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12 Photocatalysis of rare earth complexes in organic synthesis

12.1 Introduction

A traditional photochemical reaction to excite the substrate or reagents uses high-energy UV light. These reactions are often unselective, highly difficult to control and involve special equipment to carry out the reaction. Visible light has emerged as an effective reagent in photocatalysis, an effective technique in organic synthesis that utilizes photons for excitation, paving the path for sustainable chemical reactions. In this field new reactions were developed that are mostly focused on a common photo redox cycle. In addition, recently a variety of new concepts and strategies have also emerged that involve the application of visible light with variable wavelengths and intensities that tune the properties of photocatalyst to control the reactivity of the organic compounds. Evidenced by volumes of reviews published in the last decade, many research groups have turned their interest in photocatalysis [1–8]. In general, iridium- and ruthenium-based photocatalysis dominates the chemical community till now, but recently rare earth metal complexes [9, 10] are also employed as photocatalysts for various organic transformations.

12.2 General mechanistic pathways involved in photocatalysis

Photocatalysts could initiate the organic transformations through various mechanistic manners. Particularly, visible light photoredox catalysis [11–15] is documented as an effective protocol in synthetic organic conversions. The various mechanistic cycles of photocatalysis are shown in Figure 12.1. Depending on the reagents and substrates present in the reaction mixture, an excited photocatalyst (PC*) may absorb or donate a single electron after being exposed to light, enabling oxidative or reductive quenching cycles. Occasionally, a coordinated proton transfer (proton-coupled electron transfer

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Figure 12.1: Distinct catalytic approaches of photocatalytic reactions.

[PCET]) could also work in tandem with the oxidative or reductive cycles. Contrarily, photocatalytic hydrogen atom transfer (HAT) occurs either following single electron transfer (SET) events or by the homolytic breakage of C–H bonds by the PC. Additionally, photocatalysts in their excited state can transfer their energy to reactants that are not capable of absorbing light to induce a chemical reaction.

12.3 Photosensitization

Zhang et al. [16] demonstrated the synthesis of Gd^{III} complexes that can serve as photosensitizer for singlet oxygen (Figure 12.2). These Gd^{III} complexes include porphyrin,



Figure 12.2: Synthesis of Gd^{III} trans-porphodilactone complex.

porpholactone, and *cis*- and *trans*-porphodilactone, which act as ligands that coordinate to Gd^{III} ion and alters its photosensitization efficiency. One of these ligands, *trans*-porphodilactone, produced singlet oxygen with high quantum yield when stimulated in the visible to near-infrared range (NIR). In addition to its photosensitization property, Gd(III) *trans*-porphodilactone complex (2) acts as effective catalyst for photooxidative C–H bond cleavage of secondary or tertiaryamines and also efficient in natural product cholesterol photo-oxygenation.

Schelter and coworkers [17] have developed luminescent Ce^{III} complexes with two complete mixed-ligand series (Figure 12.3). The general formula of Ce^{III} complexes is $[N(SiMe_3)_2]_{3-x}Ce^{III}[(Me_3Si)_2NC(N^iPr)_2]_x$ (x = 0, **3** N; x = 1, **4** N, x = 2, **5** N; x = 3, **6** N) and $(OAr)_{3-x}Ce^{III}[(Me_3Si)_2 NC(N^iPr)_2]_x$ (x = 0, 1-OAr; x = 1, 2-OAr, x = 2, 3-OAr; x = 3, 4) has lifetimes of 117(1) ns and quantum yields of photoluminescence up to 0.81(2). These Ce^{III} photosensitizers are extensively studied for their photocatalytic activity in C–C bond formation between benzene and 4-fluoroiodobenzene.

12.4 Photoreductions

 Ce^{III} complexes have been extensively studied by Schelter et al. [18] for the photoreduction reactions of benzyl chloride (7) through single electron transfer mechanism (SET) to furnish homo-coupled products (9) (Figure 12.4). The reaction involves the formation of $Ce^{IV}Cl$ complex which is a stronger absorber of light than Ce^{III} which leads to incomplete reaction. They anticipated that the addition of NaN(SiMe₃)₂ (8) might reduce $Ce^{IV}Cl$ complex to Ce^{III} with NaCl precipitation, preventing the formation of $Ce^{IV}Cl$ complex.



