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Solvent-free copper-catalyzed trisilylation of alkynes: a practical and atom-economical approach for accessing 1,1,1-trisilylalkanes†

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Organosilicon compounds are versatile reagents in chemical synthesis and materials sciences. As an important class of organosilanes, 1,1,1-trisilylalkanes can undergo various organic transformations and serve as core units for silicon-containing hyperbranched polymers. The existing catalytic approaches for accessing 1,1,1-trisilylalkanes *via* alkyne trisilylation not only requires pre-synthesized moisture- and air-sensitive organocalcium and organolanthanum catalysts but also suffers from limited substrate scope for both alkyne and hydrosilane reagents. For example, only alkyl-substituted alkynes can undergo organocalcium-catalyzed trisilylation with alkyl hydrosilanes to provide the desired 1,1,1-trisilylalkane products. Herein, we report a selective copper-catalyzed trisilylation reaction of both alkyl- and aryl-substituted alkynes with a readily accessible copper catalyst that is generated *in situ* from $Cu(OAc)_2$ and tributylphosphine P^nBu_3. This copper-catalyzed trisilylation reaction features easy catalyst preparation, broad substrate scope, and mild solvent-free reaction conditions. Mechanistic studies reveal that this trisilylation reaction occurs through copper-catalyzed deprotosilylation of alkynes to form alkynylsilanes followed by double hydrosilylation of alkynylsilane.

Introduction

Organosilanes are useful building blocks in organic synthesis and materials sciences because of their diverse reactivity, non-toxicity, high stability, and ease of handling.[1–3] As an important family of organosilicon compounds, 1,1,1-trisilylalkanes, particularly those containing Si–H bonds which allow their further functionalization, are widely used in the synthesis of silicon polymers.[4,5] In addition, 1,1,1-trisilylalkanes can readily undergo base-induced desilylation to generate *gem*-disilyl-substituted carbanions.[6] These carbanions are stabilized by the attached silyl groups and can react with various electrophiles.[6–9] However, general approaches for preparing structurally diverse 1,1,1-trisilylalkanes from readily accessible starting materials are rather limited in scope and functional group compatibility, which in turn limits the exploration of their new reactivity. The classic synthesis of 1,1,1-trisilylalkanes has largely been based on stoichiometric reactions of trisilylmethyllithium or trisilylmethyl Grignard reagents with activated alkyl halides.[10,11] However, these reactions require stoichiometric amounts of pyrophoric reagents and generate large quantities of waste when conducted on a large scale.

Metal-catalyzed hydrosilylation of unsaturated hydrocarbons is a straightforward and atom-economical approach for preparing various families of organosilicon compounds,[12–16] such as alkylsilanes, vinylsilanes, allylsilanes, and *gem*-disilylalkanes.[17–24] Synthetic protocols based on lanthanum-catalyzed dihydrosilylation of silyl-substituted internal alkynes (Scheme 1A) and calcium-catalyzed trisilylation of terminal alkynes (Scheme 1B) to prepare 1,1,1-trisilylalkanes have also been developed but suffer from several significant limitations.[25,26] For example, the scope of alkynes for these metal-catalyzed trisilylation reactions is limited to alkyl-substituted alkynes, and aryl-substituted alkynes only undergo dehydrogenative silylation to provide alkynylsilane products.[26] In addition, the scope of hydrosilanes for these reactions is limited to alkylsilanes $RSiH_3$ because arylsilanes $ArSiH_3$ can readily undergo silane redistribution reactions to produce SiH_4, Ar_2SiH_2, or Ar_3SiH in the presence of alkaline earth metal or lanthanide catalysts.[27–30] Furthermore, the preparation of these well-defined lanthanum and calcium pre-catalysts is rather challenging because they are highly oxophilic and moisture-sensitive.[31] Lastly, the highly polar nature of metal–carbon bonds in organolanthanum and organocalcium intermediates renders these trisilylation reactions less compatible towards reactive functional groups.[32] Therefore, it

