Letter

Control Over Organometallic Intermediate Enables Cp*Co(III) Catalyzed Switchable Cyclization to Quinolines and Indoles

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Control Over Organometallic Intermediate Enables Cp*Co(III) Catalyzed Switchable Cyclization to Quinolines and Indoles

Qingquan Lu, Suhelen Vásquez-Céspedes, Tobias Gensch, and Frank Glorius*

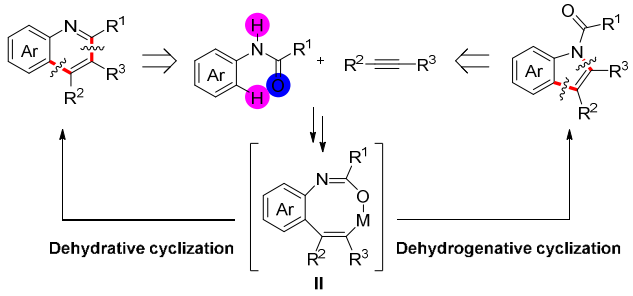
Organisch-Chemisches Institut Westfälische Wilhelms-Universität Münster Corrensstraße 40, 48149 Münster (Germany)

ABSTRACT: Achieving controllable C–H functionalization to elaborate valuable compounds from simple chemicals is attractive and highly desirable, especially if non-precious transition metal catalysts can be used. However, controlling selectivity in these transformations remains a continuous challenge to synthetic chemists. Herein, we show for the first time that control over the reactive organometallic intermediate enables the switchable synthesis of quinoline and indole from amides and alkynes through C–H activation using Cp*Co(III). The keys to this strategy are: 1) introducing a Lewis acid to greatly accelerate the dehydrative cyclization, which can out-compete dehydrogenative cyclization; 2) tuning the directing group to facilitate the dehydrogenative cyclization and inhibit dehydrative cyclization.

KEYWORDS: cobalt catalysis, C–H bond activation, switchable selectivity, dehydrative cyclization, dehydrogenative cyclization

Catalysis is a key technology for organic synthesis, and the development of more sustainable, efficient catalysts has become particularly important in modern chemistry.[1] More recently, first row transition-metal catalysts have attracted more organic chemists not only due to their unique reactivity, but also their lower toxicity, low cost, and abundant reserves.[2] In this regard, cobalt catalysis has gained prominent attention,[3] and of particular interest is the high-valent cobalt catalyst Cp*Co(III).[3c,3d] The high valence of the cobalt catalyst has proven to be effective for enabling cascade bond construction reactions that are usually elusive and difficult to achieve by other transition metals, as demonstrated by the groups of Matsunaga and Kanai,[4] Ackermann,[5] Ellman,[6] Chang,[7] Glorius[8] and others.[9] On this basis, we speculated that this innovative catalysis might serve as an alternative route to address some formidable issues faced in C–H bond functionalization.

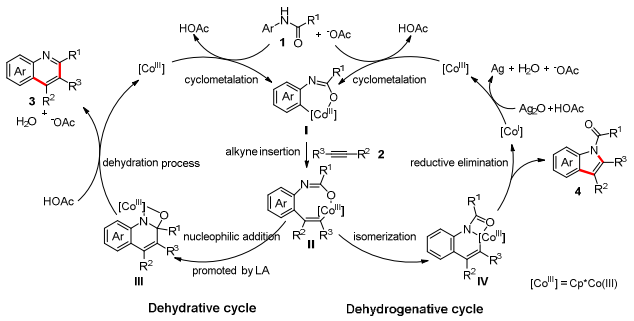
Selectivity control has always been an essential issue in organometallic chemistry,[10] and the sometimes uncontrolled reactivity of organometallic intermediates makes it more challenging to develop highly selective and efficient C–H functionalizations. An ambitious goal is the controlled synthesis of quinolines and indoles, which are privileged structures in medicinal chemistry and widely present in natural products.[11-12] As shown in Scheme 1, both types of molecules can be envisioned to arise retrosynthetically from the combination of amides and alkynes. Although great progress has been made in transition metal catalysis, up to date, the exploration of a switchable strategy for the synthesis of both quinolines and indoles has not been accomplished.[11-12] The major difficulty of this transformation is the high reactivity of the organometallic intermediate **II** generated in situ, rendering the following cyclization processes uncontrollable.



