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Copper(I)-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Terminal Alkynes with Boryldisiloxane

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By employing 1,1,3,3-tetramethyl-1,3-(pinacolboryl)disiloxane as a novel silicon source, the N-heterocyclic carbene copper complex catalyzed hydrosilylation of terminal alkynes was developed to prepare vinyldisiloxanes in a highly regio- and stereoselective manner. A number of functional groups, including ether, ester, cyano, nitro, halo, hydroxyl, cyclopropyl, and aryl groups, were tolerated under the optimized conditions. A mechanistic investigation was undertaken by using density functional theory calculations. This approach allows facile entry to unsymmetrical disubstituted (*E*)-alkenes by Pd-catalyzed cross-coupling reactions.

Vinylsilanes are versatile building blocks in organic synthesis^[1] because of their extensive applications in protodesilylations,^[2] Tamao–Fleming oxidations,^[3] Hiyama–Denmark cross-coupling reactions,^[4] and other transformations.^[5] Although numerous successful catalytic processes, such as the hydrosilylation of al-kynes with Si–H reagents,^[6] have been described to access these types of compounds, efforts to increase the catalytic activity and to control reaction selectivity with high substrate tolerance continue.

Silylcupration^[7] of carbon–carbon triple bonds followed by protonation is one of the most attractive routes to generate vinylsilanes with complete *syn* stereoselectivity. However, stoichiometric amounts of Fleming's silyl cuprate reagents (Cu–Si) by employing silyl–lithium $(Si–Li)^{[8]}$ or silyl–stannane $(Si–Sn)^{[9]}$ reagents as the silicon sources are needed for this transformation. Recently, much attention has been directed toward the catalytic formation of functionalized vinylsilanes under copper catalysis, in which the key Cu–Si species arise from activation of disilane $(Si–Si)^{[10]}$ or silylborane (Si–B) reagents^[11–14] (Scheme 1).

The first copper(I)-catalyzed system for the hydrosilylation of alkynes conjugated to carbonyl groups was reported by Molander's group, who used diphenyltetramethyldisilane to obtain β -silyl- α , β -unsaturated carbonyl mixtures with different *E/Z* ratios in moderate yields.^[10] Me₂PhSiB(pin) (pin=pinacolato), an important silylborane (Si–B) reagent owing to its versatile synthetic transformations, has been widely researched to effectively synthesize silicon- and/or boron-functionalized synthons.^[15] Loh^[11] reported that by using Me₂PhSiB(pin) as the sil-

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icon source, CuCl bearing a phosphine ligand catalyzed the hydrosilylation of terminal alkynes to selectively form α -vinylsilanes, in which the hydrogen atom was provided by added alcohols. Unfortunately, the regioselectivity was decreased with the use of electron-deficient substrates. Very recently, N-heterocyclic carbene (NHC)–copper(I) complexes were found to be more efficient catalytic systems for the above reaction, and they afforded β -(*E*)-vinylsilanes with high regio- and stereoselectivity (>98% *E* and β).^[12] During the preparation of this manuscript, Calderone and Santos^[13] and Lipshutz^[14] successively reported the copper-catalyzed hydrosilylation of electron-deficient internal alkynes by using Me₂PhSiB(pin) in water at room temperature to selectively afford β -silyl- α , β -unsaturated carbonyl compounds.

However, thus far only Me₂PhSiB(pin) has been used in all reported transformations, and the scant number of Si–B reagents available has limited broader application of copper-catalyzed hydrosilylation reactions. Considering that vinylsilanes bearing oxygen substituents at silicon have higher reactivity and more diversity of reactions than their dimethylphenyl counterparts,^[3b,4] we sought to establish the Cu¹-catalyzed hydrosilylation of terminal alkynes by employing a novel boryldisiloxanes under mild conditions.

We initiated our studies by using the known MeOMe₂SiB(pin) reagent^[16] as the oxygen-substituted silicon source for the hydrosilylation of phenylacetylene (Scheme 2). The reaction proceeded smoothly in a *cis* manner in the presence of CuCl (1 mol%), PPh₃ (1.2 mol%), and NaOtBu (1.2 mol%) in THF at room temperature for 1 h to give the constitutional isomer



Scheme 1. Cu reagents involved in the hydrosilylation of alkynes by using different silicon sources.

