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Mechanistic Investigation

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

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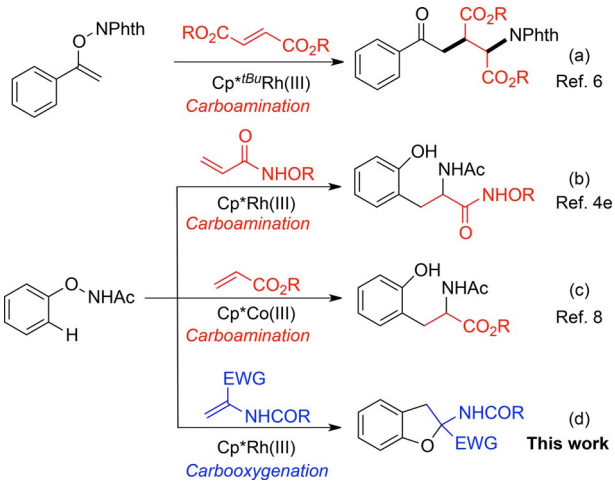
Abstract: A Cp*Rh^{III}-catalyzed annulative carbooxygenation of challenging 1,1-disubstituted alkenes triggered by C–H activation of *N*-aryloxyacetamides has been established, which affords 2,3-dihydrobenzofuran derivatives with a quaternary carbon center in good to excellent yields under mild redox-neutral conditions. An amide group on the alkenes is essential for the process, and may inhibit the β-H elimination from C(sp3)–Rh species by saturating the rhodium center through coordination. Furthermore, mechanistic insights obtained from control experiments suggest a 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 occur in natural products, bioactive compounds, and pharmaceuticals.[1] Among a wide range of synthetic methods involving C–H functionalization, alkenes are widely used as a coupling partner in Heck-type reactions.[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] Rhodium(III)-catalyzed intra- and intermolecular carboamination of alkenes or allenes triggered by C–H activation, in particular using oxidizing directing groups (N–OR), 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. The β-H-elimination was able to be inhibited by saturating the C(sp3)–rhodium intermediate through coordination with an in situ-generated bidentate directing group (Scheme 1 a). Using 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 1 b). Subsequently, Glorius' group[8] developed the carboamination of acrylates with *N*-aryloxyacetamides, and they found that the Cp*Co^{III} catalyst demonstrated unique reactivity compared with Cp*Rh^{III} in the transformation (Scheme 1 c). In contrast to the carboamination strategies, the corresponding carbooxygenation of alkenes triggered by C–H activation has rarely been investigated.[9] Consequently, developing new and efficient carbooxygenations of alkenes through C–H activation remains an important objective, and 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 1 d).



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

Inspired by the fact that a coordinating functional group on alkenes is essential to obtain high enantioselectivities in Rh^{I}-catalyzed asymmetric hydrogenation of functionalized alkenes through chelation with the rhodium center,[11] we proposed that a coordinative functional group on alkenes may also be

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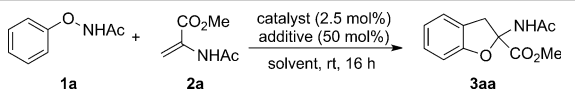
helpful to inhibit the β-H-elimination in the transition-metal-catalyzed difunctionalization of alkenes by saturating the C(sp3)–metal intermediate. We were also interested in employing 1,1-disubstituted alkenes as substrates for the difunctionalization, which are expected to generate a quaternary carbon center in the products. It is worth noting that 1,1-disubstituted alkenes represent a challenging and rarely applied coupling partner for C–H functionalizations.[5g,4j,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 the 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). However, a 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]

