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C–H Activation

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Rh^{III}-Catalyzed C–H Activation with Pyridotriazoles: Direct Access to Fluorophores for Metal-Ion Detection**

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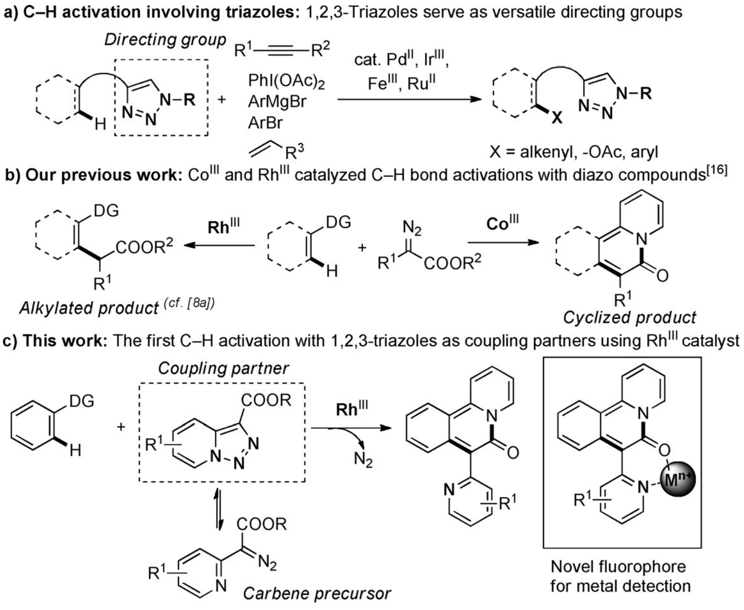
***Abstract:** The first C–H bond activation with pyridotriazoles as coupling partners is presented using a Rh^{III} catalyst. The pyridotriazoles can be used as new carbene precursors in C–H activation for direct access to novel fluorescent scaffolds. These tunable fluorophores can be applied for the detection of metal ions.*

Small-molecule fluorophores have attracted attention because of their potential applications in fluorescent bioimaging,[1] organic light-emitting diodes,[2] and as chemosensors for the detection of metal ions and biologically relevant species.[3] Over the past decades, several fluorescent scaffolds, such as naphthalimides, fluoresceins, rhodamines, and BODIPYs, have been developed.[4] In general, many organic fluorescent dyes are composed of conjugated polycyclic scaffolds possessing highly mobile electrons, which can lead to a change in the fluorescence properties during interaction with binding units.[5] Transition-metal-catalyzed C–H bond activations are widely used to construct diverse π-conjugated polycyclic ring systems, but are rarely employed in dye synthesis.[6] In this respect, novel designs and direct syntheses of new fluorescent analogues by C–H activation strategies are highly desirable.

Carbene migratory insertion has been successfully merged with reactions in which the C–H bond metalation is the initial step.[7] In recent years, diazo compounds[8] and *N*-tosylhydrazones[9] have been employed as precursors to carbenes. While diazo compounds are very versatile reagents for structurally complex products, some are potentially explosive and extremely difficult to handle on an industrial scale.[10] Although significant progress has been achieved, the development of new stable carbene precursors is still highly challenging. Recently, transition-metal catalyzed denitrogenative transformations of triazoles or tetrazoles have received attention for the construction of diverse N-heterocyclic compounds.[11] It has been demonstrated that these 1,2,3-triazoles share characteristics of diazo compounds as a result of an equilibrium of closed/opened forms.[12] Despite the remarkable advances achieved with Rh^{II}, Ni^{0}, or Cu^{I} catalysts,[13] C–H bond metalation coupled with metal carbene migratory insertion using triazoles has not been reported previously. In the C–H activation field, transformations involving 1,2,3-triazole compounds have been limited to their use as directing groups (Scheme 1 a).[14,15]


a) C–H activation involving triazoles: 1,2,3-Triazoles serve as versatile directing groups

b) Our previous work: Co^{III} and Rh^{III} catalyzed C–H bond activations with diazo compounds[16]

c) This work: The first C–H activation with 1,2,3-triazoles as coupling partners using Rh^{III} catalyst

Scheme 1. Directed C–H bond activation with carbene precursors.

