Photochemical Heterolysis of the Metal−Metal Bond in $(Me_3P)(OC)_4OsW(CO)_5$

Jonathan L. Male and Roland K. Pomeroy

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received April 2, 1997[⊗]

The photochemistry of $(Me_3P)(OC)_4OsW(CO)_5$ **(1)**, a molecule with a dative covalent metal−metal bond, was investigated. The results indicate that the photoprocess is heterolytic cleavage of the metal−metal bond, rather than homolytic cleavage as is found in compounds with nondative covalent metal−metal bonds. The principal evidence for heterolysis comes from the irradiation ($\lambda > 400$ nm) of **1** in benzene in the presence of PPh_3. The major products were $Os(CO)_4(PMe_3)$, $Os(CO)_3(PMe_3)(PPh_3)$, and $W(CO)_5(PPh_3)$. These products are consistent with a pathway that involves initial heterolysis to form $Os(CO)_4(PMe_3)$ and $W(CO)_5$ followed by trapping of the coordinatively unsaturated $W(CO)_5$ species with PPh_3. (Control experiments showed that $Os(CO)_3(PMe_3)(PPh_3)$ forms from $Os(CO)_4(PMe_3)$ and PPh_3 under the reaction conditions.) Primary photoprocesses involving either M−CO bond dissociation or Os−W bond homolysis are incompatible with the results of other experiments. For example, when the irradiation of **1** was carried out under CO, the quantum yield for disappearance of **1** increased to 0.28 ± 0.05 from its value of 0.13 ± 0.01 under N_2, a result inconsistent with M−CO dissociation as the primary photoprocess. Likewise, control experiments showed that $[W(CO)_5{}^{\bullet-}]$ was readily trapped under the reaction conditions, but all attempts to trap $[W(CO)_5{}^{\bullet-}]$ (one of the expected homolytic primary photoproducts) with the metal−radical traps benzyl chloride, CCl_4, or TMIO (1,1,3,3-tetramethylisoindoline-2-oxyl) during the photolysis of **1** were fruitless. Compound **1** reacted photochemically with CCl_4 to form *fac*-$Os(CO)_3(PMe_3)Cl_2$ (***fac*-2**) and $W(CO)_6$. The *fac*-$Os(CO)_3(PMe_3)Cl_2$ product is likely formed by a secondary photolysis of $Os(CO)_4(PMe_3)$. Control experiments showed that irradiation of $Os(CO)_4(PMe_3)$ in CCl_4 initially formed a compound believed to be $Os(CO)_3(PMe_3)(CCl_3)$-Cl, which in the presence of $W(CO)_5$ then reacted to form *fac*-$Os(CO)_3(PMe_3)Cl_2$. Small amounts of $W(CO)_6$ (8%) were also produced in the photochemical reaction of **1** with PPh_3. An experiment in a more viscous solvent system indicated that $W(CO)_6$ is not formed in a CO abstraction reaction involving the $[(Me_3P)(OC)_4Os, W(CO)_5]$ solvent cage pair. The formation of $W(CO)_6$ is attributed to a second (minor) heterolytic pathway involving an intermediate with a bridging CO that directly yields $W(CO)_6$ and $Os(CO)_3(PMe_3)$.

Introduction

In 1983, Pomeroy and co-workers reported the synthesis and structural characterization of $(OC)_5OsOs(CO)_3(GeCl_3)Cl$, a molecule with an unbridged Os−Os bond.[1] The complex was unusual because $Os(CO)_5$, a stable 18-electron molecule, acted as a Lewis base to the 16-electron $Os(CO)_3(GeCl_3)(Cl)$ fragment to form a metal−metal dative bond. Since that report, other neutral complexes with unbridged dative metal−metal bonds have been reported.[2−8] Molecules with metal−metal dative bonds are intriguing because of the possibility that on photolysis the dative metal−metal bonds may be cleaved *heterolytically*. Such cleavage would be unusual because, in general, metal−metal *homolysis* occurs when compounds with metal−metal bonds are irradiated.[9,10] The studies that demonstrated homolysis, however, were all carried out on molecules having

---

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

[1] Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

[2] Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, *273*, C33.

[3] Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *3*, 250.

[4] Del Paggio, A. A.; Muetterties, E. L.; Heinekey, D. M.; Day, V. W.; Day, C. S. *Organometallics* **1986**, *5*, 575.

[5] Einstein, F. W. B.; Jennings, M. C.; Krentz, R.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Inorg. Chem.* **1987**, *26*, 1341.

[6] Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C.; Tomas, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 3005.

[7] (a) Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984**, *106*, 2707. (b) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030. (c) Davis, H. B.; Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *J. Organomet. Chem.* **1987**, *319*, C25.

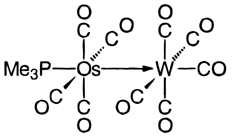
[8] Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

[9] Irradiation of metal−metal-bonded organometallic dimers generally leads to either metal−metal bond homolysis or metal−ligand bond dissociation. See: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979. (b) Meyer, T. J.; Casper, J. V. *Chem. Rev.* **1985**, *85*, 187.

[10] Photoinduced heterolytic cleavage of metal−metal bonds[11] has been suggested in several systems,[12−14] but definitive mechanistic confirmation is generally lacking. In several cases, proposed heterolyses were shown to actually involve homolytic fission followed by electron transfer.[15−17]

nondative covalent metal—metal bonds. This distinction in bond types is important because there are ample precedents for photochemical heterolyses in reactions involving dative bonds. For example, metal—ligand bond cleavage reactions from d—d excited states are generally heterolytic.[18] Because metal—ligand bonds are dative in nature, it was reasoned that bimetallic systems with dative metal—metal bonds might also undergo heterolytic cleavage.

In order to investigate the possibility that the photolysis of metal—metal dative bonds may be heterolytic,[19] we studied the photochemistry of $(Me_3P)(OC)_4OsW(CO)_5$ (**1**),[7a,b] a dinuclear complex with an unbridged, dative metal—metal bond. Herein we describe the results of our study; a preliminary account of our findings has appeared.[23]



1

Results and Discussion

Electronic Spectrum of 1. The electronic absorption spectrum of **1** in the region 300—900 nm exhibits a peak with a maximum at 368 nm ($\epsilon = 2.79 \times 10^3 \pm 1.9 \times 10^2$ L mol^{-1} cm^{-1}) and a subtle shoulder at 334 nm ($\epsilon = 2.7 \times 10^3 \pm 1.9 \times 10^2$ L mol^{-1} cm^{-1}) in C_6H_6 at 25 °C. By analogy to binuclear complexes with unbridged metal—metal bonds, the band at 368 nm is assigned to a $\sigma \rightarrow \sigma^*$ transition associated with the metal—metal bond.[24,25] For comparison, the $[H(OC)_4FeM(CO)_5]^-$ complexes (M = Cr, Mo, W), with a putative donor—acceptor metal—metal bond, also exhibit a strong absorption in the near-UV region (315—330 nm, $\epsilon \approx 10^4$ L mol^{-1} cm^{-1}).[26] These absorptions were also ascribed to the $\sigma \rightarrow \sigma^*$ transition by analogy to studies on the $[M_2(CO)_{10}]^{2-}$ (M = Cr, W) molecules.[27]

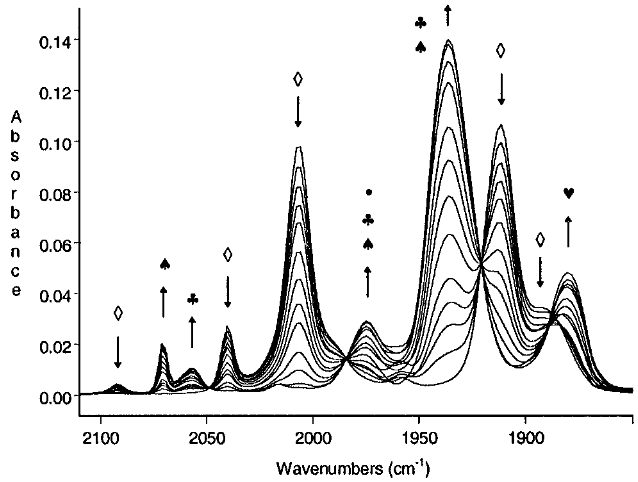


Figure 1. Infrared spectra of the photolysis ($\lambda > 400$ nm) of **1** in C_6H_6 in the presence of PPh_3. The time scale of the reaction was 0—28 min utilizing a 200 W high-pressure mercury arc lamp. The species are identified as follows: club = $Os(CO)_4(PMe_3)$; spade = $W(CO)_5(PPh_3)$; heart = $Os(CO)_3(PMe_3)(PPh_3)$; diamond = $(Me_3P)(OC)_4OsW(CO)_5$ (**1**); ● = $W(CO)_6$.

