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Rhodium-Catalyzed Formal C–O Insertion in Carbene/Alkyne Metathesis Reactions: Synthesis of 3-Substituted 3*H*-Indol-3-ols

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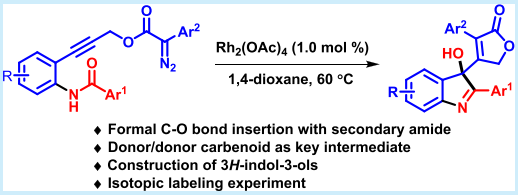
Supporting Information

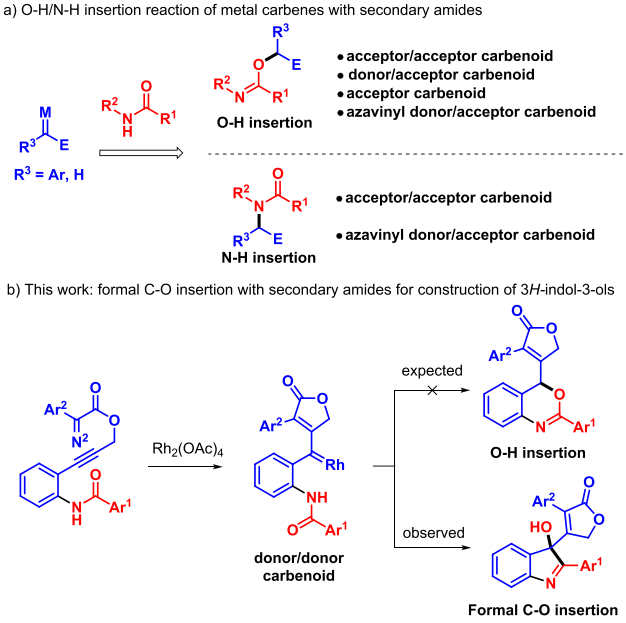
ABSTRACT: An efficient and novel rhodium-catalyzed formal C–O insertion reaction of alkyne-tethered diazo compounds for the synthesis of 3*H*-indol-3-ols is described. A type of donor/donor rhodium carbene generated *in situ* via a carbene/alkyne metathesis (CAM) process is the key intermediate and terminates in a unique transformation different from donor/acceptor carbenoids. In addition, ^{18}O-labeling experiments indicate that intramolecular oxygen-atom transfer from the amide group to the carbon–carbon triple bond occurs during this transformation.



During the past few decades, transition-metal catalyzed carbene reactions have emerged as a powerful chemical tool for the construction of carbon–carbon and carbon–heteroatom bonds.[1] Among these advances, carbene/alkyne metathesis (CAM) cascade reactions have received enormous attention owing to their extraordinary efficiency for complex molecule synthesis.[2] Since the pioneering work of Padwa[3] and Hoye[4] on the carbene/alkyne metathesis process, this kind of vinyl metal carbene intermediate has been widely explored for many metal carbene cascade reactions, including cyclopropanation,[5] cycloaddition,[6] X–H insertion,[7] cyclization,[8] the Buchner reaction,[9] and others.[10] Although donor/donor carbenoids generated via a CAM process attenuated electrophilicity compared to donor/acceptor carbenoids and acceptor carbenoids, most of reported carbene cascade transformations involving donor/donor carbenoids did not show the activity difference in chemoselectivity. Herein, we report a unique rhodium-catalyzed formal C–O insertion reaction of donor/donor carbenoids and secondary amides, which proceeds in a novel manner different from typical carbene reactions.

A survey of the literature indicated that N–H insertion[11] and O–H insertion[12] reactions were the main transformations of metal carbenes and secondary amides (Scheme 1a). Earlier, N–H insertions of acceptor/acceptor carbenoids and secondary amides were applied in the synthesis of *N*-containing heterocycles.[11a,b] Recently, Reddy reported the O–H insertion reactions of secondary amides and donor/acceptor carbenoids through zwitterionic intermediates for the synthesis of 2-aryl-4*H*-benzo[*d*][1,3]oxazine.[12b] Furthermore, for the azavinyl donor/acceptor carbenoids, Fokin found that less steric hindrance of the N–H bond of the scecondary amides preferred N–H insertion, whereas more steric hindrance of the N–H bond led to O–H insertion/rearrangement.[13] On the basis of these reactions and our interest in developing carbene transformations, we conceived that similar O–H insertion reactions would occur through the intramolecular reaction between the secondary amides and donor/donor carbenoid intermediates generated via a CAM process. Surprisingly, 3*H*-indol-3-ols were obtained via a formal C–O insertion reaction rather than O–H insertion with secondary amides, which exhibited the reactivity difference of donor/donor carbenoids and donor/acceptor carbenoids (Scheme 1b). Notably, this transformation offers a more attractive and atom-economical method compared to the known synthetic routes[14] to 3*H*-indol-3-ols, which are pivotal building blocks for the

