The Chemistry of Multielectron Excited States

DANIEL G. NOCERA
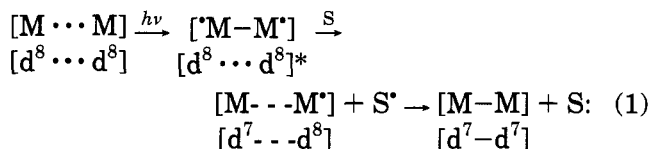
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322

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Light-initiated chemistry utilizes the energy of a harnessed photon from an excited state molecule to promote reactions that are kinetically or thermodynamically inaccessible from the ground state. Of the many reactions to investigate from the excited state, oxidation–reduction transformations provide invaluable insight into the intimate mechanistic details of electron transfer[1] and they form the basis for the metal-catalyzed photoreactions of small molecules and organic substrates.[2] The increased internal energy of the excited state complex makes it both a better oxidant and a better reductant than its ground state parent complex, and when sufficiently long-lived, the excited state can participate in intermolecular redox reactions with substrates. Whereas an extraordinarily diverse array of photoactive redox metal systems has been elaborated,[3,4] ranging from mononuclear metal complexes to metalloproteins, the basic redox chemistry of excited states has evolved little since Gafney and Adamson's[5] description of the reaction between electronically excited $Ru(bpy)_3^{2+}$ (bpy = bipyridine) and $Co(NH_3)_5Br^{2+}$ to give $Ru(bpy)_3^{3+}$ and $Co(NH_3)_5$-Br^+; namely, transition metal complexes undergo single electron transfer to or from their excited states. By itself, the single electron transfer step is limited inasmuch as most important reactions, such as small molecule activation, are multielectron processes. Accordingly, the initial single electron transfer step must be coupled to ensuing electron transfer to achieve net reactivity. Indeed, this has been the general strategy exploited in the development of the light-to-energy conversion chemistry of the past two decades.[6–8] A goal of our research is to expand the reactivity of excited states by developing new oxidation–reduction pathways extending beyond one-electron transfer. In particular, we are interested in whether discrete excited states may be designed to undergo direct multielectron reactivity.

In our endeavors to uncover new chemistry of transition metal excited states, our attention turned to binuclear metal complexes, which possess several attractive features for the elaboration of multielectron reactivity. These include the presence of a coordinatively unsaturated bimetallic core composed of metal centers that can exhibit complementary redox function in the activation process of a substrate.[9] A hint as to

the design of a bimetallic, multielectron excited state complex comes from the chemistry of $d^8 \cdots d^8$ complexes,

$$[M \cdots M] \xrightarrow{h\nu} [^{\bullet}M{-}M^{\bullet}] \xrightarrow{S}$$
$$[d^8 \cdots d^8] \quad [d^8 \cdots d^8]^*$$
$$[M{-}{-}M^{\bullet}] + S^{\bullet} \rightarrow [M{-}M] + S: \quad (1)$$
$$[d^7{-}{-}d^8] \qquad [d^7{-}d^7]$$

where multielectron reactivity is accomplished by coupling single-electron reactions of individual metal centers. Numerous spectroscopic studies have shown that the lowest energy $d^8 \cdots d^8$ excited state is metal-based with two electrons in a triplet configuration,[10,11] each localized on a metal center of a singly-bonded binuclear core.[12,13] The excited state of a binuclear d^8 compound may therefore be described chemically as a diradical tethered by a metal–metal bond ($[d^8 \cdots d^8]^* = [^{\bullet}M{-}M^{\bullet}]^*$).[14] The presence of a single electron at a coordination vacancy of an individual metal center provides a site for substrate activation by photoinduced single electron or atom transfer to yield a mixed valence $d^7{-}{-}d^8$ intermediate and the corresponding substrate radical intermediate.[14,15] Subsequent trapping of this radical by the $d^7{-}{-}d^8$ photoproduct in an ensuing thermal reaction effects overall two-electron transformations such as 2-propanol to acetone[14] and the dehydrogenation of

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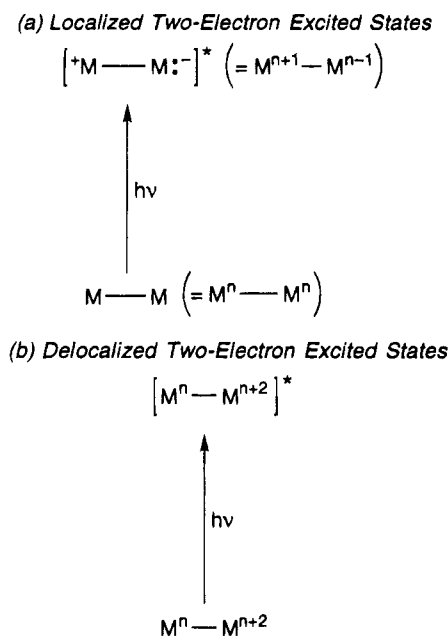(11) Rice, S. F.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1988,** *27,* 4704–4708.

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Daniel G. Nocera (born in 1957) received his undergraduate education at Rutgers University (B.A., 1979), and he performed graduate work at the California Institute of Technology (Ph.D., 1984), where he was introduced to physical-inorganic chemistry in the laboratories of Harry B. Gray. He moved in 1983 to East Lansing to take up a faculty appointment at Michigan State University and is currently a professor of chemistry. He studies the basic mechanisms of energy conversion in biology and chemistry. In addition to excited state redox mechanisms of transition metal complexes, his research interests include layered magnetism, the role of protons in mediating electron transfer, and the design of optical sensing schemes relying on a triggered luminescent response from a supramolecular active site. Recently he developed a new method to measure vorticity in highly three-dimensional turbulent flows. The laser technique has found application in solving a variety of fluid physics and engineering problems.

(a) Localized Two-Electron Excited States

$$\left[{}^{+}M \longrightarrow M \colon^{-}\right]^{*} \quad \left(= M^{n+1} \longrightarrow M^{n-1}\right)$$

$h\nu$

$$M \longrightarrow M \quad \left(= M^{n} \longrightarrow M^{n}\right)$$

(b) Delocalized Two-Electron Excited States

$$\left[M^{n} \longrightarrow M^{n+2}\right]^{*}$$

$h\nu$

$$M^{n} \longrightarrow M^{n+2}$$

Figure 1. Two strategies for designing two-electron mixed-valence excited states of binuclear metal complexes. In part a, the excited state arises from the population of orbitals that are localized on individual metal centers within the binuclear core. Thus a zwitterionic excited state is photogenerated upon metal-to-metal charge transfer $(M^{n}-M^{n} + h\nu \rightarrow M^{n+1}-M^{n-1})$ excitation of a symmetric ground state species. Alternatively (b), for complexes with delocalized metal–metal excited states, the two-electron mixed-valence excited state may be prepared from a binuclear core composed of two metals whose formal oxidation states differ by 2.

selected hydrocarbons.[16,17] With the analogy between one-electron chemistry and a biradical excited state suggested, we wondered if excited state multielectron reactions might be emphasized when two metal-localized electrons were singlet coupled within a bimetallic core.