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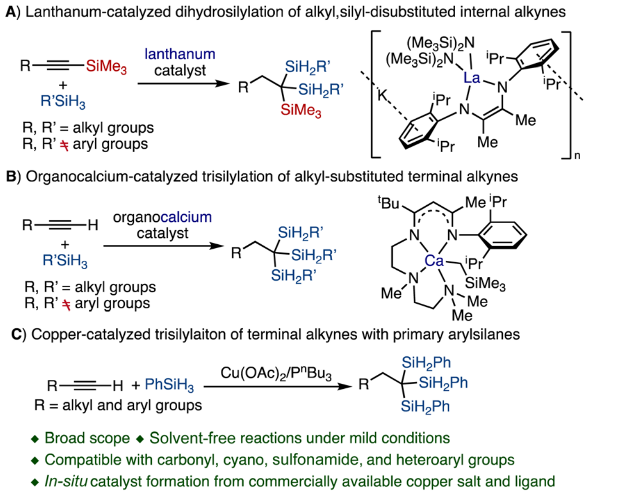


Scheme 1 Catalytic synthesis of 1,1,1-trisilylalkanes.

remains desirable to identify metal catalysts for selective alkyne trisilylation that can combine broad substrate scope, high functional group tolerance, and convenient catalyst generation.

Deprotosilylation of terminal alkynes to form alkynylsilanes with metal acetylide species as intermediates is a key step in transition metal-catalyzed alkyne trisilylation reactions. Terminal alkynes can readily react with various copper salts under mild conditions to form stable monomeric or high-nuclearity copper acetylides.[33–35] Accordingly, copper acetylide species have been proposed as reactive intermediates in a variety of alkyne functionalization reactions, such as Sonogashira coupling reactions and multi-borylation of terminal alkynes.[36–43] Recently, copper complexes have been employed to catalyze hydrosilylation and deprotosilylation of terminal alkynes to generate vinylsilanes and alkynylsilanes, respectively.[44,45] In these copper-catalyzed reactions between terminal alkynes and hydrosilanes, copper hydride and copper acetylide species have been proposed as key intermediates. Nevertheless, suitable conditions and copper catalysts have not been identified to integrate copper-catalyzed deprotosilylation and double hydrosilylation of alkynes into one process to produce 1,1,1-trisilylalkanes.

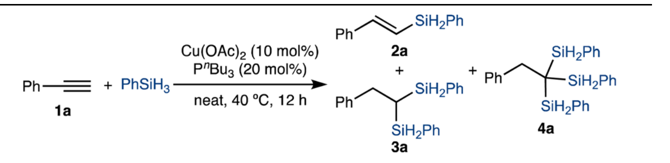
In continuation of our efforts in developing selective base-metal catalyzed synthesis of multi-organometallic compounds from readily accessible unsaturated hydrocarbons,[46–53] we became interested in identifying selective base metal catalysts for trisilylation of alkynes to access 1,1,1-trisilylalkane compounds. We envisioned that copper complexes would be potential catalysts to promote 1,1,1-trisilylation reactions of terminal alkynes because copper acetylide and copper hydride species could be formed in the reactions of terminal alkynes with hydrosilanes. Herein, we report a copper-catalyzed 1,1,1-trisilylation reaction of terminal alkynes under mild conditions with commercially available $Cu(OAc)_2$ and monophosphine ligand P^nBu_3 (Scheme 1C). Mechanistic studies suggest that alkynylcopper, alkynylsilane, and *gem*-disilylalkene species are key intermediates for this copper-catalyzed trisilylation reaction.

