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Photo-Induced *ortho*-C–H Borylation of Arenes through In Situ Generation of Rhodium(II) Ate Complexes

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ABSTRACT: Photoinduced *in situ* "oxidation" of half-sandwich metal complexes to "high-valent" cationic metal complexes has been used to accelerate catalytic reactions. Here, we report the unprecedented photoinduced *in situ* "reduction" of half-sandwich metal [Rh(III)] complexes to "low-valent" anionic metal [Rh(II)] ate complexes, which facilitate ligand exchange with electron-deficient elements (diboron). This strategy was realized by using a functionalized cyclopentadienyl (Cp^{A3}) Rh(III) catalyst we developed, which enabled the basic group-directed room temperature *ortho*-C–H borylation of arenes.

 ${
m P}$ hotoinduced transition-metal-catalyzed reactions have emerged as a new synthetic strategy through *in situ* modulation of the oxidation state of metal-containing intermediates, which provides access to complementary activation modes to those conventionally used.¹⁻⁵ Recently, a series of half-sandwich d^6 transition-metal [Ir(III), Rh(III), and Ru(II)] catalysts, which are widely used for directed ortho-C-H functionalizations of arenes by concerted-metalation deprotonation (CMD),⁶⁻¹¹ has also been combined with photoinduced reactions and allowed room temperature C-C bond formations. Since 2019, Ackermann and Greaney independently reported elegant systems of photoinduced Ru(II)-catalyzed C-H alkylation^{12,13} by *in situ* oxidation of neutral Ru(II) complex A to cationic Ru(III) complex B (Figure 1a, top). In 2020, Chang designed a sophisticated cyclopentadienyl (Cp) ligand bearing two functional domains for photosensitization and C-H carbometalation. This novel ligand enabled photoinduced Rh(III)-catalyzed C-H arylation¹⁴ through in situ generations of cationic CpRh(IV) complex B (Figure 1a, bottom). Photoinduced in situ generations of these "high-valent cationic" half-sandwich transition-metal complexes B^{1-5} facilitate rate-determining steps, including ligand exchange (LE)^{12,13} or reductive elimination (RE)¹⁴ while maintaining smooth C-H activation by CMD. However, photoinduced in situ generation of a "lowvalent anionic" half-sandwich transition-metal complex that would facilitate ligand exchange with electron-deficient coupling partners (e.g., diboron) has not been utilized in the C-H functionalizations. Here, we report ortho-C-H borylation of arenes using unprecedented photoinduced in situ generation of "anionic" CpRh(II) ate complex C through "reduction" of CpRh(III) complex A (Figure 1b). Baslé recently reported a visible-light-induced rhodium-catalyzed borylation using a sophisticated N-heterocyclic carbene-Rh(I) catalyst (Figure 1c),¹⁵ while this protocol showed a limited scope of directing groups (2-pyridyl arenes). Our strategy using the CpRh(II) ate complex C expands the scope of directing groups by the facilitation of ligand exchange with diboron reagents.

Neutral Rh(II) complexes, which have been widely used for carbenoid reactions, generally form a dimer [such as $Rh_2(OAc)_4$] to stabilize their unpaired electrons.^{16–18} In situ generations of neutral CpRh(II) complexes were also reported but not used for catalytic reactions.^{19,20} On the contrary, an anionic Rh(II) complex, which would be generated by oneelectron reduction of the corresponding Rh(III) complex, is believed to form an anionic monomer because the rhodium center is coordinatively saturated (19 electrons). However, synthesis or in situ generation of anionic CpRh(II) complexes have not been reported probably due to the low reduction potential of CpRh(III) complexes.^{21,22} Thus, their reactivities and applications to organic synthesis have been unrevealed for a long time. We hypothesized that CpRh(III) complex A bearing appropriately tuned arene and Cp ligands would be photoexcited to its triplet-state ${}^{3}A^{*}$, which would be subjected to a one-electron reduction. Besides, unlike "high-valent cationic" metal complexes B, higher-lying HOMO of anionic CpRh(II) complex C would facilitate ligand exchange with electron-deficient elements, such as boron, by strong electrostatic interaction, which would allow the photoinduced ortho-C–H borylation of arenes under mild conditions (Figure 1b).

