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Photoinduced Oxidative Addition to a Quadruply Bonded Tungsten Complex $W_2Cl_4(dppm)_2$

Single-electron transfer has proven to be a ubiquitous oxidation–reduction pathway of electronically excited transition-metal complexes.[1–4] More recently, efforts have been extended to the utilization of electronically excited molecules to promote multielectron transformations, which are required for many important chemical processes. Successful multielectron photochemical schemes to date have relied on coupling one-electron excited-state chemistry via a relay catalyst[5] or by photochemically generating reactive radical intermediates that undergo subsequent oxidation or reduction.[6,7] Our approach in designing multielectron photochemical pathways has relied on accessing the redox chemistry of electron-rich multiple metal–metal bonds. Recent studies in our laboratories have demonstrated that photoactivated quadruply bonded metal–metal ($M\overset{4}{-}M$) complexes can promote the two-electron reductions of protons[8] and organic substrates.[9] In all cases, however, this $M\overset{4}{-}M$ multielectron photochemistry is achieved by coupling the one-electron chemistry of independent metal cores. Owing to our interest in developing unique excited-state reaction pathways, we became intrigued by the possibility of exploiting the complementary redox function of the two metals of an individual core to drive multielectron photoprocesses. We now report the two-electron photoreduction of methyl iodide at $W_2(dppm)_2Cl_4$ (dppm = bis(diphenylphosphino)methane). This photoredox chemistry is unusual in that it corresponds to a multielectron transformation of a discrete photoactivated metal core.

Although CH_3I solutions of $W_2(dppm)_2Cl_4$[10] are stable indefinitely at room temperature and below in the absence of light, excitation of $W_2(dppm)_2Cl_4$ with $\lambda > 435$ nm results in the spectral changes shown in Figure 1.[11] The decrease in the $\delta^2 \rightarrow \delta\delta^*$ absorption maximum of the $M\overset{4}{-}M$ binuclear complex ($\epsilon_{734} = 2585$ M^{-1} cm^{-1}) is accompanied by the appearance of absorptions exhibiting maxima at 490 and 582 nm and a weak near-infrared absorption at 1090 nm ($\epsilon = 646$ M^{-1} cm^{-1}). Two isosbestic points are maintained throughout the course of the reaction. Absorptions characteristic of mixed-valence $M^{II}M^{III}$ species, namely $\delta \rightarrow \delta^*$ absorptions with intensities comparable to and energies considerably red-shifted (6000–8000 cm^{-1}) from the $\delta^2 \rightarrow \delta\delta^*$ absorption of their quadruply bonded counterparts,[12] are not observed.

Consistent with the presence of the isosbestic points, and the spectroscopic absence of a mixed-valence species, a single diamagnetic product is quantitatively obtained by addition of hexane to photolyzed solutions. Elemental analysis of the isolated purple solid corresponds to addition of CH_3I to the tungsten–tungsten bond.[13] Further evidence that photolysis cleanly yields the simple oxidative-addition product is provided by fast-atom-bombardment mass spectrometry (FABMS).[14] The molecular ion cluster in the FABMS spectrum of the photoproduct centered at 1418 amu represents the molecular ion, $W_2(dppm)_2Cl_4(CH_3)I^{\bullet+}$, with major fragments centered at 1383 and 1291 amu corresponding to loss of Cl and I, respectively. A simulation of the natural isotope distribution for $W_2(dppm)_2Cl_4(CH_3)I^{\bullet+}$ agrees well with the observed spectrum. The FABMS and simulation are available as supplementary material.