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Scheme 2. $MeOMe_2SiB(pin)$ reagent involved in the hydrosilylation catalyzed by a Cu^1 complex.

having the silyl group at the terminal position as the sole product in 52% yield ($\beta/\alpha > 99:1$; E/Z > 99:1). No other isomers were detected in a solution of the crude reaction mixture by 400 MHz ¹H NMR spectroscopy. Because MeOMe₂SiB(pin) is sensitive to air and moisture, strict Schlenk operations were needed for the whole reaction process.

Novel, stable Si–B reagents with high hydrosilylation activity were further developed by introducing the Si–O–Si moiety, which generally exists in stable silicates and SiO₂ materials. 1,1,3,3-Tetramethyl-1,3-(pinacolboryl)disiloxane (1) was successfully obtained as the oxygen-functionalized Si–B reagent by reaction of CIMe₂SiB(pin)^[16] with H₂O in THF at room temperature for 24 h, as shown in Scheme 3, on the basis of our knowl-



Scheme 3. Synthesis of 1,1,3,3-tetramethyl-1,3-(pinacolboryl)disiloxane (1).

edge of silylboration^[17] and hydrosilylation^[18] of 1,3-enynes. By SiO₂ column chromatography with the use of I₂ as a chromogenic agent, white solid **1** was easily isolated in 83% yield. The ¹H NMR spectrum showed two singlets at $\delta = 0.18$ and 1.22 ppm, which were attributed to the methyl groups on the silicon atom and pinacolborane, respectively.

In contrast to the previously reported Si–B reagents,^[15,16] boryldisiloxane **1** is air and moisture stable owing to the effect of the Si–O–Si structure. Single crystals were obtained from *n*-pentane solution, and the molecular structure was confirmed by X-ray crystallography (see Figure S1 in the Supporting Information). The two Si–B bonds [2.032(2) and 2.027(2) Å] are close to those of the tri- and tetrasilylborates [(Me₃Si₃)BR]Li (R=Me, SiMe₃, \approx 2.017–2.034 Å).^[19] The Si–O–Si angle of **1** is 143.46(9)°, which shows a similar structural motif in silica gel.^[20]

We first performed the hydrosilylation reaction of phenylacetylene (**2 a**, 0.3 mmol) with boryldisiloxane **1** (0.125 mmol) and methanol (4.0 equiv.) in the presence of CuCl (1 mol%) bearing monodentate ligands (1.2 mol%) and NaOtBu (1.2 mol%) as a catalyst in THF at room temperature for 2 h (Table 1). Three isomeric vinyldisiloxanes products, (α,α) -(*E*)/(α,β)-(*E*)/(β,β)-(*E*), can be provided by *cis* addition. The results demonstrate that the ligands clearly affected the activity and selectivity of the hydrosilylation. No reaction occurred in the absence of the ligand (Table 1, entry 1). The use of monodentate phosphines, such as PPh₃ and PCy₃ (Cy = cyclohexyl), generated sole product (β,β) -(*E*)-**3** a in 54 and 72% yield, respectively, with high selectivity (Table 1, entries 2 and 3), whereas a small amount of the (α,β) -(E) regioisomer was formed with PEt₃ (Table 1, entry 4). Formation of the (α, α) -(E) regioisomer became more preferable with the use of PtBu₃ and P(tBu)₂(biphenyl-2-yl), which indicates that sterically demanding phosphines are able to control the regioselectivity of the reaction (Table 1, entries 5 and 6).

Similar ligand-controlled hydrosilylation of terminal alkynes was reported by Loh and co-workers^[11] by employing Me₂PhSiB(pin) to afford α -(*E*)-vinylsilanes as the major regioisomers. CuCl bearing NHC ligands showed more reactivity to synthesize **3a** with complete regio- and stereoselectivity, and the less bulky 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) ligand provided a higher yield than 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (Table 1, entries 7 and 8). Further research showed that isolated (IMes)CuCl was also highly active for this transformation (Table 1, entry 9).

We next evaluated the scope of the copper-catalyzed hydrosilylation of terminal alkynes with boryldisiloxane **1**. With the optimized procedure and by using (IMes)CuCl as the catalyst, a variety of terminal alkynes bearing various functional groups and substitution patterns were tested in the selective synthesis of the corresponding (β , β)-(*E*)-vinyldisiloxanes, and the results are summarized in Table 2.



