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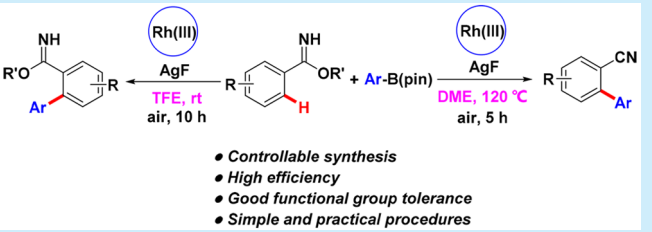
Controllable Rh(III)-Catalyzed C−H Arylation and Dealcoholization: Access to Biphenyl-2-carbonitriles and Biphenyl-2-carbimidates

Bo Jiang,[†] Songxiao Wu,[†] Jing Zeng, and Xiaobo Yang*

Institute of Catalysis for Energy and Environment, College of Chemistry & Chemical Engineering, Shenyang Normal University, Shenyang, Liaoning 110034, China

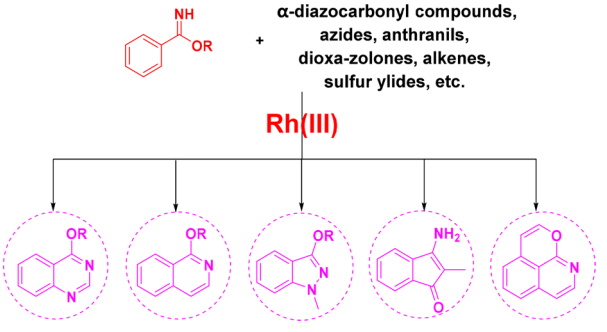
Supporting Information

ABSTRACT: A controllable Rh(III)-catalyzed C−H arylation and dealcoholization of benzimidates with arylboronic esters was developed, delivering various biphenyl-2-carbonitriles and biphenyl-2-carbimidates by simply tuning the reaction conditions. This approach features high efficiency, good functional group tolerance, and easy operation. It also provides an alternative pathway to thoroughly exploit the directing group in transition-metal-catalyzed C−H activations.



Rhodium (III)-catalyzed direct C−H transformation has emerged in the past few years as a powerful and versatile strategy for the construction of valuable molecules.[1] Among them, readily available benzimidates, which act as both directing groups and synthons for cyclization, are always employed as the reaction partners.[2] In previous works, sequential Rh(III)-catalyzed direct C−H activations and intramolecular nucleophilic additions frequently occurred between benzimidates and the coupling reactants such as α-diazocarbonyl compounds,[3] azides,[4] anthranils,[5] nitrosobenzenes,[6] dioxazolones,[7] alkenes,[8] sulfur ylides,[9] etc., thus furnishing isoquinolines, quinazolines, and other heterocycles (Scheme 1). These protocols provide a facile and step-economical strategy to access important N-containing heterocycles. However, in these transformations, the directing groups generally disappear, which deprives the chance for further functionalization based on N-unsubstituted imines.

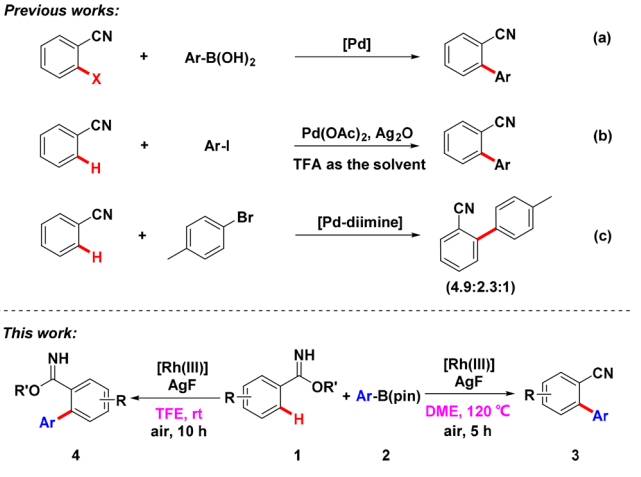
Scheme 1. Previous Works on Rh(III)-Catalyzed Direct C−H Transformation of Benzimidates



Recently, transition-metal-catalyzed C−H *ortho*-arylation of arenes represents a promising tool to form aryl−aryl bonds,[10] in which the directing group is indispensable because of the chelation-assisted strategy.[10j] Therefore, additional synthetic operations to manipulate the directing group issue are desirable. Even though several pioneering works on direct C−H arylation reactions without any directing group have been reported,[11] the rational utilization of directing groups is still challenging.

