Abstract: Photochemistry enables new synthetic means to form carbon–heteroatom bonds. Photocatalysts can catalyze carbon–heteroatom cross-couplings by electron or energy transfer either alone or in combination with a second catalyst. Photocatalyst-free methods are possible using photolabile substrates or by generating photoactive electron donor-acceptor complexes. This review summarizes and discusses the strategies used in light-mediated carbon–heteroatom bond formations based on the proposed mechanisms.

1. Introduction

The backbone of organic molecules mainly consists of C–C bonds, but the function is often derived from the presence of heteroatoms. Almost all natural products, pharmaceuticals, agrochemicals, and polymeric materials contain carbon–heteroatom bonds that are often introduced by the synthetic chemist through nucleophilic substitutions and transition metal-catalyzed cross-coupling reactions.[1] The resurgence of photochemistry[2] has resulted in a series of C–heteroatom bond formations that are complementary to traditional transformations.

The most common way to harness visible light is photocatalysis. Upon irradiation, a photocatalyst (PC) can induce chemical reactions by two modes of action (Figure 1). In photoredox catalysis (PRC), an excited PC accepts or donates a single electron, enabling oxidative or reductive quenching cycles.[3] Depending on the reaction conditions, both events can occur with the same PC. An excited photocatalyst can also transfer its excited state energy to a substrate or reagent to induce chemical reactions.[4] Photocatalysts can generally be divided into metal complexes, organic dyes and heterogeneous semiconductors (Figure 1). Ruthenium and iridium polypyridyl complexes are the

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most common photocatalysts due to their strong absorption, stability, long excited state lifetime and the straightforward tunability by ligand modifications.[5] Photoactive complexes with earth-abundant metals,[6] and organic dyes are alternatives,[7] but suffer from limited photostability. Semiconductors, such as TiO₂, CdS, CdSe or carbon nitrides (CN), are attractive heterogeneous PCs due to their straightforward preparation, high stability, and recyclability.[8]

Photocatalysis can be used in synergy with other catalytic reactions in dual catalytic processes.[9] The combination with transition metal catalysis resulted in a series of novel approaches for carbon–carbon and carbon–heteroatom cross-coupling reactions.[9,10] Here, the key is either a direct single electron (SET) or energy transfer (EnT) between the photoredox and transition metal catalyst, or the interception of a photogenerated intermediate by the transition metal catalyst.

Reactions can be also triggered by light in the absence of a photocatalyst using photolabile starting materials, in case of photoactive intermediates.[11] In addition, electron-rich and electron-poor molecules can form electron donor-acceptor (EDA) complexes that absorb light in the visible region and induce SET events to trigger chemical transformations (Figure 2).[12]

This review provides an overview of photochemical approaches for the formation of C–N, C–S, C–O, and C–P bonds. Selected examples are discussed on the basis of the underlying strategy and mechanistic proposal. A detailed discussion on the selection criteria for photocatalysts is beyond the scope of this survey and can be found elsewhere.[2–10] It is, however, important to note that photochemical transformations can be highly complex and various mechanisms might be plausible or even operating simultaneously in certain cases.[13]

2. Photocatalytic Carbon–Heteroatom Bond Formation

In this section, carbon–heteroatom couplings solely catalyzed by a PC are discussed. These reactions are triggered by the formation of highly reactive intermediates that are generated when starting materials or reagents quench the excited photocatalyst (PC*). The structures of the photocatalysts can be found at the end of this review.

2.1. Oxidative Quenching of PC*

Aryl diazonium salts (1) have a rich history as precursors of aryl radicals (4).[14] In traditional photochemical protocols, irradiation with UV light results in photodecomposition of 1, forming N₂ and an aryl radical (4) that can be converted into aryl fluorides (Balz–Schiemann reaction), but a competitive heterolytic cleavage limits this approach. More recently, aryl diazonium salts (1) became one of the most common oxidative quenchers in visible-light PRC and enable the selective generation of 4 from 1 which was used for a broad range of applications.[14,15] In the synthesis of thioanisoles (3), the aryl radical (4) was proposed to react with disulfides affording 5, that donates an electron to the oxidized photocatalyst (PCOx, Scheme 1).[16]
Scheme 2. Synthesis of aryl sulfones (A) and aryl sulfides (B) by reduction of aryl diazonium salts by PRC.

