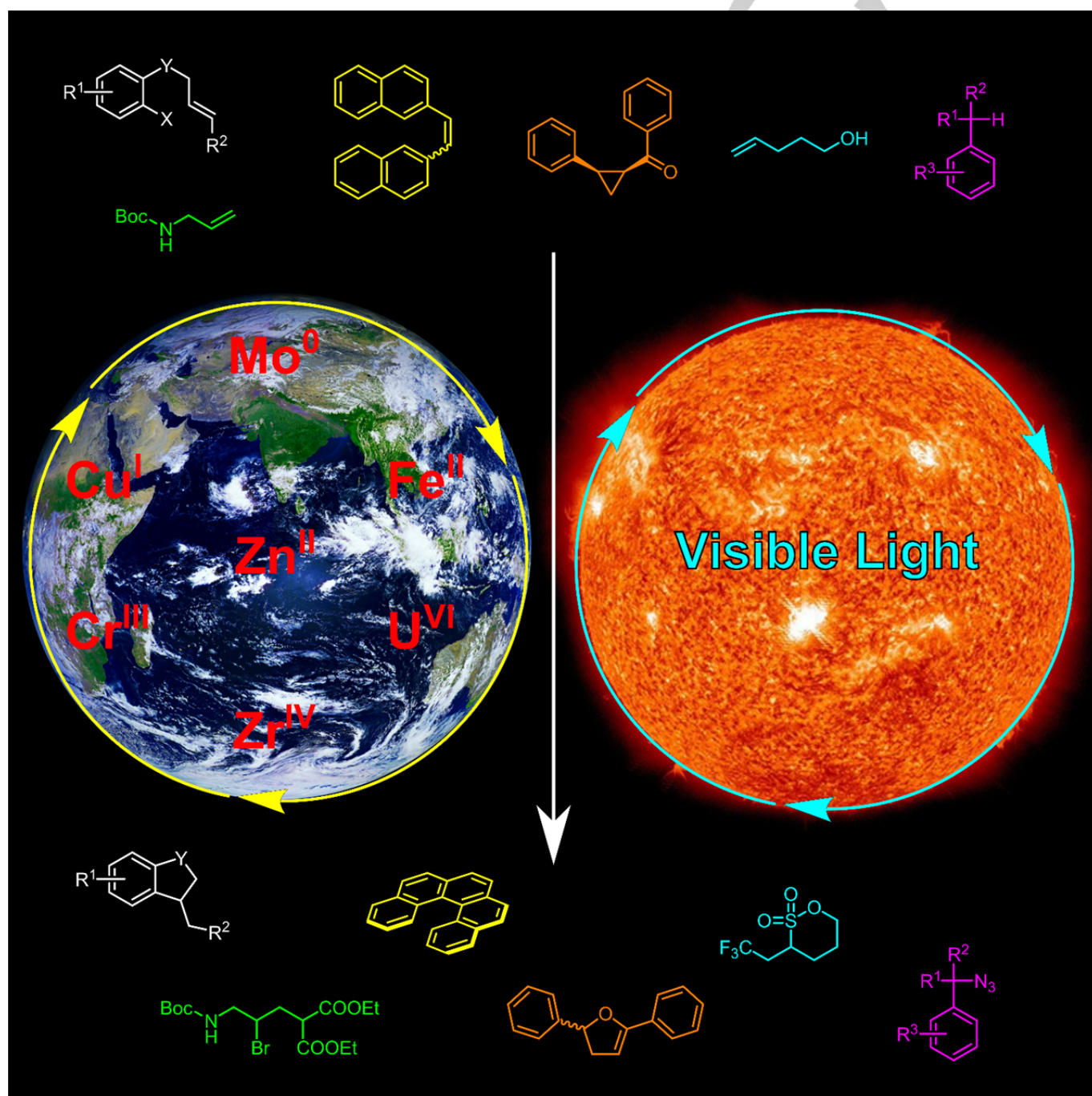# Photoredox Catalysis with Metal Complexes Made from Earth-Abundant Elements

Christopher B. Larsen,[a] and Oliver S. Wenger*[a]

Abstract: Photoredox chemistry with metal complexes as sensitizers and catalysts frequently relies on precious elements such as ruthenium or iridium. Over the past 5 years, important progress towards the use of complexes made from earth-abundant elements in photoredox catalysis has been made. This review summarizes the advances made with photoactive Cr^{III}, Fe^{II}, Cu^{I}, Zn^{II}, Zr^{IV}, Mo^{0} and U^{VI} complexes in the context of synthetic organic photoredox chemistry using visible light as an energy input. Mechanistic considerations are combined with discussions of reaction types and scopes. Perspectives for the future of the field are discussed against the background of recent significant developments of new photoactive metal complexes made from earth-abundant elements.

1. Introduction

Many complexes with the d^{6} electron configuration made from Ru^{II}, Re^{I}, Os^{II} and Ir^{III} exhibit comparatively long-lived electronically excited states in which the redox properties are drastically altered relative to the respective electronic ground states.[1] This behavior forms the basis for their application as photosensitizers in various contexts, for example in solar cells or photoredox catalysis. Particularly Ru^{II} polypyridine and cyclometalated Ir^{III} complexes have attracted much attention as light-absorbers and catalysts for a range of photoredox transformations, sometimes in combination with secondary catalytic cycles.[2]

There is a long-standing interest in replacing the precious metals in photoactive coordination complexes by more earth abundant elements,[3] but this is difficult because excited-state deactivation in first-row transition metal complexes is often extremely rapid. For example, in Fe^{II} polypyridine complexes the lowest MLCT excited state depopulates typically on the sub-picosecond timescale via lower lying d-d excited states.[4] On the other hand, there are well-known cases of 3d metal complexes with long-lived excited states, for example Cr^{III} polypyridines,[5] or Cu^{I} diimines.[6] However, with very few exceptions[7] they have only been used for photoredox catalysis in the past 5 years. Regarding other relatively earth-abundant metal elements, very recent developments made the use of Zr^{IV} and Mo^{0} for photoredox catalysis possible.[8] It is worth noting that organic dyes represent another alternative to precious metal complexes, which have been extensively reviewed elsewhere and are outside the remit of this review.[9]

This review is divided into individual sections according to transition metal elements, and it summarizes roughly 50 original studies from the past 5 years by discussing the types of reactions that were performed and by considering their mechanisms and substrate scopes. Cu^{I} complexes represent the most thoroughly investigated class of substances considered

here, and there have been 3 prior reviews of photoredox catalysis with this particular focus.[10] However, the present review is thematically broader with respect to the different Cu^{I} and non-Cu^{I} photoredox studies considered. It focuses on organic transformations that require excitation of (usually) well defined transition metal complexes that act as light-absorbers and photoredox catalysts. Polymerization initiation processes, UV-light induced click reactions, and reactions relying on the photodriven formation of catalytically active partner complexes in their electronic ground states are usually not considered.

2. Principles

Photoredox behavior arises due to excited-state redox properties being drastically altered from the corresponding ground state redox properties.[1] This can be understood at the most basic level by considering for example a metal-to-ligand charge-transfer excited state (Figure 1). In the ground state, the metal center can be oxidized (Figure 1, process i) and the ligand reduced (process ii). In the MLCT excited state, the metal center is already formally oxidized and the ligand formally reduced. Therefore, so long as the excited state is sufficiently long-lived, the metal center can more readily be reduced than in the ground state (Figure 1, process iii) and the ligand is easier to oxidize than in the ground state. (Figure 1, process iv).

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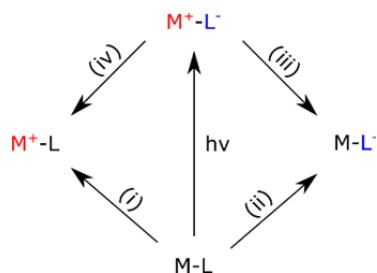   E-mail: oliver.wenger@unibas.ch

Christopher B. Larsen graduated with a BSc(Hons) – first class degree in chemistry under the supervision of Nigel T. Lucas at the University of Otago (New Zealand) in 2011. He then graduated with a Ph. D. degree under the joint supervision of Keith C. Gordon and Nigel T. Lucas at the University of Otago in 2016, following which he started a postdoctoral fellowship in the group of Oliver S. Wenger at the University of Basel (Switzerland).

Oliver S. Wenger received a Ph. D. degree after work with Hans U. Güdel at the University of Bern (Switzerland) in 2002. Following postdoctoral stays with Harry B. Gray at Caltech, and with Jean-Pierre Sauvage in Strasbourg, he started independent research as an assistant professor at the University of Geneva in 2006. In 2009, he became W2 professor (with tenure) at Georg-August-Universität Göttingen (Germany), and in 2012 he moved with his group to the University of Basel (Switzerland).

Figure 1. Example of redox processes of relevance to an MLCT (M$^+$-L$^-$) excited state. (i) metal oxidation from ground state; (ii) ligand reduction from ground state; (iii) metal reduction from excited state; (iv) ligand oxidation from excited state.

The magnitude by which the redox properties are altered between ground and excited state may be estimated using the Rehm-Weller equations:[11]

$$E_{1/2}(C^+/C^*) \approx E_{1/2}(C^+/C) - E_{00}$$
$$E_{1/2}(C^*/C^-) \approx E_{1/2}(C/C^-) + E_{00}$$

Where $E_{1/2}(C^+/C^*)$ and $E_{1/2}(C^*/C^-)$ are the excited state oxidation and reduction potentials, respectively, $E_{1/2}(C^+/C)$ and $E_{1/2}(C/C^-)$ the ground state oxidation and reduction potentials, respectively. E_{00} is the energy of the electronic origin for the excited state (the difference in energy between the 0th vibrational levels of the ground and excited states). Pragmatically, E_{00} is often estimated in one of two ways: (1) the intersection between excitation and emission bands; (2) the high-energy onset of the emission band at low temperature.

Precious metal complexes with the d^6 electron configuration typically exhibit MLCT excited states, and the underlying photophysical processes of relevance to photoredox catalysis for this class of complexes have been extensively reviewed elsewhere,[2a, 2b] and will not be revisited here.

When moving from precious metal complexes to more earth abundant analogues, one must start to take into consideration other types of excited states. The four key types of excited state relevant to metal complexes are: (1) d-d states, also known as ligand-field (LF) or metal-centered (MC) states, whereupon an electron is excited from an occupied metal d orbital to an unoccupied metal d orbital; (2) metal-to-ligand charge transfer (MLCT) states, whereupon and electron is excited from an occupied metal d orbital to an unoccupied π* orbital on the ligand; (3) ligand-to-metal charge-transfer (LMCT) states, whereupon an electron is excited from an occupied ligand-based orbital to an unoccupied metal d orbital; (4) π-π* states, whereupon an electron is excited from an occupied ligand π orbital to an unoccupied ligand π* orbital. An additional excited state that can be formed when the complex bears multiple ligands is the ligand-to-ligand charge-transfer (LLCT) state, whereupon an electron is excited from an occupied π orbital on one ligand to an unoccupied π* orbital on another.

Charge-transfer excited states (MLCT, LMCT and LLCT) are particular desirable for photoredox applications, as the charges are localized on separate parts of the complex, extending excited-state lifetimes and improving the efficiency of single electron transfer (SET). π-π* and d-d excited states typically have large wavefunction overlap with the ground state and therefore often extremely rapid excited-state relaxation occurs, lowering the efficiency of SET. It is important to note that there are exceptions for both of these classes of excited states – for example, the ^{2}E state for d^3 metal complexes is a 'spin-flip' excited state, and therefore has very long excited state lifetimes.[5a]

The earth abundant metals in their corresponding oxidation states of relevance to this review, and their corresponding electron configurations are presented in Table 1. All complexes discussed herein have the metal electron configuration as either d^0, d^3, d^6 (low spin) or d^{10}. d^0 complexes have the d orbitals completely unoccupied, precluding d-d and MLCT states as a possibility. Conversely, d^{10} complexes have the d orbitals fully occupied, precluding d-d and LMCT excited states. d^3 complexes are able to possess all four excited states, as are d^6.

