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► **To cite this version:**

Jompol Thongpaen, Romane Manguin, Vincent Dorcet, Thomas Vives, Carine Guyard-Duhayon, et al.. Visible Light Induced Rhodium(I)-Catalyzed C-H Borylation. *Angewandte Chemie International Edition*, 2019, 58 (43), pp.15244-15248. 10.1002/anie.201905924 . hal-02307077

HAL Id: hal-02307077

<https://univ-rennes.hal.science/hal-02307077v1>

Submitted on 16 Dec 2019

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Visible Light Induced Rhodium(I)-Catalyzed Directed C–H Borylation.

Jompol Thongpaen, Romane Manguin, Vincent Dorcet, Thomas Vives, Carine Duhayon, Marc Mauduit and Olivier Baslé*

Abstract: An efficient visible light-induced rhodium(I)-catalyzed regioselective borylation of aromatic C–H bonds is reported. The photocatalytic system is based on a single NHC-Rh(I) complex capable of both harvesting visible light and enabling the bond breaking/forming at room temperature. The chelating nature of the NHC-carboxylate ligand was critical to ensure the stability of the Rh(I) complexes and to provide excellent photocatalytic activities. Experimental mechanistic studies evidenced a photooxidative *ortho* C–H bond addition upon irradiation with blue LEDs that led to a cyclometalated Rh(III) hydride intermediate.

The direct functionalization of inert C–H bonds has emerged over the past two decades as an increasingly important synthetic tool.¹ In particular, transition metal (TM)-catalyzed C–H functionalization has witnessed continuing improvements in performance,² allowing to expand the toolbox available for organic material synthesis,³ natural products synthesis⁴ and drug discovery programs.⁵ In spite of this success, there is still a need for the development of C–H transformations that can efficiently operate under mild conditions with broad functional group tolerance and high selectivity. The recent enthusiasm for visible light-driven reactions has resulted in a rise in the number of innovative catalytic systems that enable C–H transformations under mild conditions.⁶ Most of these methodologies involve the photosensitization of a photoredox catalyst (PC) that promotes the transformation either *via* hydrogen atom transfer (HAT) or single electron transfer (SET) (Figure 1 a).⁷ More recently, by merging photoredox catalysis and TM-catalysis, this dual catalysis strategy has allowed the installation of unique functional groups with efficient selectivity control (Figure 1 b).⁸ An ideal alternative, would be to use a single TM catalyst capable of both harvesting visible light and enabling the bond breaking/forming within the coordination sphere of the metal center.⁹ While this strategy employing unconventional TM photocatalysts has notably led to attractive reactivities in coupling reactions,¹⁰ the field of visible light-induced TM-catalyzed C–H functionalization still requires fine catalyst engineering to address the various challenges associated with the selective transformation of unactivated C–H bonds.¹¹

Organoboron compounds are versatile intermediates for medicinal chemistry and materials science and the direct C–H

borylation of arenes is arguably the most straightforward approach to access these useful building blocks.¹² Despite the recent advances made in TM-catalyzed site selective C–H borylation,¹³ only poor regioselectivities have been observed with the few photocatalytic systems that have been reported and that rely on the use of less attractive high energy UV-light (Figure 1c).¹⁴ We report here an unprecedented visible light-induced rhodium(I)-catalyzed regioselective borylation of aromatic C–H bonds at room temperature (Figure 1d).

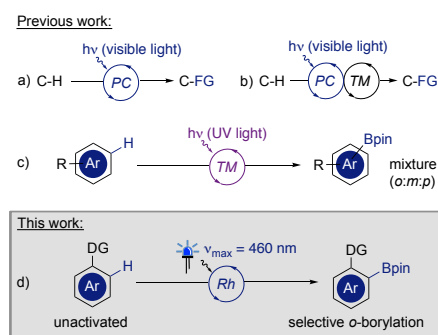


Figure 1. Light-driven catalytic C–H functionalization strategies.

The use of *N*-Heterocyclic Carbene (NHC) ligands has allowed for the preparation of TM complexes that are highly valuable materials to access efficient and selective homogeneous catalysis,¹⁵ including photocatalysis.¹⁶ Nevertheless, the use of such ligands in TM-catalyzed C–H bond borylation is scarce.¹⁷ We recently developed a new class of bidentate carboxylate NHC ligands,¹⁸ which proved to be beneficial for Cp*Rh(III)-based catalysts in aromatic and aliphatic C–H bond borylations under thermal conditions.¹⁹ These bidentate NHC-carboxylate ligands have also been recently used in the preparation of particularly robust luminescent octahedral Ir(III) complexes, which were shown to display some interesting photophysical properties useful in the context of visible light-induced catalysis.²⁰ Therefore, with the objective to achieve borylation under the mildest conditions possible, we hypothesized that the incorporation on a Rh(I) complex of a strong electron-donating bidentate NHC-carboxylate ligand in association with a relatively labile 1,5-cyclooctadiene (cod) ligand should afford simple visible-light absorbing complexes that fit the requirements to achieve the pursued photocatalytic activity. To this end, a series of amino acid-based NHC ligand precursors **1** were converted to their corresponding silver-intermediates and then transmetalated to [Rh(cod)Cl]₂ to afford the desired Rh(I) complexes in good yields (Figure 2). X-ray diffraction analysis unambiguously confirmed the structure of complex **2a**, which exhibits a slightly distorted square planar geometry (Figure 2).²¹ Importantly, UV-vis spectra of complexes **1** evidenced the expected visible light absorption (Figure S2) suitable for excitation with blue light emitting diodes (LEDs).

