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Dual Catalysis: Combination of Photocatalytic Aerobic Oxidation and Metal Catalyzed Alkynylation Reactions—C–C Bond Formation Using Visible Light

Magnus Rueping,* René M. Koenigs, Konstantin Poscharny, David C. Fabry, Daniele Leonori, and Carlos Vila^[a]

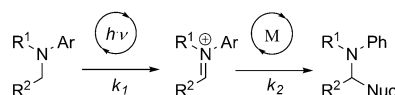
Dedicated to Professor Dr. Dr. h.c. Lutz F. Tietze on the occasion of his 70th birthday

The direct formation of new C–C bonds from unreactive C–H bonds is one of the major challenges in modern synthetic organic chemistry. To date several examples have been realized, yet, they are typically limited to the activation of sp^2 carbon atoms. In general, the activation of sp^3 C–H bonds is more challenging, as the reactions are typically conducted by employing significant amounts of precious metals or under harsh reaction conditions. For this reason, only a few examples of the activation of unreactive sp^3 C–H bonds have been realized. The oxidation of tertiary amines is an elegant alternative to overcome the intrinsically low reactivity of sp^3 C–H bonds. Following this approach highly reactive intermediate iminium ions can be generated that can be intercepted by nucleophiles to yield the desired coupling products.^[1] In such a way, oxidative cross couplings were realized with different metal catalysts in the past few years. Yet, they mainly rely on the use of stoichiometric amounts of oxidant and/or on elevated temperature for an efficient oxidation of the tertiary amine. Recently, visible-light photoredox catalysis^[2–6] has emerged as a highly promising approach to such reaction sequences. Especially with respect to the development of new sustainable and green synthetic methods, the application of visible light as a renewable source of energy is of wide general interest in modern organic chemistry. Based on single photoelectron transfer reactions,^[7,8] photoredox catalysts provide new reaction protocols that enable an environmentally benign approach under mild conditions to valuable fine chemicals.^[2,4,5]

Continuing our efforts on dual catalytic transformations,^[9] we became interested in an efficient combination of photoredox and transition-metal catalysis for C–C bond forming reactions. This would not only be the first example of this kind of combination of two metal catalysts, but it would also

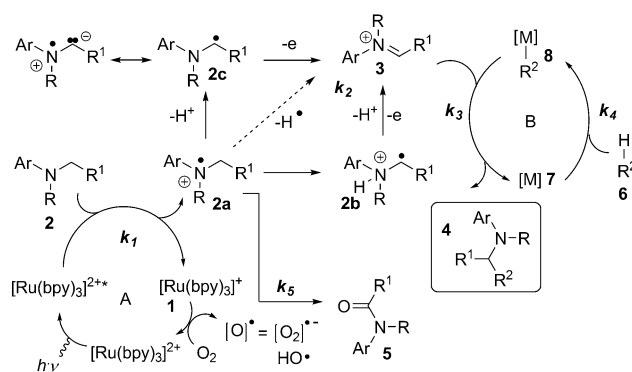
open up the way to many new methods that rely on a dual catalytic photo- and metal-catalyzed transformations.

Herein we report on the first combination of light-induced aerobic oxidation reactions and a metal-catalyzed C–C bond forming reaction (Scheme 1).



Scheme 1. Dual metal catalysis—combining photoredox catalysis and metal-catalyzed C–C bond formation.

In contrast to previous work on photoredox catalysis, special hurdles need to be overcome that arise from combining two metal catalysts. First, the appropriate choice of metal catalyst **7** is crucial for a consecutive catalytic system, based on a photoredox cycle A and a second metal catalytic cycle B. Second, metal catalysts can easily undergo oxidative or reductive degradation (Scheme 2). In particular, the metal catalyst can be easily reduced by strongly reducing intermediates that are passed in the photocatalytic cycle, which is one of the central challenges that needs to be addressed.^[10] Thus the successful development of this dual catalytic reaction is strongly reliant on the compatibility of catalysts



Scheme 2. The complex interplay of photoredox catalysis and metal catalysis.

