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Alkynylboranes: A Practical Approach by Zinc-Catalyzed Dehydrogenative Coupling of Terminal Alkynes with 1,8-Naphthalenediaminatoborane

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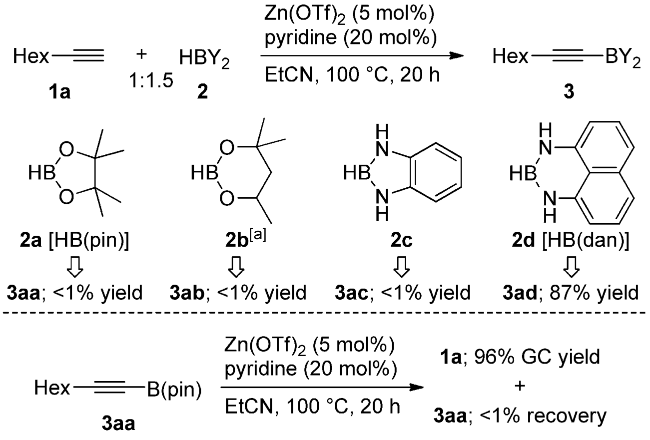
Abstract: Under zinc Lewis acid catalysis, terminal alkynes coupled dehydrogenatively with 1,8-naphthalenediaminatoborane [HB(dan)]. It is important to note that the resulting alkynylboranes with an C(*sp*)–B(dan) bond are isolable by column chromatography on silica gel (SiO_2) and are usable as coupling partners for palladium- and copper-catalyzed cross-coupling reactions with (hetero)aryl halides.

Keywords: boron; catalysis; dehydrogenation; Lewis acids; multiple bonds

Due to their broad spectrum of applications in synthetic, material, biological, and medicinal chemistry, organoboron compounds have permeated deeply into the field of chemical science.[1] Such a great importance has consistently stimulated the development of new synthetic routes to obtain target organoboron compounds more easily and efficiently. Among them, the dehydrogenative coupling of B–H and H–C bonds has seen considerable success in the past 15 years.[2,3,4] This would be due to the high availability of the two substrates. The high atom-economy of the process is also an important advantage in terms of requiring no pre-activation of the C–H bond, and thus producing no particular waste, in contrast to the two common methods. One of these is the reaction of main group organometallic reagents with trialkyl borates;[5] the other should be the coupling of organic halides with mono- or diboron reagents under palladium catalysis.[6,7] To date, transition metal complexes of Co, Ru, Rh, Pd, and Ir have had a monopoly on catalyzing the dehydrogenative borylation of C(sp^2)–H and C(sp^3)–H bonds.[2,8] This holds true for the dehydrogenative borylation of an alkynyl C–H bond, finally achieved just recently.[9] Such a dependence on the transition metals should be due to their ability to activate the inert C–H bond efficiently. Distinctly different from the preceding studies, we have found that a Lewis acid is able to participate as a catalyst in this category. We thus report on the Lewis acid-catalyzed dehydrogenative borylation, where the zinc–pyridine system exhibits remarkable catalytic performance to promote the coupling of terminal alkynes with 1,8-naphthalenediaminatoborane [HB(dan)].[10,11]

Upon preparing alkynylboranes, despite a low functional group tolerance, chemists have mainly relied on Brown's method by treating alkynyllithiums with trialkyl borates, followed by the addition of HCl/Et_2O.[5b,12] The lately reported iridium system seems to have made significant progress on the functional group compatibility, while requiring multiple steps to prepare an iridium pre-catalyst.[9] We therefore envisioned that the development of a novel C(*sp*)–H bond dehydrogenative borylation with simplicity and practicality would satisfy the needs of a variety of situations requiring alkynylboranes. On the basis of this notion, we examined the dehydrogenative borylation of 1-octyne (**1a**) with a series of hydroboranes **2** (Scheme 1). Treating **1a** and pinacolborane [**2a**, HB(pin)] with 5 mol% of $Zn(OTf)_2$ ($Tf = SO_2CF_3$) with the aid of pyridine (20 mol%) in EtCN at 100 °C for 20 h, however, gave no coupling product **3aa**. Replacing **2a** with **2b** and **2c** provided no improvements. To address why, for instance, **2a** is useless, a control experiment was conducted (Scheme 1). When **3aa** prepared by the authentic method[12b] was thus subjected to the reaction conditions, **1a** was formed in 96% GC yield, and no **3aa** was recovered, showing that **3aa** is unable to survive under the reaction conditions. The protodeborylation of **3aa** might be ascribed to the influence of water, possibly present in a small amount in the reaction solution, whereas EtCN distilled from P_2O_5 was used. The incompatibility of **2b** and **2c** might be due to the same reason. In order to



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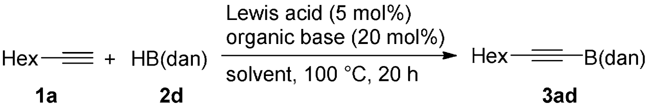
[a] Used as a 1.0 M dioxane solution.

