Borylcyanocuprates

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Borylcyanocuprate in a One-Pot Carboboration by a Sequential Reaction with an Electron-Deficient Alkyne and an Organic Carbon Electrophile**

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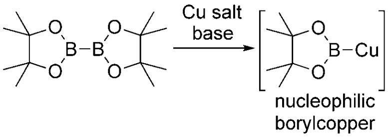
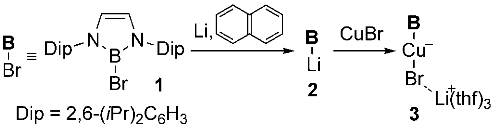
The chemistry of borylcopper species has broadened since 2000 when they were first proposed as intermediates in a reaction of bis(pinacolato)diborane(4) (B_2pin_2) with a copper salt [Eq. (1)].[1] In the presence of B_2pin_2, nucleophilic borylcopper species could catalyze many borylation reactions, such as β-borylation of α,β-unsaturated carbonyl compounds and imines,[1,2] nucleophilic borylation of polar double bonds, such as C=N and C=O,[3] S_N2' borylation of allylic and propargylic substrates,[1b,2p,4] the diboration of styrene,[5] the borylation of dienes,[6] and the borylation of aryl iodide.[7] In these reactions, the reactive borylcopper species was usually used without isolation.



(1)

Additions of borylcopper to alkynes were also reported. A simple borylcupration of terminal alkynes took place with in situ generated borylcopper.[1b,2p] Yun et al. reported the borylcupration of alkoxycarbonyl alkynes and internal alkynes and subsequent protonation with MeOH.[8] Borylcupration of propargylic carbonate and subsequent β-oxygen elimination was reported to construct an allenic skeleton.[4d] Except for the reaction of propargylic carbonate, all other borylcupration reactions of alkynes were limited to the introduction of boron and hydrogen substituents onto the C≡C bond in a *syn* fashion. Thus, although β-borylalkenylcopper species were expected to exist as intermediates, further subsequent reaction of the alkenyl copper species with electrophiles has never been reported. This may be attributed to the low reactivities of the borylalkenylcopper species.[9]

To date, three borylcopper species have been isolated. In 2005, Sadighi et al. synthesized the first borylcopper species generated from a carbene-ligated copper alkoxide complex and B_2pin_2 by a σ-bond metathesis pathway.[3b,c] In 2007, we reported syntheses of borylcopper species generated from an anionic and nucleophilic boryl anion, via a boryllithium **2** [Eq. (2)],[10] and treatment with copper chloride resulting in a nucleophilic borylation of Group 11 metal chloride.[11]



(2)

Our method for a preparation of borylcopper species differs from the typical one using copper alkoxide and diborane(4) and is similar to the synthetic methods for generating organocopper species,[12] from a copper salt and an organolithium or organomagnesium reagent. Based on our method, we could also make an anionic cuprate-type complex **3** with a formal negative charge on the copper center by treating **2** with CuBr [Eq. (2)].[13]

Herein we report the synthesis and isolation of a borylcyanocuprate **5** (see Scheme 2), its stoichiometric addition to ynoate by borylcupration, and subsequent reactions with electrophiles to give a one-pot carboboration of alkyne.[14]

Lithium borylbromocuprate **3**, generated from a stock solution of boryllithium **2** and CuBr, was allowed to react with 0.75 equivalent of diethyl acetylenedicarboxylate (DEAD) followed by protonation with MeOH to give **4**-*syn* (76 %) and *anti*-**4** (6 %) and no residual DEAD (Scheme 1). The formation of the C–B bond and the stereochemistry of the *syn*-**4** were unambiguously determined by X-ray crystallography.[15] The *syn* addition is fashion the same as that with organocuprates, indicating an intermediate boryl-substituted alkenylcuprate. Changing the copper source to $CuCN\cdot 2LiCl$ gave *syn*-**4** and *anti*-**4** in 65 % and 28 % yield, respectively.

