



Nickel Catalysis Hot Paper

***sp*³ Bis-Organometallic Reagents via Catalytic 1,1-Difunctionalization of Unactivated Olefins**Shang-Zheng Sun[†], Laura Talavera[†], Philipp Spieß, Craig S. Day, and Ruben Martin*

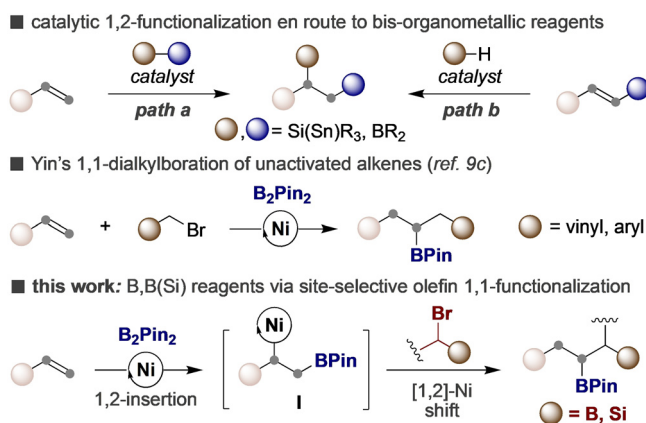
Abstract: A catalytic 1,1-difunctionalization of unactivated olefins en route to *sp*³ bis-organometallic B,B(Si)-reagents is described. The protocol is characterized by exceptional reaction rates, mild conditions, wide scope, and exquisite selectivity pattern, constituting a new platform to access *sp*³ bis-organometallics.

Metal-catalyzed cross-coupling reactions of *sp*³ mono-organometallic reagents have reached remarkable levels of sophistication as vehicles to rapidly build up *sp*³ architectures.^[1] Although *sp*³ poly-organometallics might a priori offer an improved versatility and modularity for forging *sp*³ linkages, a limited number of catalytic synthetic routes have been described for preparing these reagents from simple, yet available, precursors.^[2] At present, catalytic approaches for their synthesis include olefin 1,2-bis-metallations^[3] or 1,2-hydrometallation of vinyl metal species (Scheme 1, *top*).^[4,5] In

contrast, a de novo catalytic technique aimed at accessing *sp*³ bis-organometallics via site-selective olefin 1,1-difunctionalization still remains a desirable scenario.^[6] If successful, such a technology might not only complement existing 1,1-difunctionalizations that incorporate boron fragments across olefins,^[7–9] such as the elegant protocols described by Yin^[9a,c] and Fu,^[9d] but also offer an unrecognized opportunity to rapidly and reliably access versatile 1,2-bis-organometallic intermediates with an extra carbon.

As part of our interest in site-selective olefin functionalization and ambiphilic α -haloboranes,^[10] we recently questioned whether it would be possible to design a Ni-catalyzed 1,1-difunctionalization of olefins to generate *sp*³ bis-organometallics bearing both B and Si motifs (Scheme 1, *bottom*). However, it was unclear whether such a three-component endeavor could be implemented with an exquisite regio- and chemoselectivity pattern given the inherent propensity of transition metals for enabling 1,2-difunctionalization events.^[11] Conceptuality and practicality aside, we recognized that such a platform might offer a new blueprint for preparing densely functionalized, yet synthetically versatile, bis-organometallics from simple and readily accessible precursors while opening new complementary strategies for our ever-growing olefin functionalization portfolio.^[6–9] Herein, we report the realization of this goal with a platform consisting of a site-selective [1,2]-Ni migration via the intermediacy of **I** facilitated by the stabilization of the neighboring boron atom, thus setting the stage for establishing the 1,1-difunctionalized linkage bearing a versatile bis-organometallic B,B(Si)-reagent.^[12,13] Our method is distinguished by its excellent chemo- and regioselectivity profile, even in the context of ethylene valorization.

Inspired by Yin's and Brown's work on the catalytic borylation of olefins with B₂Pin₂,^[9c,13a] we began our work by evaluating the 1,1-difunctionalization of **1a** with **2a** and B₂Pin₂ (**3a**, Scheme 2). The choice of **2a** was not arbitrary, as α -haloboranes are readily accessible on a large scale via Matteson homologation.^[14] After some experimentation, the use of NiBr₄·TBA₂ (10 mol %), **L1** (10 mol %), *t*-BuOLi and *t*-BuOH in DME at 30 °C gave rise to **4a** in 73 % isolated yield in 30 min as a single regioisomer, with functionalization occurring at the less-hindered site of the olefin.^[15] Intriguingly, 2,2'-bipyridines or 1,10-phenanthrolines—ligands that are particularly suited for olefin functionalization—failed to provide even traces of **4a**.^[16] As shown in entries 1–5, only pyridine ligands possessing a tethered free alcohol delivered **4a**, indicating that binding of the latter to the Ni center might play a non-negligible influence on reactivity.^[9c] This notion was reinforced by the catalytic competence of Ni(**L1**)₂, hence demonstrating the importance of the N,N,O binding mode of

