Heterocycles

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Dehydrative Direct C–H Allylation with Allylic Alcohols under [Cp*Co^{III}] Catalysis**

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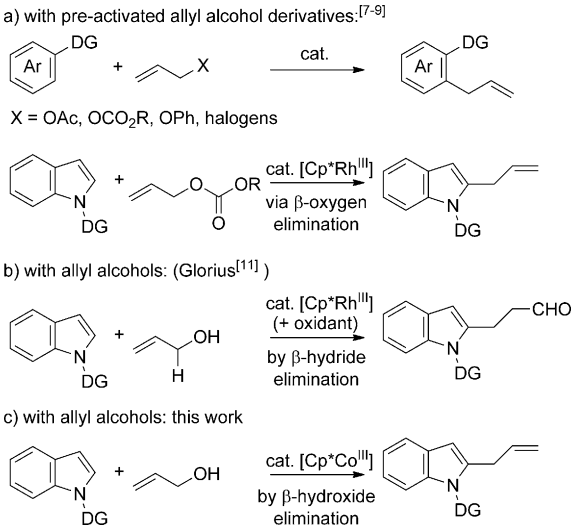
Abstract: *The unique reactivity of [Cp*Co^{III}] over [Cp*Rh^{III}] was demonstrated. A cationic [Cp*Co^{III}] catalyst promoted direct dehydrative C–H allylation with non-activated allyl alcohols, thus giving C2-allylated indoles, pyrrole, and phenylpyrazole in good yields, while analogous [Cp*Rh^{III}] catalysts were not effective. The high γ-selectivity and C2-selectivity indicated that the reaction proceeded by directing-group-assisted C–H metalation. DFT calculations suggested that the γ-selective substitution reaction proceeded by C–H metalation and insertion of a C–C double bond, with subsequent β-hydroxide elimination. The [Cp*Co^{III}] catalyst favored β-hydroxide elimination over β-hydride elimination.*

The allylation of arenes is one of the most fundamental and useful transformations in organic synthesis because allyl units can be easily manipulated to access various functionalized building blocks. In addition, isoprenylated arenes are ubiquitous structural motifs found in many biologically active natural products and pharmaceuticals.[1] Although cross-coupling reactions using prefunctionalized arenes[2] are powerful, allylation starting from a simple C–H bond of an arene[3] is more attractive in terms of atom-[4] and step-economy.[5] In this regard, the classical Friedel–Crafts allylation of arenes[6] is a straightforward approach, but problems such as low regioselectivity, over-allylation, and limited substrate scope, are often encountered. To overcome these limitations, transition-metal-catalyzed C–H allylation has been intensively studied over the last several years,[7–9] and various catalysts have been developed for a wide range of arenes. Among them, [Cp*Rh^{III}]-catalyzed allylation of arenes[7,10] under mild reaction conditions are particularly attractive, wherein the reaction is thought to proceed by insertion of a C–C double bond and subsequent β-oxygen elimination. As for the allylation reagents, however, preactivated allyl alcohol derivatives, such as allyl halides, carbonates, acetates, phosphates, and phenyl ethers, are still essential for transition-metal-catalyzed C–H allylation of arenes (Scheme 1 a).[7–9]



Scheme 1. a) C–H allylation with pre-activated reagents; b) C–H alkylation with allyl alcohols; c) C–H allylation with allyl alcohols. Cp* = C_5Me_5, DG = donating group.

We assume that the difficulty in using non-activated free allyl alcohols arises from an intrinsic preference for the β-hydride elimination pathway over the β-hydroxide elimination pathway. The C–H functionalization with allyl alcohols typically affords aldehydes via enol intermediates, as reported by Glorius, under [Cp*Rh^{III}] catalysis (Scheme 1 b).[11] To promote β-oxygen elimination towards allylated products, pre-activated allyl alcohols, such as allyl carbonates, which allow a favorable six-membered transition state, are required under [Cp*Rh^{III}] catalysis (indoles; Scheme 1 a).[7]

In 2013, as a part of our ongoing studies of first-row transition-metal catalysis,[12] we reported the utility of a cationic [Cp*Co^{III}]/arene complex as a less expensive alternative to [Cp*Rh^{III}].[13] Since then, we and others have attempted to broaden the scope of [Cp*Co^{III}] catalysis.[8,14,15] Most applications of [Cp*Co^{III}] complexes, however, are limited to

