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Organometallic Catalysis under Visible Light Activation: Benefits and Preliminary Rationales

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Dedicated to Prof. Angelo Albini on the occasion of his 75th birthday.

Abstract: Recent reports have shown that some transition metal complexes are capable of efficiently interacting with visible-light and can behave as both a photo- and a metal-catalyst. Absorption of light by these complexes can facilitate or trigger elementary steps in a catalytic cycle such as pre-catalyst reduction, oxidative addition, transmetalation and reductive elimination, as well as the ability of generating radical intermediates, widening the structural diversity offered by classical couplings. This perspective aims to highlight key examples of these light-induced or enhanced processes, with an emphasis on the underlying mechanisms involved.

Introduction

Visible light-assisted transformations play an increasingly important role in synthetic chemistry and have attracted considerable attention particularly in metal-catalyzed homogeneous reactions. The merger of organometallic catalysis and photoredox catalysis, also called metallaphotocatalysis, is an ever-expanding field of great interest to the chemical research and industrial communities [1]. Photocatalysis with Ru(II) and Ir(III) complexes has stimulated and promoted significant advances due to their strong absorption properties in the visible region, remarkable redox properties upon photoexcitation and long-lived excited states [2,3]. The merger of photoredox catalysis

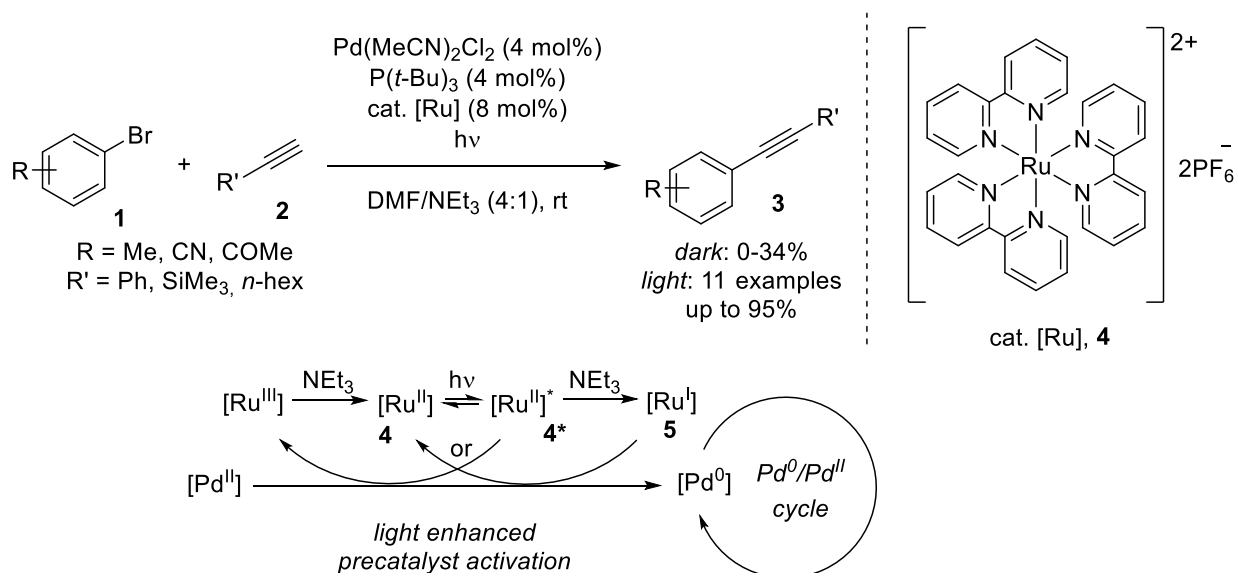
with transition metal-catalysis overcomes the limitations of both strategies, and offers unprecedented opportunities for functional group tolerance and selectivity [1,4]. The ability to harness visible light to access energy transfer reactivity is another emerging field of profound impact in organic synthesis [4,5]. Recently, further developments have revealed the ability of light to interact directly with organometallic complexes involved in the cross-coupling catalytic cycle (rather than the photocatalyst) inducing novel and unique bond-breaking/forming reactivities, thereby expanding the diversity of possible chemical transformations [6,7]. In this context, light can be used to induce or accelerate a reaction step. The aim of this perspective is to highlight and outline how visible-light can interact with an organometallic complex to trigger or accelerate a specific elementary step encountered in homogenous organometallic catalysis. We will especially focus on mechanisms that involve direct excitation of transient organometallic intermediates inducing specific transformations.

Visible-light promoted oxidative addition

One of the key steps in an organometallic catalytic cycle is the oxidative addition of the electrophile onto the metal center. Given the importance of metal catalysed cross-couplings in organic chemistry, and especially in C-C bonds formation, these processes have been thoroughly investigated [8,9]. Changing the reaction parameters, ligands and substrates can have a significant impact on reaction outcomes by facilitating the oxidative addition step. However, in cases where oxidative addition is not possible, or slow, by thermal activation, photoactivation of the system has been shown to be a viable alternative to enhance or trigger this rate-limiting step.

One of the first examples demonstrating the ability of light to enhance an organometallic reaction was reported by Akita and co-workers in 2007 describing a light mediated Sonogashira cross-coupling between aryl bromides **1** and alkynes **2** to provide phenylacetylene derivatives **3** [10] (Scheme 1). The classical combination of a strongly donating bulky phosphine $P(t\text{-Bu})_3$ with a palladium catalyst $\text{Pd}(\text{MeCN})_2\text{Cl}_2$, was merged with a photoactivation, involving a ruthenium photocatalyst and an amine, to allow cross-coupling in the absence of a copper co-catalyst. Importantly, this modification

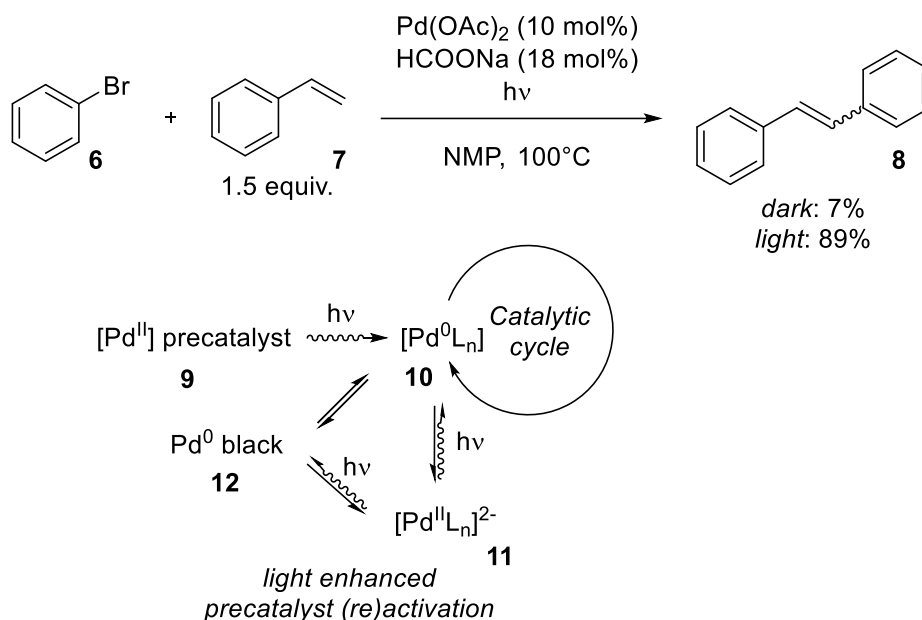
allows cross-coupling to occur at room temperature. The mechanism is thought to involve excitation of the Ru photocatalyst, Ru(bpy)₃2PF₆ **4** to the excited species [Ru(II)]* **4*** which is reduced in the presence of NEt₃ acting as a sacrificial electron donor to generate [Ru(I)] **5**. Both [Ru(II)]* **4*** and [Ru(I)] **5** are suspected to readily reduce the Pd(II) pre-catalyst to the active Pd(0) species. While the exact mechanism has remained unknown, the authors also noted that irradiation may also accelerate the oxidative addition step as preliminary experiments demonstrated the viability of using aryl chlorides as substrates.



Scheme 1 Light mediated Sonogashira cross-coupling

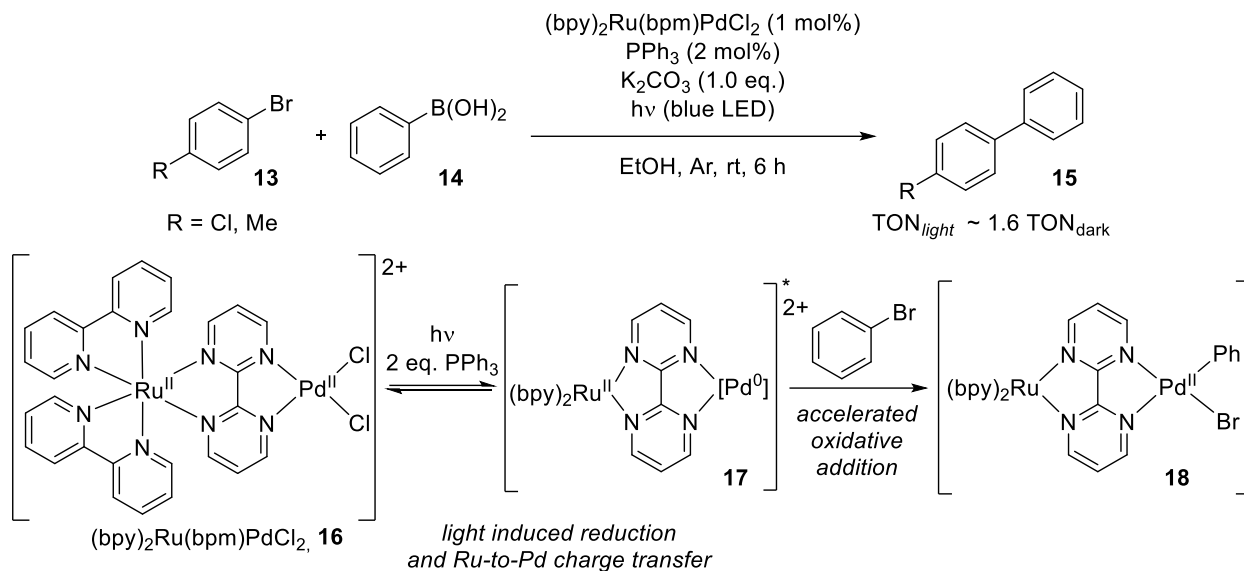
Köhler and co-workers demonstrated that visible-light can be used to enhance Mizoroki-Heck reactions between bromobenzene (**6**) and styrene (**7**) to give stilbene **8** (Scheme 2) [11]. Here, light accelerates the reduction of the Pd(II) pre-catalyst **9** by sodium formate (HCOONa) to the active Pd(0) species **10**, as evidenced by NMR and UV/Vis spectroscopic studies. Faster reduction to Pd(0) (minutes vs hours thermally) allowed reaction temperatures to be lowered (100 °C vs 120 °C) while maintaining similar yields. Additional mechanistic experiments revealed that the role of light in this reaction was more complex, as light was proposed to be involved in various Pd deactivation and reactivation pathways involving equilibrium between the active Pd(0) species **10**, anionic palladium halide complexes [Pd(II)X₄]²⁻ **11** and Pd(0) black **12** formed *in-situ*

(See scheme 2), contributing to the increased conversions observed. UV/Vis spectroscopy and DFT calculations of Pd(II) complexes suggested the participation of the ligand-to-metal charge transfer (LMCT) state in the acceleration of the reduction process of Pd(II) to Pd(0).



Scheme 2 Visible-light enhanced Pd pre-catalyst (re)activation

Similarly, Yamashita and Mori have leveraged the photoredox properties of Ru(II) polypyridine salts to reduce a Pd(II) pre-catalyst to the active Pd(0) species in Suzuki-Miyaura reactions, coupling aryl bromides (**13**) and phenylboronic acid **14** to the corresponding biphenyl derivatives **15** (Scheme 3).[12] Covalently linking the photosensitizer and Pd catalyst as a Ru-Pd bimetallic complex **16** allows light induced electron transfer from the excited Ru(II), in the presence of PPh₃, to the Pd(II) center, reducing it to an electron-rich Pd(0) active catalyst **17**. Additionally, the Pd(0) center in **17** is presumed to be more electron-rich, compared to (bpy)Pd(0), due to charge transfer from the excited Ru center, which would enhance the rate-limiting oxidative addition process and can explain the significant increase in turnover number of the reaction under light irradiation compared to dark (Scheme 3).

