

Visible-Light-Initiated Palladium-Catalyzed Cross-coupling by PPh_3 Uncaging from an Azobenzene Ruthenium–Arene Complex

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Abstract: Photo-release of triphenylphosphine from a sulfonamide azobenzene ruthenium–arene complex was exploited to activate $\text{Pd}^{\text{II}}\text{Cl}_2$ into Pd^0 catalyst, for the photo-initiation of Sonogashira cross-coupling. The transformation was initiated on demand – by using simple white LED strip lights – with a high temporal response and the ability to control reaction

rate by changing the irradiation time. Various substrates were successfully applied to this photo-initiated cross-coupling, thus illustrating the wide functional-group tolerance of our photo-caged catalyst activator, without any need for sophisticated photochemistry apparatus.

Introduction

The field of photoswitchable catalysis has emerged over the last two decades from the idea of modulating the activity of a catalyst through the use of a non-invasive external light stimulus, with high spatiotemporal response.^[1] In this respect, research efforts have focused on the incorporation of a light-responsive actuator into the structure of a functional catalyst. In practice, however, maximizing the difference in reactivity between two forms of a photoswitchable catalyst remains a challenging and hardly a predictable issue. One reason lies in the inherent efficiency of the photoswitching process (notably photostationary state composition), which can be strongly influenced by the surrounding groups required for catalytic activity. Moreover, the modulation of reactivity originates from a variety of interconnected effects and subtle variations such as steric shielding, electronic modification, change in distance between reactive sites, or solubility and aggregation effects.^[1c]

The photo-release of a chemical entity, often referred as “photo-uncaging”, is conceptually and practically a much simpler process than photoswitching, providing unidirectional and irreversible generation of chemical entities. It has consequently been employed since the late 1970s as a tool for the

control of biological processes and controlled release of bioactive substances.^[2] More recently, it has shown great promise for the development of efficient photoacid and photo-base generators targeted towards polymeric materials and photoresist application.^[3] Such approach has also been successfully exploited for the generation of a vacant site at a metal center through ligand photo-dissociation in various catalytic transformations such as alkene isomerization,^[4] and metathesis,^[5] [2 + 2] cycloadditions,^[6] allyl carbamate cleavage,^[7] or azide–thioalkyne cycloaddition^[8] (Figure 1 a). The strategy in which an organocatalyst is released from a photo-active “cage” substrate has been also explored, though only few examples involving hexylamine (thiol–Michael addition),^[9] proline (aldol, Michael and Mannich reaction),^[10] thiourea and squaramide (Michael addition),^[11] DMAP (acetylation of alcohols)^[12] and PPh_3 (aza–Morita–Baylis–Hillman reaction,^[13] Figure 1 b).^[14] To the best of our knowledge, the complementary approach involving photo-release of a ligand that could in turn generate an active catalytic species from an appropriate

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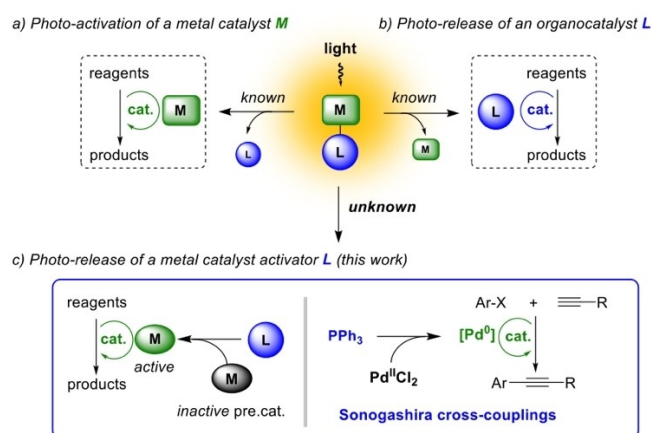


