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# Co(III)-Catalyzed [4 + 1] Annulation of Amides with Allenes via C–H Activation

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**Abstract.** A Co(III)-catalyzed [4 + 1] annulation of amides with allenes to synthesize isoindolone and 1,5-dihydro-pyrrol-2-one derivatives is reported. A wide range of aromatic and vinylic amides react with allenes to give the corresponding annulation products in good to excellent yields. The mechanistic studies strongly support that the catalytic reaction proceeds through an amide-directed C–H activation, followed by carbocobaltation of allene,  $\beta$ -hydride elimination, and an intramolecular 1,2-hydroamination.

**Keywords:** Cobalt; Allenes; Annulation; Amides; C–H Activation

The metal-catalyzed annulation reactions are one of the efficient approaches in organic synthesis because it provides straightforward method for the synthesis of cyclic products from easily accessible substrates in a rapid manner.<sup>[11]</sup> In particular, the reactions through C– H activation<sup>[2,3,4]</sup> offer an atom- and step-economical process<sup>[5]</sup> to construct complex organic molecules,<sup>[6]</sup> which has a number of applications in the synthesis of natural products, bioactive molecules, and materials.<sup>[7]</sup>

Amide is a versatile directing group in C-H functionalization to access *N*-heterocyclic compounds.<sup>[8]</sup> Similar to alkynes and alkenes, allenes<sup>[9]</sup> also underwent diverse reactions including annulation,<sup>[10a-g]</sup> allylation,<sup>[10h-j]</sup> allenylation,<sup>[10k,I]</sup> and dienylation<sup>[10m,n]</sup> with amides (Scheme 1a).<sup>[2d]</sup> However, due to the presence of orthogonal cumulative carboncarbon double bonds, allenes showed distinct reactivity from alkynes and alkenes.<sup>[11]</sup> In 2016, Lu et al reported a Rh(III)-catalyzed oxidative annulation of amides with allenes to afford  $\gamma$ - lactams.<sup>[10a]</sup> The reaction is limited to allenes bearing a hydroxyl group. The coordination of hydroxyl group to the rhodium center might be the key for the regioselectivity of the allenes (Scheme 1b).

Recently, earth-abundant first-row transition metal catalysts<sup>[3,4]</sup> have emerged as an economical alternative to precious metals. As a first-row metal, cobalt showed its unique reactivity in C–H functionalization.<sup>[4]</sup> Specifically, the reaction with allenes showed different reactivity including

hydroarylation and annulation from the three reactive carbons of allene.<sup>[10e-g,12]</sup> With this background and our continued progress in C–H functionalization,<sup>[12d-e,13]</sup> we are highly interested in developing an economical method for annulation of amides with allenes using CoCp\* catalyst system. Herein, we report a Co(III)catalyzed [4 + 1] annulation of amides with allenes to give isoindolinones and 1,5-dihydropyrrol-2-one, where allene acts as a one-carbon source.<sup>[12d,14]</sup> Isoindolinone and pyrrolone motifs have been found in many natural products and bioactive compounds.<sup>[15,16]</sup>



Scheme 1. C-H functionalization of amides with allenes.

The reaction of benzamide **1a** and allene **2a** was examined in the presence of Cp\*Co(CO)I<sub>2</sub> unde. oxidative reaction conditions (Table 1, entries 1–18). From these studies, we found the optimization conditions consisting of 10 mol% Cp\*Co(CO)I<sub>2</sub>, 20 mol% AgSbF<sub>6</sub>, 20 mol% Mn(OAc)<sub>3</sub>· 2H<sub>2</sub>O, and 1.0 equiv Ag<sub>2</sub>O in 1,2-dichloroethane (DCE) at 110 °C for 15 h (Table 1, entry 9), which gave the highest yield (87%) of annulation product **3aa**. The additive AgSbF<sub>6</sub> is essential for the success of the reaction (Table 1, entry 16); the possible role of this salt is to quickly remove the iodide from Cp\*Co(CO)I<sub>2</sub> to provide vacant sites for catalysis. In addition, a catalytic amount of acetate source plays a vital role in enhancing the reaction yield (Table 1, entry 17). These results show that a high concentration of acetate ion would suppress the coordination of substrates to the cobalt (Table 1, entries 1, 3, 5, and 6), however, a catalytic amount of acetate ion is necessary to abstract the proton in the C–H activation step. Thus, the barely soluble Ag<sub>2</sub>O or Ag<sub>2</sub>CO<sub>3</sub> acts as better oxidants, which might neutralize the AcOH produced during the reaction to maintain a low concentration of OAc<sup>-</sup> in the catalytic solution. It is noteworthy that the reaction in the presence of RhCp\* catalyst gave **3aa** in 61% yield (see supporting information), which was unsuccessful in the Lu's reaction conditions.<sup>[10a]</sup>

