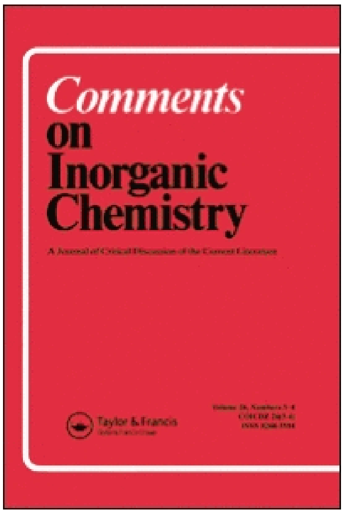

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Photogeneration of Strong One- and Two-Electron Redox Agents from Transition Metal Complexes

Richard J. Watts[a]
[a] Department of Chemistry, University of California, Santa Barbara, California

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Photogeneration of Strong One- and Two-Electron Redox Agents from Transition Metal Complexes

Key Words: *photosensitization, photo-oxidation, photo-reduction, photo-catalysis, transition metal complexes, cyclometalated complexes, ortho-metalated complexes, iridium(III) complexes, rhodium(III) complexes, photo-reduction of carbon dioxide, photochemical hydrogen production, 2,2'-bipyridine complexes, 2-phenylpyridine complexes, ortho-metalated complexes of 2,2'-bipyridine, photoconversion, solar fuel production*

I. INTRODUCTION

The thermal reaction chemistry and electrochemistry of oxidation and reduction reactions occupies a prominent position in the development of modern inorganic chemistry. The thermodynamic parameters associated with redox reactions have been extensively studied via electrochemical as well as calorimetric techniques, and these parameters provide a convenient basis for establishing equilibrium constants and spontaneity for a wide variety of redox processes. Development of theories describing electron transfer reactions[1-4] has provided, with the help of structural information, an important means of correlating these thermodynamic parameters with the kinetics of redox reactions. Thermal electron transfer reactions continue to play a central role in current inorganic chemical research in such diverse areas as theoretical and synthetic

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inorganic chemistry, inorganic polymer chemistry, and bioinorganic chemistry.

More recently, the importance of redox reactions in which the oxidizing or reducing agent is an excited state of a metal complex has been recognized,[5-9] and studies of excited state electron transfer reactions have been brought into sharp focus in the area of inorganic photochemistry.[10-15] Studies of these reactions in natural photosynthesis in plants,[16] photocatalysis in artificial photosynthetic systems,[17,18] and interfacial photoelectrochemical processes[19,20] are representative of this focus. Adaptations of theories describing thermal electron transfer processes to the description of processes in which the oxidizing or reducing agent is an excited state of a metal complex have been actively pursued[21-23] in conjunction with photochemical studies of the rates, mechanisms and product distributions for these processes.

Both the oxidizing and reducing power of any chemical species is enhanced by electronic excitation as is illustrated in Fig. 1. The absorption of a mole of photons having energy $N^{\circ}h\nu_a$ leads to an increase in the internal energy of the excited species. This species must live sufficiently long to undergo collisions with a substrate if it is to participate in bimolecular electron transfer. For excitation above the lowest energy excited state, rapid vibrational relaxation, internal conversion and intersystem crossing processes generally

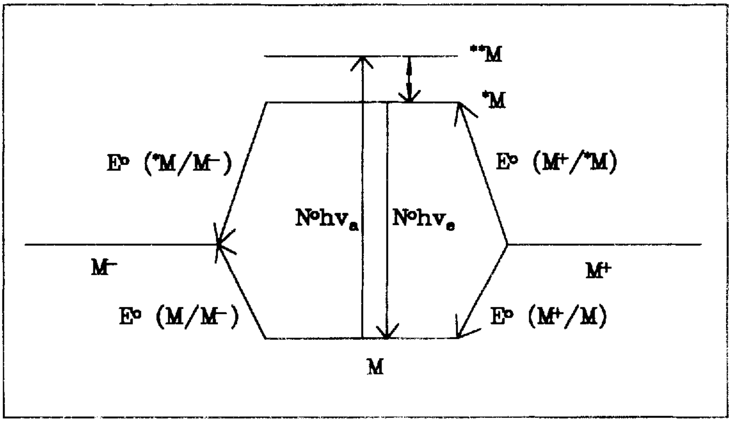

FIGURE 1 Changes of redox potentials due to electronic excitation.

lead to some loss of excitation energy to populate the lowest energy excited state which might live sufficiently long to participate in outer sphere electron transfer. The internal energy difference between this excited state and the ground state, ΔE^*, is therefore generally less than $N^o h\nu_a$ and is often taken as equivalent to the energy of a mole of emitted photons, $N^o h\nu_e$ when emission can be monitored. For processes which occur in condensed media, ΔH^* may be taken as equal to ΔE^*, so that the Gibbs free energy, ΔG^* is given by $N^o h\nu_e - T\Delta S^*$. Straightforward corrections for entropy changes due to degeneracy changes associated with spin multiplicities are sometimes used to estimate values of ΔG^* from measured emission energies. However, more important entropy changes are expected to arise from changes in solvation, and these are generally neglected.

Entropy changes are expected to be relatively small in cases where relatively little distortion of the nuclear framework or the electronic charge distribution occurs in the excited state, but the $T\Delta S^*$ term could become significant for excited states with highly distorted geometries and/or large transition dipoles. Reliable values of ΔS^* for excitation processes are generally not available, and values of $N^o h\nu_e$ are often used as estimates of ΔG^* values with recognition of some degree of inaccuracy associated with this approach.

Values of the standard half-cell potential for the ground state, $\epsilon^o(M/M^-)$ as well as the one electron oxidation product of the ground state, $\epsilon^o(M^+/M)$, are generally taken from cyclic voltammetric measurements. Values of the excited state redox potentials can then be estimated from Eqs. (1a) and (1b) below where F represent the value of the Faraday.

$$\epsilon^o(M^*/M^-) = -\Delta G^*/F + \epsilon^o(M/M^-), \tag{1a}$$

$$\epsilon^o(M^+/M^*) = \Delta G^*/F + \epsilon^o(M^+/M). \tag{1b}$$

In these equations the sign of ΔG^* is negative, reflecting the change in Gibbs free energy for a pathway leading from the excited state to the ground state. This method of determination of excited state redox potentials[24] has the advantage that it depends upon emission spectroscopic and electrochemical measurements which are often relatively straightforward. A second method based upon determination of quenching rate constants for a homologous series of quenchers as a function of the quencher redox potential provides an alternate means by which to estimate excited state redox potentials for a photosensitizer.[25] This method has the advantage that it is grounded in the kinetics of electron transfer processes which may be closely associated with the purpose for which a sensitizer is developed. However, the experimental methods for the large number of Stern–Volmer quenching studies required to determine a series of quenching constants are time consuming, and homologous series of quenchers with solubilities and well-known redox potentials suitable for studies of a particular photosensitizer are not always readily available. As a result, the combined spectroscopic/cyclic voltammetric method is generally preferred as a starting point for estimates of excited state redox potentials.

While any molecular species which absorbs light is generally a better oxidizing agent and a better reducing agent in its electronically excited states than it is in the ground state, a number of factors suggest that transition metal complexes have characteristics particularly favorable to their application as photoredox agents which can be activated by visible light. These factors have been discussed[26–29] in the context of photocatalytic cycles which employ transition metal complexes as sensitizers to shuttle electrons to and from thermal catalysts, relays, or redox substrates, in a manner which leads to a net endergonic redox reaction in the substrates. The favorable features associated with many transition metal complexes include strong visible absorption bands, relatively long excited state lifetimes in fluid solutions, and reversible oxidation and/or reduction electrochemistry. Many metal complexes also have relatively rapid excited state self-exchange rates with their oxidized and/or reduced forms,[21,22] which provides a kinetic advantage for their use in photoredox applications.