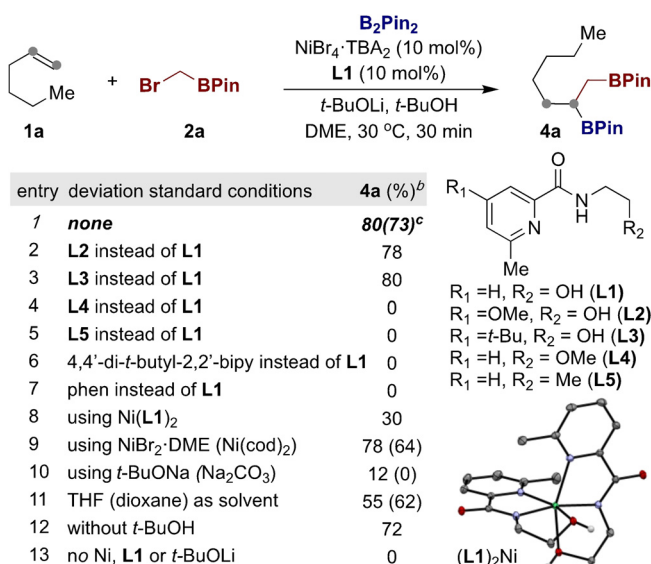


Scheme 1. Preparation of bis-organometallic reagents.

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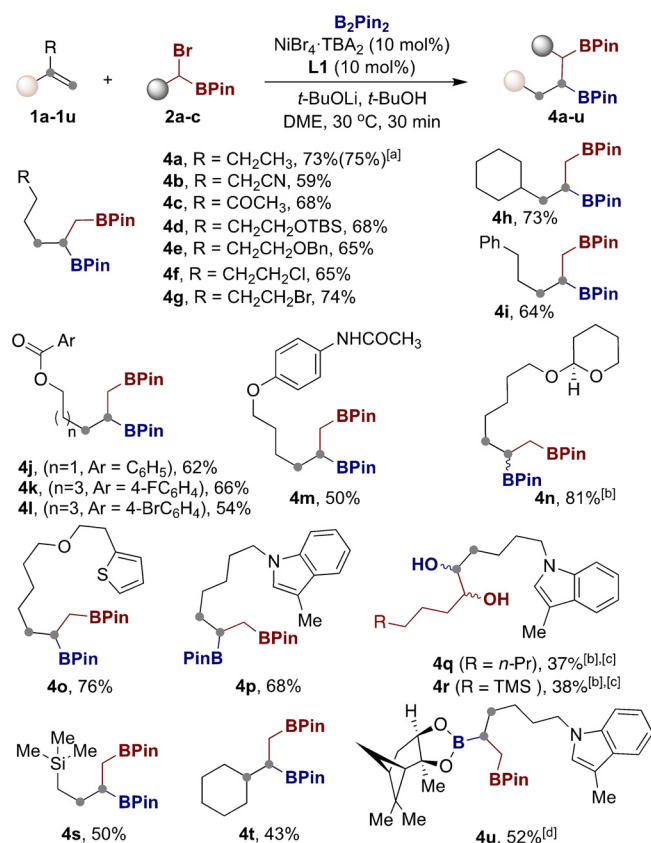


Scheme 2. Optimization of the reaction conditions. **1a** (0.20 mmol), **2a** (0.34 mmol), B_2Pin_2 (0.34 mol), $\text{NiBr}_4 \cdot \text{TBA}_2$ (10 mol%), **L1** (10 mol%), $t\text{-BuOLi}$ (0.40 mmol), $t\text{-BuOH}$ (0.80 mmol), DME (0.5 mL) at 30 °C for 0.5 h. [a] GC yields using 1-decane as internal standard. [b] Isolated yield. $\text{B}_2\text{Pin}_2 = \text{Bis}(\text{pinacolato})\text{diboron}$.

