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Metal-Free, Stereospecific Bis-Silylation of Functionalized Alkynes with NHC-Supported Silylaminosilylene

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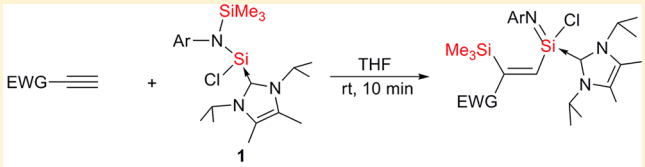
Supporting Information

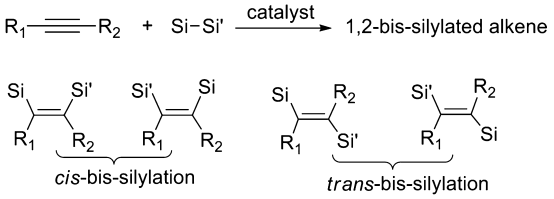
ABSTRACT: The NHC-supported silylaminosilylene Ar-($SiMe_3$)N(Cl)Si(I*i*Pr) (**1**; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, I*i*Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is an efficient and stereospecific bis-silylation reagent for a range of functionalized alkynes to yield cis-1,2-bis-silylated alkenes via a 1,4-silyl migration from the amino nitrogen atom to an alkyne carbon atom. The reaction is regio- and stereospecific for terminal alkynes with an electron-withdrawing substituent, thus providing a facile access to 1,2-bis-silylated alkenes with two different silyl groups.



EWG = CO_2Me; pyridine; CO_2Me, CN, NO_2, Cl and CF_3 substituted phenyl groups
Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Vinylsilanes are important alkene derivatives that have been widely used as synthetic intermediates, monomers for copolymer plastics, and coupling agents for hybrid silicon-containing materials.[1] Therefore, the development of efficient and selective silicon reagents for the synthesis of vinylsilanes is of great interest. Transition-metal-catalyzed hydrosilylation and bis-silylation of alkynes represent the most straightforward and atom-economic routes to vinylsilanes.[2] 1,2-Disilylated alkenes, stable alkene dianion equivalents,[3] have been obtained by catalytic addition of a Si−Si bond across a C−C triple bond (Scheme 1). Since the original reports by Kumada and Sakurai

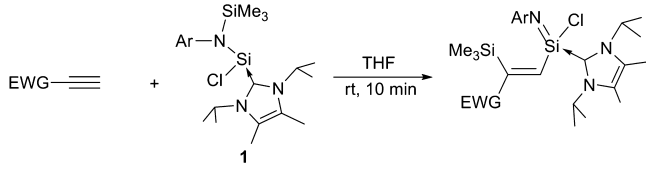
Scheme 1. Group 10 Metal Catalyzed Bis-Silylation of Alkynes with Disilanes as Bis-Silylation Reagents and the Possible Four Isomers



on palladium-catalyzed bis-silylation of alkynes with disilanes,[4] stereoselective bis-disilylation catalyzed by group 10 metal complexes in combination with suitable ligands has been extensively investigated.[5] Despite the successes in the intramolecular variants, the selective intermolecular reactions have been mostly achieved by employments of cyclic disilanes as bis-silylation reagents. The catalytic intermolecular reaction of unsymmetrical alkynes with disilanes featuring two different silicon atoms has met very limited success, due to the difficulty in controlling the stereo- and regioisomers (Scheme 1) and their separation. Thus, the development of highly selective bis-silylation reagents is still highly desirable.

Reactions of silylenes with alkynes present an alternative approach for the silylation of alkynes without the aid of transition-metal catalysts.[6] However, previous studies have been only confined to a few alkynes without functional groups as models for an understanding of the fundamental chemistry of silylenes.[7] No efforts have been devoted to the employment of silylenes for the silylation of functionalized alkynes because of the extremely high reactivity of silylenes toward various functional groups that may result in the formation of a complicated mixture. Herein we report on the bis-silylation of alkynes featuring diverse functional groups with the easily available NHC-stabilized silylaminosilylene Ar($SiMe_3$)N(Cl)Si-(I*i*Pr) (**1**; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, I*i*Pr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene)[8] under metal-free conditions (Scheme 2). Remarkably, the bis-silylation reaction has been accomplished in a stereospecific manner via a 1,4-silyl migration from the silylamino nitrogen atom to one of the alkyne central carbon atoms, representing the first successful approach for the selective bis-silylation of alkynes with a donor-supported silylene as the silylation reagent. In addition, the reaction is

Scheme 2. Stereo- and Regioselective Bis-Silylation of Terminal Alkynes with 1 as the Silylation Reagent under Metal-Free Conditions



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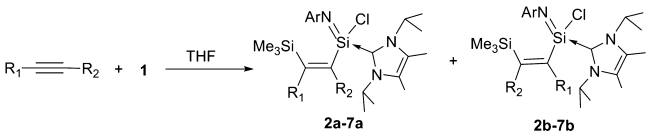
regiospecific for terminal alkynes with an electron-withdrawing group (Scheme 2).

