

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

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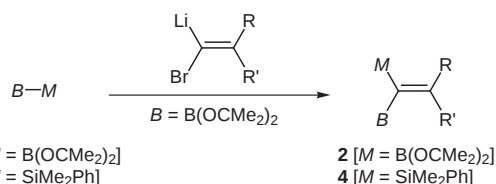
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This paper is dedicated to Professor Ryoji Noyori on the occasion of his retirement of Nagoya University, Japan

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.

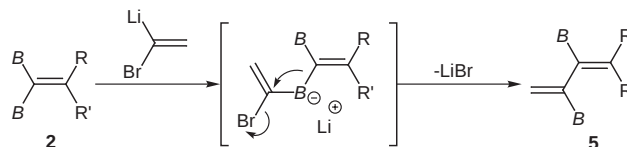
Key words: boron, lithium, carbenoids, insertion, alkenes

Alkenylboron compounds are readily accessible and extremely useful reagents in organic synthesis.¹ In contrast, bis(alkenylboron) compounds have attracted less attention probably because their facile syntheses are quite limited,² 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.³ In particular, **2** is a parent example of bis(alkenylboron) compounds (eq.).



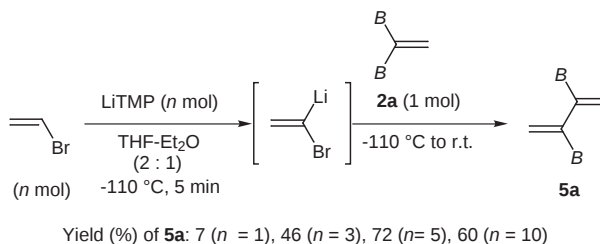
Equation

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 CH₂=CBrLi followed by 1,2-migration of a carbon (Scheme 1).¹ We report herein that the synthesis of 2,3-bisboryl-1,3-dienes is general,⁴ and bisborylated 1,3-dienes **5** serve as useful precursors of complex 1,3-dienes.⁵ In addition, introduction of two boryl groups into a 1,3-diene unit enhances the synthetic utility of the addition products.



Scheme 1 B = B(OCMe₂)₂

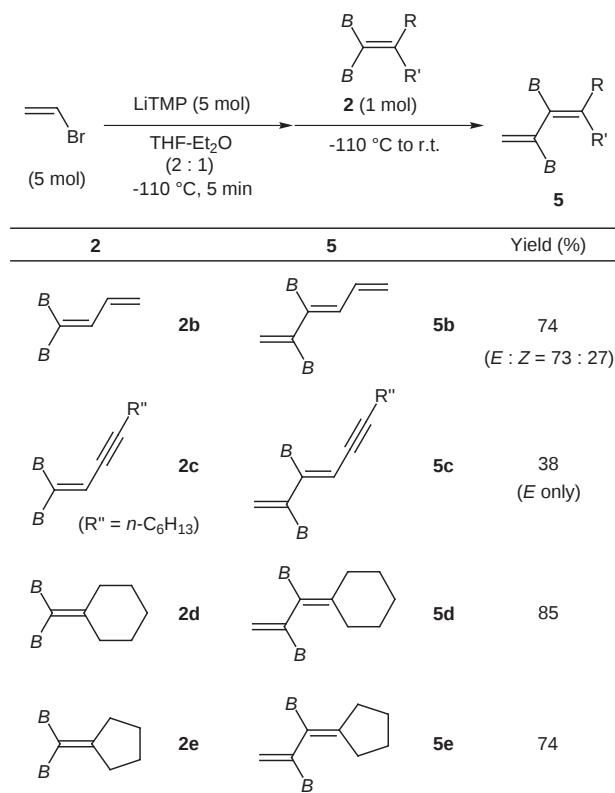
Treatment of 1-bromo-1-lithioethene (1 mol), generated from vinyl bromide and lithium 2,2,6,6-tetramethylpiperide (LiTMP) in THF-Et₂O (2:1) at -110 °C, with 1,1-bis[(pinacolato)boryl]ethene **2a** (1 mol) at -110 °C gave 2,3-bisboryl-1,3-butadiene **5a** in 7% yield (Scheme 2). In view that diboron **1** reacts with an equimolar amount of 1-bromo-1-lithioethene to give **2a** in 91% yield,³ the low yield indicates that the reaction of the carbenoid with **2a** is slower than with **1** and apparently competes with the decomposition of the lithium carbenoid. Then, we increased the amount of the carbenoid reagent, and observed that 72% yield was achieved when 5 molar equivalents of vinyl bromide and LiTMP were employed as shown in Scheme 2.^{6,7} Noteworthy is that **5a** can be purified by column chromatography on silica gel since 2-boryl-1,3-diene is reported to be highly susceptible to dimerization.⁸ Carbenoid generation carried out in the presence of **2a** gave **5a** in lower yield (59%), while reaction of 2-substituted 1-bromo-1-lithioethene with **2a** did not proceed at all.



