## Novel Synthesis of 2,3-Bisboryl-1,3-dienes from 1-Bromo-1-lithioethene and 1,1-Bisborylalkenes

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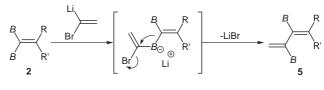
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This paper is dedicated to Professor Ryoji Noyori on the occasion of his retirement of Nagoya University, Japan

**Abstract:** Treatment of 1,1-[bis(pinacolato)boryl]alkenes with excess of 1-bromo-1-lithioethene was found to give 2,3-bis[(pinacolato)boryl]-1,3-dienes in moderate to good yields. Synthetic applications of 2,3-[bis(pinacolato)boryl]-1,3-butadiene were also demonstrated.

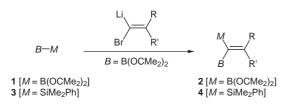
Key words: boron, lithium, carbenoids, insertion, alkenes



Treatment of 1-bromo-1-lithioethene (1 mol), generated

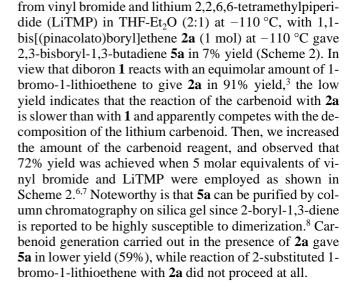
**Scheme 1**  $B = B(OCMe_2)_2$ 

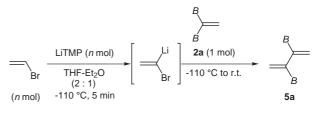
Alkenylboron compounds are readily accessible and extremely useful reagents in organic synthesis.<sup>1</sup> In contrast, bis(alkenylboron) compounds have attracted less attention probably because their facile syntheses are quite limited,<sup>2</sup> though bis(alkenylboron) compounds would be employed for an efficient synthesis of polysubstituted olefins through double carbon-carbon bond formation with retention of configuration by a simple experimental operation. Very recently, we found that treatment of bis(pinacolato)diboron **1** or (dimethylphenylsilyl)(pinacolato)boron **3** with 1-halo-1-alkenyllithium gave the corresponding 1,1-bisborylalkenes **2** or 1-silyl-1-borylalkenes **4**, respectively.<sup>3</sup> In particular, **2** is a parent example of bis(alkenylboron) compounds (eq.).



## Equation

During the course of the synthetic studies, we eventually found that 2,3-bisboryl-1,3-dienes **5a** were produced when excess of 1-bromo-1-lithioethene was treated with **1**. Formation of **5a** was ascribed to the reaction of 1,1-bisborylethene **2a** with  $CH_2$ =CBrLi followed by 1,2-migration of a carbon (Scheme 1).<sup>1</sup> We report herein that the synthesis of 2,3-bisboryl-1,3-dienes is general,<sup>4</sup> and bisborylated 1,3-dienes **5** serve as useful precursors of complex 1,3-dienes.<sup>5</sup> In addition, introduction of two boryl groups into a 1,3-diene unit enhances the synthetic utility of the addition products.

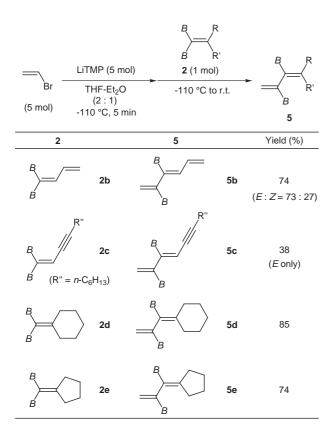




Yield (%) of **5a**: 7 (*n* = 1), 46 (*n* = 3), 72 (*n*= 5), 60 (*n* = 10)

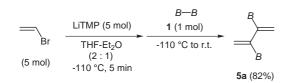
Scheme 2 Synthesis of 2,3-bisboryl-1,3-diene 5a

The optimized conditions were applied to 2-monosubstituted bisborylethenes **2b** and **2c**. The corresponding conjugated triene **5b** as a E/Z mixture (73:27) and dienyne **5c** as the only *E*-isomer were respectively isolated in 74% and 38% yields.<sup>9</sup> The stereochemical outcome indicates that 1-bromo-1-lithioethene preferentially attacks the sterically less hindered boron atom of **2**. Reaction of 2,2disubstituted-1,1-diborylethenes **2d** and **2e** also took place smoothly, giving rise to **5d** and **5e** in good yields.