Table 1. Summary of the earth abundant metals and their corresponding oxidation states of relevance to this review, their electronic configurations and preferred coordination geometries.

metal and oxidation state	electron configuration	idealized symmetry / point group
Cr^{III}	3d^3	O$_h$
Fe^{II}	3d^6	O$_h$
Cu^I	3d^{10}	T$_d$
Zn^{II}	3d^{10}	T$_d$
Zr^{IV}	4d^0	O$_h$
Mo^0	4d^6	O$_h$
U^{VI}	6d^0	D$_{\infty h}$

3. Chromium^{III}
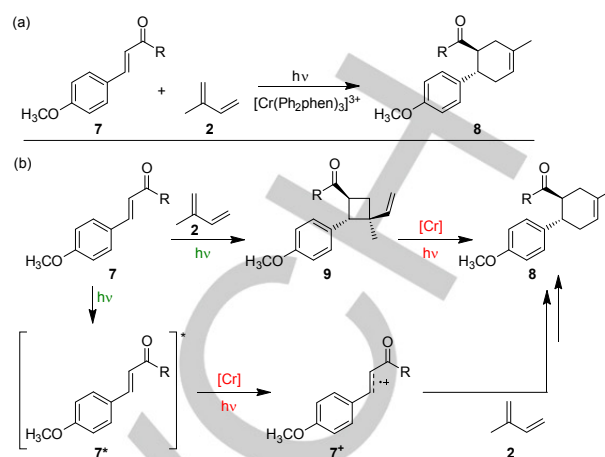
Cr^{III} polypyridine complexes have long been known as luminophores with favorable electrochemical properties,[5] but their application as photoredox catalysts in synthetic organic chemistry is yet very little explored. Recently, Shores, Ferreira and coworkers discovered that Diels-Alder reactions between electron-rich styrenes (**1**, **4**) and isoprene (**2**) or 2,3-dimethyl-1,3-butadiene (**5**) (Scheme 1a/b) can be performed at room temperature under irradiation with 300-419 nm light using the [Cr(Ph$_2$phen)$_3$]$^{3+}$ complex as a catalyst (Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline).[12]
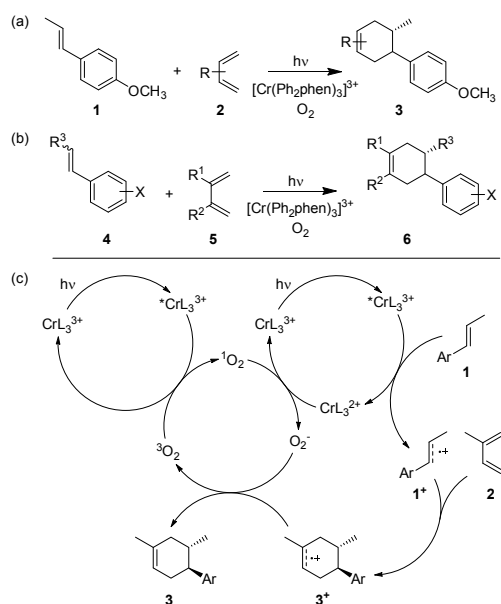
Scheme 1. (a, b) Diels-Alder reactions with electron-rich styrenes catalyzed by photoexcitation of a Cr^{III} polypyridine complex in presence of oxygen. (c) Proposed mechanism involving both photoinduced SET as well as energy transfer to O_2.[12-13]

Scheme 2. (a) Light-driven [4+2] cycloaddition reactions with electron-deficient dienophiles and a Cr^{III} photoredox catalyst. (b) Possible mechanistic pathways involving multiple photo-excitation events.[15]

Detailed mechanistic studies indicated that oxygen seems to interfere twice in the catalytic cycle of the overall cross-cycloaddition (Scheme 1c).[13] Due to its high oxidizing power (E_{ox} = 1.40 V vs. SCE), the photoexcited Cr^{III} complex can readily convert electron-rich styrenes (**1**) to their radical cationic forms (**1$^+$**), which can then form a cycloadduct radical cation (**3$^+$**) with dienes (**2**). The reductant needed for the conversion of this cycloadduct radical cation to the final Diels-Alder product is most likely superoxide anion, which is only accessible via primary formation of $^1O_2$ and subsequent reaction of $^1O_2$ with the reduced catalyst resulting from the initial photoinduced SET step with styrene. This is an unusual photoredox catalysis cycle, because it requires the input of two photons per overall turnover. It benefits from the long ^2E excited-state lifetime of the Cr^{III} complex (τ = 13 µs), which permits the accumulation of significant concentrations of $^1O_2$ (τ = 40 µs).[13] A radical chain mechanism, as observed in analogous cycloaddition reactions catalyzed by a Ru-based sensitizer,[14] seems to play a minor role with the $[Cr(Ph_2phen)_3]^{3+}$ complex.

Under photo-irradiation, the same Cr^{III} complex is also able to mediate [4+2] cycloaddition reactions with electron-deficient dienophiles (**7**) (Scheme 2a).[15] In these cases, direct oxidation of the dienophile (**7**) by the photoexcited Cr^{III} complex is not thermodynamically viable, and hence the reaction mechanism must be fundamentally different from the one outlined above. One possibility is direct photoexcitation of the dienophile (**7**), followed by [2+2] cycloaddition with the diene (**2**) to result in a vinylcyclobutane intermediate (**9**) (Scheme 2b). The latter can be oxidized more readily by the photoexcited Cr^{III} complex than any of the substrates, and in its one-electron oxidized form it could undergo rearrangement to the final product (**8**). Another mechanistic possibility that was discussed as a significant contributor to the overall conversion involves the direct reaction of photoexcited dienophile (**7***) (τ = 20-30 ns) with the photoexcited Cr^{III} complex to form a radical cation (**7$^+$**) that can subsequently react with the diene (**2**).[15] The reaction of two photoexcited species with one another is certainly unusual, but in the present case one of them has a very long lifetime (τ = 13 µs). The observation of a nonlinear dependency of the overall rate of reactivity on the light intensity is in line with a multi-photon process. Oxygen was found to be beneficial to the overall reaction progress, but unlike in the reactions from Scheme 1 it does not seem to be indispensable.
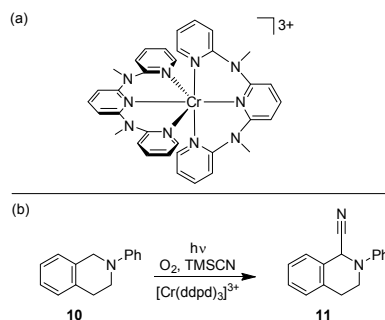
Scheme 3. (a) Molecular structure of the [Cr(ddpd)₃]³⁺ complex. [16] (b) Formation of an α-aminonitrile from a tertiary amine via ¹O₂ generation sensitized by the [Cr(ddpd)₃]³⁺ complex.

In a very recent study, Heinze, Opatz, Lochbrunner, and coworkers demonstrated that a newly developed Cr^{III} polypryidine complex enables visible light-induced cyanation of amines via ¹O₂ generation (Scheme 3).[16] Owing to particularly favorable bite angles and its comparatively electron-rich nature, the ddpd (*N,N'*-dimethyl-*N,N'*-dipyridine-2-ylpyridine-2,6-diamine) ligand permits the synthesis of a highly photostable homoleptic Cr^{III} complex with a large energy gap between the ^2E_g and $^4T_{2g}$ states, leading to a spectacularly long ^2E excited-state lifetime (898 μs).[17] This large gap impedes back intersystem crossing from the ^2E_g to the $^4T_{2g}$ state, and consequently, energy transfer from the ^2E_g state (rather than electron transfer from the short-lived $^4T_{2g}$ state) is the dominant excited-state deactivation pathway in presence of oxygen. ¹O₂ then presumably forms a charge-transfer complex with the amine substrates, and subsequent hydride transfer could lead to hydroperoxide and an iminium ion that can be trapped by cyanide (from trimethylsilylcyanide). Selective α-C-H cyanation of 5 different amine substrates (for example compound **10**) by ¹O₂ to yield α-aminonitriles has been demonstrated with Cr(ddpd)₃³⁺.[16]

4. Iron^{II}

The MLCT excited states of [Fe(bpy)₃]²⁺ depopulate to the metal-centered $^5T_2$ state within ~150 fs, and after 2-3 ps vibrational cooling of that state is complete.[4b] The $^5T_2$ state then decays to the ground state within ~650 ps, which at first glance seems too short in order to perform photoredox chemistry.[4b] Nevertheless, Cozzi, Ceroni and coworkers recently reported that [Fe(bpy)₃]²⁺ in presence of an organocatalyst can enable photoredox alkylation of aldehydes with various α-bromo carbonyl compounds.[18] Building on related work with Ru and Ir based photosensitizers,[19] they explored the reaction between hydrocinnamaldehyde (**12**) and dimethyl bromomalonate (**13**) to the asymmetric alkylation product **14** in presence of organocatalyst **15**, [Fe(bpy)₃]²⁺, and lutidine (Scheme 4a). Remarkably, product yields and enantiomeric excess were comparable to what could be achieved using [Ru(bpy)₃]²⁺. The reaction was performed with various aldehydes and bromo derivatives, and it tolerated various functional groups. Moreover, the same reaction conditions could be used for the preparation of enantio-enriched lactones via photoredox alkylation of aldehydes. For example, the addition of bromo-ester **16** to hydrocinnamaldehyde (**12**) afforded lactone **17** (Scheme 4b).
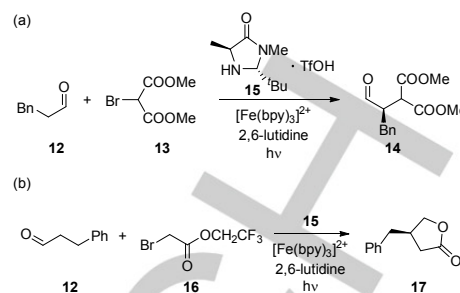
Scheme 4. Enantioselective photoredox alkylation of aldehydes with various α-bromo carbonyl compounds using an Fe^{II} photosensitizer and an organocatalyst.[18]

In mechanistic studies, spin trap experiments with N-*tert*-butyl-α-phenylnitrone provided EPR evidence for an adduct formed with the malonate alkyl radical, indicating that photoirradiation of the reaction mixture containing [Fe(bpy)₃]²⁺ does indeed lead to the formation of radicals. Furthermore, the reaction was shut down in presence of TEMPO. However, once initiated, the reaction was observed to proceed also when the light was switched off, indicating that a radical chain mechanism is operative. Thus, the role of the [Fe(bpy)₃]²⁺ photosensitizer seems to be principally that of a radical chain initiator.

The Lalevée group has further demonstrated that Fe^{II} complexes of electronically-tuned pyridyl-imines show promise, when combined with suitable additives, as photoinitiators for free radical polymerization and free radical-promoted cationic polymerization reactions.[20]

The Collins group recently reported on the formation of carbazoles from triarylamines with [Fe(phen)₃]²⁺ as a catalyst using flow chemistry and O₂ as an oxidant.[21] Currently it is unclear how this works, and it was noted that some mechanism other than photoredox catalysis via MLCT must be promoting that transformation, yet it was speculated that superoxide is involved. Light-driven triarylamine to carbazole oxidation will be discussed in more detail below.

Recently, *N*-heterocyclic carbene complexes of Fe^{II} have also been investigated as photosensitizers for light-induced water reduction, using colloidal Pt as catalysts. Short MLCT excited state lifetimes seem to impede water reduction in a manner that is as efficient as with a cyclometalated Ir^{III} complex under identical conditions.[22]

5. Copper^{I}

Bis(phenanthroline)copper^{I} complexes have long been known to possess long-lived ³MLCT excited states, and an early study by the Sauvage group already made use of a Cu^{I} complex for photoredox catalysis.[7a] Specifically, *p*-nitrobenzyl bromide was converted to bis(*p*-nitro)bibenzyl with a turnover number (TON) of 30 in presence of triethylamine in de-aerated CH₂Cl₂. In 2012, the Reiser group initiated a revival of Cu^{I} photoredox chemistry with a report on C-C bond forming atom transfer radical addition (ATRA) reactions,[23] and since then a considerable number of

different works on photoredox catalysis with Cu[I] have appeared, including 3 short reviews.[10]
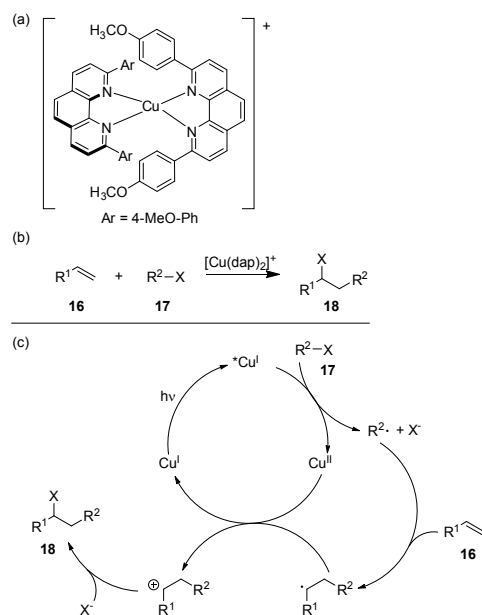
Scheme 5. (a) The [Cu(dap)$_2$]$^+$ complex (dap = 2,9-dianisyl-1,10-phenanthroline.[23-24] (b) ATRA reactions between alkenes and organobromo or organoiodo compounds.[23] (c) Reaction mechanism.

The [Cu(dap)$_2$]$^+$ (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline) complex (Scheme 5a) is a slightly stronger photoreductant than [Ru(bpy)$_3$]$^{2+}$ (-1.43 V vs. SCE) with a ^{3}MLCT lifetime of 270 ns in de-aerated CH$_2$Cl$_2$ at 25 °C.[6b, 23] In degassed solutions, irradiation of this complex at 530 nm leads to efficient ATRA reactions between a variety of alkenes (**18**) and organohalogen compounds (**19**) (Scheme 5b).[23] The reaction mechanism (Scheme 5c) is thought to involve oxidative excited-state quenching by the organohalogen compound (**19**), followed by addition of the resulting organic radical to the alkene (**18**). The neutral addition product (**21·**) is then oxidized by Cu[II] to close the catalytic cycle for the sensitizer, and to result in a cation (**21$^+$**) that can be attacked in nucleophilic manner by the halogenide anion (X$^-$) from the initial photoinduced reaction step, thereby forming the final product (**20**). These ATRA reactions are redox neutral and therefore no sacrificial reagent is required.

The same sensitizer was employed for the light-driven allylation of α-chloro- and α-bromoketones.[23] With allyltri-*n*-butyltin as a substrate this reaction proceeded in good to excellent yields in ~15 different cases, but for allyltrimethylsilane only CBr$_4$ was a suitable reaction partner.