This Account presents our approach to design multielectron chemistry based on two-electron mixed-valence excited states as described in Figure 1. For excited states derived from electrons that are weakly coupled, the multielectron excited state may be prepared by exciting a metal-to-metal charge transfer (MMCT) transition. Here electrons originally localized on the individual metal centers of a bimetallic core in the ground state are paired upon the absorption of a photon to produce an excited state that is zwitterionic, $M^{+}-M\colon^{-}$, in nature. With regard to two-electron mixed valency, a $M^{n+1}-M^{n-1}$ excited state is photogenerated from a $M^{n}-M^{n}$ ground state. Two-electron reductions of substrate may be promoted at the $\colon M^{-}$ site, whereas substrates susceptible to two-electron oxidation may react at the M^{+} site. Alternatively, for excited states derived from electrons residing in strongly coupled orbitals, the two-electron mixed-valence character must be built into the corresponding ground state complex where the formal oxidation states of the metals within the bimetallic core differ by 2, i.e., $M^{n}-M^{n+2}$. In this approach, the absorption of the photon produces a more energetic excited state that is predisposed to react in two-electron steps at the individual metal centers of the bimetallic core.

Localized Two-Electron Mixed-Valence (Zwitterionic) Excited States

Zwitterionic excited states have a long history in chemistry and physics, appearing early in valence bond[18] and molecular orbital[19] descriptions for the two-electron bond. These states were invoked early in bonding theories to describe dihydrogen at a long internuclear distance (stretched hydrogen)[19,20] and ethylene upon twisting.[21] For both of these cases, the frontier orbitals (1s orbitals of hydrogen at long distances and the orthogonal $p\pi$ orbitals of twisted ethylene) are weakly coupled, leading to four states. Two low-energy diradical states arise from one electron in each orbital with spins opposed (singlet) and parallel (triplet), and two zwitterionic singlet states are derived from the antisymmetric and symmetric linear combinations with both electrons paired in one orbital of either center. Whereas diradical states have been long established, lying at the foundation of the organic chemist's description of biradicals over the past two decades,[22-25] the zwitterionic states are more elusive, having only a transitory existence in the dissociation of a bond or the isomerization of an olefin.[26-28]

Can stable zwitterionic excited states be elaborated so that their chemistry may be explored? A cursory glance at the problem suggests that, as in the case for stretched hydrogen, the metal centers should be widely separated to achieve zwitterionic character upon MMCT excitation. Precedent for this approach comes from Taube and co-workers' classic studies of mixed valency, in which electron localization between two metal centers may be observed with the judicious choice of a bridging ligand (e.g., $[(NH_3)_5M^{III}-L-M^{II}-(NH_3)_5]^{5+}$, M = Ru, Os).[29] However, in general these complexes will not be practical excited state reagents because the oscillator strength for the MMCT transitions is too small and the metals are coordinatively saturated. In perhaps one of the great ironies of inorganic chemistry, one place to find two electrons in weakly coupled metal orbitals is in complexes that feature the shortest distances between metals, quadruple-bonded metal–metal $(M\overset{4}{-}M)$ complexes.

The overlap of the d_{z^2}, (d_{xz},d_{yz}), and d_{xy} orbitals of two d^4 metals results in a $\sigma^2\pi^4\delta^2$ ground state electronic configuration, which yields a quadruple metal–metal bond.[30] The spectroscopy of these species is dominated by metal-localized transitions with the lowest energy excited states arising from the promotion of electrons from the δ to the δ^* orbital.[31] Although this molecular orbital model aptly describes the σ and π interactions, it does not adequately

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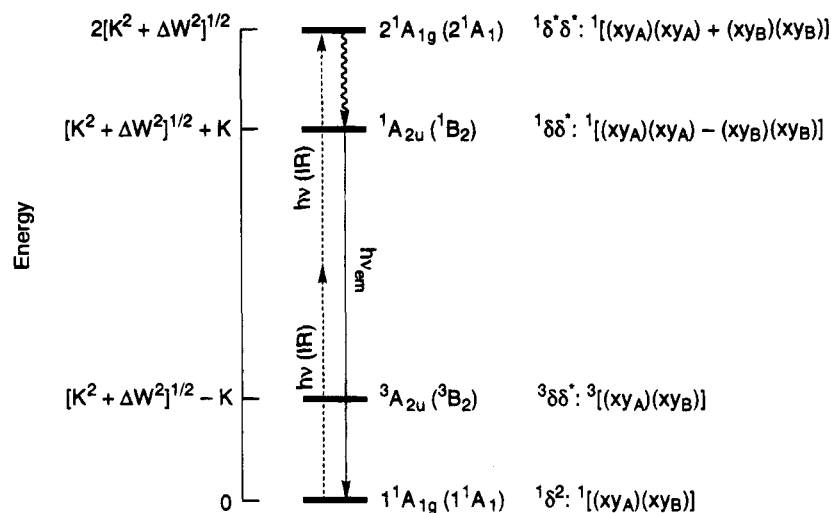(26) Schilling, C. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 2296–2298.

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Figure 2. Qualitative energy level diagram for the δ/δ^* orbital manifold of M$\stackrel{4}{-}$M complexes in accordance with a valence bond model. The state ordering is given for M$\stackrel{4}{-}$M complexes in D_{4h} and D_{2d} symmetries (with the latter parenthetically offset); the d_{xy} orbitals on metal centers A and B are designated by (xy$_A$) and (xy$_B$), respectively. The state energies are given in terms of the exchange integral, K, and the difference between the energies of the electron in a singly occupied δ and δ^* orbital, ΔW. Note that when $K \gg \Delta W$ (i.e., the two-electron energy is much greater than the one-electron energies), the diradical states are degenerate and equal to 0 whereas the zwitterionic states are degenerate and equal to $2K$. The two-photon experiment designed to detect the "zwitterionic" 2^1A_{1g} (A$_1$) excited state by laser-induced fluorescence (ref 34) is also summarized. The 2^1A_{1g} (A$_1$) state is pumped by two near-infrared photons (indicated by the dashed lines), followed by subsequent internal conversion to the highly emissive $^1A_{2u}$ (B$_2$) excited state. The red fluorescence from this state is detected.

