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Regioselective Hydroacylation of 1,3-Dienes by Cobalt Catalysis

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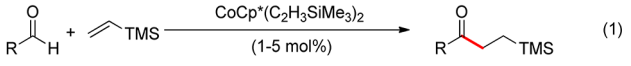
Supporting Information

ABSTRACT: We describe a cobalt-catalyzed hydroacylation of 1,3-dienes with non-chelating aldehydes. Aromatic aldehydes provide 1,4-addition products as the major isomer, while aliphatic aldehydes favor 1,2-hydroacylation products. The kinetic profile supports an oxidative cyclization mechanism involving a cobaltacycle intermediate that undergoes transformation with high regio- and stereoselectivity.

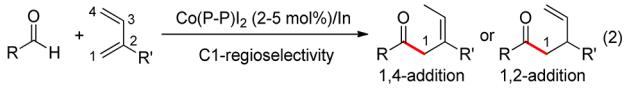
A modern challenge in organic synthesis is the invention of methods that use catalysts derived from first-row transition metals.[1] A number of valuable olefin transformations, including hydrogenation,[2] hydroformylation,[3] and hydrovinylation,[4] have been achieved by cobalt catalysis. These breakthroughs highlight Co as an attractive and complementary alternative to Rh due to its relatively low cost and high abundance. Encouraged by this progress, we recently turned our attention to developing olefin hydroacylation[5−14] by cobalt catalysis.[15] Brookhart demonstrated the first and only previously known intermolecular Co-catalyzed hydroacylation (eq 1).[15a,b] While promising, this

Brookhart's Work: C–H activation



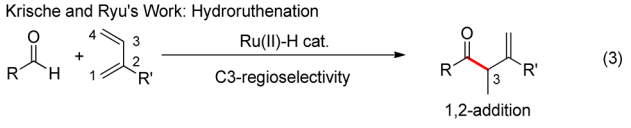
(1)

This Work: Oxidative Cyclization



(2)

Krische and Ryu's Work: Hydroruthenation

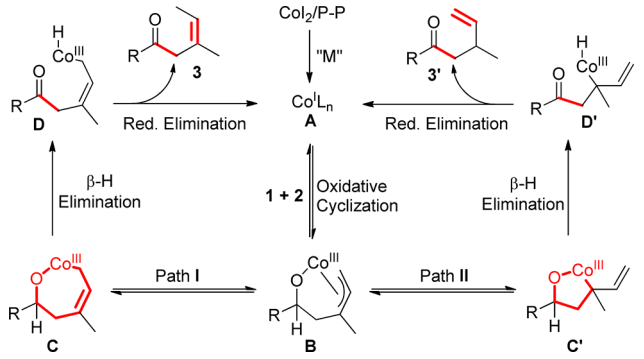


(3)

strategy was limited to vinylsilanes, and aldehyde decarbonylation remained competitive. We imagined developing a Co(I)-catalyzed cross-coupling of various aldehydes and 1,3-dienes (eq 2). Our C−H bond functionalization would yield β,γ- and/or γ,δ-unsaturated ketones with high regioselectivity and excellent atom economy. Moreover, this proposed hydroacylation would afford regiocontrol distinct from current technologies, including the relevant Ru-catalyzed pathway developed independently by Krische[11c] and Ryu[11d] (eq 3).

Our proposal draws from a mechanism established by Hilt for the Co-catalyzed hydrovinylation of olefins to generate 1,4-dienes.[4] As shown in Scheme 1, a Co(II) precatalyst can be used to generate the Co(I) catalyst.[16] We hypothesize that Co(I) catalyst **A** would promote oxidative cyclization between aldehyde

Scheme 1. Proposed Cobalt-Catalyzed Hydroacylation of Dienes by Oxidative Cyclization



1 and a 1,3-diene **2**.[17] The resulting cobaltacycle **B** exists in two η^1 forms: seven-membered cobaltacycle **C** and five-membered cobaltacycle **C′**.[4,18,19] Depending on the substrate and ligand, cobaltacycle **C** or **C′** would undergo transformation by Path I or II, respectively. A β-hydride elimination generates intermediate **D** or **D′**, which can undergo reductive elimination to yield product **3** or **3′** and regenerate catalyst **A**. In Path I, formation of the cobaltacycle intermediate requires a *cis*-olefin geometry; thus, we propose this pathway would lead to the *Z*-isomer of **3** with high levels of stereocontrol.

