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Cobalt(III)-Catalyzed Directed C−H Allylation

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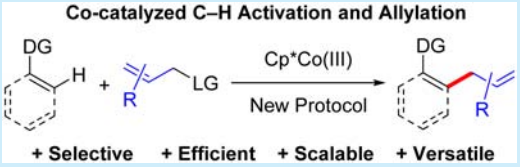
Supporting Information

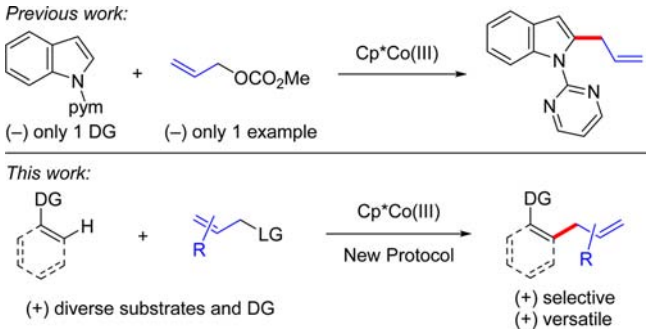
ABSTRACT: The cobalt(III)-catalyzed allylation was developed for amide-directed C−H activation of arenes, heteroarenes, and olefins. A variety of allyl sources can be employed to introduce this useful functional group.



The direct transformation of C−H bonds into useful functional groups offers great value added per step compared to conventional functional group interconversions. In this context, many effective methods have been developed, mainly using second- and third-row transition-metal catalyst systems, most notably palladium, rhodium, and ruthenium.[1] In contrast, the ability of the first-row transition metals to undergo C−H activation catalysis is just beginning to be explored. Their abundance, low price, and potentially novel reactivity motivate the research in catalysis using first-row transition-metal compounds.[2] Pioneered by the group of Matsunaga and Kanai, Cp*Co(III) complexes have been introduced as catalysts for directed C−H activation very recently and used to complement Cp*Rh(III) catalysis.[3]

The allyl moiety is an exceptionally versatile functional group, offering a wealth of opportunities for further functionalizations. In this context, allylarenes and 1,4-dienes (skipped dienes), which can be seen as allylated olefins, are interesting due to their synthetic value[4,5] and can be found in a number of biologically active molecules.[6] Allyl arenes and skipped dienes are traditionally prepared by rearrangements, electrophilic or nucleophilic substitutions, or cross-coupling reactions. These methods can suffer from competing formation of the conjugated double-bond isomers, harsh reaction conditions, and limited reaction scope and/or require syntheses of special, prefunctionalized substrates.[7] More recently, methods have been described for the direct allylation of aromatic C−H bonds using transition-metal catalysts.[8] We previously reported the use of a Cp*Co(III) catalyst for the direct functionalization of C−H bonds, including the allylation of *N*-pyrimidylindoles with allyl carbonates as reaction partners (Scheme 1).[3g,r,s] These allylation reactions proceeded with remarkable efficiency at room temperature, using only 0.5 mol % of the catalyst. With an even lower catalyst loading, we observed a turnover number (TON) of 2200. So far, both the high turnover number and the mild reaction conditions are unique for this catalyst. Intrigued by the exceptional reactivity of Cp*Co(III) in the allylation of pyrimidyl indoles, we aimed to achieve the allylation of more challenging (hetero)arenes and olefins, exploring other directing groups (DG), as well as other allyl reaction partners. Herein, we report the direct C−H allylation of (hetero)arylamides and acrylamides using Cp*Co(III) catalysis (Scheme 1).

Scheme 1. Cobalt(III)-Catalyzed C−H Allylation



We first pursued the introduction of substituted allyl moieties using a variety of allyl carbonates with pyrimidylindole **1** (Scheme 2). We found that substituents at the α-position of the allyl carbonate are generally tolerated, giving linear 2-allylindoles as mixtures of the *E*/*Z* isomers. Thus, excellent yields were obtained when alkyl-substituted allyl carbonates were used under equally mild conditions (**3a**−**c**). The more complex hexadienyl carbonate **2d** gave moderate yields with an increased catalyst loading and temperature. Cyclohexenyl carbonate **2e** and crotyl carbonate **2f** proved the applicability to terminally substituted allyl substrates, yielding the cyclohexenyl-substituted product **3e** and the branched product **3f**, respectively. Notably, no linear product **3b** was obtained from the reaction of **2f**. We also demonstrated the utility of a residue other than methyl on the carbonate, using *tert*-butyl hept-1-en-3-yl carbonate (**2c**-^{t}**Bu**). While the product yield was not affected by the change of the carbonate, the *E*/*Z* ratio was enhanced when using the *tert*-butyl rather than the methyl carbonate. Presumably, the conformation of the carbonate at the step of olefin insertion to the cobaltacycle intermediate determines the relative configuration of cobalt and carbonate in the following intermediate and thus the geometry of the resulting olefin. We showed the excellent scalability of this transformation in a gram scale reaction of **1** with **2a**. Employing 0.25 mol % of the convenient precatalyst $[Cp^*CoI_2]_2$, we obtained 98% (1.15 g) of **3a**.

