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Authors: Yuki Nagashima, Daiki Yukimori, Chao Wang, and Masanobu Uchiyama

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In Situ Generation of Silylzinc by Si–B Bond Activation Enabling Silylzincation and Silaboration of Terminal Alkynes

Yuki Nagashima,* Daiki Yukimori, Chao Wang, and Masanobu Uchiyama*

Abstract: We designed a new protocol for the *in-situ* generation of unstable Si–Zn species through the reaction of dialkylzinc, phosphine, and silylborane (Si–B). Successive reaction with various terminal alkynes using this protocol enabled highly controllable regio-/stereo-/chemoselective silylzincation and silaboration on demand without the need for a transition-metal catalyst.

Organozinc compounds are ubiquitous and versatile intermediates in modern synthetic organic chemistry.^[1] A number of preparation methods have been developed, which permit the preparation of a broad range of organozinc compounds.^[2-5] In recent years, increasing attention has been devoted to a new type of "heteroatom-zinc species" having Zn-Het bond(s) (Het = B, Si, Sn, ...),^[6] but the unstable nature of the Zn-Het bond(s) makes their stoichiometric preparation problematic. Conventional methods to prepare stable organozincs are often not appropriate or not effective: (1) halogen-zinc exchange reaction of Het-X, and deprotonative zincation of Het-H(hydrides) remain undeveloped,^[7] and (2) transmetalation by the reaction of organolithiums with zinc halides suffers from difficulty in quantitative preparation of the unstable Het-Li species, such as B-Li, Si-Li, or Sn-Li species.^[6] A recently developed protocol for activation of the B-B bond of stable diborons and successive in situ transmetalation with organozinc compounds to afford B-Zn species provides an alternative approach for the utilization of unstable/reactive B-Zn species for the borylation of aromatic halides and borylzincation of unsaturated C–C bonds.^[8] However, its simple application to commercial Si-Si compounds for the preparation of Si-Zn species has been unsuccessful due to low reactivity of the Si-Si bond. Thus, we considered the use of the readily available, storable, and easy-to-handle silylboranes,^[9] even though it initially appeared that activation of the Si-B bond would require a high activation energy,^[10] and that the transmetalation selectivity would be low, leading to the formation of a mixture of B-Zn and Si-Zn species.^[11] We anticipated that if a direct in situ activation-transmetalation method could be developed despite these issues, it would open up a versatile new avenue for silaboration and element-zincation. We were encouraged by our model calculations, which implied that if the Si-B bond could be

[*]	Y. Nagashima, D. Yukimori, Dr. C. Wang, Prof. Dr. M. Uchiyama						
	Graduate School of Pharmaceutical Sciences						
The University of Tokyo							
	7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan						
	E-mail: yuki-nagashima@g.ecc.u-tokyo.ac.jp, uchiyama@mol.f.u-						
tokyo.ac.jp							
	Dr. C. Wang, Prof. Dr. M. Uchivama						
	Cluster of Pioneering Research (CPR), Advanced Elements						
Chemistry Laboratory, RIKEN,							
2-1 Hirosawa, Wako, Saitama 351-0198, Japan							
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successfully cleaved, formation of the Si–Zn species would be thermodynamically favored over that of the corresponding B–Zn species (Scheme 1). We disclose herein the *in situ* generation of silylzinc species from silylboranes *via* a novel Si–B bond activation reaction, which enables chemoselective *cis*-silylzincation or *cis*-silaboration of various terminal alkynes.

Scheme 1. *In situ* generation of borylzinc or silylzinc species from silylborane, Lewis base, and dialkylzinc.



Based on our working hypothesis, we started with a screening study to find a suitable activator (Lewis base) for Si-B bond activation by using 1-octyne (1a), PhMe₂Si-B(pin) (2, 1.1 eq) and Me₂Zn (1.1 eq) in THF (0.25 M) at 50°C as a fixed condition (Table 1). In the absence of Lewis bases, only a trace amount of the desired silylzincated product was detected (run 1). The use of 1.1 equivalents of NaOMe promoted cis-silylzincation to afford the desired products (3a and 4a) as a mixture of regioisomers (45%, run 2), indicating the success of in situ generation of Si-Zn species. The change to other alkoxy or fluoride anion did not improve the yield or regioselectivity (runs 3 and 4). Interestingly, however, addition of a phosphine base such as ⁿBu₃P or Ph₃P gave only the 1,2-cis-silylzincated product (3a, the silyl moiety is installed at the terminal carbon), albeit in low yield (entries 5 and 6). After extensive experimentation, we found that the use of an appropriate amount of phosphine (0.3 eq) is crucial for smooth silylzincation (57%, run 7). Finally, the set of conditions shown in run 8 was found to be optimal (94%, 3a:4a = >98:2).