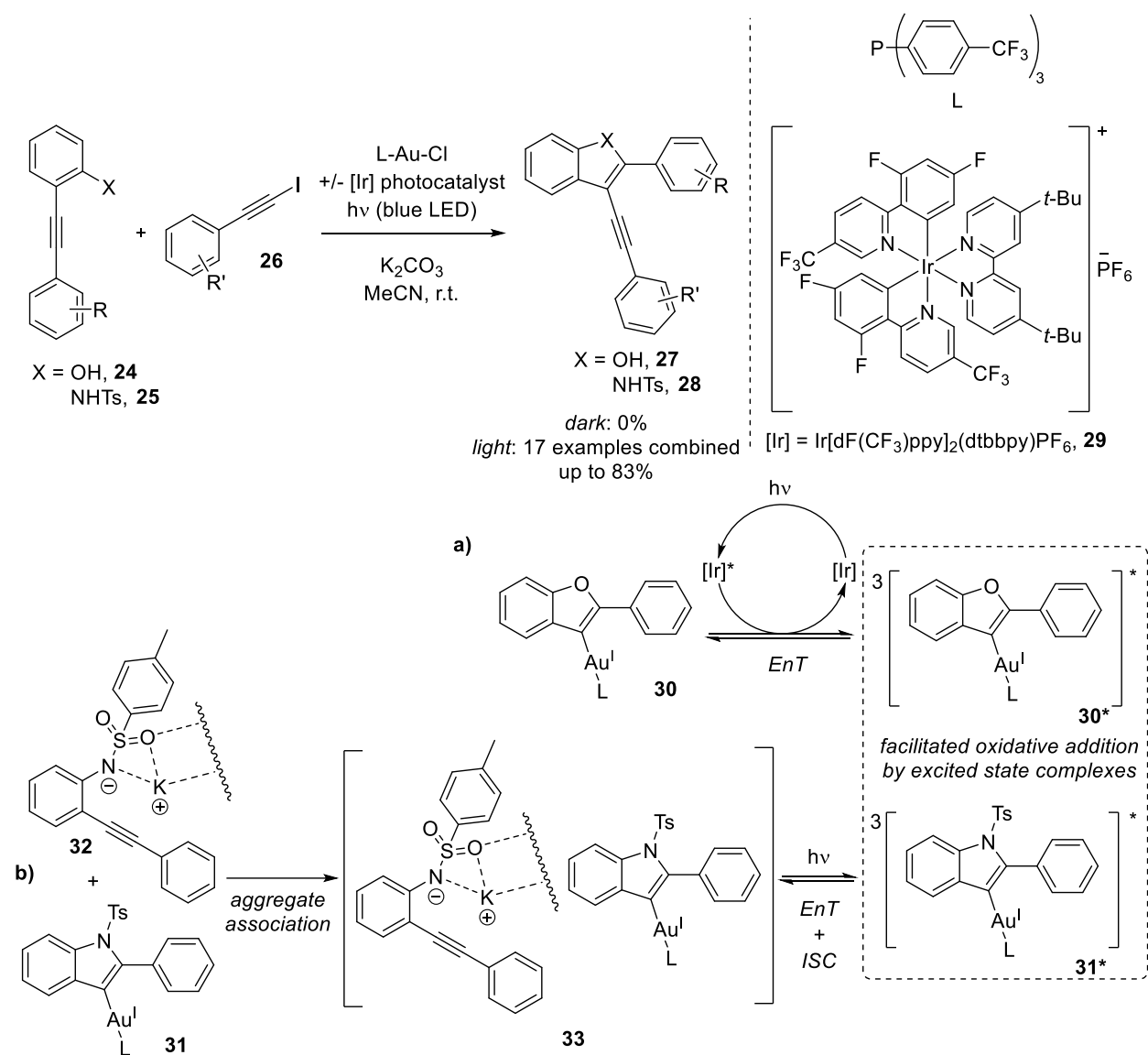


Scheme 3 Light accelerated oxidative addition using a bimetallic Ru-Pd complex

Alcázar and co-workers developed a Negishi-type cross-coupling reaction between aryl bromides **19** and a large variety of organozinc Reformatsky-type reagents **20** to give the corresponding (hetero)aryl derivatives **21** (Scheme 4) [13]. This methodology merges flow and photochemistry expanding the application of this coupling to electron-rich aryl bromides and even aryl chlorides. Mechanistic studies reveal that under reaction conditions a Pd(0)-Zn complex **22** is formed *in situ* which displays an absorption band at 430 nm. Irradiation of **22** with visible-light significantly accelerates the oxidative addition of the aryl halide substrate to give the Pd(II) intermediate **23**, via postulated excited intermediate **22***, as evidenced by NMR spectroscopic studies. The importance of light to the transformation is highlighted by the drastic decrease in yields in its absence. Alcázar and co-workers extended this strategy towards light enhanced Ni catalysed Negishi [14], and Fe catalysed Kumada [15] cross-couplings. In these transformations the low-valent electron-rich metal coordinates the nucleophilic partner, and the consequent adduct is directly excited by light thus accelerating the oxidative addition process.

ability of the Au(I) complex **30*** to undergo oxidative addition. In this case, visible-light, via the Ir photocatalyst **29** acting as an *EnT* agent, smoothly overcomes the thermodynamic limitation of this step without the use of external reagents.

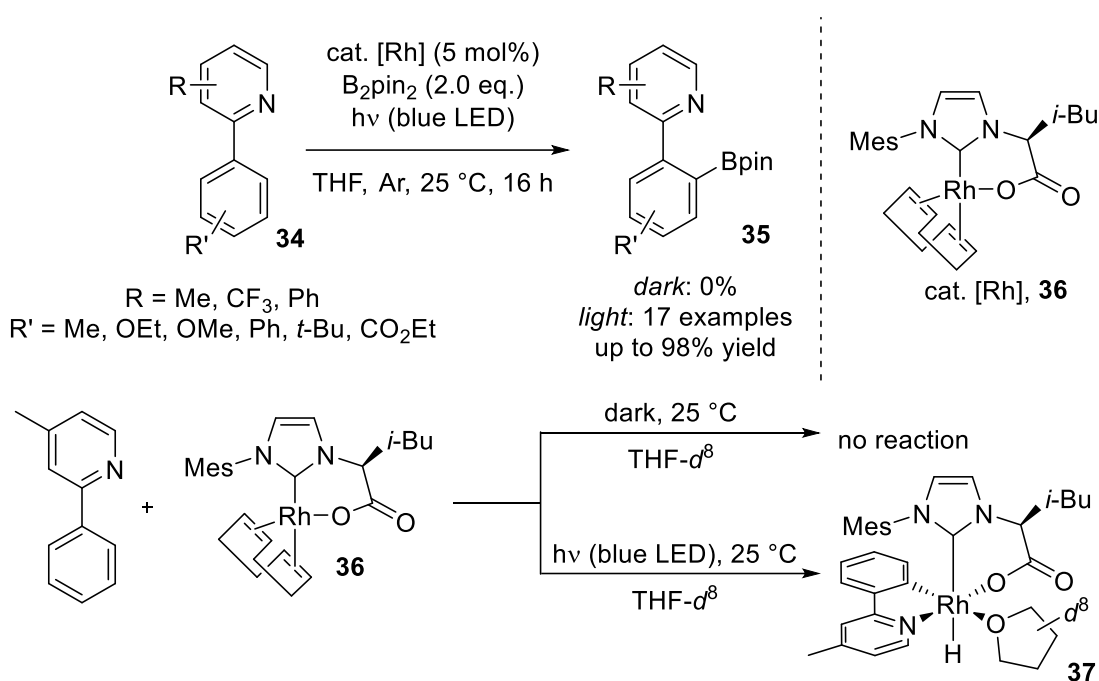
To further explore the scope of this methodology, we turned to the cyclization of *o*-alkynyl-anilines **25** to indoles and observed that, contrary to the previous system, the Au(I) catalysed reaction occurs under light irradiation without requiring an exogenous photocatalyst [22]. UV-visible absorption spectroscopic studies revealed that neither the reagents, products, nor the vinyl-Au(I) intermediate **31** were viable photocatalysts or *EnT* active species. However, in the presence of a potassium base, the corresponding potassium salt of the tosylated aniline forms an aggregate **32** in solution and in the solid state (Scheme 5b). This aggregate was shown to display an absorption band at 380 nm consistent with visible-light absorption. Quenching experiments evidenced the ability of the aggregate **32** to act as a photosensitizer, transferring energy to the Au(I) intermediate **31**, producing the excited species **31*** and mediating the C(sp)–C(sp²) cross-coupling to provide product **29**. In contrast to the previous example with phenols, excitation and subsequent energy transfer occurs through an association complex **33** composed of the potassium salt aggregate and the vinyl-Au(I), in the ground state. These two examples illustrate and highlight the possibility of visible-light triggered oxidative addition on Au(I) without the need of strong oxidant and tailored bidentate ligands.



Scheme 5 Gold(I) photosensitized alkylnative cyclization of *o*-alkynyl phenol by Iridium and photocatalyst-free indole formation from *o*-tosylaniline

Recently, Baslé and co-workers reported visible-light induced C(sp²)-H borylation of pyridine derivatives **34** mediated by a rhodium NHC-carboxylate complex **36** (Scheme 6) [23]. The authors found that Rh(I)-NHC-carboxylate complexes **36** display absorption bands in the visible region, suitable for excitation with blue light. Using pyridine as a directing group, the authors demonstrated that the Rh complex **36** could be used as a photocatalyst for the regioselective borylation of a variety of substrates under mild

conditions and in the absence of an exogenous photocatalyst to provide the ortho-borylated products **35**. Importantly, this methodology overcomes the poor regioselectivities observed with other photocatalytic systems that use higher energy UV irradiation. Mechanistic studies exclude the involvement of radical species and highlight the requirement of light for this transformation. Stoichiometric experiments using the Rh complex **36** and substrate show that photooxidative C-H bond addition only occurs in the presence of light, providing the corresponding cyclometalated Rh complex **37**. The authors postulate that excitation of the Rh complex followed by metal-to-ligand charge transfer (MLCT) allows the oxidative addition process to occur.



Scheme 6 Rh-catalysed visible-light induced C(sp²)-H bond borylation

Visible-light promoted reductive elimination/transmetalation

In addition to oxidative addition, transmetalation of a nucleophile onto the metal center, and reductive elimination of the nucleophile-electrophile adduct, are also the elementary and fundamental steps in a catalytic cycle for cross-coupling reactions. Significant advances have been made in the nature of transmetalation agents [24,25,26], expanding the range of nucleophiles available for such transformations. Rational ligand

