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Shining Light on Photoredox Catalysis: Theory and Synthetic Applications

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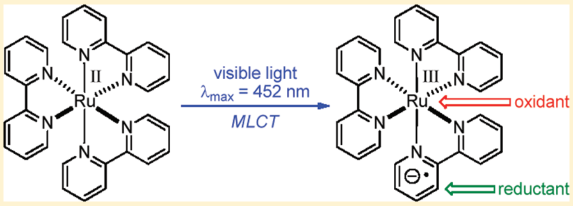
ABSTRACT: Photoredox catalysis is emerging as a powerful tool in synthetic organic chemistry. The aim of this synopsis is to provide an overview of the photoelectronic properties of photoredox catalysts as they are applied to organic transformations. In addition, recent synthetic applications of photoredox catalysis are presented.



Redox manipulations of molecules are some of the most common chemical transformations performed both in nature[1] and scientific laboratories.[2] In particular, scientists have studied the redox properties of visible light active metal complexes, such as $Ru(bpy)_3Cl_2$,[3] for decades.[4] Applications of $Ru(bpy)_3Cl_2$ include areas such as visible light induced water splitting,[5] photovoltaic cells,[6] and energy storage.[7] There are examples, dating back to the 1970s, of the utilization of the redox cycles of $Ru(bpy)_3Cl_2$ to enable synthetic manipulations of organic molecules.[8] However, it is only recently that photoredox catalysis (redox photosensitization)[9] has gained widespread recognition within the synthetic chemistry community (Figure 1).

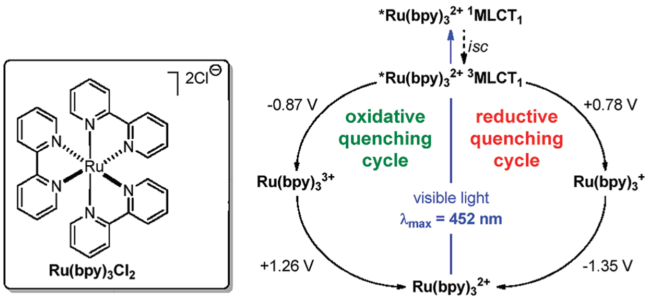


Figure 1. $Ru(bpy)_3Cl_2$: a prototypical photoredox catalyst.

Furthermore, the field of green chemistry has brought a desire for the development of new synthetic methods, including those that enable redox transformations to be performed in a more environmentally benign manner. The development of visible light promoted photochemistry has been recognized for nearly a century as a valuable goal.[10,11] The aim of this synopsis is to provide background into the photophysical properties which enable the chemistry associated with photoredox catalysis. Understanding of these processes will allow for this methodology to be more broadly employed by organic chemists. Furthermore, the specific catalysts and transformations discussed herein serve as illustrative examples to highlight certain aspects which are general to a wide array of photoredox catalysts.

■ PHOTOELECTRONIC PROPERTIES OF CATALYSTS

The synthetic community is fortunate to be able to utilize the exceptionally extensive body of work in the chemical literature describing, in detail, the modes of action of numerous photoredox catalysts. By understanding the underlying processes that govern the redox behavior of these light active complexes, appropriate reaction designs can be formulated and implemented by organic chemists.

Formation and Fate of the Catalyst Excited State. All light-promoted transformations must begin with absorption of a photon by the photocatalyst (PC) to generate a high energy excited state (*PC). It is this gain in energy that enables much of the enhanced redox processes available to these catalysts. The absorption of higher energy visible light (e.g., 400−475 nm) is desirable as it allows for the maximum potential energy gain without the possibility of undesired reactivity associated with direct excitation of organic substrates. For instance, the maximum absorbance of $Ru(bpy)_3Cl_2$ is 452 nm. However, the absorbance of organic dyes is significantly red-shifted (e.g., λ_{max}(eosin y) = 522 nm).[12] As a result, though advantageous that it avoids the use of precious metals, the excited state of eosin Y has 0.37 eV less energy to potentially apply to reaction promotion. Despite the broad absorption band typical of Ru^{2+} and Ir^{3+} polypyridyl complexes, they generally relax initially to the lowest spin-allowed metal to ligand charge transfer excited state [*PC $^1MLCT_1$] from numerous singlet excited states [*PC $^1MLCT_n$].[4b] The *PC $^1MLCT_1$ state rapidly undergoes intersystem crossing (k_{isc}) to the triplet manifold followed by internal conversion to generate a long-lived first triplet excited state, *PC $^3MLCT_1$ (Figure 2).[13] As a result, fluorescence, k_f, and internal conversion from *PC $^1MLCT_1$ are minor deactivation pathways. Furthermore, *PC $^3MLCT_1$ is sufficiently long-lived to undergo bimolecular quenching reactions. While energy transfer is an important pathway,[14] this synopsis will focus on the redox quenching processes.

