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Research Article

Photocatalytic Umpolung Synthesis of Nucleophilic π-Allylcobalt Complexes for Allylation of Aldehydes

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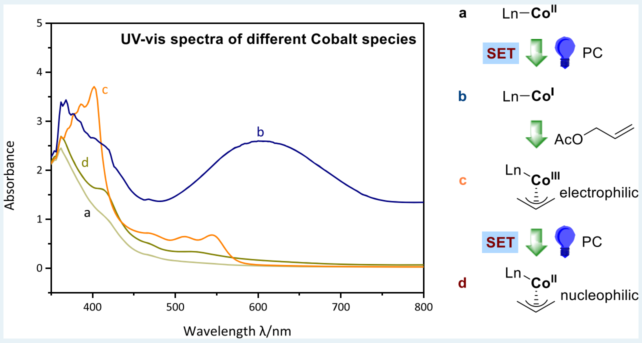
ABSTRACT: The concept of "umpolung" reactivity of π-allylmetal complexes has been developed as a powerful method for the allylation of aldehydes. This paper describes the photocatalytic umpolung strategy for the synthesis of nucleophilic allylcobalt complexes through a single-electron-transfer (SET) process. This strategy enables the metallaphotoredox allylation of carbonyls with allyl acetate using organic *N*,*N*-diisopropylethylamine as the terminal reductant bypassing the use of a stoichiometric amount of metals. Ultraviolet−visible spectroscopy was used to monitor the redox changes of cobalt in the reaction.



KEYWORDS: *π-allylcobalt complexes, photoredox catalysis, allylation, umpolung, alcohol*

Homoallylic alcohols and their derivatives are essential synthetic intermediates for the preparation of numerous natural products and medicine.[1,2] The concept of "umpolung" reactivity of π-allylmetal complexes has been developed as a powerful approach for carbonyl allylation with high regio- and diastereo-selectivity control (Scheme 1a).[3−5] Such "reverse reactivity" of π-allylmetal complexes can be controlled by the modification of their electronic environment through the use of additives and ligands. For example, π-allylpalladium complexes are known to be electrophilic and can react with a wide range of nucleophiles (Tsuji−Trost reaction), while nucleophilic π-allylpalladium complexes are also well documented to catalyze the umpolung allylation of carbonyls and imines.[6] However, an excess of metal reductants such as Et_2Zn and Et_3B is usually required for such a "reactivity switch" process.

Cobalt is an earth-abundant low-cost first-row transition metal and generally of low toxicity.[7] π-Allylcobalt complexes show similar "amphiphilic character" in organic reactions. Mita and Sato reported the nucleophilic addition of π-allylcobalt/Xantphos complexes to ketones and carbon dioxide using excess $AlMe_3$ as the reductant, in which the low-valent π-allylcobalt^{I} complexes generated through reductive elimination were proposed to be the key intermediates.[8,9] Co-catalyzed allylic alkylation and amination were reported by the groups of Kojima/Matsunaga and Li, respectively, in which the key electrophilic π-allylcobalt^{III} species was generated *in situ via* oxidative addition of allyl acetate to a low-valent Co^{I} complex.[10,11] However, the photocatalytic conversion of electrophilic π-allylcobalt to nucleophilic π-allylcobalt remains an understudied topic.[12−16]

Metallaphotoredox catalysis is a new and rapidly growing research field.[17−25] Recently, the combination of photoredox and cobalt catalysis has been developed as a distinct new option in the field of metallaphotoredox catalysis and has found numerous applications in synthetic chemistry.[26−44] Given that photoredox processes can directly modify the oxidation state of transition metals by single electron transfer (SET), we wonder whether the photoredox system can convert an electrophilic π-allylcobalt^{III} species to a nucleophilic π-allylcobalt^{II} species. If so, a novel dual photoredox and cobalt-catalyzed allylation of carbonyls based on a $2e^-$ (oxidative addition) and a $1e^-$ (SET) relay process is anticipated (Scheme 1b). In this paper, we report the first photocatalytic generation of nucleophilic π-allylcobalt complexes for carbonyl allylation through an umpolung strategy.

We selected 4-methoxybenzaldehyde **1a** and allyl acetate as the standard substrates to optimize the reaction conditions (Table 1). Following the rapid screening of different reaction conditions, we were able to identify the conditions of $CoBr_2$ (10 mol %), the photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (**Ir-1**), 4,4′-di-*tert*-butyl-2,2′-dipyridyl **L3** (10 mol %), *N*,*N*-diisopropylethylamine (DIPEA) (3 equiv), and allyl acetate (3 equiv) mixed in dimethylformamide (DMF) at room temperature. The obtained

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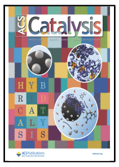

