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Perspective

Catalysis in the Excited State: Bringing Innate Transition Metal Photochemistry into Play

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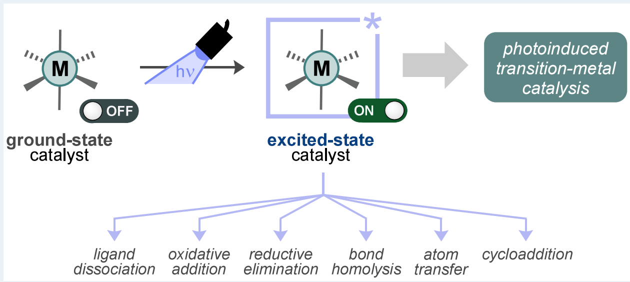
ABSTRACT: Transition metal catalysis is an indispensable tool for organic synthesis that has been harnessed, modulated, and perfected for many decades by careful selection of metal centers and ligands, giving rise to synthetic methods with unparalleled efficiency and chemoselectivity. Recent developments have demonstrated how light irradiation can also be recruited as a powerful tool to dramatically alter the outcome of catalytic reactions, providing access to innovative pathways with remarkable synthetic potential. In this context, the adoption of photochemical conditions as a mainstream strategy to drive organic reactions has unveiled exciting opportunities to exploit the rich excited-state framework of transition metals for catalytic applications. This Perspective examines advances in the application of transition metal complexes as standalone photocatalysts, exploiting the innate reactivity of their excited states beyond their common use as photoredox catalysts. An account of relevant examples is dissected to provide a discussion on the electronic reorganization, the orbitals involved, and the associated reactivity of different types of excited states. This analysis aims to provide practitioners with fundamental principles and guiding strategies to understand, design, and apply light-activation strategies to homogeneous transition metal catalysis for organic synthesis.



KEYWORDS: *photocatalysis, photochemistry, transition metal catalysis, excited states, organic synthesis*

INTRODUCTION

It is estimated that 90% of all chemical processes worldwide employ catalysis.[1] Within the arena of organic synthesis, the paramount role of transition metal catalysis in the development of efficient, selective, and novel methods to access complex architectures is widely recognized.[2] However, in the vast majority of these processes, all the reactivity occurs in the electronic ground state, and the required energy is supplied in the form of heat (thermal conditions). The utilization of excited-state reactivity (photochemical conditions), where energy is supplied by light absorption, is recognized in synthetic organic chemistry and has been historically practiced through the direct excitation of organic substrates in noncatalytic systems.[3,4] However, the application of this strategy has been traditionally hampered by two factors: (*i*) the need for highly energetic UV light (λ < 350 nm) which is required to excite most organic compounds entails possible side reactivities and requires the utilization of quartz vessels and complex/hazardous light sources; (*ii*) the reactivity of purely organic molecules is relatively narrow, typically involving a few functional groups (carbonyl, alkenes) or some activated redox-active moieties, although this mantra has been relentlessly challenged in recent years.[5] On the other hand, transition metal complexes display an extraordinarily diverse photochemistry,[6−8] owing to the variety of metals, ligands, geometries, and oxidation states which altogether strongly affect the dynamics and chemical reactivity of excited states. Moreover, unlike purely organic molecules, most transition metal complexes are colored and present significant absorption in the visible or near-UV range. Considering this, it is remarkable that light has not been broadly used as a tool to alter the reactivity of transition metal catalysis, a fact that perhaps can be ascribed to the lack of practical, economical, and well-defined light sources such as modern LEDs. In recent years, the rise of photoredox catalysis,[9−11] new technological developments,[12] and an increasingly multidisciplinary research landscape applied to chemical synthesis (involving techniques such as DFT, transient-absorption spectroscopy, etc.) has accelerated the adoption of light as the source of energy to run catalytic reactions with applications in synthetic organic chemistry in academic and industrial settings.[13]

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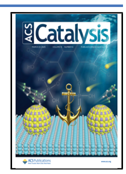


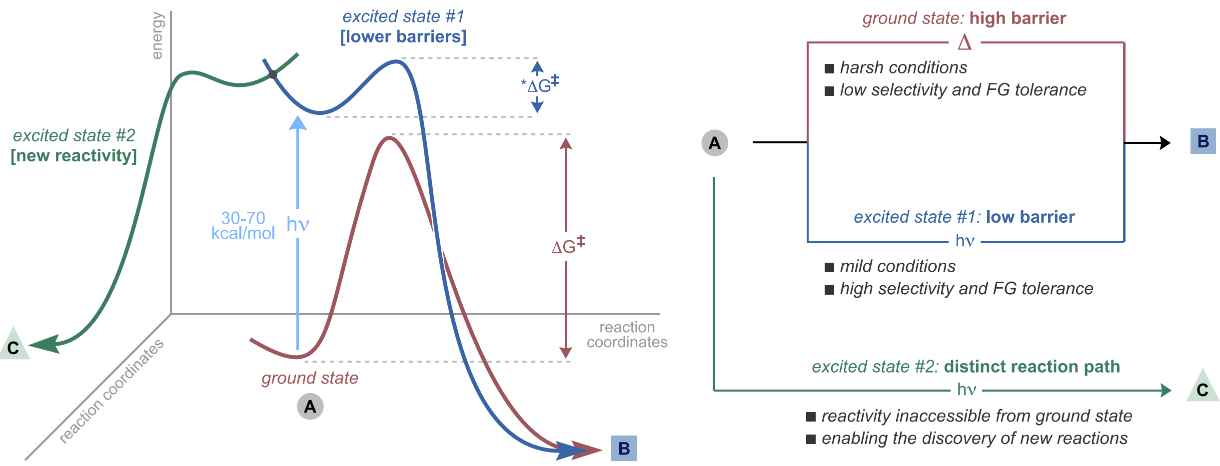


Figure 1. Advantages of excited-state versus ground-state reactivity.

In this Perspective, an account of examples of light-activated transition metal catalysis is presented, showcasing how the innate reactivity of excited states of transition metal complexes can be harnessed to design new synthetic methods. Accordingly, the focus will be placed on systems employing homogeneous transition metal catalysts that absorb light and promote chemical reactivity without the need for external photosensitizers and, therefore, dual catalytic systems (e.g., metallaphotoredox[14]) are beyond the scope of this work. Because many transition metal complexes can display long-lived excited states with enhanced redox properties, there are multiple examples of bimolecular outer-sphere SET reactivity. However, in view of their features being similar to "classic" photoredox catalysts (indeed, they are often indistinguishable), those examples are excluded and the reader is referred to excellent resources on the topic.[15−18] Likewise, examples of energy-transfer processes are not covered and can be found elsewhere.[19] Finally, while other monographs are classified according to the identity of the metal center,[20−22] this Perspective is *organized according to the nature of the excited states*, in an attempt to rationalize their reactivity, find common ground, and provide a general vision on how it can be streamlined to induce specific elementary steps to address challenges in catalysis.