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The reactivity was slightly affected by both electron-donating (e.g., –Me and –OMe) and electron-withdrawing (e.g., –Br and –NO₂) groups on the aryl ring (Table 2, entries 1–4). Substrates with a variety of functional groups, such as cyclopropyl, hydroxyl, ether, ester, and cyano, were tolerated in these reactions (Table 2, entries 7, 9–12) and gave products in excellent yields with excellent selectivity. Even the sterically crowded *tert*-butylethyne showed (Table 2, entry 13) high reactivity and selectivity [90% yield, $(\beta,\beta)/(\alpha,\beta)/(\alpha,\alpha) > 99:1:<1$].



Scheme 4. A plausible mechanism for the hydrosilylation of terminal alkynes with boryldisiloxane **1**.

In the absence of MeOH, the hydrosilylation of propargyl alcohol **2m** with boryldisiloxane **1** also proceeded smoothly under the optimized conditions. A proton was effectively provided by **2m** itself, and after hydrolysis^[21] desired product **3m** was conveniently isolated by SiO_2 flash chromatography in 90% yield.

A possible catalytic cycle for the hydrosilylation of terminal alkynes is proposed, as shown in Scheme 4. Initially, the reaction of the NHC-Cu¹Cl complex with NaOtBu smoothly proceeds to form CuOtBu complex **A**.^[22] This is followed by σ -bond metathesis with boryldisiloxane,^[23] from which silylcopper complex **B** is generated. Subsequent insertion of the terminal alkyne into the Cu–Si bond of **B** selectively affords β -silylvinylcopper complex **C** in a *cis* manner.^[13] Next, protonation^[12,13] of **C** with MeOH provides desired hydrosilylation product **D** and the NHC-CuOMe complex to complete the catalytic cycle.

According to the reaction mechanism, the regioselectivity is effectively controlled by the insertion process. To further explain this experimental behavior, two geometries of the transition states in the insertion step of the IMesCu–SiOSiB(pin) intermediate to phenylacetylene (**2**a) were optimized with DFT at the B3LYP/6-31G(d) level (Figure 1). The calculated results show that the insertion step proceeds with an activation energy barrier of 8.2 kcal mol⁻¹ from **TS1** in comparison to an activation energy barrier of 13.4 kcal mol⁻¹ from **TS2**, which means that the IMesCu¹ catalytic system tends to form intermediate **C** rather than another regioisomer, and therefore, (β , β)-(*E*)-vinyldisiloxane **D** is selectively generated as the sole isomer.

Vinyldisiloxane reagents, as the possible intermediates generated from organosilanol-based cross-coupling reactions^[24] catalyzed by palladium complexes in the presence of a strong base, are useful synthetic building blocks to afford alkene derivatives with a high degree of stereochemical retention.^[25] As expected, cross-coupling reactions of vinyldisiloxanes with 1-

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TS2: 13.4 kcal mol⁻¹

Figure 1. Transition state in the insertion step of the Cu–Si intermediate to phenylacetylene (**2a**). C: gray, Cu: orange, Si: green, B: pink, O: red, and N: blue.

iodonaphthalene and 1-chloro-4-iodobenzene catalyzed by $Pd_2(dba)_3/nBu_4NF$ (dba = dibenzylideneacetone) were successfully realized in THF at room temperature to provide (*E*)-1,2-disubstituted unsymmetrical alkynes **4a** and **4b** in 95 and 92% yields, respectively, without the formation of any other isomers or protodesilylated products (Scheme 5).

In summary, we developed an efficient procedure for the hydrosilylation of various terminal alkynes by using a novel boryldisiloxane reagent as the silicon source and an inexpensive copper complex catalyst. The products, (β , β)-(E)-vinyldisiloxanes, were obtained as the sole detectable isomers with perfect regio- and stereoselectivity. Theoretical evidence from calculations combined with experimental evidence explain the remarkable selectivity of the NHC-Cu¹ complex catalyzed hydro-



Scheme 5. Application of vinyldisiloxane for the Pd-catalyzed Hiyama cross-coupling reaction.

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silylation. Further chemical transformation by Pd-catalyzed cross-coupling reactions is an efficient approach to synthesize unsymmetrical 1,2-disubstituted (*E*)-alkenes. Extension of this method to other unsaturated substrates and their further chemical applications are in progress.

