Bulletin of the Chemical Society of Japan

Sodium-Metal-Promoted Reductive 1,2-*syn*-Diboration of Alkynes with Reduction-Resistant Trimethoxyborane

Shiori Ito, Mizuki Fukazawa, Fumiya Takahashi, Keisuke Nogi,* and Hideki Yorimitsu*

Advance Publication on the web May 29, 2020
doi:10.1246/bcsj.20200110

Sodium-Metal-Promoted Reductive 1,2-*syn*-Diboration of Alkynes with Reduction-Resistant Trimethoxyborane[#]

Shiori Ito, Mizuki Fukazawa, Fumiya Takahashi, Keisuke Nogi,* and Hideki Yorimitsu*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502

E-mail: knogi@kuchem.kyoto-u.ac.jp; yori@kuchem.kyoto-u.ac.jp

Abstract

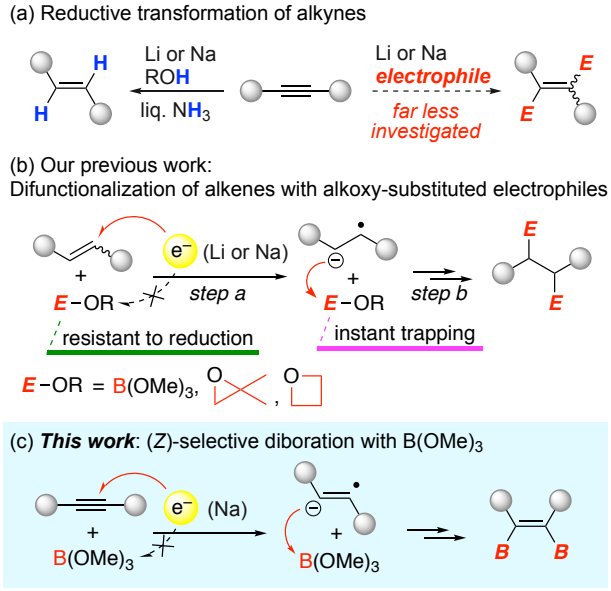
Reductive 1,2-diboration of alkynes has been accomplished by means of sodium dispersion in the presence of trimethoxyborane as a reduction-resistant boron electrophile. Two boron moieties can be introduced onto alkynes with excellent *syn* selectivity to afford the corresponding (*Z*)-1,2-diborylalkenes. Bis(borate) species generated *in situ* can be involved in one-pot Suzuki-Miyaura arylation, formal arylboration of alkynes thus being executed.

Keywords: 1,2-Diboration, Alkyne, Sodium metal

1. Introduction

As represented by *trans*-hydrogenation of alkynes, alkali-metal-promoted reduction of carbon–carbon unsaturates is a classical yet important synthetic methodology.[1,2] These transformations generally focus on construction of C–H bonds via *in situ* protonation of vinylic carbanions (Scheme 1a, left). Introduction of other atoms (or groups) by means of aprotic electrophiles has been far less investigated despite its potent synthetic utility (Scheme 1a, right). This situation would be attributed to the susceptibility of common aprotic electrophiles, like organic halides and carbonyls, toward reduction by alkali metals. Such electrophiles are preferentially reduced over alkynes, which results in the homocoupling of organic halides or carbonyls. Even worse, vinylic radical anions generated via single electron reduction (SER) of alkynes rapidly decompose via oligomerization[3] or polymerization in the absence of proper electrophiles. These difficulties have limited alkali-metal-promoted reductive functionalizations of alkynes to useful yet specific intramolecular reactions.[4]

Recently, we have developed reductive difunctionalization of alkenes by means of alkoxy-substituted boron and carbon electrophiles such as $B(OMe)_3$, isobutylene oxide, and oxetane.[5,6] Owing to the resonance effect of their oxygen atoms, alkoxy-substituted electrophiles are resistant to reduction, which allows selective SER of alkenes with alkali metals (Scheme 1b, *step a*). The radical anions generated can be instantly trapped by the co-existing alkoxy-substituted electrophiles to furnish difunctionalization products (Scheme 1b, *step b*). We envisioned that this strategy, reductive difunctionalization with alkoxy-substituted electrophiles, is applicable to alkynes for the synthesis of tetrasubstituted alkenes. Herein, we report sodium-metal-promoted 1,2-diboration of alkynes with $B(OMe)_3$ (Scheme 1c).[7,8] As opposed to the conventional *trans*-hydrogenations, our diboration proceeded with *syn* selectivity resulting in the formation of (*Z*)-1,2-diborylalkenes. In addition, bis(borate) species generated *in situ* could be employed for one-pot Suzuki-Miyaura arylation, formal arylboration of alkynes thus being executed to afford 1,2,2-triarylalkenylboronate.



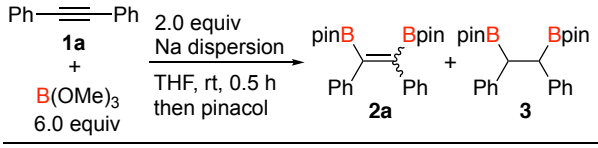
Scheme 1. Reductive difunctionalization promoted by alkali metals.

2. Results and Discussion

1,2-Diboraton of diphenylacetylene (**1a**) with $B(OMe)_3$ was chosen as a model reaction (Table 1). Na dispersion[9] (2.0 equiv) was added to a THF solution containing **1a** and $B(OMe)_3$ (6.0 equiv) at room temperature. The reaction completed within 0.5 h because of the particularly large surface area of the Na dispersion (average particle size <10 μm). After protection of the installed boron moieties with pinacol, an 89% yield of 1,2-diboration product **2a** was obtained (entry 1). In contrast to the conventional *trans*-selective hydrogenation, the present diboration proceeded in a *syn* manner exclusively, and the (*Z*)-diboration product was formed as the sole product. Of note, the order of adding the reagents was crucial for the reaction. Na dispersion must be added to the mixture of **1a** and $B(OMe)_3$. Treatment of **1a** with Na dispersion in the absence of $B(OMe)_3$ invoked instant decomposition of intermediary vinylic radical anions within 1 min, and a complex product mixture containing a trace amount of **2a** was obtained after an addition of $B(OMe)_3$ (entry 2). Instead of Na dispersion, Li powder (particle size 120–250 μm) also promoted the 1,2-diboration whereas the reaction suffered from lower conversion of **1a** even after 2 h (entry 3). The smaller surface area of Li powder caused slower electron transfer than that from Na dispersion. Although we conducted the reaction using homogeneous reduing agents, lithium and sodium naphthalenide (LiNp and NaNp), **2a** was obtained in low yields with recovery of ca. 60% of **1a** (entries 4 and 5). These results demonstrate the utility of Na dispersion in alkali-metal-promoted transformations. We then checked the effects of solvents and boron electrophiles. As the solvent, THF was found to be optimal and other ethereal solvents including Et_2O, 1,2-

dimethoxyethane (DME), and 1,4-dioxane gave the product in lower yields with recovery of ca. 20% of **1a** (entries 6–8). The use of $B(OMe)_3$ was indispensable for the present diboration; other common trialkoxyboranes such as $B(OiPr)_3$ and MeOBpin significantly lowered the yield and the stereoselectivity of **2a** (entries 9 and 10). Notably, the use of MeOBpin caused the formation of a considerable amount of diborylalkane **3** as a byproduct (entry 10, See Scheme 6c for details). Product **2a** was also obtained in 85% yield with 3.0 equivalents of $B(OMe)_3$, and eventually, a 93% yield of **2a** was obtained with an increased amount, 2.2 equivalents, of Na dispersion (entries 11 and 12).

