

Comparative Catalytic Activity of Group 9 [Cp*^{III}M] Complexes: Cobalt-Catalyzed C–H Amidation of Arenes with Dioxazolones as Amidating Reagents

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Abstract: A procedure for the [Cp*Co^{III}]-catalyzed direct C–H amidation of arenes with dioxazolone has been developed. This reaction proceeds under straightforward and mild conditions with a broad range of substrates, including anilides. A comparative study on the catalytic activity of Group 9 [(Cp*)₂MCl₂]₂ complexes revealed the unique efficiency of the cobalt catalyst.

Transition-metal-catalyzed C–H bond functionalization has emerged as a powerful synthetic strategy.^[1] This approach does not require prefunctionalized starting materials that have to be prepared in separate steps. Consequently, a diverse range of transition-metal catalytic systems has been developed for such transformations, including Pd,^[2] Rh,^[3] Ru,^[4] and Ir catalysts.^[5] Rh^{III} and Ir^{III} species with a 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) ligand have been widely used for various C–X bond-forming reactions. Despite their promising catalytic activity, earth-abundant first-row metals have not been investigated as thoroughly for such reactions.^[6] Since pioneering studies by Kanai and co-workers on the use of a [Cp*Co^{III}] catalyst for C–H activation,^[7] a handful of cobalt(III)-catalyzed reactions for direct functionalization have been developed with high synthetic potential.^[8,9] However, the [Cp*Co^{III}] system generally operates under harsh reaction conditions and shows narrow substrate scope as compared to its Rh and Ir counterparts. For example, it functions best with substrates bearing 2-pyridyl and analogous azacyclic directing groups, whereas other types of coordinating groups are less effective. Indeed, only a few examples of functionalization for substrates bearing moderate to weak directing groups, such as benzamide, have been reported.^[8b,f] For direct C–H amidation, which has been the focus of extensive recent research, the [Cp*Co^{III}] system is effective only with 2-phenylpyridine and its pyrimidylindole derivatives.^[7b,10]

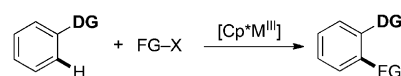
Recently, we reported a rhodium(III)-catalyzed C–H amidation protocol with dioxazolones as robust and highly efficient amidating reagents.^[11] Dioxazolones,^[12] while safe

and easy to handle, display higher coordination affinity toward the metal center of metallacyclic intermediates as compared to organic azides, which were utilized as a representative type of amidating reagent.^[3a,13] We fully elucidated this influence of binding affinity on the resultant reactivity in the [Cp*Rh^{III}]-catalyzed C–H amidation.

Along this line, we planned to take advantage of the intrinsically high coordination ability of dioxazolones to enable the development of a cobalt system that may have additional merit from a practical point of view. Described herein is the result of this research effort and a comparative reactivity study of the Group 9 triad [Cp*^{III}M, M = Co, Rh, and Ir], which revealed the highest catalytic activity for a cobalt system in the C–H amidation with a dioxazolone amidating reagent (Scheme 1).

To examine whether a [Cp*Co^{III}] system showed catalytic reactivity in C–H amidation reactions with 1,4,2-dioxazol-5-one (**2a**), we selected pivalanilide (**1a**) as a model substrate (Table 1; see the Supporting Information for details). Whereas no conversion was observed at room temperature (Table 1, entry 1), the desired product **3a** was obtained in high yield at 40 °C (entry 2). However, the product yield was lower at higher temperature (Table 1, entries 3 and 4); the decrease in yield was attributed to the formation of bisamidated by-products.^[14] Lowering of the catalyst loading led to a slight decrease in the product yield (Table 1, entry 5), but an increase in the reaction time provided the product in satisfactory yield, even with 1 mol % of the catalyst precursor [(Cp*CoCl₂)₂] in the presence of 4 mol % of AgSbF₆ (entry 6).