To avoid the isolation of potentially explosive diazonium compounds, Noël showed that aryl diazonium salts (1) can be generated in situ from the corresponding anilines (9) and subsequently undergo photocatalytic C–S cross-couplings with thiols (10, Scheme 2, B).[18] Mechanistic studies indicated that the oxidative quencher is likely a diazosulfide intermediate rather than 1.

Aryl halides (12) are also potential radical precursors but have reduction potentials that are inaccessible to most photocatalysts.[15] Irradiation of Ir(ppy)₃ (ppy = 2-phenylpyridine) results in the strongly reducing \([\text{Ir(ppy)}_3]^*\) (IrIV/IrIII* –1.76 V vs. SCE), which was demonstrated to reduce aryl iodides (12-I) and vinyl iodides (13-I) enabling C–S bond formations. (Scheme 3, A).[19] Luminescent quenching experiments and transient absorption spectroscopy showed that 12-I is reduced by the excited photocatalyst, confirming an oxidative quenching cycle. Diaryl iodonium salts (16) can be used as alternative substrates with less reducing PCs such as Eosin Y (EYox/EY* –1.11 V vs. SCE). This was demonstrated for the synthesis of aryl sulfides (11) from thiosulfates (17) under anaerobic conditions (Scheme 3, B).[20] In air, singlet oxygen (\(\text{O}_2\)) was generated, resulting in a subsequent oxidation to form the corresponding sulfoxides (18) in good to excellent yield.

Scheme 3. Synthesis of aryl and vinyl sulfides by reduction of aryl iodides (A) or diaryl iodonium salts (B) by PRC.

Minisci type radical additions to heteroaromatic systems enable the direct functionalization of (hetero)aromatic compounds[21] and were extensively studied using photocatalysis.[22] Complementary to C–S bond formation via aryl radicals, the reduction of sulfonyl chlorides (20) by oxidative quenching of an excited iridium photocatalyst results in sulfonyl radicals (24) that were coupled with heterocycles affording the corresponding sulfonylation products (22, Scheme 4).[23] At elevated temperatures, extrusion of SO₂ resulted in the formation of aryl radicals, and the corresponding C–C coupling products were obtained (23).

Scheme 4. Temperature controlled sulfonylation and arylation of heterocycles by PRC.

Aromatic and heteroaromatic amines are an important structural motif in pharmaceuticals and are usually prepared by using transition-metal catalyzed cross-couplings.[16] The formation of N-centered radicals that react with unactivated (hetero)aromatic compounds is an appealing alternative. Amidyl and sulfonamidyl radicals (25) were accessed by reductive cleavage of suitable precursors (26) such as \(N\)-sulfonyloxysulfonamides (27),[24] \(N\)-acyloxyphthalimides (28),[25] and \(N\)-aryloxyamides (29)[26] using a sufficiently strong reducing PC (Scheme 5). The electrophilic radical species (25) was proposed to react with (hetero)aromatic compounds (21), to form a radical intermediate (30), that is subsequently oxidized by the photocatalyst, closing the catalytic cycle and affording the desired products (32) after deprotonation.

Scheme 5. Amidation of heterocycles via the formation of amidyl radicals using PRC.
Aminyl radicals, on the contrary, are nucleophilic and the repulsive interaction between their lone pair and the aromatic coupling partner makes them unsuitable for reactions with (hetero)aromatics.\(^{[27]}\) Leonori and co-workers could overcome this synthetic hurdle by applying acidic conditions.\(^{[28]}\) While their initial protocol required electron-poor O-aryl hydroxylamines as radical precursors,\(^{[28a]}\) the authors developed a protocol which enabled the direct use of secondary and primary alkylamines (34, Scheme 6).\(^{[28b]}\) Key to the success was the in situ generation of N-chloroammonium species (40) using N-chlorosuccinimide (NCS) under acidic conditions. 40 readily quenches the excited PC forming a highly electrophilic amonium radical (41) which undergoes regioselective radical addition with a broad range of arenes (33), forming the respective aniline derivatives (35) in good to excellent yield.