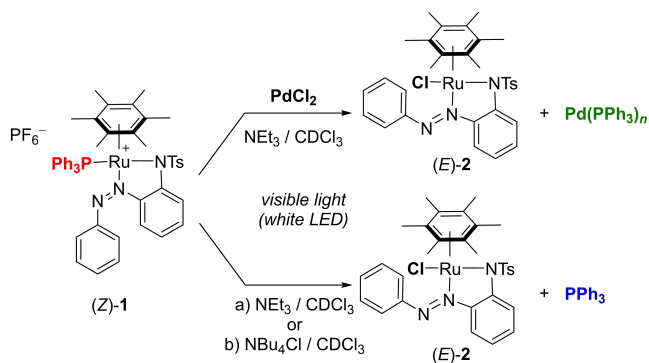
Figure 1. General paths for the induction of catalytic activity with light through “photo-uncaging”.

precatalyst has not been reported to date (Figure 1 c). As a first example of this general strategy, we explored in this work, the ability of “photo-uncaged” PPh₃ to generate catalytically competent Pd⁰ species from Pd^{II} precatalysts and applied this process to the photo-initiation of C(sp²)–C(sp) cross-couplings, namely the Sonogashira reaction. As far as we know, no prior visible-light-activated palladium-catalyzed coupling reaction has been achieved through photo-release of the metal catalyst activator, as has with these PPh₃.^[15]

Results and Discussion

Upon visible light irradiation, ruthenium complex (Z)-1^[13] can release PPh₃ and be converted into a new Ru^{II} species, through Z→E isomerization of the azobenzene core (Scheme 1). As demonstrated in our previous studies, the photo-releasing efficiency is mostly affected by the nature of the surrounding medium.^[16] Noteworthy, in weakly coordinating solvents (such as dichloromethane, chloroform, or acetone), light irradiations led to a dynamic equilibrium consisting of about 50% photo-released PPh₃ in mixture with (Z)-1 and H₂O-coordinated complex (Scheme S2 and Figure S7 in the Supporting Information), whereas quantitative phosphine release could be achieved in the presence of coordinating solvents (such as pyridine, DMSO, or acetonitrile).^[13]

In the aim of exploiting PPh₃ photo-release from (Z)-1 as a general platform for the initiation of a variety of chemical transformations with light, we decided to further investigate its reactivity with a focus on the reduction of Pd^{II}Cl₂ into active Pd⁰(PPh₃)_n under basic conditions, to photo-induce Pd-catalyzed cross-couplings.^[17] Preliminary studies revealed a good stability of (Z)-1 in the dark in a NEt₃/CHCl₃^[18] mixture, by comparison with other tested bases/solvents.^[19] Dispersing PdCl₂ (1 equiv.) along with (Z)-1 (1 equiv.) and NEt₃ (30 equiv.) in CDCl₃, after 1 h in the dark, did not lead to any reaction, such as ligand exchange, and the characteristic signals of (Z)-1 remained unchanged according to ¹H/³¹P NMR analyses (Figure 2). After 20 min of light irradiation using simple white LED (RGB) strip lights, ¹H NMR showed quasi-quantitative conversion of (Z)-1



Scheme 1. Photo-uncaging of PPh₃ from (Z)-1. Photo-induced reduction of PdCl₂ (1 equiv.) into Pd(PPh₃)_n with NEt₃ (30 equiv.; top) and photo-release of PPh₃ promoted by Cl⁻ ions (bottom). a) NEt₃ (70 equiv.); b) NBu₄Cl (5 equiv.).

