C–H Activation

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Cationic Cobalt(III) Catalyzed Indole Synthesis: The Regioselective Intermolecular Cyclization of N-Nitrosoanilines and Alkynes

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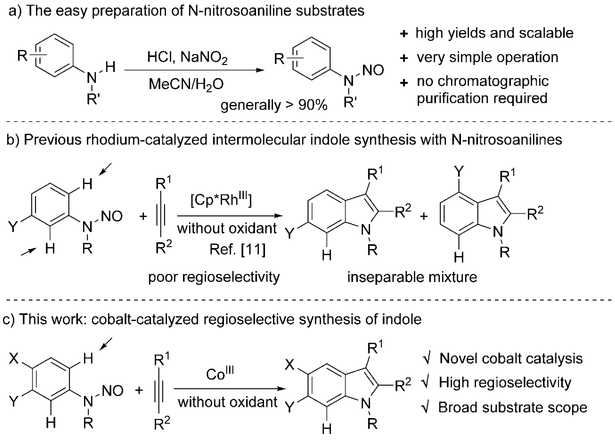
***Abstract:** The unique regioselectivity and reactivity of cobalt(III) in the direct cyclization of N-nitrosoanilines with alkynes for the expedient synthesis of N-substituted indoles is demonstrated. In the presence of a cobalt(III) catalyst, high regioselectivity was observed when using unsymmetrical meta-substituted N-nitrosoanilines. Moreover, internal alkynes bearing electron-deficient groups, which are almost unreactive in the [Cp*Rh^{III}]-catalyzed system, display good reactivity in this transformation.*

Indole motifs are widespread in natural products, bioactive compounds, and other functional molecules.[1] In light of their importance, numerous useful methods have been developed for their preparation,[2] including the well-established Fischer indole synthesis.[3] Alternatively, intermolecular cyclization of *ortho*-halogenated anilines with alkynes is the frequently used in the construction of indoles.[4] Importantly, the directed transition-metal-catalyzed C–H bond functionalization strategy has been employed in cyclization reactions for broader substrate scope and higher atom economy.[5] According to this strategy, the precious transition-metal-catalyzed (e.g., palladiumn, rhodium, ruthenium, gold) intermolecular cyclizations of anilines, or its derivatives, with alkynes through C–H annulation for the construction of indoles have been developed.[6]

In the past decades, the development of the first-row transition-metal-catalyzed transformation has attracted attention because these base metals are earth-abundant, inexpensive, have variable oxidation states, and are less toxic, etc.[7] In contrast to the instability and the sensitivity of the low-valent earth-abundant metal catalysts to air and moisture, the high-valent earth-abundant metals such as iron(III)[8] and cobalt(III)[9] are stable and easily prepared, and have exhibited incredible potential in C–H activation in recent years. Despite these elegant works, the intermolecular C–H cyclization of aniline derivatives with alkynes, catalyzed by either iron(III) or cobalt(III), has not been achieved.

More recently, by using the N-nitrosoanilines as starting materials, which are readily prepared through a very simple process (Scheme 1a),[10] an interesting rhodium-catalyzed indole synthesis through the intermolecular cyclization with alkynes has been independently disclosed by the groups of Zhu[11a] and Huang[11b] (Scheme 1b). Although [Cp*Rh^{III}] proved to be effective in this transformation, there are still some limitations which need to be addressed: 1) High loading of the expensive rhodium catalyst was used; 2) The regioselectivity was not controlled in the rhodium catalysis. When using the unsymmetrical *meta*-substituted N-nitrosoanilines as substrates, typically a pair of inseparable isomeric indole products was obtained (Scheme 1b); 3) The internal alkynes bearing electron-deficient groups were not effective. These issues may limit its application in organic synthesis. If these problems could be addressed by either an inexpensive and stable earth-abundant iron(III) or cobalt(III) catalyst, it is definitely attractive but still a challenging issue. Herein, we describe a novel highly regioselective, cobalt-catalyzed cyclization of N-nitrosoanilines and alkynes through C–H bond cleavage (Scheme 1c). To the best of our knowledge, this reaction is the first cobalt(III)-catalyzed construction of indoles through an intermolecular C–H cyclization of simple aniline derivatives with alkynes (Scheme 1c).



