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Recent synthetic additions to the visible light photoredox catalysis toolbox

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The boom in visible light photoredox catalysis (VLPC) research has demonstrated that this novel synthetic approach is here to stay. VLPC enables reactive radical intermediates catalytically generated at ambient temperature, a feat not generally allowed through traditional pyrolysis- or radical initiator-based methodologies. VLPC has vastly extended the range of substrates and reaction schemes that have been traditionally the domain of radical reactions. In this review the photophysics background of VLPC will be briefly discussed, followed by a report on recent inroads of VLPC into decarboxylative couplings and radical C-H functionalization of aromatic compounds. The bulk of the review will be dedicated to advances in synergistic catalysis involving VLPC, namely the combination of photoredox catalysis with organocatalysis, including β -functionalization of carbonyl groups, functionalization of weak aliphatic C-H bonds, and anti-Markovnikov hydrofunctionalization of alkenes; dual catalysis with gold or with nickel, photoredox catalysis as an oxidation promoter in transition metal catalysis, and acid-catalyzed enantioselective radical addition to π systems.

Introduction

Visible light photoredox catalysis (VLPC) uses visible light as a renewable energy source to promote chemical transformations involving electron transfers.¹ Photoredox catalysis has received much attention from the organic synthetic community since the independent seminal reports from the MacMillan, Yoon, and Stephenson groups almost a decade ago.² Novel applications in the field of green chemistry and dual catalysis have expanded the synthetic applications of VLPC.³ Several VLPC reactions, such as the enantioselective α -functionalization of carbonyl compounds,^{1,4} [2+2] cycloadditions,¹⁵ and dehalogenation reactions,^{1,6} are already established synthetic tools. In this review, the photophysics background of VLPC will be briefly discussed, followed by recent inroads of VLPC into other synthetic realms, including decarboxylative couplings and radical C-H functionalization of aromatic compounds. The bulk of this review will be dedicated to advances in synergistic catalysis involving VLPC, namely the combination of photoredox catalysis with organocatalysis, including β -functionalization of carbonyl groups, functionalization of weak aliphatic C-H bonds, and anti-Markovnikov hydrofunctionalization of alkenes; dual catalysis

with gold or with nickel, photoredox catalysis as an oxidation promoter in transition metal catalysis, and acid-catalyzed enantioselective radical addition to π systems. Unless otherwise mentioned, all reactions described herein are performed at room temperature.

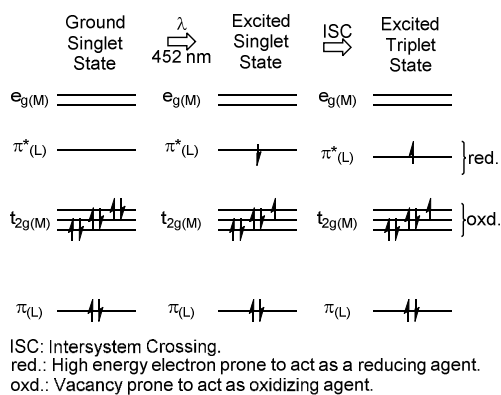
Visible light photoredox catalysis (VLPC)

$\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ is among the most common and well-studied photoredox catalysts. This d^6 octahedral complex possesses several interesting properties. Although its HOMO is centered on the $d_{t_{2g}}$ orbital of the metal, its LUMO is centered on the π^* orbital of 2,2'-bipyridyl ligands (bpy) instead of the metallic d_{eg} orbital (Scheme 1)⁷ as suggested by its UV-Vis spectrum. An absorption at the longest wavelength 452 nm is attributed to a $d_{t_{2g}} \rightarrow \pi^*$ transition, which is the band gap of LUMO and HOMO. Another absorption at 350 nm is attributed to a $d_{t_{2g}} \rightarrow d_{eg}$ transition. In addition, $\pi \rightarrow \pi^*$ transitions observed at 185, 208 and 285 nm are attributed to the bipyridyl system.⁸ During the transition corresponding to the absorption at 452 nm, one d -electron of the ground state complex is excited onto the π^* orbital of the ligand without flipping its spin. Such process is termed metal-to-ligand charge transfer (MLCT), and generates an excited singlet state. This excited singlet undergoes a rapid intersystem crossing (ISC), and quantitatively transforms itself into an excited triplet state (Scheme 2).⁹ The luminescence quantum yield of the excited triplet state of $\text{Ru}(\text{bpy})_3^{2+}$ in an organic medium is around 10%.¹⁰ This high yielding light-harvesting step accounts for the overall efficiency of VLPC.

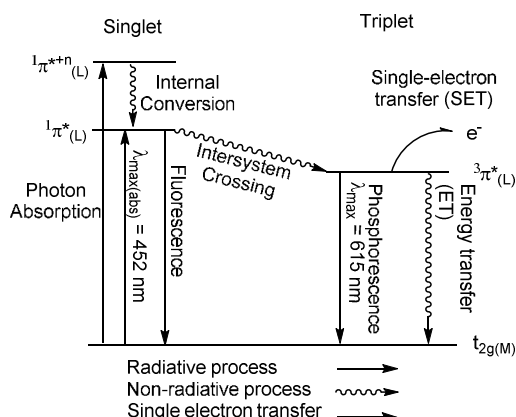
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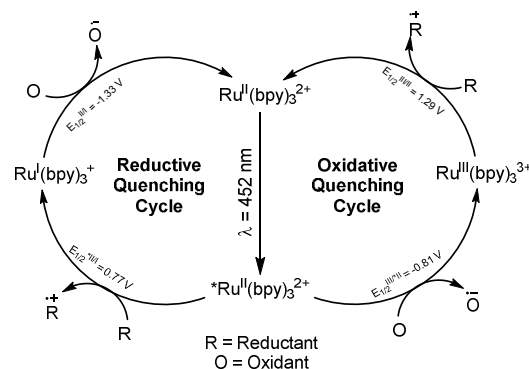
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Scheme 1: Orbital energy level diagram for the activation of $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$.