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1 and **7**. In addition, the efficiency of this dual catalytic transformation is strongly dependent on the interplay of both catalytic cycles; in particular, reaction rates need to be adapted, which is obligatory for an efficient trapping of the highly reactive iminium ion, as it can readily undergo an unwanted side reaction, leading to the formation of amide **5**,^[2] which in turn results in diminished yield of the desired reaction product **4**. The formation of the amine radical cation **2a**, the iminium ion **3**, and the reoxidation of the photocatalyst by oxygen are well known.^[11] It has been suggested that the formation of **3** is caused through a hydrogen (H[•]) abstraction of the amine radical cation **2a** by the superoxide anion formed in the regeneration of the photoredox catalyst. Mechanistically two other reaction pathways appear to be plausible. These differ in the order in which the deprotonation and the electron transfer occur: On one hand the 1,2-hydrogen transfer forms C-radical **2b**, which then provides the iminium ion **3** as a result of deprotonation by the tertiary amine or superoxide radical anion, followed by electron transfer to Ru^{II}, Ru^{II*}, or HOO[•]. On the other hand deprotonation may form the neutral C-radical **2c**, which, for example, can react with olefins or, as described here, can provide **3** by electron transfer. The iminium ion **3** formed in situ can then be transformed in the second catalytic cycle **B**, via a metal-catalyzed 1,2-addition reaction into the amine. Bearing this in mind, we decided to develop a suitable dual catalytic system for an oxidative alkynylation reaction,^[12–16] which comprises the advantages that it does not necessitate the use of ligands for the stabilization of the metal catalyst and thus circumvents problems that might occur due to redox reactions of the metal catalyst. Additionally, the application of different metal salts offers an operationally simple control of the second catalytic cycle, as the nature of the counterion has a direct influence on both reaction rates k_3 and k_4 of this catalytic cycle.

We initiated our investigations on the oxidative alkynylation reaction by examining the oxidation of *N*-phenyl-tetrahydroisoquinoline (**2a**) in the presence of photoredox catalyst [Ru(bpy)₃](PF₆)₂ (**1a**),^[10] phenylacetylene (**6a**), and different silver salts (Table 1). However, the use of blue LEDs as light source and Ag₂O₂CCF₃ as metal catalyst resulted only in the formation of a silver mirror and decomposition of the tertiary amine. Interestingly, silver benzoate proved to be more robust under the present reaction conditions, as no silver mirror was observed after a reaction time of a few days, yet, no conversion of **2a** to the desired product was observed. We therefore investigated under otherwise identical reaction conditions a ternary catalyst mixture, consisting of the photoredox catalyst, a photochemically inert silver salt, and camphor sulfonic acid, which was intended to act as a phase-transfer catalyst of Ag⁺ ions. Following this procedure, low concentrations of Ag⁺ ions can be obtained, resulting in diminished photodegradation of the metal catalyst. Employing this ternary catalyst mixture, we could indeed isolate the desired alkynylation product for the first time in 32 % yield (Table 1, entry 3). To adapt the rate of the primary photocatalytic cycle to the second metal-catalyzed re-

Table 1. Survey of different metal salts, additives, and light.

Entry ^[a]	Light source	cat/metal salt/additive	Time ^[b]	Yield [%] ^[c]
1	Blue LED	1a /Ag ₂ O ₂ CCF ₃	24	decomp
2	Blue LED	1a /AgOBz	24	— ^[d]
3	Blue LED	1a /AgOBz + CSA	72	32
4	5 W lamp	1a /AgOBz + CSA	24	50
5	5 W lamp	1b /AgOBz + CSA	16	74
6	5 W lamp	1a /Cu(OTf) ₂	16	33
7	5 W lamp	1b /Cu(OTf) ₂	16	63
8	5 W lamp	1b /(MeCN) ₄ CuPF ₆	16	88
9 ^[c]	5 W lamp	1b /(MeCN) ₄ CuPF ₆	36	— ^[d]
10	5 W lamp	(MeCN) ₄ CuPF ₆	36	— ^[d]
11	5 W lamp	1b	36	— ^[d]

