



On the scope of the Pt-catalyzed Srebnik diborylation of diazoalkanes. An efficient approach to chiral tertiary boronic esters and alcohols via B-stabilized carbanions

Andrew J. Wommack ^{a,†}, Jason S. Kingsbury ^{a,b,*}

^a Department of Chemistry, Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467, United States

^b Department of Chemistry, Ahmanson Science Center, California Lutheran University, 60 West Olsen Road, Thousand Oaks, CA 91360, United States



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ABSTRACT

Conditions milder than those previously reported are shown to be generally applicable to the Pt-catalyzed insertion of non-carbonyl-stabilized diazoalkanes into $B_2\text{pin}_2$. Selective transformation of one (pinacolato)boryl unit in the products is enabled by rapid, low-temperature deboronation in the presence of a Lewis base and genesis of a highly reactive B-stabilized carbanion.

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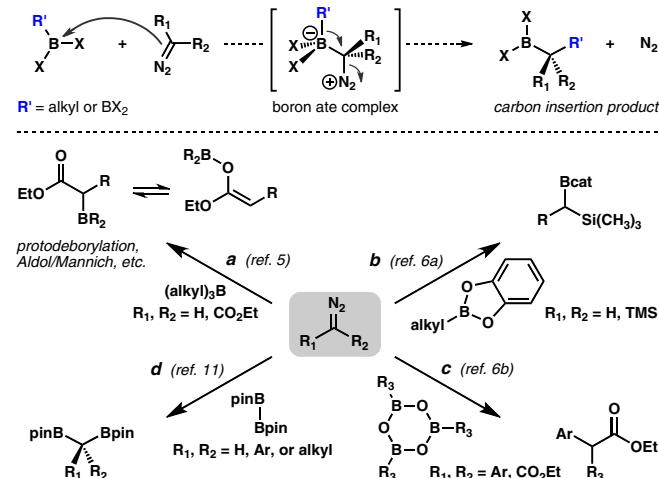
Diazoalkanes

1,1-Diborylalkanes

Deboronation

B-stabilized carbanions

The C–B bond holds a special status in organic synthesis, unrivaled as a handle for further elaboration through oxidative,¹ cross-coupling,² or homologation³ strategies. The latter of these invariably requires introduction of a carbenoid (donor–acceptor) reagent for complexation with the electrophilic boron atom prior to 1,2-rearrangement. Along with the highly reactive 1-lithio-1-halogenoalkanes popularized by Matteson,³ sulfur ylides⁴ and metalated α -chloro sulfoxides^{4b} can be applied to stereoretentive carbofunctionalization of alkylborons. Hooz, however, was the pioneer of C–B homologations with diazo compounds.⁵ With its reliance on stabilized diazoester and diazoketone nucleophiles, a Hooz reaction furnishes α -boryl carbonyls that undergo further Aldol, Mannich, or alkylation events, but the process is limited to trialkylboranes because of their greater electrophilicity relative to boronic acids or esters (Scheme 1a). Recent work⁶ has broadened the reactivity to include reaction of trimethylsilyldiazomethane and α -substituted diazoesters with catecholboranes and boroxines (respectively, Scheme 1b and c), findings that hint at generality for a range of diazoalkanes and boryl acceptors. In our own laboratory, some experience has been gained in the synthesis⁷ and solution-phase handling⁸ of diverse non-carbonyl-stabilized diazoalkanes, and catalytic methods for ketone, aldehyde, and formaldehyde



Scheme 1. Varied approaches to C–B and B–B homologation with donor–acceptor diazo compounds by complexation and 1,2-migration.

homologation have been developed.⁹ To further expand on the synthetic utility of these unique carbon nucleophiles, we began to explore various B-based electrophiles in formal carbon insertion.

* Corresponding author. Tel.: +1 (805) 493 3026.

E-mail address: jkingsbu@callutheran.edu (J.S. Kingsbury).

