

# Diboration of alkenes with bis(pinacolato)diboron catalysed by a platinum(0) complex†

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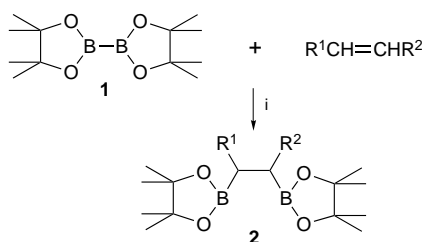
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**Bis(pinacolato)diboron selectively adds to terminal alkenes and cyclic alkenes having internal strain to provide bis(boryl)alkanes in 76–86% yields in the presence of a catalytic amount of Pt(dba)<sub>2</sub> at 50 °C.**

Increasing attention has been recently focused on the transition-metal-catalysed addition reactions of boron–heteroatom reagents, such as thioboranes,<sup>1</sup> stannylboranes,<sup>2</sup> or silylboranes<sup>3</sup> to alkenes or alkynes, as a direct procedure for preparing organoboron compounds from unsaturated hydrocarbons. We have recently reported the platinum(0)-catalysed addition of bis(pinacolato)diboron **1** to alkynes<sup>4,5</sup> and the conjugated addition to alka-1,3-dienes.<sup>6</sup> The proposed mechanism *via* the oxidative addition of **1** to the platinum(0) complex followed by insertion of an unsaturated C–C bond into the B–Pt–B complex was fully substantiated by Marder and coworkers<sup>7</sup> and Iverson and Smith.<sup>8</sup> However, the extension of this protocol to alkenes has been somewhat troublesome. Phosphine-based platinum(0) catalysts failed because the insertion of an alkene into the B–Pt bond is too slow to develop the catalytic cycle, and rhodium(i) catalysts suffered from side-reactions resulting from  $\beta$ -hydride elimination.<sup>9</sup> In 1995, Baker *et al.* first demonstrated a practical method for the diboration of styrene derivatives with a phosphine–gold(i) catalyst.<sup>9</sup> However, the previous observation,<sup>6</sup> that Pt(dba)<sub>2</sub> (dba = dibenzylideneacetone) exhibits much higher catalytic activity than Pt(PPh<sub>3</sub>)<sub>4</sub> in diboration of 1,3-dienes, prompted us to investigate the platinum(0)-catalysed diboration of alkenes (Scheme 1). The platinum(0) complex Pt(dba)<sub>2</sub> is found to be an excellent catalyst allowing alkene insertion into the B–Pt bond under mild conditions.

The diboration of aliphatic and aromatic terminal alkenes, and some cyclic alkenes having internal strain was readily achieved with Pt(dba)<sub>2</sub> (Table 1).<sup>‡</sup> When dec-1-ene (1.5 equiv.) was allowed to react with **1** (1.0 equiv.) in toluene at 50 °C in the presence of 3 mol% Pt(dba)<sub>2</sub>, the addition proceeded to completion within 1 h to afford the desired 1,2-bis(boryl)decane **2a** in 82% yield together with two unidentified products (4 : 1 ratio, *ca.* 15%), presumably arising from the  $\beta$ -hydride elimination reported in the rhodium(i)-catalysed diboration of styrene.<sup>9</sup> Among the platinum catalysts we examined, Pt(dba)<sub>2</sub> was the most efficient; combination with other ligands such as PPh<sub>3</sub>, AsPh<sub>3</sub> or P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> showed no advantages over Pt(dba)<sub>2</sub> itself.