This efficiently formed excited triplet state is responsible for the peculiar reactivity of the catalytic system for two main reasons. First, the lifetime of the excited triplet state is significantly extended to approximately 1100 ns because the direct relaxation from an excited triplet state to a ground singlet state (selection rule) is forbidden. This allows intermolecular redox reactions to take place. Second, this species can act as either a single-electron reductant or oxidant via a single-electron transfer (SET) mechanism because of the vacancy at the $d_{t_{2g}}$ orbital and the presence of a high energy electron at the bipyridyl π^* orbital, respectively.¹

Scheme 2: Simplified Jablonski diagram for a typical photocatalyst like $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$.

The amphoteric redox reactivity of the excited triplet state of $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ ($^*\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$) enables two distinct catalytic redox cycles, namely, the reductive quenching cycle (RQC) and the oxidative quenching cycle (OQC) (Scheme 3). In RQC, $^*\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ first oxidizes a reductant into a radical cation species, and reduces itself into $\text{Ru}^{\text{I}}(\text{bpy})_3^+$, which subsequently reduces an oxidant into a radical anion species, and converts itself into the ground state catalyst. OQC starts with the oxidation of the complex $^*\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ to $\text{Ru}^{\text{III}}(\text{bpy})_3^{3+}$ followed by its reduction to $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$.¹ Here arises the question of how to determine if the reaction mechanism follows an OQC or a RQC path.



Scheme 3: Oxidative vs. reductive quenching cycles.

Besides participating into a redox reaction, the $^*\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ species can relax back to the ground state through either a non-emissive process, or, an emissive process after approximately 1100 ns. The latter produces characteristic phosphorescence at 615 nm, which can be used to elucidate the nature of the catalytic cycle through a Stern-Volmer study.¹¹

The Stern-Volmer equation (eq. 1) describes the linear relationship between the relative phosphorescence intensity I_0/I and the concentration of the quenching species $[Q]$.¹

$$I_0/I = 1 + k_q \tau_0 [Q] \quad \text{eq. 1}$$

In eq 1, I_0 is the phosphorescence intensity in the absence of any quenching agent, I is the phosphorescence intensity at a concentration $[Q]$ of quenching agent. k_q is the attenuation constant, and τ_0 is the lifetime of the excited state.¹ In practice, the change of relative intensity in the phosphorescence along with that of the oxidant indicates whether a reaction follows a possible OQC path. In a RQC-driven reaction, the change of phosphorescence intensity may only be related to the concentration of reductant.

The non-radiative relaxation process, also known as energy transfer (ET) between photo-sensitive molecules, may also quench the phosphorescence at 615 nm; hence the absence of phosphorescence at 615 nm is not sufficient to distinguish SET from ET.¹² However, the secondarily excited molecules formed through ET usually produce patterns of phosphorescence different from that of $^*\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$, which can help to further elucidate reaction pathway.

Ru^{II} - and Ir^{III} -based catalysts are the most frequently used metal catalysts because of their identical d^6 electronic structure. Although belonging to the same family of Ru^{II} , $\text{Fe}^{\text{II}}(\text{bpy})_3^{2+}$ has a LUMO centered at the d_{eg} orbitals, thus lacking the MLCT required for photoredox catalysis. In addition, its labile coordination structure fosters deactivation during catalysis.¹³ Os^{II} has more similarities to Ru^{II} but its short-lived excited state (about one order of magnitude shorter) and toxicity dim its synthetic usefulness.¹⁴ Rh^{III} complexes analogous to $\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})^+$ lack an efficient MLCT, thus they are not considered to be good catalysts.¹⁵

Despite having an electronic configuration different from Ru^{II} and Ir^{III} , the redox reactivity of the excited triplet state of

Cu^{I} complexes (d^{10}) have also been demonstrated in reactions that follow an OQC pathway.^{1,16}

In addition to transition metal-based catalysts, several organic dyes that are well known sensitizers in photo-oxygenation reactions have been reported to be effective photoredox catalysts.¹⁷

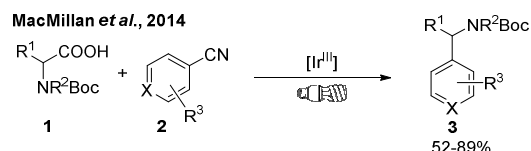
Selected applications in organic synthesis

Although many VLPC applications in organic synthesis have been covered in the seminal review of MacMillan,¹ the fast pace of VLPC research has uncovered new methodologies in radical additions to alkenes,¹⁸ alkynes,¹⁹ isonitriles,²⁰ carbon monoxide,²¹ and other π systems,²² functional group interconversions,²³ difluoroalkylations,²⁴ trifluoromethylations,²⁵ halide reductions,²⁶ oxidative couplings,²⁷ radical [2+2],²⁸ [3+2]²⁹ and [4+2]³⁰ cycloadditions, retro-cycloadditions,³¹ activation of reagents via two consecutive SET processes,³² C-C bond cleavage,³³ other radical couplings³⁴ and cleavages.³⁵

Decarboxylative couplings

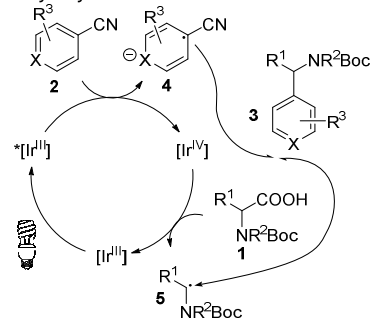
Generating radicals via decarboxylation of carboxylic acid derivatives is a particularly attractive methodology due to the general availability of carboxylic acids in nature.³⁶ However, the efficient generation of an alkyl radical from a carboxylic acid is not easy. One representative case is the Minisci reaction, in which an alkyl radical generated from the decarboxylation of a carboxylic acid adds to an azine. However, its harsh oxidative reaction conditions cannot tolerate labile functional groups. In addition, the only available acceptor of alkyl radicals in this transformation is limited to azine itself.³⁷