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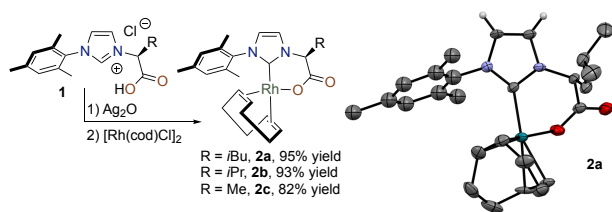
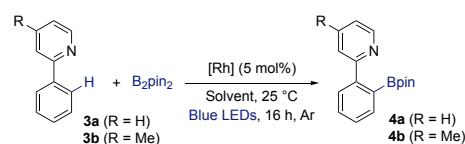


Figure 2. (NHC)Rh(cod) complexes **2** (left) and X-ray crystal structure of **2a** (right). Most hydrogen atoms are omitted for clarity. For complex **2a**: distances between C_{carbenic} and Rh = 2.04 Å, between Rh and O = 2.08 Å. Angle for C_{carbenic}-Rh-O = 85.2°. cod = 1,5-cyclooctadiene

With the new complexes in hand, we decided to investigate their photocatalytic activity in aromatic C–H borylation directed by a pyridine group using B₂pin₂ [bis(pinacolato)diboron] as borylating reagent (Table 1). The functionalization of 2-phenylpyridine (**3a**) in tetrahydrofuran (THF) in the presence of complex **2a** irradiated overnight with 20W blue LEDs allowed 90% conversion of **3a** with modest selectivity and gave the desired *ortho*-borylated product in 50% yield.²² Pleasantly, the regioselectivity outcome of the borylation reaction could be efficiently improved using 4-methylpyridine as directing group to afford the borylated product **4b** in nearly quantitative yield (entry 2). The use of other solvents dramatically impacted the catalytic activities (entries 3–5). When THF was replaced by benzene, the yield of **4b** decreased to 85%. Only traces of product were obtained in dichloromethane and no detectable amount of **4b** could be observed when performing the reaction in acetonitrile. On the other hand, the use of pinacolborane (HBpin) instead of B₂pin₂ gave the desired product in modest 51% yield (entry 6). The influence of the chelating side arm of the NHC ligand was also investigated (entries 7–10). While similar efficiency was obtained using **2b**, a noticeable decrease of the borylation efficiency was observed with the alanine-based complex **1c**. The importance of the chelating NHC ligand was further evidenced with the very poor catalytic activities observed using [Rh(cod)Cl]₂ (entry 9), or monodentate NHC-based (IMes)Rh(cod)Cl (entry 10). Finally, a series of control experiments revealed that both the rhodium catalyst and the light are essential for the reaction to proceed (entries 11 and 12).

Subsequently, the scope of the borylation reaction with respect to 2-arylpyridine based substrate **3** was studied (Table 2). The optimized conditions were utilized to examine steric and electronic influences on the reaction efficiency. The yield of the *ortho*-borylated product **4** was determined by ¹H NMR spectroscopy and the crude reaction mixture was then treated with Oxone[®] to allow the efficient isolation of the corresponding hydroxylated product **5**.¹⁹ Aryl groups bearing a substituent at *para*-(**3c**, **3d**), *meta*-(**3e**) and *ortho*-(**3f**) were well tolerated affording the functionalized products (**5c–5f**) in good isolated yields. When comparing with the result obtained with the electron-rich **3g**, a slight decrease of reactivity was observed with electron-deficient **3h** and **3i**. 2-phenylpyridine bearing a trifluoromethyl (**3j**) and a phenyl (**3k**) substituent on the pyridyl group are also amenable substrates. Borylation of the 1-naphthyl fragment of the sterically congested substrate **3l** was highly efficient and allowed the isolation of **5l** in a racemic form.²³ The isoquinoline-group were also amenable to direct the borylation in *ortho*-position of electron-rich and electron-deficient substituted aryl fragments

Table 1. Optimization of the reaction conditions.^[a]