To test our hypothesis, we chose benzaldehyde **1a** and isoprene **2a** as model substrates. Control experiments confirm that these substrates are unreactive in the absence of either Co(II) salts or reducing agents.[20] We then examined the transformation using Co(II) (a catalyst precursor for hydrovinylation)[4] with various ligands and additives to generate the requisite Co(I) catalyst. A survey of 20 commercially available phosphines reveals 1,3-bis(diphenylphosphino)propane (dppp) is the most promising ligand. With Co(II)-dppp, the desired product is observed in 11% yield by using Zn/ZnI_2, a known protocol for generating Co(I) (Table 1, entry 1).[4,16] By applying In as the reductant instead, we observe improved reactivity (21%, entry 2). Through a further survey of additives, we find that a combination of In/$InBr_3$ gives the best result (57% yield, entries 3−5). Given the role of ZnI_2 in hydrovinylation,[4] we assume $InBr_3$ similarly promotes the formation of cationic Co(I) species. In the absence of these Lewis acids, the yield is diminished (13% yield, entry 6). In all cases, we observe the β,γ-unsaturated ketone in preference to the γ,δ-unsaturated ketone (up to 19:1 selectivity). In accordance with our proposed mechanism, the

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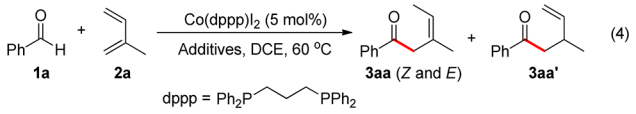
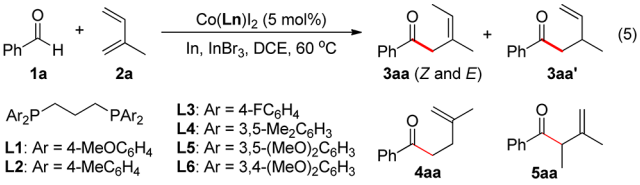
Table 1. Additives Effects for Hydroacylation[a]



entry	additives	yield (%)[b]	3aa/3aa'[c]	Z/E (3aa)[c]
1	Zn/ZnI_2	11	12:1	10:1
2	In/ZnI_2	21	14:1	16:1
3	In/InI_3	45	17:1	13:1
4	In/$InBr_3$	57	19:1	11:1
5	In/$InCl_3$	28	14:1	17:1
6	In/—	13	13:1	18:1

[a]**1a** (0.20 mmol), **2a** (0.60 mmol), Co(dppp)I_2 (5 mol%), In or Zn (20 mol%), MX_n (5 mol%), DCE (1 mL), 60 °C, 24 h. [b]Overall yield of **3aa** and **3aa'**, determined by ^{1}H NMR or GC-FID with dimethyl terephthalate (0.05 mmol) as internal standard. [c]Determined by ^{1}H NMR or GC-FID.

Table 2. Ligand Effects of DPPP Analogues[a]



entry	catalyst	yield (%)[b]	3aa/3aa'[c]	Z/E (3aa)[c]
1	Co(dppp)I_2	57	19:1	11:1
2	Co(**L1**)I_2	59	17:1	17:1
3	Co(**L2**)I_2	63	19:1	13:1
4	Co(**L3**)I_2	50	14:1	15:1
5	Co(**L4**)I_2	83	>20:1	6:1
6	Co(**L5**)I_2	95	>20:1	3:1
7	Co(**L6**)I_2	83	>20:1	20:1
8[d]	Co(**L6**)I_2	91 (87[e])	>20:1	19:1