In 2014, MacMillan reported the first Ir-catalyzed photoredox decarboxylative coupling of α -amino acids **1** and benzonitriles **2**, which renders a photoredox version of the Minisci reaction under benign conditions (Scheme 4). This transformation began with a single-electron reduction of benzonitrile **2** by an excited Ir^{III} catalyst, which then generated radical anion **4** and an Ir^{IV} complex. The Ir^{III} catalyst was regenerated from the oxidation of an α -amino acid, which after extrusion of carbon dioxide led to the formation of a nucleophilic α -amino alkyl radical **5**. The recombination of radicals **5** and **4**, and subsequent cyanide elimination led to the secondary benzyl amine **3**. Not surprisingly, the stereo configuration of the α -carbon of the original chiral amino acid was lost due to the rapid radical inversion.³⁶ Soon after, the same group extended the scope of coupling partners incorporating electron-deficient alkenes **7** and vinyl sulfones **10**, hence achieving the decarboxylative alkylation and vinylation of carboxylic acids (Scheme 5).³⁸ Tungue reported that allylic acetates, in the presence of a Pd⁰ catalyst and a photoredox catalyst, gave rise to the decarboxylation product **14** (Scheme 5). In this manner, it became possible to perform the decarboxylative allylation of carboxylic acid **12**.³⁹



X = N, CCO₂Me, CPO(OEt)₂, CSO₂Ph, CCN.
R¹ = alkyl or aryl, R² = alkyl or H

Proposed catalytic cycle



Scheme 4: Decarboxylative arylation of amino acids.

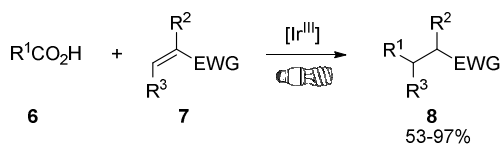
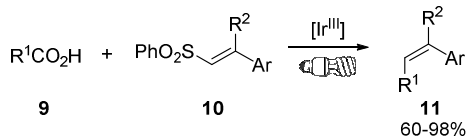
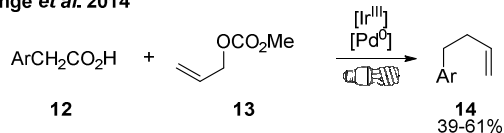
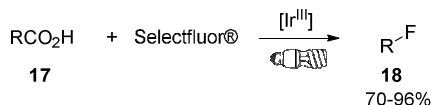
Paquin and Sammis also employed a similar strategy in the Ru-catalyzed decarboxylative fluorination of α -aryloxyacetic acid **15**. In this case, the *Ru^{II} species was first oxidized by Selectfluor into Ru^{III}, which induced the oxidative decarboxylation and fluorination steps (Scheme 5).⁴⁰ Sammis reported a similar transition metal-free photo decarboxylative fluorination of the same class of substrates; however, the reaction required a higher energy UV light source.⁴¹ Later, MacMillan's group successfully expanded the range of carboxylic acids **17** in the decarboxylative fluorination reaction by employing a heteroleptic iridium photocatalyst (Scheme 5). Primary, secondary, and tertiary radicals can be generated from the carboxylic acid precursor, and transformed into the corresponding fluorides in high efficiency (Scheme 5).⁴²

Radical C-H functionalization of aromatic compounds

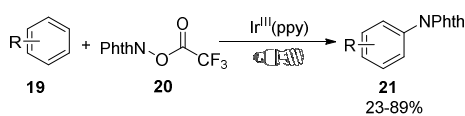
Interesting examples of VLPC radical additions to arenes have been reported; a case in point is the direct trifluoromethylation of arenes reported in 2011 by MacMillan and Nagib.⁴³

In 2014, Sanford and coworkers reported the photoredox catalytic amination of several arenes using *N*-acyloylphthalimides as *N*-radical precursor alternatives to *N*-bromophthalimides.⁴⁴ The latter were traditionally used in the UV-promoted amination of arenes, but the competitive bromination reaction that took place under the reaction conditions rendered them problematic (Scheme 6).⁴⁵

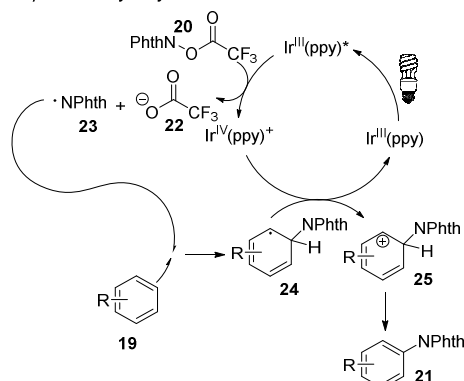
This reaction supposedly starts with a single-electron reduction of an *N*-acyloylphthalimide by *Ir^{III}(ppy), the subsequent fragmentation generates an electrophilic phthalimidoil radical **23**, which then adds to arene **19** to form a cyclohexadienyl radical **24**. Ir^{IV}(ppy)⁺ oxidizes **24** into a cyclohexadienyl cation **25**, which, upon rearomatization, furnishes product **21** (Scheme 6).⁴⁴

MacMillan *et al.* 2014MacMillan *et al.* 2014Tunge *et al.* 2014Paquin and Sammis *et al.* 2014MacMillan *et al.* 2015

Scheme 5: Photoredox-catalytic decarboxylative couplings.

Sanford *et al.*, 2014

Proposed catalytic cycle

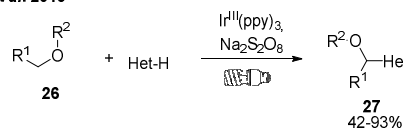
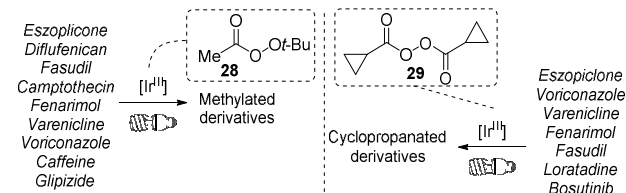


Scheme 6: Photoredox radical C-H functionalization of arenes.

In 2015, Jin and MacMillan developed the direct α -arylation of ethers and C-H functionalization of heteroarenes using a similar strategy in which the radicals are formed by the direct oxidation of ethers (Scheme 7).⁴⁶

A Merck group led by DiRocco employed a similar photoredox approach to perform the late-stage methylation

and cyclopropanation of bioactive molecules using peroxides. Although regioselectivity was hardly controlled, this procedure opened a fast and practical access to various alkylated APIs, which have appeal in medicinal chemistry (Scheme 7).⁴⁷

MacMillan *et al.* 2015DiRocco *et al.* 2014

Scheme 7: Applications of photoredox catalyzed addition of radicals to arenes.

