C–H Activation

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Cobalt(III)-Catalyzed Redox-Neutral Synthesis of Unprotected Indoles Featuring an N–N Bond Cleavage

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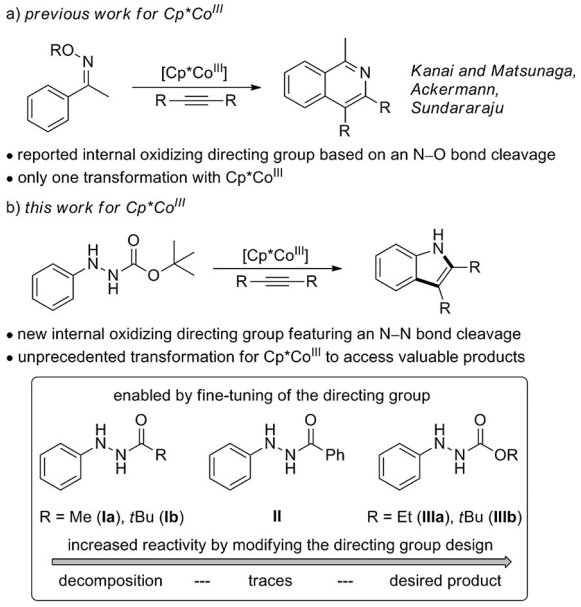
Dedicated to Professor Barry M. Trost on the occasion of his 75th birthday

Abstract: *A redox-neutral cobalt(III)-catalyzed synthetic approach for the direct synthesis of unprotected indoles showcasing an N–N bond cleavage is reported. The herein newly introduced Boc-protected hydrazines establish a beneficial addition to the limited portfolio of oxidizing directing groups for cobalt(III) catalysis. Moreover, the developed catalytic methodology tolerates a good variety of functional groups.*

Transition-metal-catalyzed C–H bond functionalization is an established and broadly applied methodology for various organic transformations and a multitude of these are well-explored with common transition-metal catalysts, such as rhodium, palladium, iridium, and ruthenium.[1] However, their low abundance and high cost create the demand for cheaper and more accessible transition-metal catalysts, such as cobalt.[2] In 2013, Kanai and Matsunaga pioneered the development of several Cp^*Co^{III} catalysts ($Cp^* = \eta\text{-}C_5Me_5$) which are comparable and complementary in reactivity to the well-established catalyst systems of Cp^*Rh^{III} and Cp^*Ir^{III}.[3] Further progress in this field has been achieved by the groups of Ellman,[4] Chang,[5] Ackermann,[6] Glorius,[7] and others.[8]

Frequently, a directing group is required for chemo- and regioselective C–H bond functionalization and several different types have been reported.[9] Especially internal oxidizing directing groups have created a renaissance for common transition-metal catalysts in the field of C–H activation, owing to the mildness and versatility that they enable.[9c,d] However, for cobalt(III) catalysis only oxime derivatives are described as oxidative directing groups for the formation of isoquinolines based on an N–O bond cleavage to date (Scheme 1 a).[10] To broaden the area of application for cobalt(III) catalysis the exploration of new oxidizing motifs as potential directing group is of major interest. Since, to our knowledge there is no redox-neutral cobalt(III)-catalyzed transformation featuring an N–N bond cleavage we wanted to explore this important motif.

Indoles are crucial structural motifs in numerous natural products, pharmaceuticals and other bioactive compounds.[11]



Scheme 1. Internal oxidizing directing groups for Cp^*Co^{III} catalysis.

Therefore the development of inexpensive, elegant, and efficient methods to achieve these target molecules is of ongoing importance.[12] Transition-metal-catalyzed C–H bond functionalization has evolved as one of the most robust tools for the synthesis of several heterocycles and different strategies using external[13] or internal[14] oxidants have been developed. In 2013, our group introduced the use of acetyl-protected hydrazine as a directing group for the rhodium(III)-catalyzed synthesis of unprotected indoles.[15] Inspired by this strategy we had to tackle the considerable challenges:

a) to design a new redox-neutral directing group for cobalt-(III)-catalyzed C–H bond functionalization
b) to develop the first efficient Cp^*Co^{III}-catalyzed synthesis of unprotected indoles.

