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Co-Catalyzed Direct Addition of Allylic C(sp^3)−H Bonds to Ketones

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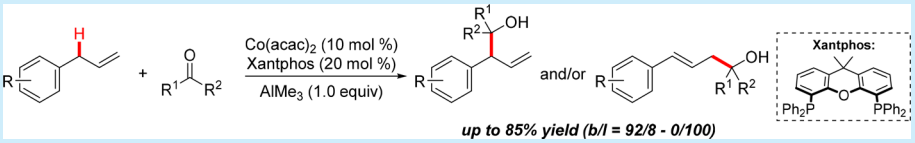
Supporting Information

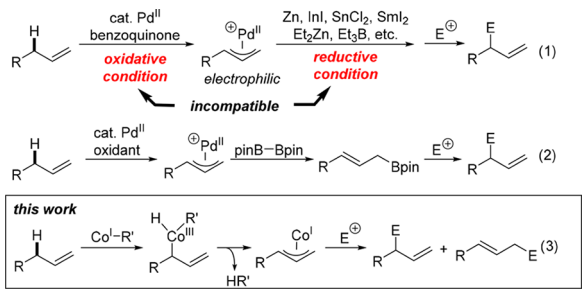


ABSTRACT: By using Co(acac)$_2$/Xantphos with AlMe$_3$, the C(sp^3)−H bonds of allylarene derivatives were cleaved for reaction with various ketones, affording the homoallylic alcohols in moderate to good yields. The branch/linear selectivity depended on the steric and electronic factors of the ketone electrophiles. The intermediate in this reaction is thought to be a low-valent allylcobalt(I) species, which exhibits high nucleophilicity toward ketones.

The C−H activation reaction has become a powerful tool, especially for the construction of C−C bonds directly from poorly reactive C−H bonds (the pK_a values are usually more than ca. 30) without using a strong base or acid.[1] Of particular interest is the functionalization of C(sp^3)−H bonds[2] because of its high potential for the synthesis of 3D complex molecules from simple aliphatic compounds. In this regard, polar carbonyl electrophiles have been less exploited,[3] although there are many successful examples of C(sp^2)−H addition to aldehydes, aldimines, and their equivalents, especially in the presence of Rh(III) and Co(III) complexes as catalysts.[4,5] We turned our attention to the allylic C(sp^3)−H bonds adjacent to alkenes, with the aim of developing a new class of carbonyl insertion reactions to C(sp^3)−H bonds.

Cleavage of the allylic C(sp^3)−H bonds of alkenes using a Pd(II) salt was first reported by Hüttel,[6a,b] and the reactive intermediate was employed for allylic alkylation by Trost.[6c] White further extended this stoichiometric activation to a catalytic variant by using a stoichiometric amount of the oxidant and a sulfoxide ligand.[7] Since the generated η^3-allylpalladium(II) complex exhibited high reactivity toward a variety of nucleophiles (Scheme 1, eq 1), it cannot be allowed to react with electrophiles. Umpolung of the electrophilic η^3-allylpalladium(II) complex was established by using various reductants or alkylmetal reagents (Zn, InI, SnCl$_2$, SmI$_2$, ZnEt$_2$, or BEt$_3$).[8] Yet, catalytic cleavage of C(sp^3)−H bonds by Pd(II) under oxidative conditions and umpolung under reductive conditions cannot be achieved in the same pot. To tackle this problem, a diboron reagent was employed for the generation of a nucleophilic allylboron under oxidative conditions, which allows the reaction of carbonyl electrophiles (eq 2).[9] However, direct conversion from an alkene by C(sp^3)−H activation without the generation of a reactive intermediate (boron/silane/stannane) would be a powerful strategy that is preferable in terms of atom and step economy (eq 3).

Scheme 1. Previous Works



To develop a new electrophilic transformation of the allylic C(sp^3)−H bonds of alkenes, we considered generating a low-valent η^3-allylmetal complex. Alkylated transition-metal species such as alkylcobalt(I) and alkylrhodium(I) were reported to cleave the allylic C−H bond of alkenes to generate an η^3-allylmetal(I) complex with the release of an alkane.[10] However, the reactivities of these complexes were not fully studied, which attracted our initial interest. After considerable experimentation, allylcobalt(I) was found to show high nucleophilicity toward CO$_2$, a poorly reactive carbonyl electrophile.[11] A combination of Co(acac)$_2$/Xantphos with AlMe$_3$ led to smooth allylic carboxylation of alkenes with CO$_2$, affording the corresponding β,γ-unsaturated carboxylic acids in high yields with high linear selectivities. Encouraged by this successful carboxylation, we focused on the development of direct addition[12] to ketones, which have not been commonly employed in C−H activation chemistry due to the low electrophilicity and potential reversibility.[13] We herein reveal a direct nucleophilic addition of allylic C(sp^3)−H bonds to various ketone electrophiles.

