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Cobalt-Catalyzed 1,1-Diboration of Terminal Alkynes: Scope, Mechanism and Synthetic Applications

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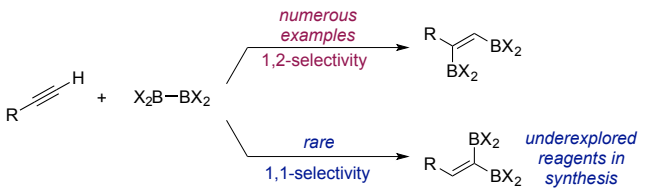
ABSTRACT: A cobalt-catalyzed method for the 1,1-diboration of terminal alkynes with bis(pinacolato)diboron (B_2Pin_2) is described. The reaction proceeds efficiently at 23 °C with excellent 1,1-selectivity and broad functional group tolerance. With the unsymmetrical diboron reagent PinB–BDan (Dan = naphthalene-1,8-diaminato), stereoselective 1,1-diboration provided products with two boron substituents that exhibit differential reactivity. One example prepared by diboration of 1-octyne was crystallized and its stereochemistry established by X-ray crystallography. The utility and versatility of the 1,1-diborylalkene products was demonstrated in a number of synthetic applications, including a concise synthesis of the epilepsy medication tiagabine. In addition, a synthesis of 1,1,1-triborylalkanes was accomplished through cobalt-catalyzed hydroboration of 1,1-diborylalkenes with HBPin. Deuterium-labeling and stoichiometric experiments support a mechanism involving selective insertion of an alkynylboronate to a Co–B bond of a cobalt boryl complex to form a vinylcobalt intermediate. The latter was isolated and characterized by NMR spectroscopy and X-ray crystallography. A competition experiment established that the reaction involves formation of free alkynylboronate and the two boryl substituents are not necessarily derived from the same diboron source.

Introduction. Organoboron compounds are among the most versatile in organic synthesis owing to their stability, ease of handling and utility for the synthesis of carbon-carbon and carbon heteroatom bonds.[1] Among this important class of reagents, alkenyldiboronates are particularly attractive because they offer two distinct boron substituents for elaboration, ideally in a site and stereoselective manner. As a consequence, alkenyldiboronates have found applications in the stereocontrolled synthesis of multisubstituted olefins,[2] an important challenge in synthesis.[3] Specifically, 1,2-diborylalkenes have been used as key intermediates en route to natural products[4] and π-conjugated materials,[5] while the utility of 1,1-diborylalkenes has been demonstrated in a concise synthesis of the anti-cancer agent tamoxifen.[6]

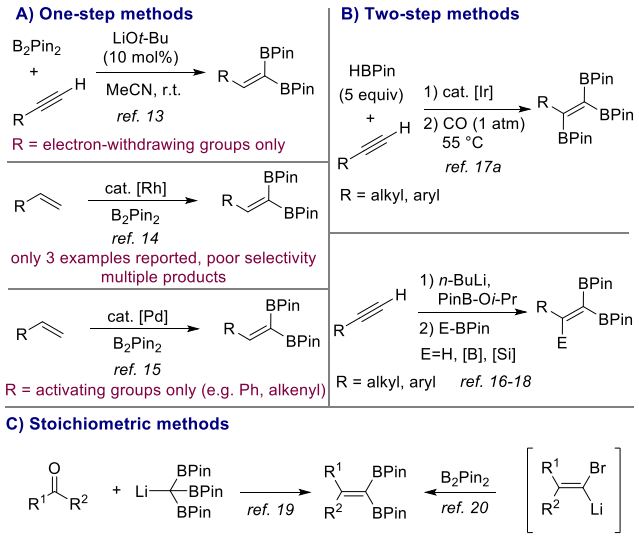
Synthesis of alkenyldiboronates is typically accomplished by diboration of terminal or internal alkynes and is often promoted by transition metal catalysts,[7] base,[8] Lewis acid,[9] and in some cases proceeds in the absence of catalysts.[10] Regardless of the synthetic route, these methods almost exclusively result in 1,2-difunctionalization,[11] a common reactivity mode for addition to C-C multiple bonds (Scheme 1).

Scheme 1. 1,2 vs 1,1-selectivity in alkyne diboration.



Since Miyaura and Suzuki's seminal discovery of platinum-catalyzed alkyne 1,2-diboration,[12] a number of catalysts for this transformation have been reported. By contrast, examples of the direct synthesis of the isomeric 1,1-diborylalkenes from terminal alkynes and diboron reagents are rare. In addition, the full potential of 1,1-diborylalkenes in synthesis has not been explored beyond the singular tamoxifen example, even though these reagents offer a significant degree of synthetic flexibility. In 2015, Sawamura and coworkers reported the direct preparation of 1,1-diborylalkenes from terminal alkynes and B_2Pin_2 using LiO*t*-Bu as the catalyst (Scheme 2A).[13] While effective and an important advance, this reaction is limited to alkynes bearing electron-withdrawing substituents such as propiolates.

Scheme 2. Summary of current methods for the synthesis of 1,1-diborylalkenes.



