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Pd-Catalyzed Reductive Heck Reaction of Olefins with Aryl **Bromides for Csp2-Csp3 Bond Formation**

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We developed a Pd-catalyzed intermolecular reductive Heck reaction to construct Csp2-Csp3 bonds between aryl bromides and olefins. Various styrene derivatives, acyclic and cyclic alkenes, were well tolerated to couple with varied aryl bromides in linear selectivity. Kinetic and deuterium labeling experiments suggested that *i*-PrOH provide a hydride through β -H elimination.

Pd-catalyzed Heck reactions are one of the most efficient and powerful tools for construction of structurally sophisticated alkenes, which have been widely applied in modern organic synthesis.1 Such transformations generally involve coupling of olefins, the alkenyl source, with aryl or vinyl electrophiles. Mechanistically, the syn migratory insertion of olefin into Ar-Pd bond and the subsequent β -H elimination are considered to be the key elementary steps in the whole catalytic cycle.² It is, however, inescapable that the migratory insertion delivers a σ -Pd-alkyl intermediate. The interception of the σ -Pd-alkyl species as the dominant quenching step leads to a Csp³centered compound but this transformation remains challenging.³ In addition, directly utilizing olefins, which are extensive, stable, inexpensive and of great diversity, as the Csp³ synthons is more synthetically practical and attractive, compared to conventional alkylmetallic reagents or alkyl halides.⁴

Reductive Heck (rH) reactions, initially disclosed by Cacchi and coworkers, referred to the conjugate addition of Ar-Pd-X to olefins and then reductive cleavage to deliver the desired arylalkyl product.⁵ Although these reactions have achieved delightful progress, some limitations and challenges still exist.⁶ First, rH-type cyclizations in an intramolecular fashion to construct Csp³ related cyclic molecules dominate in this area.⁷ In sharp contrast, the intermolecular rH reactions remain much

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strained ofering as facal substrates, such as horbornene
derivatives.9 Second, olefins with electron withdrawing groups,
such as the most commonly used conjugated enones, $^{10}\ensuremath{\text{were}}$
employed to react with Ar-Pd-X species generated in situ from
reaction mixtures. Third, in view of the regioselectivity, 1,2-
insertion or 2,1-insertion leading to the linear or branch desired
product, respectively, is also problematic while employing
inactivated olefins. ¹¹ Thus, it is of great importance to develop
a new catalytic system that exhibits wider tolerance for simple
olefins in a regioselective manner. In addition, the commonly
used reductants are formates/bases combination performing as
the hydride donor. Very recently, Nakao's and Buchwald's
groups independently employed a Pd/Cu/Si-H synergistic
catalysis in these rH transformations, in which branch rH
products were obtained when vinylarenes were utilized, ¹² while
a Ni/silane system was reported by Liu ¹³ and Zhu ¹⁴ . Moreover,
Zhu and coworkers found a Pd/H ₂ O system for enantioselective
rH reactions. ¹⁵ Nevertheless, simple reductive systems are still
worthy to develop.
In the present work, we report a Pd-catalyzed rH reaction of

less studied, except for the one utilizing special cyclic and strained olefins as ideal substrates⁸ such as norhornene

sent work, we report a Pd-cataly olefins with aryl bromides in an intermolecular fashion. This reaction provides an efficient strategy for construction of Csp²-Csp³ bonds with linear selectivity. The bidentate geometryconstrained iminopyridyl (CImPy) ligand plays an important role in stabilization of the catalytically active palladium center.





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Our recent research focuses on the bidentate CImPy ligands and their application in Pd-catalyzed C-C coupling reactions.¹⁶ We found that this ligand was able to efficiently stabilize the Pd center in the coupling reactions, especially the Pd_{CImPy}* with a highly steric environment (Schemes 1).17 In our efforts to study its effect in selective Pd-catalyzed alkene functionalization with 1a and 2a as the model substrates, we unexpectedly obtained product **3aa** that arose from the linear Csp²-Csp³ coupling when *n*-BuOH is used as the solvent, although the major product was still the normal Heck product 4a (Scheme 1). This interesting result strongly suggested that the rH reaction could occur under the current conditions in an alcoholic solvent environment. In this regards, we further examined other alcohols. Gratifyingly, using secondary alcohol *i*-PrOH, the selectivity was greatly reversed compared with the primary n-BuOH and the linear rH product 3aa was obtained in predominance (Scheme 1). Further optimization of the reaction conditions suggest that the bidentate iminopyridyl ligand is important in promoting this transformation and strong bases are crucial for the selectivity (See supplementary information). KOH was finally chosen as the reaction base.