As is illustrated in Fig. 2, the use of a metal complex as a photoredox catalyst implies that the complex must participate in both an excited state electron transfer process and a thermal electron transfer process which brings the complex back to its initial oxidation level. The metal complex which has been by far the most widely used photoredox agent in photocatalytic applications is the *tris*-2,2′-bipyridylruthenium(II) dication, $[Ru(bpy)_3]^{2+}$. Estimates

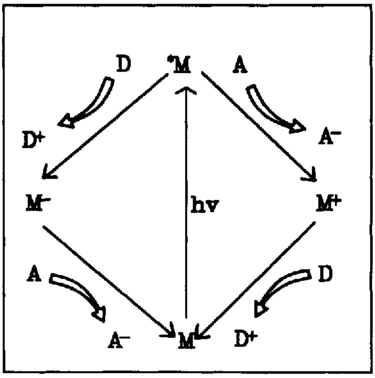

FIGURE 2 Photocatalytic cycles associated with oxidative and reductive quenching of excited states.

of the excited state redox potentials of this complex[30,31] by the method described above yields values of $\epsilon^{\circ}(^{*}\text{Ru(bpy)}_3^{2+}/\text{Ru(bpy)}_3^{+}) = +0.82$ V and $\epsilon^{\circ}(\text{Ru(bpy)}_3^{3+}/^{*}\text{Ru(bpy)}_3^{2+}) = -0.84$ V. These values are in good agreement with kinetic estimates taken from quenching studies[25] and based upon the Marcus–Hush theory for electron transfer.[1,2]

Many of the substrate redox reactions which one might wish to drive with photosensitizers require the transfer of two or more electrons, and excited state photosensitizers are typically capable of delivering or accepting only a single electron following absorption of a photon. It is possible to circumvent this photosensitizer/substrate incompatability by introducing catalysts which act as electron sinks or hole sinks to accept electrons from or deliver electrons to a photosensitizer one at a time. Having stored sufficient numbers of electrons or holes from the photosensitizer, the sink may then interact with substrates to induce multielectron redox processes. For example, Pt metal in the form of colloidal particles has often been used as an electron sink which accepts electrons from a photosensitizer and goes on to interact with 2 H+ in a two electron reduction process to produce molecular H_2. The primary advantage of this approach is in bypassing high energy pathways often associated with one-electron transfer processes, thereby producing the desired product by less energetically demanding multielectron transfer processes. For example, in the case of hydrogen reduction, the one electron transfer which reduces H^+ to H atoms requires a driving force of -2.52 V vs. NHE ($\Delta G = +243$ kJ/mol) at pH 7 as compared to a driving force of -0.41 V vs. NHE ($\Delta G = +79$ kJ/mol) for the two electron reduction of 2 H^+ to molecular H_2 at pH 7. Energetic considerations such as the one cited above have led to considerable emphasis on the coupling of thermal multielectron catalysts with photosensitizers in multicomponent heterogeneous systems which circumvent the high-energy one-electron transfer processes generally implied by direct interaction of substrates with the excited state of a photosensitizer. In these systems $Ru(bpy)_3^{2+}$, and related complexes in which the redox potentials of the complex are modified by substituents on the bpy ligand, have proven to be particularly useful since the thermodynamic demands of many of the multielectron transfer reactions of simple substrates, such as water and carbon dioxide, to form products such as H_2, O_2, CO and HCO_2^-, are readily met by the Ru(II) photosensitizers when they deliver or accept one electron per photon absorbed in interactions with an intermediary thermal catalyst. Some of the difficulties with these heterogeneous systems are associated with development of appropriate multielectron thermal catalysts which can promote the desired redox reactions of the substrates and efficiently accept electrons or holes from the photosensitizer without undergoing energy-wasting back reactions.

Due to the emphasis which has been placed upon promotion of low-energy multielectron transfer reactions mediated by thermal catalysts, relatively little attention has been directed towards the development of photosensitizers which might participate directly with substrates in one-electron transfer processes which produce high energy species. Even less attention has been directed towards development of two-electron redox agents via oxidative or reductive quenching of photosensitizer excited states. These approaches have the advantage of eliminating at least one component, an electron or hole sink, and might therefore lead more readily to homogeneous photoconversion systems. Furthermore, the development of strong photoxidizing or photoreducing agents might lead to unusual secondary or tertiary chemical reactions subsequent to production of high energy one- or two-electron transfer products.

Just how strong a one-electron photoxidizing or photoreducing agent can be activated by absorption of visible light? Two factors relevant to this question are apparent by consideration of Fig. 1

above. If one takes the 400 nm edge of the visible region as a short wavelength limit, the maximum value of ΔG^* is -3.1 V, and this is reduced to -2.5 V at 500 nm, near the maximum of the solar spectral irradiance at air mass 1.2. This leaves, then, the values of $\epsilon^\circ(\mathrm{M/M^-})$ and $\epsilon^\circ(\mathrm{M^+/M})$ which, in conjunction with ΔG^*, can be used to estimate $\epsilon^\circ(\mathrm{M^*/M^-})$ and $\epsilon^\circ(\mathrm{M^+/M^*})$ according to Eqs. (1a) and (1b) above. Practical considerations suggest that values of the ground state redox potentials in these equations should be compatible with species which are stable toward decomposition reactions such as air oxidation or disproportionation as well as with a cyclic, photocatalytic process which does not consume strong oxidizing or reducing agents in thermal reactions needed to regenerate the photosensitizer. Evaluation of these terms is therefore dependent upon specific chemical stability factors associated with the photosensitizer as well as with specific considerations related to the net reaction which will be catalyzed. It may be anticipated that these factors would generally limit $\epsilon^\circ(\mathrm{M}\backslash\mathrm{M^-})$ to values no less negative than minus a few hundred millivolts and $\epsilon^\circ(\mathrm{M^+}\backslash\mathrm{M})$ to values no less positive than plus a few hundred millivolts. Given this admittedly oversimplified generality for the ground state redox couples and ΔG^* values in the range suggested above, oxidizing agents with values of $\epsilon^\circ(\mathrm{M^*/M^-})$ or $\epsilon^\circ(\mathrm{M^+}\backslash\mathrm{M})$ in the range of $+2.2$ to $+2.8$ V might be prepared by absorption of visible light. Similarly, reducing agents with values of $\epsilon^\circ(\mathrm{M^+}\backslash\mathrm{M^*})$ or $\epsilon^\circ(\mathrm{M/M^-})$ in the range -2.2 to -2.8 V might be attainable. Comparison of these values with well-known ϵ° values of standard thermal oxidizing and reducing agents suggests that one-electron photoxidizing agents with thermodynamic potentials comparable to fluorine and one-electron photoreducing agents with thermodynamic potentials comparable to sodium might be produced by visible light excitation of relatively stable ground state species! Thermodynamic potentials, however, do not tell the whole story since excited states decay via radiative and nonradiative decay processes which compete with outer sphere electron transfer. Photoactivated redox agents are therefore subject to kinetic restrictions which are not generally applicable to strong thermal redox agents. However, the large overpotential to drive outer sphere electron transfer reactions with substrates which might be provided by strong excited state redox agents can often assure diffusion controlled electron transfer kinetics. For excited states which live more than 10^{-8} s, this may be sufficient to assure efficient electron transfer at modest substrate concentrations. The difficult problem of stopping back reactions of the oxidized/reduced photocatalyst with the reduced/oxidized substrate must then be solved, but the generation of strong photoredox agents is a first step toward facilitating new photochemical processes leading to high energy products.

The net reduction potential of the two-electron couple, M^+/M^-, which might be generated by oxidative or reductive quenching of a photosensitizer excited state, is given by

$$\epsilon^\circ(M^+/M^-) = 1/2\,\{\epsilon^\circ(M^+/M) + \epsilon^\circ(M/M^-)\}. \tag{2}$$

For reductive quenching to produce a two-electron reducing agent, M^-, the M^*/M^- couple should have a potential no less positive than a few hundred millivolts to facilitate quenching, and the M^+/M couple should have a potential no less positive than a few hundred millivolts in order to assure stability of M towards air oxidation. Thus, $\epsilon^\circ(M^+/M^-)$ might have values as negative as -1.3 V if all factors can be optimized. Similar reasoning for oxidative quenching to produce a two-electron oxidizing agent, M^+, suggests that optimization of all factors might lead to an $\epsilon^\circ(M^+/M^-)$ value as positive as $+1.3$ V.

The limitations suggested above for generation of one- and two-electron reducing agents via absorption of visible light apply to situations where the redox agent is activated by absorption of a single photon. It is possible, in principle, to generate even stronger redox agents by sequential absorption of two photons. For example, excitation followed by reductive quenching leads to a species, M^-, which might be further activated by absorption of a second photon to form $^*M^-$ which might have a reducing power approaching $\epsilon^\circ(M/^*M^-) = -4.4$ V to -5.6 V. Similarly, values of $\epsilon^\circ(^*M^+/M)$ approaching $+4.4$ V to $+5.6$ V are possible, in principle. Preparation of stronger two-electron redox agents by sequential absorption of two photons is also possible in principle. For example, absorption of one photon followed by reductive quenching to form M^- could be followed by a second absorption/reductive quenching sequence to form M^{2-}. The potential of the (M/M^{2-}) couple so-generated might approach $\epsilon^\circ = -2.6$ V, and by similar reasoning the potential of the couple (M^{2+}/M) might approach values of +2.6 V. While it is unlikely that the complex problems of assuring optimal conversion of photon energy into chemical redox potential in two sequential absorption steps will be solved in the forseeable future, optimization of the first absorption step followed by some assistance in a second step might lead to one- or two-electron redox agents stronger than those generated by absorption of a single photon.

A wide variety of one- or two-electron redox half-reactions might ultimately prove to be compatible with photo-activated redox agents. However, several of these which are of particular interest for solar fuel production have been the topic of special interest. These are summarized in Table I along with the thermodynamic potential, ϵ^0, associated with the half-reaction.

