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Cobalt-Catalyzed Hydroacylative Dimerization of Allenes Leading to Skipped Dienes

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[§] Supporting Information

ABSTRACT: A cobalt–diphosphine catalyst has been found to promote a selective 1:2 coupling reaction between aldehydes and allenes to form β,δ -dialkylidene ketones, featuring skipped diene moieties, with high regioselectivities and stereoselectivities. The reaction is distinct from previously reported, rhodium-catalyzed aldehyde–allene 1:2 coupling to afford β,γ -dialkylidene ketones bearing 1,3-diene moieties. The present hydroacylative dimerization involves a unique allene/allene oxidative cyclization mode to form a C1–C2 linkage between the allene molecules.

The transition-metal-catalyzed coupling between aldehydes and unsaturated hydrocarbons is among the most straightforward and atom-economical approaches to the synthesis of ketones.¹ While 1:1 coupling (hydroacylation) reactions between aldehydes and alkenes or alkynes have been most extensively developed in both intramolecular and intermolecular settings, allenes have also attracted significant interest as unique reaction partners for aldehydes. Thus, rhodium-catalyzed hydroacylation reactions of allenes using chelating aldehydes such as salicylaldehyde and methylthio-substituted aldehyde have been reported by groups led by Miura² and Willis,³ respectively, the latter being achieved in an enantioselective fashion.⁴ Dong and co-workers achieved ruthenium-catalyzed hydroacylation of alkynes with simple aromatic aldehydes, which involves in situ generation of allenes from the alkynes.⁵ Besides the 1:1 coupling reactions, a few examples of aldehyde/allene coupling engaging an extra π -substrate have been reported. Oonishi et al. reported rhodium(I)-catalyzed intramolecular and intermolecular [6 + 2] cycloaddition between 4-allenals and alkynes initiated by aldehyde C–H activation.⁶ Murakami and co-workers reported rhodium(I)-catalyzed 1:2 coupling reactions between aldehydes and allenes to afford β,γ -dialkylidene ketones, the regiochemistry of which is controlled by the choice of a neutral or a cationic rhodium catalyst (Scheme 1a).⁷ While this reaction was initially proposed to proceed through aldehyde/allene oxidative cyclization on rhodium(I), computational studies by Himo and co-workers later indicated that oxidative cyclization of two allene molecules is more likely to operate, forming the C–C bond between the central allenic carbons (see the box in Scheme 1a).⁸ In pursuit of our continuing

interest in low-valent cobalt catalysis⁹ for hydroacylation^{10,11} and allene transformations,^{12–14} we have found that a cobalt catalyst promotes the aldehyde/allene 1:2 coupling in a distinct fashion, compared with the rhodium catalysts (Scheme 1b). Thus, with a low-valent cobalt–diphosphine catalyst, the hydroacylative dimerization is achieved with high regioselectivities and stereoselectivities to afford β,δ -dialkylidene ketones featuring skipped diene moiety¹⁵ in good yields. The product selectivity of the present reaction is ascribed to a unique allene/allene oxidative cyclization mode, which selectively forms a C–C bond between the terminal and the central allenic carbons (see the box in Scheme 1b).

Recently, Dong and co-workers reported a cobalt-catalyzed regioselective hydroacylation reaction of 1,3-diene (Scheme 1c).^{11c} The reaction was proposed to involve oxidative cyclization of the aldehyde and the diene on cobalt(I), forming an oxacobaltacycle intermediate as the key step. Inspired by this precedent, we initially set to explore the feasibility of hydroacylation of cyclohexyl allene (**2a**) with benzaldehyde (**1a**), assuming analogous oxidative cyclization of the aldehyde and the allene. Contrary to this working hypothesis, we did not obtain any 1:1 coupling product but observed selective 1:2 coupling to afford the skipped diene isomers **3aa** and **4aa**. Upon extensive optimization studies (see Tables S1–S3 in the Supporting Information), the reaction of **1a** and **2a** (3.5 equiv) was achieved in the presence of CoI₂ (10 mol %), dppp (10 mol %), In (20 mol %), and InBr₃ (20 mol %) in toluene at 40 °C to afford **3aa** in 97% yield with

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Scheme 1. Hydroacylative Dimerization of Allenes

of the reductant and the Lewis acidic additive, In and InBr₃ gave the best result, while they could be replaced by Zn and ZnI₂, respectively, albeit with decreased yields (Table 1, entries 7 and 8). No reaction was observed when either In or InBr₃ was omitted. CoCl(PPh₃)₃ proved to work in place of CoI₂ and In, albeit with moderate activity (Table 1, entry 9), suggesting the involvement of a cationic Co(I) species. Lastly, the solvent was also found to influence the efficiency and the regioselectivity. Dichloroethane (DCE) and acetone maintained the reaction efficiency but caused slight erosion in the regioselectivity (Table 1, entries 10 and 11). No reaction was observed in more coordinating solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and acetonitrile (MeCN). The reaction could be performed using 5 mol % catalyst with a slightly diminished yield (86%), but became much sluggish with further reduction in the catalyst loading (34% with 2 mol % and 17% with 1 mol %).

