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Author(s)	Takahashi, Kou; Ishiyama, Tatsuo; Miyaura, Norio
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Addition and Coupling Reactions of Bis(pinacolato)diboron Mediated by CuCl in the Presence of Potassium Acetate

Kou Takahashi, Tatsuo Ishiyama, and Norio Miyaura*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628

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The addition of bis(pinacolato)diboron $[(\text{Me}_4\text{C}_2\text{O}_2)\text{B}-\text{B}(\text{O}_2\text{C}_2\text{Me}_4)]$ to α,β -unsaturated ketones, esters, nitriles, or terminal alkynes and the coupling with allyl bromide were carried out in DMF at room temperature in the presence of CuCl and AcOK. The transmetalation from boron to copper generating a B-Cu species was proposed as the key step of the reactions.

The addition of diborons to alkenes and alkynes is an attractive and straightforward method to introduce boryl groups into organic molecules.¹ Although tetra(alkoxo)diborons such as bis(pinacolato)diboron **1** are highly inert to ionic reactions, they oxidatively add to a low-valent transition metal with the B-B bond cleavage, thus allowing the catalyzed addition of the diboron to unsaturated organic substrates. The platinum(0) complexes were recognized to be the most efficient catalyst for such diboration of alkenes,² alkynes,³ and conjugate dienes.⁴ Here, we wish to report the addition reaction of bis(pinacolato)diboron (**1**) to α,β -unsaturated ketones, esters, or nitriles, and terminal alkynes (Eqs. 1 and 2), and the coupling reaction with allyl halides (Eq. 3) mediated by CuX and AcOK. The reaction may involve the transmetalation of **1** to CuX giving a B-Cu species (**2**). A boryl nucleophile which couples with MeI, CF₃I, and RCOCl was first synthesized by the reaction of dialkylchloroborane R₂BCl with sodium/potassium alloy yielding R₂BK.⁵ The reaction suffered from reproducibility due to the liability of R₂BK, but the present B-Cu species is stable at room temperature and undergoes the addition and coupling reaction characteristic for copper compounds.⁷ An analogous conjugate addition of **1** to enones mediated by (CuOTf)₂•C₆H₆ was recently reported by Hosomi and coworkers.⁶

The conjugate addition of **1** to the representative Michael acceptors are summarized in Table 1. The addition of **1** to

2-cyclohexenone failed in the absence of either copper(I) halide or base (Entry 1), but the yields were improved significantly by the addition of both CuX and AcOK (Entry 2). Like other related reactions mediated by copper(I) halides,⁷ the addition of LiCl as the ligand of copper(I) species improved the yields (Entry 3). The effect of bases under conditions used for entry 2 revealed the following order of yields suggesting the superiority of more basic and small potassium salts; CF₃COOK (trace), PhCOOK (15%), CH₃COOK (67%), Me₂CHCOOK (55%), and PhOK (54%). The reaction was not mediated by CuCl₂, but various copper(I) halides or pseudohalides accelerated the reaction; 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 both for CuCl and KOAc which was demonstrated in the addition to methyl vinyl ketone (Entries 4 and 5). Under analogous reaction conditions used for the ketones, α,β -unsaturated esters and nitriles afforded the corresponding addition products in moderate yields (Entries 6-10).

A preliminary result for the addition of **1** to alkynes is shown in Eq. 2. The addition to 1-decyne afforded a mixture of the internal and the terminal addition product in a ratio of 91 : 9. The reactions of alkyl-,⁸ silyl-,⁹ and stannylcuprates¹⁰ with terminal alkynes alter the regioselectivity depending on the elements on the copper metal center. Both lower order and higher order stannyl cuprates such as Me₃SnCu•SMe₂, and Me₃Sn(*n*-Bu)Cu(CN)Li₂ selectively afford the internal products whereas *n*-BuCu•MgBr₂, (*n*-Bu)₂CuLi, and (PhMe₂Si)₂Cu(CN)Li₂ yield the terminal addition products for aliphatic terminal alkynes. The origin of regioselectivity is not well understood, but the present results suggest the generation of a borylcopper species (**2**) which exhibits the internal selectivity for terminal alkynes.

Another indirect evidence for the formation of a B-Cu species was obtained by the coupling reaction with allyl chloride yielding pinacol allylboronate (Eq. 3).

We previously reported that copper(I) tetraalkylborate (**4**) has a quite analogous reactivity to organocopper(I) compounds undergoing the conjugate addition to α,β -unsaturated carbonyl compounds and the coupling with allyl and benzyl halides (Figure 1).¹¹ Although no spectral evidence is available for the present B-Cu species, the results imply the formation of a boron ate-complex (**5**) or the equilibrium dissociation of a free B-Cu species (**2**) from **5**. The addition of BuLi to **1** in toluene at

-78 °C also afforded a nucleophilic boron species, presumably a B-Li complex (**6**), that reacted with cinnamyl bromide at 50 °C giving a mixture of 3-phenyl-2-propenylborate (43%) and 1-phenyl-2-propenylborate (23%) at 50 °C.¹² Thus, available information suggests that the quarternalization of one boron atom with a negatively charged base generates a nucleophilic boron species which is synthetically equivalent to the boryl anion.