The coordination geometry about the metal–metal bond has not unequivocally been established because we have not yet been able to obtain single crystals suitable for X-ray diffraction. However, the absorption profile with its weak near-infrared and 500-nm visible absorption bands is similar to those reported for edge-sharing bioctahedral complexes,[15] which are typically ob-

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(11) Sample irradiations were performed by using a Hanovia 1000-W Hg/Xe high-pressure lamp. The beam was collimated and passed through a 10-cm circulating water filter, and the irradiation wavelength was selected with a Schott GC-435 colored glass high-energy cutoff filter. The photoreaction proceeds with a quantum yield of 0.011 (2) with 435.8-nm irradiation, as determined by ferrioxalate actinometry using the identical experimental setup with an interference filter (Oriel 56450) in place of the cutoff filter. Although the parentage of the excited-state reactivity has not yet been yet identified, no appreciable photoreactivity is observed for irradiation wavelengths greater than 600 nm. The spectral range for maximum quantum yield is energetically coincident with excitation of the metal localized $\pi\delta^*$ and $\delta\pi^*$ transitions. Time-resolved absorption studies of $M_2X_4P_4$ complexes have shown that excitation into this spectral region gives rise to transients of appreciable lifetimes (Winkler, J. R.; Nocera, D. G.; Netzel, T. L. *J. Am. Chem. Soc.* **1986**, *108*, 4451–4458).

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(13) Analysis performed by Galbraith Laboratories. Anal. Calcd (found) for $W_2(dppm)_2Cl_4CH_3I$: C, 43.1 (43.0); H, 3.31 (3.37); I, 8.93 (8.43); P, 8.72 (8.54).

(14) FABMS was performed on a JEOL HX 110 double-focusing mass spectrometer housed at the National Institutes of Health/Michigan State University Mass Spectrometry Facility. Samples were dissolved in 2-(octyloxy)nitrobenzene matrices.

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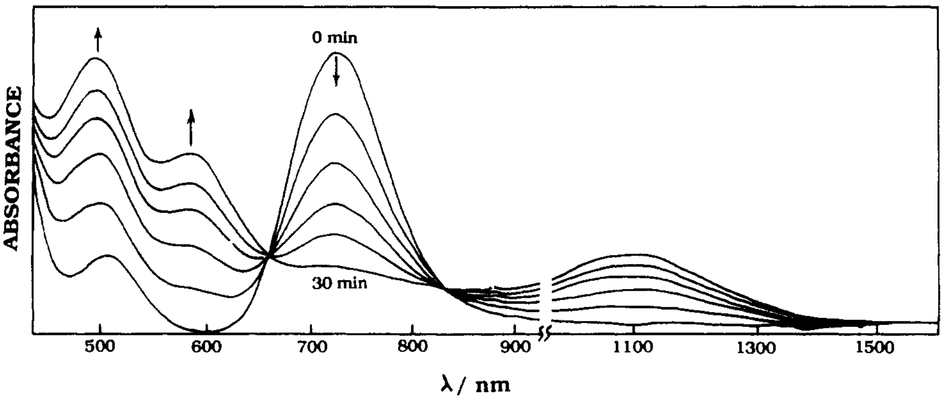
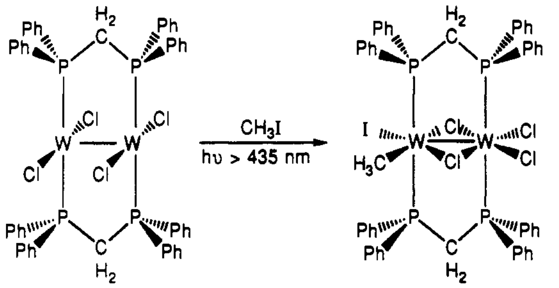


Figure 1. Electronic absorption spectral changes during photolysis ($\lambda_{exc} > 435$ nm) of deoxygenated methyl iodide solutions of $W_2Cl_4(dppm)_2$ at 0 °C. The wavelength scale in the near-infrared region (λ = 900–1600 nm) is twice that of the visible region (λ < 900 nm).

tained from addition reactions of $M_2(PP)_2Cl_4$ (PP = bridging phosphines) species.[15-17] The absorptions are predicted to arise from transitions involving the one-electron promotions between σ-, π-, and δ-symmetry orbitals of the edge-sharing bioctahedral core.[18] Insight into the coordination position of the methyl group is provided by ^{13}C NMR spectroscopy. A single ^{13}C resonance shifted 21 ppm upfield from TMS indicates that the methyl group is more likely to be in a terminal rather than bridging coordination position, as the diamagnetic anisotropy of the multiple metal–metal bond would induce a downfield shift of the resonance of a bridging ligand.[19] A photochemical transformation consistent with these observations is shown in eq 1. The coordination site of the iodide will give rise to five isomers; we show only one of the isomers in eq 1.