To test the feasibility of our working hypothesis shown in Figure 1b, we first performed time-dependent density functional theory (TDDFT) calculations of pentamethylcyclopentadienyl (Cp*) aryl Rh(III) acetates bearing different directing groups (Figure 1d).²³ The TDDFT calculation of the absorption spectrum of basic pyrazole complex A1 indicated that the visible absorption is assigned to the HOMO \rightarrow LUMO transition, and ligand-to-metal charge-transfer (LMCT)^{24–30} character is predominant (Figure S4). In

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b) This work: Photo-induced in situ "reduction" of CpRh(III) complex



c) Previous work: Photo-induced NHC–Rh(I)-catalyzed C–H borylation



Figure 1. Photoinduced *in situ* oxidation (previous works) and reduction (this work) strategies. CMD = concerted-metalation deprotonation. ISC = intersystem crossing. PS = photosensitizer.

contrast, amide complex A2 showed visible absorption assigned to the HOMO \rightarrow LUMO transition that is mainly described as a metal-centered transition. The experimental spectra of the complexes A1 and A3 showed good agreement with the calculated spectra (Figure S2). This observation indicates that Rh(III) intermediates with basic rather than neutral directing groups would possess the favorable photophysical property for the long triplet lifetime through visible light irradiation.

Based on the above anticipations, we started with a screening study to find a suitable half-sandwich d^6 transitionmetal catalyst (5 mol % metal) by using 1-phenylpyrazole (1a), bis(pinacolato)diboron (2, 2 equiv), and bases (10 mol %) under blue LED irradiation (Table 1). When using the Cp*Rh(III) catalyst, any conditions without base did not give the desired product 3a, whereas the use of NaOAc, NaOMe, and NaO^tBu slightly promoted the borylation (entries 1–4) and NaO^tBu was the base of choice. Rh(III) complexes with electron-deficient ligands (Cp^{E 31,32} and Cp^{33,34}) did not promote any reactions (entries 5 and 6). Our previously reported Cp^{A1–3}Rh(III) complexes³⁵ were also tested (entries 7–10), which revealed that the Cp^{A3}Rh(III) complex bearing the electron-rich *N*-phenylcarbamoyl moiety afforded 3a in an pubs.acs.org/JACS





[Ir(ppy)₃] = Tris(2-phenylpyridinato)iridium(III)

[lr(dtbbpy)(ppy)₂]PF₆ = (4,4'-Di-tert-butyl-2,2'-bipyridine)bis[(2-pyridinyl)phenyl]iridium(III) hexafluorophosphate

entry	catalyst	base	additive	yield (%) ^c
1	[Cp*RhCl_]	none	none	0
2	[Cp*RhCl_]	NaOAc	none	11
3	$[Cp*RhCl_2]_2$	NaOMe	none	6
1	$\begin{bmatrix} Cp * RhCl \end{bmatrix}$	NaO ^t Bu	none	10
т с	$\begin{bmatrix} C_p & RiC_{2} \end{bmatrix}_2$	NaO ^t Bu	none	19
3	$\left[C P K \Pi_2 \right]_n$		none	0
6	$[Cp^{-}RhCl_2]_2$	NaO'Bu	none	0
7	$[Cp^{A_1}RhCl_2]_2$	NaO'Bu	none	47
8	$[Cp^{A2}RhCl_2]_2$	NaO ^t Bu	none	53
9	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	none	65
10	$[Cp^{A4}RhCl_2]_2$	NaO ^t Bu	none	41
11	$[Cp*IrCl_2]_2$	NaO ^t Bu	none	0
12	[RuCl ₂ (<i>p</i> - cymene)] ₂	NaO ^t Bu	none	21
13 ^d	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	none	0
14	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	[Ir(ppy) ₃]	58
15	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	[Ir(dtbbpy)(ppy) ₂]PF ₆	67
16	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	[Ir(dF(CF ₃) ppy) ₂ (dtbbpy)]PF ₆	50
17	$[Cp^{A3}RhCl_2]_2$	NaO ^t Bu	[Ir(dFppy) ₃]	81
18	$[Cp*RhCl_2]_2$	NaO ^t Bu	[Ir(dFppy) ₃]	5
19	$[CpRhI_2]_n$	NaO ^t Bu	[Ir(dFppy) ₃]	0
20	[RuCl ₂ (<i>p</i> - cymene)] ₂	NaO ^t Bu	[Ir(dFppy) ₃]	18

