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Phosphine-free rhodium-catalyzed hydroarylation of diaryl acetylenes with boronic acids

Weiwei Zhang, Miaochang Liu, Huayue Wu, Jinchang Ding, Jiang Cheng *

College of Chemistry and Materials Science, Wenzhou University, Wenzhou 325027, PR China

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ABSTRACT

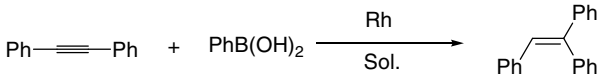
$Rh(CO)_2(acac)$ was found to be an efficient and simple catalyst in hydroarylation of diaryl acetylenes with boronic acids in the absence of phosphine ligand. Thus, triaryl-substituted olefins were prepared in good to excellent yields. No 1,4-rhodium shift was observed in the catalytic cycle.

Recently, much attention has been paid to rhodium catalysts in the formation of carbon–carbon bond since it represents a central theme in organic synthesis.[1] The addition of arylboronic acids to unsaturated C–C bond catalyzed by transition-metal has drawn considerable attention because organoboron reagents possess the advantages of low toxicity, stability to air and/or moisture, and good functional group tolerance.[2] Recently, Hayashi and Miyaura reported the rhodium-catalyzed 1,4-addition of organoboronic acids to various α,β-unsaturated compounds.[3] In these reactions, only olefins activated by the presence of a conjugated electron-withdrawing group could be used, which were generally carried out in a mixture of organic solvent and water. The regio- and stereoselective synthesis of multisubstituted olefins has been a challenge for synthetic organic chemists for years.[4] In 2001, Hayashi reported the rhodium-catalyzed hydroarylation of alkynes with arylboronic acids via 1,4-shift of rhodium.[5] Lautens described the rhodium-catalyzed regioselective addition of arylboronic acids to alkynes in water, albeit a pyridin-2-yl was required to be attached in the C–C triple bonds.[6] Genét also reported the rhodium-catalyzed addition of arylboronic acids to alkynes, employing the water soluble phosphines as ligands.[7] In addition to the rhodium-catalyzed methods,[8] the palladium or nickel-catalyzed addition of organoboron reagents to alkynes was also reported.[9] In 2004, Nolan described that NHC was an efficient ligand in the palladium-catalyzed addition of arylboronic acids to alkynes.[10] Although progress has been made for this reaction, additional ligands either phosphine or NHC ligands are still needed. However, most ligands are expensive and/or air-sensitive, which will result in the tedious procedures. It still remains a continuing and urgent goal to develop simple and versatile synthetic methods for this transformation. Our interest in the development of transition metal-catalyzed additions of arylmetallic reagents to the carbon–carbon or carbon-hetero unsaturated bonds[11] led us to explore the possibility of using a simple catalytic system for such transformation. Herein, we report a phosphine-free rhodium-catalyzed hydroarylation of alkynes with arylboronic acids, which did not involve a 1,4-rhodium shift.

Initial studies of the reaction conditions were conducted using the addition of phenylboronic acid **2a** to diphenyl acetylene **1a** as the model reaction. Since water was reported to enhance the reaction rate in many rhodium-catalyzed addition reactions, we employed toluene/H_2O = 10:1 as the co-solvents in the reaction. A series of rhodium sources were tested under various reaction conditions in the absence of any phosphine ligand. The screening results are summarized in Table 1.

During the screening process, it was observed that rhodium source played an important role in the reaction. Rh(cod)(acac) gave the desired product in 47% isolated yield with toluene and water as solvent, and the yield was increased to 74% when $Rh(cod)_2Cl$ dimer

Table 1
Effects of rhodium sources and solvents on the rhodium-catalyzed addition of phenylboronic acid to diphenyl acetylene[a]



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

Entry	Rhodium source	Solvent	Yield[b] (%)
1	Rh(cod)(acac)	Toluene/H_2O = 10:1	47
2	$Rh(cod)_2Cl$ dimer	Toluene/H_2O = 10:1	74
3	$Rh(CO)_2(acac)$	Toluene/H_2O = 10:1	90 (80)[c]
4	$Rh(CO)_2(acac)$	Toluene	<5
5	$RhCl_3·3H_2O$	Toluene/H_2O = 10:1	<5
6	$Rh(PPh_3)_3Cl$	Toluene/H_2O = 10:1	<5

[a] All reactions were run in the presence of diphenyl acetylene (36 mg, 0.2 mmol), phenylboronic acid (36 mg, 0.3 mmol), indicated rhodium source (5 mol %), and solvent (3.3 mL) under reflux for 12 h.
[b] Isolated yield.
[c] Under room temperature.