Experiments Exploring the Possibility of Heterolytic Cleavage. Irradiation ($\lambda > 400$ nm) of **1** (1.66×10^{-3} M) in the presence of PPh_3 (1.91×10^{-1} M) in deoxygenated benzene gave $Os(CO)_4(PMe_3)$, $Os(CO)_3(PMe_3)(PPh_3)$, $W(CO)_5PPh_3$, and $W(CO)_6$ in the yields shown in eq 1.

$$\underset{\mathbf{1}}{(Me_3P)(OC)_4OsW(CO)_5} + PPh_3 \xrightarrow[\text{benzene}]{h\nu\ (\lambda > 400\ \text{nm})} \underset{46\%}{Os(CO)_4(PMe_3)} + \underset{49\%}{Os(CO)_3(PMe_3)(PPh_3)} + \underset{81\%}{W(CO)_5(PPh_3)} + \underset{8\%}{W(CO)_6} \quad (1)$$

The reaction was followed by infrared spectroscopy, which showed the appearance of the product bands and the disappearance of bands for **1** over a period of 28 min (Figure 1; Table 1). The products were identified by comparison of their infrared spectra to the spectra of compounds prepared independently or to spectra reported in the literature (Table 1). (Examples of the spectra for all of the reactions followed by infrared spectroscopy described in this paper are included in the Supporting Information for this paper. Note that the percent yields in eq 1 are reported with respect to the total Os or W.) The photolyses were carried out into the low-energy tail of the $\sigma \rightarrow \sigma^*$ absorption band ($\lambda >$

---

(11) Armentrout, P. B.; Simons, J. *J. Am. Chem. Soc.* **1992**, *114*, 8627.

(12) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. J.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189.

(13) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1984**, *268*, 259.

(14) Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497.

(15) For example, the disproportionation reactions of many dinuclear complexes follow a pathway involving homolysis, followed by coordination of a ligand to form a 19-electron adduct, and then electron transfer. See: Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032—6037.

(16) For a review of disproportionation, see: Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217—240.

(17) Stufkens and Oskam reported several instances where heterolytic products are the result of photochemical homolysis followed by electron transfer between geminate cage radicals. See: (a) van Dijk, H. K.; van der Haar, J.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 75—81. (b) Knoll, H.; de Lange, W. J. G.; Hennig, H.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1992**, *430*, 123—132.

(18) For a review, see: Zinato, E. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975.

(19) Note that thermal heterolytic cleavage of metal—metal bonds has been demonstrated, for example, in the complexes $(Cp)(PMe_3)_2CoA$ [A = $Zn(Cl)_2(PMe_3)$, $Cu(Cl)(PMe_3)_2$],[20] $(CO)_4CoRh(CO)(PEt_3)_2$,[21] and $(Cp)(H)_2MM'(CO)_5$ (M = Mo, W; M′ = Cr, Mo, W)[22] and in several of the neutral unbridged complexes with a dative metal—metal bond.[2—4,6,7]

(20) Dey, K.; Werner, H. *Chem. Ber.* **1979**, *112*, 823.

(21) Roberts, D. A.; Mercer, W. C.; Geoffroy, G. L.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 1439 and ref 3 therein.

(22) Deubzer, B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1968**, *90*, 3276.

(23) Male, J. L.; Davis, H. B.; Pomeroy, R. K.; Tyler, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 9353.

(24) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 1003.

(25) Davis, H. B. Ph. D. Thesis, Simon Fraser University, Jan 1991.

(26) (a) Arndt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2617 and references therein. (b) Arndt, L. W.; Bancroft, B. T.; Darensbourg, M. Y.; Janzen, C. P.; Kim, C. M.; Reibenspies, J.; Varner, K. E.; Youngdahl, K. A. *Organometallics* **1988**, *7*, 1302. (c) Arndt, L. W. Ph. D. Thesis, Texas A&M University, May 1986.

(27) No electronic spectroscopic studies have been published on complexes with metal—metal dative bonds. However, theoretical studies suggest that the lowest energy transitions in these complexes are $\sigma \rightarrow \sigma^*$ or possibly $d\pi \rightarrow \sigma^*$ transitions. See: Nakatsuji, H.; Hada, M.; Kawashima, A. *Inorg. Chem.* **1992**, *31*, 1740. Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886—2897.

Table 1. Selected IR Data for $(Me_3P)(OC)_4OsW(CO)_5$ (1) and All Photoproducts in C_6H_6 at Room Temperature

compound	IR absorption ν(CO) bands, cm^{-1} (ϵ, L mol^{-1} cm^{-1})
$(Me_3P)(OC)_4OsW(CO)_5$	2092 (340), 2041 (1970), 2007 (6980), 1912 (7520), 1894 (2490)
$Os(CO)_4(PMe_3)$	2058 (2110), 1974 (1360), 1930 (5300)
$Os(CO)_3(PMe_3)(PPh_3)$	1881 (6870)
fac-$Os(CO)_3(PMe_3)Cl_2$	2125 (1390), 2050 (2660), 2004 (2390)
$W(CO)_6$	1976 (15500)
$W(CO)_5(PPh_3)$	2071 (1730), 1981 (423), 1937 (10500)
fac-$Os(CO)_3(PMe_3)(CH_2C_6H_5)Cl$	2098 (s), 2026 (s), 1979 (s)
fac-$Os(CO)_3(PMe_3)(CH_3)Cl$	2097 (s), 2027 (s), 1982 (s)[a]
fac-$Os(CO)_3(PMe_3)(CCl_3)Cl$	2119 (m), 2055 (m), 2010 (m)

[a] In hexane. See ref 38.