Table 1. Optimization study with **1a**

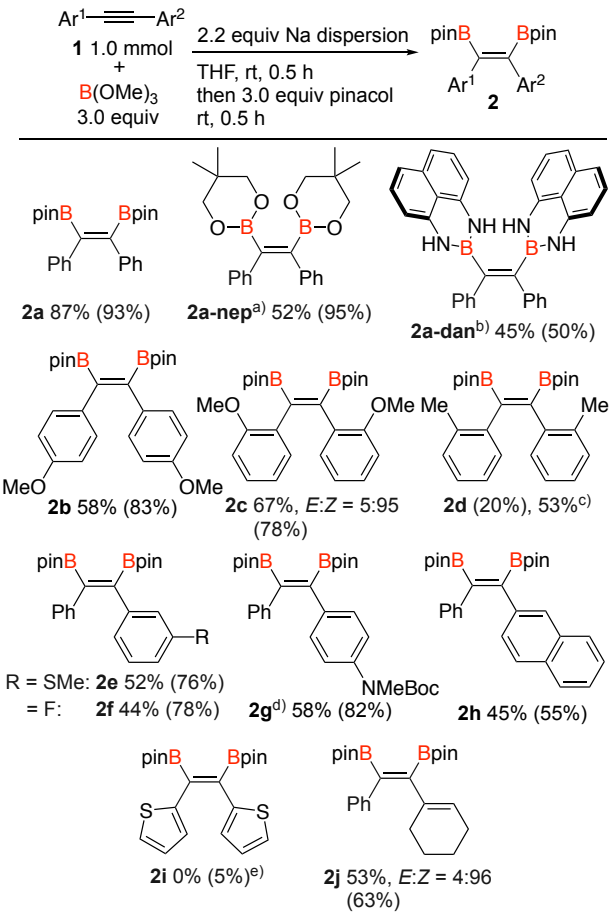


entry	deviations from above conditions	yield of **2a** (%, *Z*:*E*)	yield of **3** (%)
1	none	89 (100:0)	2
2	Na dispersion then $B(OMe)_3$[a)]	<5	0
3	Li powder instead of Na dispersion, for 2 h	50 (96:4)	6
4	LiNp instead of Na dispersion	28	1
5	NaNp instead of Na dispersion	30	1
6	Et_2O instead of THF	45 (100:0)	5
7	DME instead of THF	64 (100:0)	7
8	1,4-dioxane instead of THF	65 (88:12)	2
9	$B(OiPr)_3$ instead of $B(OMe)_3$	25 (68:32)	2
10[b)]	MeOBpin instead of $B(OMe)_3$	48 (79:21)	21
11	3.0 equiv $B(OMe)_3$	85 (100:0)	trace
12	3.0 equiv $B(OMe)_3$ and 2.2 equiv Na dispersion	93 (100:0)	0

[a)] $B(OMe)_3$ was added 1 min after completion of the addition of Na dispersion. [b)]Without addition of pinacol.

Under the optimized reaction conditions (Table 1, entry 12), **2a** was isolated in 87% yield (Scheme 2). Pinacol was found to be a suitable protective group of the boron moieties of **2a**; the isolated yield of neopentyl glycol-protected **2a-nep** was 52% because of decomposition during purification. Although 1,8-diaminonaphthalene-protected **2a-dan** was sufficiently stable during purification, the protection step suffered from lower efficiency resulting in a moderate yield of **2a-dan**.

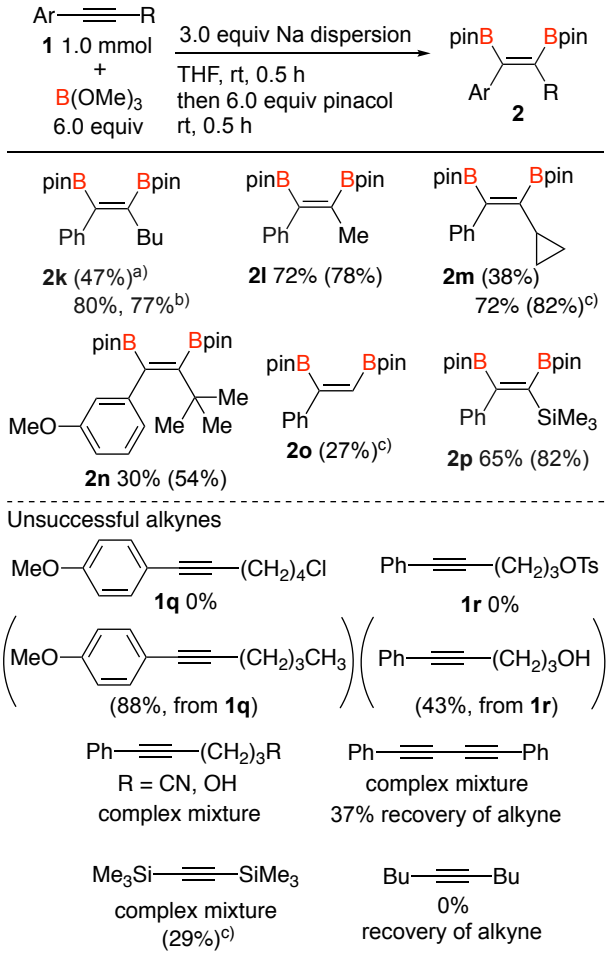
We then investigated the substrate scope with respect to diarylacetylenes. Electron-rich *para*-methoxy-substituted diarylacetylene **1b** smoothly underwent the 1,2-diboration to afford **2b** in 58% yield. *ortho*-Methoxy-substituted **1c** also took part in the reaction to yield **2c**. On the other hand, only a 20% yield of diboration product **2d** was obtained from *ortho*-methyl-substituted **1d** while most of **1d** were consumed. Because of the steric hindrance, the C–B bond formation between the radical anion generated from **1d** and $B(OMe)_3$ would be hampered, resulting in decomposition of the labile radical anion. On the other hand, coordination of the *ortho*-methoxy group to sodium cation would modulate the reactivity of **1c**. To our delight, the addition of LiI and the use of THF/TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) cosolvent system significantly improved the yield of **2d**. Such positive effects of the additive and cosolvent system were observed in our previous reductive diboration of alkenes.[5] The 1,2-diboration was compatible with several functionalities such as methylsulfanyl, fluoro, and NBoc groups to yield (*Z*)-diborylalkenes **2e**–**g**. These products might gradually decompose during purification, the isolated yields were thus modest. Naphthyl-substituted alkyne **1h** could be also involved in the reaction while the yield of **2h** was moderate. Unfortunately, di(thiophen-2-yl)acetylene (**1i**) did not provide the diboration product **2i**. Recovery of 53% of **1i** indicates that sodium metal might be consumed for cleavage of the endocyclic C–S bonds. The reaction at –78 °C also did not provide good result. Of note, the present diboration preferentially proceeded at a C–C triple bond compared to a C–C double bond. Indeed, the acetylenic moiety of enyne **1j** was converted selectively to 1,2-diboryl-1,3-diene **2j**.



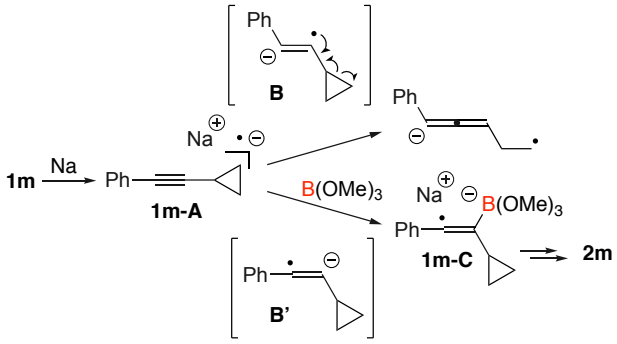
Scheme 2. Reaction scope with respect to diarylacetylenes. Yields determined by ^1H NMR analysis of the crude products are shown in parentheses. [a)]Neopentyl glycol was used instead of pinacol. [b)]1,8-Diaminonaphthalene was used instead of pinacol. The protection step was performed at 65 °C. [c)]With 2.2 equiv LiI in THF/TMEDA (v/v = 9/1). [d)]3.0 equiv Na dispersion, 4.0 equiv $B(OMe)_3$ and pinacol. [e)]At –78 °C.

