

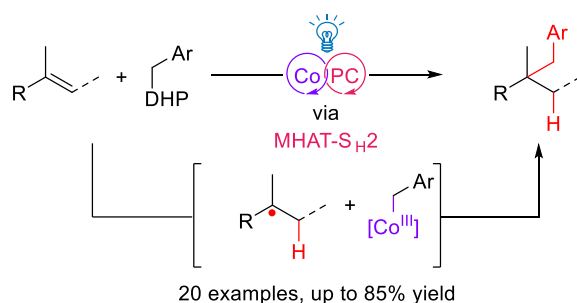
Cobalt/Photoredox Dual-Catalyzed Cross-Radical Coupling of Alkenes via Hydrogen Atom Transfer and Homolytic Substitution

Yuto Yamaguchi,^{1,2} Yuki Hirata,^{1,2} Kosuke Higashida,² Tatsuhiko Yoshino,¹ Shigeki Matsunaga^{1,2*}

¹Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo, Japan.

²Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, Japan.

MHAT, Photoredox Catalysis, Cobalt Catalysis



ABSTRACT: Cobalt-catalyzed metal hydride hydrogen atom transfer (MHAT) in combination with photoredox catalysis has emerged as a powerful synthetic method, owing to its redox nature and applicability to various radical precursors. Herein, we describe a cross-radical coupling reaction under cobalt/photoredox dual catalysis. MHAT and homolytic substitution (S_H2) processes enabled Markovnikov-selective hydrobenzylation of di/tri-substituted alkenes, affording products with a quaternary carbon center in a redox-neutral manner.

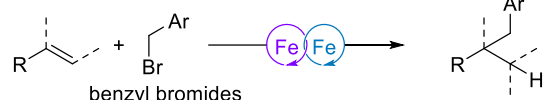
Metal hydride hydrogen atom transfer (MHAT)-type Markovnikov-selective hydrofunctionalization reactions of alkenes, catalyzed by first-row transition metal hydride species (e.g., manganese, iron, cobalt hydrides), have been extensively investigated since the pioneering report of the Drago-Mukaiyama hydration reaction.^{1,2} These reactions, initiated by the formation of radical intermediates through hydrogen atom transfer (HAT) of alkenes, are useful for synthesizing complex molecules, including natural products, due to their mild and selective conditions in contrast to hydrofunctionalization in harsh acidic conditions. Among these reactions, C–C bond-forming reactions via MHAT of alkenes have attracted attention as an efficient and chemoselective approach, especially for constructing quaternary carbons.³ For example, Shenvi and co-workers reported hydroarylation and hydroalkylation reactions employing dual catalysis with Ni/Co, Ni/Fe, and Ni/Mn.⁴ More recently, the same group developed a novel MHAT cross-coupling reaction using an iron-iron dual catalyst system to facilitate MHAT of inert alkenes and to form benzyl-iron species generated from benzyl bromides.^{5a} A homolytic substitution (S_H2) reaction provided hydrobenzylated products (Figure 1a). In addition, S_H2-type reactions have gained notice for their chemoselectivity, which enables cross-coupling of highly substituted tertiary or secondary alkyl radicals with less substituted primary radicals.⁶ The combination of cobalt MHAT catalysis with either photoredox or electrochemical conditions is useful and widely

adopted for various alkene hydrofunctionalization reactions.^{7–9} In the cobalt/photoredox dual catalysis system, the cobalt(II) catalyst is reduced by the photoredox catalyst (PC) and sequentially protonated to afford active cobalt(III) hydride species. The reductive generation of cobalt(III) hydride species under photoredox conditions is complementary to the oxidative metal(III) hydride generation system, in which a metal(II) catalyst undergoes one-electron oxidation with external oxidants and is subsequently transformed into metal(III) hydride species with organosilane reagents. Photoredox catalysts enable the use of various redox-active radical precursors;^{10,11} thus, studies to expand the scope of MHAT hydrofunctionalization processes under cobalt/photoredox dual catalysis have been actively investigated by several groups since our contribution in 2021.^{8,12}