2.2. Reductive Quenching of PC*

Single electron oxidation of arenes (33) to form arene radical cations (50) requires PCs with highly positive excited state reduction potentials such as acridinium dyes.\(^{[7]}\) The electrophilic radical 50 was coupled with nucleophiles, such as azoles (51) to form carbon–heteroatom bonds (Scheme 8).\(^{[31]}\) Molecular oxygen as terminal oxidant was problematic as the generated reactive oxygen radicals caused side reactions, as well as degradation of the organic photocatalyst. Addition of sub-stoichiometric amounts of TEMPO (55, 2,2,6,6-tetramethylpiperidine-1-oxyl) mitigated these problems, significantly improving the selectivity. It was proposed that 55 aromatizes radical intermediate 53 to yield the desired C–N coupling product (54) and 56 was regenerated by superoxide (O$_2$•–). Triplet oxygen without additional TEMPO was instead well tolerated in the sulfonamidation of pyrroles and the alkoxylation of imidazopyridines.\(^{[32]}\)

Ritter,\(^{[29]}\) Togni and, Carreira\(^{[30]}\) developed the amination of arenes (33) via the generation of N-pyridyl radical cations from triflyloxy pyridinium derivatives (45, Scheme 7). Oxidative quenching of excited Ru(bpy)$_3$(PF$_6$)$_2$ by 45 was confirmed with Stern–Volmer quenching studies. EPR experiments corroborated the existence of the N-pyridyl radical cation.\(^{[30]}\) The method yielded N-aryl pyridinium triflates (46), which were subsequently converted into the corresponding aniline (9) or piperazine derivatives (47).

Ammonium persulfate was used as terminal oxidant in the phosphorylation of arenes (33) using Ru(bpz)$_3$(PF$_6$)$_2$ (bpz = 2,2′-bipyrazine) as PC (Scheme 9).\(^{[33]}\) Stern–Volmer analysis confirmed reductive quenching of PC* (+1.45 V vs. SCE) by electron-rich arenes such as 1,2,4-trimethoxybenzene (+1.12 V vs. SCE) and 1,2-dimethoxybenzene (+1.45 V vs. SCE). Anisole was not suitable using this protocol as it does not quench PC* due to its high oxidation potential (+1.76 V vs. SCE).

An oxidant-free methodology was developed for cation radical-accelerated nucleophilic aromatic substitutions of anisole derivatives (59, Scheme 10).\(^{[34]}\) The radical intermediate (61) formed from SET oxidation and addition of the nucleophile served as an electron acceptor to close the catalytic cycle. A similar strategy was used to activate aryl triflates using acetone as triplet sensitizer using UV light to realize several C–C, C–O, and C–N bond formations.\(^{[35]}\)

If the arene has a higher reduction potential than the PC* (e.g. anisoles, 65), the coupling reaction can be initiated by oxidation of the heteroatom through reductive quenching of PC*.\(^{[36]}\) Primary amines (66), the coupling reaction can be initiated by oxidation of the heteroatom through reductive quenching of PC*.
Scheme 9. Aryl phosphorylation using photoredox catalysis. Stern-Volmer quenching plots for Ru(bpz)$_3$(PF$_6$)$_2$ in the presence of different starting materials. Reproduced with permission [ref 33].

Scheme 10. Amination of anisoles via formation of aminyl radical cations using PRC.

Scheme 11. Amination of anisoles via formation of aminyl radical cations using PRC.

Scheme 12. Synthesis of arylamines (A), sulfones (B) and phosphonates (C) by oxidation of heteroatoms using PRC.

Scheme 13. Photoredox catalyzed C–N bond formation through radical pairing or cross-dehydrogenative coupling.
radical (83) either directly couples with 82, or forms 84 after a SET event followed by cross-dehydrogenative coupling (CDC). A possibility that was not taken into account is a HAT process between 82 and 79 to form radical 83 and pyrazole (51), followed by the CDC coupling pathway.

