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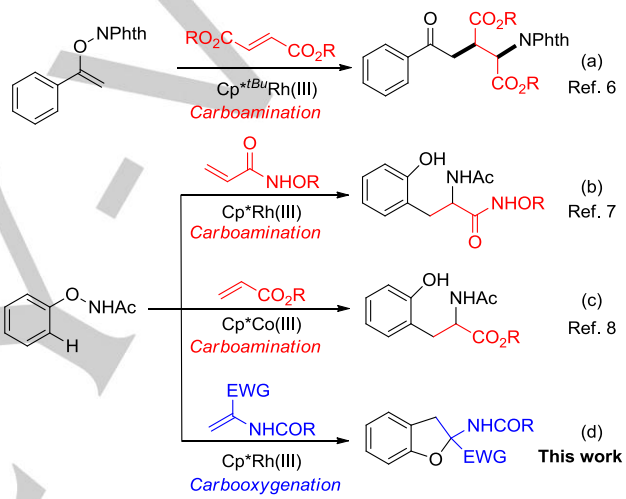
Rhodium(III)-Catalyzed Annulative Carbooxygenation of 1,1-Disubstituted Alkenes Triggered by C-H Activation

Yang Li*, Yuhai Tang, Xin He, Dandan Shi, Jun Wu and Silong Xu*

Abstract: A Cp*Rh^{III}-catalyzed annulative carbooxygenation of challenging 1,1-disubstituted alkenes triggered by C-H activation of *N*-aryloxyacetamides has been established, which affords 2,3-dihydrobenzofuran derivatives with a quaternary carbon center in good to excellent yields under mild redox-neutral conditions. An amide group on the alkenes is essential for the process, which may inhibit the β-H elimination from C(sp3)-Rh species by coordinatively saturating the rhodium center. Furthermore, mechanistic insights obtained from control experiments suggest a most likely mechanism involving a Rh^{III}-Rh^{V}-Rh^{III} catalytic cycle.

Transition-metal-catalyzed C-H functionalization has been developed as an economical and straightforward synthetic approach for the synthesis of a variety of complex core structures that are occurring in natural products, bioactive compounds as well as pharmaceuticals.[1] Among a wide range of synthetic methods involving C-H functionalization, alkenes are widely used as a coupling partner via Heck-type approaches.[2] However, difunctionalization of alkenes triggered by transition-metal-catalyzed C-H activation is still a challenge due to the competitive β-H-elimination from the resulting C(sp3)-metal-species.[2-3] Recently, C-H functionalization employing a redox-neutral strategy with oxidizing directing groups has been elegantly demonstrated.[1h, 4] In particular, with oxidizing directing groups (N-OR), rhodium(III)-catalyzed intra- and intermolecular carboamination of alkenes or allenes triggered by C-H activation has been developed for the synthesis of *N*-heterocyclic compounds.[5] In 2015, Rovis group[6] published the first Cp*^{tBu}Rh^{III}-catalyzed carboamination of 1,2-disubstituted alkenes with *N*-enoxyphthalimides affording acyclic products with excellent *syn*-selectivities, in which the β-H-elimination could be inhibited by coordinatively saturating the C(sp3)-rhodium-intermediate with an *in situ* generated bidentate directing group (Scheme 1a). With a similar strategy, by employing *N*-aryloxyacetamides as precursors, Liu and co-workers[7] reported the Cp*Rh^{III}-catalyzed carboamination of *N*-alkoxyacrylamides (Scheme 1b). Subsequently, Glorius group[8] developed the carboamination of acrylates with *N*-aryloxyacetamides and they found that Cp*Co^{III} catalyst demonstrated unique reactivity compared with Cp*Rh^{III} in the transformation (Scheme 1c). In contrast to the carboamination strategies, the corresponding carbooxygenation of alkenes triggered by C-H activation has been rarely investigated.[9] Consequently, developing new and efficient carbooxygenations of alkenes via C-H activation remains an important objective, which provides a promising approach for difunctionalization of alkenes with C-O bond formation.[10] Herein, we report a Cp*Rh^{III}-catalyzed carbooxygenation of 1,1-disubstituted alkenes with *N*-aryloxyacetamides to afford 2,3-dihydrobenzofuran derivatives with a quaternary carbon center in good to excellent yields under mild redox-neutral conditions (Scheme 1d).



