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A borylcopper species generated from bis(pinacolato)diboron and its additions to α,β-unsaturated carbonyl compounds and terminal alkynes

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Abstract

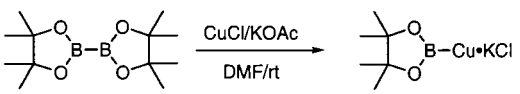
The addition of bis(pinacolato)diboron [$(Me_4C_2O_2)B–B(O_2C_2Me_4)$] to α,β-unsaturated carbonyl compounds giving β-boryl carbonyl compounds and the addition to terminal alkynes yielding either 2-boryl-1-alkenes or 1-boryl-1-alkenes were carried out in DMF at room temperature in the presence of CuCl and AcOK. The transmetalation between diboron and [Cu(Cl)OAc]K generating a borylcopper species was proposed as the key step in the reactions because CuOAc similarly mediated both addition reactions to enones and alkynes in the presence of LiCl. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diborons; Copper halides; Conjugate addition; Alkynes

1. Introduction

Tetra(alkoxo)diborons such as bis(catecholato)-diboron and bis(pinacolato)diboron are versatile reagents for borylation of unsaturated organic compounds and organic halides [1–4]. Diborons can be oxidatively added to a low-valent transition metal with B–B bond cleavage, thus allowing the catalyzed addition of diborons to unsaturated C–C bonds. Platinum(0) complexes have been shown to be the most efficient catalysts for such diboration of alkenes [5–7], alkynes [8–10], conjugate dienes [11,12], and enones [13,14]. The transmetalation of diboron to palladium(II) halides provides another convenient and direct method for borylation of organic halides and triflates. The cross-coupling reaction of diborons with aryl [15–17], 1-alkenyl [18], allyl [19,20], and benzyl [21] halides or triflates demonstrated the utility of diborons for the synthesis of variously functionalized organoboronic esters. The palladium complexes also catalyze the three-component assembling reaction of acyl chlorides, allenes, and diboron yielding 2-acylallylboronates [22]. The dehydrogenative coupling of diborons with alkanes or arenes with Rh or Ir catalysts is versatile as a method for direct functionalization of inactivated C–H bonds [23,24].

Here, we report the synthesis of a borylcopper species (**2**) from bis(pinacolato)diboron (**1**, pinB–Bpin) (Eq. (1)) and its addition to α,β-unsaturated ketones or esters and terminal alkynes (Eqs. (4) and (5)), and the coupling reaction with allyl chloride (Eq. (8)) [25]. These reactions were efficiently mediated by CuCl in the presence of AcOK at room temperature.



1 (pinB-Bpin) **2** (pinB[Cu]) (1)

The reaction may involve the transmetalation of **1** to CuCl giving a nucleophilic borylcopper species (**2**) as the key intermediate. The boryl nucleophile, which couples with MeI, RCOCl, and CF_3I, was first synthesized by the reaction of dialkylchloroborane R_2BCl with potassium metal yielding R_2BK or its amine complex $R_2BK{\cdot}NEt_3$ (Eq. (2)) [26]. These reactions suffered from poor reproducibility due to the lability of R_2BK; however, the present B–Cu species is stable at room

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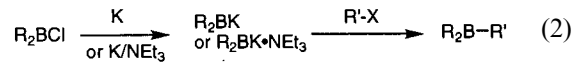
temperature and undergoes the addition and coupling reaction characteristic to copper compounds. On the other hand, the reduction of phosphine–monoiodoboranes with lithium 4,4′-di-*tert*-butylbiphenylide (LDBB) yields tricoordinate boron anions which are stable at −78°C [26] (Eq. (3)).



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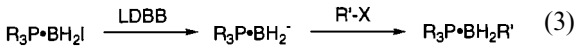
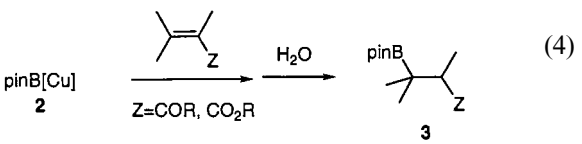


(3)

An analogous conjugate addition of **1** or bis(catecholato)diboron to enones catalyzed by CuOTf or $CuCl/Bu_3P$ was recently reported by Hosomi and coworkers [27]. Although mechanistic works are still in progress, their reactive intermediate carrying out the reaction for α,β-unsaturated ketones under neutral conditions may involve a different mechanism to that of generating borylcopper species. It has also been reported that $Pt(C_2H_4)(PPh_3)_2$ and $Pt(dba)_2$ catalyze the addition of diborons to α,β-unsaturated carbonyl compounds [13,14].