2.3. Quenching of PC* through Energy Transfer

Quenching of PC* through energy transfer rather than single electron oxidation or reduction was reported to be responsible for the photocatalytic amidation of heteroarenes (21) using benzoyl azides (86, Scheme 14).[38]

Energy transfer from PC* to the azide triggers N2 extrusion. The resulting benzoyl nitrene (89) reacts with 21 to form the desired amide (87) after deprotonation. An electron transfer pathway was excluded, as benzoyl azides are not sufficiently electron-deficient to be reduced by PC*. Furthermore, the addition of TEMPO did not affect the transformation, indicating the absence of radical intermediates.

3. Carbon–Heteroatom Bond Formation by Combining Photo- and Transition-Metal Catalysis

Transition metal catalysis plays a key role in the formation of C–C and C–heteroatom bonds.[1a,1b] While palladium catalysis is well established, more sustainable alternatives using nickel or copper are less common. High temperatures, strong bases or reducing agents, as well as air-sensitive metal complexes are required to realize catalysis with abundant metals, thus hampering their application. Recently, the combination of transition metal- and photocatalysis (metallaphotoredox catalysis) was shown to overcome these drawbacks, enabling cross-couplings with abundant metals under mild conditions.[10a] Different modes of action are possible in metallaphotoredox catalysis. In most cases, modulation of the transition metals’ oxidation state by the photocatalyst or addition of photocatalytically generated radicals are essential for product formation. Energy transfer from the excited photocatalyst can also activate intermediates in transition metal catalysis, inducing thermodynamically unfavorable processes.

3.1. Oxidation State Modulation in Metallaphotoredox Catalysis

Palladium readily performs rigid two-electron processes in Pd0/PdII systems that are responsible for carbon–heteroatom bond formations in Buchwald–Hartwig type reactions.[1a,1e] The low electronegativity of Ni enables facile oxidative addition into carbon–halide bonds, but reductive elimination is difficult.[39] While thermolysis of NiII oxametallacycles resulted in β-hydride elimination of undesired carbonyl compounds, oxidation to NiIII complexes through single electron transfer (SET) with stoichiometric oxidants was shown to induce reductive elimination of C–O coupling products.[40] Combination of nickel’s electronic versatility with photoredox catalysis rather than stoichiometric redox reagents afforded more efficient SET processes.[10c] Oxidative addition of an aryl halide (12) to Ni0 followed by ligand exchange with a suitable nucleophile (48) results in thermodynamically stable NiII complexes (94). Oxidation of 94 to a NiIII intermediate (95) by reductive quenching of PC* was proposed to trigger reductive elimination of the desired product (49, Scheme 15). Single electron oxidation of PCred restores PC and Ni0 (92) for the next turnover.

![Scheme 14. Amidation of heteroarenes through an energy transfer process.](image-url)

![Scheme 15. Nickel metallaphotoredox catalysis by oxidation state modulation.](image-url)
the macrocyclization of peptides. Replacement of the expensive iridium PCs by recyclable, heterogeneous semiconductors was feasible.

A similar mechanistic scenario is likely responsible for the coupling of 12-Br with primary and secondary amines (Scheme 17). In contrast to the C–O bond formation discussed above, unligated NiII salts were used as common ligands, such as dtbbpy (4,4'-di-tert-butyl-2,2'-bipyridine), reduced the reaction rate significantly. Computational studies indicated that the amine substrate itself acts as a ligand for the photocatalytically generated, active Ni0 species.

Reductive elimination of carbon–heteroatom coupling products from nickel complexes was also proposed to proceed through addition of a photochemically generated radical to NiII intermediates that is re-reduced to Ni1 before oxidative addition of 12 (Scheme 18, B). All three mechanistic scenarios for the amination of aryl halides (Scheme 15 and Scheme 18) are plausible and these pathways may even operate simultaneously. In fact, for the coupling of aryl iodides (12-I) with anilines or aryl azides (Scheme 19, A), the formation of amine radicals was supported by fluorescence quenching studies.

Thiyl radicals were generated from thiols, through reductive quenching of PC*, for C–S cross-couplings with aryl iodides or bromoalkynes in presence of a nickel catalyst. The thioetherification of aryl iodides (12-I) works well with aryl bromides. Similarly, sulfur- and phosphorus-centered radicals can be generated for the synthesis of sulfones and phosphine oxides respectively (Scheme 19, D & E).