Scheme 1. Reaction of Metal Carbenes with Secondary Amides



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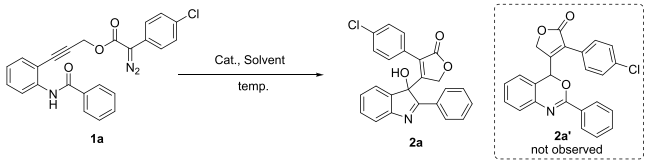
construction of natural products[15] and pharmaceutically active molecules.[16]

Initially, 3-(2-benzamidophenyl)prop-2-yn-1-yl 2-(4-chlorophenyl)-2-diazoacetate (**1a**) was treated with 1.0 mol % $Rh_2(OAc)_4$ in 1,2-dichloroethane (DCE) at room temperature (Table 1, entry 1). Interestingly, a formal C−O insertion

Table 1. Condition Optimization[a]



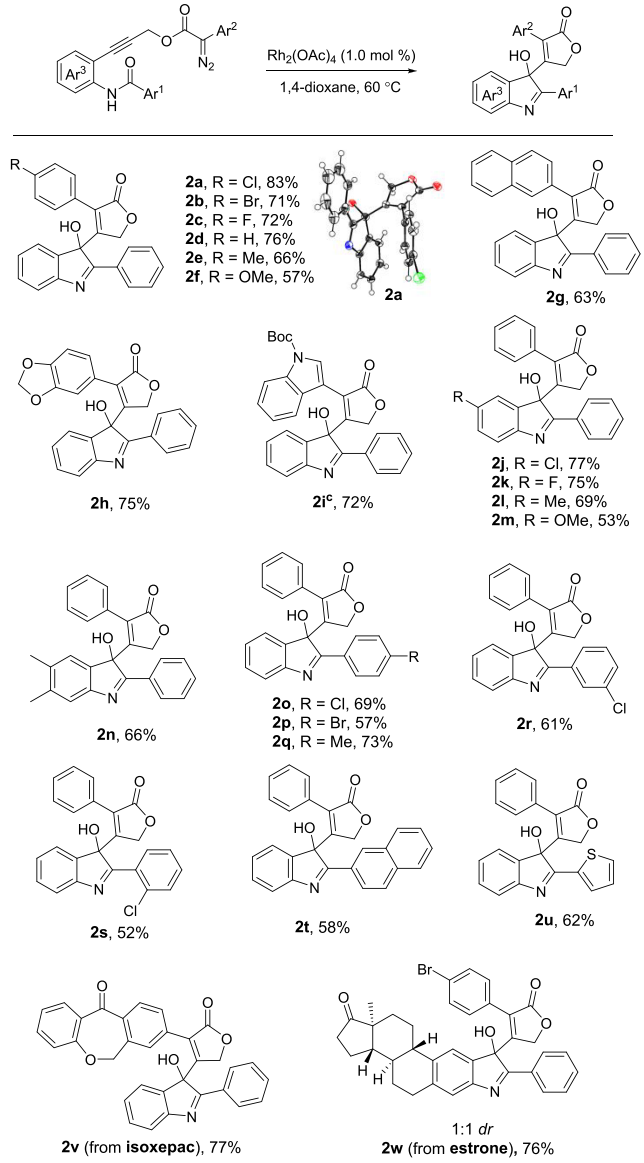
	cat. (x mol %)	T (°C)	solvent	yield (%)[b]
1	$Rh_2(OAc)_4$ (1.0 mol %)	20	DCE	47
2	$Rh_2(esp)_2$ (1.0 mol %)	20	DCE	20
3	Rh(cod)OH (1.0 mol %)	60	DCE	25
4	Ir(cod)Cl (1.0 mol %)	60	DCE	22
5	$Cu(MeCN)_4PF_6$ (5.0 mol %)	60	DCE	46
6[c]	Cp*$RhCl_2$ (5.0 mol %)	20	DCE	60
7[c]	Cp*$IrCl_2$ (5.0 mol %)	60	DCE	23
8	$Rh_2(OAc)_4$ (1.0 mol %)	60	THF	52
9	$Rh_2(OAc)_4$ (1.0 mol %)	60	1,4-dioxane	83
10[d]	$Rh_2(OAc)_4$ (1.0 mol %)	60	1,4-dioxane	76

[a]Reactions were conducted by adding **1a** (0.1 mmol) in 1 mL of the solvent to the catalyst in 1 mL of the solvent over 5 min and then stirred for another 30 min. [b]Isolated yield after column chromatography. [c]Running for 24 h. [d]With 100 mg of 4 Å molecular sieves.