Results and discussion

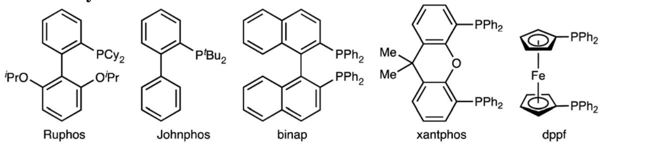
Evaluation of reaction conditions

To initiate our studies on the copper-catalyzed trisilylation of alkynes, we evaluated the reaction between phenylacetylene **1a** and $PhSiH_3$ to identify selective copper catalysts and reliable conditions that promote the formation of 1,1,1-trisilylalkane **4a** (Table 1). The major possible by-products of this reaction are (*E*)-vinylsilane **2a** and *gem*-disilylalkane **3a** from hydrosilylation and double hydrosilylation of **1a**, respectively.[10] The copper catalysts for this study were generated *in situ* by com-

Table 1 Evaluation of reaction conditions for the copper-catalyzed 1,1,1-trisilylation of terminal alkyne **1a**[a]



Entry	Variation from the standard conditions	Conversion of **1a** (%)	Yield of **4a** (%)	**2a : 3a : 4a**
1	None	>99	76	— : 12 : 88
2	P^nBu_3 (30 mol%)	>99	53	— : 16 : 84
3	P^nBu_3 (10 mol%)	88	11	31 : 38 : 31
4	PCy_3 as the ligand	86	8	65 : 23 : 12
5	P^tBu_3 as the ligand	90	—	86 : 14 : —
6	PPh_3 as the ligand	85	—	66 : 34 : —
7	Ruphos as the ligand	89	—	84 : 16 : —
8	Johnphos as the ligand	90	—	80 : 20 : —
9	xantphos as the ligand	90	<5	48 : 45 : 7
10	binap as the ligand	88	—	90 : 10 : —
11	dppf as the ligand	55	—	82 : 18 : —
12	toluene as solvent	70	5	21 : 66 : 13
13	CH_3CN as solvent	>99	44	8 : 36 : 56
14	THF as solvent	92	36	10 : 30 : 60
15	DMA as solvent	>99	68	— : 12 : 88
16	CuOAc as the precursor	>99	72	— : 24 : 76
17	CuTC[b] as the precursor	>99	74	— : 15 : 85
18	(iPr)CuCl as the catalyst[c]	30	—	20 : 80 : —

