A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition

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Accepted Article

Title: Stereoselective Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201913544
Angew. Chem. 10.1002/ange.201913544

Link to VoR: http://dx.doi.org/10.1002/anie.201913544
http://dx.doi.org/10.1002/ange.201913544

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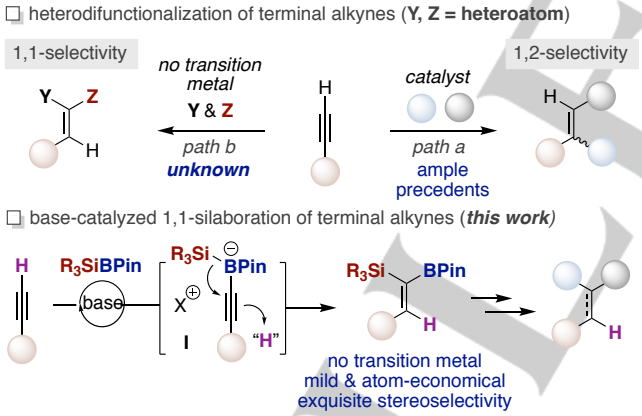
Stereoselective Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

Yiting Gu, Yaya Duan, Yangyang Shen and Ruben Martin*

Abstract: A base-catalyzed protocol that enables a stereoselective 1,1-silaboration of terminal alkynes is described. This method does not only offer a new strategy to functionalize simple and readily accessible alkynes beyond 1,2-difunctionalization events, but also provides an unconventional atom- and step-economical approach to rapidly and reliably access versatile geminal silylboranes in the absence of transition metals with an exquisite stereoselectivity pattern.

In recent years, the catalytic functionalization of π-systems has gained momentum as a powerful, yet practical, alternative to the use of organic (pseudo)halides for building up molecular complexity.[1] Among these, particular attention has been devoted to designing *de novo* catalytic routes en route to densely functionalized alkenes via site-selective difunctionalization of alkyne congeners.[2] Although 1,2-difunctionalizations of alkynes via one or two-electron manifolds have become routine (Scheme 1, *top right*),[3-5] a related 1,1-difunctionalization event is not as commonly practiced as one might initially anticipate. At present, these techniques remain primarily confined to the use of transition metal catalysts – in most instances requiring sophisticated ligand sets –,[6] or stoichiometric organometallic reagents.[7] Despite the advances realized,[8] a stereoselective catalytic 1,1-heterodifunctionalization blueprint that obviates the need for transition metals while forging two different C–heteroatom bonds still constitutes an elusive cartography in catalytic endeavors (Scheme 1, *top left*).



Scheme 1. Base-catalyzed heterodifunctionalization of terminal alkynes.

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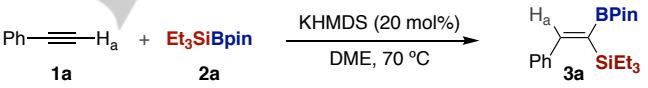
Driven by the versatility and inherent modularity of organosilicon and organoboron reagents as synthons in organic synthesis,[9] we recently wondered whether it would be possible to design an atom-economical stereoselective 1,1-silaboration of alkynes in the absence of transition metals or organometallic species. To this end, we hypothesized that a base-catalyzed protocol in the presence of readily available silylborane might be suited for our purposes (Scheme 1, *bottom*). Specifically, we anticipated that in situ generated ate-complexes of type **I** might enable a stereoselective [1,2]-silyl shift[10] with concomitant deprotonation of the acetylenic *sp* C–H bond, thus setting the basis for the base catalyst turnover. If successful, such a route would represent, conceptuality and practicality aside, a new platform for preparing geminal organometallic linkages bearing two chemically distinct, yet modular, C–B and C–Si bonds. In our continuing interest in silylation and borylation reactions,[11] we report herein the successful realization of this goal. Unlike related 1,1-diborations that typically require either transition metal catalysts or organometallic reagents,[12] our catalytic 1,1-silaboration event offers a strategic gateway to rapidly and reliably access densely functionalized alkenes in a highly stereocontrolled manner via orthogonal C–Si and C–B cleavage, thus leading to new knowledge in retrosynthetic design.