represent the δ-bonding in M$\stackrel{4}{-}$M complexes. As emphasized in Hay's theoretical study[32] of the octachlorodirhenate ion, Re$_2$Cl$_8^{2-}$ (D_{4h}), the d_{xy} orbitals on the adjacent metals of the binuclear core weakly overlap owing to their parallel disposition to each other, and consequently the electrons residing in these orbitals are weakly coupled. Like twisted ethylene or stretched hydrogen, two diradical states ($1^1A_{1g}(\delta^2)$ and $^3A_{2u}(^3\delta\delta^*)$ symmetry in D_{4h}) and two zwitterionic states ($^1A_{2u}(^1\delta\delta^*)$ and $2^1A_{1g}(^1\delta^*\delta^*)$ symmetry) are predicted (see Figure 2). Because the $^3A_{2u}$ state arises from a simple spin-flip of an electron in a relatively isolated orbital, it should lie close in energy to the ground state. Conversely the zwitterionic states derive their parentage from pairing electrons in the confined volume of atomic-like orbitals centered on individual metals (as opposed to a molecular orbital delocalized over the bimetallic core). These states are predicted to be energetically far removed from their diradical counterparts owing to large two-electron energies. Figure 2 summarizes the $^3A_{2u}$, $^1A_{2u}$, and 2^1A_{1g} state ordering relative to the 1^1A_{1g} ground state in terms of the one-electron energy ΔW ($=W_{\delta^*} - W_\delta$, which is the difference between the energies of the electron in singly occupied δ and δ^* orbitals) and the two-electron energy K (i.e., the exchange integral).[33] In the ionic limit, $K \gg \Delta W$ and therefore the difference between the energies of the zwitterionic states is zero. Thus the energetic disposition of 2^1A_{1g} relative to $^1A_{2u}$ is a direct measure of the ionicity of these zwitterionic excited states.

With this task of measuring the $^1A_{2u}$–2^1A_{1g} energy gap at hand, we undertook a comparative study of the one- and two-photon spectroscopy of M$\stackrel{4}{-}$M complexes.[34] Formally corresponding to the promotion of

two electrons from the δ orbital to the δ^* orbital, the $2^1A_{1g} \leftarrow 1^1A_{1g}$ transition had escaped detection because it is inaccessible to conventional linear absorption spectroscopy. But such a transition is allowed in the two-photon spectrum.[35] The bright red luminescence of the $^1\delta\delta^*$ ($\lambda_{em,max} = 673$ nm) excited state of Mo$_2$Cl$_4$-(PMe$_3$)$_4$ (D_{2d})[36,37] permitted us to design the two-photon experiment schematically represented in Figure 2. The 2^1A_1 state (2^1A_{1g} in the D_{4h} geometry) is pumped by two near-infrared photons (indicated by the dashed lines), followed by subsequent internal conversion to the highly emissive $^1B_2(^1\delta\delta^*)$ ($^1A_{2u}$ in D_{4h} geometry) excited state. When the two near-infrared photons are off resonance from the $1^1A_1(^1\delta^2) \rightarrow 2^1A_1$-($\delta^*\delta^*$) transition, little or no luminescence is observed from the $^1B_2(^1\delta\delta^*)$ state; but as the $2h\nu$ laser excitation frequency is tuned into the 2^1A_1 excited state, emission from $^1\delta\delta^*$ is detected. In this manner, the excitation profile of the $2^1A_1(^1\delta^*\delta^*)$ state can be mapped out by monitoring the laser-induced fluorescence from the $^1\delta\delta^*$ excited state. Indeed, intense laser irradiation of Mo$_2$Cl$_4$(PMe$_3$)$_4$ solutions with wavelengths that are 200 nm to the red ($\lambda_{exc} = 800$–950 nm) of the $^1(\delta^2 \rightarrow \delta\delta^*)$ absorption profile ($\lambda_{abs,max} = 585$ nm) results in $^1\delta\delta^*$ luminescence! The two-photon excitation profile maximizes at 455 nm, and as expected for a two-photon transition, the intensity of the fluorescence scales with the second power of the laser intensity ($I_{fl} \propto$ (power)^2).[38] The 0.7 ratio of the fluorescence intensity for circularly to linearly polarized excitation identifies the $^1A_1$ symmetry of the excited state ($\Omega = \delta_{cir}/\delta_{lin}$ should be <1.0 for a $^1A_1$ state in the D_{2d} point group[39–41]).

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The $^1B_2-2^1A_1$ energy gap, as determined from the difference between the $^1(\delta^2 \to \delta\delta^*)$ and $^1(\delta^2 \to \delta^*\delta^*)$ transition maxima, is 4800 cm^{-1}. This zwitterionic energy gap should be equivalent, to a first approximation, to that of the $1^1A_1-^3B_2$ diradical states (see the energy scale in Figure 2). This is the case. Estimates of the diradical gap come from temperature-dependent magnetic susceptibility[42] and temperature-dependent paramagnetic shifts of the ^{31}P NMR signal[43,44] arising from the $^3A_{2u}-^1A_{1g}$ spin equilibrium for twisted M_2X_4-$(P\frown P)_2$ ($P\frown P$ = bridging phosphine) complexes. The bridging phosphines induce rotation about the metal–metal bond away from an eclipsed geometry ($\chi = 0°$), where the δ bond is fully developed, to a nearly staggered geometry at $\chi = 45°$, where the d_{xy} orbital overlap, and therefore the δ interaction, is annihilated. Although the $^3B_2$ excited state for $M\overset{4}{-}M$ complexes in eclipsed geometries is too high in energy to be populated at reasonable temperatures, the $^3B_2-1^1A_1$ spin equilibrium can be observed in the temperature-dependent susceptibility and paramagnetic shifts of the ^{31}P NMR signal of the twisted $M_2X_4(P\frown P)_2$ complexes. In the case of the latter, meticulous measurements of complexes with twist angles over the range $\chi = 17-64°$ yielded singlet–triplet energy separations of 3000–1200 cm^{-1}, respectively. Extrapolation of these data to a torsional angle of $\chi = 0°$ gives an energy gap splitting of 4840 cm^{-1}, in excellent agreement with theory[45] and the spectroscopically measured zwitterionic energy gap.

The determination of the δ manifold of Mo_2Cl_4-$(PMe_3)_4$ represents the first complete experimental description of a two-center, two-electron bond. In itself, the identification of the δ-bond manifold represents a 30-year odyssey beginning in 1964 with Cotton's realization of a δ bond,[46] followed by Gray's assignment of the $^1\delta\delta^*$ excited state in 1972,[47] measurement of the $^1\delta^2-^3\delta\delta^*$ diradical energy gap and concluding with the discovery of the $^1\delta^*\delta^*$ zwitterionic excited state.

