Visible light-induced excited-state transition-metal catalysis

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Abstract

In recent years, visible light-induced, excited-state transition-metal (TM = Mn, Co, Cu, and Pd) catalysis has attracted significant attention for the development of various chemical transformations. In contrast to metal/photoredox dual catalysis that uses conventional photosensitizers and TMs cooperatively, photoexcited-state TM catalysis uses a single TM complex as both the photocatalyst and cross-coupling catalyst, resulting in more sustainable and efficient reactions. Unlike the outer-sphere mechanism active in conventional photocatalysis, these TM catalysts operate through a photoinduced inner-sphere mechanism in which the substrate-TM interaction is crucial for the bond-breaking or bond-forming steps, making this system an important advancement in efficient C–C bond formation reactions. Given the importance of these TM complexes as next-generation photocatalysts with distinct mechanisms, in this review, we highlight recent developments in photoexcited TM catalysis for C–C bond formation.

Keywords: visible-light; Excited-state; Manganese; Cobalt; Copper; Palladium

Advances in photocatalysis

Carbon-carbon (C–C) bond-forming reactions are among the most important reactions in organic chemistry, and transition-metal (TM)-catalyzed cross-coupling reactions have revolutionized the way in which such bonds are formed [1, 2]. The wide range of substrates that can be applied in these C–C bond-forming reactions and the diversity of tolerated functional groups have made metal-catalyzed cross-coupling reactions an essential synthetic tool in the chemist's toolbox. In this regard, the platform of photoredox catalysis has become an interesting avenue for the development of new bond-forming protocols and synthetic methodologies for the construction of complex molecules by using a photocatalyst (PC) and visible light [3, 4]. Mechanistically, these reactions proceed via the excitation of a photocatalyst to its **excited state** (see Glossary) by visible light, where the excited catalyst either donates/accepts electrons based on its redox potential or participates in the atom/energy transfer process (Figure 1A). As a result, the use of metal complexes (e.g., Ir, Ru, or homoleptic/heteroleptic Cu complexes of polypyridyl or phenanthroline), as well as organic dyes as PCs has attracted significant attention [4-7]. Subsequently, cooperative/dual photoredox catalysis via the combination of photocatalysis with TM catalysis has emerged, allowing facile and efficient access to cross coupling products in a new way (Figure 1B) [8, 9].

Successful dual catalysis has been achieved by **single-electron transfer** (SET) or energy transfer processes [10, 11] from the corresponding PC to the TM catalyst, enabling the cleavage of specific C–H or C–C bonds. Recently, as an alternative to combining often expensive or unstable photocatalysts with TM catalysts, the use of metal complexes (Mn, Co, Cu, and Pd) that act both as the photocatalyst and reactive catalysts for the cross-coupling reactions has emerged (Figure 1C) [12]. The most important feature in the use of TMs as PCs is the ability of a TM to exist in multiple oxidation states, each of which has distinct reactivity patterns. Unlike the **outer-sphere** mechanisms observed with conventional photosensitizers, visible light-induced TM catalysis proceeds via a photoinduced **inner-sphere** mechanism that constitutes an important

advancement in the field of efficient and economic C–C bond formations. In this review, we highlight recent advances in visible light-induced, excited-state TM catalysis (Mn, Co, Cu, and Pd) for the formation of C–C bonds. Related excited-state TM catalysis using UV irradiation is addressed elsewhere [13, 14].

Visible light-induced Mn-catalyzed C–C bond-forming reactions

Photoinduced homolytic cleavage of the weak Mn–Mn (38 kcal mol⁻¹) bond in dimanganese decacarbonyl [Mn₂(CO)₁₀] under visible-light irradiation produces two MnCO₅• (17e⁻) metallo radicals without an additional **photosensitizer** [15-17]. These Mn-radicals have a strong affinity for the halide atoms of alkyl halides, which generate carbon-centered radicals, suggesting that low-cost Mn₂(CO)₁₀ could be used to catalyze various C–C bond formations [18].