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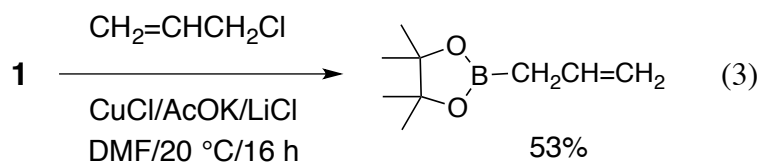
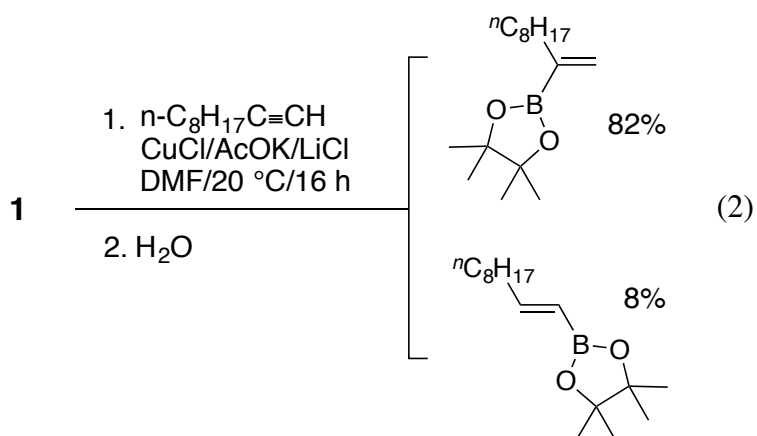
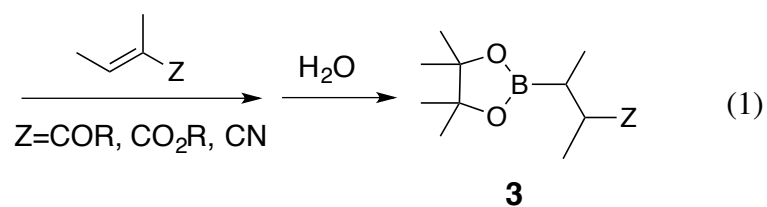
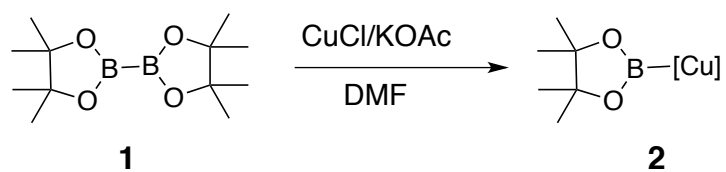


Table 1. Conjugate 1,4-Addition of Diboron^a

Entry		Acceptor	
Conditions		Yield/% ^b	
1	2-cyclohexenone	AcOK	6 ^c
2		CuCl/AcOK	67 ^c
3		CuCl/AcOK/LiCl	68 ^c
4	CH ₂ =CHCOCH ₃	CuCl/AcOK	86 ^c
5		CuCl/AcOK ^d	90
6	CH ₂ =CHCO ₂ Et	CuCl/AcOK/LiCl	59
7	CH ₂ =C(Me)CO ₂ Me	CuCl/AcOK/LiCl ^e	65
8	MeCH=CHCO ₂ Et	CuCl/AcOK/LiCl ^e	54
9	CH ₂ =CHCN	CuCl/AcOK/LiCl	57
10	MeCH=CHCN	CuCl/AcOK/LiCl ^e	49

^aA mixture of an α,β -unsaturated ketone, ester, or nitrile (1.0 mmol), diboron **1** (1.1 mmol), CuX (1.1 mmol) and a base (1.1 mmol) in DMF (6 ml) was stirred at room temperature for 16 h, unless otherwise noted. ^bIsolated yields by chromatography over silica gel. ^cGC yields. ^dThe catalyzed reaction by using CuCl (0.1 mmol) and AcOK (0.1 mmol). ^eThe reaction was conducted at 50 °C for 16 h.

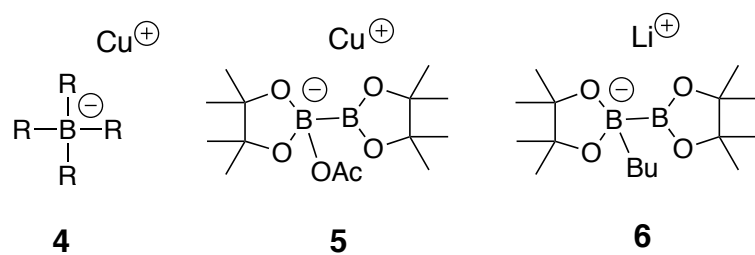


Figure 1. Nucleophilic Boron Species