This article will describe several metal complexes which have been found to be very strong one-electron photoredox agents in their excited states according to the type of analysis outlined above. Strategies to prepare strong one-electron and two-electron thermal redox agents from these will be considered. Current and possible future modifications of the structures of these species in a manner which will push towards the limits of oxidizing and reducing power one might attain via absorption of visible light will be described. Some of the factors relevant to one- and two-electron redox re-

TABLE I

Reduction potentials for one- and two-electron half-reactions at pH 7 and 298 K

Redox Couple	ϵ^0 (V vs. NHE)
$H^+ + e^- = H^\cdot$	−2.69
$H^\cdot + e^- = H^-$	+0.03
$OH^\cdot + e^- = OH^-$	+2.33
$H_2O_2 + e^- = OH^\cdot + OH^-$	+0.38
$2\,H^+ + O_2^- + e^- = H_2O_2$	+0.82
$O_2 + e^- = O_2^-$	−0.28
$CO_2 + e^- = CO_2^-$	−1.9
$2\,H^+ + 2\,e^- = H_2$	−0.41
$H^+ + 2\,e^- = H^-$	−1.33
$H_2O_2 + 2\,e^- = 2\,OH^-$	+1.35
$CO_2 + 2\,H^+ + 2\,e^- = CO + H_2O$	−0.52
$CO_2 + 2\,H^+ + 2\,e^- = HCOOH$	−0.61

actions with several of the specific substrates listed in Table I will be discussed throughout.

II. THE USE OF d^6 METAL COMPLEXES OF 2,2′-BIPYRIDINE AS PHOTOREDOX AGENTS

The photophysics of a wide range of metal–ligand combinations have been studied, and the variety of structural types which might lead to strong photoredox agents is expanding rapidly. However, rather than attempting to review all of these types, this paper will begin with the well-known d^6 Ru(II) complex, $Ru(bpy)_3^{2+}$, as a prototype of a photoredox agent, and describe structural modifications of the central metal ion and ligands which have been used to substantially modify the redox potentials of species of this general structural type.

Cyclic voltammetric studies of $Ru(bpy)_3^{2+}$ have shown[32–34] that it undergoes a reversible oxidation associated with the metal-centered Ru(II)/Ru(III) couple to form $Ru(bpy)_3^{3+}$ as well as a reversible ligand-centered bpy/bpy$^-$ reduction to form $Ru(bpy)_3^+$. The excited state can function as either an oxidizing agent to form $Ru(bpy)_3^+$ or as a reducing agent to form $Ru(bpy)_3^{3+}$. Once formed, $Ru(bpy)_3^+$ is a strong reducing agent while $Ru(bpy)_3^{3+}$ is a strong oxidizing agent. The presence of an oxidizable metal center and a reducible ligand in $Ru(bpy)_3^{2+}$ gives rise to a relatively long-lived (10^{-6} to 10^{-7} s) low energy excited state associated with metal-to-ligand charge-transfer[35–39] as well as providing oxidizable and reducible sites within the molecular framework.

These features of the $Ru(bpy)_3^{2+}$ prototype suggest that the photoredox potentials could be modified by alteration of the metal-centered redox potential and/or the ligand-centered redox potential. Due to interactions of the metal d-orbitals with the ligand π-orbitals, one type of modification can not be accomplished independently of the other, and either modification may have major effects upon a variety of properties of an excited state which might function as a photoredox agent. Perhaps the most straightforward consideration in modifying the redox potential of $Ru(bpy)_3^{2+}$ is in the charge and atomic number of the central metal ion. Other d^6 metal centers whose *tris*-bpy complexes have been studied for their photoredox properties include Os(II), Rh(III) and Ir(III). Os(II) forms a well-characterized *tris*-bpy complex in which the value of $\epsilon^o(Os(bpy)_3^{3+}/Os(bpy)_3^{2+}$ is only +0.82 V[10] compared to the ϵ^o value of +1.26 V for $(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+})$. Ligand reduction in the $(Os(bpy)_3^{2+}/Os(bpy)^{+})$ couple occurs at an ϵ^o value of −1.22 V[33] compared to the ϵ^o value of −1.28 V for $(Ru(bpy)_3^{2+}/Ru(bpy)_3^{+})$. These potentials are consistent with the anticipated ease of oxidation of the higher atomic number Os(II) ion relative to Ru(II) and the relative insensitivity of the bpy reduction to the identity of the metal center where the net charge (+2) of the metal is constant. Correlation of the MLCT energy with metal oxidation potential and ligand reduction potential[40–44] suggests that the energy of the MLCT excited state of $Os(bpy)_3^{2+}$ should be less than that of $Ru(bpy)_3^{2+}$, and this is indeed found to be the case[22] (1.8 V versus 2.1 V). The net result of these modifications leads to an MLCT excited state, $*Os(bpy)_3^{2+}$, which is a stronger reducing agent than is $*Ru(bpy)_3^{2+}$ $(\epsilon^o(Os(bpy)_3^{3+}/*Os(bpy)_3^{2+}) = -0.96$ V)[45] but a weaker oxidizing agent $(\epsilon^o(*Os(bpy)_3^{2+}/Os(bpy)_3^{+}) = +0.59$ V).[10]

Although the Rh(III) complex, $Rh(bpy)_3^{3+}$ is well known, a number of factors preclude its use as a photoactivated redox agent. The difficulty of oxidation of Rh(III) leads to a low energy excited state which is ligand-centered rather than MLCT in nature.[46–51] As a result, very little visible absorption occurs and the excited state is strongly quenched by non-radiative decay processes in fluid solutions. Although the presence of the +3 metal ion center facilitates ligand reduction in this species, reduction of $Rh(bpy)_3^{3+}$ leads eventually to loss of a bpy ligand and formation of $Rh(bpy)_2^{+}$, suggesting that reduction at the metal center is favored over ligand reduction.[52–54] As a result of these complications, $Rh(bpy)_3^{3+}$ has not found use as a photoredox agent although it is known to participate as an electron relay in photochemical H_2 production.[55–57] The nature of the complicated series of chemical reactions which lead to H_2 production subsequent to reduction of $Rh(bpy)_3^{3+}$ in aqueous solutions has been studied in great detail.[54,58–60]

Although the 1,10-phenanthroline (phen) complex, $Rh(phen)_3^{3+}$, like the $Rh(bpy)_3^{3+}$ is unstable when electrochemically reduced to $Rh(phen)_3^{2+}$ in acetonitrile,[53] the excited state of this complex has been studied as a photo-oxidizing agent.[61-63] The ground state reduction potential, ϵ^{o} ($Rh(phen)_3^{3+}/Rh(phen)_3^{2+}$) = -0.51 V[53] and the ΔG^* value of -2.75 V estimated from emission spectroscopy[47] lead to an estimated value of $+2.24$ V for ϵ^{o}($^*Rh(phen)_3^{3+}/Rh(phen)_3^{2+}$).[61] Reductive quenching of $^*Rh(phen)_3^{3+}$ by oxidizable substrates has been demonstrated,[61-63] indicating that the excited state might be used as a strong oxidizing agent. However, the absence of significant visible absorption, the difficulty of oxidation of Rh(III) to Rh(IV), the chemical instability of $Rh(phen)_3^{2+}$ and the complexity of the emission behavior of this species at room temperature, where a metal-centered as well as a ligand-centered emission have been reported,[62,64] indicate a number of complex problems might arise in the use of $^*Rh(phen)_3^{3+}$ as a photoredox agent.

This then leaves $Ir(bpy)_3^{3+}$ as the final d^6 metal-center-modified species to be considered here. The increase in ionic charge in Ir(III) relative to Ru(II) should render oxidation of Ir(III) more difficult than oxidation of Ru(II), while the increase in atomic number should facilitate oxidation of Ir(III) relative the Rh(III). The net result of these factors leads to an ϵ^{o} value of $+2.17$ V for ($Ir(bpy)_3^{4+}/Ir(bpy)_3^{3+}$).[24,65] However, the cyclic voltammetric studies[65] of $Ir(bpy)_3^{3+}$ indicate that oxidation of $Ir(bpy)_3^{3+}$ to $Ir(bpy)_3^{4+}$ is irreversible, and it is likely that the oxidation occurs at the bpy ligand rather than the metal center. As a result, there is little hope that generation of $Ir(bpy)_3^{4+}$ via oxidative quenching of $^*Ir(bpy)_3^{3+}$ is a feasible route for photoactivation of a strong oxidizing agent. Similar electrochemical behavior reported[66] for $Ir(phen)_3^{3+}$ leads to the same conclusion regarding the use of photogenerated $Ir(phen)_3^{4+}$ as an oxidizing agent.