In 2017, Frenette and Fadeyi described a Mn₂(CO)₁₀ catalyzed Minisci reaction using quinolines and organoiodides under visible-light (blue Led, wavelength range from 400 to 470 nm) irradiation (Figure 2A and 2B) [19]. In the developed protocol, traditional noble photoredox catalysts (e.g., Ir, Ru, and Au) are not required, and various primary, secondary and tertiary C₂-alkylated quinolines are obtained in good yields. Here, MnCO₅•, which was initially formed by photochemical Mn–Mn bond cleavage, promotes the subsequent chain propagation step (Figure 2C), generating an alkyl radical and MnCO₅I. The alkyl radical then nucleophilically attacks an electron-deficient position of the heteroaromatic species to form dearomatized aminyl radical cation intermediate **6**, which is deprotonated by trifluoroacetate to afford α-amino alkyl radical intermediate **7**. Finally, the single-electron oxidation of **7** by Mn(I) affords the alkylated product and regenerates the MnCO₅• radical species. To support the proposed mechanism, a laser flash photolysis experiment was performed. In these experiments, excitation at 460 nm facilitated the homolytic cleavage of the Mn–Mn bond, which in turn provides the MnCO₅• radical, as confirmed by its specific absorption at 800 nm. Surprisingly, no reaction was observed in the presence of alkyl bromide. The abstraction of bromine from cyclohexyl bromide by Mn(CO)₅• is thermodynamically less favored than the abstraction of iodide. Density functional theory (DFT) calculations also support that the

overall catalytic processes are exergonic and that the initial iodine abstraction from the alkyl iodide by $\text{MnCO}_5^\bullet$ is the rate-limiting step.

In 2018, Nagib and coworkers further reported a Mn-catalyzed synthesis of *Z*-vinyl halides from aldehydes, alkynes, and acyl iodide via the *in-situ* generation of α -oxy iodides **11** (Figure 3A) [20]. The broad substrate scope, good functional group compatibility, and excellent diastereomeric ratio (up to 20:1) of the vinyl iodide products make this method quite versatile. The formed alkyl C–I bond is very weak due to the donation of the nonbonding oxygen electrons to the antibonding ($n \rightarrow \sigma^*$) orbital of C–I through **hyperconjugation**. This phenomenon shifts the reduction potentials of **11** from -2.2 V to -1.1 V. As shown in Figure 3B, $\text{Mn}(\text{CO})_5^\bullet$ acts as an atom-transfer radical addition (ATRA) catalyst to abstract $\text{I}^\bullet$ from **11**, generating a long-lived nucleophilic ketyl radical (**12**), which further reacts with an alkyne to afford vinyl radical **13**. Subsequent oxidation followed by isomerization of **13** by $\text{Mn}(\text{CO})_5\text{I}$ via ATRA regenerates $\text{Mn}(\text{CO})_5^\bullet$ and forms the vinyl iodide products with high *Z*-selectivity. The authors also found that the catalytic turnover occurs by atom transfer with Mn–I and that the overall reaction is exothermic due to the formation of new strong vinyl C–I bond.

Very recently, Ackermann and coworkers reported a Mn(I)-catalyzed visible light-induced photoflow protocol for C–H arylation by utilizing arenes and aryl diazonium salts at room temperature in the presence of different functional groups (Figure 3C) [21]. Here, both substrates coordinate to the manganese complex to form **18** as a key intermediate, which can undergo photoexcitation and SET to produce a Mn-radical cation and aryl radical intermediate (**20**). Further addition of the aryl radical to the arene affords a biaryl radical intermediate that is rapidly oxidized by the Mn-radical cation and then deprotonated to give the desired C–H arylated product.

Visible light-induced Co-catalyzed C–C bond-forming reactions

Photoinduced carbon radical generation using a cobalt (Co) catalyst has resulted in important advances in C–C bond formation because the catalysts are environmentally benign, inexpensive, and exhibit activities comparable to Ru- and Ir-based photoredox catalysts. For example, vitamin B_{12a} and cobaloxime complexes can be used as photocatalyst to generate C–C bonds at particularly low overpotentials upon

photoexcitation [22, 23]. The resulting Co-organo intermediate undergoes photohomolysis to generate organic radicals and persistent metal-centered radicals due to the weak metal-carbon bond. The very low bond energy of the Co–C (17-30 kcal mol⁻¹) bond and high oxidation state of the metal results in a significantly lower dissociation energy compared to those of other transition metal-carbon bonds [24-26]. The photohomolysis of the Co–C bond is completely dependent on the electronic and steric effects of both the equatorial and axial ligands. The structural analyses of the alkyl-cobalt bond indicated that the lowest unoccupied molecular orbital (LUMO) of the alkyl-cobalt species is the σ^* orbital because of the interaction between the alkyl sp^3 and cobalt d_z^2 orbitals. Due to the nature of equatorial and axial ligands, an additional electron occupies the antibonding σ^* orbital from the π^* and $d_{x^2-y^2}$ orbitals of ligand and metal. This phenomenon reduces the Co–C bond strength and favors homolysis with the loss of the alkyl radical and reduced cobalt complex [27]. The donating ability of the coordinated ligands, particularly with more basic ligands, has been shown to stabilize the parent organo-cobalt complex, which marginally increases the Co–C bond dissociation energy. However, increasing the steric bulk of the axial ligands reduces the Co–C bond strength and facilitates homolytic Co–C bond cleavage even upon exposure to visible light [28].

