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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,\textsuperscript{1} distannanes,\textsuperscript{2} silylstannanes,\textsuperscript{3} and germystannanes\textsuperscript{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.\textsuperscript{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.\textsuperscript{6} This activation protocol is readily extended to the catalytic diboration of unsaturated hydrocarbons, such as alkynes,\textsuperscript{6} alkenes,\textsuperscript{7} and 1,3-dienes.\textsuperscript{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).

\[
\begin{align*}
\text{RO}_2\text{B}-\text{B(OR)}_2 + \text{\text{\scriptsize R}}^1\text{\text{\scriptsize R}}^2\text{\{H\}} & \xrightarrow{\text{Pt catalyst}} \text{\text{\scriptsize R}}^1\text{\text{\scriptsize B(OR)}_2}\text{\text{\scriptsize R}}^2\text{\{H\}} \\
\text{(RO)}_2\text{B-B(OR)}_2 & \rightarrow \text{\text{\scriptsize R}}^1\text{\text{\scriptsize B(OR)}_2}\text{\text{\scriptsize R}}^2\text{\{H\}} + \text{\text{\scriptsize R}}^1\text{\text{\scriptsize R}}^2\text{\{H\}} \text{B(OR)}_2 \tag{1}
\end{align*}
\]

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(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)_3P (85%) > (4-MeOC_6H_4)_3P.
(66%) > (C\textsubscript{6}H\textsubscript{5})\textsubscript{3}P (46%) > (C\textsubscript{6}H\textsubscript{4})\textsubscript{3}P (25%) > Me\textsubscript{3}P (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(PPh\textsubscript{3})\textsubscript{4} at 80 °C (Conditions A) or Pt(dbarg)(c-Hex)\textsubscript{3}P 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 \textsuperscript{1}H NMR spectra with authentic alcohols (Eq. 2).\textsuperscript{9}

\[
\begin{align*}
\text{B(OR)}_2 & \quad \text{H} \\
\text{R}^1 & \quad \text{B(OR)}_2 \\
\text{PhCHO} & \quad \text{1} \\
\text{AcOH} & \quad \text{2} \\
\end{align*}
\]

1. PhCHO 2. AcOH

\[\text{R}^1 = \text{Ph}, \text{MeO}, \text{MeS}\]

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(BO\textsubscript{2}C\textsubscript{2}Me\textsubscript{4})(PPh\textsubscript{3})\textsubscript{2}\textsuperscript{6} 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.\textsuperscript{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

\[
\text{cis-Pt[B(OR)]}_2(PPh_3)_2 + \text{Bu} \rightarrow \text{Pt}[B(OR)]_2 \rightarrow \text{Bu} \rightarrow \text{H} \rightarrow \text{PhCHO} \rightarrow \text{dioxane} \rightarrow \text{50 °C/6 h} \rightarrow \text{PhI} \rightarrow \text{dioxane/90 °C/16 h} \rightarrow \text{PhOH} \rightarrow 75 \%
\]

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).

\[
\begin{align*}
\text{PhCHO} & \rightarrow \text{PhI} \\
\text{PhOH} & \rightarrow 75 \%
\end{align*}
\]

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 °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


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<th>Conditions B</th>
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Table 1. The Synthesis of 3 (Eq. 1)<sup>a</sup>

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<tr>
<th>Entry</th>
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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).

Conditions A: Pt(PPh<sub>3</sub>)<sub>4</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>Regiosomeric 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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\[
\begin{align*}
(RO)_2B\quad &+ \quad \text{Pt catalyst} \\
\quad &\text{toluene} \\
\xrightarrow{\text{R}_1^1 \text{R}_2^2 \{\text{H}\}} \\
(RO)_2B &\quad \rightarrow \quad \text{(RO)}_2B \\
\quad &\quad \text{(RO)}_2B \\
\end{align*}
\]

\[
(RO)_2B(OR)_2 + \quad \rightarrow \quad \text{(RO)}_2B(OR)_2 + \\
(RO)_2B(OR)_2 \\
\]

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