Hydroboration

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Copper-Catalyzed Triboration: Straightforward, Atom-Economical Synthesis of 1,1,1-Triborylalkanes from Terminal Alkynes and HBpin

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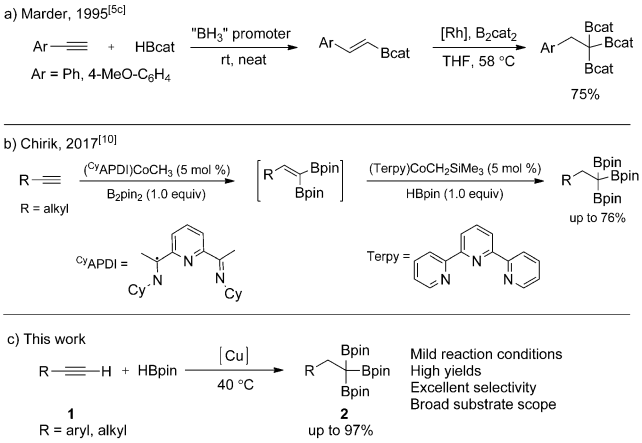
Abstract: *A convenient and efficient one-step synthesis of 1,1,1-triborylalkanes was achieved via sequential dehydrogenative borylation and double hydroborations of terminal alkynes with HBpin (HBpin = pinacolborane) catalyzed by inexpensive and readily available $Cu(OAc)_2$. This process proceeds under mild conditions, furnishing 1,1,1-tris(boronates) with wide substrate scope, excellent selectivity, and good functional-group tolerance, and is applicable to gram-scale synthesis without loss of yield. The 1,1,1-triborylalkanes can be used in the preparation of α-vinylboronates and borylated cyclic compounds, which are valuable but previously rare compounds. Different alkyl groups can be introduced stepwise via base-mediated deborylative alkylation to produce racemic tertiary alkyl boronates, which can be readily transformed into useful tertiary alcohols.*

Organoboron compounds have become, without doubt, among the most useful species in organic chemistry due to their ease of preparation and widespread application in synthesis, pharmaceuticals, and functional materials.[1] Multiborylated compounds are important in modern organic chemistry due to their various roles such as bioactive agents and synthetic building blocks.[2] Monoboronates[3] and *gem*-bisboronates[4] have been increasingly applied in organic synthesis. In contrast, 1,1,1-triboronate analogues are relatively rare, but are very interesting due to their documented reactivity arising from the stabilization of a carbanion center by the α-boronate moieties.[5] Thus, efficient methods for their synthesis are desirable, but few are currently available. A triboration of chloroform using $(RO)_2BCl$ and six equivalents of lithium metal at low temperature was developed by Matteson and co-workers.[5a,b] Mita, Sato et al. reported an Ir-catalyzed, pyridine-directed triple $C(sp^3)$–H boration of 2-ethylpyridines at 150 °C; however, good yields and selectivity resulted only when small, electron-donating substituents were present on the pyridine rings.[6] Chirik and co-workers have reported a Ni-catalyzed preparation of benzyltriboronates via triboration of benzylic C–H bonds; however, although the selectivity and yields were high, the substrate scope was quite limited.[7,8] The Huang group synthesized 1,1,1-triborylalkanes from alkenes via a Co-catalyzed double dehydrogenative borylation/hydroboration sequence, but unactivated alkenes were not suitable substrates.[9]

Terminal alkynes are very useful reagents in the synthesis of diverse organoboron compounds.[5d,11] In 1995, our group reported a Rh-catalyzed 1,1-diboration of (*E*)-styrylboronates prepared via hydroboration of the corresponding ethynylarenes with HBcat (HBcat = catecholborane; Scheme 1a), which yielded predominantly 1,1,1-triborona-



Scheme 1. Methods for the synthesis of 1,1,1-tris(boronates) from alkynes.

tes.[5c,12] In 2017, Chirik et al. achieved the synthesis of 1,1,1-triboronates via Co-catalyzed 1,1-diboration of terminal alkynes with B_2pin_2 (Scheme 1b), which underwent subsequent hydroboration with HBpin. Two different types of cobalt catalysts were used in this two-step sequence (Scheme 1b).[10] All of these methods, though useful, suffer from major or minor drawbacks, such as weak functional-group tolerance, expensive catalysts, or tedious procedures. Herein, we report a straightforward atom-economical synthesis of diverse 1,1,1-triborylalkanes from easily available and low-cost catalysts and starting materials under mild conditions (Scheme 1c).