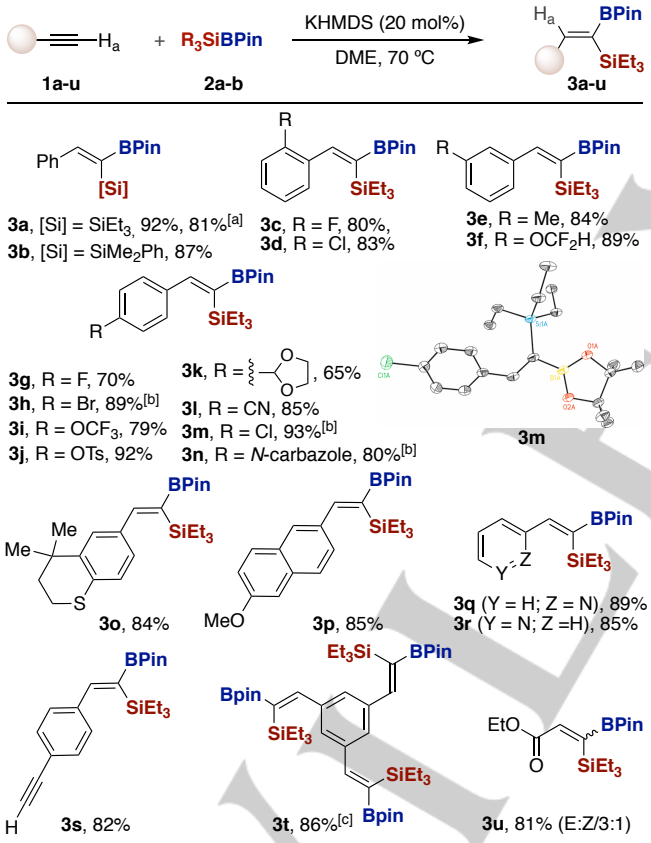


Entry	Deviation from standard conditions	**3a** (%)[a]
1	***none***	***97 (91)***[b]
2	KHMDS (10 mol%) was used	34
3	LiHMDS instead of KHMDS	15
4	NaHMDS instead of KHMDS	36
5	$Mg(HMDS)_2$ instead of KHMDS	–
6	+ 18-crown-6 (20 mol%)	–
7	*t*-BuOK instead of KHMDS	32
8	toluene instead of DME	95
9	dioxane instead of DME	32
10	reaction conducted at 25 °C	41
11	$Et_3SiSiEt_3$ (Et_3SiH) instead of $Et_3SiBPin$	–[c]
12	B_2Pin_2 instead of $Et_3SiBPin$	–[d]

Scheme 2. Optimization of the reaction conditions. **1a** (0.40 mmol), **2a** (0.4 mmol), KHMDS (0.08 mmol, 20 mol%) in DME (2 mL) at 70 °C for 12 h. [a] Yields determined by GC using decane as internal standard. [b] Isolated yield, average of two independent runs. [c] no traces of hydro(di)silylation were found. [d] no traces of hydro(di)boration were found. DME = 1,2-dimethoxyethane; BPin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl. HMDS = hexamethyldisilazide.

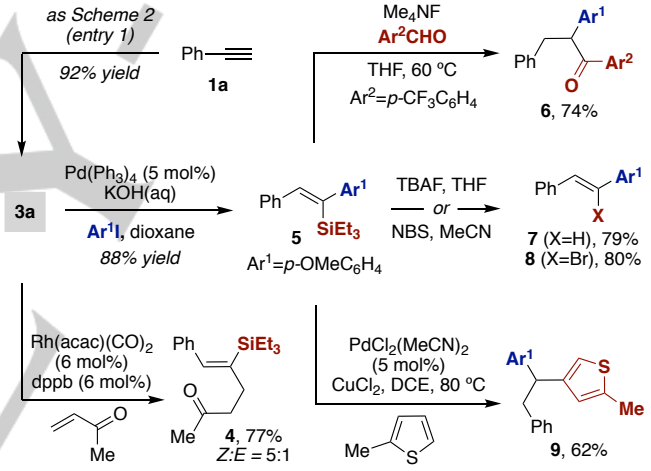
We began our investigations by studying the 1,1-silaboration of phenylacetylene (**1a**) with $Et_3SiBPin$ (**2a**) en route to **3a** (Scheme 2). The choice of **2a** instead of commonly employed $PhMe_2SiBPin$ (**2b**) was not arbitrary.[13] From a synthetic standpoint, the use of **2a** offers the advantage of selectively functionalizing the vinyl–Si bond in **3a** at later stages, thus avoiding unnecessary site-selectivity issues arising from the presence of multiple sp^2 C–Si

