

Photoreduction of Diaryl Disulfides by Quadruply Bonded Dimolybdenum and Ditungsten Complexes

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The quadruple metal–metal bonded complexes, $M_2Cl_4(dppm)_2$ ($M = Mo, W$; $dppm = \text{bis}(\text{diphenylphosphino})\text{-methane}$), photoreact with disulfides in nonaqueous solvents to yield M^{III}_2 addition products. Excitation ($\lambda_{\text{exc}} > 435 \text{ nm}$) of the dimolybdenum photoreagent in the presence of PhSSPh affords $\text{Mo}_2\text{Cl}_5(dppm)_2(\text{SPh})$. Whereas the Mo^{III}_2 edge-sharing bioctahedron is only accessible by photochemistry, $\text{W}_2\text{Cl}_4(dppm)_2$ is thermally and photochemically oxidized by PhSSPh to $\text{W}_2\text{Cl}_4(dppm)_2(\text{SPh})_2$, but reaction to the W^{III}_2 edge-sharing bioctahedron is greatly accelerated by light. The photolysis quantum yield for the $\text{Mo}_2\text{Cl}_4(dppm)_2$ photochemistry increases for excitation wavelengths to the blue of 436 nm ($\phi_p^{436} = 0.01$, $\phi_p^{405} = 0.11$, $\phi_p^{360} = 0.23$) and asymptotically approaches a maximum at wavelengths less than 320 nm ($\phi_p^{313} = 0.27$). The action spectrum red shifts by $\sim 50 \text{ nm}$ when the photoreagent is $\text{W}_2\text{Cl}_4(dppm)_2$. The wavelength dependence of $\text{M}_2\text{Cl}_4(dppm)_2$ photochemistry and the presence of long-lived intermediates in the transient absorption spectra of $\text{M}_2\text{X}_4(\text{P}^-\text{P})_2$ complexes ($M = Mo$ and $\text{P}^-\text{P} = \text{dmpm} = \text{bis}(\text{dimethylphosphino})\text{methane}$; $M = W$ and $\text{P}^-\text{P} = \text{dppm}$) suggest that reactivity is derived from metal-localized excited states lying to higher energy of the $\delta\delta^*$ excited state.

Introduction

Quadruply bonded metal–metal complexes are good photoreductants of organic substrates owing to the presence of low-energy excited states that are localized within an electron rich, coordinatively unsaturated, $d^4\text{--}d^4$ bimetallic core.¹ The precise nature of the photooxidation product depends intimately on the coordination environment surrounding the bimetallic core.² When the metal core is strapped by four bidentate ligands (D_{4h}), $d^3\text{--}d^4$ mixed-valence species are the common photoproduct. The inflexibility of the four bidentate ligands renders the coordination sphere incapable of accommodating the increased charge of a Mo^{III}_2 core, and hence, the reaction terminates at the one-electron oxidized $\text{Mo}^{\text{II}}\text{Mo}^{\text{III}}$ metal complex. For instance, $\text{Mo}_2[\text{O}_2\text{P}(\text{OC}_6\text{H}_5)_2]_4$ photoreduces 1,2-dihalocarbons to hydrocarbons in one-electron steps to yield the mixed-valence complex, $\text{Mo}_2[\text{O}_2\text{P}(\text{OC}_6\text{H}_5)_2]_4\text{Cl}$.³ As we have demonstrated, a two-electron oxidized photoproduct may be accessed if the bimetallic core is made more reducing. Substitution of $\text{O}_2\text{P}(\text{OR})_2^-$ by HPO_4^{2-} increases the reduction potential of the dimolybdenum core by 1.0 V, and accordingly, a Mo^{III}_2 tetraphosphate is obtained on the photochemical reduction of protons to hydrogen.⁴ However, $d^4\text{--}d^4 \rightarrow d^3\text{--}d^3$ photoconversions of this type are unusual when the bimetallic core is spanned by four bidentate ligands.