† Current address: Department of Chemistry, High Point University, 833 Montlieu Avenue, High Point, NC 27262, United States.

Of the available boron reagents to consider for reaction development, diboronic esters are among the most intriguing. Formal diazoalkyl insertion into a B–B bond gives mono- and di-substituted 1,1-diborylalkanes^{10,11}—molecules that have captured the interest of multiple research groups.^{12,13} The common mode of preparing these building blocks is a double hydroboration¹⁴ of terminal alkynes, for which 9-BBN^{14c,d} is the preferred reagent in the absence of Rh or Cu(I) catalysis.¹⁵ However, dihydroboration is not general; the use of internal alkyne substrates leads to regioisomeric mixtures, and this has created a gap in reaction scope for doubly carbon-substituted *geminal* diborons. Very recently, Wang and coworkers^{11a} reported a simple and convenient entry to 1,1-bis(pinacolato)diborylalkanes by merging Bamford–Stevens *N*-tosylhydrazone cleavage with high-temperature homologation of B₂pin₂ (**Scheme 1d**). A range of base-stable BCB products were prepared, but a limitation was identified in the case of internal, ketone-derived diazoalkanes: steric hindrance and low solubility of the intermediate tosylhydrazone sodium salts led to diminished yields. Therefore, the Pt(0)-catalyzed insertion of diazoalkanes into B₂pin₂, a novel transformation first discovered by Srebnik¹⁰ with diazomethane, remains a more efficient approach to fully C-substituted, sp³ hybridized 1,1-diborons. Herein, we disclose the results of our own independent study on the scope of the catalytic Srebnik¹⁰ diborylation of ‘non-stabilized’ diazo compounds. Specifically, we have lowered the temperature needed (80 °C) to observe facile carbon insertion with B₂pin₂ and further widened preparative access to the more challenging disubstituted adducts. Encouraged by the promise of *gem*-diborylalkanes as precursors to valuable quaternary carbon atoms, we further report that the products undergo a clean, high-yield conversion to chiral tertiary alkyl (pinacolato)borons by Lewis base-induced deboronation and S_N2 alkylation of the resulting B-stabilized carbanion (**Scheme 2**).

We began our studies by screening conditions reported for the syntheses of **1** and **6** (**Table 1**, entries 1 and 6), two of the four compounds that had been prepared earlier by Srebnik in 2002.^{10b} Ni(PCy₃)₂, Pd(PPh₃)₄, and Pd₂dba₃ all failed to provide any of the desired insertion product, but smooth conversion was observed with Pt(PPh₃)₄. At a catalyst loading of 3 mol %, transformation of pure methyl phenyl diazomethane¹⁶ to diboronic ester **1** was rapid enough to permit a lower reaction temperature (110 → 80 °C) and a shorter reaction time (6 h, >98% conversion of B₂pin₂). Reaction progress can be monitored by visual inspection due to the brightly colored appearance of the diazoalkane, but regardless a 6 h duration was applied to a selection of aryl alkyl diazomethanes in warm toluene.

The experimental results are compiled in **Table 1**. The method tolerates both electron-donating and -withdrawing substituents at the *para* position (entries 2–4, 7). Also of note is chemoselective reaction with the diboron reagent in the case of *p*-chlorophenyl methyl diazomethane (entry 4). The Miyaura borylation¹⁷ product is not observed, an expected result given a slow rate of oxidative addition of Pt(0) into the aryl–Cl bond. Cyclic diazo compounds can be employed to prepare diboryl tetrahydronaphthalenes and indanes (entries 6 and 7). Importantly, reaction efficiency maintains in the presence of increased steric congestion, as demonstrated by the syntheses of benzylic diborylalkanes **5** and **8** in >70% yield (entries 5 and 8). Additional reactions of internal and terminal alkyl diazoalkanes¹⁶ (entries 9–12) attest to the height-

Table 1
Doubly C-substituted 1,1-diborons by diazoalkyl insertion^a

The reaction scheme shows a diazoalkane (R₁-C≡N₂-R₂) reacting with 1.0 equiv B₂pin₂ and 3 mol % Pt(PPh₃)₄ in toluene at 80 °C for 6 h. The product is a 1,1-diboron compound where one carbon of the diazo group is replaced by a boron atom bonded to two pinacolato groups (B-OPin₂) and one R₁ group. Nitrogen gas (N₂) is also released.

