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Synthesis of Secondary and Tertiary Alkylboranes via Formal Hydroboration of Terminal and 1,1-Disubstituted Alkenes

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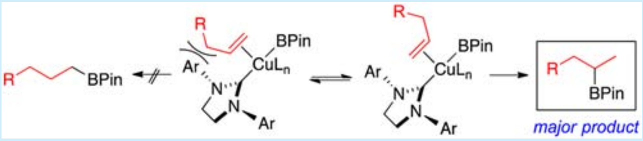
Ⓢ *Supporting Information*

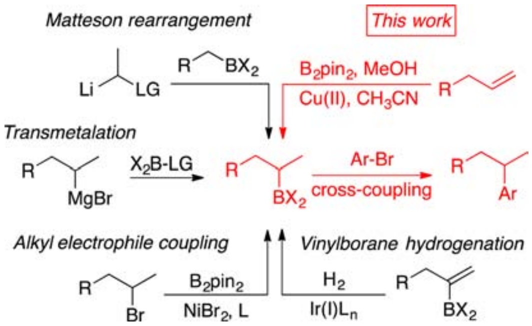
ABSTRACT: Copper-catalyzed functionalization of terminal or 1,1-disubstituted alkenes with bis(pinacolato)diboron and methanol provides formal hydroboration products with exceptional regiocontrol favoring the branched isomer. Pairing this procedure with photocatalytic cross-couplings using iridium and nickel cocatalysis provides an effective, highly regioselective procedure for the hydroarylation of terminal alkenes.



The hydroboration of simple terminal alkenes is a transformation of fundamental importance in synthesis, and the hydroboration/oxidation sequence serves as the introduction to anti-Markovnikov regioselectivity in most introductory organic chemistry courses.[1] Despite the long history of this process, a general approach to reversing the regioselectivity of hydroborations of simple alkenes bearing aliphatic substituents has remained elusive. Coupled with oxidation of the resulting organoborane, this outcome would provide a process equivalent to the acid-catalyzed hydration of alkenes with accompanying advantages in scope and functional group tolerance. Additionally, we envisioned that other processes such as metal-catalyzed cross-coupling, when paired with a reversal of regiochemistry in hydroborations, would provide a useful and simple method for the synthesis of tertiary carbon frameworks through the two-step branch-selective reductive union of alkenes and sp^2-carbon electrophiles. In view of the tremendous recent advances in cross-couplings of secondary organoboranes,[2−5] the development of more efficient methods for accessing the requisite branched organoboranes could find immediate utility.

Most catalytic hydroboration methods provide the linear alkylborane product, often with efficiencies greatly exceeding that of the direct thermal addition of boranes to alkenes.[6] Direct access to branched boranes from the hydroboration of terminal olefins is typically accompanied by chain walking,[7] which often leads to terminal or benzylic boranes. Advances in reversing the regiochemical outcome of hydroborations are often accomplished through the installation of directing groups, which can override normally expected preferences based on the alkene substitution pattern.[8] More recent advances illustrated that subtle remote electronic biases can also be used as a handle for regiocontrol.[9] Alkenes such as styrenes provide an electronic bias for the development of catalyst−substrate interactions that enable regioselectivity reversals, with notable illustrations in directly accessing benzylic boranes from the rhodium-catalyzed hydroboration of styrenes.[10] The copper-catalyzed addition of bis(pinacolato)diboron (B_2Pin_2) in the presence of methanol has been utilized by Hoveyda as a formal hydroboration of terminal alkynes with regioreversal compared with traditional strategies,[11] whereas styrenes afford the terminal borane product.[11b] The procedure, which involves borylmetalation followed by protonation of the resulting Cu−C bond, provides considerable utility as a means to access the more hindered alkenylborane products. Secondary alkylboranes, such as those that potentially could be made by a branch-selective hydroboration of terminal alkenes, are typically accessed by methods such as addition of organolithium or organomagnesium reagents to boron electrophiles,[12] conversion of alkyl halides to alkylboranes,[13] hydrogenations of vinylboranes,[14] or variations of the Matteson rearrangement, which has proven to be immensely useful in asymmetric versions (Scheme 1).[15] Impressive cascade functionalizations of terminal alkenes have enabled the preparation of secondary alkylboranes in tandem with arylation or alkenylation of the terminal alkene carbon,[16] and reports of aminoboration and carboboration were recently disclosed.[17] Furthermore, a recent approach from Ito involves the formal hydroboration of terminal alkenes via a process catalyzed by copper-phosphine complexes.[18] While these methods have enabled many

Scheme 1. Approaches to Secondary Alkylboranes



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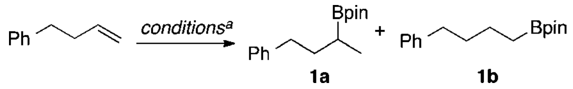
impressive advances in the synthesis and application of secondary alkylboranes, a more general approach to the hydroboration of a variety of terminal and 1,1-disubstituted alkenes to provide a regiochemical outcome opposite that of classical thermal additions of borohydrides to alkenes would provide an important entry to branched alkylboranes for utilization in synthesis. The development of a highly regio- and branch-selective hydroboration process using a copper–NHC catalyst is described herein, and the utility of the method with photocatalytic cross-couplings[3] is demonstrated.

