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Catalytic Photoredox Allylation of Aldehydes Promoted by a Cobalt Complex

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Abstract. The preparation of homoallylic alcohols by addition organometallic allyl compounds to carbonyls is an important strategy in organic chemistry. Allylating organometallic cobalt species can be generated employing stoichiometric quantities of Zn acting as reductant. To avoid the employment of stoichiometric amount of Zn, we have developed an allylation reaction of aromatic and aliphatic aldehydes promoted by photoredox catalysis in the presence of a cobalt complex, and we present herein a full account of our research. In the presence of the abundant $CoBr_2$ (10 mol%), 4,4′-di-tert-butyl-2,2′-dipyridyl (dtbbpy, 10 mol%), allyl acetate (3 equiv), $[Ir(dtbbpy)(ppy)_2]PF_6$ (ppy = 2-phenylpyridine, 2 mol%), and *N*,*N*-diisopropylethylamine (4 equiv), an allylation of aldehydes is taking place, in moderate to good yields. Substrates scope, limitations, and photophysical investigations of this new process are reported.

Keywords: Metalla photoredox catalysis; Cobalt; allylation; Aldehydes; Iridium(III) photocatalyst

Introduction

Preparation of pre-metallated C-nucleophiles, and their addition to electrophiles constitute a fundamental route for chemical synthesis. In this context, allylation of carbonyls is a relevant subject.[1] The required organometallic allylic compound was obtained from many metals (Zn, Cr, Ti, Zr, Li, Mg, and others). However, often the methodology is hazardous, requires cryogenic conditions, and, most importantly, generates stoichiometric quantities of metallic byproducts, which thwarts large scale applications.

The development of allyl-chromium reactions (Nozaki-Hiyama-Kishi or NHK)[2] and the employment of allyltitanium reagents[3] shows the possibility to install a redox cycle,[4] realized in Barbier conditions.[5] A transient organometallic specie (Figure 1, A) is obtained *in situ* by the employment of over-stoichiometric amount of sacrificial reductant such as manganese or zinc. In the titanium or chromium Barbier type allylation reaction performed using a catalytic amount of metal, the employment of a scavenger (i.e. Me_3SiCl) is needed for liberating the active metal (titanium or chromium) from the final organic product. The fundamental studies reported by Fürstner,[6] and Gansäuer,[7] that have introduced the concept of catalytic redox cycle, where further exploited to develop interesting stereoselective variant of the reactions.[8]

One of the most spectacular application of the NHK chemistry was described in the synthesis of Eribulin,[9] a large-scale synthesis on a densely functionalized molecule. As stated, one of the major drawbacks of this chemistry rely in the waste associated with the employment of a stochiometric or an over-stoichiometric amount of co-reductant. Electrochemistry[10] could be an effective solution for the drawback, and some interesting allylation reactions performed by electrochemical apparatus were reported in literature.[11] Rapidly, photoredox catalysis, started to attract a wide interest in the organic chemistry community[12] as it offers the possibility to access radical catalytic cycles, by the use of photocatalysts based on metal complexes, dyes, or semiconductors.[13] The fruitful combination of photoredox catalytic cycle with other catalytic cycles, working cooperatively,[14] opens many possibilities and reaction pathways.[15] Metallaphotoredox catalysis is the new and rapidly growing research area,[16] that is merging catalysis with metals and photocatalytic cycles. We reasoned that processes that involve a redox cycle (i.e. allylation reactions with redox active metals) can be sustained by photoredox catalysis (Figure 1, B).

