

Copper-Catalyzed *Anti*-Markovnikov Hydrosilylation of Terminal Alkynes

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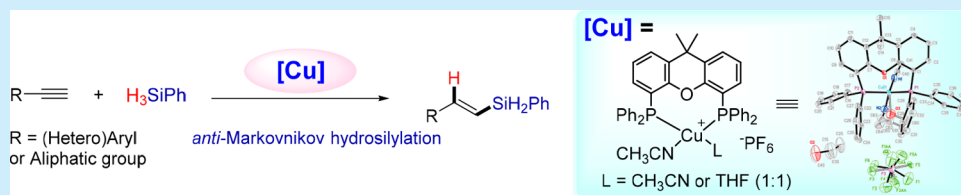
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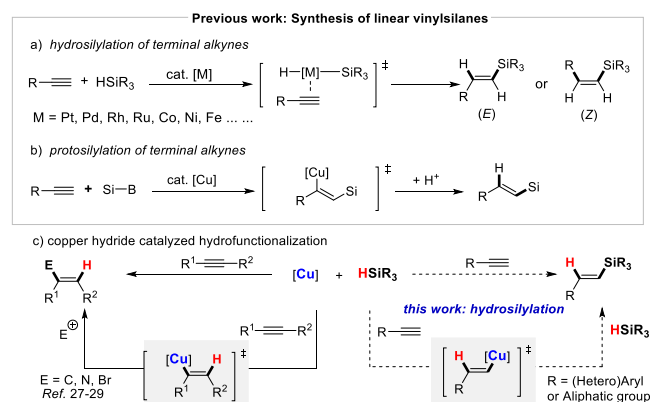
Supporting Information



ABSTRACT: A copper-catalyzed *anti*-Markovnikov hydrosilylation of alkynes with PhSiH₃ was reported. This reaction represents a notable and efficient example on copper-catalyzed hydrosilylation of alkynes, which shows excellent recognition between the terminal and internal triple bonds. Various (hetero)aromatic and aliphatic substituted terminal alkynes underwent this reaction to afford the (*E*)-vinylsilanes in high yields and with excellent regioselectivity.

The use of vinylsilanes as versatile building blocks in organic synthesis has attracted much attention in recent years.¹ Among the available methods for the synthesis of these compounds, there is no doubt that hydrosilylation of alkynes is the most atom-economical and powerful approach. So far, numerous examples on the hydrosilylation of alkynes have been well documented in the presence of different catalysts such as late transition metals Pt,² Rh,^{2a-d,3} Ru,^{2c,4} Pd,^{2c,5} Ir,^{2c,6} Ni,⁷ Co,⁸ Mn,⁹ and Fe¹⁰ as well as the early transition metals.^{11–15} On the other hand, some examples on the hydrosilylation of alkynes in the presence of heterogeneous catalysts^{2i,7f,16} also emerged. It is worth noting that alkyne hydrosilylation under radical conditions¹⁷ or catalyzed by strong Lewis acids¹⁸ has also been demonstrated in recent years. In the past 10 years, an alternative pathway to access the alkenylsilanes via copper-catalyzed protosilylation of alkynes with silylboronates has also been successfully developed by Hoveyda,¹⁹ Zhou,²⁰ Oestreich,²¹ Li,²² Carretero,²³ Santos,²⁴ Lipshutz,²⁵ our group,²⁶ and others, respectively. It should be noted that the synthetic utility of the vinylsilanes depends on their preparation methods and the level of regio- and stereoselectivity control. Therefore, the development of simple and practical catalytic system for the hydrosilylation still remains an opportunity. Compared with the wide applications of other naturally abundant first-row transition-metal catalysts in the hydrosilylation, in sharp contrast, the copper-based catalysts were scarcely employed for this kind of reaction. Despite the fact that, during the past decade, the Cu–H-catalyzed hydroamination,²⁷ hydrocarbylation,²⁸ hydrobromination,²⁹ etc. have been successfully developed with using different silanes (Scheme 1c, left), to the best of our knowledge, so far only copper-catalyzed enantioselective hydrosilylation of styrene derivatives and vinyl heterocycles

Scheme 1. Transition-Metal-Catalyzed Hydrosilylation of Terminal Alkynes



have been elegantly described by Buchwald and co-workers^{30,31} Herein, we would like to report a copper-catalyzed highly chemo- and regioselective hydrosilylation of terminal alkynes. Various aryl and aliphatic substituted alkynes could afford the desired linear alkenylsilane products in good yields.