Scheme 1. Transition-metal-catalyzed difunctionalization of alkenes triggered by C-H activaton.

Inspired by the fact that a coordinative functional group on alkenes is essential for obtaining high enantioselectivities in Rh^{I}-catalyzed asymmetric hydrogenation of functionalized alkenes due to the coordination with rhodium center in a chelating mode,[11] we proposed that a coordinative functional group on alkenes may also be helpful to inhibit the β-H-elimination in transition-metal-catalyzed difunctionalization of alkenes, by coordinatively saturating the C(sp3)-metal-intermediate. We were also interested in employing 1,1-disubstituted alkenes as substrates for the difunctionalization, which were expected to generate a quaternary carbon center in the products. Noteworthy is that 1,1-disubstituted alkenes represent a type of challenging and rarely-applied coupling partner for C-H functionalizations.[5g-h, 12] To test the proposed strategy, methyl 2-acetamidoacrylate (**2a**) was employed as a coupling alkene in the transition-metal-catalyzed C-H functionalization of *N*-phenoxyacetamide (**1a**) (Table 1). After an initial screening of catalysts, to our delight, [Cp*RhCl$_2$]$_2$ afforded an annulative carbooxygenation product 2,3-dihydrobenzofuran[13] (**3aa**) in 72% yield, without any β-H-elimination products detected (Table 1, entries 1-3). Screening of several bases revealed CsOAc as the optimal choice giving **3aa** in 83% yield (entries 3-5).

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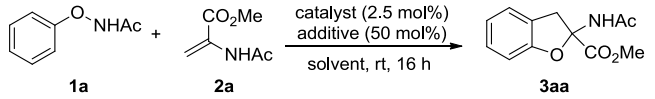
However, higher temperature exerted no effect on the reaction (entry 6). Solvents dramatically affected the yields and DCE emerged as the best solvent affording the product **3aa** in 91% yield (entries 7-10). Further optimization of the reaction conditions demonstrated that the carbooxygenation reaction was best performed in DCE in the presence of 50 mol% CsOAc, with 2.5 mol% $[Cp^*RhCl_2]_2$ as the catalyst at room temperature for 16 hours (entry 10).

Table 1. Optimization of the reaction conditions.[a]