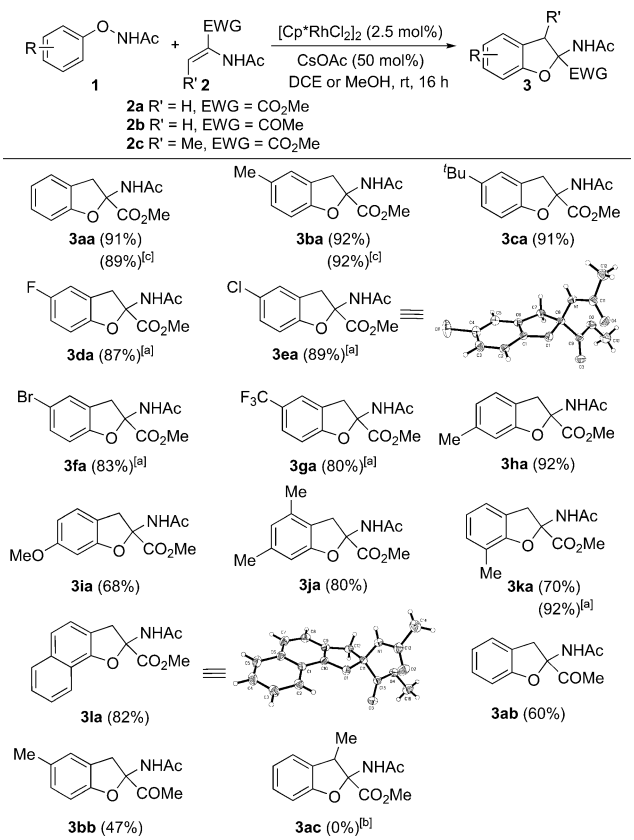


1a 2a 3aa

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

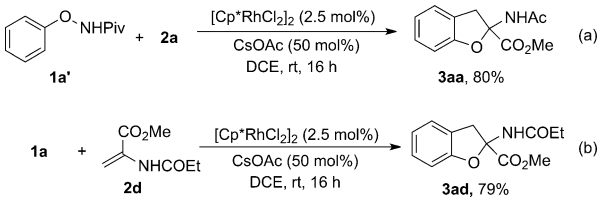
[a] Unless specified, the reactions were carried out using catalyst (2.5 mol%), additive (50 mol%), *N*-phenoxyacetamide **1a** (1.0 equiv., 0.2 mmol) and methyl 2-acetamidoacrylate **2a** (1.2 equiv., 0.24 mmol) in solvent (2 mL) at rt under N_2 for 16 h. [b] Isolated yield. [c] 60 °C. [d] 1.5 equiv. 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 the 2,3-dihydrobenzofuran products in excellent yields (**3ba**, **3ca**), whereas those with *para*-electron-withdrawing groups could not drive 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**), since the C–H activation takes place at the less-hindered C–H bond of aryloxyacetamides. The *ortho*-methylphenoxyacetamide afforded product **3ka** in a good yield of 70% under standard conditions, whereas using MeOH as the solvent increased the yield 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, which gave products **3aa** and **3ba** in 89% and 92% yield, 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, resulting in 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 impedes binding to the Rh center.



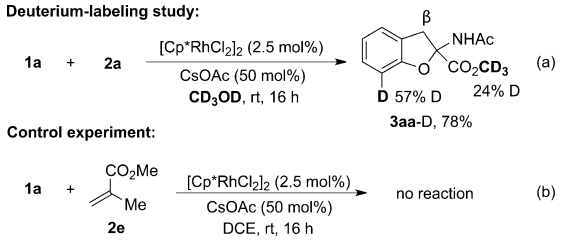
Scheme 2. The scope of the carbooxygenation reaction. Isolated yields are given. Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.24 mmol, 1.2 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), CsOAc (0.1 mmol, 0.5 equiv.) and DCE (2 mL) were sealed in a 25 mL Schlenk tube at rt for 16 h under N_2. [a] MeOH (2 mL) was used as solvent. [b] Both **1a** and **2c** were recovered. [c] 1 mmol scale. Displacement ellipsoids of **3ea** and **3la** were drawn at the 30% probability level.