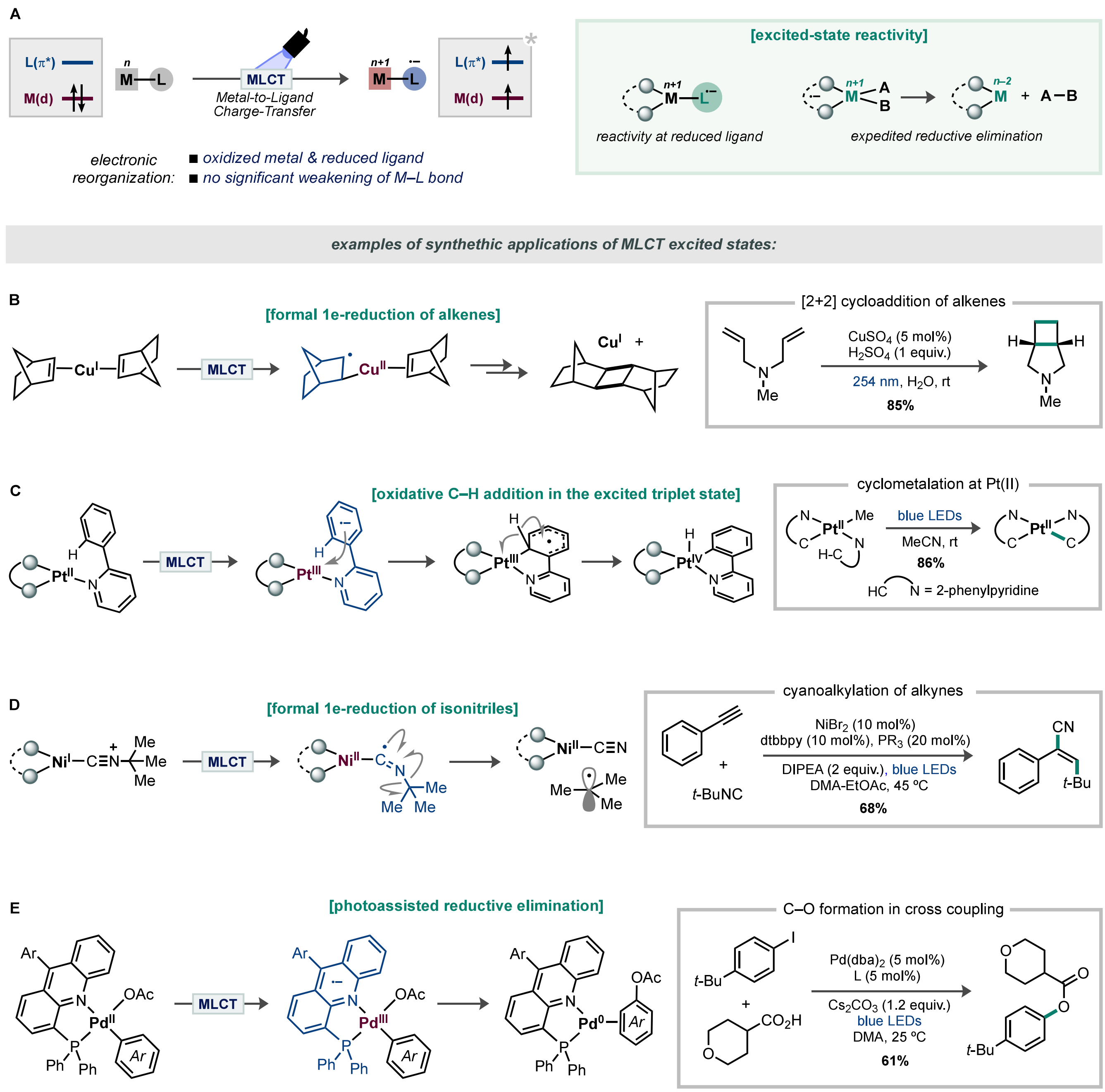
■ WHY USE EXCITED-STATE REACTIVITY?

"The chemical reactivity of a molecule is determined principally by its electron distribution."[23]

Excited states result from the reorganization of electrons at frontier orbitals to give a configuration with higher energetic content than the lowest (ground) state. This means that oxidation states and net charges can change, geometries may suffer important modifications as well as bonds, which are often strengthened or weakened resulting in bond-formation or bond-cleavage that can sometimes occur at extremely short time scales.[24] As a result, excited states must be addressed as individual entities, possessing their own physical and chemical properties which can be very different from their corresponding ground-state species.[23] This often distinct, and rather unique, reactivity can be harnessed to enable elementary steps in catalytically relevant species that are prohibitive without light excitation and recruited to design more effective synthetic routes and methodologies. As illustrated in Figure 1, let us now consider a given reaction **A** → **B** which, in the ground state (red line), presents a prohibitively high energy barrier ($\Delta G^{\ddagger}$). This path would require harsh conditions, which can result in a low functional-group tolerance, decomposition, or low selectivity due to the existence of competitive nondesired pathways. In this regard, we can consider two scenarios in which excited-state reactivity opens advantageous channels. The first one is the population of excited state #1, providing access to the energy profile represented in blue. In this case, the energy of light (in the visible range, 400−800 nm; 35−70 kcal/mol) is stored in the excited state, and due to the population of highly energetic species, the reaction leading to product **B** is highly exothermic and possesses a barrier ($^*\Delta G^{\ddagger}$) that is significantly smaller in comparison to the ground-state profile. This favorable reaction profile results in reactions that can be carried out at mild conditions under irradiation and, potentially, provide higher chemoselectivity and functional group compatibility. A typical example of this strategy is the decoordination of certain ligands (e.g., CO)[25] to create vacant coordination sites needed for catalysis which can be accessed thermally but under light excitation allows a cleaner or more desirable reaction profile. A second case is depicted with the green line, where the population of excited state #2 does not lead to **B** but rather steers toward a different product **C**, *which is inaccessible with ground-state reactivity*. This case is particularly appealing because it opens new possibilities to access the unexplored chemical space, paving the way for the discovery of new synthetic transformations. This is the case for most examples covered in this Perspective, where control experiments show that similar reactivity is not possible in the absence of light, even upon heating. On the other hand, there are also examples where ground-state and excited-state reactivities lead to different products, such as the case of Co-catalyzed hydroboration of enones, where the regioselectivity is controlled by the presence or absence of light irradiation.[26]

Since the nature of excited states (metal centers, topology, bonding character of frontier orbitals, etc.) largely determines the different physical and chemical properties in comparison to the ground state, the chemical reactivity of such states is intimately related to the type of orbitals involved. As such, a classification attending to the orbitals involved in each excited state, while being a simplification (it must be noted that most orbitals and excited states are mixed), often serves to rationalize, understand, and design excited-state reactivities. Accordingly, the following sections showcase examples of photochemically induced reactivities that have led to synthetically useful catalytic systems, organized according to the class of excited states. Each

Scheme 1. (A) Photophysical Aspects, Topology, and Common Reactivity of MLCT States; (B−E) Synthetic Applications of Photochemistry Involving MLCT States



section will display orbitals involved and the corresponding electronic reorganization in the excited state, correlated with their implications for chemical reactivity. It should be noted that while excited states in the schemes below are represented with triplet multiplicity in all cases for the sake of simplicity, a discussion of the spin state is outside the scope of this work, and the reader is referred to the original works for further analysis. Nevertheless, this analysis should serve as the starting point for a more detailed case-by-case analysis. In fact, the same type of excited state can lead to diverse reactivities, as can be readily noticed, attending to the examples covered in this Perspective.

■ MLCT STATES

In view of the large amount of metal complexes with π-accepting ligands (e.g., pyridine, imine, phosphine), it is not surprising that low-lying metal-to-ligand charge-transfer (MLCT) excited states are prevalent in transition metal catalysts. MLCT transitions typically involve the promotion of an electron from a nonbonding d orbital of the metal to a π^* orbital of the ligand, resulting in a net transfer of 1 electron from the metal (which is formally oxidized) to the ligand (which is formally reduced).[6,27] Because the electronic reorganization in the excited state does not retrieve electronic density from an M−L σ-bond nor populate orbitals with antibonding M−L character, MLCT states are often chemically stable and do not directly participate in M−L bond cleavage (Scheme 1A). As a result, MLCT states

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can often engage in bimolecular processes with additional substrates.[28,29] Their long lifetimes together with the ability to act as good oxidants and/or reductants in redox reactions played an essential role in the foundations of photoredox catalysis.[9−11] Indeed, the use and easy tunability of MLCT states of polypyridyl Ru(II) and cyclometalated Ir(III) complexes has been crucial for the spectacular growth and development of this field to date.[30] Since excited-state reactivity in those cases is limited to outer-sphere single-electron transfer (SET), these examples are not covered in this Perspective. Despite the dominance of broadly applied SET reactivity of MLCT states, there are also other interesting examples of reactivity arising from these charge-separated species, which are described below.

