Direct and Base-Catalyzed Diboration of Alkynes Using the Unsymmetrical Diborane(4), pinB-BMes₂
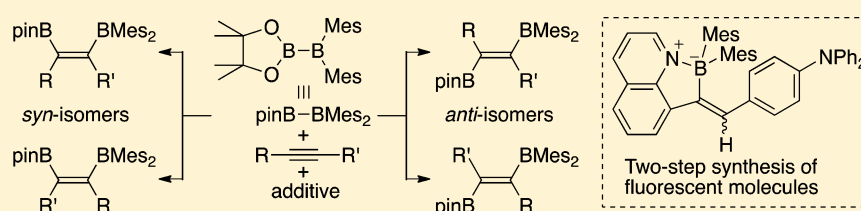
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Ⓢ *Supporting Information*

ABSTRACT: In the absence of transition metal catalysts, the unsymmetrical diborane(4), pinB-BMes₂, reacted with alkynes to afford diborylalkenes. The isomer ratio of the products could be controlled via temperature, solvent, and additive(s). A reaction mechanism was proposed on the basis of two isolated intermediates, and this reaction could furthermore be applied to synthesize a luminescent molecule.

■ INTRODUCTION

The transition-metal-catalyzed diboration of alkynes with B₂pin₂ [bis(pinacolato)diborane(4)] to form 1,2-diborylalkenes has been widely applied in organic synthesis[1] since its discovery in 1993.[2] The first diboration of alkynes in the absence of a transition metal catalyst was reported in 1959 for Cl₂B−BCl₂, which adds directly to acetylene to form Cl₂BCH=CHBCl₂ via a B−B bond cleavage. The resulting C=C double bond and the molecular weight of the product were confirmed by IR spectroscopy and vapor density, respectively (Scheme 1).[3] The

Scheme 1. Reaction of Acetylene with Tetrahalodiboranes(4)
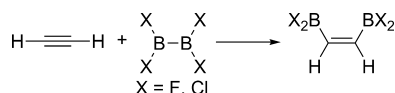
same study reported that the reaction of the corresponding tetrafluorodiborane(4) was slightly slower than that of the tetrachloro derivative. However, the formation of F₂BCH=CHBF₂ was confirmed by comparison with an authentic sample, which was prepared from 1,2-bis(dichloroboryl)-ethylene and SbF₃. Until recently, this report was the only example for a diboration of alkynes in the absence of a transition metal catalyst.

The seminal discoveries on the alkoxide-catalyzed diboration of alkenes (Scheme 2a) and on the phosphine-catalyzed β-boration of alkenes substituted with electron-withdrawing groups (EWGs) (Scheme 2b) through the activation of B₂pin₂[4,5] initiated a renaissance of the investigations into diborations of alkynes in the absence of transition metal

Scheme 2. Alkoxide-Catalyzed Diboration of Alkenes and Phosphine-Catalyzed β-Boration of Alkenes Substituted with EWGs (Key Intermediates in the Dashed Rectangles)
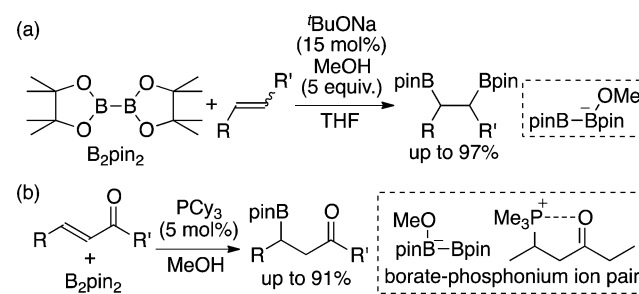

catalysts. The key steps in these activations of B₂pin₂ are the formation of a diborane−alkoxide sp²−sp³ adduct[6] and the generation of a phosphonium enolate intermediate.

In the past three years, several related diborations of alkynes in the absence of transition metal catalysts have been reported. Sawamura and Ohmiya reported that B₂pin₂ could be added to alkynoates to afford *trans*-α,β-diboryl acrylates in the presence of trialkylphosphine catalysts (Scheme 3a).[7] The proposed mechanism for this transformation involved the formation of phosphonium allenolates, which could activate B₂pin₂ in a nucleophilic fashion. The same group also found that an alkoxide base could catalyze the 1,1-diboration of EWG-substituted acetylenes with B₂pin₂ (Scheme 3b).[8] They proposed a catalytic cycle consisting of a deprotonation of