Next, we explored the reaction scope with respect to alkylarylacetylenes (Scheme 3). Under the conditions shown in Scheme 2, 1-phenyl-1-hexyne (**1k**) underwent the reaction to afford **2k** whereas the yield was 47%. Gratifyingly, the use of larger amounts of $B(OMe)_3$ (6.0 equiv) and Na dispersion (3.0 equiv) improved the yield of **2k** to 80%. The radical anion generated from **1k** would be less stable than those from diarylacetylenes. The use of such an excess amount of $B(OMe)_3$ would be important to rapidly trap the fragile radical anion. The present 1,2-diboration was applicable to gram-scale synthesis; 1.6 g (77% yield) of **2k** was obtained from 5.0 mmol of **1k** and

2.7 equivalents of Na dispersion. 1-Phenyl-1-propyne (**1l**) was uneventfully converted to the corresponding (*Z*)-1,2-diboration product **2l** in 72% yield. The reaction of (cyclopropylethynyl)benzene (**1m**) produced a 38% yield of diboration product **2m** and several byproducts including ring-opened allenylic compounds. This indicates that delocalized radical anion **1m-A** generated through SER of **1m** would undergo both of two pathways shown in Scheme 4. One is ring-opening to afford allenyl species via notional intermediate **B** having an α-cyclopropylvinyl radical.[10] On the other hand, a part of **1m-A** can react with $B(OMe)_3$ via notional intermediate **B'** because α-cyclopropylvinyl anion is reluctant to undergo ring-opening.[11] Although the two pathways compete at room temperature, the former, undesirable ring-opening via **B**, could be fairly suppressed by decreasing the reaction temperature to –78 °C to afford **2m** in 72% yield. Bulky *tert*-butyl-substituted **1n** took part in the reaction to afford product **2n** in moderate yield (Scheme 3). Terminal alkyne **1o** was hardly applicable to the reaction. Oligomerization of **1o** occurred even at –78 °C to diminish the yield of **2o**. 1-Phenyl-2-(trimethylsilyl)acetylene (**1p**) also underwent the reaction to afford **2p** in good yield. The strongly reducing conditions were detrimental to the reaction of chloro-, tosyloxy-, cyano-, and hydroxy-substituted alkynes. Although we tried the diboration of 1,4-diphenylbutadiyne, a complex product mixture was obtained with recovery of 37% of the substrate. The diyne would mainly oligomerize under the strongly reducing conditions. Alkynes should have at least one aromatic ring on the acetylenic carbon; the reaction of bis(trimethylsilyl)acetylene gave a complex product mixture while 5-decyne was fully recovered after the reaction.

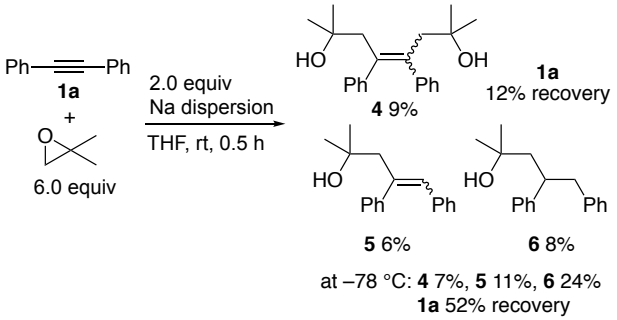


Scheme 3. Reaction scope with respect to other alkynes. Yields determined by ^{1}H NMR analysis of the crude products are shown in parentheses. [a]With 2.2 equiv Na dispersion, 3.0 equiv $B(OMe)_3$ and pinacol. [b]5.0 mmol scale. With 2.7 equiv Na dispersion. [c]At –78 °C.



Scheme 4. Possible pathways of the reaction with **1m**.

In place of alkoxy-substituted boron electrophiles, we attempted the reaction of **1a** with isobutylene oxide that can be used in our previous reductive difunctionalization of alkenes.[5] However, decomposition of **1a** preferentially occurred and the desired bis(hydroxyalkylation) product **4** was obtained only in 9% yield (Scheme 5).[12] Even at –78 °C, the yield of **4** was only 7% while 52% of **1a** was recovered.

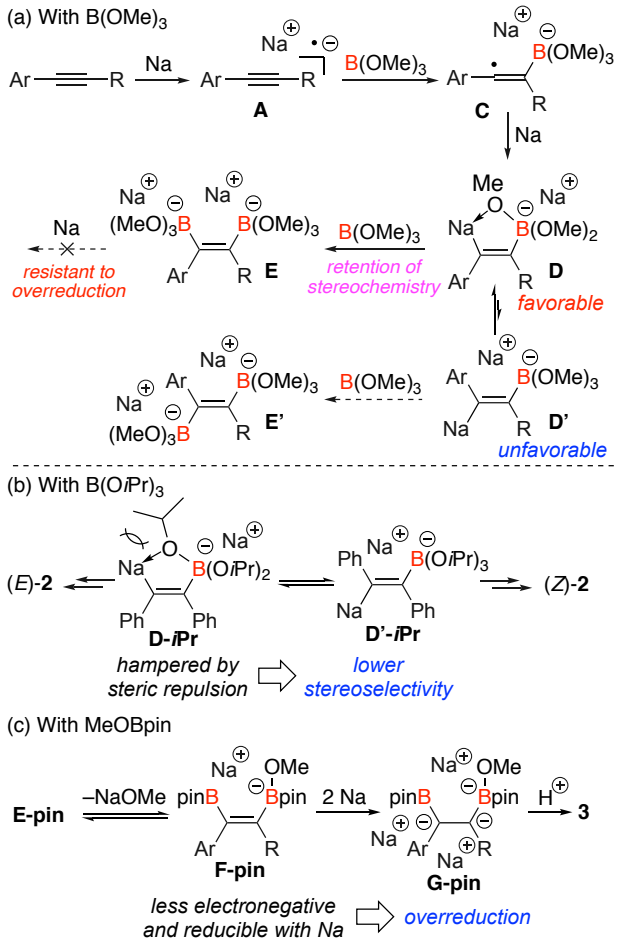


Scheme 5. Attempted bis(hydroxyalkylation) of **1a** with isobutylene oxide. Yields were determined by ^{1}H NMR analysis of crude products.

A possible reaction mechanism of the present diboration is shown in Scheme 6a. First, SER of alkyne **1** with Na dispersion would generate radical anion **A**.[13] It has been known that, at room temperature, the radical anions of an arylalkynes readily undergo dimerization in THF.[3c–f] On the other hand, in the presence of $B(OMe)_3$, the labile radical anion can be instantly trapped by $B(OMe)_3$ even at room temperature to provide **C**. Subsequent SER would form borylated carbanions **D** and its stereoisomer **D'**. Because benzylic vinyl anions easily undergo isomerization,[14] **D** and **D'** would be in equilibrium while the former would be more stable due to internal coordination of the methoxy group to the sodium on the vinylic carbon. Finally, second C–B bond formation between **D** and $B(OMe)_3$ would proceed with retention of the stereochemistry to provide (*Z*)-bis(borate) **E**. Although **E** still has a conjugated C–C double bond, the borate structure renders **E** negatively charged to suppress the overreduction with the Na dispersion.

