

## Photochemical Heterolysis of the Metal-Metal Bond in $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$

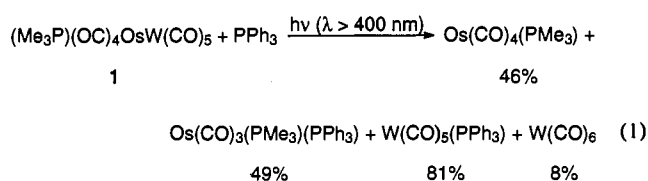
Jonathan L. Male,<sup>†</sup> Harry B. Davis,<sup>†</sup>  
Roland K. Pomeroy,<sup>†</sup> and David R. Tyler<sup>\*‡</sup>

Departments of Chemistry, University of Oregon  
Eugene, Oregon 97403  
Simon Fraser University, Burnaby  
British Columbia, Canada V5A 1S6

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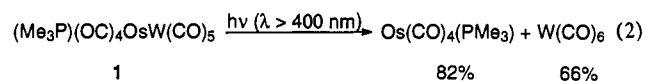
Metal-metal bond heterolysis is an elusive primary photoprocess in the photochemistry of metal carbonyl dimers.<sup>1</sup> Photoinduced heterolytic cleavage of metal-metal bonds<sup>2</sup> has been suggested in several systems,<sup>3-5</sup> but mechanistic confirmation is generally lacking. In several cases, proposed heterolyses were shown to actually involve homolytic fission followed by electron transfer.<sup>6,7</sup> Photochemical heterolyses are, however, well established in reactions not involving metal-metal bonds. For example, metal-ligand bond cleavage reactions from dd excited states are typically heterolytic.<sup>8</sup> All photochemical investigations of metal-metal-bonded dimers to date have been carried out on molecules with nondative covalent metal-metal bonds. Because heterolyses are typically observed in systems with dative bonds, we were prompted to investigate the photolysis of molecules that contain dative metal-metal bonds.<sup>9</sup> In this communication, we report the photochemistry of  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  (**1**), a molecule with a putative metal-metal dative bond (i.e., Os→W).<sup>9c</sup> The photolysis products are consistent with heterolysis of the metal-metal bond. It is also shown that metal-metal bond homolysis and M-CO dissociation, two processes that normally occur in the photolyses of metal carbonyl dimers,<sup>1</sup> are probably not occurring with low-energy excitation. Overall, the results presented herein further illustrate the difference in chemistry and bonding between complexes with dative covalent metal-metal bonds and complexes with nondative covalent metal-metal bonds.

Strong evidence for heterolytic cleavage comes from photochemical experiments carried out in the presence of a large excess of triphenylphosphine. The photochemical reaction of **1** ( $1.66 \times 10^{-3}$  M) with  $\text{PPh}_3$  ( $1.91 \times 10^{-1}$  M) in deoxygenated benzene proceeded according to eq 1.<sup>10</sup> The products were identified by



infrared and, where appropriate, electronic absorption spectroscopy.<sup>11</sup> Note the nearly quantitative conversion of  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  to the two Os products and to  $\text{W}(\text{CO})_5(\text{PPh}_3)$  and  $\text{W}(\text{CO})_6$ . This result is most readily interpreted in terms of a heterolytic primary photoprocess to give  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  and  $\text{W}(\text{CO})_5$ . Control experiments showed that  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  is photochemically converted to  $\text{Os}(\text{CO})_3(\text{PMe}_3)(\text{PPh}_3)$  under identical reaction conditions, implying that the latter product is formed in a secondary photochemical reaction in eq 1. The  $\text{W}(\text{CO})_5$  fragment, a 16-electron species, would be scavenged by  $\text{PPh}_3$  to give  $\text{W}(\text{CO})_5(\text{PPh}_3)$ . (The mechanism of  $\text{W}(\text{CO})_6$  formation is discussed below.) Control experiments also showed that  $\text{PPh}_3$  did not react thermally with  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  on the time scale of the photochemical experiments.<sup>12</sup>