Thermodynamic Parameters of Photoredox Catalysts. Photoredox catalysts offer the ability to tune the reactivity of the complex. There are two sets of reduction potentials[15] of

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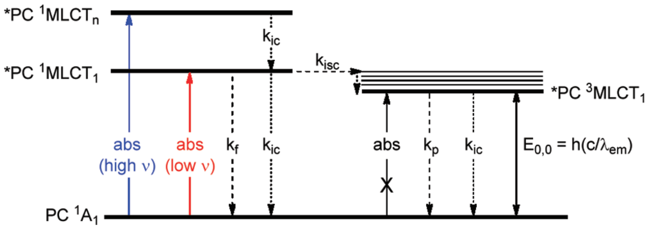

Figure 2. Generalized Jablonski diagram of photocatalysts. k_f, k_{ic}, k_{isc}, and k_p are the rate constants for fluorescence, internal conversion, intersystem crossing, and phosphorescence, respectively and λ_{em} is the maximum emission wavelength of the photocatalyst.

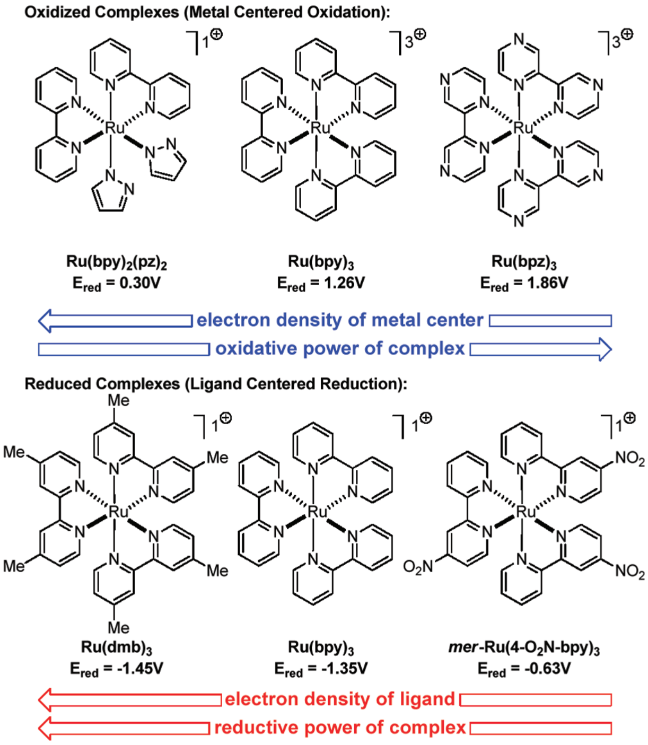

Figure 3. Ligand effects on ground-state redox properties of catalysts.

Oxidative Quenching:

$$E_{red}[PC^{+1} / {*PC}] = E_{red}[PC^{+1} / PC] - E_{0,0} \qquad (1)$$

$$Ru(bpy)_3^{3+} + e^{\ominus} \longrightarrow {*Ru(bpy)_3^{2+}}$$

77 K: $E_{red}[PS^{+1} / {*PS}] = 1.26\ V - 2.13\ V = \mathbf{-0.87\ V}$

293 K: $E_{red}[PS^{+1} / {*PS}] = 1.26\ V - 2.02\ V = \mathbf{-0.76\ V}$

Reductive Quenching:

$$E_{red}[{*PC} / PC^{-1}] = E_{red}[PC / PC^{-1}] + E_{0,0} \qquad (2)$$

$${*Ru(bpy)_3^{2+}} + e^{\ominus} \longrightarrow Ru(bpy)_3^{1+}$$

77 K: $E_{red}[{*PS} / PS^{-1}] = -1.35\ V + 2.13\ V = \mathbf{0.78\ V}$

293 K: $E_{red}[{*PS} / PS^{-1}] = -1.35\ V + 2.02\ V = \mathbf{0.67\ V}$

Figure 4. Calculations of approximate reduction potentials of $*Ru(bpy)_3$.

interest: those of the ground state and those of the excited state. Herein, “reduction potential” is exclusively used to describe the potential associated with the electrochemical half-reaction written in the direction where the more oxidized species is reduced, i.e., $Li^+ + e^- \rightarrow Li$, ($E_{red}[Li^{1+}/Li] = -3.39$ V).