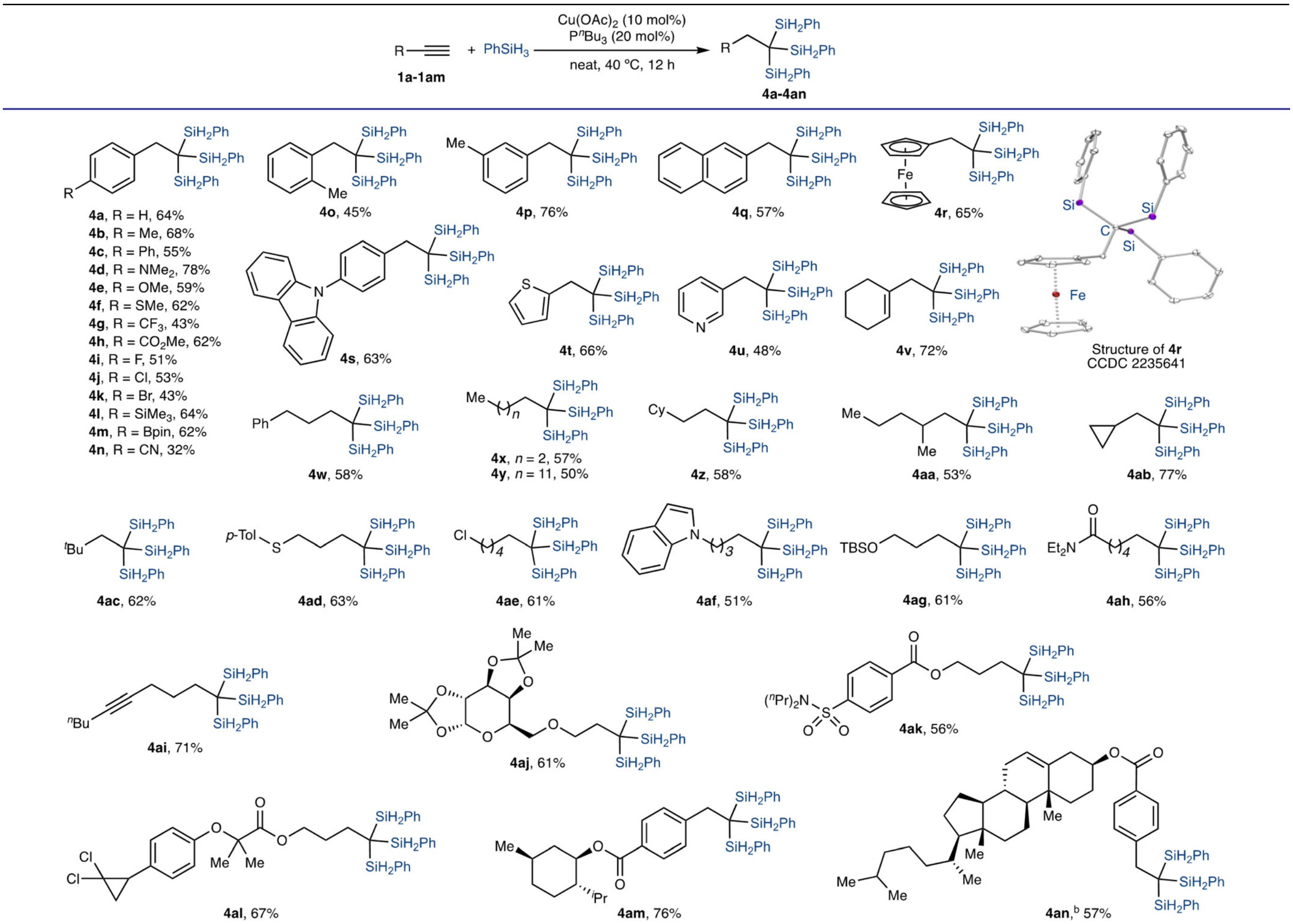


[a] Reaction conditions: phenylacetylene **1a** (0.300 mmol), $PhSiH_3$ (1.20 mmol), $Cu(OAc)_2$ (30.0 μmol), ligand (60.0 μmol for monophosphines and 30.0 μmol for bisphosphines), neat or solvent (0.3 mL) at 40 °C for 12 h; the conversion of **1a**, the yield of **4a**, and the ratios of **2a : 3a : 4a** were determined by GC analysis with tridecane as the internal standard. [b] CuTC = copper(I) thiophene-2-carboxylate. [c] NaOtBu (20 mol%) was used.

bining $Cu(OAc)_2$ and phosphine ligands and activated by their reaction with $PhSiH_3$. In general, the experiments were performed with alkyne **1a** as a limiting reagent in the presence of 4 equivalents of $PhSiH_3$ and 10 mol% copper catalyst at 40 °C. The results of the selected examples of these experiments are summarized in Table 1.

After evaluating various phosphine ligands and solvents, we found that the neat reaction between **1a** and 4 equivalents of $PhSiH_3$ proceeded smoothly in the presence of 10 mol% Cu$(OAc)_2$ and 20 mol% P^nBu_3 and afforded 1,1,1-trisilylalkane **4a** in 76% GC yield with 88% selectivity (entry 1 in Table 1). The reaction with 30 mol% P^nBu_3 showed similar selectivity (entry 2 in Table 1). However, the reaction with 10 mol% P^nBu_3 proceeded with much lower selectivity (entry 3 in Table 1). The steric properties of trialkylphosphine ligands had profound influence on selectivity. For example, the reaction conducted with 20 mol% PCy_3 showed only 12% selectivity toward 1,1,1-trisilylalkane **4a** and the reaction with 20 mol% P^tBu_3 did not generate any detectable amounts of **4a** (entries 4 and 5 in Table 1). When copper catalysts were generated from $Cu(OAc)_2$ and triphenylphosphine PPh_3 or bulky dialkylbiaryl phosphines, such as Johnphos and Ruphos, the reactions proceeded with high conversions of alkyne **1a**, but provided (*E*)-vinylsilane **2a** as the major product (entries 6–8 in Table 1). Similar results were obtained for the reactions conducted with copper catalysts containing bisphosphine ligands, such as xantphos, binap, and dppf (entries 9–11 in Table 1). In addition, we also tested various solvents for this reaction and found that the solvent effect on this trisilylation was noticeable (entries 12–15 in Table 1). The reactions conducted in toluene, acetonitrile, and THF proceeded with decreased chemoselectivity, and the reaction in *N*,*N*-dimethylacetamide (DMA) occurred with a similar selectivity compared to the neat reaction. Furthermore, we also found that copper catalysts generated *in situ* from copper(I) salts, such as CuOAc or CuTC, and P^nBu_3, were similarly active and selective for the copper-catalyzed alkyne trisilylation (entries 16 and 17 in Table 1). However, when the copper(I) complex (iPr)CuCl (10 mol%)

