

# SYNLETT Spotlight 78

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Bis(pinacolato)diboron

Compiled by Xinyu Liu

Xinyu Liu was born in Shenyang, China in 1978. He studied chemistry in Kyoto University, Japan and received his B.E. in 2002. From April 2001 to May 2003, he was a research student in the group of Prof. Tamejro Hiyama, Kyoto University, where he worked on the synthetic applications of stereoselectively generated CF<sub>3</sub>-substituted lithio-oxirane. In June 2003, he moved to ETH-Zürich, Switzerland, and is currently working towards his Ph.D. degree under the supervision of Prof. Peter H. Seeberger.

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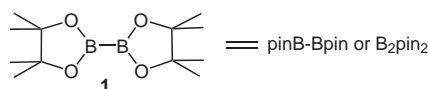
### Introduction

Since Brown's discovery of the hydroboration reaction, organoboron compounds have found wide application in organic synthesis.<sup>1</sup> The synthesis of functional organoboranes has mostly relied on either the hydroboration of unsaturated hydrocarbons or the transmetallation between an organometallic precursor and an appropriate boron compound.

In 1993, Miyaura's group reported the first platinum(0)-catalyzed *vic*-diboration of alkynes using bis(pinacolato) diboron (**1**).<sup>2</sup> This group subsequently expanded the substrates to alkenes, 1,3-dienes, allenes, and  $\alpha,\beta$ -unsaturated ketones.<sup>3</sup> These reactions provide new alternatives to access the functional organoboron compounds and also popularized diboron **1** as a new boron source.

B<sub>2</sub>pin<sub>2</sub> is used preferentially over other (alkoxo)diborons, because both the borylated products derived from it and itself can be handled in air and exhibit high stability towards hydrolysis, which facilitate reaction workup and purification.

B<sub>2</sub>pin<sub>2</sub> is commercially available from Aldrich, Lancaster, Frontier Scientific Inc, etc.

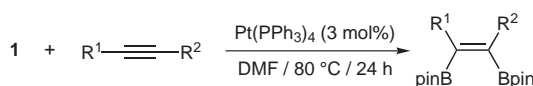


Besides the Pt-mediated *vic*-diboration of unsaturated hydrocarbon, B<sub>2</sub>pin<sub>2</sub> undergoes coupling reactions with aryl halides and allyl acetates, in the presence of Pd catalysts, to give aryl and allyl boronates.<sup>4,5</sup> More recently, B<sub>2</sub>pin<sub>2</sub> has been used in the borylation of alkanes and arenes via Rh- and Ir-mediated C-H activations.<sup>6,7</sup> Furthermore, B<sub>2</sub>pin<sub>2</sub> has found application in carbenoid chemistry, which has been explored by Hiyama's group, to generate *gem*-diborylated alkenes.<sup>8</sup>

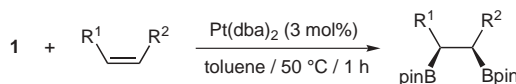
The borylated products derived from the above-mentioned strategies serve as versatile synthetic intermediates, which can undergo oxidation, allylation, and Suzuki-Miyaura cross-coupling reaction to generate more complex organic frameworks.

### Abstracts

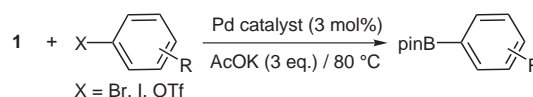
(A) In the presence of a platinum(0) catalyst, **1** undergoes addition reaction to alkynes to give exclusive *cis*-diborylated alkenes.<sup>2,9</sup> This reaction works very well on both terminal and internal alkynes. It also tolerates various functional groups in the side chain of R<sup>1</sup> and R<sup>2</sup>, such as epoxy, cyano, and carbonyl groups. The key for this type of reaction is the oxidative addition of Pt(0) to B<sub>2</sub>pin<sub>2</sub>, forming a bis(boryl)platinum(II) complex.