As anticipated from charge considerations, reduction of $Ir(bpy)_3^{3+}$ occurs[65] at a much less negative potential (ϵ^{o}($Ir(bpy)_3^{3+}/Ir(bpy)_3^{2+}$) = -0.76 V) than it does in $Ru(bpy)_3^{2+}$, and this process is a reversible one associated with reduction at the bpy ligand. The oxidation and reduction potentials of $Ir(bpy)_3^{3+}$ suggest[40-44] a relatively high energy MLCT excited state, and the long excited state lifetime of $Ir(bpy)_3^{3+}$ in low temperature glasses (~80 μs) indicate emission from a low energy ligand-centered excited state with $\Delta G^* = -2.81$ V.[67] However, unlike the $Rh(bpy)_3^{3+}$ complex, $Ir(bpy)_3^{3+}$ maintains a reasonably long lifetime in fluid solutions[68] (2.4 μs), perhaps due to some mixing of a higher energy MLCT excited state with the low-lying ligand centered state. As a result, electron transfer quenching of this excited state is quite feasible, and the excited state potentials of $\epsilon^o(^*Ir(bpy)_3^{3+}/Ir(bpy)_3^{2+}) = +2.05$ V[24] and $\epsilon^o(Ir(bpy)_3^{4+}/^*Ir(bpy)_3^{3+}) = -0.64$ V[24] indicate that $^*Ir(bpy)_3^{3+}$ is a far stronger oxidizing agent than is $^*Ru(bpy)_3^{2+}$, but a weaker reducing agent.

The oxidizing power of $^*Ir(bpy)_3^{3+}$ approaches the limits for photoactivated oxidizing agents suggested above, and if it were not for the severe difficulties originally encountered in the synthesis of this species[67] as well as in its severely limited visible absorption,[67] it might have found widespread use as a powerful photoxidant. Recently reported developments of improved synthetic routes[69,70] to this complex hold promise that at least the synthetic problem is far less severe than it once was. Modification of the complex to adjust its absorption futher into the visible region may be feasible with the recent development of new synthetic routes. This might be effected through the use of electron withdrawing substituents on one or more of the bpy ligands. To a first approximation, this might serve to facilitate the ligand reduction process to a greater extent than the metal oxidization process is rendered more difficult. This would not necessarily lower the energy of the lowest excited state since this is a ligand-centered state in $Ir(bpy)_3^{3+}$. Rather, it might serve to superimpose upon the weak ligand-centered singlet–triplet transition which gives rise to visible absorption, a rather more intense singlet–triplet charge-transfer absorption. In this way the ΔG^* value of -2.8 V might be maintained with some improvement of the visible absorption characteristics and even an enhancement of the already strong oxidizing power of the excited state. This might also modify the oxidation potential of the substituted bpy ligand to a value above the metal oxidation potential, offering the prospect of a complex with a reversible Ir(IV)/Ir(III) couple. This could lead to photogeneration of a powerful ground state oxidizing agent via oxidative quenching of the excited Ir(III) complex to the Ir(IV) species. At this point it appears that development of photo-oxidants, based upon *tris*-coordination of substituted bpy ligands to Ir(III), which absorb visible light in the 400–450 nm region and supply a driving force in excess of 2.2 V versus NHE for outer sphere electron transfer oxidation of substrates, is well within range. This approaches the potential required for oxidation of hydroxide ions to hydroxyl radicals at pH 7 ($\epsilon^\circ(OH^\cdot/OH^-) = +2.33$ V).

Although the potential needed to oxidize hydroxide ions to hydrogen peroxide ($\epsilon^\circ(H_2O_2/2\ OH^-) = +1.35$ V) at pH 7 is easily satisfied by $^*Ir(bpy)_3^{3+}/Ir(bpy)_3^{2+}$, the one-electron nature of the couple indicates that this could only occur via two one-electron oxidations of two OH^- to two $OH^\cdot$ followed by coupling of the two $OH^\cdot$ radicals. The high potential required for oxidation of OH^- to $OH^\cdot$ ($\epsilon^\circ(OH^\cdot/OH^-)) = +2.33$ V) is not supplied by $^*Ir(bpy)_3^{3+}$, but, as indicated above, it might be possible to modify the complex to meet this difficult requirement. Although the potential of the two-electron couple, ($H_2O_2/2\ OH^-$), is substantially less than that of the one-electron ($OH^\cdot/OH^-$) couple, the net free energy requirement for oxidation of 2 OH^- to H_2O_2 ($-2 \times -1.35 = +2.70$ V) is very close to the estimated value of the excited state energy of $Ir(bpy)_3^{3+}$. As a result, there appears to be little hope of developing a two-electron oxidizing agent capable of oxidizing 2 OH^- to H_2O_2 in one step on the basis of absorption of a single photon of visible light. Furthermore, potential development of a two-electron oxidizing agent as a result of sequential absorption of two photons coupled with two oxidative quenching steps to form a species such as $Ir(bpy)_3^{5+}$ is unlikely due to the known instability of $Ir(bpy)_3^{3+}$ subsequent to electrochemical oxidation.[65] Even if ligand substituents which serve to stabilize Ir(IV) are found, stabilization of Ir(V) is unlikely. As a result, the homogeneous photocatalysis of H_2O_2 formation via two-electron oxidation of 2 OH^- without formation of $OH^\cdot$ radicals does not appear to be promising, even though it should be subject to far less stringent mechanistic restrictions than four-electron oxidation of water to molecular oxygen.

A basic type of structural change which serves to enhance MLCT in the low energy excited states of Ir(III)bpy complexes arises from metalation of bpy at the C-atom adjacent to the bridge bond rather than coordination at the N-donor site. The first example of a complex of this structural type was $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ and its conjugate base, $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$.[65,71–77] The structure of this complex[78–81] as well as a closely related species which was recently reported[82] are illustrated in Fig. 3. In addition to these,

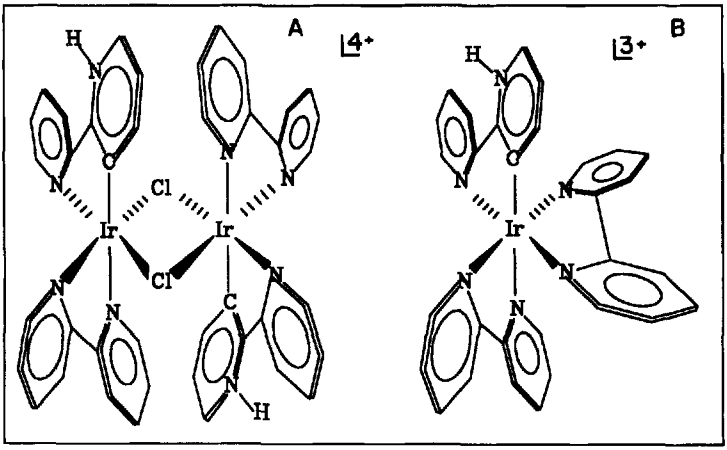

FIGURE 3 Structures of ortho-metalated Ir(III) complexes of 2,2′-bipyridine. (A) $[Ir(Hbpy\text{-}C^3,N')(bpy)Cl]_2^{4+}$; (B) $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$.

several other complexes in which Pt(II) has been found to metalate bpy or N-methyl-2,2′-bipyridine have been reported.[83,84] Of these, only the species $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$, which may be viewed as a linkage isomer of $Ir(bpy)_3^{3+}$, and its conjugate base have been studied as sensitizers.[57,73,85-89]

The estimated ΔG^* value of $[Ir(bpy)\text{-}C^3,N')(bpy)_2]^{2+}$ (-2.68 V)[73] and the $\epsilon^o([Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}/Ir(bpy\text{-}C^3,N')(bpy)_2]^+)$ value of -0.76 V[65] lead to an estimated value of $+1.92$ V for $\epsilon^o([{}^*Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}/Ir(bpy\text{-}C^3,N')(bpy)_2]^+)$. Protonation at the external nitrogen alters the value of ΔG^* to -2.55 V, but the reduction potential of the protonated couple, $\epsilon^o(Ir(Hbpy\text{-}C^3,N')(bpy)_2^{3+}/Ir(Hbpy\text{-}C^3,N')(bpy)_2^{2+})$ has not been measured. A small charge effect would be expected to lead to a slightly less negative ground state reduction potential in the protonated form relative to the deprotonated form. As a result, the value of $\epsilon^o({}^*Ir(Hbpy\text{-}C^3,N')(bpy)_2^{3+}/Ir(Hbpy\text{-}C^3,N')(bpy)_2^{2+})$ is expected to be similar to the value of $+1.92$ V for the deprotonated form. Comparison of these values to those given above for the fully N-coordinated $^*Ir(bpy)_3^{3+}$ species reveals that $[{}^*Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$ is a slightly weaker oxidizing agent due to both a less negative ΔG^* value and a more negative ground state reduction potential.