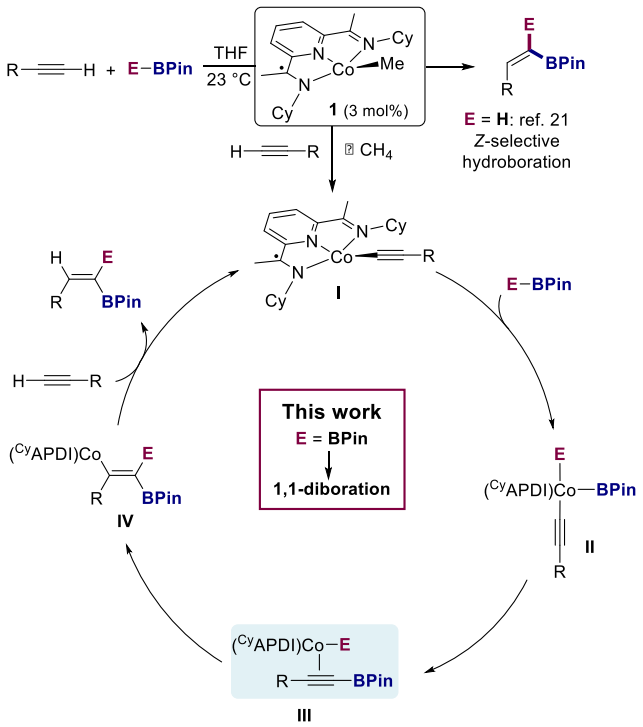
Rhodium-catalyzed dehydrogenative borylation of alkenes has been reported as a route to 1,1-diborylalkenes but the selectivity is poor as mixtures of (di)borylated products were obtained and high temperatures were required.[14] A more selective palladium-catalyzed method has since been described but is restricted to terminal alkenes bearing electronically activating groups such as aryl and alkenyl substituents (Scheme 2A).[15]

Two-step procedures starting from terminal alkynes (Scheme 2B)[16-18] and methods involving stoichiometric amounts of organo-

lithium reagents (Scheme 2C) have also been reported.[19,20] However, these approaches suffer from low volumetric throughput and poor functional group compatibility, respectively.. Given the limitations of the methods currently available for the synthesis of 1,1-diborylalkenes, the direct 1,1-diboration of terminal alkynes with simple alkyl and aryl substituents would be an attractive, atom economical method for the synthesis of these valuable building blocks and likely open new avenues for synthesis.

Our laboratory recently reported that the cyclohexyl-substituted pyridine(diimine) cobalt methyl complex **1** promotes the *Z*-selective hydroboration of terminal alkynes (Scheme 3).[21] Stoichiometric experiments, isolation of intermediates, and deuterium labeling studies established a unique mechanistic pathway involving initial formation of a cobalt acetylide (**I**) which, following engagement with pinacolborane (HBPin), forms an alkynylboronate complex (**III**). Regioselective *syn*-hydrocobaltation forms vinylcobalt intermediate (**IV**, E=H), resulting in the unusual *Z*-selectivity. The cyclohexyl-substituents were found to be important for the observed reactivity and formation of the key cobalt-acetylide intermediate. Analogous experiments with aryl-substituted bis(imino)pyridine cobalt compounds resulted in *E*–selective alkyne hydroboration due to preferential formation of the cobalt hydride over the cobalt acetylide. In the Z-selective method, the [H] and [BPin] of the borane are both transferred to the terminal carbon of the alkyne, suggesting that complex **1** may serve as a catalyst for other cobalt-catalyzed 1,1-difunctionalization methods.[22] Specifically, replacement of HBPin with B_2Pin_2 would generate a cobalt boryl intermediate (**III**), which after *syn*-borylcobaltation and product release would result in a method for the direct synthesis of 1,1-diborylalkenes (**I**-**IV**, E=BPin).

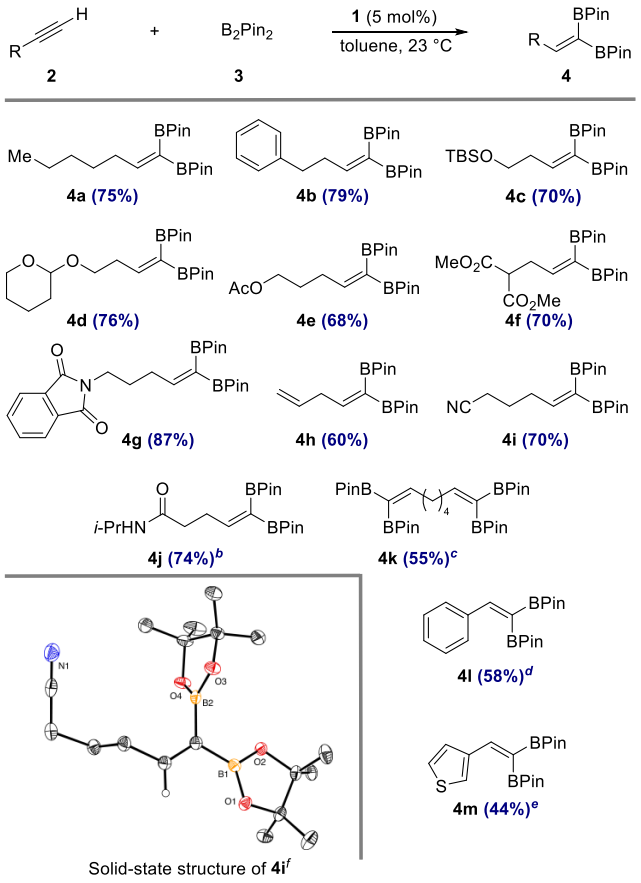
Scheme 3. Proposed mechanism for *Z*-selective hydroboration as inspiration for the 1,1-diboration of terminal alkynes.