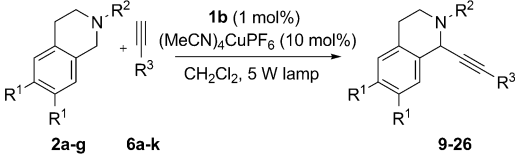
[a] Reaction conditions: 0.1 mmol **2a**, 1 mol % photocatalyst, 10 mol % metal salt/additive, 2 mL CH₂Cl₂, 5 equiv **6a**. [b] Yield after purification. [c] In the absence of oxygen. [d] No reaction.

action rate, we decided to switch the light source to a less intense 5 W fluorescent bulb; however, only moderate conversions were observed. Therefore, we changed to the more potent photoredox catalyst [Ru(bpy)₂(dtbbpy)](PF₆)₂ (**1b**). Under these reaction conditions we were able to isolate the oxidative alkynylation product in 74 % yield (Table 1, entry 5).

After having for the first time established the general conditions for the dual catalytic oxidative alkynylation, we examined different metal salts, as these could have a direct impact on the reaction rate of the second catalytic cycle (k_3 and k_4). In further studies, different copper salts were examined; these studies proved that the alkynylation reaction proceeds smoothly, regardless of whether Cu^I or Cu^{II} salts were applied. The best yield (88 %) was obtained by using the (MeCN)₄Cu^IPF₆ complex. In further optimization studies of this new dual catalytic transformation, the influence of solvent was investigated. The results showed that the transformation can be carried out most efficiently using dichloromethane or ethyl acetate as solvent, whereas all other solvents proved to be detrimental for a high efficiency.

After optimizing the reaction conditions, we examined the substrate scope of this photooxidative alkynylation reaction (Table 2). In general, a variety of different aromatic alkynes could be efficiently added to the photochemically generated reactive iminium ion intermediates. Only the *p*-*t*Bu-phenyl-substituted alkyne could not be added efficiently using the Cu^I metal catalyst; in this case only the decomposition of the starting material was observed. However, we were able to demonstrate, that in this case a silver salt can be efficiently used as a substitute for the Cu^I catalyst (Table 2, entry 3). This underlines the potential of this newly developed modular dual catalytic system: Both catalysts can be easily substituted to rapidly determine the perfect catalyst combination to obtain high yields for each individual combination of substrates. Besides different aromatic substituted alkynes, we employed different aliphatic and functionalized terminal al-

Table 2. Scope of the photooxidation–alkynylation reaction.



Entry ^[a]	H ₄ -iQ/ Alkyne	R ¹ /R ² /R ³	Product	Yield [%] ^[b]
1	2a/6a	H/Ph/Ph	9	88
2	2a/6b	H/Ph/ <i>p</i> Tol	10	71
3 ^[c]	2a/6c	H/Ph/ <i>p</i> (<i>t</i> Bu)Ph	11	77
4	2a/6d	H/Ph/ <i>p</i> PentylPh	12	95
5	2a/6e	H/Ph/6MeO-2-(Naphthyl)	13	67
6	2a/6f	H/Ph/Cyclopropyl	14	62
7	2a/6g	H/Ph/Cyclohexyl	15	50
8	2a/6h	H/Ph/Bu	16	59
9	2a/6i	H/Ph/ <i>t</i> Bu	17	51
10	2a/6j	H/Ph/CO ₂ Et	18	56
11	2a/6k	H/Ph/TPS	19	84
12	2b/6a	H/ <i>p</i> Tol/Ph	20	67
13	2c/6a	H/ <i>p</i> Et/Ph	21	65
14	2d/6a	H/ <i>p</i> ClPh/Ph	22	68
15	2e/6a	H/ <i>o</i> Tol/Ph	23	73
16	2f/6a	H/2-Naphthyl/Ph	24	85
17	2g/6a	MeO/Ph/Ph	25	70
18	2h/6d	H/ <i>p</i> Tol/ <i>p</i> PentylPh	26	56

[a] Reaction conditions: 0.1 mmol **2**, 1 mol % **1b**, 10 mol % (MeCN)₄CuPF₆, 5 equiv **6**, 2 mL CH₂Cl₂, 5 W fluorescent bulb, reaction time 16–36 h. [b] Yield after purification. [c] 10 mol % Ag(O₂CCF₃).