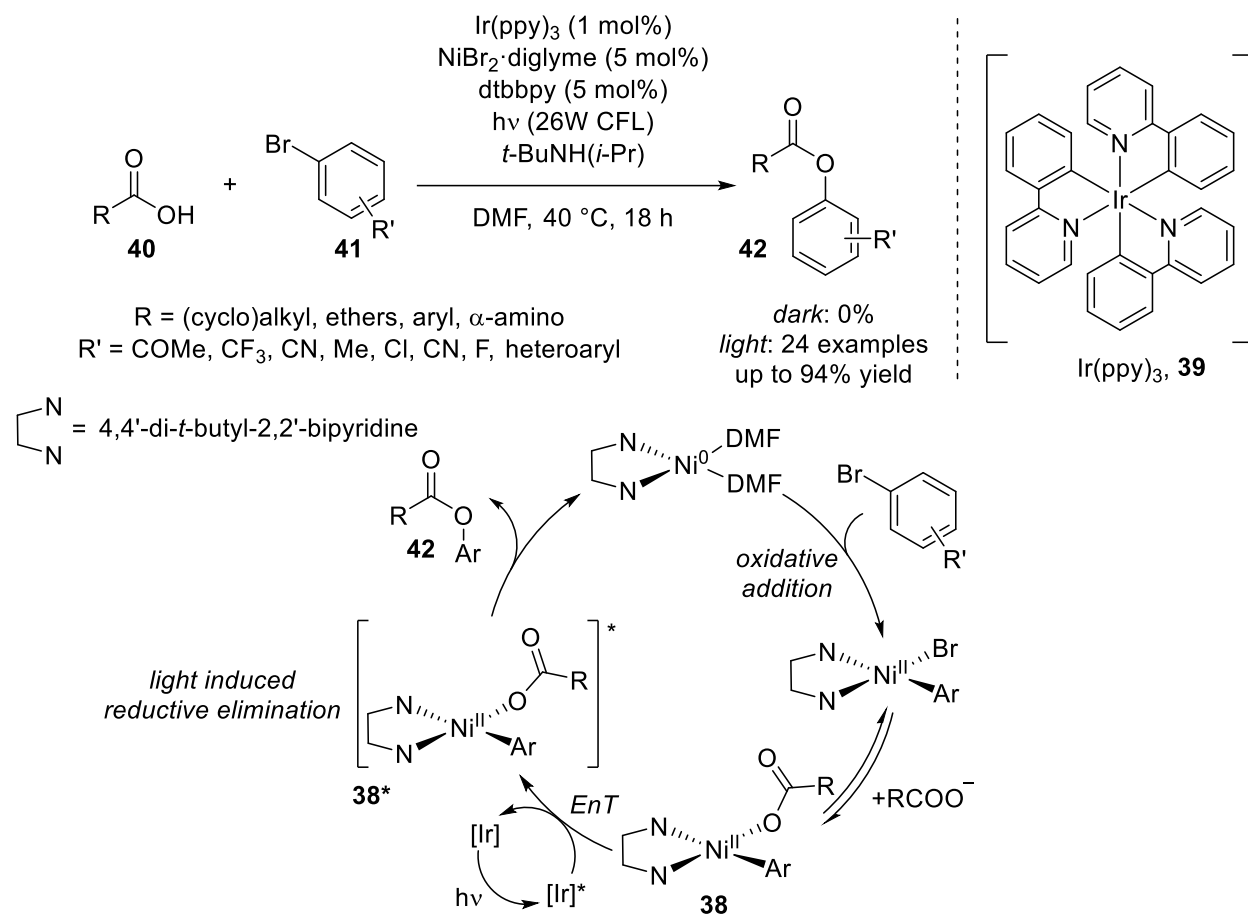
design has provided systems that can promote reductive elimination from metal centers that are usually reluctant to undergo this process. In this context, photoactivation of an organometallic system can also constitute a viable method to enhance reluctant or thermally unfavourable transmetalation or/and the reductive elimination steps in a catalytic cycle.

A seminal report by MacMillan and co-workers revealed the ability to excite a Ni(II) complex **38**, through *EnT* from an excited photocatalyst **39**, to mediate catalytic cross-coupling reactions between carboxylic acids **40** and aryl bromides **41** to provide the corresponding esters **42** (Scheme 7) [27]. Here the authors demonstrate that it is possible to access excited-state organometallic catalysis through a photosensitization mechanism by triplet-to-triplet energy transfer. The excited-state Ni(II) complex **38*** undergoes a thermally unfavourable reductive elimination to form a C-O bond. Specifically, the authors developed a methodology for the cross-coupling of various aryl and alkyl carboxylic acids with a series of aryl bromides under unprecedentedly mild conditions.

In order to explain the mechanism involved in this esterification, mechanistic studies were carried out on the *in situ* generated Ni(II) intermediate **38**, efficiently formed by oxidative addition of the aryl halide followed by ligand exchange with a carboxylic acid. Without a photocatalyst, and by direct excitation of the oxidative addition Ni(II) complex **38**, the reductive elimination product was observed in 45% yield after 120 hours. Using benzophenone as a photosensitizer resulted in 25% yield, while an optimal yield of 85% was achieved in 24 hours using Ir(ppy)₃ (**39**) as a photocatalyst. Variation of the photocatalyst revealed a cut-off for the triplet state energy (~40 kcal/mol) under which no conversion was observed. Additionally, the authors found that photocatalysts with increasing oxidizing power resulted in lower yields, lending evidence against a SET process.

Further studies were conducted on an isolable, robust and thermally stable Ni(II) oxidative addition complex. NMR spectroscopy studies confirmed the requirement of light and accelerated reductive elimination in the presence of a photocatalyst (minutes vs days without photocatalyst). Electrochemical studies revealed that oxidation of the

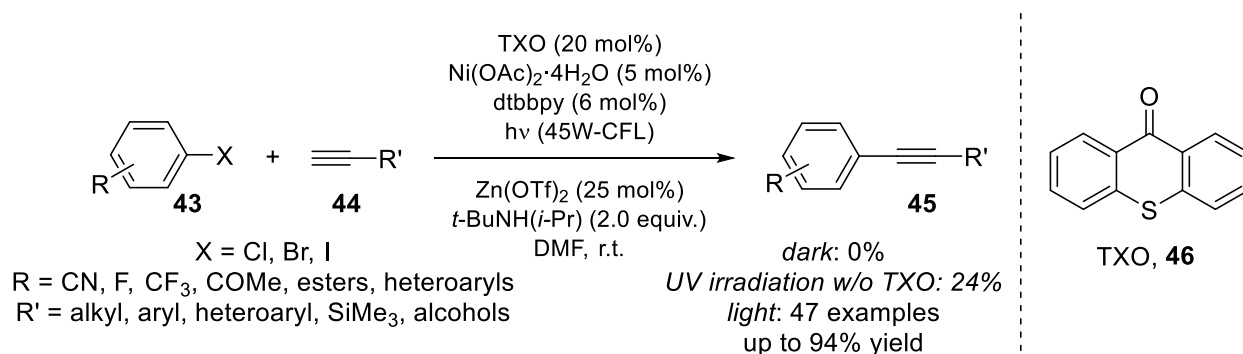
Ni(II) complex, by excited-state $[\text{Ir}^{\text{III}}]^*$ or $[\text{Ir}^{\text{IV}}]^+$ is unfavourable, again disfavoring a SET process and eliminating a redox pathway for this transformation. Finally, UV/Vis spectroscopy and Stern-Volmer quenching studies suggest that a Dexter-type *EnT* is most likely involved in this specific reaction.



Scheme 7 Access to excited-state Ni(II) catalysis via *EnT*

This strategy of excited-state Ni(II) catalysis has also been expanded by the MacMillan and other groups for the formation of C-O [28,29,30] and C-N [31] bonds using different (organo)photocatalysts. More recently, Li and co-workers have used this strategy to develop a visible-light induced Ni-catalysed Sonogashira C(sp)-C(sp²) coupling reaction between aryl halides **43** and alkynes **44** to produce phenylacetylene derivatives **45** (Scheme 8) [32]. The authors have demonstrated the ability of using thioxanthene-9-one (TXO) **46** as an alternative and cheap photosensitizer, which when combined with a

Ni catalyst allows for visible-light mediated cross-coupling of a large scope of alkynes with aryl halides under mild conditions. The reaction shows excellent functional group tolerance and even allows the coupling of aryl chlorides. Optimisation studies demonstrated that the addition of $\text{Zn}(\text{OTf})_2$ as an additive significantly improved reaction yields, here the authors suggest that *in situ* formed $\text{Zn}(\text{II})$ acetylide may increase the transmetalation process to form the prerequisite $\text{Ni}(\text{II})$ acetylide species. Mechanistic investigations reveal that **46** outperforms $\text{Ir}(\text{ppy})_3$ **39** or other organic photocatalysts as the photosensitizer of choice. Importantly, these studies evidenced that when using other strongly oxidizing photocatalysts, trace or no reductive elimination product was observed, suggesting that a process involving $\text{Ni}(\text{II})$ to $\text{Ni}(\text{III})$ is not operative in this transformation. Further support for an *EnT* process was demonstrated by no observable conversion in the absence of TXO as a photocatalyst using visible light. However, UV irradiation of the reaction mixture in the absence of TXO resulted in 24% yield, suggesting that triplet-to-triplet *EnT* is required for efficient reductive elimination. To summarise, irradiation of the reaction mixture would generate the excited-state TXO^* (**46***), which following *EnT* to the oxidative addition $\text{Ni}(\text{II})$ complex produces an excited-state $\text{Ni}(\text{II})^*$ complex from which reductive elimination can occur.



Scheme 8 Visible-light induced reductive elimination in Sonogashira cross-coupling

While light-enhanced reductive elimination was clearly demonstrated in these previous reports, it is important to note that other mechanisms than *EnT* may be operative in photocatalysed Ni cross-coupling transformations. Nocera and co-workers

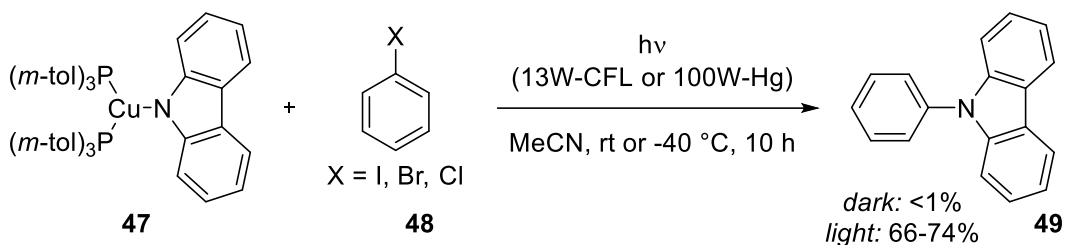
demonstrated that light and Ni catalysed C-O bond forming etherification reactions were actually photoredox mediated, where light initiates a self-sustained dark Ni(I)/Ni(III) cycle [33]. More recently, MacMillan and co-workers discovered that in light and Ni mediated C-N coupling reactions, photocatalysis initiates and perpetuates a dark Ni(I)/Ni(II) cycle rather than their previously proposed Ni(0)/Ni(II)/Ni(III)/Ni(I) mechanism [34]. Notably, Nocera and co-workers have recently demonstrated that various light mediated Ni catalysed cross-coupling reactions can be in fact accessed in the absence of light [35]. In their report the authors demonstrate that the addition of 0.02-0.5 equivalents of Zn(0) allows Ni catalysed amination, etherification/hydroxylation and esterification of a series of aryl bromides to occur in the absence of light, mimicking photoredox-like cross-coupling reactions and conditions. The authors postulate that Zn(0), functioning as a heterogenous reductant, slowly generates Ni(I) which initiates and sustains a Ni(I)/Ni(III) cycle. Here the authors caution that catalysis attributed to light mediated *EnT* may in fact be initiated by photoreduction of Ni(II) precatalyst to Ni(I).

These investigations demonstrate that various pathways may be in play regarding light-mediated Ni catalysis that exclude an energy transfer process. However, it is crucial to recognize that direct comparison of these different systems (with or without light, *EnT* vs photoredox) is intricate and should be addressed with caution as they do not involve the same substrates and product-forming transformations. This also highlights the complexity of the process.

Visible-light induced Single Electron Transfer

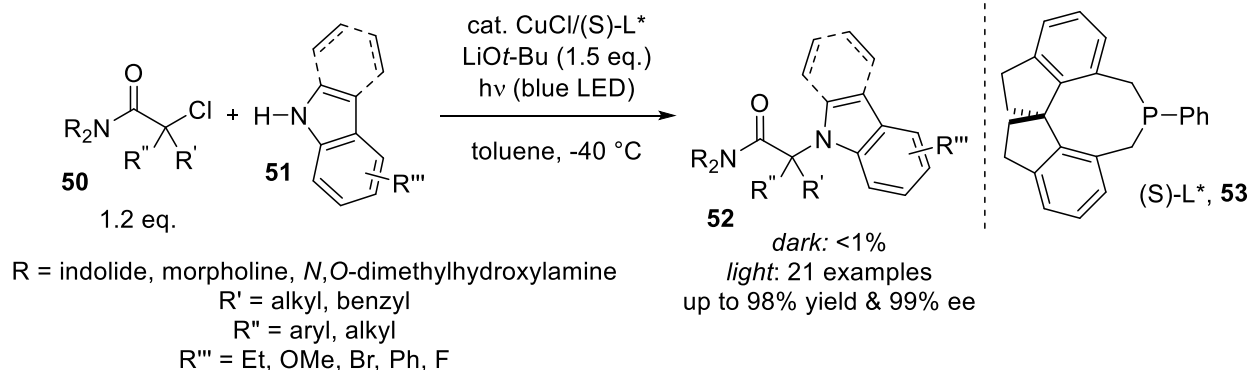
The previous section has focused on the interaction of light with organometallic complexes to induce or accelerate fundamental steps in a catalytic cycle. In parallel, strategies have emerged that harness the ability of organometallic intermediates, in the presence or absence of an exogenous photocatalyst, to interact with light to generate carbon-centered radicals that can then be engaged in cross-coupling processes. The involvement of radical species expands the scope of coupling partners and provides a means to further control the selectivity and tolerance of these transformations. This section excludes photoredox/Ni dual catalysis which has been reviewed [36].