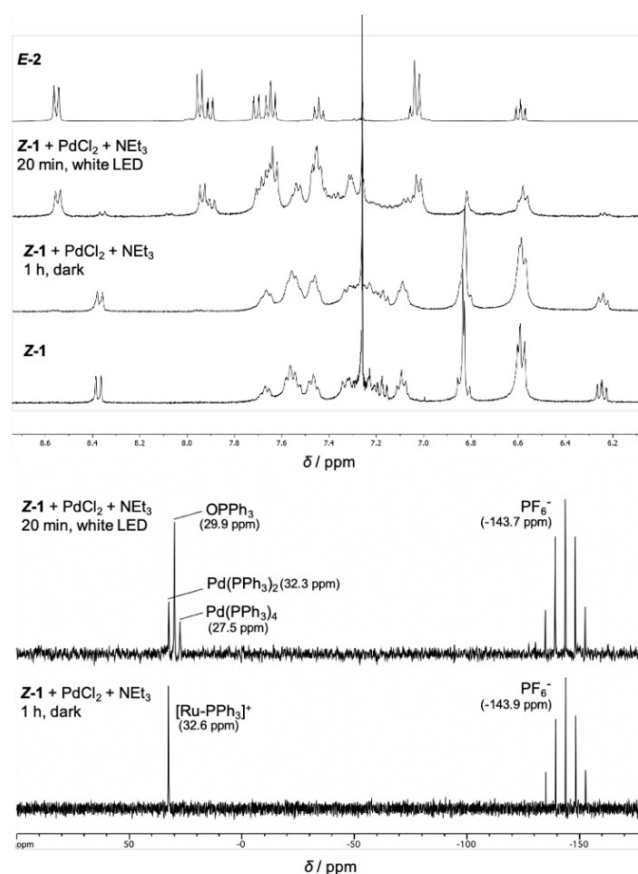
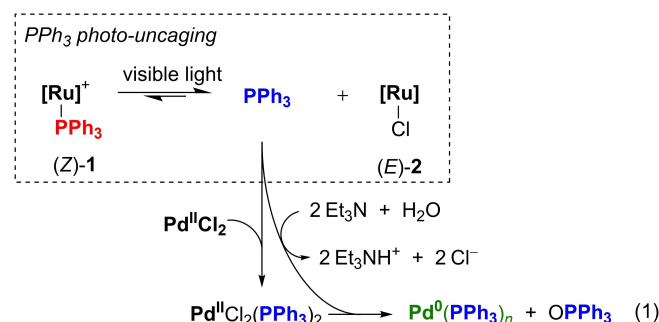


Figure 2. Evolution of ¹H (top) and ³¹P (bottom) NMR spectra of (Z)-1 in CDCl₃ (1 equiv.) along with PdCl₂ (1 equiv.) and NEt₃ (30 equiv.) after 1 h in the dark and after 20 min of light irradiation.

with concomitant formation of (E)-2 (Scheme 1, top) and ³¹P NMR revealed new peaks: an intense one at 29.9 ppm and two smaller at 32.3 and 27.5 ppm, without sign of free PPh₃ (−4.8 ppm) or PdCl₂(PPh₃)₂ (24 ppm; Figure 2). According to experimental (Table S2) and literature data,^[20] the most intense signal (29.9 ppm) was ascribed to the formation of PPh₃ oxide which might indicate the reduction of Pd^{II}Cl₂ into Pd⁰(PPh₃)_n facilitated by the presence of traces of water^[21] in the medium (Scheme 2).^[17] If the signal at 32.3 ppm can be attributed to



Scheme 2. Plausible mechanism for the photo-induced reduction of Pd^{II}Cl₂ to Pd⁰(PPh₃)_n.

Pd(PPh₃)₂ along with traces of remaining (Z)-1,^[22] the second lowest intense peak at 27.5 ppm could indicate the formation of Pd⁰(PPh₃)₄ complex according to the overall Equation (1) (Scheme 2).^[23]

In comparison, irradiation for 15 min of (Z)-1 in CDCl₃ in the presence of an excess of NEt₃ but without PdCl₂, also promoted the complete photo-releasing with the concomitant formation of chloro complex (E)-2 (Scheme 1, bottom). This finding, supported by ¹H NMR, UV-Vis absorption studies (Figures S6–S8), suggested that chloride anions, that may originate from a solvent degradation under those conditions,^[24] also favored the efficient PPh₃ uncaging.^[25] Indeed, upon light irradiations in the presence of an external source of chloride and without base, (Z)-1 was efficiently transformed into (E)-2 (Figure S9), ultimately confirming the fundamental cooperative role of chloride ions and light in the PPh₃ uncaging (Scheme 1, bottom).