First, the reaction parameters were investigated using methyl-4-allylbenzoate (**1a**) and acetone (**2a**) in the presence of various transition-metal catalysts and an alkylmetal source. According to our previously developed allylic carboxylation with CO$_2$,[11] Co(acac)$_2$ (10 mol %), Xantphos (20 mol %), and AlMe$_3$ (1.5 equiv) were employed for the reaction of allylarene **1a** and **2a** in DMF (Table 1). The corresponding homoallylic alcohol **3aa** was obtained in 59% yield with modest branch selectivity (b/l = 86/

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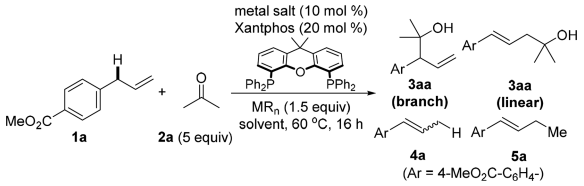
Table 1. Screening of Reaction Conditions



				yield (%)[a]			
entry	metal salt	solv	MR_n	**3aa** (b/l)	**4a**	**5a**	rec **1a**
1	$Co(acac)_2$	DMF	$AlMe_3$	59 (86/14)	28	12	–
2	$Co(acac)_3$	DMF	$AlMe_3$	59 (86/14)	27	13	–
3[b]	$Co(acac)_2$	DMF	$AlMe_3$	29 (69/31)	29	8	3
4	$Rh(acac)_3$	DMF	$AlMe_3$	–	–	–	90
5	$[Rh(cod)Cl]_2$	DMF	$AlMe_3$	–	42	–	58
6[c]	$Co(acac)_2$	DMF	$AlEt_3$	–	63	–	–
7	$Co(acac)_2$	DMF	$ZnMe_2$	11 (–/100)	25	2	54
8[d]	$Co(acac)_2$	DMF	$ZnEt_2$	–	71	–	–
9[e]	$Co(acac)_2$	DMF	BEt_3	–	88	–	–
10	$Co(acac)_2$	THF	$AlMe_3$	51 (80/20)	37	10	2
11	$Co(acac)_2$	1,4-dioxane	$AlMe_3$	49 (86/14)	23	18	–
12	$Co(acac)_2$	DMA	$AlMe_3$	75 (83/17)	15	10	–
13[f]	**$Co(acac)_2$**	**DMA**	**$AlMe_3$**	**75 (81/19)**	**16**	**8**	–

[a]Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The ratio of branched to linear products is given in parentheses. [b]1.0 equiv of CsF was added. [c]8% of methyl 4-propylbenzoate was observed. [d]29% of methyl 4-propylbenzoate was observed. [e]4% of methyl 4-propylbenzoate was observed. [f]1.0 equiv of $AlMe_3$ was used.

14), along with the olefin isomerization product **4a** (*E*/*Z* mixture) and methylated product **5a** (entry 1). When $Co(acac)_3$ was employed instead of $Co(acac)_2$, a similar product distribution was observed (entry 2). The addition of CsF, which was effective for carboxylation, did not work well in this case (entry 3). The use of Rh catalysts such as $Rh(acac)_3$ and $[Rh(cod)Cl]_2$ did not promote the desired carbonyl allylation (entries 4 and 5). Other alkylmetal reagents such as $AlEt_3$, $ZnMe_2$, $ZnEt_2$, and BEt_3 were not promising (entries 6–9), and a small amount of hydrogenated product, methyl 4-propylbenzoate, was observed when MEt_3 (M = Al, Zn, and B) was employed. Screening of potential solvents such as THF, 1,4-dioxane, and DMA revealed that DMA was the best in terms of the yield of **3aa** (entries 10–12). Eventually, the amount of $AlMe_3$ was reduced to 1.0 equiv, and the yield of **3aa** was maintained at 75% (entry 13).