The application of defined copper complexes in visible-light driven transformations is highly documented and a domain of ongoing intense interest and research [37,38,39]. One of the seminal works demonstrating the potential of visible-light-induced copper catalysis was the report by Fu, Peters and co-workers on photoinduced Ullmann coupling for C-N bond formation (Scheme 9) [40]. The authors demonstrated that irradiation of Cu complex **47**, using a 13W-CFL or 100W-Hg lamp at room temperature or -40 °C, respectively, in the presence of halobenzenes (I, Br or Cl) **48** resulted in formation of the C-N coupling product **49** in good yields (66-74%). Notably, this transformation was also demonstrated to be efficient with catalytic amounts of copper and provides a photoinduced methodology that avoids typically required thermal conditions (>90°C) needed for classical Ullmann coupling.



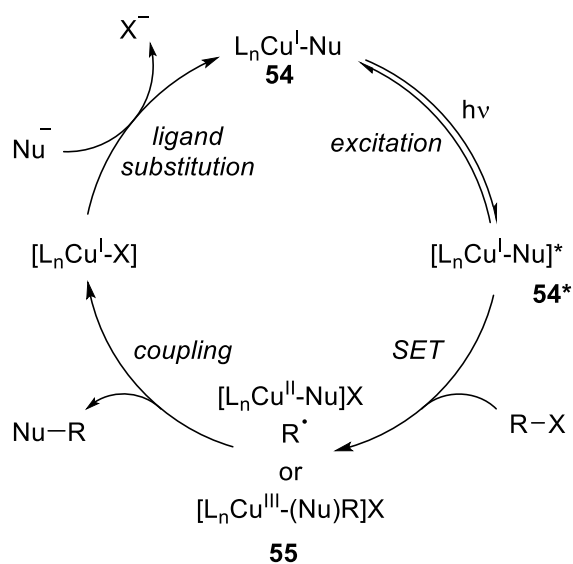
Scheme 9 Photoinduced Ullmann C-N coupling

Building on these results, a few years later Peters, Fu and co-workers [41] extended this methodology towards asymmetric C-N cross-coupling using racemic tertiary alkyl chlorides **50** as electrophiles and amines (carbazoles and indoles) **51** as nucleophiles to provide the corresponding products **52** (Scheme 10). The use of a chiral phosphine ligand **53** with a catalytic amount of CuCl allowed the coupling of a variety of tertiary alkyl chlorides and carbazoles in high yields and enantioselectivities. Importantly, they demonstrated that the reaction could now be performed using blue LEDs and at low temperatures (-40 °C).



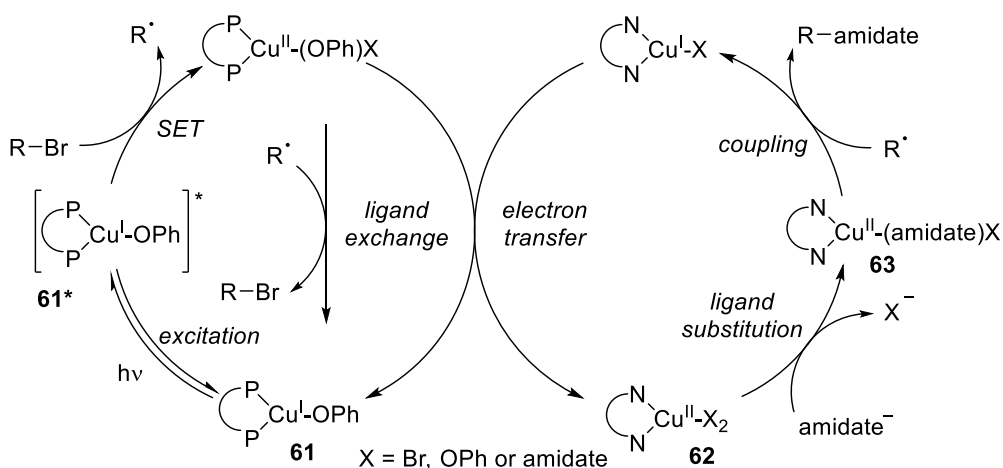
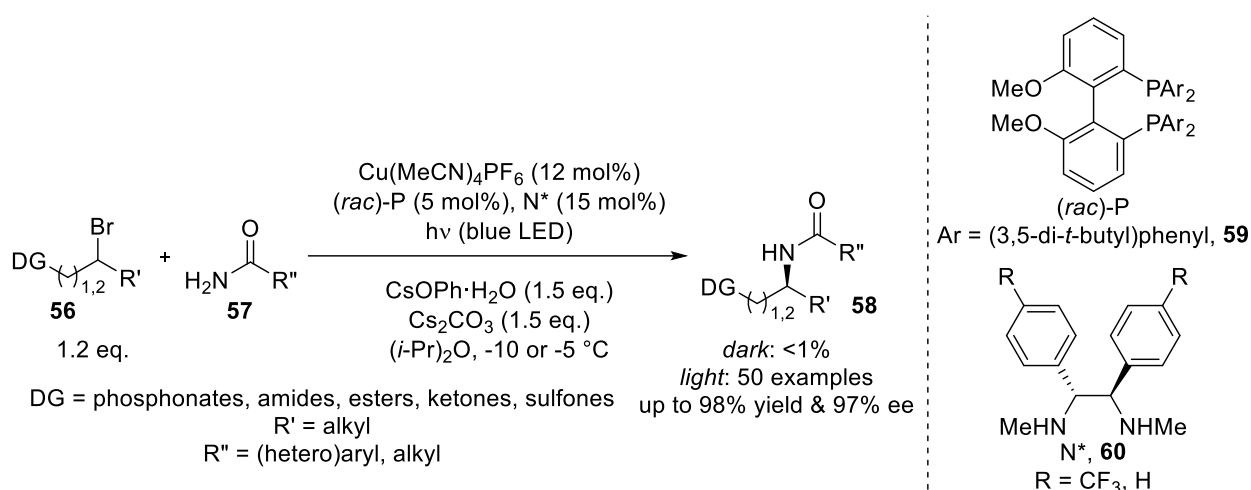
Scheme 10 Visible-light induced asymmetric Cu-catalysed C-N cross-coupling

Detailed mechanistic studies from both these reports highlight the involvement of radical intermediates in these transformations. This information, coupled with the demonstrated ability of $(\text{R}_3\text{P})_2\text{-Cu(I)}$ -carbazolide complexes like **47** to absorb visible-light allowed the authors to suggest a viable mechanism for these transformations (Scheme 11). Irradiation of the copper-nucleophile complex **54** leads to an excited state adduct **54*** that can engage in SET with the electrophile (aryl- or alkylhalide) to generate an aryl/alkyl radical and Cu(II) complex **55** which mediates the (enantioselective) bond-forming process between the aryl/alkyl radical and the nucleophile.



Scheme 11 Proposed mechanism for the photoinduced SET transfer and C-N cross-coupling from Cu-carbazolide complexes

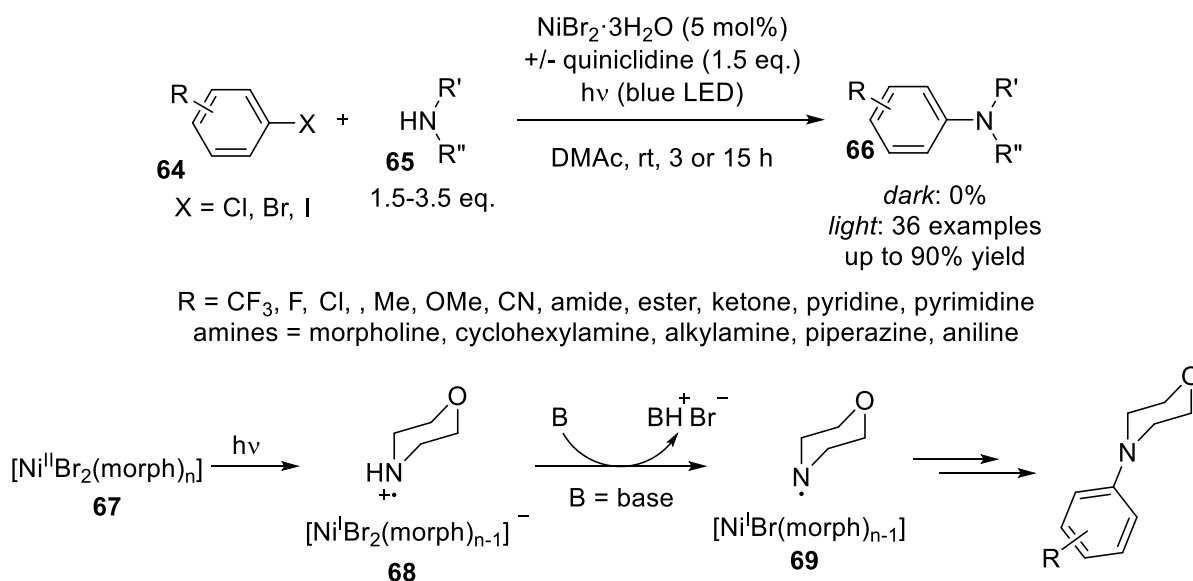
More recently, Peters, Fu and co-workers have extended this methodology even further towards the asymmetric amidation, with amides **57**, of unactivated tertiary alkyl bromides **56** bearing a remote directing group to provide chiral secondary amides **58** in excellent yields and enantioselectivities (Scheme 12) [42]. In this example the authors demonstrate the crucial combination of three distinct ligands: a phenoxide, bisphosphine **59** and a chiral diamine **60**; during the transformation the ligands would assemble *in situ* to form two distinct copper catalysts (**61** and **62**) that function cooperatively. On the one hand, the bisphosphine and phenoxide ligands coordinate the copper pre-catalyst to provide a photo-active complex **61** capable of absorbing light. The latter could reach an excited state complex **61*** which undergoes SET with the alkyl bromide and generate an alkyl radical. On the other hand, the chiral diamine forms a copper complex **62** able to coordinate the amidate nucleophile to give complex **63** and mediates the asymmetric C-N bond-forming reaction. Mechanistic studies and supporting DFT calculations evidence and support the cooperative nature of both copper catalysts and rationalize the coupling point of both cycles through either electron transfer or ligand exchange.



Scheme 12 Cooperative photoinduced Cu-catalyzed enantioselective amidation

In 2018, Miyake and co-workers reported the ability of catalytic C-N cross-coupling between aryl halides **64** and amines **65** to give the corresponding anilines **66** through the photoexcitation of Ni(II)-amine complexes **67** (Scheme 13) [43]. They demonstrated that the reaction did not need an exogenous photocatalyst, and that the active species was generated by direct irradiation of Ni-amine complexes. In this context the amine plays multiple roles as the nucleophile, ligand and base to neutralize the acid by-product. The reaction uses inexpensive Ni(II)Br₂·3H₂O, is oxygen tolerant and presents good substrate scope regarding the amine base used (primary, secondary amines and anilines). Nevertheless, electrophile aryl halides with electron-withdrawing groups were more reactive than those with electron-neutral or donating moieties. Experimental and