Other recent applications of radical C-H functionalization of arenes⁴⁸ and heteroarenes,⁴⁹ can be found elsewhere.

Synergistic catalysis involving VLPC

Synergistic catalysis—the coupling of more than one catalytic cycle in a single transformation—is an interesting concept that combines the distinct advantages of different catalytic processes although compatibility challenges may arise.⁵⁰

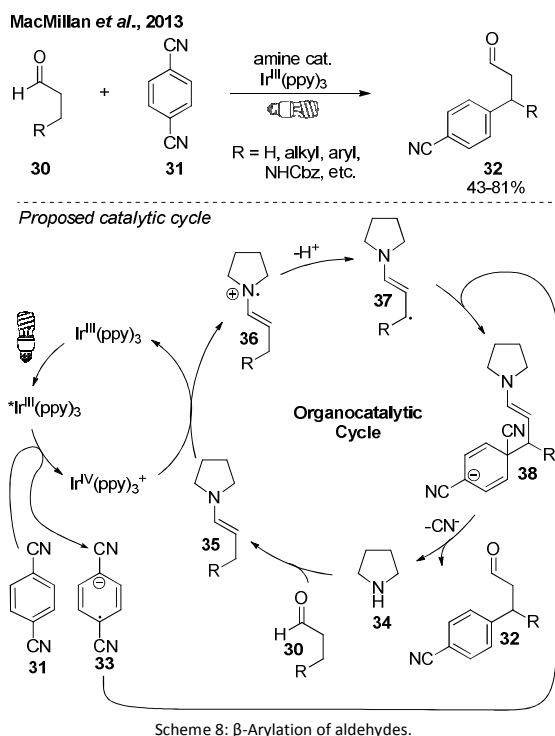
Combination of photoredox catalysis and organocatalysis

β -Functionalization of carbonyl groups

In contrast to the vastly available methods for α -functionalization of carbonyl compounds, the direct β -functionalization of saturated carbonyl compounds has been sparsely reported. One viable approach entails the quenching of a homoenolate, derived from cyclopropanol under basic conditions, by an electrophile. However, this approach is marred by the narrow substrate scope and the absence of regiocontrol during the ring-opening step of 2-substituted cyclopropanols.⁵¹ The MacMillan's group first reported a highly effective direct β -C-H arylation of carbonyl compounds using benzonitrile as aryl donor (Scheme 8),⁵² using a strategic combination of organocatalysis and photoredox catalysis.^{2a}

The proposed mechanism for this transformation follows an OQC pathway, starting with the formation of a cyclohexadienyl radical anion **33** via a single-electron reduction of benzonitrile **31** by the excited photoredox catalyst. The subsequent single-electron oxidation of enamine **35** by an Ir^{IV} species yields an enamyl radical cation **36**, and regenerates the photoredox catalyst. Notably, an external base deprotonates **36** to provide an γ -amino allyl radical **37**—an equivalent of a β -activated carbonyl—that then recombines

with radical anion **33** to furnish a cyclohexadienyl anion **38**. Upon elimination of cyanide and hydrolytically release of the amine catalyst **34**, **38** yields β -arylated carbonyl **32**.⁵² β -Substituted aldehydes and cyclohexanones are compatible substrates in this transformation, and the corresponding products are not readily accessible using the traditional homoenolate manifold.⁶ Regarding the special β -selectivity of this transformation, the authors proposed that a lesser electrophilic radical coupling partner is responsible for the β -functionalization, since the activation of the β -position would require the enamine intermediate to undergo the oxidation and deprotonation steps. A more reactive electrophilic radical, like the trifluoromethyl radical, would have quenched the enamine directly furnishing the α -functionalized product.^{52,53}

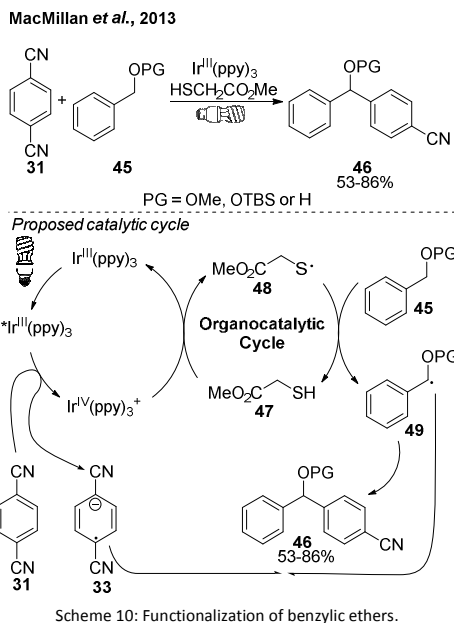
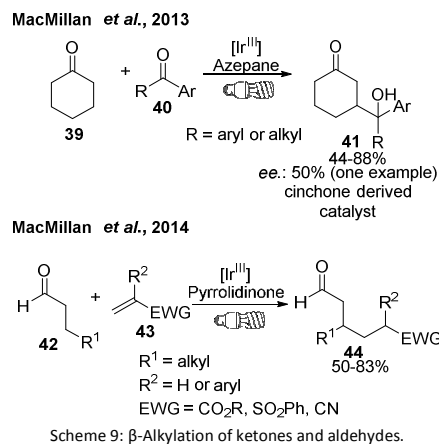


This methodology was later expanded to include the intermolecular β -hydroxyalkylation of cyclohexanones and the β -intra- and inter-molecular alkylation of aldehydes (Scheme 9).^{53,54}