The dimerization of alkenes under copper photocatalysis, known as the Solomon−Kochi reaction, provides access to cyclobutane moieties via [2 + 2] cycloaddition.[31] Due to the coordination of the olefin substrates to copper, this transformation allows the cycloaddition of nonconjugated alkenes, which typically do not absorb over 200 nm, under UV irradiation using standard photochemical reactors equipped with Hg lamps (254 nm). The commonly accepted mechanism involves the formation of a bis-alkene Cu(I) complex which, upon light absorption, populates MLCT excited states resulting in the formal 1e$^-$ reduction of the alkene (Scheme 1B).[32,33] The resulting Cu-coordinated radical anion, which is often postulated as an organometallic Cu(II) species, undergoes radical addition to the adjacent alkene and subsequently forms a second C−C bond to generate the cyclobutane [2 + 2] product and restore the Cu(I) catalyst. Notably, this reactivity mode showcases how the formal reduction of an unactivated alkene, while virtually inaccessible by direct outer-sphere SET (E_{red} < −2.5 V vs SCE), can be leveraged using excited-state pathways. Recent studies have shown that the population of MLCT states may lead in some cases to $\pi-\pi^*$ states after internal conversion, which is not accessible by direct excitation at the desired wavelengths, and provide the desired [2 + 2] reactivity via the formation of triplet diradical species.[34] The reaction conditions and scope of this transformation have been refined over the years and nowadays found application to the synthesis of bicyclic sp^3-rich building blocks of high interest for medicinal chemistry and total synthesis.[35,36] Similarly, the application of this blueprint for the [2 + 2] carbonyl-olefin photocycloaddition has also been reported.[37]

In 2016, González-Herrero and co-worker described the first aromatic C−H oxidative addition proceeding in the triplet state of a transition metal complex (Scheme 1C).[38] The authors found that cyclometalation of phenylpyridine-type ligands was possible under blue light irradiation of Pt(II) complexes, while failing under thermal conditions. Mechanistic experiments and computational calculations revealed a pathway initiated by the population of MLCT states, resulting in the generation of a formal radical anion on the phenylpyridine ligand that coordinates to the electrophilic Pt(III) center. Subsequent hydrogen atom transfer (HAT) restores aromaticity on the phenyl ring and leads to a Pt(IV) hydride intermediate, which could be experimentally detected and characterized. This photochemical reactivity has been employed in the synthesis of bis-cyclometalated platinum complexes.[39,40] In addition to these examples of stoichiometric organometallic reactivity, Baslé and co-workers postulated a similar photoinduced C−H oxidative addition step operating on aromatic C−H borylations catalyzed by rhodium,[41] while related transformations have also been proposed to benefit from reactivity arising from triplet MLCT states.[42]

Low-valent nickel complexes [i.e., Ni(I), Ni(0)] are highly electron-rich species which have found use as catalytic intermediates in synthetic methodologies, owing to their ability to activate strong bonds via oxidative addition under thermal conditions.[43,44] However, very recently Chu and co-workers have demonstrated that a fundamentally different activation mode is also viable under light irradiation of Ni(I) isonitrile complexes (Scheme 1D).[45] The authors found that the population of excited states, postulated to have MLCT character, results in the oxidation of the metal center and concomitant reduction of the coordinated isonitrile ligand, which undergo C(sp^3)−NC bond cleavage to afford a Ni(II) cyanide complex and an alkyl radical. This unusual inner-sphere reactivity can be utilized for the catalytic carbocyanation of alkynes with isonitriles to afford products resulting from the formal insertion of the alkyne into strong C(sp^3)−NC bonds. While in this reactivity the Ni species acts as standalone photocatalyst, a related hydrocyanation method was also demonstrated in the same report in the presence of an additional photoredox catalyst. A series of spectroscopic studies supported by stoichiometric and catalytic reactivity have been carried out to propose a mechanism by which the putative photoactive Ni(I) species is generated in situ in the reaction mixture, supporting as well the presence of alkyl radicals arising from the alkyl substituents of the isonitrile ligands.

While previous examples were triggered by the 1e-reduced nature of the ligand, MLCT states also serve to transiently oxidize the metal center, which can find valuable synthetic applications. For example, since high-valent metals are more prone to undergo reductive elimination,[46−48] the population of MLCT states has been postulated to accelerate reductive elimination at Ni(II) centers on the cross-coupling of aryl halides with carboxylates/amines under metallaphotoredox catalysis.[49−51] In those works, the Ni(III) character of the MLCT states of Ni(II) intermediates is proposed to be responsible for the accelerated reductive elimination to form new C−O/C−N bonds. In 2022, Iwasawa and co-workers demonstrated the applicability of a similar strategy to palladium-catalyzed cross-coupling reactions (Scheme 1E).[52] In this work, the authors employed an acridine-based bidentate phosphine ligand, which, once coordinated to palladium, sets the stage for the efficient population of low-lying MLCT states. This strategy allows the coupling of a variety of aryl halides with carboxylic acids under mild conditions under visible light irradiation, while the desired reactivity was absent in the dark. Experimental and computational studies are in line with a rate-limiting reductive elimination step, which can be accelerated via the population of an MLCT state that offers a pathway involving a barrier that is roughly 10 kcal/mol lower than that of the ground state. Indeed, while heating the aryl-acetato Pd(II) intermediate at 100 °C does not lead to the desired product, on the other hand, the same species irradiated with blue light at room temperature yields the desired C−O coupling product after reductive elimination, highlighting the key role of excited-state reactivity in this elementary step.

LMCT STATES

In ligand-to-metal charge-transfer (LMCT) states, the electronic reorganization can be described as the polarity-reverse situation to that found on MLCT states portrayed in the previous section; that is, excitation results in the promotion of an

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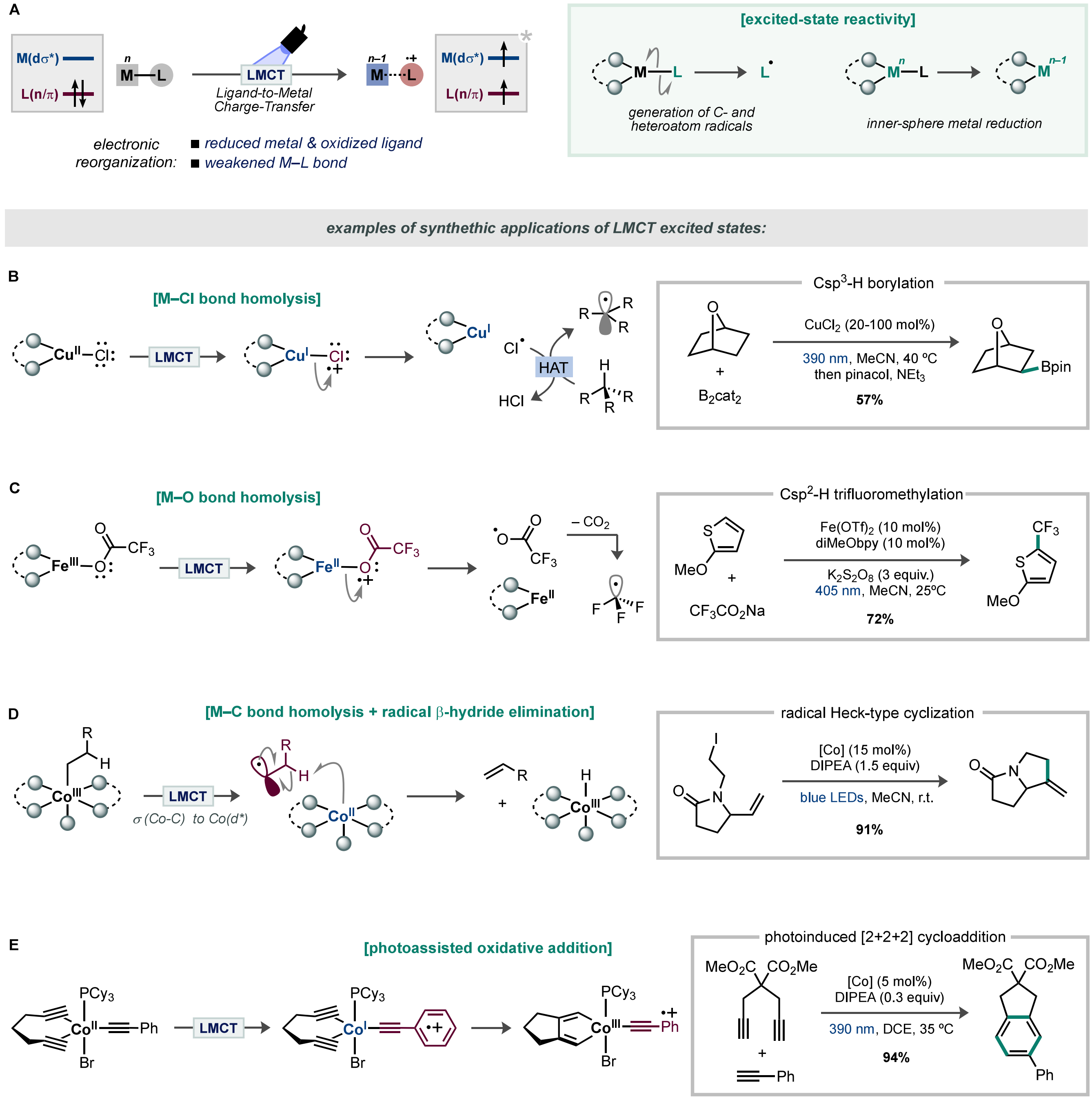
Scheme 2. (A) Photophysical Aspects, Topology, and Common Reactivity of LMCT States; (B–E) Synthetic Applications of Photocatalysis Involving LMCT States



