Synthetic Methods

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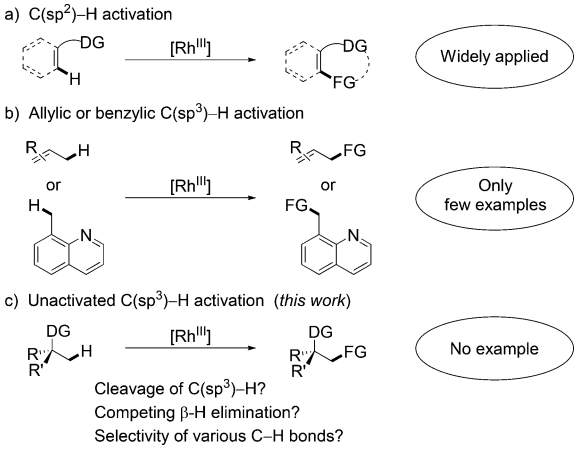
Cp*Rh^{III}-Catalyzed Arylation of C(sp^3)–H Bonds**

*Xiaoming Wang, Da-Gang Yu, and Frank Glorius**

Abstract: *The first Cp*Rh^{III}-catalyzed arylation of unactivated C(sp^3)–H bonds is presented. The unactivated primary C(sp^3)–H bond of 2-alkylpyridines can be activated by Rh^{III} and further reacts with triarylboroxines to efficiently build new C(sp^3)–aryl bonds. The methodology also provides a facile and efficient synthesis of unsymmetrical triarylmethanes by Rh^{III}-catalyzed C(sp^3)–H arylation of diarylmethanes.*

Driven by the desire to further streamline the synthesis of valuable building blocks and complex molecules, transition-metal-catalyzed C–H bond activation has evolved as an important field in organic synthesis.[1] Among them, Cp*Rh-catalyzed C–H activation has emerged as a prosperous field owing to the high efficiency, selectivity, and functional-group tolerance.[2] Although many exciting achievements have been made in Rh^{III}-catalyzed C(sp^2)–H functionalization (Scheme 1 a),[3] by comparison, much less research attention has been devoted to the activation of C(sp^3)–H bonds. Until now, only a few successful transformations dealing with the functionalization of relatively activated allylic and benzylic C–H bonds by Rh^{III} catalysis have been reported (Scheme 1 b).[4] It is considerably more challenging to achieve the direct functionalization of unactivated C(sp^3)–H bonds because of their inherent low reactivity, the lack of an adjacent heteroatom or π-system to aid metal binding, and the considerable potential for low selectivity owing to the large numbers of C(sp^3)–H bonds present in most organic compounds.[5,6] Furthermore, side-reactions resulting from β-hydride elimination may reduce the efficiency.

Therefore, selective catalytic functionalization of unactivated (i.e., not benzylic, allylic, or adjacent to a heteroatom) C(sp^3)–H bonds of alkanes remains a big challenge in the field of Rh^{III}-catalyzed C–H activation (Scheme 1 c).[2] Herein, we report the first successful Cp*Rh^{III}-catalyzed functionalization of unactivated C(sp^3)–H bonds resulting in the selective β-arylation of 2-alkylpyridine derivatives. Similar conditions can also be employed in the activation of secondary benzyl C(sp^3)–H bonds to generate important triarylmethane compounds.



Scheme 1. Types of C–H bonds in the field of Rh^{III}-catalyzed C–H activation. FG = functional group, DG = directing group.

Since the arylation of unactivated C(sp^3)–H bonds is a desirable transformation to build up pharmaceuticals and natural products,[7] we envisioned that the Rh^{III}-catalyzed reaction of 2-alkylpyridine derivatives[8] and arylboron reagents would efficiently build a new C(sp^3)–aryl bond. However, there are additional challenges, because only a few applications of arylboron reagents are known in Rh^{III}-catalyzed C–H activation reactions[9] and homocoupling[10] of these reagents may outcompete C(sp^3)–H functionalization.