2. Results and discussion

2.1. Conjugate addition to α,β-unsaturated carbonyl compounds



(4)

Table 1
Conjugate 1,4-addition of diboron (**1**) to α,β-unsaturated carbonyl compounds [a]

Entry	Acceptor	Copper reagent	Yield (%) [b]
1	2-Cyclohexenone	CuCl	Trace
2	2-Cyclohexenone	CuCl–AcOK	67 [c]
3	2-Cycloheptenone	CuCl–AcOK	82
4	CH_2=$CHCOCH_3$	CuCl–AcOK	86[c]
5	CH_2=$CHCOCH_3$	CuCl–AcOK [d]	90
6 [e]	(*E*)-MeCH=CHCOPh	CuCl–AcOK [d]	81
7	CH_2=$CHCO_2Et$	CuCl–AcOK–LiCl	59
8 [e]	CH_2=$C(Me)CO_2Me$	CuCl–AcOK–LiCl	65
9 [e]	MeCH=$CHCO_2Et$	CuCl–AcOK–LiCl	54

[a] A mixture of an α,β-unsaturated ketone or ester (1.0 mmol), diboron **1** (1.1 mmol), CuCl (1.1 mmol), LiCl (1.1 mmol), and AcOK (1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h, unless otherwise noted.

[b] Isolated yields by chromatography over silica gel.

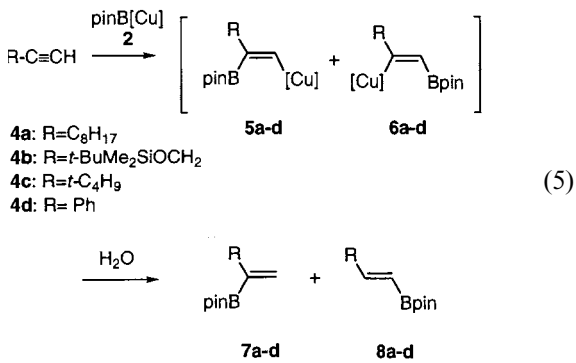
[c] GC yields.

[d] The catalyzed reaction in the presence of CuCl (0.1 mmol) and AcOK (0.1 mmol).

[e] The reaction was conducted at 50°C for 16 h.

The conjugate addition of **1** to the representative Michael acceptors (Eq. (4)) is summarized in Table 1. The addition of **1** to 2-cyclohexenone failed in the absence of either a copper(I) halide or a base (entry 1), but the yields were improved significantly by the addition of both CuCl and AcOK (entry 2). The effect of a base showed the following order of yields, suggesting the superiority of small, more basic potassium carboxylates. The following order of yields was obtained under the conditions of entry 2; CF_3COOK (trace) < PhCOOK (15%) < $Me_2CHCOOK$ (55%) < PhOK (54%) < CH_3COOK (67%). Various copper(I) halides or pseudohalides similarly accelerated the reaction in the presence of KOAc; for example, CuI (52%), CuBr (50%), and CuCl (67%), and CuCN (44%). The reaction was fast in polar solvents such as DMF (67%) and DMSO (55%), but it was very slow in THF (3%) and toluene (17%). The reaction smoothly proceeded catalytically (10 mol%) both for CuCl and KOAc, as was demonstrated with the addition to methyl vinyl ketone and (*E*)-1-phenyl-2-buten-1-one (entries 5 and 6). Under analogous reaction conditions used for enones, α,β-unsaturated esters afforded the corresponding products in moderate yields (entries 7–9). Like other related reactions mediated by copper(I) halides, the addition of LiCl (1 equivalent), as the ligand of the copper(I) species, improved the yields by 5–10% [28].