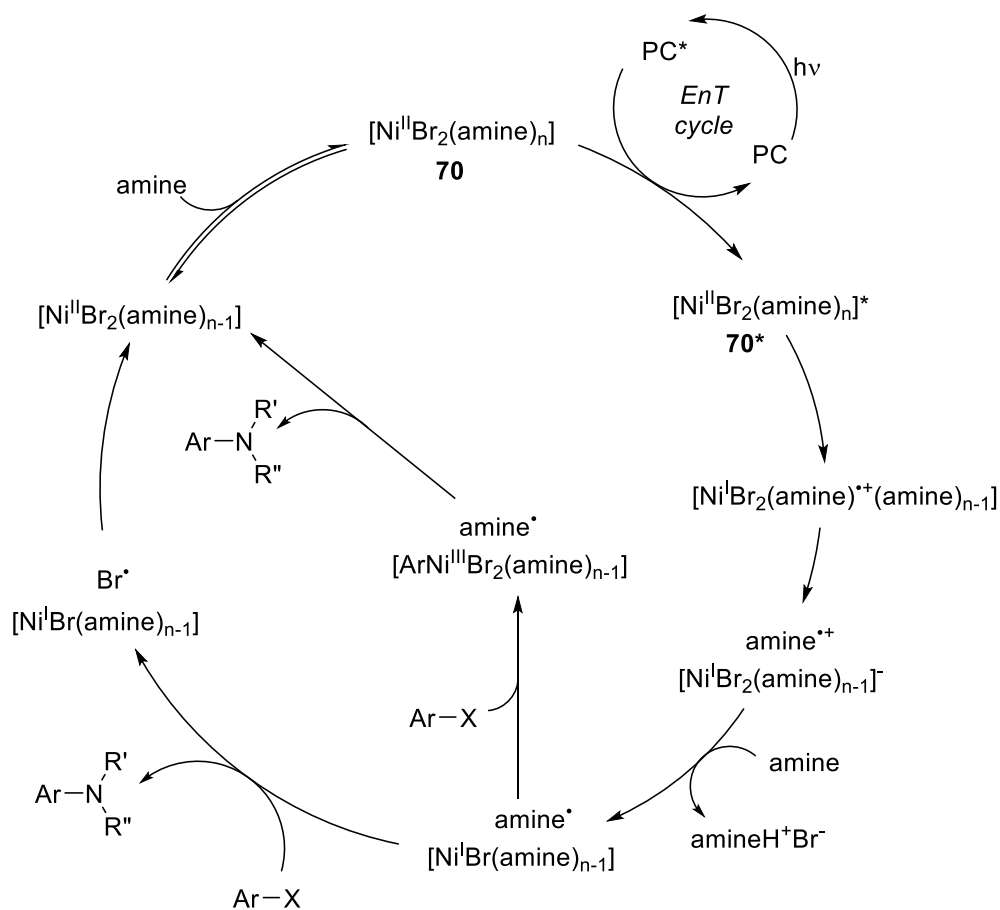
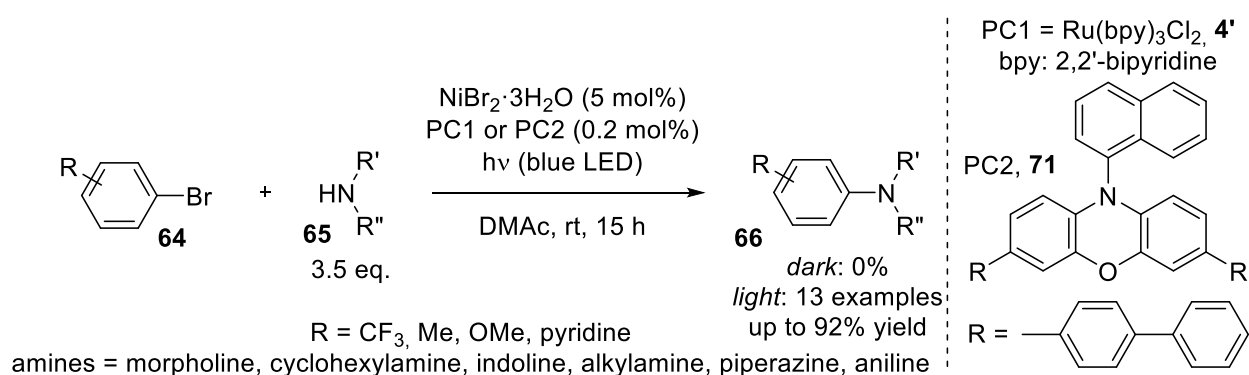
computational mechanistic studies suggest, in the presence of excess amine (morpholine for mechanistic studies), that $[\text{Ni}(\text{II})\text{Br}_2(\text{morph})_3]$ **67** was the predominant species in solution, importantly this complex blue-shifts absorption to ~ 430 nm compared to 657 nm for $\text{Ni}(\text{II})\text{Br}_2 \cdot 3\text{H}_2\text{O}$. The authors then propose that excitation of **67** allows SET from the electron-rich morpholine ligand to Ni(II) reducing it to Ni(I) forming complex **68** and generating an oxidized morpholine radical cation, which can dissociate into the corresponding ion pair. Deprotonation of the radical cation with excess base would provide the morpholine radical and neutral Ni(I) complex **69** that can generate the product through either of two pathways: i) a Ni(I)/Ni(III) cycle or ii) addition of the morpholine radical to the aryl halide.



Scheme 13 Visible-light induced photocatalyst-free Nickel-catalyzed Ullmann reaction

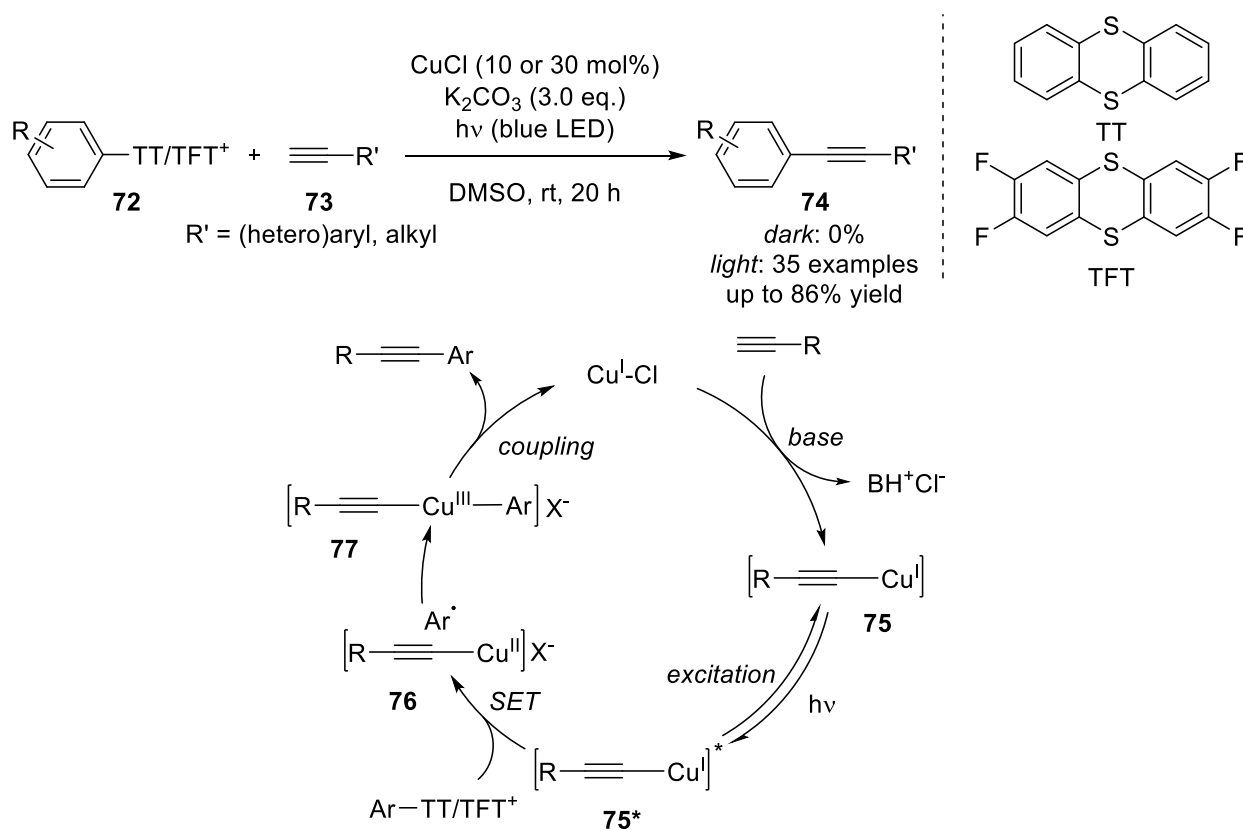
Inspired by the demonstrated ability of Ni complexes to be directly photoexcited by light without the use of a photocatalyst, Thordarson, Miyake and co-workers proposed, that in the case of dual Ni/photocatalyst systems, this may in fact suggest that the photocatalyst is performing Förster-type *EnT* to the Ni^{II} complex **70** rather than electron transfer (Scheme 14).[44] During this study the authors characterized the structure of Ni(II)-amine complex *EnT* acceptors through crystallographic and spectroscopic studies. Excited photocatalyst emission and Ni(II)-amine complex absorption overlap and

quenching experiments supported Förster-type *EnT*. Finally, using quantitative Förster theory the authors could select an organic photocatalyst **71** that proved to be more effective in the catalytic C-N cross-coupling process. Importantly, this methodology allows the reaction to now occur using lower energy light (blue, 457 nm or green, 523 nm) compared to their previous study (365 nm).



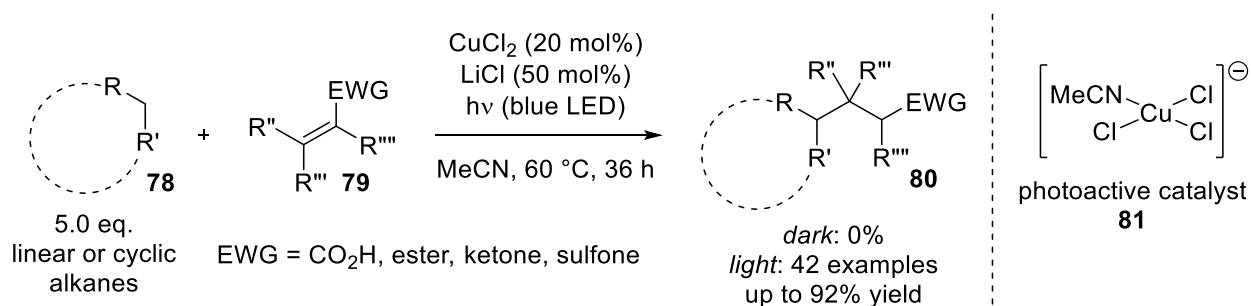
Scheme 14 Photocatalyst to Ni *EnT* enabled C-N cross-coupling

The ability of other copper complexes to function as efficient photocatalysts was recently demonstrated by Liang, Niu and co-workers (Scheme 15) [45]. Using simple CuCl, aryl sulfonium salts **72** as electrophiles and alkynes **73**, under blue light irradiation the authors report efficient and site-selective Sonogashira C(sp²)-C(sp) cross-coupling to provide phenylacetylene derivatives **74**. The use of aryl sulfonium salts **72** and a Pd-free method increases substrate compatibility and chemoselectivity of the transformation with excellent functional group tolerance. The mechanism is proposed to occur through photoexcitation of the *in situ* formed Cu(I)-acetylide complex **75**, which in the excited state (**75***) is able to reduce an aryl sulfonium salt, through SET, to generate an aryl radical. Radical recombination of the aryl radical and the Cu(II) complex **76**, produces a Cu(III) complex **77**, which following reductive elimination, produces the cross-coupling product and closes the catalytic cycle.



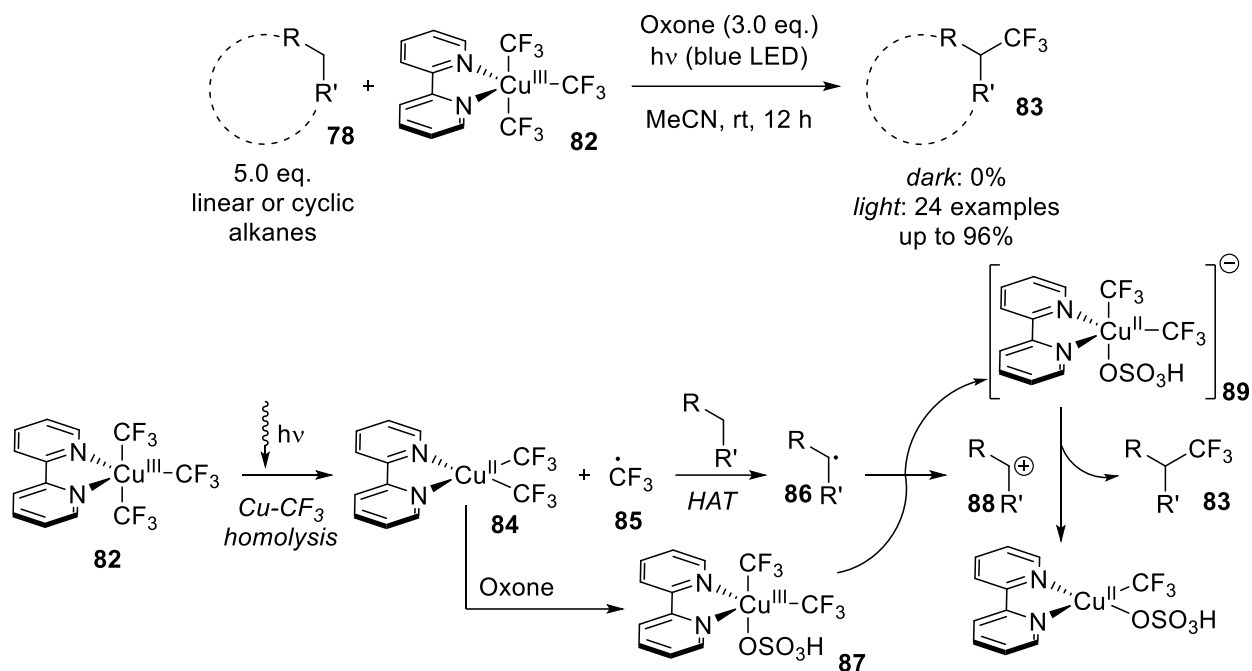
Scheme 15 Photoinduced Sonogashira cross-coupling

Treacy and Rovis showed that, under light irradiation, the simple combination of CuCl₂ and LiCl can efficiently catalyse the alkylation of unactivated C(sp³)-H bonds of alkanes **78** with alkenes **79** to provide the corresponding products **80** (Scheme 16) [46]. Under their reaction conditions, photoactive MeCNCuCl₃⁻ (**81**) is formed *in situ*, from CuCl₂ and LiCl in acetonitrile, and undergoes ligand-to-metal charge transfer LMCT to generate a chlorine radical which is capable of abstracting an H atom from unactivated C(sp³)-H bonds. Addition of the resulting radical onto the acceptor, followed by a metallation tautomerization/protodemetalation sequence provides the product.



