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Photoredox chromium and cobalt dual catalysis for carbonyl allylation with butadiene *via* allyl radical intermediates†

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Here, we report an allylation reaction of aldehydes with butadiene using cobalt and chromium catalysts *via* a metal-hydride hydrogen atom transfer (MHAT) pathway under visible light irradiation. A variety of homoallylic alcohols can be obtained with high yield and excellent diastereoselectivity. The cheap and readily available raw materials and catalysts make the reaction system have a great potential application value.

Homoallylic alcohol is a very important structural fragment that widely exists in various natural products, drug molecules, and intermediates. Therefore, its efficient synthesis has received widespread attention.[1,2] One of the most direct methods for synthesizing such compounds is the allylation of carbonyls;[3,4] however, using traditional methods usually requires the preparation of allyl metal reagents, which are unstable and require stoichiometric metallic reductants (Fig. 1a). Therefore, the use of inexpensive and readily available raw materials to develop *in situ* generated allyl metal reagents has become a focus of current research.[5]

Conjugated dienes, especially 1,3-butadiene and 1,3-cyclohexadiene, have a huge annual output and are important chemical raw materials in industry.[6] Transforming these industrial raw materials into high value-added chemical products is of great significance. Surprisingly, the allylation of butadiene with carbonyl groups has undergone rapid development in recent years.[7–9] For example, Krische's group achieved allylation of butadiene with alcohols or aldehydes using ruthenium and chiral phosphoric acid.[10] Buchwald and his team used Cu–H to catalyze the reduction coupling reaction of ketones with butadiene, exhibiting excellent regional and enantioselective control.[11] Recently, Xia's group also achieved this reaction through Ni and visible light dual catalysis.[12] These methods are based on the 2e$^-$ transfer process (Fig. 1b).

Metal hydride hydrogen atom transfer (MHAT), as an important method for functionalization of olefins, has been greatly developed in the past few decades.[13,14] Cobalt, as a cheap transition metal, has received widespread attention in the past decade, especially in the field of photocatalysis.[15–20] In traditional methods, achieving the cycle of Co–H in the reaction usually requires an equivalent amount of silane reagent and TBHP, which is not in line with the current concept of green chemistry.[21] Recently, the use of silane and

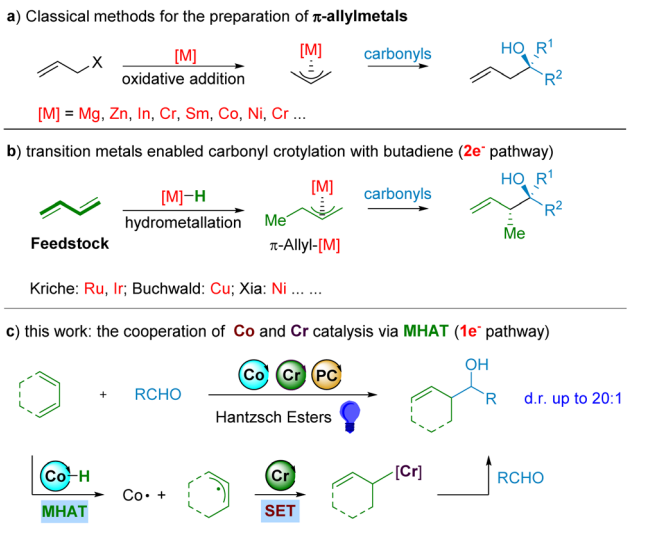

Fig. 1 (a) Previous methods for the preparation of *p*-allyl metals; (b) transition metals enabled carbonyl crotylation with butadiene; (c) novel diene functionalization by photoredox Co-MHAT and Cr dual catalysis.

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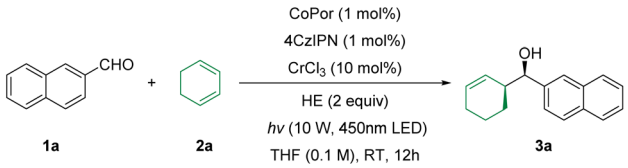
TBHP has been avoided by combining photoredox with metal catalysis.[22–27] These studies have greatly promoted the development of MHAT reactions. However, to our knowledge, the selective functionalization of butadiene through MHAT has rarely been reported.