Treating **2**, generated in situ from **1**, with CuCN allowed crystals of lithium borylcyanocuprate **5** to be isolated in 60 % yield (Scheme 2). X-ray crystallographic analysis reveals a monomeric structure with a linear B-Cu-C≡N-Li linkage and three THF molecules coordinating to the lithium atom (Figure 1). This structural motif is similar to the reported structure of an arylcyanocuprate derivative, $[(2,6\text{-}Mes_2C_6H_2)Cu\text{-}CN\text{-}Li(thf)_3]$ (**6**), which has large substituents

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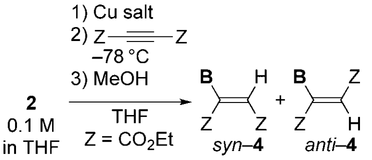
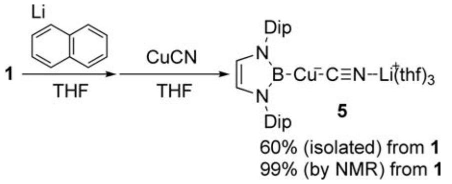


Cu salt	yield [%]	
	syn–**4**	*anti*–**4**
CuBr	76	6
CuCN•2LiCl	65	28

Scheme 1. Reaction of in situ generated borylcopper species with DEAD.



Scheme 2. Synthesis of borylcyanocuprate **5**.

on the copper-bonded aryl group.[16] The B−Cu bond length in **5** of 1.973(6) Å was shorter than those of borylcopper species.[3b,c,11,13] This shortening may come from an electron-accepting character of the cyanide group. Relatively long Cu−C bond of 1.906(7) Å in **5** compared to **6** (1.869(4) Å) reflects a strong donor ability of boryl ligand on the copper center.[11,17] On the contrary, C≡N length of 1.147(7) Å in **5** was close to that in **6** (1.159(5) Å), indicating the boryl ligand mainly functions as a σ donor, not a π donor. The ^{1}H and ^{13}C NMR spectra of **5** indicated its solution structure has D_{2h} symmetry for the boryl moiety and free rotation about the N1−Li1 bond. The ^{11}B NMR spectra showed a broad resonance signal at $\delta_{B} = 38.6$ ppm which is close to those of other borylcopper species.[3b,c,11,13] Comparison between the NMR spectra of reaction mixture in [D$_8$]THF and isolated crystals of **5** allowed us to estimate the yield by NMR spectroscopy of the reaction as 99 % from bromoborane precursor **1**. In the negative mode of ESI-TOF mass spectrum of **5** the strongest signal corresponded to an aggregated dinuclear species $[2(\mathbf{5}-\mathrm{Li\cdot 3THF})-\mathrm{CN}^{-}]^{-}$.

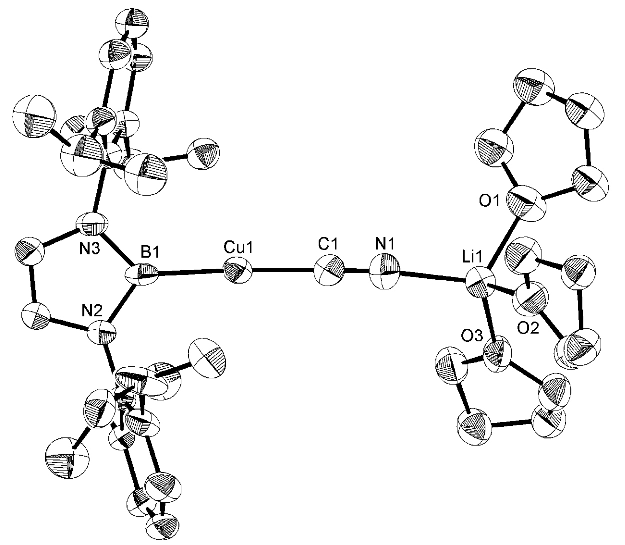
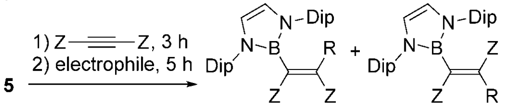


Figure 1. ORTEP drawing of **5** with thermal ellipsoids set at 50% probability (hydrogen atoms and minor disorder of the Dip moieties and THF molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: B1–Cu1 1.973(6), B1–N2 1.459(7), B1–N3 1.480(7), Cu1–C1 1.906(7), C1–N1 1.147(7), N1–Li1 2.01(2), Li1–O 1.92(2) (av.); N2-B1-N3 99.7(4), B1-Cu1-C1 176.9(2), Cu1-C1-N1 177.7(6), C1-N1-Li1 174.7(8).