Entry	Diazoalkane	Product	Yield ^b (%)
1			79
2			80
3			68
4			61
5			74
6			78
7			76
8			71
9			81
10 ^c			75
11 ^c			84
12 ^c			70

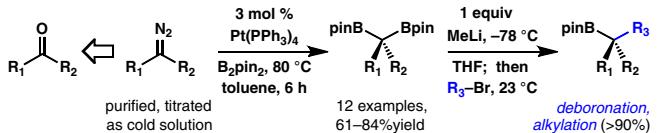
^a Conditions: 1.1 equiv diazoalkane, 1 equiv B₂pin₂ and 3 mol % Pt(PPh₃)₄ in dry toluene (0.1 M, 80 °C, 6 h).

^b Purified yields.

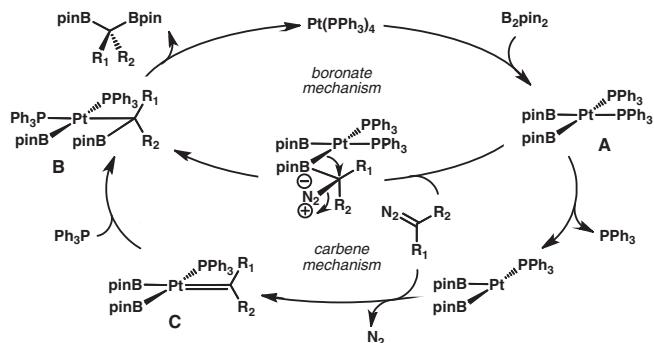
^c Run at 40 °C for 6 h.

ened reactivity that is observed in the absence of resonance delocalization. In these cases, complete conversion was achieved in 6 h at just 40 °C. All diboron products proved robust and bench-stable, and they were typically isolated as colorless crystalline solids in 60–80% yield by standard flash silica gel chromatography.

At the temperatures reported herein, efficient diborylation is not observed in the absence of Pt(0). This suggests that a Hooz pathway involving diazoalkyl addition to B₂pin₂ and a B–B bond shift (**Scheme 1**, top) is not a dominant source of products. Two other mechanisms differing only in the site of nucleophilic attack (B vs Pt) are provided in **Scheme 3**. With di(pinacolato)boryl Pt(II) complex **A** well characterized by the work of Ishiyama et al.,¹⁸ Srebnik¹⁰ postulates that boronate formation and subsequent



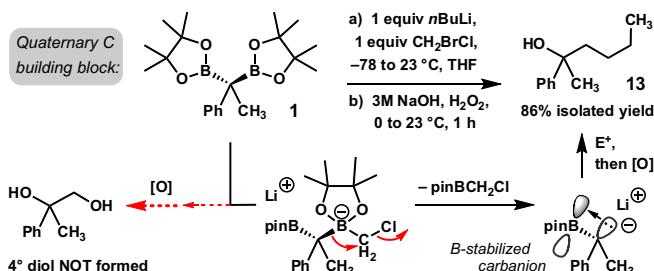
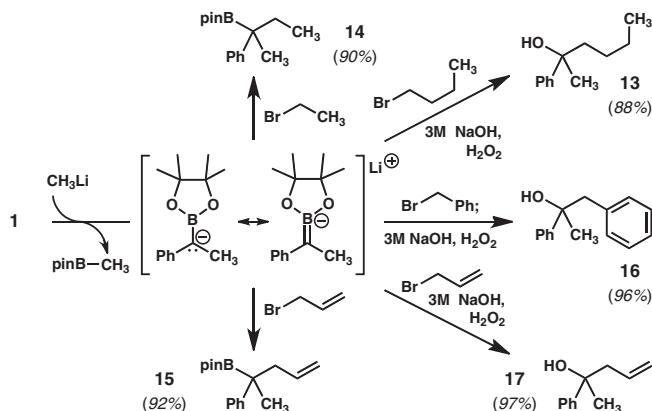
Scheme 2. A dual investigation on the scope of Pt-catalyzed Srebnik diazoalkane diborylation and selective transformation of one B group.

