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 [(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 allylmetal part and vinylmetal part in the same molecule. Although disilanes,¹ distannanes,² silylstannanes,³ and germystannanes⁴ 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).

\[
\begin{align*}
(RO)_2B-B(OR) \quad + \quad \overset{\text{Pt catalyst}}{\overset{\text{toluene}}{\longrightarrow}} \quad & \quad (RO)B-B(OR)_2 \quad + \quad (RO)B-R^1 \quad \overset{(H)}{\longrightarrow} \quad (RO)_2B \quad + \quad (RO)_2B \quad (RO)_2B \quad = \quad (RO)_2 = \text{Me}_4\text{C}_2\text{O}_2 \\
\end{align*}
\]

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).

\[
\begin{align*}
\text{R}^1 \quad \text{B(OR)}_2 \\
\text{B(OR)}_2 \quad \text{R}^1 \\
\text{H} \\
\end{align*}
\]

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)₂ 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. 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

\[
\begin{align*}
\text{cis-Pt[B(OR)]_2(PPh_3)_2} + \text{Bu}_2 &= \text{Pt(0)} \\
\text{(RO)B} &\text{Bu}_2 \\
\text{BuH} &\rightarrow \text{H} \\
\text{C}_6\text{D}_5 &\text{Pt-B} \\
\text{50 °C/6 h} &\rightarrow \text{Bu}_2 \\
\text{(RO)B} &\text{BuH} \\
\text{PhCl}_2(dppf)/aq KOH &\text{dioxane/90 °C/16 h} \rightarrow \text{Ph} \\
\text{75 %} &\rightarrow \text{Ph} \\
\text{1H NMR} &\text{d} 1.24 (s, 12 H), 1.26 (s, 12 H), 1.82 (s, 2 H), 5.58 (br s, 1 H), and 5.71 (d, 1 H, } J = 3.4 \text{ Hz); } \text{13C NMR} (100 \text{ MHz, CDCl}_3) \text{ d} 24.74, 83.05, 83.35, \text{ and } 128.44; \text{11B NMR} (128 \text{ MHz, CDCl}_3) \text{ d} 30.03 \text{ and } 33.46.
\end{align*}
\]

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).

\[
\begin{align*}
\text{cis-Pt[B(OR)]_2(PPh_3)_2} + \text{Bu}_2 &= \text{Pt(0)} \\
\text{(RO)B} &\text{Bu}_2 \\
\text{BuH} &\rightarrow \text{H} \\
\text{C}_6\text{D}_5 &\text{Pt-B} \\
\text{50 °C/6 h} &\rightarrow \text{Bu}_2 \\
\text{(RO)B} &\text{BuH} \\
\text{PhCl}_2(dppf)/aq KOH &\text{dioxane/90 °C/16 h} \rightarrow \text{Ph} \\
\text{75 %} &\rightarrow \text{Ph} \\
\text{1H NMR} &\text{d} 1.24 (s, 12 H), 1.26 (s, 12 H), 1.82 (s, 2 H), 5.58 (br s, 1 H), and 5.71 (d, 1 H, } J = 3.4 \text{ Hz); } \text{13C NMR} (100 \text{ MHz, CDCl}_3) \text{ d} 24.74, 83.05, 83.35, \text{ and } 128.44; \text{11B NMR} (128 \text{ MHz, CDCl}_3) \text{ d} 30.03 \text{ and } 33.46.
\end{align*}
\]

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.

References
<table>
<thead>
<tr>
<th>Entry</th>
<th>Allene (2)</th>
<th>Product (3a, 3b)</th>
<th>Conditions A Yield/%</th>
<th>Conditions B Yield/%</th>
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<td><img src="image14.png" alt="Image" /></td>
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<td>85&lt;sup&gt;d&lt;/sup&gt; 100:0</td>
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<td>82&lt;sup&gt;d&lt;/sup&gt; 82:18</td>
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</table>

<sup>a</sup>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<sub>3</sub>)<sub>2</sub>/80 °C/16 h. Conditions B: Pt(dba)<sub>2</sub>/(c-Hex)<sub>3</sub>P/50 °C/18 h. The exact procedure, see the text.

<sup>b</sup>Isolated yields based on 1. <sup>c</sup>Regioisomeric purity was determined by GLC and <sup>1</sup>H NMR analyses.

<sup>d</sup>0.1 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

\[
\text{(RO)}_2 \text{B} - \text{B(OR)}_2 + \text{H} = \text{Pt catalyst} \rightarrow \text{Me}_4 \text{C}_2 \text{O}_2
\]

\[
\text{Pt catalyst} \rightarrow \text{toluene} \rightarrow \text{R}^1, \text{R}^2 \{\text{H}\} + \text{RO}_2 \text{B} \text{B(OR)}_2 + \text{RO}_2 \text{B} \text{B(OR)}_2
\]