^{*a*}pin = pinacolato. ^{*b*}Catalyst (0.0050 mmol Rh, Ir, or Ru), additive (0.001 mmol), base (0.010 mmol), **1a** (0.10 mmol), **2** (0.20 mmol), and THF (1.0 mL) were used. ^{*c*}Determined by ¹H NMR using mesitylene as an internal standard. ^{*d*}Without blue LED irradiation.

improved yield of 65% (entry 9).³⁶ Half-sandwich Ir(III) and Ru(II) catalysts were ineffective for this borylation (entries 11 and 12). More importantly, the present borylation was completely shut down without blue LED irradiation (entry 13). These results indicate that the appropriately function-alized CpRh(III) complex catalyzes the *ortho*-C–H borylation through a photoexcited triplet state. We surveyed various iridium photocatalysts (1 mol %) to facilitate the electron-transfer process (entries 14–17), which revealed that the use of $[Ir(dFppy)_3]$ gave 3a in the highest yield of 81% (entry 17). This facilitation using $[Ir(dFppy)_3]$ to the present borylation was unique only to $Cp^{A3}Rh(III)$ catalyst, not to $Cp^*Rh(III)$, CpRh(III), and Ru(II) catalyst (entries 18–20).

The substrate scope of the photoinduced ortho-C-H borylation is shown in Scheme 1a. The key findings are as follows: 1) a wide variety of basic directing groups, such as pyrazoles (1a and 1b), pyridines (1c-1e), and π extended

Scheme 1. Photo-Induced ortho-C-H Borylation^a





 $^{a}[\mathrm{Cp}^{\mathrm{A3}}\mathrm{RhCl}_{2}]_{2}$ (0.0050 mmol), $[\mathrm{Ir}(\mathrm{dFppy})_{3}]$ (0.002 mmol), $\mathrm{NaO^{f}Bu}$ (0.020 mmol), 1 (0.20 mmol), 2 (0.40 mmol), and THF (2.0 mL) were used. Cited yields were determined by $^{1}\mathrm{H}$ NMR (3) or of isolated products (4). $^{b}\mathrm{Without}$ $[\mathrm{Ir}(\mathrm{dFppy})_{3}]$. $^{c}\mathrm{For}$ 72 h. $^{d}\mathrm{Bis}$ (neopentylglycolato)diboron (5) was used instead of 2. $^{e}[\mathrm{Cp}^{\mathrm{A3}}\mathrm{RhCl}_{2}]_{2}$ (0.010 mmol), [Ir(dFppy)_{3}] (0.004 mmol), NaO'Bu (0.040 mmol), 1 (0.20 mmol), 2 (0.40 mmol), and THF (2.0 mL) were used. $^{f}\mathrm{For}$ 48 h.

heteroaromatics (1i and 1j) could be used to give the corresponding arylboronates in excellent yields 2) oxygen and methylene linkers between directing groups and arenes (1f-1h) were tolerated in the reaction; 3) benzylamines (1k and 1k)

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11) were also applicable; 4) arenes bearing electron-withdrawing groups (o-F, m-/p-CF₃, m-/p-Cl, p-Br, and p-phenyl) as well as electron-donating groups (o-/m-/p-Me, m-/p-MeO, and p-alkyl) were compatible to give the corresponding borylated products in good to excellent yields; 5) sequential borylation/oxidation processes were available to give phenol products 4 without isolation of 3. In addition, arenes bearing various basic groups (1a, 1c, and 1k) participated in the present borylation even without a photocatalyst, which revealed that this broad substrate scope is derived from our developed Cp^{A3}Rh(III) catalyst.