electron from a ligand- to a metal-based orbital (Scheme 2A). Due to the nature of this electron reorganization, this type of excited state is typically present in complexes having an electrophilic, high-valent metal (possessing low-lying, empty d* orbitals) coordinated by electron-rich ligands (typically anionic, strong σ-donors or σ+π donors). Since LMCT transitions populate dσ-antibonding orbitals, the resultant excited state possesses a decreased bond order in one or several M−L bonds, an aspect which, together with the existence of 1e-oxidized ligands, often renders short-lived and chemically unstable species.[8] Accordingly, LMCT represents an extraordinarily effective channel to translate light absorption into chemical reactivity, allowing unimolecular reactivity in ultrafast time scales.[53,54] Indeed, reactivity arising from LMCT states is gaining momentum as an effective platform to generate carbon and heteroatom radicals from X-type ligands on Earth-abundant metal catalysts, since the decoordination of a 1-electron-oxidized ligand from these excited states results in the overall homolysis of M−L bonds.[55]

Due to the ubiquity of cheap and readily available chloride salts of many transition metals, it is perhaps not surprising that the homolytic cleavage of M−Cl bonds was one of the first examples of the utilization of LMCT reactivity applied to organic synthesis. Pioneering studies by Kochi in the 1960s demonstrated that stoichiometric Cu(II) chloride salts were able to release Cl• under UV light irradiation.[56] Building upon

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these seminal results, the performance of this system has been recently improved and used as a general platform for the generation of chlorine radicals in several synthetic applications.[57] For example, Aggarwal and co-workers used the ability of Cl• to undergo HAT reactions with alkanes to generate alkyl radicals (Scheme 2B).[58] In the presence of bis(catecholato) diboron (B_2cat_2) these carbon radicals can be captured to form new C−B bonds, overall representing an effective method for C(sp^3)−H borylation. This methodology allows the borylation of a broad range of substates with excellent functional group tolerance, representing a useful new strategy for this challenging and highly desirable transformation.

The possibility of using carboxylic acids as precursors of carbon radicals is one of the most notable and popular applications of photoredox catalysis.[59,60] However, although this strategy has proven to be an effective tool to generate alkyl radicals, its expansion to benzoic acids and trifluoroacetic acid has been traditionally hampered by the slow CO_2 extrusion or high oxidation potentials. In this regard, LMCT reactivity has been utilized to overcome these limitations, allowing methodologies that use aryl and trifluoromethyl radicals via decarboxylation of their corresponding acids. For example, the groups of Ritter and MacMillan disclosed methods for the decarboxylative functionalization of benzoic acids triggered by the population of LMCT states on the corresponding carboxylato Cu(II) complexes.[61,62] On the other hand, West and Juliá-Hernández simultaneously reported the use of this concept to access trifluoromethyl radicals from readily available trifluoroacetic acid or its salts (Scheme 2C).[63,64] These two works clearly showcase how the issues related to the high oxidation potential of trifluoroacetate (E_{ox} > +2 V vs SCE), which makes this process extremely challenging via outer-sphere SET, can be bypassed by recruiting inner-sphere reactivity at Fe(III) complexes via LMCT excitation. This strategy effectively unlocks the use of the most desirable source of CF_3 groups for radical chemistry, which was applied for the trifluoromethylation of arenes and the hydrotrifluoromethylation of alkenes. Importantly, this strategy has been rapidly adopted and can be now extended beyond CF_3 to access other related fluorinated C(sp^3) radicals such as difluoromethyl, perfluoroalkyl, or halodifluoromethyl via decarboxylation in different synthetic applications.[63,65−68] Besides iron catalysis, a similar design involving Ag(II) has also been proved competent for this purpose.[69] While the latter examples focused on decarboxylations, M−O bonds in alkoxide complexes can also be homolyzed upon LMCT excitation, enabling interesting synthetic applications such as C−C bond cleavage, remote C−H bond functionalization, or deracemization protocols.[70−73]

Cobaloximes and vitamin B_{12} derivatives (cobalamins) are Co(III) complexes that are the subject of many studies due to their role in biological and energy conversion processes.[74,75] Alkyl cobaloxime and cobalamin derivatives possess a relatively weak Co−C bond in the axial position that is readily homolyzed upon light irradiation. Studies on the nature of the excited state have revealed that transitions from the Co−C bond to a d* orbital of the metal center (LMCT/MC mixture) are responsible for the observed photoreactivity.[7] A notable feature of cobaloximes that sets them apart from other alkyl metal complexes is that the resultant Co(II)/alkyl radical can effectively react via HAT within the solvent cage (Scheme 2D). This results in a Co(III) hydride and an alkene, which are products derived from this stepwise, radical β-hydride-type elimination. Pioneering studies by Carreira and co-workers in 2011 demonstrated the photocatalytic performance of alkyl- and stannyl cobaloximes for the cyclization of alkyl iodides to give Heck-type products.[76] This mode of action has been increasingly used in photoinduced methods for alkene synthesis,[77] most frequently in combination with an additional photocatalyst, although their use as a standalone catalyst has also being demonstrated.[78] Interestingly, Leonori and co-workers demonstrated that regioselectivity on the alkene formation can be harnessed by controlling the HAT step, which is heavily affected by the steric and electronic effects on the ligands of Co complexes.[79]

While many LMCT states have a dissociative nature owing to the population of σ* orbitals, this class of excited states can present another type of reactivity that does not involve the homolytic cleavage of metal−ligand bonds or even result in relatively stable photoluminescent compounds.[80,81] For example, since LMCT excitation results in the formal reduction of the metal center, low-valent intermediates may be transiently generated in this fashion and their enhanced tendency toward oxidative addition harnessed for synthetic purposes. A compelling example of this blueprint was demonstrated in 2019 by Rovis and co-workers on the cobalt-catalyzed [2+2+2] cycloaddition of alkynes (Scheme 2E).[82] The authors proposed the formation of a photoactive Co(II) phenylacetilyde, which, upon LMCT excitation, results in the formation of a radical cation on the ligand and the 1e$^-$ reduction of the metal center to Co(I). This photophysical event triggers the oxidative migratory insertion leading to a Co(III) metallacycle which, after reductive elimination, renders the final cycloaddition product.