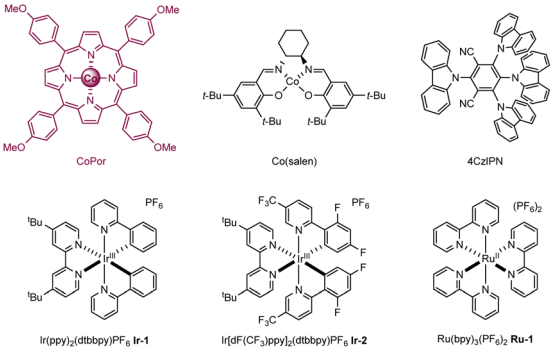
As a cheap and low toxic transition metal, chromium has been extensively studied in the past half century, especially in the Nozaki–Hiyama allylation.[28–30] With the emergence of photoredox catalysis, free radicals play a dominant role in this reaction.[31–34] However, still there are few studies on the direct allylation of aldehydes with conjugated dienes catalyzed by chromium. This is because the direct conversion of conjugated dienes to allyl chromium species usually requires the participation of Cr–H species, but the formation conditions of Cr–H species are relatively harsh.[35] In 1994, Takai reported a case of coupling of conjugated dienes and aldehydes catalyzed by Co/Cr synergistic catalysis.[36] The excessive use of chromium and the unsatisfactory diastereoselectivity of the product severely limited its application. Therefore, we envisioned whether this reaction can be carried out by combining cobalt, chromium and photoredox to reduce catalyst usage while improving product selectivity *via* a MHAT pathway (Fig. 1c).

Based on the above assumption, we attempted the reaction using commercially available catalysts and reagents (4CzIPN, HE, CoPor, $CrCl_3$, 2-naphthaldehyde, 1,3-cyclohexadiene). After screening a series of conditions, homoallylic alcohol was obtained with a yield of 89% and outstanding diastereoselectivity (dr > 20 : 1) under the optimal reaction conditions (Table 1, entry 1). In the screening of various cobalt catalysts, it was found that only CoPor can efficiently convert 1,3-cyclohexadiene into allyl radicals (entries 2–4), and different solvents led to significant differences in yield. For example, in DCM and toluene, the yield is less than 10%, while in DMF, the yield is only 33% (entries 5–9). Reducing the amount of CoPor to 0.1 mol% did not significantly bring down the yield, indicating the high efficiency of CoPor (entries 10 and 11). Other commonly used metal photosensitizers can also make the reaction proceed smoothly. Although **Ir-1** and 4CzIPN have comparable yields, from the perspective of green chemistry and economy, we chose to use 4CzIPN in this reaction. In the absence of CoPor, $CrCl_3$, 4CzIPN, HE, or visible light, the reaction is not able to proceed (entries 15–19).

Table 1 Reaction optimization[a,b,c]



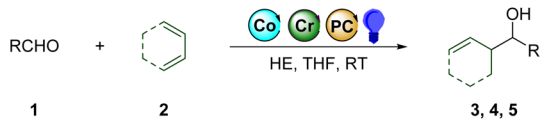
Entry	Variation from standard conditions	Yield (%)
1	None	89 (85)
2	Vitamin B12 instead of CoPor	0
3	$Co(dmgh)_2PyCl$(II) instead of CoPor	0
4	Co(salen) instead of CoPor	0
5	DCM instead of THF	<5
6	MeCN instead of THF	74
7	DMF instead of THF	33
8	PhMe instead of THF	7
9	EtOH instead of THF	75
10	CoPor (0.1 mol%) used	88
11	CoPor (0.01 mol%) used	30
12	**Ru-1** instead of 4CzIPN	72
13	**Ir-1** instead of 4CzIPN	85
14	**Ir-2** instead of 4CzIPN	79
15	No *hv*	0
16	No CoPor	0
17	No $CrCl_3$	0
18	No 4CzIPN	0
19	No HE	0



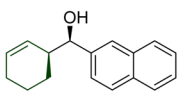
[a] Reactions were performed on a 0.2 mmol scale of **1a**, **2a** (2.0 equiv.), 4CzIPN (1 mol%), CoPor (1 mol%), $CrCl_3$ (10 mol%), HE (2.0 equiv.), THF (c = 0.1 M), 10 W blue LEDs, RT, 12 h. [b] Yields were determined by ^{1}H NMR spectroscopy *versus* dimethyl terephthalate as an internal standard. [c] Diastereomeric ratios were determined by ^{1}H NMR spectroscopy of crude products.