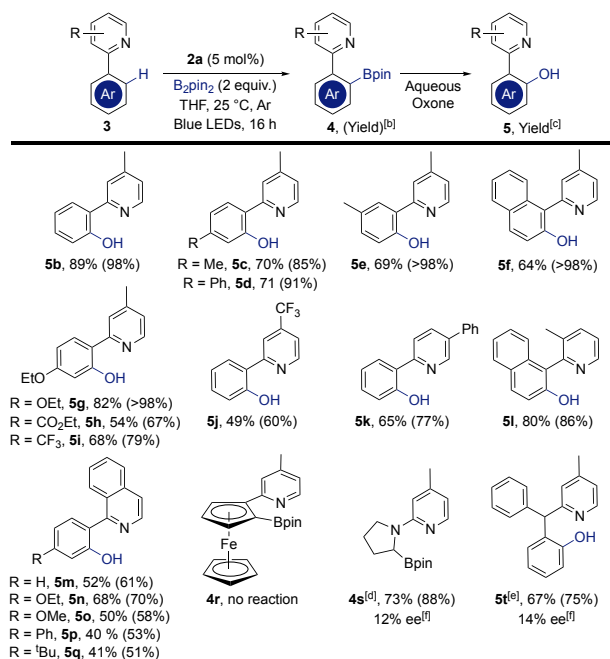


Entry	Catalyst	R	Solvent	Yield (%) ^[b]
1	2a	H	THF	50
2	2a	Me	THF	>99
3	2a	Me	C ₆ H ₆	85
4	2a	Me	CH ₂ Cl ₂	<5
5	2a	Me	CH ₃ CN	0
6 ^[c]	2a	Me	THF	51
7	2b	Me	THF	91
8	2c	Me	THF	76
9	[Rh(cod)Cl] ₂	Me	THF	<5
10 ^[d]	(IMes)Rh(cod)Cl	Me	THF	<5
11 ^[e]	2a	Me	THF	0
12	none	Me	THF	0

[a] Reaction conditions: **3** (0.1 mmol), B₂pin₂ (0.2 mmol), [Rh] (0.005 mmol), solvent (0.1M), 20W Blue LEDs (λ_{max} = 460 nm), 16 h under Ar. [b] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c] HBpin instead of B₂pin₂. [d] IMes = 1,3-Bis(2,4,6-trimethylphenyl)imidazolide. [e] Reaction performed in the dark from 25 to 80 °C.

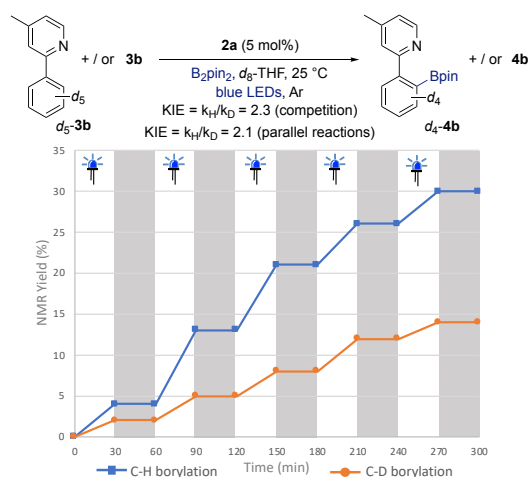
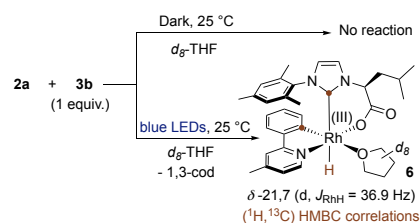
(**3m–3q**). No reaction could be observed for the prochiral ferrocenyl substrate **3r**. This lack of reactivity may originate from the strong visible light absorbance of the substrate (λ ~ 460 nm) that can interfere with the catalyst activation (Figure S3). On the other hand, the site-selective C(sp³)-H borylation of substrate **3s** could be achieved with high efficiency and low enantio-induction.²⁴ Finally, substrate **3t** was engaged in a pyridine-directed desymmetrization,²⁵ to afford the desired product **5t** in good 67% isolated yields and with similar 14% enantiomeric excess.