In subsequent studies by the same group, the scope of [Cu(dap)$_2$]$^+$ mediated ATRA was extended to reactions between benzyl halides and styrenes or silyl enol ethers, but this was limited to electron-deficient benzyl halides due to lack of more reducing power by the photoexcited Cu[I] complex.[25] The photodriven ATRA reactions with 2-nitrobenzyl bromide are

interesting because they provide rapid access to tetrahydroquinolines.
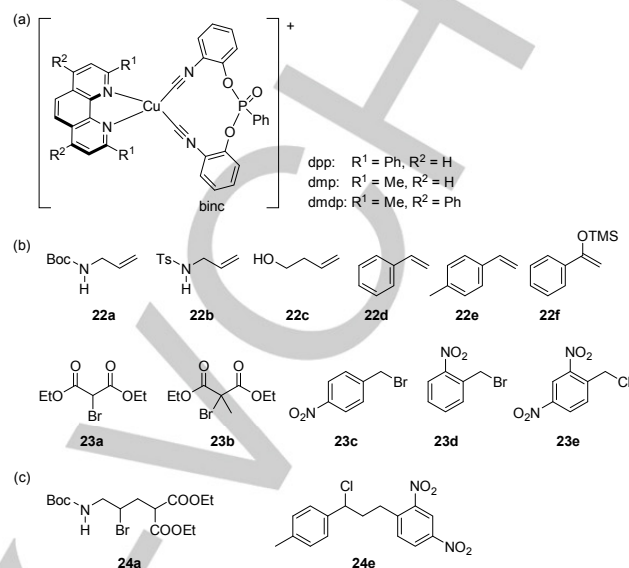
Scheme 6. (a) [Cu(dpp)(binc)]$^+$ complex with a chelating diisocyanide ligand (binc) for ATRA reactions. (b) Substrate scope with regard to alkenes (**20a** - **22f**) and ATRA reagents (**23a** - **23e**). (c) Exemplary ATRA products resulting from the reaction between **22a** and **23a** (**24a**) and from **22e** and **23e** (**24e**).[26]

Heteroleptic Cu[I] phenanthroline complexes with sterically demanding partner chelates represented a substantial development of the photophysics of emissive Cu[I] complexes, because this compound class exhibits much enhanced ^{3}MLCT lifetimes and luminescence quantum yields when compared to [Cu(dap)$_2$]$^+$ and its homoleptic congeners made from other α-diimine ligands.[27] Building on this knowledge and on prior studies of Cu[I] isocyanides,[28] the Reiser group recently developed Cu[I] complexes with one phenanthroline and one chelating diisocyanide ligand for further ATRA and allylation reactions.[26] The [Cu(dpp)(binc)]$^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline, binc = bis(2-isocyanophenyl)phenylphosphonate) complex (Scheme 6a) is a stronger excited state reductant than [Cu(dap)$_2$]$^+$ (-1.88 V vs. SCE instead of -1.43 V vs. SCE), and it exhibits a ^{3}MLCT lifetime of 17 μs in PMMA at room temperature, compared to 560 ns for [Cu(dap)$_2$]$^+$ under identical conditions. Among a series of heteroleptic complexes with binc and different phenanthroline ligands (Scheme 6a), [Cu(dpp)(binc)]$^+$ turned out to be the most active for photoredox catalysis of ATRA reactions between Boc-protected allylamine and diethyl bromomalonate. The scope of ATRA reactions (Scheme 6b) mediated by [Cu(dpp)(binc)]$^+$ encompassed different protected allylamines (**22a**, **22b**), but-3-en-1-ol (**22c**), styrenes (**22d**, **22e**), and a silylenol ether (**22f**), whereas diethyl bromomalonates (**23a**, **23b**) and various nitrobenzyl halides (**23c**-**23e**) served as ATRA reagents. The ATRA products of the reaction between **22a** and **23a**, as well as from the reaction between **22e** and **23e** are shown in Scheme 6c as representative examples (**24a**, **24e**).

[Cu(dpp)(binc)]$^+$ is able to mediate the allylation of diethyl bromomalonate using allyltrimethylsilane in good yields,[26] whereas [Cu(dap)$_2$]$^+$ can only enable allylation of CBr$_4$ when using allyltrimethylsilane.[23] Presumably, the mechanism is similar to that in Scheme 5c.[26]
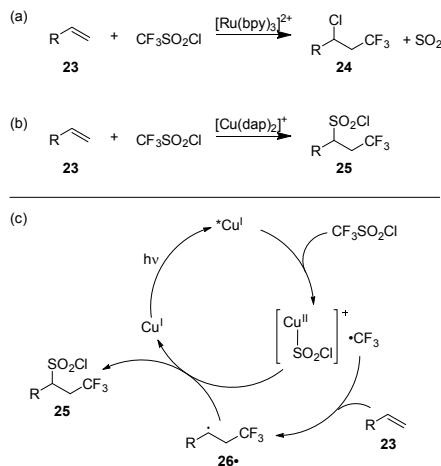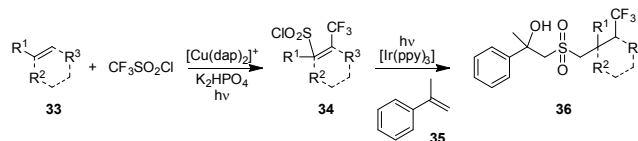

Scheme 7. (a) Trifluoromethylchlorination of alkenes via photoredox catalysis with [Ru(phen)$_3$]^{2}.[29] (b) Trifluoromethylchlorosulfonylation of alkenes via photoredox catalysis with [Cu(dap)$_2$]$^+$ and [Cu(dpp)(binc)]$^+$.[30] (c) Possible mechanism for the net addition of CF$_3$SO$_2$Cl to alkenes.

Using [Cu(dap)$_2$]$^+$ or [Cu(dpp)(binc)]$^+$ as photoredox catalysts, Reiser and coworkers succeeded in performing an unprecedented trifluoromethylchlorosulfonylation of unactivated alkenes.[30] While the [Ru(phen)$_3$]$^{2+}$ photoredox catalyst leads to trifluoromethylchlorination when reacting triflyl chloride with alkenes (Scheme 7a),[29] the Cu^I catalysts mediate a reaction without SO$_2$ extrusion in presence of K$_2$HPO$_4$, resulting in the net addition of CF$_3$SO$_2$Cl instead of only CF$_3$Cl (Scheme 7b). Terminal alkenes reacted with excellent regioselectivity to addition products with terminal CF$_3$ groups, whereas internal alkenes lead to mixtures of regio- and diastereomers. Donor atoms in close proximity to the olefin functionality leads to net CF$_3$Cl addition instead, and sterically more hindered alkenes also produce simple trifluomethylchlorination products.

Given the unique reactivity observed for the Cu^I photoredox catalysts, it was assumed that copper can weakly coordinate SO$_2$Cl$^-$, thus preventing it from decomposing rapidly into SO$_2$ in Cl$^-$ (Scheme 7c). Following addition of the ·CF$_3$ radical (generated in the initial photoinduced SET step) to the alkene, SO$_2$Cl can transfer to the radical intermediate (**28**·), coupled to reduction of Cu^{II} back to Cu^I. With the sterically less demanding [Cu(dpp)(binc)]$^+$ catalyst, the ratio between CF$_3$SO$_2$Cl and CF$_3$Cl addition products further increases, compatible with the idea of SO$_2$Cl$^-$ coordination. Evidently, steric bulk in the substrate and in the catalyst coordination environment disfavors the trifluoromethylchlorosulfonylation pathway.
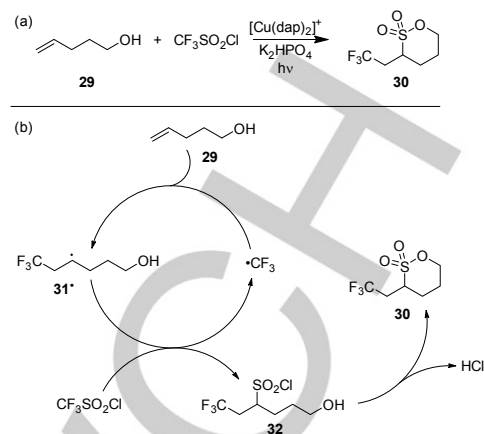
Scheme 8. (a) Trifluoromethylchlorosulfonylation of α,ω-alkenols leading to internal esters of hydroxysulfonic acids, so-called sultones. (b) Possible radical chain mechanism for sultone formation.[31]

After establishing the proof of concept, the Reiser group applied the trifluoromethylchlorosulfonylation to α,ω-alkenols and thereby gained unusually direct access to internal esters of hydroxysulfonic acids, so-called sultones.[31] Pent-4-en-1-ol (**29**) as a benchmark substrate reacts with triflyl chloride in presence of [Cu(dap)$_2$]$^+$ and K$_2$HPO$_4$ to the sultone **30** (Scheme 8a). The base acts as a scavenger for HCl that is liberated in the course of ester formation. [Ru(bpy)$_3$]$^{2+}$ and [Ir(ppy)$_3$] promote the same reaction only very poorly and primarily induce CF$_3$Cl addition. The desired sultone reaction has broad substrate scope, and it is even tolerant of phenol groups. The reaction is believed to follow the mechanism outlined above (Scheme 7c) with internal esterification (**32** → **30**) as a final step, but a radical propagation pathway in which the ·CF$_3$ addition intermediate (**31**·) reacts with CF$_3$SO$_2$Cl to liberate further ·CF$_3$ radicals could not be fully excluded (Scheme 8b), even though this calls for a somewhat uncommon attack of the trifluoromethylated radical intermediate at sulfur.


Scheme 9. Photoredox cascade leading from alkenes, triflyl chloride and styrenes to β-hydroxysulfones, using two complementary photoredox catalysts.[32]

The trifluoromethylchlorosulfonylation reaction mediated by [Cu(dap)$_2$]$^+$ was further exploited in a photoredox cascade in which β-hydroxysulfones were synthesized from triflyl chloride and alkenes.[32] In a first reaction step, trifluoromethylated sulfonyl chlorides (**34**) were obtained via Cu^I photoredox catalysis from CF$_3$SO$_2$Cl and various alkenes (**33**) (Scheme 9). The resulting ATRA products were reacted further with α-

methylstyrene (**35**) using [Ir(ppy)$_3$] as a photoredox catalyst, yielding different hydroxysulfones (**36**) using either a two-flask or a one-pot reaction. Importantly, the [Ir(ppy)$_3$] catalyst alone is unable to promote net CF$_3$SO$_2$Cl addition in the first step, while [Cu(dap)$_2$]$^+$ is not competent to mediate the coupling between α-methylstyrene (**35**) and the trifluoromethylchlorosulfonylation products (**34**), hence both catalysts are vital. The reaction sequence in Scheme 9 demonstrates the feasibility of photoredox cascades.
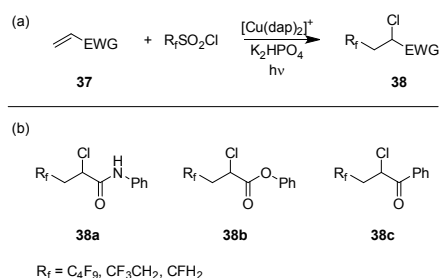

Scheme 10. (a) Reaction of fluoroalkylsulfonyl chlorides with electron-deficient alkenes catalyzed by [Cu(dap)$_2$]$^+$. (b) Representative α-chloro-β-fluoroalkylcarbonyl products.[33]

Dolbier and coworkers explored the reaction of various fluoroalkylsulfonyl chlorides with electron-deficient alkenes (such as α,β-unsaturated ketones, amides, esters, carboxylic acids) under photoredox catalysis conditions with [Cu(dap)$_2$]$^+$ (Scheme 10a).[33] Using CF$_3$SO$_2$Cl, exclusively CF$_3$Cl addition products are obtained, contrasting the CF$_3$SO$_2$Cl products observed by the Reiser group. [Cu(dap)$_2$]$^+$ clearly outperforms [Ru(bpy)$_3$]$^{2+}$ as well as [Ir(ppy)$_3$] for the reactions with CF$_3$SO$_2$Cl. The preparation of α-chloro-β-trifluoromethyl amides (**38a**), esters (**38b**), and ketones (**38c**) was possible in moderate to excellent yields at room temperature (Scheme 10b). However, since the reduction potentials of HCF$_2$SO$_2$Cl, H$_2$CFSO$_2$Cl and CF$_3$CH$_2$SO$_2$Cl are more negative than that of CF$_3$SO$_2$Cl, the reaction temperature had to be increased in these cases. Particular focus was on HCF$_2$SO$_2$Cl, with which 1:1 addition products bearing CF$_2$H and Cl were obtained in excellent yields using electron-deficient alkenes at 100 °C.
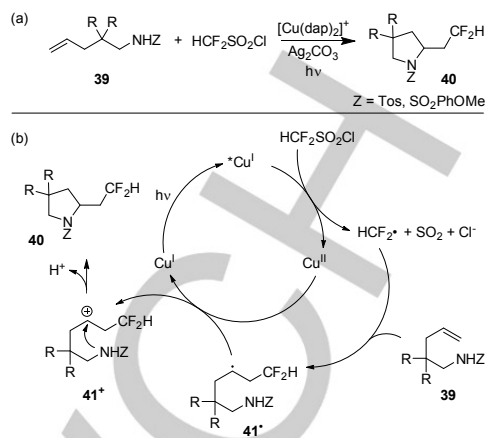
Scheme 11. (a) Intramolecular amino- and oxy-difluoromethylation of unactivated alkenes. (b) Possible reaction mechanism.[34]