To assess the light-driven ability of (Z)-1 to activate Pd^{II}-catalyzed cross-couplings through PPh₃ uncaging (and subsequent Pd^{II} reduction), the classical Sonogashira reaction was next targeted as typical procedures for this coupling involve NEt₃ as the base along with Pd^{II} pre-catalyst.^[26] We started our investigations by studying the cross-coupling between an activated aryl iodide, 4-iodoacetophenone, with trimethylsilyl (TMS) acetylene. Even though performing Sonogashira couplings in chlorinated solvents is uncommon, to our delight, the model reaction catalyzed by PdCl₂/CuI in NEt₃/CHCl₃ can be efficiently turn on (100% conv.) or off (< 5% conv.) according to the presence, or not, of PPh₃ (4 mol%; Table 1, entries 1 and 2). When the reaction was performed under similar conditions with (Z)-1 (4 mol%) in the dark or under visible light irradiations, differences of reactivity were noticed with a complete conversion into cross-coupled product under light compared with 45% conversion in the dark (entry 3). This mild conversion obtained in the dark suggested a partial PPh₃ releasing from (Z)-1 over the reaction, possibly favored by the presence of additional coordinating species (such as iodide ions). However, Cu-free Sonogashira coupling appeared not to be suitable for

this system (entry 4). Replacing (Z)-1 by (E)-2 did not promote the reaction (entry 5), thereby excluding a photosensitizing ability^[15a,b,d,f–g] for our Ru^{II} complexes (or their decomposition into catalytically competent entities^[27]) and highlighting the fundamental role of PPh₃ ligand to generate and/or stabilize active Pd⁰ species.

The effect of the solvent was next investigated. Switching to CH₂Cl₂, neutralized CHCl₃ (passed through Al₂O₃ pad), or CHCl₃ distilled over CaH₂, reduced the “off effect” in the dark (entries 6–8). These experiments might suggest that the intrinsic acidity of CHCl₃, used without further treatment, protected (Z)-1 from degradation under the cross-coupling conditions employed herein.^[28] To our delight, decreasing the amount of the base from 15 to 2.5 or 1.6 equiv. significantly improved the on-off photo-effect of the reaction. (entries 9 and 10). Indeed, a yield of 92% yield was obtained when running the reaction upon irradiation with 1.6 equiv. of NEt₃, in contrast to 10% in the dark. This result demonstrated the potential of our photocaged system to efficiently turn on a Sonogashira coupling reaction upon visible light irradiation.

To gain more insights into the photo-initiation of the coupling, conversion rates of our model reaction were investigated by ¹H NMR over time, by directly performing the reaction into an NMR tube using PPh₃ or (Z)-1 in the dark, or after light irradiations (Figure 3, top). The conversion rates appeared to be similar using PPh₃ as ligand or (Z)-1 after 20 min of light exposure with a translational time of around 15 min, attributed to the irradiation period. When the reaction was carried out in the dark with (Z)-1, no coupling occurred for 12 min and then, slowly took place. After 1 h, around 10% of product was formed even though the degradation of (Z)-1 could not be detected by ¹H NMR. On the other hand, while only negligible amount of product could be observed after 30 min in the dark, exposure to light for 10 min nicely initiated the cross-coupling, to reach almost full conversion in about one additional hour (Figure 3, bottom). Interestingly, the rate of the coupling reaction could be finely tuned by changing the

Table 1. Investigations toward visible-light-initiated Sonogashira coupling.