■ METAL−OXO LMCT STATES

Transition metal complexes having a metal−oxo bond (M═O) have been the subject of intense studies due to their relevance in catalytic oxidations and their key role in biological processes.[83] This type of compound presents a high-valent metal center bonded to an electron-rich O^{2-} ligand, which results in large contributions of metal-based empty d* orbitals and filled p(O) orbitals to the LUMO and HOMO, respectively (Scheme 3A). Accordingly, low-lying LMCT excited states are prevalent in this type of complexes. However, in contrast to other LMCT excited states, excited-state reactivity at metal−oxo complexes generally does not involve dissociation of ligands since a π-bond, rather than a σ-bond, is cleaved. A simplified representation of the electronic reorganization on the excited state would be the homolytic cleavage of an M═O double bond, leading to a 1e$^-$ reduced metal bound through a single bond to an oxygen-atom radical (M^{n-1}−O•). This topology resembles the triplet excited n-π* state frequently found in organic carbonyl compounds,[3,23] and in fact, the reactivity associated with both excited states is often alike.[84] Although the photophysics and photochemistry of different metal−oxo complexes have been studied, polyoxometalates have received most of the attention in this regard and their reactivity with organic substrates under light irradiation has been known for a long time.[85−87] Among polyoxometalates, decatungstate salts (DT, $W_{10}O_{32}^{4-}$) stand out on their use as photocatalysts due to the formation of a relatively long-lived triplet wO state.[88,89] This triplet state is accessed after internal conversion from singlet LMCT states and possesses a marked radical character in the oxygen atom, which is responsible for its high efficiency on HAT reactions driven by the formation of a strong O−H bond. This reactivity has been extensively exploited in organic synthesis to access alkyl radicals from unactivated C(sp^3)−H bonds via HAT, which are then the object of

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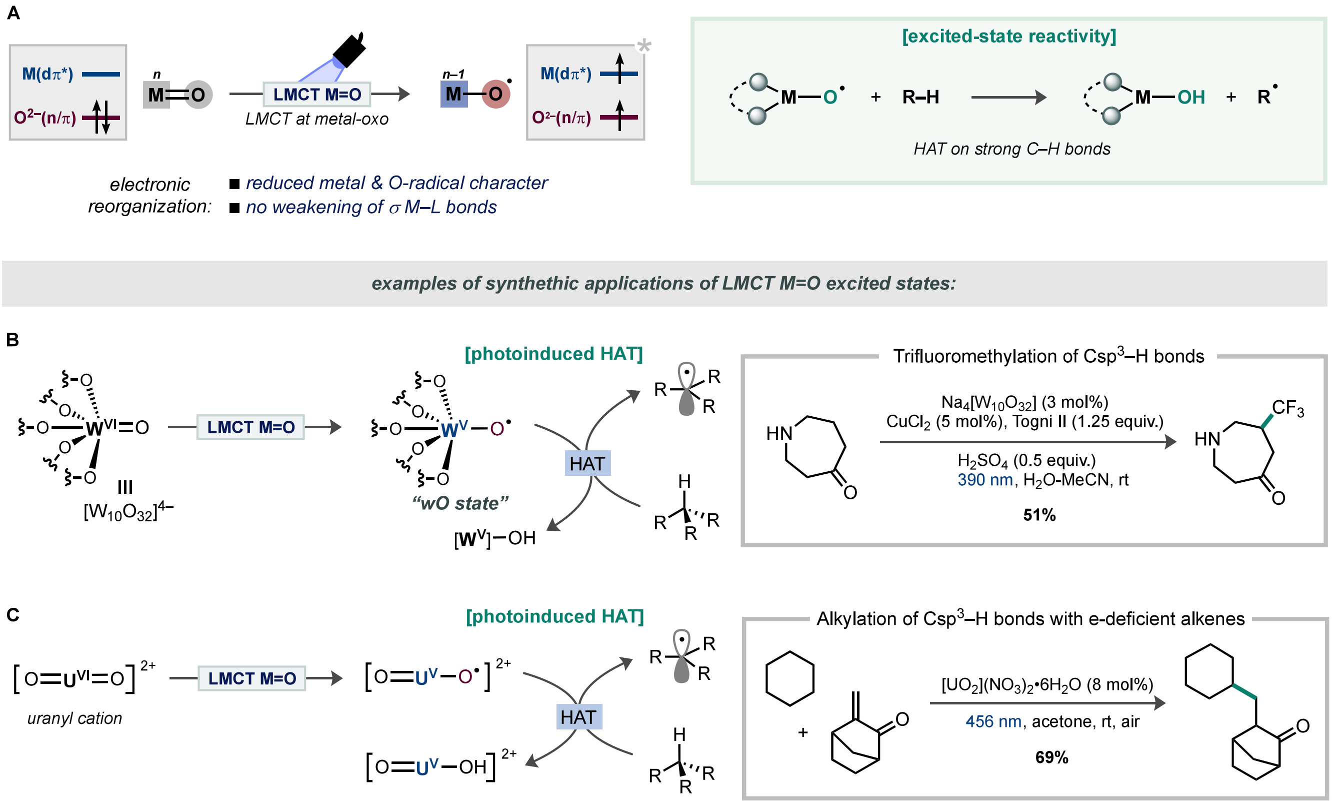
Scheme 3. (A) Photophysical Aspects, Topology, and Common Reactivity of LMCT States at Metal−Oxo Complexes; (B and C) Synthetic Applications of Photocatalysis Involving LMCT States at Metal−Oxo Complexes



subsequent functionalizations.[90−93] A notable application of this strategy was disclosed by MacMillan and co-workers in 2020, developing a method based on DT and copper catalysis to perform the trifluoromethylation of C(sp^3)−H bonds (Scheme 3B).[94] The proposed mechanism involves a photoinduced HAT from the alkane substrate to DT*, resulting in an alkyl radical that is intercepted by the Cu^{II}−CF_3 species to deliver the cross-coupled C−CF_3 products. Remarkably, this approach represents an effective way to introduce CF_3 groups at sites otherwise difficult to access, holding great interest for medicinal chemistry in view of the desirable properties of the trifluoromethyl group.[95]

However, photocatalytic activity via LMCT at M═O is not limited to polyoxometalates and can also be harnessed using monomeric species. For instance, uranyl cation (UO_2^{2+}) and derivatives have been particularly well-suited for catalytic applications.[96−101] In the excited state, UO_2^{2+} is a potent oxidant and, similarly to DT salts, an effective agent for HAT reactions that can be leveraged for C−H functionalization reactions. This reactivity mode was exploited by Ravelli and co-workers to promote the C−H alkylation of alkanes (Scheme 3C).[102] In this work, the authors employed uranyl photocatalysis to promote Giese-type radical additions of alkyl radicals generated via HAT to electron-deficient alkenes. The good absorptivity of uranyl cation in the visible range, together with the relatively large abundance of uranium, makes it an interesting alternative to DT salts. Apart from DT salts and uranyl complexes, other metal−oxo complexes such as molybdenum-,[103−105] cerium-,[106] or antimony-based[107] compounds have also shown applicability in organic synthesis.

■ MC (d−d*) STATES

Excited states resulting from electronic transitions within the metal center (i.e., metal centered, MC; also known as ligand-field, LF) are inherent to transition metal complexes, given the frequent contribution of both filled and empty d orbitals to the frontier-orbital landscape of these types of compounds. d−d* transitions commonly appear in the visible range and are responsible for the notoriously rich palette of colors that is characteristic of transition metal complexes. This also means that MC excited states often retain a low energetic content, making them susceptible to fast deactivation by vibrational coupling with the ground state according to the energy-gap law.[108,109] Notwithstanding, processes that do not require the cleavage of strong bonds (e.g., isomerization of coordination compounds[110,111]) can take place effectively competing with vibrational deactivation. MC states are spatially confined excited states and, thereby, do not involve a net charge transfer or a change in the oxidation state of the metal (Scheme 4A). However, since MC states are associated with the population of d* orbitals, their intermediacy can result in bond-breaking processes, particularly when weak metal−ligand bonds are present. In fact, some of the earliest examples on the use of photochemical conditions to trigger chemical reactivity in transition metal complexes, such as photoinduced ligand substitutions in Cr(III) complexes,[112] are mediated by MC states.