Building on these insights, intramolecular amino- and oxy-difluoromethylation of unactivated alkenes (**39**) became possible (Scheme 11a).[34] The Cl$^-$ anion resulting from the reaction between photoexcited [Cu(dap)$_2$]$^+$ and HCF$_2$SO$_2$Cl was intercepted with Ag$^+$, liberating SO$_2$ and free ·CF$_2$H radicals (Scheme 11b). The latter added to alkenes (**39**) to form alkyl radicals (**41·**) that could be oxidized to carbocations (**41$^+$**), leading to recovery of the initial Cu^I state from the Cu^{II} photoredox product. The carbocations subsequently underwent intramolecular nucleophilic attack by sulfonamides to result in pyrrolidines (**40**). When carboxylic esters were present, intramolecular cyclization resulted in lactones. It is important that the nucleophile is not easily oxidizable (Z = Tos, SO$_2$PhOMe) in order for these reactions to proceed well.
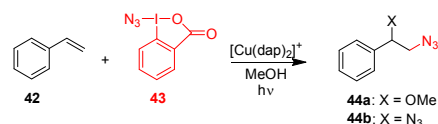
Scheme 12. Azidation of styrene-type double bonds using a hypervalent iodine compound and [Cu(dap)$_2$]$^+$.[35]

Greany and coworkers found that [Cu(dap)$_2$]$^+$ is able to catalyze azide addition to styrene-type double bonds when using a hypervalent iodine reagent (**43**) as an azide source (Scheme 12).[35] In the dark, the lifetime of the resulting benzyl radical intermediate is long enough that another azide radical can add to form bis(azide) products (**44b**). Upon photoirradiation of [Cu(dap)$_2$]$^+$, oxidation to the benzylic radical cation presumably takes place, followed by subsequent trapping with methanol (**44a**), bromide anions, or other nucleophiles. Thus, the product outcome can be controlled by either working in the dark or under illumination, resulting either in double azidation (**44b**) or differentially substituted products (**44a**). For a fairly broad range of styrene derivatives moderate to excellent yields were achievable.
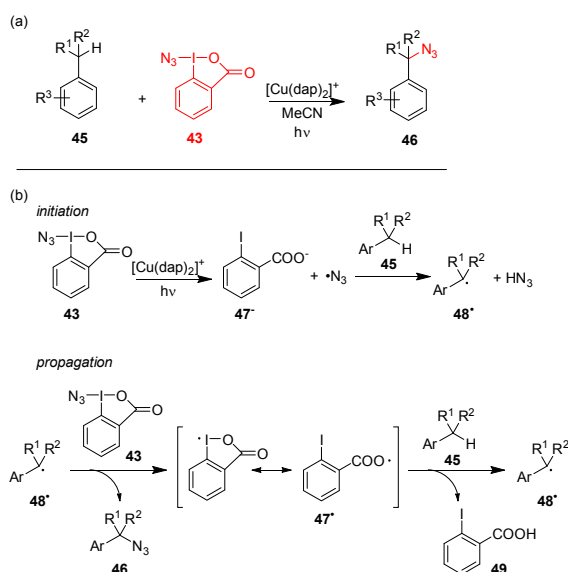
**Scheme 13.** (a) Benzylic C-H azidation leading to primary, secondary and tertiary benzylic azides. (b) Possible radical chain mechanism.[36]


Scheme 14. (a) Allylation of phenyl radical based on diaryl iodonium salts, allylsulfones, and a sacrificial electron donor. (b) Proposed reaction mechanism.[37]

Using the same hypervalent iodine compound (**43**) and [Cu(dap)$_2$]$^+$ under photoredox catalysis conditions, azides could be introduced at benzylic C-H positions (**45** → **46**, Scheme 13a).[36] Primary, secondary and tertiary benzylic azides were accessible in ~30 different cases. The reaction is thought to proceed through a radical chain mechanism (Scheme 13b) with photoinduced electron transfer from [Cu(dap)$_2$]$^+$ to the hypervalent iodine compound (**43**) as an initial step liberating an azide radical. The N$_3$ radical can abstract a benzylic hydrogen atom from the substrate (**45**) to form HN$_3$, thereby liberating a benzylic radical (**48**$^{\cdot}$). The latter then propagates the chain reaction by abstracting an azide radical from the hypervalent iodine compound (**43**) to form the main product (**46**) and a chain-carrying iodane radical (**47**$^{\cdot}$). The iodane radical subsequently abstracts an H-atom from the benzylic substrate (**45**) to result again in the benzylic radical (**48**$^{\cdot}$). Addition of TEMPO or BHT suppresses the benzylic C-H azidation, in line with expectations for a radical chain process.

Ollivier, Goddard, and Fensterbank used diaryl iodonium salts (**51**) and [Cu(dpp)$_2$]$^+$ to generate phenyl radicals under visible light irradiation.[37] In presence of the sacrificial donor diisopropylethylamine (DIPEA, **52**) and allylsulfones (**50**), photoirradiation of the copper complex at 530 nm resulted in the allylation of phenyl radical in moderate to good yields (Scheme 14a). It seems plausible that photoexcited [Cu(dpp)$_2$]$^+$ donates an electron to the iodonium species, thereby forming an unstable iodanyl intermediate (**51**$^{\cdot}$) that fragments to an iodoarene molecule and an aryl radical (Scheme 14b). The latter adds to the allylsulfone (**50**), and release of a tosylate radical leads to the final allylation product (**53**). The sacrificial donor (**52**) regenerates Cu^I from Cu^{II} to close the catalytic cycle. It was noted that the C-C bond formation seems to be efficient because the products are formed in good yields. This is remarkable because the aryl radicals are certainly very reactive when compared to the benzylic radicals appearing in some of the abovementioned studies.
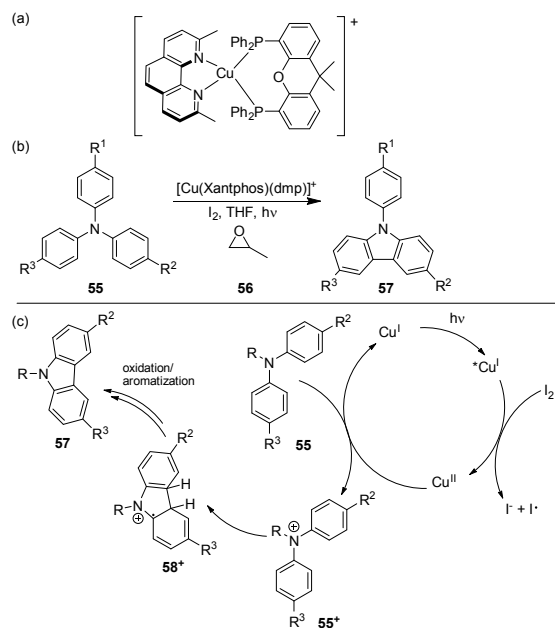
Scheme 15. (a) The [Cu(Xantphos)(dmp)]$^+$ complex.[27] (b) Photochemical conversion of triarylamines to carbazoles. (c) Possible reaction mechanism.[38]

Collins and coworkers reported on the synthesis of carbazoles from triarylamines using heteroleptic Cu^I complexes as photoredox catalysts.[10c, 38a] While the initially used [Ru(bpy)$_3$]$^{2+}$ sensitizer lead to limited success, these researcher saw the possibility of forming Cu^I complexes in situ from a mixture of [Cu(CH$_3$CN)$_4$]BF$_4$ and various N^N and P^P ligands in presence of the triarylamine reactants and an oxidant as an advantage to rapidly screen for suitable catalysts. The [Cu(Xantphos)(dmp)]$^+$ complex (Scheme 15a) in combination with I$_2$ and propylene oxide (**56**) as an oxidation system in THF turned out to be optimal, and triphenylamine (**55**) could be converted to carbazole (**57**) in 75% yield (Scheme 15b, R^1=R^2=R^3=H). Not surprisingly, triarylamines with electron-donating methoxy-groups tend to produce higher yields, whereas the synthesis of carbazoles from electron-deficient substrates using visible light irradiation is proving difficult.[38b] In that latter case, yields were found to be higher when employing UV irradiation at 300 nm. Unsymmetrical triarylamine substrates are converted to mixtures of constitutional isomers, and in many cases there is a clear preference for one of these isomers, but the origin of this selectivity in the photocyclization seems to be somewhat unclear at present. A possible mechanism for the photoredox cyclization (Scheme 15c) starts with oxidative excited-state quenching of [Cu(Xantphos)(dmp)]$^+$ by I$_2$ to result in a Cu^{II} species, I$^-$, and an iodide radical (I·). The Cu^{II} complex can oxidize the substrate (**55**) to a triarylamine radical cation (**55$^+$**), and subsequent secondary oxidation was thought to be possible via reaction with iodide radicals (I·). It was noted that molecular oxygen or I$_2$ would be necessary for re-aromatization.[38a]
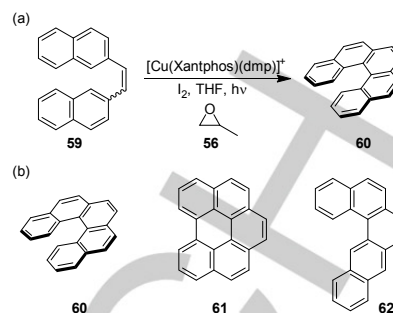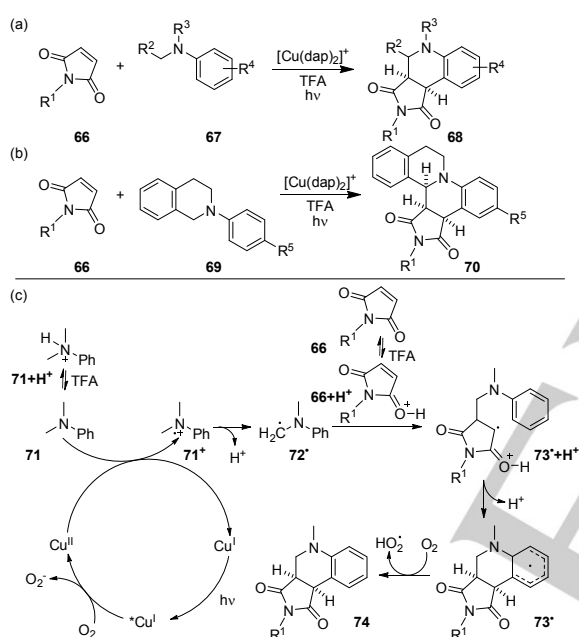

Scheme 16. (a) Cu^I catalyzed synthesis of a [5]helicene from a stilbene precursor.[10c, 39] (b) The desired photocyclization product (**60**) along with a product resulting from overoxidation (**61**) and a different regioisomer (**62**).

Helicenes consisting of *ortho*-fused aromatic rings are traditionally synthesized via UV light mediated photocyclodehydrogenation of stilbene analogues, sometimes called the Mallory reaction. Collins and coworkers reported on visible light induced reactions of this type, using different heteroleptic Cu^I complexes as photosensitizers.[39] This new method permits the synthesis of a [5]helicene (**60**) from a stilbene precursor (**59**) with significantly higher yield than the prior UV based approach (Scheme 16a), and unlike the latter it proceeds without the formation of side products resulting from intermolecular [2+2] cycloaddition or from photocyclization at other positions (Scheme 16b), commonly resulting in the formation of unwanted regioisomers (**62**). Formation of the overoxidation product benzo[*ghj*]perylene (**61**) is also not observed. Cu^I catalysts were synthesized in situ in a screening approach with different chelating diphosphine and diimine ligands, whereby the combination of Xantphos and dmp provided the best results. Using flow chemistry, the gram scale synthesis of the [5]helicene (**60**) became readily possible in THF with I$_2$ and propylene oxide (**56**) as an oxidant system. The mechanism of this photocyclization reaction has not yet been fully explored.[10c] Pyrene-helicene hybrids are accessible using the same methodology from suitable precursors,[40] and the resulting products represent novel helicene structures with increased π-surfaces.
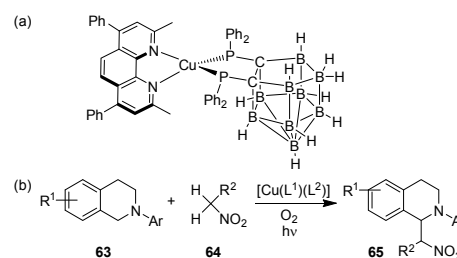
Scheme 17. (a) Cu^I complex with a monoanionic nido-carborane-diphosphine ligand. (b) Photoinduced cross-dehydrogenative coupling reactions between tetrahydroisoquinolines and nitroalkanes using the complex from (a).[41]

The Che group discovered that a Cu^I complex with a phenanthroline and a monoanionic nido-carborane-diphosphine ligand (Scheme 17a) is able to mediate photoinduced cross-dehydrogenative coupling reactions between tetrahydroisoquinolines and nitroalkanes (Scheme 17b).[41] The Cu^I-P bonds were expected to be strong, and the steric bulkiness of the carborane ligand was anticipated to prevent significant excited-state distortions, yet in degassed CH$_2$Cl$_2$ the Cu^I complex from Scheme 17a exhibits an excited-state lifetime of 1.4 µs, which is not longer than that of related [Cu(P^P)(N^N)]$^+$ species.[27] The respective complex is a strong photo-oxidant with an excited-state reduction potential of 1.01 V vs. Ag/AgCl, and consequently it is able to mediate oxidative aza-Henry reactions of tertiary amines with CH$_3$NO$_2$, C$_2$H$_5$NO$_2$ and C$_3$H$_7$NO$_2$ under aerobic conditions (Scheme 17b).[41]

overall process involving the cleavage of 2 C-H bonds and the formation of 2 C-C bonds. Interestingly, [Cu(dap)$_2$]$^+$ mediates regio- and stereoselective reactions of N-aryltetrahydroisoquinolines with N-phenylmaleimide to provide single diastereomers.