Although there are many examples of the transition-metalcatalyzed ortho-C-H borylation, these reactions suffered from harsh conditions (reagents) $^{37-44}$ and/or an excess amount of substrates.^{45,46} Thus, the present room temperature borylation with a broad substrate scope is worthy of note. Furthermore, the present borylation is highly chemoselective, and only basic groups act as directing groups because ligand-to-metal charge transfer of Rh(III) intermediates is necessary (Figure 1d). Thus, no C-H borylation at the ortho-position of the amide (1m), CF₃ (1r and 1u), halogens (1q, 1s, and 1w), and methoxy moieties (1t and 1x) were detected. Moreover, the borylation of 7 bearing both basic and neutral directing groups exclusively afforded the basic group-directed product 8, whereas a mixture of multiborylation products was generated under the previously reported Ir(I)-catalyzed conditions⁴⁷ (Scheme 1b). To demonstrate the synthetic utility of the present borylation, we examined the one-pot borylationelementalization in the presence of the basic functional groups (Scheme 2). Pleasingly, not only hydroxylation (4b) but also





chlorination (9b), deuteration (10b), alkynylation (11b), arylation (12b), alkylation (13b), and dimerization (14b) reactions smoothly proceeded in one-pot starting from 1b without isolation of boronate 3b.

We then sought to acquire mechanistic insights into the present borylation reaction. First, control experiments were examined as shown in Scheme 3a. No LED irradiation or no Scheme 3. Experimental Mechanistic Studies and Plausible Reaction Mechanisms



Rh(III) catalyst (with or without the Ir photocatalyst) shut down the reaction. The base is also essential; no reaction was observed in the absence of NaO^tBu with or without Rh(III) catalyst. In addition, the present borylation was inhibited by a single electron transfer (SET) inhibitor [nitrobenzene (15)], a radical oxidant [(2,2,6,6-tetramethylpiperidin-1-yl)oxy (16)], and oxygen (under air), whereas a radical scavenger [9,10dihydroanthracene (17)] was able to coexist. These results indicate that this reaction does not involve any free radical species but a reduction process through a single electron transfer. Since the optimum base (NaO^tBu) used in the present borylation does not promote the CMD pathway,^{47,48} Rh(III)-catalyzed C-H activation can be excluded. To identify the possibility of C-H activation with Rh(I) species generated by in situ reduction of the initial Rh(III) complex in the presence of possible reducing agents (photocatalyst and/or diboron), we synthesized Rh(I) complex 18 and examined its catalytic activity. We found that 18 can catalyze the borylation (39% yield of 3a) only under blue-light irradiation (Scheme 3b). In addition, the present reaction hardly proceeds in the absence of NaO^tBu with or without the Ir photocatalyst. These

results suggest that the current reaction might start from *in situ* reduction of the Rh(III) complex to generate Rh(I) species, and the following steps also involve the photoinduced reduction process facilitated by the base that coordinates to the diboron reagent.

Based on the experimental mechanistic studies, plausible reaction mechanisms are shown in Scheme 3c. First, as shown in the top scheme, Rh(III) di-tert-butoxide D, generated from [Cp^{A3}RhCl₂]₂ and NaO^tBu, is slowly reduced by borate complex E to give active Rh(I) complex F along with a boronate ester [tBuO-B(pin)]. In the presence of a photocatalyst [Ir(III)], rapid oxidation of borate complex E with the triplet state of the photocatalyst [Ir(III)*] results in the generation of the anionic reductive state of the photocatalyst $[Ir(II)^{-}]$, which instead reduced Rh(III) complex D to Rh(I) complex F. Then, as shown in the bottom scheme, the subsequent oxidative addition (OA, step I) of Rh(I) to the ortho-C-H bond of an arene affords aryl Rh(III) hydride G. Although the direct ligand exchange from G with diboron is difficult, photoexcitation of G generates triplet state ${}^{3}G^{*}$ that is more subject to the second reduction giving Rh(II) ate complex H (SET, step II-A). A facile ligand exchange (LE, step II-B) between electron-rich H and electron-deficient diboron forms the Rh-B bond. Subsequent oxidation with the photocatalyst affords Rh(III) boryl complex I. Finally, reductive elimination (RE, step III) affords the desired borylated product and regenerates Rh(I) complex F.

To gain detailed insight into the proposed mechanisms, model calculations using 1c, bis(ethyleneglycolato)diboron $[B_2(eg)_2]$, and $Cp^{A3}Rh(I)$ or $Cp^{A3}Rh(III)(OMe)_2$ complexes were performed. First, the initial reductive process of Rh(III) to Rh(I) species was evaluated in Figure 2a. Both of the two oxidations of borate complex INT-X to unstable boryl radical species (INT-Y) are endothermic, but they are compensated by a large energy release for the reformation of 1 equiv of diboron $[B_2(eg)_2]$. On the other hand, this process is dramatically changed to an exothermic process by employing an iridium photocatalyst. These results clearly support that the present reaction proceeds even with a single rhodium catalyst but is accelerated by an iridium cocatalyst.