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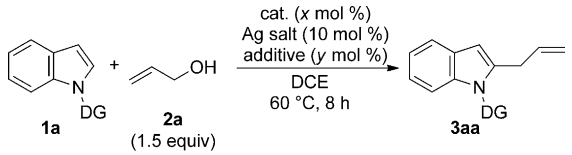
reactions similar to those developed with [Cp*Rh^{III}] complexes, except for the synthesis of pyrroloindolones by us[14b] and 6*H*-pyrido[2,1-*a*]isoquinolin-6-ones by Glorius and coworkers by utilizing the Lewis acidity of [Cp*Co^{III}].[15e] Our current research interest is in determining how the reactivity differs between [Cp*Co^{III}] and [Cp*Rh^{III}]. We hypothesized that cationic high-valent [Cp*Co^{III}] complexes are more oxophilic than [Cp*Rh^{III}] and other low-valent transition-metal complexes, and that [Cp*Co^{III}] would facilitate direct dehydrative C–H allylation with allyl alcohols through a β-hydroxide elimination pathway (Scheme 1c; this work), rather than a conventional β-hydride elimination pathway.

Optimization studies using *N*-pyrimidin-2-yl indole (**1a**) and allyl alcohol (**2a**) are summarized in Table 1. The first-generation cationic [Cp*Co^{III}]/arene complex, [Cp*Co(C$_6$H$_6$)](PF$_6$)$_2$, did not promote the desired allylation either with or without a base additive (entries 1 and 2). In contrast, a cationic [Cp*Co^{III}] catalyst generated in situ from readily available [Cp*Co(CO)I$_2$],[14c] AgPF$_6$, and AgOAc gave the C2-allylated adduct **3aa** in 88% yield (entry 3), whereas in the absence of AgPF$_6$ **3aa** was not obtained (entry 4). AgOTf was the best among the silver salts screened (entries 5–8), thus giving **3aa** in 97% yield. Other bases were not as effective as AgOAc (entry 8 versus entries 9–12). The amount of AgOAc was optimized (entries 13 and 14), with 10 mol% of AgOAc giving **3aa** in 99% yield upon isolation. No reaction proceeded in the absence of [Cp*Co^{III}] (entries 15 and 16). Other cobalt(II) and cobalt(III) salts (entries 17–20) did not afford **3aa**. To compare the catalytic activity of [Cp*Co^{III}] and [Cp*Rh^{III}] catalysts for allylation with allyl alcohol, several reaction conditions were examined (entries 21–25). Replacing [Cp*Co(CO)I$_2$] with [{Cp*RhCl$_2$}$_2$] afforded **3aa** in poor yield together with many byproducts (entry 14 versus 21). In the absence of AgOAc (entry 13 versus 22), **3aa** was not obtained under [Cp*Rh] catalysis. Other reaction conditions using AgSbF$_6$ with either bases or acids, which are often used in other C–H functionalization reactions,[10,11] also did not produce **3aa** (entries 23–25). Control experiments indicated that the cationic [Cp*Co^{III}] species was essential for selectively promoting C2-allylation with allyl alcohol (entries 15–25).

Table 1: Optimization studies and control experiments.[a]



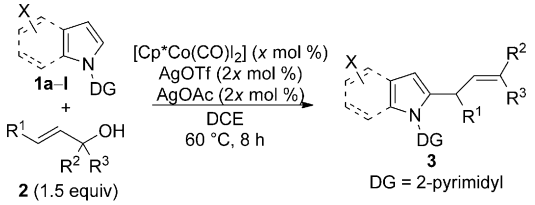
Entry	Cat. (mol%)	Ag salt	Additive (mol%)	Yield [%][b]
1	[Cp*Co(C$_6$H$_6$)](PF$_6$)$_2$ (5)	none	none	0
2	[Cp*Co(C$_6$H$_6$)](PF$_6$)$_2$ (5)	none	AgOAc (20)	0
3	[Cp*Co(CO)I$_2$] (5)	AgPF$_6$	AgOAc (20)	88
4	[Cp*Co(CO)I$_2$] (5)	none	AgOAc (20)	0
5	[Cp*Co(CO)I$_2$] (5)	AgSbF$_6$	AgOAc (20)	88
6	[Cp*Co(CO)I$_2$] (5)	AgBF$_4$	AgOAc (20)	88
7	[Cp*Co(CO)I$_2$] (5)	AgNTf$_2$	AgOAc (20)	83
8	[Cp*Co(CO)I$_2$] (5)	AgOTf	AgOAc (20)	97
9	[Cp*Co(CO)I$_2$] (5)	AgOTf	NaOAc (20)	80
10	[Cp*Co(CO)I$_2$] (5)	AgOTf	KOAc (20)	55
11	[Cp*Co(CO)I$_2$] (5)	AgOTf	CsOAc (20)	70
12	[Cp*Co(CO)I$_2$] (5)	AgOTf	Ag$_2$CO$_3$ (20)	92
13	[Cp*Co(CO)I$_2$] (5)	AgOTf	none	70
14	[Cp*Co(CO)I$_2$] (5)	AgOTf	AgOAc (10)	99[c]
15	none	AgOTf	AgOAc (10)	0
16	none	AgOTf	none	0
17	CoI$_2$ (5)	AgOTf	AgOAc (10)	0
18	Co(OAc)$_2$ (5)	AgOTf	none	0
19	[Co(acac)$_3$] (5)	AgOTf	AgOAc (10)	0
20	[Co(NH$_3$)$_6$Cl$_3$] (5)	AgOTf	AgOAc (10)	0
21	[{Cp*RhCl$_2$}$_2$] (2.5)	AgOTf	AgOAc (10)	31
22	[{Cp*RhCl$_2$}$_2$] (2.5)	AgOTf	none	0
23	[{Cp*RhCl$_2$}$_2$] (2.5)	AgSbF$_6$	AgOAc (10)	0
24	[{Cp*RhCl$_2$}$_2$] (2.5)	AgSbF$_6$	AgOPiv (10)	0
25	[{Cp*RhCl$_2$}$_2$] (2.5)	AgSbF$_6$	PivOH (10)	trace