In general, the redox behavior of ground state Ru^{3+} and Ir^{3+} polypyridyl complexes can be described by oxidations of the metal center and reductions of the ligands.[4] As such, the ground state reduction potentials can be adjusted by metal and ligand combinations. For instance, when considering the potentials associated with the Ru^{3+}/Ru^{2+} couple, the greater the electron donation from the ligand the more facile this oxidation will become. In particular, $Ru(bpy)_2(pz)_2$ bearing two anionic pyrazolo ligands make the reduction potential of the corresponding $Ru(bpy)_2(pz)_2^{1+}/Ru(bpy)_2(pz)_2$ couple significantly less positive ($E_{red} = 0.30$ V)[16] than that of $Ru(bpy)_3Cl_2$ ($E_{red} = 1.26$ V). Conversely, utilization of the stronger π-accepting ligand, 2,2′-bipyrazine, shifts the potential for the $Ru(bpz)_3^{3+}/Ru(bpz)_3^{2+}$ couple to 1.86 V.[17] Similarly, given that the reduction of complexes of this type is ligand centered, it follows that the reduction potential of the Ru^{2+}/Ru^{1+} couple will become more negative with more electron rich ligands. For example, adding methyl substituents to the bipyridine ligands shifts the reduction potential of the $Ru(dmb)_3^{2+}/Ru(dmb)_3^{1+}$ couple to −1.45 V (cf. $E_{red}[Ru(bpy)_3^{2+}/Ru(bpy)_3^{1+}] = -1.35$ V).[18] Conversely, the *mer*-$Ru(4\text{-}O_2N\text{-}bpy)_3^{2+}$/*mer*-$Ru(4\text{-}O_2N\text{-}bpy)^{1+}$ couple shifts to −0.63 V (Figure 3).[19]

The reduction potentials associated with the excited states cannot be directly measured and are typically calculated from known cyclic voltammetry (CV) and spectroscopic data.[20] As an approximation, the excited-state potentials of a catalyst are related to its ground state potentials and its zero−zero excitation energy ($E_{0,0}$).[21] $E_{0,0}$ can be estimated by the difference in energy between *PC $^3MLCT_1$ and PC $^1A_1$ and can be approximated by the maximum emission of the catalyst (Figure 2). As an example, the emission maximum for $Ru(bpy)_3Cl_2$ in MeCN has been measured to be 615 nm at room temperature and 582 nm at 77 K in a frozen MeOH/EtOH mixture.[22] This corresponds to an $E_{0,0}$ value of 2.02 eV at room temperature and 2.13 eV at 77 K. Given the ground-state reduction potentials, the excited-state reduction potentials can be calculated as shown in Figure 4.

This simple calculation gives a general approximation of the reduction potentials of the excited state complex. Variables such as temperature, solvent, concentration, and pH can affect these properties.[23] However, these numbers can serve as useful tools for reaction design.

Finally, since the excited-state and ground-state reduction potentials are related by $E_{0,0}$, designing catalysts to optimize one of these values necessarily affects the other. In particular, there are numerous Ru photocatalysts that have been measured to be particularly strong reductants (e.g., $E_{red}[Ru(bpy)_2(CN)_2^{2+}/Ru(bpy)_2(CN)_2^{1+}] = -1.68$ V). However, as a consequence of the relatively large Stokes shift typical of Ru complexes, the $E_{0,0}$ values for these complexes are lowered, making the excited states both weaker oxidants and reductants (e.g., $E_{red}[{*Ru(bpy)_2(CN)_2^{2+}}/Ru(bpy)_2(CN)_2^{1+}] = 0.37$ V).[24] This can prove detrimental to organic reaction development since more powerful redox agents are required to quench the excited state. In contrast to tertiary amines (E_{red} ranges between 0.50 and 0.96 V),[25] the oxidative power of $*Ru(bpy)_2(CN)_2^{2+}$ is thermodynamically better matched with stronger reductants, such as Cu(I) ($E_{red}[Cu^{2+}/Cu^{1+}] = -0.09$ V) or ferrocene (E_{red}[ferrocenium/ferrocene] = 0.16 V).[26]

