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

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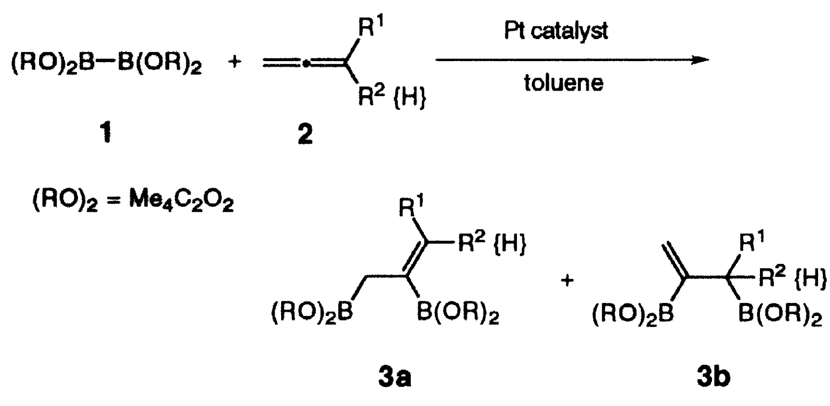
Abstract: *Addition of bis(pinacolato)diboron [$(Me_4C_2O_2)B$-$B(O_2C_2Me_4)$] to various allenes was carried out in excellent yields in the presence of $Pt(PPh_3)_4$ at 80 °C or $Pt(dba)_2/(c\text{-}Hex)_3P$ at 50 °C. The addition to internal double bond was predominant for monosubstituted allenes, whereas the terminal diboration products were regioselectively obtained when a sterically bulky phosphine ligand of $(c\text{-}Hex)_3P$ and 1,1-disubstituted allenes were used.*

The transition-metal-catalyzed addition reaction of metal-metal reagents to allenes provides a straightforward route to bis(metal)alkenes. Although such addition reactions of disilanes,[1] distannanes,[2] silylstannanes,[3] and germylstannanes[4] are readily catalyzed by palladium(0) complexes, the analogous reaction of the diborons can be best carried out by platinum(0) catalyst because their oxidative addition to palladium(0)-phosphine complexes is very slow.[5] We have recently reported various catalytic diboration reactions of unsaturated hydrocarbons such as alkynes,[6] alkenes,[7] and 1,3-dienes.[8] In the course of our study on the synthesis of organoboronic esters from diborons and unsaturated hydrocarbons, we found the platinum(0)-catalyzed addition of bis(pinacolato)diboron (**1**) to allenes (**2**) to afford **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 with 3 mol% of $Pt(PPh_3)_4$ in toluene gave the corresponding **3** in 99% yield at 80 °C. The "ligandless" platinum(0) complex $Pt(dba)_2$ catalyzed the addition even at room temperature, but the reaction resulted in a low yield (50%) because of catalyst decomposition with precipitation of metallic

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platinum. The catalytic activity was markedly influenced by phosphine ligands. Comparison of various $Pt(dba)_2/PR_3$ (1:1) at room temperature led to the following order: $(c\text{-Hex})_3P$ (85%) > $(4\text{-MeOC}_6H_4)_3P$ (66%) > $(4\text{-ClC}_6H_4)_3P$ (46%) > $(C_6H_5)_3P$ (25%) > Me_3P (7%). Less polar solvents such as toluene afforded higher yields than dioxane or DMF.

The representative results of the reaction between **1** and **2** are summarized in Table 1. A variety of allenes **2** with alkyl and aryl substituents provided the corresponding **3** (82-99%) in the presence of 3 mol% of $Pt(PPh_3)_4$ at 80 °C (Conditions A) or $Pt(dba)_2/(c\text{-Hex})_3P$ at 50 °C (Conditions B) (entries 2-6). 10 mol% of catalyst was used for electron-rich allenes having MeO or MeS groups because the reactions were very slow (entries 7 and 8). The regioselectivity can be controlled by two factors. The addition has a strong tendency to occur at the internal double bond; however, steric hindrance in both allenes and phosphine ligands forces the addition towards the terminal double bond. Thus, the reaction of monosubstituted **2** (entries 2-4) with a less bulky ligand PPh_3 preferentially produced the internal adducts (**3b**). On the other hand, the bulky ligand $(c\text{-Hex})_3P$ gave the terminal adducts (**3a**) for 1,1-disubstituted allenes (entries 5 and 6) or heteroatom-substituted allenes (entries 7 and 8). ^1H and ^{13}C NMR analyses revealed that all reactions stereoselectively produced (*Z*)- **3a** (entries 2-4, 7, and 8).

The catalytic cycle may involve oxidative addition of **1** to the platinum(0) complex to give bis(boryl)platinum(II) intermediate (**4**), the insertion of **2** into the B-Pt bond to provide vinyl- or π-allylplatinum species (**5** or **6**), and finally the reductive elimination of **3** reproducing platinum(0) (Fig. 1).