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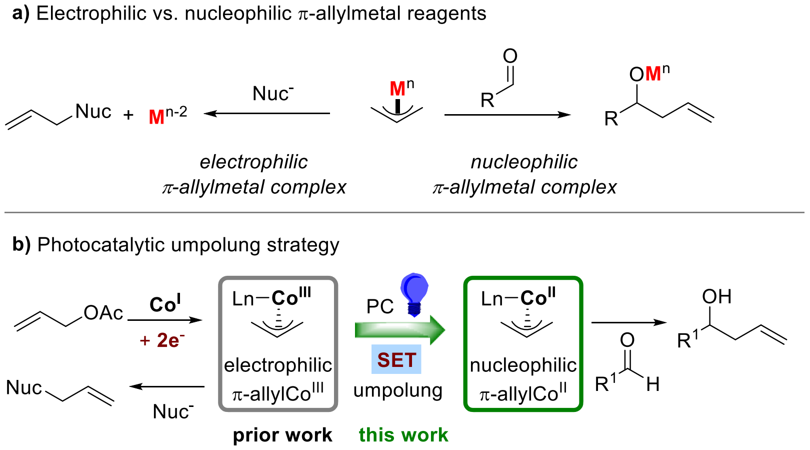
Scheme 1. (a) Concept of "Umpolung" Reactivity of π-Allylmetal Complexes and (b) Conversion of Electrophilic π-AllylCo^{III} to Nucleophilic π-AllylCo^{II} *via* SET



mixture was irradiated with a 450 nm LED lamp for 32 h and afforded the product **2a** in 58% yield (entry 1). Various solvents such as acetonitrile, tetrahydrofuran, and dichloroethane were tested, generally producing low yields in the 10−20% range. The use of Hantzsch ester as an organic electron donor instead of DIPEA resulted in no product (entry 2). Further screening of various photocatalysts, including 4CzIPN, [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (**Ir-2**), and Ru(bpy)$_3$(PF$_6$)$_2$ (**Ru-1**), revealed that they are less efficient for allylation (entries 3−5). Different ligands such as 4,7-diphenyl-1,1-phenanthroline **L1**, 1,10-phenanthroline **L2**, and 1,2-bis(diphenylphosphino)ethane **L4** (entries 6−8), were tested as replacements of **L3**. These ligands were less efficient for catalysis. Further testing of various cobalt salts showed that CoSO$_4$·H$_2$O gave the best results and increased the yield up to 80% (entries 9−13). Additive effects were tested but did not increase the yield (entries 14 and 15). Additionally, the reaction did not occur in the absence of either light, Co, DIPEA, or photocatalyst (entries 16−19). The reaction is sensitive to low light intensity, H$_2$O, and high oxygen concentration, as shown by the condition-based sensitivity testing (Supporting Information **S7**).[45]

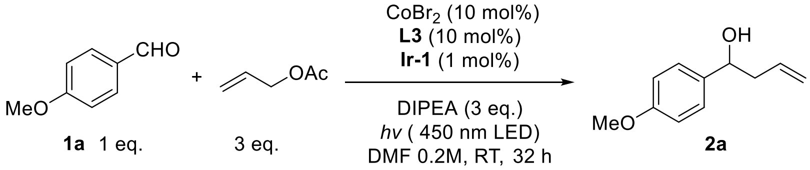
After optimizing the reaction conditions, we evaluated the scope of aldehydes for the allylation reactions (Table 2). It was clear that the reactions worked smoothly with lots of aromatic and aliphatic aldehydes producing various trans-alcohols in generally decent yields. The substituent effect of the aromatic ring has little effect on the allylation reaction. Both the electron-rich groups and electron-withdrawing groups, including methoxy **2a** and fluorine **2l**, gave homoallylic alcohols in reasonable yields. The reaction of sterically hindered mesitaldehyde **2e** was also successful. Heteroatoms did not impede the catalytic cycle, including oxygens **2g** and **2u** and the protected amine **2x**. Besides, various heteroarenes, which are widely used as core structures in medicinal synthesis, were also suitable substrates for this photoredox and cobalt catalysis, including furans **2q** and **2r** and thiophene **2p**. Due to the extremely mild photocatalytic conditions, reactions showed excellent compatibility with many synthetically important and valuable functional groups that include the free alcohol **2j**, alkene **2w**, ether **2h**, bromobenzene **2k**, and chlorobenzene **2o**. Allylation of the acid-sensitive citronellal **2w** substrate was also successful without forming a cyclization byproduct. The synthetic potential of this dual photoredox and cobalt catalysis was demonstrated by the late-stage functionalization of complicated structure molecules, such as indomethacin, probenecid, and lithocholic acid derivatives, and the desired products **3a−3c** were obtained in a decent yield.

The regio- and diastereo-selectivity of the new catalysis system was further explored using cinnamyl alcohol as the coupling substrate. It was found that *tert*-butyl cinnamyl carbonate **4** is more reactive than cinnamyl acetate for the allylation of various aldehydes, as shown in Table 3. Only branched products **5a−5l** were obtained in favor of trans-diastereoselectivity with moderate to good yields. The highest diastereoselectivity (d.r. > 20:1) was achieved with cyclohexanecarboxaldehyde (**5h**), albeit in somewhat low yield. The trans-diastereoselectivity can be elucidated based on the Zimmerman−Traxler transition state, where the oxygen atom of the carbonyls coordinates with the cobalt. The aryl group of the π-allylcobalt complexes and the R group of the aldehyde preferentially adopt an equatorial orientation, resulting in the generation of an anti-isomer of the corresponding homoallylic alcohols.[14]

The scalability of the reaction was determined by the synthesis of **5a** in a gram-scale under standard conditions. Gratifyingly, product **5a** was obtained in decent 83% isolated yield. The use of earth-abundant cobalt, wide compatibility with various sensitive functional groups, and easy to operate conditions of this reaction are appealing features for laboratory and industrial applications.