400 nm) in order to reduce the possibility of multiple excitation pathways. (Multiple pathways generally become more common as the exciting energy increases in metal–metal-bonded complexes.[9])

The results are most readily interpreted in terms of a heterolytic cleavage of the metal–metal bond in **1** to yield $Os(CO)_4(PMe_3)$ and $[W(CO)_5]$ as the initial photoproducts. The unsaturated, 16-electron $[W(CO)_5]$ fragment produced then reacts with PPh_3 to give $W(CO)_5(PPh_3)$.[28] (The mechanism for the formation of the minor product, $W(CO)_6$, will be discussed later.) A control experiment showed that $Os(CO)_4(PMe_3)$ (1.15×10^{-2} M) is photochemically converted to $Os(CO)_3(PMe_3)(PPh_3)$ in the presence of PPh_3 (1.52×10^{-1} M) under the same reaction conditions (benzene solvent; $\lambda > 400$ nm) as reaction 1.[29] This result suggests that $Os(CO)_3(PMe_3)(PPh_3)$ is formed predominantly in a secondary photochemical reaction (eq 2).

$$Os(CO)_4(PMe_3) + PPh_3 \xrightarrow[\text{benzene}]{h\nu\ (\lambda > 400\text{ nm})} Os(CO)_3(PMe_3)(PPh_3) + CO \tag{2}$$

Irradiation of $W(CO)_6$ (3.55×10^{-3} M) and PPh_3 (6.34×10^{-2} M) in deoxygenated C_6H_6 at room temperature with the same wavelengths used in eq 1 ($\lambda > 400$ nm) showed no formation of $W(CO)_5(PPh_3)$ even after 30 min of photolysis.[30] The $W(CO)_5PPh_3$ product in eq 1 is therefore not the result of a secondary reaction of $W(CO)_6$.[31]

$$\underset{\mathbf{1}}{(Me_3P)(OC)_4OsW(CO)_5} \xrightarrow[\text{benzene}]{h\nu\ (\lambda > 400\text{ nm})} \underset{82\%}{Os(CO)_4(PMe_3)} + \underset{66\%}{W(CO)_6} \tag{3}$$

The photolysis of **1** (9.08×10^{-4} M) in deoxygenated benzene without any ligands present went according to eq 3 over a 12 min period. The reaction was again monitored by infrared spectroscopy, and the products were identified by comparison to reported spectra (Table 1). In no instance was any $W(CO)_5(\eta^2\text{-}C_6H_6)$ observed in the IR spectra.[33] (Because benzene has an intense absorption in the IR spectrum close to the single ν(CO) absorption of $W(CO)_6$, it was difficult to measure the absorbance of the latter band. The concentrations of $W(CO)_6$ produced in the various reactions are thus subject to a larger than normal error.) The $W(CO)_6$ is believed to form by decomposition of some of the $[W(CO)_5]$ to give CO, which then reacts with remaining $W(CO)_5$ to give the observed product (e.g., eq 4).[34] A similar pathway was proposed to account for the formation of $W(CO)_6$ in the thermal decomposition of $[(Me)(OC)_4FeW(CO)_5^-]$ (eq 5).[26b] A maximum yield of 83% of $W(CO)_6$ would result if this were the only mechanism of formation (see below, however).

$$W(CO)_5 \longrightarrow 5\,CO + [W] \tag{4a}$$

$$CO + W(CO)_5 \longrightarrow W(CO)_6 \tag{4b}$$

$$Me(OC)_4FeW(CO)_5^- \longrightarrow MeC(O)Fe(CO)_4^- + W(CO)_6 + [W] \tag{5}$$

As a control experiment, the thermal reaction of **1** (1.1×10^{-3} M) with PPh_3 (6.0×10^{-2} M) was carried out in deoxygenated C_6H_6 under N_2 in the dark at both room temperature and 40 °C. No peaks due to products were observed in the IR spectrum of the control reaction at room temperature until 27.5 h, and signals due to **1** were still clearly visible in the spectrum after 9 days. At 40 °C, traces of $Os(CO)_4(PMe_3)$ and $W(CO)_5(PPh_3)$ were detected by IR spectroscopy after 3 h, but the absorptions of **1** were detectable up to 66 h. Even the longest photochemical experiments with **1** described in this paper were complete within 2 h, and thus the contribution of the thermal decomposition of **1** to the products can be considered negligible. Note that in the thermal control $W(CO)_5PPh_3$ and $Os(CO)_4(PMe_3)$ were the sole carbonyl-containing products. There was no evidence to suggest the presence of $Os(CO)_3(PMe_3)(PPh_3)$ or $W(CO)_6$.

Experiments Exploring the Possibility of Homolytic Cleavage. Reactions with the Radical Trap $C_6H_5CH_2Cl$. The products in eqs 1 and 3 might possibly be the result of metal–metal bond homolysis followed by fast electron transfer. To probe this possibility, a solution of **1** (1.47×10^{-3} M) in deoxygenated C_6H_6 was irradiated ($\lambda > 400$ nm) in the presence of an excess of benzyl chloride (1.47×10^{-2} M), an excellent metalloradical trap, until all of **1** had disappeared (8 min).[35] The photoproducts were identical to those in eq 3 except the yields of $W(CO)_6$ (57%) and $Os(CO)_4(PMe_3)$ (43%) were lower; no other photoproducts were observed. Furthermore, no bibenzyl was detected. (Bibenzyl is the expected organic coupling product resulting from the Cl atom abstraction from benzyl

---

[28] (a) Dennenberg, R. J.; Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 72 and references therein. (b) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.

[29] For $Os(CO)_4PMe_3$ in C_6H_6 at 400 nm, $\epsilon_{400nm} = 20$ L mol^{-1} cm^{-1}.

[30] For $W(CO)_6$ in C_6H_6, $\epsilon_{400nm} \approx 2$ L mol^{-1} cm^{-1}.

[31] When the irradiation wavelength was changed to $\lambda > 335$ nm, the following photochemical reactions were observed:[32]

$$W(CO)_6 + PPh_3 \xrightarrow{h\nu\ (\lambda > 335\text{ nm})} W(CO)_5(PPh_3) + CO$$

$$W(CO)_5(PPh_3) \xrightarrow{h\nu\ (\lambda > 335\text{ nm})} W(CO)_4(PPh_3)_2 + CO$$

[32] See ref 9a, p 68, and ref 28.

[33] Tyler, D. R.; Petrylak, D. P. *J. Organomet. Chem.* **1981**, *212*, 389.

[34] (a) Reference 9a, p 69. (b) Leventis, N.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5807. (c) Albano, V. G.; Busetto, L.; Castellari, C.; Monari, M.; Palazzi, A.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1993**, 3661.

[35] (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246. (b) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388. (c) Scott, S. L.; Espenson, J. H.; Zhu, Z. *J. Am. Chem. Soc.* **1993**, *115*, 1789.

chloride.) Continued irradiation (1 h) showed the formation of small amounts of *fac*-$Os(CO)_3(PMe_3)Cl_2$ (***fac*-2**) and the loss of $Os(CO)_4PMe_3$. (***fac*-2** is a new molecule, and its characterization will be described in a subsequent paper.[36]) A control irradiation ($\lambda > 400$ nm) of $Os(CO)_4PMe_3$ (2.17×10^{-3} M) in C_6H_6 in the presence of an excess of benzyl chloride (2.09×10^{-1} M) for 3 h gave ***fac*-2** and *fac*-$Os(CO)_3(PMe_3)(CH_2C_6H_5)$-Cl.[36,37]

Reactions with CCl_4. Complex **1** (2.18×10^{-3} M) was irradiated ($\lambda > 400$ nm) in the presence of an excess of CCl_4 (5.68×10^{-2} M) in deoxygenated C_6H_6. The reaction was monitored by infrared spectroscopy, which showed the disappearance of the starting material and the appearance of bands attributed to $W(CO)_6$ (56%) and *fac*-$Os(CO)_3(PMe_3)Cl_2$ (***fac*-2**) (72%) (eq 6; Table 1). The reaction was complete after 13 min.

$$\underset{\mathbf{1}}{(Me_3P)(OC)_4OsW(CO)_5} + CCl_4 \xrightarrow[\text{benzene}]{h\nu\ (\lambda > 400\text{ nm})} W(CO)_6 + \underset{\textbf{\textit{fac}-2}}{\textit{fac}\text{-}Os(CO)_3(PMe_3)Cl_2} \quad (6)$$

