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## Accepted Article

**Title:** Rhodium-Catalyzed Arylative Transformations of Propargylic Diols: Dual Roles of the Rhodium Catalyst

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COMMUNICATION

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# Rhodium-Catalyzed Arylative Transformations of Propargylic Diols: Dual Role of the Rhodium Catalyst

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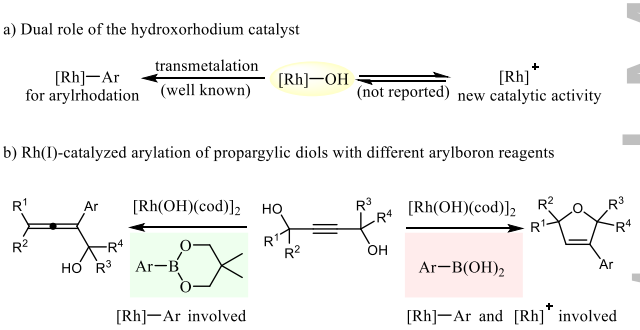
**Abstract.** Controllable synthesis of a variety of allenic alcohols and 2,5-dihydrofurans by rhodium(I)-catalyzed arylative transformations of propargylic diols is reported. The hydroxorhodium catalyst was found to play dual role: it catalyzed the arylation/dehydroxylation reaction of propargylic diols to afford allenic alcohols, and besides, it could convert to a cationic rhodium species in situ, which catalyzed the intramolecular hydroalkoxylation of allenic alcohols to form dihydrofurans. Remarkably, generation of the cationic rhodium species is dependent on the arylboron reagent used. Thus, the controllable synthesis is achieved by simply changing the arylboron reagent.

**Keywords:** rhodium; propargylic diol; arylation; allenes; dihydrofuran

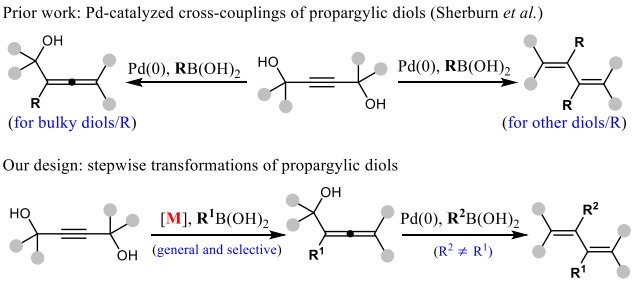
The metal catalyst, which plays an essential role in the metal-catalyzed transformations, may show disparate catalytic activities when existing in different forms, and thus greatly affects the reaction pathway and outcomes.[1] As a result, a thorough understanding of the metal catalyst, especially its existing forms during the reaction, is of great significance for development of metal catalysis. As one of the most convenient and reliable methods for the construction of C–C bonds, the rhodium(I)-catalyzed arylation reactions of unsaturated bonds with arylboron reagents have been extensively explored over the last decades.[2] In particular, the detailed reaction pathway of rhodium(I)-catalyzed arylation reactions with arylboron reagent was studied,[2,3] and it is well accepted that the rhodium(I) catalyst participates in the catalytic cycle via transmetalation with arylboron reagent to form an arylrhodium species. However, the possibility of the rhodium catalyst to form other catalytically active species during the reaction is neglected. Herein, we report our finding that the hydroxorhodium catalyst can not only catalyze the arylation process, but also convert to a cationic rhodium species under suitable reaction conditions to promote new transformations (Scheme 1a). This serendipitous finding originated from the study of the rhodium-catalyzed arylative transformations of propargylic diols, and eventually led to a controllable synthesis of a series of fully substituted allenic alcohols[4] and 2,5-dihydrofurans[5] (Scheme 1b).