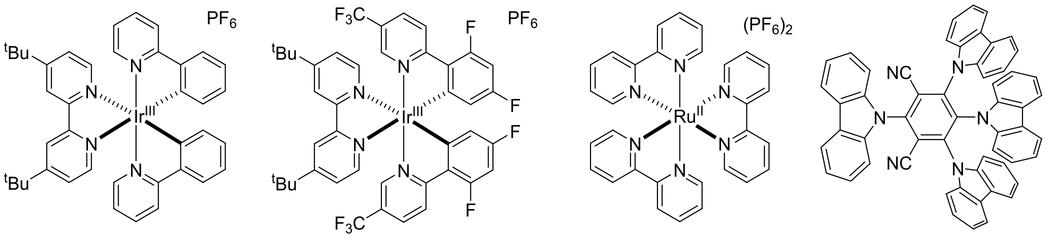
Stern−Volmer luminescence quenching studies were conducted (Supporting Information **S2**) and showed that DIPEA can readily quench the excited photocatalyst **Ir-1** at the rate of 3.42×10^8 L M^{-1} s^{-1}. Then, a series of experiments were performed to probe the different π-allylcobalt species in the catalytic cycle. First, CoBr$_2$, **L3**, and **Ir-1** were added to a solution of DIPEA in DMF (Figure 1C(a)). The resulting mixture was exposed to 450 nm LED irradiation. In the first SET process, the color of the reaction changed from green to blue (Figure 1C(b)). The ultraviolet−visible (UV−vis) spectroscopic analysis of the reaction was also performed. A broad absorption band at 550−700 nm gradually appeared within 30 min, indicating the formation of Co^I **7** species, which is consistent with previous reports (Figure 1A(b)).[27,46,47] Then, the allyl acetate was added to the resulting reaction system in the dark, and the color changed to brown (Figure 1C(c)). At the same time, UV−vis spectroscopic analysis of the reaction revealed the rapid disappearance of absorption of Co^I **7**, and a

Table 1. Optimization of the Reaction Conditions[a]

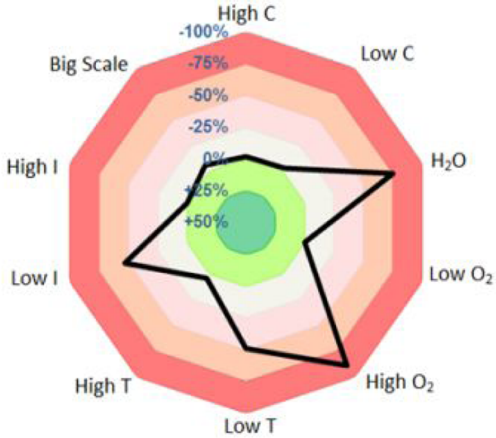


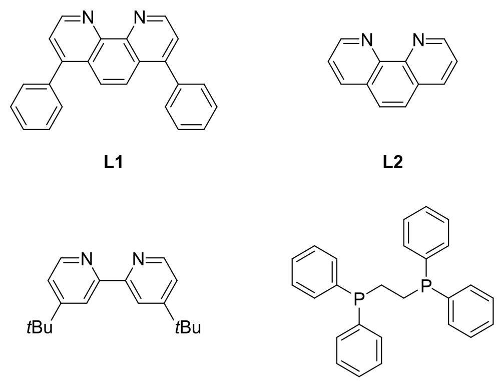
entry	variation from standard conditions	yield (%)
1	none	58
2	HE instead of DIPEA	0
3	**Ir-2** instead of **Ir-1**	trace
4	**Ru-1** instead of **Ir-1**	trace
5	4CzIPN instead of **Ir-1**	trace
6	**L1** instead of **L3**	34
7	**L2** instead of **L3**	37
8	**L4** instead of **L3**	25
9	$Co(BF_4)_2{\cdot}6H_2O$ instead of $CoBr_2$	61
10	$Co(OAc_2)_2{\cdot}4H_2O$ instead of $CoBr_2$	75
11	$Co(NO_3)_2{\cdot}4H_2O$ instead of $CoBr_2$	<5
12	$Co(acac)_3$ instead of $CoBr_2$	17
13	$CoSO_4{\cdot}H_2O$ instead of $CoBr_2$	80
14	$CoSO_4{\cdot}H_2O$, CF_3COOH	42
15	$CoSO_4{\cdot}H_2O$, K_2CO_3	40
16	no Co catalyst	0
17	no DIPEA	0
18	no photocatalyst	0
19	no light	0

[a]Reaction conditions: **1a** (0.5 mmol scale). Yields were determined by ^1H NMR spectroscopy *vs* an internal standard.



$Ir(ppy)_2(dtbbpy)PF_6$ **Ir-1** $Ir[dF(CF_3)ppy_2](dtbbpy)PF_6$ **Ir-2** $Ru(bpy)_3(PF_6)_2$ **Ru-1** 4CzIPN





L1 **L2** **L3** **L4**

new strong absorption band appeared at 380−550 nm, suggesting the formation of π-allylcobalt^{III} **8** *via* the oxidative addition of allyl acetate to a low-valent Co^{I} complex (Figure 1B(c)). The resulting **8** is known to react with various nucleophiles but not with aldehydes.[10,11] It was reported that π-allylcobalt^{III} can be further reduced to π-allylcobalt^{II} by a photocatalyst under irradiation.[41] In fact, when the reaction was further exposed to irradiation, the absorption band of the proposed Co^{III} **8** disappeared and a new absorption band appeared at 360−450 nm, indicating the generation of π-allylcobalt^{II} **9** (Figure 1B(d)). Thus, the allylation indeed occurred with irradiation and **2a** was smoothly obtained (Figure