To probe the mechanism of the visible-light induced C–H borylation process, we performed a series of mechanistic experiments. First, the catalytic borylation of substrate **3b** conducted in the presence of butylated hydroxytoluene (BHT) or TEMPO [2,2,6,6-tetramethylpiperidine-1-oxyl] proceeded without noticeable decrease of catalytic activities, which suggested that processes involving radicals are unlikely to be operative (Scheme S10). Then, the on/off experiment was combined with the kinetic isotope effect (KIE) cross-experiment (Scheme 1). When the LEDs were switched off, the reaction did not proceed in the dark, which indicated that constant photoexcitation is essential for the transformation. In addition, the KIE value of 2.1 determined by comparing the two reaction rate constants independently measured using either **3b** or its pentadeuterated analogue *d*₅-**3b** suggested that the C–H bond breaking occurs during the rate-determining step.²⁶ Further insights into the mechanism of the C–H breaking process were gained through the reaction of stoichiometric amount of complex **2a** and substrate **3b** in *d*₈-THF. Indeed, while no reaction was observed in the dark, blue LEDs irradiation of a solution of the rhodium complex **2a** with **3b** allowed

Table 2. Scope of the visible-light induced C-H borylation. [a]

[a] Reactions conditions: **3** (0.2 mmol), B_2pin_2 (0.4 mmol), THF (0.1M), 20W Blue LEDs ($\lambda_{max} = 460 \text{ nm}$), 16 h under Ar. [b] NMR yield of the borylated product **4**. [c] Isolated yield of the hydroxylated product **5**. [d] 48 h reaction. [e] **2a** (10 mol%). [f] Enantiomeric excess determined by HPLC analyses.

the formation of a new species with a characteristic Rh–H resonance at $\delta -21.7$ (d, $J_{RhH} = 36.9 \text{ Hz}$, Scheme 2) that is concomitant with release of the 1,5-cod ligand isomerized to 1,3-cod (Figure S10).²⁷ In line with the solvent effect observed during the optimization of the catalytic process (Table 1), the stoichiometric reaction between **2a** and **3b** upon blue LEDs irradiation in C_6D_6 revealed similar results, while no such Rh–H signal could be detected in CD_3CN . Additional thorough NMR spectroscopy analyses, including 2D ($^1H, ^{13}C$)-HMBC at 213 K in d_8 -THF, revealed strong correlations between the hydride ligand, the $C_{carbenic}$ and the *ortho*- C_{phenyl} atoms that allowed us to propose the expected cyclometalated Rh(III)-hydride species **6** resulting from the oxidative addition of the *ortho*-C–H bond of **3b** (Scheme 2 and Figure S13). Despite unsuccessful isolation of **6** due to pronounced instability, structural characterization of the corresponding Rh(μ -OH) species arising from hydrolysis could further confirm the octahedral geometry of the postulated cyclometalated Rh(III) intermediate (Scheme S12). Furthermore, it is important to note that no such hydride species were detected when **3b** was subsequently added in the dark to a pre-irradiated solution of complex **2a** in d_8 -THF which confirmed that light induced the C–H activation process. In analogy with the mechanistic study of Gonzalez-Herrero regarding C–H activation in the triplet excited state of Pt(II) complex,²⁸ we postulate that a metal to ligand charge transfer (MLCT) promotes oxidative *ortho* C–H addition leading to the cyclometalated Rh(III)-hydride intermediate **6**.²⁹ Although, we are unsure at this point of the exact nature of the species involved in the subsequent C–B formation event,³⁰ we propose that **6** reacts with B_2pin_2 to produce HBpin and the corresponding Rh(III)-boryl species,³¹ which undergo reductive elimination of the desired *ortho*-borylated product **4**.³²

**Scheme 1.** Time profile of the isotope cross-experiment in light and dark.**Scheme 2.** Stoichiometric photooxidative C–H bond addition experiment

In summary, rhodium-catalyzed regioselective borylation of aromatic C–H bonds can be induced by visible-light. We discovered a photocatalytic process that involves the direct visible-light absorption of a NHC–Rh(I) complex capable of breaking Csp^2 –H bonds and forming C–B bonds at room temperature. This mild approach to activate C–H bonds is anticipated to find applications in other functionalization reactions, including asymmetric transformations.

Acknowledgements

We acknowledge the CNRS; the ENSCR and the MESRI (grant to RM). This work was supported by the ANR (ANR-15-CE07-0012-01 “CHADOC” grant to OB, JT), We thanks Dr. Christian Bijani (LCC) for NMR analysis of the Rh–H intermediate.

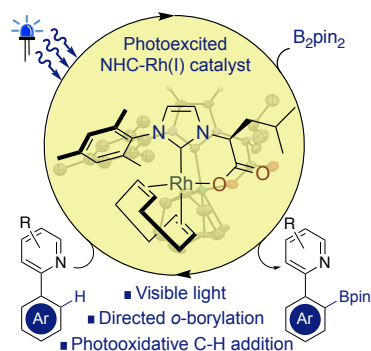
Keywords: Visible-light • borylation • NHC • rhodium • C–H activation

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COMMUNICATION

An efficient visible light-induced rhodium(I)-catalyzed regioselective borylation of aromatic C-H bonds is reported. The photocatalytic system is based on a single NHC-Rh(I) complex capable of both harvesting visible light and enabling the bond breaking/forming at room temperature. The bidentate structure of the NHC ligand was demonstrated to be critical both for the stability and the reactivity of Rh(I) complexes.



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