**Scheme 3. Recent Examples for the Diboration of Alkynes in the Absence of Transition Metal Catalysts**

**Scheme 4. Reaction of Unsymmetrical Diborane(4) 1 with CO and *tert*-Butylisocyanide**
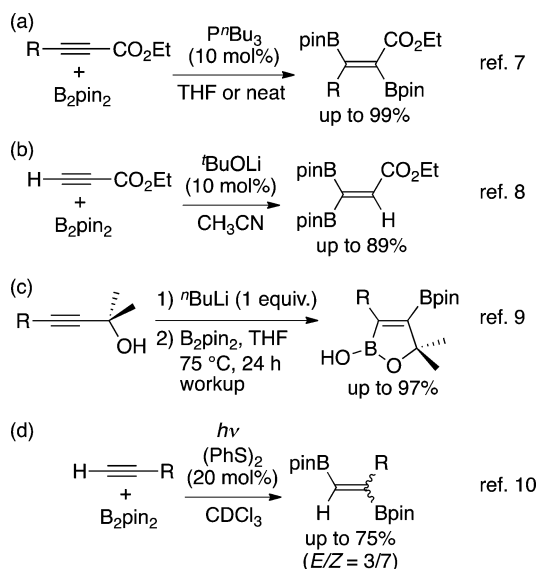
the EWG-substituted acetylene, coordination of the resulting acetylide to B_2pin_2, 1,2-migration of a pinB group under concomitant protonation to form an allene intermediate, and subsequent isomerization to furnish the 1,1-diborylalkenes. Independently, Uchiyama and Hirano reported the diboration of propargylic alcohols with B_2pin_2 in the presence of a stoichiometric amount of ^nBuLi to generate *trans*-1,2-diborylalkenes (Scheme 3c).[9] The proposed reaction mechanism involved the deprotonation of propargylic alcohols, coordination of the resulting alkoxides to B_2pin_2, migration of a pinB group and the lithium cation to form alkenyllithium intermediates, and a nucleophilic attack of the resulting alkenyl carbon to the pinB group. Ogawa and co-workers also studied the diboration of alkynes in the absence of a transition metal catalyst (Scheme 3d). They demonstrated that the irradiation of a mixture of a terminal alkyne, B_2pin_2, and a catalytic amount of diphenyl disulfide with light led to formation of a *cis/trans* mixture of diborylalkenes.[10] Even though the reaction mechanism is yet unclear, they proposed a radical chain reaction pathway involving sulfur- and boron-centered radical species on the basis of an ESR analysis of the reaction mixture and control experiments with radical initiators in the absence of light.

Recently, we reported the synthesis of a novel unsymmetrical diborane(4), $pinB\text{-}BMes_2$ (1), and its reactivity toward the C≡O and C≡N triple bonds in CO and *tert*-butylisocyanide (Scheme 4).[11] Most notably, the C≡N triple bond in the isocyanide was completely cleaved in the absence of transition metals. The key to the attractive reactivity of 1 is its strong Lewis acidity, which arises from the lowering of the LUMO as a result of the overlapping vacant p-orbitals between the two boron atoms.[12] Inspired by the reactivity of 1 toward C≡O and C≡N triple bonds, we started to explore the reactivity of 1 toward the C≡C triple bond of alkynes.[13] Herein, we report direct and base-catalyzed diborations of alkynes with 1 to afford diborylalkenes with a diarylboryl unit. The regioselectivity of this reaction can be controlled by the reaction conditions. The synthetic utility of this diboration was demonstrated by the preparation of an emissive material.
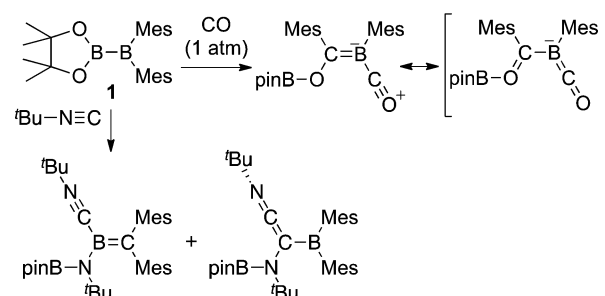
■ RESULTS AND DISCUSSION

The unsymmetrical diborane(4) 1 reacted with phenylacetylene to afford a mixture of three regioisomers (2a–c), whereby the isomer ratio depends on the reaction conditions (Table 1).

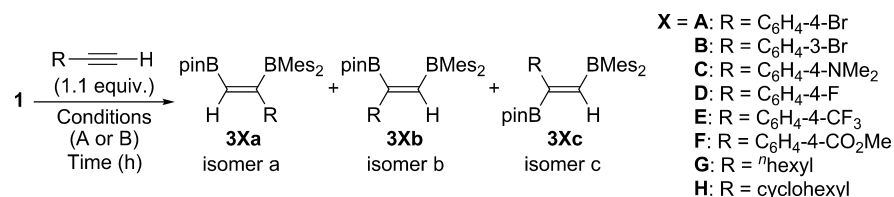**Table 1. Reaction between 1 and Phenylacetylene[a] (TMB: 1,3,5-Trimethoxybenzene; DME: 1,2-Dimethoxyethane)**
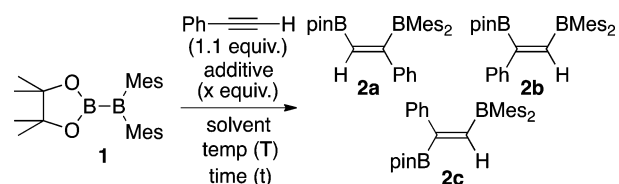
run	additive (x equiv)	solvent	T (°C)	t (h)	NMR yield (%)[b]		
					2a	2b	2c
1	–	toluene	100	37	69	30	0
2	^nBuLi (0.15)	toluene	100	17	10	61	8
3	^nBuLi (0.15)	THF	70	19	21	7	56
4	^nBuLi (0.15)	n-hexane	80	19	18	9	53
5	^nBuLi (0.15)	toluene	40	42	14	9	58
6	^nBuLi (0.15)	THF	40	88	30	14	37
7	^nBuLi (0.15)	n-hexane	40	96	34	14	23
8	^nBuLi (0.15), TMB (1)	toluene	100	1	2	9	82
9	^nBuLi (0.15), anisole (1)	toluene	100	1	2	24	44
10	^nBuLi (0.15), DME (1)	toluene	100	1	5	6	84
11	^nBuLi (0.15)	DME	70	24	12	13	63
12	^nBuLi (0.03), DME (0.03)	toluene	100	3[c]	16	9	67
13	^nBuLi (0.01), DME (0.01)	toluene	100	3[d]	23	13	44