Combining photoredox and copper catalysis enabled carbon–heteroatom cross-coupling reactions by generating alkyl radicals from redox-active esters (Scheme 20). Addition of C-centered radical that generates thyl radicals through intermolecular H-atom abstraction (Scheme 19, C). This methodology works well with aryl bromides (12-Br). Similarly, sulfur- and phosphorus-centered radicals can be generated for the synthesis of sulfones and phosphine oxides respectively (Scheme 19, D & E).

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to a copper–amido complex and the following SET oxidation by PC$^{\text{ox}}$ triggers reductive elimination of the desired product (115).

Following this strategy, anilines, amides, and sulfonamides were coupled with alkyl radicals derived from the corresponding N-hydroxyphthalimide esters (116, Scheme 21, A)[50a] or dialkyl idomesitylene dicarboxylates.[50c] The use of benzophenone imines (120) as nucleophiles resulted in 121 which was subsequently hydrolyzed, furnishing primary amines (66) in good to excellent yields (Scheme 21, B).[50b] A similar mechanistic concept was reported for the formation of aryl alkyl ethers by coupling phenols with alkyl radicals generated from 116 (Scheme 21, C).[51]

Scheme 21. Synthesis of amines (A), imines (B) and alkyl aryl ethers (C) by copper metallaphotoredox catalysis. CuX = CuBr (20 mol-%), Cu(MeCN)PF$_6$ (50 mol-%), or CuCl (20 mol-%); ester/nucleophile stoichiometry depends on the type of ester.

The copper catalyzed cross-coupling of aryl boronic acids and alcohols (Chan–Evans–Lam coupling) requires aerobic conditions to access the key Cu$^{\text{III}}$ intermediate through oxidation with triplet oxygen.[52] Kobayashi and co-workers showed that efficiency problems resulting from the limited solubility of O$_2$ in organic solvents can be addressed by combing copper and photoredox catalysis (Scheme 22).[53] This strategy also enabled the use of electron-deficient aryl boronic acids, which are troublesome under traditional conditions.

Scheme 22. Synthesis of diarylamines by copper metallaphotoredox catalysis.

3.2. Photoredox and Proton Reduction Catalysis

Most of the reactions involving single electron oxidation of arenes (33) to the corresponding radical cations (50) discussed in section 2.2 require a sacrificial single electron acceptor (O$_2$ or persulfates). These terminal oxidants can be omitted when photoredox catalysis is combined with cobalt catalysis.[54] In a seminal report, Lei showed that the N-arylation of azoles, which was originally carried out using O$_2$ in presence of TEMPO (Scheme 8),[31a] can be carried out with catalytic amounts of Co(dmgH)$_2$Cl$_2$ (dmg = dimethylglyoxime) to avoid not only the stoichiometric oxidant, but also formation of side products and catalyst degradation due to reactive oxygen species (Scheme 23).[54a] In the proposed catalytic cycle, reductive quenching of the acridinium photocatalyst affords the radical cation 50, that reacts with the azole (51) to form 53. The Co$^{\text{III}}$ catalyst is reduced to CoI by two consecutive single electron transfer events, one to regenerate the PC and one to afford cation 127 that, upon deprotonation, gives the desired amination product. The reduced cobalt catalyst is protonated to form a Co$^{\text{II}}$H species, which subsequently reacts with another proton to release H$_2$ and regenerate the cobalt catalyst.

This dual catalytic CDC approach was subsequently applied to the coupling of azoles (78) and alcohols (97) for the etherification of arenes.[54c] Stern–Volmer studies showed that both starting materials quench PC$^*$ and generation of both radical cations might be responsible for the C–N
3.3. Energy Transfer to Metal Catalysts

Activation of NiII complexes to induce reductive elimination by energy transfer rather than SET oxidation was proposed for the coupling of aryl bromides and carboxylic acids yielding the respective esters (136, Scheme 25). Key to the success was the use of Ir(ppy)3 as PC which has high triplet energy in its excited state. Further, Ir(ppy)3* is a weak SET oxidant, which avoids decarboxylative C–C cross-couplings. More recently, the same transformation was realized using organic sensitizers and heterogeneous photocatalysts, such as graphitic carbon nitrides and lead halide perovskites. A similar mechanistic scenario was proposed for the N-arylation of sulfonamides, sulfoximines, and carbamates.