Styrene and 4-methoxystyrene provided **2b** and **2c** with accompanying by products (*ca.* 10%). The addition to 4-methoxystyrene was apparently slower than to styrene itself,



Scheme 1 Reagents and conditions; i, Pd(dba)<sub>2</sub>, toluene, 50 °C, 1 h

the order of which is consistent with the relative reactivity observed on the insertion of arylacetylenes to the B–Pt–B complex.<sup>8</sup>

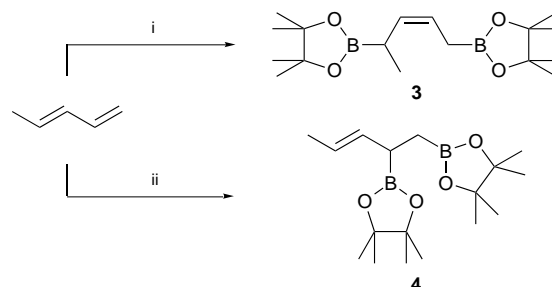
Cyclopentene (1.5 equiv.) and norbornene (3.0 equiv.) underwent a clean reaction with no byproducts. The *cis*-addition of **1** was established from the <sup>1</sup>H NMR spectrum of **2d** and its oxidation to *cis*-cyclopentane-1,2-diol. However, additions to other internal alkenes were slow, as anticipated from the order of alkene reactivity in transition-metal-catalysed reactions. Cyclooctene gave 1,2-bis(boryl)cyclooctane in low yield, but all attempts in the diboration of oct-4-ene, stilbene, cyclohexene or 2-methylpropene were unsuccessful.

Table 1 Pt(dba)<sub>2</sub>-catalysed diboration of alkenes<sup>a</sup>

Alkene	Product	Yield (%) <sup>b</sup>
Dec-1-ene	 <b>2a</b>	82
Styrene	 <b>2b</b>	86
4-Methoxystyrene	 <b>2c</b>	76 <sup>c</sup>
Cyclopentene	 <b>2d</b>	85
Norbornene	 <b>2e</b>	85 <sup>c</sup>

<sup>a</sup> All reactions were carried out at 50 °C for 1 h with Pt(dba)<sub>2</sub> (3 mol%), **1** (1.0 equiv.), alkene (1.5 equiv.), and toluene (6 ml), unless otherwise noted.

<sup>b</sup> Isolated yields based on **1**. <sup>c</sup> 3.0 equiv. of alkene was used.



Scheme 2 Reagents and conditions: i, **1**, Pt(PPh<sub>3</sub>)<sub>4</sub>, toluene, 80 °C, 84%; ii, **1**, Pt(dba)<sub>2</sub>, toluene, room temp., 92%

It is interesting that Pt(dba)<sub>2</sub> directed 1,2-addition to certain conjugated dienes, whereas 1,4-addition through a  $\pi$ -allyl-platinum(II) intermediate is an energetically more favourable process. The 1,4-addition to penta-1,3-diene at 80 °C with Pt(PPh<sub>3</sub>)<sub>4</sub> to give **3** was consistent with our previous report,<sup>6</sup> but the same reaction with Pt(dba)<sub>2</sub> selectively produced the 1,2-addition product **4** at room temperature (Scheme 2).

Further studies are in progress to elucidate the mechanism and possible synthetic applications.

#### Footnotes

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† Preliminary results were discussed at the 43rd Symposium on Organometallic Chemistry, Japan, October 31, 1996.

‡ A representative procedure for **2**: a flask was charged with Pt(dba)<sub>2</sub> (0.03 mmol) and **1** (1.0 mmol), and flushed with nitrogen. Toluene (6 ml) and dec-1-ene (1.5 mmol) were successively added, and the resulting solution was stirred at 50 °C for 1 h. Concentration and Kugelrohr distillation at 135 °C (0.1 mmHg) gave **2a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  0.79 (dd, 1 H, *J* 6.0, 15.6 Hz), 0.87 (t, 3 H, *J* 6.8 Hz), 0.87 (dd, 1 H, *J* 9.5, 15.6 Hz), 1.0–1.5 (m, 15 H), 1.22 (s, 12 H), 1.23 (s, 12 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  14.10,

22.69, 24.73, 24.77, 24.83, 24.90, 28.86, 29.28, 29.56, 29.86, 31.91, 33.83, 82.71, 82.78; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>),  $\delta$  34.14.

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