While both the metalated and fully N-coordinated complexes contain the same Ir(III) metal center, the presence of the anionic ortho-metalated ligand reduces the overall positive charge and correlates with the more negative reduction potential of the metalated complex. The second influence of the ortho-metalation in lowering the excited state energy is due to enhancement of the charge transfer character of the low energy excited state. This excited state is substantially shorter-lived (~20 μs) at 77 K[71] than the ligand-centered excited state of $Ir(bpy)_3^{3+}$. Furthermore it is longer-lived than $Ir(bpy)_3^{3+}$ in fluid solutions (~10 μs), where the emission yield is 0.35, as a result of far less quenching.[71] The lower charge-transfer energy in this complex is not reflected in the oxidative cyclic voltammetry, which displays an irreversible oxidation at about the same potential as seen in $Ir(bpy)_3^{3+}$.[65] This is probably due to similar oxidation of the bpy ligand rather than the metal center in both species. However, the enhancement of the charge-transfer character in the low-energy excited state in spite of the more negative reduction potential suggests that the potential of the Ir(IV)/Ir(III) metal-centered couple is substantially less positive in the metalated species than it is in the fully N-coordinated species. This trend toward less positive ϵ° values for the Ir(IV)/Ir(III) couple becomes more apparent with increasing numbers of metallated ligands as will be described in detail below.

The synthesis of $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$ is a low yield process[71] and there have been no published reports of methods which further promote the ortho-metalation process and improve the yields of this product. However, considerable work has been done towards studying the use of the metallated complex as a photocatalytic redox agent, and this work indicates that it does have potentially important photocatalytic properties. Initial reports of electron transfer quenching of the emission[73] as well as its function as both a sensitizer and catalyst for H_2 production in homogeneous solutions[57] appeared in 1979. The ability of this complex to catalyze homogeneous H_2 formation is surprising as it is a relatively weak reducing agent but a strong oxidizing agent in its excited state. The H_2 forming reaction occurs subsequent to oxidation of an electron donor by the excited state, which results in formation of the reduced species, $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$. Although this reduced species might function as a two-electron donor with formation of

$[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{4+}$, the estimated value of $\epsilon^o([Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{4+}/[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ of $\sim +0.7$ V is very unfavorable for H_2 production by two-electron reaction of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ with 2 H^+. Pulse radiolytic studies indicate that the complex produces H_2 from water when it is reduced by solvated electrons,[90,91] and the pH dependence of the absorption spectrum of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ indicates that this species undergoes a protonation process to form $[HIr(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ at pH $< \sim 2$.[90] The site of the second protonation is uncertain in this species and protonation at a reduced bipyridine ring, the metal center, or the metal–carbon bond are possible alternatives. The production of H_2 at pH values of 4 or greater in pulse radiolytic studies has been attributed to a disproportionation reaction illustrated in Eq. (3) below.[91]

$$2\,[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+} = [Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{1+} + [Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}. \quad (3)$$

The species, $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{1+}$, would presumably be analogous to the product of two-electron reduction of $[Ir(Hbpy\text{-}C^3,N')(bpy)]^{3+}$ which is formed in cyclic voltammetry. From the cyclic voltammetric measurement, the value of $\epsilon^o([Ir(Hbpy\text{-}C_3,N')(bpy)_2]^{2+}/[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{+})$ is estimated to be -0.96 V.[65] Given this potential and the estimated value of $\epsilon^o([Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}/[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}) = -0.76$ V,[65] the disproportionation in Eq. (1) should be thermodynamically unfavorable although a small equilibrium concentration of the two-electron reduction product could be formed. The potential of the two-electron redox couple, ($[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}/[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{+}$, $\epsilon^o = -0.86$ V, indicates a large driving force for reduction of 2 H^+ to H_2, and protonation of the monocation to form $[HIr(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ would be likely. Thus, H_2 might be formed by a reaction of the type shown in Eq. (4) below.[91]

$$[HIr(Hbpy\text{-}C^3,N')(bpy)_2]^{2+} + H^+ = [Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+} + H_2. \quad (4)$$

Application of the above rational to homogeneous photochemical generation of H_2 using $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ as a photocatalyst suggests that the initial reductive quenching step to form $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ might give rise to a small concentration of the monocation according to Eq. (3), followed by protonation and H_2 production according to Eq. (4). However, a second mechanism for formation of the monocation in the presence of the sacraficial electron donors used in photochemical H_2 production might arise from excitation of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ followed by a second reductive quenching step. Although the properties of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$ have not been extensively studied, its visible absorption spectrum[90] is known to be considerably enhanced relative to $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ due to transitions associated with the reduced bpy ligand.[92,93] Therefore excitation of this species after it is formed in an initial reductive quenching step is probable. Whether the resulting excited state is reductively quenched to form a monocation is not known at this time.

Homogeneous photochemical H_2 production is rare, and it is interesting to consider what factors might favor this process when $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ is used as a photosensitizer, but not when $Ru(bpy)_3^{2+}$, which requires an added thermal catalyst such as Pt, is used. Although $^*Ru(bpy)_3^{2+}$ is a substantially weaker oxidizing agent than the Ir(III) complex, it can be efficiently quenched by electron donors to form $Ru(bpy)_3^+$. Estimation of the value of $\epsilon^0(Ru(bpy)_3^{2+}/Ru(bpy)_3^+)$ with Eq. (2) yields a value of ~0 V, so that some H_2 might be formed in strongly acidic solutions via two electron oxidation of $Ru(bpy)_3^+$ to $Ru(bpy)_3^{2+}$ if an appropriate mechanism for combination of two protons with $Ru(bpy)_3^+$ exists. Disproportionation of $Ru(bpy)_3^+$, like disproportionation of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$, is unfavorable, but small concentrations of $Ru(bpy)_3^0$ could be formed in this way. Similarly, the two-electron reduction product might be formed by a second reductive quenching step following excitation of $Ru(bpy)_3^{1+}$, although $^*Ru(bpy)_3^{1+}$ is expected to be a weaker oxidizing agent than $[^*Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$. Although simple electrostatics would suggest that either $Ru(bpy)_3^+$ or $Ru(bpy)_3^0$ would be more prone to protonate than $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{2+}$, the presence of a metal–carbon bond which might be kinetically more susceptible to protonation than any site in $Ru(bpy)_3^0$ could be a key feature in the homogeneous H_2 production by the Ir complex. Perhaps future studies in which the ortho-metalated complex is replaced by a fully N-coordinated Ir(III) complex of bpy or a substituted bpy will serve to clarify whether or not the Ir–C bond is crucial to the function of the sensitizer as a homogeneous H_2 catalyst.

The strong oxidizing power of $[{}^*\mathrm{Ir(bpy\text{-}C^3,N')(bpy)_2}]^{2+}$ has been utilized[86] in photocatalysis of the reaction of bromide ion with oxygen to yield hydrogen peroxide and tribromide ion according to Eq. (5) below.

$$3\,Br^- + O_2 + 2\,H^+ \rightarrow H_2O_2 + Br_3^- . \qquad (5)$$

The mechanism which has been suggested to account for this process is a complicated one which includes formation of exciplexes of the excited iridium complex with bromide ion leading to formation of dibromine radical anions and the reduced $[\mathrm{Ir(bpy\text{-}C^3,N')(bpy)_2}]^+$ species.[86] The reduced iridium complex is then thought to react with O_2 in the presence of H^+ to regenerate the iridium catalyst with formation of $HO_2^{\cdot}$ radicals. While the detailed mechanism of this reaction is not known with certainty, the anticipated strongly basic character of the uncoordinated N-atom in $[\mathrm{Ir(bpy\text{-}C^3,N')(bpy)_2}]^+$ suggests that this species would protonate at this N-atom in the presence of even low concentrations of H^+ to form $[\mathrm{Ir(Hbpy\text{-}C^3,N')(bpy)_2}]^{2+}$; in strongly acidic media a second protonation to form $[\mathrm{HIr(Hbpy\text{-}C^3,N')(bpy)_2}]^{3+}$ would be expected.[90] Disproportionation reactions of $HO_2^{\cdot}$ radicals as well as dibromine radical anions could then give rise to the observed photoproducts, Br_3^- and H_2O_2.[86]

The ortho-metalated *tris*-bpy complex of Ir(III) has also been used to sensitize the valence isomerization of norbornadiene to quadricyclene under irradiation with visible light.[87,94] This process occurs with high quantum efficiency in acetonitrile solutions (0.72), and has been successfully adapted to a heterogeneous system in which the complex is supported on silica gel.[95] The sensitization mechanism is believed to be due to formation of a charge transfer exciplex in which partial oxidation of norbornadiene leads to isomerization to quadricyclene followed by fragmentation of the exciplex into the ground state catalyst and the quadricyclene product.[87] Net oxidation of norbornadiene via outer sphere electron transfer followed by isomerization and back electron transfer has been ruled out in this system due to the high energy of activation associated with isomerization of the norbornadiene radical cation to the quadracyclene radical cation. Thus, the function of the sensitizer in this system, as in the Br^-/O_2 system described above, is due to strong bonding interactions of the substrate with the excited sensitizer and not due to relatively simple outer sphere electron transfer processes.