Our investigation began with the triboration of phenylacetylene (**1a**) with HBpin in the presence of 10 mol% $Cu(OAc)_2$, 20 mol% PCy_3, and stoichiometric KF in toluene at 80 °C (Table 1, entry 1), giving the desired product **2a** in 78% yield. The effect of ligand was investigated (Table 1,

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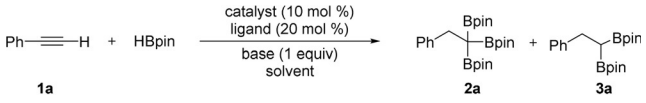
Table 1: Optimization of reaction conditions.[a]



Entry	Catalyst	Ligand	Base	Temp. (°C)	Yield **2a** (%)[b]	Yield **3a** (%)[b]
1	$Cu(OAc)_2$	PCy_3	KF	80	78	9
2	$Cu(OAc)_2$	PPh_3	KF	80	23	4
3	$Cu(OAc)_2$	P^tBu_3	KF	80	21	54
4	$Cu(OAc)_2$	P^nBu_3	KF	80	89 (84)	1
5	$Cu(OAc)_2$	–	KF	80	0	0
6	CuOAc	P^nBu_3	KF	80	80	4
7	$Cu(acac)_2$	P^nBu_3	KF	80	16	8
8	–	P^nBu_3	KF	40	0	0
9	$Cu(OAc)_2$	P^nBu_3	–	80	trace	trace
10	$Cu(OAc)_2$	P^nBu_3	KOAc	80	84 (78)	3
11	$Cu(OAc)_2$	P^nBu_3	K_2CO_3	80	71	6
12	$Cu(OAc)_2$	P^nBu_3	KOPiv	80	85 (80)	3
13	$Cu(OAc)_2$	P^nBu_3	Li_2CO_3	80	82 (75)	5
14	$Cu(OAc)_2$	P^nBu_3	KO^tBu	80	15	35
15	$Cu(OAc)_2$	P^nBu_3	DABCO	80	40	11
16	$Cu(OAc)_2$	P^nBu_3	KF	100	66	6
17	$Cu(OAc)_2$	P^nBu_3	KF	60	81	3
18	$Cu(OAc)_2$	P^nBu_3	KF	40	97 (93)	3
19[c]	$Cu(OAc)_2$	P^nBu_3	KF	40	62	10
20	$Cu(OAc)_2$	P^nBu_3	KF	r.t	58	3

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), catalyst (10 mol%), ligand (20 mol%), base (1 equiv), HBpin (4 equiv), toluene (0.25 mL), 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. [c] Using "standard conditions" except HBpin (3 equiv). Yields of isolated product are given in parentheses. acac = acetylacetonate, DABCO = 1,4-diazabicyclo[2.2.2]octane, Piv = pivalate.

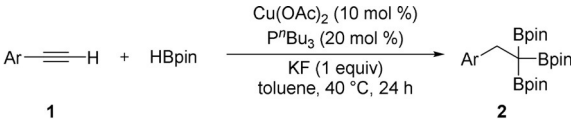
entries 1–4), and P^nBu_3 was found to be optimal compared to PCy_3, PPh_3, and P^tBu_3. In the presence of nitrogen ligands, no desired product was obtained (Table S1 in the Supporting Information), and there was no reaction in the absence of a ligand (Table 1, entry 5).

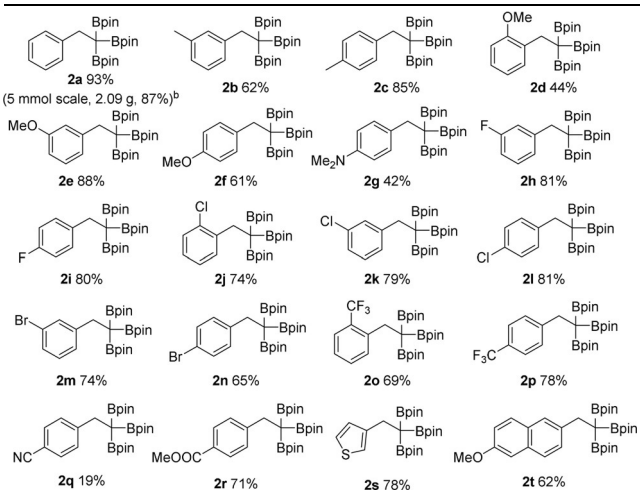
The influence of the copper precursor was studied (Table 1, entries 6–8 and Table S2), and copper(I) acetate (Table 1, entry 6) appeared to be slightly less effective than copper(II) acetate, but the difference is probably within experimental error ($85 \pm 5\%$). When $Cu(acac)_2$ (Table 1, entry 7) was used, the desired product was afforded in only 16% yield. Other copper sources such as $CuCl_2$, CuCl, and $Cu(OTf)_2$ (Table S2, entries 1–3) were also examined, but unfortunately, no desired product was detected. In the absence of a copper source, the reaction did not occur (Table 1, entry 8).

