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Sodium silylsilanolate as a precursor of silylcopper species†

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Silylcoppers function as convenient and effective sources of silicon functional groups. Commonly used precursors for those species have been limited to certain symmetric disilanes and silylboranes. This fact renders the development of silylcopper precursors desirable so that more diverse silyl groups could be efficiently delivered. Here we extend the utility of sodium silylsilanolates as competent precursors of silylcoppers. A silanolate unit operates as an auxiliary to transfer a variety of silyl groups to the copper centre, which was demonstrated in the copper-catalysed hydrosilylation of internal alkynes, α,β -unsaturated ketones, and allenes. Our mechanistic studies through DFT calculation suggested that a copper silylsilanolate undergoes intramolecular oxidative addition of the Si–Si bond to the copper centre to generate a silylcopper, in contrast to the typical formal σ -bond metathesis mechanism for conventional disilanes or silylboranes and copper alkoxides. Accordingly, sodium silylsilanolate has been established as an expeditious precursor of a variety of silylcopper species.

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Introduction

Organosilicon compounds are gathering increased attention in the areas of materials¹ and pharmaceutical sciences.² One of the most versatile reactions for the synthesis of organosilicon compounds is copper-catalysed silylation that is favoured for its high functional group tolerance and the availability of inexpensive copper salts.³ The efficiency of the reaction is critically affected by the choice of the source of the silicon functional group. Early literature on copper-mediated or -catalysed silylation reactions employed silyllithium or silylzinc as silicon sources that normally need to be prepared *in situ*.^{3b,4} Hexaorganodisilanes could also act as the precursor of silylcoppers. These species are used in a limited number of studies, since the reactions require harsh reaction conditions due to the low reactivity for activation of the Si–Si bond through a formal σ -bond metathesis (Fig. 1A(a)).^{3b,5} When disilanes are substituted with multiple heteroatoms in such form as hexaalkoxydisilanes, it is known that silylcoppers are smoothly generated on treatment with copper alkoxide *via* the efficient formation of the silicate intermediate.⁶ This phenomenon originates in the higher Lewis acidity of the silicon centre (Fig. 1A(b)). Meanwhile, such active disilanes and the silylated products are moisture-sensitive and the efforts to utilise these

alkoxydisilanes for copper-catalysed silylation remain rare. Silylboranes have thus been used as popular precursors to silylcopper reagents because of the high efficiency of the formation of active silylcopper species.⁷ It was demonstrated by means of stoichiometric experiments⁸ that the silylcopper species was generated through the reaction between a silylborane and a copper alkoxide with concomitant formation of an

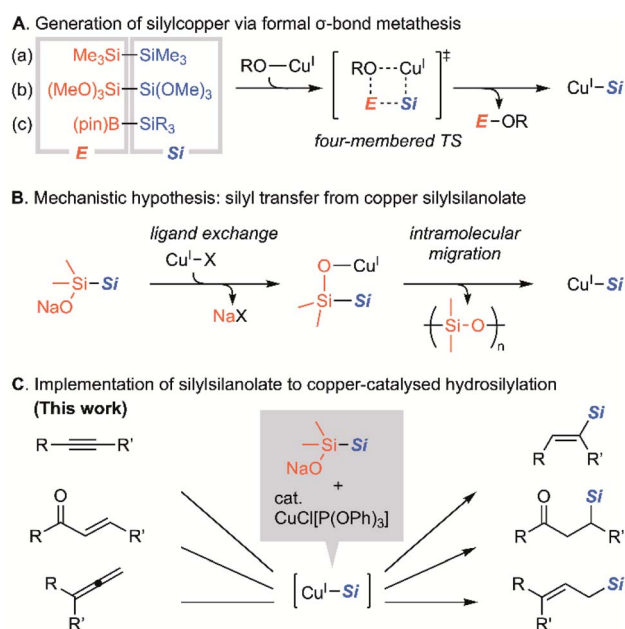


Fig. 1 Overview of the current study.

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alkoxyborane *via* formal σ -bond metathesis (Fig. 1A(c)). Despite the increasing utility of silylboranes by the refined preparative methods,⁹ sensitivity to air/moisture remains to inflict certain limitations.¹⁰ From the viewpoint of the structural diversity of silyl groups and the disadvantageous susceptibility to air and moisture, silicon sources such as hexaalkoxydisilanes or silylboranes leave room for more development. Thus, a new silylating reagent that could be complementarily used with disilanes or silylboranes has been desired as key reagents for versatile silylcupration.

