

Borylation of Olefin C–H Bond via Aryl to Vinyl Palladium 1,4-Migration

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S Supporting Information

ABSTRACT: The aryl to vinyl palladium 1,4-migration was realized for the first time. The generated alkenyl palladium species was trapped by diboron reagents under Miyaura borylation conditions, providing a new method to synthesize β,β -disubstituted vinylboronates. The excellent regioselectivity and broad substrate scope were observed for this novel transformation.

In search of more efficient and green organic transformations, the metal-catalyzed direct functionalization of C–H bonds has been playing an increasingly important role in nearly all areas of chemical science.¹ In order to activate a specific inert C–H bond, the intramolecular directing strategy is frequently applied through the introduction of a chelating² or preoxidized (such as halides)³ functional group at the neighboring position. The latter approach is often accompanied by a metal migration from the original position to a remote destination, which proved to be quite common for various used metals such as Pd,⁴ Rh,^{4,5} Ir,⁶ Co,⁷ etc.

As a result, the palladium migration has been extensively studied,⁸ and a variety of migration types including aryl to aryl,⁹ vinyl to aryl,¹⁰ alkyl to aryl,¹¹ benzylic to aryl,^{8c} aryl to alkyl,¹² and aryl to benzylic¹³ migrations have been reported.¹⁴ Although the seminal work by Larock demonstrated the vinyl to aryl palladium 1,4-migration as a reversible process in the mechanistic diagram,^{10a} no experimental evidence was provided to support this feasibility (Scheme 1a). Some subsequent experiments even hinted that the reverse process might not be possible.^{14a} One possible challenge for the palladium migration to a vinyl position may attribute to the relatively weak acidity of the vinyl C–H bond, which has a strong influence on the migration trend supported by some results indicating that palladium tends to migrate to a more acidic position.¹⁵ Thus, the vinyl moiety in relating research was usually used as a relay station via Heck addition to generate a sequent palladium migration, and no direct functionalization of a vinyl C–H bond has been reported.¹¹

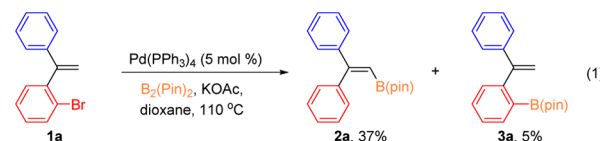
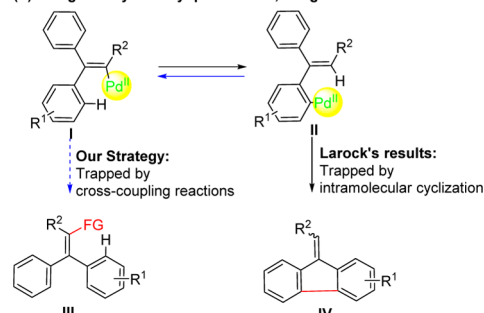
We speculate that if the migration from Larock's arylpalladium II to the alkenylpalladium I did exist,¹⁶ the resulting intermediate I could be trapped by coupling with other reagents, such as arylboronic acid, olefin or diboron reagents, and lead to a new palladium migration/functionalization process (Scheme 1b). Following this hypothesis, we tested aryl bromide **1a** under Suzuki, Heck, or Miyaura reaction conditions. To our delight, the desired 1,4-migration product **2a** was obtained in 37% yield under the Miyaura borylation reaction conditions (eq 1).^{17,18}

Scheme 1. C–H Functionalization via Palladium Migration

(a) Palladium migration between vinyl and aryl positions



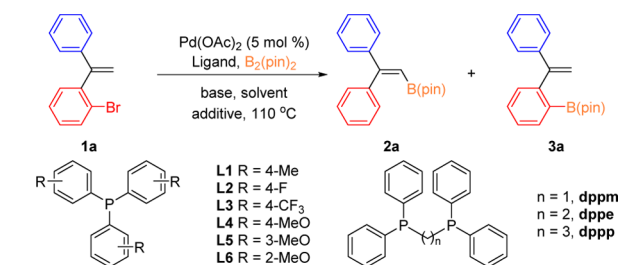
(b) Design of aryl to vinyl palladium 1,4-migration reaction