[a]The regiochemistry was determined by single-crystal X-ray diffraction analysis of the isolated products. [b]Estimated by comparison with the signals of isolated products. [c]92% conversion. [d]82% conversion.

Heating of a reaction mixture of 1 and phenylacetylene in toluene to 100 °C for 37 h (run 1) produced *syn*-adduct 2a as the major product (69%) and isomer 2b as the minor product (30%). In 2a, the $BMes_2$ substituent is attached to the carbon atom that carries the phenyl group. The regiochemistry of 2a and 2b was unambiguously determined by X-ray diffraction analysis (see Supporting Information). It should be noted that 1 started to decompose at T > 100 °C. In contrast, B_2pin_2 did not react with phenylacetylene under otherwise identical reaction conditions. In the presence of a catalytic amount of ^nBuLi (15 mol %), similar reaction conditions (T = 100 °C for

Table 2. Substrate Scope Using Terminal Alkynes (X: A–H)

X = **A**: R = C_6H_4-4-Br
B: R = C_6H_4-3-Br
C: R = C_6H_4-4-NMe_2
D: R = C_6H_4-4-F
E: R = C_6H_4-4-CF_3
F: R = C_6H_4-4-CO_2Me
G: R = ^{n}hexyl
H: R = cyclohexyl

Run	R	Conditions[a]	Time (h)	Products,[b] yield (%)[c]		
				isomer a	isomer b	isomer c
1	C_6H_4-4-Br	A	23	**3Aa**, 64 (59)	**3Ab**, 26 (24)	-
2	C_6H_4-4-Br	B	3	**3Aa**, 20	**3Ab**, 5	**3Ac**, 69 (35)
3	C_6H_4-3-Br	A	14	**3Ba**, 64 (44)	**3Bb**, 20 (9)	-
4	C_6H_4-3-Br	B	3	**3Ba**, 10	**3Bb**, 5	**3Bc**, 68 (61)
5	C_6H_4-4-NMe_2	A	6	**3Ca**, 24 (19)	**3Cb**, 76 (50)	-
6	C_6H_4-4-NMe_2	B	1.5	**3Ca**, 13	**3Cb**, 41	**3Cc**, 27[d]
7	C_6H_4-4-F	A	72	**3Da**, 66 (61)	**3Db**, 30 (21)	-
8	C_6H_4-4-F	B	5	**3Da**, 16	**3Db**, 12	**3Dc**, 53 (41)
9[e]	C_6H_4-4-CF_3	A[e]	59	**3Ea**, 69 (40)	**3Eb**, 16 (11)	-
10	C_6H_4-4-CF_3	B	8	**3Ea**, 18	**3Eb**, 6	**3Ec**, 59 (43)
11	C_6H_4-4-CO_2Me	A	28	**3Fa**, 64 (36)	**3Fb**, 17 (1)	-
12	C_6H_4-4-CO_2Me	B	42	**3Fa**, 38	**3Fb**, 10	**3Fc**, 10[d]
13	^{n}hexyl	A	4	**3Ga**, 64 (37)	**3Gb**, 33 (29)	-
14	^{n}hexyl	B	2	**3Ga**, 57	**3Gb**, 29	**3Gc**, 5[d]
15	cyclohexyl	A	9	**3Ha**, 40[d]	**3Hb**, 50[d]	-
16	cyclohexyl	B	4	**3Ha**, 37[d]	**3Hb**, 50[d]	**3Hc**, trace[d]

[a]Condition A: 0.5 or 0.6 mmol of **1**, 1.1 equiv of alkyne, 0.4 M toluene, 100 °C. Condition B: 0.5 or 0.6 mmol of **1**, 1.1 equiv of alkyne, 3 mol % of ^{n}BuLi and DME, 0.4 M toluene, 100 °C. [b]The regiochemistry was determined by single-crystal X-ray diffraction analysis (underlined) and/or diff-^{1}H NOE NMR analysis (doubly underlined). [c]^{1}H NMR yields (isolated yields in parentheses). [d]Not isolated, but tentative characterization of the mixture by NMR spectral analysis. [e]1.0 M toluene solution was used to shorten the reaction time.