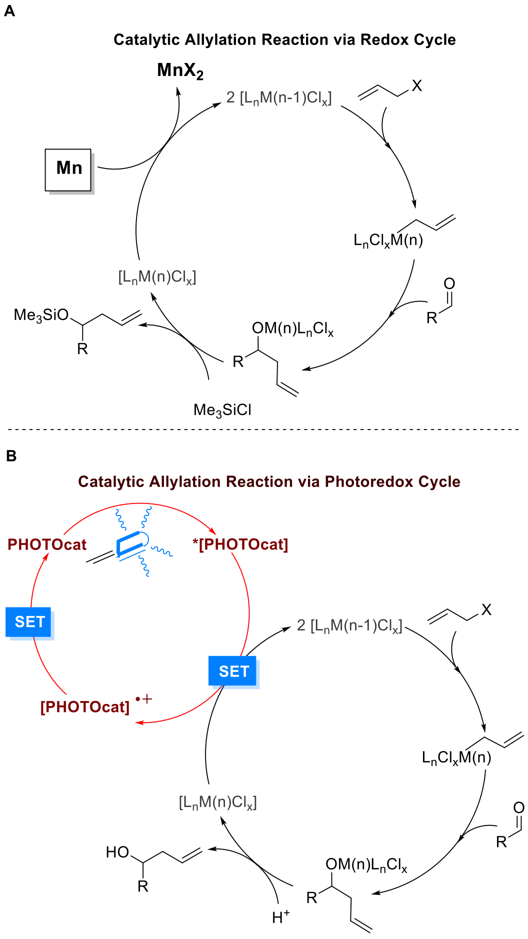


Figure 1. Comparison between an allylation reaction performed with a redox and a photoredox cycle.

In our hypothesis the combination of radical and polar chemistry, in a so-called reductive radical-polar crossover (RRPC) is realized.[17] In the process design, a metal complex at low oxidation state, generated in the reaction media by single electron transfer (SET) events, is converted in an organometallic nucleophilic specie, through a radical-radical combination or by oxidative addition with suitable organic substrates. The use of stoichiometric amount of metals, such as manganese or zinc, is avoided, as the photoredox catalyst, in combination with light, is maintaining the redox catalytic cycle. Of course, the use of other sacrificial reductant is not avoided, as the photocatalyst need to be restored in its fundamental state, but in many cases reported in literature,[12] sacrificial agents employed in photoredox reaction are cheap and available organic amines. Photoredox generation of allyl radical via oxidation, was also employed by Glorius,[18] and Kanai[19] for interesting photoredox version of the NHK reaction. In these examples the photoredox generated allyl radical is forming the allyl organometallic chromium reagent in situ, by a radical-radical combination (allyl radical and Cr(II)). Remarkably, in both the mentioned examples the use of a sacrificial co-reductant is not necessary, as the catalytic photoredox cycle is continued by the oxidation of the allyl moiety with the associated reduction of chromium(III) complexes. We have realized examples of photoredox allylation reaction, reporting a nickel based dual photoredox approach in allylation of aldehydes, with a broad scope and functional groups compatibility.[20] Quite recently, we have also reported a novel allylation photoredox methodology based on the use of Cp_2TiCl_2, using the organic dye 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile (3DPAFIPN)[21] to access $Cp_2Ti(III)Cl$ reagent, avoiding the use of stoichiometric amount metal.[22] To further expand these radical-polar crossover reaction, here, we report a full account of a practical and straightforward allylation methodology of aldehydes based on not toxic and available cobalt salts.[23]

Results and Discussion

Cobalt (Co) is the first and lightest element among the group 9 transition metals, that comprise rhodium (Rh), iridium (Ir), and meitnerium (Mt). Among these elements, Cobalt is the most abundant one in the Earth.[17] Co(II) salts are used as precatalysts in many catalytic reactions[23] in combination with zinc or manganese, in order to reduce Co(II) to the active Co(I), which is stabilized by appropriate ligand to turn it in a catalytically active species.