2.2. Addition to terminal alkynes



(5)

The results of the addition of **1** to terminal alkynes (Eq. (5)) are shown in Tables 2 and 3. The addition to 1-decyne **4a** afforded a mixture of internal **7a** and terminal addition product **8a** in a ratio of 91/9 in the presence of LiCl (Table 2, entry 2). The addition of a donating phosphine ligand such as PBu_3 and $P(i\text{-}Pr)_3$ effected to improve the terminal selectivity, yielding **8a** (entries 6 and 7), whereas all attempts at selective synthesis of **8a** were unsuccessful (entries 3–8). On the other hand, the regioselectivity was not affected by the bulkiness of potassium carboxylates (entries 9–11). The

Table 2
Addition of diboron (**1**) to 1-decyne (Eq. (5)) [a]

Entry	Copper precursor	Ligand	Yield (%) [b]	**7a**/**8a**
1	CuCl–AcOK	None	63	92/8
2	CuCl–AcOK	LiCl	90	91/9
3	CuCl–AcOK	Etpo [c]	64	83/17
4	CuCl–AcOK	$P(OPh)_3$	57	79/21
5	CuCl–AcOK	PPh_3	66	69/31
6	CuCl–AcOK	PBu_3	69	34/66
7	CuCl–AcOK	$P(i\text{-}Pr)_3$	66	31/69
8	CuCl–AcOK	$P(t\text{-}Bu)_3$	81	54/46
9	CuCl–i-$PrCO_2K$	LiCl	60	87/13
10	CuCl–t-$BuCO_2K$	LiCl	66	86/14
11	CuCl–$PhCO_2K$	LiCl	70	85/15

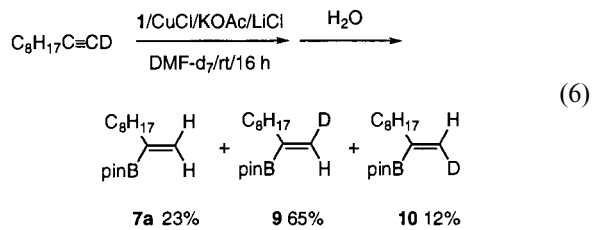
[a] A mixture of 1-decyne (1.0 mmol), diboron **1** (1.1 mmol), a copper precusor (1.1 mmol), additive (1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h.
[b] GC yields.
[c] $P(OCH_2)_3CCH_2CH_3$.

vinylcopper species is reported to be labile at room temperature and undergoes decomposition, leading to a homocoupling diene with retention of configuration at the olefinic double bond [29]; however, the formation of such dimers of **5a**/**6a** was not observed.

In contrast to the results of 1-decyne, the additions to 3-(*t*-butyl)dimethylsilyloxy (TBSO)-1-propyne (**4b**), *t*-butylethyne (**4c**), and phenylethyne (**4d**) resulted in poor regioselectivities when a combination of CuCl–KOAc–LiCl was used (entries 1, 5, and 10 in Table 3). However, the effects of phosphine ligands were significant in these three alkynes. $P(t\text{-}Bu)_3$ exhibited a high internal selectivity (91%) for **4b** (entry 4), which was comparable to that of **4a** in the presence of CuCl–KOAc–LiCl (entry 2 in Table 2). $P(i\text{-}Pr)_3$ and PBu_3 revealed a high terminal selectivity for **4c** and **4d** (entries 8 and 12). Although there were no clear correlations between phosphine ligands and regioselectivities, the internal selectivities observed in **4a** and **4b** may have a synthetic value because 2-borylalkenes are not available by conventional hydroboration of terminal alkynes [18,30]. The reaction can be applied to the borylation of other terminal alkynes, but no addition reaction was observed for heteroatom-substituted alkynes and internal alkynes such as ethoxyethyne, methylthioethyne, and 4-octyne.

The additions of alkyl- [31], silyl- [32], and stannylcuprates [33] to terminal alkynes alter the regioselectivity depending on the order of coordination and the elements on the copper metal center. Both lower-order and higher-order stannyl or alkyl cuprates such as $Me_3SnCu{\cdot}SMe_2$, $Me_3Sn(n\text{-}Bu)Cu(CN)Li_2$, $n\text{-}BuCu{\cdot}MgBr_2$, and $(n\text{-}Bu)_2CuLi$ selectively afford the internal products, whereas $(PhMe_2Si)_2Cu(CN)Li_2$ yields the terminal addition products for aliphatic terminal alkynes. The origin of regioselectivity is not well understood, but the copper atom, in general, adds to the least-hindered and more-electron-rich carbon [28]. The present results suggest the generation of an analogous copper species, that exhibits internal selectivity for less-hindered terminal alkynes (**4a** and **4b**) and terminal selectivity for hindered alkynes (**4c** and **4d**).