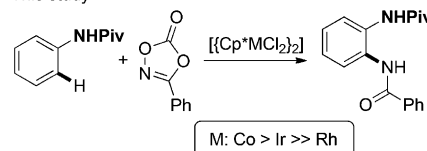
Previous study



M = Ir, Rh: broad scope
mild conditions
high catalytic activity

M = Co: limited scope
most effective for N-chelators
harsh conditions

This study



cobalt-catalyzed C–H amidation
low catalyst loading
dioxazolones as amidating reagents
broad scope and mild conditions

Scheme 1. Direct C–H bond functionalization with [Cp*^{III}M] systems.

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Table 1: Optimization of the cobalt-catalyzed C–H amidation.^[a]

Reaction scheme showing the C-H amidation of anilide **1a** with 1,4,2-dioxazol-5-one **2a** to form product **3a**. The reaction is catalyzed by a catalyst in $\text{ClCH}_2\text{CH}_2\text{Cl}$.

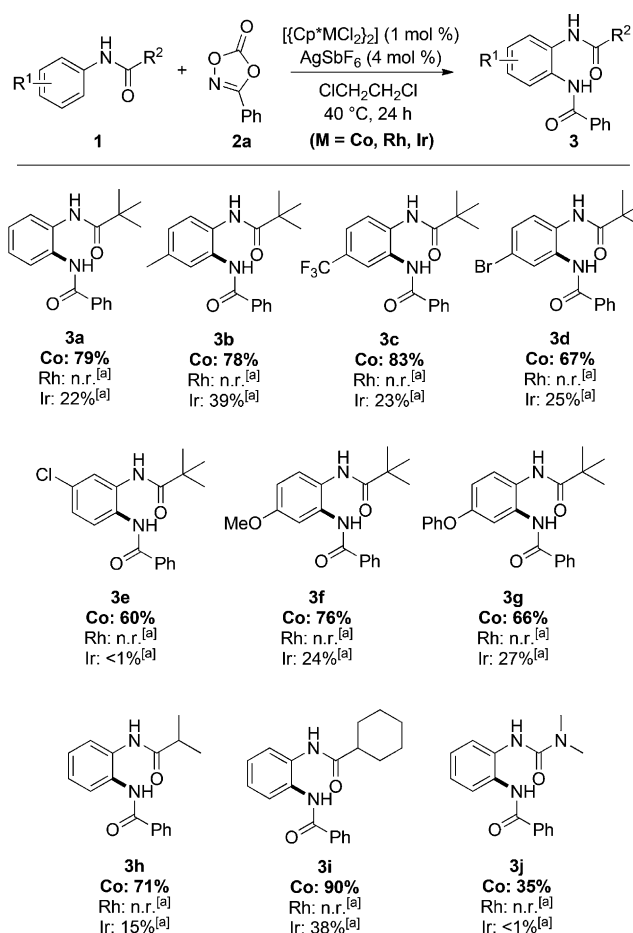
Entry	Catalyst (mol%)	<i>T</i> [°C]	<i>t</i> [h]	Yield [%] ^[b,c]
1	[(Cp*CoCl ₂) ₂] (5)/AgSbF ₆ (20)	RT	12	n.r. ^[d]
2	[(Cp*CoCl ₂) ₂] (5)/AgSbF ₆ (20)	40	12	71
3	[(Cp*CoCl ₂) ₂] (5)/AgSbF ₆ (20)	60	12	64
4	[(Cp*CoCl ₂) ₂] (5)/AgSbF ₆ (20)	80	12	60
5	[(Cp*CoCl ₂) ₂] (2.5)/AgSbF ₆ (10)	40	12	66
6	[(Cp*CoCl ₂) ₂] (1)/AgSbF ₆ (4)	40	24	83 (79)
7	[(Cp*CoCl ₂) ₂] (1)/AgOAc (4)	40	24	n.r. ^[d]
8	CoCl ₂ (2)/AgSbF ₆ (4)	40	24	n.r. ^[d]
9	[(Cp*CoCl ₂) ₂] (1)	40	24	n.r. ^[d]
10	AgSbF ₆ (4)	40	24	n.r. ^[d]
11	[(Cp*RhCl ₂) ₂] (2.5)/AgSbF ₆ (10)	80	24	n.r. ^[d]
12	[(Cp*IrCl ₂) ₂] (2.5)/AgSbF ₆ (10)	80	24	30