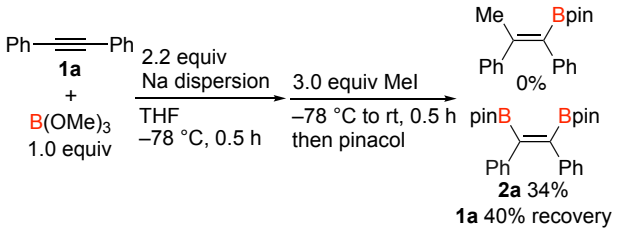
The unsuccessful result with $B(O\mathit{i}Pr)_3$ (Table 1, entry 9) would be attributable to the steric hinderance of $B(O\mathit{i}Pr)_3$. Owing to its bulkiness, trapping of anionic species **A** and/or **D-*i*Pr** would be sluggish to diminish the yield of **2a**. Moreover, the internal coordination of **D-*i*Pr** might be hampered by the bulky isopropoxy moiety, the stereoselectivity of the diboration thus decreased (Scheme 6b). Steric hinderance around the boron center poses another problem: overreduction of the diboration products observed in the reaction with MeOBpin (Table 1, entry 10). The reaction with MeOBpin would produce bis(borate) **E-**

pin, the methoxide anion of which would readily depart from the boron center because of the steric hinderance of the Bpin unit.[15] Less electronegative **F-pin** thus formed would be compelled to undergo overreduction with the remaining Na dispersion to generate **G-pin** that would be delivered to diborylalkane **3** via eventual protonation[6] (Scheme 6c). The less steric hinderance of $B(OMe)_3$ realized efficient and stereoselective C–B bond formation in the present diboration.



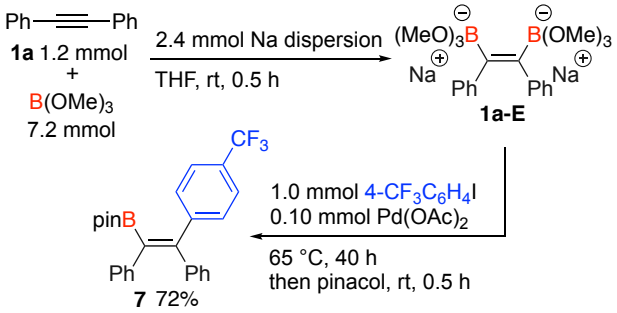
Scheme 6. A possible reaction mechanism and problems with trialkoxyboranes other than $B(OMe)_3$.

Considering the proposed mechanism, we attempted to trap borylated carbanion **D** with another electrophile for unsymmetric difunctionalization. At –78 °C, alkyne **1a** was successively treated with 1.0 equivalent of $B(OMe)_3$ and 3.0 equivalents of MeI (Scheme 7). However, no methylboration product was observed. A 34% yield of diboration product **2a** was obtained under concomitant recovery of **1a** (40%). This indicates that borylated carbanion **D** would react $B(OMe)_3$ faster than radical anion **A**.



Scheme 7. Attempted methylboration of **1a**.

Finally, to utilize *in situ* generated bis(borate) species **E**, we attempted one-pot Suzuki-Miyaura arylation without recourse to additional bases (Scheme 8). According to the Suzuki-Miyaura coupling of aryl(trimethoxy)borates,[16] we performed monoarylation of **1a-E** with 4-iodobenzotrifluoride. After generation of **1a-E** from 1.2 mmol of **1a**, 1.0 mmol of 4-iodobenzotrifluoride and 0.10 mmol of $Pd(OAc)_2$ were added. Heating the resulting mixture at 65 °C for 40 h afforded monoarylation product **7** in 72% yield.



Scheme 8. One-pot synthesis of 1,2,2-triarylalkenylboronate **7** via 1,2-diboration and Suzuki-Miyaura monoarylation.

3. Conclusion

We have developed Na-promoted reductive 1,2-diboration of alkynes with reduction-resistant and sterically less hindered $B(OMe)_3$. The reaction proceeded with excellent *syn* selectivity to provide various (*Z*)-1,2-diborylalkenes. By employing *in situ* generated bis(borate) species, one-pot synthesis of 1,2,2-triarylalkenylboronate was accomplished.

4. Experimental

Instrumentation and Chemicals

^1H NMR (600 MHz), ^{11}B NMR (192 MHz), ^{13}C NMR (151 MHz), and ^{19}F NMR (564 MHz) spectra were taken on a JEOL ECZ-600 spectrometer and were obtained in $CDCl_3$ by using $CHCl_3$ (for ^1H, δ = 7.26 ppm) and $CDCl_3$ (for ^{13}C, δ = 77.16 ppm). For the ^{11}B and ^{19}F NMR spectra, $BF_3{\cdot}OEt_2$ (δ = 0.00 ppm) and fluorobenzene (δ = –113.50 ppm) were used as an external standard, respectively. Carbons bearing boron atoms were hardly observed due to the quadrupolar relaxation mechanism of ^{11}B nucleus. Diboration product **2d** provides broad signals in their NMR spectra at 25 °C probably due to slow rotation of the C(alkenyl)–C(aryl) bonds. To obtain better signals, the NMR measurements for **2d** were conducted at 50 °C. Mass spectra were determined on a Bruker micrOTOF II spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Purification was done by column chromatography using silica gel (KANTO CHEMICAL CO., INC., Silica gel 60N, spherical neutral, particle size 100–210 μm) or done by preparative recycling gel permeation chromatography (GPC) on a JAI LC-9260 II NEXT system using $CHCl_3$ as the eluent. The reactions were carried out under an atmosphere of nitrogen while the reaction using Li powder was conducted under an atmosphere of argon. Dehydrated THF, Et_2O, and CH_2Cl_2 were purchased from KANTO CHEMICAL CO., INC. and stored under an atmosphere of nitrogen. Dehydrated 1,4-dioxane was purchased from FUJIFILM Wako Pure Chemical Corporation and stored under an atmosphere of nitrogen. DME, TMEDA, and triethylamine were purchased from commercial suppliers and

distilled prior to use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Alkynes **1a**, **1k**, **1o**, and **1p** were purchased from TCI. Alkyne **1l** was prepared from phenylacetylene and iodomethane with BuLi. Na dispersion (ca. 10 M suspension in mineral oil) was provided by KOBELCO ECO-Solutions Co., Ltd. The concentration of the Na dispersion was determined by acid-base titration: NaOMe generated via the reaction of Na dispersion with MeOH was titrated with 1 M aqueous HCl using phenolphthalein as an indicator. Li powder was prepared according to a modified procedure reported by Yus.[17] The particle sizes (120–250 μm) of the Li powder were measured by SEM (HITACHI, Miniscope TM3030Plus). LiNp and NaNp were prepared from naphthalene and Li granule and Na dispersion in THF, and titrated according to the literature.[18]

Preparation of Materials

Preparation of diarylacetylenes 1b–d and 1i: A modification of the procedure reported by Song and Lee was used.[19] The synthesis of **1b** is representative. A 100-mL two-necked flask was charged with 4-bromoanisole (2.5 mL, 20 mmol), propiolic acid (0.62 mL, 10 mmol), $PdCl_2(PPh_3)_2$ (0.35 g, 0.50 mmol), 1,4-bis(diphenylphosphino)butane (dppb, 0.43 g, 1.0 mmol), DMSO (40 mL), and DBU (3.0 mL, 20 mmol). The resulting solution was stirred at 80 °C for 32 h, before additions of saturated aqueous NH_4Cl (4 mL) and H_2O (40 mL). The mixture was extracted with Et_2O (40 mL × 4) and the combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 29/1) to give **1b** (1.2 g, 5.2 mmol, 52%) as a white solid. Alkynes **1c**, **1d**, and **1i** were prepared through the same procedure. All the resonances in the ^1H and ^{13}C NMR spectra of **1b**,[20] **1c**,[19] **1d**,[19] and **1i**[19] were consistent with the reported values.