Scheme 1. Retrosynthetic analysis of quinolines and indoles from amides and alkynes through C–H activation

Recent reports showed that cationic Cp*Co(III) complexes might be more oxophilic than other transition metal complexes such as Cp*Rh(III) and can be utilized to achieve unconventional cyclization or oxidative coupling reactions.[4a] We questioned whether a well-defined Cp*Co(III) system could offer the possibility to address the above-mentioned issues through identification of the selective cyclization processes. A proposed pathways for the switchable synthesis of quinolines and indoles is outlined in Scheme 2. After initial cyclometalation and alkyne insertion, an eight-membered organometallic intermediate **II** is generated. It is well known that the eight-membered organometallic intermediate **II** is highly reactive,[13] which could undergo intramolecular nucleophilic addition to C=O and further dehydration to furnish quinoline. In contrast, a six-membered organometallic intermediate **IV** can be formed through isomerization of **II**, which then undergoes a C–N reductive elimination to form indole. Ultimately, the relative reaction rates of dehydrative cyclization and dehydrogenative cyclization will determine the final product distribution. Thus, control over the selectivity would be accomplished if the reactivity of the intermediate **II** can be adjusted by elegant methods. On this basis, we reasoned that the cooperation of Cp*Co(III) and Lewis acids (LA) would improve the electrophilicity of the carbonyl group and further facilitate the nucleophilic addition process. Moreover, modulation of the electronic and steric properties of the directing group would also enable the dehydrogenative process and suppress the nucleophilic attack.[14] If this strategy is successful, we recognized that this new catalytic system might provide (1) a demonstration of a new strategy to switch the elusive organometallic intermediate between

dehydrative cyclization and dehydrogenative cyclization processes, (2) a direct access to quinolines by employing simple amides and alkynes through C–H activation,[15] and (3) an undeveloped Cp*Co(III) catalyzed oxidative dehydrogenative C–C/C–N cyclization reaction.

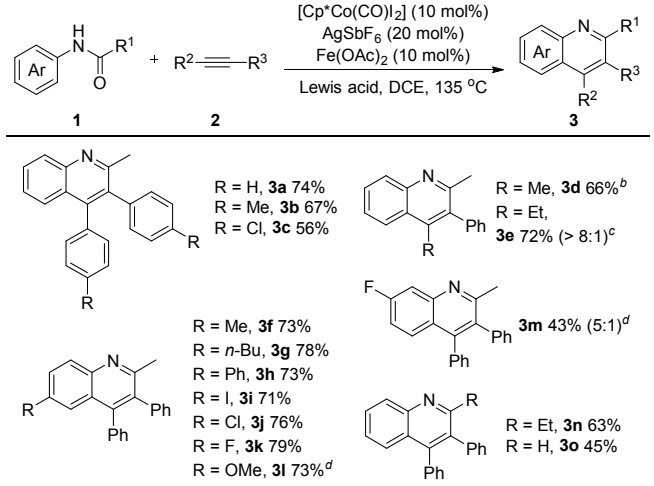


Scheme 2. Proposed pathways for switchable cyclization to quinolines and indoles from amides and alkynes through C–H activation

To validate our proposed assumption, we started our investigation by reacting acetanilide (**1a**) with diphenylacetylene (**2a**) as the model reaction. As expected, a mixture of quinoline **3a** and indole **4a** was obtained in low selectivity and low yield when **1a** and **2a** were directly reacted in the presence of $[Cp^*Co(CO)I_2]$ and $AgSbF_6$. To improve the reaction efficiency, we next screened an array of bases and the yield of quinoline **3a** slightly increased to 25% employing $Fe(OAc)_2$. (for details, see table S1 in the supporting information). The low reaction efficiency is attributed to the deactivation of Cp*Co(III) through C–N reductive elimination to form indole **4a**. On the basis of our above-mentioned hypothesis, the feasibility of this strategy relies on the selectivity after the alkyne insertion step. To facilitate the nucleophilic addition, we next attempted to use a Lewis acid to activate the C=O bond. Accordingly, the yield of quinoline **3a** increased to 72% when BF_3•OEt_2 was employed. The yield of **3a** further improved to 76% with high selectivity by increasing the temperature to 135 °C. Subsequently, to switch the reaction selectivity from quinoline to indole, we utilized an external oxidant, silver oxide, to close the dehydrogenative catalytic cycle. However, the desired indole product **4a** was obtained only in 41% yield, together with 38% yield of the quinoline. To solve this problem, we further aimed to inhibit the nucleophilic addition and facilitate the isomerization/reductive elimination process by tuning the directing group.[14] Delightfully, when the methyl group in the acetanilide (**1a**) was replaced by dimethylamino group, the corresponding indole product **4c** was isolated in 85% yield and no quinoline was detected by GC-MS analysis. Moreover, neither indole nor quinoline was detected when $[Cp^*Co(CO)I_2]$ was absent, revealing the vital role of Cp*Co(III) in this transformation.