With the optimized Co–dppp catalytic system in hand, we explored the scope of the hydroacylative dimerization. First, a variety of aldehydes were reacted with the allene **2a** (see Scheme 2). Various aromatic aldehydes participated in the

Scheme 2. Hydroacylative Dimerization of **2a** with Various Aldehydes^a

^aThe reaction was performed on a 0.2 mmol scale. The regioisomer ratio is shown in the parentheses. ^bThe reaction was performed at 80 °C.

Table 1. Effect of Reaction Conditions^a

entry	deviation from standard conditions	yield ^b (%)	3aa:4aa ^b
1	none	97	>20:1
2	CoBr ₂ instead of CoI ₂	89	>20:1
3	CoCl ₂ instead of CoI ₂	7	>20:1
4	Co(acac) ₃ instead of CoI ₂	90	>20:1
5	dppe instead of dppp	7	19:1
6	dppb instead of dppp	13	2:1
7	ZnI ₂ instead of InBr ₃	74	>20:1
8	Zn, ZnI ₂ instead of In, InBr ₃	51	>20:1
9	CoCl(PPh ₃) ₃ instead of CoI ₂ , In	41	>20:1
10	DCE instead of toluene	94	11:1
11	acetone instead of toluene	88	15:1

^aThe reaction was performed using 0.1 mmol of **1a** and 0.35 mmol of **2a**. dppp = 1,3-bis(diphenylphosphino)propane; dppe = 1,2-bis(diphenylphosphino)ethane; dppb = 1,4-bis(diphenylphosphino)butane. ^bDetermined by GC using *n*-tridecane as an internal standard.

Co(acac)₃ as the precatalyst (Table 1, entries 2 and 4), whereas the reaction became rather sluggish with CoCl₂ (Table 1, entry 3). The reaction is highly dependent on the diphosphine ligand. Thus, typical diphosphines other than dppp, including dppe and dppb, displayed much lower activities (Table 1, entries 5 and 6). As for the combination

hydroacylative dimerization to afford the desired skipped diene products **3aa–3ka** in high yields with moderate to high regioselectivities, tolerating substituents such as halogen (F, Cl, Br), trifluoromethyl, ester, and methoxy groups. The reaction of **1a** could be achieved on a gram (4 mmol) scale to afford **3aa** in 95% yield. Notably, electron-neutral and electron-poor aryl aldehydes showed excellent regioselectivities (mostly

115 >20:1), while a clear drop in the regioselectivity was observed
 116 with electron-rich aldehydes such as *p*-tolualdehyde (see **3ga**;
 117 7.5:1) and *p*-anisaldehyde (see **3ha**; 2.5:1). The molecular
 118 structure of **3ha** was unambiguously confirmed by the X-ray
 119 crystallographic analysis. Furfural, 2-thiophenecarboxaldehyde,
 120 and cinnamaldehyde also participated in the hydroacylative
 121 dimerization to afford the desired products **3la–3na** in
 122 moderate yields and regioselectivities. 3-Phenylpropanal was
 123 a somewhat sluggish substrate, but afforded the desired
 124 product **3oa** in 43% yield with excellent regioselectivity.
 125 We next examined the reaction of benzaldehyde **1a** with
 126 various allenes (**Scheme 3**). Alkyl- and benzyl-substituted

Scheme 3. Hydroacylative Dimerization of Various Allenes with 1a^a

^aThe reaction was performed on a 0.2 mmol scale. The major product is shown, together with the regioisomer ratio in the parentheses.

127 allenes were amenable to the hydroacylative dimerization to
 128 afford the expected products **3ab–3ai** in moderate to good
 129 yields with high regioselectivities (14:1 to >20:1). Substituents
 130 such as siloxy (**3ae**), allyloxy (**3af**), ester (**3ah**), and chloro
 131 (**3ai**) could be well-tolerated. Interestingly, aryl-substituted
 132 allenes were found to show opposite regioselectivity in the
 133 aldehyde–allene bond formation, affording the products **4aj–**
 134 **4an** in moderate yields with regioselectivities of 8:1 to 10:1.
 135 The structure of the product **4am** derived from 4-
 136 bromophenylallene was confirmed by X-ray crystallography.
 137 Note that 1,1-disubstituted allenes such as 1,1-dibutyl allene

and vinylidene cyclohexane and 1,3-disubstituted allenes such
 as 1,3-diheptyl allene and cyclonona-1,2-diene failed to give the
 desired products; most of them remained unreacted after 48 h
 at 80 °C.