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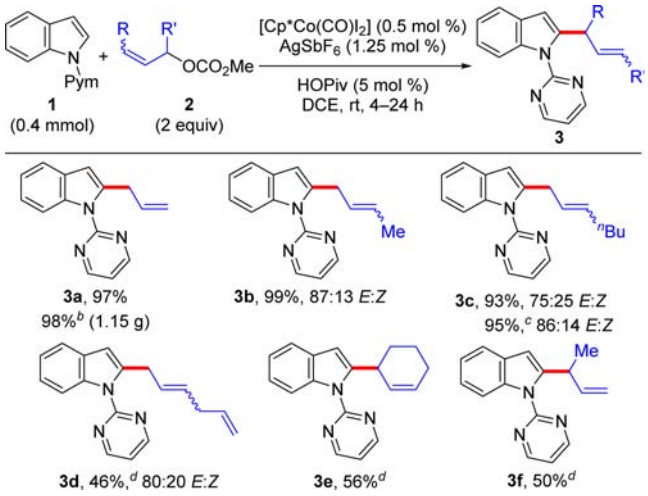
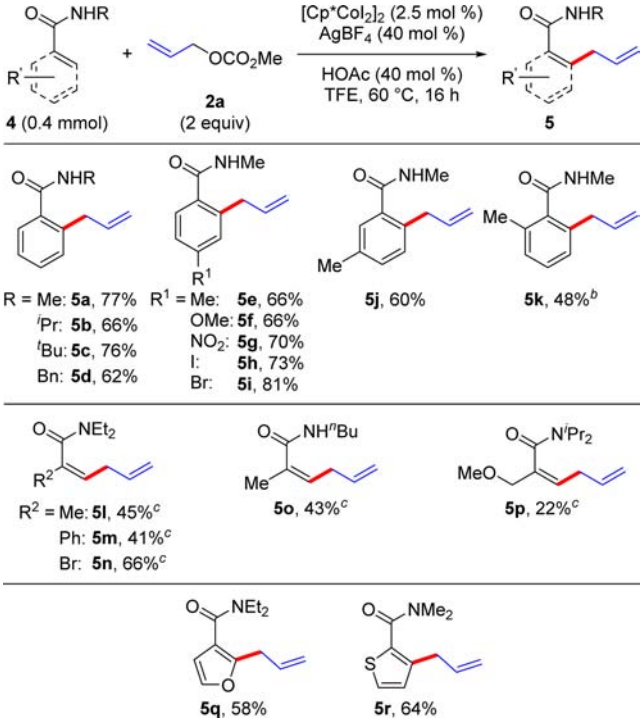
Scheme 2. Scope of Allyl Carbonates[a]



[a]Isolated yields are given. *E*/*Z* ratios were determined by ^{1}H NMR. For more detailed reaction conditions, see the Supporting Information. [b]5 mmol scale, 0.25 mol % of $[Cp^*CoI_2]_2$ was used. [c]*tert*-butyl hept-1-en-3-yl carbonate (**2c**-**^{t}Bu**) was used. [d]5 mol % of $[Cp^*Co(CO)I_2]$, 40 mol % of $AgSbF_6$, 20 mol % of HOPiv, 80 °C, 16 h.

Scheme 3. Scope of Aryl- and Alkenylamides[a]



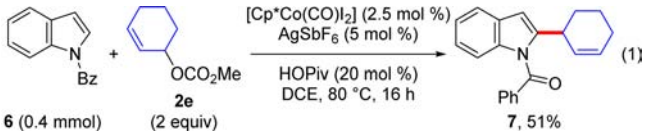
[a]Isolated yields are given. For more detailed reaction conditions, see the Supporting Information. [b]32 h. [c]110 °C.