Preparation of diarylacetylenes 1e, 1f and 1h: A modification of the procedure reported by Buchwald and Fu was used.[21] The synthesis of **1f** is representative. A 50-mL Schlenk tube was charged with 3-fluorobromobenzene (0.55 mL, 5.0 mmol), $PdCl_2(PPh_3)_2$ (90 mg, 0.15 mmol), $P(tBu)_3 \cdot HBF_4$ (39 mg, 0.30 mmol), CuI (19 mg, 0.10 mmol), diisopropylamine (0.85 mL, 6.0 mmol), and 1,4-dioxane (5 mL). Phenylacetylene (0.66 mL, 6.0 mmol) was added dropwise, and the resulting suspension was stirred at room temperature. After completion of the reaction, the mixture was passed through pads of silica gel and alumina with EtOAc as an eluent. The mixture was washed with saturated aqueous NH_4Cl and brine. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as an eluent to give **1f** (0.80 g, 4.2 mmol, 83%) as a yellow oil. Alkynes **1e** and **1h** were prepared through the same procedure. All the resonances in the ^1H and ^{13}C NMR spectra of **1e**,[22] **1f**,[23] and **1h**[23] were consistent with the reported values.

Preparation of alkynes 1g, 1m and 1n: The synthesis of **1g** is representative. A 50-mL Schlenk tube was charged with *tert*-butyl (4-iodophenyl)(methyl)carbamate (3.11g, 9.3 mmol), $PdCl_2(PPh_3)_2$ (0.16 g, 0.23 mmol), CuI (0.11 g, 0.56 mmol), degassed NEt_3 (1.9 mL, 14 mmol), and THF (14 mL). Phenylacetylene (1.2 mL, 11 mmol) was added dropwise, and the resulting suspension was stirred at room temperature. After completion of the reaction, the mixture was passed through pads of silica gel and alumina with EtOAc as an eluent. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 30/1) as an eluent to give **1g** (2.7 g, 8.7 mmol, 94%) as a white solid. Alkynes **1m** and **1n** were prepared through the same procedure. All the resonances in the ^1H and ^{13}C NMR spectra of **1m**[24] and **1n**[25] were consistent with the reported values.

Preparation of alkyne 1j: Modifications of the procedures reported by Kotschy[26] (for the fist step) and Nicolaou[27] (for the second step) were used. A 50-mL two-necked flask was charged with iodobenzene (1.1 mL, 10 mmol), 1-ethynylcyclohexanol (1.5 g, 12 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.3 mmol), CuI (0.11 g, 0.6 mmol), and diisopropylamine (20 mL), and the resulting mixture was stirred at room temperature. After completion of the reaction, the mixture was passed through pads of silica gel and alumina with EtOAc as an eluent. The mixture was washed with saturated aqueous NH_4Cl and brine. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1 to 5/1) to give 1-(phenylethynyl)cyclohexanol (1.94 g, 97 mmol, 97%) as a yellow solid. A 100-mL flask was charged with 1-(phenylethynyl)cyclohexanol (1.60 g, 8.0 mmol), CH_2Cl_2 (50 mL), and NEt_3 (3.9 mL, 28 mmol). Methanesulfonyl chloride (1.9 mL, 24 mmol) was added dropwise at 0 ˚C, and the resulting suspension was stirred at 0 ˚C for 15 min, before additions of saturated aqueous NH_4Cl (3 mL) and H_2O (30 mL). The mixture was extracted with CH_2Cl_2 (10 mL× 4). The combined organic layer was washed with saturated aqueous NH_4Cl, dried over Na_2SO_4 and concentrated under reduced pressure. DBU (12 mL, 80 mmol) was added portionwise to the residue at 0 ˚C and the resulting suspension was stirred at 0 ˚C. The solution was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as an eluent to give **1j** (1.31 g, 7.2 mmol, 90%) as a colorless oil. All the resonances in the ^1H and ^{13}C NMR spectra of **1j** were consistent with the reported values.[28]

Experimental Procedures

General procedure for 1,2-diboration of diarylacetylenes (GP1, Scheme 2): An oven-dried 20-mL Schlenk tube was charged with alkyne **1** (1.0 mmol), $B(OMe)_3$ (0.34 mL, 3.0 mmol), and THF (4.0 mL). Na dispersion (10.0 M in mineral oil, 0.22 mL, 2.2 mmol) was added dropwise, and the resulting suspension was stirred at room temperature for 30 min. Pinacol (0.36 g, 3.0 mmol) was then added, and the resulting mixture was stirred at room temperature for an additional 30 min. After an addition of aqueous HCl (2 M, 3 mL), the resulting mixture was extracted with EtOAc (2 mL × 4). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was loaded on a short silica gel column (φ = 16 mm, H = 120 mm) and 100 mL of hexane was passed through the column to remove the mineral oil in the Na dispersion. EtOAc (200 mL) was then passed through the column to elute the crude product. After the EtOAc layer was concentrated under reduced pressure, the residue was purified by GPC (eluent: $CHCl_3$).

General procedure for 1,2-diboration of alkylaryl- and arylsilylacetylenes (GP2, Scheme 3): An oven-dried 20-mL Schlenk tube was charged with alkyne **1** (1.0 mmol), $B(OMe)_3$ (0.67 mL, 6.0 mmol), and THF (4.0 mL). Na dispersion (10.0 M, 0.30 mL, 3.0 mmol) was added dropwise, and the resulting suspension was stirred at room temperature for 30 min. Pinacol (0.71 g, 6.0 mmol) was then added, and the resulting mixture was stirred at room temperature for an additional 30 min. After an addition of HCl (2 M, 3 mL), the resulting mixture was extracted with EtOAc (2 mL × 4). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 50:1).

Procedure for gram-scale synthesis of 2k (Scheme 3):

An oven-dried 50-mL Schlenk tube was charged with **1k** (0.88 mL, 5.0 mmol), $B(OMe)_3$ (3.4 mL, 30 mmol), and THF (20 mL). Na dispersion (1.35 mL, 13.5 mmol) was added dropwise, and the resulting suspension was stirred at room temperature for 30 min. Pinacol (3.55 g, 30 mmol) was then added, and the resulting mixture was stirred at room temperature for an additional 30 min. After an addition of HCl (2 M, 6 mL), the resulting mixture was extracted with EtOAc (5 mL × 4). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was loaded on a short silica gel column (φ = 32 mm, H = 120 mm) and 400 mL of hexane was passed through the column to remove the mineral oil in the Na dispersion. EtOAc (800 mL) was then passed through the column to elute the crude product. After the EtOAc layer was concentrated under reduced pressure, the residue was purified by GPC to provide **2k** (1.6 g, 3.9 mmol, 77%) as a yellow oil.

Procedure for one-pot Suzuki-Miyaura coupling followed by 1,2-diboration (Scheme 8): The arylation step was conducted according to the Suzuki-Miyaura coupling of aryl(trimethoxy)borates reported by Starichenko.[16] An oven-dried 20-mL Schlenk tube was charged with **1a** (0.21 g, 1.2 mmol), $B(OMe)_3$ (0.80 mL, 7.2 mmol), and THF (4.8 mL). Na dispersion (10.0 M, 0.24 mL, 2.4 mmol) was added dropwise, and the resulting suspension was stirred at room temperature for 30 min before additions of $Pd(OAc)_2$ (22 mg, 0.10 mmol) and 4-iodobenzotrifluoride (0.15 mL, 1.0 mmol). The resulting mixture was stirred at 65 ˚C for 40 h. Pinacol (0.85 g, 7.2 mmol) was then added, and the resulting mixture was stirred at room temperature for an additional 30 min. After an addition of HCl (2 M, 3 mL), the resulting mixture was extracted with EtOAc (2 mL × 4), The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 75:1) to provide **7** (0.34 g, 0.72 mmol, 72%) as a yellow solid.

