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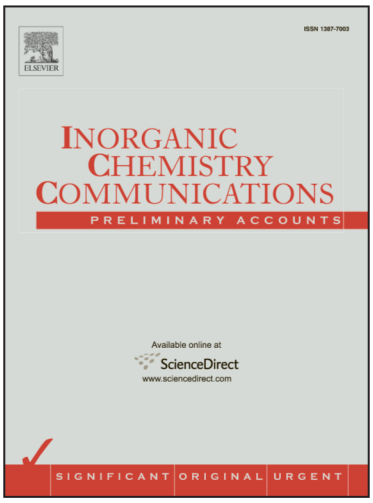

Short communication

Rhodium-Catalyzed Decarbonylation Cross-coupling Reactions of Aromatic Aldehydes and Arylboronic Acids via C-C Bond Activation Directed by a Guide Group Chelation

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Rhodium-Catalyzed Decarbonylation Cross-coupling Reactions of Aromatic Aldehydes and Arylboronic Acids via C-C Bond Activation Directed by a Guide Group Chelation

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ABSTRACT: A rhodium-catalyzed decarbonylative cross-coupling reaction of benzoquinoline-10-carbaldehydes with arylboronic acids through chelation-assisted sp^2 C−CHO bond activation has been developed. A variety of functional groups substituted phenylboronic acids or benzoquinoline-10-carbaldehydes are compatible with the reaction under the optimized reaction conditions, the corresponding 10-phenylbenzo[h]quinoline derivatives were obtained in moderate to good yields. The method affords a useful strategy for the synthesis of N-heterocyclic biaryl compounds via rhodium-catalyzed sp^2 C-CHO bond activation.

Keywords: Rhodium-catalyzed; Decarbonylation; Cross-coupling; C-C bond activation; Benzoquinoline-10-carbaldehyde

1. Introduction

Transition metal catalyzed C-C bond activation reaction can rapidly and efficiently synthesize organic compounds through reorganizing existing molecular skeletons, which has attracted much attention in recent decades. [1,2] The field is also facing challenges because of the thermodynamic and kinetic inertia of C-C bonds.

The C-C bond activation reactions usually are achieved through various activation strategies. One of the successful strategies for non-tensioned ring molecules is the use of directing groups, which introduce the transition metal catalyst into the immediate vicinity of the desired activation site via a directing group to overcome the intrinsic stability of the C-C bond. [1]

Quinolinones are good metal-directing agents that have been earlier used for directing group activation strategies. [3] The initial reactions were mainly intramolecular C-C bond activation reactions of quinolinones. Later, Wang's group reported that the reaction of direct exchange of groups between quinolinones and arylboronic acids via C-C bond activation reaction.[4] Johnson reported that rhodium-catalyzed interconversion of quinolinyl ketones with boronic acids via C−C bond activation [2a].

Compared with quinolinones, benzoquinoline is also a good metal-directing reagent, and is widely used for C-H bond activation reactions.[5] Benzoquinoline derivatives are also used in some C-C bond activation reactions. Wang's group reported that rhodium-catalyzed C-C bond activation coupling reaction of benzoquinolin-10-ethyl esters with arylboronic acids. [6]

Based on this research, we further reported that another rhodium-catalyzed C-C

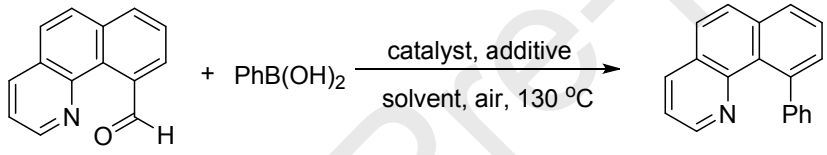
bond activation of benzoquinolin-10-methanols and arylboronic acids to afford biaryl compounds. [7] The reaction mechanism suggests that the oxidation of the primary alcohol to an aldehyde may be the key step in this cross-coupling reaction. This prompted us to study the C-C bond activation reaction of benzoquinoline-10-carboxaldehyde.