Recently, we developed a new silylating reagent, sodium silylsilanolate, which has a nucleophilic silanolate and one Si-Si bond in the molecular structure. These reagents are chemically stable to air and moisture,¹¹ and could be used in combination with palladium or nickel catalysts for the silylation reactions of aryl halides.¹² The reaction conditions are generally mild and allow the introduction of silyl groups, including *tert*-butyldimethylsilyl and allyldimethylsilyl groups that were not previously applied for coupling reactions using conventional silylating reagents. Remarkably, the reports on transferring the simplest triorganosilyl group, trimethylsilyl group, copper species such as Me_3SiCu or $(\text{Me}_3\text{Si})_2\text{CuLi}$ has relied upon using Me_3SiLi as a precursor,¹³ except for the one report that employs hexamethyldisilane.^{5a} This fact inevitably indicates the absence of a conventional method for delivering a trimethylsilyl group in copper chemistry. These results inspired us to study silylsilanolates as precursors of silylcoppers *via* an unconventional activation mechanism that is distinct from the ones for disilanes or silylboranes (Fig. 1B). We hypothesised that silylsilanolate-coordinated copper(i) formed *in situ* would undergo an activation scheme *via* four-membered transition state, which affords silylcopper(i) with concomitant formation of polysiloxane, a polymer form of the detached silanone species.

Herein, we report our studies on the copper-catalysed hydrosilylation across the unsaturated bonds of internal alkynes, α,β -unsaturated ketones, and allenes. With the aid of DFT calculation, our study demonstrates the utility of silylsilanolates as precursors of silylcopper species that function distinctively to the conventional silicon sources (Fig. 1C).

Results and discussion

Initially, we investigated the use of sodium trimethylsilyldimethylsilanolate (**1-Me**) to evaluate silylsilanolate as a precursor of silylcopper through the hydrosilylation of internal triple bond of diphenylacetylene (**2a**) as a benchmark reaction.¹⁴ Extensive screening of reaction conditions revealed that the conditions using 5 mol% of $\text{CuCl}[\text{P}(\text{O}i\text{Pr})_3]$ in DCE (1,2-dichloroethane), 2.0 equiv. *t*BuOH, 50 °C, 12 h were chosen as the standard reaction conditions. Protonation of the intermediary alkenylcopper would generate alkenylsilane **3a** that was obtained in 89% NMR yield (entry 1). In the absence of a copper catalyst or in the presence of a catalytic amount of CuCl with no ligand, no or low conversion of **2a** was observed (entries 2 and 3). Other disilanes ($t\text{BuOMe}_2\text{SiSiMe}_3$, $\text{Me}_3\text{SiSiMe}_3$) in combination with NaOSiMe_3 as a base resulted in no formation of the product, showing the

Table 1 Optimisation of the reaction conditions

Entry	Deviations from the standard conditions	Yield ^a (%)
1	None	89
2	No copper catalyst	0
3	No ligand	11
4	$t\text{BuOMe}_2\text{SiSiMe}_3/\text{NaOSiMe}_3$ instead of 1-Me	0
5	$\text{Me}_3\text{SiSiMe}_3/\text{NaOSiMe}_3$ instead of 1-Me	0
6	5 mol% CuCl + 5 mol% PPh_3	68
7	CuCl(bpy)	84
8	CuCl(dppe)	27
9	CuCl(IPr)	5
10	Toluene	60
11	THF	84
12	CH_3CN	1
13	MeOH instead of <i>t</i> BuOH	86
14	Counteranion: Li	41
15	Counteranion: K	7
16	Reaction time: 16 h	95 (86) ^b

CuCl(IPr)

CuCl(bpy)

