



# Controlled mono- and double-Heck reaction catalyzed by a dicarbene dipalladium complex



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## ABSTRACT

The phosphine-free mono- and double-Heck reaction of terminal olefins with electron-deficient and electron-rich aryl halides (iodides and bromides) is described. These reactions are catalyzed by the dicarbene dipalladium complex **1** by controlling the stoichiometry of the aryl halide and the olefine, the loading of the palladium catalyst, as well as using different base, and with or without additive. The procedure of double-Heck reaction allows  $\beta,\beta$ -diarylation and  $\beta,\beta'$ -diarylation of terminal olefins and affords trisubstituted olefins in good to excellent yields.

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## 1. Introduction

Palladium-catalyzed C–C cross-coupling reaction is one of the most important classes of organometallic reactions and finds widely applications in pharmaceuticals, fine chemicals, and natural products.<sup>1</sup> Among various coupling reactions, the Mizoroki–Heck reaction is one of the most powerful methods for C–C bond formation, and can be accomplished using a great amount of palladium catalyst precursors under various reaction conditions.<sup>2</sup> The classical intermolecular Heck reaction is mainly limited to the monoarylation of terminal alkenes, whereas the synthesis of trisubstituted alkenes by diarylation has been scarcely investigated and most synthetic protocols are only effective with aryl iodides or acrylates.<sup>3</sup> Therefore the development of an efficient process for diarylation of more general terminal alkenes with aryl halides (esp. cheap aryl bromides) would be desirable. Over the last years, the chemistry of palladium *N*-heterocyclic carbene (NHC) complexes has become an area of great interest and has been extensively studied.<sup>4</sup> We have been interested in the chemistry of bimetallic di-NHC complexes concentrated on homodinuclear and heterodinuclear complexes,<sup>5</sup> with special emphasis on developing inexpensive, user-friendly, and highly efficient precatalyst for C–C

cross-coupling reactions. The design and synthesis of binuclear palladium complexes with di-NHC are of considerable interest because the adjacent metals could function in a synergic manner in their interactions with substrate molecules. We report now that a di-NHC dipalladium complex is an appropriate precatalyst for the controlled mono and diarylation of terminal alkenes under phosphine-free conditions.

## 2. Results and discussion

The structure of di-NHC dipalladium complex **1** used in this study was shown in Chart 1. The synthesis of **1** was achieved by the reaction of PdCl<sub>2</sub> with bisimidazolium dichlorides in pyridine in the presence of K<sub>2</sub>CO<sub>3</sub> in 65% yield.<sup>6</sup>

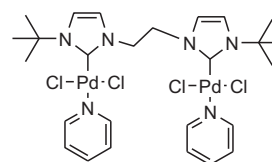


Chart 1. Palladium catalyst **1** used in this study.

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## 2.1. Monoarylation of terminal alkenes

From the previous result of screening the solvents, bases, catalyst loadings, and temperatures, the mono-arylation of styrene catalyzed by **1** can be effectively performed with 0.5 mol % of catalyst with  $K_3PO_4$  as base (1.5 equiv) in the solvent of dimethyl acetamide (DMA) at 100 °C in 5 h.<sup>6</sup> To investigate the scope of the reaction, the application of **1** in the mono-arylation of styrene with a series of aryl halides was shown in Table 1. From the results we can see that deactivated electron-rich aryl iodides and bromides are coupled with styrene in good yields (Table 1, entries 2, 11, 13, 14). Sterically hindered aryl iodide with *ortho*-substitution worked well in the reaction, whereas, the yield decreased with *ortho*-substituted bromide (Table 1, entries 14 vs 11). A wide variety of functional groups were tolerated on the aromatic ring (Table 1, entries 2–10). Unfortunately, the catalyst was not effective for aryl chloride. Furthermore, the application of **1** in the coupling reaction of various aryl halides with ethyl acrylate was shown in Table 2. The complex **1** was also highly active for the coupling of electron-rich and electron-deficient aryl halides (iodides and bromides) with ethyl acrylate. Steric effect still only plays role in the reaction of aryl bromide (Table 2, entries 10 vs 13). A wide variety of functional groups were tolerated in the coupling reaction with aryl halides.

From these results, it can be summarized that the mono-arylation of terminal alkene with aryl iodides and bromides can be performed efficiently with 0.5 mol % of the di-NHC di-Pd complex **1** using  $K_3PO_4$  as base in the solvent of DMA.


