



**A Synthesis of Allylboronates via the Palladium(0)-Catalyzed Cross-Coupling
Reaction of Bis(pinacolato)diboron with Allylic Acetates**

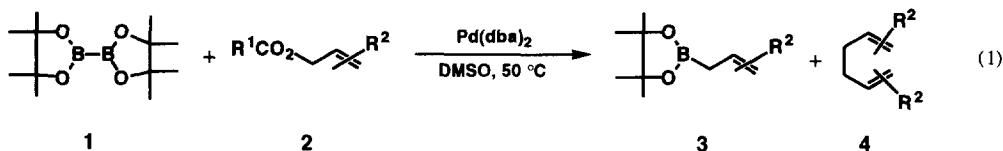
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Abstract: The cross-coupling reaction of bis(pinacolato)diboron [(Me₄C₂O₂)₂BB(O₂C₂Me₄)] with allyl acetates regio- and E-stereoselectively provided the pinacol esters of allylboronic acids in high yields. The reaction was efficiently catalyzed by Pd(dba)₂ in DMSO at 50 °C.

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Allylboron compounds are valuable reagents in organic synthesis, addition of which to the carbon-oxygen or the carbon-nitrogen double bond diastereoselectively provides homoallylic alcohols or amines via a chair-like six-membered cyclic transition state.¹ Allylboron reagents are now accessible by various methods including the transmetalation of allyllithiums or allylmagnesiums to the boron,² the coupling of 1-alkenyl halides with borylmethylzinc reagents,³ the reaction of halomethylboronates with vinylolithiums,⁴ the mono-hydroboration of 1,2- or 1,3-dienes,⁵ and the one-carbon homologation of 1-alkenylboronates.⁶ The cross-coupling of boryl nucleophiles with allylic electrophiles is a convenient and alternative method; however, this protocol has been severely limited due to the lack of suitable boron nucleophiles.⁷ We have recently reported the cross-coupling reaction of bis(pinacolato)diboron (**1**) with aryl halides giving arylboronates, which represents the first one-step procedure for preparing organoboronic esters from organic halides.⁸ We wish to report here the palladium-catalyzed cross-coupling reaction with allyl acetates (**2**) which regio- and stereoselectively affords the allylboronic esters (**3**) under neutral conditions (Eq. 1).



The representative results are summarized in Table 1. The reaction of **1** with 2-phenyl-2-propenyl acetate at 50 °C in DMSO for 16 h in the presence of Pd(dba)₂ (3 mol %) gave **3a** (89%) together with the dimer (**4**) of the allyl unit (2,5-diphenyl-1,5-hexadiene, 10%) (Entry 1). The reaction was efficiently catalyzed by the palladiums without a phosphine ligand, such as Pd(dba)₂ and Pd(OAc)₂, whereas the addition of PPh₃, dppf, or P(OPh)₃ slowed down the reaction rate. Although a combination of Pd(dba)₂ and DMSO exhibited excellent catalytic activity, the use of Pd(dba)₂ in other solvents such as DMF, dioxane or benzene resulted in quite low yields due to the catalyst decomposition precipitating palladium black at the early stage of the reaction.

A comparison of the representative allyl carboxylates demonstrated the superiority of allyl acetates (Entries 1-4). The coupling with the trifluoroacetate gave good yield of **3a** without the accompanying dimer (Entry 2), but the use of trifluoroacetates may have no advantage over the corresponding acetates because they were rather sensitive to the hydrolysis with the base. The carbonate predominantly provided its dimer (Entry 4).

The results of other allylic acetates are summarized in Entries 5-10. Allyl acetate itself and its derivatives having methyl or phenyl substituents at the α - or β -carbon provided the corresponding **3** in high yields (Entries 1, 5-7 and 10). The reaction with γ -substituted allyl acetates such as cinnamyl acetate took longer, presumably due to their slow oxidative addition to the palladium(0) (Entries 8 and 9). All attempts at the borylation of 3-methyl-2-butenyl acetate were unsuccessful; however, the corresponding tertiary allyl acetate can be used for the same purpose because the boron atom exclusively bonds to its primary carbon (Entry 7). Both (*E*)- and (*Z*)-cinnamyl acetate gave (*E*)-cinnamylboronate *via* the isomerization during the cross-coupling (Entries 8 and 9).