In general terms, the most frequent use of excited MC states in catalysis is the heterolytic dissociation (decoordination) of ligands. Under irradiation a given compound can increase the rate of ligand substitution up to 15 orders of magnitude,[7,24] a feature of tremendous utility when the creation of a coordination

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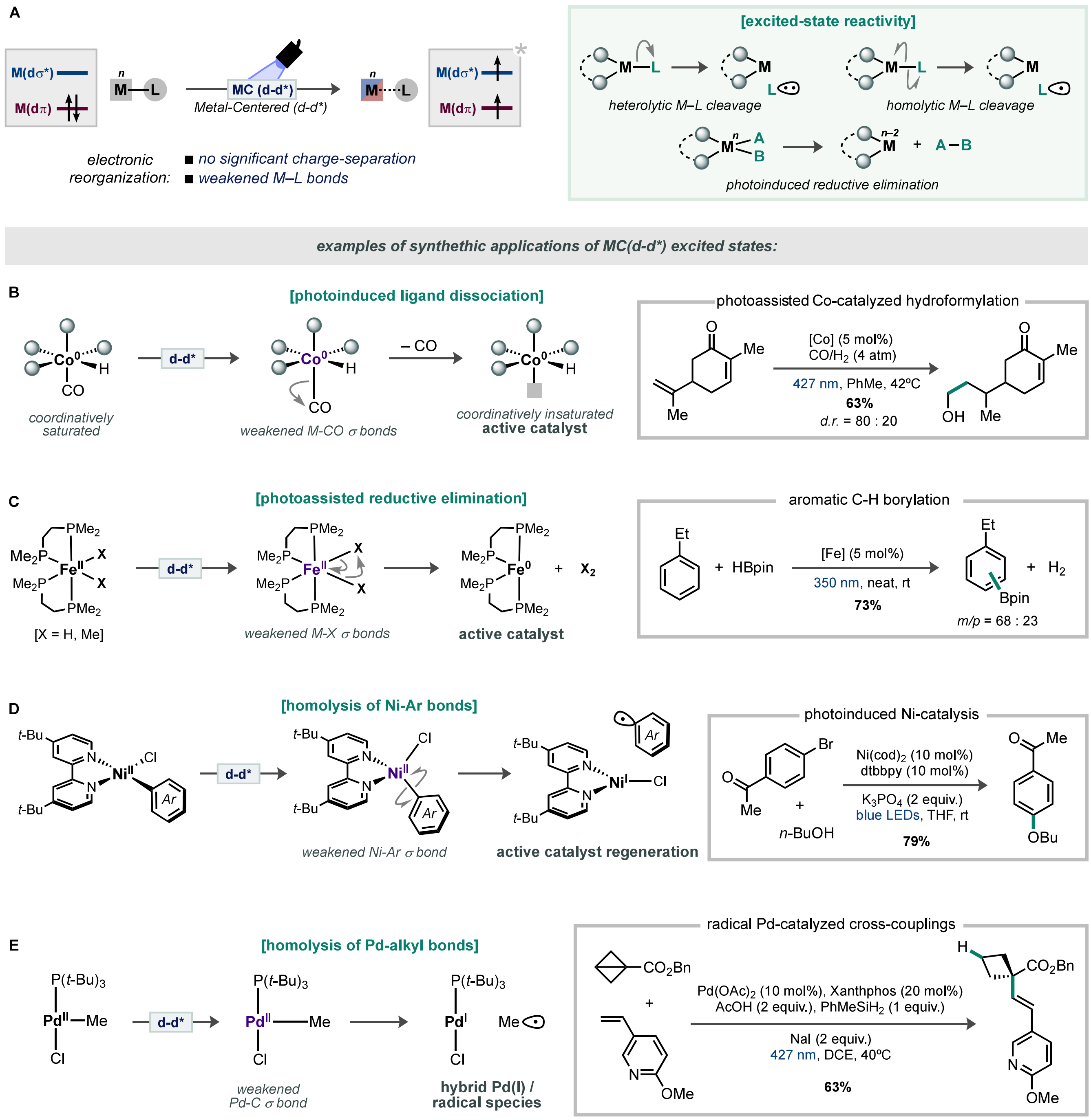
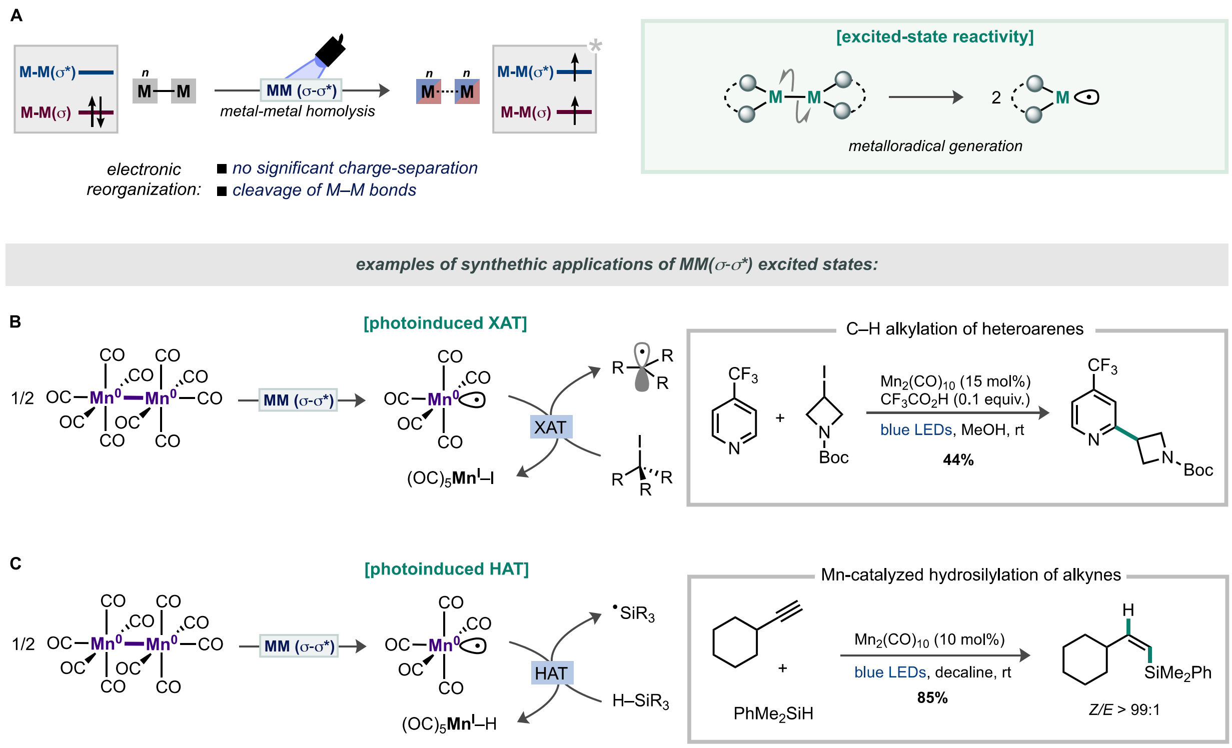
Scheme 4. (A) Photophysical Aspects, Topology, and Common Reactivity of MC States; (B–E) Synthetic Applications of Photocatalysis Involving MC States



vacancy to allow the binding of substrates is an energetically demanding step. In this situation, light irradiation circumvents the need for high temperatures, allowing milder conditions that often result in better selectivities. A well-known example is catalysis mediated by carbonyl complexes, where light irradiation is a widely used approach to generate catalytically active species by facilitating CO dissociation.[7,25,113] Although photoinduced CO dissociation is long-standing,[114,115] its use remains frequent in the fields of organometallic chemistry and transition metal catalysis. For example, Chirik and co-workers reported in 2022 the Co-catalyzed hydroformylation of alkenes with syngas (CO/H_2) under visible light irradiation (Scheme 4B).[116] The authors propose a mechanism by which a Co hydride species dissociates one of its CO ligands upon blue light absorption to form the active form of the catalyst, enabling alkene coordination and subsequent migratory insertion into the Co–H bond. This results in a hydroformylated product that is hydrogenated in situ to give the desired alcohol. This methodology presents a good scope on both activated and unactivated alkenes and excellent selectivity for linear alcohol products. Taking advantage of the possibility to dissociate CO photochemically and thermally, the groups of Teskey and Chirik have reported the operation of divergent mechanistic pathways under these two conditions for Co catalysis.[26,117] Other metal