Functionalization of weak aliphatic C-H bonds

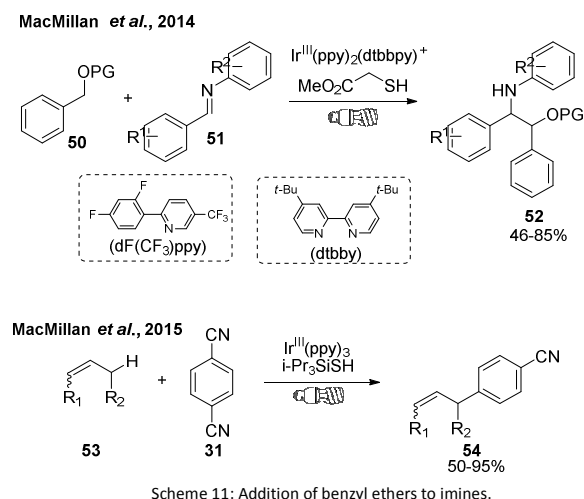
Another reaction that makes use of the combination of organocatalysis and VLPC is the functionalization of weak C-H bonds. In this context, the photoredox catalytic arylation of benzylic ethers **45** in the presence of a mercaptoacetate co-catalyst reported in 2013 by MacMillan's group is noteworthy (Scheme 10). The proposed mechanism for this reaction begins with an SET from the excited photoredox catalyst to benzonitrile, which produces a cyclohexadienyl radical anion **33** and the oxidized catalyst. The latter abstracts one electron from mercaptoacetate co-catalyst **47** to furnish a sulfur radical

(**48**). It is interesting to note that the direct oxidation of **47** ($E_{1/2}^{\text{red}} = +0.85$ V) by the complex $\text{Ir}^{\text{IV}}(\text{ppy})_3^+$ ($E_{1/2}^{\text{IV/III}} = +0.77$ V) is a thermodynamically unfavorable process but adding a base (e.g., K_2HPO_4) drives the reaction through a concerted proton-coupled electron transfer (PCET) pathway, in which the deprotonation and oxidation of thiol **47** can occur simultaneously.⁵⁵ The radical **48** then abstracts a benzylic hydrogen from ether **45** to furnish the benzylic radical intermediate **49**. The recombination of radical species **51** and **33** gives rise to the formation of a cyclohexadienyl anion, which furnishes the diarylmethyl derivative **46** after cyanide elimination.⁵⁵



Later, the same group reported a similar VLPC coupling reaction of benzyl ether **50** and imine **51** to produce β -amino ether **52**. In contrast to the previously discussed arylation reaction, which follows a provisional OQC pathway, the Stern-Volmer quenching study in this report shows the linear

relationship between the relative phosphorescence intensity and the concentration of mercaptoacetate, hence supporting a RQC pathway for the formation of a sulfur radical. In addition, the thermodynamically unfavorable reduction of imine ($E_{1/2}^{\text{red}} = -1.98$ V) by $^*\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})^+$ ($E_{1/2}^{\text{IV/III}} = -0.96$ V) further excludes the possibility of an OQC pathway (Scheme 11). In this work, the challenging oxidation of thiol **47** was achieved by using a more electron-deficient complex $\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})^+$ ($E_{1/2}^{\text{III/II}} = +0.66$ V) in the presence of an acetate, via a PCET mechanism.⁵⁶



The authors also evaluated the effect of the reaction vessel on reaction kinetics. It was observed that an increase in surface-to-volume ratio of the reaction vessel accelerates the reaction. The optimum reaction rate was achieved when the reaction was conducted in an NMR tube. This result indicates that the effective number of photons absorbed by the reaction mixture limits the process.⁵⁶

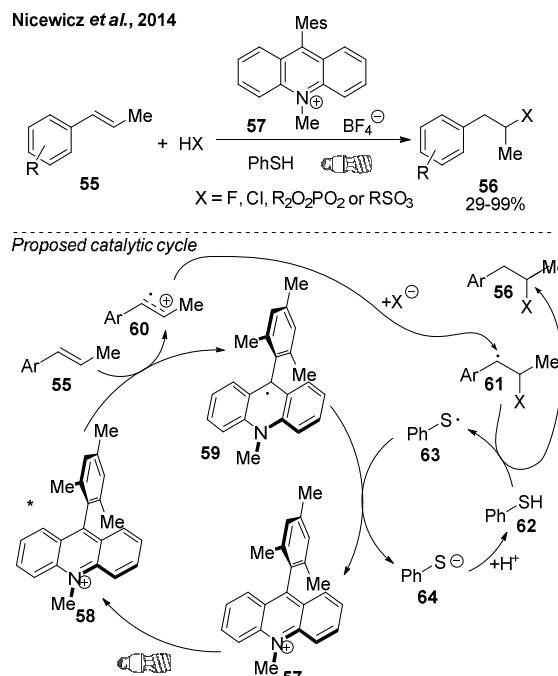
Recently, the MacMillan group reported a direct arylation of allylic C-H bond under photocatalytic conditions with a silylthiol co-catalyst (Scheme 11).⁵⁷ In these arylation reactions, electron rich bases like amines cannot be used to assist the PCET process because they compete with the thiol co-catalyst in the oxidation reaction. Inorganic bases are better alternatives.^{55,56,57}

The combination of organocatalysis and photoredox catalysis has also been used for functional group interconversion⁵⁸, polar radical crossover cycloadditions⁵⁹, and radical addition to π systems.⁶⁰

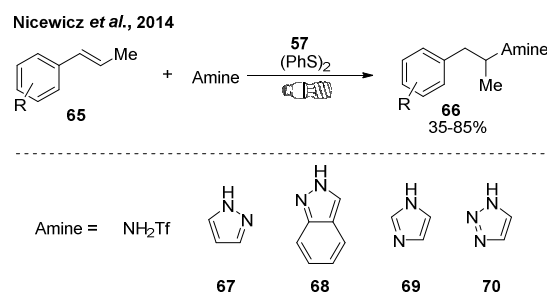
Anti-Markovnikov hydrofunctionalization of alkenes

Anti-Markovnikov hydrofunctionalization of alkenes has also recently become associated with VLPC, particularly due to the efforts of the Nicewicz's group, who used organic sensitizers as photoredox catalysts in place of Ru/Ir complexes. Some work in this area has already been reviewed.^{17,61} More recently, Nicewicz reported the anti-Markovnikov addition of mineral acids to styrenes (Scheme 12).⁶²

The proposed mechanism for these transformations has been recently supported by mechanistic studies.⁶³ Oxidation of styrene **55** by the excited photocatalyst **58** (either excited singlet or triplet) results in a radical cation **60**. The addition of nucleophile **X** leads to the radical intermediate **61**, which then abstracts hydrogen from thiol **62** to furnish product **56**.