When KF was omitted from the reaction mixture, trace amounts of the 1,1,1-tris(boronates) were formed (Table 1, entries 9). Much lower yields were obtained when the KF loading was reduced to 20 mol% and 50 mol% (31% and 58% yield, respectively; Table S6, entries 1 and 2), which indicated that KF possibly promotes this transformation. Then, a series of bases (Table 1, entries 10–15) were evaluated, with KOAc, K_2CO_3, KOPiv, and Li_2CO_3 being slightly less effective than KF. Remarkably, as illustrated in entries 16–19, the desired product can be obtained in up to 97% yield at 40°C, while either higher or lower temperatures gave inferior results.

With optimized reaction conditions identified, we examined the scope of this novel Cu-catalyzed triboration reaction (Table 2). Generally, a wide range of both donor- and acceptor-substituted aromatic alkynes were found to work well, providing the corresponding 1,1,1-triborylated alkanes in moderate to good yields (**2a**–**2t**). Substrates containing electron-donating substituents, such as methyl (**2b**/**2c**), methoxy (**2d**/**2e**/**2f**), and dimethylamino (**2g**) groups, afforded the corresponding products in moderate to good yields of isolated product, ranging from 42% to 88%. This catalytic system was also efficient for substrates containing electron-withdrawing groups (up to 81% isolated yield), such as F (**2h**/**2i**), Cl (**2j**/**2k**/**2l**), Br (**2m**/**2n**), CF_3 (**2o**/**2p**), CN (**2q**), and CO_2Me (**2r**). It should be noted that reaction of haloaryl-substituted alkynes (**2h**–**2n**) occurred selectively to form the desired products, and no C–X (X = F, Cl, Br) bond boration was detected, thus opening the door for further functionalization. Furthermore, heteroaromatic and polyaromatic substrates, for example, thienyl-substituted (**2s**) and naphthyl-substituted (**2t**) acetylenes, are suitable substrates for this sequential dehydrogenative borylation/double hydroboration reaction (78% and 62% yield, respectively). This method enables convenient gram-scale synthesis (5 mmol) without significant loss of yield, as demonstrated for **1a** (**2a**: 2.09 g, 87%).

Table 2: Substrate scope for the Cu-catalyzed triboration of aromatic alkynes.[a]

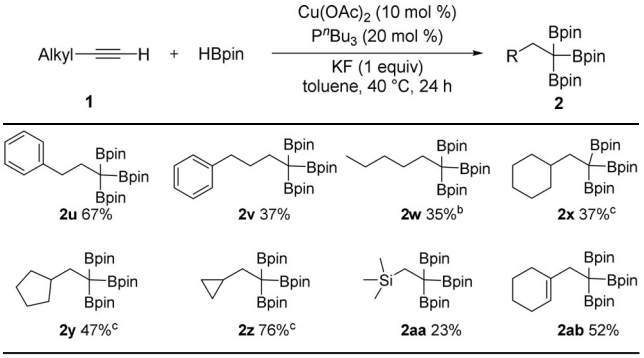




[a] Standard conditions: in an argon-filled glove box, **1** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol%), P^nBu_3 (20 mol%), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), 40°C, 24 h; yield of isolated product. [b] In an argon-filled glove box, **1** (5 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol%), P^nBu_3 (20 mol%), KF (1 equiv), HBpin (4 equiv), toluene (5 mL), 40°C, 24 h.