Scheme 5. (A) Photophysical Aspects, Topology, and Common Reactivity of MM States; (B and C) Synthetic Applications of Photocatalysis Involving MM States



carbonyls can also benefit from this strategy, as shown by Chen and co-workers on the Rh-catalyzed coupling of imides with alkynes, where photoinduced CO dissociation is key to enable catalytic turnover.[118] On the other hand, photoinduced dissociation is not only restricted to CO and can be leveraged to cleave other M−L bonds. For instance, Koenigs and co-workers revealed that visible light irradiation on Rh-catalyzed C−H functionalizations plays a pivotal role to decoordinate the directing group, which is needed to facilitate the protodemetalation step.[119]

Beyond ligand dissociation, excitation to d−d* states can result in changes in the oxidation state of the metal center as well. In particular, $2e^-$ reductions can be achieved via photoinduced reductive elimination, a strategy that has been exploited to generate active low-valent species *in situ* by irradiating thermally stable precursors, i.e., $[M^{(n+2)}X_2] \rightarrow [M^n] + X_2$ (X = H and/or alkyl). A classic example of this reactivity is the photoinduced reductive elimination of H_2 from Ir(III) or W(IV) diihydrides with concomitant generation of active Ir(I) or W(II) species, which assisted the development of seminal works in the field of metal-mediated C−H activation.[120−122] In these metal hydride complexes the HOMO is generally a nonbonding d orbital from the metal while the LUMO is an M−H(dσ*),[123] giving rise to photochemically active excited states with different degrees of MC/MLCT character. Thereby, population of such excited states in many transition metal dihydrides triggers a fast and efficient reductive elimination of H_2 which can proceed within 40 fs.[124] As a result, photoinduced reductive elimination from dihydrido- and dialkyl-metal complexes has been historically capitalized to generate catalytically active species for a variety of processes, being of particular interest in C−H activation protocols[125] all the way from their inception to more recent works. For example, Darcel and co-workers reported in 2015 the iron-catalyzed C−H borylation of arenes under UV light irradiation (Scheme 4C).[126] This work capitalizes on the ability of $Fe(P\wedge P)_2X_2$ ($P\wedge P$ = diphosphine, X = H or Me) complexes to eliminate H_2 or ethane to deliver low-valent, coordinatively unsaturated $Fe(P\wedge P)_2$ species,[127] which present high activity on Csp^2−H borylation reactions in the presence of HBpin. This excited-state reactivity mode has found use in other applications beyond synthetic chemistry.[128,129] Photoinduced C−O and C−F reductive eliminations have been reported for Au(III), although the nature of the excited state was not discussed in detail in those cases.[130,131]

Previous examples showcased photoinduced $2e^-$ processes, but MC states can also induce radical reactions. Recently, Doyle and co-workers disclosed a study on the mechanism of photoinduced C−O cross-coupling reactions involving nickel catalysis (Scheme 4D).[132] Through a series of computational studies, spectroscopic measurements, and reactivity experiments, the authors propose the formation of a Ni(II) aryl complex, resulting from the oxidative addition of aryl bromide substrates, which presents photochemical reactivity. After light absorption into MLCT states, the excited state dynamics leads to a relatively long-lived, low-lying triplet MC state which not only involves a geometry change from square planar to tetrahedral but also presents a significantly weakened Ni−aryl bond. This eventually results in the homolytic cleavage of the organometallic bond leading to an aryl radical and a 1e-reduced Ni(I) species, which presents high activity in cross-couplings. This mechanistic paradigm establishes photoinduced reactivity as a way to initiate and sustain "dark" (ground-state) catalytic cross-couplings based on Ni(I), a concept that has been proposed by other groups as well.[133,134] It is worth noting that metallaphotoredox systems based on Ni catalysis present rich and intriguing pathways, and their mechanistic features have been the subject of intense debate with equally diverse

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conclusions on the nature of the operative excited states and their reactivities.[50,135−140]

While homolysis is a relatively well-established pathway in Ni and other 3d metals, noble metals (e.g., Pd, Ir, Rh, etc.) present a much lower tendency to participate in odd-electron reactivity.[141] However, such a paradigm is not retained in the excited state, and therefore, photochemical activation represents a highly attractive gateway to enter the $1e^-$ regime in noble metals to overcome challenges typically encountered in thermal pathways. For instance, the ability of alkyl Pd(II) complexes to participate in homolytic cleavage leading to Pd(I) and alkyl radicals has been known for decades,[142−145] but only recently has this reactivity been systematically exploited for catalytic purposes.[18,146] Such "hybrid" Pd(I)/C-radical species generated under photochemical conditions play a key role in a number of catalytic applications in synthetic organic chemistry,[147−156] enriching the capabilities of Pd catalysis under light irradiation (e.g., box in Scheme 4E). Unfortunately, although the synthetic utility of this strategy is evident, the nature of the excited state is often undisclosed. In this context, Carrow and co-workers reported in 2023 a detailed mechanistic analysis to shed light on the nature of the excited states involved in the light-induced Pd−C homolysis of T-shaped Pd(II) alkyl complexes (Scheme 4E).[157] Interestingly, the authors found that simple monophosphine ligand complexes were more efficient than other analogues containing chromophoric diimine ligands, in line with the hypothesis of an MC (rather than an MLCT excited state involving low-lying π^* orbitals) as responsible for the observed reactivity. Computational calculations predict low energy transitions from filled Pd(d) orbitals to orbitals being a mixture of Pd(d*)/Pd−CH_3(σ^*). The resultant MC/MLCT states have a Pd−CH_3 bond that is weakened by 20 kcal/mol with respect to that found in the ground state as a result of the population of a σ^* orbital, allowing efficient homolysis of this bond at room temperature. Taken together, it could be hypothesized that analogous MC states may be responsible for the formation of "hybrid" Pd(I)/C-radicals previously mentioned.

■ MM (σ–σ^*) STATES

In previous sections, the focus has been placed on monomeric metal complexes. However, excited-state reactivity can also play a key role in multimetallic systems.[158] Transition metal complexes containing more than one metal center, and sometimes presenting metal−metal bonds, exhibit a variety of orbitals which are even richer, leading to distinct excited states that are not present in discrete, monomeric species. Perhaps the most characteristic example of photochemistry arising from multimetallic systems is metal−metal bond homolysis.[159] Compounds bearing a metal−metal bond often present a frontier orbital diagram in which the HOMO has large contributions of the σ(M−M) bond, while the LUMO has a marked antibonding character, i.e., σ^*(M−M) (Scheme 5A). The resultant excited state (MM, σ–σ^* state) is largely dissociative because it removes electronic density from a σ-bonding orbital to place it in an σ-antibonding orbital around the same bond, leading to the ultrafast homolytic cleavage to generate monomeric species. Interestingly, the ensuing complexes are frequently $17e^-$-complexes with a singly occupied d_{z^2} orbital which is highly directional, conferring upon them a radical-type character.[160] These metalloradicals have a strong tendency to undergo electron- or atom-transfer to fulfill the 18-electron rule, leading to intriguing reactivities.[161]

Although photoinduced metal−metal homolysis is known for many metal complexes and studies on the reactivity of the resultant metalloradicals appeared decades ago,[159] the manganese carbonyl dimer complex $Mn_2(CO)_{10}$ has been predominant over the rest on their catalytic performance for organic synthesis. Upon visible light irradiation, a homolytic cleavage of the Mn−Mn bond of the dimer results in the effective generation of the $17e^-$ metalloradical $(CO)_5Mn$●, which displays a remarkable ability to undergo atom-transfer reactions and fulfill the $18e^-$ rule (Scheme 5B). In particular, the high affinity for halogen-atom transfer (XAT) reactions[162] has been used to generate carbon radicals from their corresponding halides, with applications in organic synthesis pioneered by the groups of Parsons and Freidstad.[163−165] These seminal studies have propelled more recent applications, such as the Minisci-type C−H alkylation of heteroarenes with alkyl iodides under $Mn_2(CO)_{10}$ photocatalysis.[166] This work, reported in 2017 by Frenette, Fadeyi, and co-workers, showcases the utility of manganese photocatalysis for the late-stage functionalization of densely functionalized compounds and bioactive molecules under mild conditions. Photogenerated $(CO)_5Mn$● can also participate in the HAT events. For example, Zhang and Zhang demonstrated the synthetic utility of this blueprint on the hydrosilylation of alkynes (Scheme 5C).[167] The key step of this methodology is the HAT between the metalloradical and different alkyl and aryl silanes, offering high regio- and stereoselectivity when aryl alkyne substrates are used. This reactivity was also extended to hydrogermylation in the same report.