However, Ir complexes typically experience smaller Stokes shifts relative to similar Ru based complexes. For instance, Bernhard, Malliaras and co-workers observed a Stokes shift of 205 nm for $Ru(bpy)_3$ when irradiated at 400 nm, while the Stokes shift of $Ir(ppy)_2(dtbbpy)$ was significantly smaller, 181 nm.[27] As a consequence of this and its increased HOMO−LUMO gap, this complex is still easily quenched by tertiary amines while the reduction potential of $Ir(ppy)_2(dtbbpy)PF_6$ is more negative by approximately 150 mV (E_{red}[Ir(ppy)$_2$(dtbbpy)$^{3+}$/Ir(ppy)$_2$(dtbbpy)$^{2+}$] = −1.51 V).

Kinetic Parameters of Electron Transfers. While favorable thermodynamics are critical, the successful implementation of a reaction design requires the proper kinetics for the various steps associated with the net electron-transfer process. In addition, for any closed photoredox catalytic cycle there are at least two outer-sphere electron transfer processes that must occur: (1) an electron transfer to quench the excited state and (2) a subsequent electron transfer to regenerate the ground-state catalyst. For an example, Figure 5A depicts the various steps required to generate the net products associated with the oxidative quenching of a photocatalyst excited state (*PC). The reaction must begin with the association of *PC and the quencher, Q, to form a solvated precursor complex, **A**. The electron transfer, k_{et}, may then occur to form **B**. This successor complex may then undergo charge recombination, k_{cr}, to regenerate the quencher along with the ground-state photocatalyst. Alternatively, the components of **B** may escape the solvent cage, k_{esc}, to give the desired products of the oxidative quenching process, **C**. The relative rates of all of these processes are critical in order to have productive generation of the quenching products.[28] Marcus theory allows for the relation of the rate of the key electron-transfer process, k_{et}, to several thermodynamic parameters.[29]

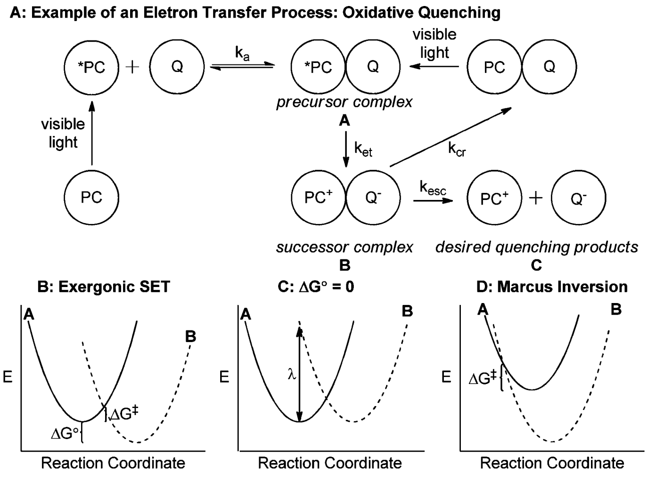

Figure 5. Steps and reaction coordinates associated with outer-sphere electron transfer.

Unlike a typical organic transformation, outer-sphere electron transfer does not result in the making or breaking of bonds. However, electron transfer changes the electronic configuration of the reaction partners as well as instigates a reorganization of the solvent cage. Furthermore, according to the Franck−Condon principle, electronic motions are very rapid relative to nuclear reorganization. Consequently, an activation barrier must be overcome in order for electron transfer to take place.

Figure 5B depicts the reaction coordinate of an exergonic electron transfer as viewed within the framework of Marcus theory. The energy surfaces of the precursor and successor complex are depicted as parabolas shifted vertically by $\Delta G°$, a value related to the reduction potentials of the reaction partners. The intersection of these curves represents the activation barrier, $\Delta G^‡$. Figure 5C depicts a similar reaction coordinate with $\Delta G° = 0$. The value λ, called the reorganization energy, represents the energy required for the reorganization of the precursor complex to the same configuration of the successor complex without the corresponding transfer of an electron. Application of Marcus theory allows for the expression of k_{et} based on these values (eq 3).

$$k_{et} = \frac{2\pi}{\hbar}|H_{A,B}|^2\frac{1}{\sqrt{4\pi\lambda k_b T}}e - \frac{(\lambda + \Delta G°)^2}{4\lambda k_b T} \quad (3)$$