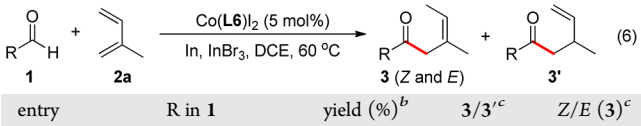
[a]**1a** (0.20 mmol), **2a** (0.60 mmol), Co(II) (5 mol%), In (20 mol%), $InBr_3$ (5 mol%), DCE (1 mL), 60 °C, 24 h. [b]Overall yield of **3**, determined by ^{1}H NMR or GC-FID with dimethyl terephthalate (0.05 mmol) as internal standard. [c]Determined by ^{1}H NMR or GC-FID. [d]In (10 mol%), DCE (0.5 mL). [e]Isolated yield.

stereochemistry of the resulting trisubstituted olefin is *Z*, as confirmed by 2D NOESY analysis.

To tune the catalyst, we prepared six analogues of dppp by varying the substitution pattern on the aryl groups (**L1**−**L6**, Table 2). From this study, we find that **L6** (where Ar = 3,4-$(MeO)_2C_6H_3$) gives high yield, regioselectivity, and stereocontrol (87% isolated yield, >20:1 regioselectivity, and 19:1 *Z*/*E*, entry 8). With **L6**, the amount of In powder can be reduced to 10 mol% (entry 8). A trace amount of *γ*,*δ*-unsaturated ketone **4aa** is observed as a minor product (**3aa**/**4aa** >20:1, entry 8). Our cobalt catalyst favors the 1,4-hydroacylation product **3aa** over the 1,2-addition isomer **5aa** which has been accessed with Ru(II) catalysis.[11c,d] Thus, cobalt enables a rare type of hydroacylation that occurs across a conjugated *π*-system rather than a single *π*-bond.

With this protocol in hand, we explored the hydroacylation of diene **2a** using 18 different aldehydes (Table 3). In general, good to high yields are obtained with various aromatic aldehydes **1** (60−97% yields, entries 1−13). In the case of electron-rich aryl aldehyde **1h**, we observe a drop in stereoselectivity (2:1) due to

Table 3. Variation in the Aldehyde Scope[a]



entry	R in **1**	yield (%)[b]	3/3'[c]	Z/E (3)[c]
1	Ph (**1a**)	87	>20:1	19:1
2	4-BrC_6H_4 (**1b**)	92	>20:1	>20:1
3	4-ClC_6H_4 (**1c**)	96	>20:1	>20:1
4	4-FC_6H_4 (**1d**)	60	>20:1	>20:1
5	4-$CF_3C_6H_4$ (**1e**)	78	>20:1	>20:1
6	4-$MeO_2CC_6H_4$ (**1f**)	88	>20:1	>20:1
7	4-MeC_6H_4 (**1g**)	90	>20:1	6:1
8	4-$MeOC_6H_4$ (**1h**)	97	>20:1	2:1
9[d]	4-$MeOC_6H_4$ (**1h**)	83	>20:1	11:1
10	3-BrC_6H_4 (**1i**)	64	>20:1	>20:1
11	3-ClC_6H_4 (**1j**)	89	>20:1	>20:1
12	2-furyl (**1k**)	94	>20:1	>20:1
13	2-naphthyl (**1l**)	94	>20:1	6:1
14	(*E*)-styryl (**1m**)	86	>20:1	6:1
15	Cy (**1n**)	17	2:1	n/a
16[e]	Cy (**1n**)	82	1:8	n/a
17[e]	*n*-C_5H_{11} (**1o**)	78	1:5	n/a
18[e]	*n*-C_6H_{13} (**1p**)	83	1:4	n/a
19[e]	*n*-C_7H_{15} (**1q**)	91	1:5	n/a
20[e]	$BnCH_2$ (**1r**)	74	1:4	n/a