Very recently we and others reported the dehydrochlorination of chlorosilanes by N-heterocyclic carbenes (NHCs) for the generation of N-heterocyclic silylenes and NHC-stabilized silylenes.[9] We have shown that an NHC-stabilized cyclic (silole) silylene is highly nucleophilic and could generate an alkenyl anion intermediate upon treatment with phenylacetylene.[10] In order to have an insight into the mechanism of this type of reaction, the NHC-stabilized aminochlorosilylene **1** was employed for the reaction. Stirring a mixture of **1** with phenylacetylene in THF led to a rapid color change from light green to yellow. The proton NMR analysis indicated the formation of the two products **2a,b** in high yield with a **2a**/**2b** molar ratio of 1.3/1 (Table 1). They have been separated by

Table 1. Bis-Silylation of Internal Alkynes[a]



entry	R_1	R_2	time	regioisomers (a:b); yield[b] (%)
1	C_6H_5	H	10 min	**2a**/**2b** = 1/1.3; 74 (65)
2	C_6H_5	C_6H_5	4 h	**3a** = **3b**; 100 (71)
3	CO_2Me	CO_2Me	10 min	**4a** = **4b**; 100 (74)
4	CO_2Me	Me	10 min	**5a**/**5b** = 2.3/1; 71[c]
5	C_6H_5	Me	6 h	**6a**/**6b** = 1.8/1; 70[c]
6	CO_2Me	C_6H_5	10 min	**7a**; 100 (78)

[a]Reaction conditions: in THF, room temperature. [b]NMR yield, isolated yields given in parentheses. [c]NMR yield of the mixtures.

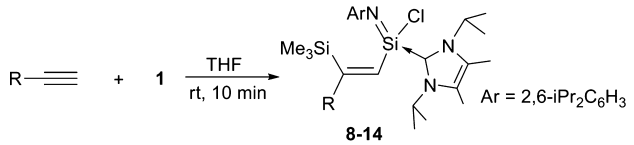
extraction with *n*-hexane. The multinuclear NMR spectroscopic and X-ray single crystal analysis (see Figures S7 and S8 in the Supporting Information) of **2a,b** disclosed the formation of the two cis-bis-silylated alkenes. The results prompted us to investigate the reaction mechanism and the scopes and limitations of the reaction with various alkynes, as the reaction is not only mechanistically novel but is also promising for stereospecific bis-silylation of alkynes under mild conditions in the absence of metal catalysts.

For simplicity, we first examined three symmetrical alkynes with phenyl, $SiMe_3$, and MeO_2C groups. It was found, by proton NMR analysis, that phenyl- and MeO_2C-substituted alkynes reacted smoothly with **1** in C_6D_6 at room temperature to give cis-bis-silylated alkenes **3** and **4** (Table 1) in quantitative yield, while the Me_3Si-substituted alkyne did not react with **1** under the same conditions, probably due to steric reasons. **3** and **4** have been fully characterized by multinuclear NMR spectroscopy and elemental analysis. The structure of **3** was confirmed by X-ray single-crystal analysis (Figure S9 in the Supporting Information). Heating of **4** in C_6D_6 at 70 °C yielded the corresponding bis-silylated maleic anhydride with the elimination of dimethyl ether, indicating the cis-bis-silylated structure of **4**. These reactions suggested that **1** is a cis-bis-silylation reagent for alkynes.

Next, several unsymmetrical internal alkynes were employed for the investigation of the steric and electronic factors of the substituents of alkynes on the reaction. It was found that the alkynes with an ester group significantly accelerated the reaction (entries 3, 4, and 6 in Table 1). The reactions of ester-substituted internal alkynes with **1** are complete in 10 min, while those of the other alkynes complete in several hours. In addition, dialkyl-substituted alkynes led to very slow and sluggish reactions. For $MeO_2CC{\equiv}CMe$ (entry 4) and $PhC{\equiv}CMe$ (entry 5), regioisomeric mixtures were obtained and could not be easily separated. It is noteworthy that the reaction of $MeO_2CC{\equiv}CPh$ (entry 6) only gave one isomer, **7a**, in high yield, indicating that it is possible to control the regioselectivity of the bis-silylation reaction by regulation of the electronic and steric factors of the alkyne substituents.