The products in eq 1 could conceivably be the results of a homolytic photoprocess that is followed by a fast electron transfer. To check this possibility, experiments were carried out to trap the radical products of homolytic cleavage. Homolysis of the Os-W bond in **1** would yield  $[\text{Os}(\text{CO})_4(\text{PMe}_3)]^{+\bullet}$  and  $[\text{W}(\text{CO})_5]^{-\bullet}$  radicals. However, all experiments aimed at trapping these radicals were unsuccessful. Thus, irradiation of **1** ( $1.47 \times 10^{-3}$  M) in deoxygenated benzene that contained excess ( $1.4 \times 10^{-2}$  M) benzyl chloride (a good metal-radical trap<sup>13</sup>) gave as the only metal carbonyl products those shown in eq 2. Identical



products were obtained in the absence of benzyl chloride. In addition, no bibenzyl was detected in the experiment with benzyl chloride. As a control experiment, the irradiation of  $[n\text{-Bu}_4\text{N}]_2[\text{W}_2(\text{CO})_{10}]$  (**2**) in  $\text{CH}_3\text{CN}$  ( $\lambda > 420$  nm) was carried out to generate  $[\text{W}(\text{CO})_5]^{-\bullet}$  radicals.<sup>14</sup> Irradiation of a solution of **2** (0.011 M) and benzyl chloride (0.89 M) in  $\text{CH}_3\text{CN}$  for 1.5 min gave  $[\text{W}(\text{CO})_5\text{Cl}]^{-}$  as the only metal-containing product. Al-

<sup>†</sup> Simon Fraser University.

<sup>‡</sup> University of Oregon.

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(6) The disproportionation reactions of many dimers follow a pathway involving homolysis, followed by coordination of a ligand to form a 19-electron adduct, and then electron transfer. See: (a) Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032-6037. (b) Stieglitz, M.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217-240.

(7) Stufkens and Oskam have reported several instances where heterolytic products are the result of photochemical homolysis followed by direct 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.

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

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(10) The lowest energy electronic absorption band in **1** is at 368 nm ( $\epsilon = 2790 \text{ M}^{-1} \text{ cm}^{-1}$ ) in benzene solution. By analogy to the dimers with nondative covalent metal-metal bonds,<sup>1</sup> this band is assigned to the metal-metal bond  $\sigma \rightarrow \sigma^*$  transition. Photochemical irradiations for this study were carried out into the low-energy tail of this band ( $\lambda > 400$  nm). Quantum yields were measured at 368 nm. So as to avoid any problems with product absorptions, less than 15% of the dimer was allowed to react in these measurements.

(11) Product yields were determined using infrared spectroscopy by comparing product peak areas to those of authentic samples of known concentrations. The  $\nu(\text{CO})$  bands for the photoproducts are as follows:  $\text{Os}(\text{CO})_4(\text{PMe}_3)$ , 2058 (m), 1974 (m), 1930 (s);  $\text{W}(\text{CO})_6$ , 1976 (vs);  $\text{W}(\text{CO})_5(\text{PPh}_3)$ , 2071 (m), 1981 (w, sh), 1937 (vs);  $\text{Os}(\text{CO})_3(\text{PMe}_3)(\text{PPh}_3)$ , 1881 (vs). Note that the yield of  $\text{W}(\text{CO})_6$  is essentially unchanged (7%) when  $[\text{PPh}_3] = 0.018 \text{ M}$ .

(12) In a previous study, qualitative results showed that **1** reacted with  $\text{PPh}_3$  slowly at room temperature to yield products consistent with heterolytic cleavage of the metal-metal bond.<sup>9c</sup> This reaction was repeated under greater scrutiny; the thermal reaction of **1** ( $1.1 \times 10^{-3}$  M) with  $\text{PPh}_3$  ( $6.0 \times 10^{-2}$  M) in deoxygenated benzene under  $\text{N}_2$ , in the dark, was studied at room temperature and at 40 °C. No products were observed in the control reaction at room temperature even after 24 h. At 40 °C, traces of  $\text{W}(\text{CO})_5(\text{PPh}_3)$  and  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  were detected by infrared spectroscopy after 3 h. Even the longest of the photochemical experiments described herein was over within 60 min.

(13) (a) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388-391. (b) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246-4251.

(14) It has previously been proposed that irradiation of  $[\text{W}_2(\text{CO})_{10}]^{2-}$  yields  $[\text{W}(\text{CO})_5]^{-\bullet}$  radicals. See: (a) Silavwe, N. D.; Pan, X.; Tyler, D. R. *Inorg. Chim. Acta* **1988**, *144*, 123-128. (b) Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. *Inorg. Chem.* **1989**, *28*, 1231-1236. (c) Phillips, J. R.; Troglor, W. C. *Inorg. Chim. Acta* **1992**, *198*, 633-638.

though the inability to capture  $[\text{W}(\text{CO})_5]^-$  radicals in the irradiation of **1** does not necessarily imply that the radicals are not forming, the ease with which  $[\text{W}(\text{CO})_5]^-$  was captured in the control experiment strongly suggests that if the radicals were to form during the irradiation of **1**, they could be trapped.