Figure 12.3: Synthesis of series of luminescent Ce^{III} complexes.

Pioneer in photocatalysis, Schelter and coworkers [19] revealed a robust method for the photo reduction of aryl chloride (**10**) to reduced aryl compounds (**11**) by using hexachlorocerate(III) $[Ce^{III}Cl_6]^{3-}$ (Figure 12.5). This complex is produced by in situ reaction of Et₄NCl and CeCl₃ in acetonitrile solutions (Figure 12.6). The main advantage

PhCH₂Cl + NaN(SiMe₃)₂
$$\xrightarrow{10 \text{ mol}\% \text{ Ce}^{III}}$$
 PhCH₂CH₂Ph
7 8 9 $Ce^{III} = Ce \left(N \left(N \left(N \right)^{SiMe_3} \right)_3 \right)$

Figure 12.4: Photoreduction of benzyl chloride.



Figure 12.5: Photo reductive dehalogenation of aryl halides.

$$[NEt_4]_3[Ce^{III}CI_6] \xrightarrow{1 eq. NEt_4CI} [NEt_4]_3[Ce^{III}CI_6] \xrightarrow{toluene/CH_3CN (1:4)} [NEt_4]_3[Ce^{III}CI_6] \xrightarrow{12 N_2, r.t.} 13$$

Figure 12.6: Synthesis of Ce^{III} complex.

of [Ce^{III}Cl₆]³⁻ complex is the low photo reduction potentials and fast quenching kinetics which facilitates the dehalogenation of aryl chloride via aryl radical.

12.5 Photooxidations

Chen et al. [20] succeeded in developing an efficient protocol for the visible light driven photooxidation of diarylalkynes (141) to diketones (15) (Figure 12.7) and thioethers (16) to sulfoxides (17) (Figure 12.8). The team have prepared four isostructural lanthanides with same coordinated ligand 3,7-diamino-9,10-anthraquinone-2,6-disulfonatecomplexes via hydrothermal method. The complexes are [Er(H₂O)₈]•[Er(L)(H₂O)₆]•2 L•8H₂O (Er-L), [Tm(H₂O)₈]• [Tm(L)(H₂O)₆]•2 L•8.5H₂O (Tm-L), [Yb(H₂O)₈]•[Yb(L)(H₂O)₆]•2 L•9H₂O (Yb-L), [Lu(H₂O)₈] • [Lu(L)(H₂O)₆]•2 L•9H₂O (Lu-L), respectively. Based on single crystal X-ray analysis, the structure of these complexes is determined, and it also discloses the presence of free and coordinated ligand in the crystal structure. These complexes act as heterogeneous photooxidative catalysts. Among the four lanthanide complexes, the Er-L is superior over other complexes for visible light driven photooxidation. The advantage of Er-photocatalyst includes easy isolation of catalyst after the completion of photooxidation through simple filtration, and it can be used without activation for up to five catalytic cycles.



Figure 12.7: Photooxidation of arylalkynes to diketones.



Figure 12.8: Photooxidation of thioethres to sulfoxides.

12.5.1 General procedure for the preparation of 3,7-diamino-9, 10-anthraquinone-2,6-disulfonic acid (H₂L)

2,6-Diamino-9,10-anthracenedione (4 g) was added gently to a stirring solution of 20 mL 20% oleum in 50 mL two-necked flask under cooling. To the reaction mixture H_2O_2 (30%, 0.5 mL) was added and run for 5 h at 100 °C. The resulting dark brown precipitate was filtered, washed cleanly with CH₃CN, and vacuum-dried to provide 5.4 g of product (a yield of 80%).

12.5.2 General procedure for the preparation [Er(H₂O)₈]•[Er(L)(H₂O)₆]•2L•8H₂O (Er-L)

A mixture of H_2L (19.8 mg, 0.05 mmol) and $ErCl_3 \cdot 6H_2O$ (38.2 mg, 0.1 mmol) was dissolved in a glass container into 3.0 mL water. The glass container was wrapped with a cap and heated to a temperature of 100 °C for 24 h. Then reaction mixture was gently cooled to room temperature to produce give reddish brown crystals, which were then filtered out, cleaned with CH_3COCH_3 , and allowed to dry at ambient temperature. Yield: 65% according to H_2L .