We commenced the study by testing the hydrosilylation of phenylacetylene (**2a**) with PhSiH₃ as the model reaction. First, the catalytic system established by Buchwald's group was

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Table 1. Copper Catalyzed Regioselectively Hydrosilylation of Alkynes^a

Reaction scheme: $\text{Ph-C}\equiv\text{C-R} + \text{PhSiH}_3 \xrightarrow[\text{solvent, N}_2, 60^\circ\text{C, 1 h}]{\text{catalyst / ligand}}$ $\text{Ph-C}=\text{C}(\text{R})\text{-SiH}_2\text{Ph}$ (3a) + $\text{Ph-C}(\text{SiH}_2\text{Ph})_2$ (4a) + $\text{Ph-C}(\text{SiH}_2\text{Ph})_2\text{-R}$ (5a)

entry	catalyst (mol %)	ligand (mol %)	PhSiH ₃ (equiv)	solvent (0.5 mL)	yield (%)	
					3a/4a	5a
1 ^b	Cu(OAc) ₂ (4)	(s,s)-Ph-BPE (4.4)	3.0	THF (0.4 mL)	12 (67:33)	0
2 ^b	Cu(OAc) ₂ (4)	(s,s)-Ph-BPE (4.4)	5.0	none	13 (70:30)	0
3	Cu(CH ₃ CN) ₄ PF ₆ (10)	DPEphos (10)	3.0	THF	13 (92:8)	4
4	Cu(CH ₃ CN) ₄ PF ₆ (10)	BINAP (10)	3.0	THF	10 (100:0)	trace
5	Cu(CH ₃ CN) ₄ PF ₆ (10)	PPh ₃ (10)	3.0	THF	11 (91:9)	trace
6	Cu(CH ₃ CN) ₄ PF ₆ (10)	Xantphos (10)	3.0	THF	60 (97:3)	7
7	Cu(CH ₃ CN) ₄ PF ₆ (10)	no	3.0	THF	0	0
8	1a (10)	no	3.0	THF	63 (99:1)	5
9	1a (10)	no	3.0	DME	76 (99:1)	6
10	1a (5)	no	3.0	DME	77 (74) ^c (99:1)	6
11	1b (5)	no	3.0	DME	0	0
12	1a (5)	no	2.0	DME	68 (99:1)	10
13	1a (5)	no	1.2	DME	50 (98:2)	14
14 ^d	1a (5)	no	3.0	DME	25 (98:2)	0
15 ^e	1a (5)	no	3.0	DME	24 (98:2)	0
16 ^f	1a (5)	no	3.0	DME	trace	0

L = CH₃CN or THF (1:1)
1a^g

1b^g

^aConditions: **2a** (0.2 mmol), PhSiH₃ (0.6 mmol) in solvent (0.5 mL). The yields were determined by ¹H NMR using Cl₂CHCHCl₂ as an internal standard. ^bBuchwald's group reported catalytic system. ^cIsolated yield of **3a** and **4a**. ^dEt₂SiH₂ replaced PhSiH₃. ^ePh₂SiH₂ replaced PhSiH₃. ^fPhMe₂SiH replaced PhSiH₃. ^gSee the Supporting Information for the crystal structures of **1a** and **1b**. DPEphos = bis(2-diphenylphosphinophenyl)ether; BINAP = 1,1'-Binaphthyl-2,2'-diphenyl phosphine; Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; DME = 1,2-dimethoxyethane.

applied to this reaction. Unfortunately, only about 13% NMR yield of the hydrosilylation product was detected (Table 1, entries 1 and 2). Therefore, continuous efforts to improve the product yield were made. When the reaction was run in the presence of 10 mol % Cu(CH₃CN)₄PF₆ and 10 mol % of DPEphos in THF at 60 °C in an oil bath the desired product was obtained in 13% yield with 92:8 regioselectivity (Table 1, entry 3). Next, different phosphine ligands were examined to improve the reaction efficiency. It was found that the Xantphos ligand could improve the product yield to 60% without diminishing the selectivity (Table 1, entry 6). However, no reaction occurred in the absence of ligand (Table 1, entry 7). In order to determine the exact species of copper catalyst, the copper complex **1a** (CCDC no. 2014784) was prepared with using equivalent Cu(CH₃CN)₄PF₆ and Xantphos in THF. When complex **1a** was used as catalyst, similar yield and regioselectivity of product **3a** were observed (Table 1, entry 8). When DME was used instead of THF, the yield of product was improved to 76% (Table 1, entry 9). Further studies showed that the reaction completed within 1 h by using 5 mol % of **1a** and furnished the desired product in 74% isolated yield and with 99:1 regioselectivity (Table 1, entry 10). When the neutral copper complex³² **1b** (CCDC no. 2014786) was used as catalyst, no reaction occurred (Table 1, entry 11). Subsequently, we tested the loading of PhSiH₃ used in the reaction. When the amount of PhSiH₃ was reduced to 2.0 or 1.2 equiv, the yield of product **3a** decreased accompanied with the formation of more dihydrosilylation product **5a** (Table 1,