■ MISCELLANEOUS EXCITED-STATE REACTIVITY

The previous sections covered the most frequent types of chemically active excited states utilized in catalysis. However, the broad diversity of transition metal complexes results in assorted sets of excited states involving different topologies and associated reactivities. This section is intended to illustrate this diversity by briefly commenting on some miscellaneous examples that could serve as a starting point for curiosity-driven readers.

Apart from MLCT and LMCT, other excited states that involve charge separation can result in interesting reactivities. For example, when both HOMO and LUMO are in different ligands and have reduced contributions from metal orbitals, ligand-to-ligand charge transfer (LLCT) excited states are predominant. The main reactivity associated with LLCT states is electron-transfer, which has been observed in Cu complexes[168] that are catalytically active for C−N bond cross-couplings.[169] On the other hand, LLCT states at main group catalysts can also lead to synthetically useful transformations, such as the homolytic cleavage of Bi−O bonds to form CF_3 radicals at bismuth catalysts.[170] Ligand-centered (LC) states are also prevalent in many metal complexes, but their reactivity (or its absence) is largely variable and case-by-case dependent. For example, an LC state involving intraligand charge transfer (ILCT) within a bipyridine ligand decorated with two carbazole moieties has been used to improve the performance of Ni as standalone catalyst in cross-coupling reactions under visible light irradiation.[171] On the other hand, Au(III) complexes using a donor−acceptor dye as ligand present ILCT states accessible with green light which, after unidentified excited-state dynamics, trigger the generation of chlorine radicals.[172]

It is also worth noting that, although a given excited state presents an electronic distribution that is in line with similar compounds, sometimes it can lead to different pathways resulting in unique outcomes. A clear example is the photochemistry of cyclopentadienyl Ir(III) hydrides having bipyridine ligands. In this class of compounds long-lived MLCT excited states—resulting from the promotion of an electron from a d orbital of the metal to a π^* orbital of bipyridine—are populated, which can react with another molecule of the same complex in the ground state (bimetallic self-quenching mechanism) resulting in disproportionation reactions enabling hydrogen evolution.[173] Similarly, cyclometalated derivatives can also be active in proton-coupled electron transfer (PCET) or HAT photocatalytic hydrogenation reactions.[174,175]

The availability of f orbitals in lanthanides results in MC states with different properties in comparison to lighter transition metals. For example, Ce(III) amidato complexes display long-lived excited states resulting from 4f → 5d (SOMO to SOMO +1) transitions, having metalloradical character due to the presence of an unpaired electron on the highly directional d_{z^2} orbital.[176] These types of excited states are able to participate in both inner- and outer-sphere SET reactions with aryl iodides, bromides, and benzyl chlorides. Recently, it has also been proposed that an MC state at Ni(II) presenting inverted valence plays a key role promoting photocatalytic C−H arylation reactions via an unusual concerted metalation deprotonation (CMD) mechanism,[177] further emphasizing the heterogeneity in the reactivity of d−d* states.

Finally, multimetallic systems can also present other reactivities beyond the formation of metalloradicals by homolysis of metal−metal bonds via the population of MM states. In fact, there are dinuclear d^8 species with metal−metal interactions in which a bimetallic bond is not cleaved but formed in the excited state as a result of a $d\sigma^* \rightarrow p\sigma$ transition.[178,179] The resulting excited state is often long-lived and has the topology of a diradical species, making them suitable for bimolecular reactivities that have found some catalytic applications, with Au and Pt dimers being the most relevant in this regard.[180,181]

■ CONCLUSIONS

The modulation of specific elementary steps has been a crucial factor within the arena of transition metal catalysis to overcome key challenges hampering the desired catalytic performance.[2] This approach has been routinely implemented over the years through the careful selection of metal centers and ligands to enable the desired "thermal" reactivity. Nevertheless, such a blueprint only considers the influence over a single, electronically relaxed ground state. Light absorption represents a practical and effective gateway to access a much more diverse landscape of chemical reactivity offered by the population of diverse excited states, each of them having distinct physical and chemical properties. As such, *photochemical conditions should not only be considered as a mere alternative to thermal conditions as the source of energy to fuel a chemical process, but rather recognized as a channel to access reactivity landscapes that are inaccessible in ground-state chemistry*. While the photophysics and photochemistry of transition metal complexes has been a subject of intense study for many decades,[6,23,110] the transpiration of this knowledge into the field of organic chemistry has been historically sporadic. However, renewed interest in photochemical conditions to enable the development of synthetic methods has stimulated interest in the use of excited-state reactivities at transition metal complexes for catalytic applications. Moreover, well-defined, low-cost, and practical photochemical setups are nowadays more accessible than ever before, breaking the barriers to their quick adoption in any synthetic lab.

So the question is how can photochemical conditions modulate the intrinsic reactivity of a transition metal catalyst to enable the desired reactivity or discovery of new ones? Is there any rationale behind this strategy, or is it just a "black box" where the outcome of irradiation is completely unpredictable? How can one promote a given photochemical process or access a desirable type of excited state of interest? Certainly all these questions cannot be answered in a general fashion or solved in a single piece of work, but I hope this Perspective aids to rationalize the outcome of representative photoinduced reactions and helps to bridge the gap between the fields of organic chemistry, coordination chemistry, and photophysics and photochemistry. Within this Perspective, it can be realized how the interplay of excited-state reactivity and subsequent, ground-state organometallic reactivity results in highly effective and rather unique systems. While the application of photochemical conditions has been used for decades on organometallic systems based on precious metals,[7] their application was typically reduced to the creation of coordination vacancies by ligand dissociation or the generation in situ of low-valent metal species by reductive elimination. Conversely, now the greater appreciation of different excited states−particularly those involving charge-transfer−by the homogeneous catalysis community as well as the increasing interest in catalysis using Earth-abundant 3d-metals,[141] more prone to 1e-pathways, have materialized on a diverse palette of reactivity profiles. Here it is shown how the reactivity of many excited states can be rationalized attending to the electronic redistribution after light absorption, and although in some cases the excited state dynamics are too complex to be generalized, reactivity in similar classes of metal complexes can be predicted, optimized, and used for synthetic purposes.

While the benefits of this strategy are obvious, there are several future challenges that remain in this field. The excited states involved in many photoinduced reactions, for example, in a key field such as C−H activation,[182] are still unknown or not being discussed in detail. While this entails a gap of knowledge, it represents a great opportunity for nonsynthetic research groups to step in and perform spectroscopic or computational studies a posteriori, aimed at providing further insights that aid the design of future related catalytic manifolds. Regarding mechanistic studies, a simple HOMO−LUMO analysis or studies based on UV−vis absorption spectroscopy can be a good starting point to understand the photochemical reactivity of a given compound or perform preliminary studies, but it should always be taken into account that this inspection gives information only about the first excited states that are populated after photon absorption, which are not necessarily responsible for the observed reactivity. The excited-state dynamics can lead to other states via internal conversion, intersystem crossing, or conical intersections, complicating the interpretation. This complexity, together with the short lifetime of the species generated after photoexcitation, represents an additional challenge to unraveling the mechanism of a photoinduced reaction involving transition metal catalysts. For this reason, the frequent multidisciplinary collaboration between purely synthetic chemists with other groups specialized in photophysical studies or computational calculations is required to shed light on these processes. Lastly, further research efforts should be devoted to the systematic use of certain photocatalytic manifolds

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and their extension to different synthetic transformations rather than a sporadic appearance in one work for a single application. In this regard, the use of photoexcited palladium catalysis is an evident success story, enabling a myriad synthetic opportunities.[18,146]

In short, this account provides an analysis of selected up-to-date advances on photoinduced processes exploiting the innate reactivity of metal complexes in the excited state without the need for additional photosensitizers. It can be envisioned that many more systems will be discovered over the next years, due to the increasing number of researchers using photocatalysis and its outstanding potential as a synthetic tool. Hence, the future seems bright in this field, demonstrating that innovation can be just one photon away.

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Notes

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