[a]**1** (0.20 mmol), **2a** (0.60 mmol), Co(**L6**)I_2 (5 mol%), In (10 mol%), $InBr_3$ (5 mol%), DCE (0.5 mL), 60 °C, 20−24 h. [b]Isolated yield of all isomers. [c]Determined by GC-FID or ^{1}H NMR; trace amount of product **4** was observed as minor isomer (**3**/**4** >20:1) for aldehydes **1a**−**m**. [d]DCE/toluene (1:1, 0.5 mL) was used solvent. [e]**1** (0.20 mmol), **2a** (0.60 mmol), Co(dcpe)I_2 (5 mol%), In (20 mol%), $InBr_3$ (5 mol%), DCE/EtOAc (3:1, 0.5 mL), 50 °C, 20−24 h.

competitive olefin isomerization. The use of a mixed solvent (1:1 DCE/toluene) presumably inhibits isomerization and allows isolation of the desired product in good yield and higher stereoselectivity (11:1, entry 8 vs 9). This catalyst promotes hydroacylation of heteroaromatic aldehyde **1k** (94% yield, entry 12). Moreover, the hydroacylation of isoprene **2a** with *α*,*β*-unsaturated aldehyde **1m** provides a conjugated ketone in 86% yield and >20:1 regioselectivity (entry 14).

With catalyst Co(**L6**)I_2, aliphatic aldehyde **1n** is less reactive and undergoes hydroacylation with lower regioselectivity (Table 3, entry 15). Toward addressing this challenge, we investigated a range of parameters and found promising reactivity with a more electron-rich phosphine ligand, 1,2-bis(dicyclohexylphosphino)ethane (dcpe).[20] The resulting ketone products are obtained in good yields with a dramatic switch in regiocontrol (entry 15 vs 16). Generally, the 1,2-hydroacylation products **3'** are afforded as the major isomer with regioselectivities ranging from 4:1 up to 8:1 for aliphatic aldehydes **1n**−**r** (entries 16−20). In these cases, we observe high C1-regioselectivity (C−C bond formation at 1-position of diene **1a**) instead of C3-regioselectivity (eq 2 vs 3).

Next, we examined the scope of dienes (Table 4). For benzaldehyde, high yields (77−97%) and excellent regio- and stereoselectivities (>20:1 for both) are achieved for hydroacylation of 2-aryl-substituted butadienes, despite varying electronic and steric properties of substituents (entries 1−9). The catalyst loading can be reduced to 2 mol% for the coupling of benzaldehyde **1a** and 2-phenylbutadiene (entry 2). The use of 2-cyclohexylbutadiene gives *β*,*γ*-unsaturated ketone **3aj** with

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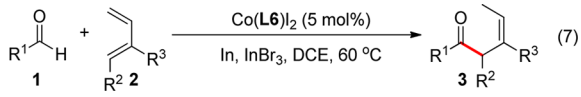
Table 4. Variation of the Diene Partner[a]



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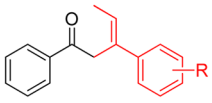
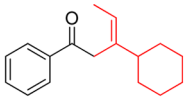
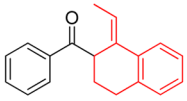
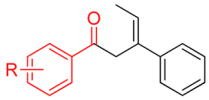
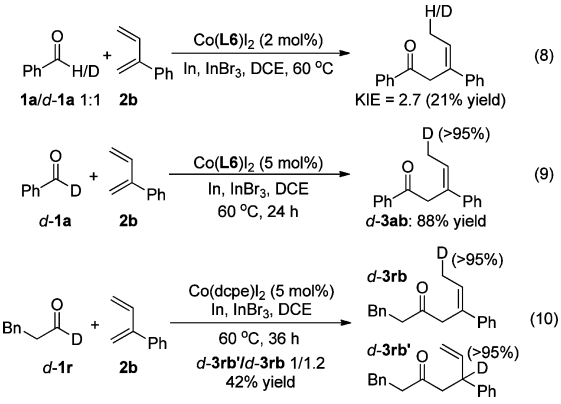
Entry	3	R in 3	Yield (%)
1		H	88 (**3ab**)
2		H	86 (**3ab**)[b]
3		4-Br	92 (**3ac**)
4		4-F	81 (**3ad**)
5		4-CF_3	90 (**3ae**)
6		4-MeO	77 (**3af**)
7		4-Me	97 (**3ag**)
8		3-Cl	97 (**3ah**)
9		2-Cl	89 (**3ai**)
10		n/a	87 (**3aj**)
11		n/a	61 (**3ak**)
12		4-Br	78 (**3bb**)
13		4-F	73 (**3db**)
14		4-CF_3	81 (**3eb**)
15		4-CO_2Me	88 (**3fb**)
16		4-Me	82 (**3gb**)
17		4-MeO	80 (**3hb**)