In order to explain the formation of ***fac*-2**, it was hypothesized that irradiation of $Os(CO)_4(PMe_3)$ in the presence of CCl_4 gave ***fac*-2**. To test this hypothesis, $Os(CO)_4(PMe_3)$ (5.64×10^{-3} M) was irradiated ($\lambda > 400$ nm) in the presence of an excess of CCl_4 (5.53×10^{-2} M) in deoxygenated C_6H_6. Infrared spectroscopic monitoring of the reaction, however, showed complete conversion of $Os(CO)_4(PMe_3)$ to a product thought to be $Os(CO)_3(PMe_3)(Cl)(CCl_3)$ (***fac*-3**; ν(CO) = 2119 (m), 2055 (m), and 2010 (m) cm^{-1})[36] after 32 min of irradiation (eq 7). The spectrum did not change in intensity after a further 160 min in the dark at room temperature.

$$Os(CO)_4PMe_3 + CCl_4 \xrightarrow[\text{benzene}]{h\nu\ (\lambda > 400\text{ nm})} \underset{\textbf{\textit{fac}-3}}{Os(CO)_3(PMe_3)(Cl)(CCl_3)} \quad (7)$$

The results above were puzzling because irradiation of $Os(CO)_4(PMe_3)$ in the presence of CCl_4 led to ***fac*-3** (eq 7), while the irradiation of **1** (which forms $Os(CO)_4$-(PMe_3)) led to ***fac*-2** (eq 6). These results prompted the additional experiment of irradiating $Os(CO)_4(PMe_3)$ (2.02×10^{-3} M) in deoxygenated C_6H_6 with CCl_4 (2.36×10^{-1} M) *in the presence of* $W(CO)_6$ (1.99×10^{-3} M). (Excitation wavelengths of $\lambda > 335$ nm were used in this experiment to generate $[W(CO)_5]$; recall $W(CO)_6$ does not react when it is irradiated with $\lambda > 400$ nm.) The experiment was designed to determine if the $[W(CO)_5]$ fragment promotes the formation of ***fac*-2** from ***fac*-3**. In fact, this appears to be the case. Infrared spectroscopic monitoring of the reaction showed the disappearance of the bands due to $Os(CO)_4(PMe_3)$ (after 2 min) and the formation of ***fac*-3**. With continued irradiation, conversion of ***fac*-3** to ***fac*-2** was complete in about 1 h.[39] (A control reaction showed that irradiation of ***fac*-3** at $\lambda > 335$ nm for 2 h gave no photochemical reaction. A slight thermal reaction did occur to give trace amounts of ***fac*-2**.)

No products that could be considered the result of radical fragments containing tungsten were trapped during the photolysis of **1** ($\lambda > 400$ nm) in the presence of an excess of CCl_4. The only photoproduct containing tungsten detected by IR spectroscopy was $W(CO)_6$. Species such as $[W(CO)_5Cl]^-$,[40] $[W(CO)_4(Cl)_2]$,[41] or $[W(CO)_5Cl]$,[42] which could result from the formation of W-containing radical species, were not detected.

Thermal control reactions of **1** with CCl_4 in deoxygenated C_6H_6 in the absence of light at room temperature demonstrated that the same products are produced as in the photochemical reaction (eq 6). The thermal pathway, however, is much slower; no change was detected in **1** by infrared spectroscopy until after 3.5 h. The products observed when **1** is photolyzed in the presence of CCl_4 are therefore due to a photochemical process alone and not a thermochemical pathway.[43,44]

To summarize, it is proposed that the initial product produced in the photolysis of $Os(CO)_4(PMe_3)$ in the presence of CCl_4 is ***fac*-3,** which subsequently converts to ***fac*-2**. It is known that complexes with the $M-CCl_3$ unit are unstable and readily convert to the corresponding $M-Cl$ derivative.[45] That different products are observed in the irradiation of **1** with CCl_4 or $Os(CO)_4$-(PMe_3) with CCl_4 under similar conditions appears to indicate that the $[W(CO)_5]$ fragment plays a key role in the reactivity. Just what that role is remains uncertain. It is suggested that the $W(CO)_5$ fragment may interact with CCl_4 to form a chlorinating reagent that reacts differently from CCl_4.[46] Finally, there is no evidence that metal radicals form during the irradiation of **1** in C_6H_6 in the presence of an excess of the radical traps $C_6H_5CH_2Cl$ or CCl_4.[47]

---

[36] Male, J. L.; Einstein, F. W. B.; Leong, W. K.; Pomeroy, R. K.; Tyler, D. R., submitted to *J. Organomet. Chem.*

[37] The *fac*-$Os(CO)_3(PMe_3)(CH_2C_6H_5)Cl$ (ν(C≡O) in benzene: 2098 (s), 2026 (s), and 1979 (s) cm^{-1}) was identified by comparison to *fac*-$Os(CO)_3(PMe_3)(CH_3)Cl$[38] (ν(C≡O) in hexane: 2097 (s), 2027 (s), and 1982 (s) cm^{-1}).

[38] Bellachioma, G.; Cardaci, G.; Macchioni, A.; Zanazzi, P. *Inorg. Chem.* **1993**, *32*, 547−553.

[39] Note that substantial amounts of $W(CO)_6$ still remained after this time.

[40] (a) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068. (b) King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157.

[41] Borowczak, D.; Szymanska-Buzar, T.; Ziólkowski, J. J. *J. Mol. Catal.* **1984**, *27*, 355.

[42] (a) Krausz, P.; Garnier, F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 437. (b) Krausz, P.; Garnier, F.; Dubois, J. -E. *J. Organomet. Chem.* **1976**, *108*, 197.

[43] Thermal control reactions were carried out in which **1** (1.47×10^{-3} M) was stirred in the dark with CCl_4 (1.45×10^{-1} M) in deoxygenated C_6H_6 under N_2. No change in the infrared spectrum of the reaction mixture was detected until 3.5 h, after which time trace amounts of ***fac*-2** and $W(CO)_6$ were detected in the solution. Even after 58 h at room temperature in the dark the reaction was far from complete: bands due to **1** were clearly visible. In another thermal control reaction, $Os(CO)_4(PMe_3)$ (1.79×10^{-3} M) was stirred in the dark with CCl_4 (1.45×10^{-1} M) in deoxygenated C_6H_6 under N_2. Bands attributed to ***fac*-3** were observed in the IR spectrum of the solution immediately after mixing. Continued monitoring of the reaction showed the slow disappearance of $Os(CO)_4(PMe_3)$, which was complete after 58 h. During this period all of ***fac*-3** had converted to ***fac*-2**.

[44] That the radical trapping reagents CCl_4 and $C_6H_5CH_2Cl$ reacted differently with $Os(CO)_4(PMe_3)$ may be attributed to the fact that CCl_4 is considerably more oxidizing than benzyl chloride. (See: White, R. C.; Buckles, R. E. *J. Photochem.* **1978**, *8*, 67.) Thus, oxidative addition to $Os(CO)_3(PMe_3)$ may simply be more energetically favorable in the case of CCl_4. Another possibility is that the $C_6H_5CH_2Cl$ reaction is less efficient because two molecules are required to form the product.

[45] (a) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167. (b) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 1206. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

[46] Irradiation of $W(CO)_6$ in the presence of CCl_4 has been proposed to produce a variety of chlorinating agents, including phosgene. See, for example, refs 41 and 42.

