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Rhodium(III)-catalyzed diamidation of olefins *via* amidorhodation and further amidation†

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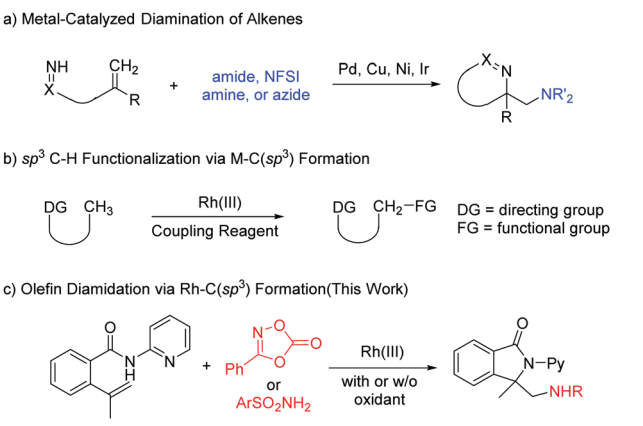
Rh(III)-catalyzed synthesis of vicinal diamides has been realized *via* elaboration of an authenticated Rh–C(sp^3) species generated *via* initial intramolecular amidorhodation of olefins. The second amidation was achieved using both electrophilic and nucleophilic amidating reagents. The reactions proceeded under mild conditions with good yield, broad substrate scope, and excellent functional-group tolerance.

Nitrogen-containing organics, especially vicinal diamines, represent an important family that have been employed as synthetic building blocks, biologically active molecules, and privileged ligands in transition metal catalysis.[1] Consequently, great efforts have been made in nitrogenation of diverse substrates.[2] Among reported methods, metal-catalyzed C–N coupling reactions have been increasingly employed for direct functionalization of readily available substrates.[3] Traditional C–N coupling strategies include Buchwald–Hartwig coupling, the Goldberg reaction, and the Chan–Lam reaction. However, they may suffer from limited efficiency or compatibility during the introduction of two nitrogen groups. Significantly, Shi and others made important progress in diamination of olefins using strained aminating reagents.[4] Subsequently, diamination of diverse olefins has been realized using Pd,[5] Cu,[6] Ni,[7] and Ir[8] catalysts (Scheme 1a), as in the reports by Muinz, Wang, Rovis, and others.[9] Despite the significant progress, the coupling systems suffer from intramolecular diamination or employment of limited classes of nitrogen sources such as amides,[6a] amines,[6h,i] NFSI,[3e,f,10] and organoazides.[6b] Therefore, it is necessary to develop new diamination/diamidation methods using readily available electrophilic and nucleophilic reagents.

The successful development of olefin diamination boils down to generation and subsequent efficient transformation of an M–C(sp^3) bond. Regarding this organometallic species, lessons can be drawn from chelation-assisted C(sp^3)–H activation, particularly by Rh(III) catalysis[11] (Scheme 1b). C(sp^3)–H activation generates a Rh–C(sp^3) intermediate that can be functionalized by a diverse array of coupling reagents such as alkyne,[11b] olefins,[12] diazo compounds,[13] and aminating reagents.[3j,k,14] We reasoned that such organorhodium could be alternatively accessed *via* cyclization of an olefin bearing a proximal nitrogen nucleophile. Of note, although cyclization of alkynes bearing a proximal nucleophile has been studied in Rh(III)-catalyzed coupling reactions,[15] the cyclization of olefins has been rarely studied. We now report diamidation of olefins using both electrophilic and nucleophilic amidating reagent, where a rhodium(III) alkyl species has been authenticated as an intermediate (Scheme 1c).

We initially investigated olefin diamidation using reactive dioxazolone[16] as the external, electrophilic amidating reagent. *N*-Substituted 2-(prop-1-*en*-2-yl)benzamide (**1a**) was employed as a substrate. It was found that the N-group had profound effects on the reaction efficiency under Rh(III)-catalyzed reaction conditions (Table S1 in the ESI†). Thus, employment of N–OMe or –NHPh groups only resulted in simple cyclization of the



Scheme 1 Formation of C(sp^3)–M bond en route to C–N coupling.