**Scheme 1.** Dual role of the rhodium catalyst and divergent transformations of propargylic diols.

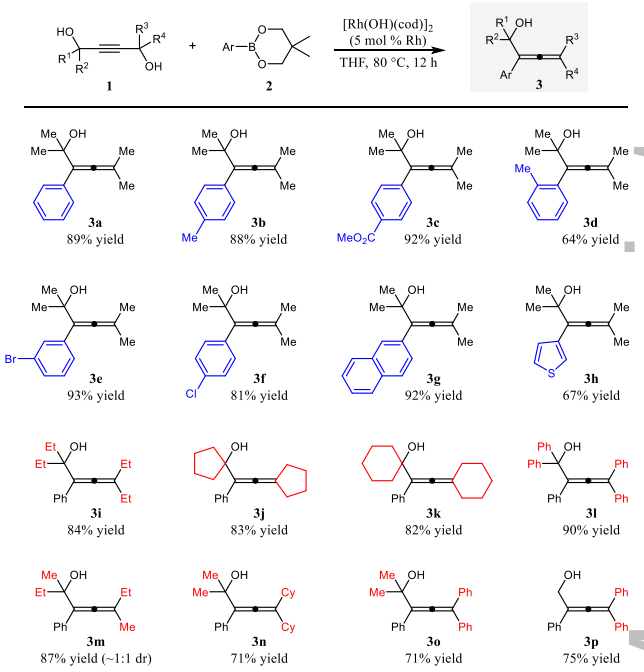
Propargylic 1,4-diols are attractive substrates for organic synthesis in terms of availability and economy, since they are bench stable, inexpensive, and easily prepared from abundant acetylene and ketones. However, the transformations of propargylic diols were mainly restricted to cyclization reactions to furnish heterocyclic compounds.[6] Recently, Sherburn and co-workers developed an elegant palladium-catalyzed Suzuki–Miyaura-like cross-coupling of propargylic diols to prepare 1,3-butadienes or allenic alcohols,[7] which greatly expanded the synthetic utilities of those readily available reagents (Scheme 2). This palladium-catalyzed reaction provided a novel and reliable method for the synthesis of a series of 1,3-butadienes via twofold cross-coupling and allenic alcohols via

single cross-coupling, respectively. However, there are still several challenges to be addressed. For example, the direct twofold cross-coupling could only introduce the same substitution group at 2,3-positions on the final products, hence limited the diversity of 1,3-butadienes accessible. Moreover, the allenic alcohol synthesis was only applicable to the bulky substrates (bulky diols or bulky aryl boronic acids should be used), and other substrates were not able to stop at the allenic alcohol step, but directly underwent twofold cross-couplings. We then envisaged that a selective and stepwise synthesis may overcome the aforementioned limitations. For instance, a suitable metal catalysis may provide a general method to access allenic alcohols, which could be further transformed to dienes bearing different substitutions by the palladium-catalyzed cross-coupling.[8] As part of our ongoing interests in the transformations of propargylic alcohols,[9] we embarked on a project aiming at the general and selective synthesis of allenic alcohols from propargylic diols and their further transformations to unsymmetrical 1,3-butadienes (Scheme 2).