With the optimized reaction conditions in hand, the generality of this protocol to synthesize quinolines was first investigated and the results are given in Table 1. Diphenylacetylenes bearing either electron-donating or electron-withdrawing groups, such as *p*-methyl and *p*-chloro, efficiently underwent dehydrative cyclization, giving good yields of the desired quinolines **3b** and **3c**. Notably, when one of the aromatic groups in diphenylacetylene was replaced with an alkyl chain, the corresponding products (**3d**-**3e**) were obtained with high regioselectivity. Nevertheless, aliphatic alkynes or terminal alkynes, such as octyne and phenylacetylene, were not amenable to this protocol. Furthermore, a series of acetanilides substituted with electron-donating groups (MeO, Me, *n*-Bu,) and electron-withdrawing groups (F, Cl, I) proved to be well tolerated and converted to the expected quinolines **3f**-**3m** in moderate to good yields. The tolerance of halides, in particular the iodo, demonstrated the potential utility of the present protocol. For *meta*-substituted acetanilide, as exemplified by fluoro, the reaction gave two regioisomers with moderate selectivity. When the sterically hindered *ortho*-methyl substituted acetanilide was employed, only trace amounts of the desired product could be detected. Variation of the *N*-acyl moiety of the anilide substrate was found to be feasible as well. Anilides bearing not only ethyl group, but also a hydrogen, proceeded to give the expected products **3n** and **3o** in moderate to good yields.

Table 1. Substrate scope for dehydrative cyclization to quinolines[a]



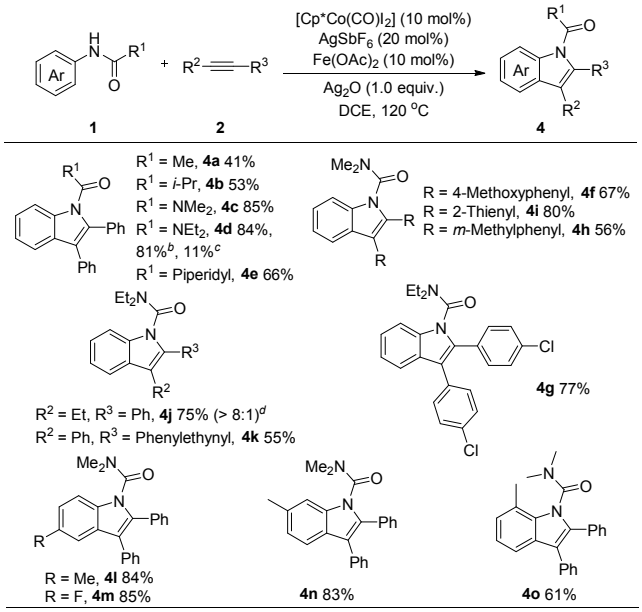
[a]Unless otherwise specified, all reactions were carried out using **1** (0.2 mmol), **2** (0.8 mmol), $[Cp^*Co(CO)I_2]$ (10 mol%), $AgSbF_6$ (20 mol%), $Fe(OAc)_2$ (10 mol%), and BF_3•OEt_2 (0.16 mmol) in DCE (1.0 mL) at 135 °C under argon for 12 h, isolated yield. [b]Single product was isolated. [c]Major isomer was shown. [d]$B(C_6F_5)_3$ (0.16 mmol) was used and 24 h.

So far, most of the Cp*Co(III) catalyzed transformations are limited to reactions known with established transition metal catalysts. We next compared the reactivity of the state-of-the-art precatalysts widely employed in C–H activation, such as $[(p\text{-cymene})RuCl_2]_2$, $[Cp^*RhCl_2]_2$, $Pd(OAc)_2$ and $[Cp^*IrCl_2]_2$, under otherwise identical conditions (see Table S2 in the supporting information). All of these showed to be inactive in this new challenging transformation and most of the starting material remained inert after reaction, further emphasizing the specificity of Cp*Co(III). The unique catalytic efficiency of Cp*Co(III) might be attributed to its Lewis acidity and the more nucleophilic alkenyl-Cp^*Co^{III} species.[4a]