Efforts to access branched alkylboranes from terminal alkenes began with exploration of hydroborations using HBPin with Ni, Pd, Pt, Co, and Rh catalysts and the N-heterocyclic carbene ligands IMes, SIMes, IPr, and SIPr (Table 1, entries 1–7; selected data). In all cases, the terminal alkylborane product was favored, with Co- and Rh-catalyzed processes most strongly favoring the linear products, and no more than a 21% yield of the desired branched product was observed in any case. We next examined additions using B_2Pin_2 with methanol and Cu(I) catalysts given the success seen in regiochemistry reversals involving terminal alkynes by Hoveyda with similar catalyst systems.[11] The combination of CuCl with IMes provided a nearly 2:1 ratio of regioisomers favoring the branched isomer **1a** (Table 1, entry 8), whereas the use of SIPr provided excellent regioselectivity favoring **1a**, albeit in modest yield (Table 1, entry 9). A solvent screen illustrated that CH_3CN provided superior conversions compared with THF and other common solvents, and a variety of Cu(I) and Cu(II) precatalysts were therefore examined in CH_3CN for yield optimization (Table 1, entries 10–13). In cases where Cu(II) precatalysts are effective, it is likely that a Cu(I) species generated under the reaction conditions functions as the active catalyst.[19] Among the cases explored, the use of the preformed complex Cu(Cl)IPr with B_2Pin_2/MeOH (Table 1, entry 11) provided an optimum outcome in terms of conversion, regioselectivity, and reproducibility across various substrate classes, and this protocol was thus selected for further study.

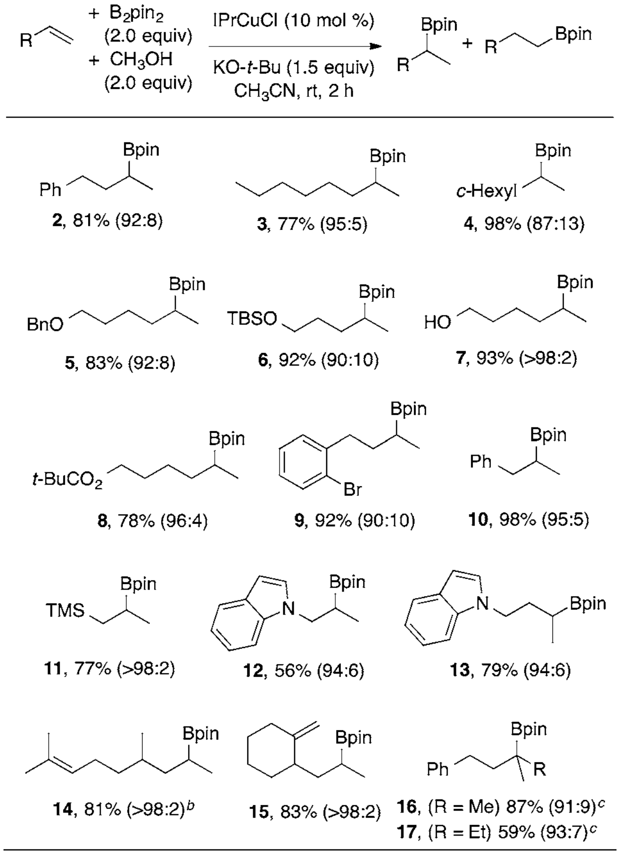
Table 1. Optimization of Branched Alkylborane Synthesis



entry	catalyst	ligand[b]	reagent	solvent	1a:1b (yield, %)[c]
1	Pd_2dba_3	IMes	HBPin	THF	17:83 (62)
2	Pd_2dba_3	SIPr	HBPin	THF	21:79 (47)
3	$Ni(cod)_2$	IMes	HBPin	THF	21:79 (14)
4	$Ni(cod)_2$	SIPr	HBPin	THF	13:87 (<5)
5	$PtCl_2$	SIPr	HBPin	THF	7:93 (74)
6	$CoBr_2$	SIPr	HBPin	THF	<2:98 (62)
7	$Rh(PPh_3)_3Cl$	SIPr	HBPin	THF	<2:98 (33)
8	CuCl	IMes	B_2Pin_2	THF	67:33 (3)
9	CuCl	SIPr	B_2Pin_2	THF	79:21 (48)
10	CuCl	SIPr	B_2Pin_2	CH_3CN	95:5 (52)
11	Cu(Cl)IPr	–	B_2Pin_2	CH_3CN	92:8 (81[d])
12	$Cu(OAc)_2$	SIPr	B_2Pin_2	CH_3CN	93:7 (62)
13	$CuBr_2$	SIPr	B_2Pin_2	CH_3CN	96:4 (78)