The calculated pathways from generated Rh(I) species depicted in Figure 2b show that oxidative addition from Cp^{A3}Rh(I) (step I, INT1 to INT2) and reductive elimination from ArCp^{A3}Rh(III)B(eg) (step III, INT5 to INT6) smoothly proceed ($\Delta G^{\ddagger} < 10 \text{ kcal mol}^{-1}$). On the other hand, the CMD process with Cp^{A3}Rh(III)(OMe)₂ (step I', INT1' to INT2') is kinetically unfavored ($\Delta G^{\ddagger} = 32.2$ kcal mol⁻¹) and thus excluded from the plausible pathway.^{47,48} In addition, the interconversion from INT2 to INT3' is also excluded because the release of unstable NaH with a large endothermic energy $(35.6 \text{ kcal mol}^{-1})$ is required. In the Cp^{A3}Rh(I)/(III) catalytic cycle, the rate-limiting step is the ligand exchange (step II, INT3 to INT4), in which the highest activation energy (40.3 kcal mol⁻¹) is required. In contrast, the blue-light induced excitation of INT2 followed by ISC leads to a triplet ³INT2* (Figure 2c). This excitation might also be accelerated with an excited iridium photocatalyst via the triplet energy transfer from ³Ir(III) to INT2 [Rh(III)] ($\Delta G = -19.7 \text{ kcal mol}^{-1}$). In the excited triplet state, a single electron transfer from the iridium photocatalyst or borate complex INT-X proceed with a large energy release (-43.2 or -3.5 kcal mol⁻¹, respectively) to in situ generate Rh(II) ate complex INT2-Rh(II), which is preferred to the endothermic direct ligand exchange (³INT2*

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Figure 2. Theoretical mechanistic studies. The changes of the Gibbs free energies calculated at the M06/6-311+G^{**} (C, H, O, and N), SDD (Rh) levels using PCM(THF)//M06/6-31G^{*} (C, H, O, and N) and LANL2DZ (Rh) levels are shown in kcal mol⁻¹.

to ³INT3^{*}).⁴⁹ Compared with Rh(III) complex INT3, cationic aryl Rh(IV) complex INT3-Rh(IV), which could be generated by a single-electron oxidation,¹²⁻¹⁴ still requires a high activation energy (32.2 kcal mol⁻¹) (Figure 2d). Indeed, the structure of TS2-Rh(IV) is similar to that of TS2-Rh(III), and stabilization by the cationic complex was not observed (Figure S3). In contrast, Rh(II) ate complex INT3-Rh(II) smoothly affords the neutral Rh(II) complex and borate hydride species INT3-2-Rh(II) ($\Delta G^{\ddagger} = 10.5 \text{ kcal mol}^{-1}$), and subsequent rapid ligand exchange of the boryl group forms the Rh-B bond with a low activation energy $(1.8 \text{ kcal mol}^{-1})$ (Figure 2e). The formation of borate hydride species is limited to the case of the in situ generation of the Rh(II) ate complex. Thus, all attempts to locate a similar borate hydride species from INT3-Rh(III) or INT3-Rh(IV) resulted in a geometric rearrangement to starting complexes without a barrier. These comparisons support that in situ generation of the Rh(II) ate complex allows the present photoinduced borylation reaction.

In conclusion, we have developed the first protocol for *in situ* generations of "low-valent anionic" Rh(II) ate complexes through photoexcited "reduction" of functionalized Cp (Cp^{A3}) Rh(III) intermediates. This "reductive" strategy enables room temperature C–H borylation of arenes by access to alternative reaction pathways [ligand exchange with an electron-deficient element (boron)], which has never been available by conventional photoinduced "oxidative" strategies to form "high-valent cationic" complexes. We believe that the present

"reductive" protocol provides complementary activation modes to conventionally used "oxidative" ones in photoinduced transition-metal-catalyzed reactions. Further applications of this strategy to C–H functionalizations with electron-deficient elements other than boron, such as silane and tin, and the synthesis of a range of bioactive and functional compounds are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c05859.

Experimental details, analytical data, and spectral reproductions for all new compounds, and details of computational studies (PDF)

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Notes

The authors declare no competing financial interest.

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