Transient Spectroscopy of $M\overset{4}{-}M$ Complexes Derived from Zwitterionic Excited States

The spectroscopic results unequivocally establish that transitions associated with the δ-orbital manifold are MMCT in character to yield an electron pair, singlet coupled (:M$^-$–M$^+$ = d^5–d^3), within the binuclear core. More quantitatively, the spectroscopically ascertained values of ΔW and K (determined from the difference between the $^1(\delta^2 \to \delta\delta^*)$ and $^1(\delta^2 \to \delta^*\delta^*)$ energy gaps) in conjunction with the effective $d_{xy}(A)-d_{xy}(B)$ overlap (as evaluated from the oscillator strength of the $^1(\delta^2 \to \delta\delta^*)$ transition[33]) reveal that the $^1\delta^2$ ground state possesses 34% ionic character, which increases significantly to 68% in the excited

state. Nevertheless, the presence of a long-lived, ionic, excited state in $M\overset{4}{-}M$ complexes does not in itself ensure multielectron photochemistry. The $^1\delta\delta^*$ (Ψ_-) and $^1\delta^*\delta^*$ (Ψ_+) zwitterionic states are described by the following linear combinations:

$$\Psi_\pm = \begin{array}{c} :M^-\text{–}M^+ \pm M^+\text{–}M:^- \\ [d^5\text{–}d^3] \pm [d^3\text{–}d^5] \end{array} \qquad (2)$$

Although these states are ionic, they are nonpolar because :M$^-$–M$^+$ and M$^+$–M:$^-$ contribute equally to the linear combination as long as a center of inversion is maintained within the molecule and its environment. However, intermolecular or intramolecular perturbations that remove the center of inversion will lead to dissimilar contributions of the :M$^-$–M$^+$/M$^+$–M:$^-$ states in eq 2, thereby polarizing the system.

Rapid localization of the charge within the zwitterionic state may be induced externally. Fluctuations in the solvent (which may be far removed from the bimetallic core) can cause ionic character from one of the ionic states to be mixed with the other, thereby giving rise to unequal contributions of the two states in eq 2. This localization in charge by solvent, which can further reorganize to trap the ionic intermediate, is familiar in the guise of sudden or instantaneous polarization.[48,49] In the case of $M\overset{4}{-}M$ complexes, it has long been observed that an increase in solvent polarity causes the $^1\delta\delta^*$ emission band to shift to lower energies and increase in bandwidth. Recent studies show that the dipole moment of the electronically excited $Mo_2Cl_4(PMe_3)_4$ is 4.0 D (the ground state dipole is 0) in benzonitrile.[50] Moreover, the temporal evolution of the emission spectrum was observed by time-resolved emission spectroscopy to occur on the time scale of the microscopic solvent relaxation time. Presumably, the Franck–Condon transition produces the $^1\delta\delta^*$ excited state with a solvent configuration that is appropriate for the apolar ground state. The polar ionic intermediate is stabilized as solvent moves to accommodate the localized charge induced by the sudden polarization of solvent. Hence the emission spectrum evolves to its steady-state profile on the time scale of solvent motion. This result verifies that solvent is an important controlling factor of the dynamics of $^1\delta\delta^*$ luminescence and is consistent with the valence bond description of a M^IM^{III} mixed-valence excited state.

The two-electron character of the excited state may also be trapped by intramolecular distortions within the ligation sphere. In the zwitterionic excited state of the $M\overset{4}{-}M$ complexes, one center of the binuclear core is oxidized. A recurrent theme in $M\overset{4}{-}M$ chemistry is that oxidation of the binuclear metal core is accompanied by rearrangement of the ligating sphere to confacial or edge-sharing bioctahedral geometries,[30,51,52] which stabilize the binuclear metal core by ensuring an octahedral coordination geometry about the oxidized metal centers. Is the same true

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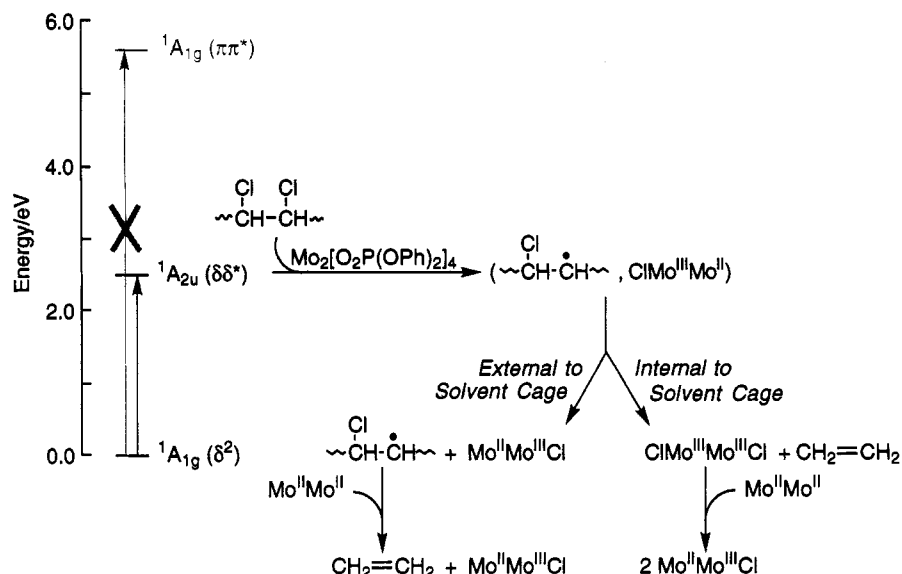
Figure 3. Mechanism for the photochemical reduction of 1,2-dichlorocarbons by $Mo_2[O_2P(OC_6H_5)_2]_4$ (refs 56 and 57). In nonaqueous solution, the lifetime of $^1\delta\delta^*$ is sufficiently long-lived to permit photoreaction from this low-energy excited state. Subsequent reaction of the primary photoproducts may occur internal or external to a solvent cage.

for the excited state? Transient absorption spectroscopy of $M_2X_4(P\frown P)_2$ complexes suggests that intramolecular distortion to a bioctahedral intermediate is indeed important. These complexes exhibit a long-lived transient whose lifetime (10−100 μs) is much longer than that of the $^1\delta\delta^*$ excited state (10−500 ps)[53] and whose absorption spectra are similar to those of $M_2Cl_6(P\frown P)$ edge-sharing bioctahedral complexes.[54,55] This has led us to propose that the long-lived, nonluminescent transient of $M_2X_4(P\frown P)_2$ complexes arises from chemical distortion to an edge-sharing bioctahedral intermediate:

$$(3)$$
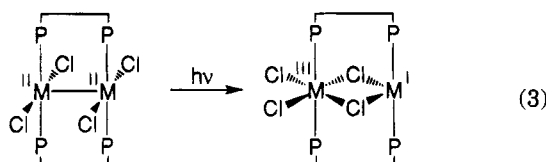
Such a ligand rearrangement provides cooperative stabilization of a charge-separated core by achieving an octahedral geometry about the oxidized M^{III} center and by diminishing the donation of electron density from the halides about the reduced M^I center. It should be noted that charge transfer within the bimetallic core does not appear to be solely sufficient to promote rearrangement because the structurally distorted transient intermediate is not observed to form upon $^1\delta\delta^*$ excitation, but rather is observed when metal-localized transitions (e.g., $\delta \rightarrow \pi^*$, $\pi \rightarrow \delta^*$) immediately to higher energy of $^1(\delta^2\rightarrow\delta\delta^*)$ are excited. These states not only possess charge transfer character, but their population should also lead to diminished metal−metal π bonding relative to that in the ground state molecule. This feature is expected to enhance 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.