We recently reported a Co^{III}-catalyzed C–H bond functionalization with diazo compounds, which provides access to a new family of fluorescent extended π-systems (Scheme 1 b).[16] Inspired by our previous work, we envisioned that C–H activation followed by insertion of 1,2,3-triazole-derived diazo compounds as coupling partners might be possible if the diazoimine form is present. In consideration of

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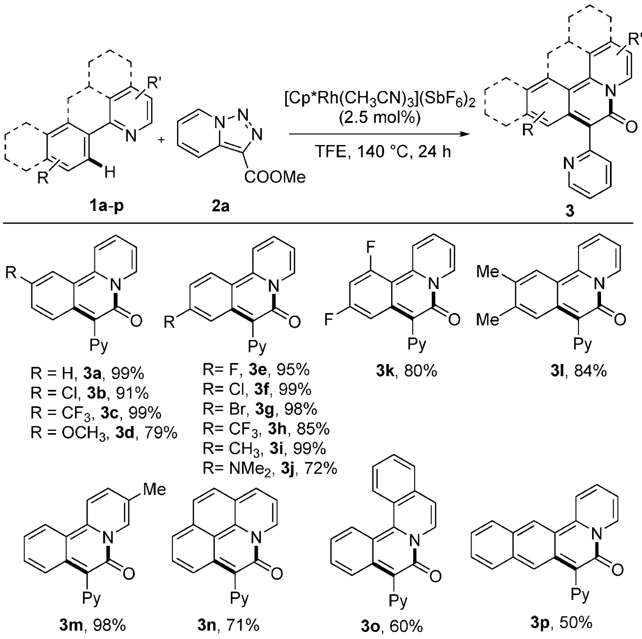
the structural differences between triazoles and diazo compounds, new analogous 1,2,3-triazole compounds, facilitating the open diazoimine form of triazole, need to be explored. In this regard, pyridotriazoles are especially attractive owing to the facile formation of the diazoimine form, which could be trapped with C–H bond metalated compounds to form a pyridiyl carbene intermediate.[11c,12,17] Furthermore, the pyridyl moiety on this new class of fluorescent compounds may offer a site for metal coordination, which can be potentially used for metal-ion sensors (Scheme 1c). Herein, we describe the first C–H bond activation with pyridotriazoles as innovative carbene precursors using the Cp*Rh^{III} (Cp* = η-C_5Me_5) catalyst, which provides direct synthetic access to novel fluorescent scaffolds for selective metal-ion detection. In this transformation, there are some intricate challenges:

1) The position of the equilibrium between the cyclic triazole and the open diazoimine form is governed by the substitution pattern, solvent polarity, and temperature.[17a] Although N-fused triazoles show an equilibrium shift towards the diazoimine form, the equilibria still favor the bicyclic structures in all cases studied to date. The equilibrium shift to the diazoimine form is essential to avoid unexpected side reactions.
2) Both the pyridine and 1,2,3-triazole groups are strongly coordinating directing groups that can lead to competing undesired C–H bond activation.[14,15,18]
3) Moreover, the pyridine groups in the substrate and product can coordinate strongly to the metal center, which may poison the catalyst.[19]