Gosmini have reported some years ago a cobalt catalyzed coupling reaction of allyl acetates with carbonyl compounds using zinc dust as a reducing agent, leading to homoallylic alcohols.[24] In this methodology, homoallylic alcohols were obtained by a reaction that occurs with a cobalt catalyst ($CoBr_2$) and zinc dust, in CH_3CN as reaction solvent. The suggested mechanism for the reaction considered the formation of a low valent cobalt species that undergoes oxidative addition with the allylic acetate. The formed allylcobalt(III) is further reduced by zinc to the active allylcobalt(II), that is able to perform nucleophilic attack to carbonyls. As this scheme is coherent with a redox cycle, we wondered if the allylation performed by cobalt could be merged with photoredox catalysis. Besides broadening the scope of the radical-polar cross over reactions, cobalt is considered less toxic and more suitable for industrial application with respect to nickel catalysis.[23] Although cobalt-catalyzed allylic substitution has received much less attention from synthetic point of view,[25] an interesting example of photoredox cobalt mediated processes was recently reported by Kojima, Matsunaga, and co-workers.[26] However, this nice work reported the cobalt catalysed highly branched selective allylic alkylation of sodium malonate with allylic electrophiles. To the best of our knowledge, the photoredox cobalt mediated allylation of aldehydes was not described yet. Therefore, we settled up a model reaction investigating several reaction parameters and Table 1 reports key experiments for implementing the general reaction conditions. 2-Naphthaldehyde and allyl acetate were used in the model reaction. Alter a preliminary screening of solvents, cobalt catalysts and temperature (for full details of optimization, see SI), in Table 1 we report the salient observation regarding the photoredox process.[20]

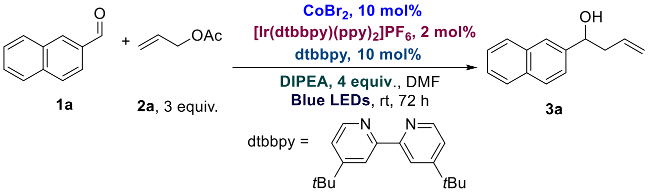


Table 1. Cobalt catalyzed allylation of aldehyde **1a**.

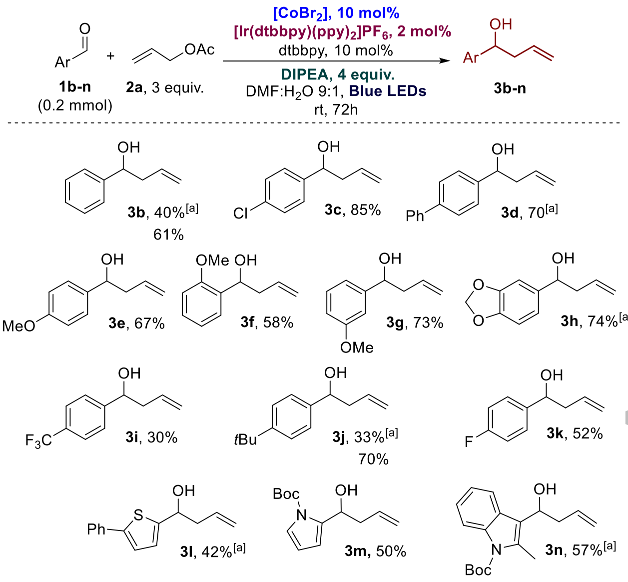
Entry[a]	Deviations from standard conditions	Yield(%)[b]
1	None	91 (60)
2	$CoBr_2$ 5 mol%	28
3	$Co(OAc)_2$ instead of $CoBr_2$	89 (51)
4	TEA instead of DIPEA	85 (53)
5	$\{Ir[dF(CF_3)ppy]_2(dtbbpy)\}PF_6$ as photocatalyst	37 (25)
6	$[Ru(bpy)_3]Cl_2$ as photocatalyst	0
7	No photocatalyst	0
8	No light	0
9	No dtbbpy	0
10	dppe as ligand instead of dtbbpy	0
11	dppf as ligand instead of dtbbpy	0
12	PPh_3 as ligand instead of dtbbpy	32 (23)
13	bpy as ligand instead of dtbbpy	44 (38)
14	CH_3CN as reaction solvent	55 (33)
15	DCE as reaction solvent	64 (50)
16	DMSO as reaction solvent	33 (25)
17	DMF:H_2O 9:1 instead of DMF	97 (76)
18	Scale up to 0.8 mmol scale	96 (74)[c]