In addition to the parameters discussed above, $|H_{A,B}|$ represents the electronic coupling of the reaction partners[30] and T the absolute temperature. As discussed previously, favorable thermodynamics ($\Delta G°$) are critical for the kinetics of this step. In addition, the reorganization energy, λ, plays a crucial role and is dependent on both the differences in molecular configuration of the reactants and products as well as reorganization of the solvent cage. In summary, the consideration of thermodynamics alone is insufficient when designing a reaction system. In fact, after a point, increasingly exergonic electron transfer reactions result in a decreased k_{et}. This is known as the Marcus inverted region (Figure 5D).[31]

SYNTHETIC APPLICATIONS OF PHOTOREDOX CATALYSTS

Organic intermediates bearing an unpaired electron are particularly attractive to synthetic chemists due to their unique and powerful reactivity.[32] The use of photoredox catalysts under mild reaction conditions (i.e., irradiation by visible light, ambient temperature) offers an attractive alternative to more traditional reaction systems.[33] The following are examples, grouped by reaction type, of organic transformations selected to give an overview of the type of reactivity accessible using photoredox catalysis.

Oxidative Generation of Reactive Intermediates. Photoredox catalysis has found applications in a variety of synthetically useful reductions of organic compounds.[8] Recently, Stephenson and co-workers investigated a tin-free reductive dehalogenation reaction. In this work, ^{i}Pr$_2$NEt was used as a reductive quencher, and the corresponding trialkylammoniumyl radical cation was determined to be prone to oxidation to generate an iminium ion.[34] On the basis of this preliminary evidence, several groups have utilized this reactivity for the functionalization of amines. Initially in 2010, Stephenson and co-workers reported that employing Ir(ppy)$_2$(dtbbpy)PF$_6$ and atmospheric oxygen afforded an oxidative aza-Henry reaction between tetrahydroisoquinolines and nitroalkanes.[35] Subsequently, other groups have shown this methodology to be viable for the nucleophilic trapping of oxidized benzylic amines.[36] Finally, Stephenson and co-workers recently reported an improved protocol for the generation of the iminium intermediate, which allowed for the successful utilization of a broad range of nucleophiles.[37,38] In addition, MacMillan and co-workers have described the generation of α-amino radicals via deprotonation of ammoniumyl radical cations and their subsequent coupling with electron deficient cyanoarenes (Figure 6A).[39,40] Finally, Yoon and co-workers have utilized photoredox catalysis to afford the oxidation of electron rich styrenes to afford intramolecular 2 + 2 and 4 + 2 cycloaddition reactions of the corresponding styrenyl radical cations.[41]

Carbon−Carbon Bond Formations via Displacement Reactions. Early work, performed by Deronzier and co-workers, nicely demonstrated the application of the electron transfer properties of photoredox catalysts in the context of intramolecular C−C bond-forming reactions. This group reported a Pschorr-type reaction initiated by the reduction of aryl diazonium salts by the Ru(bpy)$_3$Cl$_2$ excited state.[42] It was found that direct irradiation of the diazonium salt (λ_{ex} = 370 − 410 nm) afforded very little of the Pschorr products. Instead,

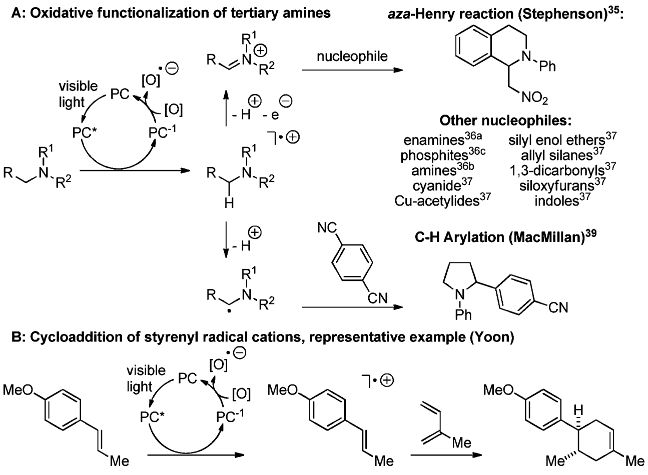

Figure 6. Oxidative generation of reactive intermediates.

conversion to the acetamide was observed. However, irradiation ($\lambda_{ex} > 410$ nm) in the presence of Ru(bpy)$_3$Cl$_2$ affords clean and rapid conversion to the phenanthrene product. This exemplifies one advantage of photoredox catalysis: the reaction control afforded due to the inability of the majority of organic molecules to absorb low energy visible light.