Table 2 Scope of terminal alkynes for $Cu(OAc)_2/P^nBu_3$-catalyzed trisilylation[a]



[a] Reaction conditions: terminal alkyne **1** (0.300 mmol), $PhSiH_3$ (1.20 mmol), $Cu(OAc)_2$ (30.0 μmol), P^nBu_3 (60.0 μmol), 40 °C, 12 h, and yields of the isolated products. [b] Alkyne **1an** (0.100 mmol) was used.

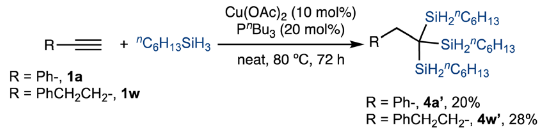
together with NaO^{t}Bu (20 mol%) was used as the catalyst for the trisilylation reaction, the reaction proceeded with a low conversion and did not form a detectable amount of 1,1,1-trisilylalkane product **4a** (entry 18 in Table 1).

Substrate scope of terminal alkynes

With an active copper catalyst in hand and reliable conditions identified for this Cu-catalyzed 1,1,1-trisilylation (entry 1 in Table 1), we explored the scope of terminal alkynes that undergo this trisilylation reaction, and the results are gathered in Table 2. In general, a wide range of aryl- (**1a–1u**), alkenyl- (**1v**), and alkyl-substituted alkynes (**1u–1ai**) reacted smoothly with $PhSiH_3$ in the presence of 10 mol% $Cu(OAc)_2$ and 20 mol% P^nBu_3 to afford the corresponding 1,1,1-trisilylalkanes (**4a–4ai**) in moderate to high isolated yields (up to 78%). Furthermore, several alkynes (**1aj–1an**) derived from commonly used drugs and bioactive molecules also underwent this Cu-catalyzed trisilylation reaction to form 1,1,1-trisilylalkane products (**4aj–4an**) in good yields (56–76%). The structure of 1,1,1-trisilylalkane **4r** was confirmed by single-crystal X-ray diffraction analysis.

This Cu-catalyzed 1,1,1-trisilylation reaction tolerates various reactive groups. For example, alkynes containing sulfide (**4f** and **4ad**), carboxylic ester (**4h** and **4ak–4an**), fluoro (**4i**), chloro (**4j**, **4ae**, and **4al**), bromo (**4k**), silyl (**4l**), pinacol boronic ester (**4m**), cyano (**4n**), siloxy (**4ag**), carboxylic amide (**4ah**), acetal (**4aj**), and sulfonamide (**4ak**) moieties are compatible with the identified reaction conditions. In addition, alkynes containing heterocyclic aromatic groups also reacted with $PhSiH_3$ to provide the desired 1,1,1-trisilylalkanes containing carbazole (**4s**), thiophene (**4t**), pyridine (**4u**), and indole (**4af**) in good yields.