Trapping of a possible intermediate, β-borylalkenylcopper, which is generated from **5** and DEAD, was successfully accomplished as described below. In situ generated **5** was treated with DEAD, and then with benzoyl chloride or allyl bromide at −78 °C or room temperature to give carboboration product (Table 1). At low temperature, reaction with benzoyl chloride afforded the protonated products *syn*-**4** and *anti*-**4** in 48 % and 32 % yields (Table 1, entry 1), indicating that the boryl-substituted alkenylcuprate intermediate did not react with benzoyl chloride at −78 °C. Elevating the temperature to room temperature afforded the *anti*-adduct, *anti*-**7**, in 71 % yield with a selectivity of *syn*/*anti* = 1/ > 99 (entry 2). Changing the electrophile to allyl bromide gave the corresponding *syn*-adduct, *syn*-**8**, in 93 % yield accompanied with a trace amount of *anti*-adduct *anti*-**8** (entry 3). In the reaction with allyl bromide at room temperature, *anti*-**8** was obtained as the major product in 60 % and *syn*-**8** was given in 36 % yield (entry 4). The stereochemistry of these products was unambiguously confirmed by X-ray crystallography (Figure 2 for *anti*-**7** and Supporting Information for others). The products can be considered as formally carboborated products[13] of DEAD. It should be noted that MeOTf and PhCHO were not suitable electrophiles for this reaction. Trials for catalytic borylation reaction using boryllithium **2** with a catalytic amount of copper were unsuccessful to date.

Table 1: Sequential reaction of **5** with DEAD (Z = CO$_2$Et) and an electrophile.



syn–**7**: R = PhCO *anti*–**7**: R = PhCO
syn–**8**: R = allyl *anti*–**8**: R = allyl

Entry	Electrophile	*T* [°C]	Products (yield[a] [%])	*syn*/*anti*
1	PhCOCl	−78	*syn*-**4** (48), *anti*-**4** (32)	60/40
2	PhCOCl	RT	*anti*-**7** (71)	1/99 >
3	allylBr	−78	*syn*-**8** (93)	99 > /1
4	allylBr	RT	*syn*-**8** (36), *anti*-**8** (60)	38/62

[a] Yield of isolated product based on DEAD.

Proposed mechanism was depicted in Scheme 3. Reaction of lithium borylcyanocuprate **5** with DEAD led to a formation of alkenylcuprate intermediate *syn*-**9**. Protonation or reaction with allyl bromide at low temperature gave *syn* adducts *syn*-**4** or *syn*-**8**. Formation of *anti*-adducts *anti*-**7** and *anti*-**8** can be explained by a reaction of organic electrophiles with *anti*-alkenylcuprate *anti*-**9** generated by an isomerization

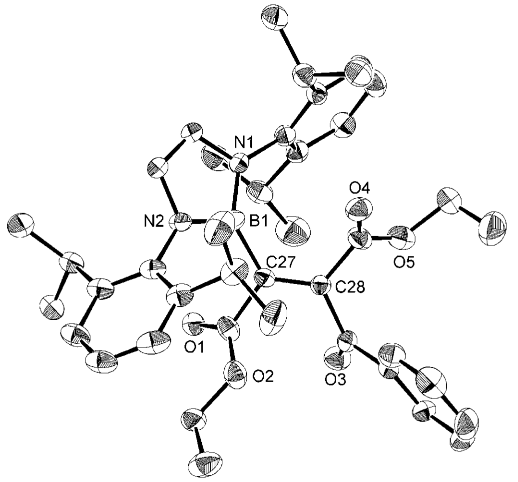
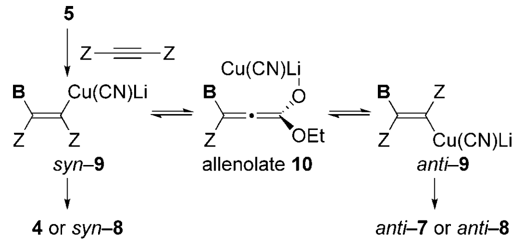


Figure 2. ORTEP drawing of *anti*-**7** with thermal ellipsoids set at 50% probability (hydrogen atoms and minor disorder of the alkene moieties is omitted for clarity).