Table 2. Selected IR Data for the Irradiation of $[Bu^n{}_4N]_2[W_2(CO)_{10}]$ (4) in CH_3CN at Room Temperature

compound	IR absorption ν(CO) bands, cm^{-1}	IR media	ref
$[Bu^n{}_4N]_2[W_2(CO)_{10}]$	1940 (m), 1891 (vs), 1788 (s)[a]	CH_3CN	this work, 49
$W(CO)_6$	1975 (s)	CH_3CN	this work, 49
$[Et_4N][W(CO)_5Cl]$	2061 (w), 1904 (s), 1869 (m)	KBr	40
	2061 (w), 1904 (s), 1869 (m)	$CHCl_3$	41
$[Bu^n{}_4N][W(CO)_5Cl]$	2064 (w), 1919 (s), 1846 (m)	CH_3CN	this work
$[Et_4N][W(CO)_5Br]$	2064 (w), 1904 (s), 1868 (m)	KBr	40
	2066 (w), 1922 (s), 1851 (m)	CH_3CN	this work
$W(CO)_5(CH_3CN)$	2085 (w), 1948 (vs), 1931 (s)	C_6H_{14}	54a
	2075, 1940	CH_3CN	54a
	2078 (w), 1939 (s)	CH_3CN	this work
cis-$W(CO)_4(CH_3CN)_2$	2024 (m), 1900 (vs), 1842 (s)	CH_3CN	54a
trans-$W(CO)_4(CH_3CN)_2$	1898 (s)	CH_3CN	49
$W(CO)_4(CH_3CN)_2$	2020 (vw), 1898 (m), 1840 (w)	CH_3CN	this work

[a] Relative intensities of the IR absorption bands: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

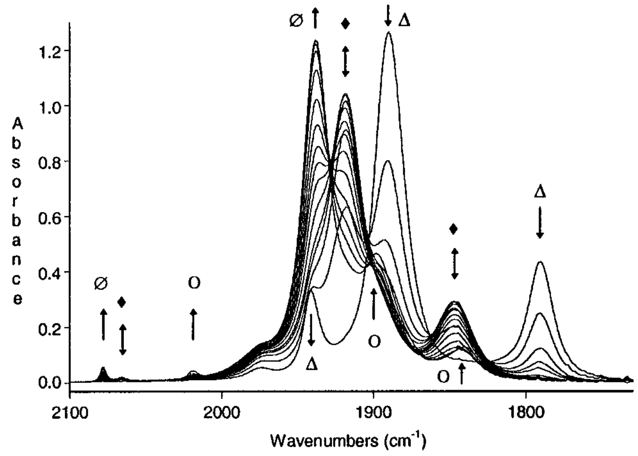


Figure 2. Irradiation ($\lambda > 400$ nm) of $[Bu^n{}_4N]_2[W_2(CO)_{10}]$ (**4**) (9.52×10^{-3} M) in CH_3CN in the presence of an excess of $C_6H_5CH_2Cl$ (9.99×10^{-1} M). The time scale of the reaction was 0−1 min utilizing a 200 W high-pressure mercury arc lamp. The species are identified as follows: Δ = $[W_2CO_{10}]^{2-}$; ♦ = $[W(CO)_5Cl]^-$ (the initial photoproduct); Ø = $W(CO)_5(CH_3CN)$ (product of secondary photochemistry); O = $W(CO)_4(CH_3CN)_2$ (product of secondary photochemistry).

Photoreactions of $[W_2(CO)_{10}{}^{2-}]$. In order to probe whether CCl_4 or $C_6H_5CH_2Cl$ could capture $[W(CO)_5{}^{\bullet -}]$ if it were to form, $[Bu^n{}_4N]_2[W_2(CO)_{10}]$ (**4**) was irradiated ($\lambda > 400$ nm) in CH_3CN in the presence of these traps.[48] Acetonitrile was used as a solvent because **4** is not sufficiently soluble in C_6H_6 to give a satisfactory IR spectrum. Irradiation ($\lambda > 400$ nm) of **4** (9.52×10^{-3} M) in deoxygenated CH_3CN in the presence of an excess of $C_6H_5CH_2Cl$ (9.99×10^{-1} M) caused the complete disappearance of **4** within 10 s and the emergence of $W(CO)_5Cl^-$ and $W(CO)_5(CH_3CN)$ (eq 8). Upon further irradiation for 50 s, the $W(CO)_5Cl^-$ was completely converted to $W(CO)_5(CH_3CN)$ and trace amounts of $W(CO)_4(CH_3CN)_2$ (Figure 2). The products were identified by IR spectroscopy (Table 2).[51] As in complexes containing nondative metal−metal bonds, it is suggested that irradiation of **4**[55] leads to homolysis of the W−W bonds to form $[W(CO)_5{}^{\bullet -}]$, and this radical subsequently reacts with $C_6H_5CH_2Cl$ in an atom abstraction reaction to form $[W(CO)_5Cl^-]$.

$$\underset{\mathbf{4}}{W_2(CO)_{10}{}^{2-}} + C_6H_5CH_2Cl \xrightarrow[CH_3CN]{h\nu\ (\lambda > 400\ \mathrm{nm})}$$

$$2\,W(CO)_5Cl^- \xrightarrow[CH_3CN]{h\nu\ (\lambda > 400\ \mathrm{nm})} W(CO)_5(CH_3CN) \quad (8)$$

Because the secondary photolysis of $W(CO)_5Cl^-$ is so fast, it might be suggested that if $W(CO)_5Cl^-$ were produced in the reaction of **1** with benzyl chloride, then it might not be observed. However, $Os(CO)_4(PMe_3)Cl^+$ or $Os(CO)_3(PMe_3)Cl_2$ would also be formed in the reaction.[56] Recall that the primary Os-containing product was $Os(CO)_4PMe_3$, which upon secondary photolysis *slowly* yielded ***fac*-2**. These experiments therefore strongly suggest that homolysis of the Os-W bond in **1** does not occur.

The photochemical reaction of **4** (9.8×10^{-3} M) was also attempted in CH_3CN with CCl_4 (9.4 × 10−1 M) as a radical trap. The CCl_4, however, immediately reacted with **4**, without exposure to light. Infrared spectroscopy

---

(47) Experiments were also carried out with the radical trap 1,1,3,3-tetramethylisoindoline-2-oxyl, TMIO (see: Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632). One of the advantages of using TMIO is that when it interacts with a metal radical the TMIO does not generate new radicals that can then undergo further chemistry, unlike CCl_4 or $C_6H_5CH_2Cl$. Photolysis ($\lambda > 400$ nm) of **1** (1.53×10^{-3} M) in deoxygenated C_6H_6 at room temperature in the presence of an excess of TMIO (6.86×10^{-3} M) gave $W(CO)_6$ (22%) and $Os(CO)_4(PMe_3)$ (75%), which are identical to the products formed in the photolysis of **1** in the absence of any other reagent and similar to the initial products formed by irradiation of **1** and $C_6H_5CH_2Cl$.

(48) It has been previously proposed that **4** cleaves to yield $[W(CO)_5{}^{\bullet -}]$ radicals upon photolysis.[49,50]

(49) (a) Silavwe, N. D.; Pan, X.; Tyler, D. R. *Inorg. Chim. Acta* **1988**, *144*, 123. (b) Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. *Inorg. Chem.* **1989**, *28*, 1231.

(50) Phillips, J. R.; Trogler, W. C. *Inorg. Chim. Acta* **1992**, *198*, 633.

(51) The yellow compound $[Et_4N][W(CO)_5Cl]$ has its lowest energy electronic absorption band maximum at 417 nm ($\epsilon = 3.10 \times 10^3$ L mol^{-1} cm^{-1}) in methanol,[52] and $[Bu^n{}_4N][W(CO)_5Cl]$ would not be expected to display vastly different absorption characteristics in CH_3CN due to the slight modification of the cation or the solvent. Irradiation at $\lambda >$ 400 nm, in the aforementioned reaction, would therefore photoexcite $[W(CO)_5Cl]^-$. Irradiation ($\lambda > 436$ nm) of $[W(CO)_5Br]^-$ at 280 K in CO saturated $CHCl_3$ is known to yield $W(CO)_6$.[53] The analogous reaction where CH_3CN is the entering ligand into $[W(CO)_5]$ would, therefore, appear plausible, particularly since the concentration of CH_3CN is greater than that of CO. The complex $W(CO)_5(CH_3CN)$ could then undergo further photochemical substitution to yield $W(CO)_4(CH_3CN)_2$. It is known that upon photolysis of $W(CO)_6$, at higher energy wavelengths, a mixture of $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$ is formed quickly.[54]

(52) McLean, R. A. N. *J. Chem. Soc., Dalton Trans.* **1974**, 1568.