a) Reactions were performed on 0.2 mmol of **1a** in DMF (1 mL) under 23W Blue LED stripe irradiation. b) Determined by ^1H NMR analysis of the reaction crude. Yield in parenthesis are isolated yields after chromatographic purification. The discrepancies observed in the yields determined by ^1H NMR and the yields after chromatographic purification are ascribable to the difficulties encountered during purification, due to contamination of some fractions of the eluted product **3a** with dtbbpy. dppe = 1, ,2-Bis(diphenylphosphino)ethane; dppf = 1,1′-Ferrocenediyl-bis(diphenylphosphine). c)The scale up was performed using a KESSIL® Lamp (40W) for 72 hours.

We found that the best photocatalyst is $[Ir(dtbbpy)(ppy)_2]PF_6$, as other photocatalysts gave lower yields (Table 1, entry 5) or no conversion (Table 1, entry 6). Contrary to our nickel mediated process,[20] $[Ru(bpy)_3]Cl_2$ is unable to form an active cobalt complex. The reaction is not occurring in the absence of the photocatalyst or in the dark (Table 1 entries 7 and 8). Amines are suitable sacrificial agents for the reactions, and we observe very similar conversion by employing TEA (triethylamine) instead of DIPEA (diisopropylethylamine). The reaction seems insensitive to the cobalt source employed as different cobalt salts gave similar yields and conversions (Table 1 entry 3 and supporting information). DMF:H_2O in 9:1 ratio is the solvent for this reaction (Table 1 entry 16).

Although the addition of water slightly improved the isolated yields in the case of 2-naphthaldehyde, in case of other aldehydes we observe a decisive role in the addition of water. The chelating di-*tert*-butylbipyridine is the adapted ligand for the reaction, and other ligands are less effective (See SI for full list of ligands tested). As in many reports on the use of cobalt complexes, phosphines are able to stabilize cobalt in low oxidation state (i.e. in Reformatsky reaction),[27] we have also tested mono or chelating phosphines (Table 1, entries 10-12). In the case where dtbbpy was substituted by PPh_3 we observed a strongly reduced reactivity, whereas other phosphines were ineffective in the reaction.

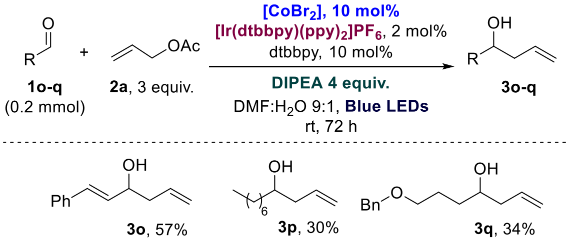
With the optimized conditions in hand, we investigated the scope of the reaction with variously substituted aromatic, heterocyclic, and aliphatic aldehydes. In general, the reaction work effectively with aromatic aldehydes, as specified in Scheme 1.



[a] Reaction performed in DMF

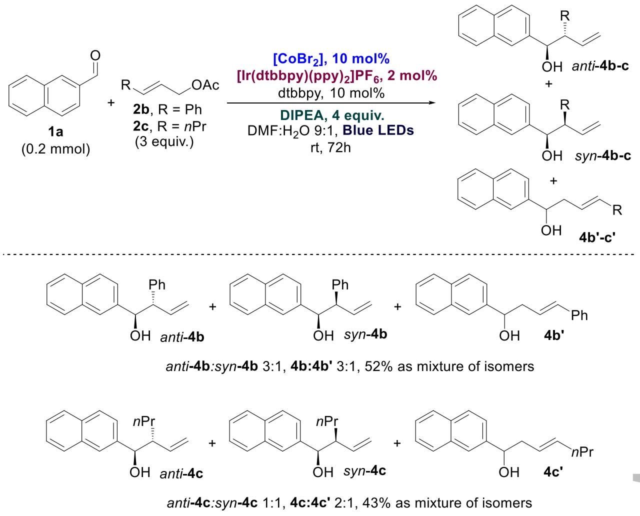
Scheme 1. Scope of the cobalt-promoted photoredox allylation reaction with aromatic aldehydes.