Subsequently, the generality of this protocol to synthesize indoles was investigated. As shown in Table 2, the structure of **4c** was confirmed unambiguously by X-ray crystallographic analysis.[16] Other *N*-phenylureas, such as, 1,1-diethyl-3-phenylurea and *N*-phenylpiperidine-1-carboxamide, also display high reactivity in this protocol, affording the corresponding indole products **4d** and **4e** in 84% and 66% yields, respectively. Diphenylacetylenes substituted with methyl,

methoxy and chloro were viable in this transformation, furnishing the desired products **4f**-**4h** in moderate to good yields. The heterocyclic alkyne 1,2-bis(2-thienyl)acetylene proved suitable for this dehydrogenative cyclization and gave the desired product **4i** in 80% yield. For unsymmetrical arylalkyl substituted alkyne, the reaction proceeded smoothly with high regioselectivity, delivering the expected product **4j** in 75% yield. Importantly, a diyne can also be successfully utilized in this transformation, affording the corresponding product **4k** with highly selective monoannulation. Only trace amount of the expected indole product was detected when octyne or phenylacetylene was submitted. Furthermore, various *ortho*, *meta* and *para*-substituted *N*-arylureas were examined next. Methyl as an electron-donating group and fluoro as an electron-withdrawing group did not alter the reactivity of the *N*-arylureas, providing the desired products **4l** and **4m** in 84% and 85% yields. It is particularly notable that the *meta*-substituted *N*-arylurea gave the single product **4n** in 83% isolated yield. When methyl was located at the *ortho*-position, **4o** was isolated in 61% yield.

Table 2. Substrate scope for dehydrogenative cyclization to indoles[a]



[a]All reactions were carried out using **1** (0.2 mmol), **2** (0.4 mmol), [Cp*Co(CO)I$_2$] (10 mol%), $AgSbF_6$ (20 mol%), $Fe(OAc)_2$ (10 mol%), and Ag_2O (0.2 mmol) in DCE (1.0 mL) at 120 °C under argon for 12 h, isolated yield. [b][Cp*RhCl$_2$]$_2$ (5 mol%) was used. [c][Cp*IrCl$_2$]$_2$ (5 mol%) was used. [d]Major isomer was shown. The synthetic utility of this Cp*Co(III)-catalyzed oxidative dehydrogenative cyclization strategy was further illustrated by the removal of the carbamoyl moiety. For example, **4c** can be easily transformed into the corresponding unprotected indole in 76% yield by a simple operation (see Scheme S1 in the supporting information).

As mentioned above, the key cobaltacycle intermediate **II**, determines the efficiency of the dehydrative cyclization or dehydrogenative cyclization processes. When acetanilide (**1a**) reacted with diphenylacetylene under the dehydrogenative cyclization conditions, the corresponding indole **4a** was isolated in 41% yield while 38% yield of quinoline **3a** was generated concurrently. However, when *N*-phenylisobutyramide was submitted under identical condition, the corresponding indole product **4b** was isolated in 53% yield while only about 3% yield of the corresponding quinoline can be detected. These results indicate that the bigger R^1 group in cobaltacycle intermediate **II** might hinder the dehydrative cyclization, probably through supression of the nucleophilic addition process. Moreover, the nucleophilic addition will be favored for the amides due to the decreased electrophilicity of the urea motif, as evidenced by the significant upfield shift of the urea carbonyl carbon in ^{13}C-NMR, relative to acetanilide. For example, the chemical shift of the carbonyl group in *N*-(*p*-tolyl)acetamide and 1,1-dimethyl-3-(*p*-tolyl)urea are 168.6 and 156.0 ppm, respectively.

To better understand the origin of the observed selectivity, the mechanism of the alkyne insertion was studied computationally (Figure 1). Alkyne insertion in **I** occurs readily to form the eight-membered cobaltacycle **II**. Nucleophilic attack in this intermediate is favored to the acetamide (R = Me) relative to the urea derivative (R = NMe_2) by 1.7 kcal mol^{-1}. Isomerization to a 6-membered, N,O-chelating cobaltacycle **IV** has a lower barrier by ca. 10 kcal mol^{-1} for either substrate. Subsequent reductive elimination to the indole (**V**) is favored for the more electron-rich urea derivative by 2.7 kcal mol^{-1} over the acetamide. Interestingly, from **IV** the acetamide derivative has a slightly lower barrier for the isomerization back to the 8-membered intermediate **II** (+31.5 kcal mol^{-1}) than the reductive elimination (+32.2 kcal mol^{-1}), which means that the overall lowest barrier for product formation is the nucleophilic attack to the 6-membered ring **III** (+29.3 kcal mol^{-1}). Based on these results, a slight preference for the formation of quinolines over indoles should be expected from acetanilide substrates, as opposed to a selective formation of indole from arylurea. Importantly, the role of BF_3 can be rationalized to decrease the high barrier for nucleophilic addition by coordination to **II**.