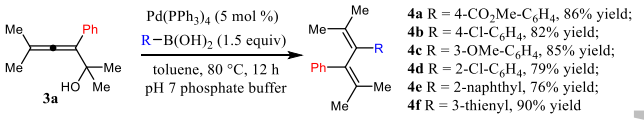



**Scheme 2.** Synthesis of allenic alcohols and 1,3-butadienes from propargylic diols.

Our group is particularly interested in the rhodium-catalyzed transformations of propargylic alcohols,[9] and we recently developed a rhodium(I)-catalyzed arylation reaction of *γ*-alkyl *tert*-propargylic alcohols for the synthesis of allenes.[9a] We then speculated that this method might be amendable to the synthesis of allenic alcohols from propargylic diols. However, the challenge is the bulkiness associated with the *tert*-propargylic diols, which is not favourable for the projected arylation reaction. Nevertheless, we commenced our study by investigating the arylation of *tert*-propargylic diol **1a**. To our delight, the reaction proceeded smoothly with $[Rh(OH)(cod)]_2$ as the catalyst, and when phenylboronic acid neopentylglycol ester **2a** was used as the arylboron reagent,[10] the desired allenic alcohol product **3a** was obtained in 89% yield. The generality of the reaction was then investigated. As shown in Scheme 3, diverse arylboronic acid neopentylglycol esters, including those bearing substitutions with both electron-donating and electron-withdrawing characters, halogen substitutions, as well as heterocyclic arylboron reagent, were all suitable in this reaction system (**3a**–**3h**). Besides, different propargylic diols prepared from diverse ketones were well-tolerated (**3i**–**3p**). In particular, when unsymmetrical diols were used, the aromatic ring was introduced preferentially to the less hindered side (**3n**–**3p**). It should be noted that most of the allenic alcohols reported here are not accessible by the previous method.[7] Using **3a** as the model substrate, we verified our hypothesis that unsymmetrical 1,3-butadienes could be achieved selectively (Scheme 4).

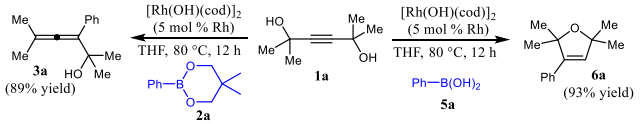



**Scheme 3.** Scope of the allenic alcohol synthesis.




**Scheme 4.** Cross-coupling of **3a** to unsymmetrical dienes.

During our study of the model reaction between propargylic diol **1a** and various phenylboron reagents. It was found that divergent reaction outcomes were obtained when different phenylboron reagents were used (see Table S1 in the Supporting Information for details). For example, when phenylboronic acid neopentylglycol ester **2a** was used, allenic alcohol **3a** was formed exclusively. However, under otherwise identical reaction conditions, replacement of **2a** with phenylboronic acid **5a** resulted in the formation of dihydrofuran **6a** as the sole product (Scheme 5).




**Scheme 5.** Divergent products with different arylborons.

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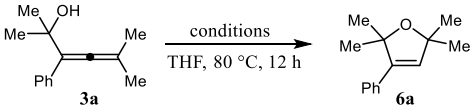
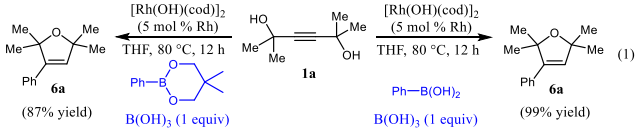
In the literature precedence, combination of the same rhodium catalyst with different arylboron reagents usually led to the change of reactivity, rather than the reaction pathway.[2,10] We speculated that there should be different catalytically active species present in the reaction system when different arylboron reagents were used. Thus, these extraordinary results prompted us to further investigate the reasons behind.

