO)_{10}$ (14 mM) and PPh_3 (40 mM) or PBu_3 (50 mM) gave $W(CO)_5PR_3$ and $W(CO)_5{}^{2-}$:

$$W_2(CO)_{10}{}^{2-} + PR_3 \xrightarrow{\lambda > 420\,\text{nm}} W(CO)_5PR_3 + W(CO)_5{}^{2-} \quad (10)$$

R = Ph, Bu

The products were identified by infrared spectroscopy (Table I) and no $W(CO)_6$ or other possible products were detected. Identical results were obtained using $(n\text{-}Bu_4N)_2W_2(CO)_{10}$ rather than $Na_2W_2(CO)_{10}$. The quantum yield (436 nm in CH_3CN) for reaction 10 (R = Ph) is 0.06.

To make certain that the absence of $W(CO)_6$ in the reactions above was not due to reaction (11), a control reaction was done.

$$W(CO)_6 + PR_3 \xrightarrow{h\nu} W(CO)_5PR_3 + CO \quad (11)$$

Irradiation ($\lambda > 420$ nm) of a CH_3CN solution of $W(CO)_6$ (50 mM) and an excess of PPh_3 (0.8 M) gave no $W(CO)_5PPh_3$ or other substitution products, as monitored by infrared spectroscopy. Reaction (11) was thus excluded as the source of $W(CO)_5PR_3$. [Note, however, that when higher energy radiation ($\lambda > 350$ nm) was used, the $W(CO)_6$ was quickly consumed and $W(CO)_5PPh_3$ and *cis*-$W(CO)_4(PPh_3)_2$ were formed [17].]

Irradiation of $W_2(CO)_{10}{}^{2-}$ and I^- in CH_3CN

The neutral metal–metal bonded dimers disproportionate when irradiated in the presence of halides and pseudo-halides [18]. $W_2(CO)_{10}{}^{2-}$ was therefore irradiated in the presence of I^- to determine if a similar reactivity occurred with this dimer. Irradiation ($\lambda > 420$ nm) of $(n\text{-}Bu_4N)_2[W_2(CO)_{10}]$ (8 mM) and $(n\text{-}Bu_4N)I$ (100 mM) in CH_3CN produced only a very slow decrease in the intensity of bands due to the dimer and a correspondingly slow growth of a band at 1740 cm^{-1} attributed to $W(CO)_5^{2-}$. The dimer remained largely unreacted even after irradiating for over six minutes, and the $W(CO)_5I^-$ complex was not detected [19].

Irradiation of $W_2(CO)_{10}^{2-}$ in the Presence of 4-Cyanopyridine

During the course of this study, Kaim reported the ESR spectra of the $M(CO)_5L^-$ complexes (M = Cr, Mo, W; L = 4-cyanopyridine (4-cypy), 4-acylpyridine) [20]. The complexes were generated by either reducing the 18-electron $M(CO)_5L$ complexes with potassium metal or reacting the metal dimers $M_2(CO)_{10}^{2-}$ with an appropriate ligand L:

$$M_2(CO)_{10}^{2-} \xrightarrow[THF]{L} M(CO)_5L^- \xleftarrow[THF]{K} M(CO)_5L \qquad (12)$$

The existence of the $W(CO)_5(4\text{-cypy})^-$ complex provides a convenient test for homolysis of the metal–metal bond in $W_2(CO)_{10}^{2-}$. Thus, if homolysis occurs we would expect the formation of $W(CO)_5(4\text{-cypy})^-$ by the following route:

$$W_2(CO)_{10}^{2-} \xrightarrow{h\nu} 2W(CO)_5^- \xrightarrow{4\text{-cypy}} W(CO)_5(4\text{-cypy})^- \qquad (13)$$