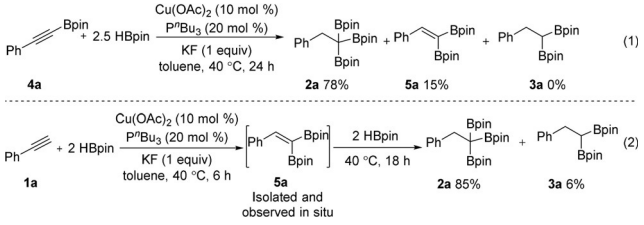
Unlike the previous synthetic method for preparing 1,1,1-triborylalkanes from alkynes,[9] our Cu-catalyzed system is not limited to aryl alkenes, since it can be extended to readily available unactivated alkyl alkynes (Table 3). Alkynes with linear alkyl groups were converted into the corresponding 1,1,1-tris(boronates) in moderate yields (**2u** to **2w**, 35–67%). Reaction of cyclohexylacetylene and cyclopentylacetylene gave the triboration product **2x** in 37% and **2y** in 47% yield of isolated product, respectively, but reaction of cyclopropylacetylene afforded the product **2z** in higher yield (76%). Trimethylsilylacetylene **1aa** gave the desired product **2aa** in 23% yield. For the conjugated 1,3-enyne 1-ethynylcyclohexene (**1ab**), no boration occurred at the double bond, and **2ab** was isolated in 52% yield, thus confirming the high chemoselectivity of this reaction.

Table 3: Substrate scope for Cu-catalyzed triboration of alkyl alkynes and a 1,3-enyne.[a]



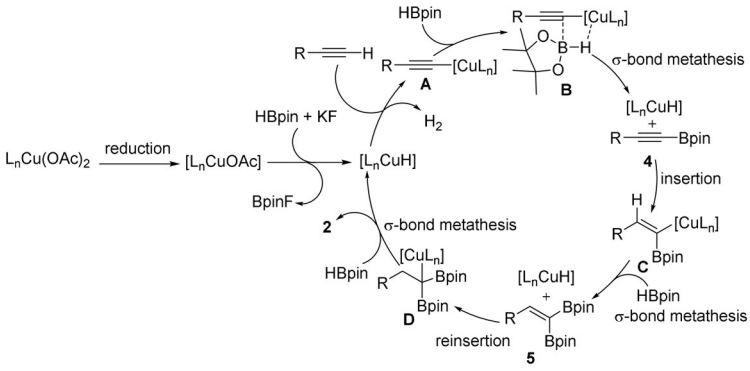
[a] Standard conditions: in an argon-filled glove box, **1** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol%), P^nBu_3 (20 mol%), KF (1 equiv), HBpin (4 equiv), toluene (0.25 mL), at 40°C for 24 h; yield of isolated product. [b] Reaction time 36 h. [c] Reaction time 12 h.

A series of studies was carried out to gain insight into the reaction mechanism (for details, see Part IV of the Supporting Information). Alkynylboronate **4a** gave **2a** in 78% yield with the concomitant generation of **5a** as a side product in 15% yield [Scheme 2, Eq. (1)]. This indicated that alkynylboronate **4a** may serve as an intermediate in the catalytic reaction. When **2a** was reacted with 2 equiv of HBpin, 1,1-diborylalkene **5a** was observed as the major product by GC–MS after 6 h, with the concomitant generation of byproduct **3a** via double hydroboration of terminal alkyne **1a**. When another 2 equiv of HBpin were added to the reaction mixture, **2a** was isolated in 85% yield after 18 h, and no 1,1-diborylalkene **5a** remained, as evidenced by GC–MS [Scheme 2, Eq. (2)], thus suggesting that the 1,1-diborylalkene is an intermediate in the catalytic cycle and undergoes hydroboration to form the final product.



Scheme 2. Mechanistic investigation.