L1 (entry 8).^[17,18] In addition, subtle changes on the nickel precatalyst, inorganic base or solvent, invariably led to lower yields of **4a** (entries 9–12). Control experiments revealed that all of the reaction parameters were critical for success (entry 13).^[19]

The excellent reactivity encountered for **1a** suggested that our protocol could be equally extended to a wide variety of olefin counterparts. Gratifyingly, the 1,1-difunctionalization event showed an excellent chemoselectivity profile, as nitriles (**4b**), ketones (**4c**), silyl ethers (**4d**), esters (**4j**, **4k**, **4l**), amides (**4m**) or heterocycles (**4n**, **4o**, **4p**) were perfectly accommodated (Scheme 3). Notably, organosilanes (**4s**), alkyl halides (**4f**, **4g**) and aryl halides (**4k**, **4l**) were all well-tolerated, thus providing ample opportunities for further derivatization via conventional cross-coupling reactions.^[20] Remarkably, the reaction could be conducted on a gram scale, affording **4a** in 75 % yield. In addition, 1,1-disubstituted olefins could be employed as substrates (**4t**) whereas the successful preparation of **4q** and **4r** indicates that secondary α -haloboranes might pave the way for accessing diborane fragments at secondary sp^3 alkyl sites. The preparation of **4u** is particularly noteworthy, as it allows for incorporating both a chiral boron entity and two structurally different sp^3 C–B bonds in a synergistic manner. Note, however, that lower yields and diastereoselectivities were found in these cases. Unfortunately, internal olefins, styrenes and α -bromoalkyl boronic esters bearing quaternary carbon centers failed to provide the targeted products.

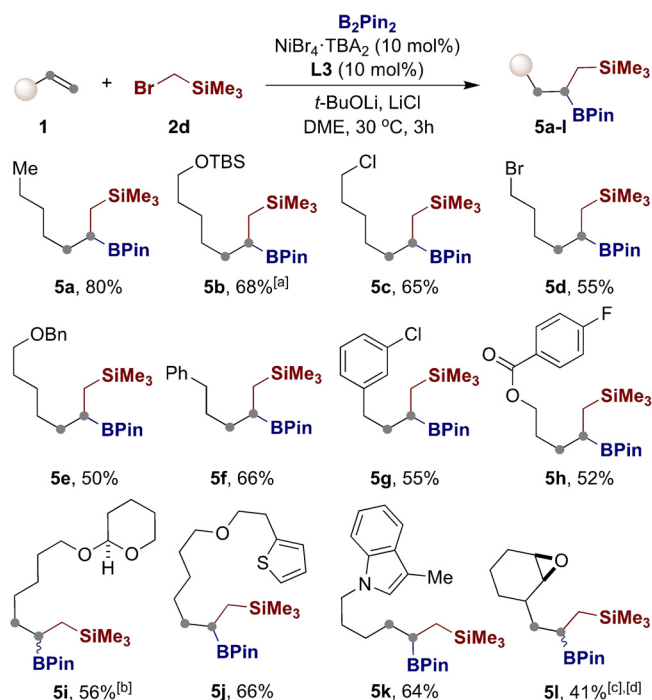
Encouraged by the results shown in Scheme 3, we wondered whether our catalytic 1,1-difunctionalization of olefins could be extended to ambiphilic organometallic partners other than α -haloboranes.^[21] This was particularly important, as such scenario would give access to 1,2-*bis*-organometallic reagents with intrinsically different $\text{C}(sp^3)$ -



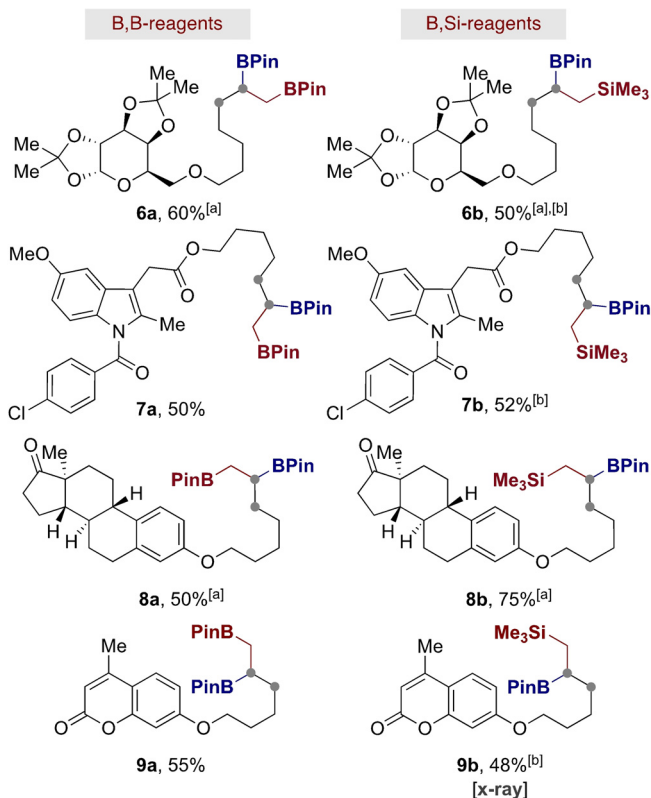
Scheme 3. Scope of 1,1-difunctionalization with α -bromoboranes. As Scheme 2 (entry 1); isolated yields, average of two independent runs. [a] 5.0 mmol scale. [b] dr = 1:1. [c] Isolated as diol upon quenching with $\text{NaBO}_3 \cdot \text{H}_2\text{O}$. [d] dr = 1:1.