**Scheme 3.** Two possible catalytic cycles for formal carbon insertion.

1,2-migration afford intermediate **B**. Reductive elimination then turns over the catalyst. Alternatively, metalation at platinum(II) could occur after dissociation of a phosphine ligand. Formation of carbene¹⁹ **C**, followed by migratory insertion and reductive elimination, would also complete the catalytic cycle.²⁰

1,1-Diborylalkanes are useful synthons marked by a growing list of strategies for further transformation. Of particular value are those that chemoselectively divert one boryl unit toward C–C bond formation. For monosubstituted derivatives with an α -C–H, deprotonation with LTMP and nucleophilic addition/elimination with ketones gives alkenyl boronates that are direct precursors to tetrasubstituted olefins through Suzuki–Miyaura cross coupling.²¹ Shibata and coworkers also identified mild conditions in which terminal pinacol 1,1-diboronic esters participate outright as cross coupling nucleophiles.²² In this context, enabling features are an incipient hydroxy boronate that serves to direct transmetalation and stabilization of the resulting aryl Pd-alkyl intermediate by the remaining, proximal boronyl. Hall and coworkers^{15b} achieved similar success with chiral 1,1-diborons prepared by catalytic asymmetric conjugate borylation in which chemoselectivity for arylation or vinylation derives from differentiated boron groups.

Judging that severe steric crowding would pose new challenges for Pd-catalyzed cross coupling, we chose a more classical mode of reaction to initially probe the utility of the quaternary diboron products. As shown in **Scheme 4**, a Matteson homologation was attempted under the standard conditions for chloromethyl lithium formation in situ, and a basic peroxide workup was performed to oxidize any remaining C–B bonds. Naively, we were surprised to find that none of the homologous quaternary 1,2-diol is formed under these conditions. Rather, a tertiary alcohol incorporating a butyl fragment (**13**, **Scheme 4**) is produced cleanly in high yield. It became clear that *n*-butyl bromide, the byproduct of lithium–bromine exchange, had served as electrophile in an unforeseen S_N2 alkylation. Instead of rendering the attached C–B bond more electron-rich toward 1,2-migration, ate complex formation allows for rapid deboronation. The result is a B-stabilized carbanion that clearly represents a competent electrofuge. To test this notion,

**Scheme 4.** Attempt to produce quaternary diol gives tertiary alcohol.**Scheme 5.** 1,1-Diborons are precursors to tertiary boronic esters and alcohols due to the ease with which deboronation/substitution occurs.

the same experiment was repeated, this time with benzyl bromide (1 equiv) added to outcompete the *n*-butyl bromide formed in situ. Homobenzylic tertiary alcohol **16** (see **Scheme 5**) was recovered in 91% purified yield under the conditions of this experiment.