(53) (a) Dahlgren, R. M.; Zink, J. I. *J. Chem. Soc., Chem. Commun.* **1978**, 863. (b) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154−3161.

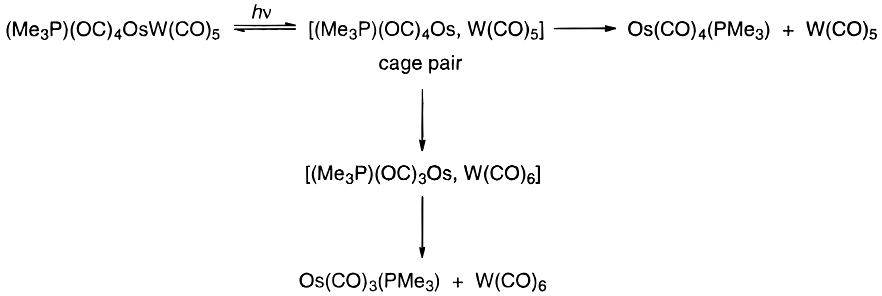
(54) (a) Dobson, G. R.; Amr El Sayed, M. F.; Stolz, I. W.; Sheline, R. K. *Inorg. Chem.* **1962**, *1*, 526. (b) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730.

(55) Compound **4** has absorption band maxima at 347 nm ($\epsilon = 7.21 \times 10^3$ L mol^{-1} cm^{-1}) and 390 nm (shoulder, $\epsilon = 4.84 \times 10^3$ L mol^{-1} cm^{-1}) in CH_3CN.[49]

(56) Although the stability of this complex is unknown, $Os(CO)_4(PMe_3)CH_3{}^+$ [38] and $Os(CO)_5Cl^+$ [57] are known and are stable in solution.

(57) Rushman, P.; Van Buuren, G. N.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693−694.

Scheme 1



showed the formation of [W(CO)$_5$Cl]$^-$, W(CO)$_6$, and W(CO)$_5$(CH$_3$CN) (Table 1).[58]

Metal–Ligand Bond Dissociation. Irradiation (λ > 400 nm) of **1** (2.96×10^{-3} M) in a CO-saturated C$_6$H$_6$ solution (7.4×10^{-3} M)[61] at room temperature gave Os(CO)$_4$(PMe$_3$) (81%) and W(CO)$_6$ (74%), analogous to eq 3. Recall that when **1** was irradiated (λ > 400 nm) in the absence of any ligand, W(CO)$_6$ was formed in 66% yield (eq 3). The increased yield in the presence of CO is similar to the increase in the amount of W product formed in the presence of PPh$_3$, where 89% tungsten-containing products were detected (eq 1). The quantum yield[62] for disappearance in the photoreaction (λ = 368 nm) of **1** in deoxygenated benzene under 1 atm of N$_2$ at 23 ± 1 °C was determined to be 0.13 ± 0.01. Under the same conditions but with 1 atm of CO, the quantum yield *increased* to 0.28 ± 0.05. If the initial photoprocess was loss of a CO or PMe$_3$ ligand, then the initial process would be inhibited and the quantum yield for the disappearance of **1** would be reduced in the presence of an excess of free ligand such as CO or PPh$_3$. That the quantum yield under CO *increases* strongly suggests that the initial step in the photolysis is not M–CO bond cleavage. Furthermore, irradiation of **1** in deoxygenated C$_6$H$_6$ in the presence of excess PPh$_3$ (eq 1) did not yield [OsW(CO)$_8$(PMe$_3$)(PPh$_3$)], which might be expected if M–CO dissociation occurred. These results further support the view that heterolysis of the Os–W bond results from the excitation of **1**. In the presence of CO, the recombination of the fragments from the heterolysis would be inhibited because the [W(CO)$_5$] fragment would be trapped by CO rather than recombine with Os(CO)$_4$PMe$_3$. This would increase the quantum yield for the disappearance of **1**, as observed.

Formation of W(CO)$_6$. The results discussed to this point are all consistent with a Os–W heterolytic photoprocess. However, a heterolytic pathway does not necessarily account for the formation of W(CO)$_6$ in eq 1. This section discusses several experiments designed to probe how W(CO)$_6$ is formed. As indicated in eq 1, W(CO)$_6$ was formed in about 8% yield even in the presence of a large excess of PPh$_3$ ([**1**]:[PPh$_3$] 1:115, [PPh$_3$] = 1.91×10^{-1} M).[63] A possible mechanism for the formation of W(CO)$_6$ is that it results from CO abstraction by W(CO)$_5$ from Os(CO)$_4$(PMe$_3$) in the geminate caged intermediate [Os(CO)$_4$(PMe$_3$), W(CO)$_5$] (Scheme 1).[64] The high reactivity of W(CO)$_5$ and its ability to abstract ligands from other moieties has ample precedent.[26b,28,33,34] To probe this possibility, the photolysis (λ > 400 nm) of **1** (1.22×10^{-3} M) was repeated in a more viscous medium of biphenyl (2.87 M) in C$_6$H$_6$ at 25 °C (absolute viscosity 1.2 cP as compared to C$_6$H$_6$ absolute viscosity 0.601 cP at 25 °C[65,66]) in the presence of an excess of PPh$_3$ (1.36×10^{-1} M). If W(CO)$_6$ is formed in a geminate cage reaction, then, in a more viscous medium, cage escape should be hindered and the yield of W(CO)$_6$ should be increased. However, the reaction in the more viscous solvent gave the same yield of W(CO)$_6$ (8%). The reaction was also carried out under similar conditions but with mineral oil added to C$_6$H$_6$ to create the more viscous solvent (mineral oil 30.3% v/v in C$_6$H$_6$ at 28 °C (absolute viscosity 1.1 cP)). When this solvent system was used, the yield of W(CO)$_6$ was again 8%.[67] These experiments strongly suggest that a CO abstraction mechanism taking place in a caged intermediate is not responsible for the formation of the W(CO)$_6$.

Another possible origin of the W(CO)$_6$ is that it forms in a reaction of W(CO)$_5$ with the CO that is liberated during the secondary photolysis of Os(CO)$_4$(PMe$_3$). To

---

[58] It has been reported that the electrochemical oxidation of **4** in THF in the presence of an excess of CH$_2$Cl$_2$ with a supporting electrolyte of tetrabutylammonium perchlorate gave W(CO)$_5$(THF) and [W(CO)$_5$Cl]$^-$ as the products.[50] The electron affinity of CCl$_4$ (2.12 eV, first $E_{1/2} = -0.25$ V in DMF with [Bu$^n{}_4$N][Br] as supporting electrolyte) is much greater than that of CH$_2$Cl$_2$ (1.32 eV, first $E_{1/2} = -2.14$ V in DMF with [Bu$^n{}_4$N][Br] as supporting electrolyte).[59,60] Thus if there were an electron transfer reaction and the process involved an oxidation/reduction couple, CCl$_4$ would be more reactive than CH$_2$Cl$_2$. One possible explanation for the products observed would be that **4** forms a charge-transfer complex with CCl$_4$ in the polar solvent CH$_3$CN in the dark which yields [W(CO)$_5$Cl]$^-$ and W(CO)$_5$(CH$_3$CN), analogous to the electrochemical reaction of **4** and CH$_2$Cl$_2$ mentioned above. It was shown that, after the photolysis of W(CO)$_6$ in CH$_3$CN, if the reaction mixture was allowed to remain in the dark at room temperature, then substantial quantities of W(CO)$_6$ were re-formed.[54a] This implies that an equilibrium exists between the W(CO)$_6$ and W(CO)$_5$(CH$_3$CN) species, and this may explain the presence of W(CO)$_6$ in the reaction of **4** with CCl$_4$.