bonds in **3b**.[14] After systematic optimization,[15] a protocol based on KHMDS (20 mol%) in DME at 70 °C provided the best results, (entry 1).[16] This transformation merits some further discussion: 1) no transition metal complex is required; 2) the reaction is conducted with a **1a:2a** ratio of 1:1 and catalytic amounts of KHMDS, thus offering an atom- and step-economical route to **3a**; 3) two different, yet chemically distinguishable, organometallic bonds can be forged from available alkynes with exquisite control of the stereoselectivity. Intriguingly, the escorting cation exerted a profound influence on the reaction outcome. Indeed, the corresponding Li, Na or Mg analogues provided lower yields of **3a**, if any (entries 2-5), possibly due to the different size and coordination ability of the cation. The key role of potassium counterions was further corroborated by observing no conversion of **1a** to **3a** with 18-crown-6 (entry 6) whereas lower yields were found when KO^{t}Bu was used (entry 7). Likewise, the nature of the counteranion and the solvent employed was equally important (entry 8 and 9). The importance of boron–interelement reagents was illustrated by the lack of reactivity found when employing either Et_3SiH,[17] $(Et_3Si)_2$ or B_2Pin_2, respectively (entry 11 and 12).



Scheme 3. Scope of terminal alkyne. Reaction conditions: As scheme 2, entry 1; Yield of Isolated product, average of at least two independent runs. [a] 10 mmol scale. [b] T = rt. [c] **2a** (3.5 equiv).

With a reliable set of conditions in hand, we focused our attention on studying the generality of our method (Scheme 3). As evident from the results compiled in Scheme 3, the 1,1-silaboration turned out to be widely applicable for a wide range of arene substituents at the alkyne terminus. Moreover, **3b** was within reach in an otherwise identical yield to that shown for **3a**. Notably, the presence of nitriles (**3l**), carbazoles (**3n**) or esters (**3u**) could all be well-accommodated. Interestingly, aryl halides (**3c, 3d, 3g, 3h** and **3m**),[18] sulfonates **3j**), ethers (**3f**, **3i, 3k** and **3p**) or sulfides (**3o**) – all common counterparts in the cross-coupling arena –[19] did not interfere with our targeted 1,1-silaboration, hence opening up an orthogonal gateway for further derivatization via conventional transition metal-catalyzed reactions. Particularly noteworthy was the observation that the 1,1-silaboration of **1a** could be executed on a gram scale, delivering **3a** in 81% yield without noticeable erosion in yield or diastereoselectivity. The ability to obtain **3q** and **3r** as single products is particularly noteworthy if one takes into consideration the known proclivity of silylboranes to enable C2– or C4–silylation of electron-poor azines under basic conditions via nucleophilic aromatic substitution (S_NAr) pathways.[11a] Substrates bearing more than one terminal alkyne can either be selectively (**3s**) or exhaustively coupled with silylborane (**3t**) by carefully adjusting the stoichiometry of the reaction. As shown for **3u**, the reaction can be applied to non-aromatic acetylenes, yet with significant lower selectivity, suggesting that allene-type intermediates might come into play in certain cases (see below).[20]



Scheme 4. Synthetic Applicability.

