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Two-electron photoelimination reactions from edge-sharing bioctahedral dimolybdenum(III) complexes

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Dimolybdenum(III) edge-sharing bioctahedral (ESBO) complexes, $Mo_2X_6(dtbppm)_2$ [dtbppm = *bis*(di(4-*tert*-butylphenyl)phosphinomethane), X = Cl, Br, I], photoreact when irradiated with near-UV light, cleanly producing the corresponding quadruple metal–metal bonded complexes, $Mo_2X_4(dtbppm)_2$.

Metal complexes in electronic excited states typically exhibit one-electron oxidation–reduction chemistry. Conversely, the small molecule activation processes of most energy conversion schemes encompass multielectron transformations. This discontinuity between the intrinsic redox stoichiometries of electronic excited states and the reactions that they are targeted to thermodynamically drive has prompted us to explore conceptually new excited state reaction pathways, extending beyond the single electron. A strategy occupying our recent efforts is predicated on the chemistry of two-electron mixed-valence excited states. As one-electron mixed valence complexes promote single electron transfer reactions, a two-electron mixed valence complex can promote reactions in two-electron steps at the individual metal centers of the bimetallic core.[1] In one approach we have shown that excitation of quadruply bonded metal–metal ($M\overset{4}{-}M$) dimers pairs two electrons in a d_{xy} orbital localized, for the most part, at one center of the bimetallic core with a corresponding two-electron hole at the other metal center.[2] The resultant $^{+}M–M:^{-}$ zwitterion (formally, a $M^{III}M^{I}$ intermediate for M = Mo and W) exhibits reactivity that establishes it as an excited state analog of Vaska's complex;[3] $M_2X_4(PP)_2$ (M = Mo, W; X = halide; PP = bridging phosphine) complexes undergo two-electron photoadditions of substrates to yield $M^{III}{}_2$ complexes with edge-sharing bioctahedral (ESBO) geometries.[4,5] An extensive reaction chemistry of the past decade shows these ESBO photoproducts to be inert, especially when metal–halide bonds compose the core.[6] This stability has hampered the construction of cyclic reaction schemes based on $M^{II}M^{II} \leftrightarrow M^{III}M^{III}$ photoreactivity. Accordingly, we became interested in developing the two-electron photoreduction chemistry of ESBO complexes. We now report the photoactivation of the metal–halogen bonds of the ESBO framework and subsequent two-electron photoconversion of $Mo_2X_6(PP)_2$ to $Mo_2X_4(PP)_2$.

Early efforts to investigate ESBO photochemistry were hampered by the limited solubility of $Mo_2X_6(PP)_2$ compounds in common solvents possessing moderate dielectric constants. We overcame this problem by introducing *tert*-butyl groups at the *para* position of the phenyl rings of bis(diphenyl)phosphinomethane (dppm). Reaction of $Cl_2PCH_2PCl_2$ with 12 equiv. of Bu^t-4-PhMgBr in diethyl ether at –78 °C under the N_2 atmosphere of a glove box, followed by procedures standard to a Grignard work-up, afforded bis(di-(4-*tert*-butylphenyl)-phosphinomethane) (dtbppm), which was recrystallized from acetonitrile: yield, 89%.† The introduction of the dtbppm ligand onto bimetallic cores proceeds smoothly according to literature procedures.[7] Treatment of $Mo_2(O_2CMe)_4$ with 4 equiv. of Me_3SiX and 2.2 equiv. of dtbppm in THF resulted in conversion to $Mo_2X_4(dtbppm)_2$, which was recrystallized from pentane and benzene.† Halogen oxidation of $Mo_2X_4(dtbppm)_2$ produced paramagnetic $Mo_2X_6(dtbppm)_2$ in good yields.† The electronic absorption spectra of the $Mo_2X_4(dtbppm)_2$ and $Mo_2X_6(dtbppm)_2$ complexes‡ are similar to those of their dppm counterparts,[7c,8] with only slight differences observed in absorption maxima and intensities. Fig. 1 shows the evolution of the absorption profiles for the photolysis of $Mo_2X_6(dtbppm)_2$ in THF. Each photoreaction behaves similarly. The initial spectrum, which is maintained indefinitely in the absence of light, promptly changes when THF solutions of the compound and a non-coordinating base such as 2,6-lutidine (2,6-dimethylpyridine) are irradiated with light in the blue and UV spectral regions. Well anchored isosbestic points maintained throughout the irradiation attest to a clean and quantitative photoreaction. With the appearance of the final absorption spectrum, no additional changes are observed with continued irradiation. For each photolysis reaction shown in Fig. 1, a single product is isolated with electronic absorption and $^{31}P\{^{1}H\}$ NMR spectra identical to those of independently prepared $Mo_2X_4(dtbppm)_2$ complexes. The photochemistry proceeds in THF only when carried out in the presence of at least a 2 equiv. excess of 2,6-lutidine (per equiv. of metal complex), though the photoconversion efficiency is independent of the concentration of base to excesses of 10^4 equiv. These results are consistent with THF acting as an *in situ* trap of