Since the reaction of the terminal alkyne $PhC{\equiv}CH$ with **1** is rapid, terminal alkynes with an electron-withdrawing group would be ideal choices for the probe of the electronic factors of alkyne substituents. Thus, the reactions of terminal alkynes substituted by MeO_2C and a series of substituted-phenyl groups with an electron-withdrawing group including C(O)R, CO_2Me, CN, NO_2, Cl, and CF_3 groups with **1** have been studied. Surprisingly, these reactions, in general, are complete in 10 min and gave only one isomer in good to quantitative yields on the basis of proton NMR analysis of the crude products (Table 2), with the exception of carbonyl-substituted alkynes, which led to the formation of a complicated mixture that could not be characterized.

Table 2. Stereo- and Regiospecific Bis-Silylation of Terminal Alkynes[a]



entry	R	product	yield[b] (%)
7	CO_2Me	**8**	100 (90)
8	*o*-pyridine	**9**	80 (50)
9	*p*-CO_2Me-C_6H_4	**10**	100 (76)
10	*p*-CN-C_6H_4	**11**	100 (79)
11	*p*-NO_2-C_6H_4	**12**	100 (62)
12	*p*-Cl-C_6H_4	**13**	76 (65)
13	*p*-CF_3-C_6H_4	**14**	100 (79)

[a]Reaction conditions: in THF, 10 min, room temperature. [b]NMR yield, isolated yield given in parentheses.

The bis-silylated products **7a** and **8**−**14** have been fully characterized by multinuclear NMR spectroscopy, IR spectroscopy, and elemental analysis. The structures of **7a**, **8**, and **9** were confirmed by X-ray single-crystal analysis (see Figures S10−S12 in the Supporting Information). The structures of **10**, **11**, **13**, and **14** were determined by ^1H and ^{13}C NMR and ^{13}C HMBC (heteronuclear multiple bond correlation) experiments, from which it can be seen that the substituted phenyl group is on the same vinyl carbon atom as the Me_3Si group (see Figures S1−S4 in the Supporting Information). Compound **12** is not stable and decomposed in solution within 1 h.

The novel stereoselective bis-silylation reaction apparently results from the 1,4-$SiMe_3$ migration from the nitrogen atom of the amino ligand to one of the central alkyne carbon atoms. The NHC-stabilized silylene **1** can be represented by two resonance forms, as depicted in Scheme 3. Owing to the highly nucleophilic nature of the silicon center of **1**, it tends to attack the polarized alkynes to afford the zwitteranionic species **A**, in which the carbanion may interact with the $SiMe_3$ group to form the five-membered-ring intermediate or transition state **B** with a hypervalent silicon atom followed by complete cleavage of the

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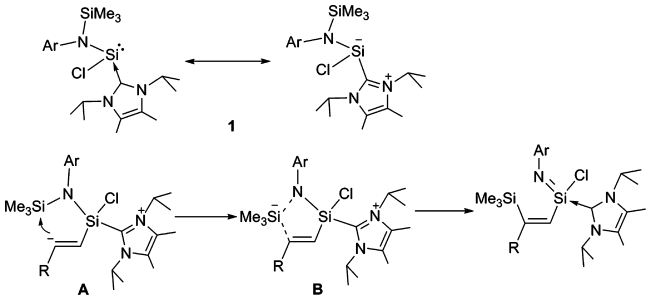
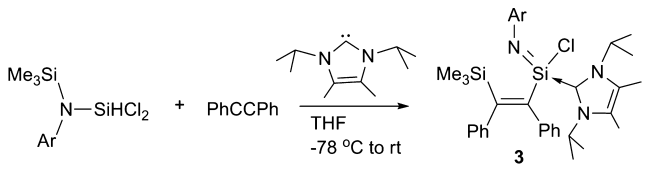
Scheme 3. Proposed 1,4-Silyl Migration Mechanism for the Selective Bis-Silylation