Two-electron chemistry is more typically observed when two of the four bidentate ligands are replaced by monodentate

ligands, usually halides. It is well established that $\text{M}_2\text{X}_4(\text{P}^-\text{P})_2$ ($\text{P}^-\text{P} = \text{bidentate phosphine}$) complexes reduce a variety of substrates (YZ) by two electrons to yield $\text{M}_2\text{X}_4(\text{P}^-\text{P})_2\text{YZ}$ edge-sharing bioctahedron (ESBO) species.^{5–7} Here, the ability of the ligand coordination sphere to stabilize an ESBO structure facilitates the reaction by enforcing an octahedral geometry about the individual metal centers of the oxidized bimetallic core. For the same reason, formation of ESBO species is also prominent in the two-electron photochemistry of these species.^{1,2,8} We now report the facile photoreaction of $\text{M}_2\text{X}_4(dppm)_2$ ($M = Mo$ or W ; $dppm = \text{bis}(\text{diphenylphosphino})\text{-methane}$) in the presence of PhSSPh to give ESBO species. The wavelength dependence of $\text{M}_2\text{X}_4(dppm)_2$ photochemistry correlates with the presence of long-lived intermediates as detected by transient absorption spectroscopy.

Experimental Section

General Procedures. Syntheses of $\text{Mo}_2\text{Cl}_4(dppm)_2$,⁹ $\text{Mo}_2\text{Cl}_4(\text{dmpm})_2$ ($\text{dmpm} = \text{bis}(\text{dimethylphosphino})\text{methane}$),¹⁰ $\text{Mo}_2\text{Cl}_6(dppm)_2$,¹¹ $\text{W}_2\text{Cl}_4(dppm)_2$,¹² and $\text{W}_2\text{Cl}_6(dppm)_2$ ¹³ were carried out by using standard Schlenk techniques. The bidentate phosphines and diphenyl disulfide were purchased from Aldrich Chemicals, and the former was used without further purification. Diphenyl disulfide was recrystallized and dried under vacuum. Toluene was freshly distilled from sodium/

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potassium benzophenone ketyl, and dichloromethane was distilled from P_2O_5 . All other chemicals were reagent grade and used as received.

Methods. Sample irradiations were performed by using a collimated beam from a Hanovia 1000-W Hg/Xe high-pressure lamp. Excitation wavelengths in the ultraviolet and visible spectral regions were selected by using Schott glass, high-energy cutoff filters. Photolysis experiments were performed on solutions at constant temperature contained in two-arm evacuable cells equipped with Kontes quick-release Teflon valves. Solutions were prepared by bulb-to-bulb distillation of solvent on a high-vacuum manifold. For quantum yield measurements, the excitation wavelength was isolated by using an interference filter purchased from Oriol Corporation with a half-width of less than 10 nm at the given mercury line. Absorption spectra for photolysis and quantum yield experiments were recorded on a Cary 2300 or Cary 17 spectrometer. Extinction coefficients were calculated from Beer–Lambert plots composed of at least seven points. Quantum yields were determined on CH_2Cl_2 or toluene solutions containing 1.4×10^{-3} M $M_2Cl_4(dppm)_2$ and a 20-fold excess of diphenyl disulfide. The quantum yield for photoreaction was determined by monitoring the disappearance of the $\delta^2 \rightarrow {}^1\delta\delta^*$ transition of $M_2Cl_4(dppm)_2$, and it was standardized by using a ferrioxalate actinometer.

Picosecond and nanosecond transient absorption measurements were made with the pulse–probe technique utilizing instrumentation¹⁴ housed in the LASER (Laser Applications in Science and Engineering Research) Laboratory at Michigan State.

Fast atom bombardment mass spectrometric (FAB/MS) analyses were performed on a JEOL HX-110 double focusing mass spectrometer housed in National Institutes of Health/ Michigan State University Mass Spectrometry Facility. Samples were dissolved in 2-(octyloxy)-nitrobenzene matrices and were operated in the positive ion detection mode. Electrospray mass spectrometric (ES/MS) analyses were obtained with a Finnegan mat (San Jose, CA) quadrupole mass spectrometer using a CH_3CN mobile phase. A CH_3CN solution of the sample was infused directly into the vaporization nozzle of the electrospray ion source at a flow rate of $3 \mu L \text{ min}^{-1}$. Nitrogen was used as the nebulizing gas at a pressure of 35 PSI.