Here we describe a cobalt-catalyzed method for the synthesis of 1,1-diborylalkenes from readily available terminal alkynes and diboron reagents. In contrast to all other transition metal-catalyzed diborations reported to date, the cobalt-catalyzed reaction documented here proceeds with excellent 1,1-selectivity. The new method exhibits broad scope and functional group tolerance, and its utility and mildness was demonstrated in a concise synthesis of tiagabine, a medication for the treatment of epilepsy. To highlight the synthetic versatility of the 1,1-diborylalkene products, they were used to access a diverse set of structural motifs, including 1,1-dihaloalkenes, a carboxylic acid, a 1,1-diborylalkane, and 1,1,1-triborylalkanes. In addition, the method could be extended to stereoselective synthesis of trisubstituted olefins through 1,1-diboration of terminal alkynes with the mixed diboron reagent PinB–BDan. The chemically differentiated boron substituents allowed selective cross coupling at [BPin]. Finally, mechanistic studies established the intermediacy of a cobalt vinyl intermediate that was crystallographically characterized.

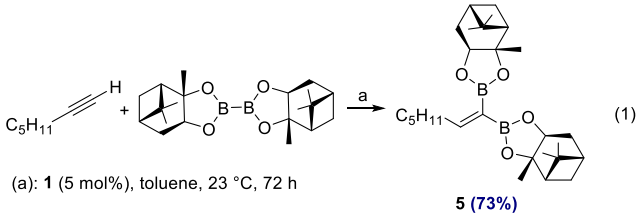
Results and Discussion. Initial catalyst evaluation was conducted with equimolar quantities of 1-heptyne and B_2Pin_2 in the presence of 5 mol% of **1** at 23 °C for 13 hours in a 1.0 M toluene solution. Analysis of the unpurified reaction mixture by ^{1}H NMR spectroscopy established clean and complete conversion to 1,1-diborylalkene **4a**, which was isolated in 75% yield (Scheme 4). A control experiment demonstrated that no 1,1-diborylalkene product formed in the absence of cobalt complex **1**. As shown in Scheme 4, a range of alkynes participated in cobalt-catalyzed 1,1-diboration to yield 1,1-diborylalkene products **4b**-**4m**. Common organic functional groups such as *tert*-butyldimethylsilyl ether (**4c**), acetal (**4d**), ester (**4e**, **4f**), phthalimide (**4g**), nitrile (**4i**), and secondary amides (**4j**) were all compatible with the reaction conditions. Remarkably, a substrate bearing a terminal olefin underwent chemoselective 1,1-diboration of the alkyne without isomerization of the double bond (**4h**).

Scheme 4. Scope of the 1,1-diboration of terminal alkynes with B_2Pin_2 and (^{Cy}APDI)CoCH$_3$ (**1**).[a]



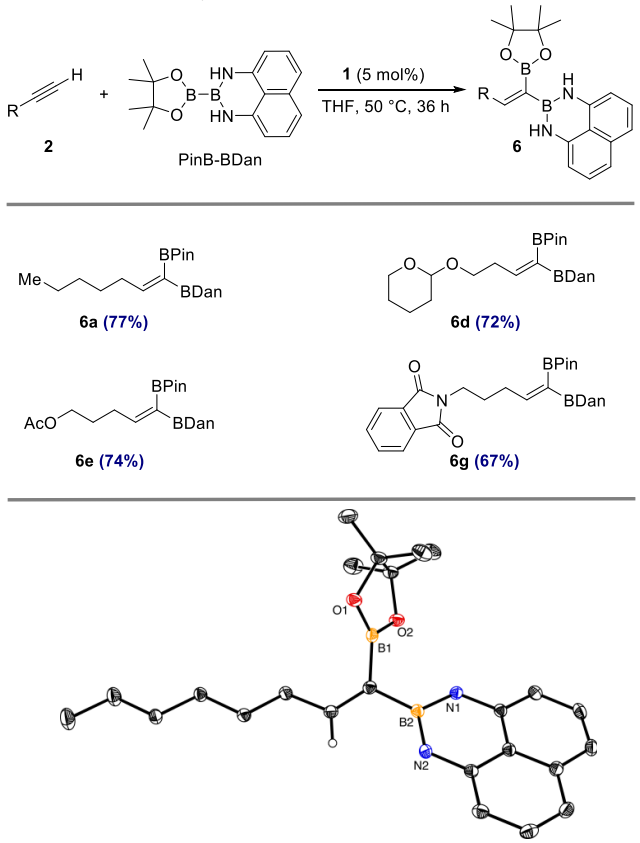
[a]Reaction conditions: alkyne **2** (0.50 mmol), B_2Pin_2 (0.50 mmol, 1.0 equiv), **1** (0.025 mmol, 5 mol%), toluene (0.5 mL), 23 °C. Numbers in parentheses are yields of isolated products obtained after purification by flash chromatography on silica gel. [b]0.25 mmol **2**, 0.25 mmol **3**, 10 mol% **1**. [c]2.0 equiv **3**. [d]4.0 equiv **3**. [e]1.5 equiv **3**. [f]Thermal ellipsoids at 50% probability.