Although the cyclic voltammetry of $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$ in acetonitrile is characterized[65] by an irreversible oxidation wave, several studies indicate that the complex can be oxidatively quenched in aqueous solutions.[73,88] The oxidized species has been characterized by absorption spectroscopy,[88] and it is found to be stable at low pH (< 1.5) for at least two hours. This oxidized species has been found to be capable of oxidizing Cl^- to Cl_2^-. The oxidant could be $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{3+}$, which might be stabilized in water relative to acetonitrile by solvation effects, or it may be a secondary product formed in a reaction subsequent to oxidation. For example, cleavage of an Ir–N bond followed by metalation of a second bpy ligand to form $[Ir(bpy\text{-}C^3,N')_2(bpy)]^{2+}$, as has been suggested on the basis of studies of transient absorption of the complex following laser flash photolysis,[85] would enrich the electron density at the metal and stabilize development of an Ir(IV) species. An oxidized species, such as $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{3+}$ or $[Ir(bpy\text{-}C^3,N')_2(bpy)]^{2+}$, could function as a two-electron oxidizing agent in a couple such as $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{3+}/[Ir(bpy\text{-}C^3,N')(bpy)_2]^{+}$ or $[Ir(bpy\text{-}C^3,N')_2(bpy)]^{2+}/[Ir(bpy\text{-}C_3,N')_2(bpy)]^{0}$. A rough estimate of the maximum anticipated ϵ^{o} for either of these couples, taken from the potentials of the irreversible oxidation wave (+2.17 V) and the reversible reduction wave (−0.76 V) in the cyclic voltammetry of $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$ in acetonitrile,[65] yields a value of about +0.7 V. Although this is sufficient to drive a two-electron oxidation of $2\ I^-$ to I_2, it is substantially less than the thermodynamic requirement for two-electron oxidations of $2\ Br^-$ to Br_2, $2\ Cl^-$ to Cl_2 or $2\ OH^-$ to H_2O_2. This limitation as well as the unknown mechanistic details for the two-electron oxidations suggest that the primary use of an oxidant formed in oxidative quenching of $[Ir(bpy\text{-}C^3,N')(bpy)_2]^{2+}$ is likely to be as a one-electron rather than a two-electron oxidizing agent.

III. THE USE OF d^6 METAL COMPLEXES OF ORTHO-METALATED 2-PHENYLPYRIDINE AS PHOTOREDOX AGENTS

The success of $[\mathrm{Ir(Hbpy\text{-}C^3,N')(bpy)_2}]^{3+}$ and its conjugate base as both a sensitizer and a catalyst has been followed by further investigations of the photophysics, photochemistry and electrochemistry of more traditional ortho-metalated species.[96–129] The characteristics of the *tris*-ortho-metalated species, *fac*-$\mathrm{Ir(ppy)_3}$,[117,118] serves to demonstrate the manner in which Ir–C bonding radically alters the excited state redox properties of these species relative to the Ir–N bonded bpy complexes. This is illustrated in the modified Latimer diagram for $\mathrm{Ir(ppy)_3}$ shown in Fig. 4. This diagram shows that the ground state potential for $\mathrm{Ir(ppy)_3^+/Ir(ppy)_3}$ has a value of $\epsilon^o = \sim +1.0$ V[110] whereas the potential for the $\mathrm{Ir(ppy)_3/Ir(ppy)_3^-}$ couple is $\epsilon^o = \sim -2.0$ V.[110] Thus, this complex is far easier to oxidize but much more difficult to reduce than the fully N-coordinated $\mathrm{Ir(bpy)_3^{3+}}$ or the partially ortho-metalated $[\mathrm{Ir(Hbpy\text{-}C^3,N')(bpy)_2}]^{3+}$. Furthermore, reversible oxidative and reductive chemistry occurs on the timescale of the cyclic voltammetric measurements which have been made[110] in contrast to the irreversible oxidative waves seen in cyclic voltammetry of the *tris*-bpy Ir(III) complexes. The wide range of ground state redox potentials as-

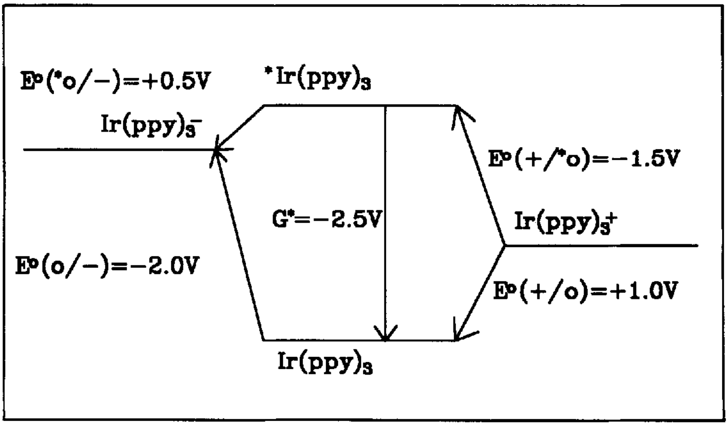

FIGURE 4 Modified Latimer diagram for $\mathrm{Ir(ppy)_3}$ and $\mathrm{{}^*Ir(ppy)_3}$.

sociated with Ir(III) complexes of ppy and bpy is indicative of the versatility of the Ir(IV)/Ir(III) couple when Ir–C σ-bonding comprises a portion of the coordination sphere. Furthermore, the $Ir(ppy)_3$ complex emits from a MLCT excited state at $\Delta G^* = -2.5$ V with a lifetime of 2.0 μs and a luminescence quantum yield of 0.4 in room temperature acetonitrile solutions.[117] The luminescence lifetime of 5 μs in 77 K glasses suggests a luminescence quantum yield near unity at low temperatures. Based upon values of ΔG^* and ϵ^o, the excited state potentials are estimated to be $\epsilon^o(Ir(ppy)_3^+/{}^*Ir(ppy)_3) = -1.5$ V and $\epsilon^o({}^*Ir(ppy)_3/Ir(ppy)_3^-) = +0.5$ V. Thus, $^*Ir(ppy)_3$ is seen to be a far superior reducing agent than any of the (*tris*) bpy metal complexes, but a very weak oxidizing agent. Kinetic-based studies of Stern–Volmer quenching of this complex by a series of electron acceptors confirm the above estimate of $\epsilon^o({}^*Ir(ppy)_3/Ir(ppy)_3^+)$ and indicate that $^*Ir(ppy)_3$ might be of some use in photocatalysis of the cyclization of α,β-unsaturated keto- and aldehydo-esters via a reductive mechanism.[117,118]

The use of $^*Ir(ppy)_3$ as a reducing agent is limited by the availability of only one electron from the $Ir(ppy)_3^+/{}^*Ir(ppy)_3$ couple. However, the potential of $\epsilon^o = -1.5$ V for this couple approaches the potential for one-electron reduction of CO_2 to CO_2^-, $\epsilon^o(CO_2/CO_2^-) = -1.9\ V \pm 0.2$ V.[130–134] Modifications of the ppy ligand with substituents might enhance the reducing power of a (*tris*) ortho-metalated complex of Ir(III) to meet the thermodynamic requirement for one-electron reduction of CO_2, but the kinetic limitations of the excited state give rise to the requirement for an overpotential sufficient to drive the reduction during the limited excited state lifetime. The extent of the required overpotential can be estimated from the excited state lifetime of 2.0 μs and the self-exchange rates for (CO_2/CO_2^-) and $(Ir(ppy)_3^+/{}^*Ir(ppy)_3)$. Recent estimates of the CO_2/CO_2^- self-exchange rate, k_{se}, indicate a value of 1.4×10^{-3} L mol^{-1} s^{-1} when the value of $\epsilon^o(CO_2/CO_2^-)$ is taken to be -1.9 V.[134,135] A prior estimate of k_{se} for CO_2/CO_2^- suggested a smaller value of 10^{-5} M^{-1} s^{-1}.[136] Although the rate of self-exchange for $(Ir(ppy)_3^+/{}^*Ir(ppy)_3)$ has not been measured, a maximum value of $k_{se} \sim 1 \times 10^8$ can be taken from estimates of the self-exchange rate for $Ru(bpy)_3^{3+}/{}^*Ru(bpy)_3^{2+}$.[10] For relatively slow electron transfer in a precursor complex of $^*Ir(ppy)_3|CO_2$ which is formed with an equilibrium constant of unity, the quenching constant, k_q, monitored in a Stern–Volmer quenching study may be taken to be equal to the electron transfer rate, k_{et},[21] for formation of the successor complex, $Ir(ppy)_3^+|CO_2^-$ from the precursor complex. Given the solubility of CO_2 in aqueous solution at room temperature of about 3×10^{-2} M, and a requirement that the product, $k_q[CO_2] = 10^5\ s^{-1}$ to obtain readily measureable shortening of the excited state lifetime due to quenching, a value of k_{et} of about $3 \times 10^6\ M^{-1}\ s^{-1}$ is required. The value of the overpotential needed to attain this electron transfer rate can be estimated from the Marcus–Hush theory of electron transfer using Eq. (6) below.[21]

$$k_{et} = (k_{11}k_{22}K_{12}f_{12})^{1/2}. \tag{6}$$

In this equation, k_{11} and k_{22} are the self-exchange rates of the donor and acceptor, K_{12} is the equilibrium constant for the redox reaction, and f_{12} is given by Eq. (7) below.