Herein, we report our efforts to address these challenges giving a meaningful addition to the portfolio of internal oxidizing directing groups in this field.

We began our studies using the reported acetyl hydrazide (Scheme 1 b, **Ia**). However, when we applied a cobalt(III) catalyst to this substrate no formation of the desired indole product, just the decomposition of the starting material, mostly to the corresponding aniline, was observed. This result prompted us to explore the design of other substituents at the hydrazine-β-nitrogen atom to create a more reactive substrate

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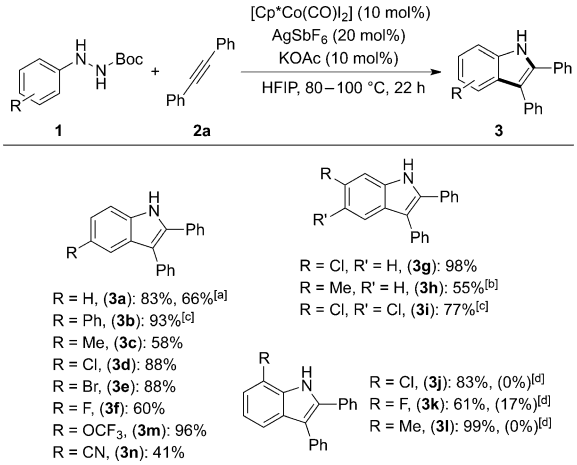
with a more Lewis basic carbonyl-oxygen atom for the highly reactive and Lewis acidic cobalt(III) catalyst. Upon switching from the acetyl hydrazide (**Ia**) and the bulkier, non enolizable pivaloyl hydrazide (**Ib**) to the benzoyl hydrazide (**II**), traces of product could be observed. To our delight, the introduction of a carbamate group, such as the ethyl hydrazinecarboxylate (**IIIa**) and the *tert*-butyl hydrazine carboxylate (**IIIb**), enabled the formation of the desired product (Scheme 1b, see the Supporting Information).

Comparing the ethyl-2-phenylhydrazine-1-carboxylate **IIIa** with Boc-phenylhydrazine **IIIb**, we found that **IIIb** led to a completely selective formation of the desired product. Therefore Boc-phenylhydrazine was used for optimization with diphenylacetylene as standard substrate. After intensive screening, the annulation reaction afforded the desired unprotected indole (**3a**) in 83% yield, using [Cp*Co(CO)I_2] (10 mol%), $AgSbF_6$ (20 mol%), and KOAc (10 mol%) in HFIP (0.2 M) at 80°C (Scheme 2). Note that the standard

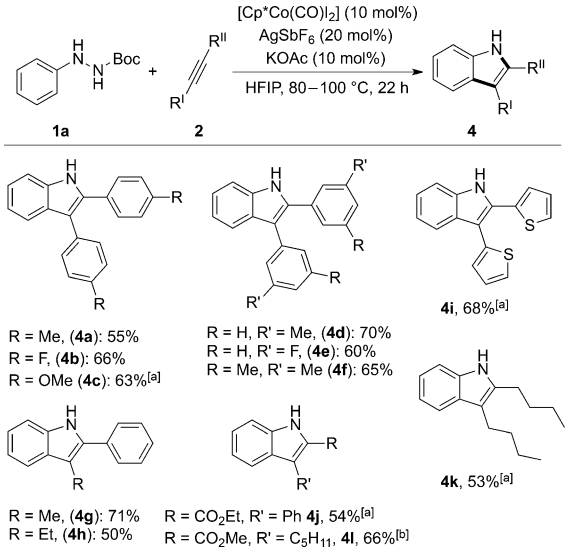


Scheme 2. Variation of different substituted 1-Boc-arylhydrazines with diphenylacetylene. Yields of isolated product are given. **1** (0.8 mmol), **2a** (0.4 mmol), [Cp*Co(CO)I_2] (10 mol%), $AgSbF_6$ (20 mol%), and KOAc (10 mol%) in HFIP (0.2 M) at 80°C for 22 h. [a] 5.0 mmol scale using [Cp*Co(CO)I_2] (5 mol%), $AgSbF_6$ (20 mol%), and KOAc (10 mol%) in HFIP (0.2 M) at 80°C for 46 h. [b] 100°C. [c] 0.3 mmol scale. [d] [Cp*$RhCl_2$]$_2$ instead of [Cp*Co(CO)I_2] (optimized conditions of Ref. [15a] used). HFIP = hexafluoro isopropanol.

reaction is finished within 6 h on an 0.1 mmol scale. However, for a more general methodology, the reaction time was increased to 22 h. With these conditions in hand, the substrate scope of Boc-protected arylhydrazines was investigated.

