

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

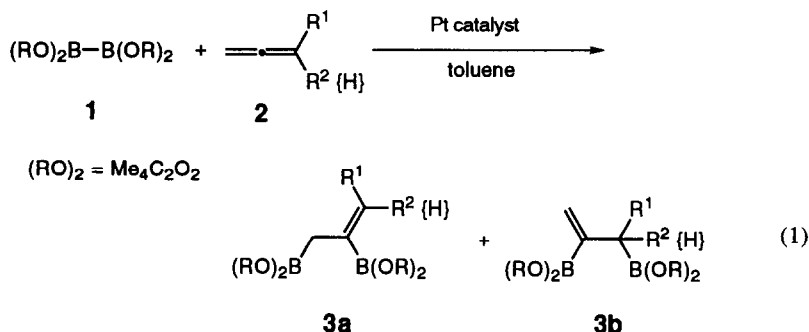
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Abstract: Addition of bis(pinacolato)diboron [(Me₄C₂O₂)B-B(O₂C₂Me₄)] to various allenes was carried out in excellent yields in the presence of Pt(PPh₃)₄ at 80 °C or Pt(dba)₂(c-Hex)₃P at 50 °C. The addition to internal double bond was predominant for monosubstituted allenes, whereas the terminal diboration products were regioselectively obtained when a sterically bulky phosphine ligand of (c-Hex)₃P and 1,1-disubstituted allenes were used. © 1998 Elsevier Science Ltd. All rights reserved.

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 germylstannanes⁴ 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).



1,2-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(PPh₃)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

platinum. The catalytic activity was markedly influenced by phosphine ligands. Comparison of various $\text{Pt}(\text{dba})_2/\text{PR}_3$ (1:1) at room temperature led to the following order: $(c\text{-Hex})_3\text{P}$ (85%) > $(4\text{-MeOC}_6\text{H}_4)_3\text{P}$ (66%) > $(4\text{-ClC}_6\text{H}_4)_3\text{P}$ (46%) > $(\text{C}_6\text{H}_5)_3\text{P}$ (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 $\text{Pt}(\text{PPh}_3)_4$ at 80 °C (Conditions A) or $\text{Pt}(\text{dba})_2/(c\text{-Hex})_3\text{P}$ 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 $(c\text{-Hex})_3\text{P}$ 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).

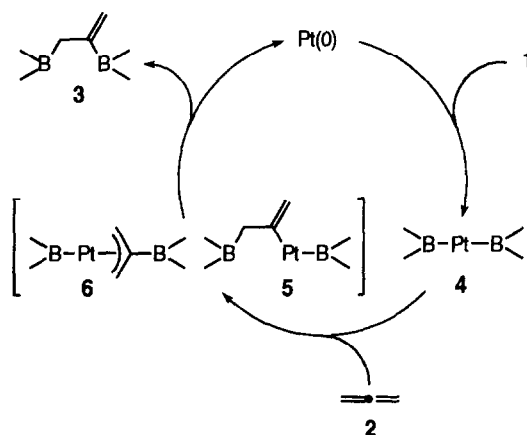


Figure 1. The Catalytic Cycle for the Diboration

The oxidative addition of **1** to $\text{Pt}(\text{PPh}_3)_4$ gave *cis*- $\text{Pt}(\text{BO}_2\text{C}_2\text{Me}_4)_2(\text{PPh}_3)_2$ (**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** ($\text{R}^1=\text{C}_4\text{H}_9$, $\text{R}^2=\text{H}$) (**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

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

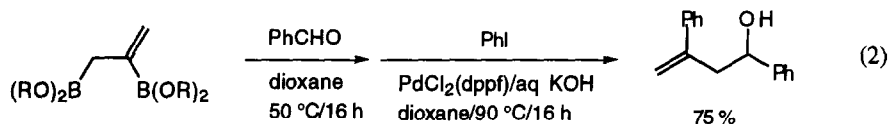
Conditions A: Pt(PPh₃)₄/80 °C/16 h. Conditions B: Pt(dba)₂/(*c*-Hex)₃P/50 °C/18 h. The exact procedure, see the text.

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

^d0.1 mmol of catalyst was used.

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 PdCl₂(dppf) (3 mol%) and aqueous KOH (3 mmol).



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.

References

- (a) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343. (b) Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 617.
- (a) Mitchell, T. N.; Schneider, U. *J. Organomet. Chem.* **1991**, *407*, 319. (b) Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318.
- Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354.
- Mitchell, T. N.; Schneider, U.; Fröhling, B. *J. Organomet. Chem.* **1990**, *384*, C53.
- Sakaki, S.; Kikuno, T. *Inorg. Chem.* **1997**, *36*, 226. Gui, Q.; Musaeu, G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355.
- (a) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713. (b) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018.
- Ishiyama, T.; Yamamoto, M.; Miyaura, N. *J. Chem. Soc., Chem. Commun.* **1997**, 689.
- Ishiyama, T.; Yamamoto, M.; Miyaura, N. *J. Chem. Soc., Chem. Commun.* **1996**, 2073.
- Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137. Iverson, C. N.; Smith III, M. R. *Ibid.* **1996**, *15*, 5155.