Photochemistry of $Mo_2Cl_4(P^{\wedge}P)_2$ ($P^{\wedge}P$ = dppm and dmpm) with PhSSPh. $Mo_2Cl_4(dppm)_2$ (0.05 g, 0.045 mmole) was dissolved in CH_2Cl_2 containing a 20-fold molar excess of diphenyl disulfide and irradiated at $\lambda > 435$ nm (16 ± 0.5 °C). The solution was concentrated to 5 mL, and the photoproduct was precipitated from solution by adding hexane. The compound was further purified by chromatography on a Florisil packed column with CH_2Cl_2/CH_3CN as the eluent. Fast atom bombardment mass spectrometry displayed a mass ion cluster with a peak at 1246 amu, corresponding to the molecular weight of $Mo_2Cl_5(dppm)_2(SPh)$. Single crystals of the photoproduct were obtained by layering a toluene solution with cyclohexane. The same photoproduct was obtained for an excitation wavelength range 305–435 nm and in either CH_2Cl_2 or toluene; only the yield was perturbed by the nature of the solvent (33% for $\lambda > 435$ nm in CH_2Cl_2 and 52% for $\lambda > 335$ nm in toluene). FAB/MS of $Mo_2Cl_5(dppm)_2(SPh)$: 1246 ($[M]^+$), 1211 ($[M-Cl]^+$), and 1137 ($[M-SC_6H_5]^+$) amu. UV–vis for $Mo_2Cl_5(dppm)_2(SPh)$ in CH_2Cl_2 : 527 (752), 457 (1120), and 407 nm (898 $M^{-1}cm^{-1}$). In the absence of PhSSPh substrate, no photoreaction was observed even with hard UV excitation ($\lambda > 265$ nm).

A similar photoreaction was observed for $Mo_2Cl_4(dmpm)_2$ (0.08 g, 0.13 mmole) dissolved in CH_2Cl_2 containing PhSSPh (0.043 g, 0.20 mmole) irradiated under the same conditions as described above. The isolation and purification procedures developed for the dppm complex were also successful for the dmpm product. ES/MS of $Mo_2Cl_5(dmpm)_2(SPh)$: 715 ($[M-Cl]^+$), 680 ($[M-2Cl]^+$), and 632 ($[M-SC_6H_5]^+$) amu. UV–vis for $Mo_2Cl_5(dmpm)_2(SPh)$ in CH_2Cl_2 : 700, 520, and 410 nm. Solutions of $Mo_2Cl_4(dppm)_2$ and PhSSPh showed no reaction at room temperature in the absence of light.

Photoreaction of $W_2Cl_4(dppm)_2$ and PhSSPh. Toluene solutions of $W_2Cl_4(dppm)_2$ (0.035 g, 0.027 mmol) and a 20-fold excess of PhSSPh were photolyzed ($\lambda > 495$ nm at -10 °C) to completion within 45 min, as determined by UV–vis spectroscopy. The product, isolated and purified (47% yield) as described above, exhibited a UV–vis and

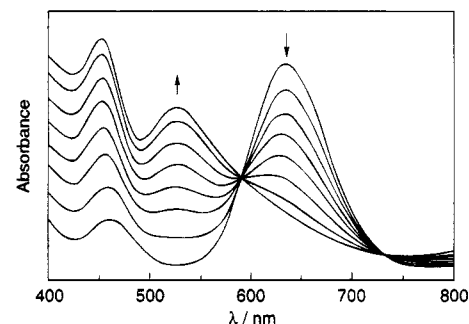


Figure 1. Electronic absorption spectral changes during the photolysis ($\lambda_{exc} > 435$ nm) of $Mo_2Cl_4(dppm)_2$ with a 20-fold excess of PhSSPh in deoxygenated dichloromethane at 16 °C. Spectra were recorded at 0–210 min in 30 min intervals.

FAB/MS identical to those of $W_2Cl_4(dppm)_2(SPh)_2$, which was independently prepared. FAB/MS: 1496 ($[M]^+$), 1419 ($[M-C_6H_5]^+$), and 1387 ($[M-C_6H_5-S]^+$) amu. UV–vis (toluene): 730 and 504 nm. Similar to $Mo_2Cl_4(dppm)_2$ photochemistry, no photoreaction is observed in the absence of substrate.

Thermal Reactions of $M_2Cl_4(dppm)_2$ ($M = Mo$ and W) and PhSSPh. $Mo_2Cl_4(dppm)_2$ (0.06 g, 0.054 mmol) and PhSSPh (0.06 g, 0.28 mmol) were mixed in toluene and rigorously shielded from light. No reaction was observed at room temperature. Under reflux conditions for 12 h, an unidentified orange-brown solid precipitated out of the solution. The product was isolated by washing with hexane to remove excess disulfide. Parent ion clusters at 1263 and 1279 amu in the FAB/MS are consistent with a trinuclear cluster product (UV–vis (CH_2Cl_2): 460 (m) and 375 nm (sh)).