In this context it is important to note, that Vollhardt and others developed visible light induced a dicarbonylcyclopentadienyl cobalt ($CpCo(CO)_2$)-mediated [2+2+2] cycloaddition (Vollhardt reaction) to afford macrocyclic aromatic or non-aromatic compounds with long-chain diynes, monoalkynes, and carbon-heteroatom multiple bonds [29-33]. The proposed mechanism of cobalt mediated [2+2+2] alkyne cyclotrimerization involves the replacement of two carbonyl ligands on the cobalt metal by the alkyne units forming dialkyne cobalt intermediate that undergoes spontaneous oxidative addition to give Cp-cobaltacyclopentadiene intermediate. This intermediate coordinates with next reactive unsaturated component to form the metallacycloheptatriene. Finally, the seven membered cobalta cycle undergoes reductive elimination to liberate the cycloaddition product and CpCo-catalyst. The supporting studies suggested that a SET event is not operative in these reactions.

In 1990, Scheffold and coworkers first reported the cobalt-catalyzed, visible light-induced homolytic Co–C bond cleavage and intramolecular radical addition to alkenes and alkynes to form the core of prostaglandin $F_{2\alpha}$ via SET [34]. This pioneering work utilizes vitamin B_{12a} as a catalyst and alkyl bromides as the carbon radical source under photo- and electrochemical conditions. Later, other groups applied the same principle to Heck reactions. The Carreira group developed the first cobaloxime-catalyzed intramolecular Heck-type reaction with alkyl iodides and olefins under visible-light irradiation [35, 36]. The proposed mechanism involves the formation of an alkyl-Co(III) intermediate with the liberation of $ISnPh_3$ upon initial irradiation, followed by a 5-exo-trig cyclization with subsequent β -H elimination and metal reduction to give the olefinated product and a Co(I) complex. Later, a similar strategy for the Co-catalyzed, intermolecular Heck-type reaction of alkyl iodides and olefins was successfully developed by the Martin and Carreira groups [37]. The reaction allows the synthesis of numerous allylic trifluoromethanes from styrenes and trifluoroethyl iodide. However, aliphatic alkenes were not compatible with the system, which tolerates only a wide range of styrenes with different functional groups.

Following the reports by Martin and Carreira, the Gryko group extended the formal homolysis of alkyl-Co bonds to acyl-Co bonds and used 2-S-pyridyl thioesters as acyl radical precursors and vitamin B_{12} as a Co catalyst under visible-light irradiation (Figure 4A) [38]. The proposed mechanism (Figure 4B) involves the oxidative addition of an electrophilic 2-S-pyridyl thioester to a nucleophilic Co(I) catalyst to yield acyl-cobalt complex **25**, which undergoes homolysis to afford acyl radical **26** and a Co(II) species upon visible-light irradiation. Then, the reaction between **26** and **22** with subsequent single-electron reduction affords the alkylated product and reduced Co(I) using Zn as the reducing agent. Additionally, the authors confirmed the intermediacy of the acyl-cobalt complex by mass spectrometry. The reaction has a wide substrate scope, including aryl and alkyl thioesters and electron-deficient alkenes.

In 2018, Hanan and Colman's coworkers developed strong electron-donating six-membered chelating ligands containing two new homoleptic Co(III) photoredox complexes, **A** and **B** (Figure 4C) [39]. The redox and photophysical properties of the

newly developed low-spin cobalt catalysts make them a good alternative for Ir and Ru photoredox catalysts. For example, the excited-state oxidation (Ox) and reduction (Red) potentials of both **A** and **B** were calculated to be $E_{\text{Ox}}^* = -1.26 \text{ V}$ and -1.15 V and $E_{\text{Red}}^* = 2.26$ and 2.75 V (vs. SCE), respectively. To show the photoredox activities of these cobalt catalysts in chemical transformations, the authors explored a visible light-induced regioselective C–H trifluoromethylation of polycyclic aromatic hydrocarbons, which was achieved in good yields. To date, these cobalt complexes have been found to be good photooxidants and are rare examples of ligand-to-metal charge transfer emissive catalysts with high excited-state energies.