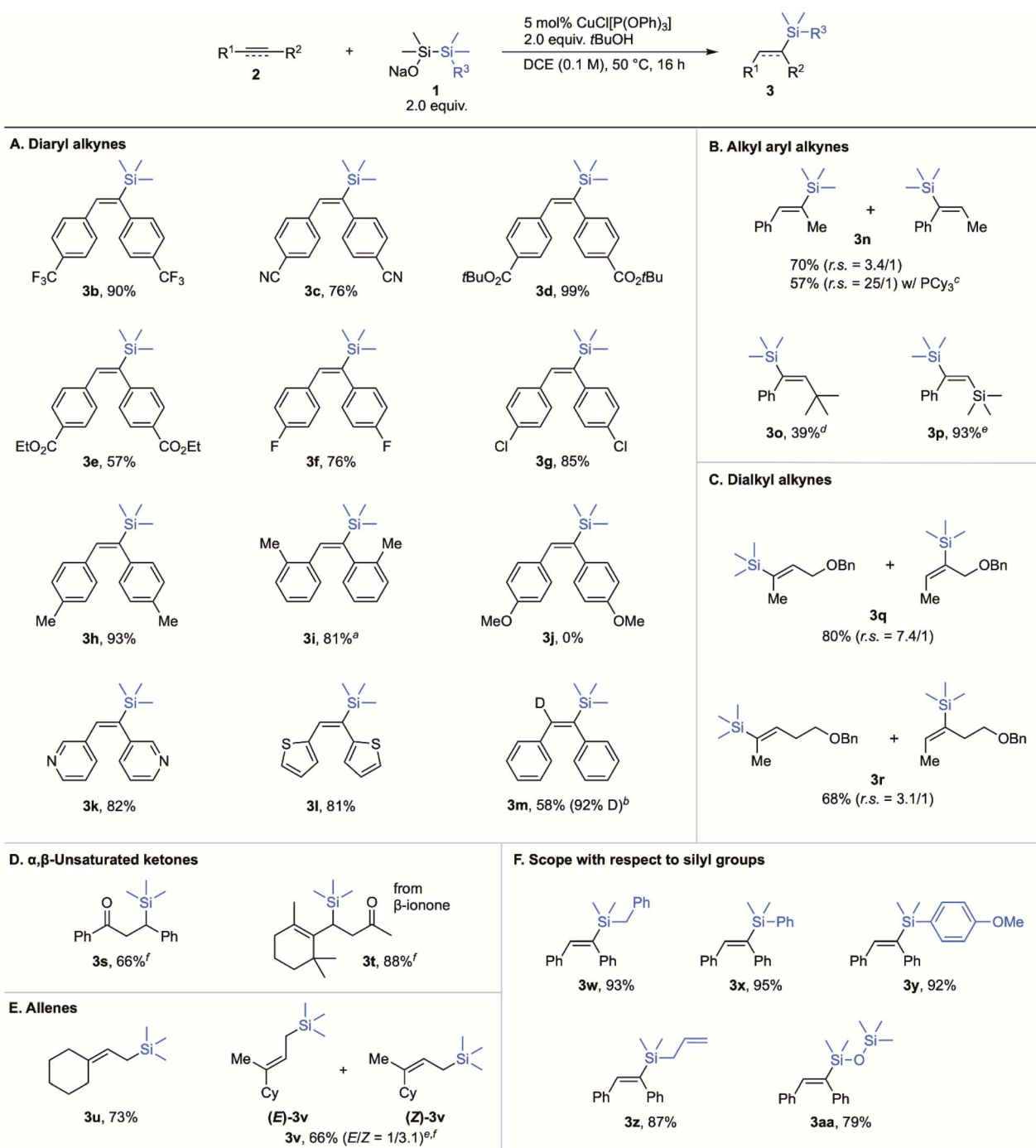
CuCl(dppe)

^a Yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^b Isolated yield (0.50 mmol scale).

importance of the silanolate unit for the reactivity (entries 4 and 5). Regarding the ligands of copper catalysts, slightly lower yields (68% and 84%) were observed with monodentate phosphine ligand, PPh_3 , or 2,2'-bipyridyl (entries 6 and 7). Much lower yields (27% and 5%) were observed with a bidentate phosphine ligand, dppe, or an *N*-heterocyclic carbene ligand, IPr (entries 8 and 9). The reaction in toluene or THF was similarly efficient (60% and 84%) though almost no product was obtained in CH_3CN due to the low conversion (8%) of the substrate (entries 10–12). MeOH showed almost the identical utility with *t*BuOH as a proton source and the desired product was obtained in a slightly lower yield of 86% (entry 13). The use of lithium or potassium trimethylsilyldimethylsilanolate showed much lower efficiency (entries 14 and 15). Finally, extending the reaction time to 16 h forced the reaction to the completion to give the desired product in 95% NMR yield and 86% isolated yield (entry 16). The conditions for entry 16 were set to be optimal for this reaction.

