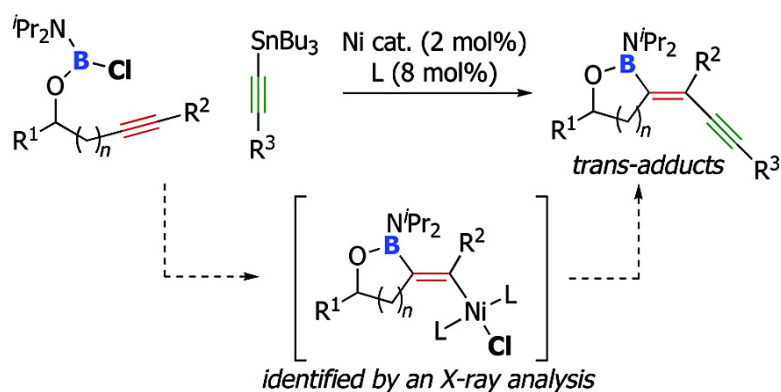


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Nickel-Catalyzed *trans*-Alkynylboration of Alkynes via Activation of a Boron–Chlorine Bond

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Remarkable progress has been achieved during the past decade in utilizing organoboron compounds in C–C bond forming reactions with the aid of transition metal catalysts. In addition to the significant improvement in the efficiency and scope of the Suzuki–Miyaura coupling reaction,¹ several new Rh-catalyzed reactions, including enantioselective conjugate additions of organoboronic acids, have appeared.² To fully take advantage of the rapid development of those boron-based reactions, exploration of efficient synthetic routes to new functionalized organoboron compounds is eagerly desired.

Addition of organoboron compounds to unsaturated organic molecules is recognized as one of the most efficient methods to produce functionalized organoboron compounds.^{1b} Recent developments in this area mainly concern transition metal catalyzed additions because of the high efficiency and regio- and stereochemical controllability.^{3–5} We have been interested in carboboration reactions, which allow concomitant introduction of carbon and boron substituents to organic frameworks, possibly in a regio- and stereoselective fashion. As the first example of carboboration, we have recently reported regio- and stereoselective cyanoboration, which allowed convenient synthesis of β -boryl- α,β -unsaturated nitriles.⁶ In this paper, we describe another example of carboboration of alkynes. The reaction proceeds through the activation of the boron–chlorine bond by a nickel catalyst,^{7,8} followed by delivery of an organic group from organostannanes,⁹ affording formal *trans*-carboboration products.

A chloroboryl ether **1a** ($R^1 = H$, $R^2 = Et$) was prepared from 3-hexyn-1-ol and reacted with alkynylstannane **2a** ($R^3 = Ph$) in the presence of a catalyst prepared from $Ni(cod)_2$ (2 mol %) and triphenylphosphine (8 mol %) at 80 °C (Scheme 1; Table 1, entry 1). We observed formation of the alkynylboration product **3aa** in 93% yield, which was derived from 5-exo cyclization of **1a** with incorporation of the alkynyl unit of **2a**. It became clear by the subsequent screening of the phosphine ligands that triphenylphosphine was superior to other phosphine ligands, such as trimethylphosphine and tricyclohexylphosphine, with respect to the reaction yield. The ligand screening also suggested that the Ni/P ratio of 1/4 showed the highest catalyst efficiency in the reaction. Our interest then focused on the geometry of the C=C bond. Careful inspection of the stereochemistry of the C=C bond by nOe experiments for **3** and other related products shown below suggested that the alkynylboration took place in a *trans* fashion.

Under the optimized reaction conditions, the chloroboryl homopropargylic ethers **1** underwent *trans*-alkynylboration (Table 1). Because of the instability of the primary product **3** toward moisture, the crude reaction mixtures were treated with pinacol and acetic anhydride in the presence of a base to produce pinacolborane derivatives **4**, which could be isolated by silica gel chromatography. As the alkynylstannane components, those derived from phenylacetylene, 1-pentyne, and trimethylsilylacetylene were found to be

Scheme 1

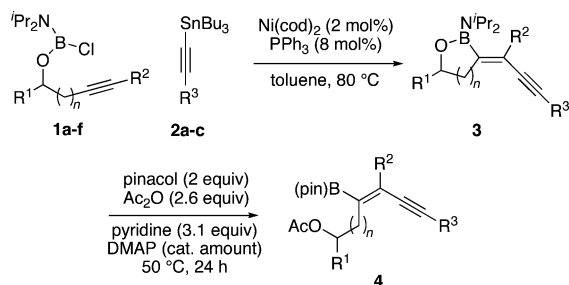


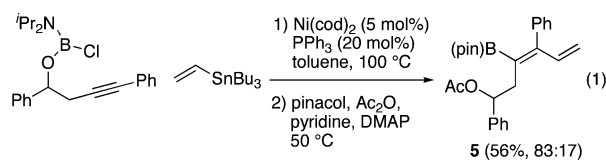
Table 1. Ni-Catalyzed Reactions of Chloroboryl Ethers of Alkynols with Alkynylstannanes^a

entry	<i>n</i>	R ¹	R ²	R ³	product	% yield of 3 ^b	% yield of 4 ^c
1 ^d	1	H	Et	Ph	aa	93	85
2	1	H	Et	<i>n</i> -Pr	ab	98	81
3	1	H	Et	Me ₃ Si	ac	78	70
4	1	H	Ph	Ph	ba	99	85
5	1	H	CH=CMe ₂	Ph	ca	76	67
6	1	Ph	Ph	Ph	da	89	61
7	1	Me	Et	Ph	ea	nd	90
8 ^e	2	H	Me	Ph	fa	nd	71