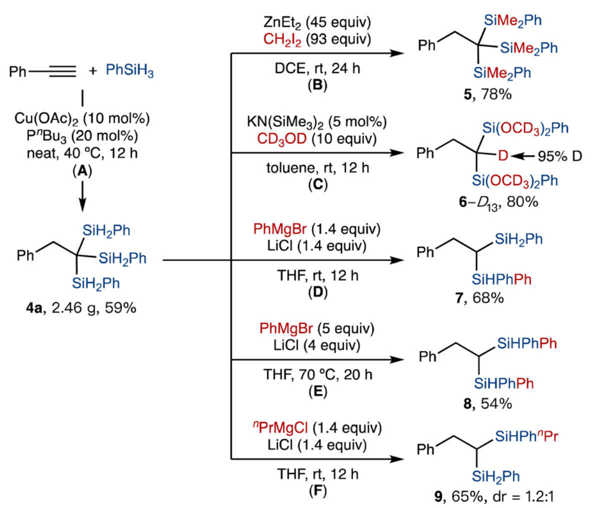
We also conducted the copper-catalyzed 1,1,1-trisilylation of terminal alkyne **1a** and **1w** with $^nC_6H_{13}SiH_3$, an alkyl-substituted hydrosilane. These two reactions proceeded to form the desired 1,1,1-trisilylalkanes **4a′** and **4aw′**, respectively, albeit in low isolated yields (eqn (1)).



(1)

Synthetic utilities

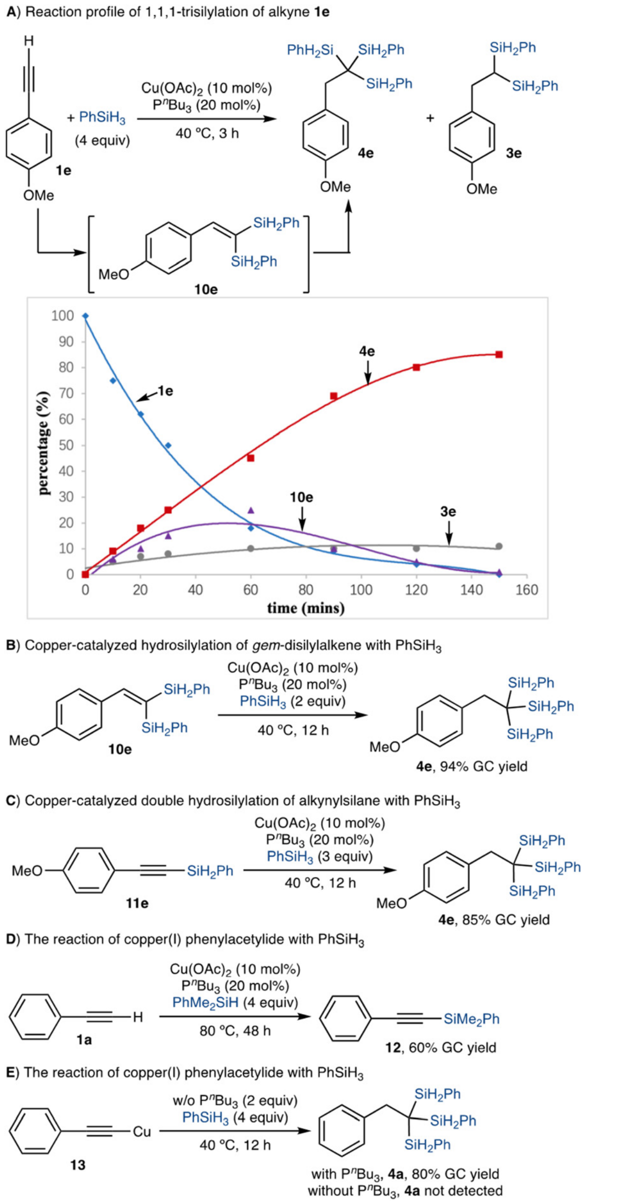
After establishing the scope of this 1,1,1-trisilylation reaction, we subsequently showed the synthetic utility of this protocol (Scheme 2). A gram-scale reaction of phenylacetylene **1a** with $PhSiH_3$ was performed, and this reaction proceeded smoothly under standard conditions to afford 1,1,1-trisilylalkane **4a** (2.46 g) in 59% isolated yield (Scheme 2A). Trisilylalkane products from these trisilylation reactions contain three primary silyl groups and they can be readily converted to other organosilicon compounds. For example, CH_2 carbene formed from CH_2I_2 and Et_2Zn could readily be inserted into all six Si–H bonds of **4a** to produce trisilylalkane **5**, which contains three tertiary silyl groups, in 78% isolated yield (Scheme 2B).[54] Sequential alkoxylation/protodesilylation of **4a** with methanol-D_4 in the presence of KHMDS as a catalyst generated *gem*-disilylalkane **6**-D_{13} in 80% isolated yield (Scheme 2C).[55] Compound **4a** could undergo arylation/desilylation and diarylation/desilylation reactions with a phenyl Grignard reagent to form *gem*-disilylalkanes **7** and **8** in good yields, respectively (Scheme 2D and 2E).[56] The corresponding sequential alkylation/desilylation reaction with *n*-propylmagnesium chloride afforded *gem*-disilylalkane **9** in 65% isolated yield (Scheme 2F).