We subsequently examined the scope of this rH reaction with a variety of aryl bromides and aryl olefins (Table 1).¹⁸ The aryl bromides with electron-donating groups were found to proceed well in good yields (Table 1, 3ab-3ae), while the ones with electron-withdrawing substituents, such as CF₃, F and Cl, were less efficient under the standard condition. It is important to note that the de-bromination of aryl bromides occurred for these electron-deficient aryl bromides due to the facile reduction under the current reductive condition.12 To our delight, increasing the amount of aryl bromide and base could efficiently address this issue, significant improvements were observed and the desired reductive products were isolated in moderate to good yields (Table 1, 3af-3ah). The sterically hindered aryl bromides could smoothly undergo the reductive coupling reaction with 1a in good yields under the modified conditions (Table 1, 3ai and 3aj). However, the reaction with the heteroaromatic compound 8-bromoquinoline proceeded with much lower yield (Table 1, 3am).

With respect to the innate character of olefins, the catalytic reactions appeared quite general toward varied styrene derivatives (Table 1, 3bb-3fb). 4-Vinylpyridine was also compatible to give 60% yield (3gb). Furthermore, we tested 1,1and 1,2-disubstituted styrenes, which are usually considered to be less active in Heck reactions.¹⁹ More interestingly, the rH arylation of 1,2-disubstitited alkenes results in the formation of a potentially chiral center. It was found that the reaction applying α -methyl styrene furnished the corresponding reductive arylated product 3hb in 58% yield. trans-Anethole reacted smoothly with 4-bromotoluene 2b affording 3ib in the moderate yield. However, one utilizing 1.1diphenylethylene exhibited much lower conversion to give only 19% yield of the desired product 3jb. Similarly, trans-stilbene was less active under the current conditions (Table 1, 3kb).

Table 1. Pd-catalyzed rH reactions with aryl bromides and aryl olefins. a





^{*a*} Reaction conditions: [PdCImPy*] (2 mol%), olefin (1 mmol), ArBr (1.5 mmol), KOH (2.5 mmol), 75 °C, *i*-PrOH (7.0 mL), 12 h. Isolated yields were obtained. ^{*b*} ArBr (3 mmol), KOH (3.5 mmol); ^{*c*} ArBr (3 mmol), KOH (2.5 mmol). ^{*d*} The regioselectivity is 10:1 for β:α arylated product basing on ¹H NMR analysis. ^{*e*} NMR yield was obtained.

Inactivated aliphatic olefins were also investigated. As shown in Table 2, the olefins bearing primary alkyl (11), secondary alkyl (1m), ether (1n) and carboxyl (1o) groups could be successfully transferred to the corresponding rH products in acceptable yields. It is well known that aliphatic olefins that lack directing groups and electronic bias give a mixture of isomers in Pdcatalyzed Heck reactions.^{2b} Similarly, the regioselective outcomes were observed in this rH process. Linear and branched products were isolated in ca. 3:1 regioselectivity according to the ¹H NMR analysis (Table 2, 1). For the relatively steric olefins, such as 1m, the linear regioselectivity was increased with the ratio of 6:1 (linear : branched). To our delight, the internal 4-octene worked well in this rH reaction and provided 72% yield. Particularly, cheap and readily available cyclic alkenes were investigated under the optimal conditions. The reaction applying 2,3-dihydrofuran (1q) gave the major arylated product with 67% yield. Application of this protocol to cyclic alkenes revealed dramatically reduced efficiency as the ring size increased. Cyclopentene (1r) could smoothly transferred to the desired product in moderate yield, and cyclohexene (1s) displayed less active, whereas cyclooctene (1t) was almost inert in the reaction condition with the formation of less than 5% of the desired product. Instead, a large amount of the Heck product coupled with related isomers was observed. We reasoned that the increased steric encumbrance of the larger cyclic olefins play little effect of the alkene insertion,²⁰ but obviously slow down the following reduction step.