$$\log(f_{12}) = (\log K_{12})^2/4 \log(k_{11}k_{22}/Z^2). \tag{7}$$

The rate constant for bimolecular collisions due to diffusion, Z, is taken as $10^{11}\ M^{-1}\ s^{-1}$. Application of Eq. (6) to this calculation suggests that an overpotential of about 0.6 V is required in order to drive the electron transfer quenching with the required rate. A similar calculation of the intrinsic barrier for reduction of CO_2 to CO_2^- also yields a value of 0.6 V for the intrinsic barrier.[134] Thus, approximately 2.5 V ± 0.2 V of reducing power versus NHE would be needed in order to obtain a reasonable level of quenching during the excited state lifetime. This calculation does not take into account potentially important effects which might arise from solvation or from some tendency of the electron-rich excited state to bind CO_2, and either of these effects might serve to reduce the estimated overpotential by several hundred millivolts. This type of diminution of the overpotential estimated by Marcus–Hush theory described above could prove to be crucial in achieving one-electron reduction of CO_2 by a visible light activated sensitizer. The uncertainties in the reduction potential of the couple (CO_2/CO_2^-) and in the self-exchange rates for this couple as well as the Ir(IV)/*Ir(III) couple render the above estimate quite rough. However, under the most favorable of circumstances it appears that an excited state with an ϵ° (Ir(IV)/*Ir(III)) value more negative than −2.0 V would be required before oxidative quenching of the excited state by one-electron reduction of CO_2 to CO_2^- might be expected to occur.

Modification of the excited state redox potentials of $Ir(ppy)_3$ through introduction of ligands with electron-donating substituents might provide a means to enhance the excited state reducing power toward the above-estimated potential required for reduction of CO_2 to CO_2^-. However, modification of the ground state potential for the Ir(IV)/Ir(III) couple in these complexes is likely to affect other important parameters including the value of ΔG^* and the excited state lifetime. Furthermore, the synthetic chemistry associated with preparation of *tris*-ortho-metalated complexes poses a rather more serious problem than does the synthesis of most *tris*-coordinated complexes of substituted bpy. However, a synthetic procedure for high yield preparation of *tris*-ortho-metalated complexes of substituted ppy has recently been developed,[137] and this method has facilitated preparation of a series of these complexes in which an electron-donating substituent is attached to the phenyl-ring system of ppy.[138,139] The values of ΔG^*, τ and ϵ° (Ir(IV)/Ir(III)) are listed in Table II along with values estimated for the excited state potential, ϵ°(Ir(IV)/*Ir(III)); excited states with ϵ° (Ir(IV)/*Ir(III)) values as negative as about −1.6 V have been prepared. Further ligand modifications might well be expected to eventually yield species in which ϵ°(Ir(IV)/*Ir(III)) reach the thermodynamic requirement for CO_2/CO_2^- reduction. Due to the high overpotential estimated for outer sphere electron transfer to CO_2, success in accomplishing the reduction to CO_2^- will probably depend upon some binding of CO_2, either in the ground state or in the excited state (excimer formation). Binding of CO_2 might serve to cause some bending of linear CO_2 towards the bent geometry of CO_2^-,[140–142] thereby lowering the Franck–Condon barrier to electron transfer.[136] Binding would further imply a lowering of the electron transfer rate constant needed to bring about quenching in the excited state due to an increase in the value of the equilibrium constant for precursor complex formation. The *Ir(III) reducing

TABLE II

Emission and cyclic voltammetric data for *fac-tris*-ortho-metalated Ir(III) complexes

Complex	τ (μs)[a]	ΔG^{*b}(V)	$\epsilon^\circ(1+/0$[c]	$\epsilon^\circ(1+/{*}0)$[d]
Ir(ppy)$_3$	1.90	−2.51	+1.01	−1.50
Ir(4-methylppy)$_3$	1.94	−2.52	+0.94	−1.58
Ir(4-propylppy)$_3$	1.93	−2.50	+0.91	−1.59
Ir(4-*tert*-butylppy)$_3$	1.97	−2.49	+0.90	−1.59
Ir(4-fluoroppy)$_3$	2.04	−2.65	+1.21	−1.44
Ir(4-trifluoromeppy)$_3$	2.16	−2.51	+1.32	−1.19
Ir(4-methoxyppy)$_3$	2.24	−2.58	+0.99	−1.59
Ir(5-methoxyppy)$_3$	2.86	−2.30	+0.79	−1.51

[a] Emission lifetime in degassed acetonitrile at room temperature.

[b] Taken from shortest wavelength feature in emission spectrum in ethanol/methanol glass (1:1 by volume) at 77 K.

[c] Reduction potential for [Ir(R-ppy)$_3$]$^+$/Ir(R-ppy)$_3$ taken from cyclic voltammogram.

[d] Reduction potential for [Ir(R-ppy)$_3$]$^+$/*Ir(R-ppy)$_3$ estimated from difference in emission energy and $\epsilon^\circ(+1/0)$.

agents should provide a means for testing whether or not a visible light driven one-electron reduction of CO$_2$ to CO$_2^-$ at or near the thermodynamic potential of the CO$_2^-$ couple can be achieved using an excited state reducing agent.

A second approach to utilizing excited states such as *Ir(ppy)$_3$ to drive difficult chemical reductions consists of reductively quenching the excited state with an electron donor to produce Ir(ppy)$_3^-$. The reversible reduction waves in the cyclic voltammetry of Ir(ppy)$_3$[110] suggest that this thermal reducing agent has sufficient stability to last for at least several ms, and the ϵ°(Ir(ppy)$_3$/Ir(ppy$_3^-$) value of −2.0 V provides the thermodynamic potential for the CO$_2$/CO$_2^-$ reduction. Ir(ppy)$_3^-$ is not subject to the kinetic limitation imposed by competing excited state decay processes in the use of *Ir(ppy)$_3$ as a reducing agent, and modification of the potential for (Ir(ppy)$_3$/Ir(ppy)$_3^-$) to more negative values with electron-donating substituents of the pyridine ring, which is believed to be the site of reduction,[110] is likely to occur.

Another aspect of photochemically generated reducing agents such as Ir(ppy)$_3^-$ which might be put to use resides in the possibility of utilizing two-electron couples, such as (Ir(ppy)$_3^-$/Ir(ppy)$_3^+$). The potential for this couple, estimated to be -0.5 V, provides a rather rare example of a case where the combination of reversible ground state oxidation and reduction potentials of a metal complex in conjunction with ΔG^* gives rise to the possibility of generating a moderately powerful two-electron reducing agent. The value of $\epsilon^o(\mathrm{Ir(ppy)_3^-/Ir(ppy)_3^+})$ estimated above, for example, is adequate to drive reduction of 2 H^+ to H_2 at pH 7 ($\epsilon^o = -0.41$ V) and approaches the thermodynamic values of the potentials required for two-electron reduction of CO_2 to CO at pH 7 ($\epsilon^o = -0.52$ V) or CO_2 to HCOOH at pH 7 ($\epsilon^o = -0.61$ V). Modification of the ppy ligands with electron donating substituents should serve to facilitate photogeneration of two-electron reducing agents with ϵ^o values substantially more negative than -0.5 V, so that the thermodynamic requirements of any of the above two-electron reductions could be met. However, unlike the relatively simple mechanistic, but demanding energetic, requirements of one-electron transfer to produce CO_2^- from CO_2, the modest energy requirements of these two-electron transfer reactions are accompanied by more stringent mechanistic demands. The two-electron reductions require not only the availability of the two-electron reducing agent but also a means to bring CO_2 and H^+ into close proximity during the reduction process. A variety of ways in which this might be achieved in heterogeneous systems which employ surface sites to bring about the proximity requirements can be envisioned, but it is more difficult to envision how homogeneous photocatalysts could meet the stringent requirements anticipated in two-electron transfer mechanisms.[143–148] At any rate, the photogeneration of strong thermal reducing agents, such as $\mathrm{Ir(ppy)_3^-}$, via reductive quenching of an excited state appears to be feasible. This and related species may be able to function as either one-electron reducing agents with sufficient power to drive reductions with potentials more negative than -2.0 V or as two-electron reducing agents with sufficient power to drive reductions with potentials more negative than -0.5 V.