[59] Wawzonek, S.; Duty, R. C. *J. Electrochem. Soc.* **1961**, *108*, 1135.

[60] Briegleb, G. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 617.

[61] Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids—A Critical Evaluation of Gas/Liquid Systems in Theory and Practice*; John Wiley & Sons: Chichester, 1991; pp 2, 277.

[62] Typical concentrations of **1** for the quantum yield measurements were 2.90×10^{-4} M. The quantum yields were measured at 368 nm in order to obtain the maximum absorption possible for species **1** while seeking to avoid problems with absorptions due to products (for W(CO)$_6$ at 368 nm, ϵ = 220 L mol^{-1} cm^{-1}, for Os(CO)$_4$(PMe$_3$) at 368 nm, ϵ = 98 L mol^{-1} cm^{-1} in C$_6$H$_6$ at room temperature). Less than 15% of the bimetallic complex **1** was allowed to react in these measurements. Note that the quantum yields reported in this paper differ from those reported in ref 23 by a factor of 2.23. We used an incorrect quantum yield for the Aberchrome 540 actinometer in our prior calculations.

[63] The yield of W(CO)$_6$ was essentially unchanged at 7% when the ratio of the concentrations was altered ([**1**]:[PPh$_3$] = 1:10; [PPh$_3$] = 1.83×10^{-2} M).

[64] Covert, K. J.; Askew, E. F.; Grunkemeier, J.; Koenig, T.; Tyler, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 10446.

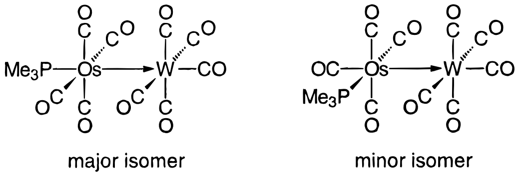
[65] Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: Oxford, 1994; p 833, C27.

[66] Lide, D. R. *Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boston, 1990; pp 6–142.

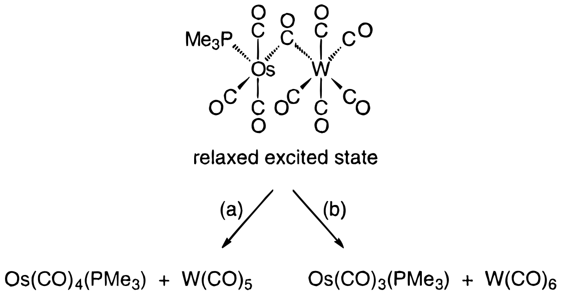
[67] In the latter reaction, concerns arose over the possibility of preferential solvation of the photoproducts due to the differences in polarity and shape of mineral oil and C$_6$H$_6$. This problem was believed to be less of a problem with the biphenyl/C$_6$H$_6$ solvent system because of the similar natures of the solvent and the viscosity enhancer.

test this possibility, $Os(CO)_4(PMe_3)$ (1.81×10^{-3} M) and $W(CO)_5(PPh_3)$ (1.58×10^{-3} M) were irradiated ($\lambda > 400$ nm) in benzene at room temperature in the presence of PPh_3 at a concentration similar to that used in reaction 1 (1.85×10^{-1} M). ($W(CO)_5(PPh_3)$ was used as the source of $W(CO)_5$ in this experiment rather than $W(CO)_6$ because $W(CO)_6$ is the potential product of the reaction. Note that irradiation of $W(CO)_5(PPh_3)$ at $\lambda = 405$ nm is claimed to generate $W(CO)_5$.[53] Also, recall that $W(CO)_6$ will not react photochemically with PPh_3 for $\lambda > 400$ nm.) The reaction was monitored by infrared spectroscopy, which showed the disappearance of the starting material bands and the appearance of new bands at 1881 cm^{-1} assigned to $Os(CO)_3(PMe_3)(PPh_3)$ (Table 1) and at 2018, 1920, and 1898 cm^{-1} assigned to $W(CO)_4(PPh_3)_2$.[68] There was no band at 1976 cm^{-1}, however, that would indicate the formation of $W(CO)_6$. (If small amounts of $W(CO)_6$ were formed, it would likely have been detected because the molar absorption coefficient of the absorption at 1976 cm^{-1} is large; Table 1.) This result suggests that, under the reaction conditions in eq 1, CO is not competitive with PPh_3 in its reactions with $W(CO)_5$.

Other possibilities for the formation of $W(CO)_6$ are based on the supposition of two different excited states. There are two isomers of $(Me_3P)(OC)_4OsW(CO)_5$ in solution,[69] one with the phosphine ligand *trans* to the metal−metal bond (major isomer) and the other with the phosphine ligand *cis* to the metal−metal bond (minor isomer).[7,25] The isomers are in dynamic equilibrium in solution at room temperature.[7,25] Irradiation of the two isomers of **1** would produce two slightly different Franck−Condon excited states. The two Franck−Condon states could relax differently, one to give the major products (i.e., $Os(CO)_4(PMe_3)$ and $[W(CO)_5]$) and the other to give $[(Me_3P)(OC)_3Os(\mu\text{-}CO)W(CO)_5]$ (Scheme 2). The intermediate with the bridging CO ligand could then cleave to yield $W(CO)_6$ and $[Os(CO)_3(PMe_3)]$ (route b, Scheme 2). The latter unsaturated complex would then react to form $[Os(CO)_3(PMe_3)(PPh_3)]$. This mechanism is consistent with the results from the reaction carried out in a more viscous medium because a caged pair is not required. It should be pointed out that the singly bridged intermediate could cleave the other way (route a, Scheme 2) to produce $Os(CO)_4(PMe_3)$ and $[W(CO)_5]$; that is, it could also account for the major products formed in the photolysis.



Scheme 2



Pathway b in Scheme 2 cannot account for the 66% yield of $W(CO)_6$ that is formed in the photolysis of **1** in the absence of an incoming ligand (eq 3). (This result can be stated with certainty because $W(CO)_6$ does not absorb light at the wavelengths used in this experiment. Thus, $W(CO)_6$ yields would be 66% in the presence of ligands if pathway b were followed exclusively.) The major production of $W(CO)_6$ (eq 3) is believed to be from the reaction of $[W(CO)_5]$ with CO arising from partial decomposition of $[W(CO)_5]$[26b] (eq 4) or by $[W(CO)_5]$ abstracting a CO from other species present.[34]

The relaxed excited state in Scheme 2 might have two bridging CO ligands rather than one. A similar transition state species, although containing an Os−W dative metal−metal bond, was proposed to account for the nonrigidity and thermal decomposition products of $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W).[7,25] There are again two decomposition pathways for a species with two bridging CO ligands: Symmetric cleavage of the $Os(\mu\text{-}CO)_2W$ unit (pathway a) would yield $Os(CO)_4(PMe_3)$ and $[W(CO)_5]$ and asymmetric cleavage (pathway b) would give $W(CO)_6$ and $[Os(CO)_3(PMe_3)]$. As before, the formation of $W(CO)_6$ by route b would be independent of the presence of PPh_3 and viscosity of the medium. Note that there are precedents for the asymmetric cleavage of a bimetallic species with two bridging CO ligands in both thermal[70] and photochemical reactions.[71]

Conclusions. The photochemical reactions of **1** in C_6H_6 can be interpreted in terms of the heterolytic cleavage of the metal−metal bond. Irradiation ($\lambda > 400$ nm) of **1** in C_6H_6 in the presence of an excess of PPh_3 yielded predominantly $Os(CO)_4(PMe_3)$, $W(CO)_5(PPh_3)$, and a secondary photochemical product, $Os(CO)_3(PMe_3)(PPh_3)$. Attempts to trap radicals that would be produced by homolytic cleavage of the metal−metal bond were unsuccessful. Although this latter result does not eliminate a homolytic route, in conjunction with the PPh_3 experiments, it strongly suggests that homolysis does not occur. Quantum yield determinations for the disappearance of **1** in C_6H_6 under N_2 and under CO demonstrated that the quantum yield increased in the presence of CO. This result provides evidence that metal−ligand photodissociation is not the reaction pathway in the photolysis of **1**.