Yang and coworkers reported on the use of [Cu(dap)$_2$]$^+$ as an initiator for visible light induced radical polymerization of methacrylates.[43] This is interesting because UV light can result in undesirable photochemical decomposition reactions, and [Cu(dap)$_2$]$^+$ gave good linear evolution with low polydispersity indexes. N,N-dimethylaniline served as a reductant to regenerate Cu^I from the oxidized Cu^{II} complex.

Scheme 19. (a) The [Cu(DPEphos)(Me$_2$Ph$_2$phen)]$^+$ complex.[44] (b) Reduction of aryl halides. (c) Photoredox cyclization of aryl iodides. (d) Arylation of heteroarenes with aryl iodides.
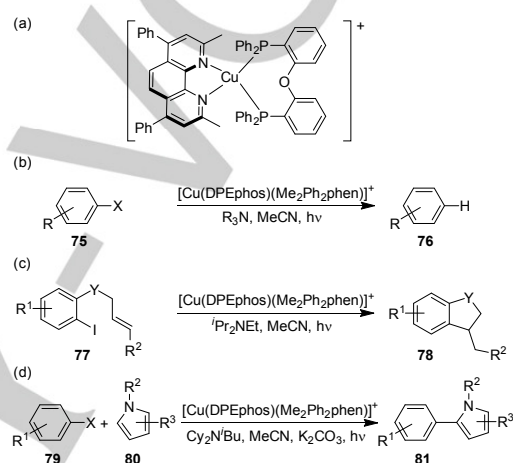

Scheme 18. (a, b) Direct α C-H functionalization of N,N-dialkylanilines and N-aryltetrahydroisoquinolines.[42] (c) Possible mechanism.

Using [Cu(dap)$_2$]$^+$ as a photoredox catalyst, Bissember and coworkers were able to perform direct α C-H functionalization of amines.[42] Specifically, reactions of N,N-dialkylanilines (67) and N-aryltetrahydroisoquinolines (69) with electron-deficient alkenes (66) yielded a range of annulated tetrahydroquinolines (68) and tetrahydroisoquinolines (70) at room temperature under aerobic conditions (Scheme 18a/b). The reaction likely proceeds via oxidative excited-state quenching by O$_2$ (Scheme 18c), followed by oxidation of the amine (71) by Cu^{II}. Subsequent deprotonation of the oxidized amine (71$^+$) then gives an α-amino radical (72$^.$). Radical addition with protonated N-phenylmaleimide (66+H$^+$) could lead to an intermediate (73$^.$+H$^+$) that is able to undergo intramolecular cyclization (73$^.$), and aerobic oxidation as a final step could lead to the observed annulated products (74). Trifluoroacetic acid is crucial for the

Evano, Moucheron, and coworkers used the [Cu(DPEphos)(Me$_2$Ph$_2$phen)]$^+$ complex (Scheme 19a) for the reduction of aryl iodides and electron-deficient aryl bromides (75) to hydrodeiodinated arenes (76) (Scheme 19b).[44] Intramolecular C-C bond formation was possible for a range of iodoarene substrates (77) (Scheme 19c), leading to indolines (78, Y = NR^3), dihydrobenzofurans (78, Y = O), and indanes (78, Y = CR^{3}R^4). The direct arylation of C(sp^2)-H bonds in arenes (Scheme 19d) was performed with pyrroles as bimolecular reaction partners (80), because they are known to react rapidly with radicals. The mechanism for these photoredox transformations likely involves reductive quenching of the photoexcited Cu^I complex.[44]
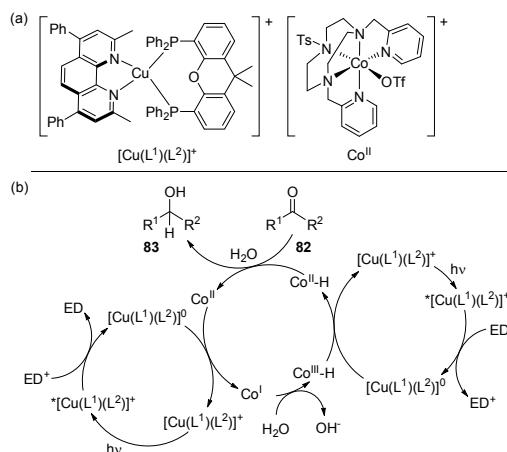
Scheme 20. Dual catalytic system for the photoreduction of aromatic ketones and aldehydes.[45] ED = electron donor.

A dual cobalt-copper catalysis cycle was recently found to enable the reduction of aldehydes and aromatic ketones in aqueous media using trialkylamines as electron donors (ED) (Scheme 20a).[45] The commonly expected reactivity of aromatic ketones under sufficiently reducing photochemical conditions is the formation of ketyl radicals via SET, followed by dimerization to pinacols. Experiments with cyclopropane radical clock molecules suggest that a SET-HAT mechanism (HAT = hydrogen atom transfer) is indeed operative but other evidence points towards the involvement of a hydride transfer mechanism. In particular, a Co^{II}-hydride species (known from water reduction catalysis)[46] is a likely intermediate that can reduce aldehydes and ketones (Scheme 20b). It was noted that depending on substrate reduction potential different reaction pathways (SET-HAT or hydride transfer) could be prevalent.
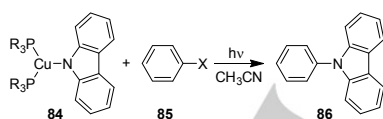
Scheme 21. Reaction of a Cu^I-carbazolide complex with bromo- and iodobenzene under UV photoirradiation.[47]

In the course of studies of Cu^I amido complexes,[48] the Peters group found that complexes such as [Cu(carbazolide)(PPh$_3$)$_2$] are photoluminescent, and this sparked interest in exploiting the favorable excited-state properties of this class of complexes for synthetic applications. In a combined effort between the groups of Peters and Fu, a conceptually novel, synthetically highly useful and broadly applicable approach to photoredox catalysis emerged. In the initial landmark study,[47] it was demonstrated that the [Cu(carbazolide)(PR$_3$)$_2$] complex (R = *meta*-tolyl) (**84**) (Scheme 21) reacts with iodobenzene and bromobenzene (**85**) under UV photoirradiation at -40°C to an Ullmann coupling product (**86**). Experiments with radical probes signaled the intermediacy of photogenerated radicals, and the reactivity

patterns observed with various halogenated arenes were compatible with C-X cleavage via an SET process. Importantly, CuI was able to serve as a catalyst for the photoinduced Ullmann couplings, presumably due to the *in situ* formation of a copper-carbazolide complex.[47]
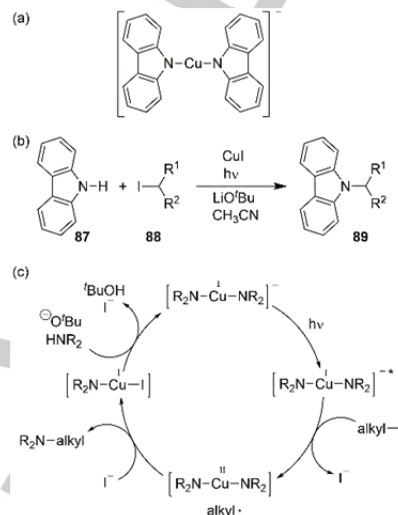
Scheme 22. (a) A [Cu(carbazolide)$_2$]$^-$ complex formed in situ from CuI, carbazole, and base. (b) Coupling of carbazoles with alkyl iodides. (c) Reaction mechanism.[49]

One of the radical probes used in the initial study lead to the formation of a C(sp^3)-N bond,[47] and this encouraged systematic investigations on the coupling of carbazoles (**87**) and alkyl iodides (**88**) (Scheme 22b).[49] A rather wide range of secondary and hindered primary alkyl iodides are amenable to this reaction, using CuI as a pre-catalyst and LiO^{t}Bu as a base. A 100 W Hg lamp was employed for photoirradiation of CH$_3$CN solutions at 0 °C. It was hypothesized that a [Cu(carbazolide)$_2$]$^-$ complex (Scheme 22a) is formed under the reaction conditions and may be an intermediate in the overall reaction mechanism. The respective complex was synthesized and structurally characterized, and when irradiating it in presence of cyclohexyl iodide, the expected N-C coupling product (**89**) was indeed observed. The proposed mechanism (Scheme 22c) starts with photoexcitation of [Cu(carbazolide)$_2$]$^-$ and subsequent SET to generate I$^-$ and an alkyl radical. The latter then reacts with one of the carbazolide ligands on Cu^{II} to form the N-C coupling product and a Cu^I iodo complex. Coordination of a new carbazolide ligand closes the catalytic cycle.[49] A very recent study also discusses the involvement of a photo-excited lithium carbazolide species in reactions with alkyl bromides.[50]
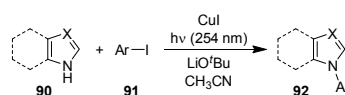
Scheme 23. Photoinduced Ullmann couplings between aryl iodides and indoles, benzimidazoles, and imidazoles.[51]

In following investigations, the concept of photoinduced Ullmann couplings was extended to new families of nucleophiles and electrophiles. Since the previously investigated reactions seemed to rely on photoexcitation of copper-substrate complexes (in particular the copper-carbazolide complexes mentioned above), it was not a priori clear whether this would also be possible with other nucleophiles. In a first step, nitrogen nucleophiles such as indoles, benzimidazoles, and imidazoles were explored (Scheme 23).[51] A key finding is that photoirradiation at 254 nm (rather than at 350 nm) becomes of key importance, presumably because the involved Cu-substrate complexes only absorb well at shorter wavelengths. Aside from aryl iodides, aryl bromides and activated aryl chlorides react with various alkenyl and alkynyl halides to C-N coupling products (**92**) at room temperature.[51]
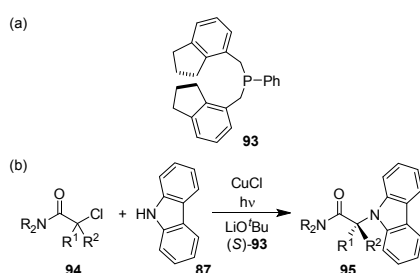

Scheme 24. (a) Chiral phosphine ligand. (b) Enantio-convergent cross coupling of racemic tertiary alkyl halides to carbazoles and indoles under photoirradiation.[52]

Using a commercially available chiral phosphine ligand (**93**, Scheme 24a) and CuCl, the enantio-convergent cross coupling of racemic tertiary alkyl halides to carbazoles and indoles under photoirradiation became possible (Scheme 24b).[52] The chiral ligand controls the absolute configuration of the product regardless of the stereochemistry of the starting electrophile, and cleavage of the C-Cl bond of the electrophile seems to be essentially irreversible. It was assumed that a photoexcited copper-substrate complex reduces the alkyl halide, and the ensuing steps are similar to those outlined above for other N-C couplings (Scheme 22c). A heteroleptic Cu^I complex with one chiral phosphine ligand and a carbazolide was structurally characterized, and this complex was found to exhibit basically the same reactivity with regard to Ullmann coupling as the mixture of CuCl and free phosphine ligand under the typically employed reaction conditions. Thus, the mechanistic studies suggest that a single catalyst is responsible for both the photochemistry and the enantioselective bond formation.
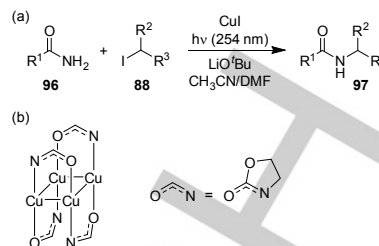
Scheme 25. (a) Monoalkylation of primary alkyl and aryl amides with CuI as a pre-catalyst. (b) Tetrameric Cu^I oxazolidinyl complex as a model of presumed catalytically active Cu^I amidate species.[53]

Subsequent further studies demonstrated that the nucleophilic Ullmann reaction partner does not necessarily have to contain an aromatic ring but can be a primary amide instead.[53] This is not self-evident given the very likely involvement of photoexcited Cu-nucleophile adducts in the overall N-C coupling mechanism. Using CuI as a pre-catalyst, un-activated secondary (and hindered primary) alkyl bromides and iodides (**88**) can be used for the photodriven monoalkylation of primary alkyl and aryl amides (**96**) (Scheme 25a). A Cu^I-amidate complex was postulated as a likely critical intermediate in the catalytic cycle. Relevant monomeric Cu^I complexes could not be isolated, but instead a small cluster made from 4 Cu^I ions and 4 oxazolidinyl ligands (Scheme 25b) was structurally characterized. This tetramer could indeed be used instead of CuI for photoinduced N-alkylation of an amide. The reaction mechanism was thought to proceed via photoexcitation of the Cu^I-amidate complexes formed with the substrate, followed by SET to the alkyl halide, in analogy to the mechanisms discussed above.
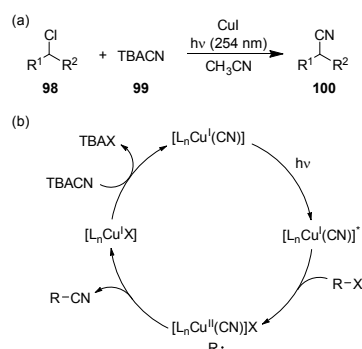
Scheme 26. (a) Cyanation of un-activated secondary alkyl chlorides to afford nitriles. (b) Proposed mechanism.[54]