**Table 1.** Optimization studies<sup>[a,b]</sup>

1:		Cp*Co(CO)I <sub>2</sub> Additive 1 (2 Additive 2 (2 Oxidant (X DCE, 110	(10 mol%) 0 mol%) (0 mol%) c, 15 h 3aa	- Ph
Entry	Additive 1	Additive 2	Oxidant	Yield (%)
1 <sup>[c]</sup>		AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	0
2 <sup>[c]</sup>		AgSbF <sub>6</sub>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	trace
3 <sup>[c]</sup>	Mn(OAc) <sub>2</sub>	AgSbF <sub>6</sub>	CuO	31
4 <sup>[c]</sup>		AgSbF <sub>6</sub>	Mn(OAc) <sub>2</sub>	11
5	Mn(OAc) <sub>2</sub>	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	70
6 <sup>[c]</sup>		AgSbF <sub>6</sub>	AgOAc	37
7	Mn(OAc) <sub>2</sub>	AgSbF <sub>6</sub>	$Ag_2CO_3$	65
8	Cu(OAc) <sub>2</sub>	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	77
9	$Mn(OAc)_3 \cdot 2H_2O$	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	87
10	Fe(OAc) <sub>2</sub>	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	65
11	NaOAc	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	24
12	AcOH	AgSbF <sub>6</sub>	Ag <sub>2</sub> O	63
13	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	AgOTf	Ag <sub>2</sub> O	16
14	$Mn(OAc)_3 \cdot 2H_2O$	AgPF <sub>6</sub>	Ag <sub>2</sub> O	15
15	$Mn(OAc)_3 \cdot 2H_2O$	NaSbF <sub>6</sub>	Ag <sub>2</sub> O	0
16	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O		Ag <sub>2</sub> O	0
17		AgSbF <sub>6</sub>	Ag <sub>2</sub> O	20
18 <sup>[d]</sup>	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	$AgSbF_6$	$O_2$	30

<sup>[a]</sup> Unless otherwise mentioned, all reactions were carried out using **1a** (0.18 mmol), **2a** (0.27 mmol), Cp\*Co(CO)I<sub>2</sub> (0.018 mmol, 10 mol%), additive 1 (0.036 mmol), additive 2 (0.036 mmol), oxidant (0.18 mmol) and DCE (2.5 mL) at 110 °C for 15 h under N<sub>2</sub>. <sup>[b]</sup> Yields were determined by the <sup>1</sup>H NMR integration method. <sup>[c]</sup> Oxidant (0.36 mmol). <sup>d</sup>Reaction at 80 °C under O<sub>2</sub> balloon.

With the optimized reaction conditions, we investigated the scope of different amides 1 with benzyl allene 2a (Scheme 2). Thus, the reaction of unsubstituted amide 1b with 2a afforded the annulation product 3ba in 81% yield. Likewise, electron-donating, halogen, and electron-withdrawing group substituted benzamides 1c-g proceeded

smoothly under the optimized reaction conditions to give products 3ca-ga in good to excellent yields. o-Substituted substrates 1h-j reacted well with allene 2a, to provide the corresponding products **3ha-ja** in good yields. In the reactions of 3-methyl and 3,4-dimethoxy substituted benzamides 1k-l, the C-H activation highly favored the less-hindered ortho position of amides to give products 3ka and 3la, respectively. It is mentioning that electron-rich worth 23dimethoxybenzamide 1m and thiophene containing amide **1n** went well with the reaction conditions, affording products **3ma-na** in 80 and 63% yields, respectively. Different N-substituted benzamides 10-p also involved in the reaction, however, N-methyl benzamide was the best one. The present reaction was not limited to aromatic amides; it was also viable with vinylamide 1q to provide annulation product 3qa, albeit in lower yield. Furthermore, the structures of 3ia, 3ka, and 3la were unambiguously confirmed by X-ray crystallographic analysis.<sup>[17]</sup>



Scheme 2. Co(III)-Catalyzed Coupling of Amides 1 with Allene 2a. Standard reaction conditions: 1 (0.30 mmol), 2a (0.45 mmol), Cp\*Co(CO)I<sub>2</sub> (0.030 mmol), AgSbF<sub>6</sub> (0.060 mmol), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.060 mmol), Ag<sub>2</sub>O (0.30 mmol), and DCE (4.0 mL) at 110 °C for 15 h under N<sub>2</sub>; Isolated yields.

Next, we examined the scope of allenes for the catalytic reaction. A variety of allenes **2b-1** with benzamide **1a** were tested (Scheme 3). The reaction of benzamide **1a** with *ortho-*, *meta-*, and *para-*substituted benzylallenes **2b-g** proceeded efficiently under the optimized reaction conditions, to afford the desired products **3ab-ag** in 68-87% yields. Likewise, 1-naphthylmethyl allene **2h** also furnished product **3ah** in good yield. The use of long chain aryl and alkyl allenes **2i-j** with **1a** provided the annulation products **3ai-aj** in 61% and 45% yields, respectively. 1,3-Disubstituted cyclic allene **2k** was transformed into the

desired spiro compound 3ak, albeit in 39% yield. Unsymmetrical 1,3-disubstituted allene 2l also underwent annulation reaction with 1a to form regioisomeric products, **3al+3al'**, in a 2:1 ratio. Finally, electron-poor benzamides 1g was tested with allenes 2b and 2g to give products 3gb and 3gg. These results show that the catalytic reaction highly favors electronpoor benzamides and allenes. Moreover, a concerted metallation-deprotonation mechanism is operative in C-H activation step.<sup>[18]</sup> However, the present reaction failed to afford the desired annulation products with 1,1-disubstituted and simple aliphatic allenes containing ester, silyl, and hydroxyl group. It is noteworthy that hydroxymethylallene does not undergo annulation with benzamide 1a, in contrast to RhCp\*-catalyzed the oxidative annulation reaction.[10a]