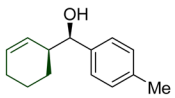
After optimal reaction conditions were obtained, various aldehyde substrates were used to test the compatibility of the system (Table 2). First, for aromatic aldehydes, electron-donating substituents can afford the target products in excellent yield and diastereoselectivity (**3b**, **3c**), while electron-withdrawing substituents can maintain good yield with a lower diastereoselectivity (**3d**). Halogens also do not affect the reaction (**3e–3g**). The presence of S atoms, which often lead to catalyst deactivation, can still lead to homoallylic alcohol products with outstanding yield and diastereoselectivity in this reaction (**3h**). The substrates with aromatic heterocyclic rings can also react well giving moderate yields and excellent selectivity (**3i**, **3j**). Aliphatic aldehydes, both primary and secondary, can still complete the reaction perfectly and maintain diastereoselectivity (**3k–3n**). 1,3-Butadiene, an industrial raw material for large-scale production, was also suitable for this reaction system. For various aliphatic aldehydes, homoallylic alcohols can be obtained in good yields as well as maintaining perfect diastereoselectivity (**4a–4j**). The substituents on aromatic aldehydes have a significant impact on product yield and diastereoselectivity. Generally, halogen substituted aromatic aldehydes have satisfactory yields and diastereoselectivity (**4m**, **4n**, **4p**), while for electron-donating substituents, diastereoselectivity was reduced slightly (**4l**). Electron-poor groups showed splendid yield and without reduction in diastereoselectivity (**4o**). Aromatic heterocyclic substrates can also provide products with moderate yield and diastereoselectivity (**4r–4u**). For isoprene and 2,3-dimethyl butadiene, homoallyl

Table 2 Scope of allylation reactions[a,b]

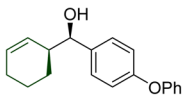


1,3-cyclohexadiene

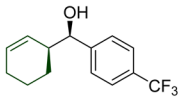

3a 85% (d.r.>20:1)



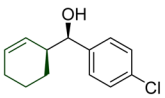
3b 78% (d.r.>20:1)



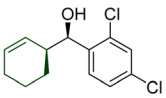
3c 83% (d.r.>20:1)



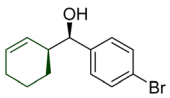
3d 62% (d.r.=7:1)



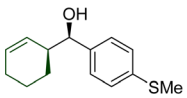
3e 79% (d.r.>20:1)



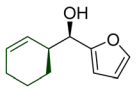
3f 76% (d.r.>20:1)



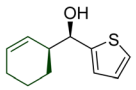
3g 95% (d.r.>20:1)



3h 90% (d.r.>20:1)



3i 60% (d.r.=18:1)



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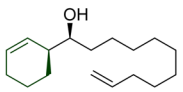
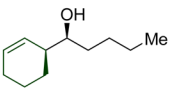
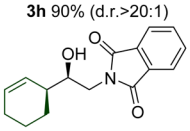


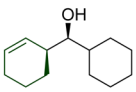
3k 82% (d.r.>20:1)



3l 85% (d.r.>20:1)

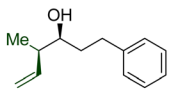


3m 83% (d.r.>20:1)

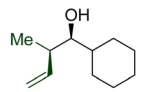


3n 79% (d.r.>20:1)

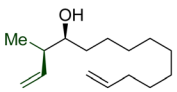
1,3-butadiene



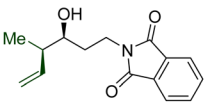
4a 77% (d.r.>20:1)



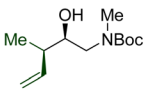
4b 78% (d.r.>20:1)



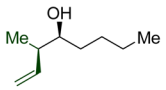
4c 71% (d.r.>20:1)



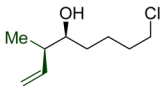
4d 56% (d.r.>20:1)



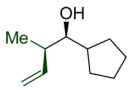
4e 76% (d.r.>20:1)



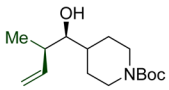
4f 74% (d.r.>20:1)



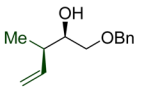
4g 82% (d.r.>20:1)



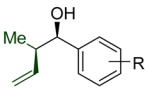
4h 45% (d.r.>20:1)



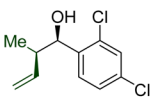
4i 85% (d.r.>20:1)



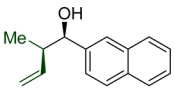
4j 80% (d.r.>20:1)



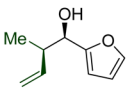
4k (X=H), 45% (d.r.=14:1)
4l (X=p-CH_3), 78% (d.r.=10:1)
4m (X=p-Cl), 74% (d.r.=18:1)
4n (X=p-Br), 62% (d.r.=18:1)
4o (X=p-CF_3), 83% (d.r.=19:1)



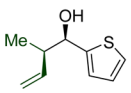
4p 70% (d.r.=15:1)



