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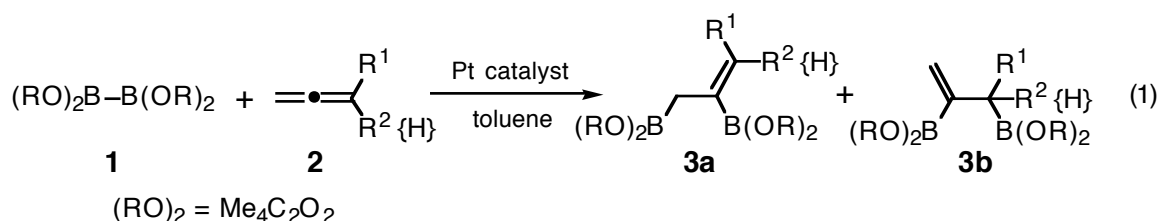
Platinum(0)-Catalyzed Diboration of Allenes with Bis(pinacolato)diboron

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Abstract: Bis(pinacolato)diboron [(Me₄C₂O₂)B-B(O₂C₂Me₄)] added to allenes in the presence of Pt(PPh₃)₄ at 80 °C or Pt(dba)₂/(*c*-Hex)₃P at 50 °C to afford 2,3-bis(boryl)-1-propenes in excellent yields. The one-pot synthesis of substituted homoallyl alcohols was also examined by the allylboration of aldehydes with diborated products followed by the coupling with organic halides.

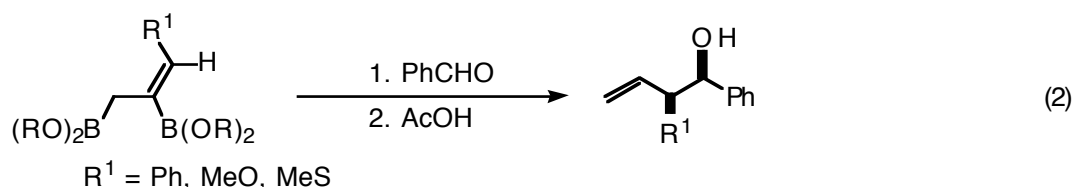
Transition-metal-catalyzed addition reaction of metal-metal reagents to allenes provides a straightforward route to 2,3-bis(metal)-1-propene and its analogs, which include synthetically useful allylmethyl part and vinylmetal part in the same molecule. Although disilanes,¹ distannanes,² silylstannanes,³ and germylstannanes⁴ are known to add to allenes in the presence of palladium(0) catalyst, the corresponding reaction of diborons has not been reported so far presumably due to difficulties in the boron-boron bond activation by its oxidative addition to the palladium(0) complexes.⁵ Recently, we have found that platinum(0) complex effectively activates the boron-boron bond by the oxidative addition to give bis(boryl)platinum(II) complex.⁶ This activation protocol is readily extended to the catalytic diboration of unsaturated hydrocarbons, such as alkynes,⁶ alkenes,⁷ and 1,3-dienes.⁸ In the course of our study, we wish to disclose herein the platinum(0)-catalyzed addition of bis(pinacolato)diboron (**1**) to allenes (**2**) to afford 2,3-bis(boryl)-1-propenes (**3**) (Eq. 1).



1,2-Propadiene (1.5 mmol) was allowed to react with **1** (1.0 mmol) for 16 h to optimize the reaction conditions. The addition completed at 80 °C with 3 mol% of Pt(PPh₃)₄ in toluene, producing the corresponding **3** in 99% yield. Ligand less platinum(0) complex such as Pt(dba)₂ also gave **3** even at room temperature, but the yield of the adduct is rather low (50%) because of catalyst decomposition. The catalytic activity of platinum(0) complex is markedly influenced by the nature of ligand. Comparison of the reaction rate at room temperature with Pd(dba)₂/PR₃ (1:1) elucidates the effectiveness of more sterically demanding ligand: e.g., (*c*-Hex)₃P (85%) > (4-MeOC₆H₄)₃P

(66%) > (4-ClC₆H₄)₃P (46%) > (C₆H₅)₃P (25%) > Me₃P (7%). As for the solvents, less polar one such as toluene is more favorable than dioxane or DMF.

The representative results of the reaction between **1** and **2** are summarized in Table 1. A variety **2** having alkyl and aryl substituents were smoothly converted into the corresponding **3** (82-99%) in toluene by using of Pt(PPh₃)₄ at 80 °C (Conditions A) or Pt(dba)₂/(*c*-Hex)₃P at 50 °C (Conditions B) (Entries 1-6), while strong electron-donating substituents on **2** such as MeO or MeS groups sufficiently slowed down the addition rate (Entries 7 and 8). The regioselectivity of the addition depends upon both the substituents of **2** and the bulkiness of ligands. The reaction of monosubstituted **2** (Entries 2-4) with less bulky ligands preferentially afforded the internal adducts (**3b**), whereas that of 1,1-disubstituted (Entries 5 and 6) or heteroatom-substituted **2** (Entries 7 and 8) with more bulky ligands tend to give the terminal adducts (**3a**). The (*Z*)-configuration of **3a** (Entries 4, 7, 8) was immediately established by their conversion into known homoallyl alcohols and the comparison of ¹H NMR spectra with authentic alcohols (Eq. 2).⁹



The catalytic cycle for the present reaction may involve the oxidative addition of **1** to platinum(0) complex to give bis(boryl)platinum(II) intermediate (**4**), the insertion of **2** into B-Pt bond to provide vinyl- or p-allylplatinum(II) species (**5** or **6**), and the reductive elimination of **3** (Fig. 1). The stoichiometric reaction between 1,2-heptadiene and *cis*-Pt(BO₂C₂Me₄)₂(PPh₃)₂⁶ resulted in an 83% yield of **3** (**3a**:**3b** = 17:83), strongly supporting the above catalytic cycle (Eq. 3). The slow reaction of **2** having strong electron-donating groups (Entries 7 and 8) may reflect the rate of insertion step, which was consistent with the relative reactivity observed on the insertion of diarylacetylenes to the B-Pt bond.¹⁰ The selective formation of **3a** in the reaction of 1,1-disubstituted **2** may be due to the steric requirement; however, the observed regio- and stereoselectivity for monosubstituted and heteroatom-substituted **2** remains controversial.