entries 12 and 13). Finally, we explored the catalytic performance of complex **1a** with other hydrosilanes. It was found that the secondary hydrosilanes (Et₂SiH₂ and Ph₂SiH₂) only afforded the corresponding products in poor yields (Table 1, entries 14 and 15), and the tertiary hydrosilane (PhMe₂SiH) was unreactive under the optimized reaction conditions (Table 1, entry 16). Therefore, the optimal reaction conditions were established as follows (entry 10): the mixture of alkyne (0.2 mmol), PhSiH₃ (0.6 mmol), and **1a** (5 mol %) in DME (0.5 mL) was stirred for 1 h at 60 °C in an oil bath under nitrogen atmosphere.

With the optimized reaction conditions in hand, the hydrosilylation of various (hetero)aryl-substituted alkynes with PhSiH₃ were tested. The results are summarized in Figure 1. The substrates bearing an electron-donating group or electron-withdrawing group could all afford the corresponding products in good yields and with excellent regioselectivities. Different functionalities such as methyl, methoxy, halides, acetal,³³ and ester etc. all were well tolerated during the transformation (Figure 1). Moreover, the 3-ethynylthiophene was also smoothly applied to this hydrosilylation to give the product **3m** in good yield and with excellent regioselectivity. Importantly, when the 1-ethynyl-4-vinylbenzene bearing a vinyl and an alkynyl group on the phenyl ring was subjected to this reaction, it was found that the PhSiH₃ exclusively reacted with a triple bond under the optimal reaction conditions (**3n**). Furthermore, when the reaction was performed with the alkyne **2o** which contained a terminal and an internal alkynyl group,

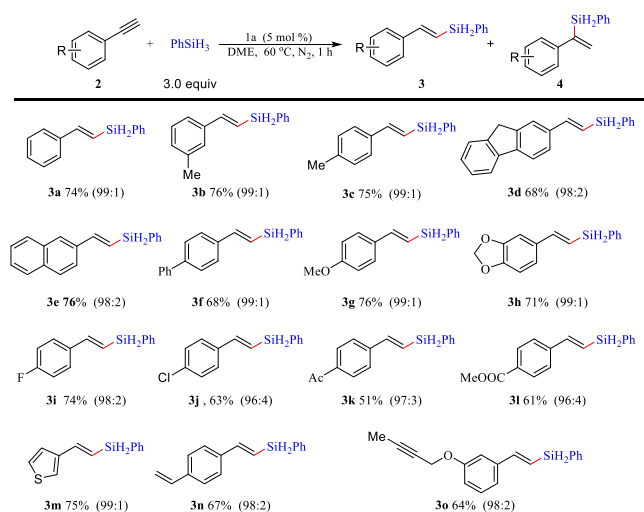


Figure 1. Substrate scope of aromatic alkynes. The mixture of alkyne (0.2 mmol), PhSiH_3 (0.6 mmol), and catalyst **1a** (5 mol %) in DME (0.5 mL) was stirred for 1 h at 60 °C in an oil bath.

the internal triple bond was well tolerated to yield the product **3o** in good yield. This result demonstrates higher reactivity of terminal alkynyl group than the internal one in this hydrosilylation reaction.

In addition to the aromatic substituted terminal alkynes, this hydrosilylation reaction was also applied to diverse aliphatic substituted alkynes. The corresponding desired products were also obtained in satisfactory yields and with excellent regioselectivities (Figure 2). First, different alkynes tethering