12.6 Photocycloadditions

Anhua and coworkers [21] developed a robust [5 + 2] cycloaddition methodology upon reacting cycloalkonols (**18**) and electron deficient alkenes (**19**) by employing synergistic combination of a PET catalyst (photo-induced electron transfer catalyst–anthracene complex) and LMCT catalyst (cerium compound) for the construction of synthetically complex bridged lactones(**20**) (Figure 12.9). These bridged lactones are important scaffolds commonly found in natural products, such as hushinone [22], nepalactones [23], dendromonilisides [24], and tutin [25]. The process for the generation of alkoxy radical under SET mechanism is shown in Figure 12.10 by using photocatalyst anthracene complex. The reaction proceeds in a stepwise manner (Figure 12.11) in such a way that first the α -hydroxy C–C bond of alkoxy radical (**21**) could be selectively cleaved to give alkyl radical (**22**) and then undergo [5 + 2] cycloaddition with electron-deficient alkenes to give higher ring alcohol (**25**) followed by lactonization upon treatment with acid affording bridged lactones (**20**).



Figure 12.9: LMCT catalyst and PET catalyst-mediated photocycloaddition.



Figure 12.10: Generation of alkanol radical.

An efficient, mild and intermolecular [2+2] cycloaddition of indoles (26) with activated olefins (27) mediated by visible violet light-induced Gd(III) catalyst toward the construction of complex scaffolds cyclopenta[*b*]indoles (28) and indolines (29) (Figure 12.12) through one-pot, multistep fashion was developed by Glorious et al. [26]. The [2+2] cycloaddition takes place in an unusual head-to-head fashion rather than traditional head-to-tail



Figure 12.11: Photocycloaddition reaction mechanism.



Figure 12.12: Gd(OTf)₃-induced photocycloaddition of indoles with alkenes.

fashion. The tethered pyrazole moiety acts as directing group when there is no substituent present at 3-position leads to cyclopenta[*b*]indole derivatives, whereas presence of substituent at 3-position, pyrazole moiety acts as both masking amination reagent and a directing group leads to dearomative cyclopenta[*b*]indoline derivatives (Figure 12.13).

12.7 Photocatalytic C–C/C–heteroatom bond construction

Zuo and coworkers [27] have developed an excellent and efficient straightforward protocol for C–C bond construction by employing inexpensive cerium photocatalysis (Figure 12.14). The reaction involves generation of in situ alkyl radical (42) upon irradiation of simple alcohols (41) by dehydroxymethylation (loss of formaldehyde). The obtained alkyl radical undergoes various cross-couplings, including hydrogenation, alkenylation, amination, alkylation, and oxidation under mild reaction parameters.



Figure 12.13: Mechanism of Gd(OTf)₃-induced photocycloaddition of indoles with alkenes.

Qiao et al. [28] achieved first-ever photo-induced Miyura borylation of sp² carbon by a rare earth photoreductant hexachlorocerate(III) anion ($Ce^{III}Cl_6$)^{3–}(Figure 12.15). The developed photo-induced Miyura borylation was coupled with Suzuki–Miyura reaction resulting in the preparation of variety of biaryls from aryl chlorides.

Zuo et al. [29] developed a general protocol for δ C–H activation of primary alcohols (**52**) by employing inexpensive cerium photocatalysis (Figure 12.16). The advantage of this method is that it does not require prefunctionalization of primary alcohols for distal functionalization. This protocol involves LMCT (ligand-to-metal charge transfer) mechanism (Figure 12.17) for the direct activation of substrates containing heteroatom functionalities.

Inspired by the previous work, Zuo et al. [30] realized the photo-induced rare earth metal catalyzed HAT (hydrogen atom transfer) strategy for the activation of highly inert substrates methane, ethane, propane, and butane (**58**) to form C-heteroatom bonds (Figure 12.18). The reaction sequence involves excitation of alcohol to form alkoxy radical which in turn triggers the inert alkanes to produce an alkyl radical which was then reacted with array of electron deficient substrates to form desired C-C/C-heteroatom bonds.