Aryl- and heteroaryl acetylenes also were suitable substrates (**4l**, **4m**), although increased amounts of diboron reagent were required to suppress competitive homodimerization of the alkynes to the corresponding enynes. It is noteworthy that this side reaction was not observed when alkyl-substituted alkynes were used (**4a**-**4k**). To highlight the practicality of the method, products **4a** and **4g** were prepared on gram scale in 68 and 81% yield, respectively, with a reduced catalyst loading of 2 mol% (see SI for details). Diboron reagents other than B_2Pin_2 also participated in the catalytic reaction (eq. 1), andcobalt-catalyzed reaction of 1-heptyne with bis[(+)-pinanediolato]diboron afforded 1,1-diborylalkene **5** in 73% yield.



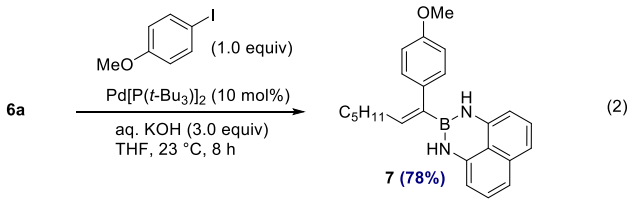
Stereoselective 1,1-diboration. The stereocontrolled synthesis of alkenes is fundamentally important in organic synthesis.[3] In this context, a stereoselective cobalt-catalyzed 1,1-diboration with an unsymmetrical diboron reagent would result in the formation of a trisubstituted olefin of well-defined configuration, providing access to an underexplored class of diborylalkenes. In 2010, Iwadate and Suginome reported the use of PinB–BDan (Dan = naphthalene-1,8-diaminato) in Pt- and Ir-catalyzed 1,2-diboration of alkynes.[2d] The reaction was regioselective, leading to exclusive transfer of the [BDan] substituent to the terminal carbon. As shown in Scheme 5, cobalt-catalyzed 1,1 diboration of 1-heptyne with PinB–BDan proceeded efficiently and stereoselectively to afford **6a** in 77% yield. A related 1,1-diborylalkene derived from 1-octyne and PinB–BDan was also prepared and crystallized. Its structure and stereochemistry were confirmed by X-ray crystallography (Scheme 5, bottom). The generality and functional group compatibility of this stereoselective process was demonstrated with selected, representative alkyne substrates bearing common functional groups to afford products **6d**, **6e** and **6g** (Scheme 5).

Scheme 5. Stereoselective cobalt-catalyzed 1,1-diboration of terminal alkynes with PinB–BDan.[a]



[a]Reagents and conditions: alkyne **2** (0.50 mmol), PinB–BDan (0.50 mmol), **1** (5 mol%), THF, 50 °C, 36 h. Numbers in parentheses are yields of isolated products obtained after purification by flash chromatography on silica gel. Thermal ellipsoids in ORTEP diagram at 50% probability, hydrogen atoms except vinyl C–H omitted for clarity. Olefin geometry of products **6a, 6d, 6e, 6g** assigned by analogy to the solid state structure.

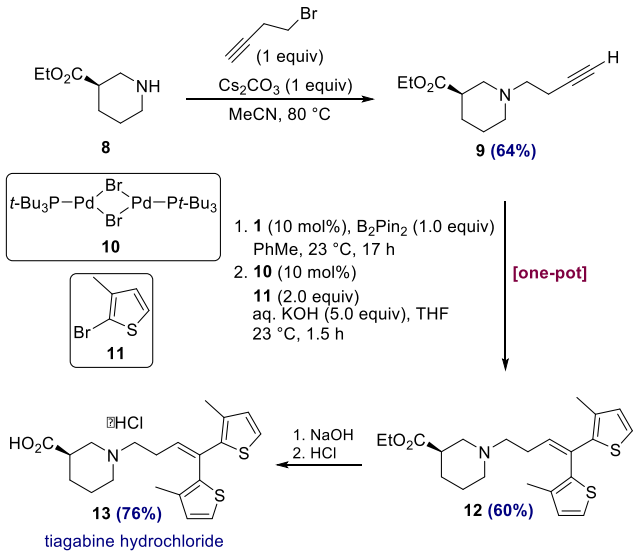
The differential reactivity of the two boron substituents in **6a** allowed selective Suzuki-Miyaura cross coupling at BPin to proceed efficiently, furnishing **7** in 78% yield (eq. 2). The olefin geometry in **7** was confirmed by NOESY (see SI). From a synthetic perspective, the two-step sequence of 1,1-diboration and cross coupling to give **7** represents a formal 1,1-carboboration of 1-heptyne.[23]