N−Si bond and formation of a Si−C bond to give the bis-silylated alkenes (Scheme 3). The proposed mechanism is in line with the observed stereo- and regioselectivity in this work. Apparently, the existence of an electron-withdrawing group on the terminal alkynes facilitates the attack of the highly polarized alkynes by **1** and stabilizes the intermediate **A**. The exclusive formation of cis-bis-silylated alkenes is due to the favorable five-membered silicate intermediate or transition state **B**. Silyl migration, such as silyl migration from a carbon to an oxygen atom (Brook rearrangement), is a ubiquitous process in the chemical reactions of organosilanes. However, silyl migration from a nitrogen to a carbon atom has been rarely investigated.[11] Because the Lewis acidic site of the silylene **1** is blocked by the coordinated NHC, it is not easily attacked by other Lewis basic groups and is thus chemoselective.

Since the NHC-supported silylene **1** has been obtained by the dehydrochlorination of $Ar(SiMe_3)NSiHCl_2$ with 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene in THF,[8a] it is possible that the bis-silylation reaction could be carried out in one pot without the isolation of the NHC-stabilized silylene **1**. As a representative example, addition of a THF solution of PhCCPh to a mixture of the silane $Ar(SiMe_3)NSiHCl_2$ and diphenylacetylene in THF from −78 °C to room temperature indeed resulted in the formation of **3**. The bis-silylated product **3** has been isolated in ca. 47% yield after workup (Scheme 4). It

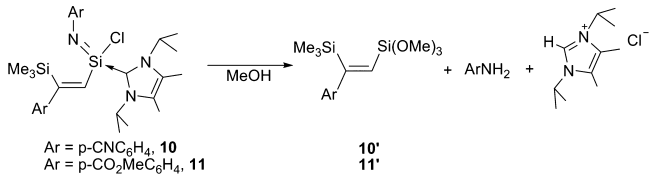
Scheme 4. Representive Example of Bis-Silylation of an Alkyne in One Pot



can be concluded that the bis-silylation reaction proceeded via the initial formation of **1**. This process is more practical than that of the direct employment of **1** as the silylation reagent. However, the almost quantitative reaction of activated alkynes with **1** as the silylation reagent greatly simplifies the workup process.

All of the resulting bis-silylated alkenes feature a reactive silicon center that contains a coordinated NHC, a formal Si═N double bond, and one chloride ligand. The NHC-stabilized silaimines (Si═N double bond) have been previously reported by us.[8b] We thought that it would be possible to convert this silyl group into a simple activated group that may be used for further transformation such as cross-coupling reactions[12] and to recover the N-heterocyclic carbene. It is envisioned that the alcoholysis of these products might be an ideal choice for these purposes, as it could generate an activated carbon−$Si(OR)_3$ unit by the cleavage of the Si═N and Si−Cl bonds and transform the NHC to the corresponding imidazolium salt simultaneously. Indeed, dissolving **10** and **11** in MeOH at room temperature led to a complete conversion of the NHC-coordinated silyl group to the $Si(OMe)_3$ group with the formation of the imidazolium salt, which can be easily separated by filtration (Scheme 5). The trimethoxylsilyl-substituted

Scheme 5. Alcoholysis of 10 and 11 for the Recovery of the NHC



alkenes **10′** and **11′** can be purified by distillation and have been characterized by standard spectroscopic methods. The sequence of reactions with these disilylated alkenes might be invaluable in synthesis.

In summary, we have developed a metal-free route for the stereo- and regiospecific bis-silylation of typical functionalized terminal alkynes with the NHC-stabilized silylaminosilylene **1** as the silylation reagent. The silylation reaction is tolerant to a range of functional groups, demonstrating that NHC-stabilized silylenes have unique reaction patterns. In addition, the reaction can be carried out in one pot without the isolation of **1** and the resulting products can be easily converted to simple trimethoxylsilyl-substituted alkenes featuring the activated C−Si bond by alcoholysis with an excess of MeOH, thus providing a practical route for the bis-silylation of activated alkynes for the preparation of cis-disilylated alkenes with two different silyl groups. The bis-silylation reaction is mechanistically distinct from known catalytic bis-silylation, in which noble-metal catalysts should be employed for the activation of a Si−Si bond. Since NHC-stabilized silylaminosilylenes are easily available, they are potentially promising metal-free bis-silylation reagents for various unsaturated substrates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving details of the synthesis and characterization data for the compounds reported in this paper and CIF files giving crystallographic data for compounds **2a**,**b**, **3**, **7a**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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