Biphenyl-2-carbonitriles, as versatile synthetic intermediates, are of great importance in the chemical synthetic industry.[12] Traditional approaches to access these compounds were accomplished via Pd-catalyzed Suzuki reactions of *ortho*-halogenated aromatic carbonitriles (Scheme 2a).[13] In contrast, transition-metal-catalyzed C−H *ortho*-arylation is privileged in the synthesis of them due to high atomic efficiency and low cost.[10] In 2011 and 2013, Sun's group[14] and Hsieh's group[15] independently reported a Pd-catalyzed C−H *ortho*-arylation using cyano as the directing group for the synthesis of biphenyl-2-carbonitriles (Scheme 2b). It has shown good yields and step-

Scheme 2. Strategies for the Synthesis of Biphenyl-2-carbonitriles



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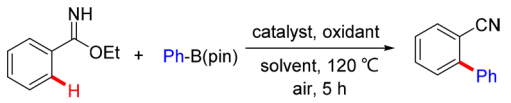
economy, but corrosive strong acid of TFA was used as the solvent, making this transformation less attractive. Recently, Hong and co-workers disclosed a novel Pd−diimine complex for the direct C−H *ortho*-arylation of simple arenes (Scheme 2c).[16] Even though the corresponding biphenyl-2-carbonitrile was obtained in moderate yield, the regioselectivity was still unsatisfactory.

To address the above-mentioned issues and approach closer to the rational utilization of directing groups, as the continuation of our interest on Rh(III)-catalyzed C−H activations,[17] herein, we report a novel Rh(III) catalytic system for the direct C−H *ortho*-arylation of benzimidates using common arylboronic esters as the arylation sources. This practical catalytic system allowed controllable synthesis of biphenyl-2-carbonitriles and biphenyl-2-carbimidates through simple tuning of the reaction conditions.

To evaluate the feasibility of this Rh(III) catalytic system, as shown in Table 1, we launched our study with the reaction of

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3aa**

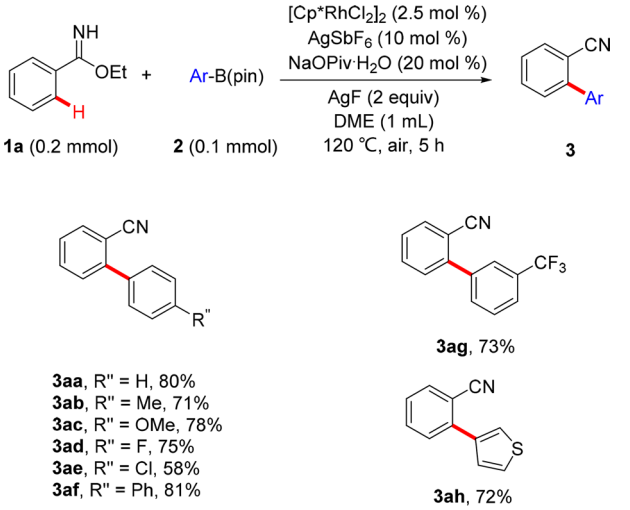
entry	catalyst	oxidants	solvent	yield (%)[b]
1	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	DCE	64
2	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	EGME[e]	12
3	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	DME[f]	80
4	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	EtOH	trace
5	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	toluene	64
6	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	H_2O	28
7	$[Cp^*RhCl_2]_2/AgSbF_6$	AgOAc	DME	trace
8	$[Cp^*RhCl_2]_2/AgSbF_6$	Ag_2CO_3	DME	22
9	$[Cp^*RhCl_2]_2/AgSbF_6$	Ag_2O	DME	13
10	$[Cp^*RhCl_2]_2/AgSbF_6$	$Cu(OAc)_2$	DME	0
11	$[Cp^*IrCl_2]_2/AgSbF_6$	AgF	DME	17
12	$Cp^*Co(CO)I_2/AgSbF_6$	AgF	DME	0
13	$[RuCl_2(p\text{-cymene})]_2$	AgF	DME	0
14	$Mn_2(CO)_{10}$	AgF	DME	0
15[c]	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	DME	48
16[d]	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	DME	50
17[g]	$[Cp^*RhCl_2]_2/AgSbF_6$	AgF	DME	61