	Solvent	Co-catalysts	NEt ₃ [equiv.]	Yield [%] ^[a] Irr. LED	Dark
1 ^[b]	CHCl ₃	CuI	15	–	< 5
2 ^[b]	CHCl ₃	PPh ₃ /CuI	15	–	100
3	CHCl ₃	(Z)-1/CuI	15	100	45
4 ^[c]	CHCl ₃	(Z)-1	15	10	< 5
5	CHCl ₃	(E)-2/CuI	15	< 5	–
6	CH ₂ Cl ₂	(Z)-1/CuI	15	100	95
7	CHCl ₃ ^[d]	(Z)-1/CuI	15	100	79
8	CHCl ₃ ^[e]	(Z)-1/CuI	15	93	55
9	CHCl ₃	(Z)-1/CuI	2.5	100	30
10	CHCl ₃	(Z)-1/CuI	1.6	92	10

Reaction scale: iodoaryl (0.057 mmol; 38 mM); PdCl₂ (5 mol%) and co-catalysts: CuI (6 mol%), (Z)-1, PPh₃ or (E)-2 (4 mol%). [a] NMR yields were determined from crude ¹H NMR after workup based on the relative integrals product/remaining iodoaryl substrate. [b] Run under ambient light. [c] 4 h reaction time. [d] Neutralized through Al₂O₃ pad. [e] distilled over CaH₂.

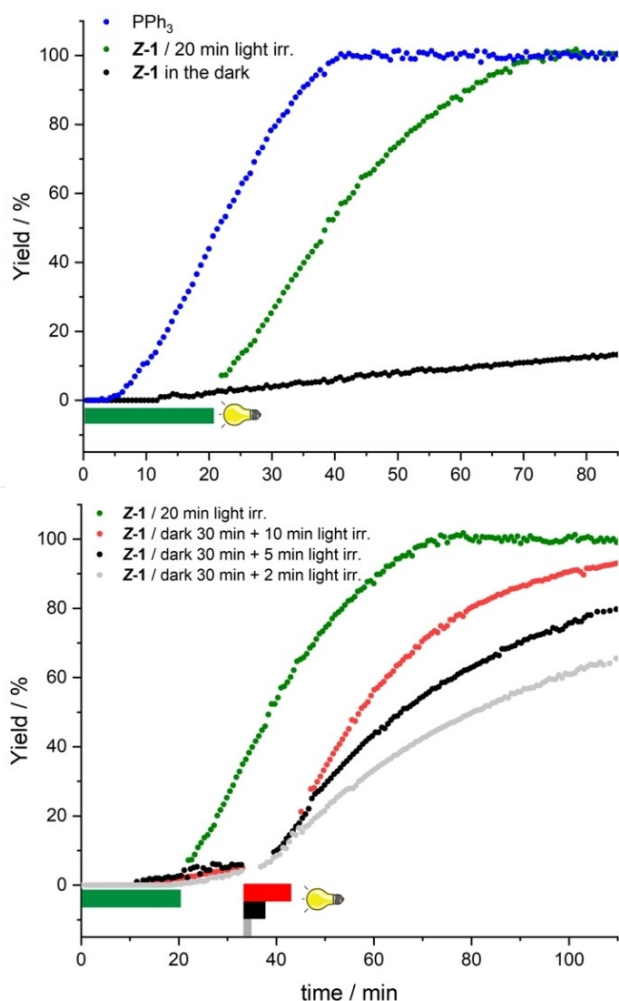


Figure 3. Yields of Sonogashira coupling between 4-iodoacetophenone and TMS acetylene (conditions: Table 1, entry 10) determined by ^1H NMR spectroscopy. Colored bars show length of visible light irradiation.

irradiation time for PPh_3 photo-releasing to 5 or 2 min. These experiments highlight the ability of our photocaged system to gradually respond to visible light exposure time on demand.