17 h) afforded **2b** (61%) as the major product (run 2) together with minor amounts of **2a** and *anti*-isomer **2c**. The regiochemistry of **2c** was also determined by X-ray diffraction analysis. Using THF or *n*-hexane as the solvent at 70 or 80 °C (runs 3 and 4), or lowering the reaction temperature to 40 °C (run 5), furnished **2c** as the major product. This result suggests that the polarity of the solvent should not affect the selectivity. Detailed DFT-assisted studies to examine the solvent effect will be reported in due course. Reactions in THF and *n*-hexane at a lower temperature (40 °C) led to a longer reaction time and a decrease in selectivity toward **2c** (runs 6 and 7). During the determination of the NMR yields for these reactions, we found that the addition of 1,3,5-trimethoxybenzene (TMB), which was originally used as an internal standard, altered the selectivity and reaction rate. The presence of TMB (1 equiv) under conditions otherwise identical to those of run 2 shortened the reaction time and increased the selectivity toward **2c** (run 8). In contrast, addition of anisole (1 equiv) decreased the selectivity toward **2c** (run 9). Changing the oxygen-containing additive from TMB to 1,2-dimethoxyethane (DME) afforded a similarly short reaction time and a comparably good selectivity toward **2c** (run 10). Considering the lower boiling point of DME relative to that of TMB, we

decided to use DME as an additive for the purification of the products. Using DME as a solvent caused a longer reaction time, as the boiling point of DME is lower than that of toluene, even though the selectivity remained unaffected (run 11). Decreasing the quantity of ^{n}BuLi and DME to 3 mol % also furnished **2c** as the major product (run 12). A further decrease of ^{n}BuLi and DME to 1 mol % led to lower selectivity toward **2c** (run 13). At this point, the exact role of the ethereal additives toward the reaction rate and selectivity is unclear. However, we expect that the additive molecules would coordinate with Li^+ cations during the reactions (see below for the study on the isolation of the intermediates) and the fluxionality of the coordination under the reaction conditions would affect the reaction rate and selectivity. Our ongoing DFT studies are expected to provide insight into this issue.

This diboration could also be applied to various other terminal alkynes, resulting in the formation of the corresponding isomers **3Xa**, **3Xb**, and **3Xc**, whereby the product distribution depended on the reaction conditions. In general, condition A (direct diboration) afforded the two *syn*-isomers **3Xa** and **3Xb**, while condition B (base-catalyzed diboration with 3 mol % of ^{n}BuLi; identical conditions of run 11, Table 1) furnished three isomers (Table 2). 4-Bromo- and 3-bromo-

substituted phenylacetylenes afforded product distributions for **3Aa-c** and **3Ba-c** similar to those reported in Table 1 (runs 1−4), probably on account of the fact that the bromo substituents on the 3- and 4-position do not alter the electronic and steric properties of the benzene rings toward the reaction center substantially. It should also be noted that the Br functionality remained intact.[14] The presence of an electron-donating Me_2N group in the phenylacetylene substrate accelerated the direct reaction in the absence of a base and inversed the selectivity toward the *syn*-isomers **3Ca/3Cb** (run 5). Increasing the electron density of the alkyne moiety may lower the activation barrier of its nucleophilic attack to the Lewis-acidic $BMes_2$ moiety. Due to the acceleration of the direct diboration in run 5, the selectivity toward *anti*-isomer **3Cc** under the base-catalyzed conditions in run 6 was lower in comparison to those observed in runs 2 and 4. A 4-fluoro derivative revealed selectivity results (runs 7 and 8) similar to those observed for bromo derivatives in runs 1−4, probably due to the diminished steric effect of the 4-fluoro substituent. It should be noted that the longer reaction time in run 7 compared to run 5 may arise from the slightly electron-withdrawing 4-fluoro substituent.[15] The presence of an electron-withdrawing 4-CF_3 substituent resulted in a similar selectivity toward *syn*-isomers **3Ea** and **3Eb** (run 9), but the reaction was decelerated as observed in run 7. This is the reason why a higher concentration was used in run 7. Under base-catalyzed conditions (run 10), a substrate with a 4-CF_3 substituent afforded a selectivity toward *anti*-isomer **3Ec** over *syn*-isomers **3Ea** and **3Eb**, which is similar to those obtained in runs 2 and 4. Direct diboration of 4-methoxycarbonyl-substituted phenylacetylene (run 11) also led to the formation of two *syn*-isomers **3Fa/3Fb** with a selectivity toward the former, being similar to the case of runs 1 and 3, while the reaction was less decelerated. In contrast, the reaction of the same substrate under base-catalyzed conditions afforded *anti*-isomer **3Fc** as the minor product (run 12). Considering the relatively lower mass balance in run 12, side products might arise from the possible reactions of *n*BuLi with the ester substituent. Under direct reaction conditions, 1-octyne was also rapidly converted into **3Ga** and **3Gb** with a selectivity (run 13) that was similar to that of run 1. The observed decreased reaction time may reflect the increased reactivity of a more electron-rich alkyne with an alkyl substituent. Converting 1-octyne under base-catalyzed reaction conditions decreased the yield of *anti*-product **3Gc** (run 14). The presence of a slightly bulkier cyclohexyl ring decreased the reaction rate and reversed the selectivity toward the *syn*-isomers **3Ha/3Hb** (run 15). The corresponding base-catalyzed diboration (run 16) yielded trace amounts of *anti*-product **3Fc**. Considering the results of runs 14 and 16, the generation of the *anti*-isomer in the base-catalyzed reactions may be suppressed due to the lower acidity of the acetylenic proton. Therefore, the relative product ratios and reaction rates given in Table 2 were determined via the electronic and steric factors of the substituents on the alkyne substrate. It should be noted that all of the products listed in this table are not luminescent, although many examples of fluorescent β-diarylborylstyrene compounds can be found in the literature.[16,17]