Photochemistry of M$\underline{\underline{4}}$M Complexes

The stabilization of the two-electron mixed-valence intermediate in eq 3 is critical for multielectron

activation. When the metal core is strapped by four bidentate ligands (D_{4h}), d^3-d^4 mixed-valence species are the common photoproducts. The inflexibility of the four bidentate ligands renders the coordination sphere incapable of accommodating the increased charge of a $M^{III}M^{III}$ core, and hence the reaction terminates at the one-electron-oxidized $M^{II}M^{III}$ metal complex. In these cases, photochemistry is not derived from a zwitterionic excited state, but multielectron photochemistry may be achieved by coupling stepwise one-electron chemistry via a mixed-valence $M\underline{\underline{3.5}}M$ intermediate. The photochemistry of quadruply bonded $Mo^{II}Mo^{II}$ tetrakis phosphates and phosphonates in aqueous and nonaqueous solutions, respectively, exemplifies these reactivity patterns.

The $Mo^{II}Mo^{II}$ tetrakis diphenyl phosphate, $Mo_2[O_2P(OC_6H_5)_2]_4$, is luminescent in nonaqueous solutions, and $^1\delta\delta^*$ is sufficiently reducing and long-lived ($\tau_0 = 68$ ns) to permit its reaction with organic substrates.[56] Visible irradiation of halocarbon solutions of $Mo_2[O_2P(OC_6H_5)_2]_4$ leads to the two-electron reduction of dihalocarbons to olefin (eq 4). As summarized in Figure


$$(4)$$
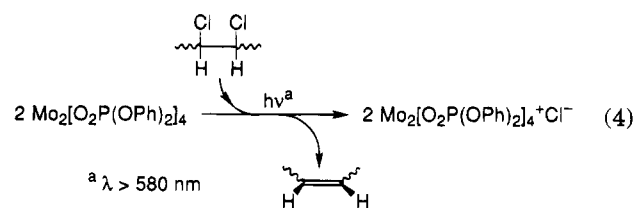
3, the photochemistry proceeds via one-electron intermediates with the primary photoevent comprising initial chlorine atom abstraction to give the mixed-valent $Mo^{II}Mo^{III}$ complex, $Mo_2[O_2P(OC_6H_5)_2]_4Cl$. The

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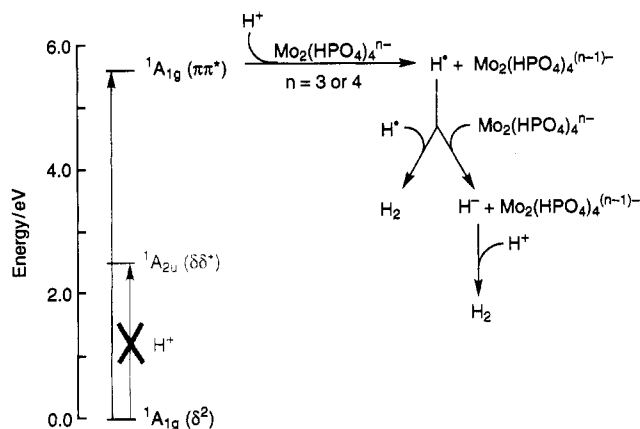
Figure 4. Energy level diagram summarizing the mechanism for the photochemistry of the quadruply bonded dimer $Mo_2(HPO_4)_4^{4-}$ in acidic solution (ref 58). The $^1\delta\delta^*$ excited state is not long-lived in aqueous solution, and photochemistry proceeds exclusively from the high-energy metal-localized $^1\pi\pi^*$ excited state. This scheme is also valid for the mixed-valence complex $Mo_2(HPO_4)_4^{3-}$; the photoproduct is the triply bonded metal–metal complex $Mo_2(HPO_4)_4^{2-}$ thus giving the overall stoichiometry for eq 5.

chemistry has been generalized to include unsaturated chlorocarbons as well,[57] but here too the primary photoevent appears to be chlorine atom abstraction.

A two-electron-oxidized photoproduct may be accessed if the bimetallic core is made more reducing, but the reaction again proceeds through a one-electron mixed-valence intermediate. Whereas substitution of $O_2P(OR)_2^-$ by HPO_4^{2-} does little to perturb the electronic structure, the reduction potential of the dimolybdenum core is increased by 1.0 V. In acidic aqueous solutions, ultraviolet irradiation of $Mo_2(HPO_4)_4^{4-}$ yields the triply bonded metal complex $Mo_2(HPO_4)_4^{2-}$ and H_2,[58] a net two-electron photoreaction. But detailed mechanistic studies show that the reaction proceeds in one-electron steps via the powerfully reducing $^1\pi\pi^*$ excited state (the $^1\delta\delta^*$ excited state is susceptible to efficient quenching by protons in aqueous solution[59]) of the quadruple bond complex (Figure 4) to yield the one-electron mixed-valence species $Mo_2(HPO_4)_4^{3-}$. This complex is subsequently excited by another ultraviolet photon into its $\pi\pi^*$ excited state, which like its quadruple-bond parent can react with protons to yield 0.5 equiv of H_2:
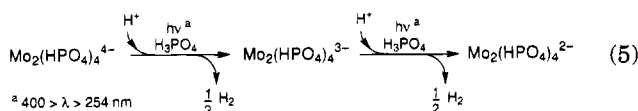
One-photon, two-electron reactivity may be realized when two of the four bidentate ligands are replaced by monodentate ligands, usually halides. As suggested by transient absorption spectroscopy of the $M_2X_4(P \frown P)_2$ complexes, the terminal halide ligands can rearrange to form an edge-sharing bioctahedral coordination about the photooxidized metal center of the electronically excited binuclear core. From eq 3, we see that absorption of a photon produces a charge-

separated state of singlet character and simultaneously provides an open coordination site at the reduced metal center. These properties represent the basic tenets for substrate activation by oxidative-addition.[60] Accordingly, the photoactivity of M_2X_4-$(P \frown P)_2$ complexes was explored along these lines.