metal bonds, thus setting the stage for promoting site-selective sp^3 cross-coupling reactions at later stages. As shown by the results compiled in Scheme 4, this turned out to be the case and the utilization of readily accessible (bromomethyl)trimethylsilane resulted in a useful entry point to 1,2-silylboranes by means of catalytic 1,1-difunctionalization of olefins. In this case, however, the targeted products were obtained under a $\text{Ni}/\text{L3}$ regime with LiCl as additive.^[15] These conditions could be employed across a wide number of unactivated olefins bearing silyl ethers (**5b**), alkyl halides (**5c**, **5d**), aryl halides (**5g**, **5h**), heterocycles (**5i–5k**) or even epoxides (**5l**). With a reliable set of conditions in hand for forging both 1,2-diboranes and 1,2-silylboranes from unactivated olefins, we turned our attention to apply these techniques in advanced synthetic intermediates (Scheme 5).^[22] As shown, a variety of products bearing either a diborane (**6a–9a**) or silylborane motif (**6b–9b**)^[23] could easily be accessed from common precursors. These results are particularly noteworthy, as these intermediates might be used as vehicles to access libraries of compounds of interest in drug discovery programs via site-selective C–B or C–Si bond-functionalization.

The synthetic value of our site-selective 1,1-difunctionalization is further illustrated in Scheme 6. As shown, ethylene—the largest-volume organic chemical produced in industry—could be employed as substrate, even at atmospheric

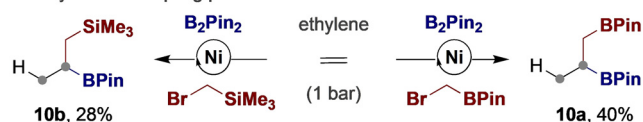


Scheme 4. Scope of 1,1-difunctionalization with α -bromosilanes. As Scheme 2 (entry 1), with **2d** (0.50 mmol), **L3** (10 mol%), $t\text{-BuOLi}$ (0.50 mol), LiCl (0.40 mol), DME (0.2 mL); isolated yields, average of two independent runs. [a] **2d** (0.60 mmol), 6 h. [b] $\text{dr} = 1:1$. [c] starting alkene with $\text{dr} = 1:1$. [d] $\text{dr} = 1.5:1.5:1:1$.

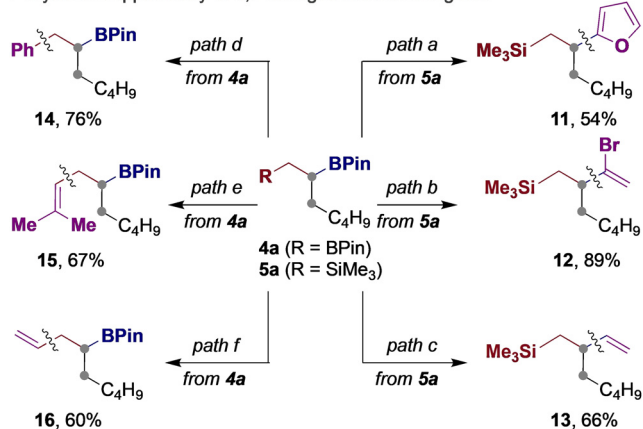


Scheme 5. Olefin 1,1-difunctionalization in advanced synthetic intermediates. α -bromoborane coupling (left): as Scheme 2 (entry 1); α -bromosilane coupling (right): as Scheme 4; isolated yields, average of two independent runs. [a] $\text{dr} = 1:1$. [b] (bromomethyl)trimethylsilane (0.60 mol), 6 h.