The possibility of performing analogous photoinduced C-C couplings with carbon nucleophiles was demonstrated on the example of cyanation of un-activated secondary alkyl chlorides (**98**) to afford nitriles (Scheme 26a).[54] Irradiation at 254 nm provides significantly better yields than excitation at 300 or 350 nm, presumably due to weak extinction of Cu^I cyanide complexes at the longer wavelengths. ESI-MS signals the presence of the [Cu(CN)$_2$]$^-$ complex in the reaction mixture, and

photoexcitation of this or related Cu^I cyanide complexes was assumed to trigger SET to alkyl chlorides (Scheme 26b), followed by reaction of the alkyl radical with a Cu^{II}-bound CN$^-$ ligand.
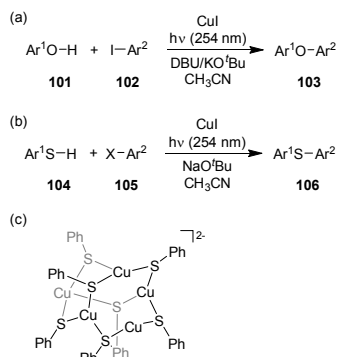


Scheme 27. (a) Photodriven coupling of phenols and aryl iodides to diaryl ethers.[55] (b) Coupling of aryl thiols to aryl halides.[56] (c) Isolated pentameric Cu^I thiolate complex that is presumably in equilibrium with catalytically active [Cu(SPh)$_2$]$^-$ and [Cu$_2$(SPh)$_3$]$^-$ species.[56-57]

Based on the same type of photoinduced copper-catalyzed chemistry, phenols (**101**) can be coupled to aryl iodides (**102**) to generate diaryl ethers (**103**) (Scheme 27a).[55] This reaction likely follows a pathway similar to those discussed above for the corresponding C-N and C-C couplings with a Cu^I-phenoxide complex as a photoactive species. The phenolic reaction partners can bear electron-withdrawing or electron-donating substituents, and even sterically hindered substrates react well. The scope with regard to the electrophile is similarly broad.

Essentially the same methodology is applicable to photoinduced C-S bond formation between aryl thiols (**104**) with aryl halides (**105**) (Scheme 27b).[56] Sterically hindered, electron-deficient, electron-rich, and heterocyclic thiols all react well with aryl iodide. Expectedly, shorter reaction times are required for aryl iodides than for aryl bromides due to greater ease of reduction, but on the other hand even an activated aryl chloride could be coupled to a thiol at 0 °C. The combination of CuI, PhSH and NaO^{t}Bu in CH$_3$CN afforded a pentameric Cu^I thiolate complex (Scheme 27c), and ESI-MS provided evidence for [Cu(SPh)$_2$]$^-$ and [Cu$_2$(SPh)$_3$]$^-$ species in the reaction mixture. It seems plausible that solution equilibria lead to Cu^I-thiolate complexes that act as photoactive species. This view was corroborated by in-depth mechanistic investigations on a discrete [Cu(SAr)$_2$]$^-$ complex.[57] The use of 2,6-dimethyl substituted arylthiolate permitted the isolation of a monomeric Cu^I thiolate complex with an excited-state lifetime of 7 µs and an oxidation potential of -2.6 V vs. SCE in that excited-state. EPR and UV-Vis data signal the formation of a Cu^{II}-thiolate when the [Cu(SAr)$_2$]$^-$ complex is irradiated in presence of aryl iodide and NaSAr. Experiments with radical clocks that undergo intramolecular cyclizations with well-known first-order rate constants indicate that C-S bond formation likely occurs very rapidly within the solvent cage around the aryl radical and the Cu^{II}-thiolate. Quantum yield studies support the view that the overall reaction proceeds via a non-chain process.

The mechanistic picture that emerges from these investigations is fully compatible with the views expressed in the prior studies (Scheme 22c).[47, 49, 51-57]

A very recent study by the groups of Fu and Peters reported on photoinduced, copper-catalyzed decarboxylative C-N couplings as an alternative to the Curtius rearrangement.[58]
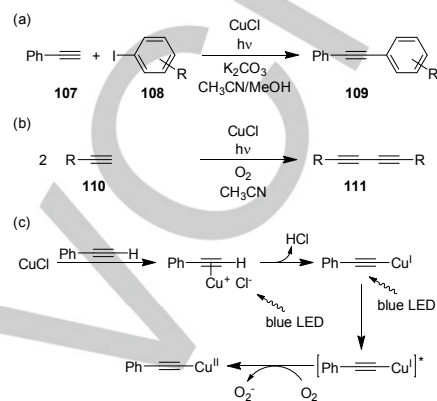

Scheme 28. (a) Photoinduced Sonogashira coupling reaction.[59] (b) Visible-light driven C(sp)-C(sp) homocoupling of terminal alkynes. (c) Presumed mechanism.[60]

Hwang and coworkers reported on copper-catalyzed alkynylations of aryl halides (**108**) aided by visible light irradiation, i. e., photo-driven Sonogashira couplings (Scheme 28a).[59] Addition of CuCl to pre-formed copper phenylacetylide lead to a reaction rate enhancement, and this was attributed to LMCT absorptions of copper complexes formed between Cu^I and the triple bond of the phenylacetylide. Photoexcitation of this species was assumed to reduce the aryl halide, thereby setting the stage for attack of an aryl halide onto the copper-bound acetylide.[61] This method works well for coupling between aryl iodides and bromides but not for aryl chlorides. The reaction is sensitive to molecular oxygen. Its presence leads primarily to homocoupling and so-called Glaser products.[59]

A subsequent study by the same group exploited this fact by demonstrating that C$_{sp}$-C$_{sp}$ homocoupling of terminal alkynes (**110**) can be driven by visible light in presence of CuCl (Scheme 28b) for the synthesis of 1,3-conjugated diynes (**111**).[60a] This reaction proceeds without base and permits homocoupling reactions of electron-deficient aromatic terminal alkynes. It was assumed that a π-alkyne complex that makes the terminal H of alkynes more acidic is the first step in the reaction mechanism (Scheme 28c). Photoexcitation of this species presumably results in the formation of Cu^I phenylacetylide without the need for any base. Secondary photoexcitation of the Cu^I-phenylacetylide complex was assumed to trigger SET to O$_2$, leading to a Cu^{II} species that was thought to dissociate to permit the formation of homocoupling products in the presence of O$_2$.

The same methodology is applicable to the cross coupling between electron-deficient and electron-rich terminal alkynes leading to unsymmetrical diynes.[60b] Presumably, the cross coupling is mediated by a hetero-dimeric Cu^I intermediate in

which one alkyne binds to Cu^I in σ-fashion while the second alkyne undergoes a π-bond. Such pre-organization in an intermediate could explain the good selectivity for heterocoupling products in presence of only 1.8 equivalents of excess of one of the alkyne reactants.
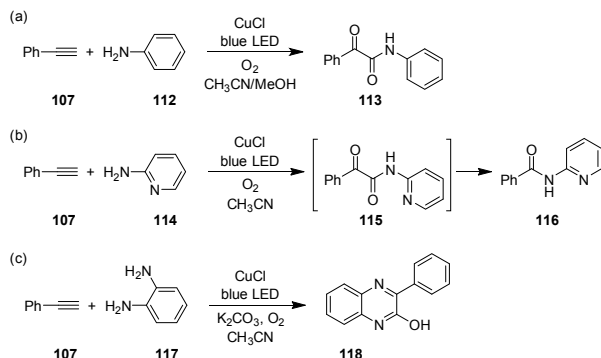

Scheme 29. (a) Oxidative coupling of anilines and terminal alkynes to yield α-ketoamides.[62] (b) Oxidative coupling of 2-aminopyridine to alkynes yielding pyridyl amides.[63] (c) One-pot synthesis of 3-phenyl-2-hydroxy-quinoxalines.[64]

When using anilines (**112**) as reaction partners with terminal alkynes, the same methodology is useful for the synthesis of α-ketoamides (**113**) (Scheme 29a).[62] Similar to the reactions discussed above, the likely key intermediate is an in situ formed Cu^I-phenylacetylide. Homocoupling reactions can be suppressed by keeping the phenylacetylene concentration low, and then the amidation/diketonation reaction is possible for a broad range of alkynes and anilines, but aliphatic amines and N-substituted anilines are not tolerated. The reaction mechanism was presumed to involve copper peroxo complexes as intermediates that are responsible for oxygen incorporation into the final products.

When using 2-aminopyridine (**114**) as a reaction partner for terminal alkynes under essentially the same conditions, the resulting pyridyl α-ketoamides (**115**) decarbonylates, and the final product is a pyridyl amide (**116**) (Scheme 29b).[63] This reaction proceeds well with a range of phenylacetylides, and it was assumed that a Cu^{II} superoxo or peroxo complex (generated after photo-excitation of an in situ formed Cu^I-phenylacetylide), is the key catalyst for the oxidative cleavage of pyridyl α-ketoamide to pyridyl benzamide. The presence of TEMPO (2,2,6,6-tetramethylpipyeridine-1-oxyl) inhibits the overall reaction, compatible with a radical process.

With ortho-phenylenediamines (**117**) instead of anilines as reaction partners for terminal alkynes, the methodology introduced by Hwang and coworkers gave rapid access to quinoxalines (**118**) (Scheme 29c).[64] As in the prior studies, a Cu^I phenylacetylide complex is a likely key intermediate, and the reaction proceeds well with o-phenylenediamines bearing electron-donating or electron-withdrawing substituents. In combination with a range of possible terminal alkyne reaction partners, the facile one-pot synthesis of a variety of different 3-phenyl-2-hydroxy-quinoxalines was feasible.
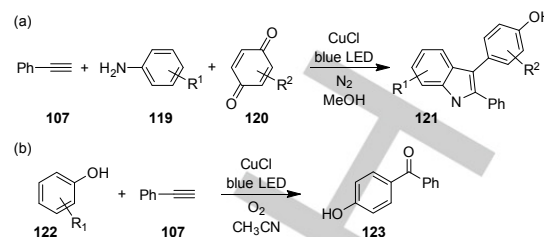
Scheme 30. (a) One-step regioselective synthesis of functionalized indoles.[65] (b) Oxidative coupling of phenols and terminal alkynes to yield functionalized ketones.[66]

Further extension of the same methodology was possible by using ternary reactant mixtures comprised of anilines, terminal alkynes, and benzoquinones.[65] Photoirradiation of this mixture with 5 mol % CuCl permits the regioselective synthesis of 39 different functionalized indoles (**121**) in one reaction step (Scheme 30a). This process works with both electron-rich and electron-neutral anilines (**119**), and it can be readily scaled up to the gram scale. Electron-rich as well as electron-deficient phenylacetylenes were tolerated, and substituted benzoquinones (**120**) did also undergo successful reaction. The reaction mechanism was assumed to start with photoinduced SET from Cu^I-phenylacetylide to benzoquinone and subsequent binding of quinone anion to the resulting Cu^{II} complex, thereby setting the stage for the formation of a C-C bond between benzoquinone and the alkyne. Nucleophilic attack at the C≡C triple bond by aniline could then be a key step for incorporation of the aniline reaction partner into the final product.

Hwang and coworkers also succeeded in performing the direct oxidative coupling of phenols and terminal alkynes using CuCl as a key ingredient.[66] This method allowed the regioselective synthesis of 47 different hydroxy-functionalized aryl and alkyl ketones (**123**) (Scheme 30b). Photoinduced SET from Cu^I-phenylacetylide to O$_2$ seems to be a key step, and ^{18}O-labeling experiments indicate that the oxygen atom in the ketone products originate from O$_2$. Presumably, a Cu^{II} superoxo complex that is formed concurrently can oxidize phenol to benzoquinone, and the latter undergoes Paterno-Büchi type [2+2] cycloaddition to Cu^{II}-phenylacetylide to form an oxotene ring. Subsequent rearrangement and fragmentation reactions, including further reaction with O$_2$ and extrusion of CO$_2$ then leads to the ketone products. Quantum yield investigations indicated that this is not a chain process.