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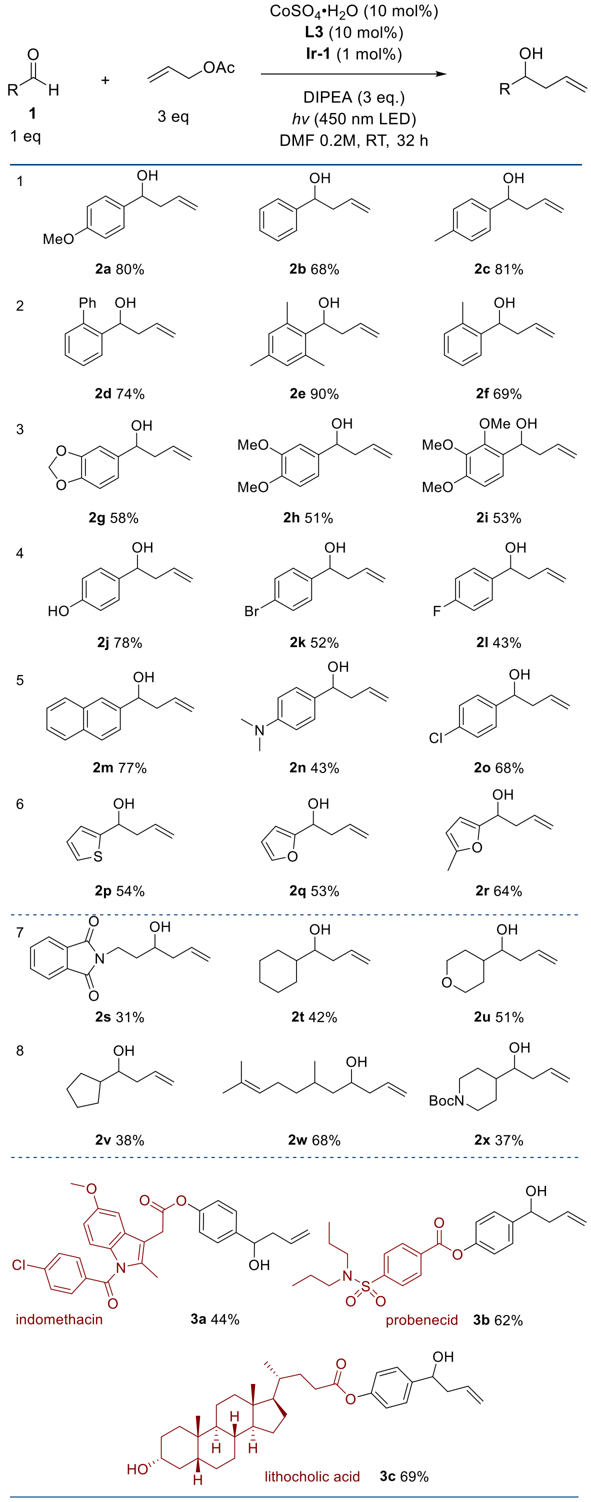
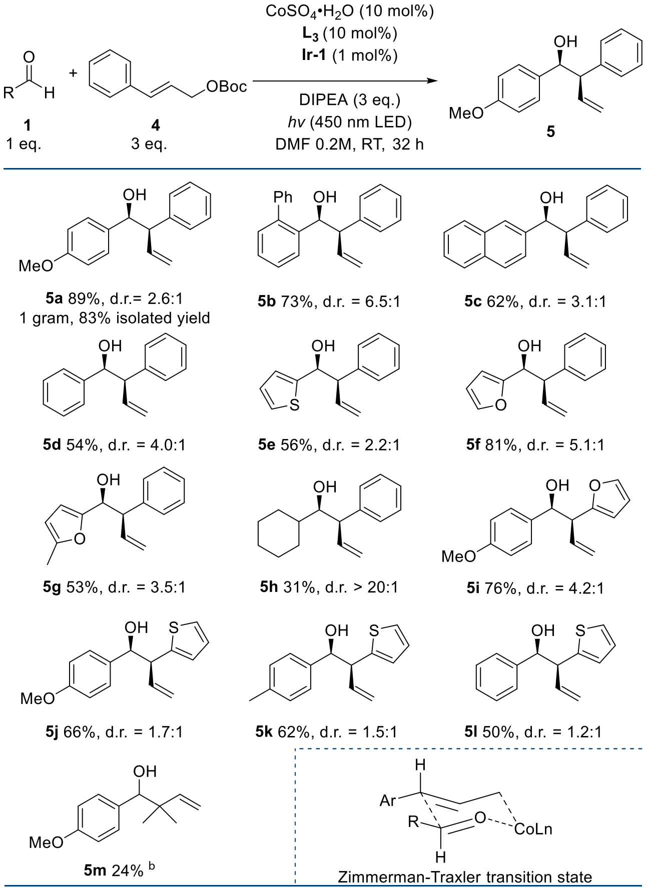
Table 2. Scope of Aldehydes in Allylation Reactions[a]



[a]Reaction conditions: **1a** (0.5 mmol scale). Yields were determined by ^{1}H NMR spectroscopy *vs* an internal standard.

1C(d)). This finding indicated that the nucleophilic π-allylcobalt^{II} **9** (dark orange) was formed *via* SET and most likely is the key active intermediate toward the aldehydes.[48,49] In addition, the quantum yield was determined to be 0.012, suggesting that the radical-chain mechanism is not likely (Supporting Information **S4**).