When a THF solution of $W_2(CO)_{10}^{2-}$ and 4-cyanopyridine was kept in the dark the solution was ESR silent. However, when irradiated ($\lambda > 420$ nm) or exposed to bright room light, the solution changed color from orange–yellow to olive green and a strong ESR signal identical to the one observed by Kaim [20] for $W(CO)_5(4\text{-cypy})^-$ was obtained. During the irradiation, the intensity of the CO stretching bands of the dimer gradually decreased in intensity and gave way to new bands at 2058w and 1914vs cm^{-1}. The bands are assigned to $W(CO)_5(4\text{-cypy})^-$ by comparison to the 18-electron complex $W(CO)_5(4\text{-cypy})$ which has bands at 2075w, 1933vs and 1913sh cm^{-1} and a $\nu(C{\equiv}N)$ stretch at 2355vvw cm^{-1}. The $\nu(C{\equiv}N)$ band of the 19-electron complex could not be located, probably because it was too weak (as is that of the 18-electron analog). Another band which appeared at 1977 cm^{-1} is assigned to $W(CO)_6$. In addition, new bands appeared at 2110w [assigned to $\nu(C{\equiv}N)$] and 1870m [assigned to $\nu(C{\equiv}O)$]. Throughout the irradiation the band attributed to $W(CO)_6$ steadily grew in intensity at the expense of those at 2110 and 1870 cm^{-1}, especially after all the starting material dimer had been consumed. In fact, after almost all the dimer had been consumed the bands at 2110 and 1870 cm^{-1} started decreasing while those at 2058 and 1914 cm^{-1} did not change in intensity, a result which strongly suggests that the two sets of bands do not belong together. The complex with bands at 2110 and 1870 cm^{-1} was not identified but two possibilities are the $W(CO)_5CN^-$ species [21] and the N-bonded nitrile isomer of $W(CO)_5(4\text{-cypy})^-$.

Chemical Reduction of $W(CO)_5(4\text{-cypy})$

Reduction of the $W(CO)_5(4\text{-cypy})$ complex (7 mM) in THF with a large excess of cesium metal led to a change in the color of the solution from orange–yellow to orange–green. After addition of the cesium metal, an infrared spectrum of the solution showed bands at 2069w cm^{-1} (assigned to unreacted starting material) and 2058w cm^{-1} [assigned to $W(CO)_5(4\text{-cypy})^-$]. There was also a band at 1929s cm^{-1} and a broad shoulder around 1895 cm^{-1}. These bands were assigned to the overlapping bands of $W(CO)_5(4\text{-cypy})$ (1933 cm^{-1}) and $W(CO)_5(4\text{-cypy})^-$ (1914 cm^{-1}). No bands were observed at 2110 and 1870 cm^{-1}.

Irradiation of $Fe_2(CO)_8^{2-}$ with Phosphines

Irradiation ($\lambda > 350$ nm) of $Na_2Fe_2(CO)_8$ and various phosphines [$PPh_2(i\text{-}Pr)$, $P(i\text{-}Pr)_3$, PPh_2Bu, PPh_3, PPh_2Me, PBu_3] in CH_3CN resulted in the formation of $Fe(CO)_4PR_3$, $Fe(CO)_3(PR_3)_2$, and $HFe(CO)_4^-$. The products were identified by infrared spectroscopy (Table I).

$$Fe_2(CO)_8^{2-} \xrightarrow[PR_3]{\lambda > 350\ \text{nm}} HFe(CO)_4^- + Fe(CO)_4PR_3 + Fe(CO)_3(PR_3)_2 \qquad (14)$$

Although $Fe(CO)_4^{2-}$ is the expected product of the disproportionation, the formation of $HFe(CO)_4^-$ is not unreasonable. $Fe(CO)_4^{2-}$ is very basic and Finke showed that it reacts with traces of H_2O (in the solvent or adsorbed on the walls of glassware) to form $HFe(CO)_4^-$ [22, 11, 23]. The use of CaF_2 infrared cells as our reaction vessel necessarily prevented us from rigorously removing all H_2O. In one experiment with $PBuPh_2$, however, extraordinary care was taken to remove H_2O from the reagents and from the Schlenk glassware used to prepare the reaction solutions. Following irradiation, a band was observed at 1750 cm^{-1}, indicating the formation of $Fe(CO)_4^{2-}$. Even with these precautions, however, bands attributable to $HFe(CO)_4^-$ were also observed.