Scheme 1. Zinc-catalyzed dehydrogenative borylation of 1-octyne, and the control experiment to ascertain the stability of **3aa**. Yields determined by ^{1}H NMR are shown here.

Table 1. Lewis acid-catalyzed dehydrogenative borylation of 1-octyne with HB(dan).[a]



Entry	Lewis acid	Organic base	Solvent	Yield [%][b]
1	$Cu(OTf)_2$	pyridine	EtCN	<1
2	AgOTf	pyridine	EtCN	<1
3	$In(OTf)_3$	pyridine	EtCN	<1
4	$Bi(OTf)_3$	pyridine	EtCN	<1
5	$Sc(OTf)_3$	pyridine	EtCN	<1
6	$Zn(NTf_2)_2$	pyridine	EtCN	76
7	$Zn(ONf)_2$[c]	pyridine	EtCN	80
8	$Zn(OAc)_2$	pyridine	EtCN	18
9	ZnF_2	pyridine	EtCN	63
10	$ZnCl_2$	pyridine	EtCN	29
11	$Zn(OTf)_2$	quinoline	EtCN	45
12	$Zn(OTf)_2$	DMAP[d]	EtCN	61
13	$Zn(OTf)_2$	Et_3N	EtCN	55
14	$Zn(OTf)_2$	DBU[e]	EtCN	27
15	$Zn(OTf)_2$	none	EtCN	18
16	$Zn(OTf)_2$	pyridine	1,4-dioxane	33
17	$Zn(OTf)_2$	pyridine	Bu_2O	2
18	$Zn(OTf)_2$	pyridine	PhCl	68
19	$Zn(OTf)_2$	pyridine	PhMe	58
20	$Zn(OTf)_2$[f]	pyridine	EtCN	40
21	none	pyridine	EtCN	<1

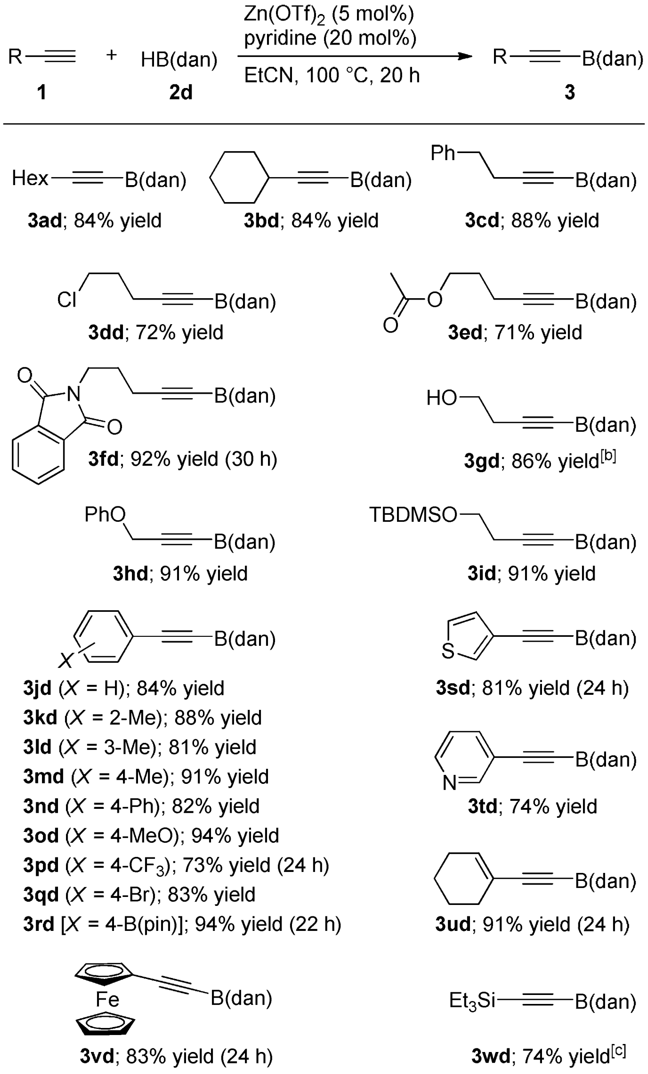
[a] *Reagents:* **1a** (0.40 mmol), **2d** (0.60 mmol), Lewis acid (20 μmol), base (80 μmol), solvent (0.40 mL).
[b] Determined by ^{1}H NMR.
[c] $Nf = SO_2C_4F_9$.
[d] DMAP = 4-(dimethylamino)pyridine.
[e] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.
[f] $Zn(OTf)_2$ (8.0 μmol) was used.