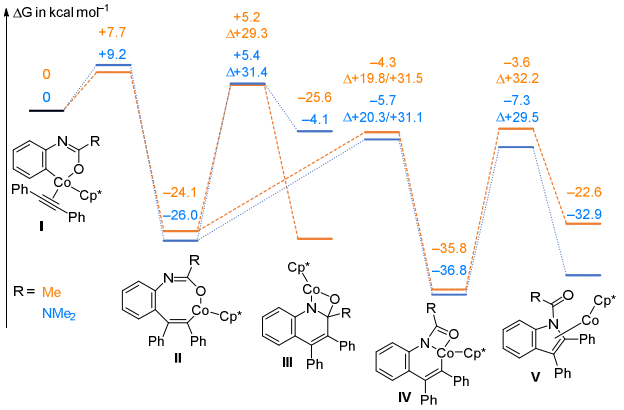
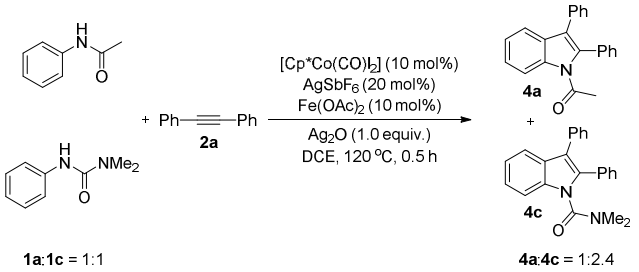


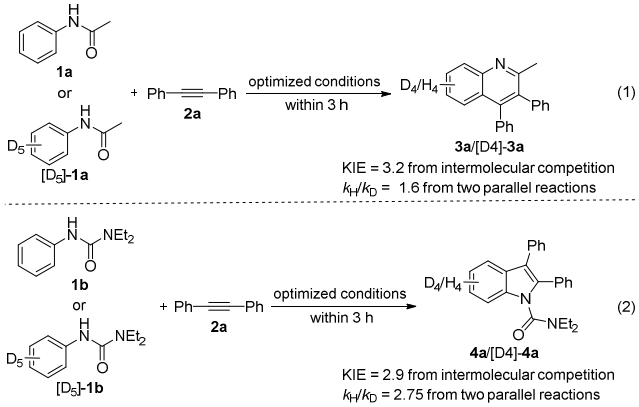
Figure 1. Free-energy profiles for two competitive reaction pathways at the IEFPCM(1,2-DCE)/M06/6-311G**//M06-L/6-31G**+LANL2DZ(Co) level. For details, please see the Supporting Information.

In addition, a competition experiment between **1a** and **1c** was conducted (Scheme 3). The result showed that the reaction of **1c** with **2a** displayed a faster reaction rate than **1a** with **2a**, and the ratio of the final indole products **4a** and **4c** is 1:2.4. This result could serve as an experimental evidence to support density functional theory calculations.



Scheme 3. Competition experiment between 1a and 1c

Furthermore, for the dehydrative cycle, the KIE value from the intermolecular competition experiment was 3.2 while a k_H/k_D = 1.6 was observed from two parallel reactions. The KIE results from the dehydrogenative cycle were 2.9 and 2.75, respectively, from the corresponding intermolecular competition experiment and two parallel reactions (Scheme 4). These results suggest that the cleavage of the C–H bond is plausibly involved in the rate determining step.



Scheme 4. The kinetic isotope effect (KIE) experiments

In summary, we have successfully developed a general strategy to control the reaction selectivity by tuning the reactivity of the organometallic intermediate, in which an earth-abundant metal catalyst and easily available chemicals are utilized to synthesize valuable quinolines and indoles. The significant aspects of our work are: (1) the strategy to switch the elusive organometallic intermediate between dehydrative cyclization or dehydrogenative cyclization processes is demonstrated; (2) the discovery that the cooperation of Cp*Co(III) and Lewis acid is feasible, which can efficiently promote dehydrative cyclization reaction; (3) the vital role of directing groups is uncovered by density functional theory calculations and experiments; (4) the unique activity of Cp*Co(III) is explored in comparison to other precious transition metal catalysts, which could provide useful clues for further novel reaction design. These results provide not only a solution for tuning the chemical-selectivity of C–H bond transformations, and also offer valuable information for a better understanding of Co(III) chemistry.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedure, characterization data, computational details and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

glorius@uni-muenster.de

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(15) A Co(III)-catalyzed redox-neutral coupling between arenes and alkynes for the synthesis of quinolines was just reported: Kong, L.; Yu, S.; Zhou, X.; Li, X. *Org. Lett.* **2016**, *18*, 588–591.
(16) CCDC 1441958 (4c) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif since November 12. 2015.

Table of Contents (TOC):