The strong oxidative nature of Ir(III) complexes of bpy and the strong reductive character of Ir(III) complexes of ppy suggest that it should be possible to adjust the redox character of Ir(III) complexes between the extremes of these two types with combinations of bpy-like and ppy-like ligands bonded to Ir(III). That this is indeed the case is illustrated by consideration of the values of ΔG^*[110,118] and the ground state redox potentials[110,112,114] of $[Ir(bpy)_2(ppy)]^+$. The ΔG^* value of -2.33 V in combination with values of $\epsilon^o([Ir(bpy)_2(ppy)]^+/[Ir(bpy)_2(ppy)]^0) = -1.10$ V and ϵ^o $[(Ir(bpy)_2(ppy)]^{2+}/[Ir(ppy)_2(bpy)]^+ = +1.54$ V lead to estimates of excited state redox potentials of $\epsilon^o[(Ir(ppy)_2(bpy)]^{2+}/{}^*[Ir(ppy)_2(bpy)]^+ = -0.79$ V and $\epsilon^o({}^*[Ir(ppy)_2(bpy)]^+/[(Ir(ppy)_2(bpy)]^0$ $= +1.23$. Cyclic voltammetric studies indicate reversible oxidation as well as reversible reduction of the ground state, and the two-electron redox couple, $([Ir(ppy)_2(bpy)]^{2+}/[Ir(ppy)_2(bpy)]^0)$, has an ϵ^o value of $+0.22$ V. Oxidative, as well as reductive quenching, of ${}^*[Ir(ppy)_2(bpy)]^+$, which has a luminescence lifetime of ~340 ns in fluid toluene solutions,[110,118] has been demonstrated[112]; this indicates that preparation of the oxidant, $[Ir(ppy)_2(bpy)]^{2+}$, or the reductant, $[Ir(ppy)_2(bpy)]^0$, should pose no great problems. However, the relatively small oxidizing potential available from the two-electron couple indicates that major modifications are needed before two-electron oxidation of substrates such as water, bromide ion or even iodide ion could be approached. The synthetic procedures used in preparation of $[Ir(ppy)_2(bpy)]^+$[110,114,149,150] are relatively simple and result in high yields of the complex, so that the use of substituted ppy and/or bpy ligands to prepare modified complexes is straightforward. Stronger two-electron oxidants based upon substitution of ppy and bpy ligands in $[Ir(ppy)_2(bpy)]^+$ could be prepared by attaching electron-withdrawing groups to both the ppy and bpy ligands. This should facilitate reduction, which occurs at the bpy ligand, while rendering oxidation of Ir(III) to Ir(IV) more difficult, leading to more positive values of the potentials for the two-electron couples in the derivatized complexes.

The combination of Ir(III) with two bpy ligands and only one ppy ligand,[116] as expected, leads to further enhancement of the oxidative character relative to $[Ir(ppy)_2(bpy)]^+$. Thus, the redox potentials of $[Ir(ppy)(bpy)_2]^{2+}$ are found to be $\epsilon^o([Ir(ppy)(bpy)_2]^{3+}/[Ir(ppy)(bpy)_2]^{2+}) = +2.3$ V and $\epsilon^o([Ir(ppy)(bpy)_2]^{2+}/[Ir(ppy)(bpy)_2]^+) = -0.96$ V.[116] These values, in combination with a ΔG^* value of -2.6 V, lead to estimated excited state redox potentials of $\epsilon^o([Ir(ppy)(bpy)_2]^{3+}/{}^*[Ir(ppy)(bpy)_2]^{2+}) = -0.3$ V and $\epsilon^o({}^*[Ir(ppy)(bpy)_2]^{2+}/[Ir(ppy)(bpy)_2]^+) = +1.64$ V. While ${}^*[Ir(ppy)(bpy)_2]^{2+}$ has slightly less oxidizing power than either

*$[Ir(bpy)_3]^{3+}$ or *$[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$, it does have the advantage of a possible reversible two electron couple, $[Ir(ppy)(bpy)_2]^{3+}/[Ir(ppy)(bpy)_2]^{+}$ for which $\epsilon^\circ = +0.67$ V. At this point in time, very little work has been done in studies of complexes composed of two bpy and one ppy ligand, largely due to the difficult and inefficient synthetic chemistry which has been encountered in preparation of $[Ir(ppy)(bpy)_2]^{2+}$.[116] However, the possibility for development of one- or two-electron oxidizing agents via oxidative quenching of the excited states of these species offers an advantage over the use of $[Ir(bpy)_3]^{3+}$ or of $[Ir(Hbpy\text{-}C^3,N')(bpy)_2]^{3+}$ which appear to be limited to use as one-electron oxidizing agents in their excited states due to the irreversible electrochemistry associated with oxidation of their ground states. This advantage is due to the ability of ppy to stabilize Ir(IV) sufficiently to facilitate oxidation of Ir(III) to Ir(IV) at potentials less positive than the potentials at which the bpy ligands are oxidized.

IV. SUMMARY AND CONCLUSIONS

The initial recognition that visible excitation of transition metal complexes could produce strong excited state redox reagents has spurred extensive study of model photoconversion systems based upon electron transfer reactions of excited states. Factors which limit the applicability of these excited state reagents include kinetic limitations based upon the decay of the excited state back to the ground state and mechanistic limitations related to the general participation of these excited states only in one-electron transfer reactions. These limitations, in concert with the large potential required for many of the known one-electron reactions of simple substrates such as CO_2, OH^-, H^+, Cl^-, etc. have led to an emphasis upon the development of intermediary thermal catalysts to assist in promoting multi-electron oxidation and reduction reactions of these substrates, thereby bypassing one-electron mechanisms requiring the production of high-energy radicals. However, with the advent of metal complexes in which a large portion of the energy of an absorbed visible photon is converted to oxidizing or reducing power in the excited state, it may become feasible to promote one-electron oxidation or reduction reactions of these substrates to produce high-energy radicals.

A second type of redox chemistry which becomes feasible with the development of strongly oxidizing or reducing excited state species results from generation of one- or two-electron thermal redox agents via oxidative or reductive quenching of the excited states. The presence of a reversibly oxidizable metal center and a reversibly reducible ligand is common in many d^6 metal complexes of coordinating bpy, ortho-metalating ppy and structurally related ligands. When the excited state, $^*M$, of one of these species is a strong one-electron oxidizing agent, the species M^+, which can be generated via oxidative quenching of $^*M$, is generally a strong thermal one-electron oxidant. The M^+ species may further be a strong two-electron oxidant through the M^+/M^- couple. Similarly, reductive quenching of a strong one-electron excited state reductant, $^*M$, can yield a species, M^-, which is a strong one-electron reductant as well as a two-electron reductant through the M^+/M^- couple. The applicability of these two-electron couples is largely unexplored, and the mechanistic requirements of bringing several reactants together as well as providing adequate driving force to bring about a two-electron redox process constitutes a challenging chemical problem. Resolution of this problem would provide materials in which the present functions of photosensitizers and thermal catalysts might be combined in one chemical species which could function in homogeneous solutions.

The concept of combining the energy of several low-energy photons in order to drive one-electron at high potentials, referred to as the two-photosystem concept, has been discussed in general terms[151] as it applies to natural photosynthesis, and has been applied in the development of semiconductor devices such as p/n junction photoelectrolysis cells.[152] Application of this concept to a homogeneous photocatalyst might be realized in sequential excitation/redox quenching steps of a metal complex, M, to produce a two-electron oxidation (M^{2+}) or reduction (M^{2-}) product. Although the one-electron redox potential available in the M^{2+}/M^+ or M^-/M^{2-} couple so produced would be much less than the energy of the two photons needed to produce M^{2+} or M^{2-}, either of these might be a substantially stronger one-electron redox agent than M^+ or M^-. Furthermore, these species might be strong two-electron redox agents, which could operate in accordance with the one-photosystem concept through the M^{2+}/M or M/M^{2-} couple. Even three-electron redox couples of the type M^{2+}/M^{-} or M^{+}/M^{2-} might arise from two sequential excitation/redox quenching steps beginning with M. The development of most of the above-mentioned redox couples presently appears to be possible in complexes of Ir(III) with ligands based upon bpy and ppy. However, the general structural feature which leads to the possibility of utilizing these redox couples is found in the simultaneous presence of distinct oxidizable and reducible sites within a single molecular structure. This might be achieved through a combination of one or more oxidizable metal centers with one or more reducible ligands, as in the examples cited here, but other combinations of oxidizable and reducible sites are undoubtedly possible. The exploration of these possibilities may lead to the photochemical production, with visible photons, of thermal redox agents capable of producing high-energy radicals. Similarly, absorption of several visible photons coupled with redox quenching might lead to the production of homogeneous multi-electron redox reagents.

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RICHARD J. WATTS
Department of Chemistry,
University of California,
Santa Barbara, California 93106

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