product **2a** was generated instead of the expected cyclization product **2a′**. To improve the yield of product **2a**, various transition metal catalysts were tested, such as other rhodium(II), rhodium(I), rhodium(III), copper, iridium(I), and iridium(III) complexes (Table 1, entries 2−7). Most of the screened catalysts could promote the conversion of **1a**, although low yields were observed in most cases. Although Cp*$RhCl_2$ led to a better improvement in the reaction and **2a** was obtained in 60% isolated yield, the transformation required a longer time of 24 h.[17] Therefore, further optimizations of the reaction conditions were carried out at higher reaction temperatures using THF and 1,4-dioxane (Table 1, entries 8−9). By employing 1,4-dioxane instead of DCE, **2a** was obtained in 83% yield, finally establishing the optimal reaction conditions (Table 1, entry 9). Notably, the addition of 4 Å molecular sieves led to a slight decrease in yield (Table 1, entry 10).

With these optimized reaction conditions in hand, we investigated the substrate generality of the formal C−O insertion reaction. As shown in Scheme 2, the current strategy showed very good substrate scope tolerating different aryl-substituted (from electron-withdrawing to electron-donating) diazoacetates **1** and resulting in the desired products **2** in 57−83% yields (**2a**−**2f**). Meanwhile, incorporating 2-naphthyl substitute and heterocyclic substitutions did not affect the efficiency of reaction (**2g**−**2i**). Subsequently, we investigated the variation of Ar^3. The results showed that different substituents on the phenyl rings were suitable for the reaction; products **2j**−**2l** were obtained in good yields. An obvious decrease in yields was observed for the diazo compounds with methoxy substitution on the aryl ring (**2m**). Furthermore, the scope of Ar^2 with respect to the amide group was examined.

Scheme 2. Substrate Scope[a,b]



[a]Unless otherwise indicated, the reaction was performed at a 0.3 mmol scale. [b]Isolated yield after column chromatography. [c]Running at a 1.0 mmol scale starting from diazo compound precursor.

Substituents on the *para*-, *meta*-, and *ortho*- positions of the aromatic amide group gave the desired products **2o**−**2s** in 52−73% yields. 2-Naphthyl and 2-thienyl substitutions were also successfully employed for the O-transfer cyclization to afford products **2t** and **2u**, respectively, in moderate yields. Next, the potential of this approach for late-stage functionalization was examined, with the aim to enrich the structural diversity of the 3*H*-indol-3-ols using diazo compounds generated from bioactive compounds.[18] Starting from isoxepac, alkyne-tethered diazo compound **1v** was also well tolerated under these conditions, affording the desired product **2v** in 77% yield. Similarly, diazoacetate **1w** which was derived from estrone was also tested in this reaction and the corresponding product was obtained in 76% yield with 1:1 dr (**2w**). Meanwhile, we found that the desired products were not formed when we employed alkyne-tethered diazo compounds substituted with an acetamide group or diarylurea group.[19] In addition to other

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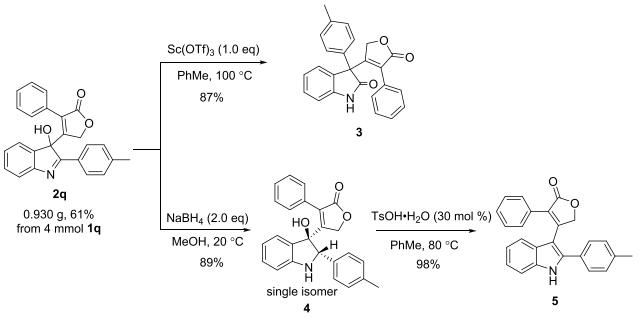
spectroscopic studies, the structure of the desired product was determined by X-ray analysis of **2a** (CCDC 1898648).[20]

To exhibit the potential utility of our method, a gram-scale reaction was carried out by using 4 mmol of **1q**. We found that the reaction proceeded smoothly under standard conditions to give the desired product **2q** in 61% yield (0.93 g). Further transformations with **2q** were conducted to show the synthetic potential of this strategy (Scheme 3). For instance, under the