Table 3. Scope of Substituted Allyl Carbonates in Allylation Reactions[a]



[a]Reaction conditions: **1a** (0.5 mmol scale). Yields were determined by ^{1}H NMR spectroscopy *vs* an internal standard. Diastereomeric ratios were determined by ^{1}H NMR spectroscopy. [b]*tert*-Butyl prenol carbonate was used.

According to previous reports in the literature and the results of this study, we tentatively propose a catalytic cycle, as shown in Figure 2. Initial excitation of the **Ir-1** photocatalyst produces the photoexcited ***Ir-1**^{III} species. The ***Ir-1**^{III} catalyst ($E_{1/2}^{red}$ [*Ir^{III}/Ir^{II}] = +0.66 V *vs* SCE in CH_3CN) is reduced by DIPEA (E^{ox} (DIPEA) = +0.65 V) via SET to produce a reducing **Ir-1**^{II} species and [DIPEA]$^{•+}$. Reduction of the ligand-coordinated Ln−Co^{II} **6** by **Ir-1**^{II} ($E_{1/2}^{red}$[Ir^{III}/Ir^{II}] = −1.51 V *vs* SCE in CH_3CN) affords Ln−Co^{I} **7** species and **Ir-1**^{III}. Then, Ln−Co^{I} **7** reacts with the allylic acetate by oxidative addition and generates the electrophilic π-allylcobalt^{III} **8** species that is readily reduced by another **Ir-1**^{II} photocatalyst to the key nucleophilic π-allylcobalt^{II} **9** species. The addition of **9** to aldehydes forms a new C−C bond in the alkoxycobalt product. Hydrolysis of the oxygen−Co bond releases Ln−Co^{II} **6** and the alcohol product. Finally, **Ir-1** can regenerate Ln−Co^{I} **7** for the next catalytic cycle.

CONCLUSIONS

In summary, this work reports a novel photocatalytic allylation of carbonyls through dual cobalt and photoredox catalysis. This eco-friendly photoredox reaction enables the allylation of numerous aldehydes with easily available allyl acetate using organic DIPEA as the terminal reductant and bypassing the use of the stoichiometric amount of metals. The success of the

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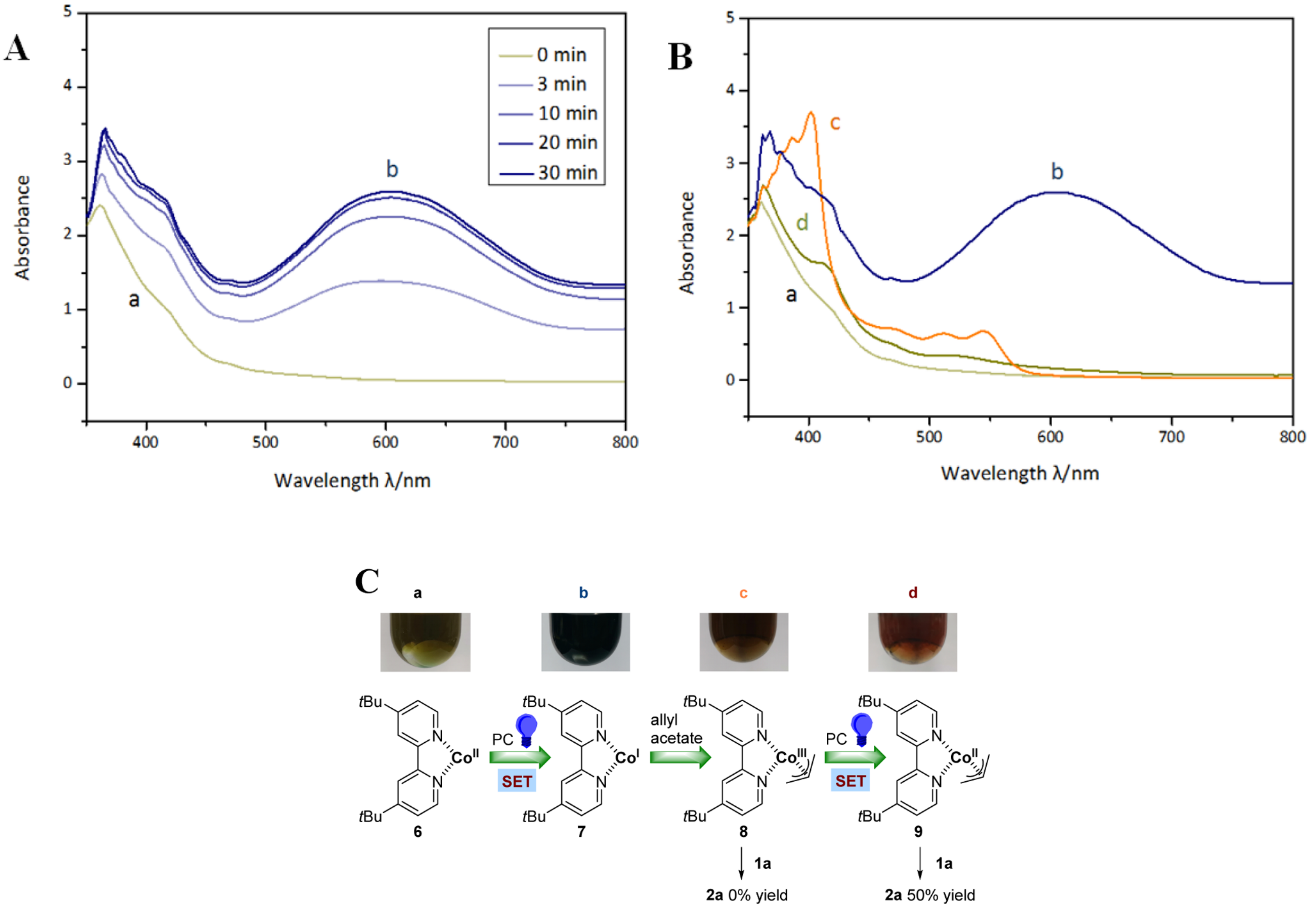