In recent studies, the possibility of using [Cu(dap)$_2$]$^+$ for the photoredox mediated synthesis of tetrahydrofurans and pyrrolidines starting from 1,2-diols and β-amino alcohols was explored, but this Cu^I complex was not a suitable catalyst for this purpose.[67] Similarly, [Cu(dap)$_2$]$^+$ turned out to be unsuitable for the tandem cyclization of vinyl radicals to indolines via photoredox catalysis, but instead an iridium catalyst was employed successfully.[68]

Lastly we note that Cu^I complexes have become of significant interest for photocatalytic hydrogen production, but this is beyond the scope of this review.[69] New classes of Cu^I complexes have been developed recently, and their application

in photoredox catalysis of organic reactions is yet to be explored.[70]

6. Zinc[II]

Zn[II] porphyrins have received significant attention for fundamental investigations of photoinduced electron transfer, for example in donor-acceptor dyads, triads, and tetrads.[71] However, until now metalloporphyrins have received limited attention as photoredox catalysts in the context of organic synthesis. Recently, Boyer and coworkers demonstrated that Zn[II] porphyrins can specifically activate trithiocarbonates that can then engage in the polymerization of styrene, (meth)acrylates, and (meth)acrylamides (Scheme 31).[72] The overall PET-RAFT process involves photoinduced electron transfer (PET) between the sensitizer and a trithiocarbonate (124), as well as subsequent reversible addition – fragmentation chain transfer (RAFT). It was noted that [Zn(TPP)] (TTP = tetraphenylporphyrin) is unique when compared to Cu, Ir, or Ru based sensitizers in that it selectively activates trithiocarbonates over other thiocarbonylthio compounds, presumably due to specific molecular recognition. [Zn(TPP)] turned out to enable controlled living polymerization by wavelength variation and by simply turning the light on and off. Moreover, the living radical polymerization could be performed under aerobic conditions.
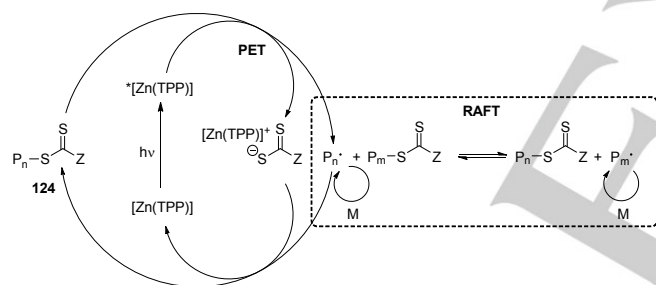
Scheme 31. Polymerization of styrene, (meth)acrylates, and (meth)acrylamides via a PET-RAFT process relying on trithiocarbonate and its specific interaction with a Zn[II] porphyrin photoredox catalyst.[72]

7. Zirconium[IV]

Milsmann and coworkers recently made the important fundamental discovery that a Zr[IV] complex with two terdentate π-donating chelating ligands exhibits LMCT luminescence in fluid solution at room temperature (Scheme 32a).[8a] The ligand contains two pyrrolide ligands with amide character at the N atom, which allows for extended delocalization of π-electron density. The luminescence quantum yield of the resulting Zr[IV] complex is comparable to that of $[Ru(bpy)_3]^{2+}$, and a reduction potential of -0.07 V vs. Fc$^+$/Fc was estimated for the excited complex. This excited state can be quenched reductively by a methylated derivative of the well-known BIH reductant to afford the corresponding one-electron reduced Zr complex in its electronic ground state. The respective Zr[III] species is oxidized

at a potential of -2.16 V vs. Fc$^+$/Fc, and consequently is a very strong reductant. This was exploited in several photoredox catalysis experiments (Scheme 32b).[8a] For example, ethyl bromodifluoroacetate (125) is efficiently dehalogenated upon irradiation of the Zr[IV] complex in presence of the BIH reductant, and diethyl maleate (127) is readily reduced to diethyl succinate (128). The reductive coupling of benzyl bromide (129) to bibenzyl (130) was also possible, and in this case the addition of 2,6-lutidine (to intercept HBr) prevented rapid catalyst degradation.
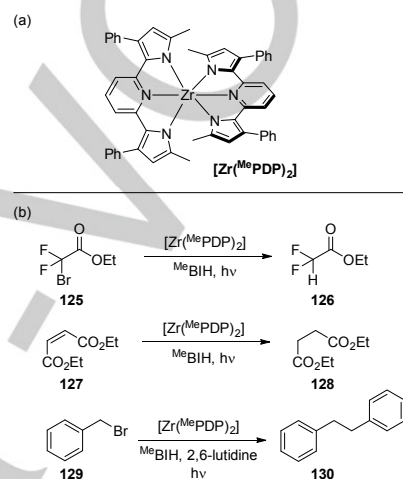
**Scheme 32.** (a) Photoactive Zr[IV] complex with pyrrolide ligands. (b) Photoredox reactions explored with this complex.[8a]

8. Molybdenum[0]

Building on prior work on W[0] complexes with monodentate arylisocyanide ligands,[73] the Wenger group recently discovered that homoleptic Cr[0] and Mo[0] complexes with chelating diisocyanide ligands exhibit long-lived [3]MLCT excited states that are amenable to photoredox chemistry.[8b, 74] The [Mo(CNAr$_3$NC)$_3$] complex (Scheme 33a) was able to mediate the visible-light driven conversion of an acyl cyclopropane (131) to a 2,3-dihydrofuran (134) in an overall redox-neutral reaction (Scheme 33b). A plausible reaction mechanism starts with oxidative excited-state quenching by the acyl cyclopropane substrate (*trans*-131) to result in the formation of an enolate (132⁻). The reduction of this substrate is energetically very demanding, but with an oxidation potential of -2.6 V vs. Fc$^+$/Fc, the [3]MLCT-excited [Mo(CNAr$_3$NC)$_3$] complex is a very strong electron donor, and in transient absorption studies it was found to reduce acetophenone to its ketyl radical anion.[74a] The enolate (132⁻) can be oxidized to a diradical intermediate (133) by the Mo[I] species, thereby leading to catalyst regeneration. The diradical (133) can either revert to the starting material (thereby forming a mixture of *cis*- and *trans*-isomers (131) out of an initially isomerically pure substrate), or it can form the desired 2,3-dihydrofuran product (134). The overall yield for the pericyclic rearrangement in Scheme 33b was 86% with a

catalyst loading of 5%, corresponding to a TON of 17, but no optimization was made.
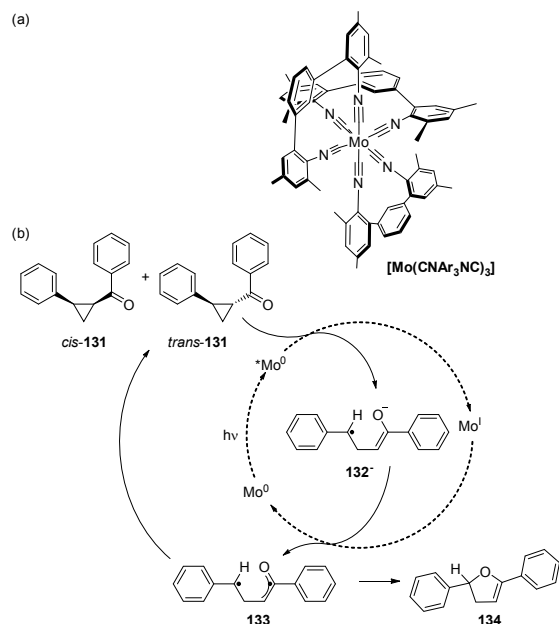

Scheme 33. (a) Mo[0] isocyanide complex as a highly reducing analogue of [Ru(bpy)$_3$]$^{2+}$. (b) Photoredox-catalyzed rearrangement of an acyl cyclopropane to a 2,3-dihydrofuran.[74a]

9. Uranium[VI]

Uranium has long been synonymous with the applications of its fissile isotope, ^{235}U, in energy and weaponry. However, its non-fissile isotope, ^{238}U, accounts for 99.3% of natural uranium – with an earth abundance exceeding that of molybdenum.[75] This association has led to the avoidance of uranium coordination chemistry, which has only started growing in recent years.[76] Despite this, the uranyl cation ([UO$_2$]$^{2+}$) has been extensively investigated for its photochemical properties.[77] Early work by the Bakac group exploited its absorption in the visible spectrum and long-lived LMCT excited state with an oxidation potential of 2.6 V vs SHE to perform challenging hydrocarbon photooxidations under aerobic conditions.[78] It was demonstrated that a range of unsubstituted alkanes, alkenes and alcohols effectively quenched the *[UO$_2$]$^{2+}$ excited state, and that cyclopentane (**135**) could be catalytically oxidised to cyclopentanone (**136**, Scheme 34a). An important observation was that cyclopentanol was not observed in any quantity, ruling out the possibility of a two-step oxidation with cyclopentanol as an intermediate. In conjunction with an H/D kinetic isotope effect (KIE) of 2.4, this observation is consistent with a mechanism wherein hydrogen-atom abstraction by the photoexcited catalyst is followed by rapid alkylperoxyl radical formation (Scheme 34c). Following radical rearrangement, a hydroxy radical is expelled and cyclopentanone is formed. The reduced catalyst is then

autooxidised to regenerate the active catalyst, forming H$_2$O$_2$ as a by-product, which was observed in significant quantities.
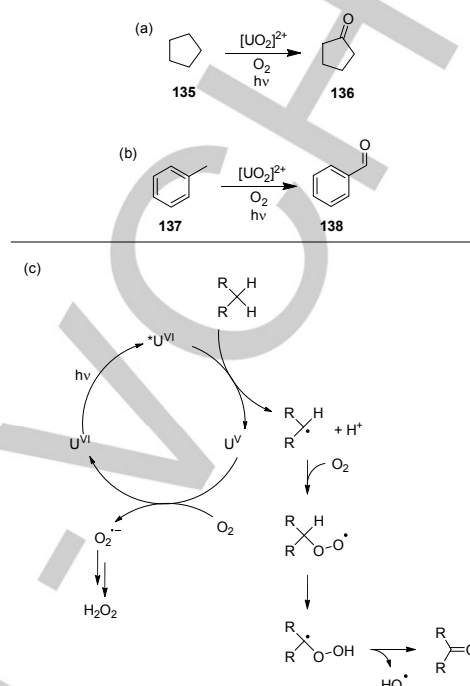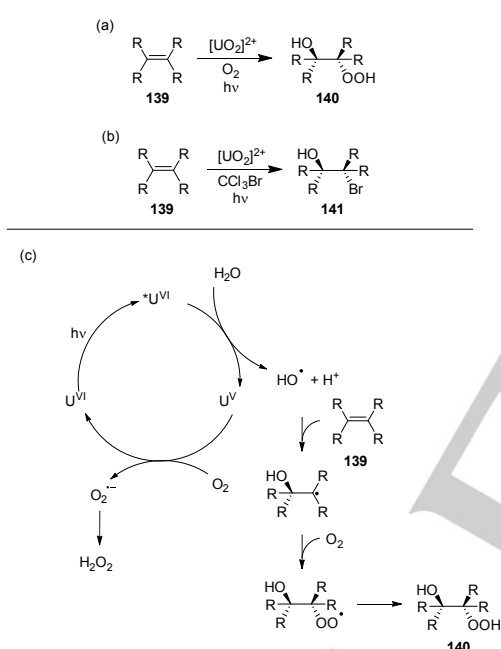

Scheme 34. [UO$_2$]$^{2+}$-catalyzed photooxidation of (a) cyclopentane and (b) toluene. (c) Presumed mechanism.[78]

A subsequent study reported on the photooxidation of toluene (**137**) to benzaldehyde (**138**).[79] This reaction is far less efficient than the oxidation of cyclopentane, and afforded a H/D KIE of only 1.2. Previous reports had observed *toluene-[UO$_2$]$^{2+}$ exciplexes,[80] and this was proposed to represent an unproductive decay pathway, resulting in no net chemical change. Competition between photooxidation and exciplex formation was proposed to be responsible for the lower efficiency and KIE.[79] In contrast to cyclopentane oxidation where the formation of a cyclopentanol intermediate remained completely unobserved, benzyl alcohol was observed in ~30% yield, indicating an alternate mechanism is at play. Due to the enhanced stability of the benzyl radical, hydroxyl radical expulsion is significantly slower – facilitating bimolecular reaction between to benzylperoxyl radicals to form one molar equivalent of benzaldehyde and one of benzyl alcohol.

Photooxidation of alcohols by [UO$_2$]$^{2+}$ under aerobic conditions was shown to yield the corresponding aldehydes, and acetaldehyde was oxidised to acetic acid.[78] Cyclohexene photooxidation was reported to occur via the same mechanism as for cyclopentane, yielding 2-cyclohexen-1-one. This is inconsistent with earlier findings by the Sato group that [UO$_2$]$^{2+}$ could sensitise the photooxidation of alkenes (**139**) to β-hydroxy hydroperoxides (**140**, Scheme 35a),[81] which was proposed to occur through quenching of *[UO$_2$]$^{2+}$ by water to yield a hydroxyl

radical that can add to the olefin (Scheme 35c). The subsequently formed radical was then proposed to be quenched by O_2, yielding the observed anti-addition product. To further probe this mechanism, O_2 was excluded, and bromotrichloromethane added to quench the formed radical (Scheme 35b). The product of this reaction was the expected β-bromoalcohol (**141**), consistent with the proposed mechanism.