ethylene as coupling partner



synthetic applicability of 1,2-bisorganometallic reagents

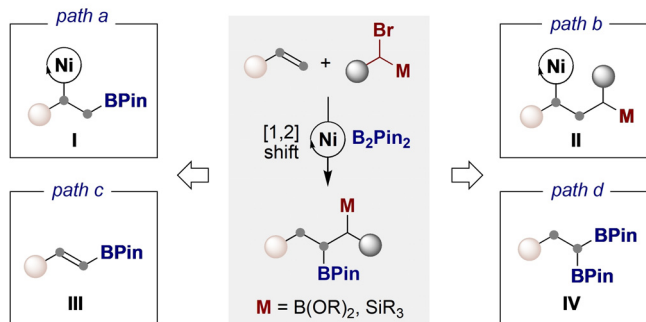


Scheme 6. Synthetic applications. *path a*: furan (0.30 mmol), $n\text{BuLi}$ (0.30 mmol), **5a** (0.25 mmol), then NBS (0.30 mmol). *path b*: **5a** (0.30 mmol), vinyl bromide (0.60 mmol), LDA (0.60 mmol) then I_2 (0.66 mmol). *path c*: **5a** (0.40 mmol), vinylMgBr (1.60 mmol) then I_2 (1.60 mmol), NaOMe (3.20 mmol). *path d*: **4a** (0.40 mmol), PhBr (0.60 mmol), $\text{Pd}(\text{OAc})_2$ (5 mol%), RuPhos (5 mol%), KOH (1.20 mmol), THF/ H_2O (10:1), 70 °C. *path e*: as path d, 1-chloro-2-methyl-1-propen (0.60 mmol). *path f*: as path d, 1,2-dichloroethane (1.20 mmol).

pressure, delivering **10a** or **10b** in an unoptimized 40% and 28% yield, respectively.^[24] More importantly, a site-selective C-B or C-Si bond-cleavage platform could be implemented by employing **4a** or **5a** as substrates, tacitly indicating that our technology might be used as a formal linchpin for selectively incorporating structurally-different carbon linkages into simple olefin backbones. Interestingly, **14–16** were easily within reach via site-selective sp^3 C-B bond-cleavage from **4a**.^[25] Under the limits of detection, no cross-coupling reaction arising from the cleavage of the secondary sp^3 C-B bond was observed in the crude mixtures. Interestingly, the utilization of **5a** instead delivered **11–13** via exclusive C-B cleavage by using appropriately substituted Grignard reagents^[26] or organolithium compounds.^[27,28]

Our available data did not allow us to clarify the mode of action by which our 1,1-difunctionalization operated. The following mechanistic scenarios are a priori conceivable: (a) migratory insertion of in situ generated Ni-BPin via **I**, followed by 1,2-[Ni] migration via chain-walking^[29] thus allowing to locate the Ni center adjacent to a boron atom due to the valence deficiency of the latter prior to coupling with **2**^[30] (Scheme 7, *path a*); (b) single electron transfer from Ni^0 to **2**, generating a boron-stabilized radical that adds across the olefin followed by recombination with Ni^{I} (**II**), chain-walking and coupling with B_2Pin_2 (*path b*); (c) formation of a vinyl-BPin intermediate **III** prior to coupling with **2** (*path c*); (d) addition of two BPin fragments across the olefin in a 1,1-selective manner (**IV**) followed by cross-coupling with **2** via C-B cleavage (*path d*).^[9d] While the two latter pathways could

■ possible mechanistic scenarios



Scheme 7. Mechanistic experiments.

be ruled out based on the lack of reactivity found by exposing **19** or **20** under our optimized reaction conditions (Scheme 7, middle), there was no easy clear-cut choice about the first two hypotheses.^[31] We anticipated, however, that if a radical pathway comes into play, 5-*exo-trig* cyclization should be observed with **17**. Interestingly, this was not the case, and **18a** was solely observed in the crude mixtures, reinforcing the notion that a non-radical pathway operates via migratory insertion of Ni-BPin species prior to chain-walking (path a).^[32] Notably, significant deuterium incorporation was observed at C3 by exposing **21** under our optimized conditions (bottom), thus indirectly confirming the [1,2]-Ni migration via **I** (Scheme 1 & Scheme 7, path a).

In summary, we have developed a highly modular and site-selective 1,1-difunctionalization of unactivated olefins en route to bis-organometallic reagents. This reaction is characterized by its broad scope, mild conditions and exquisite chemo- & regioselectivity, thus offering a complementary new blueprint for preparing densely functionalized, yet synthetically versatile, 1,2-bisorganometallics from simple and readily accessible precursors.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bis-organometallic · chain-walking · Ni catalysis · olefin functionalization

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- [31] A competitive experiment of **19** and 1-hexene under our optimized conditions revealed no crossover, with 1,1-difunctionalization occurred exclusively in the latter and **19** being recovered unaltered.
- [32] These results are consistent with EPR monitoring experiments performed under the standard catalytic conditions. Under the limits of detection, no signals corresponding to organic radicals were observed in the crude mixtures. See ref. [15].

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