

HOKKAIDO UNIVERSITY

| Title | Platinum(0)-catalyzed diboration of allenes with bis(pinacolato)diboron |
|------------------|---|
| Author(s) | Ishiyama, Tatsuo; Kitano, Takahiro; Miyaura, Norio |
| Citation | Tetrahedron Letters, 39(16), 2357-2360 https://doi.org/10.1016/S0040-4039(98)00199-3 |
| Issue Date | 1998-04-16 |
| Doc URL | http://hdl.handle.net/2115/56475 |
| Туре | article (author version) |
| File Information | (16) B-B + Allene (Com).pdf |

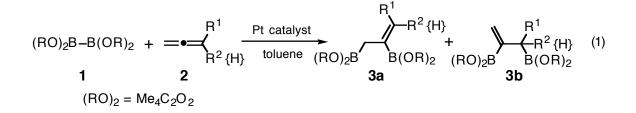


Platinum(0)-Catalyzed Diboration of Allenes with Bis(pinacolato)diboron

Tatsuo Ishiyama, Takahiro Kitano, and Norio Miyaura* Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

Abstract: Bis(pinacolato)diboron $[(Me_4C_2O_2)B-B(O_2C_2Me_4)]$ added to allenes in the presence of Pt(PPh_3)_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.

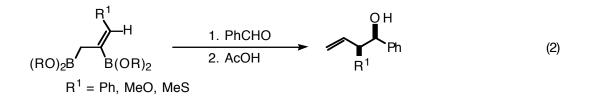
Transition-metal-catalyzed addition reaction of metal-metal reagents to allenes provides a straightforward route to 2,3-bis(metal)-1-propene and its analogs, which include synthetically useful allylmetal part and vinylmetal part in the same molecule. Although disilanes,¹ distannanes,² silylstannanes,³ 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(pinacoalto)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

 $(66\%) > (4-ClC_6H_4)_3P (46\%) > (C_6H_5)_3P (25\%) > Me_3P (7\%)$. 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(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.

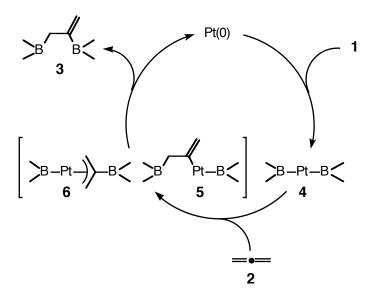
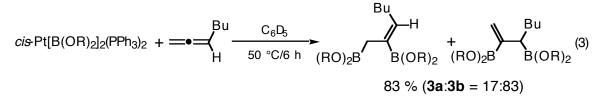
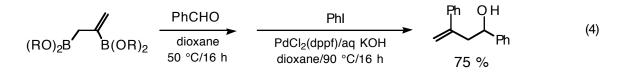


Figure 1. The Catalytic Cycle for the Diboration



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 $Pt(PPh_3)_4$ (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); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) d 24.74, 83.05, 83.35, and 128.44; ¹¹B NMR (128 MHz, CDCl₃) d 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.

- 3. Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. J. Chem. Soc., Chem. Commun. 1985, 354.
- 4. Mitchell, T. N.; Schneider, U.; Fröhling, B. J. Organomet. Chem. 1990, 384, C53.
- 5 Sakaki, S.; Kikuno, T. Inorg. Chem. 1997, 36, 226.
- (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.
- 7. Ishiyama, T.; Yamamoto, M.; Miyaura, N. J. Chem. Soc., Chem. Commun. 1997, 689.
- 8. Ishiyama, T.; Yamamoto, M.; Miyaura, N. J. Chem. Soc., Chem. Commun. 1996, 2073.
- (a) Hoffmann, R. W.; Kemper, B.; Metternich, R.; Lehmeier, T. *Liebigs Ann. Chem.* 1985, 2246.
 (b) Hoffmann, R. W.; Kemper, B. *Tetrahedron* 1984, 40, 2219.
 (c) Coxon, J. M.; Simpson, G. W.; Steel, P. J.; Trenerry, V. C. *Aust. J. Chem.* 1984, 37, 65.
- 10. Iverson, C. N.; Smith III, M. R. Organometallics 1996, 15, 5155.

| Entry | $\mathbf{A}_{\mathbf{I}}(\mathbf{a})$ | Product (3a , 3b) | Conditions A | | Conditions B | |
|-------|---------------------------------------|--|--------------------------------|-------|--------------------------------|-------|
| Entry | Allene (2) | Floduct (3a, 3b) | Yield/% ^b $3a:3b^c$ | | Yield/% ^b $3a:3b^c$ | |
| 1 | _• _ | >B B< | 99 | | 99 | |
| 2 | =• ≓ H | BU B B B B B B B B B B B B B B B B B B | 97 | 6:94 | 90 | 16:84 |
| 3 | $= - H^{-CO_2Et}$ | EtO_2C H CO_2E B B B B CO_2E | it 90 | 7:93 | 82 | 8:92 |
| 4 | =• ≓< | $\rightarrow B$ $B < \rightarrow B$ $B < B < B < B < B < B < B < B < B < B $ | 94 | 29:71 | 84 | 68:32 |
| 5 | | $>_B B < >_B B < >_B B < B < B < B < B < B < B < B < B < B$ | 96 | 50:50 | 84 | 85:15 |
| 6 | —•=∢ Me | B B B B B | 98 | 76:24 | 99 | 98:2 |
| 7 | —•=≺ H | MeO B B | 81 ^d | 100:0 | 85 ^d | 100:0 |
| 8 | =•= H | B B B B B | 48 ^{<i>d</i>} | 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: $Pt(dba)_2/(c-Hex)_3P/50$ °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

Tatsuo Ishiyama, Takahiro Kitano, and Norio Miyaura*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060, Japan