(2)

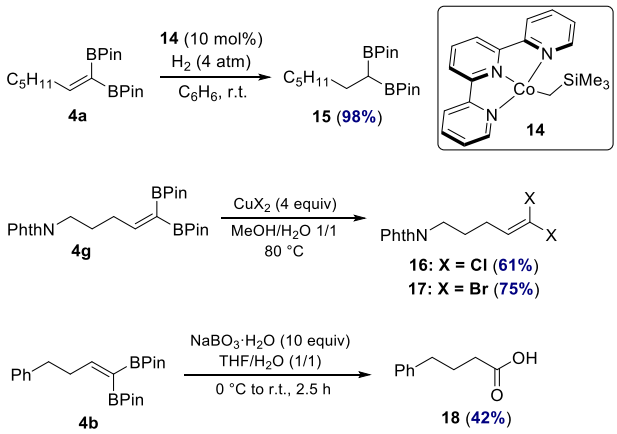
Synthetic applications of 1,1-diborylalkenes. The synthetic utility of the 1,1-diboration method was demonstrated as an enabling step in the highly concise synthesis of of tiagabine (**13**), an epilepsy medication (Scheme 6). Alkylation of commercially available (*R*)-ethyl piperidine-3-carboxylate (**8**) with 4-bromo-1-butyne gave terminal alkyne **9** in 64% yield. A one-pot sequence consisting of cobalt-catalyzed 1,1-diboration followed by Suzuki-Miyaura cross-coupling yielded tiagabine ethyl ester **12** in 60% yield over 2 steps. Importantly, the reaction conditions were compatible with the ester and amine functionality, and the integrity of the stereogenic center was preserved throughout the sequence of reactions (see SI for SFC traces). Ethyl ester **12** was then converted to tiagabine hydrochloride via a known series of steps involving saponification of the ester and formation of the hydrochloride salt.[24]

Scheme 6. Synthesis of tiagabine hydrochloride via one-pot 1,1-diboration/cross-coupling.



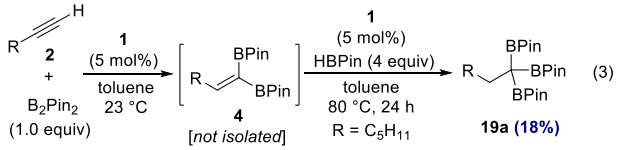
To highlight the versatility of the 1,1-diborylalkene products, they were also elaborated to other useful building blocks (Scheme 7). Hydrogenation of **4a** catalyzed by terpyridine-ligated cobalt complex **14** afforded the corresponding 1,1-diborylalkane **15** in 98% yield. 1,1-diborylalkanes have recently received increasing attention due to their utility in cross-coupling and alkylation reactions.[25] In addition, 1,1-dichloro- and 1,1-dibromoolefins **16** and **17** were prepared by treating **4g** with the appropriate cupric salt. The 1,1-dihaloolefin motif is found in a number of commercial insecticides[26] as well as in natural products.[27] Oxidation of 1,1-diborylalkene **4b** with sodium perborate furnished carboxylic acid **18**. The sequence of 1,1-diboration/oxidation is thus formally equivalent to oxidative hydration of a terminal alkyne.[28] Importantly, the transformations yielding products **16**-**18** have not been previously reported.

Scheme 7. Synthetic applications of 1,1-diborylalkenes.



Synthesis of 1,1,1-triborylalkanes. The use of 1,1-diborylalkenes in the synthesis of an unusual class of organoboron compounds was also explored. Selective hydroboration of 1,1-diborylalkenes would provide a unique route to 1,1,1-triborylalkanes, an underexplored class of reagents with considerable potential in organic synthesis. Huang recently reported high yields in deborylative alkylation reactions between 1,1,1-triborylalkanes and simple alkyl bromides,[29a] while our own laboratory demonstrated the utility of benzyltriboronates in diastereoselective conjugate additions.[29b] While the synthesis and reactivity of 1,1-diborylalkanes have received considerable attention due to their aforementioned utility in cross-coupling and alkylation reactions,[25] the chemistry of the corresponding 1,1,1-triboronates is by comparison much less developed. This is likely due to the paucity of reliable and general synthetic methods for their synthesis. More than four decades ago, Matteson reported a synthesis of triborylmethane by reaction of chloroform with $ClB(OR)_2$ in the presence of lithium metal.[19,30] All methods developed since have been limited to narrow sets of substrates, such as derivatives of 2-ethylpyridine,[31] styrene,[29,32] or toluene.[33] Accordingly, a two-step, one-pot sequence consisting of Co-catalyzed 1,1-diboration of terminal alkynes followed by selective hydroboration would provide a general synthesis of 1,1,1-triboronates with a set of structurally diverse alkyl groups attached to the triborylated carbon.