Scheme 1. Cobalt-catalyzed regioselective indole synthesis through C–H functionalization. Cp* = C_5Me_5.

With our continued interest in the use of inexpensive metals, such as iron, copper, manganese, and cobalt, to catalyze C–N bond-formation reactions[12] and the efficient synthesis of indoles,[6b] we initially tried to execute the intermolecular cyclization of *N*-methyl-*N*-phenylnitrous amide (**1a**) with diphenylacetylene (**2a**) by using iron(III)

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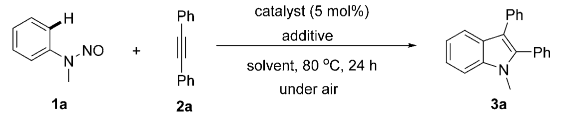
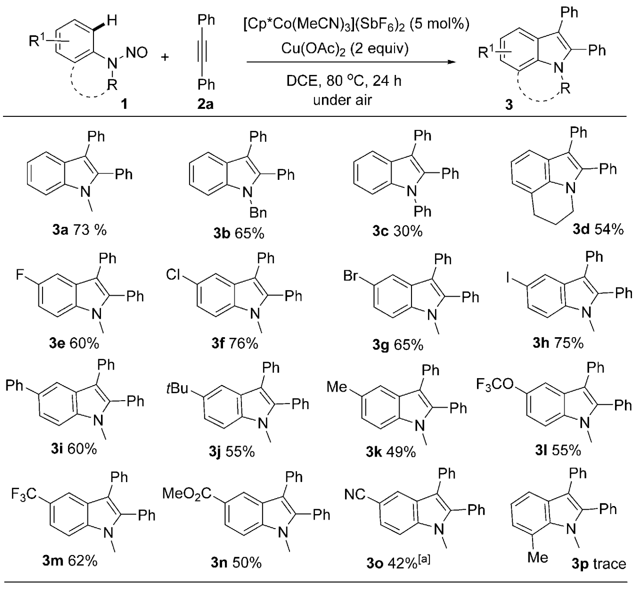
Table 1: Optimization studies.[a]



Entry	Catalyst	Additive (equiv)	Solvent	Yield [%][b]
1	FeF_3	–	DCE	–
2	$Fe(OTf)_3$	–	DCE	–
3	$[Cp^*Co(CO)I_2]$	–	DCE	–
4	$[Cp^*Co(MeCN)_3](SbF_6)_2$	–	DCE	7
5	$[Cp^*Co(MeCN)_3](SbF_6)_2$	–	MeOH	–
6	$[Cp^*Co(MeCN)_3](SbF_6)_2$	–	AcOH	–
7	$[Cp^*Co(MeCN)_3](SbF_6)_2$	LiOAc (2)	DCE	–
8	$[Cp^*Co(MeCN)_3](SbF_6)_2$	NaOAc (2)	DCE	–
9	$[Cp^*Co(MeCN)_3](SbF_6)_2$	KOAc (2)	DCE	–
10	$[Cp^*Co(MeCN)_3](SbF_6)_2$	AgOAc (2)	DCE	<5
11	$[Cp^*Co(MeCN)_3](SbF_6)_2$	$Cu(OAc)_2$ (2)	DCE	73
12	$[Cp^*Co(MeCN)_3](SbF_6)_2$	$Cu(OAc)_2$ (1)	DCE	66
13	$[Cp^*Co(MeCN)_3](SbF_6)_2$	$Zn(OAc)_2$ (2)	DCE	46
14	$[Cp^*Co(MeCN)_3](SbF_6)_2$	$Fe(OAc)_2$ (0.5)	DCE	51
15	–	$Cu(OAc)_2$ (2)	DCE	–

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (5.0 mol%), additive (0.5–2.0 equiv), solvent (1 mL), 80°C for 24 h. [b] Yield of isolated product. DCE = 1,2-dichloroethane, Tf = trifluoromethanesulfonyl.