Next, the reaction scope with respect to symmetric diaryl alkynes was surveyed under the optimised reaction conditions (Scheme 1A). The reaction could tolerate various electron-withdrawing groups at *para*-positions on aromatic rings. The substrate with trifluoromethyl or cyano group was transformed





Scheme 1 Scope of hydrosilylation of unsaturated bonds. ^a3.0 equiv. **1-Me** and 3.0 equiv. *t*BuOH were used. ^bCH₃OD was used instead of *t*BuOH. Reaction time: 20 h. ^cConcentration: 0.5 M. 5 mol% [CuCl(PCy₃)₂]. 3.0 equiv. **1-Me** and 3.0 equiv. *t*BuOH were used. ^dTemperature: 80 °C. Concentration: 0.5 M. 10 mol% CuCl[P(OPh)₃] was used. ^eConcentration: 0.5 M. 10 mol% CuCl[P(OPh)₃] was used. ^fReaction time: 12 h.

to **3b** or **3c** in excellent yield. *Tert*-Butoxycarbonyl group was compatible under the reaction conditions to give **3d** while ethoxycarbonyl group seemed to be partially hydrolysed and **3e** was afforded in 57% yield. Substrates with fluoro and chloro substituents gave the hydrosilylated products (**3f**, **3g**) in 76% and 85% respective yields. In the case of methyl groups as substituents, both *p*-tolyl and *o*-tolyl substrates gave the products **3h** and **3i** in good yields. For the sterically hindered *o*-tolyl

product **3i**, increased amounts of silylsilanolate and *t*BuOH were needed. In the case of *p*-methoxy substrate, no hydrosilylated product **3j** was observed while recovering the substrate in 85% yield. Heteroaryl-substituted acetylenes were also successfully transformed into the corresponding alkenylsilanes in good yields (**3k**, **3l**). When CH₃OD was used in place of *t*BuOH for the hydrosilylation of **2a**, the corresponding deuterated alkenylsilane **3m** was obtained in 58% yield with 92%



deuterium incorporation. This result indicates that alkenylcopper generated *in situ* is protonated by alcohols. The scope of alkyl aryl acetylenes is shown in Scheme 1B.

1-Phenyl-1-propyne (**2n**) was converted to the desired alkenylsilane **3n** in good yield, but with low regioselectivity (r.s. = 3.4 : 1). In this case, PCy_3 instead of P(OPh)_3 improved the regioselectivity up to r.s. = 25 : 1. 1-Phenyl-2-*tert*-butylacetylene (**2o**) showed low conversion and provided **3o** only in 39% yield even at higher temperature. **3o** was obtained selectively as a single isomer, probably due to the steric hindrance of the *tert*-butyl group that drives the incoming silyl group away to the distal position. The substrate bearing bulky trimethylsilyl group **2p** also gave a sole regioisomer, and **3p** was obtained in excellent yield (93%). The difference of the yield between **3o** and **3p** could be ascribed to the fact that the intermediate alkenylcopper for **3p** is thermodynamically stabilised by the presence of the adjacent silicon–carbon bond.¹⁵ Dialkyl alkynes are also applicable and hydrosilylated products **3q**, **3r** were obtained in good yields with moderate to low regioselectivity (Scheme 1C). The regioselectivity is seemingly affected by the intramolecular coordination of the ether moiety to the silyl-copper intermediate, which would direct the copper atom to the proximal position of the triple bond. Ethynylbenzene was found unreactive and no hydrosilylated product was obtained. This result indicates that terminal alkyne substrate is not compatible. It is noteworthy that the current copper-catalysed hydrosilylation could also be applied to α,β -unsaturated ketones^{4c,5a,16} and allenes¹⁷ which are known to be good substrates for these reactions (Scheme 1D and 1E).^{3b} Chalcone (**2s**) and β -ionone (**2t**) were amenable to the optimised reaction conditions, affording the products of conjugate silylation **3s** and **3t** in 66% and 88% respective yields.¹⁸ Symmetric terminal allene **2u** provided the corresponding allylsilane **3u** in good yield. Terminal allene **2v** was also converted to allylsilane **3v** as a mixture of *E* and *Z* isomers (*E/Z* = 1/3.1). We believe that this stereoselectivity is due to the steric hindrance around the bulkier cyclohexyl group that propels the silylcopper to the opposite face. Aldehydes¹⁹ and imines²⁰ are known as good substrates in copper-catalysed silylation reactions in the presence of silylborane. However, in the current reaction system, benzaldehyde and *N*-tosylbenzethanimine afforded no desired products since these substrates are not compatible with silylsilanolate reagents.