Figure 1. UV−vis spectroscopy studies of different π-allylcobalt species in the reaction (for details, please see Supporting Information S8).

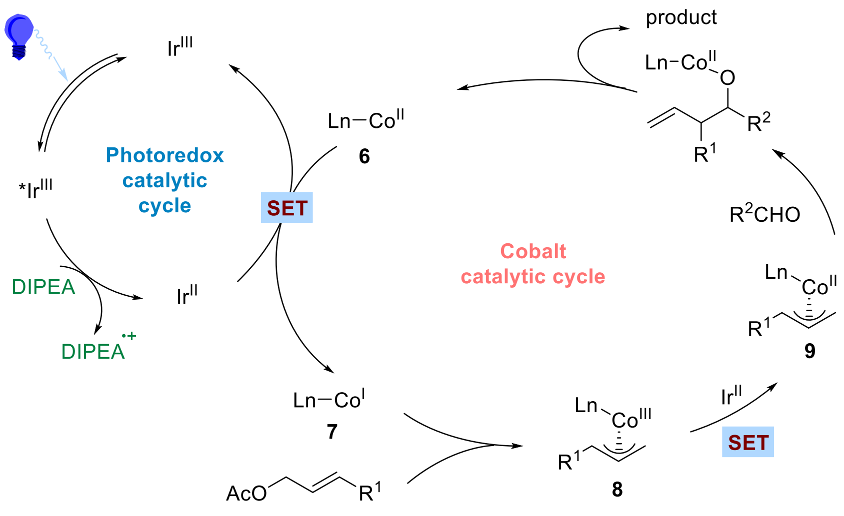

Figure 2. Proposed catalytic cycle.

reaction relies on the generation of nucleophilic allylcobalt^{II} complexes based on the photocatalytic umpolung strategy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05330.

Experimental details, characterization data of compounds, and NMR spectra (PDF)

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Author Contributions

C.S. and F.L. contributed equally. The manuscript was written through contributions of all authors.

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Notes

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■ REFERENCES

(1) Denmark, S. E.; Fu, J. Catalytic Enantioselective Addition of Allylic Organometallic Reagents to Aldehydes and Ketones. *Chem. Rev.* **2003**, *103*, 2763−2794.

(2) Knochel, P.; Dohle, W.; Gommermann, N.; Kneisel, F. F.; Kopp, F.; Korn, T.; Sapountzis, I.; Vu, V. A. Highly Functionalized Organomagnesium Reagents Prepared through Halogen-Metal Exchange. *Angew. Chem., Int. Ed.* **2003**, *42*, 4302−4320.

(3) Spielmann, K.; Niel, G.; de Figueiredo, R. M.; Campagne, J.-M. Catalytic Nucleophilic "Umpoled" π-allyl Reagents. *Chem. Soc. Rev.* **2018**, *47*, 1159−1173.

(4) Huang, H.-M.; Bellotti, P.; Glorius, F. Transition Metal-catalysed Allylic Functionalization Reactions Involving Radicals. *Chem. Soc. Rev.* **2020**, *49*, 6186−6197.

(5) Pitzer, L.; Schwarz, J. L.; Glorius, F. Reductive Radical-polar Crossover: Traditional Electrophiles in Modern Radical Reactions. *Chem. Sci.* **2019**, *10*, 8285−8291.

(6) Zanoni, G.; Pontiroli, A.; Marchetti, A.; Vidari, G. Stereoselective Carbonyl Allylation by Umpolung of Allylpalladium(II) Complexes. *Eur. J. Org. Chem.* **2007**, *2007*, 3599−3611.

(7) (a) Giedyk, M.; Goliszewska, K.; Gryko, D. Vitamin B12 Catalysed Reactions. *Chem. Soc. Rev.* **2015**, *44*, 3391−3404. (b) Frei, A.; King, A. P.; Lowe, G. J.; Cain, A. K.; Short, F. L.; Dinh, H.; Elliott, A. G.; Zuegg, J.; Wilson, J. J.; Blaskovich, M. A. T. Nontoxic Cobalt(III) Schiff Base Complexes with Broad-Spectrum Antifungal Activity. *Chem.—Eur. J.* **2020**, *27*, 2021.

(8) Michigami, K.; Mita, T.; Sato, Y. Cobalt-Catalyzed Allylic C(sp^3)-H Carboxylation with CO$_2$. *J. Am. Chem. Soc.* **2017**, *139*, 6094−6097.

(9) Mita, T.; Hanagata, S.; Michigami, K.; Sato, Y. Co-Catalyzed Direct Addition of Allylic C(sp^3)-H Bonds to Ketones. *Org. Lett.* **2017**, *19*, 5876−5879.