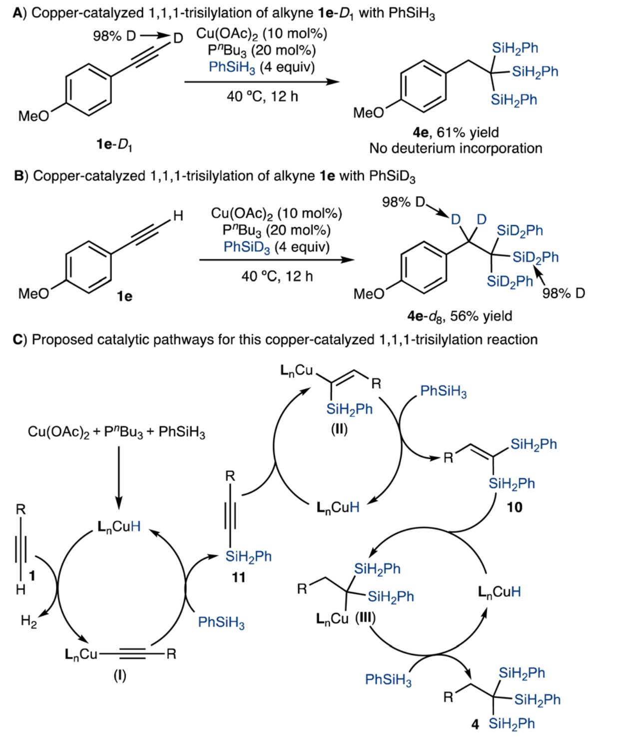
Scheme 2 Gram-scale synthesis of and derivatization of **4a**.

Mechanistic considerations

To get a preliminary understanding of this copper-catalyzed trisilylation process, we monitored the reaction of 4-ethynylanisole **1e** with $PhSiH_3$ with an attempt to identify potential intermediates. The GC-MS analysis of the reaction mixture showed that a significant amount (up to 25% GC yield) of *gem*-disilylalkene **10e** was formed in the early stage of the reaction and then **10e** was fully consumed in the late stage of the reaction (Scheme 3A). To verify the intermediacy of *gem*-disilylalkenes in this trisilylation reaction, we prepared *gem*-disilylalkene **10e** and subjected it to this copper-catalyzed trisilylation reaction. As expected, **10e** was converted to 1,1,1-trisilylalkane **4e** in 94% GC yield (Scheme 3B). In addition, we found that alkynylsilane **11e** reacted with $PhSiH_3$ to afford 1,1,1-trisilylalkane **4e** in 85% yield under standard conditions (Scheme 3C), suggesting that alkynylsilane **11e** is a potential intermediate for the trisilylation reaction of alkyne **1e**. Indeed, the reaction of phenylacetylene **1a** with $PhMe_2SiH$, a bulky hydrosilane, in the presence of $Cu(OAc)_2/P^nBu_3$ stopped at the dehydrogenative silylation stage and afforded alkynylsilane **12** in 60% GC yield (Scheme 3D). Furthermore, we also carried out the stoichiometric reaction between copper(I) phenylacetylide **13** and 4 equivalents of $PhSiH_3$ in the presence of 2 equivalents of P^nBu_3, and this reaction provided trisilylalkane **4a** in 80% GC



