C–H Activation

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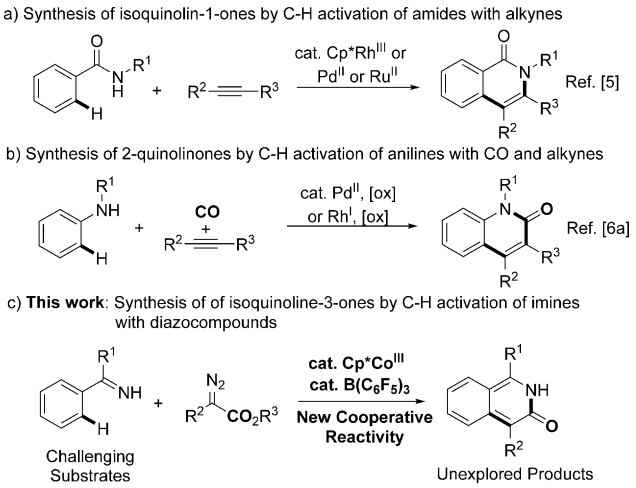
Cooperative Lewis Acid/Cp*Co^{III} Catalyzed C–H Bond Activation for the Synthesis of Isoquinolin-3-ones

*Ju Hyun Kim, Steffen Greßies, and Frank Glorius**

Abstract: *A facile route toward the synthesis of isoquinolin-3-ones through a cooperative $B(C_6F_5)_3$- and Cp*Co^{III}-catalyzed C–H bond activation of imines with diazo compounds is presented. The inclusion of a catalytic amount of $B(C_6F_5)_3$ results in a highly efficient reaction, thus enabling unstable NH imines to serve as substrates.*

Transition-metal-catalyzed C–H bond activation strategies have emerged as powerful tools for the assembly of complex molecules.[1] From both an environmental and economic point of view, catalysts consisting of the earth-abundant metal cobalt have gained attention as alternatives to those of second -row transition metals such as Pd, Ru, and Rh.[2] Although remarkable progress in the field of cobalt-catalyzed C–H bond activation has been made in the past few years, significant challenges still remain, such as achieving efficient catalyst turnover and the development of novel transformations.[2a] C–H bond-activation reactions using high-valent Cp*Co^{III} catalysts are generally limited in substrate scope due to the requirement of strong directing groups.[2c] Thus, efficient catalyst systems and new directing groups, specifically non-azacyclic compounds, need to be explored.

Isoquinolin-3-ones are prevalent structural motifs in a wide variety of natural[3] and biologically active compounds.[4] The basic framework of quinolinones has several regioisomers: 2-quinolinones, isoquinolin-1-ones, and -3-ones. In the last decade, many elegant methods toward the synthesis of isoquinolinones have been developed through C–H activation reactions. However, most of these studies are focused on the synthesis of isoquinolin-1-ones[5] and 2-quinolinones[6] (Scheme 1 a,b). Conversely, despite their broad utility, no general methods have been reported to access isoquinoline-3-ones, an important structural class present in natural compounds (Figure 1),[3] cardiotonic drug candidates,[4] as well as heteroacenes as a result of the unique feature of equilibrium with the tautomeric hydroxyisoquinolines.[7] Traditionally, isoquinolin-3-ones are prepared in multistep syntheses under harsh reaction conditions and exhibit limited substitution patterns.[8] Therefore, the development of an efficient one-pot method to give isoquinoline-3-ones is highly desirable.



Scheme 1. Synthetic methods for the preparation of isoquinolinones and quinolinones based on C–H activation strategies.

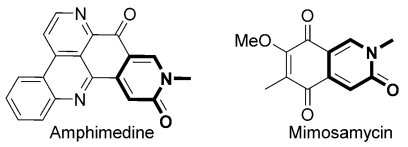


Figure 1. Naturally occurring compounds containing isoquinolin-3-one motifs.

As part of our ongoing research on Cp*Co^{III}-catalyzed C–H activation[9] and considering the interest in isoquinolin-3-ones as an important structural motif, we proposed that imines may serve as competent directing groups for Cp*Co^{III}-catalyzed C–H activation reactions with diazo esters[10] to provide isoquinoline-3-ones (Scheme 1 c). To facilitate this transformation, it was first necessary to develop an efficient Cp*Co^{III} catalyst system to enable unstable NH imines to act as directing groups. Transformations with NH imine directing groups would be the most atom-economic way to access N-unsubstituted isoquinoline-3-ones, as no prefunctionalization or additional deprotection would be required. However, NH imines are not widely used as a directing group in C–H activation reactions for the following considerations:[11]

1) Imines are mildly basic and can form iminium salts which are easily hydrolyzed to the ketone or can undergo nucleophilic addition to the electrophilic carbon atom.[11,12]
2) The relatively weak N–H bond could generate a metal–iminyl bond, which can lead to competing, undesired reactions.[13,14]