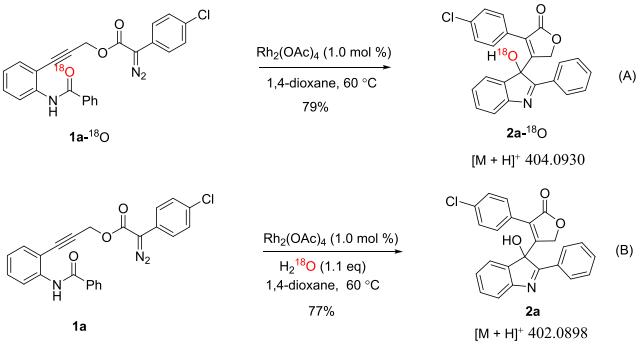
Scheme 3. Derivatization of 2q



action of $Sc(OTf)_3$, 3,3-disubstituted oxoindole **3** was obtained in 87% yield from the rearrangement from **1q**. On the other hand, reduction of **2q** to indoline **4** as a single isomer proceeded with $NaBH_4$ in 89% yield, and the relative configuration of indoline **4** was determined by NOE analysis. Subsequently, indoline **4** could be efficiently converted into 2,3-disubstituted indole **5** in 98% yield under dehydration conditions.

To gain some insight into the reaction mechanism, isotopic labeling experiments were conducted.[20] When ^{18}O was incorporated into the carbonyl group of **1a** [Scheme 4, eq

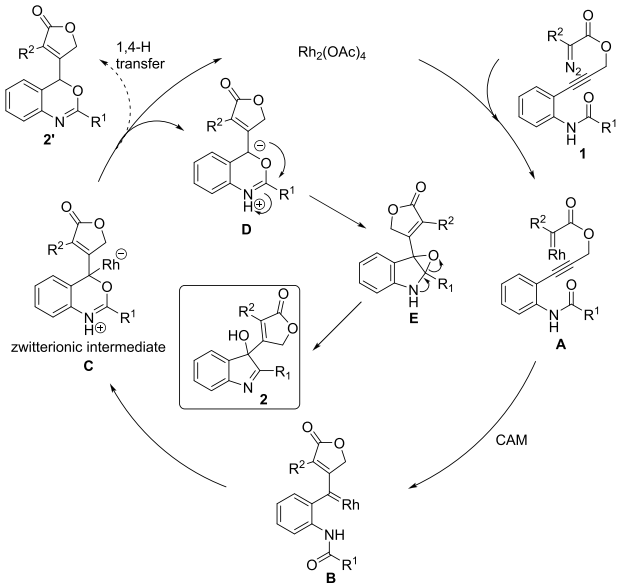
Scheme 4. ^{18}O-Labelling Experiments



A], ^{18}O-labeled product was obtained under the reaction conditions. Conversely, when $H_2{}^{18}O$ was introduced in this reaction, only normal product **2a** was observed [Scheme 4, eq B]. These results verified that intramolecular oxygen-atom transfer (OAT) from the amide group to the carbon−carbon triple bond occurred during the reaction process.

On the basis of the preliminary mechanistic studies and previous work,[21] a plausible cyclization pathway is proposed in Scheme 5. First, alkyne-tethered diazo compounds **1** formed rhodium carbene **A** in the presence of $Rh_2(OAc)_4$, which was converted into donor/donor rhodium carbene **B** via a carbene/alkyne metathesis (CAM) process. The carbonyl of the amide group attacked the carbene to form zwitterionic intermediate **C** (**C** could be trapped by imine in an intermolecular manner,

Scheme 5. Proposed Reaction Mechanism



which indicated that **C** was the key intermediate).[22] Then zwitterionic intermediate **D** was obtained, followed by dissociation of the rhodium catalyst. A conventional O−H insertion product **2′** could be generated via 1,4-H transfer; however, the zwitterionic intermediate **D** possessed higher nucleophilicity than the similar intermediate generated from the donor/acceptor carbenoid.[12b] Subsequently, epoxy intermediate **E** was generated via an intramolecular trapping process,[21b] which proceeded to afford the corresponding product **2** by ring opening and intramolecular H-transfer. The facilitation of H transfer and stabilization of the zwitterionic intermediate might account for the increase of yield in polar solvent, 1,4-dioxane.

In summary, we have developed an efficient method for the construction of 3-substituted 3*H*-indol-3-ol derivatives in good yields via formal C−O insertion reactions. The key reaction intermediate donor/donor rhodium carbene was formed via a carbene/alkyne metathesis (CAM) process. Notably, this transformation is an additional example that can show the reactivity difference between donor/donor carbenoids and donor/acceptor carbenoids. Besides, ^{18}O-labeling experiments demonstrated that intramolecular OAT occurred during this transformation, and a trapping experiment indicated the existence of the zwitterionic intermediate. Derivatization of the 3*H*-indol-3-ol to 3,3-disubstituted oxoindole and 2,3-disubstituted indole shows the potential utility of our method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01492.

Experimental procedure and spectroscopic data for all compounds (PDF)

Accession Codes

CCDC 1898648 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam-

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Notes

The authors declare no competing financial interest.

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