In preliminary experiments, benzylic dibutyl-substituted 2-ethylpyridine (**1a**) was selected as the standard substrate. There are several C(sp^3)–H bonds in the molecule which could be activated and controlling selectivity for a specific C(sp^3)–H bond is challenging. The first reaction was carried out with [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (5.0 mol%), Ag$_2$O (1.5 equiv), and PhBF$_3$K (3.0 equiv) in DMF at 100 °C for 24 h (Scheme 2). Unfortunately, the pyridine substrate **1a** was completely unreactive. Among alternative arylboron coupling partners, triphenylboroxine proved to be the best, leading to product **3a** in 79% yield. Further experiments, including the investigations of the solvents and oxidants, showed that DMF and Ag$_2$O were most effective. In addition, [{Cp*IrCl$_2$}$_2$]/AgSbF$_6$ was also tested as a catalyst, but it was ineffective.[11] Because the undesired homocoupling was consuming both oxidant and the arylboron reagent, increasing the amount of Ag$_2$O to 2.5 equivalents and triphenylboroxin to 2.0 equiv-

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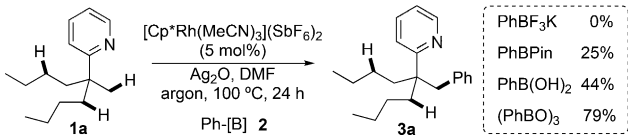
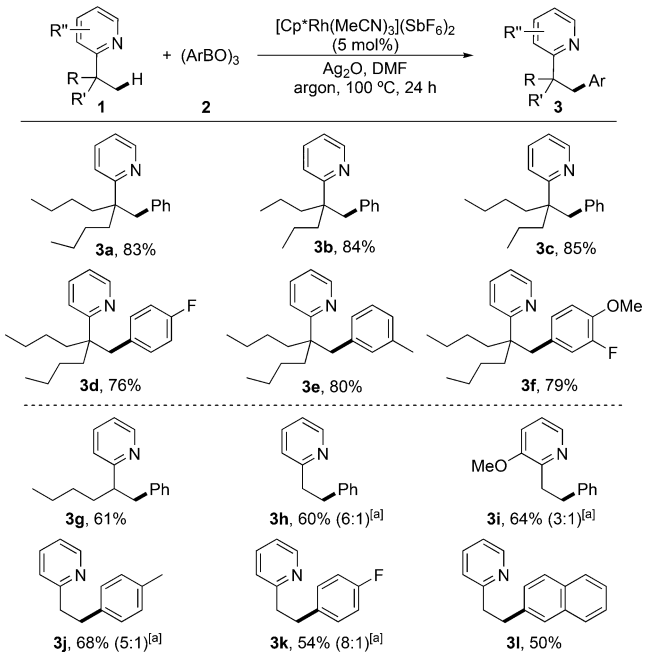


Scheme 2. Optimization of the Rh^{III}-catalyzed arylation of 2-alkylpyridine **1a**. Various Ph-[B] **2** and the resulting yields are shown in the box on the right.

alents led to higher yield (83%; see the Supporting Information). In all the investigations, only the arylated product **3a** was formed, which showed extremely high selectivity for the functionalization of the primary $C(sp^3)$–H bond over the secondary $C(sp^3)$–H bonds and all other C–H bonds present in the molecule.

Subsequently, we investigated the substrate scope of the catalysis using 2-ethylpyridine derivatives as the substrates and several kinds of triarylboroxine as the aryl source. As shown in Scheme 3, a series of arylated products was