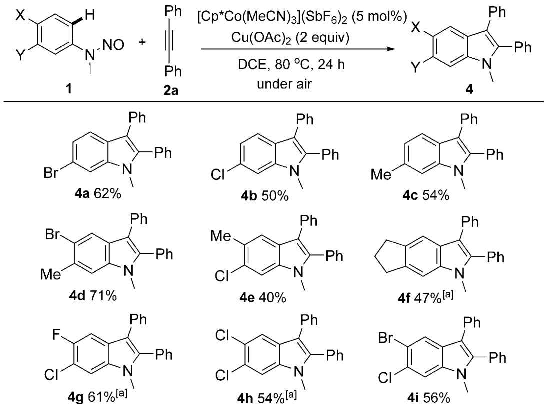


Scheme 2. Reactions of diverse substituted N-nitrosoanilines with diphenylacetylene. [a] $[Cp^*Co(MeCN)_3](SbF_6)_2$ (10 mol%) was used, 49 h.

and cobalt(III) catalysts (Table 1). Unfortunately, some iron salts, and the $[Cp^*Co(CO)I_2]$ were totally unreactive (entries 1–3). Delightfully, the use of the cationic $[Cp^*Co(MeCN)_3](SbF_6)_2$ afforded the desired product **3a** in 7% yield (entry 4). Other solvents such as MeOH and HOAc were less effective (entries 5 and 6). Further screening revealed that the key to achieving this transformation in decent yield is the identification of a suitable base, and we found that adding $Cu(OAc)_2$ improved the yield notably, whereas the efficiency decreased significantly when bases such as LiOAc, NaOAc, KOAc, and AgOAc were used (entries 7–12). It is noteworthy that the addition of $Zn(OAc)_2$ and $Fe(OAc)_2$ can furnish the desired **3a** in moderate yields, and thus convinced us that this reaction indeed proceeded without an external oxidant, and that the $Cu(OAc)_2$ served as a base, not an oxidant in this transformation (entries 13 and 14). No reaction was observed in the absence of the cobalt catalyst (entry 15).

With the optimized reaction conditions in hand, the substrat scope was then investigated. The generality of the reaction is showcased by the remarkable compatibility with various functional groups on the phenyl ring and the tolerance of different N-substituents (Scheme 2). When using other N-phenyl- or N-benzyl-substituted substrates, slightly decreased yields were obtained, and may be attributed to steric effects (**3b**,**c**). Interestingly, the fused tricyclic indole framework, which is widely present in natural products, can be easily constructed using this method (**3d**). It is important to stress that N-nitrosoanilines bearing a variety of important functional groups, such as the halogens (F, Cl, Br, I) and phenyl, alkyl groups (*t*Bu, Me), trifluoro methoxy (OCF_3), and electron-deficient (CF_3, CO_2Me, CN) groups, at the *para*-position of the phenyl ring generally react well under the present catalytic system (**3e**–**o**), thus allowing many important substitution patterns to be incorporated into the indole skeleton. Whereas this reaction seems sensitive to steric hindrance, the substrate bearing an *ortho*-substituent retarded the reaction (**3p**).

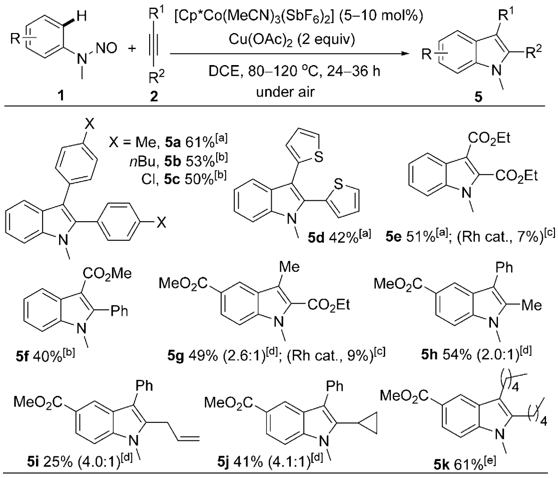
The superior regioselectivity of $[Cp^*Co^{III}]$ compared to that of $[Cp^*Rh^{III}]$ was observed when unsymmetrical *meta*-substituted N-nitrosoanilines were employed (Scheme 3). For example, the *meta*-bromo- and *meta*-chloro-substituted N-nitrosoanilines gave the desired product with impressively high regioselectivity (i.e., only one isomer was obtained; **4a**,**b**). In comparison, by using the $[Cp^*Rh^{III}]$-catalyzed system for the same substrates, inseparable mixtures, (1:1.15) and (1:1.64), were obtained, respectively.[11a] Additionally, *meta*-methyl-substituted N-nitrosoaniline also underwent the cyclization with high site-selectivity (**4c**). It is worthy mentioning that our method is not only compatible with diverse monosubstituted, but also disubstituted N-nitrosoanilines as well (**4d**–**i**). Among them, the dihalogen-substituted