Quantum yield measurements showed that M–CO bond dissociation is also an unlikely photoprocess. Thus, irradiation of  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  in deoxygenated benzene solution under 1 atm of  $\text{N}_2$  gave the products indicated in eq 2 with a quantum yield of 0.059.<sup>10</sup> Under 1 atm of CO, the quantum yield for the disappearance of **1** increased to 0.13 (and the yield of  $\text{W}(\text{CO})_6$  increased to 80%). This increase in the quantum yield under CO almost certainly rules out an initial step involving M–CO bond cleavage because inhibition of the reaction would result if this were the pathway.<sup>15</sup>

As indicated in eq 1,  $\text{W}(\text{CO})_6$  forms in about 8% yield, even in the presence of a large excess of  $\text{PPh}_3$ . A geminate cage reaction,<sup>16</sup> involving CO abstraction by  $\text{W}(\text{CO})_5$  from  $\text{Os}(\text{CO})_4(\text{PMe}_3)$ , is one interpretation of this result. To check this possibility, the photolysis shown in eq 1 was repeated in a more viscous medium,<sup>17</sup> a change that would increase the yield of any products formed by reaction of geminate cage species. However, the amount of  $\text{W}(\text{CO})_6$  formed in the more viscous medium remained constant ( $\approx 8\%$ ). It is unlikely, therefore, that cage abstraction of CO is occurring.<sup>16</sup> An alternative explanation is that the two Franck–Condon states (which arise from the two  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  isomers in solution<sup>19</sup>) relax differently: one to give  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  and  $\text{W}(\text{CO})_5$  and the other to give  $(\text{Me}_3\text{P})(\text{OC})_3\text{Os}(\mu\text{-CO})\text{W}(\text{CO})_5$ ; this singly bridged

(15) M–CO bond dissociation is also ruled out by the observation that no  $\text{PPh}_3$ -substituted dimer was observed in these experiments.

(16) Covert, K. J.; Askew, E. F.; Grunkemeier, J.; Koening, T.; Tyler, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 10446–10448.

(17) Reaction 1 was repeated in a solution consisting of bibenzyl (2.87 M) in benzene (1.2 mPa s, 25 °C). Benzene has a viscosity of 0.56 mPa s at 30 °C.<sup>18</sup>

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

(19) There are two isomers of  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$  in solution, 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).<sup>9c</sup> Irradiation of each isomer would produce a different Franck–Condon state.

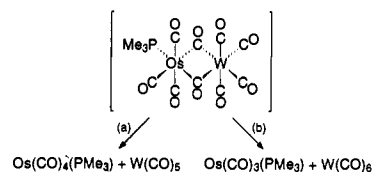
intermediate could decompose to  $\text{W}(\text{CO})_6$  8% of the time. This explanation does not account for all of the  $\text{W}(\text{CO})_6$  formed in eq 2. However, it is known that  $\text{W}(\text{CO})_5$  can abstract a CO ligand from other saturated or unsaturated species.<sup>20</sup> In reaction 2, the likely source is another  $\text{W}(\text{CO})_5$  fragment or CO arising from the decomposition of this fragment.<sup>21</sup>

In summary, convincing evidence was presented that irradiation of  $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ , a molecule believed to contain a metal–metal dative bond, leads to heterolytic rather than homolytic cleavage of the metal–metal bond. Trapping experiments suggest that the dominant mode of heterolysis is to form  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  and  $\text{W}(\text{CO})_5$ , but heterolysis to form  $\text{Os}(\text{CO})_3(\text{PMe}_3)$  and  $\text{W}(\text{CO})_6$  occurs to a small extent. These results illustrate an inherent difference between dative and nondative metal–metal bonds because photochemical heterolysis does not occur with nondative metal–metal bonds.

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(20) (a) Reference 1b, p 69. (b) Leventis, N.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5807–5809. (c) Albano, V. G.; Busetto, L.; Castellari, C.; Monari, M.; Palazzi, A.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1993**, 3661–3666.

(21) A doubly bridged intermediate with two bridging CO ligands cannot be completely ruled out.<sup>22</sup>



From this species two decomposition pathways are then possible: symmetric cleavage of the  $\text{Os}(\mu\text{-CO})_2\text{W}$  unit (pathway a) to yield  $\text{Os}(\text{CO})_4(\text{PMe}_3)$  and  $\text{W}(\text{CO})_5$ , and a minor pathway, namely, asymmetric cleavage (pathway b) to give  $\text{W}(\text{CO})_6$  and  $\text{Os}(\text{CO})_3(\text{PMe}_3)$  fragments. The formation of  $\text{W}(\text{CO})_6$  by the latter route would be independent of the presence of  $\text{PPh}_3$ .

(22) A similar intermediate was proposed to account for the nonrigidity and the thermal decomposition products of  $(\text{R}_3\text{P})(\text{OC})_4\text{OsM}(\text{CO})_5$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ).<sup>9c</sup>