Other heterocycles and benzamides can also be allylated using Cp*Co(III) catalysis, albeit not with the exceptional efficiency of the pyrimidylindoles. Increasing the catalyst loading to 5 mol % and the amount of additives to 40 mol %, as well as changing the solvent to 2,2,2-trifluoroethanol (TFE), gave the allylated benzamide **5a** in satisfactory yield. We found that $[Cp^*CoI_2]_2$ (2.5 mol %), $AgBF_4$, and HOAc are superior and convenient replacements for $[Cp^*Co(CO)I_2]$, $AgSbF_6$, and HOPiv, respectively. Under these conditions, benzamides are allylated in moderate to good yields, giving exclusively the γ-substituted allyl compounds (Scheme 3). Secondary alkyl- or benzylamides can be used as directing groups with similar utility (**5a**−**d**). Electron-donating (**5e**,**f**) and -withdrawing substituents (**5g**) are tolerated just as well as halides (**5h**,**i**). The effect of the position of a substituent was explored using *p*-, *m*-, and *o*-methylbenzamides **4e**, **4j**, and **4k**. We found that *meta*-substitution has only a slight detrimental effect on the transformation, leading to functionalization in the less hindered position *para* to the methyl group (**5j**). Even a substituent *ortho* to the directing group led to a reasonable conversion with only an increase of the reaction time (**5k**).

Considering the importance of skipped dienes and the scarcity of olefinic C−H activation using Cp*Co(III) catalysts, we next explored the direct C−H allylation of acrylamides (Scheme 3). When the reaction was carried out at elevated temperatures, the allylation was found to proceed with acceptable yields for 2-substituted secondary and tertiary acrylamides. Notably, besides alkyl and phenyl substituents (**5l**,**m**,**o**), bromo (**5n**) and methoxy (**5p**) groups were tolerated in the reaction as well.

Finally, we could demonstrate the applicability of the C−H allylation to other heteroarenes with amides as directing groups. Tertiary amides of furan and thiophene were allylated in satisfactory yields (**5q**,**r**) exclusively *ortho* to the directing group. As expected, in the case of the 3-amidofuran **4q**, functionalization occurred in the more reactive 2- instead of the 4-position.

We were interested in using other directing groups for the selective 2-allylation of indole. While *N*-acetyl, *N*-diethylcarbamoyl, and *N*-Boc indole failed to yield any desired reaction product, we finally found the first example of an acyl-directed C−H activation with the Cp*Co(III) catalyst when *N*-benzoylindole (**6**) was used, giving exclusively allylation at the 2-position of indole. Functionalization of the phenyl was not observed (eq 1).



Under the acidic conditions employed in the allylation reactions, the hypothetical $[Cp^*Co]^{2+}$ fragment should display a high Lewis acidity. Thus, we performed a number of control experiments to ascertain that a C−H metalation mechanism was operational, as opposed to a Lewis acid catalyzed electrophilic substitution (Table 1). When using other cobalt compounds such as Co(II) salts or $Co(acac)_3$, or even another strong Lewis acid such as $Sc(OTf)_3$, no reactivity was observed at all. The presence of a silver salt for the abstraction of iodide from the precatalyst was crucial, yet the Cp*Co complex introduced by the group of Ellman (see Table 1, entry 4)[3h] featuring very weakly coordinating perfluorophenyl borate counterions proved to be unsuitable for this reaction.

Further experiments were conducted to gain insight into the reaction mechanism (Scheme 4). The kinetic isotope effect was determined in parallel and competition experiments. While we observed a large KIE of 6.4 in the latter experiment, the parallel reactions resulted in a lower k_H/k_D of 2.0. The observed isotope effect is more pronounced than in previously reported mechanistic data for Cp*Co(III)-catalyzed C−H activation

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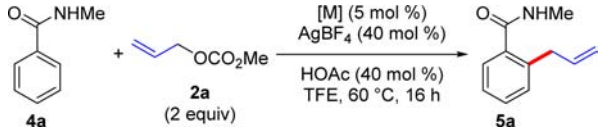
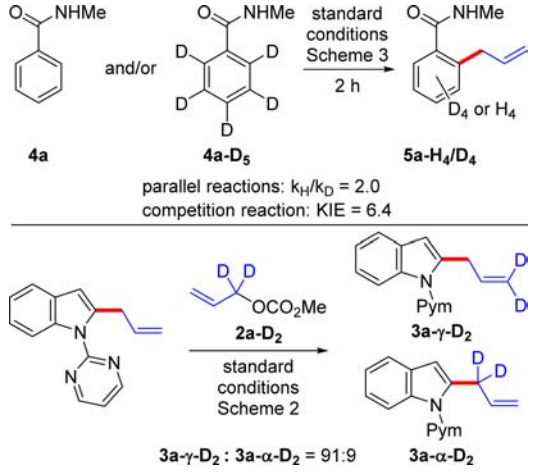
Table 1. Control Reactions



