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

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Abstract: Bis(pinacolato)diboron \([(\text{Me}_4\text{C}_2\text{O}_2)\text{B}-\text{B}(\text{O}_2\text{C}_2\text{Me}_4)]\) added to allenes in the presence of Pt(PPh\(_3\))\(_4\) at 80 °C or Pt(dba)\(_2\)/((c-Hex))\(_3\)P 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 germystannanes\(^4\) 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(pinacolato)diboron (1) to allenes (2) to afford 2,3-bis(boryl)-1-propenes (3) (Eq. 1).

\[
\text{Pt catalyst} \quad \begin{array}{c}
\text{toluene} \\
(\text{RO})_2\text{B}=\text{B}(\text{OR})_2 \\
\text{(RO)}_2 = \text{Me}_4\text{C}_2\text{O}_2
\end{array} + \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array} = \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array} \begin{array}{c}
\text{B}(\text{OR})_2 \\
\text{B}(\text{OR})_2
\end{array} + \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array} \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \text{B}(\text{OR})_2
\]

(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-Hex)\(_3\)P (85%) > (4-MeOC\(_6\)H\(_4\))\(_3\)P
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 of 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).

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(BO₂C₆H₄Me₃)(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

\[
\text{cis-Pt[B(OR)]}_2(PPh_3)_2 + \underbrace{\text{Bu} \equiv \text{H}}_{\text{C}_6\text{D}_5} \xrightarrow{50 \degree \text{C}/6 \text{ h}} \text{Bu}_{\equiv \text{H}} \xrightarrow{\text{PdCl}_2(\text{dppf})/\text{aq KOH}} \text{Bu}_{\equiv \text{H}} \]

\[
83 \% \ (3a:3b = 17:83)
\]

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).

\[
\begin{align*}
\text{(RO)}_2\text{B} & \xrightarrow{\text{dioxane} 50 \degree \text{C}/16 \text{ h}} \text{PhCHO} & \xrightarrow{\text{PdCl}_2(\text{dppf})/\text{aq KOH}} & \text{PhOH} \\
\text{75 } \% & &
\end{align*}
\]

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 \degree 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 \degree C/0.1 mmHg (oven temperature); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 24.74, 83.05, 83.35, and 128.44; \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) \( \delta \) 30.03 and 33.46.

References
Table 1. The Synthesis of 3 (Eq. 1)<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allene (2)</th>
<th>Product (3a, 3b)</th>
<th>Conditions A</th>
<th>Conditions B</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Yield/ %&lt;sup&gt;b&lt;/sup&gt; 3a:3b&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Yield/ %&lt;sup&gt;b&lt;/sup&gt; 3a:3b&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>1</td>
<td></td>
<td></td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>97 6:94</td>
<td>90 16:84</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>90 7:93</td>
<td>82 8:92</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>94 29:71</td>
<td>84 68:32</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>96 50:50</td>
<td>84 85:15</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>98 76:24</td>
<td>99 98:2</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>81&lt;sup&gt;d&lt;/sup&gt; 100:0</td>
<td>85&lt;sup&gt;d&lt;/sup&gt; 100:0</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>48&lt;sup&gt;d&lt;/sup&gt; 50:50</td>
<td>82&lt;sup&gt;d&lt;/sup&gt; 82:18</td>
</tr>
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<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).

<sup>b</sup>Conditions A: Pt(PPh<sub>3</sub>)<sub>4</sub>/80 °C/16 h. Conditions B: Pt(db)₂(c-Hex)<sub>3</sub>P/50 °C/18 h. The exact procedure, see the text.

<sup>c</sup>Isolated yields based on 1. <sup>d</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
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\[
(\text{RO})_2B-B(\text{OR})_2 + \text{allen} \xrightarrow{\text{Pt catalyst}} \text{product}
\]

(\text{RO})_2 = \text{Me}_4\text{C}_2\text{O}_2