Unsymmetrical diborane(4) **1** also reacted with internal alkynes, even though lower reaction rates were observed (Scheme 5). For example, the reaction of **1** with 4-propyne furnished tetrasubstituted *syn*-diboryl-alkyne **4** as the sole product in 82% yield. Diphenylacetylene did not react with **1**, while the use of 1-phenylpropyne generated an isomer mixture

Scheme 5. Reaction of 1 with Internal Alkynes (¹H NMR Yields in Parentheses)
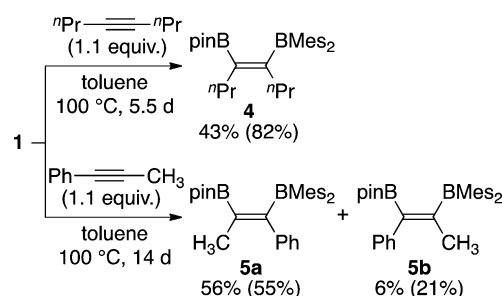
of **5a** and **5b**. The regiochemistry of the major product **5a** was unambiguously determined by single-crystal X-ray diffraction analysis.

Compounds **6(thf)₂** and **7(thf)₂** were isolated as two potential reaction intermediates for the base-catalyzed diboration (Scheme 6). Reaction of **1** with lithium phenylacetylide

Scheme 6. Synthesis and Reactivity of Intermediates 6(thf)₂ and 7(thf)₂ (¹H NMR Yields in Parentheses)
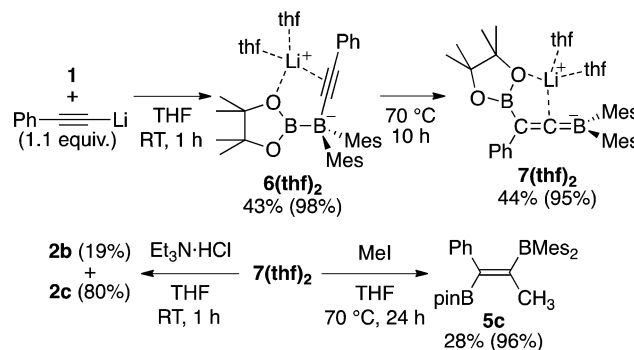
afforded sp^2–sp^3 diborane **6(thf)₂**. The ¹¹B NMR spectrum of **6(thf)₂** revealed resonances at δ_B −23 and 27 ppm, whereby the former suggests that the sp^3 borate structure is retained in solution. Single-crystal X-ray diffraction analysis of **6(thf)₂** showed an intramolecular coordination of the alkynyl π moiety and of one oxygen atom of the Bpin group to the Li^+ cation (Figure 1). The C≡C bond length [1.215(3) Å] of the alkynyl moiety was similar to that of the C≡C triple bond in phenylacetylene [1.2114(8) Å; electron diffraction at 319 K].[18] Despite the B−C bond formation and the presence of a negative charge on the boron center, the B−B bond in **6(thf)₂** [1.717(4) Å] was nearly identical to that of **1** [1.722(4) Å].[11] In the IR spectrum of **6(thf)₂**, characteristic C≡C vibrations (2101, 2120 cm⁻¹) were observed, which were confirmed by DFT calculations (for the calculated displacement vector, see Figure S118). Gentle heating (70 °C, 10 h) of **6(thf)₂** resulted in the formation of borataallene **7(thf)₂**, which was structurally characterized by single-crystal X-ray diffraction analysis (Figure 2).[19] In the crystalline state, **7(thf)₂** exhibits an orthogonal relationship between the B1 and C2 planes as confirmed by the torsion angle [C4−B1−C2−C5 = −87.7(3)]. The linear borataallene moiety exhibited a characteristic coordination mode to the Li^+ cation via the formally neutral central carbon atom. This result indicates that a significant negative charge is localized on the allenic carbon atom. Addition of $Et_3N·HCl$ to **7(thf)₂** furnished *syn*-product **2b** and *anti*-product **2c**, indicating that **7(thf)₂** should be the common intermediate
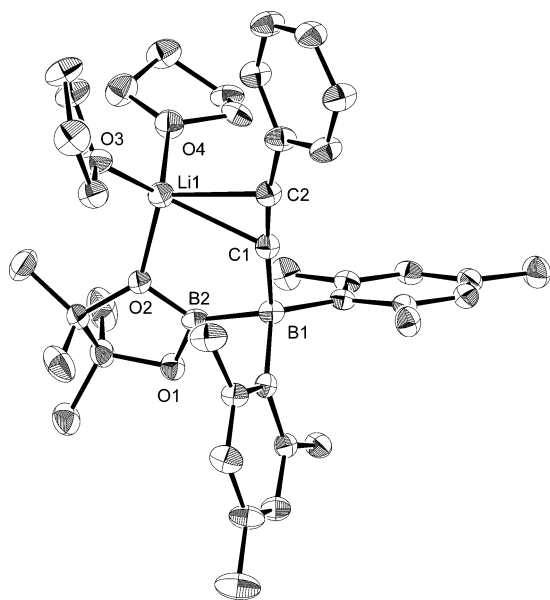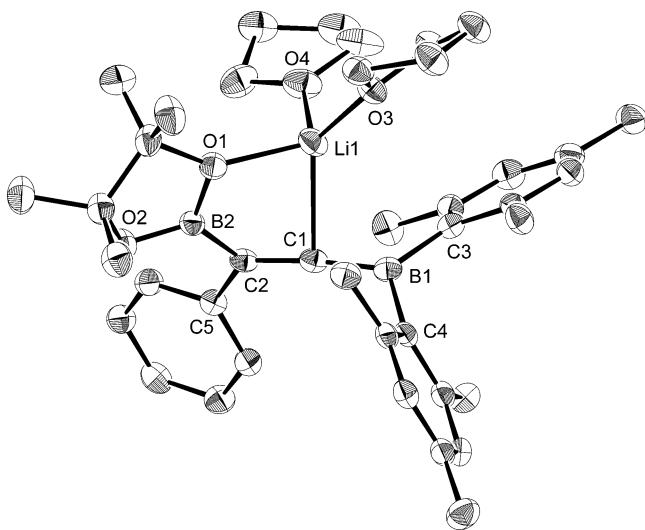
Figure 1. Molecular structure of $6(thf)_2$ (thermal ellipsoid at 50% probability; hydrogen atoms, minor parts of disordered moieties, and one cocrystallized molecule of THF are omitted for clarity). Selected bond distances (Å) and angles (deg): B1−B2 1.717(4), C1−C2 1.215(3), Li1−C1 2.414(5), Li1−C2 2.443(5), Li1−O2 1.912(4), Li1−O3 1.915(4), Li1−O4 1.948(5), C1−B1−B2 107.21(19), C2−C1−B1 173.8(2), O1−B2−B1 130.9(2), O1−B2−O2 108.6(2), O2−B2−B1 119.5(2).