(10) Ghorai, S.; Chirke, S. S.; Xu, W.-B.; Chen, J.-F.; Li, C. Cobalt-Catalyzed Regio- and Enantioselective Allylic Amination. *J. Am. Chem. Soc.* **2019**, *141*, 11430−11434.

(11) Takizawa, K.; Sekino, T.; Sato, S.; Yoshino, T.; Kojima, M.; Matsunaga, S. Cobalt-Catalyzed Allylic Alkylation Enabled by Organophotoredox Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 9199−9203.

(12) Huang, H.-M.; Bellotti, P.; Daniliuc, C. G.; Glorius, F. Radical Carbonyl Propargylation by Dual Catalysis. *Angew. Chem., Int. Ed.* **2021**, *60*, 2464−2471.

(13) Schwarz, J. L.; Huang, H.-M.; Paulisch, T. O.; Glorius, F. Dialkylation of 1,3-Dienes by Dual Photoredox and Chromium Catalysis. *ACS Catal.* **2019**, *10*, 1621−1627.

(14) Schwarz, J. L.; Schäfers, F.; Tlahuext-Aca, A.; Lückemeier, L.; Glorius, F. Diastereoselective Allylation of Aldehydes by Dual Photoredox and Chromium Catalysis. *J. Am. Chem. Soc.* **2018**, *140*, 12705−12709.

(15) Li, F.-S.; Chen, Y.-Q.; Lin, S.-J.; Shi, C.-Z.; Li, X.-Y.; Sun, Y.-C.; Guo, Z.-W.; Shi, L. Visible-light-mediated Barbier Allylation of Aldehydes and Ketones via Dual Titanium and Photoredox Catalysis. *Org. Chem. Front.* **2020**, *7*, 3434−3438.

(16) Li, F.-S.; Lin, S.-J.; Chen, Y.-Q.; Shi, C.-Z.; Yan, H.-P.; Li, C.-C.; Wu, C.; Lin, L.-Q.; Duan, C.-Y.; Shi, L. Photocatalytic Generation of π-allyltitanium Complexes via Radical Intermediates. *Angew. Chem., Int. Ed.* **2021**, *60*, 1561−1566.

(17) Twilton, J.; Le, C. C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*, 52.

(18) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Single-Electron Transmetalation via Photoredox/Nickel Dual Catalysis: Unlocking a New Paradigm for sp^3-sp^2 Cross-Coupling. *Acc. Chem. Res.* **2016**, *49*, 1429−1439.

(19) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. *Chem. Rev.* **2016**, *116*, 10035−10074.

(20) Gentry, E. C.; Knowles, R. R. Synthetic Applications of Proton-Coupled Electron Transfer. *Acc. Chem. Res.* **2016**, *49*, 1546−1556.

(21) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075−10166.

(22) Staveness, D.; Bosque, I.; Stephenson, C. R. J. Free Radical Chemistry Enabled by Visible Light-Induced Electron Transfer. *Acc. Chem. Res.* **2016**, *49*, 2295−2306.

(23) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. Visible Light Mediated Photoredox Catalytic Arylation Reactions. *Acc. Chem. Res.* **2016**, *49*, 1566−1577.

(24) Lin, S.-J.; Chen, Y.-Q.; Li, F.-S.; Shi, C.-Z.; Shi, L. Visible-light-driven Spirocyclization of Epoxides via Dual Titanocene and Photoredox Catalysis. *Chem. Sci.* **2020**, *11*, 839−844.

(25) Chen, Y.-Q.; Lin, S.-J.; Li, F.-S.; Zhang, X.-H.; Lin, L.-Q.; Shi, L. $Cp_2Ti^{III}Cl$ Catalysis in a New Light. *ChemPhotoChem* **2020**, *4*, 659−663.

(26) Kojima, M.; Matsunaga, S. The Merger of Photoredox and Cobalt Catalysis. *Trends Chem.* **2020**, *2*, 410−426.

(27) Cao, H.; Kuang, Y.; Shi, X.; Wong, K. L.; Tan, B. B.; Kwan, J. M. C.; Liu, X.; Wu, J. Photoinduced site-selective alkenylation of alkanes and aldehydes with aryl alkenes. *Nat. Commun.* **2020**, *11*, 1956.

(28) Yu, W.-L.; Luo, Y.-C.; Yan, L.; Liu, D.; Wang, Z.-Y.; Xu, P.-F. Dehydrogenative Silylation of Alkenes for the Synthesis of Substituted Allylsilanes by Photoredox, Hydrogen-Atom Transfer, and Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 10941−10945.

(29) Meng, Q.-Y.; Schirmer, T. E.; Katou, K.; König, B. Controllable Isomerization of Alkenes by Dual Visible-Light-Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 5723−5728.

(30) Grenier-Petel, J.-C.; Collins, S. K. Photochemical Cobalt-Catalyzed Hydroalkynylation To Form 1,3-Enynes. *ACS Catal.* **2019**, *9*, 3213−3218.

(31) Claros, M.; Ungeheuer, F.; Franco, F.; Martin-Diaconescu, V.; Casitas, A.; Lloret-Fillol, J. Reductive Cyclization of Unactivated Alkyl Chlorides with Tethered Alkenes under Visible-Light Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 4869−4874.

(32) Cao, H.; Jiang, H.; Feng, H.; Kwan, J. M. C.; Liu, X.; Wu, J. Photo-induced Decarboxylative Heck-Type Coupling of Unactivated Aliphatic Acids and Terminal Alkenes in the Absence of Sacrificial Hydrogen Acceptors. *J. Am. Chem. Soc.* **2018**, *140*, 16360−16367.