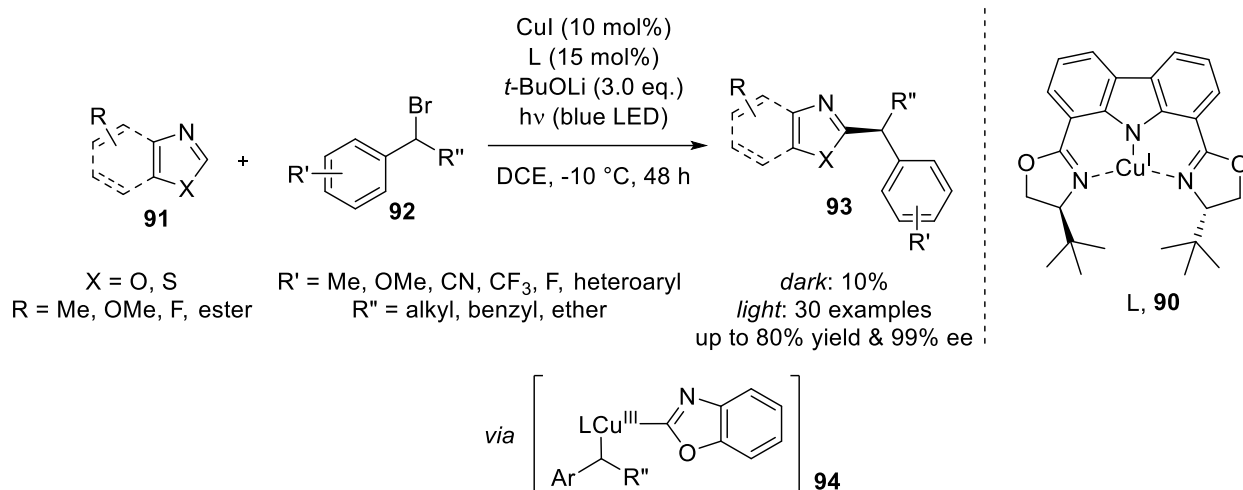
Scheme 16 Light induced Cu catalysed alkylation of unactivated C(sp³)-H bonds

Similar activation of strong C(sp³)-H bonds of alkanes **78** was recently evidenced by their trifluoromethylation (**83**) by Hong and co-workers (Scheme 17) [47]. They reported that the irradiation of bipyridine-Cu(III)-(CF₃)₃ complex **82** generates a trifluoromethyl radical **85**, which following HAT, produces an alkyl radical **86**. Under reaction conditions, Oxone would oxidize the resulting bipyridine-Cu(II)-(CF₃)₂ complex **84** to bipyridine-Cu(III)-(CF₃)₂(OSO₃H) **87**, which can oxidize the alkyl radical to the corresponding cation **88**. The resulting anionic bipyridine-Cu(II)-(CF₃)₂(OSO₃H) complex **89** then acts as a CF₃ anion source, which would add to the alkyl cation to provide the desired product **83**. This strategy provides access to trifluoromethylated alkane derivatives with tolerance towards ketone, ester, acid and amide functional groups, and can be used for the late-stage trifluoromethylation of a series of natural products and bioactive molecule derivatives.



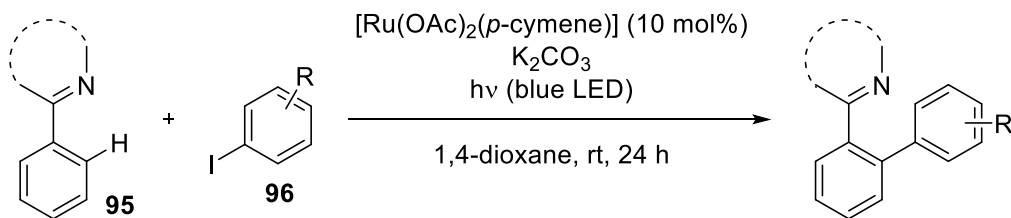
Scheme 17 Visible-light induced trifluoromethylation of unactivated C(sp³)-H bonds

Recently, Zhang and co-workers demonstrated the ability of photoactive Cu(I)-carbazole-based bisoxazoline complexes **90** to efficiently mediate the enantioselective alkylation of azoles **91** with benzyl bromide derivatives **92** (Scheme 18) [48]. Blue LED light excitation of these Cu(I) complexes (**90**) results in an excited state that can perform a SET with the electrophile to provide the corresponding azole-Cu(III)-electrophile complex **94**. Reductive elimination provides the desired product and regenerates the Cu(I) complex and the catalytic cycle is closed by the regeneration of the Cu(I) complex.



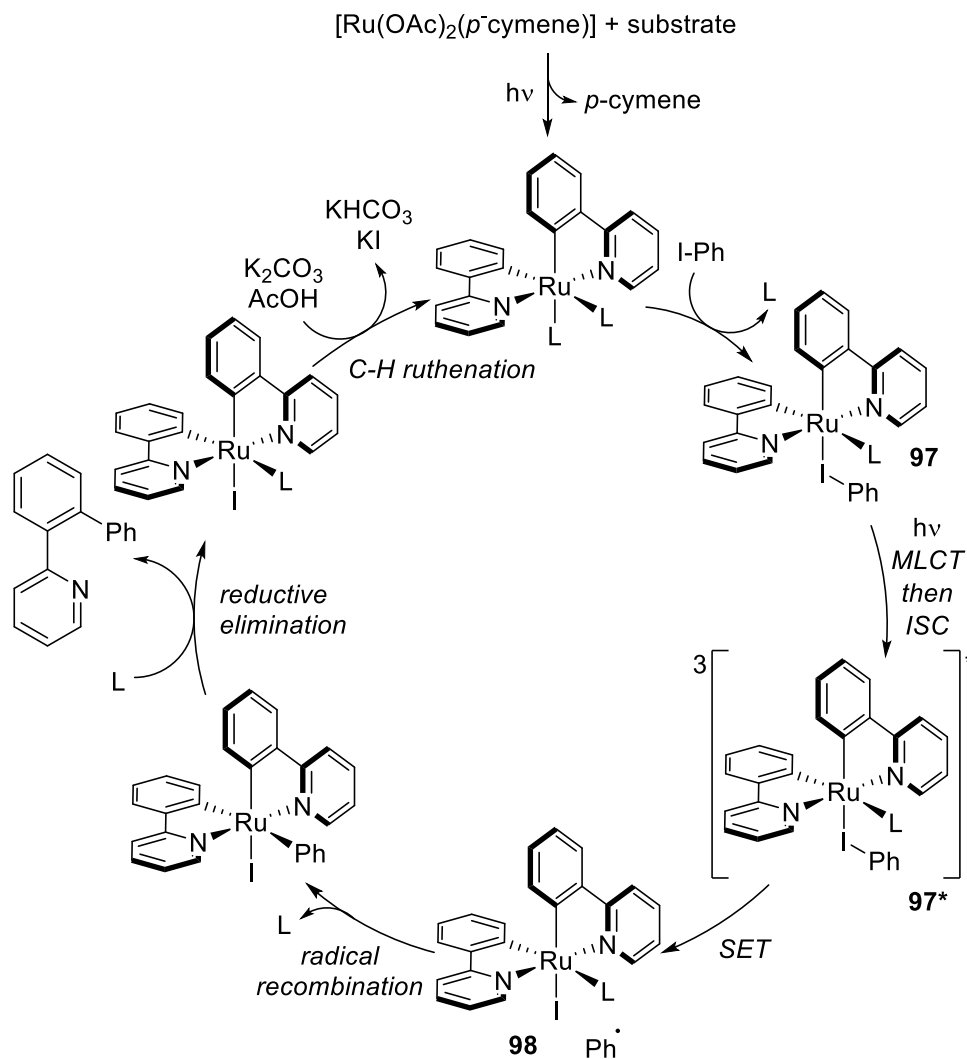
Scheme 18 Visible-light induced enantioselective alkylation of azoles

Similar SET reactivity from the excited state complexes has been observed with other metals, for example ruthenium as reported by Ackermann and co-workers in 2020 (Scheme 19) [49]. In this work the authors demonstrate that under visible-light irradiation, and in the absence of photocatalysts, Ru complexes are able to catalyse the C-H arylation of a variety of functionalized pyridines, pyrazoles, triazoles as well as nucleosides and nucleotides (**95**) with aryl iodides (**96**) with excellent functional group tolerance. The use of light in this case avoids the thermal conditions (100-140 °C) needed to accomplish this reaction. Mechanistic studies revealed that the bis-cyclometalated ruthenium complexes (generated in solution through carboxylate assisted C-H ruthenation) coordinating the aryl halide (**97**) absorb light at ~460 nm. Calculations suggested that excitation of this complex, through MLCT, followed by intersystem crossing leads to a triplet excited state complex **97*** that can be engaged in SET with the coordinated aryl iodide leading to complex **98**, which following radical combination and reductive elimination provides the coupling product and closes the catalytic cycle.



N-group = pyridine, pyrimidine, triazole, pyrazole, oxazoline, ketimine
 R = *meta*, *para* substitution, ester, indole, carbazole

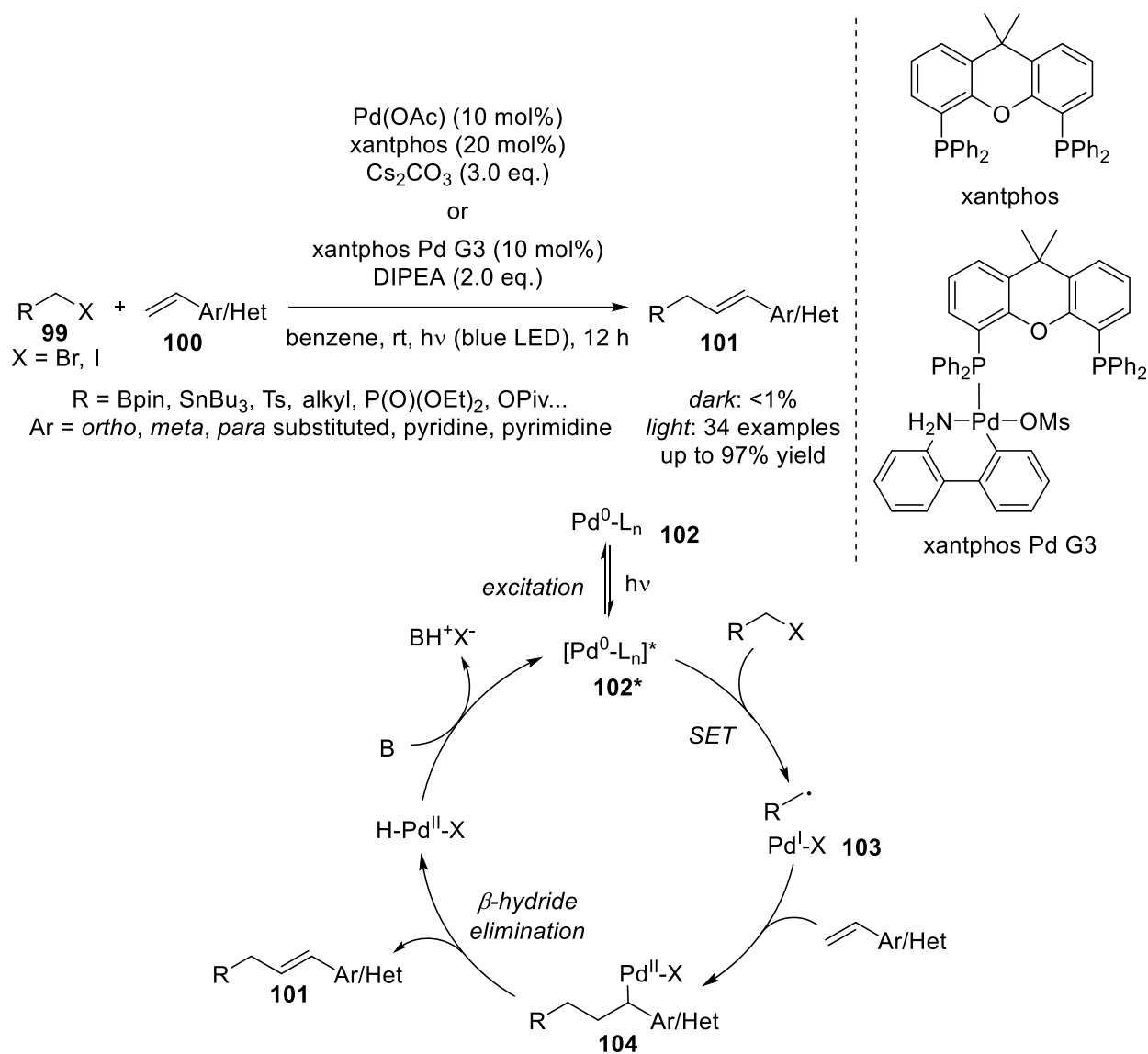
dark: 12%
 light: 50 examples
 up to 97% yield