entry	[M] =	% yield[a]
1	$[Cp^*CoI_2]_2$[b] (standard conditions)	77
2	$[Cp^*CoI_2]_2$,[b] allylic alcohol instead of **2a**	20
3	$[Cp^*CoI_2]_2$[b,c]	0
4	$Cp^*Co(C_6H_6)[B(C_6F_5)_4]_2$[c]	0
5	none	0
6	$Co(acac)_3$	0
7	$Co(OAc)_2 \cdot H_2O$	0
8	$CoCl_2$	0
9	$Sc(OTf)_3$	0

[a]Determined by GC-FID. [b]2.5 mol % of $[Cp^*CoI_2]_2$. [c]No $AgBF_4$.

Scheme 4. Mechanistic Experiments

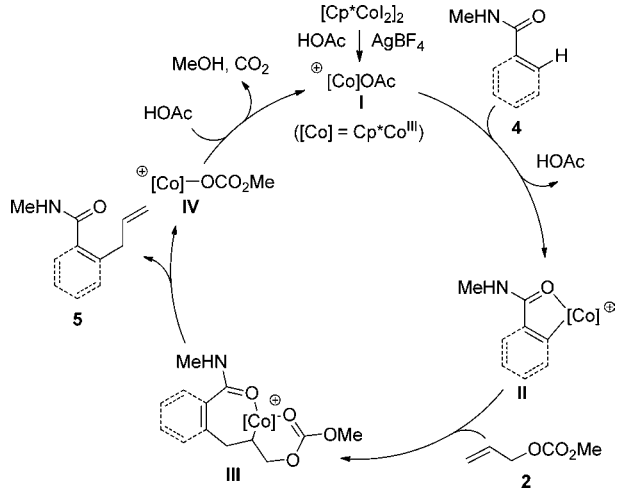


with phenylpyridine and -pyrazole.[3f,i,j,n,p] The values indicate that C−H activation likely occurs in the rate-limiting step of our transformation. H/D scrambling was observed when deuterated substrate **4a-D_5** was subjected to the standard reaction conditions in the absence of allyl carbonate, indicating the reversibility of the C−H activation process. While single regioisomers were obtained in the reactions using substituted allyl carbonates, a 91:9 mixture of α:γ deuterium substitution was observed in a reaction with γ-deuterated allyl carbonate **2a-D_2**. Considering the complete regioselectivity in the substituted products **3b−f**, the ability of allylic alcohol to serve as allyl transfer reagent (see Table 1, entry 2),[9] and a recent related mechanistic analysis of cobalt catalyzed allylation,[3s] we propose the mechanism shown in Scheme 5.

Formation of a catalytically active cobalt species **I** from the precursors is followed by C−H activation to cobaltacycle **II**. Olefin insertion leads to intermediate **III** that is stabilized by intramolecular coordination. In this geometry, β-hydride elimination is disfavored, and β-oxygen elimination leads to the allylated product. Yet, considering the observed deuterium distribution, we cannot rule out other pathways, possibly involving the formation of π-allyl species from the allyl precursors.

In conclusion, we have demonstrated the utility of the cobalt(III)-catalyzed C−H allylation. A variety of substituted allyl carbonates can be employed to introduce this useful

Scheme 5. Proposed Mechanism



functional group by means of directed C−H activation. Besides methyl carbonates, *tert*-butyl carbonates and even allylic alcohol can serve as allyl sources. This transformation can also be applied to substrates other than the privileged *N*-pyrimidylindoles, as the amide directing group proved to be versatile for the allylation of arenes and heteroarenes with low catalyst loadings. Notably, the use of acrylamides allows for the synthesis of skipped dienes. We showed the first example of an acyl directed C−H functionalization using the Cp*Co(III).

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, and copies of NMR spectra of new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01701.

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Notes

The authors declare no competing financial interest.

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(9) Likewise, the reaction of pyrimidyl indole **1a** with allylic alcohol gives full conversion to the allylated product **2a** using 5 mol% of $[Cp^*Co(CO)I_2]$.

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