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.1 equiv), 1,2-dichloroethane (0.5 mL). [b] The yield was determined by NMR spectroscopy of the crude reaction mixture with dibromomethane as an internal standard. [c] The yield of the isolated product is given in parentheses. [d] n.r. = no reaction.

None of the desired product was formed when other silver salts, such as AgOAc or AgPF₆, were used in place of AgSbF₆ (Table 1, entry 7). CoCl₂ was totally ineffective, and [(Cp*CoCl₂)₂] or the Ag salt alone also did not display any reactivity (Table 1, entries 8–10), thus indicating that the cationic [Cp*Co^{III}] species is essential for the present amidation reaction with 1,4,2-dioxazol-5-ones. Interestingly, other Group 9 metal analogues of the type [Cp*M^{III}] (M = Rh and Ir) were much less effective, even at a higher catalyst loading and higher temperatures (Table 1, entries 11 and 12).

Under the optimized conditions with the cobalt catalyst, the scope of the C–H amidation with 1,4,2-dioxazol-5-one **2a** was subsequently evaluated in terms of the substituents on the substrate (Scheme 2). Electronic variation of the anilide aromatic ring barely affected the reaction efficiency, and the desired amidated products **3b–g** were obtained in satisfactory yield. Trifluoromethyl, bromo, and chloro groups were compatible with the present conditions (products **3c–e**). The reaction is regioselective in that the amidation took place at the sterically less hindered site of a *meta*-substituted anilide to give product **3e**. Alteration of the *N*-acyl moiety of the anilide substrate was also found to be feasible. For example, the amidation of anilides bearing an isopropyl or a cyclohexyl group proceeded to give products **3h** and **3i**, respectively, in high yield. Interestingly, the C–H amidation of *N*-phenylurea occurred to afford the desired product **3j**, albeit in low yield. To the best of our knowledge, this transformation is the first successful functionalization of anilides by the action of a [Cp*Co^{III}] catalyst.

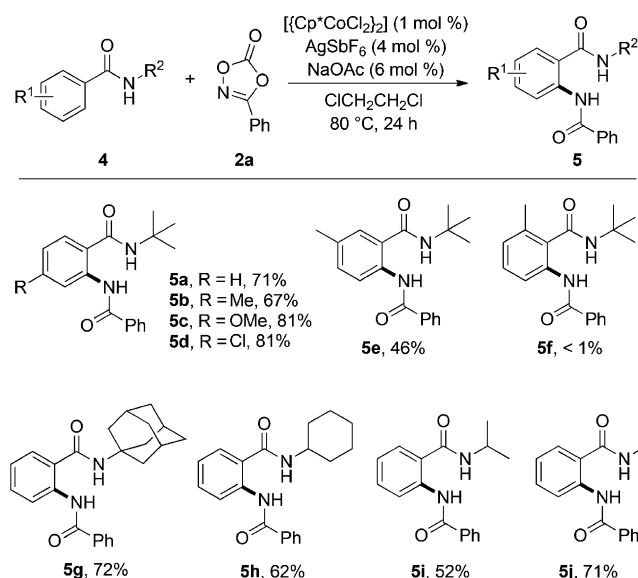
Notably, when [(Cp*RhCl₂)₂] was employed as the catalyst instead of the cobalt analogue, no catalytic reactivity was observed under otherwise identical conditions. On the other hand, [(Cp*IrCl₂)₂], another well-studied catalyst of the Group 9 triad, was found to mediate the present C–H