The photochemistry of the $M_2Cl_4(dppm)_2$ (M = Mo, W; dppm = (diphenylphosphino)methane) is consistent with classic oxidative-addition reactivity. Excitation of solutions of $M_2Cl_4(dppm)_2$ and alkyl iodides[61,62] or aryl disulfides[55] with wavelengths that are energetically coincident to those required for the production of the long-lived transient yield $M^{III}M^{III}$ edge-sharing bioctahedral photoproducts. For the case of M = W, the former photoreaction has been thoroughly investigated. Although CH_3I (MeI) solutions of W_2Cl_4-$(dppm)_2$ are indefinitely stable at room temperature in the absence of light, excitation with $\lambda > 495$ nm quantitatively affords a single product, $W_2Cl_4(dppm)_2$-$(CH_3)(I)$.[61] ^{13}C NMR indicates that the methyl group is more likely to be in a terminal than a bridging position, a result that is consistent with addition of the substrate to the open coordination site of a single tungsten center of a photogenerated edge-sharing bioctahedral intermediate. Simple photoaddition is not observed, however, when the alkyl iodide is CH_3-CH_2I (EtI).[62] Photolyzed solutions of $W_2Cl_4(dppm)_2$ and EtI yield $W_2Cl_4(dppm)_2I_2$ and $W_2Cl_5(dppm)_2I$, and unlike MeI photochemistry, the appearance of the photoproducts is adversely affected by the presence of radical inhibitors. These observations are signatures of a free radical photoreaction where the M_2Cl_4-$(P \frown P)_2$ complex photoreacts with substrate to produce a mixed-valence $M_2Cl_4(P \frown P)_2I$ primary photoproduct that disproportionates by either chlorine or iodine atom transfer.[62] This latter disproportionation reaction is confirmed by the electrochemical oxidation of $W_2Cl_4(dppm)_2$ in the presence of I^-, which permits the mixed-valence $W_2Cl_4(dppm)_2I$ intermediate to be accessed independently of a photochemical reaction pathway.

The reactivity trends of $W_2Cl_4(dppm)_2$/alkyl iodide photochemistry provide an excited state analogy to the oxidative-addition chemistry of mononuclear d^8 square-planar metal complexes. As is the case for W_2Cl_4-$(dppm)_2$ photochemistry, the d^8 archetype, Vaska's complex, *trans*-$IrCl(CO)(PR_3)_2$, reacts with MeI by simple addition and with EtI by one-electron radical pathways.[63,64] A radical chain mechanism has been proposed for EtI, based on the attenuation of the rate in the presence of radical inhibitors. Conversely the rate is unaffected by radical inhibitors when MeI is the reactant. The solvent dependence and large negative activation entropy with MeI as the oxidative-addition substrate are consistent with a nucleophilic S_N2 mechanism that entails the addition of the electropositive $H_3C^{\delta+}$ to the metal center followed by rapid

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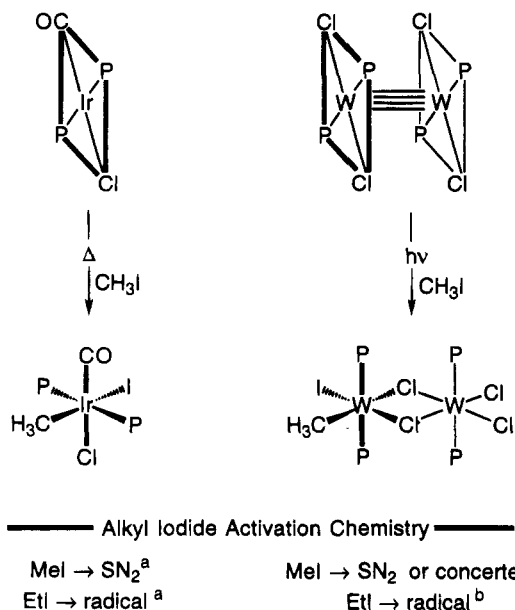
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──── Alkyl Iodide Activation Chemistry ────

| MeI → SN$_2$[a] | MeI → SN$_2$ or concerted [b] |
| EtI → radical [a] | EtI → radical [b] |

Figure 5. A comparison between the thermal chemistry of Vaska's complex and photochemistry of W$_2$Cl$_4$(dppm)$_2$ for the oxidative-addition of alkyl iodides; (a) refs 63 and 64; (b) ref 62. The atom label P signifies monodentate or bridging phosphine.

addition of the displaced I$^-$. However, a mechanism involving a very short-lived radical cage cannot be ruled out. Similarly, this is the case for the photoreaction of MeI with W$_2$Cl$_4$(dppm)$_2$. It is not yet known whether the addition of MeI across a tungsten center of the bimetallic core proceeds by sequential one-electron transfer within a solvent cage or via a concerted transition state.

Figure 5 summarizes the parallels between W$_2$Cl$_4$-(dppm)$_2$ photochemistry and the thermal chemistry of Vaska's complex. Addition of MeI in both cases is promoted at a low-valent, coordinatively unsaturated ML$_4$ center to yield an octahedral geometry at the site of activation.[65] Though not directly involved in the activation step, the neighboring ML$_4$ fragment for the M$\stackrel{4}{-}$M pathway plays the important role of initiating the two-electron chemistry by reducing the active site upon excitation. This neighboring ML$_4$ unit enforces a cis addition of MeI to the ML$_4$ fragment, as opposed to the trans addition observed for Vaska's complex.

Delocalized Two-Electron Mixed-Valence Excited States

Is direct multielectron reactivity of a binuclear metal complex restricted to the excited states of M$\stackrel{4}{-}$M complexes? In the context of preparing two-electron mixed-valence excited states by pairing two electrons within the binuclear core, M$\stackrel{4}{-}$M species are unique. Most excited states are derived from the population of molecular orbitals that are delocalized over the entire bimetallic core, and consequently, in such cases it is not appropriate to think about electron pair localization. For this reason, multielectron schemes based on zwitterionic excited states are difficult to generalize to most other classes of binuclear complexes, and new approaches must be developed. One promising line of research is the synthesis of complexes with the two-electron mixed valency already present in the ground state.

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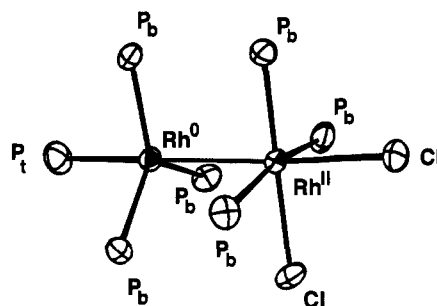
Figure 6. An ORTEP view of Rh$_2$[CH$_3$N(PF$_2$)$_2$]$_3$Cl$_2$(PF$_3$) where P$_b$ represents the phosphines of the bridging bis(difluorophosphino)methylamine and P$_t$ is the phosphine of the terminal PF$_3$ ligand.