[a] All of the experiments were conducted at rt for 2 h at 0.2 M under a nitrogen atmosphere. Experiments with B_2Pin_2 also used CH_3OH (2 equiv). B_2Pin_2 = bis(pinacolato)diboron. [b] Ligand HCl salts were used with KO-*t*-Bu; IMes·HCl = 1,3-bis(mesityl)imidazolium chloride; SIPr·HCl = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. [c] With the exception of entry 11, NMR yields using 1,3,5-trimethoxybenzene as an internal standard are shown. Regioselectivity ratios were determined on crude reaction mixtures. [d] Isolated yield.

Scheme 2. Scope of Branched Alkylborane Synthesis[a]

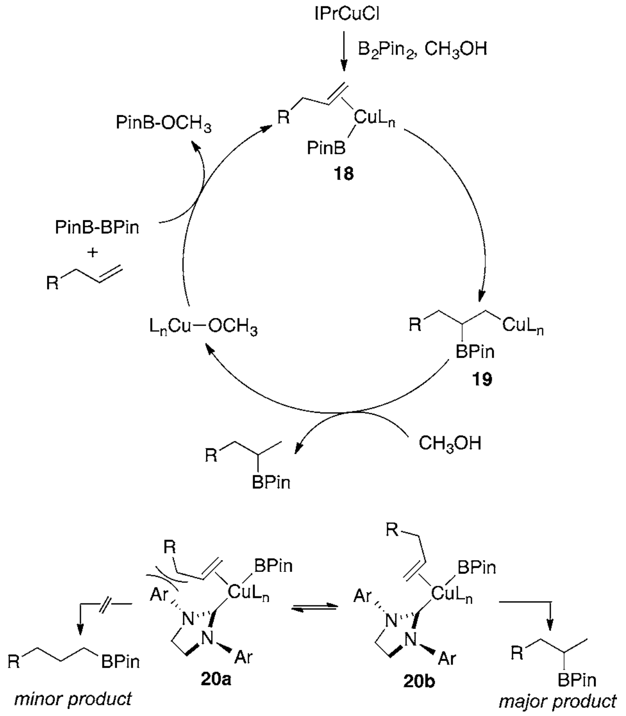


[a] B_2Pin_2 = bis(pinacolato)diboron; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. Regioselectivity ratios were determined on crude reaction mixtures. Isolated yields are given. [b] Diastereomeric ratio = 1:1. [c] The reaction was conducted in CH_2Cl_2 using NaO-*t*-Bu at rt.

A range of simple terminal olefins were examined in the regioselective formation of branched alkylborane products. With 4-phenyl-1-butene and 1-octene, excellent yields and regioselectivities favoring the branched isomer were observed (compounds **2** and **3**, Scheme 2). Branching at the allylic position was tolerated (compound **4**, Scheme 2). Other tolerated functional groups included benzyl ethers, silyl ethers, unprotected hydroxyls, pivalate esters, and bromoarenes (compounds **5**–**9**, Scheme 2). Allylbenzene was a highly effective substrate, and no isomerization to the styrene or to the corresponding benzylic borane product was noted (compound **10**, Scheme 2). Notably, compound **10** was previously prepared in highly enantioselective fashion from prop-1-en-1-ylbenzene via Cu–NHC-catalyzed hydroboration.[20] Examination of similar chiral NHCs in the current procedure using allylbenzene as the substrate led to poor enantioselectivities (see the Supporting Information for details). Therefore, the current procedure will be most useful for non-styrenyl substrates in comparison with this alternative method that is highly effective for styrene hydroborations. As additional examples, allylsilanes were tolerated in the procedure, leading to 1,2-bismetalated products (compound **11**, Scheme 2). Indoles were also tolerated to afford products borylated at the *β*- or *γ*-position of the *N*-alkyl chain (compounds **12** and **13**, Scheme 2). To explore selectivity among different olefin classes, hydroboration of a substrate possessing both a trisubstituted alkene and a monosubstituted alkene afforded complete selectivity for the terminal alkene (compound **14**, Scheme 2). Similarly, complete selectivity was seen for hydroboration of the terminal alkene when a 1,1-disubstituted alkene was present (compound **15**, Scheme 2). While alkenes that possess two or more substituents were generally unreactive, 1,1-disubstituted alkenes could be converted to tertiary borane products under modified conditions (compounds **16** and **17**, Scheme 2).[21]