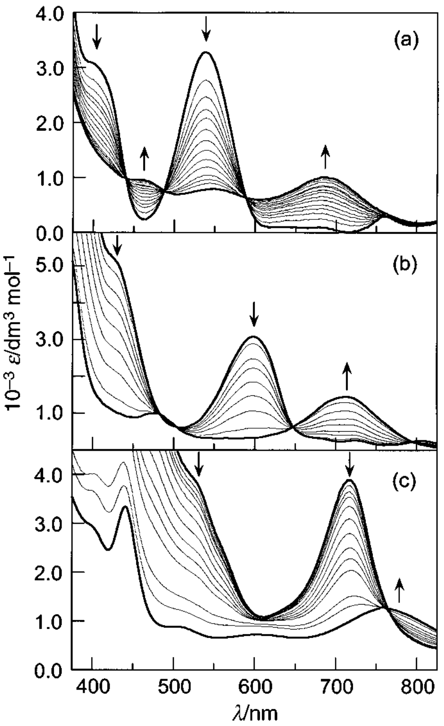

Fig. 1 The absorption profiles demonstrate the conversion of THF solutions of $Mo_2X_6(dtbppm)_2$ (*ca.* 10^{-5} M) in the presence of 20 equiv. of 2,6-lutidine at 0 °C: (a) X = Cl (λ_{exc} > 335 nm), (b) X = Br (λ_{exc} > 335 nm), and (c) X = I (λ_{exc} > 495 nm). The arrows indicate the disappearance of $Mo_2X_6(dtbppm)_2$ and appearance of $Mo_2X_4(dtbppm)_2$. Spectra were recorded over the span of 12 h for (a) and (c) and 2 h for (b).

Table 1 Product quantum yields for $Mo_2X_6(dtbppm)_2$ photolysis at selected excitation wavelengths

	$10^2\phi_p[Mo_2X_6(dtbppm)_2]^a$		
λ_{exc}/nm	X = Cl	Br	I
312	1.4(2)	0.38(4)	—
335	0.0012(1)	0.010(1)	—
365	0.0045(5)	0.0036(4)	—
405	0.00045(4)	0.0010(1)	—
470	—	—	0.0090(9)
510	—	—	0.0013(1)

[a] The quantum yield experiments were performed in THF at 0 °C containing 2,6-lutidine in 20 equiv. excess of $Mo_2X_6(dtbppm)_2$. The $Mo_2I_4(dtbppm)_2$ photoproduct decomposes when $\lambda_{exc} < 436$ nm.

photoeliminated X, arising from the susceptibility of the weak C_α–H bonds of THF toward atom abstraction.[9] In support of this contention, NMR spectra of photolyzed solutions exhibit a broad high frequency signal at δ 16.8 and a sharp methyl resonance at δ 2.9 of 2,6-lutidinium halide ($lutH^+X^-$); independently prepared lutidinium bromide exhibits a resonance at δ 16.3 for the acid proton and δ 2.96 for the methyl groups in $CDCl_3$. Moreover, integration of these resonances establish a stoichiometry of 2 equiv. of HX produced per equiv. of $Mo_2X_6(dtbppm)_2$ photoreagent to establish the following photoprocess of eqn. (1).

$$Mo_2X_6(dtbppm)_2 \xrightarrow[\text{THF, lut}]{h\nu} Mo_2X_4(dtbppm)_2 + 2\ lutH^+X^- \qquad (1)$$