remedy this situation, we focused on the B(dan) group that was first introduced by Suginome's team as a masked boryl group, capable of offering a stable C(sp^2)–B bond, even under the conditions for the Suzuki–Miyaura cross-coupling.[13] To our delight, use of HB(dan) (**2d**) as the boron source provided the desired octynylborane (**3ad**) in 87% yield. No alkenyl- and/or alkylboranes derived from hydroboration of **1a** with **2d** were present as contaminants in **3ad**. Of importance to note here is that inexpensive $Zn(OTf)_2$ and pyridine are available as the catalyst system.

Inspired by the above results, we studied the effects of changing the reaction conditions (Table 1). In stark contrast to the outstanding performance of $Zn(OTf)_2$, other triflate salts were totally inactive (entries 1–5). Zinc salts other than $Zn(OTf)_2$ also catalyzed the dehydrogenative borylation, but were less effective (entries 6–10). These results indicate that the use of zinc Lewis acids is crucial for the progress of the dehydrogenative borylation, and an anionic ligand with strong electron-withdrawing character is likely to be necessary on zinc(II), possibly to impart strong Lewis acidity to the zinc salt. We then found that adding an organic base is important because the absence of a base led to the much lower conversion of **1a**, and that pyridine is the most reliable (entries 11–15). These observations may suggest that the electronic and steric properties of the organic bases have a significant influence on the reaction rate [the pK_a value of each base: quinoline (4.9), pyridine (5.3), DMAP (9.7), Et_3N (11.0), DBU (11.9)].[14] Thus, a stronger base than pyridine might impair the catalytic activity of the zinc Lewis acid, possibly by strong coordination to the zinc center. Quinoline, which is slightly less basic and, in addition, is more bulky compared to pyridine, could be disadvantageous in forming a transition state structure (see Scheme 3). A continuous survey of the solvent effect showed that the choice of EtCN is suitable (entries 16–19). Lowering the loading of $Zn(OTf)_2$ to 2 mol% made the dehydrogenative borylation much slower, and no dehydrogenative borylation was observed without $Zn(OTf)_2$. (entries 20 and 21).

With the promising reaction conditions in hand, we explored the substrate scope of the dehydrogenative borylation (Table 2). In addition to **1a**, a range of aliphatic terminal alkynes **1** with branched or functionalized alkyl groups were successfully borylated in a dehydrogenative fashion (**3ad**–**3id**). Importantly, whereas both of the C(sp)H and OH groups underwent borylation when using 3-butyn-1-ol (**1g**), silica gel column chromatography for purification caused protodeborylation of only the OB(dan) part to give **3gd** in 86% yield. A series of aryl- and heteroarylacetylenes with different electronic and steric natures participated well in this strategy (**3jd**–**3td**); for instance, all of the regioisomeric ethynyltoluenes coupled with **2d**, providing **3kd**–**3md** in high yields. The C=C moiety of 1-

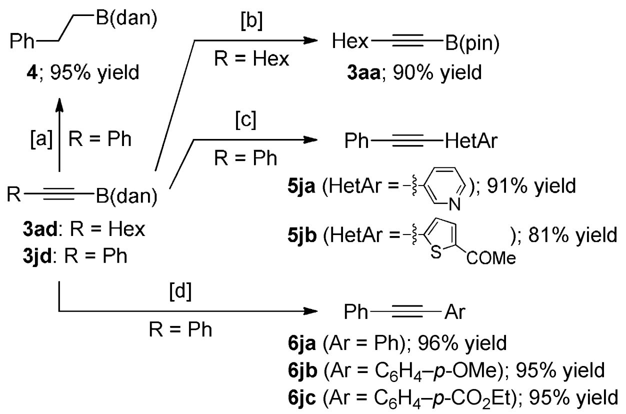
Table 2. Zinc–pyridine-catalyzed dehydrogenative borylation of terminal alkynes with HB(dan).[a]



[a] *Reagents:* **1** (0.40 mmol), **2d** (0.60 mmol), $Zn(OTf)_2$ (20 μmol), pyridine (80 μmol), EtCN (0.40 mL). Yields of isolated **3** based on **1** are shown here. TBDMS = *t*-$BuMe_2Si$.

[b] **2d** (1.2 mmol) was used.