Concerning the scope of the reaction, we found the allylation method particularly adapted to aromatic electron rich aldehydes, while electron withdrawing group are compromising the reaction outcome (See SI for examples). Hindrance of the substituent is also affecting the yields, as evidenced by the examples with the different methoxy substituted aldehydes (**3e-g**). Chelating group in ortho position is not hampering the reaction (**3f**). Substrates sensitive to acidic conditions such as pyrrole and indole derivatives, can be employed in the reaction. For the aldehydes **3b** and **3j** we have clearly observed the role played by water in the reaction conditions. In the absence of water, the yields for these substrates were quite reduced. For other aldehydes the presence or absence of water did not change the yields. This puzzling observation was more dramatic in the case of aliphatic aldehydes (Scheme 2).



Scheme 2. Investigation of the cobalt allylation reaction with aliphatic and unsaturated aldehydes.

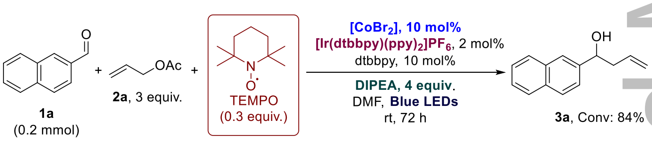
The substrates were generally found quite less reactive in comparison to aromatic aldehydes, and in the selected example of many others, in which we can isolate the desired product, the presence of water in the reaction mixture is decisive. At the present time, given the complexity of the reaction system, we can only speculate that the role played by water in enhancing yields and reactivity is probably due to the coordination of some cobalt intermediate that can effectively return in the catalytic cycle as pointed out by Fillon.[28]



Scheme 3. Investigation of the cobalt allylation reaction with aliphatic and unsaturated aldehydes.

The possibility to use γ-substituted allyl acetates was explored (Scheme 3). Cinnamyl acetate and hexenyl acetate (**2b,c**) were employed and the product were obtained with moderate regioselectivity in favor of the branched products. Satisfactory selectivity was obtained with cinnamyl derivative, whereas no selectivity was observed for hexenyl one.

Some mechanistic investigation about the possible reaction pathway was carried out. The introduction of radical scavengers like TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) is not blocking the reactions.



Scheme 4. Investigation of the cobalt allylation reaction in the presence of TEMPO.

A photophysical analysis of the photocatalytic system was carried out. The quenching of the photocatalyst luminescence by each of the components of the reaction was tested; in particular, no change of the decay of the emission intensity of $[Ir(dtbbpy)(ppy)_2]PF_6$ was observed upon addition of allyl acetate 0.6 M, di-*tert*-butylbipyridine 0.02 M, $CoBr_2$ 0.02 M or $CoBr_2$ together with the ligand di-*tert*-butylbipyridine (same concentrations used to perform the reaction, Figure S4). On the other hand, DIPEA and 2-naphthaldehyde quench the emission of the photocatalyst with quenching constants of 4.7 x 10^8 $M^{-1}s^{-1}$ and 1.9 x 10^7 $M^{-1}s^{-1}$, respectively, as determined by Stern-Volmer plots (Figures S5 and S6). This result demonstrates that the quenching of $[Ir(dtbbpy)(ppy)_2]PF_6$ obtained with DIPEA is more efficient; furthermore, under the reaction conditions reported in Scheme 1, the concentration of DIPEA is four times higher than the one of 2-naphthaldehyde.