On the other hand, transition-metal-catalyzed decarbonylation of aldehyde is a topic of concern for many decades.[8] The activation of sp^2 C-CHO band of this type still remains a challenge, there is no coupling reaction using aldehydes as decarbonylative substrates. In this study, we describe a rhodium-catalyzed decarbonylative coupling reaction of benzoquinoline-10-carbaldehydes with arylboronic acids through chelation-assisted sp^2 C−CHO bond activation.

2. Results and discussion

To optimize this reaction, benzoquinoline-10-formaldehyde (**1aa**) and phenyl boronic acid (**2aa**) were initially applied in the decarbonylative cross-coupling reaction. Based on previous research work, [7] we further investigated the effects of additives and bases on the reaction. The results are summarized in Table 1.

Table 1 Optimization of the reaction conditions for the decarbonylative coupling reaction[a]



1aa 2aa 3aa

entry[a,b]	catalyst	additive	base	yield (%)[c]
1	$(PPh_3)_3RhCl$			40
2	$(PPh_3)_3RhCl$	$CuCl_2$		62
3	$(PPh_3)_3RhCl$	$Cu(OAc)_2$		49
4	$(PPh_3)_3RhCl$	CuCl		80
5	$(PPh_3)_3RhCl$	CuI		75
6	$(PPh_3)_3RhCl$	Ag_2O		52
7	$(PPh_3)_3RhCl$	$AgBF_4$		43
8	$(PPh_3)_3RhCl$	CuCl	K_2CO_3	89
9	$(PPh_3)_3RhCl$	CuCl	Cs_2CO_3	86
10	$(PPh_3)_3RhCl$	CuCl	K_3PO_4	82
11	$(PPh_3)_3RhCl$	CuCl	Et_3N	45
12	$(PPh_3)_3RhCl$	CuCl	C_5H_5N	37
13		CuCl	K_2CO_3	0

[a] Reaction conditions: **1aa** (0.1 mmol), **2aa** (0.15 mmol), catalyst (0.007 mmol,7mol%) , additive (0.1 mmol) and base (0.1 mmol) in 1 mL of xylene in air at 130 °C; [b] Reaction time:20 h; [c] Isolated yields.

When $(PPh_3)_3RhCl$ was used as the catalyst, the desired product **3aa** can be obtained in 40% of yield at 130 °C in xylene for 20 h (entry 1). In order to further improve the yield of product **3aa**, the effect of additives on the reaction was investigated.

Several copper salts and silver salts all contributed to the reaction (entries 2-7). In particular, CuCl provided the desired **3aa** in the best yield of 80% (entry 4).

Investigations on different bases revealed that the use of a proper base can further increase the yield of the cross-coupling reaction. K_2CO_3 provided the best yield of 89% (entry 8). Cs_2CO_3 and K_3PO_3 can slightly increase the yield to 86% or 82% (entries 9, 10). However, the addition of Et_3N or C_5H_5N inhibited the progress of this reaction (entries 11, 12). In addition, the reaction can not occur without catalyst $(PPh_3)_3RhCl$ (entry 13).

Based on these results, the optimized catalytic system for this transformation is $(PPh_3)_3RhCl$ (7 mol%) with CuCl (1.0 eq.) and K_2CO_3 (1.0 eq.) in xylene at 130 °C for 20 h.

Under optimized reaction conditions, the suitable range of rhodium-catalyzed decarbonylative activation reaction was studied. The results are shown in Table 2. When **1aa** was reacted with phenylboronic acid, the desired product **3aa** was obtained in 89% yield. The phenylboronic acids with an electron-donating group at para-position, including a methyl, methoxy, t-butyl group, were well-tolerated and afforded the corresponding products **3ab**-**3ad** in good yields (83-87%).