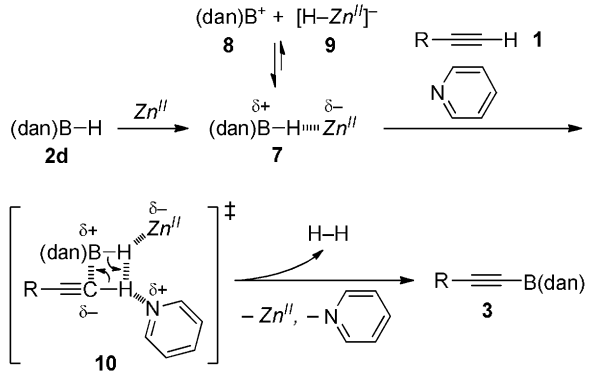
[c] 4-Methoxypyridine instead of pyridine was used.



Scheme 2. Synthetic applications of $RC\equiv CB(dan)$. Isolated yields of products are shown here. HetAr = heteroaryl. Ac = acetyl. SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl. Ar = aryl. DMI = 1,3-dimethyl-2-imidazolidinone. *Reaction conditions:* [a] 10% Pd/C (0.7 mol% on Pd), H_2 (balloon), 1,4-dioxane, room temperature, 80 min; [b] pinacol (3.0 equiv.), 6 M aqueous HCl (6.0 equiv.), 1,4-dioxane, room temperature, 12 h; [c] Br–HetAr (0.67 equiv.), $Pd(OAc)_2$ (5 mol%), SPhos (10 mol%), K_2CO_3 (3.0 equiv.), toluene, 100 °C, 5 h for **5ja** or 7 h for **5jb**; [d] I–Ar (0.83 equiv.), CuCl (10 mol%), PPh_3 (10 mol%), K_2CO_3 (1.0 equiv.), DMI, 120 °C, 12 h.

ethynylcyclohexene was also retained without suffering hydroboration (**3ud**). Metalloborylacetylene **3vd**, which could be potentially useful as a key unit for optoelectronic materials, was obtained in a high yield. Borylsilylacetylene **3wd**, which might be a platform to synthesize mutli-substituted alkenes, can be adopted as a target structure.[15] As shown thus far, the compatibility of the functional groups, Cl, OCOMe, phthalimidoyl, OH, $OCH_2C\equiv C$, TBDMSO, CF_3, Br, $C(sp^2)$–B(pin), pyridyl, C=C, ferrocenyl, is noteworthy. Our unique system also allows us to perform preparative scale syntheses; for example, the treatment of 5 mmol of **1a** or phenylacetylene (**1j**) with **2d** (1.2 equiv.) under the standard reaction conditions furnished 1.18 g (84% yield) of **3ad** or 1.19 g (86% yield) of **3jd**, respectively.[16] The achievement of scalable synthesis, which will be important as a synthetic reaction, would enhance the practicality of our method. An additional feature of this reaction is that products, $RC\equiv CB(dan)$ **3**, can be safely purified on silica gel columns without any special precautions. This means the following two things: (i) using $B(OH)_3$-impregnated SiO_2 to suppress confounded over-adsorption to silica gel in the purification process of common organoboron compounds is unnecessary;[17,18] (ii) $RC\equiv CB(dan)$ molecules are stable enough to silica gel in contrast to likely the most commonly used alkynylboranes, $RC\equiv CB(pin)$, the isolation of which has only been achieved by distillation.[19] Accordingly, our method can thus be applied to prepare $RC\equiv CB(dan)$ with high molecular weight without regard to their boiling points.

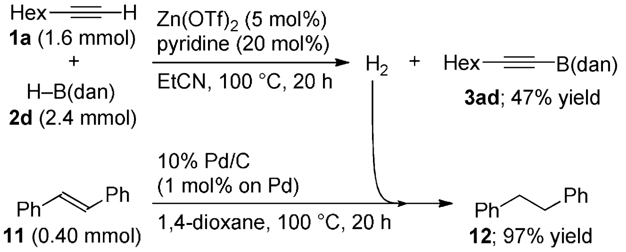
Because $RC\equiv CB(dan)$ molecules that have ever been reported in the literature are restricted to the case where R is hydrogen,[20] there is little information concerning their utility in organic synthesis. We therefore examined potential applications of $RC\equiv CB(dan)$ **3** as a virtually new class of alkynylboranes (Scheme 2). As the opening application, we prepared alkylboranes, which are also useful in synthetic and medicinal chemistry.[21] Thus, the palladium-catalyzed hydrogenation of **3jd** proceeded smoothly to provide alkylborane **4** in 95% yield. The ligand exchange of



Scheme 3. A possible reaction mechanism.