$W_2Cl_4(dppm)_2$ (0.05 g, 0.04 mmol) and excess PhSSPh were dissolved in toluene, and the solution was shielded from light at -20 °C. The reaction was complete in 24 h, as monitored by UV–vis spectroscopy. Electronic absorption and mass spectra showed that the isolated product was $W_2Cl_4(dppm)_2(SPh)_2$ (45%).

Results and Discussion

Figure 1 shows the spectral changes associated with the irradiation of CH_2Cl_2 solutions ($\lambda > 435$ nm) of $Mo_2Cl_4(dppm)_2$ and PhSSPh. Isosbestic points are maintained during the course of the photoreaction in the low-energy absorption range for the disappearance of the $\delta^2 \rightarrow {}^1\delta\delta^*$ absorption band. Isosbestic behavior in the ultraviolet spectral region, however, is not observed, indicating a more complicated chemistry. The absorption spectrum of the photoproduct compares well to that of $Mo_2Cl_5(dppm)_2(SPh)$ ($\lambda_{max} = 527$ and 457 nm), and indeed, the crystal structure of the photoproduct is the ESBO with SPh^- bridging the Mo^{III}_2 core as previously reported by Cotton and co-workers.¹⁵ The formation of $Mo_2Cl_5(dppm)_2(SPh)$ is consistent with the production of a $Mo^{II}Mo^{III}$ primary photoproduct. We have previously observed the formation of $M_2Cl_5(P^{\wedge}P)_2Y$ and $M_2Cl_4(P^{\wedge}P)_2Y_2$ photoproducts upon the photolysis of the parent quadruple bond complex in the presence of substrate $Y-Y$.^{1,16} The $M_2Cl_4(P^{\wedge}P)_2$ complex photoreacts with the substrate to produce a mixed-valence $M_2Cl_4(P^{\wedge}P)_2Y$ primary photoproduct that disproportionates by either chlorine or Y atom transfer. A similar disproportionation mechanism involving halogen atom transfer between mixed-valence intermediates for the photochemical reaction of diplatinum pyrophosphite with aryl halides has been proposed.¹⁷ For the case here, we only observe $Mo_2Cl_5(dppm)_2(SPh)$ in the disproportionation because $Mo_2Cl_4(dppm)_2(SPh)_2$ appears to have limited stability. Whereas

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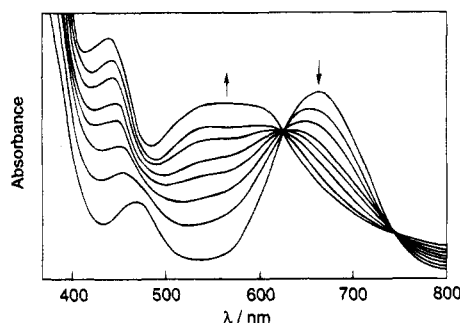


Figure 2. Electronic absorption spectral changes during the photolysis ($\lambda_{\text{exc}} > 365$ nm) of a toluene solution of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ with excess of PhSSPh at 8 °C; spectra were recorded at 0, 36, 70, 105, 140, 185, 235, and 300 min. The irradiation was interrupted when the 600 nm band had attained a maximum absorption value.

Table 1. Wavelength Dependence of Quantum Yields for Photoreaction of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and $\text{W}_2\text{Cl}_4(\text{dppm})_2$ with PhSSPh

$\lambda_{\text{exc}}/\text{nm}$	$\phi_p[\text{Mo}_2\text{Cl}_4(\text{dppm})_2]^a$	$\phi_p[\text{W}_2\text{Cl}_4(\text{dppm})_2]^b$
546	$< 10^{-5}$	0.025
436	0.010	0.048
405	0.11	0.075
365	0.23	0.15
313	0.27	0.39

^a $T = 16$ °C in CH_2Cl_2 . ^b $T = 0$ °C in toluene.