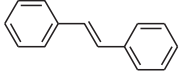
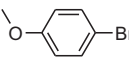
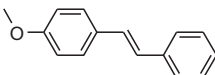
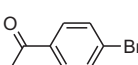
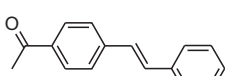
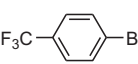
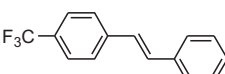
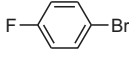
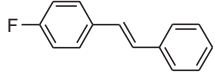

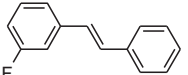
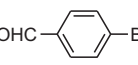
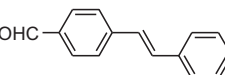

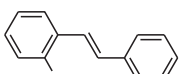

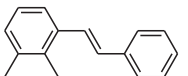
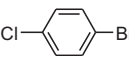
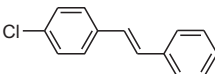

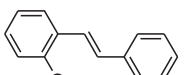

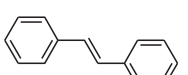
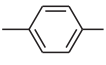
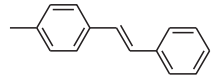

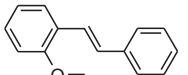
## 2.2. Diarylation of terminal alkene

To develop a general protocol for the diarylation of terminal olefins, we initially tested the reaction of ethyl acrylate (1 equiv) with bromobenzene (2.2 equiv) with tetra-*n*-butylammonium bromide (TBAB) as additive and higher loading of Pd catalyst (1 mol %) in DMA in presence of different bases (2.5 equiv) (Table 3). The diarylated product was obtained in 10% when  $K_3PO_4$  was used as the base, and 18% of monoarylated product was observed at the meanwhile (Table 3, entry 1).  $Cs_2CO_3$  did not work for both diarylation (5%) and monoarylation (8%). Moreover, NaOH failed in diarylation, whereas gave 65% of monoarylation product. However, when NaOAc or  $K_2CO_3$  was employed, the yield of diarylation was dramatically increased to 88% or 82% and no monoarylated product was detected for NaOAc. TBAB is necessary for the successful diarylation, otherwise, only 76% of monoarylation product was obtained with NaOAc under the same conditions (Table 3, entry 4). To optimize the reaction conditions, a few other solvents including toluene, DMF, DMSO, and TBAB were screened. DMA is the best solvent tested for diarylation, and relatively low yield was observed in DMF, toluene, and TBAB. No diarylation product was found in DMSO used as solvent. Therefore, all diarylation reactions below were carried with 1 mol % of Pd, TBAB (2 equiv), NaOAc (2.5 equiv) in DMA at 120 °C for 18 h.

Under the optimized conditions, the  $\beta,\beta$ -diarylation of alkyl acrylates was suitable to various aryl iodides and even less reactive aryl bromides, however, electron-rich trimethoxy(vinyl)silane does not couple at all (Table 4). Generally, the reactions of alkyl acrylates with unactivated aryl iodides containing electron-donating substituents gave good yields of trisubstituted olefine (Table 4, entries 8–10), whilst, the reactions with aryl bromides gave diarylation product in moderate to good yields (Table 4, entries 1–6). To further determine the scope of this catalytic system with other kinds of terminal olefins, different styrene substrates were chosen to react with aryl bromides or iodides under identical conditions. These reactions were afforded the desired product in good yield (Table 4, entries 13–17).

**Table 1**

Mizoroki–Heck cross-coupling reactions of styrene with aryl halides

Entry <sup>a</sup>	Aryl halide	Product	<b>2</b> Yield (%) <sup>b</sup>
1			84 ( <b>2a</b> )
2			95 ( <b>2b</b> )
3			82 ( <b>2c</b> )
4			80 ( <b>2d</b> )
5			86 ( <b>2e</b> )
6			80 ( <b>2f</b> )
7			68 ( <b>2g</b> )
8			83 ( <b>2h</b> )
9			97 ( <b>2i</b> )
10			93 ( <b>2j</b> )
11			47 ( <b>2k</b> )
12			83 ( <b>2a</b> )
13			82 ( <b>2l</b> )
14			88 ( <b>2k</b> )

<sup>a</sup> Reaction conditions: 0.005 mmol of **1**, 1 mmol of aryl halides, 1.2 mmol of styrene, and 1.5 mmol of  $K_3PO_4$  in 2 mL of DMA.

<sup>b</sup> Isolated yield.

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