**Scheme 3.** Co(III)-catalyzed coupling of amide **1a** with allenes **2**. The reaction conditions are similar to that in Scheme 2 footnote. <sup>[a]</sup> Reaction with **2** (0.60 mmol).

In addition, phenylallene **2m** was also subjected to the annulation conditions (Scheme 4). The reaction gave [4 + 2] annulation product **4am** in 30% yield,<sup>[10e]</sup> along with other unidentified products. Although a number of conditions had been tested, we failed to improve the yield of product **4am**.



Scheme 4. Co(III)-catalyzed [4 + 2] annulation of amide 1a with phenylallene 2m.

In order to gain insight into the mechanism of this cobalt-catalyzed oxidative annulation of amides with allenes, a series of isotope-labeling experiments were conducted (Scheme 5). Thus, heating penta-deuterated benzamide [D<sub>5</sub>]-1b without 2a under standard reaction conditions gave 1b with 50% D/H exchange at the ortho position of amide (Scheme 5a), whereas the reaction of [D<sub>5</sub>]-1b with 2a gave the annulation product [D<sub>5</sub>]-3ba in 80% yield with a trace of D/H exchange. These results indicate that the C-H activation step becomes irreversible in the presence of allene likely due to the faster allene insertion than protonation of C-cobalt bond. Next, the competitive and parallel experiments of [D<sub>5</sub>]-1b with 2a provided an intermolecular kinetic isotopic effect (KIE) of 3.5 and 1.9, respectively (Scheme 5b). Similarly, the reaction of  $[D_1]$ -1b with 2a gave an intramolecular KIE of 3.2 (Scheme 5c). These results clearly evidence that the C-H bond cleavage is the rate-limiting step. Moreover,  $[D_7]$ -2a was subjected to the annulation reaction with 1b for 1 h, giving [D7]-3ba in 30% yield where a benzylic deuterium was completely transferred to the methyl group in  $[D_7]$ -3ba (Scheme 5d). This result is in agreement with the proposed mechanistic steps (III-V) in Scheme 6.



Scheme 5. Mechanistic studies.

Based on our preliminary mechanistic studies and precedent, [10a, m, n, 12e, 14c, 19] literature plausible а mechanism for cobalt-catalyzed [4 + 1] annulation of benzamides with allenes is depicted in Scheme 6. The reaction starts with the formation of active cobalt species **I** from  $CoCp^*(CO)I_2$ , AgSbF<sub>6</sub>, and  $Mn(OAc)_3 \cdot 2H_2O$ . Coordination of amide **1b** with **I** and C–H cobaltation give five-membered ortho cobaltacycle II. Then, insertion of allene 2a, followed by  $\beta$ -hydride elimination delivers intermediate IV. The Co–H in **IV** inserts into the diene moiety to form **V**, which then undergoes reductive elimination to give product **3ba**. The cobalt(I) species generated from the catalytic cycle is reoxidized by Ag<sub>2</sub>O to give active cobalt(III) catalyst I.



Scheme 6. Plausible catalytic cycle.

In conclusion, we have demonstrated a first-row transition metal Co(III)-catalyzed oxidative annulation of amides with allenes to form isoindolinones and 1,5-dihydro-pyrrol-2-one. The reaction tolerated different amides and allenes. The mechanistic studies strongly indicate that the reaction proceeds through C–H activation, diene formation, and an intramolecular 1,2-hydroamination. Further studies on the reactivity of allenes with different arenes in the presence of first-row metal catalysts are underway.

#### **Experimental Section**

**General procedure for the synthesis of 3**: To a sealed tube, *N*-methyl benzamides **1** (0.30 mmol), allenes **2** (0.45 mmol), CoCp\*(CO)I<sub>2</sub> (0.030 mmol), Ag<sub>2</sub>O (0.30 mmol), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.060 mmol) and AgSbF<sub>6</sub> (0.060 mmol) were added inside a glove box and the tube was sealed with a rubber septum. DCE (4.0 mL) was added to the sealed tube via syringe and the reaction mixture was allowed to stir at 110 °C for 15 h. Then, the reaction mixture was cooled and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The reaction mixture was filtered through a celite pad and the celite pad washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using *n*-hexane/ethyl acetate (50% EA) as eluent to afford the desired pure product **3**. Benzamides **1a-q**, [D<sub>1</sub>]-**1b**, [D<sub>5</sub>]-**1b**<sup>[20a,b]</sup> and allenes<sup>[12e,20c]</sup> were synthesized according to literature procedures.

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