The formation of $Fe(CO)_3L_2$ in reaction (14) is also expected. This species undoubtedly forms by simple substitution of $Fe(CO)_4L$ [17a, p. 120; 17b, p. 148].

$$Fe(CO_4)L \xrightarrow[L]{h\nu} Fe(CO)_3L_2 + CO \qquad (15)$$

Infrared spectral monitoring of reaction (14) clearly shows that $Fe(CO)_4L$ is the initial product and that continued irradiation causes this product to disappear and $Fe(CO)_3L_2$ to appear. In addition, control experiments established that irradiation ($\lambda > 350$ nm) of $Fe(CO)_4PR_3$ with various phosphines yields $Fe(CO)_3(PR_3)_2$.

Discussion

The results above clearly establish that the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ dimers disproportionate when irradiated in the presence of various phosphine ligands (eqns. (10) and (14)). The mechanisms of the disproportionation reactions were not studied, but it is likely that these reactions proceed via a chain pathway analogous to the one in Scheme 1. Three experimental results support this mechanistic conjecture. First, the electronic spectra of the complexes are very similar to those of the neutral metal—metal bonded complexes such as $Mn_2(CO)_{10}$, $Cp_2Mo_2(CO)_6$, etc. These latter complexes undergo homolysis when irradiated in their lowest energy absorption bands ($d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$) and it is likely, therefore, that $Fe_2(CO)_8^{2-}$ and $W_2(CO)_{10}^{2-}$ will also react this way. Homolysis, of course, is the initiating step in the chain reaction. Second, irradiation of $W_2(CO)_{10}^{2-}$ and 4-cypy yields the known $W(CO)_5(4\text{-cypy})^-$ complex (eqn. (13)) [20], a result suggestive of W—W bond homolysis followed by 19-electron adduct formation. Reaction of a 17-electron radical with a ligand to form a 19-electron complex is the key step in the disproportionation reaction, and this result indicates that the $W(CO)_5^-$ fragment can react in this way. Third, note that I^- will not disproportionate the $W_2(CO)_{10}^{2-}$ dimer, although I^- will disproportionate many of the neutral metal—metal bonded dimers. This result is expected if the pathway in Scheme 1 is followed because there will be a considerable Coulombic barrier for $W(CO)_5^-$ and I^- forming an adduct. Other pathways, however, are less likely to be effected. For example, direct heterolysis of $W_2(CO)_{10}^{2-}$ would initially yield $W(CO)_5^{2-}$ and $W(CO)_5$. The latter primary photoproduct could then react with I^- to give $W(CO)_5I^-$, a known complex [19]. Thus, there are no inherent barriers to reaction of $W_2(CO)_{10}^{2-}$ with I^- if this pathway is followed, and the inability of I^- to disproportionate $W_2(CO)_{10}^{2-}$ is therefore inconsistent with a direct heterolysis pathway.

The one result perhaps inconsistent with the chain pathway in Scheme 1 is the low quantum yield for the disproportionation of $W_2(CO)_{10}^{2-}$ by PPh_3 ($\Phi = 0.06$). Quantum yields greater than one are observed in many disproportionation reactions [3], but the small quantum yield is probably attributable to some inherently inefficient step [for example, the analog of the electron-transfer step (eqn. (7)) in Scheme 1.

In summary, the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ complexes photochemically disproportionate with phosphines and the chain mechanism in Scheme 1 is a likely pathway. The implication is that the 19-electron $W(CO)_5PR_3^-$ and $Fe(CO)_4PR_3^-$ complexes are key intermediates. Studies are currently underway in our laboratory to determine if these species are, in fact, intermediates in the disproportionation reactions.

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