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

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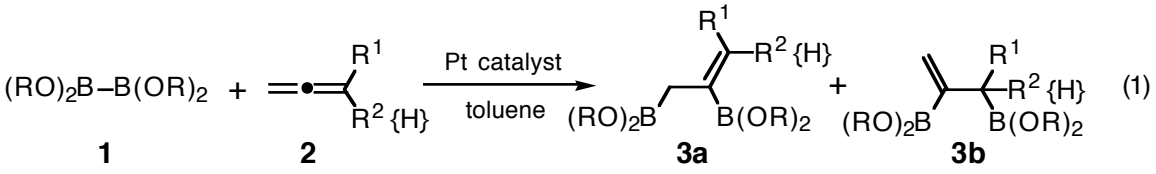
Abstract: Bis(pinacolato)diboron [$(Me_4C_2O_2)B\text{-}B(O_2C_2Me_4)$] added to allenes in the presence of $Pt(PPh_3)_4$ at 80 °C or $Pt(dba)_2/(c\text{-}Hex)_3P$ at 50 °C to afford 2,3-bis(boryl)-1-propenes in excellent yields. The one-pot synthesis of substituted homoallyl alcohols was also examined 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 allylmetal part and vinylmetal part in the same molecule. Although disilanes,[1] distannanes,[2] silylstannanes,[3] and germylstannanes[4] 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(pinacoalto)diboron (**1**) to allenes (**2**) to afford 2,3-bis(boryl)-1-propenes (**3**) (Eq. 1).

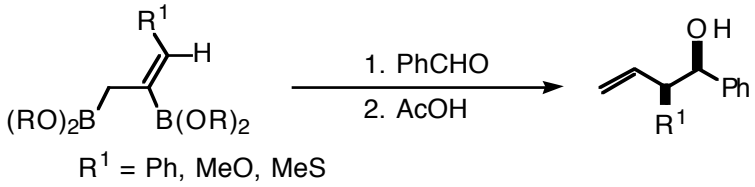


(1)

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 $Pt(PPh_3)_4$ 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 $Pd(dba)_2/PR_3$ (1:1) elucidates the effectiveness of more sterically demanding ligand: e.g., $(c\text{-}Hex)_3P$ (85%) > $(4\text{-}MeOC_6H_4)_3P$

(66%) > (4-$ClC_6H_4)_3P$ (46%) > $(C_6H_5)_3P$ (25%) > Me_3P (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 $Pt(PPh_3)_4$ 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]



R^1 = Ph, MeO, MeS (2)

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*-$Pt(BO_2C_2Me_4)_2(PPh_3)_2$[6] 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.

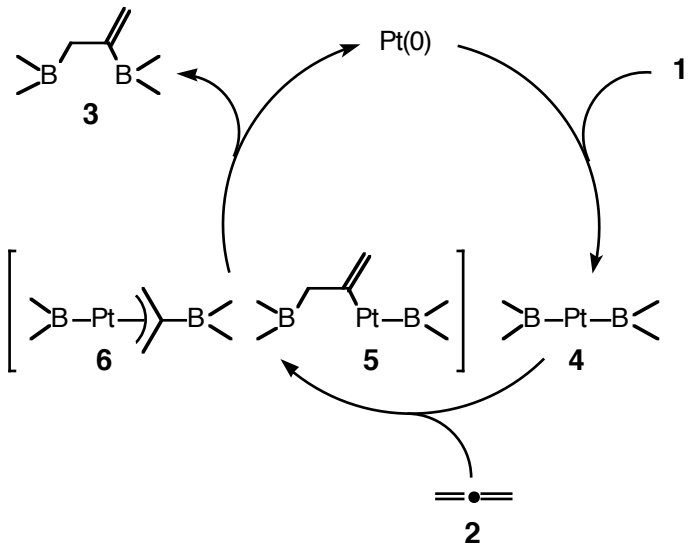
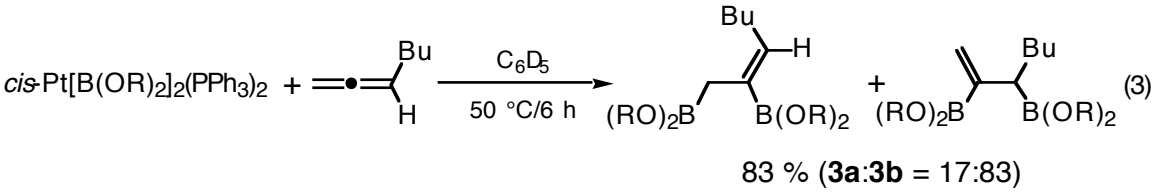
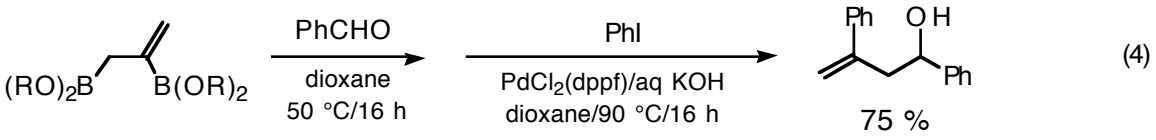


Figure 1. The Catalytic Cycle for the Diboration



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 $PdCl_2$(dppf) (3 mol%) and aqueous KOH (3 mmol) gave the corresponding homoallyl alcohol in 75% yield (Eq. 4).