Table 1 lists the product appearance quantum yields (ϕ_p) for selected irradiation wavelengths. Quantum yields are high for near-UV excitation, but they decrease precipitously as λ_{exc} is moved into the visible spectral region. Moreover, the wavelength onset of this decrease red shifts along the series Cl < Br < I. A parallel shift of the near-UV absorption profiles (2900 and 5100 cm^{-1} red shift upon substitution of chloride by bromide and bromide by iodide, respectively) indicates that the action spectra are governed by the population of ligand-to-metal charge transfer states. Though no definitive assignments have been forthcoming in the absence of detailed spectroscopic investigation, computation[10] and experiment[11] identify the low-energy absorption profile of Fig. 1 to be derived largely from d and p metal-based orbitals with some halide character resulting from X p_π-mixing. The intense absorptions to higher energy are due to the Mo_2X_6 σ-framework, comprising metal in-plane π orbitals admixed with X p_σ-orbitals. Depopulation of these metal–halide σ-orbitals (and population of the correspondingly σ* orbitals) will result in significant disruption of the Mo_2X_6 equatorial framework, accounting for the high photoconversion efficiencies associated with near-UV excitation.

Photoelimination from oxidized cores of $M\overset{n}{\text{—}}M$ complexes has only previously been observed for the alkyl ligands axially coordinated to a pre-established $W^{III}{}_2L_6$ core.[12] In view of the preponderance of ESBO compounds in multiply bonded metal–metal chemistry, the photochemistry reported here provides a general framework in which to develop multielectron photoredox schemes based on $M\overset{n}{\text{—}}M$ photoreagents. Recent work in our group shows that metal–halide bonds are susceptible to photochemical activation along reaction pathways featuring two-electron mixed-valence species.[1b] Is the same M^+–$M:^-$ two-electron mixed valence zwitterion, responsible for promoting $M\overset{4}{\text{—}}M$ photoaddition reactions,[3–5] facilitating ESBO photoelimination chemistry? Alternatively, disproportionation of a photogenerated $Mo^{II}Mo^{III}$ complex could also lead to the observed photochemistry. In ongoing work, we are addressing such mechanistic issues by investigating the ESBO photochemistry with transient absorption and Raman spectroscopy, with the aim of directly establishing the precise nature of the photointermediate that leads to ESBO activation.

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Notes and references

† *Selected Data* for dtbppm: mp, 180–183 °C. Calc. for $C_{41}H_{54}P_2$: C, 80.88; H, 8.94; P, 10.18. Found: C, 80.72; H, 9.08; P, 10.25%. ^1H NMR (acetone-d_6), δ 1.24 (s), 2.90 (s), 7.50 (m); $^{31}P\{^1H\}$ NMR ($CDCl_3$, ext. 85% H_3PO_4) δ −24.1 (s).

For $Mo_2X_4(dtbppm)_2$: $^{31}P\{^1H\}$ NMR (C_6D_6, ext. 85% H_3PO_4) δ 15.24 (s), 16.94 (s), 13.64 (s) for X = Cl, Br and I, respectively.

For $Mo_2X_6(dtbppm)_2$: pink $Mo_2Cl_6(dtbppm)_2$ was obtained by oxidation with $PhICl_2$ in CH_2Cl_2, 95% yield. Calc. for $C_{82}H_{108}Mo_2P_4Cl_6$: C, 60.71; H, 6.71. Found: C, 60.85; H, 6.85%. $Mo_2Br_6(dtbppm)_2$ and $Mo_2I_6(dtbppm)_2$ were obtained by oxidation with Br_2 and I_2, respectively, in benzene. X = Br (pine green), 92% yield. Calc. for $C_{82}H_{108}Mo_2P_4Br_6$: C, 52.14; H, 5.76. Found: C, 52.21; H, 5.85. X = I (sepia), 85% yield. Calc. for $C_{82}H_{108}Mo_2P_4I_6$: C, 45.37; H, 5.01. Found: C, 45.08; H, 5.16%.

‡ Absorption spectra were recorded in THF. Absorption coefficients were determined from Beer–Lambert plots constructed from absorption measurements recorded at 5–7 different concentrations. Each experiment was repeated and in all cases the measured ε value was accurate to three significant figures. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) for $Mo_2X_4(dtbppm)_2$, X = Cl: 340 (5720), 460 (740), 694 (1550); X = Br: 369 (3110), 448 (1100), 713 (1760); X = I: 442 (7500), 496 (1570), 600 (440), 772 (2540). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) for $Mo_2X_6(dtbppm)_2$, X = Cl: 288 (17200), 335 (11400), 400 (3190), 540 (3400), 750 (300); X = Br: 311 (13000), 371 (13300), 425 (4520), 600 (3400); X = I: 296 (27200), 352 (12400), 424 (10200), 467 (6440), 524 (4300), 718 (4200).

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