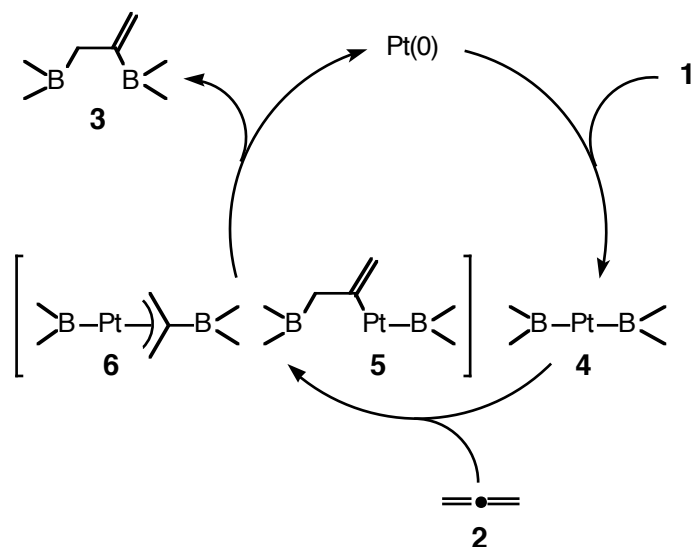
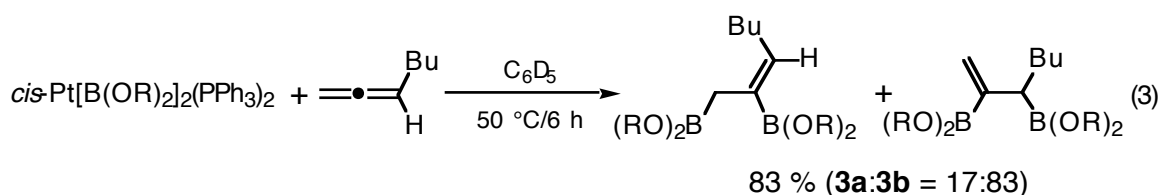
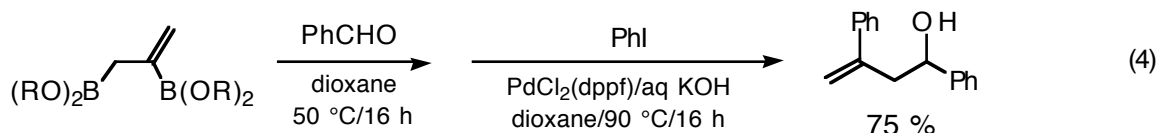


Figure 1. The Catalytic Cycle for the Diboration



The ready availability of various **3** from **2** now offers a simple route to substituted homoallyl alcohols. For example, the sequential reaction involving the allylboration of benzaldehyde (1.1 mmol) with 2,3-bis(boryl)-1-propene (1.0 mmol) in dioxane and the cross-coupling with iodobenzene (1.1 mmol) in the presence of PdCl₂(dppf) (3 mol%) and aqueous KOH (3 mmol) gave the corresponding homoallyl alcohol in 75% yield (Eq. 4).



A representative procedure for 3: To Pt(PPh₃)₄ (0.03 mmol) and **1** (1.0 mmol) were successively added toluene (6 ml) and 1,2-propadiene (1.5 mmol), and the resulting solution was then stirred at 80 °C for 16 h in a sealed reaction tube. Concentration of the reaction mixture and Kugelrohr distillation gave 2,3-bis(boryl)-1-propene: bp 130 °C/0.1 mmHg (oven temperature); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (s, 12 H), 1.26 (s, 12 H), 1.82 (s, 2 H), 5.58 (br s, 1 H), and 5.71 (d, 1 H, *J* = 3.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 24.74, 83.05, 83.35, and 128.44; ¹¹B NMR (128 MHz, CDCl₃) δ 30.03 and 33.46.

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Table 1. The Synthesis of **3** (Eq. 1)^a

Entry	Allene (2)	Product (3a , 3b)	Conditions A		Conditions B	
			Yield/% ^b 3a:3b ^c		Yield/% ^b 3a:3b ^c	
1			99	—	99	—
2			97	6:94	90	16:84
3			90	7:93	82	8:92
4			94	29:71	84	68:32
5			96	50:50	84	85:15
6			98	76:24	99	98:2
7			81 ^d	100:0	85 ^d	100:0
8			48 ^d	50:50	82 ^d	82:18

^aAll reactions were carried out in toluene (6 ml) using **1** (1.0 mmol), **2** (1.5 mmol), and platinum catalyst (0.03 mmol).

Conditions A: Pt(PPh₃)₄/80 °C/16 h. Conditions B: Pt(dba)₂/(*c*-Hex)₃P/50 °C/18 h. The exact procedure, see the text.

^bIsolated yields based on **1**. ^cRegioisomeric purity was determined by GLC and ¹H NMR analyses.

^d0.1 mmol of catalyst was used.

PLATINUM(0)-CATALYZED ADDITION REACTION OF DIBORON REAGENT TO ALLENES

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