Scheme 2. Catalytic activity of Group 9 [Cp*MCl₂]₂ complexes in the amidation of anilides. Reaction conditions: **1** (0.2 mmol), **2a** (1.1 equiv), ClCH₂CH₂Cl (0.5 mL). The yields shown for the cobalt-catalyzed reactions are for the isolated product. [a] The yield was determined by NMR spectroscopy of the crude reaction mixture with dibromomethane as an internal standard; n.r. = no reaction.

amidation of anilides with 1,4,2-dioxazol-5-one, but with significantly lower efficiency as compared to the corresponding cobalt catalyst system. However, the exact reason why the [Cp*Co^{III}] catalyst is much superior to its rhodium and iridium analogues is not clear at the present stage, thus requiring more comprehensive mechanistic elucidation. This comparative study clearly demonstrates that the cobalt catalyst could be superior to rhodium or iridium in its reactivity in certain C–H functionalization reactions.

Next, we investigated an additional substrate type, benzamides (Scheme 3). Although the optimized conditions described above were found to be less effective in this case, the addition of a catalytic amount of an acetate salt greatly improved the reaction efficiency at higher temperature.^[15] When the [(Cp*CoCl₂)₂] precursor (1 mol %) was used in the presence of AgSbF₆ (4 mol %) and NaOAc (6 mol %), the amidation of *N*-*tert*-butylbenzamide (**4a**) with **2a** at 80 °C (24 h) afforded the desired product **5a** in good yield. This high efficiency of amidation was also observed with benzamide derivatives bearing methyl, methoxy, or chloro substituents at the *para* position (products **5b–d**), thus demonstrating again

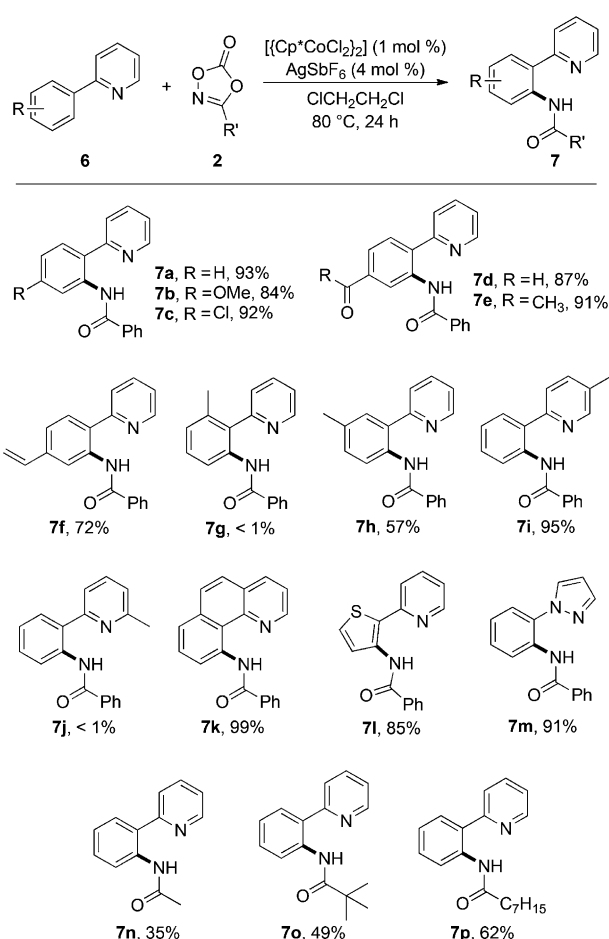


Scheme 3. Amidation of benzamide substrates. Reaction conditions: **4** (0.2 mmol), **2a** (1.1 equiv), $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.5 mL). Yields are for the isolated product.

that the reaction is not influenced by electronic variation. In contrast, the efficiency was shown to be sensitive rather to steric factors. For example, whereas a *meta*-substituted benzamide underwent the amidation highly regioselectively, albeit in moderate yield, to give product **5e**, when the same substituent was located at the *ortho* position, the desired amidation did not occur under these conditions to give **5f**. Variation of the *N*-alkyl group in the benzamide substrates, on the other hand, turned out to be more flexible. For example, the amidation of benzamides bearing not only sterically bulky adamantyl, cyclohexyl, or isopropyl groups, but also a methyl group, proceeded smoothly to give the corresponding products **5g–j** in moderate to good yields.