To evaluate the efficiency of this light induced Sonogashira coupling on a broader substrate scope, the optimized conditions (Table 1, entry 10) were first applied to unsubstituted iodobenzene ($\text{R}^1 = \text{H}$) along with TMS-acetylene, inducing a good on/off photo-effect with 65% yield upon irradiation versus traces of product when the reaction was performed in the dark (Figure 4; bar chart). To our delight, when the amount of base was increased to 15 equiv., the conversion was raised to 80%. Same conditions were applied to other iodoaryl substrates, bearing deactivating substituents with electro-donation or steric bulk.^[29] The reaction tolerated a wide range of functional groups on the arene ring, namely ketone, ester, alcohol, ether, amine. For all examples, turning the light on improved significantly the reaction reactivity as compared to the dark (Figure 4; bar chart). Aromatic and aliphatic acetylenes such as phenylacetylene or hex-1-yne were also suitable

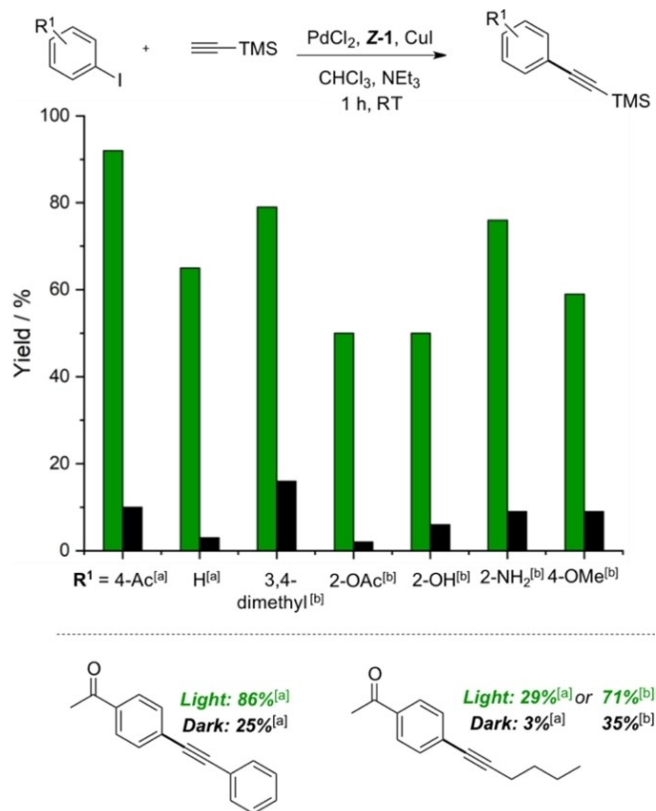


Figure 4. Light-induced Sonogashira cross-coupling between iodobenzene derivatives and acetylene derivatives by using (Z)-1. Bar chart: variation of iodoaryl derivatives with TMS acetylene. Reaction conditions: PdCl_2 (5 mol%), CuI (6 mol%), (Z)-1, (4 mol%), NEt_3 ([a] 1.6 or [b] 15 equiv). All yields were determined by ^1H NMR spectroscopy.

substrates for this reaction, yielding 86 and 71% of product with light, compared with 25 and 35% in the dark, respectively (Figure 4; bottom).

Conclusion

Ruthenium complex (Z)-1, acting as a light-gated PPh_3 , was shown to promote the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2$ into $\text{Pd}^0(\text{PPh}_3)_n$ species upon irradiation with visible light from simple white LED strips under basic conditions in CHCl_3 . This process, which does not require sophisticated photochemistry apparatus, was applied to the photo-initiation of Sonogashira cross-couplings, whose rate could be finely tuned by changing the irradiation time. We anticipate that this concept could be transposed to other Pd^0 -catalyzed transformations, or other metal catalytic systems, and open new horizons in the field of multicatalysis with the possibility of drastically changing the activity of a catalyst for relayed processes through external-light stimulus.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: arene ruthenium · azobenzene · photochemistry · Sonogashira cross-coupling · triphenylphosphine

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