* Corresponding author. Tel./fax: +86 577 88156826.
E-mail address: jiangcheng@wzu.edu.cn (J. Cheng).

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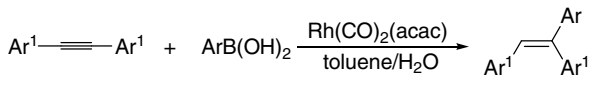
Table 2
Hydroarylation of symmetrical alkynes with boronic acids[a]



1 2 3

Entry	Alkyne	Aryl	Product	Yield[b] (%)
1	Ph—≡—Ph	Ph **2a**	**3aa**	90
2	**1a**	4-MeO–C_6H_4-**2b**	**3ab**	70
3		4-Cl–C_6H_4-**2c**	**3ac**	85
4		2-Me–C_6H_4-**2e**	**3ae**	83
5		4-CF_3–C_6H_4-**2f**	**3af**	80
6		*trans*-Ph–CH=CH-**2g**	**3ag**	83
7		4-Me–C_6H_4-**2h**	**3ah**	86
8	3-Tol—≡—3-Tol	Ph **2a**	**3ba**	72
9	**1b**	4-Cl–C_6H_4-**2c**	**3bc**	81
10	4-Tol—≡—4-Tol	Ph **2a**	**3ca**	91
11	**1c**	4-MeO–C_6H_4-**2b**	**3cb**	67
12		4-Cl–C_6H_4-**2c**	**3cc**	80
13	2-nap—≡—2-nap	Ph **2a**	**3da**	76
14	**1d**	4-Cl–C_6H_4-**2c**	**3dc**	72
15	2-thio—≡—2-thio **1e**	Ph **2a**	**3ea**	70

[a] Reaction conditions: alkyne (0.2 mmol), boronic acid (0.3 mmol), $Rh(CO)_2(acac)$ (2.6 mg, 5 mol %), toluene/H_2O (3.3 mL, 10/1), 110 °C, 12 h.
[b] Isolated yield.

was employed (Table 1, entry 2). The Wilkinson catalyst was totally ineffective in this transformation. To our delight, the yield was dramatically increased to 90% in the presence of $Rh(CO)_2(acac)$ (5 mol %) in toluene/H_2O (Table 1, entry 3). In dry toluene, $Rh(CO)_2(acac)$ did not produce the desired product.

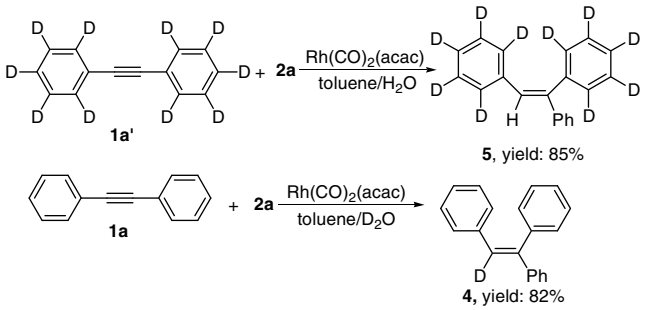
With the optimized conditions in hand, we then explored the scope of the addition reaction in the presence of a variety of functional groups of the substrates, as shown in Table 2.