Characterization Data

***tert*-Butyl methyl[4-(phenylethynyl)phenyl]carbamate (1g):** ^{1}H NMR: δ 7.51–7.53 (m, 2H), 7.48 (dt, J = 8.9, 2.1 Hz, 2H), 7.31–7.36 (m, 3H), 7.23 (d, J = 8.2 Hz, 2H), 3.27 (s, 3H), 1.46 (s, 9H); ^{13}C NMR: δ 154.57, 143.86, 131.95, 131.71, 128.49, 128.36, 125.19, 123.40, 120.01, 89.37, 89.19, 80.80, 37.19, 28.46. HRMS (APCI-MS, positive): m/z = 308.1633. calcd for $C_{20}H_{22}NO_2$: 308.1645 $[M+H]^+$.

(*Z*)-1,2-Diphenyl-1,2-bis(pinacolatoboryl)ethene (2a): Synthesized via **GP1**. Purification was done by GPC without short silica gel column chromatography. White solid (0.38 g, 0.87 mmol, 87%). All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[29]

(*Z*)-1,2-Bis[(neopentyl glycolato)boryl]-1,2-diphenylethene (2a-nep): Synthesized via **GP1** by using 2,2-dimethylpropane-1,3-diol (0.31 g, 3.0 mmol) instead of pinacol. White solid (0.22 g, 0.52 mmol, 52%). ^{1}H NMR: δ 7.06–7.09 (m, 4H), 7.02 (t, J = 7.8 Hz, 2H), 6.96–6.98 (m, 4H), 3.72 (s, 8H), 1.01 (s, 12H); ^{13}C NMR: δ 141.70, 129.39, 127.58, 125.71, 72.83, 31.89, 22.18; ^{11}B NMR: δ 27.22 (br), 18.36. HRMS (APCI-MS, positive): m/z = 512.2352. calcd for $C_{24}H_{31}B_2O_4$: 512.2349 $[M+H]^+$.

(*Z*)-1,2-Bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)-1,2-diphenylethene (2a-dan): Synthesized via **GP1** by using 1,8-diaminonaphthalene (0.47 g, 3.0 mmol) instead of pinacol. The protection step was performed at 65 ˚C. Purification was done by column chromatography on silica gel (eluent: hexane to hexane/EtOAc = 1/1) according to **GP2**. White solid (0.23 g, 0.45 mmol, 45%). ^{1}H NMR: δ 7.09–7.17 (m, 6H), 6.98–7.07 (m, 12H), 6.20 (d, J = 6.6 Hz, 4H), 5.85 (s, 4H); ^{13}C NMR: δ 142.30, 140.77, 136.35, 129.77, 128.26, 127.71, 126.50, 119.84, 118.09, 106.35; ^{11}B NMR: δ 28.78 (br). HRMS (APCI-MS, positive): m/z = 404.2330. calcd for $C_{34}H_{27}B_2N_4$: 404.2333 $[M+H]^+$.

(*Z*)-1,2-Bis(4-methoxyphenyl)-1,2-bis(pinacolatoboryl)ethene (2b): Synthesized via **GP1**. White solid (0.29 g, 0.58 mmol, 58%). All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra of were consistent with the reported values.[29]

(*Z*)-1,2-Bis(2-methoxyphenyl)-1,2-bis(pinacolatoboryl)ethene (2c): Synthesized via **GP1**. White solid (0.33 g, 0.67 mmol, 67%, E:Z = 5:95). ^{1}H NMR: δ 7.00 (dd, J = 8.7, 7.5 Hz, 2H), 6.71 (d, J = 7.8 Hz, 2H), 6.63 (d, J = 7.5 Hz, 2H), 6.52–6.54 (m, 2H), 3.74 (s, 6H), 1.31 (s, 24H); ^{13}C NMR: δ 157.07, 132.25, 131.00, 127.40, 120.22, 109.48, 83.70, 55.05, 25.05; ^{11}B NMR: δ 30.81 (br). HRMS (APCI-MS, positive): m/z = 492.2862. calcd for $C_{28}H_{38}B_2O_6$: 492.2859 $[M]^+$.

(*Z*)-1,2-Bis(2-methylphenyl)-1,2-bis(pinacolatoboryl)ethene (2d): Synthesized via **GP1** in the presence of 2.2 equivalents of LiI under THF/TMEDA (v/v = 9/1) cosolvent conditions. Purification was done by GPC using toluene as the eluent. White solid (0.24 g, 0.53 mmol, 53%). ^{1}H NMR (at 50 °C): δ 6.93 (d, J = 7.5 Hz, 2H), 6.90 (t, J = 7.5 Hz, 2H), 6.84 (br, 4H), 2.20 (br, 6H), 1.28 (s, 24H); ^{13}C NMR (at 50 °C): δ 135.04, 129.36 (br, 2C), 125.97, 124.75 (br, 2C), 83.92, 24.93, 20.32 (br); ^{11}B NMR (at 50 °C): δ 30.07 (br). HRMS (APCI-MS, positive): m/z = 461.3034. calcd for $C_{28}H_{39}B_2O_4$: 461.3039 $[M+H]^+$.

(*Z*)-1-[3-(Methylsulfanyl)phenyl]-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2e): Synthesized via **GP1**. White solid (225 mg, 0.52 mmol, 52%). ^{1}H NMR: δ 7.07–7.10 (m, 2H), 7.02–7.05 (m, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.93–6.96 (m, 3H), 6.77–6.79 (m, 2H), 2.14 (s, 3H), 1.33 (s, 12H), 1.32 (s, 12H); ^{13}C NMR: δ 141.95, 141.31, 137.21, 129.35, 127.87, 127.71, 127.55, 126.27, 126.05, 124.82, 84.27 (2C), 25.04, 25.00, 15.72; ^{11}B NMR: δ 30.03 (br). HRMS (APCI-MS, positive): m/z = 478.2527. calcd for $C_{27}H_{36}B_2O_4S$: 478.2524 $[M]^+$.

(*Z*)-1-(3-Fluorophenyl)-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2f): Synthesized via **GP1**. White solid (0.20 g, 0.44 mmol, 44%). ^{1}H NMR: δ 6.96–7.10 (m, 4H), 6.92–6.95 (m, 2H), 6.65–6.73 (m, 3H), 1.31 (s, 24H); ^{13}C NMR: δ 162.40 (d, J = 244.2 Hz), 143.76 (d, J = 8.7 Hz), 140.94, 129.15, 128.89 (d, J = 8.7 Hz), 127.73, 126.25, 125.30 (d, J = 2.9 Hz), 116.29 (d, J = 21.7 Hz), 112.78 (d, J = 21.7 Hz), 84.36, 84.30, 25.01, 24.98; ^{19}F NMR: δ –115.01; ^{11}B NMR: δ 30.27 (br). HRMS (APCI-MS, positive): m/z = 451.2627. calcd for $C_{26}H_{34}B_2O_4F$: 451.2631 $[M+H]^+$.

(*Z*)-1-[4-(*N*-Methyl-*N*-*tert*-butoxycarbonylamino)phenyl]-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2g): Synthesized via **GP1** by using 3.0 equivalents of Na dispersion (10.0 M, 0.30 mL, 3.0 mmol) and 4.0 equivalents of $B(OMe)_3$ (0.45 mL, 4.0 mmol). White solid (323 mg, 0.58 mmol, 58%). ^{1}H NMR: δ 7.05–7.08 (m, 2H), 7.02 (t, J = 7.8 Hz, 1H), 6.94–6.96 (m, 2H), 6.88–6.92 (m, 4H), 3.17 (s, 3H), 1.38 (s, 9H), 1.32 (s, 12H), 1.32 (s, 12H); ^{13}C NMR: δ 154.95, 141.62, 141.38, 138.39, 129.63, 129.43, 127.61, 125.93, 124.55, 84.22 (2C), 80.07, 37.23, 28.42, 25.02; ^{11}B NMR: δ 31.23 (br). HRMS (APCI-MS, positive): m/z = 561.3442. calcd for $C_{32}H_{45}B_2O_6N$: 561.3438 $[M]^+$.