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olefin (**3aa′**, 24–84% yield), indicating that the cyclization proceeded well but the Rh–C bond was rapidly protonolyzed. To ensure stability of the organorhodium intermediate, an *N*–Py chelating group was installed. Indeed, the desired diamidation product **3aa** started to be observed in DCE (entries 6–8), and the simple cyclization by-product was inhibited when the acid additive was omitted (entry 8).

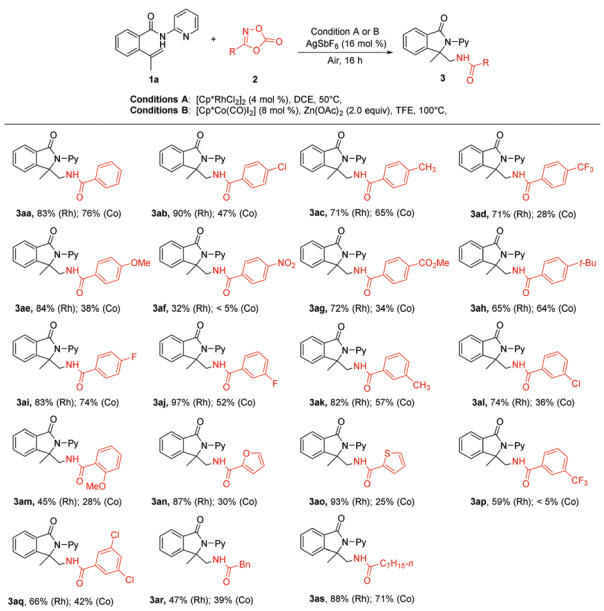
We next conducted further optimization studies using substrate **1a** (Table S2 in the ESI†). It was found that both the $[Cp^*RhCl_2]_2$ catalyst and silver salt were essential to the catalytic system (entries 3 and 4). After screening several other parameters (entries 5–18), we found that an air atmosphere was beneficial for the reaction and $AgSbF_6$ turned out to be the optimal activator, and the desired product **3aa** was isolated in 83% yield (entry 7). Given reported comparable catalytic activities in amidation,[16e] the Co(III) congener was also explored, and **3aa** was eventually isolated in 76% yield when $[Cp^*Co(CO)I_2]$ (8 mol %) was used as a catalyst in the presence of $Zn(OAc)_2$ in TFE solvent (see Table S3 in the ESI†).

With the optimal catalytic conditions in hand, the scope of the two metal-catalyzed systems was next examined (Scheme 2). The Co(III)-catalyzed method generally afforded the target product in low to moderate yield, and *p*-NO_2 and *m*-CF_3 group-substituted dioxazolones failed to undergo any coupling with **1a**. The low yield of this system is probably due to catalyst decomposition, and this negative influence has been observed in our reported work.[16e] To our delight, this limitation was resolved when our Rh(III)-catalyzed conditions were applied (conditions A). Further studies revealed that dioxazolones bearing an electron-donating (**3ac**, **3ae**, and **3ah**), -withdrawing (**3ad** and **3ag**), or halogen group (**3ab** and **3ai**) at the *para* position coupled smoothly under the rhodium-catalyzed conditions in superior yields. The negative effect of *p*-NO_2 and *m*-CF_3 groups was resolved by rhodium catalysis (**3af** and **3ap**). The introduction of *m*-Me and –Cl groups was also tolerated (**3ak**, **3al**), and the *m*-F group greatly favored the reaction, affording the desired product (**3aj**) in excellent yield (97%). An *o*-methyl-substituted dioxazolone also reacted smoothly, yielding product **3am** with moderate efficiency. In addition, furyl-, thienyl-, and alkyl-substituted dioxazolones were also compatible (**3an**, **3ao**, **3aq**, and **3as**).