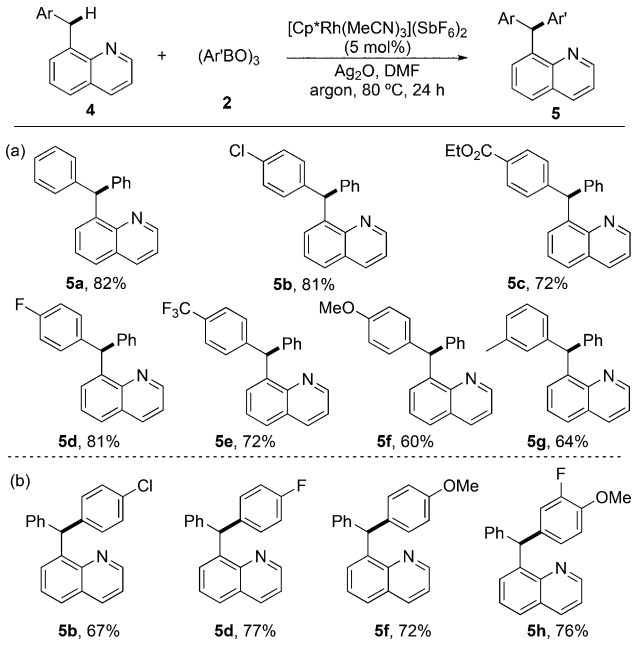


Scheme 3. The reactions of diverse 2-alkylpyridine derivatives with $(ArBO)_3$. Reactions were carried out using $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5.0 mol%), Ag_2O (2.5 equiv), **1** (0.2 or 0.4 mmol), and $(ArBO)_3$ (2.0 equiv) in DMF for 24 h at 100°C. [a] The combined yield of isolated mono- and diarylated products. The ratio of mono:diarylation is shown in parentheses.

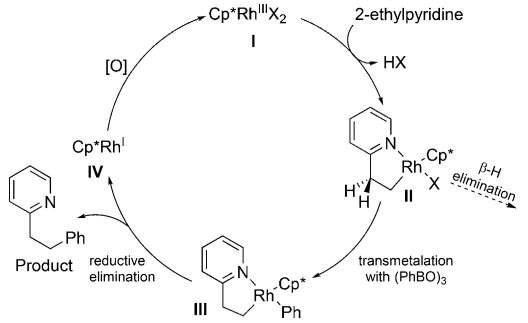
synthesized in moderate to good yields. This method was compatible with some important functional groups on the phenyl ring of the triarylboroxine or pyridine, such as fluorine and methoxy substituents, which could be subjected to further synthetic transformations. For the benzylic dialkyl-substituted substrates, the reactions led to the desired product (**3a**–**3c**) in good yields (83–85%), indicating that the catalysis can be compatible with different alkyl chains at the benzylic site. *para*- and *meta*- mono-substituted as well as disubstituted triarylboroxines were tested and gave the corresponding products **3d**–**3f** in 76%–80% yields. In all the examples discussed up till now, the presence of additional alkyl substituents at the benzylic position of the pyridine substrates **1** could be accelerating the catalysis by steric crowding which favors the orientation of the primary C–H bond towards the coordinated metal and the formation of the rhodacyclic intermediate (Thorpe–Ingold effect).[12] Next, we tried more challenging substrates that had less substitution at the benzylic position. Pleasingly, using a substrate which features only one butyl chain at the benzylic site of the pyridine ring could also afford the arylated product **3g** in 61% yield. Furthermore, the catalysis is also compatible for simple 2-ethylpyridine, while a derivative with a methoxy substituent on the pyridine was also successfully applied (**3h**,**i**). In addition, 2-ethylpyridine can react smoothly with several differently substituted triarylboroxines, such as methyl and fluorine-substituted triarylboroxine and β-naphthylboroxine, indicating that this catalytic system could be widely applicable for the arylation of substrates containing only β hydrogen atoms. In some cases, some amounts of diarylated products were observed in the reactions using 2-ethylpyridine, presumably a result of the relatively small steric hindrance of the monoarylated products. The reaction between substrate **1a** and trimethylboroxine was also tried under the standard conditions, however, the desired product was not observed.