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

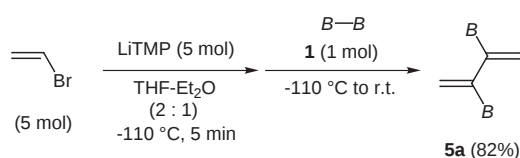
The optimized conditions were applied to 2-monosubstituted bisborylethenes **2b** and **2c**. The corresponding conjugated triene **5b** as a *E/Z* mixture (73:27) and dienyne **5c** as the only *E*-isomer were respectively isolated in 74% and 38% yields.⁹ The stereochemical outcome indicates that 1-bromo-1-lithioethene preferentially attacks the

sterically less hindered boron atom of **2**. Reaction of 2,2-disubstituted-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**

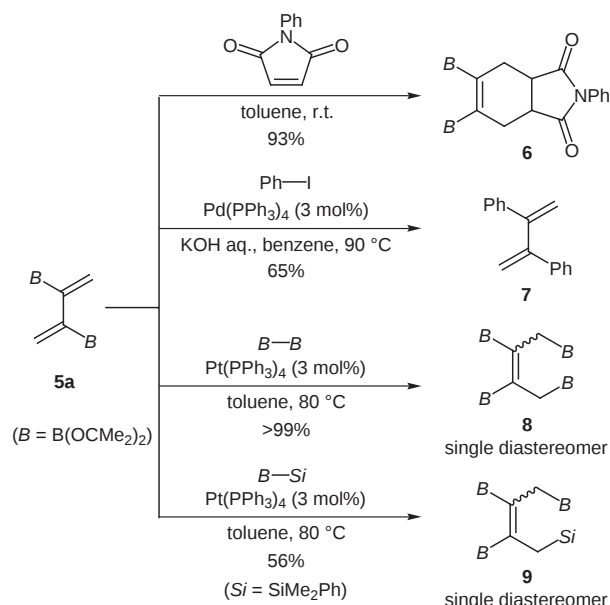
One-pot synthesis of **5a** from **1** is possible. As shown in Scheme 4, treatment of vinyl bromide (**5** mol) with LiTMP (**5** mol) followed by the addition of diboron **1** produced **5a** in 82% yield.



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.^{8,10} Cross-coupling reaction with iodobenzene catalyzed by Pd(PPh₃)₄ allowed us to prepare 2,3-diphenyl-1,3-butadiene **7**.¹¹ 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)(pinacolato)diboron **3**.¹²

The highly borylated compounds **8** and **9** contain both alkenyl- and allylmethyl 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 2,3-bisboryl-1,3-dienes from 1-bromo-1-lithioethene and 1,1-bisborylalkenes. We can transform 2,3-bisboryl-1,3-dienes 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.

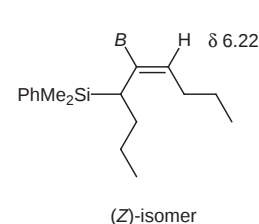
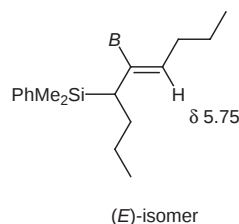
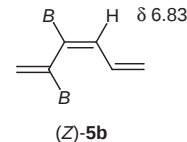
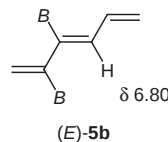
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- (6) Further insertion of the carbenoid reagent appears to be inhibited; a reason is unclear at present.
- (7) Representative procedure of **5a**: Butyllithium in hexane (1.56 M, 321 μ L, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (84 μ 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 μ L, 0.50 mmol) at -110 °C and 1,1-[bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-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_4Cl , 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 acetate-hexane = 1:10) to give **5a** (22 mg, 72% yield). Mp: 140 °C (dec). TLC: R_f 0.33 (hexane-ethyl acetate = 10:1). ^1H NMR (200 MHz, CDCl_3) δ 1.28 (s, 24H), 5.85 (d, J = 3.9 Hz, 2H), 5.96 (d, J = 3.9 Hz, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 24.8, 83.5, 130.6; IR (nujol) 1460, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm^{-1} ; MS (70 eV) m/z 307 (M^+ +1, 7.0), 306 (M^+ , 40.0), 305 (M^+ -1, 19.6), 291 (M^+ -Me, 8.5), 165 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{B}_2\text{O}_4$: C, 62.80; H, 9.22. Found: C, 62.53; H, 9.42.
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- (10) The detail of Diels-Alder reaction of **5a** will be reported in due course.
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