^a **1** (0.20 mmol) and **2** (0.20 mmol) in toluene (0.25 mL) were heated at 80 °C in the presence of $Ni(cod)_2$ (0.0040 mmol) with PPh_3 (0.016 mmol), unless otherwise noted. After 3–24 h, yields of **3** were determined by NMR using internal standard. Then, pinacol (0.40 mmol), Ac_2O (50 μ L), pyridine (50 μ L), and DMAP (3.0 mg) were added. The mixture was allowed to react at 50 °C for 24 h. ^b NMR yield. ^c Isolated yield (PTLC) for two steps. ^d On a 2.5 mmol scale. ^e At 110 °C.

equally reactive (entries 1–3). The alkynyl carbon atoms of the homopropargyl moieties of **1** could bear phenyl and even alkenyl groups (entries 4–6). It is noteworthy that the alkynylboration of **1** having phenyl groups at the alkynyl carbons was remarkably facilitated (entries 4 and 6), completing within 3 h, while the alkyl-substituted derivatives required around 24 h to reach completion (entries 1–3 and 7). We were pleased to find successful six-membered ring formation by using a homologous alkynol ($n = 2$) (entry 8). Although higher temperature was required, the reaction provided *trans*-alkynylboration product **4fa** in good yield.

Besides alkynylstannanes, vinylstannane was found to take part in the reaction. Using 5 mol % of $Ni(cod)_2$ at 100 °C, tributylvinylstannane afforded the corresponding *trans*-addition product **5** as the major isomer (83:17) in moderate yield after the pinacol/ Ac_2O treatment (eq 1).



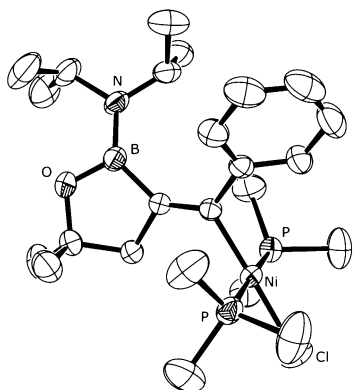
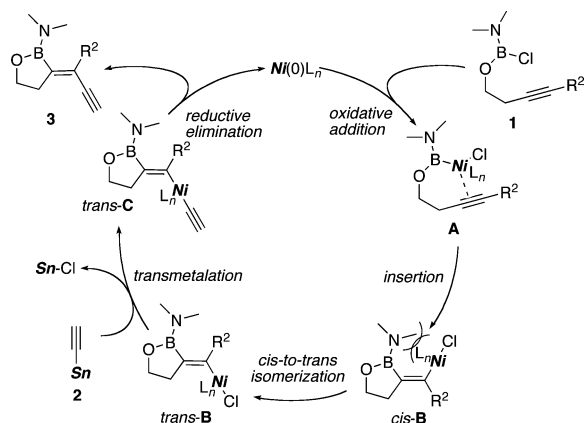


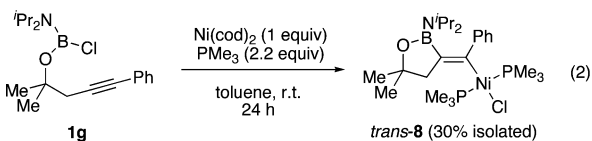
Figure 1. Single-crystal X-ray structure of *trans*-8.

Scheme 2. Proposed Mechanism for the *trans*-Alkynylboration^a



^a L = PPh₃.

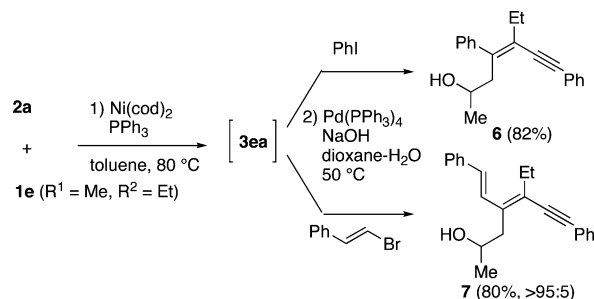
The origin of the observed *trans*-addition mode of the present reaction seems interesting from the mechanistic point of view. In an attempted stoichiometric reaction of **1g** with a Ni(0)–PMe₃ complex, we could isolate alkenylnickel(II) chloride complex *trans*-8, in which the boron and nickel are located in a *trans* fashion (eq 2). The structure of the nickel complex was determined by a single-crystal X-ray analysis (Figure 1). On the basis of this result, the catalytic cycle of the *trans*-alkynylboration may be presumed as shown in Scheme 2. The proposed mechanism involves an oxidative addition of the B–Cl bond to nickel,^{8,10} followed by insertion of the triple bond to the B–Ni bond in a *cis*-addition manner, producing *cis*-B. The transmetalation step may be slow, allowing isomerization of *cis*-B to *trans*-B (corresponding to *trans*-8).^{11,12} The *trans*-B may be more favorable than *cis*-B due to the considerable steric repulsion in *cis*-B between the chlorobis-(triphenylphosphine)nickel moiety and the diisopropylamino group.



The synthetic utility of the alkynylboration has been demonstrated by the one-pot alkynylboration/Suzuki–Miyaura cross-coupling sequence (Scheme 3). The highly substituted conjugated enyne **6** and dienyne **7** were isolated in high yields on treating the crude alkynylboration mixture containing **3ea** with the corresponding organic halides, base, and Pd(PPh₃)₄.

In summary, we report new *trans*-carboration reactions catalyzed by nickel complexes. Although mechanistically still

Scheme 3



unclear, the reaction provides a new, stereoselective access to highly functionalized organoboron compounds, which are otherwise difficult to synthesize.

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Supporting Information Available: Experimental procedures, details of the X-ray analysis of *trans*-8, and spectral data for the new compounds (29 pages, print/PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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