Experimental Section

Synthesis of 1,1,3,3-tetramethyl-1,3-(pinacolboryl)disiloxane: Under a N₂ atmosphere, H₂O (36 mg, 2.0 mmol) and pyridine (160 mg, 2.0 mmol) were sequentially added by syringe to a solution of CIMe₂SiB(pin) (220 mg, 1.0 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature for 24 h. Then, the solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to give the desired disiloxane (160 mg, 83 % yield) as a white solid. No 1,1,3,3-tetramethylpinacolborylsilanol was observed by ¹H NMR spectroscopy. ¹H NMR (400 MHz, CDCl₃): δ = 1.22 [s, 24H; -C(CH₃)₂], 0.18 ppm [s, 12H; -Si(CH₃)₂]; ¹³C NMR (100 MHz, CDCl₃): δ = 83.4, 25.3, 2.3 ppm; IR (film): \tilde{v} = 2981, 2933, 2897, 1376, 1247, 1146, 1034, 837, 781 cm⁻¹; HRMS (EI): *m/z*: calcd for C₁₀H₂₄BO₃Si: 259.1355 [M–B(pin)]⁺; found: 259.1357.

Single crystals were obtained from *n*-pentane solution at -35 °C. Diffraction data were collected at 77 K with a Bruker SMART-CCD diffractometer by using graphite-monochromated MoK_a radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods^[26] and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed by using the SHELXTL^[27] crystallographic software packages. CCDC-977410 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Hydrosilylation of alkynes catalyzed by IMesCuCl catalyst: Inside an Ar-filled glove box, a vial was charged with (IMes)CuCl (4.0 mg, 1 mol%), NaOtBu (1.2 mg, 1.2 mol%), and THF (2 mL). After 30 min stirring at room temperature, phenylacetylene (2 a, 1.0 mmol), 1,1,3,3-tetramethyl-1,3-(pinacolboryl)disiloxane (0.5 mmol), and MeOH (4.0 mmol, 4.0 equiv.) were sequentially added to the solution. The resulting mixture was stirred at room temperature for 2 h. After removal of the solvents under reduced pressure, the crude product was purified by silica gel column chromatography (hexane) to afford **3a** as a colorless liquid (88% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.51$ (d, J = 7.4 Hz, 4H; PhH), 7.39 (t, J =7.4 Hz, 4H; PhH), 7.33 (t, J=7.4 Hz, 2H; PhH), 7.05 (d, J=19.2 Hz, 2H; PhCH=), 6.54 (d, J=19.2 Hz, 2H; PhCH=CH-), 0.36 ppm [s, 12 H, $-Si(CH_3)_2$; ¹³C NMR (100 MHz, CDCl₃): $\delta = 144.7$, 138.4, 128.8, 128.5, 126.9, 1.2 ppm; IR (film): v = 3082, 3020, 2959, 1617, 1575, 1499, 1253, 1048, 989, 848, 784, 689 cm⁻¹; HRMS (El): *m*/

1499, 1253, 1048, 989, 848, 784, 689 cm $^{\circ}$; HRMS (EI): *m*/ *z*: calcd for C₂₀H₂₆OSi₂: 338.1522; found: 338.1532 (reported in Ref. [25a]).

Cross-coupling reaction of vinyldisiloxanes: $Pd_2(dba)_3$ (5 mg, 5 mol%), 1-iodonaphthalene (51 mg, 0.2 mmol), and nBu_4NF (52 mg, 2.0 equiv.) were added to a solution of disiloxane **3a** (33 mg, 0.1 mmol) in THF (2.0 mL). The resulting mixture was stirred at RT for 30 min. After removal of the solvents, the residue was purified by column chromatography (hexane) to afford (*E*)-1-styryl-naphthalene (44 mg, 95% yield) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 (d, J = 8.0 Hz, 1 H),

7.84–7.90 (m, 2H), 7.79 (d, J=8.2 Hz, 1H), 7.74 (d, J=7.2 Hz, 1H), 7.61 (d, J=8.2 Hz, 2H), 7.48–7.53 (m, 3H), 7.39 (t, J=7.8 Hz, 2H), 7.29 (dt, J=1.2, 7.4 Hz, 1 H), 7.14 ppm (d, J=16.0 Hz, 1H) (reported in Ref. [28]).

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Copper(I)-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Terminal Alkynes with Boryldisiloxane



Put a pin in it: The highly regio- and stereoselective hydrosilylation of terminal alkynes with 1,1,3,3-tetramethyl-1,3- (pinacolboryl)disiloxane as a novel silicon source with the use of a copper catalyst gives functionalized (β , β)-

(*E*)-vinyldisiloxanes in good yields. Further chemical transformation through Pd-catalyzed cross-coupling results in the synthesis of unsymmetrical 1,2disubstituted (*E*)-alkenes.