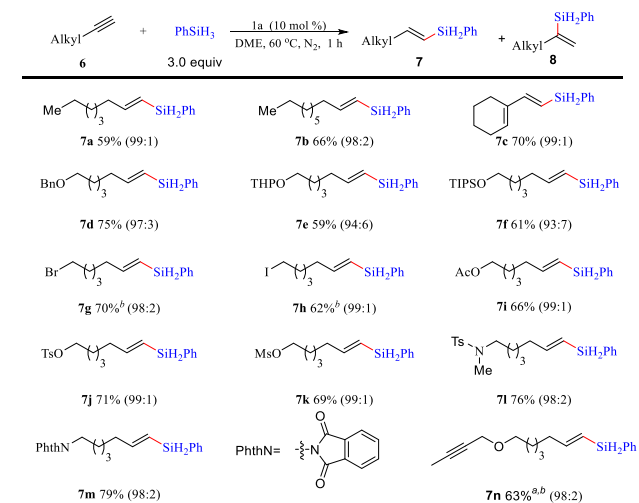


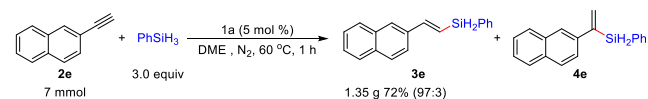
Figure 2. Substrate scope of aliphatic alkynes. The mixture of alkyne (0.2 mmol), PhSiH_3 (0.6 mmol), and catalyst **1a** (10 mol %) in DME (0.5 mL) was stirred for 1 h at 60 °C in an oil bath. (a) PhSiH_3 (6.0 equiv). (b) $t = 3$ h.

with long-carbon-chain could be transformed into the desired products smoothly (Figure 2, **7a**, **7b**). When the 1-ethynylcyclohex-1-ene underwent this hydrosilylation reaction, a diensilane product **7c** was formed in 70% yield and with 99:1 regioselectivity. Next, different functionalities were installed on the carbon chain to test their tolerated ability. It was observed that the substrates with the functional groups such as ether, silyl ether, halides, ester, tosyl, mesyl, tertiary amine, or amide group all were compatible to afford the

corresponding products (Figure 2, **7g–m**). Similarly, when the reaction was performed with **6n**, only the terminal alkynyl group selectively reacted with PhSiH_3 to produce the product **7n**.

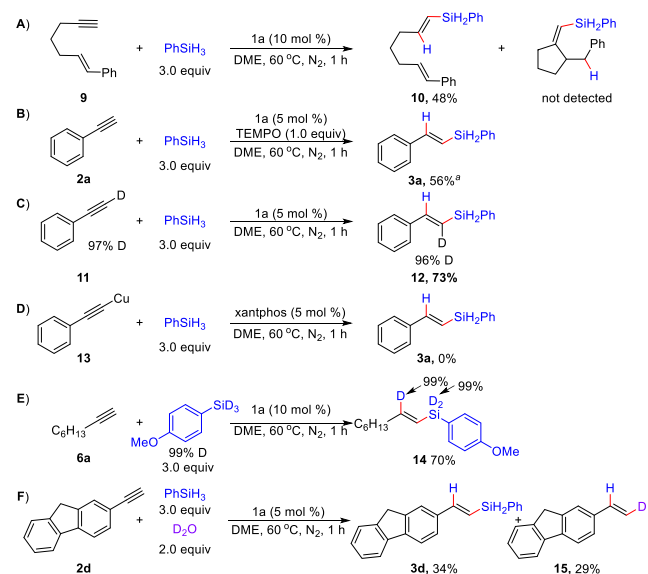
To demonstrate the utility of current strategy, a gram-scale reaction between 2-ethynyl-naphthalene (**2e**) with phenylsilane was carried out. The desired product **3e** was obtained in 72% isolated yield with 97:3 regioselectivity (Scheme 2).

Scheme 2. Gram-Scale Synthesis of Vinylsilanes **3e**



Several control experiments were carried out to clarify the possible reaction pathway. The hydrosilylation of (*E*)-hept-1-en-6-yn-1-ylbenzene (**9**) afforded the desired product in 48% yield without any cyclization product formation (Scheme 3A).

Scheme 3. Control Experiments^a



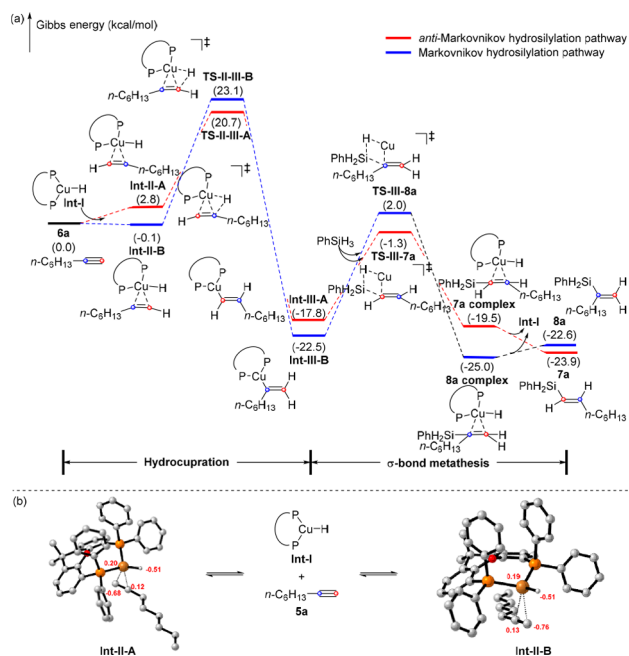
^aThe yield was determined by ^1H NMR with using $\text{Cl}_2\text{CHCHCl}_2$ as an internal standard.