Scheme 3 Synthesis of 2,3-bisboryl-1,3-diene 5

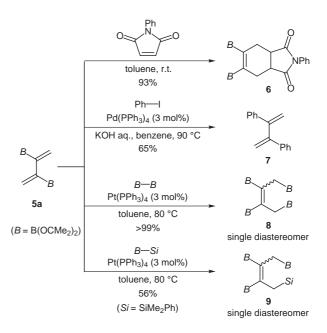
One-pot synthesis of 5a from 1 is possible. As shown in Scheme 4, treatment of vinyl bromide (5 mol) with LiT-MP (5 mol) followed by the addition of diboron 1 produced 5a in 82% yield.



Scheme 4 One-pot synthesis of 5a from 1

Synthetic utility of 2,3-bisboryl-1,3-butadiene **5a** is demonstrated in Scheme 5. Diels–Alder reaction of **5a** is particularly accelerated by the two boryl groups and indeed proceeded with maleimide even at room temperature to give 1,2-bisborylated cyclohexene **6** in 93% yield.<sup>8,10</sup> Cross-coupling reaction with iodobenzene catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> allowed us to prepare 2,3-diphenyl-1,3-butadiene **7**.<sup>11</sup> 1,2,3,4-Tetraboryl-2-butene **8** or 1-silyl-2,3,4-tris(boryl)-2-butene **9** was synthesized as a single diastereomer by Pt-catalyzed 1,4-addition reaction with bis(pinacolato)diboron **1** or (dimethylphenylsilyl)(pina-

colato)boron **3**.<sup>12</sup> The highly borylated compounds **8** and **9** contain both alkenyl- and allylmetal moieties and thus may serve as valuable synthetic reagents.



Scheme 5 Synthetic applications of 2,3-diboryl-1,3-butadiene

In summary, we have established a novel synthesis of 2,3bisboryl-1,3-dienes from 1-bromo-1-lithioethene and 1,1bisborylalkenes. We can transform 2,3-bisboryl-1,3dienes into various types of complex molecules using the boron functionality as a key element before/after unique reactions of 1,3-dienes. Further studies based on 2,3-bisboryl-1,3-dienes are in progress in our laboratory.

## Acknowledgement

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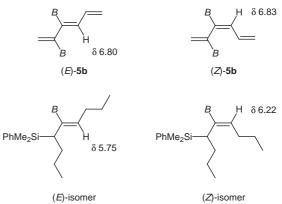
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- (7) Representative procedure of 5a: Butyllithium in hexane (1.56 M, 321 µL, 0.49 mmol) was added to a solution of 2,2,6,6tetramethylpiperidine (84  $\mu$ L, 0.50 mmol) in a mixture of THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. To this solution was added a THF solution of vinyl bromide (1.0 M, 500 µL, 0.50 mmol) at -110 °C and 1,1-[bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)]ethene (2a) (25 mg, 0.10 mmol) in THF (0.1 mL) successively. The resulting mixture was gradually allowed to warm up to room temperature and stirred for 12 h. The reaction mixture was quenched with three drops of sat. aq NH<sub>4</sub>Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200 mesh silica gel, ethyl acetatehexane = 1:10) to give 5a (22 mg, 72% yield). Mp: 140 °C (dec). TLC:  $R_f 0.33$  (hexane-ethyl acetate = 10:1). <sup>1</sup>H NMR  $(200 \text{ MHz}, \text{CDCl}_3) \delta 1.28 \text{ (s, 24H)}, 5.85 \text{ (d, } J = 3.9 \text{ Hz}, 2\text{H}),$

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- (9) Stereochemistry of **5b** was assigned by <sup>1</sup>H NMR with 6-(dimethylphenylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-4-nonene as a reference compound. Suginome, M.; Ohmori, Y.; Ito, Y. *J. Organomet. Chem.* **2000**, *611*, 403-413.



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