With the optimized conditions in hand, we examined the 1,2silylzincation (3) of various terminal alkynes, as summarized in Table 2. Not only primary aliphatic alkyl substituents (runs 1 and 4), but also secondary aliphatic substituents (runs 2 and 3) gave the product in high yield with excellent selectivity (>98%). Various polar functional groups, including alkyl chloride (run 5), ether (run 6), protected hydroxyl group (run 7), amine (run 8) and cyano group (run 9), are tolerated in the reaction. The functional group specificity of this silvlzincation is very high because of the transition-metal-free condition (internal alkyne 11 or terminal olefin 1m was intact), and the products 3I and 3m were obtained chemoselectively (runs 10 and 11). Moreover, the results of runs 2 and 11 provided some mechanistic insight, i.e., the radical mechanism is not plausible, since ring-opening of the cyclopropyl group and 5-exo-trig cyclization by-products were not detected at all.^[12] Aryl alkynes were also reactive. The electronic effect at acetylene carbons had little influence on the reactivity/regioselectivity, and various phenylacetylene derivatives with an electron-donating group (o/p-MeO and Ph₂N) as well as an electron-withdrawing group (CF₃, Br, and CO₂Me) on the phenyl ring were efficiently converted to the

corresponding products (runs 12-18). As the result of run 10 indicates, internal alkynes were not converted to the corresponding silylzincated product at all (run 20). The resultant silylzincated intermediates can be utilized as vinyl anion equivalents (Scheme 2). For instance, the intermediate generated by 1,2-silylzincation of 1-octyne (**1a**) or phenylacetylene (**1n**) was treated with allyl bromide to give the corresponding olefin (**3ab** or **3na**) in high yield. The vinylzinc intermediate also underwent copper-catalyzed methylation (**3ab** and **3nb**), and LiCI-mediated iodination (**3ac**).^[13] Thus, the present methodology for *in situ* generation of silylzinc species enables versatile synthesis of densely functionalized vinylsilanes.

 Table 1. Optimizing the conditions of silylzincation

<u> </u>	H + PhMe ₂ Si—B(pin) 1a 2 (x eq)	Me ₂ Zn (1.1 eq) Lewis Base THF (0.25 M) 50°C, 18 h; D ₂ O "1,2-sil)	H SiMe ₂ Ph PhN 3a //zincation" "2	H He2Si D 4a 2,1-sily/zincation"
Run	Si–B	Additive	Yield (%) ^[a]	Ratio (3a:4a) ^[b]
1	1.1 eq	-	trace	-
2	1.1 eq	NaOMe (1.1 eq)	45	56:44
3	1.1 eq	NaO ^t Bu (1.1 eq)	trace	-
4	1.1 eq	CsF (1.1 eq)	37	83:17
5	1.1 eq	ⁿ Bu ₃ P (1.1 eq)	33	>98:2
6	1.1 eq	Ph ₃ P (1.1 eq)	27	>98:2
7	1.1 eq	ⁿ Bu ₃ P (0.3 eq)	57	>98:2
8	1.5 eq	ⁿ Bu ₃ P (0.3 eq)	94 (92 ^[c])	>98:2

[a] NMR yield determined by ¹H NMR analysis. [b] Ratio of **3a:4a** determined by ¹H NMR analysis. [c] Isolated yield.