Alkylation of the vinylcopper intermediates (**5**/**6**) would provide further functionalized vinylboron compounds. However, alkylation of **5a**/**6a** with benzyl bromide, trimethylsilyl chloride, or allyl chloride failed to yield coupling products. Treatment of the reaction mixture with D_2O indeed resulted in no deuterium incorporation in **7a**, indicating that the vinylcopper species was not present in the solution. Thus, the protonolysis of **5**/**6** occurs in competition with the addition reaction to alkynes.



(6)

The addition to 1-d-1-decyne gave a complex mixture of an unlabeled isomer **7a** (23%) and two mono-deuterium isomers **9** and **10** (65 and 12%) (Eq. (6)). The addition of **2** to the triple bond may proceed through a *cis*-insertion, similar to related addition reactions such as carbo-, silyl-, and stannylcupration of alkynes [31–33]. The reaction indeed gave a *cis*-insertion product (**9**)

Table 3
Addition of diboron (**1**) to $TBSOCH_2$-, *t*-butyl-, and phenylethyne (Eq. (5)) [a]

Entry	Alkyne (R =)	Copper reagent	Yield (%) [b]	**7**/**8**
1	$TBSOCH_2$	CuCl–KOAc–LiCl	77	50/50
2	$TBSOCH_2$	CuCl–KOAc–PBu_3	66	63/37
3	$TBSOCH_2$	CuCl–KOAc–$P(i\text{-}Pr)_3$	67	71/29
4	$TBSOCH_2$	CuCl–KOAc–$P(t\text{-}Bu)_3$	62	91/9
5	*t*-Bu	CuCl–KOAc–LiCl	45	43/57
6 [c]	*t*-Bu	CuCl–KOAc–LiCl	64	49/51
7 [c]	*t*-Bu	CuCl–KOAc–PBu_3	45	15/85
8	*t*-Bu	CuCl–KOAc–$P(i\text{-}Pr)_3$	54	9/91
9	*t*-Bu	CuCl–KOAc–$P(t\text{-}Bu)_3$	40	24/76
10	Ph	CuCl–KOAc–LiCl	38	38/62
11	Ph	CuCl–KOAc–PBu_3	56	1/99
12[c]	Ph	CuCl–KOAc–PBu_3	65	6/94
13	Ph	CuCl–KOAc–$P(i\text{-}Pr)_3$	45	16/84
14	Ph	CuCl–KOAc–$P(t\text{-}Bu)_3$	80	28/72

[a] A mixture of alkyne (1.0 mmol), diboron **1** (1.1 mmol), CuCl (1.1 mmol), KOAc (1.1 mmol), and additional ligand (if used, 1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h, unless otherwise noted.
[b] GC yields.
[c] At 50°C for 16 h.

Table 4
Addition reactions of diboron (**1**) mediated by CuOAc [a]

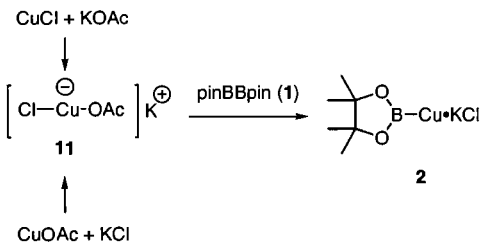
Entry	Substrate	Copper reagent	Yield (%) [b]
1	2-Cyclohexenone	CuOAc	9
2	2-Cyclohexenone	CuOAc–LiCl	46
3	2-Cyclohexenone	CuOAc–LiCl [c]	51
4	1-Decyne	CuOAc	7 (80/20) [d]
5	1-Decyne	CuOAc–LiCl	70 (86/14) [d]

[a] A mixture of 2-cyclohexenone or 1-decyne (1.0 mmol), diboron **1** (1.1 mmol), CuOAc (1.1 mmol), and LiCl (if used, 1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h.
[b] GC yields.
[c] A catalyzed reaction in the presence of 10 mol% of CuOAc and LiCl.
[d] Ratio of **7a**/**8a**.

predominantly. However, the mechanism of the C–Cu bond protonolysis and the source of protons are not obvious from these results. The protons are not derived from the acetylenic hydrogen or the solvent because no di-deuterium isomer was observed in the reaction mixture of Eq. (6) and an analogous reaction of 1-decyne in DMF-d_7 resulted in no deuterium incorporation.