Figure 2. Molecular structure of $7(thf)_2$ (thermal ellipsoid at 50% probability; hydrogen atoms, minor parts of disordered moieties, and one cocrystallized molecule of THF are omitted for clarity). Selected bond distances (Å) and angles (deg) and torsion angles (deg): B1−C1 1.435(4), C1−C2 1.340(4), C1−Li1 2.365(6), O1−Li1 2.056(6), O3−Li1 1.921(5), O4−Li1 1.965(5), B1−C1−C2 173.4(3), B1−C1−Li1 92.4(2), C1−C2−B2 118.9(2), O2−B2−O1 111.2(3), O2−B2−C2 126.1(3), O1−B2−C2 122.5(3), O1−Li1−C1 85.2(2), C4−B1−C2−C5 −87.7(3).

for formation of both isomers. $7(thf)_2$ also reacted with CH_3I to furnish *anti*-diborylalkene **5c** as the sole product. The high regioselectivity of the present reaction should be a result of the steric repulsion between CH_3I and the $Li(thf)_2$ moiety in $7(thf)_2$. Such a stoichiometric and stepwise conversion of phenylacetylene to **5c** would provide a complementary method

for the direct reaction of **1** with phenylacetylene to form **5a** and **5b**.

Based on the observed regioselectivity and the structure of the intermediates, we would like to propose the following mechanism (Scheme 7). In the absence of additives, phenyl-

**Scheme 7. Proposed Reaction Mechanism for the Direct and Base-Catalyzed Diboration of Phenylacetylene**
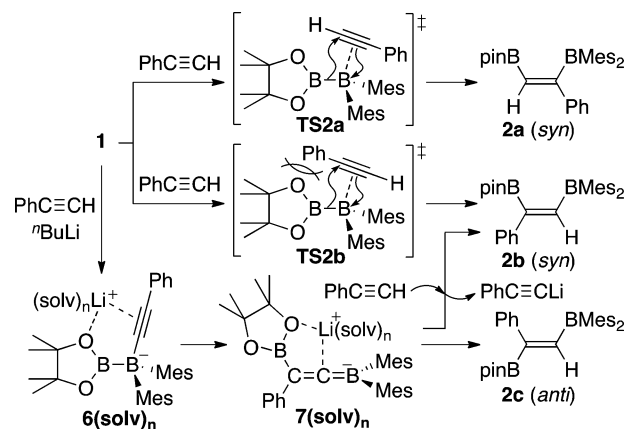
acetylene directly adds to **1** via two possible transition states (**TS2a** and **TS2b**) by coordination of the triple bond to the vacant p-orbital of the $BMes_2$ moiety.[20] The transition states should be characterized as a nucleophilic attack of the alkyne to the $BMes_2$ moiety. This characterization is consistent with the experimentally observed acceleration for electron-rich alkynes. The observed regioselectivity toward **2a** should arise from the steric repulsion between the pinB moiety and the alkyne substituents. The exact structures of these two transition states have not been determined yet so far. In the presence of ^nBuLi, the reaction between **1** and phenylacetylene should afford the sp^2−sp^3 diborane, $6(solv)_n$, which should furnish borataallene $7(solv)_n$ after B−B bond cleavage and pinB migration. Subsequently, the central carbon atom of $7(solv)_n$ should deprotonate phenylacetylene to form **2b** and **2c** under concomitant regeneration of PhC≡CLi. The isomer ratio between **2b** and **2c** would then be controlled by the characteristics of $7(solv)_n$, the reaction temperature, and the additive(s). Base-catalyzed reactions that afford mixtures of **2a**–**2c** may involve direct reaction pathways to form **2a** and **2b**. Further theoretical studies on possible pathways are currently ongoing. Their results, which should afford deeper insights into the detailed reaction mechanisms under different reaction conditions, will be reported in due course.