We began our investigation utilizing 2-phenylpyridine (**1a**) and pyridotriazole **2a** as model substrates. In accordance with our previous work,[16] this reaction was investigated with a {Cp*Co^{III}} catalyst, but neither the cyclized nor the alkylated products were detected (Table S1 in the Supporting Information). Gratifyingly, it was found that employing the [{Cp*$RhCl_2$}$_2$]/AgOAc combination or [Cp*$Rh(CH_3CN)_3$](SbF_6)$_2$ in 2,2,2-trifluoroethanol (TFE) afforded only the desired product **3a** in 96% and 87% yield, respectively (Table S1), without any of the alkylated product (Scheme 1b). It is noteworthy that the Rh^{III} catalyst can conduct the cyclization in this transformation, which indicates that the pyridyl moiety might play a crucial role in the cyclization. Further improvement of the yield (99%) was achieved in the presence of 2.5 mol% of [Cp*$Rh(CH_3CN)_3$](SbF_6)$_2$ at 140°C. The structure of **3a** was unambiguously confirmed by X-ray crystallographic analysis.[20] In addition, the reaction can be conducted effectively on a gram scale (1 g of **3a**, 97% yield).

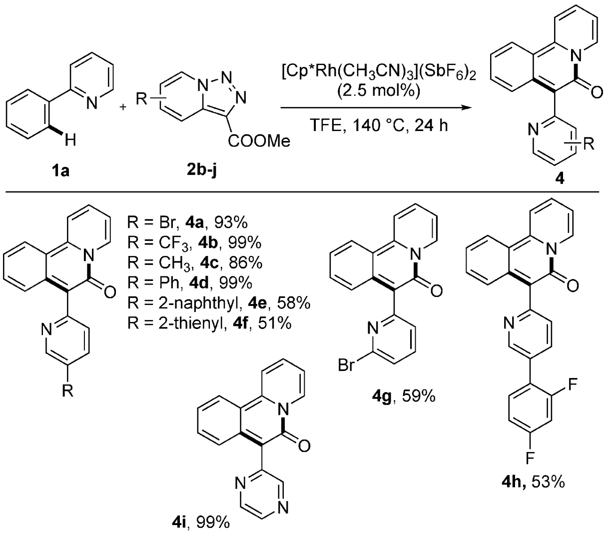
Under the optimal conditions, the scope of this reaction was explored with various 2-arylpyridines (Scheme 2). Mono or di-substituted substrates bearing both electron-donating groups (R = Me, OMe, NMe_2) and electron-withdrawing groups (R = Cl, Br, F, CF_3) on the aryl moiety were well-tolerated under the reaction conditions, and afforded the corresponding products **3b–3l** in good to excellent yields ranging from 72% to 99%. Moreover, the reaction with methyl substituents on the pyridine also proceeded efficiently and afforded **3m** in high yield. We were pleased to observe that this transformation is not restricted to a benzene platform and is applicable to extended π-systems **1n–1p** only requiring a slightly increased catalyst loading.



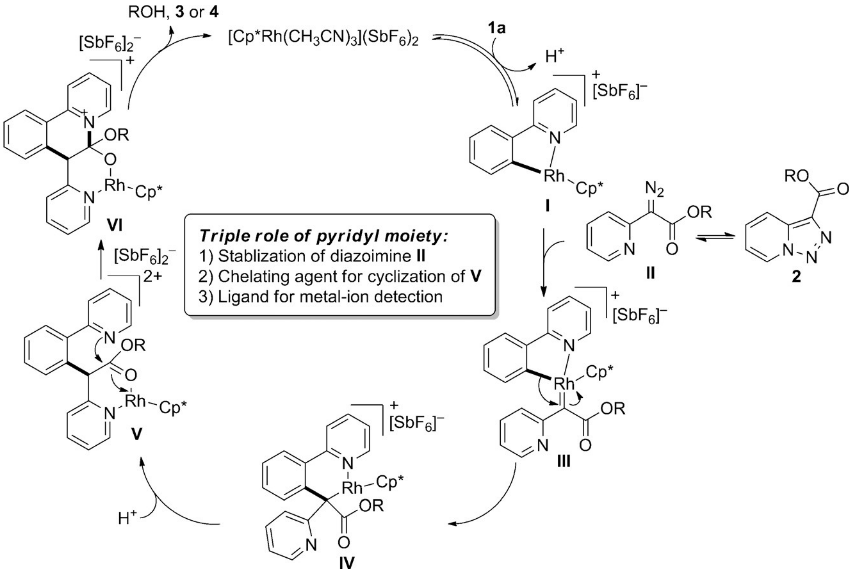
Scheme 2. Substrate scope of various 2-arylpyridines. For reaction conditions, see Supporting Information.