Based on our experimental observations and previous reports,[13,14] a possible catalytic cycle for the Cu-catalyzed sequential dehydrogenative boration and hydroboration of terminal alkynes is proposed (Scheme 3). [L_nCuOAc], generated by reduction of $Cu(OAc)_2$ in the presence of phosphine,[15,16] reacts with HBpin and KF to afford a copper hydride intermediate, as well as FBpin, with the latter being confirmed by in situ $^{11}B\{^1H\}$ and ^{19}F NMR studies (Figures S1 and S2 in the Supporting Information).[17] The copper hydride can react with terminal alkynes to give the alkynylcopper intermediate **A** and H_2.[18] The highly polarized copper–carbon bond could undergo a σ-bond metathesis with HBpin (**B**) to afford intermediate alkynyl boronic ester **4** and [L_nCuH].[14,19] *Syn* addition of [L_nCuH] to alkynyl boronic ester **4** would afford alkenyl copper species **C**,[20] which then reacts with HBpin via σ-bond metathesis to give intermediate 1,1-diborylalkene **5** (see above).[21] Then, **5** undergoes Cu-catalyzed hydroboration to furnish the 1,1,1-tris(boronate), thereby regenerating [L_nCuH].[22]

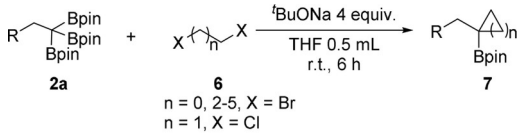


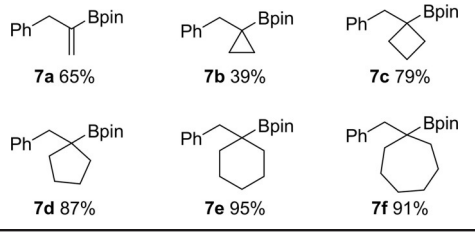
Scheme 3. A plausible mechanism.

While multiple borylated compounds such as *gem*-diborylalkanes are important synthetic intermediates for preparing organoboron compounds via C–C bond formation,[4m–o,23] by comparison, the use of 1,1,1-tris(boronates) is much less developed.[6,7,9] Herein, we describe an alkoxide-promoted deborylative alkylation of 1,1,1-tris(boronates) via the generation and electrophilic trapping of α-boryl carbanions. Using 1,*n*-dihalides as electrophiles and ^{t}BuONa as a base, we found that double deborylative alkylation of 1,1,1-tris(boronates) reliably delivered α-vinylboronates **7a** and carbocyclic derivatives **7b**–**7f** at room temperature in high yields within 6 h (Table 4). This strategy provides an efficient, straightforward route to useful α-vinylboronates and cyclic organoboronates.[4f]

In addition, different alkyl groups can be introduced in a stepwise manner via two sequential base-mediated deborylative alkylations to furnish tertiary boronic esters **9** with three different alkyl groups. Oxidation of the tertiary boronic

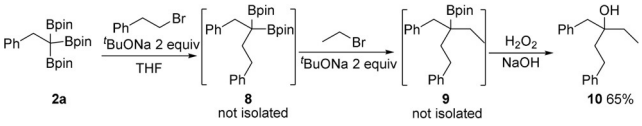
Table 4: Deborylative alkylation for the construction of carbocyclic organoboronates.[a]





[a] Standard conditions: in an argon-filled glove box, **2a** (0.11 mmol, 1.1 equiv), **6** (0.1 mmol), ^{t}BuONa (4 equiv), THF (0.5 mL), r.t., 6 h; yield of isolated product.

ester with H_2O_2/NaOH proceeded with reasonable efficiency, giving tertiary alcohol **10** in 65% yield of isolated product. Importantly, the transformation of 1,1,1-tris(boronate) products into tertiary alcohols can be performed in a one-pot, three-step fashion without the requirement for isolation of the intermediates (Scheme 4).



Scheme 4. Stepwise deborylative alkylation and oxidation to prepare a tertiary alcohol.

In conclusion, a general, atom-economical method for the synthesis of 1,1,1-trisboronates from terminal alkynes catalyzed by readily available and inexpensive $Cu(OAc)_2$ and phosphine ligands has been developed. A wide range of aryl and alkyl alkynes underwent this transformation, producing the corresponding 1,1,1-triborylalkanes in modest to high yields. The reaction can be readily conducted on a gram scale in high yield. We have also demonstrated that 1,1,1-triborylalkanes are useful synthetic intermediates for the construction of carbocyclic organoboronates and α-vinylboronates, which were difficult to synthesize using previously reported methods. A one-pot, stepwise deborylative functionalization of 1,1,1-triborylated alkanes gave an unsymmetrical $R_1R_2R_3C(OH)$ tertiary alcohol. Further applications of 1,1,1-tris(boronates) for the construction of diverse tertiary and quaternary carbon centers are under investigation in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boronic acid · cross-coupling · dehydrogenative borylation · *gem*-bisboronates · hydroboration

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