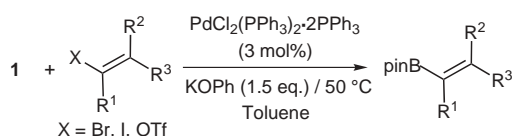
(B) By modifying the platinum catalyst to Pt(dba)<sub>2</sub>, **1** undergoes *cis*-fashion addition to alkenes very smoothly.<sup>10</sup> However, the substrate alkenes are limited to terminal alkenes and strained cyclic alkenes (cyclopentene and norbornene) under the given conditions.



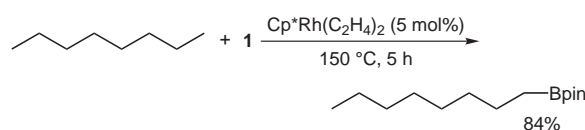
(C) In the presence of a Pd catalyst, a direct cross-coupling reaction between **1** and aryl halides (including triflates) occurs.<sup>11</sup> This reaction is now mostly referred to the Miyaura boration reaction in the literature. It has very broad functional group tolerance on the aromatic ring, hence has become a powerful method to construct aryl boronate for Suzuki-Miyaura coupling. It has been applied to the key diaryl synthesis in several natural product total syntheses.<sup>12</sup>



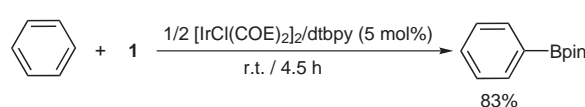
(D) By properly adjusting the palladium catalysts, bases, and solvents, a direct cross-coupling between **1** and alkenyl halides (including triflates) was achieved with the retention of the geometry of double bonds.<sup>13</sup> This strategy allowed more diversified access to alkenyl boronates, in addition to the hydroboration reaction. By adopting this strategy, a one-pot synthesis of unsymmetrical 1,3-dienes was realized.



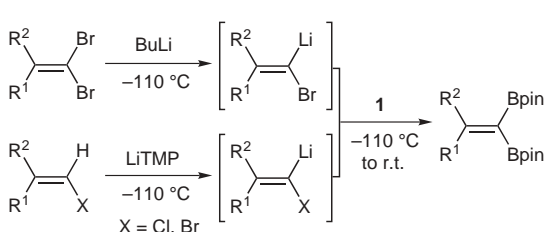
(E) Hartwig's group achieved the catalytic terminal borylation of linear alkanes in the presence of a Rh catalyst under thermal conditions for the first time.<sup>6a</sup> The key intermediate was postulated as a rhodium mono(boryl) complex, which can activate the terminal C–H bond of a linear alkane. This reaction was applied to the functionalization of polyolefins in the melt by the same group.<sup>6b</sup>



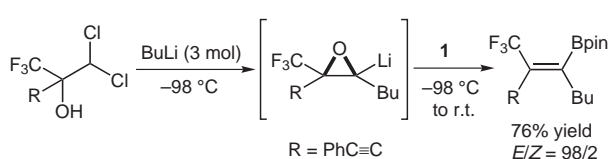
(F) A mild protocol for catalytic borylation of arenes was developed by using a Ir(I)/2,2'-bipyridine complex.<sup>7a</sup> The potential intermediate for this reaction was identified as an unusual iridium-tri(boryl) complex by single crystal x-ray diffraction. Further modification of the Ir(I) precursor to [Ir(OMe)(cod)]<sub>2</sub> allowed the first-time borylation of arenes in the presence of a stoichiometric amount of arene and **1**.<sup>7b</sup>



(H) In contrast to the extensive use of B<sub>2</sub>pin<sub>2</sub> in transition-metal catalyzed reactions, Hiyama's group disclosed that **1** reacts with alkylidene type carbenoids, which are available from 1,1-dihaloalkenes and 1-haloalkenes, to give *gem*-diborylated alkenes.<sup>14</sup> The reaction proceeds via the borate complex formation between **1** and 1-halo-1-lithio alkene, followed by stereospecific 1,2-migration of the boron substituents.



(I) Diboron **1** undergoes smooth reaction with the stereoselectively generated CF<sub>3</sub>-substituted lithio-oxirane to afford β-CF<sub>3</sub> alkenylborane in excellent diastereoselectivity.<sup>15</sup>



## References

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