



Digest paper

Recent advances in dual transition metal–visible light photoredox catalysis



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ABSTRACT

In this Digest Letter, we collected and shortly summarized the recently developed dual transition metal–visible light photoredox catalytic processes including arylation, alkynylation, alkenylation, allylation, alkylation, fluoroalkylation, benzylation, acylation, and cyclization reactions. The utilization of multi-metallic catalytic systems provides new synthetic strategies for the synthesis and functionalization of versatile and novel organic compounds.

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Introduction

The transition metal catalyzed cross-coupling reactions,¹ C–H bond activation² and the photoredox catalysis³ separately have been well investigated. In the last decade, the photocatalysis is experiencing a renaissance, considering the number of recent publications. The conversion of visible light into chemical redox energy

is beneficial and contributes to the development of milder reaction conditions and more energy-efficient transformations. Radicals are formed by the photo-triggered single electron transfer (SET), which provides reactivity as driving force. On the other hand, the expandable regioselectivity generally remained unresolved. Thus, the exploitation of the possibilities in the integration of photolytically generated radicals into transition metal catalysis has been initiated. Reasonably, in a co-operative photoredox and transition metal catalyzed coupling, the opportunity to modulate the oxidation state of transition metal species opens new pathways for efficient syntheses.⁴

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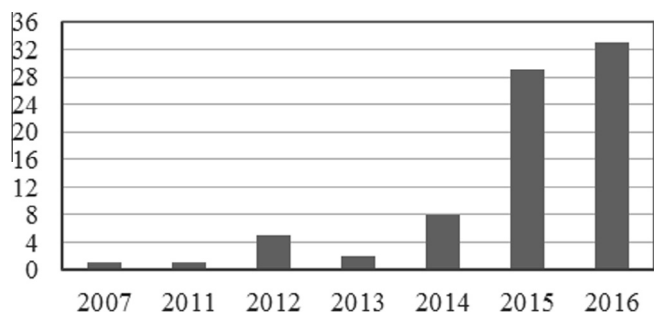


Figure 1. The evolution of photoredox-transition metal catalysis. Number of publications versus year (until middle of July, 2016).

In these processes, the reactivity and the selectivity are ensured at the same time by the two catalytic cycles. Herein, we intend to summarize recent solutions for combined, 'dual' photoredox-transition metal catalyzed syntheses. On theoretical grounds, the term of 'dual catalysis' can include two main types of mechanisms. First, the two catalytic cycles can work separately and (a) the produced fragments react with each other, (b) the produced intermediate consecutively consumed by the other cycle. Second, the two catalytic cycles are synergistically coupled, the catalysts must collide to push forward the reaction. Alternatively, in borderline case, these two roles can be played simultaneously by one bifunctional catalyst, but now these are not discussed here.

The beginning of this era is dated back to 2007, and the dual transition metal-photoredox catalysis become a hot topic in organic chemistry by now, since in the last 2 years the number of papers increased almost fourfold (see Fig. 1).

At a closer inspection of these dual systems, we can conclude that, on the side of photoredox catalysts primarily the widely used but extremely expensive Ir complexes are prevalent. Nevertheless, we can find abundantly examples for application of $\text{Ru}(\text{bpy})_3^{2+}$ catalysts. Exploitation of organic dyes in this field of visible light induced photocatalysis is in early stage. In view of the utilized transitional metals, in the catalytic cycle of the coupling Ni complexes are most widespread, although Pd, Au, and Cu species are also extensively applied. Considering the type of the transformations C–C and C–X (X = N, O, S, P) bond formations can be highlighted, including arylation, alkynylation, alkenylation, allylation, alkylation, fluoroalkylation, benzylation, acylation, and cyclization reactions. As shown, the opportunity is given to introduce several functional groups into substrates like (hetero)aromatic, saturated heterocyclic, (un)saturated aliphatic systems. Therefore, the reagents can be diverse, but trends are outlined in the application of aryl iodides and bromides, α - CH_2 -amines, carboxylic acids and their derivatives, diazonium salts, potassium trifluoroborate salts, or hypervalent silicones.

Lewis acid supported photocatalysis

In these transformations, the transition metal catalysts serve as Lewis acids and the reactive electrophiles are generated in the photocatalytic cycle.