Sodium silylsilanolates were also confirmed to be viable for the introduction of other silyl groups (Scheme 1F). Alkenylsilane **3w** substituted with benzyldimethylsilyl group was obtained from the corresponding silylsilanolate **1-Bn** in 93% yield. For aryl dimethylsilyl groups, both phenyl- and anisyl-substituted alkenylsilanes **3x**, **3y** were obtained in excellent 95% and 92% yields regardless of the electronic property of the aryl groups. Allyl-substituted silylsilanolate **1-allyl** enabled the transfer of the allyldimethylsilyl group and gave **3z** in 87% yield. Delivery of the siloxysilyl group with silylsilanolate **1-OSiMe₃** afforded the corresponding adduct **3aa** in 79% yield. Among these silyl groups, this study represents the first case of introducing anisyl dimethylsilyl and dimethyl(trimethylsiloxy)silyl groups through copper-catalysed silylation reactions. These results demonstrate that silylsilanolates represent important

substitutes for the conventional silylating reagents that mediate copper-catalysed silylation reactions.

A possible overall reaction mechanism for the hydrosilylation of diphenylacetylene (**2a**) is shown in Fig. 2A. Initially, copper(i) silylsilanolate **4** would be generated by the reaction between copper(i) chloride and sodium silylsilanolate **1**. Copper(i) silylsilanolate **4** would provide silylcopper **5** accompanied by the generation of polysiloxane. Silylcopper **5** would undergo silylcupration across **2a** to afford alkenylcopper **6**. Keeping in mind that the pK_a of silanol is generally smaller than that of alcohol,²¹ *t*BuOH would be the only protic species in the reaction mixture. Thus, the protonation of **6** with *t*BuOH would give CuOtBu (**8**) with the formation of alkenylsilane **7**. Finally, the ligand exchange of **8** with sodium silylsilanolate **1** would furnish NaOtBu with the regeneration of **4**. DFT calculations revealed that the sum of free energies of copper(i) silylsilanolate **4** and NaOtBu is almost the same as that of CuOtBu and sodium silylsilanolate **1** ($\Delta G = 0.57 \text{ kcal mol}^{-1}$, see ESI†). These data support the potential equilibrium of ligand exchange between the silanolate and the alkoxide on the copper atom.

To figure out the mechanism of the migration of the silyl groups of silylsilanolates to the copper atom, DFT calculations were carried out. Given that the optimised copper catalyst CuCl [P(OPh)_3] is known to form a cluster that could complicate the calculation,²² 2,2'-bipyridyl, the second-best ligand in the hydrosilylation reaction, was employed to model the calculation. Since disilanes were believed to undergo σ -bond metathesis *via* four-membered transition state as in Fig. 1A,^{5e} one possible pathway to form silylcopper could be the reaction between CuOtBu generated *in situ* and sodium silylsilanolate, which would furnish silylcopper through the σ -bond metathesis between the Si–Si bond of silylsilanolate and the Cu–O bond of CuOtBu, without going through silylsilanolate-coordinated copper(i) like **4** in Fig. 2A. From the fact that hexamethyldisilane and monoalkoxydisilane without anionic silanolate unit did not give any product (Table 1, entries 4,5), the formal σ -bond metathesis mechanism seems unlikely. Our extensive effort on DFT calculation toward locating the transition state for such a pathway led only to a futile result. Next, copper complex **INT-1** coordinated with silylsilanolate like **4** was chosen as a starting point of the calculated pathway. The pathway for the migration of the silyl group directly from **INT-1** to afford silylcopper was initially examined (Fig. 2B). The pathway from **INT-1** to **INT-A3** was found to be endergonic because of the thermodynamically unfavourable generation of a dimethylsilanone. Thus, we calculated the migration pathway in the presence of activators.