Softer nucleophiles were also compatible in this reaction, as demonstrated by the same group in the anti-Markovnikov hydroamination of olefins (Scheme 13).⁶⁴

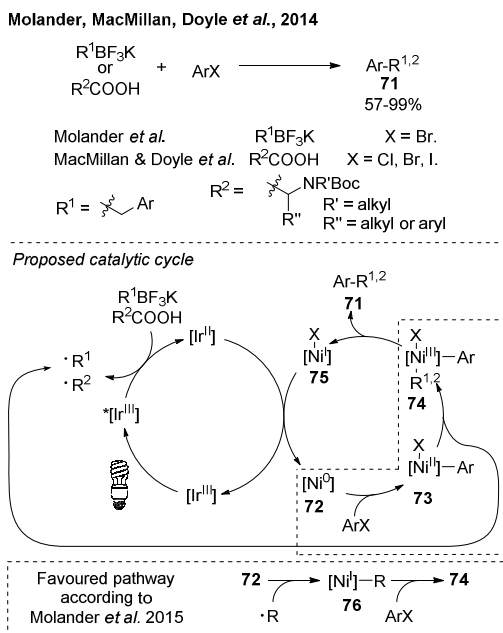


Combination of photoredox catalysis with transition metal catalysis

Dual catalysis with nickel

Nickel catalyst has demonstrated its versatility in a variety of transformations.⁶⁵ Besides being earth-abundant and cost efficient, undesired β -hydride elimination is less prone to take place in nickel catalysis compared to Pd-catalyzed

transformations. In other words, a much wider scope of substrates can be tolerated in nickel-catalyzed transformations. Moreover, its capability for tolerating both odd and even oxidation numbers allows the incorporation of radical species generated under photoredox catalysis conditions in nickel-catalyzed coupling reactions.⁶⁶ In 2014, Molander, MacMillan and Doyle first demonstrated the practicability of this concept in back-to-back communications (Scheme 14).⁶⁷

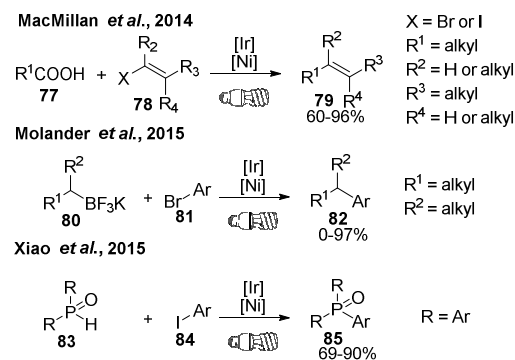


Scheme 14: Combination of VLPC with nickel catalysis.

In the initially proposed mechanism, the Ni^0 species adds oxidatively to the aryl halide to generate a Ni^{II} intermediate **73**. Simultaneously, the photocatalyst generates a radical species either from the oxidation of alkyl trifluoroborate or the decarboxylation of carboxylic acid. The corresponding radical then adds to **73**, resulting in a Ni^{III} complex that undergoes reductive elimination to give the product **71** and a Ni^{I} species that can then be reduced by the photocatalyst to restart the catalytic cycle.⁶⁷ However, a recent mechanistic investigation by Molander indicated that a more favorable pathway is the radical addition to the Ni^0 species followed by the oxidative addition of aryl halide to the Ni^{I} complex (Scheme 14).⁶⁸ According to Molander, this methodology is also complementary to classical coupling reactions involving a two-electron transmetalation step, because in the photoredox catalyzed process the reactivity order is $sp^3 > sp^2 > sp$, while in the traditional two-electron transmetalation step, the order of reactivity is $sp > sp^2 > sp^3$.^{67a} In addition, Molander's group showed that, in the presence of a chiral bisoxazoline ligand, a product with moderate enantioselectivity was obtained from the coupling reaction of a *sec*-benzyl boronate, thus demonstrating its potential for enantioselective radical coupling reactions.^{67a,69}

In 2014, the MacMillan group expanded the scope of coupling partners to include vinyl halides, thus furnishing decarboxylative Heck coupling products (Scheme 15).⁷⁰ More recently, Molander demonstrated the feasibility of coupling a secondary organoboronate and an aryl bromide using this methodology (Scheme 15).⁷¹ Xiao also reported a similar procedure in the arylation of diorganophosphine oxides (Scheme 15).⁷²

A highlight report on dual catalysis with nickel appeared at the time this review was being submitted.⁷³

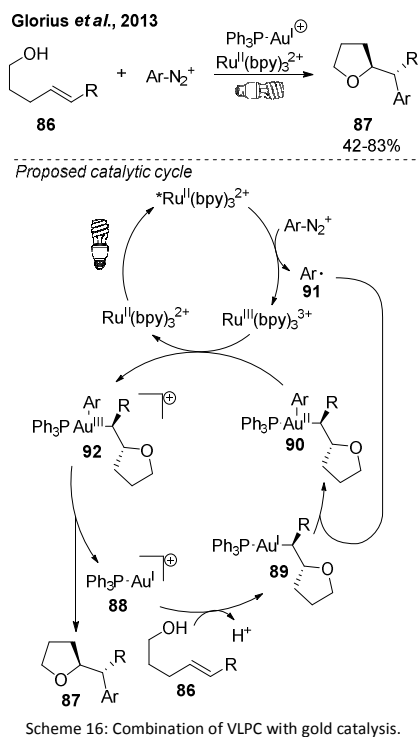


Scheme 15: Applications of the combination of VLPC with nickel catalysis.