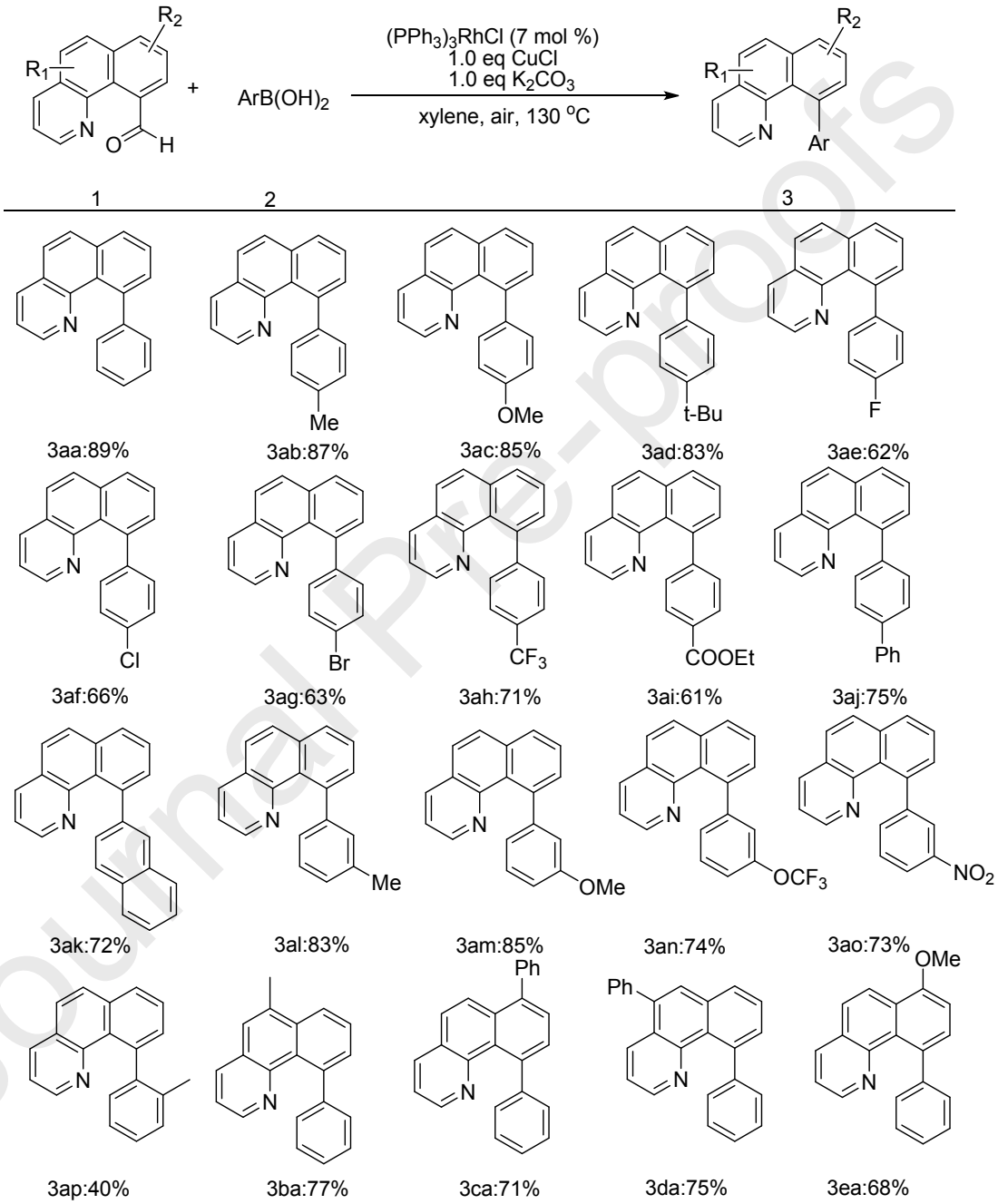
When benzoquinoline-10-carbaldehyde (**1aa**) was reacted with phenylboronic acids bearing a -F, -Cl, or -Br group at the para-position under the standard reaction conditions, the corresponding products **3ae**-**3ag** were obtained in moderate yields (62-66%). In this type of rhodium-catalyzed coupling reaction, when the halide substituted phenylboronic acids are used, the reaction product may be partially debrominated or dechlorinated.[9] At the same time, there is an advantage that the product **3af** or **3ag** can be further modified by functional groups. The phenylboronic acid substituted with a -CF_3 also can afford the product **3ah** in 71% yield. However, phenylboronic acid with a -COOEt group gave the coupling product **3ai** in 61% yield. The reaction results indicate that the phenylboronic acids with electron-donating groups are advantageous for this reaction. [1,1'-Biphenyl]-4-ylboronic acid and naphthalen-2-ylboronic acid also reacted with **1aa** to give the corresponding coupling products **3aj** and **3ak** in 75% and 72% yields, respectively.