The feasibility of the transformation of a third type of substrate, compounds with a chelating nitrogen atom, was also examined with the optimized cobalt catalyst system. Pleasingly, 2-phenylpyridine and its derivatives were shown to undergo smooth amidation with 1,4,2-dioxazol-5-ones as the amidating reagent and a 1 mol % loading of the $[\text{Cp}^*\text{CoCl}_2]_2$ catalyst precursor at 80 °C (Scheme 4). Aryl pyridines with *para* substituents underwent the reaction to afford the corresponding amidated products in good yield, irrespective of the electronic properties of the substituents (products **7b,c**).

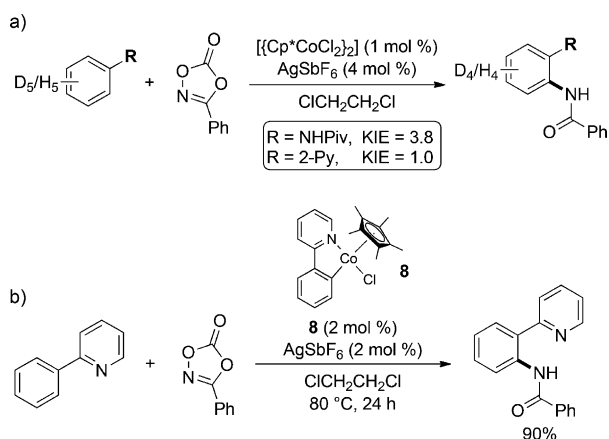
The reaction is compatible with sensitive functional groups, such as aldehyde, ketone, and vinyl groups (products **7d–f**). In contrast, arenes containing an aldehyde group were not tolerated under the conditions of iridium-catalyzed amidation.^[13b,16] As in the case of benzamides, whereas an *ortho* substituent retarded the reaction (product **7g**), the amidation of a substrate bearing a *meta* substituent on the phenyl ring was regioselective (product **7h**). The desired product **7i** was obtained in high yield from a substrate with a substituent at the 5-position of the pyridyl moiety, whereas no amidation to give **7j** occurred with 6-methyl-2-phenylpyridine.



Scheme 4. Amidation of heteroarene substrates. Reaction conditions: **6** (0.2 mmol), **2** (1.1 equiv), $\text{ClCH}_2\text{CH}_2\text{Cl}$ (0.5 mL). Yields are for the isolated product.

An additional array of heterocycles were also effective directing groups in guiding the amidation. For example, the reaction of benzo[*h*]quinoline took place smoothly to afford the desired product **7k** in quantitative yield (Scheme 4). Furthermore, a thienyl moiety was efficiently amidated under the optimized cobalt catalytic conditions (product **7l**). Pyrazole was found to be an efficient directing group in the reaction to give product **7m**, which was obtained in excellent yield. We also briefly examined the alteration of the 1,4,2-dioxazol-5-one amidating reagent. By replacing the phenyl group in the dioxazolone **2a** with alkyl groups, alkyl amides were readily installed at the desired position of 2-phenylpyridine to give products **7n–p**. These products are difficult to access by previously reported amidation methods with azides.^[17]