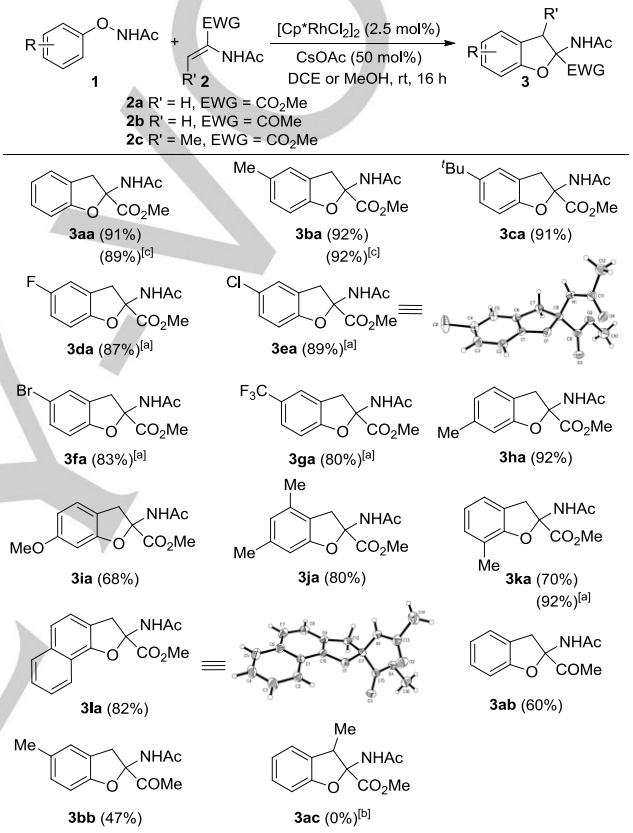


1a **2a** **3aa**

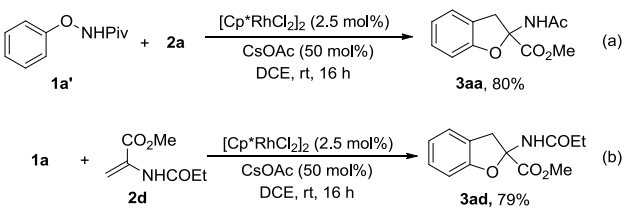
entry	catalyst	solvent	additive	yield (%)[b]
1	$[Cp^*IrCl_2]_2$	MeOH	NaOAc	trace
2	$[RuCl_2(p\text{-cymene})]_2$	MeOH	NaOAc	n.r
3	$[Cp^*RhCl_2]_2$	MeOH	NaOAc	72
4	$[Cp^*RhCl_2]_2$	MeOH	KOAc	60
5	$[Cp^*RhCl_2]_2$	MeOH	CsOAc	83
6[c]	$[Cp^*RhCl_2]_2$	MeOH	CsOAc	82
7	$[Cp^*RhCl_2]_2$	CF_3CH_2OH	CsOAc	trace
8	$[Cp^*RhCl_2]_2$	dioxane	CsOAc	42
9	$[Cp^*RhCl_2]_2$	THF	CsOAc	26
10	$[Cp^*RhCl_2]_2$	DCE	CsOAc	91
11[d]	$[Cp^*RhCl_2]_2$	DCE	CsOAc	91

[a] Unless specified, the reactions were carried out using 2.5 mol% catalyst, 50 mol% additive, 1.0 equiv of *N*-phenoxyacetamide **1a** (0.2 mmol) and 1.2 equiv of methyl 2-acetamidoacrylate **2a** (0.24 mmol) in 2 mL solvent at rt under N_2 for 16 h. [b] Isolated yield. [c] 60 °C. [d] 1.5 equiv of **2a**. n.r = no reaction.

With the optimized reaction conditions in hand, we investigated the scope of the Cp^*Rh^{III}-catalyzed annulative carbooxygenation of 1,1-disubstituted functionalized alkenes (Scheme 2). Various *N*-aryloxyacetamides were tested in the reaction with 2-acetamidoacrylate (**2a**) and the corresponding products could be isolated in good to excellent yields (**3aa-la**, 68-92%). Aryloxyacetamides with *para*-electron-donating groups gave 2,3-dihydrobenzofuran products in excellent yields (**3ba**, **3ca**), while those with *para*-electron-withdrawing groups could not proceed the reaction, probably due to their poor solubility in DCE. However, using MeOH instead of DCE as the solvent, the reaction occurred smoothly affording the corresponding products in 80-87% yields (**3da-ga**). *Meta*-substituted aryloxyacetamides delivered the corresponding products in good yields as a single regioisomer (**3ha-ja**) with the C-H activation taken place at the less hindered C-H bond of aryloxyacetamides. The o*rtho*-methylphenoxyacetamide afforded product **3ka** in a good yield of 70% under standard conditions, while using MeOH as the solvent the yield increased to 92%. For *N*-(naphthalen-1-yloxy)acetamide, the corresponding product was isolated in 82% yield (**3la**). To assess the efficiency and potential for applications of this method, we carried out a scale-up experiment and products **3aa** and **3ba** are obtained in 89% and 92% yields, respectively. The absolute molecular structures for **3ea** and **3la** were confirmed by X-ray crystallography (see Scheme 2 and the Supporting Information). Furthermore, acetyl-substituted *N*-vinylacetamide (**2b**) was investigated in the reaction, which could also afford the corresponding carbooxygenation products (**3ab**, **3bb**), albeit with moderate yields. However, trisubstituted alkene **2c** was incompatible under the optimized conditions, probably due to the bulkiness that impeded the binding to the Rh center.