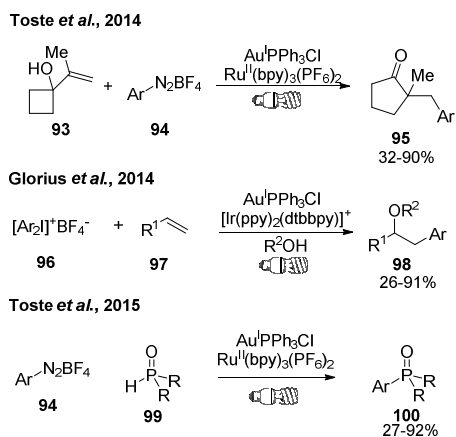
Dual catalysis with gold

Homogeneous gold catalysis has gained traction in recent years. The highly Lewis acidic and π -philic nature of the gold catalyst enabled a wide scope of selective transformations of alkynes, allenes and alkenes.⁷⁴ Conversely, processes involving redox transformations of gold catalysts are not common; the majority of the reported studies require an extra strong co-oxidant.⁷⁵ The incorporation of VLPC in the field of homogeneous gold catalysis provided access to a broader range of gold catalyzed oxidative transformations, thus extending the substrate scope. In 2013, Glorius reported a two-component oxyarylation of alkenol **86** by aryl diazonium salts using a combination of $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$ and a cationic Au^{I} catalyst. This dual catalytic system allowed the synthesis of 2-benzyl tetrahydrofuran **87** (Scheme 16).⁷⁶ The proposed mechanism for this transformation involves two coupled catalytic cycles. In the photoredox cycle, a diazonium salt is reduced to an aryl radical **91** after taking an electron from an excited Ru-catalyst and extruding dinitrogen. In the gold-catalytic cycle, *trans*-oxyarylation of alkenol **86** produces an alkylgold^I intermediate **89**, which, after two consecutive single-electron oxidations, first by the aryl radical and then by the oxidized Ru-catalyst, is converted into a cationic diorganogold^{III} intermediate **92**. Intermediate **92** releases the product and regenerates the catalyst upon reductive elimination.¹

In a subsequent report, the Glorius group used a diaryliodonium salt as aryl donor in a three-component oxyarylation reaction with an alkene and an alcohol in the presence of an Ir-sensitizer and a gold catalyst (Scheme 17).⁷⁷



Toste reported the synthesis of cyclopentanone **95** via a semi-pinacol rearrangement/oxidative arylation cascade transformation of 1-alkenyl cyclobutanol **93** and aryl diazonium salt **94** under similar reaction conditions. However, contrary to the Glorius' proposed mechanism, Toste's mechanistic study, which was based on time-resolved FT-IR spectroscopy, indicated that the addition of aryl radical to the gold catalyst occurs before the coordination of gold to the olefin (Scheme 17).⁷⁸



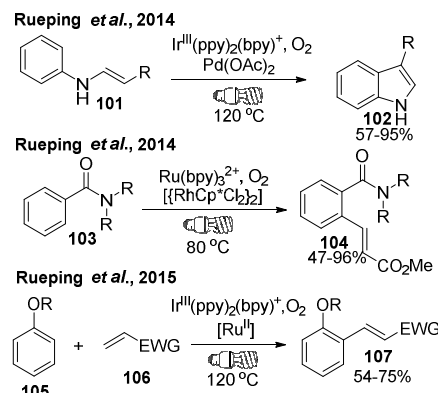
Scheme 17: Applications of the combination of VLPC with gold catalysis.

More recently, Toste reported the arylation of diorganophosphine oxide **99** using a combination of gold catalysis and photoredox catalysis (Scheme 17).⁷⁹

It has been reported that binuclear gold complexes can also perform photoredox catalysis; this strategy has been applied in radical additions to π systems⁸⁰ functional group inter-conversions⁸¹ and other radical coupling reactions.⁸²

Photoredox catalysis as an oxidation promoter in transition metal catalysis

Rueping reported Pd/Rh/Ru-catalyzed oxidative cyclization and C-H functionalization reactions under photoredox conditions using dioxygen as oxidant (Scheme 18). Heating was necessary for these reactions, presumably because the rate limiting step was not in the photoredox catalytic cycle.⁸³ Indeed, the photoredox catalysis system presumably only oxidizes intermediates pertaining to the main catalytic cycle. This method underscores the potentiality of introducing photoredox catalysis in lieu of other oxidizing agents, like copper salts, in oxidative C-H functionalization transformations.⁸⁴

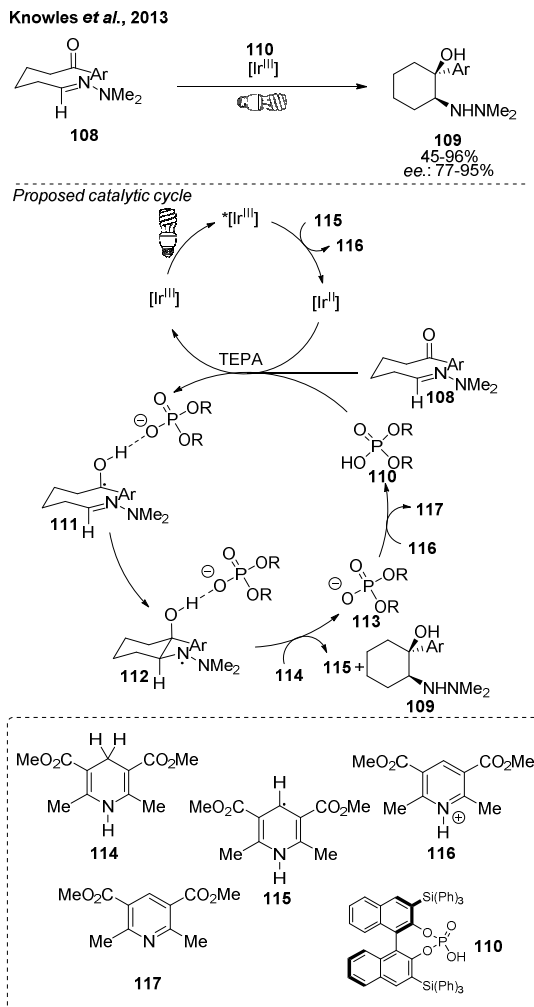


Scheme 18: Photoredox catalysis in oxidative couplings.

Other binary VLPC catalytic systems coupled with transition metal catalysts such as palladium,⁸⁵ copper,⁸⁶ and cobalt,⁸⁷ have either been previously reviewed,¹ or recently published⁸⁵⁻⁸⁷ and will not be discussed herein.