In our previous report, the pathway for the migration of the silyl group to the palladium atom was calculated through the activation by sodium trimethylsilanolate dimer **9** that was modelled as a simplified form of sodium silylsilanolate dimer.^{12a} Based on this result, the energy profile of the migration pathway with the aid of **9** was calculated. The result is summarised in Fig. 2C. The complexation of **INT-1** with **9** was found to be exergonic to provide **INT-B2**. Oxidative addition of the Si–Si bond to the copper atom in **INT-B2** affords **INT-B3** *via* **TS-B1** that bears the elongated Si–Si bond (2.55 Å).²³ This is



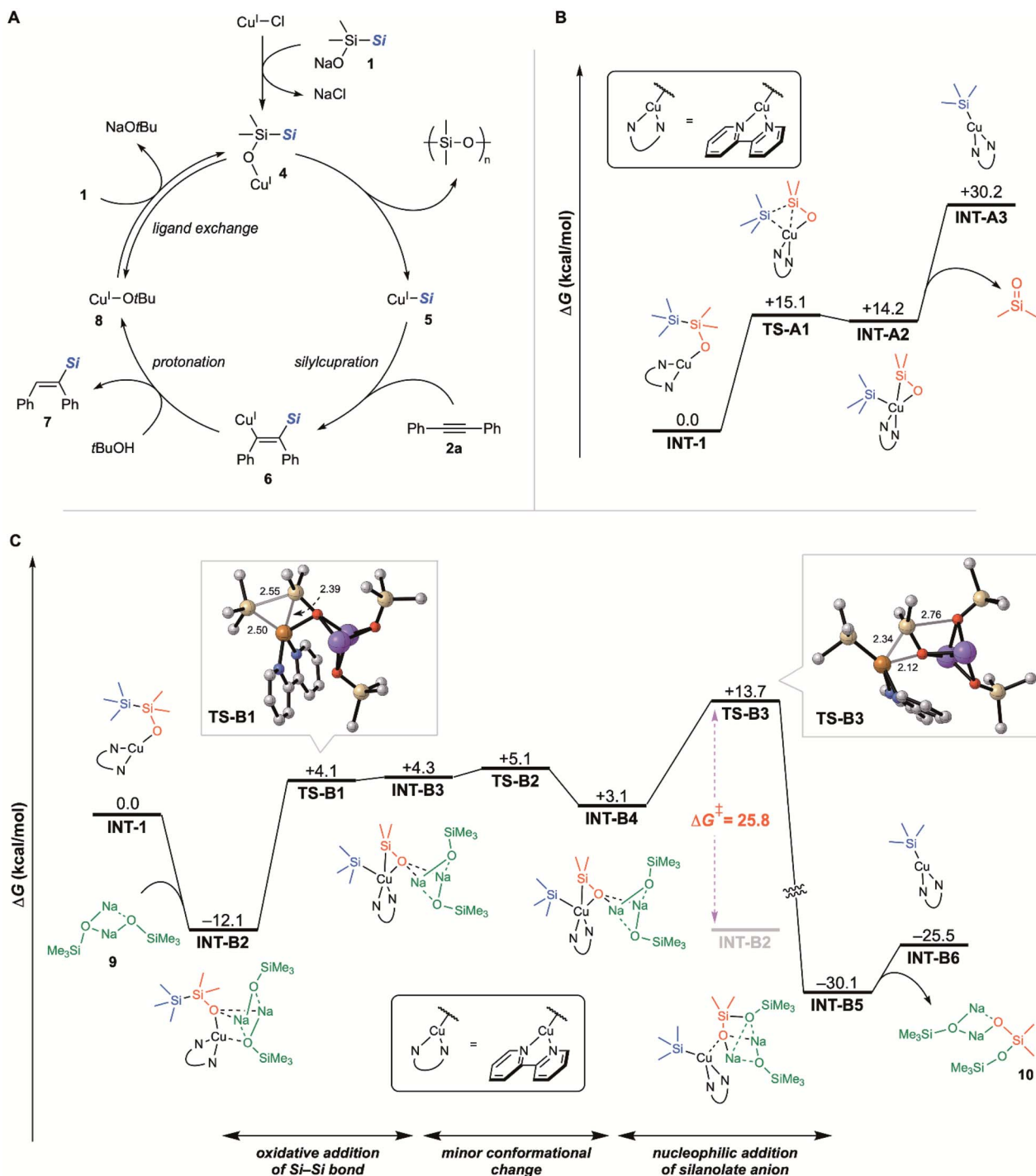


Fig. 2 (A) Possible reaction mechanism. (B) Energy profile for migration of silyl group of silylsilanolate to copper atom directly from INT-1 at the ω B97X-D/def2-TZVP/SMD (DCE)//B3LYP-D3BJ/def2-SVP level of theory at 323.15 K. (C) Energy profile for migration of silyl group of silylsilanolate to copper atom from copper silylsilanolate with the assistance of sodium trimethylsilanolate dimer 9 at the ω B97X-D/def2-TZVP/SMD (DCE)//B3LYP-D3BJ/def2-SVP level of theory at 323.15 K. Bond lengths are given in ångström [Å].

followed by a minor conformational change to provide INT-B4 via TS-B2. The intramolecular attack of trimethylsilanolate (green) to the silicon atom (red) via TS-B3 (Si-O = 2.76 Å) provides INT-B5 through sufficiently low activation barrier ($\Delta G^\ddagger = 25.8$ kcal mol⁻¹). Finally, dissociation of a silanolate bearing disiloxane moiety 10 from INT-B5 affords INT-B6. This

calculation results show that the formation of the Cu-Si bond proceeds via oxidative addition of the Si-Si bond to the copper atom. The presence of the Si-Si bond in the vicinity of the copper atom in INT-B2 may kinetically promote oxidative addition of the Si-Si bond. To the best of our knowledge, this is the first example of an indication that silylcopper could be