To gain insight into the mechanism of the present silylzincation, we performed DFT calculations using model compounds (Figures 1 and 2). The gas-phase calculations indicate that the reaction pathway of generation of putative Si-Zn species shown in Figure 1 is the most probable (see Supporting Information). In this pathway, the addition of PMe₃ to Me₂Zn occurs first to form an association complex CP1. The formation of this intermediate activates the methyl transference aptitude of Me₂Zn. Thus, one of the methyl groups bound to the Zn atom can migrate smoothly along the intrinsic reaction coordinate to the vacant orbital of the boron atom of the silvlborane with an activation energy of 13.6 kcal/mol. All attempts to locate a TS for the Me transfer to the Si atom of the silvlborane resulted in no-barrier rearrangement of the geometry to generate CP2. This borate formation (CP2) causes Si-B bond activation and the Si group migrates smoothly to the Zn atom to produce the Si-Zn species (A). The stabilization energy of the second step is very large (-26.8 kcal/mol) which can compensate for the energy loss of the first step to afford the zwitterionic complex (CP2). This scenario is consistent with the experimental detection of Me-B(pin) (B) by GC-MS analysis in the present silylzincation. Having obtained structural information for Si-Zn species A, which is likely to be theoretically and experimentally relevant, we next performed DFT calculations to investigate the silylzincation reaction of terminal alkynes. We identified two plausible pathways for the silylzincation reaction, through TS_{α} (2,1-silylzincation TS) and TS_{θ} (1,2-silylzincation TS), as shown in Figure 2. The activation energy of the 1,2-silylzincation TS is lower by several kcal/mol than that of the 2,1-silylzincation TS, probably because of the steric factor, in good agreement with the experimental selectivity.

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[a] Isolated yield (NMR yield, determined by ¹H NMR analysis, is shown in parentheses). In all cases, the ratio of regioselectivity (1,2-silylzincation:2,1-silylzincation) was >98:2, as determined by ¹H NMR analysis. [b] Run at 75°C.

Scheme 2. In situ electrophilic trapping of the silylzincated intermediate





Figure 1. Energy profile for *in situ* generation of silylzinc species (M06/631SVP (SVP for Zn, and 6-31+G* for others)). For each step, the energy change (ΔE) is shown below the arrow and values in italics above the arrow are activation barriers (ΔE^{\ddagger}) in kcal/mol.

Table 2. 1,2-Silylzincation of terminal alkynes

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Figure 2. Energy profile for silylzincation of 1-propylene (M06/631SVP; energy in kcal/mol). The structures of TS_a and TS_β are shown in the dotted boxes.

Scheme 3. Proposed mechanism of Zn-catalyzed silaboration reaction



Table 3. Optimizing the conditions of silaboration

	H + PhMe₂Si—B(pin 1a 2 (2 eq)	Me ₂ Zn (0.3 eq) Lewis Base solvent 75°C, 18 h; D ₂ O "1,2-si	H SiMe ₂ Ph Phl 5a laboration "	H Me ₂ Si B(pin) 6a '2,1-silaboration"
Run	solvent	Additive	Yield (%) ^[a]	Ratio (5a:6a) [b]
1	THF (0.25 M)	ⁿ Bu ₃ P (0.3 eq)	43	>98:2
2	MTBE (0.25 M)	ⁿ Bu ₃ P (0.3 eq)	73	>98:2
3	MTBE (0.5 M)	ⁿ Bu ₃ P (0.3 eq)	86	>98:2
4	MTBE (0.5 M)	Ph₃P (0.3 eq)	94	>98:2
5 ^[c]	MTBE (0.5 M)	Ph ₃ P (0.3 eq)	86 (83 ^[d])	>98:2

[a] NMR yield determined by ¹H NMR analysis. [b] Ratio of **5a:6a** determined by ¹H NMR analysis. [c] 1.5 eq of **2** was employed. [d] Isolated yield.

Next, we envisioned silaboration reaction via Zn-B exchange reaction of the in-situ-generated silylzincation intermediate C (Scheme 3) to afford the corresponding silaboration product D with regeneration of dialkylzinc. In fact, the combination of a catalytic amount of Me₂Zn (0.3 eq) with an excess amount of silvlborane (2, 2 eq) at higher temperature (75°C) gave the cis-1,2-silaborated product (5a) in 43% yield accompanied with the cis-1,2-silylzincated product (26% yield) (Table 3, run 1), indicating that silaboration proceeds via a stepwise mechanism, as expected. To our knowledge, this reaction is the first example of an ionic silaboration of unactivated acetylene without any transition-metal catalyst.^[9,14,15] The use of MTBE (methyl tertbutyl ether), instead of THF, and a higher concentration (0.5 M) the borylation step promoted without reducing the regioselectivity (runs 2 and 3). The change of ⁿBu₃P to Ph₃P gave the best yield of 1,2-silaboration (94%, 5a:6a = >98:2, run 4), and in this case, reducing the amount (1.5 eq) of PhMe₂Si-B(pin) (2) also gave comparable results in terms of reactivity and selectivity (run 5).