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3) Primary aryl alkyl imines could undergo imine/enamine tautomerization,[14] which may alter the chelation ability. In this regard, few transformations that utilize primary aryl alkyl imines as directing groups have been reported in C–H activation reactions.[15]

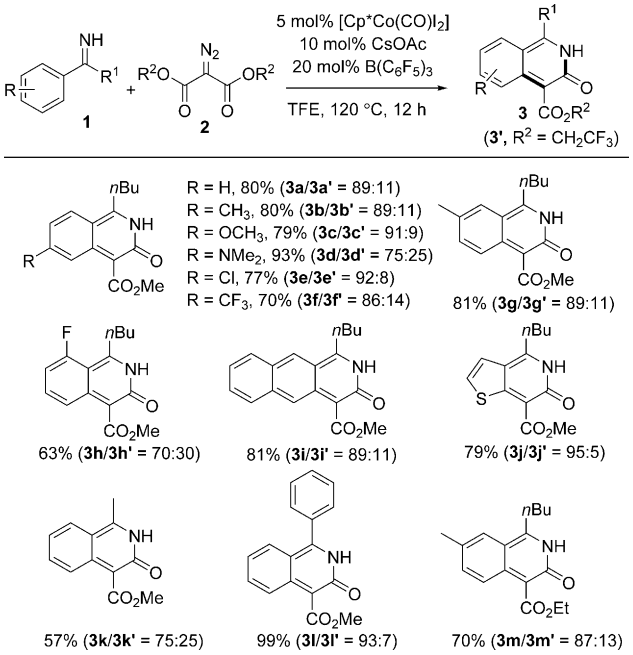
In the last few years, cooperative catalytic systems have attracted attention to enable C–H bond activations that could not previously be achieved by first-row transition-metal catalysts.[16] Interestingly, we found that the addition of catalytic amounts of $B(C_6F_5)_3$ dramatically accelerates the reaction rates and facilitates C–H bond activation. Herein, we report the first Lewis acid promoted Cp*Co^{III}-catalyzed C–H bond activation of imines with diazo compounds. Arguably, this approach represents the first synthetic method toward isoquinoline-3-ones through C–H bond activation.

To examine whether NH imines are competent directing groups for Cp*Co^{III}-catayzed C–H activation with diazo compounds, we selected 1-(*p*-tolyl)pentan-1-imine (**1b**) and dimethyl 2-diazomalonate (**2a**) as model substrates. In an initial set of experiments, silver salts and acetate bases were investigated with a Cp*Co^{III} catalyst.[2,17] To our delight, the desired product **3b** and its transesterification derivative **3b′**, derived from the solvent, were formed in the presence of CsOAc (10 mol%) and $AgSbF_6$ (10 mol%) in 29% yield (Table S1 in the Supporting Information). We suspected that the reactivity could be improved by the presence of a Lewis acid.[16] After extensive screening, we were pleased to find that the yield of **3b**/**3b′** improves significantly up to 80% on introduction of $B(C_6F_5)_3$ (20 mol%), while other Lewis acids, including $Zn(OTf)_2$, $Sc(OTf)_3$ and $BF_3{\cdot}OEt_2$ were less effective (Table S1). Finally, it was found that the addition of silver was not required for the reaction (Table S1). Structurally similar substrates, including a range of ketoximes (*N*-OH, *N*-OMe, *N*-OPiv) and *N*-PMP-substituted imines (PMP = *N*-*p*-methoxyphenyl) did not give any desired product (Table S1).[18]

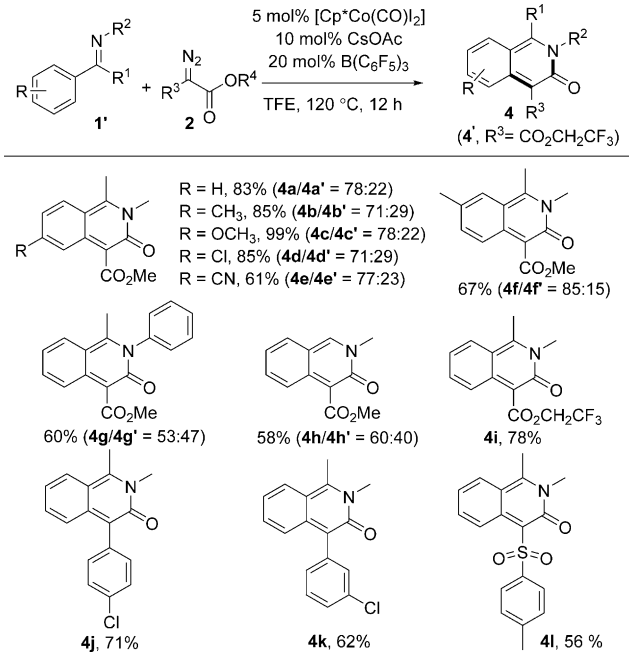
With the optimized conditions in hand, the substrate scope was investigated with various NH imines and diazo compounds (Scheme 2). Electron-donating and -withdrawing substituents on the aryl moiety were tolerated. The reaction proceeded regioselectively when functional groups were located at the *meta* and *ortho* positions. In a similar fashion, *m*-naphthyl-substituted substrate **1i** and heteroarene **1j** were also tolerated. Variation of the R^1 substituents and alteration of the diazo ester had little effect on the reaction efficiency.