Furthermore, a wide range of pyridotriazoles were investigated as coupling partners. As shown in Scheme 3, the coupling reactions between 2-phenylpyridine (**1a**) and substituted pyridotriazoles **2** proceeded smoothly to furnish the corresponding products **4** in moderate to excellent yields.

To better understand the reaction mechanism, we conducted a series of experiments (see Supporting Information). A competition experiment between electronically different arylpyridines **1a** and **1j** showed that an electron-rich substrate is more favored than an electron-deficient one by a 3:1 ratio, thus suggesting that the C–H bond activation process may be



Scheme 3. Substrate scope of various pyridotriazoles. For reaction conditions, see Supporting Information.



Scheme 4. Proposed reaction mechanism.

electrophilic in nature. Interestingly, competition experiments for the preference of electronically different triazole compounds did not noticeably affect the reactivity. A deuterium labeling experiment indicated that the C–H activation step is reversible under the conditions with the H/D scrambling being observed. The KIE value ($k_H/k_D = 1.7$) from two parallel reactions suggests that the cleavage of the C–H bond is not involved in the rate-limiting step. To probe the order of events, ^{1}H NMR spectroscopy and ESI-MS analyses of the stoichiometric reaction were conducted (see Supporting Information). The results show that C–H activation and rhodacycle formation with phenyl pyridine **1a** occur readily even at room temperature. The intermediate after carbene insertion in the reaction of the cyclometalated phenyl pyridine with pyridotriazole **2a** has also been characterized.

On the basis of the these experiments and previous reports,[8,16,21] a plausible reaction mechanism is proposed in Scheme 4. The transformation is initiated by the coordination of substrate to the cationic Rh center, followed by a reversible C–H bond cleavage to produce cationic rhodacycle **I**. Next, the Rh^{III} carbene intermediate **III** is generated by N$_2$ loss from the in situ generated diazoimine **II**. Intermediate **III** undergoes migratory insertion leading to rhodacyclic intermediate **IV**. After proto-demetalation to **V**, nucleophilic addition to the activated ester carbonyl occurs to give **VI** with the aid of {Cp*Rh^{III}} as a Lewis acid. Upon elimination of alcohol from intermediate **VI**, product **3** or **4** is formed with regeneration of the catalyst. Notably, the pyridyl group facilitates this transformation instead of poisoning the catalyst. Presumably, chelation of rhodium between the pyridyl and ester groups in **V** activates the carboxylate for the nucleophilic cyclization.

The pyridine and carbonyl moieties in the products constitute binding sites for cations, making them bidentate luminophores with sensing capabilities. To demonstrate their ability to discriminate between metal ions, we have monitored the changes in the UV/Vis absorption and emission spectra in the presence of Cu^{II} and Zn^{II} owing to the high binding affinity with ligands containing oxygen or nitrogen donor atoms.[22]

Upon addition of Zn(ClO$_4$)$_2$, the absorption maxima appear visibly blue-shifted, an effect that is more pronounced with Cu(ClO$_4$)$_2$, which causes a stronger hypsochromic shift (Figures 1 a,c, Figures S1–S10, and Table S3). This observa-