3ad with pinacol could also be performed easily, affording **3aa** in 90% yield. The B(dan) group connected with a C(sp^2) atom has now been recognized as being a masked boryl group, and thus does not participate in carbon–carbon bond-forming reactions under the palladium-catalyzed Suzuki–Miyaura cross-coupling conditions.[13] Accordingly, the transformation of **3ad** to **3aa** should be meaningful to offer active substrates for such carbon–carbon bond elongation. However, it was simply surprising that the boryl group of **3jd** is directly transformable to the heteroaryl unit under the Suzuki–Miyaura cross-coupling conditions, thereby giving **5ja** and **5jb** in high yields. Other than the palladium catalysis, we presently find that a copper salt highly effectively catalyzes C(sp)–aryl bond-forming reactions, the efficiency of which is equal to that of the original using RC≡CB(pin) instead under the same reaction conditions.[22] The results on the cross-coupling reactions show that the reactivity of the C(sp)–B(dan) unit is significantly different from that of the C(sp^2)–B(dan), and could be roughly similar to that of the C(sp)–B(pin). RC≡CB(dan) with sufficient reactivity, but with stability isolable on SiO_2 columns, would thus have a good potential to be used in organic synthesis.

We previously confirmed in the corresponding dehydrogenative silylation that the zinc–pyridine system in the nitrile medium has no ability to activate the C–H bond of terminal alkynes, but is able to activate the H–Si bond of hydrosilanes.[10] Therefore, the present dehydrogenative borylation operated by the same system in the same medium seems likely to start with activation of the H–B bond. On the basis of our preceding study as well as other significant reports, a possible route is proposed in Scheme 3. The beginning should thus be activation of the H–B bond of **2d** by $Zn(OTf)_2$ (*Zn^II^*) for enhancing the electrophilicity of the boron center (**7**), thereby possibly giving boron cation **8** and zinc hydride **9**.[23,24] On the other hand, pyridine, which remarkably accelerates the reaction rate, may support a process by enhancing the nucleophilicity of the terminal carbon atom of **1**. Accordingly, electrophilic boron species **7** should react with nucleophilic **1**, assisted by pyridine through possible transition state **10** to make the B–C bond and to regenerate Zn^{II} and pyridine as well as to release hydrogen gas.



Scheme 4. Trapping experiment for evolved hydrogen gas.

Finally, in order to confirm the evolution of the hydrogen gas, a trapping experiment was conducted, as shown in Scheme 4. Thus, the palladium-catalyzed hydrogenation of *trans*-stilbene (**11**) was carried out with the intention of capturing the hydrogen gas that would be released from the dehydrogenative borylation of **1a** with **2d**.[25] As a result, 1,2-diphenylethane (**12**) was obtained in 97% yield. This result should support the possibility of the reaction mechanism proposed in Scheme 3.

In closing, we have disclosed that a catalyst system consisting of $Zn(OTf)_2$ and pyridine can be used to connect terminal alkynes with HB(dan) in a dehydrogenative manner. This is the first example of the dehydrogenative borylation of terminal alkynes catalyzed by a Lewis acid. Our method features a broad range of substrate coverage with a high functional group tolerance. In terms of the promotion of sustainable chemistry, the use of a common metal, zinc, for the catalyst is also a distinct advantage of our strategy. Noteworthy is that the alkynyl moiety of RC≡CB(dan) proved to have reactivity to transmetallate onto Pd(II) and Cu(I) metals, in contrast to the C(sp^2)-based organic unit bound to the B(dan) group. This indicates that RC≡CB(dan) have a considerable potential as substrates for organic synthesis. Further studies on the mechanism and synthetic applications are in progress in our laboratory.

Experimental Section

General Procedure Exemplified by the Synthesis of 3ad on a 5-mmol Scale

$Zn(OTf)_2$ (90.9 mg, 0.250 mmol) was placed in a 50-mL Schlenk tube, which was heated at 150 °C under vacuum for 2 h. The tube was cooled down to room temperature and filled with argon. HB(dan) (**2d**) (1.01 g, 6.00 mmol) and EtCN (5.0 mL) were added to the tube, and the resulting mixture was stirred at room temperature for 3 min. To this were added 1-octyne (**1a**) (551 mg, 5.00 mmol) and pyridine

(79.1 mg, 1.00 mmol) successively, and the resulting solution was then stirred at 100 °C for 20 h. A saturated NH_4Cl aqueous solution (2 mL) was added to the mixture, and the aqueous phase was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (3 mL) and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 10:1) gave 2,3-dihydro-2-(1-octyn-1-yl)-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine (**3ad**); yield: 1.17 g (84%).

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