Owing to the attractive biological properties of functionalized quinolines,[13] direct arylation of the $C(sp^3)$–H bond of 8-benzylquinoline was also examined. Although there are a few examples of primary C–H bond activation on 8-methylquinolines,[4c,d] to our knowledge, there is no report on Rh^{III}-catalyzed secondary $C(sp^3)$–H activation with quinoline as a directing group. Triarylmethanes and their derivatives have found widespread applications in material sciences and medicinal chemistry;[14] however, general methods[15,16] for the synthesis of unsymmetrical triarylmethanes by secondary C–H bond arylation are less developed.[17] Therefore, we wondered if this transformation could be utilized to straightforwardly synthesize triarylmethanes through Rh^{III}-catalyzed $C(sp^3)$–H arylation of diarylmethanes **4**. We were delighted to see that the reaction afforded the desired product **5a** in 82% yield at a lower temperature (80°C) with a lower loading of the triarylboroxine and the oxidant. As shown in Scheme 4a, the reactions proceeded well for the substrates with a variety of important functional groups on the phenyl ring, such as halogens (fluoro and chloro), ester, CF_3 and OMe groups, and gave the corresponding products **5a**–**5g** in 64%–82% yields. These results show that the substrates with electron-deficient aryl groups are more favorable for the triarylmethane synthesis, possibly owing to their $C(sp^3)$–H bond being more acidic and prone to undergo C–H activation. Subsequently, the scope of triarylboroxines was investigated and all the reactions worked well (Scheme 4b). Especially the introduction of useful substituents in the substrates or triarylboroxines allows the direct construction of functionalized products, thus providing an excellent opportunity for further modification of the triarylmethanes.

Based on the results and previous studies, we propose the following mechanism using 2-ethyl pyridine as the example



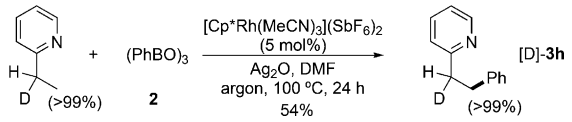
Scheme 4. The reactions of diverse **4** with $(Ar'BO)_3$. Reactions were carried out using $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5.0 mol%), Ag_2O (1.5 equiv), **4** (0.4 mmol), and $(Ar'BO)_3$ (0.4 mmol) in DMF (2 mL) for 24 h at 80°C.



Scheme 5. Proposed mechanistic pathway.

(Scheme 5). The coordination of the Cp^*Rh^{III} (**I**) with 2-ethyl pyridine is followed by the formation of the key rhodacyclic complex (**II**) after activation of primary $C(sp^3)$–H bond. Transmetalation of **II** with triphenylboroxine would lead to complex **III**. It is also possible that intermediate **III** forms from the transmetalation of **I** followed by C–H activation. Then, reductive elimination from **III** furnishes the desired coupling product and a Rh^I species **IV**. Reoxidation of Rh^I to Rh^{III} would complete the catalytic cycle. However, there is another possible sequence for substrates with β hydrogen atoms. The rhodacyclic complex (**II**) may undergo β-hydride elimination to generate 2-vinylpyridine, which could insert to an in situ generated Rh-Ar complex. Finally, protonation of the benzylrhodium complex could generate the product.

To determine which sequence is operating, we carried out a reaction starting from mono-deuterated-2-ethyl pyridine with deuterium at the benzylic position under the standard conditions. As shown in Scheme 6, the deuteration ratio of the product [D]-**3h** was the same as in the substrate, which shows



Scheme 6. Reaction of 2-ethyl pyridine deuterium-labeled in the benzyl position with $(PhBO)_3$.

that no β-hydride elimination is taking place and the arylation of 2-ethylpyridine derivatives arises from the direct functionalization of an unactivated $C(sp^3)$–H bond. This could be further supported by the efficient transformations of benzylic dibutyl substituted substrates and diarylmethanes **4** (all without β-H). Presumably because of the strong coordinating ability of pyridine and fast transmetalation/reductive elimination, β-hydride elimination from intermediate **II** is generally slow, making it amenable to subsequent functionalization.[18]

In summary, we have developed a Rh^{III}-catalyzed arylation of $C(sp^3)$–H bonds, including the activation of challenging unactivated homobenzylic $C(sp^3)$–H bonds and secondary benzylic $C(sp^3)$–H bond. Various 2-alkylpyridine derivatives can react smoothly with diverse triarylboroxines, efficiently building new $C(sp^3)$–aryl bonds and affording functionalized pyridine derivatives. In addition, we have also developed a facile and efficient methodology for the synthesis of unsymmetrical triarylmethane derivatives by Rh^{III}-catalyzed $C(sp^3)$–H bond arylation of diarylmethanes.

Keywords: arylation · boroxines · Rh^{III} catalysis · $C(sp^3)$–H activation · triarylmethanes

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