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, *N*-phenoxypivalamide (**1a′**) was tested in the reaction with alkene **2a**, generating product **3aa** 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 **3ad** with a propionamido group (EtCONH-) in 79% yield (Scheme 3b). These results indicate that the amide group in annulative products comes from the alkenes rather than the *N*-aryloxyamides, which intriguingly also provides important evidence for the reaction mechanism (vide infra).



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

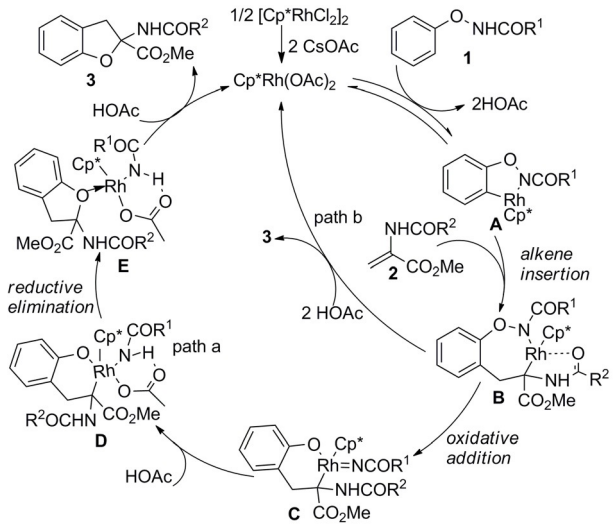
To further shed light on the mechanism of the reaction, a deuterium labeling study was conducted by performing the reaction of **1a** and **2a** in CD_3OD under otherwise identical conditions. The deuterated product **3aa**-D was obtained in 78% yield, with 57% deuterium incorporated on the benzene ring at the *ortho*-position of the directing group, and 24% deuterium on the methyl group by transesterfication (Scheme 4a).



Scheme 4. Mechanistic studies.

This result indicates that the C–H activation step is reversible under the reaction conditions. The absence of deuterium at the β-position of the 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). This suggests that the amide group in alkenes is crucial for the carbooxygenation, and is believed to coordinate with the rhodium center in the reaction.

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. Through this mechanism, the reactants bearing two different amide groups would deliver either mixed products or a single product with an 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 featuring the amide groups originating from the coupling alkenes (Scheme 3). Taking into consideration the above results, a 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, the rhodium center could be saturated by coordinating the oxygen atom of the amide group on the alkene.[5,6,4e] As a result, β-H elimination is suppressed, thereby 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 the Rh^{V}-intermediate **D**. The formation of the Rh^{V}-intermediate is supported by recent computational studies by Houk and Wu,[14] which showed that the oxidative addition to the O–N bond of the 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 path (path b) also cannot be ruled out, in which intermediate **B** undergoes an intramolecular substitution to give product **3**,[4s] however this type of cleavage of the O–N bond in *N*-aryloxyacetamides usually proceeds under acidic conditions.[4e]



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. This 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 of the C(sp3)–Rh species has been avoided, most likely since the amide coordinates to, and saturates, the rhodium center. In contrast with the generally accepted Rh^{III}-Rh^{I}-Rh^{III} mechanism, a probable 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 these new transformations triggered by transition-metal-catalyzed C–H activations are ongoing in this lab.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: 1,1-disubstituted alkenes · annulation · carbooxygenation · C–H activation · Cp*Rh^{III} catalysis

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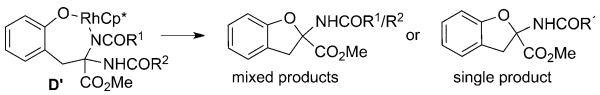
[14] For the Rh^{III}-Rh^{I}-Rh^{III} catalytic cycle, a Rh^{III}-interemediate **D′** is formed, which leads to either mixed products or a single product featuring the amide group derived from *N*-aryloxyamides. For details, see the Supporting Information.



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