The stereoselective synthesis of densely functionalized olefins – fundamental motifs in pharmaceuticals, material sciences and liquid crystals –,[21] continues to pose a challenge in preparative organic chemistry.[22] Driven by this observation, we wondered whether our 1,1-silaboration platform could be used for such purpose by selectively functionalizing two distinguishable organometallic C–Si and C–B bonds at later stages.[23] As shown in Scheme 4, this was indeed the case. Specifically, **4** and **5** could easily be obtained from **3a** via Pd-catalyzed Suzuki-Miyaura coupling with an aryl iodide[24] or Rh-catalyzed 1,4-addition with α,β-unsaturated ketones.[25] The versatility of the triethylsilyl group as a masked nucleophile is evident by the results compiled in Scheme 4 (*right pathways*). Indeed, proto– or bromodesilylation could easily be accomplished from **5** with TBAF (**7**) or NBS (**8**) whereas sp^3–sp^3 bonds can easily be forged with Me_4NF and an appropriate aldehyde counterpart (**6**).[7a] The conversion of **1a** into **9** via **5** is particularly noteworthy, allowing to incorporate three different aryl groups via β-selective C–H functionalization with Pd catalysts and Cu(II) as oxidant.[26] Taken together, the results

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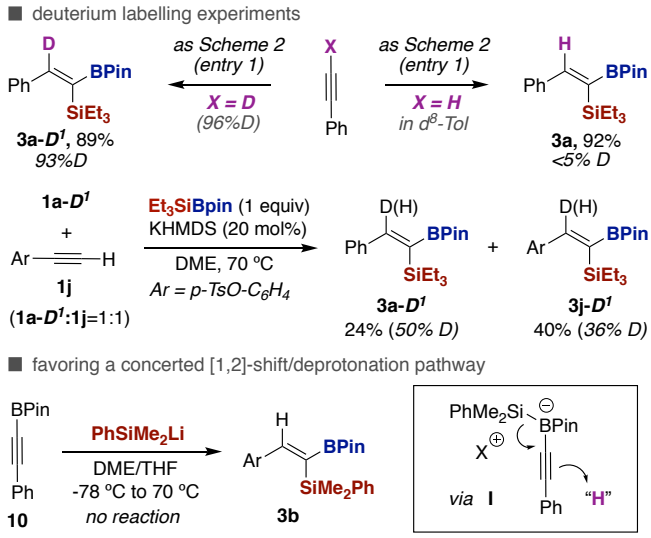
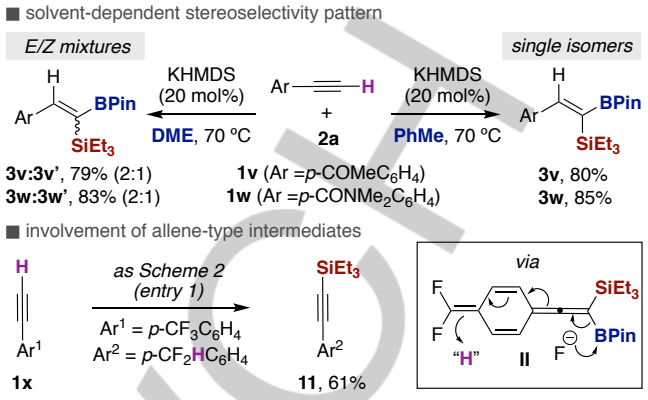
shown in Scheme 4 stand as a testament to the prospective impact of our base-catalyzed 1,1-silaboration of terminal alkynes.



Scheme 5. Deuterium labelling experiments.