In the area of materials chemistry, molecules that contain intramolecular N-coordination of a heteroaromatic ring to a diarylboryl group have been widely used to construct π-functional molecules with low-lying LUMOs, which exhibit desirable photoelectronic properties.[21] For the application of nitrogen-coordinated sp^3 diarylboron compounds, two seminal discoveries have been reported. In 2000, Wang reported that hydroxyquinolinato-coordinated diarylboron compounds can be used as the light-emitting layer in OLEDs.[22] In 2006, Yamaguchi and Wakamiya used the intramolecular N-coordination of a thiazole ring to a diarylboryl unit to construct completely planar biaryl π-functional molecules with low-lying LUMOs for electron-transporting materials.[23] After these reports, many applications of compounds with intramolecular nitrogen-diarylboryl coordination have emerged.[24] The in-

troduction of a diarylboryl unit normally requires multiple steps such as lithiation of aryl bromides followed by reaction with diarylhaloboranes. Therefore, the development of synthetic improvements for the introduction of the diarylboryl unit should represent a significant advancement in the area of organomaterials chemistry.

Inspired by the reactivity of **1** toward triple bonds and its strong Lewis acidity, the present diboration was then applied to a short synthesis of fluorescent molecules possessing an intramolecular B−N coordination bond (Scheme 8). Reaction

Scheme 8. Two-Step Synthesis of the Fluorescent Molecules 11a,d
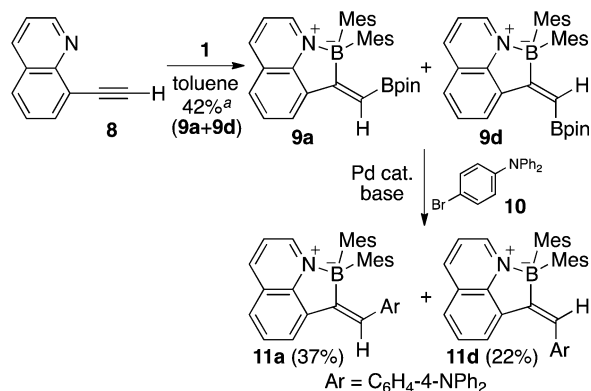
*a*Yield for isomer mixture.

of **1** with 8-ethynylquinoline (**8**) afforded an isomer mixture of diborylalkenes **9a,d**, which contained intramolecular N−BMes$_2$ bonds. The regioselectivity of the reaction that afforded *anti*-diborylalkene **9d**, in which the Bpin group is attached to the H-substituted carbon atom, was not observed in the previous section. Subsequently exposing a reaction mixture consisting of **9a,d** and **10** to Suzuki−Miyaura coupling conditions furnished **11a** (37%) and **11d** (22%).[25] The major isomer (**11a**) was structurally characterized by single-crystal X-ray diffraction analysis (Figure 3). The intramolecular Mes$_2$B−N coordination bond [1.717(3) Å] in **11a** was slightly longer than that of a similar B−N coordination bond in a three-carbon-containing
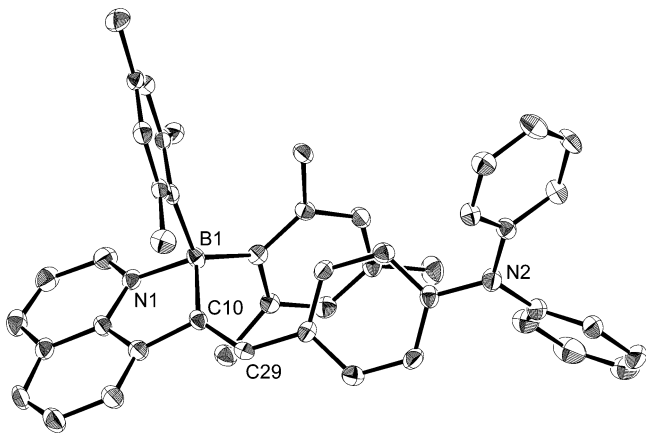
Figure 3. Molecular structure of **11a** (thermal ellipsoid at 50% probability; hydrogen atoms, and one cocrystallized molecule of C$_6$H$_6$ are omitted for clarity). Selected bond distances (Å) and angles (deg): N1−B1 1.717(3), C10−B1 1.651(4), C10−C29 1.357(3), C10−B1−N1 94.48(19), C29−C10−B1 133.8(2).

five-membered ring,[23,24e,f,l,o,q,26] probably due to the ring strain of the fused tricyclic system in **11a**. A similar structural characterization of **11d** by X-ray diffraction analysis was prevented by the isomerization of **11d** to **11a** upon recrystallization.