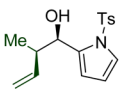
4q 90% (d.r.=12:1)



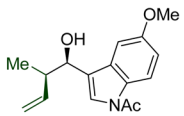
4r 55% (d.r.=11:1)



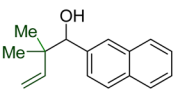
4s 50% (d.r.=9:1)



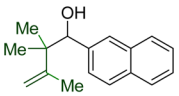
4t 70% (d.r.=3:1)



4u 50% (d.r.=3:1)

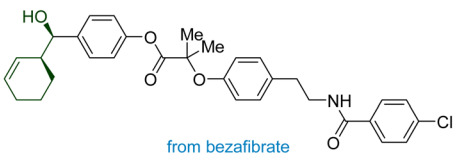


4v 88% (r.r.=9:1)

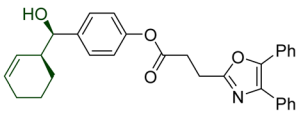


4w 85%

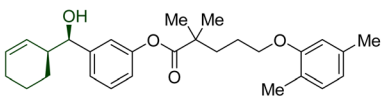
late-stage functionalization of structurally complex molecules



from bezafibrate
5a 68% (d.r.>20:1)



from oxaprozin
5b 63% (d.r.>20:1)



from gemfibrozil
5c 65% (d.r.>20:1)

[a] Reported yields are those of the isolated products. Reactions conditions: aldehydes **1** (0.5 mmol, 1 equiv.), diene **2** (2.0 equiv.), 4CzIPN (1 mol%), CoPor (0.1 mol%), $CrCl_3$ (10 mol%), HE (2.0 equiv.), THF (c = 0.1 M), 10 W blue LEDs, RT, 12 h. [b] dr was determined by ^{1}H NMR analysis of crude products.

alcohols can be obtained (**4v**, **4w**). The potential application of this synergic catalytic strategy was further demonstrated. We investigated the aldehydes derived from drugs (bezafibrat, oxaprozin and gemfibrozil) and obtained the target products with good yield and excellent diastereoselectivity (**5a–5c**). The mild reaction conditions allow the system to be compatible with

various functional groups, including halogen (**3e**, **3g**, **4g**), ether (**3c**, **4j**), OMe (**3r**, **3v**), SMe (**3h**), CF_3 (**3d**, **4o**), ester (**5a–5c**), amide (**3m**), and unsaturated alkene (**4c**).

In principle, Co(Por)(H) **6** hosts a cobalt center with a square pyramidal geometry, which lacks *cis*-vacant sites required for alkene coordination, thereby making hydrometallation of butadiene with Co(Por)(H) **6** impractical. To assess the MHAT mechanism of butadiene and Co(Por)(H) **6**, we performed DFT calculations through an unrestricted open-shell method, given the potential involvement of radical species. Gas phase optimization of intermediates and transition states was executed using the ωB97XD method. The LANL2TZ(f) basis set was used to model the Co atom, while the 6-31G(d,p) basis set was employed for butadiene, N atoms of the porphyrin ring, and the hydride atom. Meanwhile, the 6-31G basis set was used for other atoms of the porphyrin, and STO-3G was utilized for atoms of porphyrin ring substituents. Frequency calculations were conducted using the same level of theory to confirm the minima or transition state structures and obtain zero-point energy and thermal energy corrections under standard conditions of 298.15 K and 1 atm pressure. Single-point solvation energies were calculated using the ωB97XD functional, the def2-TZVP basis set, and the SMD solvation model (solvent = tetrahydrofuran). The transition state, **TS7**, exhibited partially radical pair character and was spin-polarized (see Fig. 2b). Moreover, the computed bond lengths of Co–H (1.49 Å) and C–H (1.62 Å) of the transition state TS6 were elongated. After the MHAT process, an allyl radical **8b** and Co^{II} species **8a** were generated. DFT calculations revealed that the overall MHAT reaction was exergonic by 18.7 kcal