Next, a variety of N-substituted imines were examined under the optimized reaction conditions (Scheme 3). Pleasingly, the reaction of *N*-methyl-1-phenylethan-1-imine (**1′a**) proceeded smoothly to give **4a** in 83% yield. Electronic variation of the *para*- and *meta*-substituents on the aryl group did not affect the reaction efficiency and afforded **4b**–**4f**. The structure of **4c** was confirmed by X-ray crystallographic analysis.[19] The *N*-phenyl-substituted imine **1′g** as well as the aldimine **1′h** were also competent substrates. Notably, product **4h** is an important scaffold in natural compounds (Figure 1). Other diazo compounds were also tolerated.

For a better understanding of the role of the reaction additives, we conducted a series of experiments (Scheme 4).



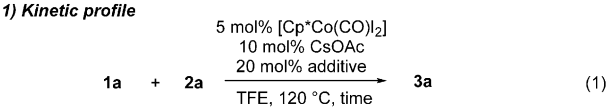
Scheme 2. Substrate scope of primary ketimines and diazo compounds. For the reaction conditions, see the Supporting Information. TFE = 2,2,2-trifluoroethanol.



Scheme 3. Substrate scope of secondary ketimines, aldimines, and diazo compounds. For the reaction conditions, see the Supporting Information.

First, the stability of NH imine **1a** was tested. Significant decomposition (27%) of **1a** was observed within 1 h in the absence of a diazo compound under the optimized conditions (see the Supporting Information). Previous conditions with $AgSbF_6$ gave 62% decomposition in the same time. It was, therefore, concluded that an increased reaction rate was the

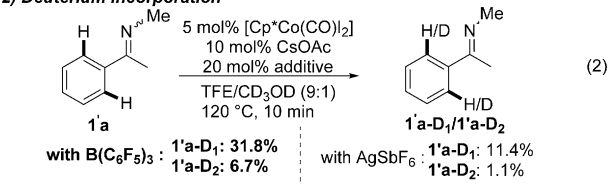
1) Kinetic profile



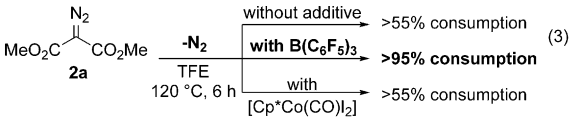
time	10 min	20 min	40 min	80 min
with $B(C_6F_5)_3$/yield[a]	**15%**	**32%**	**38%**	**43%**
with $AgSbF_6$/yield[a]	9 %	16 %	18 %	27 %

[a] ^{1}H NMR yield

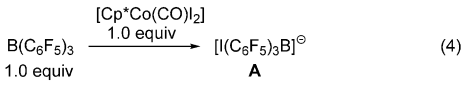
2) Deuterium incorporation



3) Carbene formation



4) Abstraction of iodide from the Co^{III} precatalyst



Scheme 4. Studies on the role of $B(C_6F_5)_3$.

key to achieving high yields. Hence, we investigated the initial rate for the reaction between imine **1a** and diazo compound **2a** in the presence of different additives [Eq. (1) in Scheme 4]. The experiments showed that the addition of $B(C_6F_5)_3$ clearly resulted in a significant rate enhancement compared to $AgSbF_6$. The origin of the high reactivity and the role of $B(C_6F_5)_3$ are ambiguous, and further comprehensive mechanistic studies are required. However, a number of experimental observations are noteworthy:

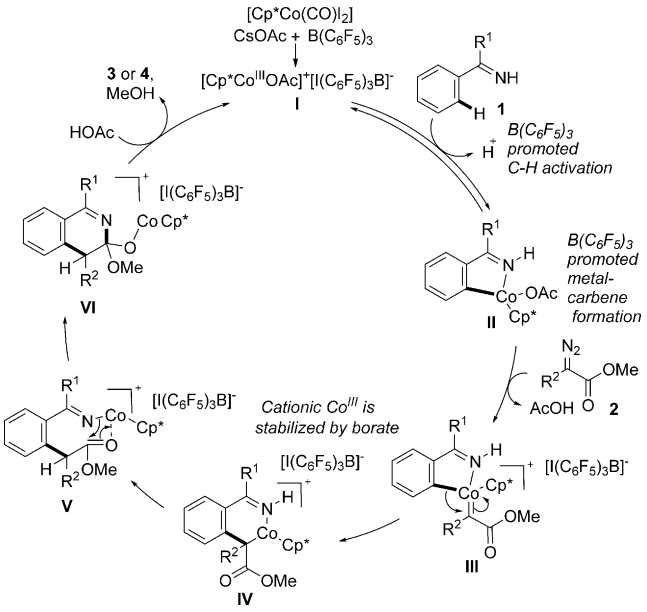
1) When parallel reactions of imine **1′a** with different additives were performed in deuterated co-solvent for 10 min, D_1 incorporation in **1′a** was 32% under the optimized conditions, while only 11% with $AgSbF_6$ [Eq. (2) in Scheme 4].
2) ^{1}H NMR experiments of the diazo compound **2a** with different additives indicated that the formation of the carbene on extrusion of nitrogen is accelerated in the presence of $B(C_6F_5)_3$ [Eq. (3) in Scheme 4].
3) When $B(C_6F_5)_3$ was treated with stoichiometric amounts of $[Cp^*Co(CO)I_2]$, the ^{11}B NMR spectra showed that the borate anion **A** is formed readily even at room temperature by iodide abstraction from the cobalt catalyst precursor [Eq. (4) in Scheme 4].

Combining the above pieces of information, it is plausible that $B(C_6F_5)_3$ plays a dual role:

1) The generation of a catalytically active cationic Co^{III} species might be facilitated by the strong Lewis acid $B(C_6F_5)_3$, which forms a noncoordinating borate anion such as $[I(C_6F_5)_3B]^-$. The cationic Co^{III} species would be stabilized by this borate anion.[20]
2) The inclusion of $B(C_6F_5)_3$ may accelerates the rate of the C–H activation step and subsequent formation of the Co^{III}–carbene intermediate **III**.

Additional preliminary experiments were carried out to gain insight into the mechanism (see the Supporting Information). Two competition experiments were performed. First, a competition between *p*-CH_3-substituted imine **1′b** and imine **1′a** with diazo ester **2a.** In the second experiment, *p*-Cl-substituted imine **1′d** and imine **1′a** were mixed with diazo ester **2a**. Both experiments suggested that this transformation is more favorable for electron-rich imines. Next, a series of deuterium labeling experiments were carried out. The use of a deuterated cosolvent demonstrated that the C–H activation was reversible (see the Supporting Information). Kinetic studies from parallel reactions revealed a KIE value (k_H/k_D) of 1.1, thus suggesting that the C–H bond cleavage of the imine is probably not the rate-limiting step.

Based on the above results and previous reports,[9,10,14] a plausible reaction mechanism is proposed (Scheme 5). First, the reactive cationic Cp^*Co^{III} species **I** is generated with the



Scheme 5. Proposed reaction mechanism.

assistance of $B(C_6F_5)_3$. Subsequently, Cp^*Co^{III} species **I** coordinates to substrate **1**, and a reversible C–H bond cleavage forms cobaltacycle **II**. The reaction with the diazo compound might then occur to give the metal–carbene intermediate **III** by extrusion of N_2. After migratory insertion to provide **IV**, rearrangement gives **V**. Nucleophilic addition to the ester carbonyl group occurs in the presence of Lewis acidic Co^{III} to give **VI**. Finally, elimination of the methoxy group from **VI** and proton transfer gives the desired products with regeneration of the catalyst.

In summary, we have successfully developed a Cp^*Co^{III}-catalyzed C–H activation of imines with diazo compounds to provide the first example of an expedient method to access highly substituted isoquinolin-3-ones with broad substrate scope and good functional-group tolerance. In this reaction, the addition of catalytic amounts of $B(C_6F_5)_3$ results in high reaction efficiency, thus unstable NH imines could serve as the directing groups. Given the high reactivity, the newly

developed $Cp^*Co^{III}/B(C_6F_5)_3$ cooperative catalytic system could allow new transformations.

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Keywords: carbenes · C–H activation · cobalt · cooperative catalysis · isoquinolinones

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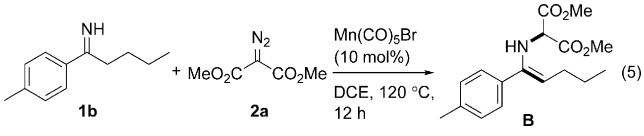
[14] An undesired reaction was observed: When the reaction of imine **1b** with diazo compound **2a** was employed with Mn^I catalyst, **B** was formed as the major product (see the Supporting Information). This result clearly showed that formation of a metal–iminyl bond and imine/enamine tautomerization occurred under the reaction conditions [Eq. (5); DCE = 1,2-dichloroethane].



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