Furthermore, an interesting experiment was conducted utilizing $\mathrm{Ru(4,4'\text{-}(^iPrO_2C)_2\text{-}bpy)_3^{2+}}$. This complex functions as a less powerful reductant in its excited state ($E_{red}[\mathrm{Ru(4,4'\text{-}(^iPrO_2C)_2\text{-}bpy)_3^{3+}/{*}Ru(4,4'\text{-}(^iPrO_2C)_2\text{-}bpy)_3^{2+}}] = -0.38$ V).[43] In addition, the ligand modification has a profound effect on the size of the coordination sphere of the complex. Thus, two of parameters of the Marcus equation, namely $\Delta G°$ and $|H_{A,B}|$, have been adversely modified. This is manifested in the rate constants for the luminescence quenching of $\mathrm{Ru(4,4'\text{-}(^iPrO_2C)_2\text{-}bpy)_3^{2+}}$ ($k_q = 0.42 \times 10^9$ L mol^{-1} s^{-1}) and Ru(bpy)$_3$ ($k_q = 3.5 \times 10^9$ L mol^{-1} s^{-1}) by the aryl diazonium salt. Recently, the Sanford group has shown that the reduction of aryl diazonium salts by photocatalysts can be merged with high-valent Pd catalysis to afford a C−H arylation transformation (Figure 7).[44]

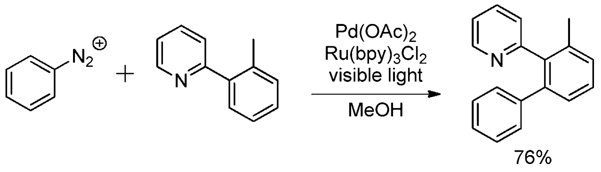

Figure 7. Merger of photoredox and high-valent Pd catalysis.

In 2008, the MacMillan group successfully merged photoredox catalysis with their ongoing research program in organocatalysis to develop a method for the α-functionalization of aldehydes. Their initial studies concerned the reduction of activated α-bromo ketones and esters,[45] and subsequent studies expanded the scope of this transformation to enantioselective perfluoroalkylation[46,47] and benzylation.[48] This general reaction design, with careful choice of catalyst, has proven capable of introducing a variety of functionality. For instance, a strong reductant was required to efficiently reduce benzyl bromides to the corresponding radical. *fac*-Ir(ppy)$_3$ was identified as a viable catalyst, since the excited state reduction potential, $E_{red}[\mathrm{Ir(ppy)_3^{4+}/{*}Ir(ppy)_3^{3+}}]$, is calculated to be −1.73 V (Figure 8).[4a]

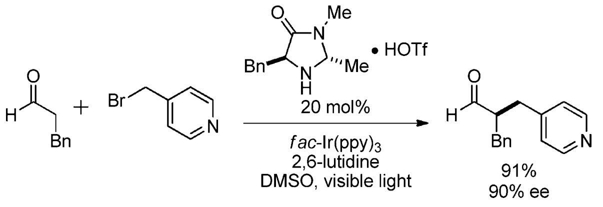

Figure 8. α-Functionalization of carbonyls mediated by photoredox catalysis (representative example).

The generation of alkyl radicals and their subsequent intra- and intermolecular addition to unsaturated carbon−carbon bonds have been utilized by several groups.[49] For instance, Stephenson and co-workers have developed several intra- and intermolecular radical functionalizations reactions.[50] Their studies have also resulted in the implementation of photoredox catalysis in the synthesis of the heterodimeric indole alkaloid (+)-gliocladin C.[51] In addition, Gagné and co-workers have reported a method for the synthesis of C-glycosides via the reduction of glycosyl halides (Figure 9).[52] This work was followed by an insightful mechanistic study which suggested that the prolonged reaction time is due primarily to a nonproductive charge recombination process.[53] To facilitate escape and solvation of the components of the successor complex, the addition of water as a cosolvent increased the effective quenching rate for Ru(bpy)$_3$(PF$_6$)$_2$. Likewise, the more hydrophobic catalyst Ru(dmb)$_3$(PF$_6$)$_2$ experienced increased quenching rates in anhydrous solvents.[54] Furthermore, increased synthetic utility is provided in the radical addition to unsaturated bonds in the form of atom transfer radical addition (ATRA) reactions, which introduce functionality at both of the alkene carbons. An early report by Barton and co-workers indicated the transfer of the S−Se bond of PhSeTos across alkenes (Figure 9).[55] Recently, Stephenson and co-workers reported a mechanistically similar ATRA transformation utilizing the photocatalyst, Ir(dF(CF$_3$)$_2$-ppy)$_2$(dtbbpy)PF$_6$, which afforded C−C bond formations with a variety of alkenes.[56]