Inspired by this preliminary result, extensive screening of the reaction conditions was carried out to further promote this palladium migration/borylation reaction, and some representative results are outlined in Table 1. As a frequently used solvent in many palladium migration reactions, DMF significantly improved the regioselectivity (**2a/3a** = 12:1), albeit with 27% reaction yield (entry 1). If the solvent was switched to toluene, DCM, or dioxane, the reaction yields were slightly improved, however the regioselectivities were compromised (entries 2–4). THF proved to be the best choice giving the highest yield and regioselectivity (67% yield of **2a**; **2a/3a** = 14:1; entry 5). High regioselectivities were observed with acetate and pivalate salts as bases. While the use of K_2CO_3 and PhOK decreases the ratio of **2a** and **3a** to 1:1 (entries 8 and 9), CsF and K_3PO_4 showed reverse regioselectivities (entries 10 and 11). The effectiveness of acetate and pivalate compared with other base suggested the C–H activation step might occur via a concerted metalation deprotonation (CMD) process, where they played as internal bases for proton abstraction.¹⁹ The ligand effect was also

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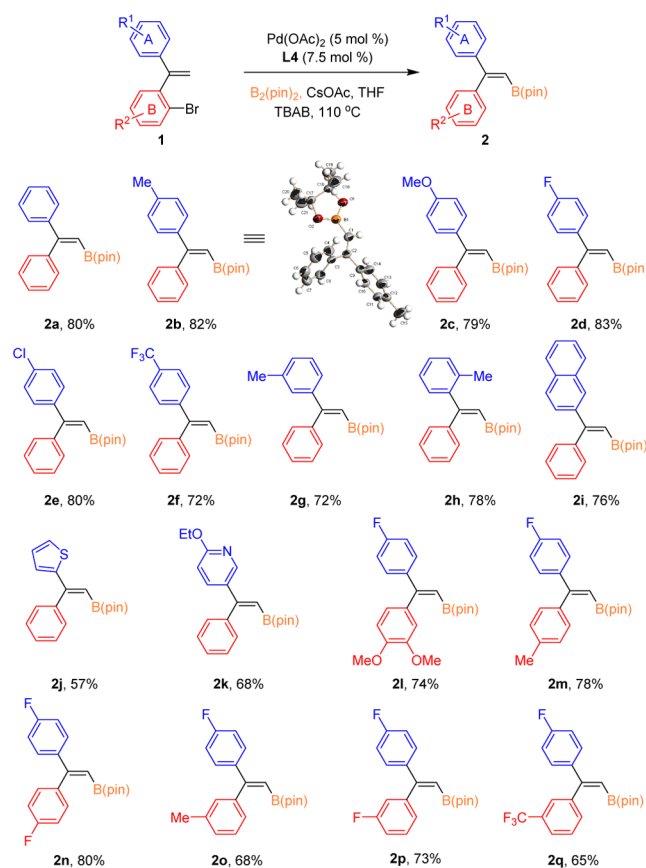
Table 1. Reaction Conditions Optimization^a

entry	solvent	base	ligand	yield of 2a (%) ^b	2a/3a ratio ^c
1	DMF	KOAc	PPh ₃	27	12:1
2	toluene	KOAc	PPh ₃	41	3:1
3	DCM	KOAc	PPh ₃	28	4:1
4	dioxane	KOAc	PPh ₃	38	5:1
5	THF	KOAc	PPh ₃	67	14:1
6	THF	CsOAc	PPh ₃	70	11:1
7	THF	CsOPiv	PPh ₃	73	8:1
8	THF	K ₂ CO ₃	PPh ₃	10	1:1
9	THF	PhOK	PPh ₃	26	1:1
10	THF	CsF	PPh ₃	13	1:3
11	THF	K ₃ PO ₄	PPh ₃	4	1:10
12	THF	TEA	PPh ₃	trace	—
13	THF	CsOAc	L1	77	10:1
14	THF	CsOAc	L2	58	6:1
15	THF	CsOAc	L3	37	8:1
16	THF	CsOAc	L4	85	10:1
17	THF	CsOAc	L5	73	10:1
18	THF	CsOAc	L6	48	>20:1
19 ^d	THF	CsOAc	dppm	nd	—
20 ^d	THF	CsOAc	dppe	67	>20:1
21 ^d	THF	CsOAc	dppp	75	>20:1
22 ^e	THF	CsOAc	L4	85	>20:1
23 ^{e,f}	THF	CsOAc	L4	89 (80) ^g	>20:1