(*Z*)-1-(2-Naphthyl)-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2h): Synthesized via **GP1**. White solid (0.22 g, 0.45 mmol, 45%). ^{1}H NMR: δ 7.67–7.68 (m, 1H), 7.62–7.64 (m, 1H), 7.54 (s, 1H), 7.48 (d, J = 8.9 Hz, 1H), 7.34–7.37 (m, 2H), 6.97–7.04 (m, 6H), 1.34 (s, 12H), 1.33 (s, 12H); ^{13}C NMR: δ 141.30, 139.11, 133.29, 132.00, 129.57, 128.26, 128.11, 128.07, 127.67, 127.62, 126.86, 126.01, 125.51, 125.39,

84.27 (2C), 25.06, 25.03; ^{11}B NMR: δ 30.35 (br), 22.36. HRMS (APCI-MS, positive): *m/z* = 482.2806. calcd for $C_{30}H_{37}B_2O_4$: 482.2804 $[M+H]^+$.

(*Z*)-1-(1-Cyclohexeyl)-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2j): Synthesized via **GP1**. White solid (0.21 g, 0.53 mmol, 53%, *E*:*Z* = 4:96). ^{1}H NMR: δ 7.19–7.22 (m, 2H), 7.15–7.17 (m, 2H), 7.10–7.13 (m, 1H), 5.36–5.38 (m, 1H), 1.87–1.91 (m, 2H), 1.67–1.69 (m, 2H), 1.36–1.40 (m, 4H), 1.33 (s, 12H), 1.27 (s, 12H); ^{13}C NMR: δ 142.50, 138.56, 128.76, 127.41, 125.87, 125.79, 83.97, 83.72, 28.49, 25.55, 24.99, 24.93, 22.95, 22.13; ^{11}B NMR: δ 29.74 (br), 22.25. HRMS (APCI-MS, positive): *m/z* = 436.2958. calcd for $C_{26}H_{38}B_2O_4$: 436.2960 $[M]^+$.

(*Z*)-1-Phenyl-1,2-bis(pinacolatoboryl)-1-hexene (2k): Synthesized via **GP2**. Purification was done by short silica gel column and GPC according to **GP1**. Yellow oil (0.35 g, 0.84 mmol, 80%) was obtained from 1.05 mmol (0.17 g) of **1k**. All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[30]

(*Z*)-1-Phenyl-1,2-bis(pinacolatoboryl)propene (2l): Synthesized via **GP2**. Purification was done by short silica gel column and GPC according to **GP1**. Yellow oil (0.27 g, 0.73 mmol, 72%) was obtained from 1.02 mmol (0.12 g) of **1l**. All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[29]

(*Z*)-1-Cyclopropyl-2-phenyl-1,2-bis(pinacolatoboryl)ethene (2m): Synthesized via **GP2**. The diboration step was conducted at –78 °C. Yellow solid (0.27 mg, 0.68 mmol, 72%). ^{1}H NMR: δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.16–7.18 (m, 1H), 1.56–1.60 (m, 1H), 1.35 (s, 12H), 1.23 (s, 12H), 0.77–0.74 (m, 2H), 0.57–0.60 (m, 2H); ^{13}C NMR: δ 142.58, 129.29, 127.70, 125.66, 84.04, 83.76, 25.55, 24.86, 15.95, 7.81; ^{11}B NMR: δ 29.87, 22.36. HRMS (APCI-MS, positive): *m/z* = 396.2644. calcd for $C_{23}H_{34}B_2O_4$: 396.2646 $[M]^+$.

(*Z*)-1-(3-Methoxyphenyl)-3,3-dimethyl-1,2-bis(pinacolatoboryl)-1-butene (2n): Synthesized via **GP2**. Purification was done by short silica gel column and GPC (eluent: toluene) according to **GP1**. White solid (0.13 g, 0.30 mmol, 30%). ^{1}H NMR: δ 7.11 (t, *J* = 7.8 Hz, 1H), 6.67–6.71 (m, 3H), 3.76 (s, 3H), 1.38 (s, 12H), 1.16 (s, 12H), 0.98 (s, 9H); ^{13}C NMR: δ 158.66, 145.63, 128.18, 121.36, 113.77, 111.48, 83.90, 83.70, 55.24, 38.38, 31.82, 25.69, 24.76; ^{11}B NMR: δ 29.95 (br), 22.32. HRMS (APCI-MS, positive): *m/z* = 442.3068. calcd for $C_{25}H_{40}B_2O_5$: 442.3065 $[M]^+$.

(*Z*)-1-Phenyl-1,2-bis(pinacolatoboryl)-2-(trimethylsilyl)ethene (2p): All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[31]

(*E*)-1,2-Diphenyl-1-pinacolatoboryl-2-[4-(trifluoromethyl)phenyl]ethene (7): All the resonances in the ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[32]

Acknowledgement

This work was supported by JSPS KAKENHI Grant Numbers JP16H04109, JP18H04254, JP18H04409, JP19H00895, JP18K14212, and JP20K15275 as well as JST CREST Grant Number JPMJCR19R4. We thank KOBELCO ECO-Solutions Co., Ltd. for providing Na dispersion. We also thank Prof. Makoto Yamashita, Dr. Kengo Sugita (Nagoya University), and Dr. Atsushi Kaga (Kyoto University) for preparing and providing Li powder, and Prof. Shohei Saito and Mr. Takuya Yamakado (Kyoto University) for measurement of the particle size of the Li powder.

[#]Dedicated to Professor Eiichi Nakamura on the occasion of his 70th birthday.