Therefore, we suggest the catalytic cycles depicted in Figure 2. The mechanistic suggestion is based on the electrochemical studies on allylation reaction developed by Gosmini. Buriez and Labbé have found[29] that reduction of Co(II) precursor occurred at -1.3 V vs SCE, followed by a fast complexation with the allyl acetate. The resulting Co(III)allyl complexes is then reduced at the same potential to an active allylCo(II) complex.[24] The inability of $[Ru(bpy)_3]^{2+}$ to act as a catalyst for this reaction, in contrast to the photoredox nickel promoted allylation with allylacetate[20] is certainly due to the major reduction potential necessary to reduce the cobalt complexes. The absence of quenching between cobalt complexes and Ir(III) are ruling out the direct reduction of the Co(II) by the photocatalyst. On the other hand, the ground state reduction potential of $[Ir(dtbbpy)(ppy)_2]PF_6$ is -1.51 V ($E_{1/2}$ $[Ir]^+/[Ir]$ vs SCE),[30] that make the reduction of cobalt complexes thermodynamically favored.

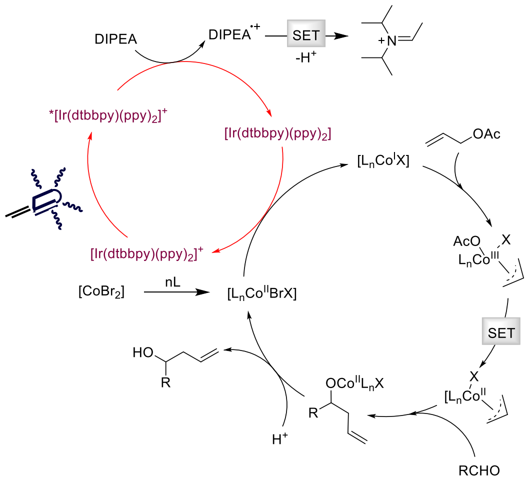


Figure 2. Mechanistic proposal for the cobalt mediated allylation of aldehydes.

Conclusion

In this study, we have introduced a simple photoredox allylation reaction based on cobalt(II), and we have fully studied the process. The reaction is effective for aromatic substrates, while application of the methodology to aliphatic aldehydes suffers from quite reduced reactivity. Employment of additive such as Lewis acids are unable to increase the reactivity. Detailed photophysical investigations have clarified the catalytic cycle. As the major drawbacks of the procedure is the challenge to form an active low valent Cobalt complex and the employment of expensive iridium photocatalysts, presently we are trying to improve conditions and outcome by the systematic investigation with strong reducing organic dyes, and we will report in due time these results

Experimental Section

General Methods. All commercial chemicals and dry solvents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals and used without additional purifications. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 NMR instrument with a 5 mm probe. All chemical shifts are referenced using deuterated solvent signals. Flash chromatography purifications were carried out using VWR or Merck silica gel (40-63 µm particle size). Thin-layer chromatography was performed on Merck 60 F254 plates

General allylation procedure: A dry 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar and an argon supply tube, was first charged with cobalt di bromide (0.02 mmol, 4 mg) and the salt was dried under vacuum and gently heating until color changed from purple to green . The tube was filled with argon and dtbbpy (0.02 mmol, 5 mg), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.004 mmol, 3.7 mg), DMF (0.9 mL) and water (0.1 mL) were added. The reaction mixture was further subjected to a freeze-pump-thaw procedure (three cycles) and the vessel refilled with argon. Then, DIPEA (0.8 mmol, 0.103 g, 0.139 mL), ally acetate (0.6 mmol, 0.060 g, 0.065 mL) and aldehyde (0.2 mmol) were added. The reaction was irradiated under vigorous stirring for the 72 h. After that the reaction was quenched with water (approx. 4 mL) and extracted with AcOEt (4 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was subject of flash column chromatography (SiO_2) to afford the products **3** in the stated yields.

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