Energy transfer to copper intermediates was reported to be responsible for the light-mediated coupling of carbazoles (139) with aryl iodides (12-I, Scheme 26). Coordination of amide results in a Cu complex that is promoted to an excited state by PC*. Electron transfer from 144 to 12-I generates an aryl radical (4) that reacts with the CuI intermediate (145) to afford the desired arylamines (34).

4. Photocatalyst-Free Carbon–Heteroatom Coupling Reactions

Photocatalysts are not always necessary for reactions involving visible light as an energy source. Photolabile starting materials,
the formation of electron donor-acceptor complexes (EDA), or intermediates that absorb visible light can also trigger photochemical carbon–heteroatom bond formations.

4.1. Photolabile Starting Materials

The direct enantioselective α-amination of aldehydes (147, Scheme 27) was realized by generating N-centered radicals (151) from dinitrophenylsulfonyloxy (ODNS) substituted amides (148) upon irradiation with UV light in presence of an imidazolidinone catalyst (150).[64] The carbamoyl radical (151) can react with an enamine intermediate (152) formed from the condensation of 150 and 147 which, after SET oxidation, eliminates the desired product. A variety of protected amines and aldehydes were successfully coupled with high enantiomeric excess.

Visible light was used to form aryl radicals (4) form azosulfones (155) for photocatalyst-free C-S and C-B bond formation (Scheme 28, A).[65] These protocols are variations of the reactions discussed in section 2.1 involving diazonium salts (1, Scheme 1 & Scheme 2). In fact, 155 were synthesized from the corresponding diazonium salts (1) using sodium methanesulfinate. Similarly, aryl radicals can also be accessed through photoinduced cleavage of aryl halides (12) for C-P bond formation (Scheme 28, B).[66] While visible light (405 nm) was suitable for the activation of aryl iodides, chlorides and bromides required photons with higher energy (254 nm) as well as tetra- butylammonium iodide (TBAI) as additive.

4.2. Electron Donor-Acceptor Complexes

Miyake and co-workers showed that aryl halides (12) and thio phenolates form an EDA complex with an absorption maximum of 306 nm. If the concentration of this EDA complex is high, visible light absorption up to 515 nm was observed which enabled the synthesis of diaryl sulfides (158) using visible light (Scheme 29).[67] The choice of the base was crucial and the best results were obtained with Cs₂CO₃ and K₂CO₃, whereas Na₂CO₃ gave only low yields under otherwise identical conditions. The same catalytic system also works for the C–S coupling of aryl halides and sulfinate salts.[68]

N-ethoxy-2-methylpyridinium (161) is a good electron acceptor and was shown to form EDA complexes that absorb above 400 nm with electron donors such as arylamines (133).[70] SET results in a nitrogen centered radical that reacts with diarylphosphanes to form 160 (Scheme 31, A).[70] Chloropyridines (162) were activated towards C–P couplings by formation of an EDA complex with potassium tert-butoxide (Scheme 31, B).[71] Blue light irradiation induced the formation of two radical species. The tert-butoxy radical activates phos-

Scheme 27. Enantioselective α-amination by combining a photolabile starting material with organocatalysis.

Scheme 28. Synthesis of aryl sulfides (A) and phosphonates (B) by photochemical generation of aryl radicals without photocatalysts.

Scheme 29. Thioetherification via EDA complex formation.

The arylation of phosphites (57) can be significantly accelerated using visible light, as an EDA complex is proposed to result from the combination of diarylodonium triflates (159) and 57 (Scheme 30).[69] The EDA complex could, however, not be detected by UV/Vis or NMR spectroscopy as it is presumably labile and forms only in low concentration. EPR analysis in the presence of a spin trap and 405 nm irradiation showed two spin adducts which were assigned as the phenyl radical and the phosphorus radical anion, indirectly proving the existence of the EDA complex.

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Scheme 30. Arylation of phosphites via EDA complex formation.

Scheme 31. α-Phosphorylation of arylamines (A) and phosphorylation of heteroaryl halides (B) via EDA complex formation.