Visible light-induced Cu-catalyzed C–C bond-forming reactions

Copper-based photoredox catalysis using visible light has become a rapidly growing research area in organic transformations due to its sustainability and low costs [40, 41]. A recent example of Cu-photoredox catalysis involved the direct irradiation of a simple Cu salt (CuI) with UV light, and this method is widely used for various coupling reactions. Although this process employs an inexpensive CuI as the catalyst [42, 43], it is dramatically limited by the use of a harmful UV-light source. Recently, Cu(I) complexes have been developed as new photoredox catalysts with low-energy visible-light irradiation. In this context, Reiser and coworkers reported the homoleptic Cu-based photoredox catalysis $\text{Cu}(\text{dap})_2\text{Cl}$ (dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline) [44-51], which has successfully facilitated numerous coupling reactions, including C–C cross-coupling, cycloaddition, and ATRA reactions. These complexes were also used for selective oxo-azidation of vinyl arenes, where $\text{Cu}(\text{dap})_2\text{Cl}$ is converted to a catalytically active Cu^{II} -species in the presence of molecular oxygen to give the expected product via an inner-sphere mechanism [52]. Apart from these Cu catalysts, Collins and coworkers [53-57] reported heteroleptic Cu^{I} -based photosensitizers that can be tuned via their ligands (e.g., $\text{Cu}(\text{Xantphos})(\text{neo})\text{BF}_4$ -complex), and these complexes are superior to homoleptic $\text{Cu}(\text{dap})_2\text{Cl}$ catalysts due to their longer excited-state lifetimes [56]. Importantly, the Reiser group also developed various heteroleptic $[\text{Cu}(\text{phenanthroline})(\text{bisisonitrile})]^+$ -complexes as efficient photoredox-catalysts with enhanced excited-state lifetimes if compared to homoleptic $\text{Cu}(\text{dap})_2\text{Cl}$ catalysts [58].

In contrast to the well-established photoredox catalytic systems, *in situ*-formed Cu-photoredox catalysis can form C-C/C-X bonds within the coordination sphere, where the true photocatalyst is generated by the *in situ* interaction between the Cu salt (i.e., CuCl) and the substrates to form covalently bound Cu-substrate complexes (Figure 5A) [59]. In 2012, Fu, Peters, and coworkers reported the photoinduced Cu(I)-catalyzed Ullmann C-N coupling of carbazoles and aryl/alkyl halides [60, 61]. The supporting studies showed that the reaction involves an *in situ*-formed Cu-carbazolide complex that follows a radical based SET pathway under ultraviolet-light conditions [60, 61]. Later, the same group reported photoactivated, Cu-catalyzed cross-coupling reactions including C-S, C-O, and C-C bond forming reactions [61-66]. Similarly, Hwang and coworkers also reported Cu-catalyzed C-C/C-N cross-coupling and annulation reactions however by using visible light-irradiation [67-71].

Given the breadth of reported Cu-photoredox catalysis systems [5, 12, 41], herein we cover mostly visible light-mediated, Cu-catalyzed C-C cross-coupling reactions, especially **Sonogashira**-type cross-coupling which are representative of the general strategy. The Sonogashira reaction, one of the most important bond-forming processes, is widely used for sp^2 - sp cross-couplings [72-74]. Conventional Sonogashira cross-coupling reactions rely on both Pd and Cu complexes [72-74]. In 2005, Albini and coworkers reported that the cross coupling of electron-rich aryl chlorides and alkynes could be achieved by UV-light irradiation (254 or 310 nm) in the absence of a TM catalyst at room temperature [75]. However, the use of high-energy UV light may cause the photolytic decomposition of the starting materials and products. In 2012, the Hwang group reported the first visible light-induced Sonogashira C-C cross-coupling of terminal alkynes and aryl halides using a CuCl catalyst without additives or ligands (Figure 5B) [70]. The control experiments also revealed that the exclusion of light, Cu, or base resulted in no product formation. A variety of substituted aryl iodides and bromides **31** were efficiently coupled with terminal alkynes **30** to give C-C cross-coupled products **32** (Figure 5B). Mechanistic and photophysical studies revealed that the *in situ*-generated Cu(I)-phenylacetylide acts as the light-absorbing species ($\lambda_{abs} = 476$ nm), allowing ligand-to-metal charge transfer (LMCT) and intersystem crossing (ISC) to the triplet-excited state [67, 76, 77]. Additionally, the excited-state lifetime ($\tau = 15.95$ μ s) and redox

potential (-2.048 vs. SCE in CH₃CN) of the Cu(I)-phenylacetylide complex indicated a SET mechanism [67].