[a] The reaction was performed in 0.10 mmol of **1a** and 0.15 mmol of **2a**. [b] Determined by ^{1}H NMR analysis with an internal standard. [c] Yield of **3aa** after purification by silica gel column chromatography. Piv = pivaloyl, Tf = trifluoromethanesulfonyl.

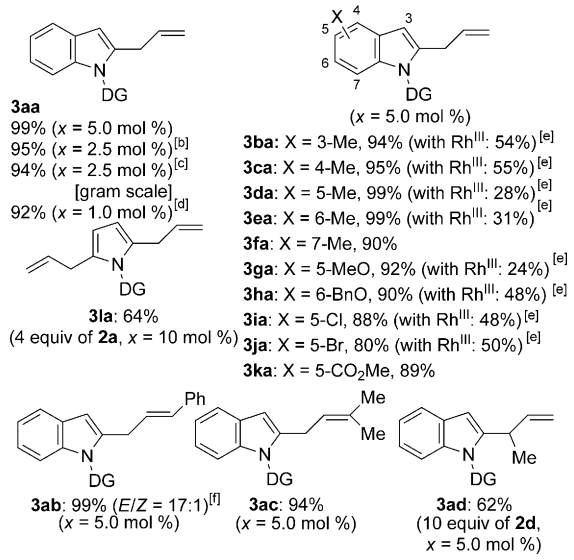
The scope of the allylation and trials to reduce catalyst loading are summarized in Table 2 and Scheme 2.[16] The reaction of **1a** with **2a** proceeded smoothly with 2.5 mol% of the [Cp*Co^{III}] catalyst, and 1.32 grams of **3aa** (94%) were obtained from the 6.0 mmol scale experiment.[17] Good yield (92%) of **3aa** was retained even with 1.0 mol% of the [Cp*Co^{III}] catalyst. The indoles **1b–f**, bearing a methyl substituent at either the 3-, 4-, 5-, 6-, or 7-position, gave the allylated products **3ba–fa** in 90–99% yield. Functionalized indoles bearing electron-donating (**1g**: MeO, **1h**: BnO) and electron-withdrawing groups (**1i**: Cl, **1j**: Br, **1k**: CO$_2$Me) also gave the products **3ga–ka** in 80–92% yield, thus showing good functional-group compatibility. The superior catalytic activity of [Cp*Co^{III}] catalysis over that of [Cp*Rh^{III}] catalysis was reconfirmed with several substrates (see results given within parentheses in Table 2). With the pyrrole **1l**, the double allylated product **3la** was obtained in 64% yield by using 4 mol equivalents of **2a**. As for the scope of allyl alcohols, the secondary alcohol **2b** selectively afforded the γ-substituted product **3ab** with *E*/*Z* = 17:1 in 99% yield. The reaction with the tertiary alcohol **2c** also proceeded with γ-selectivity, and the isoprenylated **3ac** was obtained in 94% yield. Furthermore, the methyl-substituted primary allyl alcohol **2d** reacted predominantly at the sterically more hindered γ-position to give **3ad** in 62% yield, thus indicating that reaction pathways via an allylic cationic intermediate or a π-allyl metal intermediate are less likely. From the results in Table 2, undesired isomerization of C–C double bonds was not observed under the present reaction conditions. As to the arene scope, not only electron-rich indoles and pyrrole, but also another arene was applicable. As shown in Scheme 2, C–H allylation of **1m**, bearing a pyrazole directing group, proceeded smoothly to give **3ma** in 79% yield.