In an initial experiment, an additional 5 mol%of cobalt complex **1** (5 mol%) and HBPin (4 equiv) were added to a 1,1-diboration reaction of 1-heptyne that had reached completion as judged by GC analysis. Although a new product was observed by GC analysis after a few hours, the reaction was sluggish. Heating the reaction mixture to 80 °C resulted in increased conversion and the major product, 1,1,1-triboronate **19a**, was isolated in 18% yield after 24 hours (eq. 3).

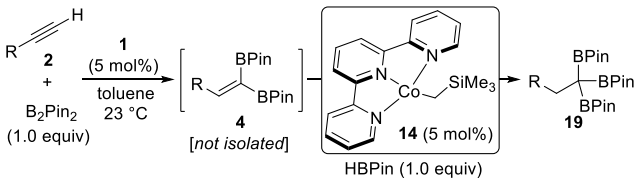


(3)

Having established that selective cobalt-catalyzed hydroboration of 1,1-diborylalkenes was possible, a more active alkene hydroboration catalyst was sought. Our laboratory recently reported a terpyridine cobalt complex that is active for the hydroboration of unactivated, trisubstituted alkenes,[34] a relatively challenging class of substrates. Use of this complex in the hydroboration of styrene led to

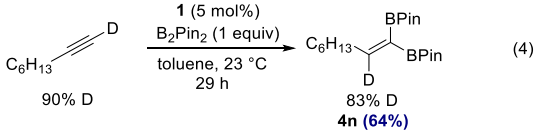
branched selectivity,[34] likely involving a benzylcobalt intermediate. Accordingly, its use with 1,1-diborylalkenes could proceed via intermediacy of a stabilized α-borylcobalt intermediate.[35] As shown in Scheme 8, sequential 1,1-diboration-hydroboration of terminal alkynes involving (^{Cy}APDI)CoCH$_3$ (**1**) and (Terpy)Co(CH$_2$SiMe$_3$) (**14**)[34] furnished a collection of 1,1,1-triboronates **19** in 50-76% yield over two steps. Importantly, carbonyl-based functional groups were compatible with this hydroboration protocol, as evidenced by the synthesis of triboronates **19e**, **19i**, and **19g**.

Scheme 8. One-pot, sequential 1,1-diboration-hydroboration of terminal alkynes.[a]



[a]Reaction conditions: alkyne **2** (0.50 mmol), B_2Pin_2 (0.50 mmol, 1.0 equiv), **1** (0.025 mmol, 5 mol%), toluene (0.5 mL), 23 °C; then **14** (0.025 mmol, 5 mol%), HBPin (0.50 mmol, 1.0 equiv). Numbers in parentheses are yields of isolated products after purification by flash chromatography on silica gel. [b]2 equiv of B_2Pin_2 and HBPin were used.

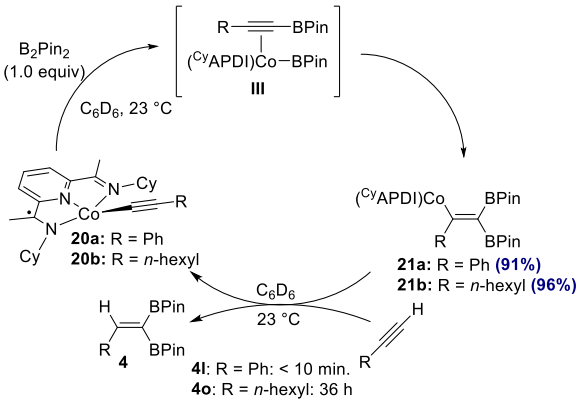
Mechanistic Studies. Having established the scope and utility of the 1,1-diboration method, attention was devoted toward understanding the mechanistic features of the transformation. Cobalt-catalyzed 1,1-diboration of 1-*d*$_1$-octyne (90% isotopic purity) with B_2Pin_2 furnished 1,1-diborylalkene **4n** with the deuterium label at the internal alkene carbon, as judged by ^{1}H and quantitative ^{13}C NMR spectroscopy (eq. 4). This result is consistent with the mechanism depicted in Scheme 3.