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), catalyst (2.5 mol %), $AgSbF_6$ (10 mol %), oxidant (0.2 mmol), and $NaOPiv{\cdot}H_2O$ (20 mol %) in solvent (1 mL) at 120 °C under air for 5 h. [b]Isolated yield. [c]Reaction temperature is 80 °C. [d]Reaction temperature is 150 °C. [e]EGME = 2-ethoxyethanol. [f]DME = 1,2-dimethoxyethane. [g]Under pure oxygen atmosphere.

ethyl benzimidate (**1a**) with phenylboronic acid pinacol ester (**2a**), employing $[Cp^*RhCl_2]_2/AgSbF_6$ as the catalyst, DCE as the solvent, in the presence of AgF and $NaOPiv{\cdot}H_2O$ at 120 °C for 5 h. Fortunately, the biphenyl-2-carbonitrile **3aa** was obtained in 64% yield through Rh(III)-catalyzed C−H arylation and dealcoholization. To identify the optimized reaction conditions, several other solvents such as DME or EGME were tested, employing $[Cp^*RhCl_2]_2/AgSbF_6$ as the catalyst in the presence of AgF. Toluene showed a similar performance, delivering the desired product **3aa** in 64% yield (entry 5). A trace amount of **3aa** was obtained in EtOH, and the major product was the C−H *ortho*-arylation product (entry 4). EGME and water were also capable of realizing this reaction, giving **3aa** in 12 and 28% yields, respectively (entries 2 and 6). In comparison to DME and other solvents, DME is the best solvent choice (entry 3). Three other Ag salts were screened in addition to AgF, all of which provided lower yields (entries 7−9). Employing $Cu(OAc)_2$ as the oxidant mainly led to an extensive decomposition of **1a** (entry 10). Switching the metal catalyst to $[Cp^*IrCl_2]_2/AgSbF_6$ only produced a 17% yield of **3aa** and afforded some dual *ortho*-arylated product (entry 11 and see details in the Supporting Information (SI) section V). When the Rh catalyst was replaced with three other transition metal catalysts, including $Cp^*Co(CO)I_2$, $[RuCl_2(p\text{-}cymene)]_2$, and $Mn_2(CO)_{10}$, no target product **3aa** or C−H *ortho*-arylation product was detected (entries 12−14). Control experiments verified the importance of proper reaction temperature (entries 15 and 16) as both lower and higher reaction temperature fell short of high reaction efficiency. In addition, when the reaction was performed under pure oxygen atmosphere, the yield of **3aa** decreased to 61% (entry 17).

With the optimized C−H arylation and dealcoholization conditions in hand, various arylboronic acid pinacol esters were selected to realize this sequential C−H arylation and dealcoholization. As depicted in Scheme 3, a series of *para*-

Scheme 3. Arylboronic Acid Pinacol Esters Scope in Rh(III)-Catalyzed Sequential C−H Arylation and Dealcoholization



substituted phenylboronic acid pinacol esters participated in this transformation successfully, giving the corresponding biphenyl-2-carbonitriles in moderate to good yields (**3aa**−**3af**). Several useful functional groups such as ether (**3ac**), fluoro (**3ad**), and chloro (**3ae**) were well tolerated. Apart from *para*-substituted phenylboronic acid pinacol esters, (3-(trifluoromethyl)phenyl) boronic acid pinacol ester (**1g**) also reacted with **1a** smoothly, delivering **3ag** in 73% yield. Notably, thiophen-3-ylboronic acid pinacol ester (**1h**) as a valuable heterocyclic source was proven as a viable substrate to produce **3ah** in 72% yield.

Furthermore, the generality and compatibility of this sequential C−H arylation and dealcoholization were then scrutinized using of a wide variety of functionalized benzimidates (Scheme 4). In most cases, the reaction proceeded well, producing the desired biphenyl-2-carbonitriles efficiently. Ethyl benzimidates, regardless of containing electron-donating or electron-withdrawing groups, all resulted in good and excellent yields (**3bc**−**3dc**, **3bi**, **3ci**, **3ba**, **3bj**, **3be**, **3bh**), suggesting that this catalytic activity was not predominantly