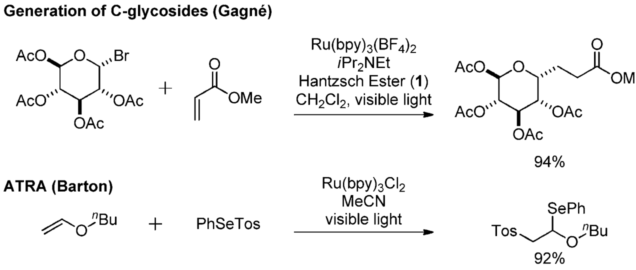

Figure 9. Radical additions mediated by photoredox catalysis (representative examples).

Transformation Initiated by Ketyl Radical Formation.

In addition to displacement reactions, the reduction of carbonyl moieties by photoredox catalysts has led to the development of a variety of transformations. Okada and Oda have reported a photocatalytic decarboxylation reaction of *N*-(acyloxy)-phthalimides to afford alkyl radicals which undergo a variety of transformations.[57] Reduction of the oxypthalamide starting material by Ru(bpy)$_3^{1+}$ generates the unstable radical anion intermediate. Decarboxylative fragmentation then affords the alkyl radical along with the phthalamide anion (Figure 10A). Yoon and co-workers have recently reported several examples utilizing photocatalysts to afford the single electron reduction

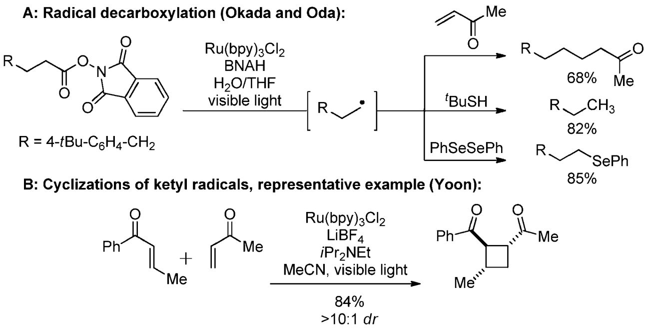

Figure 10. Reactions of ketyl radical intermediates.

of tethered bis-enones to afford varied synthetically useful transformations, including formal 2 + 2,[58] hetero 4 + 2,[59] and 3 + 2[60] cycloadditions as well as reductive cyclizations.[61] This has also been expanded to intermolecular 2 + 2 cycloadditions of enones (Figure 10B).[62] Through this work, the Yoon group has nicely demonstrated that through thoughtful design of substrates and careful control of reaction conditions these varied transformations can be achieved, giving rise to a diverse set of products.

■ CONCLUSION

The potential of photoredox catalysis in the realm of organic synthesis is just beginning to be realized by the chemical community. Although they have been studied intensively by multiple synthetic groups for only a short time, numerous and varied examples of chemical reactivity initiated or mediated by photoredox catalysts have been discovered. By applying the rich base of knowledge gained about complexes of these types through decades of study, organic chemists have the tools to further advance this promising and exciting new field.

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Notes

The authors declare no competing financial interest.

Biography

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Joseph Tucker completed his undergraduate studies at The College of William and Mary before beginning his Ph.D. work in the lab of Corey Stephenson at Boston University. Corey Stephenson completed his Ph.D. in Prof. Peter Wipf's group at the University of Pittsburgh and was a postdoctoral researcher in the group of Prof. Erick Carreira at the ETH-Zurich. He joined the faculty at Boston University in 2007 where his research group has focused on catalysis and natural product synthesis.

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(9) Herein, the term "photoredox catalysis" is used synonymously with "redox photosensitization". Often "catalyst" implies an intimate association of the additive with the rate determining step of the reaction mechanism, but this is not necessarily the case with the complexes discussed.

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