In 2018, the Lalic group reported a photoinduced Cu-catalyzed aliphatic Sonogashira reaction at room temperature (RT) (Figure 5C) [78]. An optimization study revealed that the presence of a specific terpyridine ligand (4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine, **L1**) is necessary for the selective alkylation of terminal alkynes. The reaction is compatible with various terminal alkynes and unactivated 1°, 2°, and 3° alkyl halides and affords the corresponding C–C cross-coupled products (**34a-c**; 43 to 84% yield). Cu-Acetylide complex **35**, which is a light-absorbing species, is excited, generating triplet-state **36** ($E_{1/2} = -1.77$ V vs. SCE) [76], which reduces alkyl halides via a SET process (Figure 5D) [78, 79]. The alkyl radical then attacks Cu(II)-acetylide intermediate **36** to deliver the cross-coupled products **34** (or **32**). Very recently, Hwang and coworkers reported the Cu-catalyzed denitrogenative C–C cross-coupling of pyridinyl hydrazines and terminal alkynes via a C–N bond cleavage at RT [80]. This process is compatible with a wide range of substrates and provides alkyl/arylethynyl pyridines in moderate to good yields. The mechanistic studies suggested that a SET process is operative in the presence of O₂ and involves a photoexcited Cu^I-phenylacetylide complex [68, 71].

Recently, Xiao and coworkers reported a Cu-photoredox catalyzed C–C cross-coupling reactions by a three-component radical cross-coupling of oxime esters, styrenes, and boronic acids [81]. A Cu^I/Cu^{II}/Cu^{III}-based catalytic cycle was proposed in which the oxime ester gets initially reduced by the photoexcited or ground state LCu^I complex resulting in the iminyl radical and oxidized LCu^{II} species. The iminyl radical then underwent a subsequent β -scission to give a cyanoalkyl radical. This radical is trapped by styrene leading to a new benzylic radical that underwent coupling with boronic acid-derived LCu^{II}Ph giving a Cu^{III} complex. Further successful reductive elimination of the Cu^{III}-complex gave the C–C cross-coupled product and regenerated the active Cu^I-catalyst

Visible light-induced Pd-catalyzed C–C bond-forming reactions

Pd^0 , Pd^{II} , and Pd^{IV} are the common oxidation states of palladium, and these ions participate in $\text{Pd}^0/\text{Pd}^{\text{II}}$ and $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ catalytic cycles from their ground state via two-electron redox processes. Although ground-state Pd catalysis is well developed, the use of alkyl halides in Pd catalysis is problematic due to the dominant β -hydride elimination side reaction from the alkyl palladium species [82]. Although the elegant works by Fu [83], Alexanian [84], and Zhou [85] addressed the issue, the scope of these reactions can be limited, and the reactions of 3° alkyl halides with an eliminable β -H had not been reported.

Recent pioneering work by the Gevorgyan [86] and Fu [87] groups on visible light-induced Pd catalysis have resolved the issue, and they have demonstrated that a SET from a photoexcited Pd^0 to an alkyl halide generates an alkyl- Pd^{I} radical hybrid species (*vide infra*) that subsequently add to a C=C double bond to promote the olefination [88]. In this context, Gevorgyan reported the first visible light-induced, Pd-catalyzed RT Heck reaction of α -functionalized alkyl halides **38** with vinyl arenes/heteroarenes **39** producing diverse allylic species **40** (Figure 6A) [86]. A variety of secondary and primary alkyl iodides with FG, such as boronates, silanes, stannanes, pivalates, phosphonates, phthalimides, germanes, and tosylates, were suitable substrates. The same group also reported an improved photocatalytic system for an efficient Heck reaction using tertiary alkyl halides [89]. Simultaneously, Fu and coworkers also independently developed a visible light-induced, Pd-catalyzed Heck reaction at RT with a variety of 1° , 2° , and 3° alkyl bromides using PPh_3 and Xantphos as a dual phosphine ligand system (Figure 6B) [87]. Studies using radical scavengers revealed that the generated alkyl radical exists as alkyl Pd-radical hybrid species **43**. Furthermore, X-ray photoelectron spectroscopy (XPS) measurements confirmed the presence of palladium in the Pd^0 , Pd^{I} , and Pd^{II} oxidation states in the reaction mixture. A mechanism for all these Heck reactions involving a Pd-intercepted radical was proposed (Figure 6C) [86, 87, 89]; upon photoirradiation, the Pd^0 complex is excited to give $^*\text{Pd}^0$, which is quenched by an alkyl halide via a SET process forming alkyl Pd-radical hybrid species **43**. The hybrid radical species then adds to the olefin moiety of **39**, and subsequent β -H elimination delivers product **40/42** and regenerates the Pd^0 catalyst.