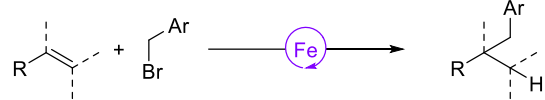
In this context, we envisioned the utility of cobalt/photoredox dual catalysis for hydroalkylation reactions of alkenes via a MHAT-S_H2 process. During our preparation of this manuscript, Shenvi,^{5a–c} Baran,^{5c} and MacMillan^{5d} reported closely related hydroalkylation reactions of alkenes via a MHAT-S_H2 process utilizing single iron catalysis (Figures 1b,1c) and manganese-nickel-photoredox triple catalysis (Figure 1d). In their reports, benzyl bromides, redox-active NHPI esters, and alcohols, respectively, were used as precursors for the cross-coupling reactions. To further broaden the utility of MHAT-S_H2 type hydroalkylation reactions of alkenes, we report our efforts using

Hantzsch esters as a coupling partner under cobalt/photoredox dual catalysis (Figure 1e).

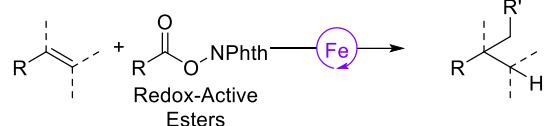
a. Fe/Fe Dual-Catalysis, using benzyl bromides (Shenvi, 2023)



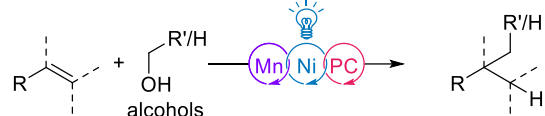
b. Fe Single-Catalysis, using benzyl bromides (Shenvi, 2024)



c. Fe Single-Catalysis, using RAEs (Baran, Shenvi, 2024)



d. Mn/Ni/PC Triple-Catalysis, using alcohols (MacMillan)



e. Cobalt/photoredox dual catalysis, using DHPs [This work]

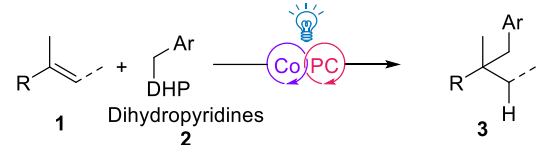


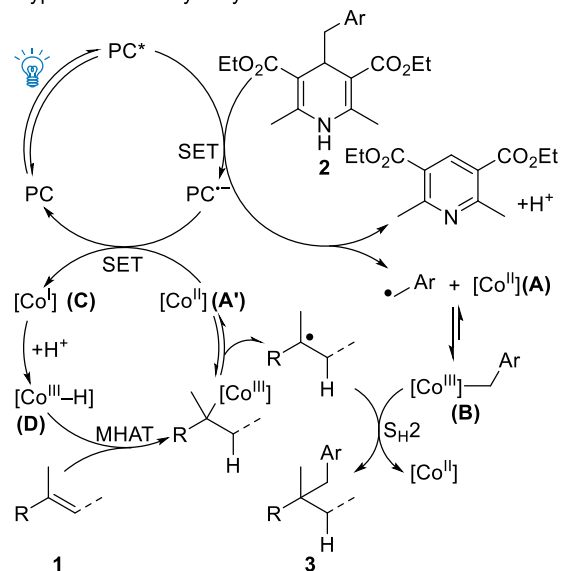
Figure 1. Examples of MHAT-S_H2 hydroalkylation reactions of alkenes.

Our reaction scheme for the hydroalkylation of alkene **1** is illustrated in Figure 2a. Through one-electron oxidation by photo-excited PC, Hantzsch ester **2** is converted into a primary alkyl radical, pyridine, and proton. The free radical would be efficiently captured by the cobalt(II) (A), forming a medium-lifetime alkyl-cobalt(III) complex (B) in equilibrium, which is equivalent to a persistent radical. Another cobalt(II) (A') catalyst is reduced by the radical anion of PC into cobalt(I) (C) and protonated, thus generating the MHAT-active cobalt(III) hydride [Co^{III}-H] (D). [Co^{III}-H] promotes MHAT to alkene **1**, producing a transient tertiary-alkyl radical intermediate. This species exists in equilibrium with an alkylcobalt(III) intermediate (E). Subsequently, the radical intermediate and the aforementioned alkylcobalt(III) (B) would undergo an S_H2 reaction,¹³ providing hydroalkylated product **3** and regenerating the cobalt(II) catalyst (A).