Acid-catalyzed enantioselective radical addition to π systems

Enantioselective radical additions to π systems have demonstrated that it is possible to tame the high reactivity of radicals in such a way that near total stereocontrol can be achieved.⁶⁹ A case in point is the VLPC-mediated enantioselective α -alkylation.² More recently, other creative approaches have been introduced to achieve enantioselective radical addition to prochiral π systems. In 2013, Knowles first reported an intramolecular enantioselective aza-pinacol coupling of the ketohydrazone **108** under photoredox catalytic conditions with the assistance of another chiral phosphoric acid catalyst and a Hantzsch's ester as reducing agent (Scheme 19). The hydrogen bond between the chiral phosphoric acid and the radical anion intermediate shortens their spatial distance, and assures enantioselective addition of the radical anion to the imine.⁸⁸

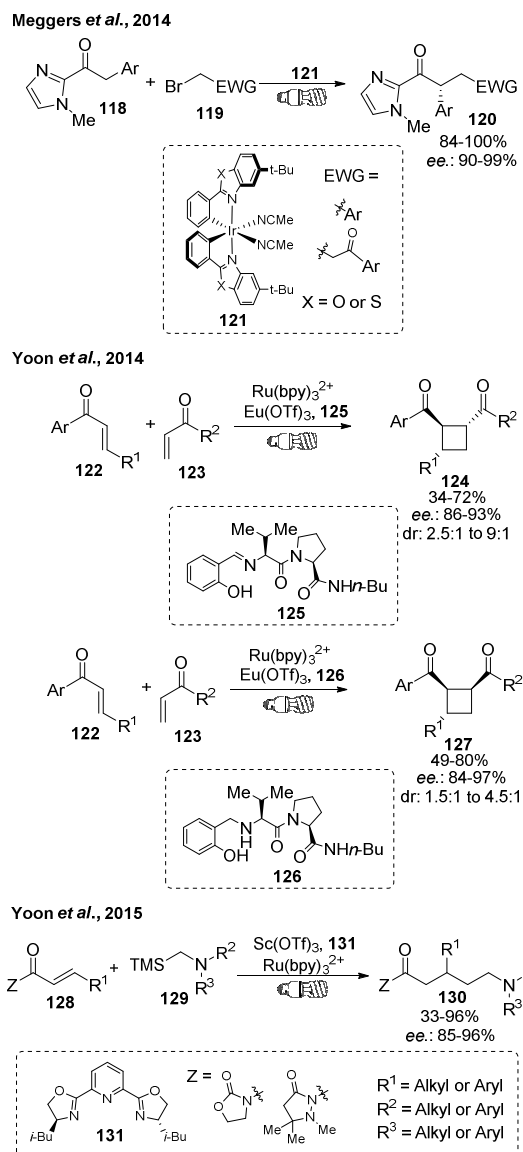


Meggers group reported the enantioselective α -alkylation of ketones using the Ir-complex **121**, which serves both as photoredox catalyst and chiral Lewis acid in this transformation.⁸⁹ This approach was employed in the oxidative coupling between carbonyl compound **118** and the activated organic bromide **119** (Scheme 20).⁹⁰

The Yoon group developed an enantioselective Lewis acid-assisted photocatalytic radical [2+2] cycloaddition in 2014. In the absence of a Lewis acid catalyst, the reaction was completely shut down. The authors proposed that the Lewis acid catalyst enhanced the electron-deficiency of enones, hence allowing a SET from the excited photocatalyst to **122** to take place. This radical underwent a [2+2] radical cyclization with enone **123** to furnish either the enantioenriched product **124** or **127**. It is interesting to note that a simply reduction of chiral ligand **125** to **126** led to the formation of products with completely different diastereoselectivities.^{5^b}

In addition, the Yoon group recently reported the enantioselective conjugate addition of an α -amino radical to an α,β -unsaturated carbonyl substrate **128** using $\text{Sc}(\text{OTf})_3$ and

the chiral ligand **131** under photoredox catalysis conditions (Scheme 20).⁹¹



Scheme 20: Cooperation of VLPC and Lewis acid catalysis.

The combination of VLPC and acid catalysis has also been used for functional group interconversions.⁹²

Conclusions

VLPC has added new transformations to the synthetic toolbox, improving known reaction processes to the point of eliminating the use of stoichiometric amounts of reductants or oxidants. Other advantages include the fact that, for the most part, the reaction conditions do not demand additional heating or cooling; instead, energy is harvested from photons from within the visible spectra. Most published works use simple

light sources such as fluorescent lamps or LED's, though the potential to use solar light is evident. As opposed to UV photochemistry, visible light does not excite the majority of functional groups. This allows for the selective irradiation of the photocatalyst, hence preventing undesired decomposition of substrates or side reactions.

One issue that is not often discussed is the light penetration power in these reactions. Although the quantum yield of excited triplet is high, the presence of other light-absorbing or -scattering factors, including solvents, substrates, and solid reagents, may reduce the actual photon-harvesting efficiency of photocatalysts. Moreover, with the thickening of the reaction medium, light intensity at the center of the reactor will be reduced according to Beer's law, which may limit the reaction to those areas close to the light source. Thus, the size and shape of the reactor, the intensity and wavelength of the light source, and the color or turbidity of the reaction medium have to be considered during trouble-shooting and scaling-up. Continuous flow reactor has been found to be an ideal solution to this problem.⁹³

With regards to the choice of ligands, visible light photoredox chemistry using transition metal catalyst has shown its dependence on polyaromatic ligands, such as bipyridyls and phenanthrolines, which are known to be DNA intercalating agents. Newly developed organic photoredox catalysts may be less toxic alternatives, although knowledge about their biological activity remains limited. Organic sensitizers may not be cost-effective compared to well-studied metallic catalysts whose ligands are easily tunable. The reactivity of catalysts and functional groups towards redox processes can be estimated based on electrochemical data, although the irreversibility of some radical reactions makes it hard to determine some redox potentials. The complexes used in VLPC do usually exhibit good stability, which allows for a low loading of catalyst (in general less than 5 mol%). However, in some catalytic reactions (particularly redox neutral), the presence of paramagnetic impurities, like dioxygen and iron rusts, could impair the catalysis process.

Notwithstanding the above shortcomings, VLPC has already shown its prowess in the construction of complex molecules, in total synthesis or in late stage functionalization of biologically active molecules.

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