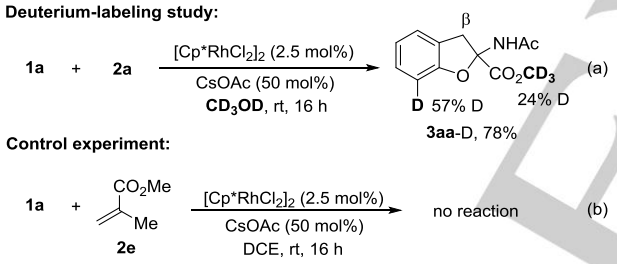
Scheme 2. The scope of the carbooxygenation reaction. Isolated yields are given. Reaction conditions: **1** (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (2.5 mol%), CsOAc (0.1 mmol, 0.5 equiv) and DCE (2 mL) were sealed in a 25 mL Schlenk tube at rt for 16 h under N_2. [a] MeOH (2 mL) was used as solvent. [b] Both **1a** and **2c** were recovered. [c] 1 mmol scale.



Scheme 3. Carbooxygenation of alkenes with *N*-aryloxyamides bearing different amide groups

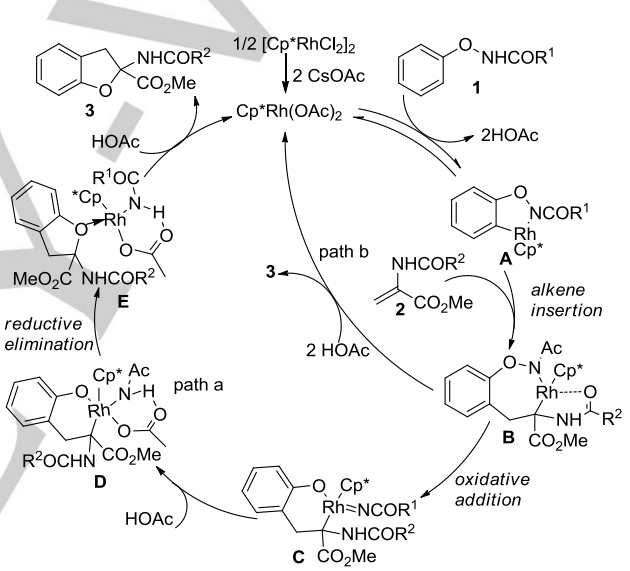
To further demonstrate the scope and at the same time clarify the source of the amide group in products, reactants with different amide groups were employed. Under standard reaction conditions, when *N*-phenoxypivalamide (**1a'**) was tested in the reaction with alkene **2a**, product **3aa** was generated in 80% yield without the incorporation of the pivalamido group (PivNH-) (Scheme 3a). On the other hand, the reaction of methyl 2-propionamidoacrylate **2d** with *N*-phenoxyacetamide **1a** produced the product **3ad** with a propionamido group (EtCONH-) in 79% yield (Scheme 3b). These results indicate that the amide group in annulative products come from the alkenes rather than the *N*-aryloxyamides, which, intriguingly, also provides an important clue for the reaction mechanism (*vide infra*).

To further shed light on the mechanism of the reaction, a deuterium-labeling study was conducted by performing the reaction of **1a** and **2a** in CD_3OD under otherwise identical conditions. The deuterium product **3aa**-D was obtained in 78% yield with 57% deuterium incorporated on the benzene ring at the *ortho*-position of the directing group, and 24% deuterium on the methyl group by transesterfication (Scheme 4a). This result indicates that the step of C-H activation is reversible under the reaction conditions. The absence of deuterium at the β-position of 2,3-dihydrobenzofuran product (**3aa**-D) also implies that β-H elimination is not involved in the reaction mechanism. In addition, methyl methacrylate (**2e**) was applied in the reaction with **1a** under standard conditions, but no product was detected (Scheme 4b). It suggests that the amide group in alkenes is crucial for the carbooxygenation and is believed to coordinate with rhodium center in the reaction.



Scheme 4. Mechanistic studies.