$\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ converts to $\text{Mo}_2\text{Cl}_5(\text{dppm})_2(\text{SPh})$ in CH_2Cl_2 ; evidence for $\text{Mo}_2\text{Cl}_4(\text{dppm})_2(\text{SPh})_2$ is provided when the photolysis is halted prior to its completion in toluene. In contrast to the isoenergetic disappearance of the $\delta^2 \rightarrow {}^1\delta\delta^*$ absorption band in Figure 1, toluene solutions display a 600 nm absorption in the low-energy spectral region (Figure 2). We have not successfully crystallized the compound responsible for this absorption, even at low temperature. However, FAB/MS and ES/MS analysis of solids isolated during intermediate stages of the photolysis showed the presence of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2(\text{SPh})_2$ as the major product, with $\text{Mo}_2\text{Cl}_5(\text{dppm})_2(\text{SPh})$ present as well. Partially photolyzed solutions containing $\text{Mo}_2\text{Cl}_4(\text{dppm})_2(\text{SPh})_2$, left standing in the dark, converted completely to $\text{Mo}_2\text{Cl}_5(\text{dppm})_2(\text{SPh})$ as monitored by UV-vis spectroscopy and FAB/MS. We believe that $\text{Mo}_2\text{Cl}_4(\text{dppm})_2(\text{SPh})_2$ may be present in both CH_2Cl_2 and toluene photolyses. Its stability however appears to be solvent dependent, reacting with facility in CH_2Cl_2 but stable enough in toluene solutions to be observed.

The formation of the Mo^{III}_2 ESBO from $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ is unique to the photochemical reaction pathway. Solutions of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and PhSSPh are indefinitely stable at room temperature. Upon refluxing, an as of yet unidentified orange-brown solid is obtained whose FAB/MS is consistent with a higher nuclearity cluster species. Presumably, the difficulty in oxidizing the Mo^{II}_2 core hinders the formation of the Mo^{III}_2 ESBO along a thermal reaction pathway. This is not the case, however, for $\text{W}_2\text{Cl}_4(\text{dppm})_2$. Electronic absorption, FAB/MS, and ES/MS spectra of thermally and photochemically ($\lambda > 495$ nm) reacted toluene solutions of $\text{W}_2\text{Cl}_4(\text{dppm})_2$ and PhSSPh are identical to independently prepared samples of the ESBO, $\text{W}_2\text{Cl}_4(\text{dppm})_2(\text{SPh})_2$, which has been previously synthesized and characterized.¹⁵ Although the same product is obtained in both cases, the thermal reaction occurs over days as opposed to only hours for the photolysis.

The action spectrum of $\text{M}_2\text{Cl}_4(\text{dppm})_2/\text{PhSSPh}$ photochemistry is consistent with reactivity originating from the metal complex. Table 1 summarizes the wavelength dependence of the photoreaction quantum yield, ϕ_p . The onset for $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ photoreaction occurs at ~ 436 nm ($\phi_p = 0.01$), and ϕ_p

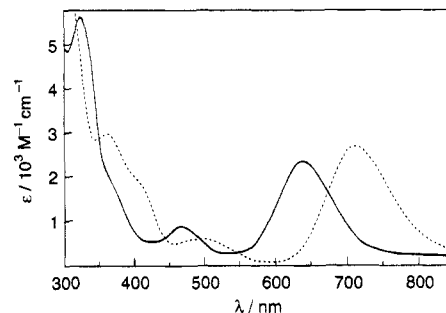


Figure 3. Electronic absorption spectra of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ (—) and $\text{W}_2\text{Cl}_4(\text{dppm})_2$ (---) complexes in dichloromethane and benzene, respectively.