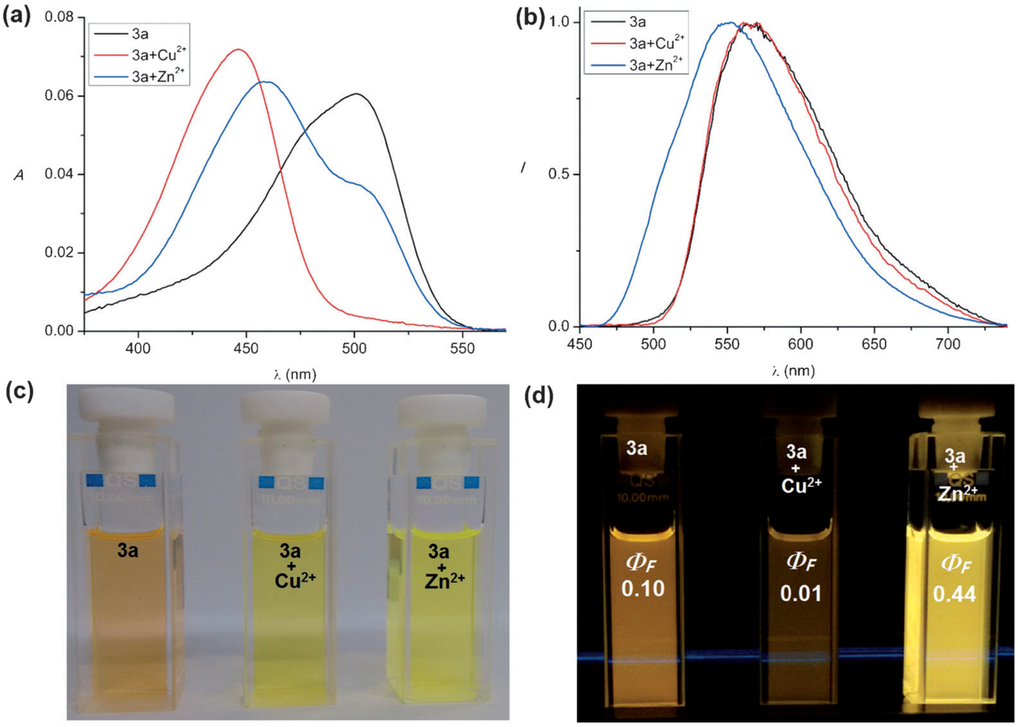


Figure 1. a) Absorption and b) emission spectra of compound **3a** in the presence of Cu(ClO$_4$)$_2$ or Zn(ClO$_4$)$_2$. Photos of **3a** in a solution of CH$_2$Cl$_2$ and with Cu(ClO$_4$)$_2$ and Zn(ClO$_4$)$_2$ under c) ambient light and d) UV light. For detailed conditions, see Supporting Information.

tion can be explained in terms of electrostatic ground-state stabilization by complexation, an effect that is enhanced by the open-shell character of Cu^{II} (d^9 configuration) as opposed to the closed d-shell structure of Zn^{II} (d^{10}) which shields the nuclear charge more effectively. If compared with the free ligands, the addition of $Zn(ClO_4)_2$ leads to enhanced fluorescence intensities and slightly blue-shifted emission spectra, whereas $Cu(ClO_4)_2$ rather acts as a quencher without affecting the emission wavelengths (Figures 1 b, d, Figures S1–S10, and Table S3). Coordination to Zn^{II} probably enhances the rigidity of the emissive states and thus an increase in the quantum yields occurs, whereas the unpaired electron of the Cu^{II} decreases the quantum yields by radiationless deactivation in spite of rigidifying the complexes.

In summary, the first example of Rh^{III}-catalyzed C–H bond activation and subsequent carbene insertion with pyridotriazoles as carbene precursors has been reported. The pyridyl moiety of the pyridotriazoles plays three vital roles:

1) for stabilization of the in situ generated diazoimine form
2) acting as a chelating agent for coordination with the catalyst, facilitating cyclization
3) as a ligand for detection of metal ions with the products.

Mechanistic investigations elucidated that C–H bond activation is the first step before rhodium carbene formation. We have demonstrated that these compounds constitute dual sensors for Cu^{2+} and Zn^{2+} ions, as both the absorption wavelengths and the fluorescence intensities are significantly affected upon coordination. Owing to the advantages of ease of visualization and tunable properties, this new class of fluorophores can be useful for a variety of applications, such as chemo/bio-sensing.

Keywords: carbene · C–H activation · fluorophore · rhodium · triazole

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[20] CCDC 1402347 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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