2.3. Reaction mechanism

The reaction of CuCl with KOAc in DMF generates [Cu(Cl)OAc]K (**11**), which was suggested by an analogous reaction mediated by CuOAc in the presence of KCl (Table 4 and Eq. (7)).

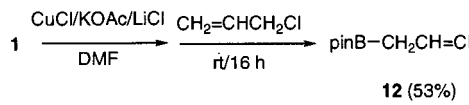


(7)

The additions of **1** to 2-cyclohexenone and 1-decyne with CuOAc failed (entries 1 and 4), but the same reaction in the presence of 1 equivalent of LiCl afforded comparable results to that of a CuCl–KOAc combination (entries 2, 3, and 5). Thus, addition of KOAc to CuCl generates **11** as an active species for transmetalation with diboron.

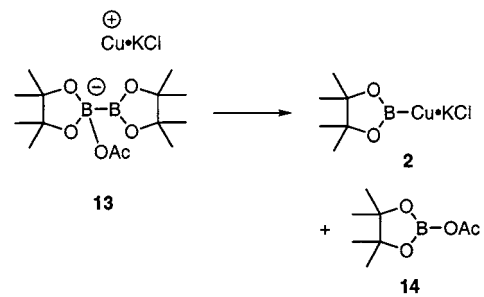
A ^{1}H-NMR study revealed the generation of a new species when **11** was treated with **1** in DMF-d_7. Addition of **1** to a mixture of CuCl–KOAc at room temperature resulted in the formation of a new signal at 1.19 ppm as well as the original signal at 1.21 ppm (singlet, four methyl of **1**). The former signal slowly increased from 9% (30 min) to 99% (8 h) by standing at room temperature. The same signal at 1.19 ppm was also observed as the major product when **1** was added to CuOAc in DMF-d_7. To gain an insight into the B–B bond cleavage, samples were withdrawn at hourly intervals from a reaction mixture of **1**, CuCl, and KOAc in DMF and then hydrolyzed with water. Judging from the recovery of **1**, the reaction between **1** and **11** was completed within 8 h, presumably, via transmetalation involving B–B bond cleavage. The diboron recovered was 70% (30 min), 26% (3 h), and <4% (8 h). On the other hand, **1** remained intact for 16 h in the absence of either CuCl or KOAc. The results are in stark contrast to the similar addition reactions of diborons to enones catalyzed by CuOTf or CuCl/PBu_3 because these catalysts do not cleave the B–B bond in the absence of substrates [27].

Indirect evidence of the formation of a borylcopper species was also obtained by trapping the intermediate with allyl chloride. Analysis of the reaction mixture revealed the formation of allylboronate **12** (53%) (Eq. (8)).



(8)

A possible mechanism that might account for the additions to both enones and alkynes, the coupling with allyl chloride, and the B–B bond cleavage by [Cu(Cl)OAc]K **11** is one proceeding through a free borylcopper species (**2**) which could be generated by the equilibrium dissociation from a boron ate–complex (**13**) (Eq. (9)). Such complexation prior to transmetalation might be a crucial steps in essentially all ionic reactions of organoboron compounds because of their highly electrophilic but weakly nucleophilic natures [34]. As a result of complex formation, the transfer of an activated boryl group to the copper center will then follow [35]. Results of the study on the B–B bond cleavages by NMR and the recovery of **1** at hourly intervals suggested that the transmetalation to yield **2** is slow, taking about 8 h at room temperature.



(9)

In summary, the generation of nucleophilic borylcopper species from diboron **1** provides a new access to β-boryl carbonyl compounds and alkenylboronates. Because of the simple experimental procedure using CuCl and KOAc in DMF, we anticipate further applications of the reagent **2** for the synthesis of boron compounds.

3. Experimental

3.1. Materials and reagents

Bis(pinacolato)diboron [36], 3-[(*tert*-butyldimethylsilyl)oxy]-1-propyne [37], and 1-deuterio-1-decyne [38] were synthesized by the reported procedures. Potassium pivalate was prepared by the reaction of pivalic acid with a molar amount of aqueous KOH in methanol. Other materials and reagents are commercial products.