Several mechanistic experiments were performed to gain
 insight into the present hydroacylative dimerization. The
 reaction between deuterated benzaldehyde (**1a–1d**) and **2a**
 afforded the product **3aa–3d** with clean deuterium incorpo-
 ration into the δ -position (**Scheme 4a**). The reaction between

Scheme 4. Mechanistic Experiments

1a–1d and **2j** furnished **4aj–4d** with the same pattern of
 deuterium incorporation (**Scheme 4b**). Note that the reaction
 using **1a–1d**, 4-methoxycarbonylbenzaldehyde (**1f**), and **2a**
 afforded **3aa–3d** and **3fa** without any H/D crossover.
 Comparison of parallel independent reactions of **1a** and **1a–**
1d with **2a** gave a kinetic isotope effect (KIE) of 1.3 (see
Scheme 4c, as well as **Figure S4** in the Supporting
 Information), indicating that C–H bond cleavage is not a
 distinct rate-limiting step of the present reaction. It is notable
 that this KIE is much smaller than the KIE of 2.7 observed in
 Dong's cobalt-catalyzed hydroacylation of 1,3-diene (**Scheme**
1c), which was attributed to rate-limiting β -hydride elimination
 of the oxacobaltacycle intermediate.^{11c} Kinetic experiments
 indicated that the reaction rate depends on the concentration
 of **1a** (range = 0.2–0.8 M) with an approximate order of 0.6,
 while virtually zero-order dependence on the concentration of
2a was observed within a range of 0.35–1.4 M (see **Figure S5**
 in the Supporting Information). In addition, the reaction
 displayed approximately first-order dependence on the catalyst
 concentration. This kinetic profile is also distinct from Dong's
 diene hydroacylation, which displayed zero-order dependence

with respect to both the aldehyde and the diene.^{11c} Competition reactions between benzaldehyde and substituted benzaldehydes revealed faster relative rates of electron-deficient aldehydes with a positive Hammett ρ value of 1.00 (see Scheme 4d, as well as Figure S6 in the Supporting Information), which was comparable in magnitude to the ρ values for the allylation using allylzinc, indium, and tin reagents.¹⁶

On the basis of the above observations, we propose a possible mechanism of the present reaction in Scheme 5, which

Scheme 5. Proposed Reaction Pathways

is initiated by oxidative cyclization of two allene molecules on a Co^{I} species **A**. This oxidative cyclization step has to ensure the C1–C2 linkage between two allenes, which is distinct from the C2–C2 linkage in Murakami's reaction (Scheme 1a),^{7,8} as well as in other known examples of allene oxidative cyclization on Rh^{I} ,^{17,18} Ir^{I} ,¹⁹ Pd^0 ,²⁰ and Ni^0 .^{21,22} The resulting cobaltacycle **B**, featuring alkenyl- and allyl-Co bonds, undergoes allylation of the aldehyde to produce oxacobaltacycles **C** or **C'**. Subsequent β -hydride elimination forms alkenyl(hydrido)cobalt species **D** or **D'**, followed by reductive elimination to afford the product **3** or **4**, respectively. According to this mechanism, as well as the observed KIE, rate dependence, and Hammett correlation, the aldehyde allylation would be the step in which the reaction rate is significantly influenced and the regioselectivity is determined.^{16,23,24} Besides this mechanism, one can also conceive an alternative mechanism initiated by aldehyde/allene oxidative cyclization (see Scheme S1 in the Supporting Information), which, however, appears inconsistent with the kinetic dependence on the aldehyde and the allene. Note also that such a mechanism requires bond formation between the aldehyde and the C3 (when $\text{R}^2 = \text{alkyl}$) or C1 (when $\text{R}^2 = \text{aryl}$) atom of the allene and generation of an alkenyl–Co bond. This is distinct from the common regioselectivity pattern in known oxidative cyclizations of an allene and a different π -component on low-valent metals including cobalt, which engages the allene C2 carbon in C–C bond formation and leads to an allyl–metal bond.^{12a,13a,25} In agreement with the inference that the allene/allene oxidative cyclization is more likely to operate, DFT calculations on allene/allene and aldehyde/allene oxidative cyclizations on a cationic (diphosphine) Co^{I} species suggested that the former is energetically much more preferred to the latter (see Figures S7 and S8 in the Supporting Information).

The DFT calculations also suggested that allene/allene oxidative cyclization on cobalt prefers to form C1–C2 linkages than C2–C2 linkages, because of smaller distortion energies of the allene molecules in the former pathway (see Scheme S2 in the Supporting Information).

The product of the present reaction is amenable to a series of functional group transformations (Scheme 6). Wittig

Scheme 6. Product Transformations

olefination of **3aa** afforded the skipped triene **5** in good yield. Electrophilic olefin functionalizations such as epoxidation and bromination occurred exclusively on the *cis*-1,2-disubstituted olefin moiety, rather than the 1,1-disubstituted olefin moiety, thus affording the products **6** and **7**, respectively, as a mixture of diastereomers. Reduction with NaBH_4 also proceeded smoothly to afford the alcohol **8** with a decent diastereoselectivity of 5:1.

In summary, we have reported highly regioselective and stereoselective hydroacylative dimerization of allenes catalyzed by a cobalt–diphosphine complex, which affords ketones bearing skipped diene moieties. The present reaction features distinct a reaction pathway, compared with that observed with the known rhodium catalysts, and displays a broad scope, with respect to aldehydes and allenes. The product selectivity is proposed to originate from a unique regioselectivity in oxidative cyclization of two allene molecules. Further exploration of cobalt-catalyzed coupling and cycloaddition reactions engaging allenes is underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02465.

Experimental procedures and spectral data for all new compounds (PDF)

Accession Codes

CCDC 1920309 and 1920310 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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