Based on the working hypothesis shown in Figure 2a, we explored the optimal reaction conditions using alkene **1a** and Hantzsch ester **2a** as model substrates (Table 1). A bulky and electron-deficient cobalt salophen complex **4a** (Figure 2b), previously identified as an optimal catalyst for our MHAT enamide synthesis,^{8g} gave hydrobenzylated product **3aa** in 85% isolated yield when combined with Ir(dFppy)₃ as a photoredox catalyst (entry 1). The use of a different cobalt salen **4b**, cobalt salophen complexes **4c-4d**, and cobalt tetraphenylporphyrin complex Co(TPP) resulted in a decreased yield (entries 2–5). Electron-withdrawing trifluoromethyl groups in **4a** improved the

reaction efficiency (entry 1 vs entries 3, 4). We assume that electron-deficient cobalt **4a** would be more favorable in the S_H2 process from the alkyl-cobalt(III) complex (B) to release cobalt(II) species (A), as shown in Figure 2a. In entry 6, the iron-tetraphenylporphyrin complex Fe(TPP)Cl also promoted the MHAT-S_H2 process, albeit with modest efficiency. Finally, control experiments were performed (entries 7–9). In the absence of a photoredox catalyst, cobalt catalyst, or blue LED irradiation, the reaction did not proceed at all. Thus, all catalyst components and photoirradiation were essential for promoting the present hydrobenzylation reaction.

a. Hypothetical catalytic cycle



b. Catalysts in this study

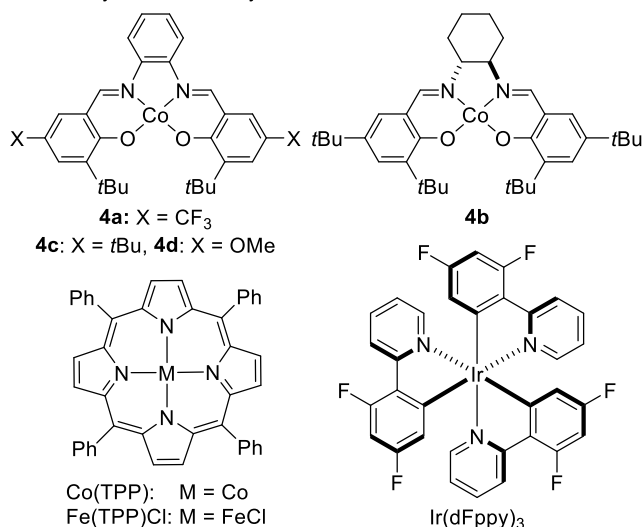
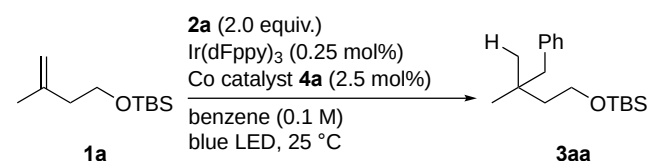


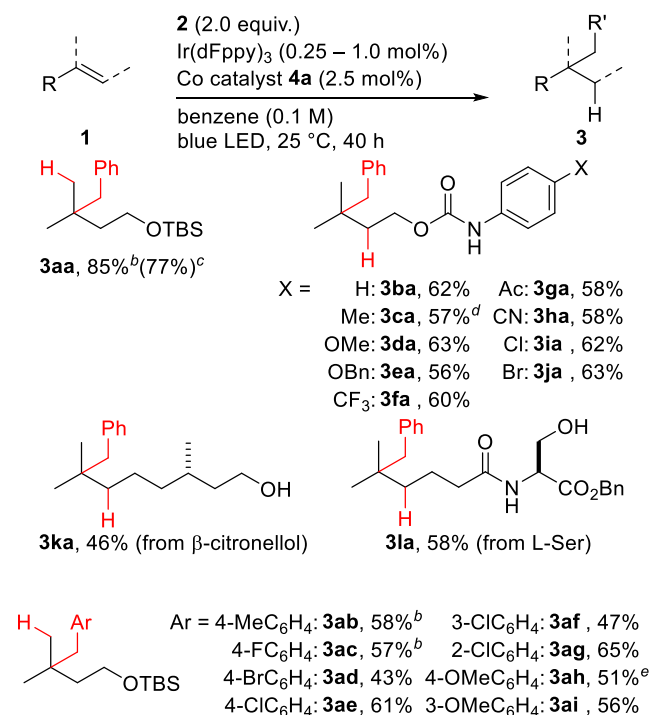
Figure 2. (a) Hypothetical catalytic cycle to realize MHAT-S_H2 hydrobenzylation of alkenes with Hantzsch esters under cobalt-photoredox dual catalysis; (b) Catalysts used in this study.