^aReactions conditions: **1a** (0.3 mmol), B₂(pin)₂ (0.345 mmol), Pd(OAc)₂ (0.015 mmol), ligand (0.0225 mmol), and base (0.6 mmol) in solvent (6 mL) at 110 °C for 3 h unless otherwise noted. ^bDetermined by ¹H NMR spectroscopy using CH₂Br₂ as an internal standard. ^cDetermined by ¹H NMR. ^dReaction time was prolonged to 4 h. ^eTBAB (0.03 mmol) was added. ^f12 mL THF was used. ^gIsolated yield, which was about 10% lower than ¹H NMR yield due to the product instability on silica gel. TBAB = tetra-*n*-butylammonium bromide; nd = not detected.

examined. While electron-rich monophosphine ligands provided higher reaction yields of **2a**, electron-deficient ones reduced both the reaction yield and regioselectivity (entries 13–16). Sterically hindered monophosphine **L6** significantly improved the regioselectivity to an excellent level (**2a/3a** > 20:1) but with a reduced reactivity (entry 18). This trend was also in accordance with the results with bis-phosphine ligands dppe and dppp, with which moderate reaction yields and excellent regioselectivities were obtained (entries 20 and 21). This dependence of the regioselectivity on the steric hindrance of ligands hints that the driving force of this palladium migration may be attributed to the less steric encumbrance of the vinyl position compared with the original aryl position. With the most active tris(4-methoxyphenyl)phosphine **L4** as ligand, further screening of reaction conditions revealed the remarkable effect of TBAB for the regioselectivity (entry 22). The reaction yield was further improved to 89% when it was run in a slightly diluted concentration (entry 23).

With optimal reaction conditions in hand, the scope of the palladium-catalyzed 1,4-migration/borylation reaction for the synthesis of β,β -diarylated vinylboronates was explored (Table 2).²⁰ Excellent regioselectivities and good reaction yields were

Table 2. Synthesis of β,β -Diarylated Vinylboronates^a

^aReactions conditions: **1** (0.3 mmol), B₂(pin)₂ (0.345 mmol), Pd(OAc)₂ (0.015 mmol), **L4** (0.0225 mmol), TBAB (0.03 mmol) and CsOAc (0.6 mmol) in THF (12 mL) at 110 °C for 3 h unless otherwise noted. Isolated yields. The possible *E/Z* isomers were estimated to be <1% compared with the desired products (see Supporting Information for details).

obtained for all the tested substrates. The substituent effect on the phenyl ring **A** was first examined. The reaction works efficiently on the substrates containing electron-donating groups (such as Me (**2b**) or MeO (**2c**)) or electron-withdrawing groups (such as F (**2d**), Cl (**2e**) or CF₃ group (**2f**)) on the para-position of the phenyl ring **A**. Compared with the substitution on the para-position, the shift of methyl group to meta- or ortho-position gave reduced reaction yields (**2g** and **2h**). Notably, alkenes with the phenyl ring **A** replaced by a naphthyl, 2-thienyl or 3-pyridinyl group were competent substrates for this reaction (**2i–2k**). The reaction with substrates bearing different substituents on the phenyl ring **B** also proceeded smoothly to afford the borylated products in good reaction yields (**2l–2q**). In addition, the structure of **2b** was verified by X-ray crystallographic analysis.

Encouraged by the above result, we tried to test the replacement of the aromatic ring **A** by other substituents (Table 3). The reaction with substrates bearing alkyl substituents took place smoothly, affording the desired products in good yields (entries 1–3). CO₂Me and CN groups were also tolerated, albeit in reduced reaction yields (entries 4 and 5).

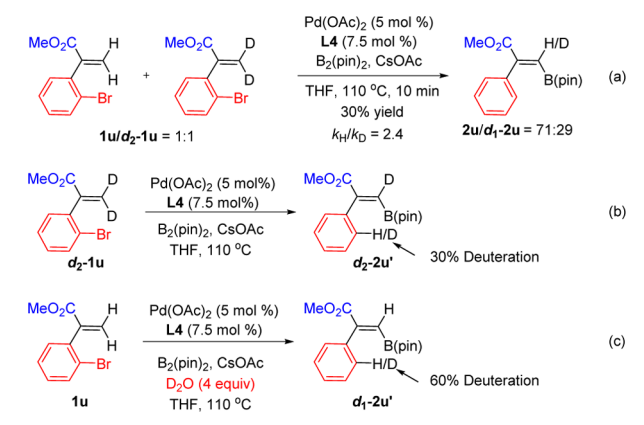
Table 3. Synthesis of Other β,β -Disubstituted Vinylboronates^a

entry	R	product	yield (%) ^b
1	Me	2r	57
2	Et	2s	66
3	<i>n</i> -Pr	2t	71
4	CO ₂ Et	2u	40
5	CN	2v	33 ^c

^aReactions conditions: **1** (0.3 mmol), B₂(pin)₂ (0.345 mmol), Pd(OAc)₂ (0.015 mmol), L4 (0.0225 mmol), TBAB (0.03 mmol) and CsOAc (0.6 mmol) in THF (12 mL) at 110 °C for 3 h. ^bIsolated yields unless otherwise noted. ^cDetermined by ¹H NMR spectroscopy.