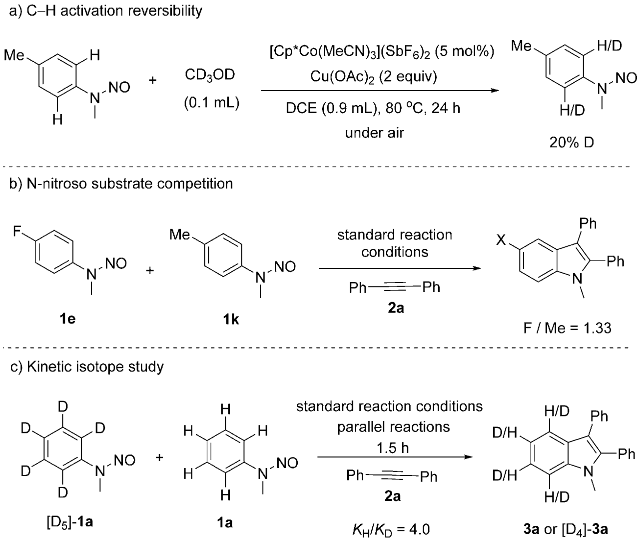
Scheme 3. Reactions of *meta*-substituted N-nitrosoanilines with diphenylacetylene. [a] $[Cp^*Co(MeCN)_3](SbF_6)_2$ (10 mol%) was used.

N-nitrosoanilines were found to be efficient reaction partners, thus offering products suitable for further structural elaboration (**4g–i**). The reason for the excellent regioselectivity may be attributed to the smaller ionic radius of cobalt compared to that of rhodium, thus resulting in a stronger steric repulsion between the substrate and the Cp* ligand of [Cp*Co^{III}]. Therefore, it is much easier for [Cp*Co^{III}] to distinguish between the two different *ortho* sites in the unsymmetrical *meta*-substituted N-nitrosoanilines.[9k]

We next tested the scope with respect to the internal alkynes (Scheme 4). To our delight, various symmetric diaryl-substituted alkynes can react smoothly with **1a** to generate the desired products (**5a–d**). More attractively, according to the previous reports[11] and our observations,[13] the reaction is less efficient under the [Cp*Rh^{III}]-catalyzed reaction conditions with an internal alkyne bearing either two electron-deficient groups or one alkyl group and one electron-deficient group, such as an ester group (COOEt). In contrast, it is noteworthy to find that these alkynes displayed good reactivity in the present protocol, furnishing the desired product in synthetically acceptable yield (**5e–g**). In addition, unsymmetrical alkyl aryl alkynes and carboxy aryl alkynes could also participate in this reaction, giving the corresponding products in reasonable yields as well as good to excellent regioselectivity (**5f–j**). Surprisingly, for the unsymmetrical alkyl aryl alkynes, different selectivity was observed between [Cp*Co^{III}] and [Cp*Rh^{III}][11] catalysis. For the [Cp*Co^{III}] catalyst, products with an aryl group at the 3-position were favored (**5h–j**; and further confirmed by HMBC, HSQC and NOESY experiments). Gratifyingly, the reaction of an alkyl alkyne also proceeded efficiently (**5k**).