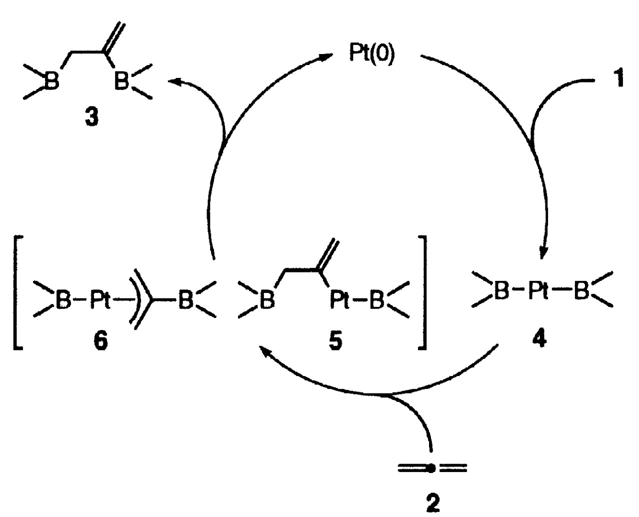
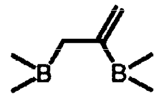
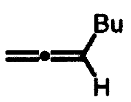
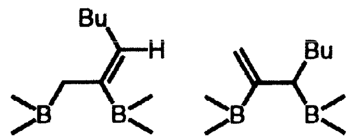
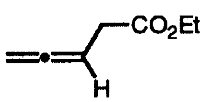
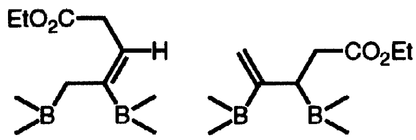
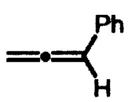
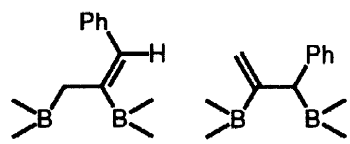
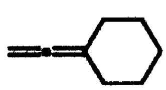
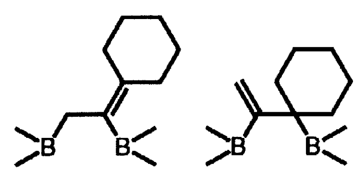
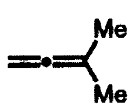
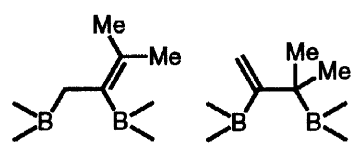
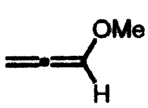
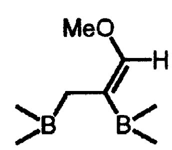
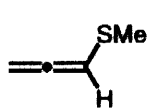
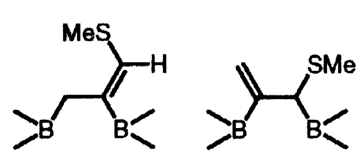


Figure 1. The Catalytic Cycle for the Diboration

The oxidative addition of **1** to $Pt(PPh_3)_4$ gave *cis*-$Pt(BO_2C_2Me_4)_2(PPh_3)_2$ (**4**) which was previously isolated and characterized by X-ray analysis.[6] The stoichiometric reaction between 1,2-heptadiene and **4** at 50 °C in C_6D_6 indeed afforded an 83% yield of **3** ($R^1=C_4H_9$, $R^2=H$) (**3a**:**3b** = 17:83), thus supporting the above catalytic cycle. The stereoselective formation of (*Z*)-**3a** suggests the insertion giving **5** rather than the π-

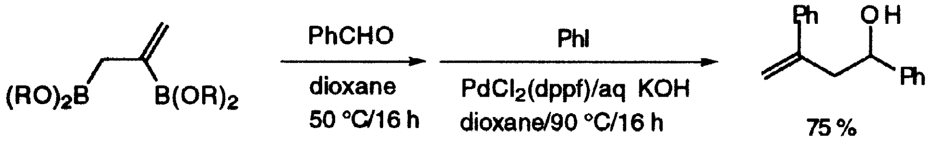
Table 1. The Synthesis of **3** (Eq. 1)[a]

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

[a]All 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.

allylplatinum intermediate (**6**); however, it is still uncertain because this step is too rapid to observe the intermediate. Similarly to the diboration of alkynes and alkenes,[6-9] a hetero-substituent strongly retards the addition due to slow insertion of B-Pt in the electron-rich double bond.

The ready availability of various allylic boronates *via* the diboration of allenes now offers a simple route to substituted homoallyl alcohols. For example, the homoallyl alcohol shown in Eq. 2 was obtained in 75% yield when the allylboration of benzaldehyde (1.1 mmol) with 2,3-bis(boryl)-1-propene (1.0 mmol) in dioxane was followed by cross-coupling with iodobenzene (1.1 mmol) in the presence of $PdCl_2$(dppf) (3 mol%) and aqueous KOH (3 mmol).



(2)

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, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.74, 83.05, 83.35, and 128.44; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.03 and 33.46.

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