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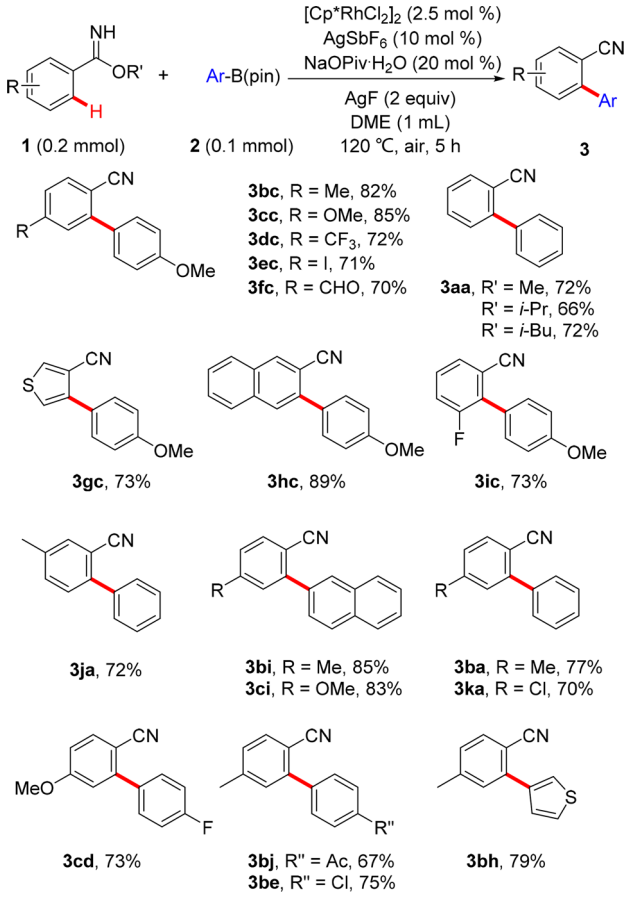
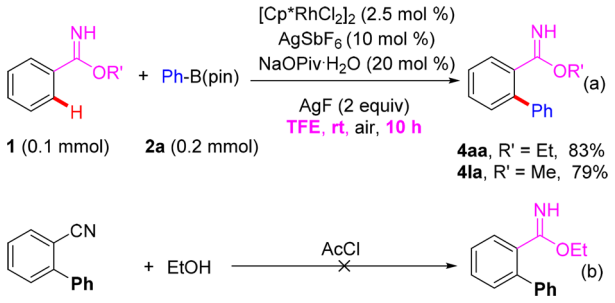
Scheme 4. Benzimidates' Scope in Rh(III)-Catalyzed Sequential C−H Arylation and Dealcoholization



affected by electronic variations. The other three alkyl benzimidates also provided the sequential arylation and dealcoholization products in good yields (**3aa**). Substituents at different positions on the phenyl ring of benzimidates showed no obvious influence on the yields, giving one regioisomer each (**3ic**, **3ja**). It is noteworthy that the reaction standard conditions tolerated some useful functional groups such as fluoro (**3ic**, **3cd**), chloro (**3ka**, **3be**), iodo (**3ec**), and acetyl (**3bj**), providing a potential possibility for further elaboration. Surprisingly, an aldehyde group in benzimidate was well compatible during the reaction, delivering the formyl product **3fc** in 70% yield. Moreover, imidates containing fused phenyl rings and heterocyclic rings were also able to carry out this reaction with good regioselectivity, affording the desired 2-carbonitriles (**3gc**, **3hc**) in satisfactory yield.

In the above Rh(III)-catalyzed reactions, C−H arylation and dealcoholization always occurred together, along with transformation of the directing group into nitriles. Although aromatic nitriles play a central role in the synthetics industry, under some circumstances, the directing group still needs to remain. To achieve this goal, further optimization was conducted (see details in the SI section VI), and the biphenyl-2-carbimidates **4aa** and **4la** with the directing group reserved were successfully obtained under very mild reaction conditions (Scheme 5a). This transformation was accomplished easily by adjusting the substrate ratio, the solvent, and the reaction temperature. With the aid of the imidate, here is a chance to fulfill the second C−H activation and cyclization for the synthesis of more useful molecules. More importantly, after the verification, it was not

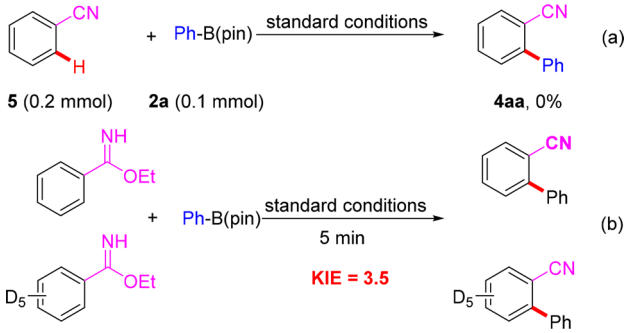
Scheme 5. Rh(III)-Catalyzed C−H Arylation for the Synthesis of Biphenyl-2-carbimidates



possible to synthesize biphenyl-2-carbimidate **4aa** via traditional nucleophilic addition from the corresponding aromatic nitriles (Scheme 5b).