increases monotonically between 320 and 380 nm, asymptotically approaching a limiting quantum yield of 0.27 at $\lambda < 313$ nm. The action spectrum tracks the rising absorption edge of transitions immediately to higher energy of the $\delta^2 \rightarrow {}^1\delta\delta^*$ transition ($\lambda_{\text{max}} = 635$ nm). This coincidence between the wavelengths of absorptions immediately to higher energy of $\delta^2 \rightarrow {}^1\delta\delta^*$ and the action spectrum of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ are preserved in $\text{W}_2\text{Cl}_4(\text{dppm})_2$ photochemistry. The ~ 50 nm red shift of the $\text{W}_2\text{Cl}_4(\text{dppm})_2$ action spectrum as compared to its $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ homologue, is consistent with a respective 50 nm red shift of the absorption spectrum of the ditungsten complex (see Figure 3). This wavelength dependence of the photochemistry excludes the possibility of a reaction derived from direct homolysis of the disulfide bond to produce RS^\bullet radicals. Organic disulfides add to acetylenes to afford 1,2-diarylmecaptoethenes in high yields via a free radical pathway, resulting from the photochemically induced cleavage of the disulfide bond, but the reaction occurs at higher wavelengths than reported here.¹⁸ We have irradiated PhSSPh in the presence of methylacetylene or 1-heptyne with wavelengths coincident with $\text{M}_2\text{Cl}_4(\text{dppm})_2$ photochemistry. No reaction is observed for $\lambda > 380$ nm, and only trace reaction is observed at lower excitation wavelengths. With decreasing wavelength, the 1:1 adduct is observed with the highest yields occurring for irradiation wavelengths coincident with the absorption maximum of PhSSPh at $\lambda = 240$ nm, a result that is consistent with Heiba and Dessau's original observations of free radical addition of PhSSPh to these alkynes.¹⁹ The parallels between the quantum yields listed in Table 1 and the absorption profiles of the quadruply bonded metal-metal complexes, and their disparity with the action spectrum of PhSSPh photochemistry, establish that $\text{M}_2\text{Cl}_4(\text{dppm})_2/\text{PhSSPh}$ photochemistry is derived from the quadruple bond complex.

A comparison of the action spectra of the dimolybdenum and ditungsten complexes provides some insight into the excited state responsible for the observed photochemistry. Substitution of Mo by W in quadruply bonded metal-metal halophosphine complexes typically leads to a blue shift in ligand-to-metal transitions owing to the greater difficulty associated with reducing W^{II} .²⁰ Conversely, metal-localized transitions exhibit a red shift as demonstrated by the shift in the $\delta^2 \rightarrow {}^1\delta\delta^*$ transitions from 635 nm for $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ to 710 nm for $\text{W}_2\text{Cl}_4(\text{dppm})_2$ (see Figure 3). Along these lines, the Mo \rightarrow W red shift of the action spectrum implies that the parentage of $\text{M}_2\text{Cl}_4(\text{dppm})_2$ (D_{2h}) photochemistry is metal-localized. These

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results are in contrast to the spectroscopy and photochemistry of D_{2d} quadruply bonded halophosphines. For $M_2Cl_4(PR_3)_4$ complexes, a distinct blue shift specific to ligand-to-metal charge transfer transitions is observed in the near-ultraviolet spectral region upon substitution of Mo with W.²⁰ Accordingly, the photochemistry of these complexes is characteristic of ligand-to-metal charge transfer reactivity.²¹ One reason for these differences between the D_{2d} and D_{2h} mixed-halide phosphine complexes is the splitting of the π_{xz} and π_{yz} orbitals levels of the latter.²² Consequently, higher energy metal-localized transitions of the D_{2d} complexes may be red shifted in the spectra of the D_{2h} counterparts. The presence of metal-localized transitions in the near-ultraviolet region is likely manifested in the metal-localized photochemistry reported here.

Photochemical studies were complemented by the investigations of the transient absorption spectroscopy of $M_2X_4(P^{\wedge}P)_2$ complexes upon visible and near-ultraviolet excitation. In the case of $M = Mo$, a complete wavelength study could not be achieved owing to stimulated emission from dppm ($\lambda_{max} = 460$ nm, $\tau \sim 1$ ns²³) when samples were excited with high-energy light ($\lambda_{exc} = 355$ nm). Specifically, stimulated emission in the 450–520 nm spectral range, although weak, was problematic because the changes in optical density (ΔOD s) for the transient absorption bands of $Mo_2Cl_4(dppm)_2$ in this range were small. The stimulated emission was eliminated upon replacement of the dppm by dmpm, thereby allowing us to obtain a sufficiently high signal-to-noise ratio to detect absorptions with ΔOD s < 0.05. Because $Mo_2Cl_4(dmpm)_2$ is structurally and electronically analogous to $Mo_2Cl_4(dppm)_2$, we believe the transient spectroscopy of the dmpm system to be representative of $Mo_2Cl_4(dppm)_2$. The absorption spectrum of $Mo_2Cl_4(dmpm)_2$ is nearly identical to that of $Mo_2Cl_4(dppm)_2$ but blue shifted by ~ 40 nm.¹⁰ Moreover, $Mo_2Cl_4(dmpm)_2$ photochemistry is parallel to that of $Mo_2Cl_4(dppm)_2$ with the production of $Mo_2Cl_5(dmpm)_2(SPh)$ as the photoproduct. For the case of $W_2Cl_4(dppm)_2$, the red shift in the electronic absorption spectrum permitted us to obtain transient spectra at high- and low-energy excitation wavelengths without the signal being obscured by stimulated emission from the sample.