Survey of the literature reveals a number of examples in which terminal *gem*-organoborons undergo base-induced deborylation as part of another transformation. 1,1-diborane intermediates give only primary alcohols upon direct oxidation due to the rapid rate of protodeboronation,^{14b,23} but the use of H₂O₂ in acidic medium²⁴ furnishes the expected aldehydes in good yield. Treatment with 2 equiv of *n*-BuLi gives dianionic 1-lithio-1-borato alkanes²⁵ that can be quenched with carbon dioxide to yield alkylmalonic acids. Use of only 1 equiv of *n*-BuLi produces 1-lithio boranes which can add to aldehydes and ketones to form alkenes.²⁶ A boron enolate has been prepared from 1,1-diborylhexane by sequential exposure to methylolithium and methyl benzoate.²⁷ Finally, *gem*-diborylalkanes presenting a leaving group at the 3- or 4-position have given rise to the corresponding cyclopropyl or cyclobutyl boranes by intramolecular cyclization.^{14a,b} Thus, despite useful precedents for forming resonance-delocalized α -boryl anions by metalation/deborylation, B–C–B structures stay underappreciated as precursors to tertiary organoborons by a simple substitution event.²⁸ Moreover, to our knowledge, we are the first to conduct such a sequence on an internal, fully substituted diboronic ester.

Additional experiments that underscore the remarkable facility with which *gem*-diborons experience net substitution

Table 2

Performance of α -boryl anion in boron–Wittig olefinations^a

1	1 equiv MeLi THF, -78 °C, 10 min; then H ⁺ -78 °C to 23 °C, 3 h	
		77% (E/Z 5.3:1)
		81% (E/Z 4.8:1)
		64% (E/Z 3.6:1)
		72% (E/Z 4.4:1)
		75% (E/Z 5.1:1)
		79% (E/Z 5.0:1)

^a Conditions stated; yields represent major isomer. E/Z ratios by ¹H NMR.

upon metalation are illustrated in **Scheme 5**. In these cases, the acetophenone-derived product **1** was treated with a commercial solution of methylolithium (1 equiv, THF, –78 °C) followed by an alkyl bromide with warming. Chiral tertiary (pinacolato)borons **14** and **15**, derived from alkylation with ethyl and allyl bromide, are isolated in 90–92% yields. If desired, the sequence can also be extended to include oxidation of the second C–B bond. Boronate formation, as before, followed by reaction with *n*-butyl, benzyl, or allyl bromide and sodium hydroxide/hydrogen peroxide upon workup affords tertiary alcohols **13**, **16**, and **17** in excellent yield.

As shown in **Table 2**, the efficient production of trisubstituted alkenes from various aromatic aldehydes lends added support to a boryl-ylide intermediate. Boron–Wittig reagents are commonly accessed by deprotonating secondary dimethylboranes, wherein a base is sterically prevented from adding to the vacant p orbital on boron.²⁹ Deprotonation is irrelevant here starting with the ketone-derived insertion product **1**. Nonetheless, these examples serve to complement other known alkylidenations of B-stabilized anions and confirm the applicability of a user-friendly pinacolato ester.³⁰ Selected functional groups (ether, ester, nitrile, or thiophene) are well tolerated, and *E/Z* selectivity approaching >5:1 is possible in certain cases (**18**, **20**, and **23**). Also noteworthy is the fact that an alkynyl trimethylsilyl function (in **20**) remains intact during the nucleophilic addition/elimination. The presence of any unreacted methylolithium at the time an electrophile is introduced is unlikely given the high rate of initial metalation/deboronation.

In summary, we report an expanded scope for the Pt-catalyzed diazoalkane diborylation reaction, particularly for disubstituted (pinacolato)borons. An opening attempt at desymmetrizing the products led to the precedented discovery that 1,1-diboroalkanes undergo bond-selective substitution upon treatment with a Lewis base and alkyl halide. The underlying deboronation mechanism is now advanced as a convenient and practical route toward chiral tertiary boronic esters. Although highly enantioselective methods have been achieved for this class of compounds,³¹ the universal importance of organoborons as nucleophiles for Suzuki–Miyaura cross coupling³² and Rh-catalyzed 1,4-/1,2-addition³³ renders the innate modularity and generality of our findings very compelling.

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Supplementary data

Supplementary data (experimental procedures, characterization data, and copies of ¹H and ¹³C NMR spectra) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2014.03.135>.

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