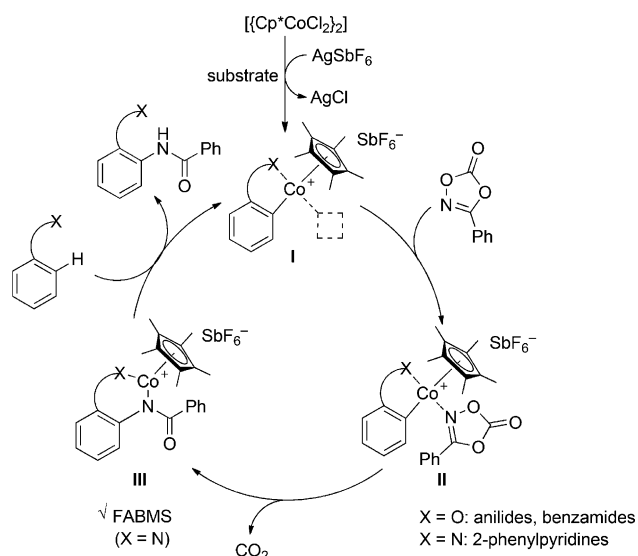
To examine the scalability of this $[\text{Cp}^*\text{Co}^{\text{III}}]$ -catalyzed C–H amidation procedure, we attempted a gram-scale reaction. We were pleased to observe that the reaction of 2-phenylpyridine (5.0 mmol) with 1,4,2-dioxazol-5-one **2a** (1.1 equiv) proceeded smoothly with 0.5 mol % of the catalyst precursor $[\text{Cp}^*\text{CoCl}_2]_2$ under the otherwise standard optimized conditions to afford the desired product in 81 % yield (1.1 g of the product).



Scheme 5. Preliminary mechanistic studies. Piv = pivaloyl, 2-Py = 2-pyridyl.

To shed light on the reaction pathway, we carried out a series of preliminary experiments (Scheme 5; see the Supporting Information for details). A primary kinetic isotope effect (KIE ; $k_{\text{H}}/k_{\text{D}} = 3.8$) was observed in the amidation of pivalanilide (Scheme 5a), thus indicating that the C–H bond cleavage of the anilide is probably the rate-determining step. In contrast, no detectable intermolecular KIE value ($k_{\text{H}}/k_{\text{D}} = 1.0$) was measured for 2-phenylpyridine. Although we failed to isolate a cobaltacycle derived from one of the anilides, we prepared **8**, the cobalt metallacycle of 2-phenylpyridine, according to the known procedure.^[8a] The complex **8** was observed to efficiently catalyze the amidation of 2-phenylpyridine upon the addition of a silver salt (Scheme 5b), thus implying that, as we presupposed, the metallacycle is involved in the catalytic cycle as a cationic active species.

On the basis of the above experiments and previously reported studies,^[10,11,13e,18] we propose the mechanistic pathway depicted in Scheme 6. The neutral dimeric complex



Scheme 6. Proposed mechanism of the $[\text{Cp}^*\text{Co}^{\text{III}}]$ -catalyzed amidation of arenes.

$[(\text{Cp}^*\text{CoCl}_2)_2]$ is assumed to be converted initially into the cationic species **I** upon treatment with a silver salt. As we have previously characterized a dioxazolone-bound rhodacycle,^[11] coordination of the amidating reagent to the cobaltacycle and then amido insertion are proposed to occur in tandem to afford an amido-inserted species **III** with the release of CO_2 as a single by-product. Finally, protodemetalation of **III** is believed to deliver the desired amidated product to regenerate the cobaltacycle species. Although we failed to isolate the dioxazolone-bound cobaltacycle intermediate **II**, the treatment of cobaltacycle **8** with a stoichiometric amount of the dioxazolone and the silver salt led to the formation of the amido-inserted species **III**, as detected by FABMS analysis.

In summary, we have developed a $[\text{Cp}^*\text{Co}^{\text{III}}]$ -catalyzed C–H amidation of arenes with 1,4,2-dioxazol-5-ones as amidating reagents. The amidation was found to be applicable to a broad range of substrates, including benzamide, phenylpyridine, and anilide derivatives. This cobalt catalyst system is suitable for practical applications, as a low catalyst loading was sufficient for the formation of amidated products in high yield under mild conditions. Mechanistic investigations to explain the observation that cobalt exhibits higher catalytic activity than its Group 9 cousins are under way.

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Keywords: amidation · anilides · C–H activation · cobalt catalysis · dioxazolones

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