To further gain insight into the reaction mechanism, preliminary experiments were performed, as demonstrated in Scheme 6. At the outset, the simple benzonitrile was employed

Scheme 6. Experiments for the Mechanistic Study



to achieve this transformation under the standard reaction conditions (Scheme 6a), and no conversion was observed, indicating that the cyano group could not coordinate with the Rh(III) complex to furnish the direct C−H *ortho*-arylation. In the above Rh(III)-catalyzed sequential C−H *ortho*-arylation and dealcoholization, direct C−H *ortho*-arylation was deemed to be the first step. The kinetic isotope effect (KIE) was determined to be 3.5 through an intermolecular competitive reaction using **1a** and [$\mathbf{D_5}$]-**1a** as the substrates (Scheme 6b). The KIE result reveals that the C−H bond cleavage probably involves in the turnover-limiting step.

Based on the above preliminary experiments and previous reports on Rh- or Ir-catalyzed direct C−H arylation,[10,18,19] a possible mechanism for this controllable Rh(III)-catalyzed C−H arylation and dealcoholization is proposed as follows (Scheme 7). First, $[Cp^*RhCl_2]_2$ reacts with $AgSbF_6$, followed by the C−H cleavage of **1a**, to afford a cyclometalated Rh(III) species **I**. Then a transmetalation occurs between the Rh(III) complex **I** and an in situ generated arylboronic ester with silver fluoride to produce intermediate **II**. Next, Rh(IV) intermediate **III** is formed from the oxidation of intermediate **II** with Ag(I). Subsequently, the desired product **4aa** and Rh(II) species **IV** are generated from the reductive elimination. Finally, the Rh(II) species **IV** is oxidized by another equivalent of Ag(I) to regenerate the Rh(III) complex **I**; meanwhile, the other product **3aa** is probably obtained via dealcoholization.

In summary, we have developed a facile and easy-to-handle protocol for the synthesis of biphenyl-2-carbonitriles and

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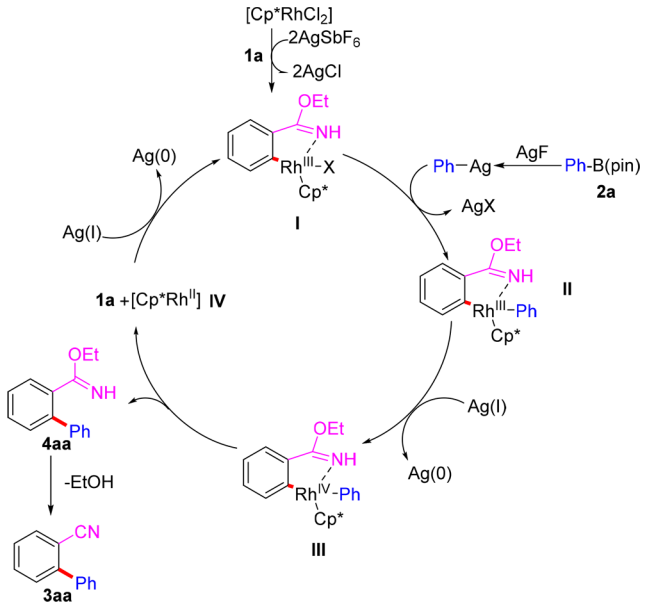
Scheme 7. Tentative Mechanism



biphenyl-2-carbimidates via Rh(III)-catalyzed C−H arylation and dealcoholization of benzimidates with arylboronic esters. In this protocol, through simple control of the reaction conditions, a variety of biphenyl-2-carbonitriles and biphenyl-2-carbimidates was synthesized in high efficiency and regioselectivity. It provides an alternative pathway for rational utilization of directing groups in chelation-assisted C−H activation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02915.

General and experimental information, the procedures and optimization of this C−H arylation and dealcoholization, details about KIE studies, analytical data and NMR spectra of the biphenyl-2-carbonitriles and biphenyl-2-carbimidates (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bxy1223@gmail.com or yangxb@synu.edu.cn.

ORCID

Xiaobo Yang: 0000-0003-0684-8419

Author Contributions

†B.J. and S.W. contributed equally.

Notes

The authors declare no competing financial interest.

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