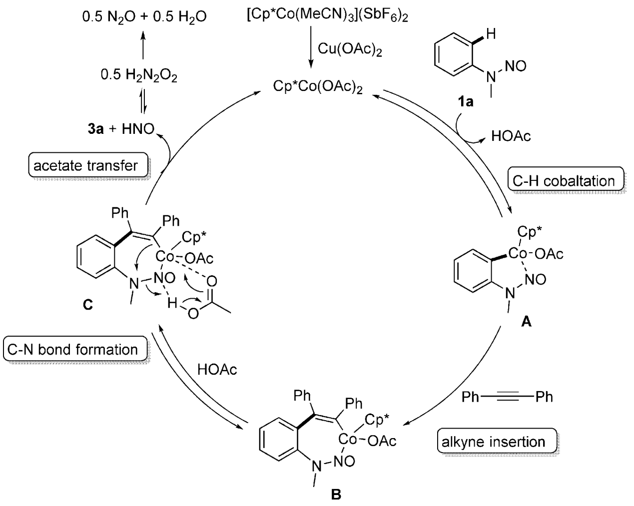
Scheme 4. Scope with respect to the internal alkynes. [a] **1** (0.2 mmol), **2** (0.3 mmol), catalyst (5 mol%), Cu(OAc)$_2$ (0.4 mmol), DCE (1 mL), 80 °C, 24 h. [b] **1** (0.2 mmol), **2** (0.3 mmol), catalyst (10 mol%), Cu(OAc)$_2$ (0.4 mmol), DCE (1 mL), 100 °C, 36 h. [c] The number within the parentheses is the yield obtained when [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ was used as the catalyst. [d] **1** (0.2 mmol), **2** (0.4 mmol), catalyst (10 mol%), Cu(OAc)$_2$ (0.4 mmol), DCE (1 mL), 120 °C, 24 h. [e] **1** (0.4 mmol), **2** (0.2 mmol), catalyst (10 mol%), Cu(OAc)$_2$ (0.4 mmol), DCE (1 mL), 120 °C, 24 h.



Scheme 5. Mechanistic studies.

To gain more insight into the mechanism, some experiments were conducted (Scheme 5). A significant level of deuterium incorporation (20%) was observed at the *ortho*-position of **1k** when it was subjected to the present cobalt-catalyzed system in CD$_3$OD, in the absence of an alkyne, thus indicating that the cobalt-mediated C–H bond cleavage is reversible (Scheme 5a). Moreover, a competition reaction was also performed to determine the electronic preference of this transformation. When **1e** was and **1k** were reacted at the same time, the reaction favored the electron-deficient N-nitrosoaniline in a 1.33:1 ratio (Scheme 5b), thus implying that the C–H activation probably occurs by a concerted metalation-deprotonation (CMD) mechanism.[14] Moreover, a notable primary kinetic isotope effect was observed ($K_H/K_D = 4.0$), thus suggesting that C–H bond cleavage should be involved in the rate-limiting step (Scheme 5c).

Based on the mechanistic studies and the relevant reports,[9,11] a plausible mechanism is proposed (Scheme 6). The reaction begins with an anion exchange to generate the



Scheme 6. Proposed catalytic cycle.

active catalyst [Cp*Co(OAc)$_2$], which coordinates to **1a** and subsequently undergoes the acetate-assisted C−H bond cleavage to furnish the five-membered metallacyclic intermediate **A**. Next, alkyne insertion forms the intermediate **B**. An intramolecular substitution may then occur to form the C−N bond and break the N−N bond with the aid of HOAc.[15] The product **3a** is thus formed and the active catalyst [Cp*Co(OAc)$_2$] is regenerated to complete the catalytic cycle.

In summary, we have demonstrated an efficient and direct cobalt-catalyzed cyclization of N-nitrosoanilines with alkynes and it provides expedient access to various N-substituted indoles. The unique regioselectivity and reactivity of cobalt(III) in the direct cyclization of N-nitrosoanilines with alkynes is demonstrated for the first time. Moreover, electron-deficient internal alkynes can be tolerated in the present protocol. Mechanistic studies revealed that the C−H activation is reversible through a concerted metalation-deprotonation (CMD) mechanism. Considering the cost-effective nature of earth-abundant cobalt and the diversity of accessible covalent linkages for the nitroso group, as well as the excellent regioselectivity of the present protocol, this method should be of high synthetic utility. Further applications of this transformation are ongoing in our laboratory.

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Keywords: C−H activation · cobalt · indoles · reaction mechanisms · regioselectivity

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