Recently, the Gevorgyan group reported an interesting excited-state Pd-catalyzed radical relay Heck reaction for the selective remote alkenylation of unactivated β -, γ -, and δ -C(sp³)-H sites of aliphatic alcohols with a broad substrate scope [90]. The Si-based auxiliary used in this method has enabled selective I-atom/radical translocation (1,*n*-hydrogen atom transfer (HAT)), giving the iodine-atom transfer intermediate, which couples with an olefin to produce the remote Heck product. A similar radical relay strategy has been employed by the same group for the selective synthesis of unsaturated alcohols [91]. In 2018, the Gevorgyan group also reported an excited-state Pd-catalyzed, 1,5-HAT/atom-transfer radical cyclization (ATRC) cascade reaction of vinyl iodide to give iodomethyl cyclopentane and spiro-annulated cyclopentane derivatives via a similar Pd-radical hybrid mechanism [92]. In their mechanism, excited $^*\text{PdL}_n$ is quenched by the vinyl iodide, forming a vinyl Pd-radical hybrid species that undergoes a 1,5-HAT and a 5-exo-trig cyclization, generating a primary alkyl radical species that delivers the target product upon subsequent iodine-atom transfer from Pd^I.

More recently, the Rueping group reported an excited-state Pd-catalyzed decarboxylative alkylation of α,β -unsaturated acids **46** with unactivated alkyl bromides along with DFT support (Figure 6D) [93]. A mechanism involving a barrier-less, photoinduced inner-sphere SET oxidative addition of Pd to the alkyl bromide was proposed. Under visible light, the singly occupied molecular orbital (SOMO) of the triplet-state $^*\text{Pd}(\text{PPh})_3$ is delocalized on the PPh₃ ligands with a minor Pd contribution, while the lowest unoccupied molecular orbital (LUMO) of the alkyl bromide **41** corresponds to the σ^* orbital of the Br-C bond. During SET (intermediate structure halfway along the potential energy surface (PES)), the SOMO of $^*\text{Pd}(\text{PPh})_3$ localizes on Pd and gets stabilized by mixing with the LUMO of **41**, leading to the rupture of the Br-C bond and the formation of the Pd-Br bond resulting an alkyl palladium-radical hybrid species **43**. The latter is a species containing two unpaired electrons i.e. two unpaired electrons localized on Pd and on the alkyl group separately. The thus-formed alkyl Pd-radical hybrid species attacks the double bond of an α,β -unsaturated acid, giving product **48** via a neutral decarboxylation. In addition, the Yu group developed a visible light-induced, Pd-catalyzed direct cross-coupling of alkyl halides and *N*-aryl tetrahydroisoquinolines [94]. A variety of tertiary, secondary, and primary alkyl

bromides, including benzyl chlorides, were efficiently coupled with *N*-aryl tetrahydroisoquinolines at the α -position. In their mechanism, excited-state $^*\text{PdL}_n$ is quenched by the alkyl bromide to give Pd^{I} and the alkyl radical species. The Pd^{I} species is then reduced by the tetrahydroisoquinoline to afford a radical amino cation and regenerate the Pd^0 catalyst. Base-assisted deprotonation of the radical amino cation intermediate then gave the α -amino carbon radical, which underwent radical-radical cross coupling with the alkyl radical, giving the α -alkylated product. In addition to $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ cross-coupling reactions, the authors also reported the intra- and intermolecular alkylations of indoles and other heteroarenes under identical photoinduced conditions.