References

1. K. N. Campbell, L. T. Eby, *J. Am. Chem. Soc*. **1941**, *63*, 216.
2. Reviews: a) K. N. Campbell, B. K. Campbell, *Chem. Rev.* **1942**, *31*, 77. b) D. J. Pasto, Reduction of C=C and C≡C by Noncatalytic Chemical Methods. in *Comprehensive Organic Synthesis*, ed. by B. M. Trost, I. Fleming, Pergamon, Oxford, **1991**; pp. 471–488.
3. a) L. I. Smith, H. H. Hoehn, *J. Am. Chem. Soc.* **1941**, *63*, 1184. b) E. H. Braye, W. Hübel, I. Caplier, *J. Am. Chem. Soc.* **1961**, *83*, 4406. c) D. Dadley, A. G. Evans, *J. Chem. Soc. B* **1967**, 418. d) D. A. Dadley, A. G. Evans, *J. Chem. Soc. B* **1968**, 107. e) G. Levin, J. Jagur-Grodzinski, M. Szwarc, *J. Am. Chem. Soc*. **1970**, *92*, 2268. f) A. G. Evans, J. C. Evans, P. J. Emes, T. J. Phelan, *J. Chem. Soc., B* **1971**, 315. g) M. Saito, M. Nakamura, T. Tajima, M. Yoshioka, *Angew. Chem. Int. Ed.* **2007**, *46*, 1504.
4. a) S. Yamaguchi, C. Xu, K. Tamao, *J. Am. Chem. Soc.* **2003**, *125*, 13662. b) C. Xu, H. Yamada, A. Wakamiya, S. Yamaguchi, K. Tamao, *Macromolecules* **2004**, *37*, 8978. c) C. Xu, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2004**, *6*, 3707. d) C. Xu, A. Wakamiya, S. Yamaguchi, *J. Am. Chem. Soc.* **2005**, *127*, 1638. e) S. Yamaguchi, C. Xu, H. Yamada, A. Wakamiya, *J. Organomet. Chem.* **2005**, *690*, 5365. f) H. Yamada, C. Xu, A. Fukazawa, A. Wakamiya, S. Yamaguchi, *Macromol. Chem. Phys.* **2009**, *210*, 904. g) H. Zhang, T. Karasawa, H. Yamada, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2009**, *11*, 3076. h) J. F. Araneda, B. Neue, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2012**, *51*, 8546. i) J. Zhao, C. Ru, Y. Bai, X. Wang, W. Chen, X. Wang, X. Pan, J. Wu, *Inorg. Chem.* **2018**, *57*, 12552.
5. M. Fukazawa, F. Takahashi, K. Nogi, T. Sasamori, H. Yorimitsu, *Org. Lett*. **2020**, *22*, 2303.
6. Our recent report on borylation chemistry with alkali metals and bis(pinacolato)diboron (B_2pin_2). F. Takahashi, K. Nogi, T. Sasamori, H. Yorimitsu, *Org. Lett.* **2019**, *21*, 4739.
7. Reviews on 1,2-diboration reactions: a) J. Takaya, N. Iwasawa, *ACS Catal.* **2012**, *2*, 1993. b) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091. c) A. B. Cuenca, R. Shishido, H. Ito, E. Fernández, *Chem. Soc. Rev.* **2017**, *46*, 415.
8. Selected recent examples of 1,2-diboration of alkynes: a) C. Kojima, K.-H. Lee, Z. Lin, M. Yamashita, *J. Am. Chem. Soc.* **2016**, *138*, 6662. b) A. Yoshimura, Y. Takamachi, K. Mihara, T. Saeki, S.-I. Kawaguchi, L.-B. Han, A. Nomoto, A. Ogawa, *Tetrahedron* **2016**, *72*, 7832. c) A. Verma, R. F. Snead, Y. Dai, C. Slebodnick, Y. Yang, H. Yu, F. Yao, W. L. Santos, *Angew. Chem. Int. Ed.* **2017**, *56*, 5111. d) T. Ohmura, Y. Morimasa, M. Suginome, *Chem. Lett.* **2017**, *46*, 1793. e) L. Ferrand, Y. Lyu, A. Rivera-Hernández, B. Fallon, M. Amatore, C. Aubert, M. Petit, *Synthesis* **2017**, *49*, 3895. f) S. Peng, G. Liu, Z. Huang, *Org. Lett.* **2018**, *20*, 7363.
9. Recent reports on reductive transformations with Na dispersion as a highly reactive but easy-to-handle reducing agent: Ref. 5 and 6 and a) J. An, D. N. Work, C. Kenyon, D. J. Procter, *J. Org. Chem.* **2014**, *79*, 6743. b) M. Han, X. Ma, S. Yao, Y. Ding, Z. Yan, A. Adijiang, Y. Wu, H. Li, Y. Zhang, P. Lei, Y. Ling, J. An, *J. Org. Chem.* **2017**, *82*, 1285. c) M. Han, Y. Ding, Y. Yan, H. Li, S. Luo, A. Adijiang, Y. Ling, J. An, *Org. Lett.* **2018**, *20*, 3010. d) P. Lei, Y. Ding, X. Zhang, A. Adijiang, H. Li, Y. Ling, J. An, *Org. Lett.* **2018**, *20*, 3439. e) B. Zhang, H. Li, Y. Ding, Y. Yan, J. An, *J. Org. Chem.* **2018**, *83*, 6006. f) Y. Ding, S. Luo, A.

Adijiang, H. Zhao, J. An, *J. Org. Chem.* **2018**, *83*, 12269. g) S. Asako, H. Nakajima, K. Takai, *Nat. Catal.* **2019**, *2*, 297. h) S. Asako, M. Kodera, H. Nakajima, K. Takai, *Adv. Synth. Catal.* **2019**, *361*, 3120. i) Y. Ding, S. Luo, L. Ma, J. An, *J. Org. Chem.* **2019**, *84*, 15827.

10. a) J. K. Crandall, G. L. Tindell, A. Manmade, *Tetrahedron Lett.* **1982**, *23*, 3769. b) T. G. Back, K. R. Muralidharan, *J. Org. Chem*. **1989**, *54*, 121. c) E. Mainetti, L. Fensterbank, M. Malacria, *Synlett* **2002**, *6*, 923. d) K. K. Milnes, S. E. Gottschling, K. M. Baines, *Org. Biomol. Chem.* **2004**, *2*, 3530.
11. S. E. Gottschling, T. N. Grant, K. K. Milnes, M. C. Jennings, K. M. Baines, *J. Org. Chem.* **2005**, *70*, 2686.
12. Although we conducted reductive disilylation of **1a** using $Si(OEt)_4$ as an alkoxy-substituted electrophile, a complex product mixture was obtained.
13. In the presence of an excess of metallic Li or Na, the radical anion of diphenylacetylene can be further reduced to the corresponding dianion while the reduction step would be rather slow. See ref 3e and A. Maercker, M. Kemmer, H. C. Wang, D.-H. Dong, M. Szwarc, *Angew. Chem. Int. Ed*. **1998**, *37*, 2136.
14. a) A. N. Nesmeyanov, A. E. Borisov, *Tetrahedron* **1957**, *1*, 158. b) D. Y. Curtin, J. W. Crump, *J. Am. Chem. Soc.* **1958**, *80*, 1922. c) R. Knorr, E. Lattke, *Tetrahedron Lett.* **1977**, *18*, 3969.
15. A. A. Thomas, A. F. Zahrt, C. P. Delaney, S. E. Denmark, *J. Am. Chem. Soc.* **2018**, *140*, 4401.
16. H.-J. Frohn, N. Y. Adonin, V. V. Bardin, V. F. Starichenko, *J. Fluorine Chem.* **2003**, *122*, 195.
17. M. Yus, P. Martínez, D. Guijarro, *Tetrahedron* **2001**, *57*, 10119.
18. C. G. Screttas, M. Micha-Screttas, *J. Organomet. Chem*. **1983**, *252*, 263.
19. K. Park, G. Bae, J. Moon, J. Choe, K. H. Song, S. Lee, *J. Org. Chem*. **2010**, *75*, 6244.
20. B. Schmidt, R. Berger, A. Kelling, U. Schilde, *Chem. Eur. J.* **2011**, *17*, 7032.
21. T. Hundertmark, A. F. Littke, S. L. Buchwald, G. C. Fu, *Org. Lett*. **2000**, *2*, 1729.
22. Q. H. Chen, P. N. P. Rao, E. E. Knaus, *Bioorg. Med. Chem.* **2005**, *13*, 6425.
23. T. Truong, O. Daugulis, *Org. Lett*. **2011**, *13*, 4172.
24. J. Teske, B. Plietker, *Org. Lett.* **2018**, *20*, 2257.
25. M. Ociepa, J. Turkowska, D. Gryko, *ACS Catal.* **2018**, *8*, 11362.
26. M. Csékei, Z. Novák, A. Kotschy, *Tetrahedron* **2008**, *64*, 975.
27. K. C. Nicolaou, T. Montagnon, T. Ulven, P. S. Baran, Y. L. Zhong, F. Sarabia, *J. Am. Chem. Soc.* **2002**, *124*, 5718.
28. A. A. Almasalma, E. Mejía, *Chem. Eur. J.* **2018**, *24*, 12269.
29. H. Yoshida, S. Kawashima, Y. Takemoto, K. Okuda, J. Ohshita, K. Takaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 235.
30. N. Nakagawa, T. Hatakeyama, M. Nakamura, *Chem. Eur. J.* **2015**, *21*, 4257.
31. J. Jiao, K. Hyodo, K. Nakajima, Y. Nishihara, *J. Org. Chem*. **2014**, *79*, 289.
32. Y. Zhou, W. You, K. B. Smith, M. K. Brown, *Angew. Chem. Int. Ed.* **2014**, *53*, 3475.