Scheme 19 Photoinduced C-H bond arylation

Similarly, this was also observed with Pd as reported by Gevorgyan and co-workers in 2017 (Scheme 20) [50]. The authors demonstrated that visible-light, without exogenous photocatalyst, could be used to mediate Heck cross-coupling between alkyl halides **99**

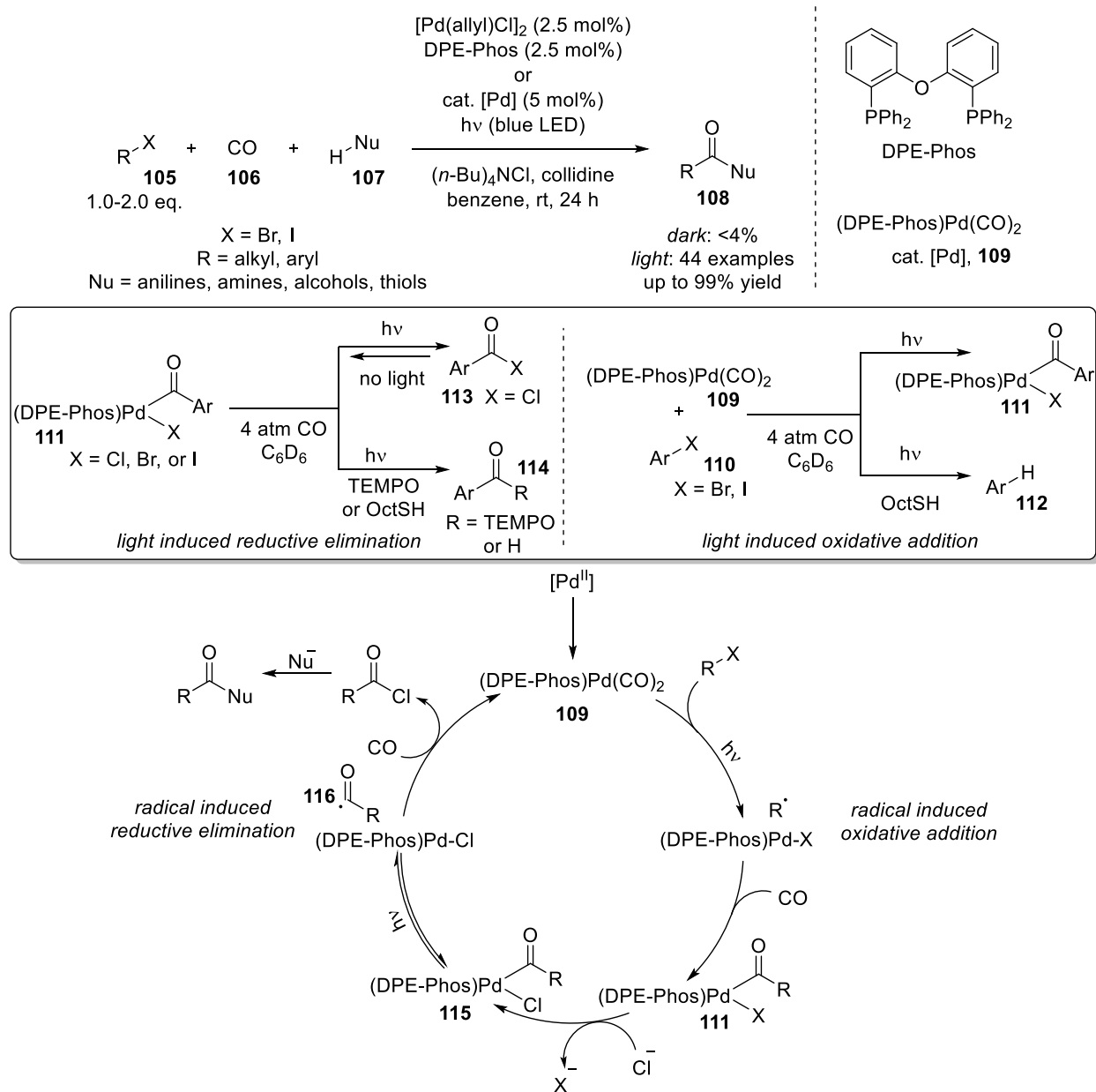
and vinyl (hetero)arenes **100** at room temperature to furnish the corresponding products **101**. Importantly, this methodology circumvents the usual high temperatures needed for this reaction to work (65-110 °C). The reaction features a general scope with regards to the alkene and alkyl halide employed and generates products that can be further post-functionalised (in one- or two-pot processes). Mechanistic investigations suggest that excitation of the *in situ* generated Pd(0) complex **102** results in an excited state complex **102*** which can be engaged in a SET with the alkyl halide, generating an alkyl radical and a Pd(I) complex **103**. Addition of the radical to the alkene, followed by β -hydride elimination from **104** furnishes the product and closes the catalytic cycle.



Scheme 20 Visible-light induced Heck cross-coupling

Arndtsen and co-workers developed a light-driven carbonylative cross-coupling reaction using aryl or alkyl halides **105**, carbon monoxide (CO, **106**) and various nucleophiles **107** to generate various carbonyl derivatives such as acyl chloride, amides, esters, ketones and thioesters (**108**) (Scheme 21) [51]. Importantly, this methodology circumvents the limitations of classical catalytic reactions with respect to oxidative addition (electron-rich catalysts) and reductive elimination (high temperatures), allowing the room temperature coupling of unactivated substrates (alkyl halides) and less

reactive nucleophiles such as anilines or *N*-heterocycles, tertiary alcohols, sterically hindered amines. The methodology allows access to a wide range of carbonyl derivatives with an excellent functional group tolerance and moderate to excellent yields. In this unique report, light was determined to intervene in two distinct steps within the catalytic cycle, inducing both oxidative addition and reductive elimination. The presumed *in situ* formed active catalyst (DPE-Phos)Pd(0)(CO)₂ **109** was independently synthesised and found to absorb blue light. Irradiation of this **109**, in the presence of an aryl halide **110**, leads to the corresponding oxidative addition Pd(II)-acyl halide complex **111** (62%) with concurrent formation of a biaryl product (25%) resulting from the coupling of the aryl halide and benzene (reaction solvent) implying the presence of radical species. Addition of a thiol (OctSH) as a hydrogen-atom donor completely inhibits oxidative addition leading only to the reduced arene **112** (from the corresponding aryl halide). Notably, only 17% of the oxidative addition product was observed in the absence of light. Additionally, experimental studies confirmed the necessity of light for reductive elimination. Mechanistic investigations on the oxidative addition Pd(II)-acyl halide intermediate **111** reveal that this complex absorbs blue light as well. Irradiation of this complex under CO pressure (4 atm) results in the formation of the desired acyl chloride **113** in near quantitative yields accompanied with the regeneration of the starting Pd(0) complex **109**. Interestingly, this process was found to be reversible and in the absence of light the reaction mixture reverted back to the starting Pd(II) complex **111**. The presence of radical intermediates was confirmed by trapping the presumed acyl radical with TEMPO or thiols to provide the corresponding ester or aldehyde **114**. To summarise, the mechanism is proposed to start from the (DPE-Phos)Pd(CO)₂ complex **109** which under irradiation induces radical mediated oxidative addition to provide the corresponding Pd(II)-acyl halide complex **111**. Ligand exchange provides the Pd(II)-acyl chloride complex **115** which upon excitation releases an acyl radical **116**. The latter induces a stepwise reductive elimination to provide the desired acyl chloride which can finally react with a nucleophile in solution to furnish the desired carbonyl product.



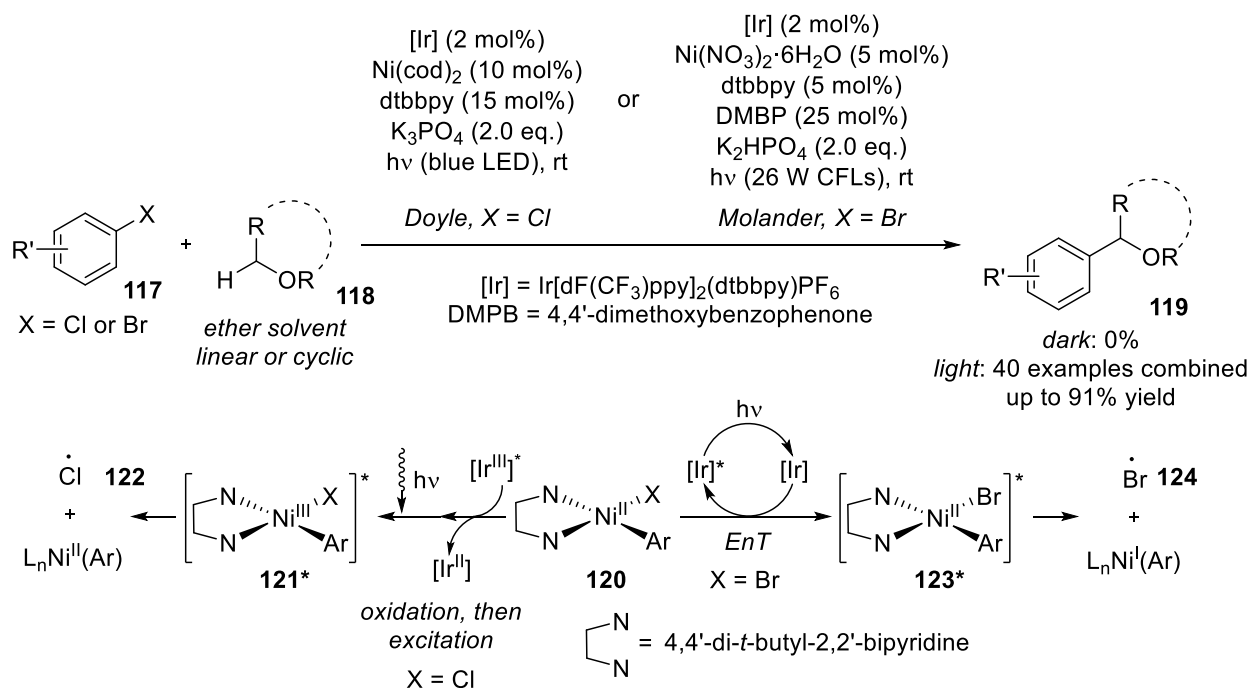
Scheme 21 Visible-light induced carbonylative cross-coupling of organohalide substrates and nucleophiles

The direct photoexcitation of nickel complexes has been so far limited to only a few examples, but it is clearly an emerging and intense area of research. Following the report of Nocera on the halogen photoelimination from Ni(III) complexes [52], significant development, simultaneously reported by the Doyle [53,54] and Molander [55] groups, was the discovery that Ni(II) aryl halide complexes could catalytically generate Cl or Br

radicals respectively, allowing for direct C(sp³)-H cross-coupling (Scheme 22). Both groups reported the coupling of aryl halides **117** with ethers **118** (as reaction solvent) to provide the corresponding coupling products **119** in good to high yields. Operationally both methods are very similar, oxidative addition provides a Ni(II) aryl halide complex **120**, which upon irradiation, and in the presence of a photocatalyst, generates a halogen radical from the homolysis of the Ni-X bond. The halogen radical undergoes chemo- and regioselective HAT with the ether coupling partner generating an alkyl radical, which following reductive elimination from Ni provides the final product. However, experimental, and theoretical investigations revealed drastic differences in the underlying mechanisms involved in both processes.