In 2018, the Zhou group reported the selective intermolecular alkyl radical addition to electron-deficient arenes at the *para*-position under thermal conditions as well as by visible light-induced Pd catalysis [95]. Recently, the Shang and Fu groups also reported the excited-state Pd-catalyzed direct C–H alkylation of heteroarenes with secondary and tertiary alkyl bromides using a dual phosphine ligand system [96]. In 2018, the Fu [97] and Glorius [98] groups independently developed decarboxylative Heck-type coupling reactions by generating alkyl radicals from *N*-(acyloxy)phthalimides via excited-state Pd catalysis (Figure 6E). In their mechanism, the Pd catalyst becomes excited in the presence of visible light, inducing a single-electron reduction of *N*-(acyloxy)phthalimides **49**, giving an alkyl Pd-radical hybrid species that is quenched by the alkene to give Heck product **51** and regenerate the Pd^0 species. The use of stable and readily available carboxylic acid-derived substrates to generate alkyl radicals under mild reaction conditions makes these processes versatile and attractive. Recently, Yu and coworkers used visible light-induced Pd catalysis for the selective oxy-alkylation of allylamines with alkyl bromides and CO_2 [99]. In this newly developed three-component reaction, the alkyl radical species that are generated from photoexcited $^*\text{PdL}_n$ and the alkyl halide add to the allyl carbamate, which is generated in situ from allylamine and CO_2 , producing a stable benzyl radical intermediate. The radical intermediate then reduces the Pd^{I} species, forming a cation intermediate that cyclizes to the oxazolidinone product. Furthermore, the Wang, Jurca, and Ong groups revealed the dual role of the Pd catalyst with a carbodicarbene ligand framework as both a photoredox catalyst and

as a cross-coupling catalyst in a one-pot tandem directed C–H arylation and coupling of aldehydes with amines [100]. The above results demonstrate that visible light induced excited state Pd-catalysis offers new perspectives in C–C bond forming reactions.

Concluding remarks

As demonstrated by the examples discussed, excited-state TM catalysis will lead to the development of a wide range of novel photocatalytic transformations with broad synthetic applications (see Outstanding Questions). These excited-state TM-catalysis systems (Figure 1C) use simple metal complexes as the catalysts and have various advantages over the conventional/cooperative photocatalysis systems, which rely on photocatalyst with finely tuned redox potentials (Figure 1A and 1B). In contrast to the common outer-sphere mechanisms observed in conventional photocatalysis, visible light-induced TM catalysis proceeds *via* a substrate-metal interaction (photoinduced inner-sphere mechanism), which is new and versatile and will serve as a platform for developing new chemical transformations. However, the field of excited TM catalysis also suffers from some limitations, such as the difficulty of developing enantioselective approaches and other organic transformations due to poor ligand tunability, which need to be addressed in future research.

Disclaimer Statement

The authors declare no conflicts of interest.

Glossary

Excited state: an energy level of a system (atom, ion or molecule) in which an electron is at higher energy level (high energy orbital) than its ground state.

Hyperconjugation: a resonance process that increases the stability of the system through the interaction of the electrons in an σ -orbital with an adjacent empty or partially filled p- or π -orbital to provide an extended molecular orbital.

Inner sphere mechanism: an electron transfer process in which the electrons are transferred between two redox partners via formation of a direct bond or a strong electronic interaction between redox partners.

Outer-sphere mechanism: an electron transfer process in which the electrons are transferred between two redox partners without formation of a direct bond or without any electronic interaction between redox partners.

Photosensitizer: a substance capable of initiating a chemical reaction by absorbing light energy and transferring the energy to the desired reactants.

Sonogashira reaction: is the cross coupling reactions of an organohalides with terminal alkynes to give the C-C cross-coupled products.

Single-electron transfer: is the transfer of electron from one atom or molecule to another. In redox chemistry, the donor atom or molecule loses electrons (oxidation) while the acceptor gains the electron (reduction).

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Figure Captions

Figure 1. (A) A general representation of different possible photocatalytic pathways such as energy transfer, oxidative and reductive quenching cycles. (B) Dual catalysis strategy combining photoredox with transition-metal catalysis. (C) Topic of the present review: visible light-induced, excited-state TM catalysis.

Figure 2. Manganese-catalyzed Minisci reactions by visible light. (A) The developments of a $\text{Mn}_2(\text{CO})_{10}$ -photoredox catalyzed Minisci reaction in the presence of heteroarenes and alkyl halides. (B) Selected examples for C-H alkylation of heteroarenes and highly functionalized drug molecule. (C) The proposed mechanism for photochemical cleavage of the Mn-Mn bond and Minisci reaction via SET events. Abbreviations: TFA, trifluoroacetic acid; LED, light-emitting diode; SET, single electron transfer; Boc, *tert*-butoxycarbonyl.