Based on the above results, the generally accepted C-H functionalization mechanism involving a Rh^{III}-Rh^{I}-Rh^{III} catalytic cycle[1-5] is supposed to be unlikely for the Cp*Rh^{III}-catalyzed annulative carbooxygenation. By this mechanism, the reactants bearing two different amide groups would deliver either mixed products or single product with amide group derived from *N*-aryloxyamides through a reductive elimination/oxidative addition pathway.[14] However, this is contradicted by the observation that single products are obtained with the amide groups originating from the coupling alkenes (Scheme 3). Taking into consideration the above results, a most likely Rh^{III}-Rh^{V}-Rh^{III} catalytic cycle (path a) is proposed in Scheme 5. The catalytically active species $Cp^*Rh(OAc)_2$ is generated by anion exchange with CsOAc, then a facile and reversible C-H activation of *N*-aryloxyacetamides **1** affords a 5-membered rhodacycle intermediate **A**, which is followed by alkene insertion, forming a 7-membered rhodacycle intermediate **B** with a C(sp3)-Rh bond. In the C(sp3)-Rh species, rhodium center could be coordinatively saturated by the oxygen atom of the amide group on the alkene.[5-7] As a result, β-H elimination is suppressed avoiding C-H olefination products. This is followed by an oxidative addition step which breaks the O-N bond and forms a high oxidation state Rh^{V}-nitrenoid intermediate **C**, which then is coordinated by a molecule of HOAc to generate a Rh^{V}-intermediate **D**. The formation of the Rh^{V}-intermediate could be supported by recent computational studies by Houk and Wu,[14] which showed that the oxidative addition to the O-N bond of oxidizing directing group is much more favorable than the reductive elimination.[15] This Rh^{V}-intermediate **D** subsequently undergoes a C-O bond reductive elimination to give intermediate **E**, which affords the products **3** and regenerates the catalyst by ligand exchange with HOAc. An alternative way (path b) that intermediate **B** undergoes an intramolecular substitution to give product **3** cannot be ruled out,[4s] however, this type of cleavage of the O−N bond in *N*-aryloxyacetamides usually proceeds under acidic conditions.[7]



Scheme 5. Proposed mechanism for the carbooxygenation.

In conclusion, an efficient intermolecular Cp*Rh^{III}-catalyzed annulative carbooxygenation of 1,1-disubstituted functionalized alkenes with *N*-aryloxyacetamides has been established, which affords 2,3-dihydrobenzofuran derivatives with a quaternary carbon center in good to excellent yields under mild redox-neutral conditions. By strategically installing an amide group on the alkenes, the β-H elimination from C(sp3)-Rh species has been prohibited probably due to the amide coordinatively saturating the rhodium center. In addition, in contrast with the generally accepted Rh^{III}-Rh^{I}-Rh^{III} mechanism, a most likely Rh^{III}-Rh^{V}-Rh^{III} catalytic cycle is proposed based on mechanistic studies for the annulative carbooxygenation. Further studies to elucidate the mechanism and exploit this new transformations triggered by transition-metal-catalyzed C-H activations are undergoing in this lab.

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Keywords: C-H activation • Cp*Rh(III) catalysis • annulation • carbooxygenation • 1,1-disubstituted alkenes

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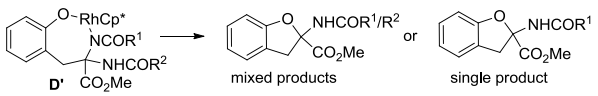
[14] For the Rh^{III}-Rh^{I}-Rh^{III} catalytic cycle, a Rh^{III}-interemediate **D'** is formed which leads to either mixed products or single product with the amide group derived from *N*-aryloxyamides. For details, see the Supporting Information.



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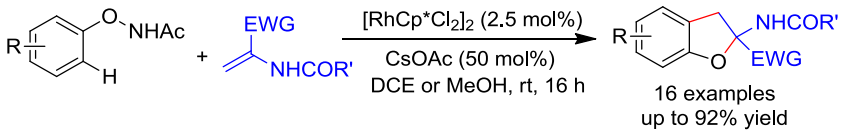

Carbooxygenation of 1,1-disubstituted alkenes: An efficient Cp*Rh^{III}-catalyzed annulative carbooxygenation of challenging 1,1-disubstituted functionalized alkenes with *N*-aryloxyacetamides triggered by C-H activation is established. An amide group on alkenes is strategically introduced by inhibiting β-H elimination from C(sp3)-Rh species. Mechanistic investigations suggest a most likely mechanism involving a Rh^{III}-Rh^{V}-Rh^{III} catalytic cycle.

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Rhodium(III)-Catalyzed Annulative Carbooxygenation of 1,1-Disubstituted Alkenes Triggered by C-H Activation