In addition, meta-substituted phenylboronic acids were also used in this reaction. A methyl and methoxy-substituted phenylboronic acids produced **3a1** and **3am** in 83% and 85% yield in this reaction, respectively. Phenylboronic acid with an -OCF_3 or -NO_2 group can also smoothly react to give the corresponding products **3an** or **3ao** with 74% or 73% of yields. A methyl group ortho-substituted phenylboronic acid was also applied in the reaction, as a result, the product **3ap** was only obtained in 40% yield. The reaction results indicate that steric hindrance inhibits the progress of the reaction, and the nature of the substituent group has an influence on the reaction. Phenylboronic acid with electron-donating substituents are facilitate to the reaction.

The effect of substituents on benzoquinoline-10-carbaldehydes was also investigated. 6-Methyl-benzo[h]quinoline-10-carbaldehyde (**1ba**), a methyl group at the 6-position of the benzo[h]quinoline ring, was well-tollerated and reacted with phenylboronic acid to give **3ba** in 77%. Moreover, substituents of benzoquinoline-10-carbaldehyde with a −Ph group at the 7-position or at the 5-position both were suitable

for optimizing reaction conditions and afforded the corresponding products **3ca** in 71% yield and **3da** in 75% yield, respectively. When benzoquinoline-10-carbaldehyde with an −OMe group at the 7-position on the benzo[h]quinoline ring, the reaction also proceeded smoothly to afford the product **3ea** in 68% yield.

Table 2 Decarbonylative cross-coupling reactions of benzoquinoline-10-formaldehydes and various arylboronic acids [a]



[a] Reaction conditions: 1 (0.10 mmol), 2 (0.15 mmol), $Rh(PPh_3)_3Cl$ (7 mol %), CuCl (0.10 mmol), K_2CO_3 (0.10 mmol) in 1 mL of xylene in air at 130 °C for 20 h; Isolated yields.

The mechanism of the reaction is similar to that of the previous studies, [6,7] the reaction is subjected to a mechanism involving oxidative addition and reductive elimination of rhodium complex to obtain the desired products.

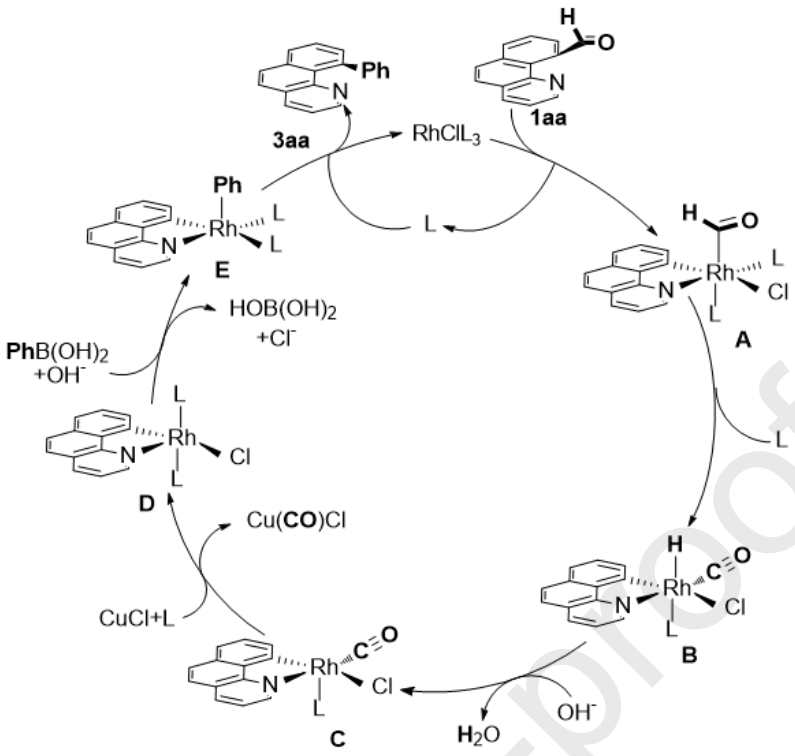


Figure 1. Proposed mechanism for rhodium-catalyzed the reaction of benzoquinoline-10-carbaldehydes with arylboronic acids.