(1)

The observed photochemistry is in contrast to the thermal oxidations of $M_2(dppm)_2Cl_4$, which do not necessarily yield products corresponding to quantitative oxidative addition of the substrate to the metal–metal bond. For example, the thermal oxidation of $Mo_2(dppm)_2Cl_4$ by PhSSPh results in the production of $Mo_2(dppm)_2Cl_5SPh$.[16] We have found that a pentachloro product is ubiquitous to free-radical addition reactions of these complexes[20] and is produced in the thermal reactions of $W_2(dppm)_2Cl_4$ with alkyl iodides. The pentachloro product $W_2(dppm)_2Cl_5I$ has been identified by FABMS (included in supplementary material), which shows a molecular ion isotopic cluster centered at 1441 amu. In addition, a parent ion cluster centered at 1531 amu corresponding to $W_2(dppm)_2Cl_4I_2^{\bullet+}$ is observed. The identity of $W_2(dppm)_2Cl_4I_2$ as a product in the thermal reaction has been verified by comparison of the absorption and FABMS spectra to those of independently prepared samples. We can account for the formation of $W_2(dppm)_2Cl_5I$ and $W_2(dppm)_2Cl_4I_2$ by invoking a radical mechanism wherein the W^{II}_2 complex reacts with RI to produce the mixed-valence $W_2(dppm)_2Cl_4I$, which disproportionates by either chlorine or iodine atom transfer to yield $W_2(dppm)_2Cl_5I$ or $W_2(dppm)_2Cl_4I_2$, respectively, and the appropriate quadruply bonded complex. A similar disproportionation mechanism involving halogen atom transfer between mixed-valence intermediates has previously been proposed for the reactions of binuclear platinum complexes with aryl halides.[21] We believe this mechanism may be typical of the thermal oxidation chemistry of $M_2(PP)_2Cl_4$ complexes. Nevertheless, the issue of interest here is that the photochemical reaction of $W_2(dppm)_2Cl_4$ with CH_3I results in the direct addition of the substrate to the metal–metal core, and products that would arise from free radical pathways such as $W_2(dppm)_2Cl_4I_2$ and $W_2(dppm)_2Cl_5I$ are not observed. The absence of free-radical pathways is further supported by GC/MS analysis of samples obtained by Toepler pumping photochemical reaction mixtures, which gave no evidence of the production of ethane.

Thus the two-electron photoreduction of CH_3I by $W_2(dppm)_2Cl_4$ has been effected at a discrete binuclear core with a visible photon. An issue of significant interest is the nature of the multielectron transformation. The distinct absorption profiles of the $M\overset{n}{-}M$ species (n = 3, 3.5, and 4) will allow for the disappearance of the photoreactant and formation of the products to be precisely monitored along either the one- or two-electron photochemical reaction pathway. Accordingly we are now in a position to investigate the intimate mechanistic details of multielectron chemistry by defining the kinetics of the $W_2(dppm)_2Cl_4/CH_3I$ system. Picosecond transient absorption experiments are currently underway.

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Supplementary Material Available: Figures showing the FABMS of the isolated photoproducts and thermal products for the reaction of $W_2Cl_4(dppm)_2$ and CH_3I and the relative isotopic distribution of the molecular ion cluster for $W_2Cl_4(dppm)_2(CH_3)(I)$ (2 pages). Ordering information is given on any current masthead page.

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