**Table 1.** Intramolecular hydroalkoxylation of allenic alcohol **3a**.[a]

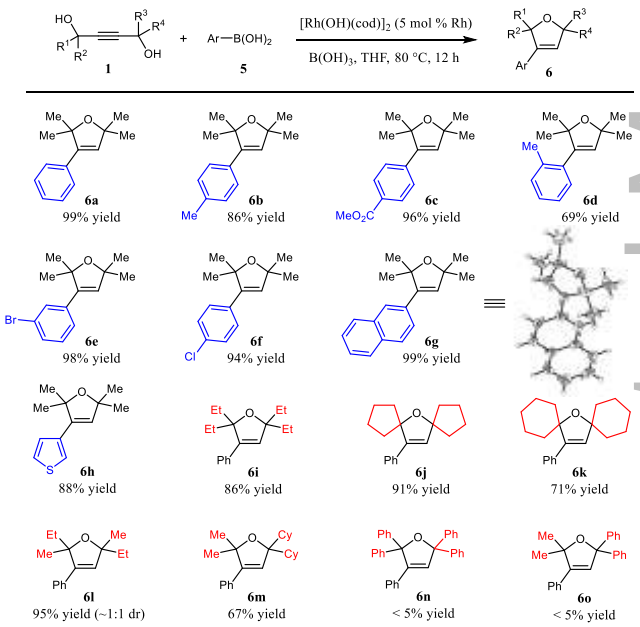



| Entry | Conditions | Yield [%][b] |
|---|---|---|
| 1 | $[Rh(OH)(cod)]_2$ (5 mol % Rh) | n.r. |
| 2 | $PhB(OH)_2$ (1 equiv.) | n.r. |
| 3 | $B(OH)_3$ (1 equiv.) | n.r. |
| 4 | $[Rh(OH)(cod)]_2$ (5 mol % Rh) + $B(OH)_3$ (1 equiv.) | 83 |
| 5 | $[RhCl(cod)]_2$ (5 mol % Rh) + $B(OH)_3$ (1 equiv.) | n.r. |
| 6 | $[RhCl(cod)]_2$ (5 mol % Rh) + $PhCO_2H$ (10 mol %) | n.r. |
| 7 | $[Rh(cod)_2]BF_4$ (5 mol % Rh) | 84 |
| 8 | $[RhCl(cod)]_2$ (5 mol % Rh) + $AgBF_4$ (5 mol %) | 78 |

[a] The reactions were carried out with **3a** (0.20 mmol) under indicated conditions.
[b] Isolated yield of **6a**. n.r.: no reaction.




For the reaction producing **6a** as the final product, both **6a** and **3a** could be detected at the early stage. Thus, we hypothesized that dihydrofuran **6a** was formed by the intramolecular hydroalkoxylation of allenic alcohol **3a**,[5] and various conditions were investigated to identify the species which enabled the transformation. As shown in Table 1, neither the hydroxorhodium catalyst nor the phenylboronic acid promoted the reaction (entries 1 & 2). Boric acid was generated during the arylation reaction when phenylboronic acid was used, so it was tested as the additive. Surprisingly, although the boric acid itself was not catalytically active (entry 3), its combination with the hydroxorhodium catalyst efficiently promoted the formation of **6a** (entry 4). Inspired by Breit's work on the rhodium-catalyzed hydroalkoxylation of allenes,[11] we initially hypothesized that the reaction might proceed via a rhodium(III) hydride intermediate, which might be generated by oxidative addition of rhodium(I) to the boric acid O–H bond. However, when the hydroxorhodium catalyst was changed to the rhodium chloride catalyst, which was used in Breit's system, the reaction did not proceed at all (entry 5). Further studies of other conditions[12] to produce the rhodium(III) hydride species all failed to enable the reaction (entry 6, see Table S2 in the Supporting Information for more conditions). Being aware that the hydroxorhodium is slightly basic[13] while boric acid is a weak acid, we then considered the possibility of a simple acid-base reaction to form a cationic tetrahydroxoborato-rhodium(I) complex $[Rh(cod)]^+B(OH)_4^-$ in equilibrium,[14] which accounted for the observed cyclization reaction. Indeed, the cationic rhodium catalyst, either preformed or generated in situ, facilitated the conversion of **3a** to **6a** without additives (entries 7 & 8). The possibility of boric acid simply serving as a proton donor[15] was also excluded as no additional proton donor was required for this transformation (entries 7 & 8). To further validate our conclusion, boric acid was introduced as the additive to the reactions in Scheme 5, and as anticipated, dihydrofuran **6a** was formed exclusively regardless of the arylboron reagent used (eq 1). To our delight, with the additional boric acid, **6a** could be obtained quantitatively using phenylboronic acid as the aryl source.