The only difference between the two reactions was the chosen solvent (1:1 H_2O/CH_3CN for cyclopentene photooxidation, pyridine for alkene photooxidation to β-hydroxy hydroperoxides). It was rationalised that the difference in reactivity likely originates from the difference in $[UO_2]^{2+}$ redox potentials in the two solvents.[78] Due to the oxidative potency of $*[UO_2]^{2+}$, it is also possible that pyridine quenches the excited state – forming an intermediate that leads to the observed products.
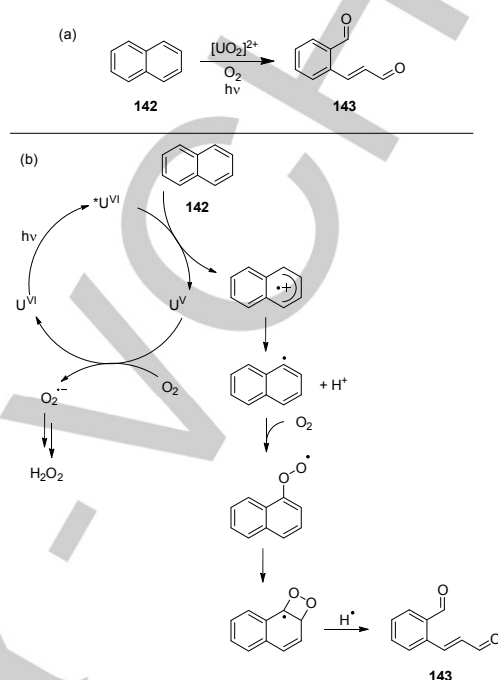

Scheme 35. $[UO_2]^{2+}$-catalyzed photooxidation of alkenes in the presence of (a) oxygen or (b) bromotrichloromethane. (c) Proposed mechanism.[81]

The Bakac group further demonstrated that $[UO_2]^{2+}$ could photooxidise naphthalene (**142**), yielding the ring-opened 2-formylcinnamaldehyde (**143**) as a product (Scheme 36a).[82] Whilst photooxidation of hydrocarbons by $[UO_2]^{2+}$ was well-established by this stage, they typically occurred by a hydrogen-abstraction mechanism.[78-79] In this study, the naphthalene radical cation was directly observed, indicative of an outer-sphere electron-transfer mechanism (Scheme 36b). As with toluene photooxidation, exciplex formation appeared to limit the efficiency of the reaction.

The naphthalene radical cation rapidly deprotonates to afford the naphthyl radical ($C_{10}H_8^{\cdot}$). Typically, naphthalene oxidations in aqueous media form naphthols – either through direct addition of the hydroxyl radical to naphthalene or hydrolysis of the naphthyl

radical.[83] In the present case of photoreaction with $*[UO_2]^{2+}$, O_2 presumably adds to naphthalene to form a proposed four-membered cyclic peroxide, which can ring-open to afford **143**.[82]

Scheme 36. (a) $[UO_2]^{2+}$-catalyzed photooxidation of naphthalene. (b) Proposed mechanism.[82]

A recent study by the Sorensen group has further expanded the chemistry of $[UO_2]^{2+}$-catalyzed photoreactions, developing a fluorination method for unactivated $C(sp^3)$-H bonds (Scheme 37a).[84] The proposed mechanism (Scheme 37b) involves abstraction of a hydrogen-atom by $*[UO_2]^{2+}$, forming an alkyl radical that can abstract a fluorine-atom from N-fluorobenzosulfonimide (NFSI), yielding the fluorinated product and the NFSI radical, which can abstract a hydrogen-atom from the reduced and protonated catalyst, regenerating the active U^{VI} species. As with previous $[UO_2]^{2+}$-catalyzed photooxidations, aromatic substrates were far less active than aliphatic substrates due to unproductive exciplex formation. Interestingly, species containing heteroatoms exhibited essentially no conversion. This was proposed to arise from either competitive unproductive inner-sphere electron-transfer processes or coordination to U^{VI}. The authors recognized that this behavior is highly discriminating, opening the possibility for selective fluorination in the presence of motifs that inhibit classical fluorination reactions.
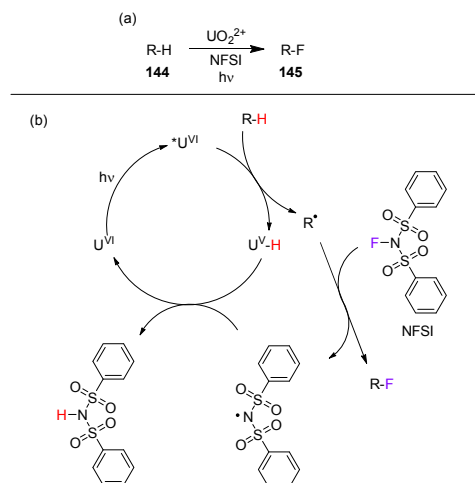
Scheme 37. (a) [UO₂]²⁺-catalyzed sp³-fluorination. (b) Proposed mechanism.[83]

10. Summary and Conclusions

A range of earth abundant metal complex photocatalysts have been considered herein, which can be classed into the two distinct categories of photoreductants and photooxidants. Relevant photophysical properties for complexes for which data are readily available are presented in Table 2. The precious metal complexes [Ru(bpy)₃]²⁺ and [Ir(ppy)₃] have been included for reference.

Cu^I complexes currently represent the most thoroughly investigated class of photoredox active compounds based on earth-abundant metal elements. A significant portion of studies makes use of traditional Cu^I bis(α-diimine) complexes developed by the groups of McMillin and Sauvage a long time ago,[6] typically resulting in ordinary outer-sphere electron transfer processes similar to those observed with the substitution-inert Ru^{II} or Ir^{III} congeners. However, in some cases the reactivity of these complexes involves substrate ligation, and the ensuing inner-sphere mechanisms lead to reaction products that would be inaccessible otherwise. This aspect can represent a significant advantage of relatively substitution-labile first-row transition metal complexes with respect to the considerably more substitution-inert 4d or 5d elements.

In several investigated cases, the photoredox active species itself is a Cu^I-substrate complex that is formed in situ from simple Cu^I halide salts, and this represents a valuable reaction pathway that is not typically accessible with the classically used Ru^{II} or Ir^{III} photoredox catalysts. In selected cases, inner-sphere photoredox pathways with Cu^I even permit enantioselective reactions, or they give rise to products that are inaccessible via outer-sphere reaction pathways.

Cr^{III} polypyridine complexes are typically very robust and substitution-inert, and these two characteristics along with their strongly oxidizing properties in their long-lived ^2E_g excited states make them interesting for light-driven reactions requiring high oxidizing power in one of the elementary SET steps. So far, their dual role as electron donors and $^1O_2$ sensitizers has been exploited mostly in cycloaddition reactions, but other applications seem readily possible, particularly because some of these complexes are very strongly oxidizing and possess excited-state lifetimes extending nearly into the millisecond regime, especially recently developed complexes.[17]

Cu^I complexes, Cr^{III} polypyridines, and possibly Zn^{II} compounds (in the form of porphyrin complexes) are currently most developed with regard to photoredox applications that are relevant for organic synthesis. For the other earth-abundant metal elements considered herein, proof-of-principle studies were reported, but further developments of these systems seem necessary before they can become as broadly applicable as their more robust counterparts made from precious metals. However, recent developments in the field of inorganic photophysics and photochemistry are highly encouraging in that regard. New Fe^{II} complexes with excited-state lifetimes in the 10-37 ps regime are being developed,[85] and conceptually novel approaches based on Fe^{III} or Zr^{IV} with LMCT excited-states seem very promising.[8a, 86] Another interesting avenue may open up with d^0 complexes given the recent developments on emissive W^{VI} complexes.[87] Newly explored luminescent Cr^0,[8b, 74b, 88] Mo^0,[8b, 74a] and W^0 [8b, 73] isocyanide complexes are d^6 systems with MLCT excited-state structures similar to the abovementioned Ru^{II} and Ir^{III} complexes, and in several regards they represent interesting alternatives made from comparatively earth-abundant metal elements.[8b] Some of the diisocyanide chelate ligands developed for these d^6 metals can also stabilize the d^{10} species Ni^0, leading to MLCT emission similar to isoelectronic Cu^I diimines.[89]

Some of the newly developed systems may be particularly interesting for niche applications in photoredox catalysis, for example for reactions requiring unusually high reducing or oxidizing power, but others seem to have the potential to become true competitors for more traditional photoactive complexes made from precious metals.

Table 2. Summary of relevant photophysical properties for complexes for which data are readily available.

photoreductants								
complex	$E_{1/2}(C^+/C)$ / V vs SCE	$E_{1/2}(C^+/C^*)$ / V vs SCE	λ_{abs} (ε) / nm (10^3 M^{-1} cm^{-1})	λ_{em} (φ) / nm	E_{00} / eV	τ_{ex}	assign.	ref.
[Cu(dap)₂]$^{+\,a}$	0.62	-1.43	400-600 (-)	670 (-) ^{a}	2.05	270 ns	MLCT	[23,

complex	$E_{1/2}(C/C^-)$ / V vs SCE	$E_{1/2}(C^*/C^-)$ / V vs SCE	λ_{abs} (ε) / nm (10^3 M^{-1} cm^{-1})	λ_{em} (φ) / nm	E_{00} / eV	τ_{ex}	assign.	ref.
				760 (-) [b] 590 (-) [c]		130 ns [b] 560 ns [d] [a]		[26]
[Cu(dpp)(binc)]$^{+\,a}$	0.69	-1.88	400-600 (-)	-	2.57	17 µs [d]	MLCT	[26]
[Cu(dpp)$_2$]$^{+\,a}$	0.69 [b]	-1.11	441 (3.6)	710 (0.001)	1.80	250 ns	MLCT	[6b]
[Cu(carbazolide)(PPh$_3$)$_2$]$^{+\,b}$	0.50	-2.6	380 (-)	420 (-)	3.1	-	LLCT[90]	[47]
[Cu(SAr)$_2$]$^{-\,b}$	-0.18	~-2.6	~290 (~11)	675 (-)	~2.4	~7 µs	MLCT/LLCT	[57]
[Mo(CNAr$_3$NC)$_3$]^c	0.18 [g]	-2.0 [g]	350-560 (~20)	617 (0.006)	2.2	74 ns	MLCT	[74a]

photooxidants								
complex	$E_{1/2}(C/C^-)$ / V vs SCE	$E_{1/2}(C^*/C^-)$ / V vs SCE	λ_{abs} (ε) / nm (10^3 M^{-1} cm^{-1})	λ_{em} (φ) / nm	E_{00} / eV	τ_{ex}	assign.	ref.
[Cr(Ph$_2$phen)$_3$]$^{3+\,b}$	-0.27	1.40	300-400(*)	-	1.67	425 µs	^{2}E$_g$	[12]
[Cr(ddpd)$_3$]$^{3+\,b}$	-0.65 [f]	0.95 [g]	435 (~4)	778 (0.12)	1.60	898 ns	^{2}E$_g$	[17a]
[Cu(Ph$_2$Me$_2$phen)(P^P-carborane)]^a	-1.44 [f]	0.97 [f]	449 (4.63)	602 (0.05)	2.40	1.4 µs	MLCT	[41]
[UO$_2$]$^{2+\,e}$	-0.29 [h]	2.36 [h]	420 (0.01)	514 (-)	2.65	11 µs	LMCT	[91]

both photoreductants and photooxidants									
complex	$E_{1/2}(C^+/C)$ / V vs SCE	$E_{1/2}(C^+/C^*)$ / V vs SCE	$E_{1/2}(C/C^-)$ / V vs SCE	$E_{1/2}(C^*/C^-)$ / V vs SCE	λ_{abs} (ε) / nm (10^3 M^{-1} cm^{-1})	λ_{em} (φ) / nm	E_{00} / eV	τ_{ex}	assign.	ref.
[Cu(DPEphos)(Me$_2$Ph$_2$phen)]$^{+}$ [b]	1.25	-1.02	-1.64	0.63	~470 (-)	545 (-)	2.27	819 ns	MLCT	[44]
[Zr(^{Me}PDP)$_2$]^c	1.5 [g]	-0.6 [i]	-1.58 [g]	0.51 [g]	528 (27.0)	594 (0.08)	2.09	-	LMCT	[8a]
[Ru(bpy)$_3$]$^{2+\,b}$	1.29	-0.81	-1.33	0.77	452 (14.6)	615 (0.08)	2.10	950 ns	MLCT	[2b, 92]
[Ir(ppy)$_3$]^b	0.77	-1.73	-2.19	0.31	375 (~7)	514 (0.40) [a]	2.50	1.9 µs	MLCT	[92-93]

- Data not readily available. [a] Recorded in CH$_2$Cl$_2$. [b] Recorded in CH$_3$CN. [c] Recorded in THF. [d] Recorded in PMMA film. [e] Recorded in H$_2$O. [f] Reported vs Ag/AgCl, converted to SCE by subtracting 45 mV.[94] [g] Reported vs Fc, converted to Ag/AgCl according to ref. [95] then to SCE by subtracting 45 mV.[26, 94] [h] Reported vs SHE, converted to SCE by subtracting 244 mV . [i] Data not reported, calculated from $E_{1/2}(C^+/C)$ and E_{00} using the Rehm-Weller equations.[11]

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REVIEW

This review summarizes the advances made with photoactive earth-abundant complexes in the context of synthetic organic photoredox chemistry using visible light as an energy input. Mechanistic considerations are combined with discussions of reaction types and scopes.
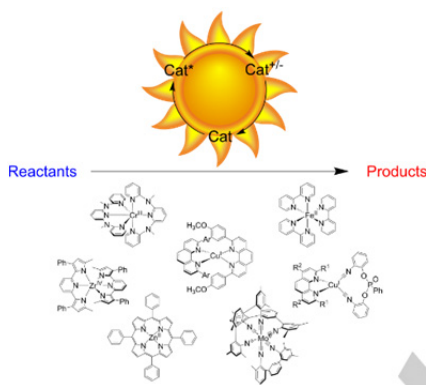
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Photoredox Catalysis with Metal Complexes Made from Earth-Abundant Elements