4.3. Photoinduced Metal Catalysis

Analysis of the mechanism of the copper-catalyzed Ullmann-type C–N bond formation unveiled a light-mediated coupling protocol between carbazoles (139) and aryl as well as alkyl halides (165, Scheme 32).\textsuperscript{[72]} Lithiation of 139, followed by transmetalation of 141 by the copper catalyst generates a Cu\textsuperscript{II} carbazolide that absorbs UV-light. A photoinduced electron transfer from 169 to the iodide 165-I\textsuperscript{−}, results in a Cu\textsuperscript{II} species and radical 171. The reaction of the alkyl radical (171) with the Cu\textsuperscript{II} intermediate (170) affords the desired C–N bond. The scope of this reaction was extended with regard to both coupling partners.\textsuperscript{[73]}

Using a chiral ligand, the enantioconvergent coupling of carbazoles (139) and racemic tertiary alkyl chlorides (172) was achieved (Scheme 33).\textsuperscript{[74]} Remarkably, the chiral phosphine ligand (174) not only enabled asymmetric copper-catalyzed cross-couplings but also allowed the use of visible light instead of UV irradiation.

Doyle and co-workers carefully studied the photophysical properties of Ni\textsuperscript{II} aryl halide complexes, that are proposed intermediates in nickel metallaphotoredox catalyzed reactions.\textsuperscript{[75]} The UV/Vis spectrum of 175 exhibits an absorption band in the visible region which is attributed to a metal-to-ligand charge transfer transition (MLCT). A photoinduced electron transfer (PET) between the excited 3MLCT complex 176 and the ground state complex 175 results in disproportionation to Ni\textsuperscript{I} (177) and Ni\textsuperscript{III} (178, Scheme 34). Based on their findings, the authors showed that a combination of Ni(COD)\textsubscript{2} (COD = 1,5-cyclooctadiene) and dtbbpy is catalytically active towards the cross-coupling of alcohols and aryl halides using blue light and proposed that the photogenerated Ni\textsuperscript{I} complex (177) is the catalytically active species.

Scheme 32. Coupling of alkyl halides and carbazoles induced by photoexcitation of a copper complex.

Scheme 33. Enantioselective coupling of tertiary alkyl chlorides and carbazoles by photoexcitation of copper complexes.

Scheme 34. Photoactivation and disproportionation of a nickel aryl halide complex.
A photocatalyst-free amination through direct sensitization of nickel complexes with UV-light was also reported (Scheme 35). The coupling of aryl halides (12) with a series of primary and secondary amines (34) was proposed to start by coordination of two to three amine molecules to NiBr$_2$·H$_2$O. The resulting Ni$^{II}$Br$_2$(NHR$_2$)$_n$ complexes were found to absorb visible light (550 nm for $n = 2$, 430 nm for $n = 3$) enabling photoinduced amine-to-metal electron transfer that generates aminyl radical species (183, Scheme 35). The C–N coupling likely results from direct reaction of 183 with 12, followed by addition of a bromine radical to 182. Alternatively, oxidative addition of the aryl halide to Ni$^{III}$Br(NH$_2$)$_2$ can generate a Ni$^{III}$ complex (184). This intermediate can react with the aminyl radical to form the desired C–N coupling product.

Scheme 35. Aryl amination by photoexcitation of nickel complexes.

5. Summary and Outlook

Light is a sustainable and traceless reagent for chemical transformations that can be used by various strategies. Visible light irradiation of a photocatalyst can trigger the plethora of carbon-heteroatom bond formations by generating reactive intermediate from otherwise unreactive starting materials or reagents. Thermodynamically prohibited processes in transition metal catalysis can be triggered by using the combination with photochemistry. The vast majority of visible light-mediated protocols is currently carried out in the presence of a suitable photocatalyst. The recent development of photocatalyst-free approaches, especially via EDA complexes and photoinduced metal catalysis is promising but is still in its infancy.

The examples listed in this review showcase how applying photochemistry to improve pre-existing techniques often resulted in discovering completely new reactivities. This partially explains why photochemistry has attracted large interest in the last decade and will certainly play a key role in the future of organic synthesis.
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