In 2012, Rueping and Zhu presented a mild functionalization and arylation of glycine derivatives.⁵ In their work, indoles in position C2 were successfully coupled with alkyl 2-(arylamino)acetates in the presence of Lewis acidic $\text{Zn}(\text{OAc})_2$ and 1 mol % $[\text{Ir}(\text{ppy})_2\text{bpy}]\text{PF}_6$ photocatalyst.

Similarly, Wu's group reported an alkylation reaction of secondary amines (Fig. 2) in 2013.⁶ For the C–N bond formation 10 mol % of copper(II) triflate was used as Lewis acid, and the photocatalytic cycle was driven by 1 mol % of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ photocatalyst under blue light irradiation.

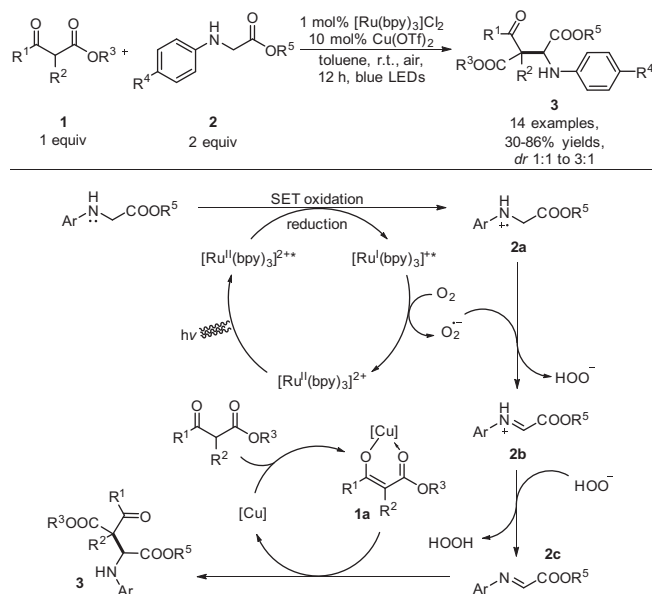


Figure 2. Combining visible-light catalysis and transition metal catalysis for the alkylation of secondary amines.

The proposed mechanism of this reaction is based on a separated dual catalytic system. First, the alkyl-aryl amine is oxidized in the photocatalytic cycle to form a radical cation (**2a**), which loses the α -hydrogen atom by interaction with a superoxide radical anion to form the highly reactive iminium cation (**2b**). An additional deprotonation provides the electrophile *N*-aryl imine (**2c**), which can be attacked by the nucleophilic copper chelated β -keto esters (**1a**) to give the desired product.

In 2016, Wu and co-workers reported a C–C bond forming reaction of copper chelated β -keto esters and isochromans in the visible light driven catalytic transformation of two different C–H bonds. The applicability of the developed procedure was demonstrated on 16 examples, and the appropriate C2-alkylated isochroman derivatives were isolated in 28–83% yields.⁷ They utilized $\text{Cu}(\text{OTf})_2$ as Lewis acid and organic photocatalyst for the coupling reaction (10 mol % of Fukuzumi's catalyst, 9-mesityl-10-methylacridinium perchlorate, $[(\text{NMeAc}^+ - \text{Mes})\text{ClO}_4]$. The reaction mixture was irradiated with blue light to generate the electrophilic 3,4-dihydroisochromenylium intermediate. This oxonium species react with the ketoester activated by the copper based Lewis acid to form the desired C–C bond.

Cross-coupling-like dual catalysis

This chapter covers a truly diverse and spacious field of dual transition metal and photoredox catalysis. As initial trials the ruthenium photocatalyzed copper-free Sonogashira coupling of aryl bromides was reported by Akita and co-workers.⁸ Recently, the cross-coupling reaction of aryl diazonium tetrafluoroborate salts with acetylenes⁹ and trimethylsilylacetylenes¹⁰ were investigated utilizing a synergistic Au–Ru dual catalytic system. Additionally, Cu–Ru($\text{bpy})_3^{2+}$ catalyzed trifluoromethylation of arylboronic acids with CF_3I was described by Ye and Sanford.¹¹

In 2016, Doyle and Joe introduced a method for direct C-acylation of tertiary amines (**4**) in the α -C(sp^3) position at room temperature (Fig. 3).¹² The α -amino radicals (**4a**) generated from the tertiary amine (**4**) by the excited Ir(III) complex in the photoredox cycle. The radical species enters into the transition metal driven cycle, and interacts with the Ni(II) coupling catalyst to form a Ni(III) species. After a reductive elimination step the desired C–C

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