3. Conclusion

In summary, rhodium-catalyzed C-C activation of aromatic aldehydes was investigated. 10-Phenylbenzo[h]quinoline derivatives were synthesized by the decarbonylative cross-coupling reaction of benzoquinoline-10-carbaldehydes with arylboronic acids. $(PPh_3)_3RhCl$ was confirmed to be a useful catalyst with CuCl and K_2CO_3 as additives. Under optimized reaction conditions, a variety of functional group substituted arylboronic acids or benzoquinoline-10-carbaldehydes are suitable for this reaction and the desired products were obtained in moderate to good yields. Further efforts to discover other directing groups in this catalytic reaction methodology are currently underway in our laboratory.

4. Experimental section

General information: ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained on Bruker AV 400 spectrometers with $CDCl_3$ as solvent. For ^1H NMR, the chemical shift is reported in ppm relative to $CDCl_3$ (δ = 7.26), for ^{13}C NMR, the central $CDCl_3$ resonance is (δ = 77.0). NMR data of known compounds are in agreement with literature values. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

The starting materials 10-phenylbenzo[h]quinolines were synthesized and purified according to the literature procedures. [7] Other chemicals or reagents were obtained from commercial sources. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of air. Reactions were monitored by analytical thin layer chromatography (TLC), which was performed on 0.20 mm silica gel plates, spots were detected by flash chromatography through UV-absorption.

Column chromatography was performed on silica gel (100-200 mesh).

General Experimental Procedure for the Preparation of 10-Phenylbenzo[h]quinolines.

To an oven-dried screwed vial were added substituted benzoquinoline-10-carbaldehyde (0.1 mmol), substituted arylboronic acid (0.15 mmol), $(PPh_3)_3RhCl$ (0.007 mmol, 6.48 mg), CuCl (0. 1 mmol, 9.9 mg), K_2CO_3 (0. 1 mmol, 13.8 mg) and xylene (1 mL). The mixture was vigorously stirred at 130 ^oC under air to the end of the reaction. Organic solvents were removed in *vacuo*, and then the residue was purified by a silica gel column chromatography to give the desired product.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at the Publications website.

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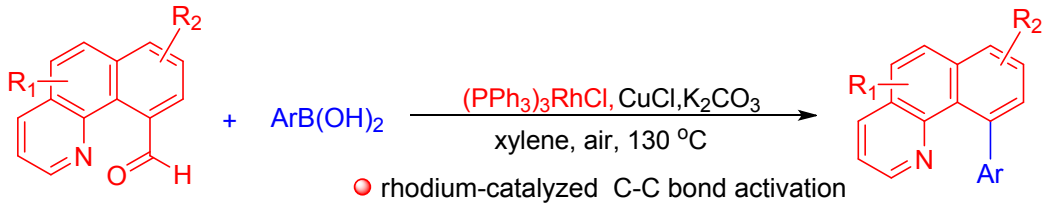
Highlights

- Rhodium-catalyzed sp^2 C-CHO bond activation.
- A broad range of arylboronic acids are suitable.
- One-step to synthesize 10-phenylbenzo[h]quinoline derivatives.
- A variety of 10-phenylbenzo[h]quinoline derivatives were obtained in medium to high yields.

Author Statement

Xiaobo Yu collected the experimental data, performed data ana-lysis, and wrote the manuscript. Guanchen Liu performed apart of data analysis. Shudong Geng performed apart of data analysis.



- rhodium-catalyzed C-C bond activation
- one step synthesis
- medium to high product yields