As expected, all substrates reacted smoothly under the reaction conditions and provided the desired hydroarylation products in good to excellent yields. Furthermore, electron-withdrawing arylboronic acids generally reacted with alkynes easily and gave triaryl-substituted olefins in much higher yields, while the electron-donating analogues provided the desired products with relatively lower yields. The hindrance in the aromatic ring of the boronic acids had little influence on the reaction. For example, comparing with **3aa**, **3ae** was produced in slightly decreased 83% yield (Table 2, entry 4). Heteroarylboronic acids were not proper substrates in the procedure. This may be at least partly because the heteroatoms in the heteroaryl boronic acid may coordinate to the transition metal. But interestingly, the di-heteroarylacetylene **1e** worked well in the procedure, and **3ea** was prepared in 70% yield (Table 2, entry 15). It was noteworthy that *trans*-Ph–CH=CH–$B(OH)_2$ **1g** was still a good reaction partner in the procedure and delivered the conjugated diene **3ag** in 83% yield (Table 2, entry 6). The reaction could run smoothly at room temperature, despite the yield of **3aa** was slightly decreased to 80% (Table 2, entry 1). However, the feasibility of employing the dialkyl or aryl alkyl acetylenes and dimethyl but-2-ynedioate analogues in the procedure was failed.

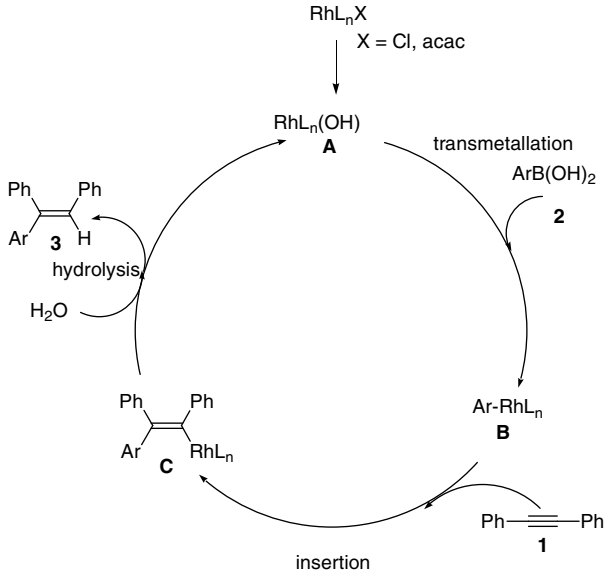
To further understand the mechanism, diphenyl alkyne-*d*[10] **1a′** was prepared,[12] and labeling studies were conducted (Scheme 1).

This result indicated that the reaction did not involve a 1,4-rhodium shift, which was firstly reported by Hayashi.[5] Further labeling studies clearly showed that the H attached to the C=C bond was derived from the solvent (Scheme 1).

Based upon the above experimental results, a plausible mechanism is outlined in Scheme 2. The catalytic cycle may contain four steps: (1) RhL_nX undergoes hydrolysis to form $RhL_n(OH)$ **A**; (2) $ArB(OH)_2$ transmetallates with **A** to form intermediate **B**; (3) intermediate **B** inserts into the triple bond, and intermediate **C** is produced; and (4) intermediate **C** directly hydrolyzes[13] to deliver the hydroarylation product **3** and the true catalytic species **A** is regenerated.



Scheme 1. Labeling studies of the hydroarylation reaction.



Scheme 2. Plausible mechanism.

In conclusion, we developed a phosphine-free rhodium-catalyzed hydroarylation of alkynes with arylboronic acids. The addition reaction was proved to be an efficient, simple and versatile method for the synthesis of triaryl-substituted ethene derivatives. Furthermore, the reaction did not involve a 1,4-rhodium shift.[14]

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.140.

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13. The ligand feedback effect of CO is stronger than that of dppe. Thus, the electron density of R–Rh$(CO)_2$ is higher than that of R–Rh(dppe). The intermediate **C** directly underwent hydrolysis rather than the 1,4-rhodium shift, which may at least partly be caused by the weaker Lewis acidity of R–Rh$(CO)_2$ than that of R–Rh(dppe). Example of rhodium-catalyzed hydroarylation of alkynes with boronic acids that did not involve 1,4-rhodium shift, see: Ref. 4.
14. *General procedure:* Under air, a reaction tube was charged with diaryl alkynes (0.2 mmol), boronic acids (0.3 mmol), Rh$(CO)_2$(acac) (2.6 mg, 5 mol %), and toluene/H_2O (3.3 mL, 10/1). The mixture was heated under air at 110 °C for 12 h, then cooled to room temperature. The mixture was concentrated in vacuo and the residue was purified by flash column chromatography on a silica gel to give the desired product.