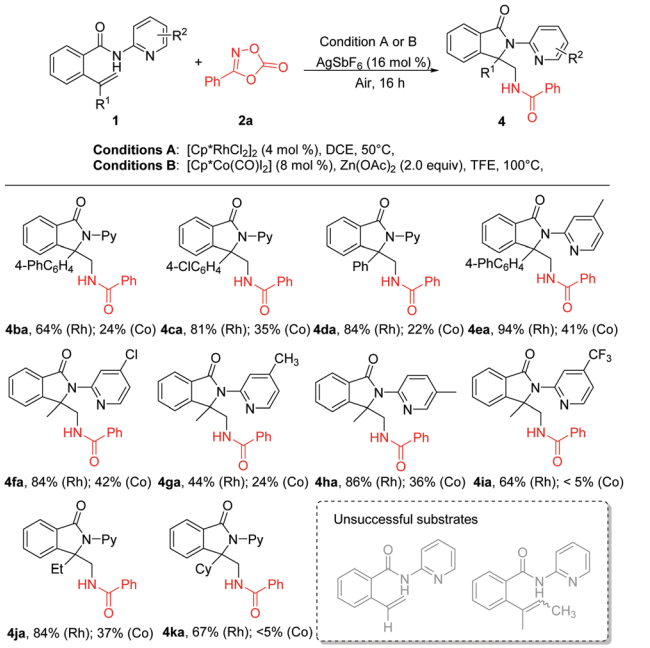
The scope of alkene substrates was next explored using **2a** as a coupling partner (Scheme 3). As expected, the Co(III)-catalyzed system generally gave lower reactivity. As for the rhodium-catalyzed system, variation of R^1 from methyl group (**1a**) to ethyl, cyclohexyl, and substituted aryl groups had little influence on the activity of the diamidation (**4ba**–**4ea**, **4ja**–**4ka**). By varying the R^2 group in the pyridine ring to alkyl, halogen, and CF_3 groups, the reactions also proceeded smoothly to yield the corresponding products (**4fa**–**4ia**) in satisfactory yields. Unexpectedly, both vinyl and internal olefin were incompatible with the standard reaction conditions.

To better explore the scope of the amidating reagents, we next investigated aryl sulfonamides as nucleophilic amidating reagents in the presence of a $PhI(OAc)_2$ oxidant.[3k,l] It was found that aryl sulfonamides bearing an electron-withdrawing group (*p*-CF_3 and *p*-CN) in the phenyl ring underwent diamidation in good yields (**4aa**, **4ad**) when catalyzed by a cationic Rh(III) catalysts in the presence of NaOAc (Scheme 4). Meanwhile, *p*-Cl and *p*-Me substituted aryl sulfonamides exhibited higher reactivity under the same conditions (**4ab** and **4ac**). Comparably high efficiency was observed for a phenyl-substituted alkene (**4ae** and **4af**).

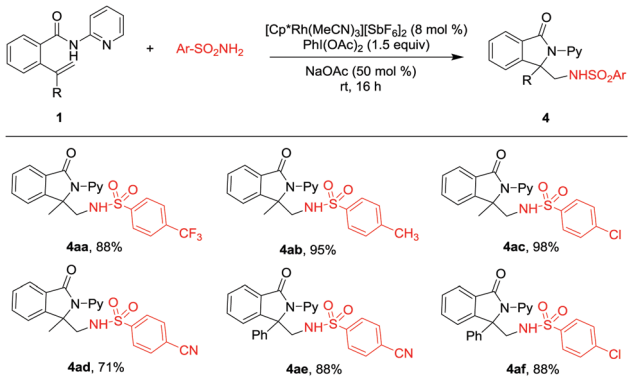
To gain insight into the mechanism of the diamidation system, several experiments have been performed (Scheme 5).



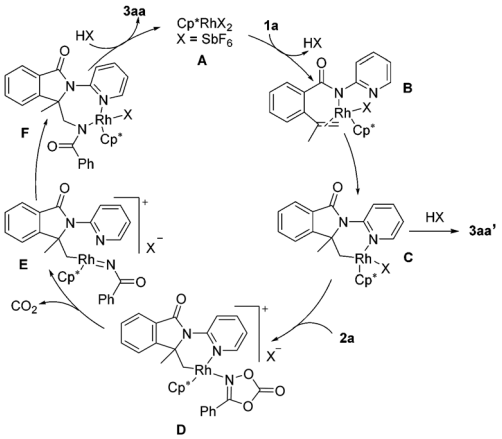
Scheme 2 Scope of dioxazolones in the amidation reaction. Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), solvent (1.5 mL) under air for 16 h. Isolated yield.