3.2. General procedure for conjugate addition of diboron to α,β-unsaturated carbonyl compounds (Table 1)

A 25 ml flask equipped with a magnetic stirring bar, a septum inlet, a reflux condenser, and a nitrogen bubbler was charged with CuCl (1.1 mmol) and LiCl (if used, 1.1 mmol). The flask was flushed with nitrogen and then DMF (6 ml) was added. After being stirred at room temperature for 1 h, diboron **1** (1.1 mmol), KOAc (1.1 mmol), and an α,β-unsaturated carbonyl compound (1.0 mmol) were added successively. The mixture was stirred at room temperature or at 50°C for 16 h and then treated with water at room temperature. The product was extracted with benzene, washed with water to remove DMF, and dried over $MgSO_4$. Analytically pure product was isolated by column chromatography over silica gel.

A catalyzed reaction was carried out by using of CuCl (0.1 mmol) and KOAc (0.1 mmol).

The following compounds were prepared by the above general procedure.

3.2.1. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-cyclohexanone

IR (neat) 1710 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 12H), 1.42–1.50 (m, 1H), 1.58–1.67 (m, 1H), 1.69–1.80 (m, 1H), 1.85–1.90 (m, 1H), 2.03–2.11 (m, 1H), 2.25–2.40 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.7, 24.7, 26.5, 28.4, 41.9, 42.6, 83.5, 212.3; MS (ITD) *m*/*e* 83 (100), 110 (78), 129 (52), 153 (37), 166 (99), 181 (24), 196 (28), 209 (32), 224 ([M^+], 64); exact mass Found: 224.1583; $C_{12}H_{21}BO_3$ Calc.: 224.1584.

3.2.2. 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-cycloheptanone

IR (Nujol) 1710 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 12H), 1.27–1.32 (m, 1H), 1.41–1.53 (m, 2H), 1.55–1.65 (m, 1H), 1.77–1.85 (m, 1H), 1.89–1.98 (m, 2H), 2.45–2.57 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.3, 24.7, 24.8, 31.1, 31.9, 43.8, 44.9, 83.5, 215.5; MS (ITD) *m*/*e* 83 (35), 152 (25), 165 (10), 180 (100), 195 (6), 223 (5), 238 ([M^+], 14); exact mass Found: 238.1737; $C_{13}H_{23}BO_3$ Calc.: 238.1740.

3.2.3. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butanone

IR (neat) 1720 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.91 (t, 2H, $J = 7.1$ Hz), 1.24 (s, 6H), 1.24 (s, 6H), 2.13 (s, 3H), 2.59 (t, 2H, $J = 7.1$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.7, 29.3, 38.4, 83.1, 209.2; MS (ITD) *m*/*e* 43 (31), 55 (30), 83 (26), 99 (20), 112 (16), 140 (100), 183 (13), 198 ([M^+], 2); exact mass Found: 198.1427; $C_{10}H_{19}BO_3$ Calc. 198.1427.

3.2.4. 1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butanone

IR (neat) 1690 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.06 (d, 3H, $J = 7.3$ Hz), 1.25 (s, 6H), 1.26 (s, 6H), 1.38–1.49 (m, 1H), 3.12 (d, 2H, $J = 6.8$ Hz), 7.44 (t, 2H, $J = 7.3$ Hz), 7.54 (tt, 1H, $J = 7.3$ and 2.0 Hz), 7.96 (d, 2H, $J = 7.3$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.1, 24.7, 24.7, 42.9, 83.0, 128.0, 128.4, 132.7, 137.1, 200.2; MS (ITD) *m*/*e* 84 (33), 105 (100), 120 (48), 130 (56), 174 (29), 191 (26), 216 (73), 259 (16), 274 ([M^+], 7); exact mass Found: 274.1735; $C_{16}H_{23}BO_3$ Calc.: 274.1740.

3.2.5. Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propionate

IR (neat) 1740, 1210, 1160 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.02 (t, 2H, $J = 7.6$ Hz), 1.23–1.26 (m, 15H), 2.43 (t, 2H, $J = 7.6$ Hz), 4.12 (q, 2H, $J = 7.1$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.2, 24.7, 28.8, 60.2, 83.1, 174.7; MS (ITD) *m*/*e* 83 (41), 142 (37), 170 (100), 183 (15), 213 ([M^+-CH_3], 10); exact mass Found: 213.1294; $C_{10}H_{18}BO_4$ ([M^+-CH_3]) Calc: 213.1298.