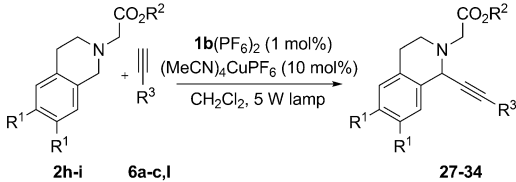
kynes, which could be added to the photochemically generated iminium ions. However, yields are lower than the yield of aromatic alkynes. Use of triphenylsilylacetylene gave an excellent yield of 84 % of the desired product (Table 2, entry 11).

Apart from different alkynes we also investigated the influence of the substituents attached to the isoquinoline. A variety of different *N*-arylated isoquinolines and different isoquinoline cores were subjected to the general reaction conditions and the desired alkynylation products were obtained in good isolated yields.

Besides the variation of aromatic amines, we were interested in a further expansion of the substrate scope to non-aromatic amines. To date the photochemical synthesis of imines with visible light was almost exclusively carried out with substrates that yielded *N*-aryl imines.^[4] We therefore decided to investigate the photochemical oxidation of different glycine derivatives, which can be oxidized with photoredox catalyst **1b** to the corresponding iminium ions, yielding propargylamines upon alkynylation. Different glycine esters,^[17] tetrahydroisoquinoline backbones and alkynes were investigated, yielding the desired propargylic amines in good yields (Table 3).^[18,19]

In summary, we herein describe the first dual catalytic system that consists of a photoredox catalyst and a metal catalyst. Besides the perfect interplay of both catalytic cycles the choice of reaction parameters, and notably the light source, the photoredox catalyst, and the metal catalyst

Table 3. Extension of the substrate scope to *N*-alkyl tetrahydroquinolines.



Entry ^[a]	H ₄ -iQ/Alkyne	R ¹ /R ² /R ³	Product	Yield [%] ^[b]
1	2h/6a	H/Me/Ph	27	67
2	2h/6b	H/Me/ <i>p</i> Tol	28	73
3	2h/6c	H/Me/ <i>p</i> (<i>t</i> Bu)Ph	29	67
4	2i/6a	H/ <i>t</i> Bu/Ph	30	57
5	2i/6b	H/ <i>t</i> Bu/ <i>p</i> Tol	31	64
6	2i/6c	H/ <i>t</i> Bu/ <i>p</i> (<i>t</i> Bu)Ph	32	53
7	2i/6l	H/ <i>t</i> Bu/cyclohexenyl	33	57
8	2j/6a	OMe/Me/Ph	34	43

[a] Reaction conditions: 0.1 mmol **2**, 1 mol % **1b**, 10 mol % (MeCN)₄CuPF₆, 5 equiv **6**, 2 mL CH₂Cl₂, 5 W fluorescent bulb, reaction time 16–36 h. [b] Yield after purification.

are essential for the successful realization of this dual catalytic transformation, as many side reactions need to be circumvented. For instance, strongly reducing intermediates of the photoredox catalyst are passed throughout the photocatalytic cycle (e.g. [Ru(bpy)₃]⁺), which can easily degrade the metal catalyst. In addition, the intermediate iminium ion can be degraded by oxidation to the undesired amide. We also demonstrated that a dual catalytic system can be realized in the oxidative alkynylation reaction. It features a highly modular catalytic system and mild reaction conditions. Reactions can be carried out using visible light as a source of energy for the oxidation of various tertiary amines, yielding valuable propargylic amines in good to excellent yields. Moreover, we were able to demonstrate for the first time that besides *N*-aryl amines also alkyl amines, namely glycine esters, can be subjected to this photoredox-catalyzed functionalization of sp³ C–H bonds. The high modularity of the catalytic system allows an easy adaption of this concept to other substrates. The realization of this concept is an important advancement in the area of both dual catalytic as well as photoredox catalytic transformations. Current investigations are focussed on extending the repertoire of dual metal-catalyzed transformations with visible light.

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