Experimental Section

General Methods. All manipulations were performed under nitrogen or argon by using standard Schlenk, drybox,

---

(68) (a) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876. (b) Darensbourg, D. J.; Bischoff, C. J. *Inorg. Chem.* **1993**, *32*, 47.

(69) The ratio of the isomers was determined by the integration of the two sets of doublets in the ^1H NMR spectrum in C_6D_6 over the range 6−26 °C. At 26 °C, the ^1H NMR spectrum of **1** showed a minor isomer with $\delta = 0.83$ (d, Me, 9H, $^2J_{P-H} = 10.2$ Hz) and a major isomer with $\delta = 0.63$ (d, Me, 9H, $^2J_{P-H} = 10.3$ Hz). The major:minor isomer ratio was 2.6:1.0. At 6 °C, the major:minor isomer ratio was 2.7:1.0. There seems, therefore, to be little variation in the ratio of the isomers in the temperature range 6−26 °C, the temperature range expected during the photolysis of **1**. For this reason, the determination of the potentially different molar absorption coefficients of the two isomers of **1** in this solvent was not possible. Carrying out the studies at a higher temperature would increase the probability of thermal reactions occurring in conjunction with photochemical reactions.

(70) Leonhard, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 649.

(71) Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 1779.

or vacuum line techniques, unless stated otherwise. Drybox manipulations were carried out using a Vacuum Atmospheres HE-493 Dri-Lab with attached Dri-Train.

Materials. Tetrahydrofuran was freshly distilled from potassium benzophenone ketyl, hexanes and benzene were distilled from potassium, dichloromethane and acetonitrile were distilled from calcium hydride, and carbon tetrachloride was distilled from P_2O_5 twice and used immediately with minimum exposure to light. Benzyl chloride was refluxed with $MgSO_4$ and then fractionally distilled under reduced pressure; the middle fraction was collected. Triphenylphosphine was recrystallized from hexanes and stored under nitrogen in the dark. TMIO was freshly sublimed at 35 °C and 1×10^{-4} mmHg prior to usage.[72] Bibenzyl was recrystallized from 30−60 °C petroleum ether; mineral oil (345/350 viscosity; specific gravity at 25 °C, 0.865−0.925) was stirred with sodium overnight and then filtered under N_2 and finally subjected to three freeze−pump−thaw cycles prior to usage. Carbon monoxide gas (Linde/Union Carbide, C. P. grade) was used as provided. The complexes $(Me_3P)(OC)_4OsW(CO)_5$, (**1**),[7] $Os(CO)_3(PMe_3)(PPh_3)$,[25] and $W(CO)_5(PPh_3)$[7,26,73] were prepared according to the literature and recrystallized from C_6H_{14}/CH_2Cl_2. The mononuclear complex $Os(CO)_4(PMe_3)$[74] was prepared according to the literature method except that a temperature of 360 ± 24 °C was employed.[74] $[Bu^n{}_4N]_2[W_2(CO)_{10}]$ (**4**) was prepared by a literature route.[75,76]

Instrumentation. Infrared spectra were measured by using a Bomem Michelson model 120 FT-IR instrument, a Nicolet 5DXB FT-IR spectrometer, a Nicolet Magna 550 FT IR spectrometer, or a Perkin-Elmer 983G IR spectrophotometer. Samples were prepared as solutions usually in NaCl (path length 0.0965 or 0.442 mm) or CaF_2 (path length 0.116 or 0.105 mm) cells. For mechanistic work, a known amount of solid was dissolved in the deoxygenated solvent containing known quantities of other reagents, if appropriate, and transferred to the IR cell via a gastight syringe.

Solution UV−vis spectra were measured with a Perkin-Elmer Lambda 6 series UV−vis spectrophotometer, a (Varian) Cary 210 UV−vis spectrophotometer, or a Hewlett-Packard 8452A diode array spectrophotometer. All NMR data were recorded at the temperatures specified on a Bruker AMX 400. The variable temperature ^1H NMR spectra of **1** in C_6D_6 at 6, 11, 16, 21, and 26 °C were allowed 20 min to equilibrate at the desired temperature in the 5 mm tube prior to collection of the data. The temperature controller of the spectrometer had previously been calibrated by using both a thermocouple and a method based on the chemical shifts of methanol.[77] The temperature values were found to be accurate to ±1 °C.

Photochemical reactions were carried out with an Oriel 200 W or an Oriel 100 W high-pressure mercury arc lamp with a 10 cm water filter with quartz windows to reduce IR emissions. Corning glass filters were used for broad band irradiations: CS 3-73 ($\lambda > 420$ nm), CS 3-74 ($\lambda > 400$ nm), CS 3-75 ($\lambda > 365$ nm), CS 4-72 ($\lambda > 335$ nm). Solutions for mechanistic experiments were scrupulously protected from extraneous light. Quantum yield determinations were carried out with an Oriel 200 W high-pressure mercury arc lamp coupled with a Beckman DU monochromator and a Merlin radiometer system, model 70100 (Oriel Corp.).[78] Light intensity was determined by actinometry using Aberchrome 540 in toluene ($\phi_{368} = 0.20$).[79] The cuvettes used for the quantum yield determinations were 1 cm in pathlength and had freeze−pump−thaw side arms. The solutions (of 4.00 mL volume) were stirred using magnetic stir bars during the irradiation. The quantum yields at 368 nm (lamp intensities were typically $I_a = (2.28 \pm 0.01) \times 10^{-10}$ einsteins s^{-1}) were determined by the initial (<15%) rates of disappearance of the UV-vis absorption band maximum at 368 nm in complex **1**. The cuvettes were maintained at 23 ± 1 °C; a flow of compressed air was passed through the cell holder during the photolysis to prevent warming and thermal reaction.[64] All quantum yields were corrected with a linear correction factor for nonabsorption. Kinematic viscosities of the solutions were measured with a calibrated Cannon−Fenske viscometer and corrected to absolute viscosities. Yields of the products were determined from the absorbances of appropriate CO stretches in the infrared spectra of the solutions. All products were independently synthesized to obtain their extinction coefficients.

The preparation and characterization of *fac*-$Os(CO)_3(PMe_3)(Cl)_2$ (***fac*-2**) and $Os(CO)_3(PMe_3)(CCl_3)(Cl)$ (***fac*-3**) will be discussed in a forthcoming paper.[36]

Acknowledgment is made to the U.S. National Science Foundation and the Natural Sciences and Engineering Research Council of Canada for financial support of this research. We also thank Dr. H. B. Davis for assistance in the initial stages of this study.

Supporting Information Available: Nine figures showing the infrared spectroscopic changes for the reactions reported herein (4 pages). Ordering information is given on any current masthead page.

OM970275W

---

(72) (a) Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397. (b) See also ref 47.

(73) (a) Matthews, C. N.; Magee, T. A.; Wotiz, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 2273. (b) Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200.

(74) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

(75) Ungurenasu, C.; Palie, M. *J. Chem. Soc., Chem. Commun.* **1975**, 388.

(76) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

(77) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(78) Lindfors, B. E.; Nieckarz, G. F.; Tyler, D. R.; Glenn, A. G. *J. Photochem. Photobiol.* **1996**, *94*, 101.

(79) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.