Figure 4 shows transient absorption profiles for $Mo_2Cl_4(dmpm)_2$ following a 3 ps excitation pulse at 600 nm. A prominent feature at 460 nm decays monoexponentially to ground state with a lifetime of 40(8) ps. Concurrent with this absorption decay is the recovery of the $\delta\delta^*$ bleach at 630 nm on the same time scale, thereby establishing the assignment of the transient absorption in Figure 4 to the $\delta\delta^*$ excited state. The excitation of the $\delta\delta^*$ transition of $W_2Cl_4(dppm)_2$ also affords a short-lived intermediate (<1 ns), which is generally true of all $M_2X_4(P^{\wedge}P)_2$ complexes that we have surveyed to date. The short lifetimes of the $\delta\delta^*$ transient account for the absence of $M_2Cl_4(dppm)_2/PhSSPh$ photochemistry upon $\delta\delta^*$ excitation.

A long-lived intermediate is observed, however, when the absorption profile immediately to higher energy of the $\delta\delta^*$ transition is excited. Dichloromethane solutions of $Mo_2Cl_4(dmpm)_2$, excited at $\lambda_{exc} = 355$ nm, display the transient absorption spectrum ($\lambda_{max} = 520$ nm) shown in Figure 5. The transient profile is spectrally similar to the absorption spectrum of the edge-sharing bioctahedron, $Mo_2Cl_6(dmpm)_2$.²⁴ A similar

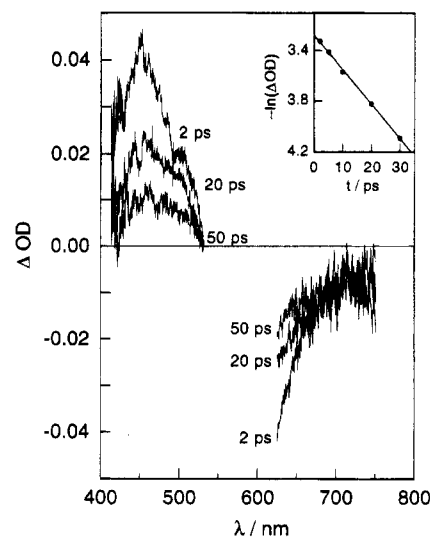


Figure 4. Time evolution of the disappearance of the picosecond transient absorption of $Mo_2Cl_4(dmpm)_2$ in dichloromethane. The spectra were obtained at 2, 20, and 50 ps after a 600 nm, 3 ps excitation pulse. The inset shows a plot of the $\ln(\Delta OD)$ for the transient absorption at 630 nm vs time.

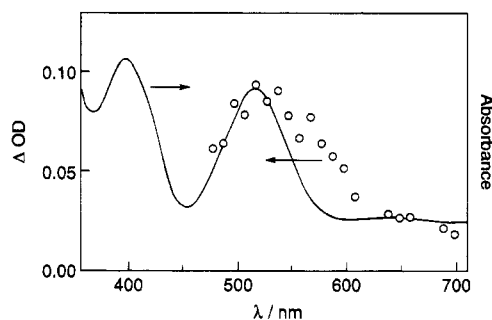


Figure 5. Transient difference spectrum (○) of a deoxygenated dichloromethane solution of $Mo_2Cl_4(dmpm)_2$ recorded 1 μ s after 355 nm, 10 ns excitation and electronic absorption spectrum of $Mo_2Cl_6(dppm)_2$ (—) in dichloromethane.

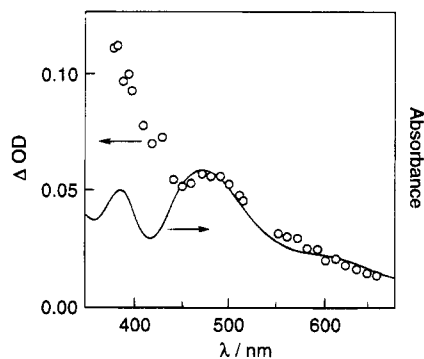


Figure 6. Transient difference spectrum (○) of a deoxygenated benzene solution of $W_2Cl_4(dppm)_2$ collected 100 ns after 532 nm, 10 ns excitation and electronic absorption spectrum of $W_2Cl_6(dppm)_2$ (—) in dichloromethane.