Scheme 3. Mechanism for the formation of *syn* and *anti* adducts.

from *syn*-**9** via an allenolate intermediate **10**. An allenolate-type intermediate for the isomerization of alkenylcopper species has been proposed based on NMR spectroscopy[18] and DFT calculation.[19] Thus, the results in Table 1 could be explained as follows: 1) At low temperature, *syn*-alkenylcuprate intermediate *syn*-**9** reacted with unhindered allyl bromide affording the *syn* adduct (entry 3) and did not react with relatively bulky benzoyl chloride (entry 1). 2) At room temperature (entries 2 and 4), isomerization from *syn*-**9** to *anti*-**9** took place because of steric repulsion between bulky boryl group and alkenylcyanocuprate center, therefore, *anti* products *anti*-**7** and *anti*-**8** were selectively obtained.

In conclusion, we achieved a one-pot carboboration of alkynes by a sequential reaction of a boryllithium compound with CuCN·2LiCl, ester-substituted alkyne, and an organic electrophile. A key reaction intermediate, lithium borylcyanocuprate, was isolated and fully characterized. By changing the reaction temperature, the *syn*/*anti* ratio of the carboborated products could be changed. The *anti*-selectivity may come from steric effects of the reactive intermediate, borylalkenylcuprate.

Experimental Section

5: In a glovebox, a 20 mL vial equipped with a glass-coated stir bar was charged with bromoborane **1** (469 mg, 1.00 mmol), lithium powder (38.1 mg, 5.49 mmol), and naphthalene (24.8 mg, 0.193 mmol). The mixture was cooled at −35 °C, and precooled THF (3.0 mL, −35 °C) was added. The resulting mixture was stirred at −35 °C for 12 h. After the solution was quickly filtered through a pad of Celite at room temperature, a precooled solution of CuCN (90.2 mg, 1.01 mmol) in THF (1.0 mL) at −35 °C was added to the filtrate at −35 °C. The reaction mixture was stirred at room temperature for 1 h. All volatiles were removed under reduced pressure, and hexane (3 mL) was added to the mixture. The volatiles were evaporated again to remove the THF completely. The residue was extracted with hexane and the resulting suspension was filtered through a pad of Celite to remove inorganic salts. The crude product was recrystallized from hexane/THF (30/1) at −35 °C to give colorless crystals (422 mg, 0.603 mmol, 60%) of **5**. M.p. 142.1–144.9 °C (decomp.); ^{1}H NMR (C_6D_6, 500 MHz): $\delta = 1.32$–1.35 (m, 24 H), 1.45 (d, $J = 7$ Hz, 12 H), 3.36 (t, $J = 7$ Hz, 12 H), 3.67(sept, J=7 Hz, 4 H), 6.45 (s, 2 H), 7.20 ppm (s, 6 H); ^{13}C NMR (C_6D_6, 100 MHz): $\delta = 24.4$ (CH_3), 25.5 (CH_3), 25.5 (CH_2), 28.5 (CH_2), 68.2 (CH_2), 119.6 (CH), 122.9 (CH), 126.1 (CH), 144.8 (4°), 146.9 (4°), 157.3 ppm (CN); ^{11}B NMR (C_6D_6, 160 MHz): $\delta = 38.6$ (br, s); ^{7}Li NMR (C_6D_6, 194 MHz): $\delta = -1.35$ (s); IR (KBr): 2131 cm^{-1} (C≡N); HRMS-ESI TOF (*m*/*z*): $[2(\mathbf{5}{-}\mathrm{Li}{\cdot}3\mathrm{THF}){-}\mathrm{CN}^-]^-$ Calcd for $C_{53}H_{72}B_2Cu_2N_5$, 926.4584, 928.4575; found, 926.4578, 928.4575.

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