The mechanism for the cross-coupling reaction can be analogous to that of the cross-coupling reactions of disilanes⁹ or distannanes¹⁰ (Fig. 1). The oxidative addition of **2** to a palladium(0) complex leads to a π -allylpalladium(II) acetate (**5**). The transmetalation between **5** and **1** forms a π -allyl(boryl)palladium(II) intermediate (**6**), and the reductive elimination of **3** reproduces the palladium(0) complex.

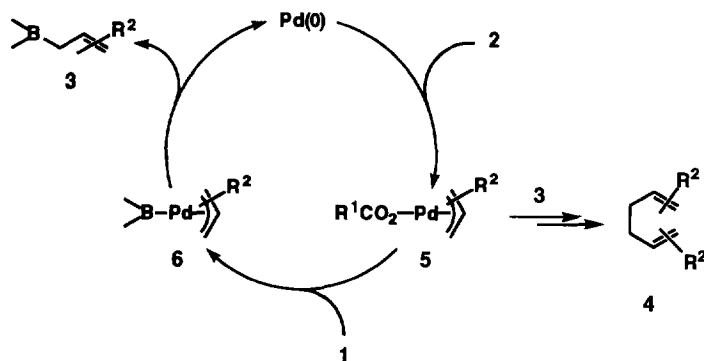


Figure 1. The Catalytic Cycle for the Cross-Coupling

In contrast to the cross-coupling reaction of organoboron compounds with organic halides,¹¹ the present reaction smoothly proceeded under neutral conditions because the oxidative addition of **2** directly produces an (acetoxo)palladium(II) species¹² (**5**). The high reactivity of the oxopalladium complex toward the transmetalation with organoboron compounds can be attributed to both the high reactivity of the Pd-O bond, which consists of a soft acid and a hard base combination, and the high oxophilicity of the boron center. Indeed, the relative reactivity of **2** was in the order of nucleophilicity of the carboxylato ligands in **5** ($\text{MeOCO}_2 > \text{MeCO}_2 > \text{PhCO}_2 = \text{CF}_3\text{CO}_2$) which is reverse to that of the oxidative addition rate. The exclusive formation of **3** over **4** suggests that the transmetalation of **5** with the diboron is reasonably faster than the reaction with **3**. The coupling with the less hindered allylic carbon (Entries 7 and 10) and the formation of (*E*)-**3e** from (*Z*)-cinnamyl acetate *via* the isomerization of *anti*- π -allylpalladiums (**5** or **6**)

Table 1. The Synthesis of Allylboronates (Eq. 1)^a

Entry	Ester (2)	Product	Compound No.	Time/h	Yield/% ^b	
					3	4
1			3a	16	89 ^c	10
2		3a		22	86	0
3		3a		18	55	15
4		3a		16	3 ^c	80
5			3b	16	68	n.d.
6			3c	16	70	n.d.
7			3d	16	83	n.d.
8			3e	26	73 ^d	~13
9		3e		24	65 ^d	~1
10		3e		16	83 ^d	~8

^aAll reactions were carried out in DMSO at 50 °C using **1** (1.1 mmol), **2** (1.0 mmol) and Pd(dba)₂ (0.05 mmol). For the experimental procedure, see the text. Assigned structures are consistent with ¹H and ¹³C NMR, and MS data.

^b GLC yields based on **2**.

^c Pd(dba)₂ (0.03 mmol) was used.

^d (*E*)-isomeric purity over 99% was determined by GLC and ¹H NMR analyses.

to the more stable *syn*-complexes¹³ (Entry 9) are closely similar to other palladium-catalyzed coupling reactions of allyl electrophiles.¹⁴

The representative procedure: Pd(dba)₂ (dba is dibenzylideneacetone) (29 mg, 0.05 mmol) and **1** (280 mg, 1.1 mmol) were placed in a flask flushed with nitrogen. DMSO (6 ml) and 2-phenyl-2-propenyl acetate (1.0 mmol) were successively added, and the resulting solution was then stirred at 50 °C for 16 h. The product was extracted with benzene, washed with brine, and finally dried over MgSO₄. An analytically pure product was isolated by Kugelrohr distillation. **3a**: ¹H NMR (CDCl₃) δ 1.16 (s, 12 H), 2.16 (s, 2 H), 5.10 (s, 1 H), 5.36 (s, 1 H), 7.2-7.3 (m, 3 H), 7.46 (d, 2 H, *J* = 8.4 Hz); ¹³C NMR (CDCl₃) δ 24.62, 83.41, 112.22, 125.86, 127.21, 128.05, 141.84, 144.37 (Due to quadrupolar relaxation, the carbon attached to the boron atom was not detected); ¹¹B NMR (CDCl₃) δ 33.16.

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