Figure 12.14: CeCl₃-induced photocatalytic C–H, C–C, and C–heteroatom bond-forming reaction.



Figure 12.15: CeCl₃-induced photocatalytic C–B atom bond formation reaction.

12.8 Photocatalytic C–C bond cleavage

Guo and coworkers [31] demonstrated an efficient strategy for amination of cycloalkanols (65) by C–C bond cleavage through cerium complex catalyzed visible lightinduced photoredox catalysis (Figure 12.19). This method is relevant to a wide array of



Figure 12.16: CeCl₃-induced photocatalytic δ C–H amination.



Figure 12.17: Mechanism of photocatalytic δ C–H amination.

secondary and tertiary cycloalkanols. The mechanism involves exposure of cerium chloride/alcohol complex (67) to radiation; the photo-excited state (68) is produced. The photo-excited Ce^{III} complex would result in a Ce^{IV} species (69) via a single electron transfer (SET) process with nitrogen radical intermediate (71). As anticipated, the extremely oxidized Ce^{IV} species (69) might facilitate the hard β -scission process to produce carbon radical (70). Then DBAD is coupled with extremely reactive radical species (70) to produce nitrogen-centered intermediate radical 71, which subsequently produce the product through SET reduction (Figure 12.20).

Based on the previous C–C bond cleavage of cycloalkanols, the same group had continued the research on C–C bond scission of cyclic and acyclic ketones. They employed cooperative Lewis acid and cerium complex photocatalysis to selectively scission C–C bonds of different ketones by utilizing the ligand-to-metal charge transfer (LMCT) excitation method (Figure 12.21) [32]. This C–C bond scission reaction serves as an alternate to Norrish type l reaction. Many acyclic and cyclic ketones, ranging from straightforward, strained cyclobutanone (72) to intricate, less strained androsterone

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Figure 12.18: CeCl₃-induced photocatalytic inert sp³ C–H amination, alkylation, and arylation.



Figure 12.19: CeCl₃ Photo mediated C–C bond scission and amination.

(cyclopentanone) (**75**), could successfully undergo C–C bond scission and converted into useful chemical feed stocks. The obtained substrate from strained ketones was easily converted to desired lactams (**77**). The substrates from unstrained ketones (cyclohexanone), the C–C bond scission would result in the production of ω -aminated acyl cyanide (**76**), which would yield a carboxylic ester upon alcohol hydrolysis with a wide range of synthetic applications.

Coming over to linear ketone compounds (77), C–C bond scission was accomplished successfully, installing carboxylic ester (78) and hydrazine derivatives (79) at altered carbon fragments without any intervention of Norrish type II reaction (Figure 12.22). In







Figure 12.21: Cerium photocatalyzed C-C bond cleavage of strained ketones, unstrained.



Figure 12.22: Cerium photocatalyzed C–C bond scission of acyclic ketones.

unsymmetrical linear ketones, more substituted α -C–C bond with greater stabilized radical could cleave precisely to furnish corresponding products.

Xiao et al. [33] published first report of cyanation of strained cyclopropylketones (**80**) via C–C cleavage by combining photoredox catalysis with Lewis acid catalysis (triple catalysis) and copper catalysis for the preparation of γ -cyanoketones (**82**) (Figure 12.23). The synthetic application of the present protocol has been showcased through the preparation of piperidine scaffolds (**84**) and (**85**) (Figure 12.24).



Figure 12.23: C-C bond scission of cyclopropylketones by triple catalysis.



Figure 12.24: Synthetic utility of triple catalysis for the construction of piperidines.

12.9 Conclusions

In conclusion, rare earth metal complexes can act as redox-neutral Lewis acids as well as redox-active centers in photochemical reactions. The redox properties of rare earth complexes trigger the activation of halogen compounds, carboxylic acid derivatives, alcohols, unsaturated systems, and chalcogens, while switching to Lewis acid character they are able to activate a plethora of compounds containing carbonyl functionality. There is plethora of queries still unanswered with respect to mechanism of lanthanide photocatalysis.

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