Mechanistic studies by Doyle and Shields revealed that the combination of both a strong oxidant and light were necessary for product formation. They proposed that the Ir photocatalyst served to oxidize the post-oxidative addition Ni(II) complex **120** to Ni(III) complex, which was then directly excited by light to an excited state Ni(III)* complex **121*** from which Ni-Cl bond homolysis occurs to release the chlorine radical **122**. Stoichiometric experiments using a strong chemical oxidant such as tris(4-bromophenyl)aminium hexachloroantimonate ([TBPA]SbCl₆) and light irradiation resulted in the formation of coupling products, however in the absence of either light or oxidant no cross-coupling products were formed confirming the requirement for both oxidation and light for an efficient transformation.

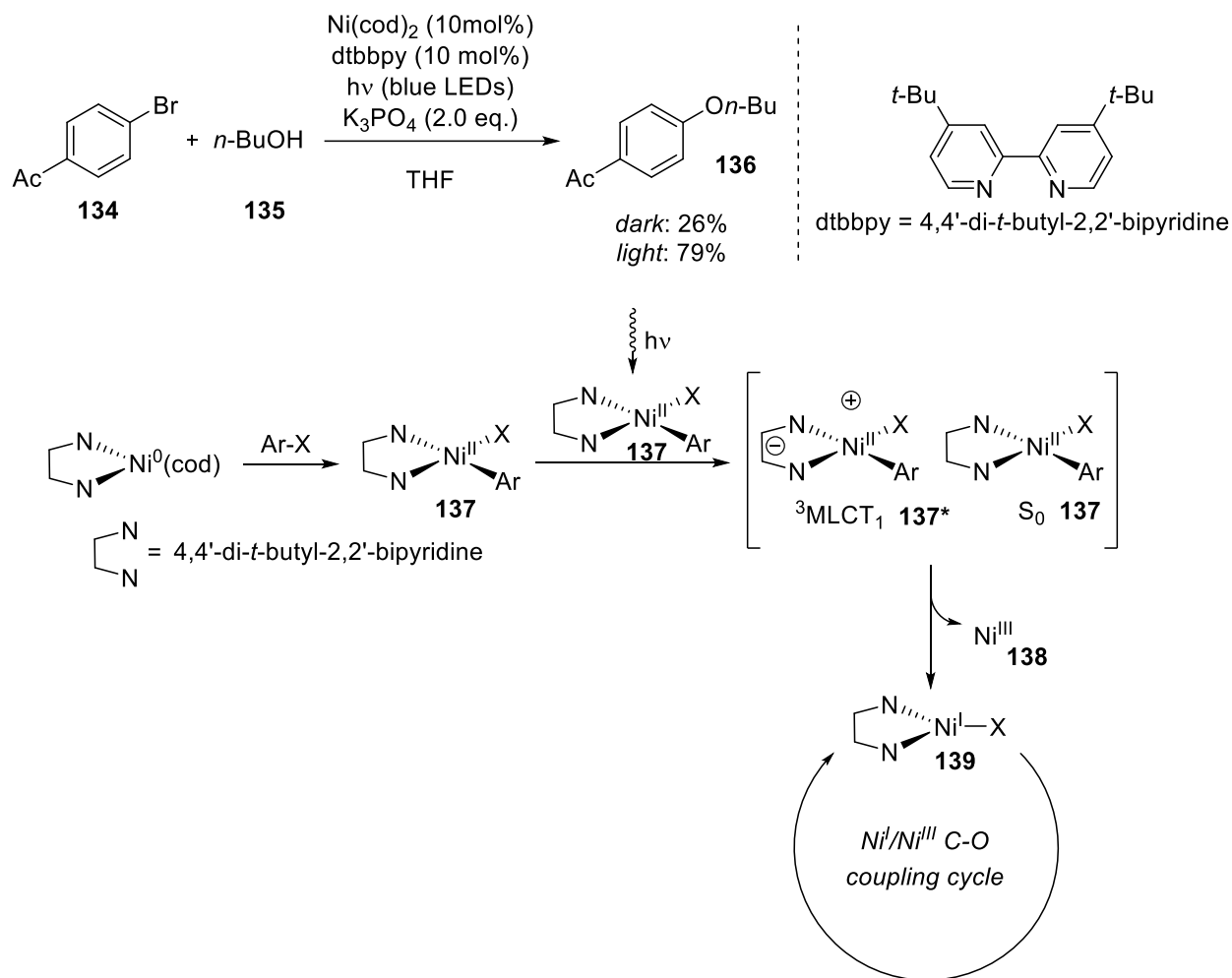
Conversely, Molander and co-workers excluded a Ni(II) to Ni(III) process by exposing their Ni(II) aryl bromide complexes **120** to strongly oxidizing photocatalysts and did not observe formation of cross-coupling products. However, direct UV-B irradiation of the Ni(II) aryl bromide complex **120** allowed formation of coupling products. This led the authors to suggest that reactivity was correlated with triplet state energies rather than excited state oxidation potentials. These findings and suppositions combined allowed the authors to invoke a triplet-triplet *EnT* process from the Ir photocatalyst to Ni(II) complex **120** to generate an excited state Ni(II)* complex **123*** from which Ni-Br bond homolysis occurs to release bromine radical **124**.



Scheme 22 Visible-light induced Ni-halide bond homolysis

A recent report by Hou, Zhu and co-workers leverages the ability of Ni complexes to generate chlorine radicals under visible-light irradiation, in the absence of an exogenous photocatalyst, for the phosphorylation of aryl halides **125** with phosphine oxides **126** (Scheme 23) [56]. Irradiation of the *in situ* formed Ni(II)-1,10-phenanthroline complex **128** results in LMCT which allows the homolysis of a Ni-Cl bond to provide the corresponding Ni(I) complex **129** and a chlorine radical **130**. The chlorine radical **130** can then abstract a H from the phosphine oxide coupling partner **126**, to generate the corresponding phosphorus atom-centered radical **131**. Concurrently, the Ni(I) complex **129** undergoes oxidative addition with the aryl halide electrophile, resulting in the corresponding Ni(III) aryl halide complex **132**. Combination of the Ni(III) complex **132** with the phosphorus radical **131** gives the corresponding Ni(IV) complex **133** from which reductive elimination occurs to release the desired product **127** and close the catalytic cycle. This methodology could be successfully applied to the coupling of various aryl phosphine oxides with aryl halides in moderate to good yields.

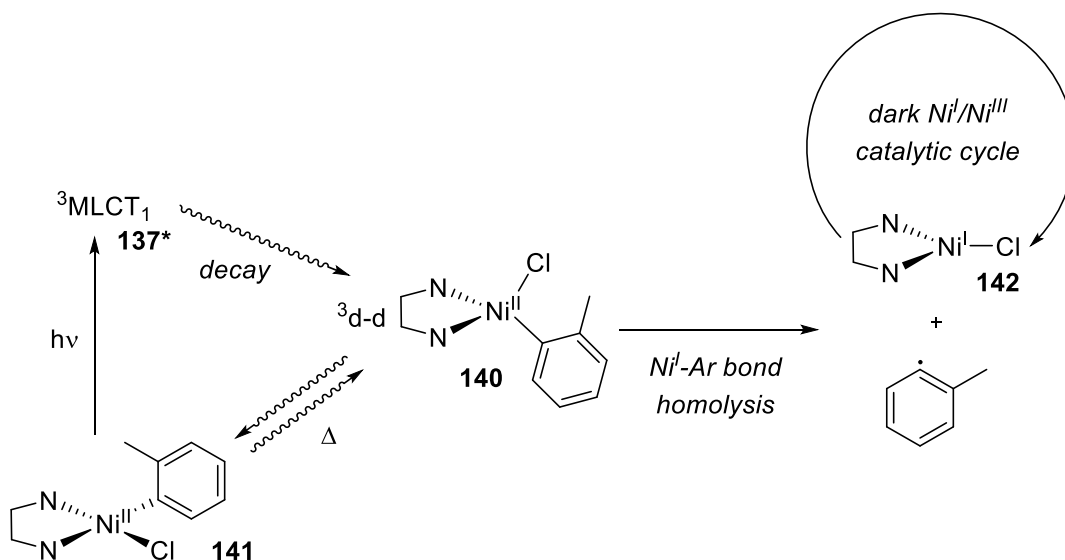
coupling of 4-bromoacetophenone and *n*-butanol under visible-light irradiation, providing the coupling product **136** in 79% yield (compared to 29% in the dark). In this context the Ni complex functions as a photocatalyst that initiates a Ni(I)/Ni(III) cycle through electron transfer from one excited state Ni(II) complex **137*** to another in the ground state.



Scheme 24 Ni(I) generation through photo-induced electron transfer between an excited and a ground-state Ni^{II} complex

However, two years later the same group revised their previous mechanism after detailed experimental spectroscopic and mechanistic investigations into the excited states of these Ni complexes [58] (Scheme 25). Through further experimental studies, the authors found that the previously computationally assigned ³MLCT₁ state **137***, although generated upon excitation, decays to another long-lived state. This state was

determined to be a tetrahedral ^3d-d state **140** with an energy of ~ 0.5 eV (~ 12 kcal/mol), the low energy of this state suggests that it is thermally accessible at room temperature. The electronic, high-spin, nature of the ^3d-d state **140** has occupied metal-ligand σ^* orbitals, resulting in weaker metal-ligand bonds. This led the authors to suggest that photoinduced Ni(II)-Ar bond homolysis could occur from this excited ^3d-d state. These propositions were confirmed by irradiating Ni(II)-(dtbbpy)(*o*-tolyl) chloride **141** with blue light and observing through ^1H NMR spectroscopy studies the formation of paramagnetic Ni(I) dimers, and through spin-trapping experiments the formation of aryl radicals by EPR spectroscopy. Once the Ni(I) complex **142** is generated it can enter into a dark Ni(I)/Ni(III) catalytic cross-coupling cycle. These new findings combined shed light onto the highly complex mechanisms involved in photoinduced cross-coupling with Ni complexes and raise the question as to whether other processes, such as photoinduced reductive elimination, operate via a photoinitiated dark Ni(I)/Ni(III) catalytic cycle (*vide supra*).



Scheme 25 Ni(I) generation through Ni^{II}-Csp² bond homolysis

Conclusion

Visible-light activation strategies occupy an important role in organometallic catalysis and notably in cross-coupling reactions. Photoactivation overcomes kinetically

challenging cycle-determining steps, such as oxidative addition in the case of Au(I)/Au(III) complexes or reductive elimination, and significantly increases the efficiency of catalysis by promoting an intermediate to a highly reactive excited state, likely to perform the rate-limiting step. Another interest of visible light activation is to enhance the redox properties of organometallic complexes allowing them to generate radicals, by SET, that can then engage in cross-coupling transformations, offering an expansion in compatible coupling partners and structural diversity of products. This photoactivation can occur through direct absorption by an intermediate complex or through photosensitization by a photocatalyst, which can readily be excited by the incident light and prone to transfer its energy to an organometallic complex, enhancing the reactivity of the latter.

The examples highlighted in this review demonstrate the power and potential of organometallic catalysis under light activation. The interaction of light and organometallic complexes grants access to unprecedented reaction mechanisms and transformations adding richness to the synthetic chemist's toolbox and to the complexity of products attainable. While there have been significant advances in delineating and understanding the underlying mechanisms of these transformations, much remains unknown. Further work in truly understanding the fundamental steps at play, where light and complexes interact, is needed. Better understanding and control of these concepts will undoubtedly spur significant developments in catalysis and synthetic chemistry.

Acknowledgements

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Conflict of interest:

There is no conflict of interest to declare.

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