Various electron-donating (**3a–3c**, **3h**, **3l–3m**) and electron-withdrawing (**3d–3g**, **3i–3k**, **3n**) functional groups are tolerated by this catalytic methodology. *Meta*-substituted Boc-arylhydrazines led to a regioselective formation of the desired product (**3g–3i**). We were delighted to observe a superior reactivity of the cobalt(III) catalyst compared to the rhodium(III) catalyst when *ortho*-substituted Boc-arylhydrazines were applied (**3j–3l**). In this particular reaction excellent yields could be obtained for several *ortho*-substituted Boc-arylhydrazines, which can only be rarely utilized in rhodium(III) catalysis.[15a] Pleasingly, the reaction could be scaled-up using a lower catalyst loading without any detrimental impact on its efficiency (**3a**).

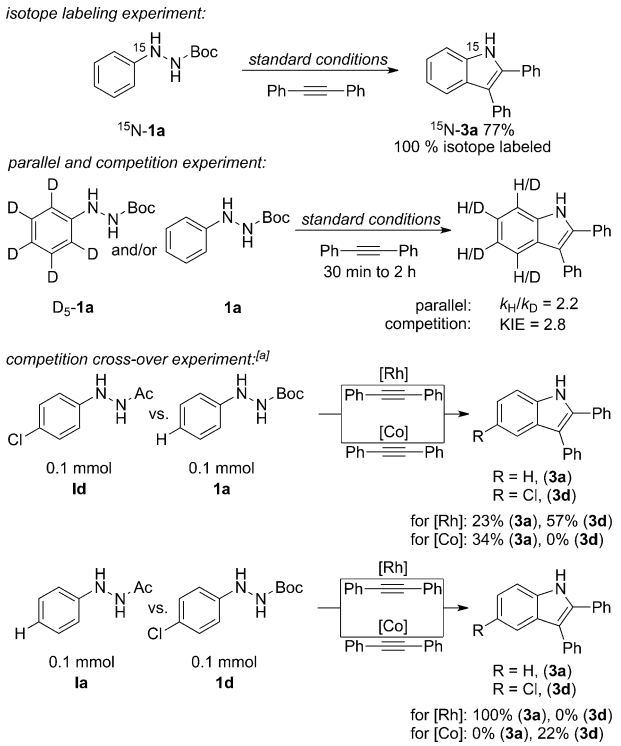
Then, we investigated the scope of several internal alkynes (Scheme 3). Different symmetrical disubstituted diarylalkynes led to the corresponding indole products in good yields (**4a–4e**). Gratifyingly, the reaction also tolerated



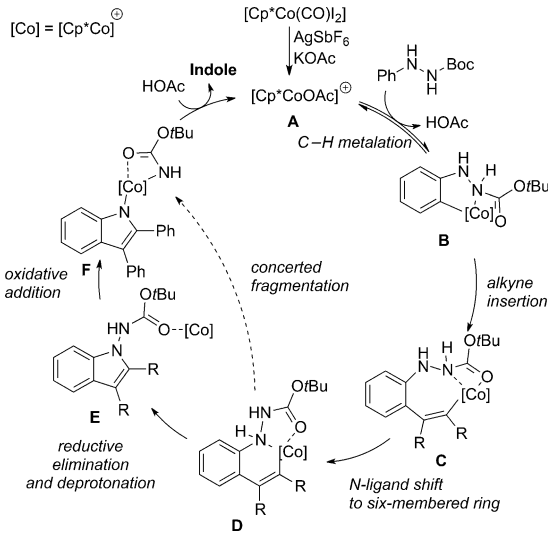
Scheme 3. Variation of several internal alkynes with 2-Boc-1-phenyl hydrazine. Yields of isolated product are given. **1a** (0.8 mmol), **2** (0.4 mmol), [Cp*Co(CO)I_2] (10 mol%), $AgSbF_6$ (20 mol%), and KOAc (10 mol%) in HFIP (0.2 M) at 80°C for 22 h. [a] 100°C. [b] 0.2 mmol scale, **1a** (0.8 mmol), 100°C.