Moreover, when radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was introduced into the reaction, there was still 56% yield of **3a** product obtained (Scheme 3B). These results showed that a radical pathway could be ruled out in this reaction. The hydrosilylation of deuterated phenylacetylene gave the corresponding product in 73% yield without H/D exchange (Scheme 3C). No reaction occurred when (phenylethynyl)copper was prepared to react with PhSiH_3 (Scheme 3D). Thus, a mechanism involving copper(I) acetylide generation process could be excluded. Next, the hydrosilylation of **6a** with (4-methoxyphenyl)silane- d_3 under the standard conditions was investigated, which produced the deuterated product **14** in 70% yield (Schemes 3E). This result implies that the copper hydride generated from copper complex and phenylsilane should initiate the hydrosilylation of alkynes. Additionally, the reaction pathway was also proved by generation of (*E*)-2-(vinyl-2-d)-9H-fluorene (**15**) from the reaction of 2-ethynyl-9H-fluorene with PhSiH_3 in the presence

of D₂O (Scheme 3F). Therefore, the formation of an active alkenyl-copper(I) species via a *cis*-addition process of Cu–H to the alkynyl bond was further confirmed.

To provide some insights into the reaction process, density functional theory (DFT) calculations were performed on the hydrosilylation of **6a** with PhSiH₃ using Xantphos ligand (Scheme 4).³⁵ The computational results indicate that the

Scheme 4. Computational Investigation of Copper-Catalyzed Regioselective Hydrosilylation of Terminal Alkynes^a



^a(a) Gibbs energy profiles for the Cu-catalyzed hydrosilylation of **6a** with Xantphos ligand. Free energies in solution (in kcal/mol) at the M06/6-311+G(d,p)-SDD/SMD(THF)//B3LYP-D3(BJ)/6-31G(d,p)-SDD/SMD(THF) level are displayed. (b) ADCH charges on the Cu, H, and two alkyne C atoms of **Int-II-A** and **Int-II-B**. 3D structures were generated by CYLview.³⁴ All of the hydrogens atom of C–H bond are omitted for clarity.

stereoselectivity is determined by the irreversible hydrocupration step, which occurs more selectively via **TS-II-III-A** than via **TS-II-III-B** (20.7 kcal/mol versus 23.1 kcal/mol), affording vinylcopper(I) species **Int-III-A** with an obvious energy decrease of 17.8 kcal/mol. The lower energy of **TS-II-III-A** than **TS-II-III-B** can be addressed by the different electronegativity of the alkyne carbon atoms on **Int-II-A** and **Int-II-B** (Scheme 4b).³⁴ The partially positive charged Cu atom is prone to migrate to the more electronegative terminal alkyne carbon atom with the hydride attached to Cu migrating to the internal alkyne carbon atom simultaneously. Subsequent σ -bond metathesis of **Int-III-A** via **TS-III-7a** produces the **7a**–Cu–H complex, which dissociates to give the linear product **7a** and regenerate Cu–H.

In summary, an unprecedented copper-catalyzed regio- and stereoselective hydrosilylation of alkynes was reported, which could highly recognize the terminal alkyne group from different functionalities. The reaction can be performed under mild reaction conditions, and a broad range of aliphatic and aromatic alkynes underwent this reaction in high efficiency. A gram-scale synthesis of vinylsilane **3e** without

diminishing the product yield or regioselectivity demonstrates that the current hydrosilylation reaction is a highly useful and practical methodology. Mechanistic studies and computational rationalization show that this reaction involves a Cu–H addition step to the alkynyl bond and a sequential σ -bond metathesis process with hydrosilane.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c02952>.

Experimental details, characterization data, and copies of ¹H NMR and ¹³C NMR spectra (PDF)

Accession Codes

CCDC 2014784 and 2014786 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(35) For details of the DFT calculations and references, see the [Supporting Information](#).