(33) Hu, X.; Zhang, G.; Bu, F.; Lei, A. Selective Oxidative [4+2] Imine/Alkene Annulation with H_2 Liberation Induced by Photo-Oxidation. *Angew. Chem., Int. Ed.* **2018**, *57*, 1286−1290.

(34) Hou, J.; Ee, A.; Feng, W.; Xu, J.-H.; Zhao, Y.; Wu, J. Visible-Light-Driven Alkyne Hydro-/Carbocarboxylation Using CO_2 via Iridium/Cobalt Dual Catalysis for Divergent Heterocycle Synthesis. *J. Am. Chem. Soc.* **2018**, *140*, 5257−5263.

(35) Hu, X.; Zhang, G.; Bu, F.; Luo, X.; Yi, K.; Zhang, H.; Lei, A. Photoinduced Oxidative Activation of Electron-rich Arenes: Alkenylation with H_2 Evolution Under External Oxidant-free Conditions. *Chem. Sci.* **2018**, *9*, 1521−1526.

(36) Ravetz, B. D.; Ruhl, K. E.; Rovis, T. External Regulation of Cobalt-Catalyzed Cycloaddition Polymerization with Visible Light. *ACS Catal.* **2018**, *8*, 5323−5327.

(37) Kalsi, D.; Dutta, S.; Barsu, N.; Rueping, M.; Sundararaju, B. Room-Temperature C-H Bond Functionalization by Merging Cobalt and Photoredox Catalysis. *ACS Catal.* **2018**, *8*, 8115−8120.

(38) Call, A.; Casadevall, C.; Acuña-Parés, F.; Casitas, A.; Lloret-Fillol, J. Dual cobalt-copper Light-driven Catalytic Reduction of Aldehydes and Aromatic Ketones in Aqueous Media. *Chem. Sci.* **2017**, *8*, 4739−4749.

(39) Abrams, D. J.; West, J. G.; Sorensen, E. J. Toward a Mild Dehydroformylation Using Base-metal Catalysis. *Chem. Sci.* **2017**, *8*, 1954−1959.

(40) Yang, Q.; Zhang, L.; Ye, C.; Luo, S.; Wu, L.-Z.; Tung, C.-H. Visible-Light-Promoted Asymmetric Cross-Dehydrogenative Coupling of Tertiary Amines to Ketones by Synergistic Multiple Catalysis. *Angew. Chem., Int. Ed.* **2017**, *56*, 3694−3698.

(41) Thullen, S. M.; Rovis, T. A Mild Hydroaminoalkylation of Conjugated Dienes Using a Unified Cobalt and Photoredox Catalytic System. *J. Am. Chem. Soc.* **2017**, *139*, 15504−15508.

(42) Zheng, Y.-W.; Chen, B.; Ye, P.; Feng, K.; Wang, W.; Meng, Q.-Y.; Wu, L.-Z.; Tung, C.-H. Photocatalytic Hydrogen-Evolution Cross-Couplings: Benzene C-H Amination and Hydroxylation. *J. Am. Chem. Soc.* **2016**, *138*, 10080−10083.

(43) Ruhl, K. E.; Rovis, T. Visible Light-Gated Cobalt Catalysis for a Spatially and Temporally Resolved [2+2+2] Cycloaddition. *J. Am. Chem. Soc.* **2016**, *138*, 15527−15530.

(44) West, J. G.; Huang, D.; Sorensen, E. J. Acceptorless Dehydrogenation of Small Molecules Through Cooperative Base Metal Catalysis. *Nat. Commun.* **2015**, *6*, 10093.

(45) Pitzer, L.; Schäfers, F.; Glorius, F. Rapid Assessment of the Reaction-Condition-Based Sensitivity of Chemical Transformations. *Angew. Chem., Int. Ed.* **2019**, *58*, 8572−8576.

(46) Du, P.; Knowles, K.; Eisenberg, R. A Homogeneous System for the Photogeneration of Hydrogen from Water Based on a Platinum(II) Terpyridyl Acetylide Chromophore and a Molecular Cobalt Catalyst. *J. Am. Chem. Soc.* **2008**, *130*, 12576−12577.

(47) Lazarides, T.; McCormick, T.; Du, P.; Luo, G.; Lindley, B.; Eisenberg, R. Making Hydrogen from Water Using a Homogeneous System Without Noble Metals. *J. Am. Chem. Soc.* **2009**, *131*, 9192−9194.

(48) Buriez, O.; Labbé, E.; Périchon, J. Electroanalytical Investigation of the Cobalt-catalyzed Electrochemical Dimerization of Allylic Acetates. Role Played by Iron(II) Ions. *J. Electroanal. Chem.* **2003**, *543*, 143−151.

(49) (a) Gualandi, A.; Rodeghiero, G.; Perciaccante, R.; Jansen, T. P.; Moreno-Cabrerizo, C.; Foucher, C.; Marchini, M.; Ceroni, P.; Cozzi, P. G. Catalytic Photoredox Allylation of Aldehydes Promoted by a Cobalt Complex. *Adv. Synth. Catal.* **2021**, *363*, 1105−1111. (b) Gomes, P.; Gosmini, C.; Périchon, J. Allylation of Carbonyl Compounds by Allylic Acetates Using a Cobalt Halide as Catalyst. *Synthesis* **2003**, 1909−1915.