Figure 3. Manganese-catalyzed single electron transfer reactions. (A) The utility of $\text{Mn}_2(\text{CO})_{10}$ -photocatalysis as a tool for generation of ketyl radicals from aldehydes and their redox-neutral coupling with alkynes with selected examples. (B) The proposed catalytic cycle for Mn-catalyzed redox-neutral ketyl radical generation and atom transfer radical addition reaction. (C) Developments and proposed mechanism for Mn-catalyzed C-H arylation of arenes by visible-light photoflow. Abbreviations: OTf, trifluoromethylsulfonate; DCM, dichloromethane; DIPEA, *N,N*-diisopropylethylamine; LED, light-emitting diode; equiv, equivalent; SET, single electron transfer; Cp, cyclopentadienyl; DMSO, dimethyl sulfoxide.

Figure 4. Cobalt-catalyzed single electron transfer reactions. (A) The use of vitamin B_{12} -photoredox catalysis in Giese-type acylation reaction and its selected examples. (B) Proposed mechanism for Co-catalyzed acyl radicals generation from 2-S-pyridyl thioesters. (C) Studies and applications of new Co(III) ligand to metal charge transfer emissive complexes with high excited-state energy. Abbreviations: Cat, catalyst; equiv, equivalent; LED, light-emitting diode; EWG, electron withdrawing group; DCM, dichloromethane; dgpy, diguanidylpyridine; dgpyz, diguanidylpyrazine.

Figure 5. Visible light-induced Cu-catalyzed C-C cross-coupling reactions: (A) Schematic of the in situ formation of Cu-substrate light-absorbing species. (B) Hwang's approach for the cross-coupling of alkynes and aryl halides [65]. (C) Lalic's aliphatic Sonogashira reaction of alkynes and aliphatic iodides [73]. (D) A general mechanism for the visible light-driven copper photoredox-catalyzed Sonogashira coupling. Abbreviations: SET, single electron transfer; LED, light-emitting diode; abs, absorbance.

Figure 6. (A) Visible light-induced Heck reaction of functionalized alkyl halides with vinyl arenes/heteroarenes [81]. (B) Irradiation-induced Heck reaction of unactivated alkyl halides [82]. (C) A general mechanism for the visible light-induced Heck reaction. (D) Decarboxylative alkylation of α,β -unsaturated carboxylic acids by excited state Pd-catalysis [88]. (E) Irradiation-induced Pd-catalyzed decarboxylative Heck reaction of activated aliphatic carboxylic acids [92, 93]. Abbreviations: FG, functional group; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; DMA, *N,N*-dimethylacetamide; THF, tetrahydrofuran; LED, light-emitting diode.

Figures

(A) Different photocatalytic pathways

PC = photocatalyst
A = acceptor
D = donor

(B) Cooperative/dual photocatalysis

S = substrate
R = reactant
P = product

(C) Present topic: Transition metal complex (ML_n) acting as both photosensitizer and as cross-coupling catalyst

Figure 1.

(A) Photo-induced Minisci C-H alkylation

(B) Selected examples of heteroarene C-H alkylation with alkyl iodides

(C) Proposed cycle for Mn-photoredox Minisci protocol

Figure 2.

(A) Photoinduced ketyl radical generation and synthetic utility

Selected examples for redox-neutral ketyl radical coupling

(B) Proposed mechanism: homolysis of $\text{Mn}_2(\text{CO})_{10}$ and ketyl radical reactivity

(C) Manganese-catalyzed photoflow strategy

Figure 3.

(A) Vitamin B₁₂-catalyzed acylation of olefins and selected examples

(B) Proposed mechanism for Co(I)-catalyzed radical acylation

(C) Photoinduced cobalt(III)-trifluoromethylation

Figure 4.

(A) General illustration for in-situ forming Cu-substrate photocatalyst

(B) Hwang's (2012) photoinduced Sonogashira C-C coupling

(C) Lalic's (2018) photoinduced aliphatic Sonogashira C-C coupling

(D) Plausible mechanism for photoinduced Cu-catalyzed Sonogashira coupling

Figure 5.

(A) Heck reaction of alkyl halides with vinyl arenes by Gevorgyan, 2017

(B) Heck reaction of unactivated alkyl halides by Fu, 2017

(C) General mechanism for the visible light-induced Heck reaction

(D) Visible light-induced decarboxylative alkylation by Rueping, 2019

(E) Pd-catalyzed decarboxylative Heck reaction of activated aliphatic acids

Figure 6.