Next, we turned our attention to unravelling the mechanistic intricacies of our 1,1-silaboration event via deuterium-labelling experiments (Scheme 5, *top*). As shown, reliable deuterium transfer en route to **3a-*D*¹** was only observed if **1a-*D*¹** was used as substrate (*top left*), arguing against radical-type scenarios via hydrogen atom transfer (HAT) with solvents possessing weak C–H bonds such as toluene (*top right*).[27] Notably, a deuterium-labelling crossover experiment with **1a-*D*¹** and **1j** revealed a non-negligible H/D scrambling in the 1,1-silaboration products **3a** and **3j**. These experiments suggested that our 1,1-difunctionalization might operate via initial deprotonation of the acetylenic *sp* C–H bond (pK_a (PhC≡C–H) = 23) by KHMDS (pK_a = 27) followed by addition to $Et_3SiBPin$. The resulting silylboronate species (**I**, Scheme 1) might evolve via a concerted pathway consisting of a [1,2]-shift[28] followed by a downhill protonolysis of an in situ generated vinyl organometallic reagent ($pK_a \approx$ 40-45) with the acetylenic *sp* C–H bond, thus turning over the key potassium acetylide species.[29-31] This notion could be corroborated by the lack of reactivity found when exposing **10** to $PhSiMe_2Li$ (*bottom*). While our available data suggested a stereoselective [1,2]-shift of in situ generated **I** en route to *Z*-configured 1,1-silylborylated alkenes (**3a-3u**, Scheme 3), care should be taken when generalizing this. Indeed, we found an intriguing dichotomy exerted by both the substituents on the arene and the solvent utilized (Scheme 6). Specifically, a significant erosion in stereoselectivity was found upon exposing **1v** or **1w** to **2a** in DME (*top left*), whereas *Z*-configured **3v** and **3w** were exclusively obtained under a toluene regime (*top right*). The former result can tentatively be interpreted on the basis of the strong coordination of DME to the escorting potassium counterion,[32] thus generating a separated silylboronated ion pair that precedes the formation of allene-type intermediates via [1,2]-shift from **I**.[8],[33] This notion was corroborated by the formal defluorosilylation of **1x** observed under our optimized reaction conditions (Scheme 6, *bottom*) as well as by the *E*/*Z* mixtures obtained for **3u** (Scheme 3). In toluene as solvent, however, a contacted ion pair is more likely, thus attenuating the reactivity of **I** while forming the targeted **3v-3w** in a highly stereoselective fashion.



Scheme 6. Solvent-dependent selectivity and intermediacy of allene species.

In summary, we have documented an unconventional atom-economical 1,1-silaboration of terminal alkynes enabled by catalytic amounts of KHMDS. This protocol is characterized by its excellent stereoselectivity pattern, constituting a complementary approach to existing methods en route to geminal organometallic reagents that typically require transition metal complexes and a new gateway to rapidly and reliably convert simple alkynes into stereodefined trisubstituted alkenes via orthogonal C–Si and C–B bond-cleavage. Further extensions to other related processes are currently underway in our laboratories.

Acknowledgements

We thank ICIQ and FEDER/MICIU – AEI/PGC2018-096839-B-100 for financial support. Y. G. and Y. S. thank Severo and China Scholarship Council (CSC) for predoctoral fellowships.

Keywords: alkyne • 1,1-difunctionalization • silaboration • atom-economy

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[12] For a remarkable exception, see ref. 8.

[13] $Et_3SiBPin$ is available in bulk quantities in one-step from cheap Et_3SiH (Gelest; 25 g, 39 $) and B_2pin_2 (Bepharm, 100 g, 60 $): A. B. Boebel, J. F. Hartwig, *Organometallics* **2008**, *27*, 6013–6019. Unlike related R_3SiLi nucleophilic reagents, the inherent stability of $Et_3SiBPin$ offers the advantage of avoiding cryogenic conditions.

[14] The utility of $PhR_2SiBPin$ reagents (R = alkyl, aryl) as functional handles is somewhat hampered due to site-selectivity issues arising from the presence of multiple sp^2 C–Si bonds.

[15] See Supporting information for details.

[16] The mass balance accounts for recovered starting material

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[18] CCDC 1960717 (**3m**) contain the supplementary crystallographic data for this paper and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac/uk/data_request/cif

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10.1002/anie.201913544

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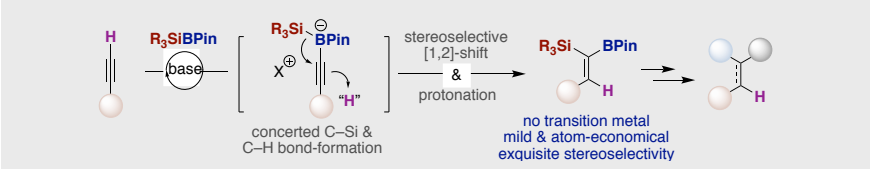

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Stereoselective Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

A base-catalyzed protocol that enables an atom-economical 1,1-silaboration of terminal alkyne is described. This protocol is distinguished by its mild conditions and exquisite stereoselectivity pattern, offering a complementary approach to conventional 1,2- or 1,1-difunctionalization techniques that typically require transition metal complexes or stoichiometric organometallics, and an opportunity to build up molecular complexity by subsequent orthogonal C–Si and C–B cleavage.