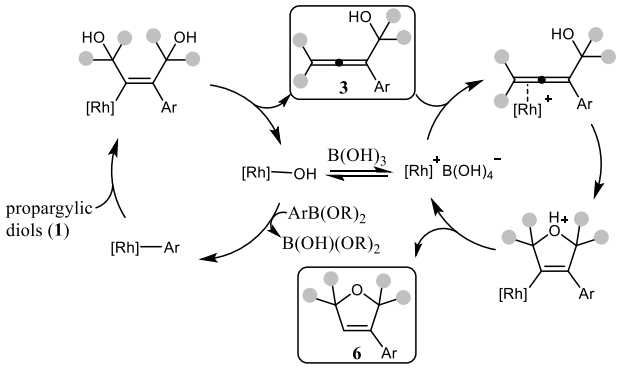



**Scheme 6.** Scope of the 2,5-dihydrofuran synthesis.

The scope of the dihydrofuran synthesis was then examined, which is summarized in Scheme 6. Arylboronic acids bearing electron-donating or electron-withdrawing substitutions and halogen substitutions at different positions on the phenyl ring, as well as other types of arylboronic acids were all suitable in this reaction system, and delivered the desired 2,5-dihydrofurans in high efficiency (**6a**–**6h**, up to 99% yield). The structure of the dihydrofuran products was unambiguously confirmed by single-crystal X-ray diffraction analysis of **6g**.[16] In addition

to various arylboronic acids, propargylic diols derived from diverse alkyl ketones worked well under optimal reaction conditions (**6i**–**6m**). However, as a limitation of current method, when propargylic diols bearing aromatic substitutions were employed, the reaction did not proceed further to give the dihydrofurans, but yielded allenic alcohols as the major product (**6n**–**6o**).

Based on the experimental results and literature precedence, a plausible mechanism of the reaction was proposed. As illustrated in Scheme 7, the arylrhodium intermediate was first generated by transmetalation of the hydroxorhodium catalyst with arylboron reagents,[3] followed by an arylrhodation/β-OH elimination process[9a,17] to furnish allenic alcohols **3**. In the presence of boric acid (generated in situ or added as the additive), a cationic rhodium complex $[Rh(cod)]^+B(OH)_4^-$ was assumed to be formed, which served as the Lewis acid catalyst to promote the intramolecular hydroalkoxylation of allenic alcohols to generate dihydrofurans.[5]




**Scheme 7.** Proposed reaction mechanism.

In summary, we have reported that the hydroxorhodium catalyst could exist in different forms when used in combination with different arylboron reagents, thus led to divergent reaction pathways in the rhodium(I)-catalyzed arylation reactions. The controllable synthesis of allenic alcohols and 2,5-dihydrofurans from readily available propargylic diols was achieved based on this new finding. The more comprehensive understanding of the rhodium catalyst shall help further development of the well-established rhodium-catalyzed arylation reactions. Further study of the mechanism and application of this new finding to other useful synthetic transformations are currently ongoing in our laboratory.

## Experimental Section

**General Procedure for the Synthesis of Allenic Alcohols**

$[Rh(OH)(cod)]_2$ (2.3 mg, 5 μmol, 5 mol % Rh), propargylic diol **1** (0.20 mmol), and arylboronic acid neopentylglycol ester **2** (0.30 mmol) were placed in an oven-dried Schlenk tube under nitrogen. Anhydrous THF (1.0 mL) was added and the resulting solution was stirred at 80 °C for 12 h. Upon completion, the reaction was diluted with water (5 mL), and extracted with ethyl acetate (5 mL*2). The organic phase was combined and the solvent was removed on a rotary evaporator. The crude product was subjected to silica gel chromatography with petroleum ether/ethyl acetate (20/1) to give allenic alcohol **3**.

**General Procedure for the Synthesis of 2,5-Dihydrofurans.**

$[Rh(OH)(cod)]_2$ (2.3 mg, 5 μmol, 5 mol % Rh), propargylic diol **1** (0.20 mmol), boric acid (0.20 mmol), and arylboronic acid **5** (0.30 mmol) were placed in an oven-dried Schlenk tube under nitrogen. Anhydrous THF (1.0 mL) was added and the resulting solution was stirred at 80 °C for 12 h. Upon completion, the reaction was diluted with water (5 mL), and extracted with ethyl acetate (5 mL*2). The organic phase was combined and the solvent was removed on a rotary evaporator. The crude product was subjected to silica gel chromatography with petroleum ether/ethyl acetate (40/1) to give 2,5-dihydrofuran **6**.

## Acknowledgements

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# Rhodium-Catalyzed Arylative Transformations of Propargylic Diols: Dual Role of the Rhodium Catalyst

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