With the optimal conditions ($Co(acac)_2$ (10 mol %), Xantphos (20 mol %), and $AlMe_3$ (1.0 equiv) in DMA at 60 °C) in hand, we investigated the substrate scope and limitations of ketone electrophiles (Figure 1). The carbonyl character of the employed ketones was elucidated by the C=O stretch in the IR spectrum. The reaction was applicable to not only acetone (**2a**) but also other aliphatic ketones, including 2-butanone (**2b**) and 3-pentanone (**2c**). However, the amount of linear products increased as the alkyl chain was elongated. Since these three ketones appeared to be equally reactive based on the C=O stretch (**2a**: 1715, **2b**:1717, and **2c**: 1716 cm^{-1}), the difference in their regioselectivities mainly depended on steric bulkiness. In contrast, aromatic ketones such as acetophenone (**2d**) and benzophenone (**2e**), which are much bulkier than aliphatic ketones, resulted in selective generation of the linear product. The double bond character of **2d** (1686 cm^{-1}) and **2e** (1659 cm^{-1}) was lower than that of **2a** (1715 cm^{-1}) because of the conjugation effect from the aromatic ring. To exclude the steric factor of electrophiles, substituted acetophenones **2f**–**2h** were examined: electron-withdrawing substituents favored the formation of

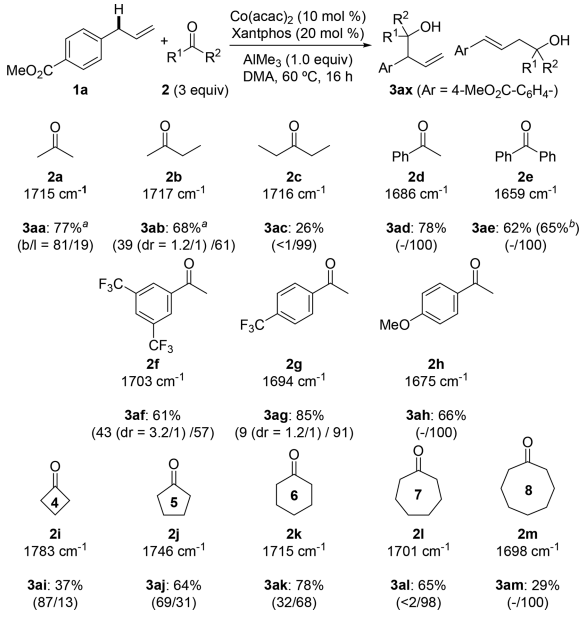


Figure 1. Substrate scope and limitations. Isolated yields are shown. [a]5 equiv of ketones was employed. [b]With 1 mmol of **1a**.

branched products, whereas electron-donating substituents selectively promoted linear addition. This trend was in accordance with the strength of the C=O bonds (**2f**: 1703, **2g**: 1694, and **2h**: 1675 cm^{-1}). In the case of cyclic ketones, the linear selectivity increased with an increase in the ring size. In these cases, as the strength of the C=O bond (**2i**: 1783; **2j**: 1746; **2k**: 1715; **2l**: 1701; **2m**: 1698 cm^{-1}) was reduced by ring expansion, the ratio of the linear product gradually increased. On the basis of the structural bulkiness and the C=O stretching of **2**, we concluded that sterically compact and/or reactive ketones (higher double bond character) such as acetone (**2a**), cyclobutanone (**2i**),

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and cyclopentanone (**2j**) were favored for branch selectivity, whereas sterically crowded ketones were favored for linear selectivity.

Next, several allylarenes were investigated using acetone (**2a**) and acetophenone (**2d**) (Figure 2). High branch selectivity was

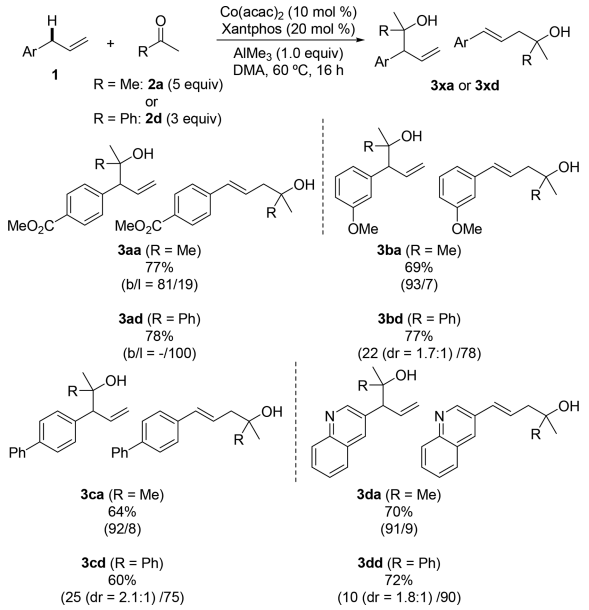
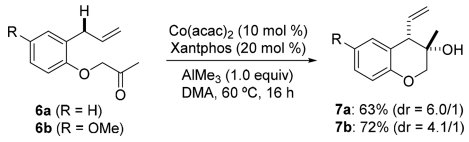


Figure 2. Substrate scope and limitations. Isolated yields are shown.

observed in the reaction of arylarenes **1a**, **1b**, **1c**, and **1d** with **2a**. Conversely, the reaction with **2d** led to a dramatic change in the regioselectivity to yield linear products predominantly, although the diastereoselectivities of **3bd**−**3dd** were not very high.