Although the occurrence of two-electron mixed-valence compounds is for the most part rare,[66] they can be prepared for binuclear cores strapped by bis-(difluorophosphino)methylamine. This unique bidentate ligand was first synthesized by Nixon in the late 1960s,[67] and subsequently it was popularized in transition metal chemistry by King and co-workers during the 1970s.[68] Bis(difluorophosphino)methylamine reacts smoothly with the symmetric Rh^{I}Rh^I dimer, [RhX(PF$_3$)$_2$]$_2$ (X = halide), to yield the singly bonded metal−metal complex Rh$_2$[CH$_3$N(PF$_2$)$_2$]$_3$X$_2$(PF$_3$) (designated Rh^{0}Rh^{II}X$_2$).[69] The overall reaction corresponds to an intramolecular disproportionation of the Rh^{I}Rh^I starting material to produce a mixed-valence Rh^{0}Rh^{II} complex. The two-electron mixed-valence Rh^0-Rh^{II} core is established by the coordination sphere about the dirhodium center, which is reproduced in Figure 6 for the chloride complex. Pseudooctahedral and trigonal-bipyramidal geometries are structural hallmarks of metal−metal-bonded rhodium in divalent and zero oxidation states, respectively.[70] The flexibility of the bis(difluorophosphino)methylamine ligand allows the coordination asymmetry about the dirhodium core to be accommodated with facility. In addition, the ligand's special electronic properties undoubtedly play a crucial role in the stabilization of both the high and low oxidation states of the unusual mixed-valence Rh^{0}Rh^{II} core. Specifically, the three N−P bonds adjacent to the P−Rh^{II} are 0.030(3) Å shorter than those N−P bonds adjacent to the P−Rh^0. We interpret this asymmetry in the fluorophosphine backbone to disparate N pπ donation to the P dπ orbitals. The shorter N−P(Rh^{II}) distances are consistent with donation of the electrons of the N lone pair to the dπ orbitals of P, which diminishes the π-withdrawing ability of the PF$_2$ groups bonded to the Rh^{II}. This feature enables the high oxidation state metal to be stabilized. With the N lone pair electron density channeled away from the PF$_2$ groups bonded to the Rh^0, the strong dπ accepting properties of the PF$_2$ group are maintained and hence the Rh^0 is stabilized. In this manner, we believe that the CH$_3$N(PF$_2$)$_2$ ligand is special in promoting M^n−M^{n+2} formation.

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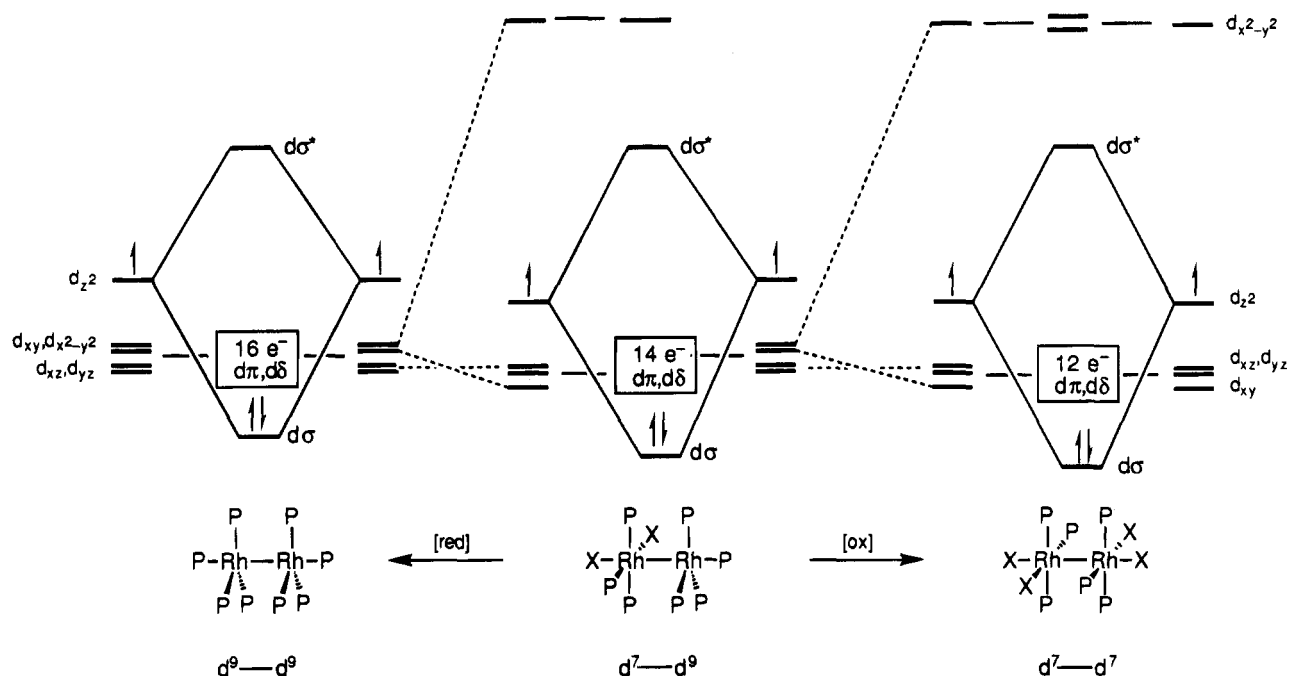
Figure 7. The center panel shows the simple molecular orbital diagram for the mixed-valence Rh^0Rh^{II} complex arising from the interaction of a C_{3v} Rh^0P_4 fragment with a C_{4v} $Rh^{II}P_3X_2$ fragment. The $d\pi$- and $d\delta$-symmetry orbitals are filled, and this manifold is indicated by the box. To minimize level congestion, $X\sigma$ and $X\sigma^*$ orbitals and low-symmetry splittings within the $d\pi$ and $d\delta$ levels of the $Rh^{II}P_3X_2$ fragment are not considered. The d-orbital correlation diagram is shown for the oxidized and reduced complexes. Upon oxidation of the mixed-valence complex, the $d_{x^2-y^2}$ orbital is depopulated and raised in energy because of a M−L σ^* interaction. Conversely, upon reduction, the $d_{x^2-y^2}$ orbital is stabilized and filled by two electrons. Accordingly, a similar electronic structure and a lowest energy, photoreactive $d\sigma^*$ excited state are preserved across the four-electron series.