Scheme 3 Control experiments and monitoring of 1,1,1-trisilylation of alkyne **1e**.



Scheme 4 Deuterium-labelling experiments and proposed catalytic cycles for this copper-catalyzed 1,1,1-trisilylation of terminal alkynes.

yield (Scheme 3E). However, the corresponding reaction in the absence of P^nBu_3 did not produce any detectable amount of **4a**.

Deuterium-labelling experiments were also carried out on this trisilylation reaction. For example, 4-ethynylanisole **1e**-D_1 reacted with $PhSiH_3$ under standard conditions to afford trisilylalkane **4e** in 61% isolated yield and no deuterium incorporation was detected by ^2H NMR spectroscopic analysis (Scheme 4A). The corresponding reaction between alkyne **1e** and $PhSiD_3$ produced **4e**-D_8 with deuterium atoms located at the benzylic carbon and silicon atoms (Scheme 4B).

Based on the results of the above mechanistic experiments and the precedent for copper-catalyzed hydrosilylation/silylation reactions of terminal alkynes,[44,45] we proposed a plausible catalytic pathway for this copper-catalyzed 1,1,1-trisilylation reaction, as depicted in Scheme 4C. The activation of $Cu(OAc)_2$ with $PhSiH_3$ in the presence of P^nBu_3 (**L**) forms a copper hydride species **L**$_n$CuH, which then reacts with an alkyne to form an alkynylcopper intermediate (**I**) with the concomitant release of hydrogen gas, which was detected by GC analysis. σ-Bond metathesis between copper acetylide **I** and $PhSiH_3$ produces alkynylsilane **11** and regenerates **L**$_n$CuH. Hydrocupration of alkynylsilane **11** with **L**$_n$CuH forms an alkenylcopper species (**II**), which then reacts with $PhSiH_3$ to give *gem*-disilylalkene intermediate **10**. Subsequently, hydrocupration of *gem*-disilylalkene **10** with **L**$_n$CuH generates an alkylcopper intermediate (**III**), which then reacts with $PhSiH_3$ to afford 1,1,1-trisilylalkanes **4**. Based on the reaction profile of the trisilylation of terminal alkyne **1e** (Scheme 3A), accumulation of *gem*-disilylalkene **10e** was observed, which suggests that the hydrosilylation of *gem*-disilylalkene **10** to generate 1,1,1-trisilylalkane **4** is the slowest reaction compared to dehydrogenative silylation of alkynes **1** and hydrosilylation of alkynylsilane **11** as shown in Scheme 4C.

Conclusions

In summary, we have developed an effective and practical protocol to access 1,1,1-trisilylalkanes by copper-catalyzed 1,1,1-trisilylation of terminal alkynes with $PhSiH_3$. A series of alkyl-and aryl-substituted alkynes undergo this trisilylation reaction in the presence of $Cu(OAc)_2$ and P^nBu_3. Mechanistic studies reveal that this trisilylation reaction proceeds through a reaction sequence combining copper-catalyzed dehydrogenative hydrosilylation and double hydrosilylation of alkynylsilane intermediates. These 1,1,1-trisilylalkane products can be readily converted to other multi-silylated compounds by manipulating their Si–H bonds. Further development of copper-catalyzed multi-functionalization reactions of unsaturated hydrocarbons and the synthetic application of 1,1,1-trisilylalkanes will be the subject of future studies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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