Table 2. Pd-catalyzed rH reactions with aliphatic olefins. ^a



Entry

1

2

3

4

5

6

7

8

9

Cv

BnO

HOOC

1a

cyclopentane

1r

cvclohexene 1s

Cyclooctene 1t



ò 3qb'

3rb

3sb

3tb

p-Tol

p-Tol

p-To

67%

(17:1)

48%

16%

<5%

^a Reaction conditions: [Pd_{CImPy*}] (2 mol%), olefin (1 mmol), 2b (1.5 mmol), KOH (2.5 mmol), 75 °C, 12 h. i-PrOH (7.0 mL). b Isolate yields of 3 and 3' were obtained. The ratios of 3 and 3' in parentheses were determined by ¹H NMR after column chromatography. ^c KOH (3.5 mmol). ^d NMR yield was obtained using 1,2-dibromoethane as the internal standard.

For the potential mechanism of this Pd-catalyzed rH reaction, three possible pathways were proposed (Scheme 2). Alkene insertion to Ar-Pd-X species produces the key intermediate I, which is prone to release H-Pd-X species. Subsequently, the normal Heck product is obtained through the facile β -H elimination step. If the resulted Heck product is reduced under the Pd/i-PrOH conditions, the targeted saturated rH product will be generated (Scheme 2, Path a).^{10e, 21} The second possible route involves that the intermediate I undergoes direct protonolysis in the presence of *i*-PrOH to give the desired product (Scheme 2, Path b).²² The third possibility involves that the alcoholysis of the intermediate I under strongly basic environment followed by $\beta\text{-}H$ elimination results in the formation of Csp³-Pd-H species III, which will finally undergo reductive elimination to produce the reductive hydroarylation product (Scheme 2, Path c).²³ To evaluate the above mentioned three possible pathways, further experiments were carried out.

The Heck product was always observed either changing olefin and aryl bromide or modification of the reaction conditions, Path a seems like the most possible pathway. Under the standard conditions, the reaction of 1a with 2a (eq 1) was carefully investigated. As shown in Figure 1 (A), the normal Heck DOI: 10.1039/C8CC02571A COMMUNICATION

product 4a was accumulated in a small amount accompanied by the formation of the rH product 3aa. Meanwhile, the reduction of 4a under the same conditions with eq 1 was also performed. The experimental results showed only trace amount of 3aa formed. These observations strongly supported to rule out the possibility of Path a.







Figure 1. Mechanism experiments. (A) Kinetic profiles of eq (1) and eq (2). (B) Deuterium labeling experiment.

Moreover, a deuterium labeling experiment applying 1a and 2i in (CD₃)₂CDOD was carried out, providing 3ai-d in 63% yield with 98% deuterium incorporation. In contrast, no reaction occurred when t-BuOH was used as the solvent. Furthermore. when the reaction was performed in (CH₃)₂CHOD, 3ai without deuterium incorporation was obtained in 67% vield (Figure 1. B). These results exclude the possibility that the solvent serves as proton source (Path b). Therefore, Path c is the most plausible pathway for this reaction, in which i-PrOH is a reductant serving as a hydride donor through the β -H elimination process. It is noteworthy that slightly higher temperature (90 °C) and extended reaction time (18 h) were needed for the deuterium labeling experiment, revealing that the alcoholysis by alcohol or the following β -H elimination is likely the rate-limiting step in the catalytic cycle.

In conclusion, we have developed an efficient protocol to construct Csp²-Csp³ bonds through a Pd-catalyzed intermolecular reductive Heck reaction, in which inactivated olefins and aryl bromides are reductive coupled using *i*-PrOH as the reductant. The geometry-constrained iminopyridyl ligand

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plays an important role in stabilization of the catalytically active Pd centers. Various substituents on styrene derivatives exhibit good tolerance to react with varied aryl bromides with excellent linear selectivity. Aliphatic olefins are also suitable partners while giving the mixtures of linear and branched isomers. Mechanistic studies suggest that *i*-PrOH is the reductant providing a hydride through β -H elimination. Further investigations via modifying ligands for improving this strategy are ongoing in our group.

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Conflicts of interest

There are no conflicts to declare.

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