3.2.6. Methyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propionate

IR (neat) 1740, 1210, 1150 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (dd, 1H, $J = 15.9$ and 7.1 Hz), 1.12 (dd, 1H, $J = 15.9$ and 7.6 Hz), 1.20 (d, 3H, $J = 7.1$ Hz), 1.24 (s, 6H), 1.24 (s, 6H), 2.64–2.73 (m, 1H), 3.66 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.4, 24.7, 24.8, 35.3, 51.5, 83.1, 177.7; MS (ITD) *m*/*e* 69 (14), 83 (26), 127 (16), 155 (9), 170 (100), 197 (5), 213 ([M^+-CH_3], 7); exact mass Found: 213.1290; $C_{10}H_{18}BO_4$ ([M^+-CH_3]) Calc.: 213.1298.

3.2.7. Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyrate

IR (neat) 1730, 1200, 1140 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.00 (d, 3H, $J = 7.3$ Hz), 1.23–1.26 (m, 15H), 1.33–1.42 (m, 1H), 2.36 (dd, 1H, $J = 16.3$ and 6.6 Hz), 2.43 (dd, 1H, $J = 16.3$ and 7.6 Hz), 4.12 (q, 2H, $J = 7.1$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.3, 15.0, 24.6, 24.7, 37.7, 60.1, 83.1, 173.9; MS (ITD) *m*/*e* 83 (80), 114 (35), 142 (44), 184 (100), 197 (19), 227 (19), 242 ([M^+], 5); exact mass Found: 242.1692; $C_{12}H_{23}BO_4$ Calc.: 242.1689.

3.3. General procedure for addition of diboron to terminal alkynes (Tables 2 and 3)

CuCl (1.1 mmol) was added to a 25 ml flask equipped with a magnetic stirring bar, a septum inlet, a reflux condenser, and a nitrogen bubbler. The flask was flushed with nitrogen and then charged with DMF (6 ml) and a ligand (if used, 1.1 mmol). After being stirred at room temperature for 1 h, diboron 1 (1.1 mmol), a base (1.1 mmol), and an alkyne (1.0 mmol) were added successively. The mixture was stirred at room temperature or at 50°C for 16 h and then treated with water at room temperature. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. Column chromatography over silica gel gave analytically pure product. GC yields determined by using an appropriate internal standard are shown in Tables 2 and 3.

The following compounds were prepared by the above general procedure.

3.3.1. 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decene

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.24–1.42 (m, 24H), 2.13 (t, 2H, $J = 7.6$ Hz), 5.59 (s, 1H), 5.75 (d, 1H, $J = 3.4$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 29.2, 29.3, 29.5, 31.9, 35.3, 83.3, 128.7; MS (ITD) m/e 84 (100), 101 (41), 138 (66), 153 (40), 209 (24), 251 (19), 266 ([M^+], 15); exact mass Found: 266.2430; $C_{16}H_{31}BO_2$ Calc.: 266.2417.

3.3.2. 3-[(tert-Butyldimethylsilyl)oxy]-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.92 (s, 9H), 1.26 (s, 12H), 4.28 (s, 2H), 5.88 (t, 1H, $J = 2.0$ Hz) 5.96 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ −5.34, 24.7, 25.9, 27.1, 29.1, 64.5, 83.3, 127.1; MS (ITD) m/e 83 (48), 99 (25), 101 (21), 141 (100), 241 (50), 283 ([M^+-CH_3], 7); exact mass Found: 283.1893; $C_{14}H_{28}BO_3Si$ ([$M^+ - CH_3$]) Calc.: 283.1901.

3.3.3. (E)-3,3-Dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 9H), 1.28 (s, 12H), 5.35 (d, 1H, $J = 18.3$ Hz), 6.64 (d, 1H, $J = 18.3$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.8, 28.8, 29.5, 35.0, 83.0, 164.4; MS (ITD) m/e 84 (100), 101 (47), 138 (63), 153 (52), 195 (16), 209 ([M^+-H], 27); exact mass Found: 209.1712; $C_{12}H_{22}BO_2$ ([M^+-H]) Calc.: 209.1713.

3.3.4. (E)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 12H), 6.17 (d, 1H, $J = 18.5$ Hz), 7.26–7.36 (m, 3H), 7.40 (d, 1H, $J = 18.3$ Hz), 7.49 (d, 2H, $J = 6.8$ Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.8, 83.4, 127.1, 128.6, 128.9, 137.4, 149.5; MS (ITD) m/e 105 (25), 130 (100), 144 (92), 157 (22), 172 (22), 187 (18), 215 (30), 230 ([M^+], 79); exact mass Found: 230.1470; $C_{14}H_{19}BO_2$ Calc.: 230.1478.