Representative results illustrating the scope of the present silaboration are summarized in Table 4. Various aliphatic alkyl substituents gave the desired products in high yield with high regio-/stereoselectivity (runs 1-5); various polar functional groups (runs 6-9), an internal C-C triple bond, and a terminal olefin (runs 10 and 11) were tolerated. On the other hand, aromatic alkynes such as phenylacetylene (**1n**) did not effectively undergo 1,2-silaboration (**5n**), but gave the 1,2-

hydrosilylated product (3n), probably because the intermediary vinylzinc species is too stabilized both electronically and sterically for the borylation step to occur (run 12). The silaboration products (5) are versatile platforms for further chemical elaborations. For instance, 1,2-silaborated product 5a, generated by 1,2-silaboration of 1-octyne (1a), was treated under cross-coupling conditions to give the arylated vinylsilane (5aa, eq 1) in 83% yield. 5a also underwent selective oxidation in high yield to give 1-silylketone (5ab, eq 2), which is normally synthesized via a complex multi-step synthetic procedure. In contrast, chemoselective desilyliodination of 5a proceeded smoothly with N-iodosuccimide to give the boryliodinated product (5ac, eq 3). The present strategy enables versatile synthesis of various vinylsilanes and vinylborons as platforms for obtaining regio-controlled trisubstituted olefins and functionalized materials.

Table 4. 1,2-silaboration of terminal alkynes and transformations of the intermediate (5a)



[a] Isolated yield (NMR yield, determined by ¹H NMR analysis, is shown in parentheses). [b] The ratio of **5:6** (1,2-:2,1-silaboration) was determined by ¹H NMR analysis. Unless otherwise noted, all ratios were >98:2. [c] 2 eq of **2** was employed. [d] Run at 100°C. [e] 1,2-Hydrosilylated product (**3n**) was obtained.

During this silaboration study, we fortuitously found that removal of phosphine from the present 1,2-silaboration reaction mixture resulted in completely opposite regioselectivity of silaboration (Table 5). Although further theoretical and spectroscopic studies of the present 2,1-silaboration are needed to elucidate the reaction pathway, it seems that a distinct species is generated that facilitates the selectivity.

Table 5. 2,1-Silaboration of terminal alkynes

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[a] Isolated yield (NMR yield, determined by ¹H NMR analysis, is shown in parentheses) [b] The ratio of **5**:**6** (1,2-:2,1-silaboration) was determined by ¹H NMR analysis.

Scheme 4. Summary of conditions for Zn-mediated silylmetalations



In summary, we have developed a new method for *in-situ* generation of highly reactive silylzinc species (Si–Zn) *via* a novel activation of the stable Si–B bond with dialkylzinc and phosphine. This method can provide highly controllable regio-/stereo-/chemo-selective silylmetalations, i.e., 1,2-silylzincation, 1,2-silaboration and 2,1-silaboration, on demand (Scheme 4). We believe that the present protocols might also offer a new approach for the activation of other inert bonds and provide access to a wide variety of hetero element-zinc species. Further work to expand the scope of this methodology and to apply this approach to a variety of reactions is in progress.

Keywords: zinc • silicon • silylmetalation • silylborane • alkyne

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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In-situ generation of silylzinc species was achieved by reaction of dialkylzinc, phosphine, and silvlborane, based on model DFT calculations indicating that Si-B bond cleavage would afford the Si-Zn species. Using this protocol, successive reaction with various terminal alkynes enabled highly controllable regio-/stereo-/chemoselective silylzincation and silaboration of terminal alkynes on demand, affording synthetically densely versatile and functionalized vinylsilane and vinylboron derivatives.



Yuki Nagashima,* Daiki Yukimori, Chao Wang, and Masanobu Uchiyama*

Page No. – Page No.

In Situ Generation of Silylzinc by Si–B Bond Activation Enabling Silylzincation and Silaboration of Terminal Alkynes