*A representative procedure for **3***: To $Pt(PPh_3)_4$ (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); ^{1}H NMR (400 MHz, $CDCl_3$) d 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); ^{13}C NMR (100 MHz, $CDCl_3$) d 24.74, 83.05, 83.35, and 128.44; ^{11}B NMR (128 MHz, $CDCl_3$) d 30.03 and 33.46.

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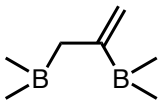
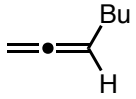
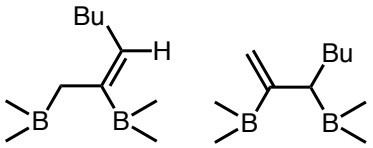
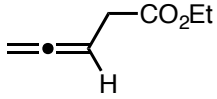
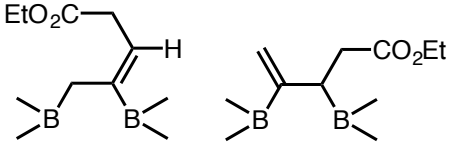
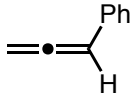
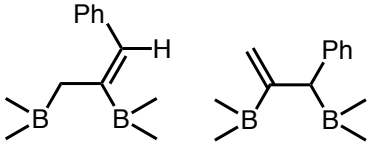
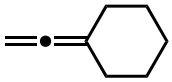
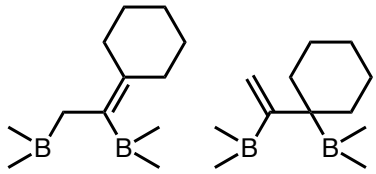
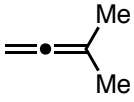
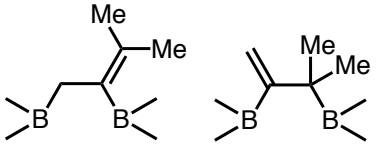
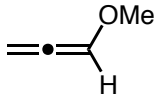
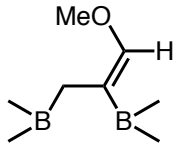
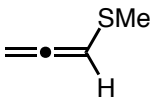
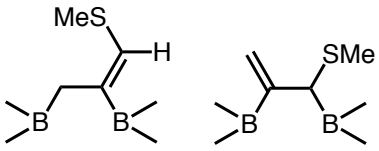
Table 1. The Synthesis of **3** (Eq. 1)[a]

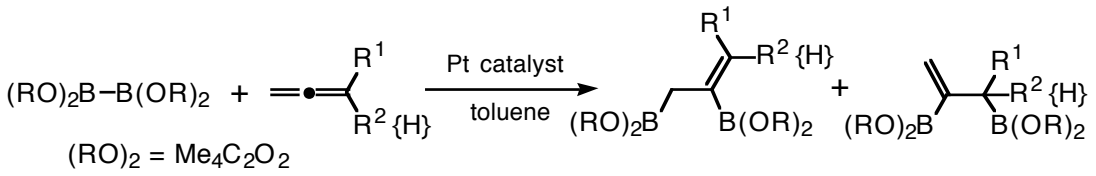
Entry	Allene (**2**)	Product (**3a**, **3b**)	Conditions A		Conditions B	
			Yield/%[b]	**3a**:**3b**[c]	Yield/%[b]	**3a**:**3b**[c]
1			99	——	99	——
2			97	6:94	90	16:84
3			90	7:93	82	8:92
4			94	29:71	84	68:32
5			96	50:50	84	85:15
6			98	76:24	99	98:2
7			81[d]	100:0	85[d]	100:0
8			48[d]	50:50	82[d]	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: $Pt(PPh_3)_4$/80 °C/16 h. Conditions B: $Pt(dba)_2$/(*c*-Hex)$_3$P/50 °C/18 h. The exact procedure, see the text.

[b]Isolated yields based on **1**. [c]Regioisomeric purity was determined by GLC and ^{1}H NMR analyses.

[d]0.1 mmol of catalyst was used.

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

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