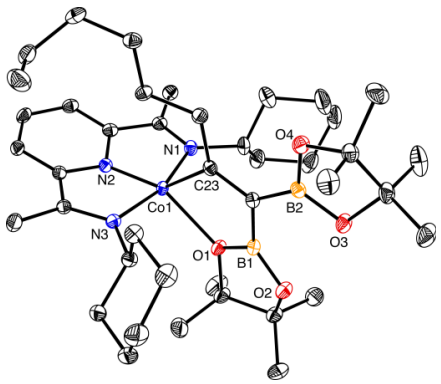
A set of stoichiometric experiments aimed at observing and isolating the proposed vinylcobalt intermediates were also conducted. Cobalt acetylide complexes **20a** and **20b**, derived from phenylacetylene and 1-octyne, respectively, were prepared by a previously described procedure.[21] As shown in Scheme 9, treatment of cobalt acetylide complex **20a** with 1 equivalent of B_2Pin_2 in benzene-*d*$_6$ cleanly generate a single new species within 60 hours as judged by ^{1}H and ^{13}C NMR spectroscopy. In contrast, the reaction of **20b** with B_2Pin_2 to give vinylcobalt **21b** proceeded to 95% conversion within 4 hours. Recrystallization of vinylcobalt complex **21b** from pentane at –35 °C yielded single crystals suitable for X-ray diffraction analysis. A representation of the solid-state structure is presented in Scheme 9 (bottom). The cobalt is five-coordinate with coordination sphere defined by the tridentate pyridine(diimine), the carbon of the alkenyl group and an oxygen (d(Co-O) = 2.2071(12) Å) of the *syn* [BPin] substituent. The bond distances of the bis(imino)pyridine are consistent with one-electron reduction[36] as evidenced by the slightly elongated C_{imine}–N_{imine} bonds of 1.326(2) Å and 1.334(2) Å as well as the slightly contracted C_{imine}–C_{ipso} bonds of 1.438(2) Å and 1.431(2) Å.

To assess its catalytic competence, complex **21a** was treated with one equivalent of phenylacetylene, and analysis by ^{1}H NMR spectroscopy established the presence of only cobalt acetylide **20a** and 1,1-diborylalkene **4l**, with vinylcobalt **21a** having been completely consumed within 10 minutes. The analogous experiment with complex **21b** and one equivalent of 1-octyne resulted in slow conversion to the cobalt acetylide **20b** and 1,1-diborylalkene **4o** over the course of approximately 36 hours. These results indicate that the relative rates of the individual steps (formation of vinylcobalt and protonation) are dependent on the identity of the alkyne. With aliphatic alkynes such as 1-octyne, the protonation is likely rate-determining, as was observed in the previously reported *Z*-selective hydroboration.[21] In contrast, with more acidic alkynes such as phenylacetylene, the protonation step is comparatively fast, such that formation of the vinylcobalt complex is likely rate-determining.

Scheme 9. Synthesis of vinylcobalt complexes, solid-state structure of **21b** and single-turnover experiments.[a]



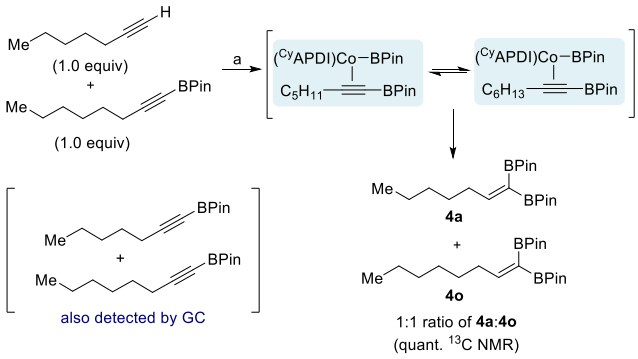
Solid state structure of complex 21b[a]



[a]Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity.

The intermediacy of a cobalt-alkynylboronate complex (**III**) was probed with a competition experiment. If dissociation of the alkynylboronate is competitive with insertion, the two BPin substituents in the product may not necessarily be derived from the same molecule of B_2Pin_2. Indeed, cobalt-catalyzed reaction of 1-heptyne with one equivalent of B_2Pin_2 in the presence of one equivalent of 1-octynyl-BPin resulted in formation of a 1:1 ratio of the two 1,1-diborylalkene products **4a** and **4o** (Scheme 10). In addition, both alkynylboronates were observed by GC analysis upon complete consumption of B_2Pin_2. This result is consistent with alkynylboronates being intermediates en route to the 1,1-diborylalkenes, and confirms that the alkynylboronate is labile in the presence of excess alkynylboronate.

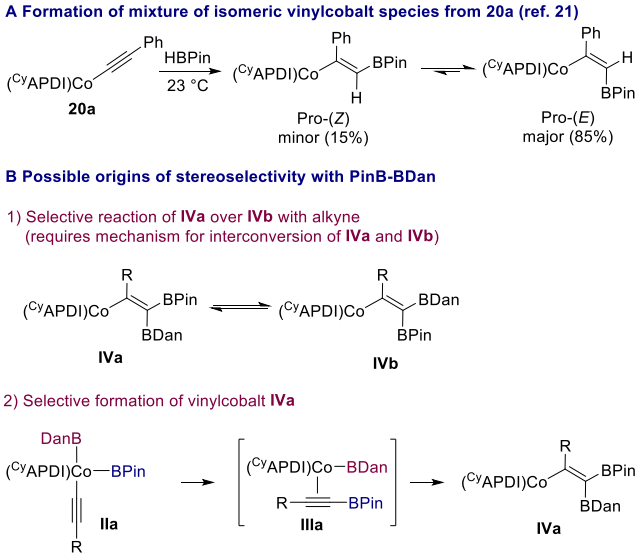
Scheme 10. Competition experiment probing formation of free alkynylboronate.[a]



[a]Reagents and conditions: (a) 1-heptyne (0.50 mmol), 1-octynyl-BPin (0.50 mmol), B_2Pin_2 (0.50 mmol), **1** (5 mol%), toluene (0.5 mL), 23 °C, 15 h.