result is obtained for $W_2Cl_4(dppm)_2$ in benzene at room temperature. Figure 6 shows that the transient absorption, which decays even more slowly ($\tau = 46 \mu$ s) than that observed for its molybdenum congener, is also similar to that of $W_2Cl_6(dppm)_2$.²⁴ The correlation between the spectra of the long-lived nonluminescent transients and the edge-sharing bioctahedra suggests that the transient may be derived from a chemically distorted ESBO-intermediate.²⁵ The formation of such an intermediate is consistent with the electronic structure of quadruply bonded metal–metal complexes. Metal-localized excited states associ-

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ated with promotion of electrons to and from the δ and δ^* orbitals exhibit charge transfer character (i.e., $M^{II}_2 \rightleftharpoons M^I M^{III}$).^{26,27} Chemical distortion to an ESBO can stabilize this charge transfer within the bimetallic core by providing cooperative stabilization with an octahedral geometry about a partially oxidized metal center and diminished donation of electron density from the halides about the partially reduced metal center. Whereas the activation barrier associated with the intramolecular ligand rearrangement may prevent access to an ESBO-type intermediate from the $\delta\delta^*$ excited state, population of the higher energy metal-localized transitions can lead to diminished metal-metal π bonding relative to that in the ground state molecule. This feature is expected to enhance the formation of a bioctahedral intermediate because interactions of the metal d_{yz} (or d_{xz}) orbitals with those of ligands in the equatorial plane of an edge-sharing bioctahedron occur at the expense of M-M π interactions. Notwithstanding, the generation of long-lived intermediates upon

excitation of the absorption profile to higher energy of the $\delta\delta^*$ transition is consistent with our observations of $M_2Cl_4(dppm)_2$ photochemistry over this same excitation range.

The photochemistry of $M_2Cl_4(dppm)_2$ is analogous in many ways to the thermal oxidative-addition chemistry of mononuclear d^8 square planar metal complexes. In the d^8 archetype, Vaska's complex, *trans*-IrCl(CO)(PR₃)₂, a reduced, coordinatively unsaturated ML₄ center adds substrate to yield an octahedral, two-electron oxidized metal center.²⁸ The same is true of $M_2Cl_4(dppm)_2$ inasmuch as the ML₄ fragments composing the quadruply bonded metal-metal core are oxidized to yield a two-electron oxidized ESBO. The analogy is even more striking when a chemically distorted ESBO is considered. A ML₄ fragment provides the reducing equivalent to and accepts two terminal ligands from its ML₄ neighbor, thereby creating a single active site susceptible to substrate addition. More practically, the presence of a chemically distorted intermediate is necessary for $M_2Cl_4(dppm)_2$ photochemistry. As transient spectroscopy shows, the $\delta\delta^*$ excited state is too short for its reaction with substrate. However, a chemically distorted intermediate provides a means of trapping the charge-separated character of the metal-localized excited states of quadruply bonded metal-metal complexes at sufficiently long lifetimes to permit their reaction with substrate.

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- (25) Although the electron counts of the chemically distorted ESBO transient ($M^I M^{III} = d^5-d^3$) and $M_2X_6(P/P)_2$ complexes ($M^{III}_2 = d^3-d^3$) are different, the spectra of the two species may be similar for several reasons. The energy ordering of the molecular orbitals of an ESBO are $\sigma < \pi < \delta^* \sim \delta < \pi^* < \sigma^*$ with a very small δ^*/δ splitting (Shaik, S.; Hoffman, R.; Fisel, R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555-4572. Chakravarty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Roth, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 971-976. Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438-7445). Consequently, transitions such as $\pi \rightarrow \delta^*$, $\pi \rightarrow \delta$, and $\delta^* \rightarrow \pi^*$ in d^3-d^3 are predicted to be energetically similar to $\delta \rightarrow \pi^*$ and $\delta^* \rightarrow \pi^*$ in a chemically distorted d^5-d^3 ESBO. Even greater similarities between the spectra of the two intermediates will result if the two additional electrons of the chemically distorted intermediate occupied the in-plane π orbital of the ESBO as a lone pair. In this case, the electron count of a chemically distorted ESBO would be $d^3-d^3(\pi_{in-plane})^2$, and metal-based transitions within the metal-based d orbitals would be similar to the native d^3-d^3 ESBO.
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