[a] **1** (0.30 mmol), **2** (0.20 mmol), Co(**L6**)I_2 (5 mol%), In (10 mol%), $InBr_3$ (5 mol%), DCE (0.5 mL), 60 °C, 16 h. Only one isomer was observed, except for **3aj** (*E*/*Z* 6:1). The geometry of **3ab** and **3ak** was assigned by NOESY spectra. [b] Co(**L6**)I_2 (2 mol%).

moderate stereoselectivity (6:1) and good yield (87%, entry 10). Hydroacylation of a 1,2-disubstituted diene occurs with moderate yield (entry 11),[21] while 2-phenylbutadiene **2b** couples well with a variety of aldehydes (entries 12−17). Throughout these studies, we observe no aldehyde decarbonylation, the byproduct expected for hydroacylations involving C−H bond activation of non-chelating aldehydes.

Finally, we report mechanistic studies that further support our proposed oxidative cyclization mechanism, in preference to a C−H activation pathway.[15a,b] First, a kinetic isotope effect (KIE, k_H/k_D) of 2.7 is observed from competition experiments between benzaldehyde **1a** and *d*-**1a** (eq 8).[22] If hydroacylation occurs through a traditional C−H activation mechanism, either oxidative addition of Co(I) to the aldehyde or insertion of the diene into the Co−H will be the turnover-limiting step.[5d] However, we observe a zero-order dependence on both aldehyde and diene concentrations,[20,23] thus disfavoring a C−H activation pathway. The KIE is consistent with β-hydride or reductive elimination as the turnover-limiting step in Path I (Scheme 1).[22] Moreover, the zero-order dependence on both the aldehyde and the diene concentrations supports the possibility of metallacycle **C** or **D** as catalyst resting state (Scheme 1).

When the hydroacylation is performed with deuterio-benzaldehyde *d*-**1a**, the deuterium atom is incorporated at the



4-position of diene **2b** without any detectable deuterium at other positions (eq 9). This result suggests that the hydroacylation with aromatic aldehydes proceeds through a 1,4-addition pathway (Path I, Scheme 1). For hydroacylation with aliphatic aldehyde *d*-**1r**, the deuterium atom is incorporated completely at the β- and δ-position of products *d*-**3rb**′ and *d*-**3rb**, respectively (eq 10). While further studies are warranted, our observations support a mechanistic proposal where Path I or II is favored (Scheme 1), depending on the properties of both the ligand and the substrate.

In contrast to the traditional mechanism of hydroacylation catalyzed by Rh(I) or Co(I), we propose an oxidative cyclization mechanism that avoids decarbonylation. Our catalyst promotes C1-regioselective hydroacylation of dienes and can be tuned to favor either 1,4- or 1,2-hydroacylation. Through the 1,4-hydroacylation pathway, we achieve the stereoselective synthesis of trisubstituted olefins, which are key building blocks that are challenging to access.[24] Ongoing efforts will focus on studying other catalysts for achieving higher selectivities and greater scope. Our study contributes to the emerging strategies available for hydroacylation via non-precious-metal catalysis.[13,15]

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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