generated through oxidative addition.²⁴ Compared with the pathway to silylcopper without any activation shown in Fig. 2B, the pathway with the assistance of the sodium trimethylsilanolate dimer **9** is found to be overall exergonic probably due to the formation of a thermodynamically stable disiloxane **10** instead of the formation of a silanone. Mass spectroscopic analysis of the finished reaction mixture shows molecular weight distribution that fitted with the Gaussian distribution with interval of 74 mass units corresponding to the repeat unit of polydimethylsiloxane, dimethylsilanone (see ESI†). This result indicates the formation of dimethylsilanone surrogates such as **10** that is assumed in our DFT calculations. It was also found that the migration process of the silyl group could proceed using NaOtBu dimer as an activator instead of **9** with a little higher activation barrier ($\Delta G^\ddagger = 28.4 \text{ kcal mol}^{-1}$, see ESI†). This result indicates that the NaOtBu generated *in situ* could also be involved in the migration pathway of silyl groups as an activator.

Conclusions

We revealed that sodium silylsilanolates function as precursors to silylcopper species in the presence of an appropriate copper catalyst. Through the demonstrations of hydrosilylation that was applied for alkynes, α,β -unsaturated ketones, and allenes, facile *in situ* generation of reactive silylcopper species was corroborated. The reaction allows the delivery of a series of silyl groups by the choice of the silylsilanolate reagent. DFT calculations unveiled the possible reaction mechanism for the formation of the silylcopper from copper(i) silylsilanolates, which proceeds through an unprecedented pathway *via* oxidative addition of the Si–Si bond to the copper(i) centre. We believe the present study would propose a new versatile approach for the generation of silylcopper species.

Data availability

Data for all compounds in this manuscript are available in the ESI† which includes experimental details, characterisation data and copies of ¹H, ¹³C and ²⁹Si NMR spectra.

Author contributions

J. S. and H. Ya. conceived the project. J. S. and H. Yo. directed the research. H. Ya. and K. H. performed the experiments. H. Ya. conducted the DFT calculations. H. Ya. and J. S. composed the manuscript and the ESI† section. All authors contributed to the editing.

Conflicts of interest

There are no conflicts to declare.

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