Low-temperature glasses and solids of $Rh^0Rh^{II}X_2$ complexes exhibit red luminescence that is strongly temperature dependent. Spectroscopic and photophysical studies are consistent with luminescence arising from a $d\sigma^*$ excited state,[71] which is an emerging trend observed in the spectroscopy of M−M cores spanned by bridging ligands.[72-74] The occurrence of a discrete $d\sigma^*$ excited state for this mixed-valence structure is consistent with a simple picture of the electronic structure of singly bonded d^7-d^7 (e.g., $Mn_2(CO)_{10}$) and d^9-d^9 (e.g., $Co_2(CO)_8$) dimers.[75,76] A qualitative molecular orbital diagram for $Rh^0Rh^{II}X_2$ complexes is shown in the central panel of Figure 7. The Rh^0P_4 fragment is the building block of a d^9-d^9 complex with eight electrons residing in $\pi(d_{xz},d_{yz})$ and $\delta(d_{xy},d_{x^2-y^2})$ orbitals; the odd electron occupies the σ-(d_{z^2}) orbital. In the case of the d^7 $Rh^{II}P_3X_2$ fragment, the $d_{x^2-y^2}$ level is displaced to very high energy owing to the destabilizing σ^* interactions of the metal with the ligands in the equatorial plane. Consequently, as in Rh^0P_4, the odd electron of the d^7 $Rh^{II}P_3X_2$ fragment resides in the $\sigma(d_{z^2})$ orbital, with the remaining six electrons occupying the lower energy $\pi(d_{xz},d_{yz})$ and δ-(d_{xy}) orbitals. Formation of a Rh−Rh single bond results from the pairing of the electrons in the spatially directed d_{z^2} orbitals of the individual fragments, and the lowest energy excited states arise from

population of the $d\sigma^*$ orbital.[69,71,77] For these reasons, the d-electron count for the d^7-d^9 $Rh^{II}Rh^0$ mixed-valence complex is best represented as $(d^6)d^1-d^1(d^8)$.

An intriguing point about the luminescent (and hence potentially reactive) $d\sigma^*$ excited state of the Rh^0-Rh^{II} binuclear complex is that it can be synthetically tailored into a homologous four-electron series.[77] The $Rh^0Rh^{II}X_2$ mixed-valence dimer can be oxidized to the symmetrical $X_2Rh^{II}Rh^{II}X_2$ complex $Rh_2[CH_3N(PF_2)_2]_3X_4$, where a pseudooctahedral geometry is now observed about each of the dirhodium centers. Alternatively, reduction of the mixed-valence complex gives the Rh^0-Rh^0 dimer with its trigonal-bipyramidal core to complete a homologous d^7-d^7, d^7-d^9, d^9-d^9 series. The electronic consequences of these synthetic conversions are illustrated in Figure 7. Upon oxidation of the Rh^0 center of the mixed-valence dimer, the $d_{x^2-y^2}$ orbital is emptied and destabilized since it is now M−L σ^* in character. Conversely, the $d_{x^2-y^2}$ orbital is stabilized and occupied upon reduction of the Rh^{II} center. Thus the electronic structures of the d^7-d^7 (i.e., $(d^6)d^1-d^1$-(d^6)) and d^9-d^9 (i.e., $(d^8)d^1-d^1(d^8)$) complexes are for the most part unchanged, with lowest energy transitions resulting from promotion of electrons to the $d\sigma^*$ orbital. Not surprisingly, the absorption and luminescence spectra across the Rh^0Rh^0, $Rh^0Rh^{II}X_2$, and $X_2Rh^{II}Rh^{II}X_2$ series are similar, and all the complexes possess a lowest energy $d\sigma^*$ excited state, from which a similar temperature-dependent luminescence is observed.

Because the $d\sigma^*$ excited state presents the possibility for interconverting among the Rh^0Rh^0, $Rh^0Rh^{II}X_2$, and $X_2Rh^{II}Rh^{II}X_2$ cores via two-electron steps, the system offers a foundation for the design of four-

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electron photocatalytic schemes. Dissociative photochemistry for $Rh^0Rh^{II}X_2$ is suggested by the disappearance of the $d\sigma^*$ luminescence in fluid solutions, and we therefore are investigating the photochemistry of the $Rh^0Rh^{II}X_2$ binuclear complexes. In THF solutions containing the Br_2 trap tetramethylethylene (TME), $Rh^0Rh^{II}Br_2$ is cleanly converted to Rh^0Rh^0,[78]
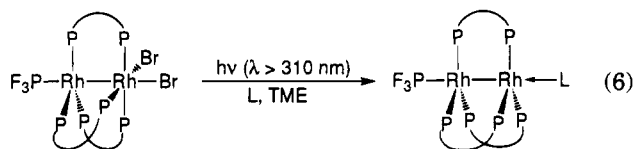
We believe that THF occupies the vacant axial coordination site of the rhodium center from which bromine elimination took place. This two-electron photoreductive elimination is noteworthy because a metal halide usually represents a kinetic and/or thermodynamic sink in a photochemical cycle. It probably is in this case, too, but the reactive $d\sigma^*$ excited state permits us to overcome the barrier to halide elimination. We can now think reasonably of replacing X_2 with HX in eq 6. The goal here would be to oxidatively add 2 equiv of HX to Rh^0Rh^0 to produce $Rh^{II}Rh^{II}$ hydrido halide species and utilize the $d\sigma^*$ excited state to reductively eliminate H_2 and X_2. While this approach to multielectron excited state chemistry is still in its infancy, the dirhodium fluorophosphine system clearly delineates a promising line of research for the future elaboration of multielectron excited states: the continued design of homologous binuclear or cluster series coupled by two-electron changes in the formal oxidation states of the metals composing the polynuclear core. If a discrete excited state can be preserved across the homologous series, then the rational design of photocatalytic, multielectron schemes should be possible.

Concluding Remarks and the Outlook

The chemistry described in this Account offers a complementary approach to effecting multielectron transformations based on coupling the one-electron reactions of electronic excited states. Discrete multielectron reactions of excited states may be realized; however, one-electron reactions must be circumvented by controlling the electronic structure of the excited

state. Two-electron mixed-valence excited states within binuclear cores provide a framework to logically advance excited state redox chemistry from conventional one-electron to multielectron pathways. As illustrated here, the development of two-electron mixed-valence excited states opens the window to photochemical oxidative-addition and reductive-elimination reactions. Yet the excited states described in this Account offer much more with regard to new reaction chemistry. Two-electron atom transfer reactions are evident when one considers the $M^+–M:^-$ character of $M\stackrel{4}{–}M$ excited states. An electron pair situated on a coordinatively unsaturated metal center is well-suited to receive an X^+ or oxygen atom.[79-81] Similarly, the M^n center of $M^n–M^{n+2}$ excited states may also be susceptible to two-electron atom transfers. Moreover, excited state multielectron processes will undoubtedly assume a prominent role in our future understanding of the mechanisms of multielectron redox reactions. The issue of sequential versus concerted electron transfer in multielectron transformations of transition metals was clearly posed over 45 years ago in Westheimer's studies of chromic acid oxidations.[82] Though often discussed,[83] this issue remains relatively undefined in comparison to our extensive understanding of single electron transfer processes. The ability to initiate a multielectron event with a photon from ultrafast lasers significantly expands the temporal window within which this important and fundamental mechanistic issue may be explored. More generally, as the chemistry of two-electron excited states continues to emerge, they will undoubtedly play a prominent role as key intermediates in the energy conversion chemistry of biomimetic and chemical assemblies.

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