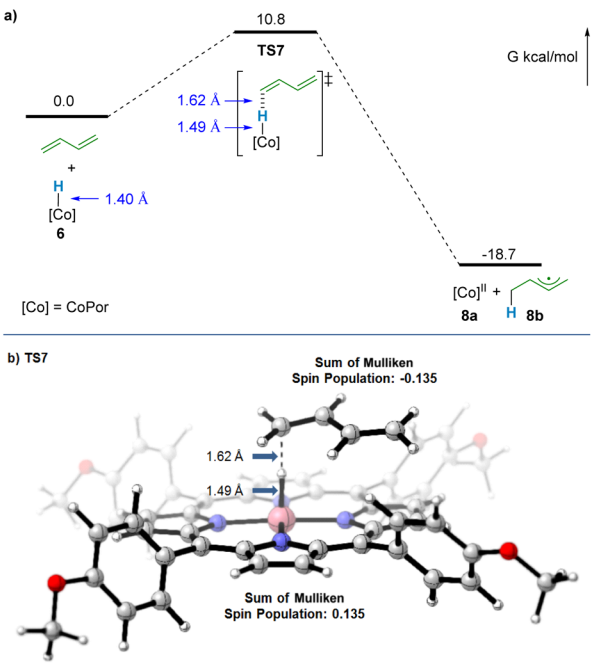


Fig. 2 (a) Computed energy profile of the MHAT between H-CoPor and 1,3-butadiene. (b) Computed structure of the transition state **TS7** of the MHAT between the CoPor hydride complex and 1,3-butadiene.

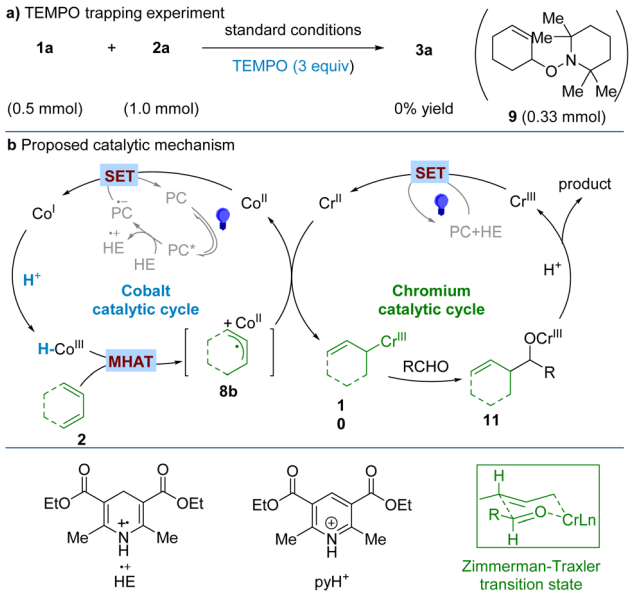


Fig. 3 Mechanistic studies.

mol^{-1}. The MHAT from Co–H to butadiene to produce allyl radicals and CoII species had a relatively small activation energy barrier of 10.8 kcal mol^{-1} at 25 °C, which is consistent with the experimentally observed fast reaction rate under the photo conditions.

The experiment of free radical trapping shows that the reaction may be carried out through a free radical pathway (Fig. 3a). Based on the above experimental results and previous studies, we proposed a possible catalytic cycle (Fig. 3b). First, 4CzIPN was excited to produce 4CzIPN* [$E_{1/2}$ (4CzIPN*/4CzIPN$^{\bullet-}$) = +1.43 V *vs.* SCE],[37] which was transformed to 4CzIPN$^{\bullet-}$ by HE ($E_{HE^{\bullet+}/HE}$ = +1.0 V *vs.* SCE) through SET.[38] The formed $HE^{\bullet+}$ continues to participate in the reaction by losing electrons and protons; Co^{II} [$E_{1/2}$ (Co^{II}/Co^{I}) = −0.70 V *vs.* SCE][39] and Cr^{III} [$E_{1/2}$ (Cr^{III}/Cr^{II}) = −0.51 V *vs.* SCE][40] were reduced to Co^{I} and Cr^{II} by 4CzIPN$^{\bullet-}$[$E_{1/2}$ 4CzIPN/4CzIPN$^{\bullet-}$ = −1.24 V *vs.* SCE],[37] and Co^{I} captured H^{+} to form Co^{III}–H species, which converted butadiene into an allyl radical by MHAT. Then the allyl radicals were rapidly captured by Cr^{II} to form an allylCr^{III} species, which was coupled with aldehydes to obtain homoallyl alcohol through protolysis, and the Cr^{III} was released. The diastereoselectivity of homoallylic alcohols can be explained by the Zimmerman–Traxler transition state in which the oxygen of the aldehyde coordinates to Cr.

Conclusions

In summary, we have developed a novel photoredox Cr and Co dual-catalysis system that enables carbonyl allylation with 1,3-butadiene and cyclohexadiene providing expedient access to valuable homoallylic alcohols. In this catalytic system, the selective HAT of Co–H to butadiene and the rapid capture of allyl radicals by Cr are key to the success of the reaction. The

low-cost and readily available substrates and catalysts make this method more advantageous in practical applications.

Conflicts of interest

There are no conflicts to declare.

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