The observed C2-selectivity and γ-selectivity indicates that the present reaction proceeded by directing-group-assisted C–H metalation, rather than a Friedel–Crafts-type pathway via either an allylic cationic intermediate or a π-allyl metal intermediate.[6] DFT calculations, at the B3LYP-D3//B3LYP level of theory, of a model [CpCo^{III}] catalyst lacking

Table 2: Substrate scope of [Cp*Co^{III}]-catalyzed C–H allylation with allyl alcohols.[a]



2a: R^1, R^2,R^3 = H; **2b**: R^1, R^3 = H, R^2 = Ph
2c: R^1 = H, R^2, R^3 = Me; **2d**: R^1= Me, R^2, R^3 = H



[a] The reactions were run with 0.10 mmol of **1** and 1.5 equiv of **2** unless otherwise noted. Yields of isolated **3** after purification by silica gel column chromatography are listed. [b] Used 0.20 mmol of **1a**. [c] Used 6.0 mmol of **1a**, and 1.32 g of **3aa** was obtained. [d] Used 0.50 mmol of **1a**. [e] Number within parentheses was obtained using [{Cp*RhCl$_2$}$_2$] (2.5 mol%) instead of [Cp*Co(CO)I$_2$] (see, entry 21 of Table 1; yield determined by ^{1}H NMR spectroscopy with an internal standard). [f] *E*/*Z* ratio was determined by ^{1}H NMR analysis of the crude reaction mixture.

Scheme 2. [Cp*Co^{III}]-catalyzed C–H allylation of 1-phenyl-pyrazole.

the pentamethyl units suggested that the S_N2' concerted substitution mechanism is unfavorable, and that insertion of the C–C double bond with a subsequent β-oxygen elimination is more favorable. The β-hydroxide elimination pathway was found to be 2.4 kcal mol^{-1} more favorable than the β-hydride elimination pathway, thus supporting the experimental results (see Figure S1 and Figure S2 in the Supporting Information for details on DFT calculation).

A plausible catalytic cycle is shown in Figure 1. Initial halide abstraction from [Cp*Co(CO)I$_2$] by AgOTf in the presence of AgOAc would form a neutral [Cp*Co^{III}(OAc)$_2$] complex, which would be the resting complex. Based on our

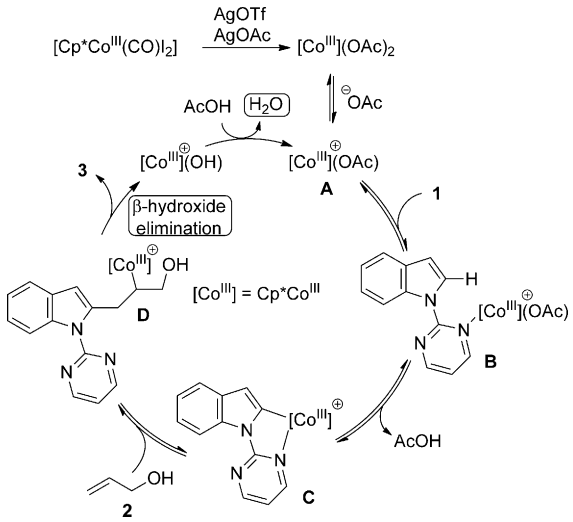


Figure 1. Plausible catalytic cycle of dehydrative direct C–H allylation with non-activated free allyl alcohols via β-hydroxide elimination.

previous mechanistic studies,[14b] we speculate that the monocationic [Cp*Co^{III}(OAc)]$^+$ (**A**) would be a catalytically active species. A C–H bond metalation (from **B** to **C**) would proceed by concerted metalation-deprotonation (CMD)[18] assisted by the acetate ion or electrophilic aromatic substitution mechanism. Insertion of the C–C double bond would proceed by direction of the hydroxy group (**D**), followed by a key β-hydroxide elimination, thus affording the product **3** and a [Cp*Co^{III}(OH)] species. The active catalyst (**A**) would be regenerated by reaction with acetic acid.

In conclusion, we demonstrated the unique reactivity of a [Cp*Co^{III}] catalyst compared with analogous [Cp*Rh^{III}] catalysts. The [Cp*Co] catalyst favored β-hydroxide elimination rather than β-hydride elimination. Thus, allyl alcohols were successfully used directly as substrates for dehydrative C–H allylation of indoles, pyrrole, and 1-phenyl-pyrazole. Allylated products were obtained with high γ-selectivity in 62–99% yield, and good turnover numbers, of up to 92, were observed. Further studies to broaden the scope with respect to the arenes as well as other unique applications of [Cp*Co^{III}] catalysts are ongoing in our laboratory.

Keywords: C–H activation · cobalt · heterocycles · homogeneous catalysis · transition metals

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