Compounds **11a** and **11d** absorb light in the visible region and exhibit fluorescence both in solution and in the solid state (Figures 4 and 5, Table 3). In the UV−vis spectrum, **11a**
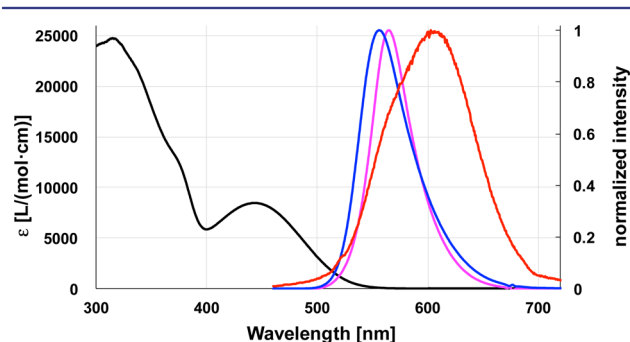
Figure 4. UV−vis absorption (black: toluene solution) and emission spectra of **11a** (excited at 450 nm; blue: from powder without benzene, purple: from crystal with benzene, red: from toluene solution).
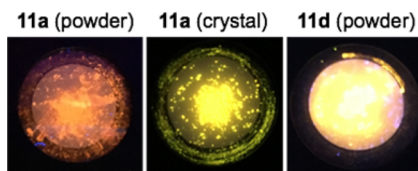
Figure 5. Pictures of solid samples of **11a** and **11d** under irradiation with UV light (365 nm).

Table 3. Photophysical Properties of 11a and 11d

	absorption		emission[d]		
compd (state)	λ_{abs}[c] (ε)		λ_{em}[c]	Φ	τ (ns)
11a (toluene)[a]	317(24700), 443 (8450)		603	0.065	1.7
11a (powder)	−		556	0.276	3.6
11a (crystal)[b]	−		565	0.578	7.2
11d (toluene)[a]	450 (3990)		610	0.041	1.7
11d (powder)	−		576	0.518	6.7

*a*Solution. *b*Cocrystallized with C$_6$H$_6$ (1 equiv). *c*In nm. *d*λ_{ex} = 450 nm.

showed two absorption maxima at 317 and 443 nm. The UV−vis spectrum of **11d** exhibited a similar profile with one absorption maximum at 450 nm, which exhibited a smaller molar absorption coefficient, although no absorption maximum was observed around 320 nm. Based on our TD-DFT calculations for **11a** and **11d**, which considered solvent effects for benzene, the maximum absorptions at longer wavelengths were assigned to the HOMO−LUMO transitions. The HOMO of **11a** mainly spreads over the [4-(diphenylamino)phenyl]-alkenyl moiety, while the LUMO is localized on the quinoline π-system (Figure 6; see SI for **11d**). The small orbital overlap between the HOMO and the LUMO should cause the relatively small molar absorption coefficient that is typically observed for the intramolecular charge transfer, while BODIPY dyes, in contrast, usually show very high ε values.[27] The difference in the observed molar absorption coefficients was
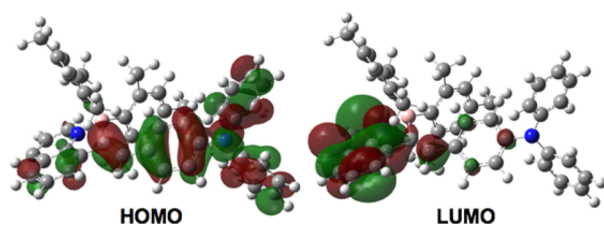
Figure 6. Frontier orbitals of **11a**.

also reproduced by our TD-DFT calculations, which showed different oscillator strengths. Similar emission maxima were observed for toluene solutions of **11a** (603 nm) and **11d** (610 nm), which is probably due to the same substituent set around the alkene moiety in these regioisomers. The emission from a powder sample of **11a** was stronger than that from its toluene solution, which was confirmed by the higher quantum yields. In the case of **11d**, the quantum yield was even higher than that of **11a** (0.518 for **11d**, 0.276 for **11a**). The suppression of nonradiative decay, probably due to a densely packed structure in the solid state, should contribute to the higher quantum yield, as we could confirm a longer fluorescence lifetime for the solid state compared to the toluene solutions. The wavelengths of the emission maxima from powder samples of **11a** (556 nm) and **11d** (576 nm) were shifted to lower wavenumbers, probably on account of the restricted rotation of the substituents, which may inhibit smooth relaxation to the lowest-excited state. It should be noted that the emission from crystalline **11a**, which contained a cocrystallized molecule of benzene, has a higher quantum yield (0.578). The exact reason for this phenomenon remains so far unclear.

CONCLUSION

In conclusion, we established a simple and versatile protocol for the preparation of diborylalkenes based on the reaction between unsymmetrical diborane(4), pinB-BMes$_2$, and a variety of alkynes. Considering the proposed mechanism, the present reaction may be regarded as a combination of (a) an electrophilic activation of alkynes with a Lewis acidic borane reagent[3] and (b) a nucleophilic borylation of alkynes by the pinB moiety of an sp^2–sp^3 diborane species.[4,6,28]

ASSOCIATED CONTENT

S **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03686.

 Experimental and computational details (PDF)
 Crystallographic data (CIF)
 Crystallographic data (CIF)
 DFT coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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