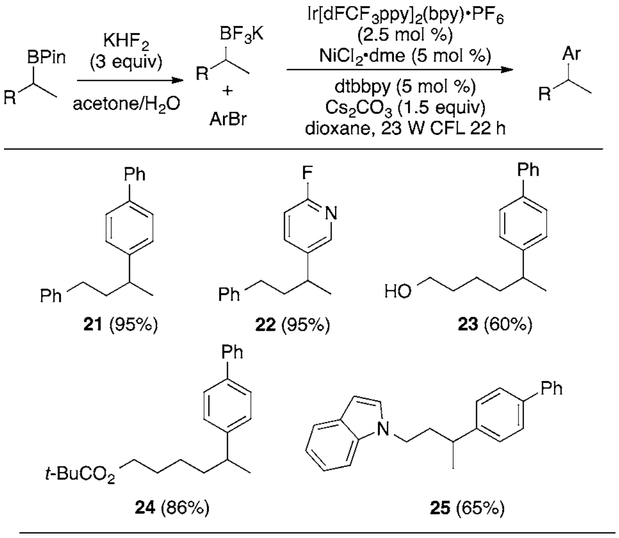
In analogy with other reports of copper-catalyzed additions of B_2Pin_2 and methanol to alkynes and styrenes,[11,17] the mechanism of the process likely involves addition of a copper borane intermediate to the terminal alkene as the regiochemistry-determining step, as depicted in the conversion of **18** to **19** in Scheme 3. Formation of the linear borane is disfavored as the ligand size increases (compare Table 1, entries 8 and 9) because of the developing steric interactions experienced in complex **20a**.[22] Alternatively, complex **20b**, which leads to the observed branched product, avoids steric interactions between the ligand and the alkene substituent. Following the sterically preferred formation of **19**, protonation of the metal−copper bond produces the desired product along with the formation of a copper methoxide species, which is converted to the reactive Cu−BPin complex by the reaction with B_2Pin_2.

Scheme 3. Mechanism of Secondary Alkylborane Formation



Recent advances in Suzuki couplings can benefit from the facile entry to secondary alkylboranes provided by this procedure.[2,3] For example, pairing the nickel-catalyzed photocatalytic cross-coupling procedure recently developed by Molander[3b] with the above developments provides a convenient and versatile method for the direct conversion of terminal alkenes to tertiary branched motifs. Alkyl(BPin) derivatives accessed by the catalytic, regiocontrolled addition of B_2Pin_2 with methanol to terminal alkenes (Scheme 4) are readily converted to the corresponding trifluoroborate derivatives[3a,23] while maintaining the versatile functional group tolerance of the hydroboration procedure (Scheme 4). The resulting functionalized trifluoroborate derivatives then directly participate in nickel-catalyzed cross-couplings in the presence of iridium photocatalysts following the Molander protocol. Both electron-rich and electron-deficient bromoarenes participate in the sequence (**21** and **22**, Scheme 4). Notably, the functional group tolerance demonstrated in the synthesis of branched alkylboranes is carried through the trifluoroborate synthesis/photocatalytic cross-coupling sequence to provide the preservation of sensitive functional groups such as free alcohols, esters, and indoles (**23**−**25**, Scheme 4).

Scheme 4. Photocatalytic Cross-Couplings of Branched Trifluoroalkylboranes[a]



[a]Isolated yields for the photocatalytic cross-coupling step are provided in the table. Details of the synthesis of the RBF_3 salts are provided in the Supporting Information. $dFCF_3ppy$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; dme = dimethoxyethane; dtbbpy =4,4′-di-*tert*-butyl-2,2′-bipyridine.

In summary, the regiodivergent hydroboration of a broad range of simple terminal alkenes may now be readily accomplished.[24] While a range of thermal or catalyzed additions of boranes provide access to linear alkylboranes according to previous reports, the copper-catalyzed addition of B_2Pin_2 with methanol reported herein provides highly regioselective access to the isomeric branched alkylboranes. This procedure complements previous methods for accessing secondary alkylborane structures, and the utilization of the obtained products in nickel-catalyzed photocatalytic cross-couplings provides a branch-selective strategy for the reductive cross-coupling of alkenes and aryl bromides. Further exploration of asymmetric versions of the formal hydroboration is in progress, and utilization of the racemic organoboranes will be possible with emerging developments in stereoconvergent cross-couplings.[3]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03090.

Synthetic details and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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