To gain some mechanistic insight into the present transformation, several deuterium-labeling experiments were conducted. An intermolecular competition between aryl bromide **1u** and its dideuterated analogue **d₂-1u** showed a kinetic isotope effect $k_{\text{H}}/k_{\text{D}} = 2.4$ (Scheme 2a), suggesting the C–H bond

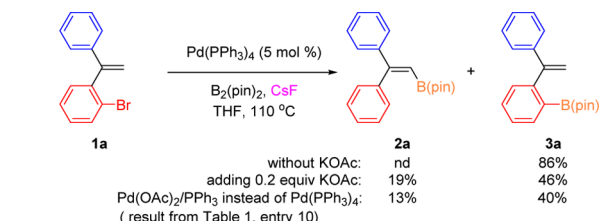
Scheme 2. Deuterium-Labeling Experiments



cleavage is involved in the rate-determining step. In palladium migration reactions, a simultaneous migration of hydrogen in the opposite direction usually will occur. We tested the dideuterated aryl bromide **d₂-1u** under reaction conditions and found 30% incorporation of deuterium into the ortho-position of phenyl ring (Scheme 2b). The loss of deuterium could be explained by the H–D exchange between palladium migration intermediates and the reaction media, which was supported by the high deuterium incorporation ratio when aryl bromide **1u** was subjected to this reaction in the presence of 4 equiv of D₂O (Scheme 2c).

Furthermore, due to the well-known facilitation effect of acetate on both C–H activation and the Miyaura borylation step, an experiment to further probe the role of the acetate for this palladium migration reaction was also performed (Scheme 3). Using CsF as a base, the borylation smoothly took place in the original place, while the migration product was totally suppressed, a sharp contrast to the result with Pd(OAc)₂/PPh₃ as catalyst, where migration product could be generated in 13% yield. As anticipated, the ability of migration was recovered by adding a small amount of acetate. These results clearly

Scheme 3. Effect of Acetate for the Migration Product



demonstrated the key effect of the acetate for the palladium migration, most possibly on the C–H activation step.

Based on the above experimental observations, a proposal on the palladium migration mechanism is outlined in Figure 1.

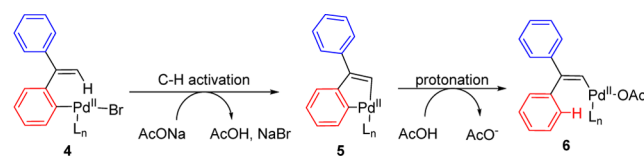


Figure 1. Plausible palladium migration mechanism.

Oxidative addition of aryl bromide to palladium(0) generates the intermediate **4**. Instead of a second oxidative addition to form palladium(IV) species, theoretical studies have revealed that a CMD mechanism would be energetically favored for the next C–H activation step.¹⁹ Although the effectiveness of carboxylates supports an intramolecular base-assisted proton abstraction, an intermolecular mode cannot be ruled out with the awareness of the success of bis-phosphine ligands.^{19c} The generated five-membered palladacycle **5** was protonated to render a net 1,4-palladium shift from the aryl to vinyl position and then proceeds through the following Miyaura borylation sequences to afford the vinylboronate **2a**.²¹

In summary, the first aryl to vinyl palladium 1, 4-migration was realized by a rationally designed experiment. The resulting alkenyl palladium intermediate was trapped by diboron reagents under Miyaura borylation conditions, providing a new method to synthesize β,β -disubstituted vinylboronates.²² The excellent regioselectivity and broad substrate scope were observed for this reaction. The key C–H activation step was believed to proceed via a CMD mechanism, which was implied by the effectiveness of acetate or pivalate salts in this reaction and was consistent with the preliminary deuterium-labeling experiments. Further studies to elucidate the mechanism of this reaction and investigations into the application of this palladium migration mode are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11990.

Crystallographic data for **2b** (CIF)

Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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