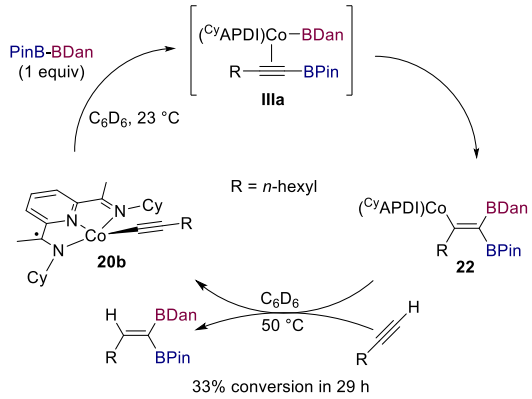
In the cobalt-catalyzed *Z*-selective hydroboration of alkynes with HBPin, a mixture of (*Z*) and (*E*)-vinylcobalt species were formed upon addition of HBPin to acetylide complex **20a**, and found to interconvert (Scheme 11A).[21] The high stereoselectivity observed in the 1,1-diboration with PinB–BDan could be a result of selective reaction of one vinylcobalt intermediate over another (**IVa** vs. **IVb**), but is also consistent with the more Lewis acidic boron substituent (BPin)[37] being transferred to the alkyne first and the resulting alkynyl–BPin cobalt complex (**IIIa**) undergoing *syn*-borylcobaltation to give **IVa** selectively (Scheme 11B).

Scheme 11. Mechanistic possibilities for the origin of stereoselectivity.



In the latter scenario, the structure of or relative rates of reductive elimination from complex **IIa** could affect what type of alkynylboronate complex (e.g. **IIIa**) forms. A stoichiometric experiment was performed to probe this question. Treatment of cobalt acetylide **20b** with 1 equivalent of PinB–BDan in benzene-d_6 at room temperature resulted in formation of a single new species as judged by ^{1}H and ^{13}C NMR spectroscopy (Scheme 12). Addition of one equivalent of 1-octyne to **22** in benzene-d_6 at room temperature resulted in only 5% conversion to diborylalkene product and complex **20b** over the course of 18 hours. However, after heating the solution in the NMR tube to 50 °C for 29 hours, a 33/66 mixture of **20b**/**22** along with a single diborylalkene product was detected by ^{1}H NMR spectroscopy This result is consistent with the requirement for heating 1,1-diborations with PinB–BDan and indicates that the protonation step is considerably slower when the vinylcobalt bears a BDan substituent instead of BPin. The observation of a single new species upon addition of PinB–BDan to **20b** suggests that stereoselective formation of vinylcobalt **22** may be the origin of the overall high stereoselectivity of the process.

Scheme 12. Stereoselective synthesis of vinylcobalt species **22** and single-turnover experiment.



Concluding Remarks. In summary, a general method for the 1,1-diboration of terminal alkynes catalyzed by a cyclohexyl-substituted pyridine diimine cobalt complex has been developed. The reaction proceeds under mild conditions, displays broad scope and functional group tolerance, and furnishes 1,1-diborylalkene products with excellent selectivity. Chiral as well as unsymmetrical diboron

reagents participate in the reaction, and the latter furnished alkene products with two different boron substituents in stereoselective fashion. When used in tandem with Pd-catalyzed cross coupling, this resulted in a formal 1,1-carboboration of the terminal alkyne. A one-pot 1,1-diboration/cross-coupling sequence enabled a highly concise synthesis of tiagabine, an approved treatment for epilepsy. The synthetic versatility of the 1,1-diborylalkene products was further demonstrated in C–halogen, C–O, C–H, and C–B bond formation. The latter gave access to a set of 1,1,1-triborylalkanes that are inaccessible by existing methods. Mechanistic studies revealed that the 1,1-diboration proceeds via the intermediacy of a vinylcobalt species, in analogy to the previously reported *Z*-selective hydroboration and suggest this approach may be general for 1,1-difunctionalization strategies.

ASSOCIATED CONTENT

Supporting Information. Experimental details, characterization data, NMR spectra, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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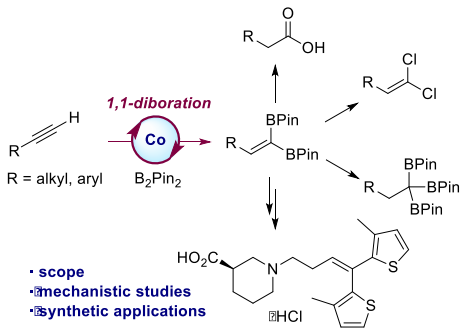
1,1-diboration
Co
R = alkyl, aryl
B2Pin2
BPin
HO2C
N
S
HCl
· scope
· mechanistic studies
· synthetic applications