3.4. Addition of diboron to 1-deuterio-1-decyne (Eq. 6)

An addition of diboron **1** (1.1 mmol) to 1-deuterio-1-decyne (1.0 mmol) was carried out in the presence of CuCl (1.1 mmol), LiCl (1.1 mmol), and KOAc (1.1 mmol) in DMF (6 ml) at room temperature for 16 h. The resulting mixture was treated by the usual manner shown in Section 3.3. Isolation by column chromatography over silica gel gave 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decene ($D = 77\%$, $Z{:}E = 84{:}16$). Spectral data of (*Z*)-1-deuterio-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decene are as follows: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.7$ Hz), 1.24-1.42 (m, 24H), 2.13 (t, 2H, $J = 7.4$ Hz), 5.73 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.7, 29.2, 29.3, 29.5, 31.9, 35.3, 83.2, 128.3 (t, $J = 23.2$ Hz); MS (ITD) m/e 84 (100), 101 (36), 139 (39), 210 (16), 252 (11), 267 ([M^+], 13); exact mass calcd for $C_{16}H_{30}DBO_2$ 267.2479, found 267.2481.

3.5. Addition of diboron to 2-cyclohexenone and 1-decyne mediated by CuOAc (Table 4 and Eq. (7))

A mixture of 2-cyclohexenone or 1-decyne (1.0 mmol), diboron **1** (1.1 mmol), CuOAc (1.1 mmol), and LiCl (if used, 1.1 mmol) in DMF was stirred at room temperature for 16 h and then treated with water. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. GC yields are summarized in Table 4. A catalyzed reaction was carried out in the presence of 0.1 mmol of CuOAc and LiCl.

3.6. Reaction of diboron with CuCl and KOAc (Eq. (7))

An NMR tube was charged with diboron **1** (0.01 mmol), CuCl (0.01 mmol), KOAc (0.01 mmol), and DMF-d_7 (0.75 ml). The mixture was stirred at room temperature by occasional shaking. The progress of the reaction was monitored on ^{1}H-NMR by measuring a ratio of integrals for a new singlet at 1.19 ppm and that at 1.21 ppm (four methyl groups in **1**). The ratios of integrals at specific intervals are as follows: 9:91 (0.5 h), 32:68 (3 h), and 99:1 (8 h). The new signal at 1.19 is assigned to be either of four methyl groups of **2** or acetoxypinacholborane.

A mixture of diboron **1** (1.0 mmol), CuCl (1.1 mmol), KOAc (1.1 mmol), and DMF (6 ml) was stirred at room temperature. At suitable time intervals, portions of solution were sampled with a syringe (ca. 0.5

ml) and poured into a stirred mixture of benzene and water. The recoveries of **1** determined by GC at specific intervals are as follows: 70% (0.5 h), 26% (3 h), and 4% (8 h).

3.7. Coupling of diboron with allyl chloride (Eq. (8))

In a 25 ml flask equipped with a magnetic stirring bar, a septum inlet, a reflux condenser, and a nitrogen bubbler were placed CuCl (1.1 mmol) and LiCl (1.1 mmol). The flask was flushed with nitrogen and then charged with DMF (6 ml). After being stirred at room temperature for 1 h, diboron **1** (1.1 mmol), KOAc (1.1 mmol), and allyl chloride (1.0 mmol) were added successively. The mixture was stirred at room temperature for 16 h. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. GC analysis revealed a formation of 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene in 53% yield. Kugelrohr distillation at 60°C (30 mmHg) gave analytically pure product: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 12H), 1.73 (d, 2H, $J = 7.3$ Hz), 4.93 (ddt, 1H, $J = 10.1$, 2.1, and 1.3 Hz), 5.01 (ddt, 1H, $J = 17.1$, 1.8, and 1.8 Hz), 5.87 (ddt, 1H, $J = 17.2$, 9.9, and 7.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 24.8, 83.3, 114.9, 134.1; MS (ITD) m/e 57 (100), 67 (21), 85 (94), 101 (10), 109 (16), 125 (24), 140 (10), 153 (25), 168 ([M^+], 21); exact mass Found: 168.1294; $C_9H_{17}BO_2$ Calc.: 168.1321.

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