Scheme 3 Scope of alkenes in amidation reactions. Reaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol), solvent (1.5 mL) under air for 16 h. Isolated yield.



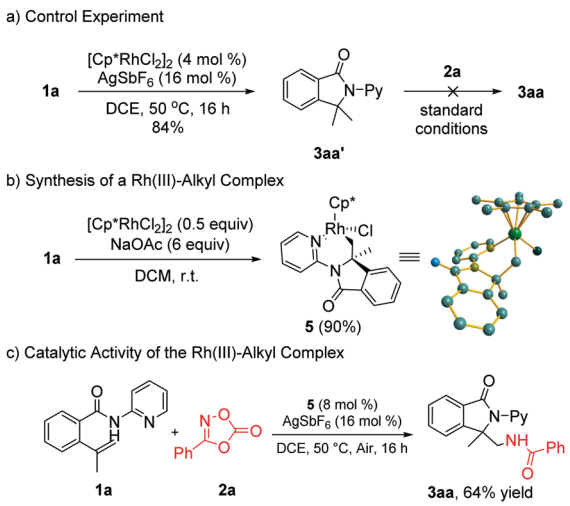
Scheme 4 Scope of sulfonamides in amidation. Reaction conditions: **1** (0.1 mmol), sulfonamides (0.1 mmol), DCM (1.5 mL) under air for 16 h. Isolated yield.



Scheme 6 Proposed mechanism.

Subjection of the simple cyclization product **3aa**′ to the standard conditions only led to recovery of this reactant (Scheme 5a), and the same scenario was observed in amidation using $TsNH_2$. This suggests that the reaction should not proceed *via* cyclization with subsequent pyridine-directed C–H activation. To explore the putative Rh(III)-alkyl intermediate, a stoichiometric amidorhodation reaction has been conducted, from which rhodacycle **5** was isolated as a single diastereomer (90% yield) and was characterized by X-ray crystallography (CCDC 1957959).† Complex **5** proved to be catalytically active for the coupling of **1a** and **2a** (Scheme 5c). Thus, it is a plausible intermediate or a direct precursor to this intermediate.

Based on the above observations and reported diamination of alkenes,[8,16e,f,17] we proposed a plausible mechanistic pathway (Scheme 6). The catalytic cycle starts from an active catalyst $[RhCp^*X_2]$ (X = SbF_6) species **A**. Subsequent chelation of alkene **1a** affords the intermediate **B**, together with an acid HX. Olefin complex **B** is proposed to undergo migratory insertion of the Rh–N bond to give a Rh(III)-alkyl **C** that is stabilized by pyridyl chelation. Coordination of dioxazolone **2a** gave an intermediate **D**.



Scheme 5 Mechanistic studies.

Elimination of the CO_2 produces a rhodium(v)–nitrene species **E**, which undergoes nitrene insertion to give a seven-membered amidate species **F**. Protonolysis of the Rh–N bond releases the diamidated product **3aa** together with regeneration of the active Rh(III) catalyst.

In summary, we have realized Rh(III)/Co(III)-catalyzed diamidation of amide-tethered olefins using dioxazolones and arylsulfonamides as different classes of amidating reagents. The reaction proceeded *via* initial intramolecular amidorhodation of the olefin to generate a Rh(III)–methyl species that is functionalized by both electrophilic and nucleophilic amidating reagents. The coupling systems were conducted under mild conditions with high efficiency. In addition, the Rh(III)- and Co(III)-catalyzed reactions have been compared. This strategy offers a rapid entry to vicinal diamides and might be useful in the synthesis of biologically active molecules.[1d,18]

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Conflicts of interest

There are no conflicts of interest to declare.

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