a diheteroarylalkyne and a multisubstituted diarylalkyne (**4i**, **4f**) in synthetically useful yields. Moreover, only one regioisomer could be isolated when unsymmetrical alkyl–aryl and alkyl–ester alkynes were employed (**4g–4h**, **4l**),[16] whereas the unsymmetrical ethyl-3-phenyl propiolate afforded the desired product in a 6:1 mixture of regioisomers (**4j**).

For the analysis of the reaction mechanism further experiments were carried out (Scheme 4). In a competition experiment the *p*-chloro-Boc-phenylhydrazine showed a higher reactivity compared to the *p*-methyl-Boc-phenylhydrazine (see the Supporting Information) and therefore a CMD-type mechanism is proposed for the reaction reported herein.[3c,15] Furthermore the ^{15}N-isotope-labeled Boc-phenylhydrazine ^{15}N-**1a** was synthesized to determine which nitrogen atom of the hydrazine is placed in the corresponding indole product. The pure isotope-labeled indole product ^{15}N-**3a** was isolated in 77% yield containing 100% of the labeled nitrogen atom as analyzed by ^{15}N-NMR spectroscopy and ESI-MS. The kinetic-isotope effect (KIE) was studied in parallel and competition experiments. A k_H/k_D value of 2.2 for the parallel experiment and a KIE of 2.8 for the competition experiment were observed. These results indicate that the C–H bond activation presumably occurs in the rate-determining step of the reaction. Moreover the particular difference in reactivity of the cobalt(III)-catalyst system regarding our directing group was investigated in competition



Scheme 4. Mechanistic studies. [a] Conditions: for [Rh] standard conditions from Ref. [15a]; for [Co] standard conditions reported herein. In each reaction 0.1 mmol of alkyne was used. Yields were determined by GC-FID.



Scheme 5. Proposed catalytic cycle.

cross-over and decomposition studies (Scheme 4, and see the Supporting Information). The results demonstrate that **Ia**/**Id** and **1a**/**1d** are both suitable substrates for the Rh^{III} system, whereas only **1a**/**1d** are successful in the Co^{III} system. Thus it is clear that the electronic properties and substitution pattern of the directing group inherently enable reactions in the corresponding Co^{III} and Rh^{III} systems.

Based on literature precedent and preliminary mechanistic experiments we propose the following reaction mechanism (Scheme 5).[15,17] After formation of the catalytically active cobalt species **A**, the C–H metalation takes place to form the cobaltacycle **B** which presumably is additionally stabilized by the Boc group.[18] After alkyne insertion, the 7-membered intermediate **C** can be formed, followed by the N-ligand shift to the 6-membered ring to create species **D**.[10] Originating from **D**, two different pathways could lead to the desired product. A reductive elimination could form intermediate **E**, followed by an oxidative addition of the N–N bond to cobalt to form the species **F**. As an alternative, a concerted fragmentation of species **D** to afford intermediate **F** is also included as possible pathway.[19] Protonation of intermediate **F** affords the desired indole product and regenerates the active catalyst **A**.

In conclusion, we have designed a new oxidizing directing group for cobalt(III) catalysis and employed this for an efficient redox-neutral synthesis of unprotected indoles featuring an N–N bond cleavage. The newly introduced directing group is a beneficial addition to the limited portfolio of oxidizing directing groups for cobalt(III) catalysis. Moreover, the developed methodology tolerates a variety of functional groups on both the arylhydrazine and the alkyne and permits several substitution patterns without impacting the reaction efficiency.

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Keywords: C–H activation · Cp^*Co^{III} catalysis · N-N bond cleavage · redox-neutral · indoles

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