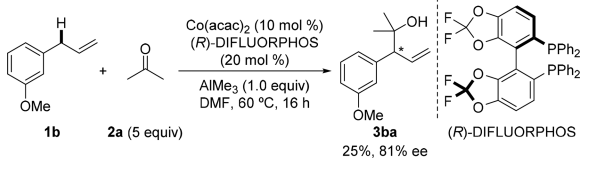
The C(sp^3)−H addition to ketones was expanded to an intramolecular variant using ketones **6a** and **6b**. Under the optimal conditions, cyclized products **7a** and **7b** were obtained in 63% and 72% yields, respectively, without generation of intermolecular products (Scheme 2). The structure of the major diastereomer was determined to be *syn* by NOE spectroscopy.[14]

Scheme 2. Intramolecular Cyclization



Finally, we conducted the reaction of **1b** with acetone (**2a**) in the presence of a chiral ligand (Scheme 3). Screening of several potential chiral ligands revealed that (*R*)-DIFLUORPHOS was the most promising in terms of enantioselectivity. Branched **3ba** was obtained in 25% yield, with 81% ee, in DMF without the

Scheme 3. Enantioselective Variant Using Chiral Ligands



generation of the linear isomer. Since enantioselective C−H activation is still limited,[15] there is much potential for further research in this direction. This result also suggested that the allylcobalt species bearing a diphosphine ligand, and not an allylaluminum species, was the actual intermediate for ketone addition.

A proposed mechanism for this reaction is depicted in Figure 3. First, a low-valent methylcobalt(I) species would be generated

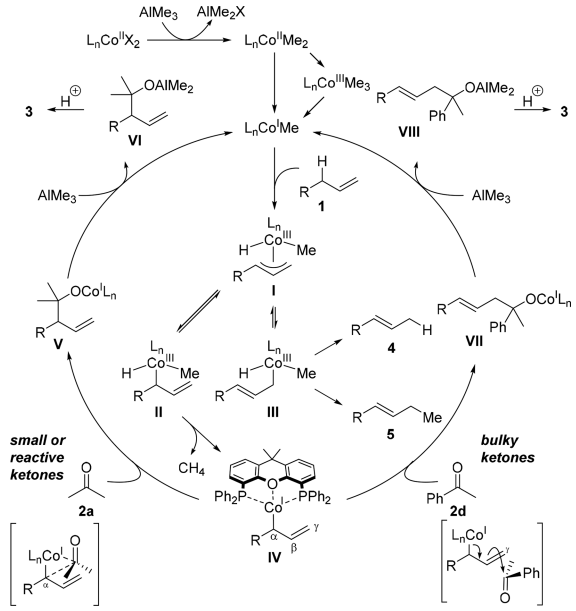


Figure 3. Plausible catalytic cycle.

from a cobalt salt and $AlMe_3$.[16] Dimethylcobalt(II) is known to undergo disproportionation to form methylcobalt(I) and trimethylcobalt(III),[17] and the latter is further reduced to methylcobalt(I) via reductive elimination. Next, the allylic C(sp^3)−H bond of an alkene is oxidatively added to methylcobalt(I) to generate intermediate **I**, which would be under equilibrium to generate **II** and **III**. Intermediate **II**, which can be stabilized by an aryl substituent,[18] would be further reduced to form low-valent η^1-allylcobalt(I) **IV** along with the release of methane. Subsequently, C−C bond formation with compact and/or reactive ketones would proceed preferentially at the α-position to produce cobalt alkoxide **V**.[19,20] Finally, **V** is transmetalated with $AlMe_3$ to afford aluminum alkoxide **VI** with regeneration of the methylcobalt(I) species. In contrast, when sterically demanded ketones are used, γ-addition[8,11−13] of **IV** is preferable due to steric repulsion between the ketone and the Xantphos ligand, affording cobalt alkoxide **VII**. Olefin isomerization product **4** and methylated product **5** would be generated through the reductive elimination of **III**. The oxygen atom in Xantphos plays a crucial role in coordinating to cobalt, which would assist the tautomerization of η^3-allylcobalt **I** to η^1-allylcobalt complex **II**.[21,22]

In conclusion, we have successfully developed the first cobalt-catalyzed nucleophilic addition of the C(sp^3)−H bonds of allylarene derivatives to ketones. We are now conducting computational studies to reveal the detailed mechanism for explaining the observed regioselectivity. Much effort toward the development of an asymmetric variant is also ongoing, and the results will be reported in due course.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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