Table 1. Optimized conditions and their variations.



Entry	Deviation from the above conditions	% yield ^a
1	none	80 (85) ^b
2	Co cat. 4b instead of 4a	45
3	Co cat. 4c instead of 4a	70
4	Co cat. 4d instead of 4a	61
5	Co(TPP) instead of 4a	37
6	Fe(TPP)Cl instead of 4a	13
7	without PC	N.D.
8	without Co catalyst	N.D.
9	without blue LED irradiation (dark)	N.D.

^a Determined by ¹H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. ^b Isolated yield after purification by column chromatography.

Table 2. Substrate scope of hydrobenzylation.^a

^a Reaction conditions (unless otherwise noted): **1** (0.20 mmol), **2** (0.40 mmol), Ir(dFppy)₃ (2.0 μmol) and **4a** (5.0 μmol) in benzene (2.0 mL) at 25 °C under irradiation with blue LEDs. Isolated yields are shown. ^b Ir(dFppy)₃ (0.50 μmol) was used. ^c 1.0 mmol scale at 45 °C. ^d Isolated yield was determined after epoxidation of remaining starting alkene in the crude mixture [mCPBA (0.20 mmol), DCM (0.20 M)] and purification by silica gel column chromatography. ^e 20 hours.

To demonstrate the utility of this hydrobenzylation method, we next investigated the substrate scope (Table 2). The reaction of alkene **1a** was successfully carried out on a 1.0-mmol scale, giving product **3aa** in 77% yield. In addition to terminal 2,2-disubstituted alkene **1a**, the reaction proceeded with internal tri-substituted alkenes to afford products with various functional groups, including electron-donating (**3ca–3ea**), electron-withdrawing (**3fa–3ha**), and halide groups (**3ia**, **3ja**). A natural terpene, β-citronellol, was also converted into benzylated product **3ka** in a moderate yield. A coordinative nitrile and a free alcohol group did not interfere with this reaction (**3ha**, **3ka**). Alkene with an amino acid unit also yielded the corresponding hydrobenzylated product (**3la**). Next, we investigated the scope of Hantzsch esters **2b–2i**. Several benzyl radicals were tolerated, and hydrobenzylated products **3ab–3ag** were obtained from 4-, 3-, or 2-substituted benzyl radical precursors. Additionally, benzyl radicals with both electron-donating (4-OMe) and electron-withdrawing (3-OMe) substituents were tolerated (**3ah** and **3ai**).

In conclusion, we established a hydrobenzylation method under cobalt/photoredox dual catalysis. In this system, Hantzsch esters served as one-electron reductants and as a source of benzylic radicals and protons to generate the cobalt-hydride species. Thus, two distinct alkyl radicals were generated in situ, leading to cross-radical coupling for constructing a quaternary carbon center in a redox-neutral manner. Further application of cobalt/photoredox dual catalysis in MHAT-S_H2 type reactions is ongoing in our group.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Experimental procedures, characterization of the synthesized compounds, and NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

Shigeki Matsunaga – Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan; orcid.org/0000-0003-4136-3548; Email: smatsuna@kuchem.kyoto-u.ac.jp

Authors

Yuto Yamaguchi – Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan and Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan

Yuki Hirata – Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan and Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan

Kosuke Higashida – Department of Chemistry, Kyoto University, Kyoto 606-8502, Japan; <https://orcid.org/0000-0002-0999-0763>; Email: higashida.kosuke.2h@kyoto-u.ac.jp

Tatsuhiko Yoshino – Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan;

Notes

The authors declare no competing financial interest.

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