Silylation Reactions

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Direct *Syn* Addition of Two Silicon Atoms to a C$\equiv$C Triple Bond by Si–Si Bond Activation: Access to Reactive Disilylated Olefins

Maha Ahmad, Annie-Claude Gaumont, Muriel Durandetti, and Jacques Maddaluno**

Abstract: *A catalytic intramolecular silapalladation of alkynes affords, in good yields and stereoselectively, syn-disilylated heterocycles of different chemical structure and size. When applied to silylethers, this reaction leads to vinylic silanols that undergo a rhodium-catalyzed addition to activated olefins, providing the oxa-Heck or oxa-Michael products, depending on the reaction conditions.*

Silicon is a fascinating element to organic chemists, and is a kind of "big brother" of carbon but with very different character. These two Group 14 elements share fundamental properties; for instance, a strong tendency to establish four covalent bonds, but differ also in crucial characteristics, such as covalent radius or electronegativity. When introduced into organic molecules, silicon transforms the chemical and physicochemical characteristics and adds unique properties to the resulting structure. In particular, a carbon–silicon swap increases the chemical diversity in drug design[1] since it alters both the physiological and biological properties of usual active principles.[2] Beyond pharmacy,[3a–d] fragrances that include silicon atoms have recently been synthesized and evaluated.[3e–f] In the field of materials science, the heat-resistance, light-stability, and light-transparency often displayed by organosilicon materials make them attractive targets.[4] All these applications infer that simple accesses to original silylated synthons through reliable and cheap methods are sought. Recently, many silylation procedures have appeared that give access to new organosilicon building blocks.[5] Among those, the attractive vinylsilanes[6] are available by methods such as hydrosilylation,[7] Heck coupling,[8] or "soft" silylmetalations (zincation,[9] boration,[10] or stannation[11]).

Within this context, molecules juxtaposing two vicinal silicon atoms with different functionalities can become particularly advanced substrates.[12] Preparing such compounds by a "silyl-silylation" of alkynes is appealing since the two silicon atoms would be delivered synchronously and, possibly, in a stereocontrolled fashion. The relatively weak Si–Si bond (ca. 54 kcal mol^{-1})[13] suggests that disilanes can be an appropriate source of silicon and precedents in the literature hint that a metal-induced dissociation is conceivable. However, except in a few particular cases, only one silicon is usually transferred.[14] A first exception was evidenced by Sakurai et al. who showed, in 1975, that a strained cyclic disilane reacts with three activated alkynes to provide disilyla-cycloheptenes (Figure 1 a).[15] Subsequently, Ito and colleagues described a palladium-catalyzed intramolecular *syn* bis-silylation of the triple bond of activated propargylic oxydisilanes, furnishing tetrasubstituted (*Z*)-olefins (Figure 1 b).[16] Very recently, Matsuda and Ichioka have observed an intramolecular Rh$^{\text{I}}$-catalyzed transformation of aryldisilanes into silylbenzosilanes (Figure 1 c).[17] Intriguingly, the authors showed that when rhodium is replaced by palladium, the reaction derails and affords a fused four-member sila heterocycle (benzosiletane). In a footnote, they also mention that the "*trans* bis-silylation failed to occur when the tether link was increased by one carbon", limiting the scope of the method. Worthy of note is the result reported recently by Stratakis and colleagues, who have shown that gold nanoparticles supported on metal oxides activate the Si–Si bond. This process, which applies to terminal alkynes only, leads to *Z*-isomers, which gradually isomerize into the corresponding *E*-isomers under the reaction conditions.[18]

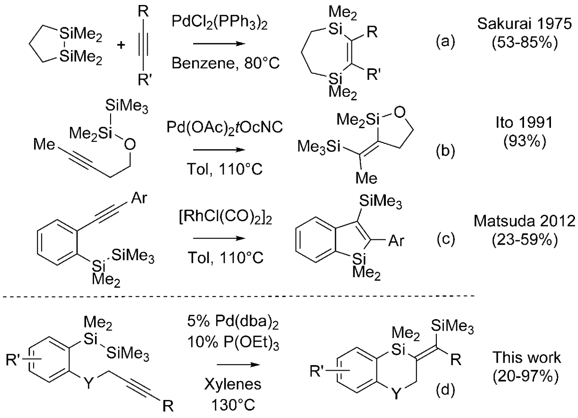

Figure 1. Inter- and intramolecular metallo-catalyzed disilylation of alkynes.

These promising results, while restricted to specific cases, highlight the potential synthetic value of fragmentation of the Si–Si bond of non-activated disilanes. Herein, we show that the palladium-catalyzed activation of the Si–Si bond suffices to trigger a direct intramolecular disilylation of alkynes,

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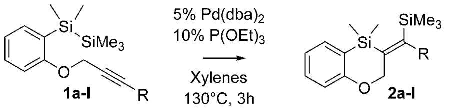
providing straightforward access to a large set of *syn*-disilylated olefins.

Inspired by Matsuda's works, we prepared substrate **1a** in 92% yield from the known *o*-disylanylphenol[19] and 1-bromobut-2-yne. Our study began using Ito's catalytic conditions, based on the Pd-*t*OcNC system that afforded the expected disilylated product **2a** with 35% conversion after 24 h at reflux in toluene. Optimizing[20] the source of Pd^0, the ligand, the solvent, and the temperature, led to a remarkably simple system (5% Pd(dba)$_2$ + 10% P(OEt)$_3$), which was able to perform this same transformation with a high 97% isolated yield—even in relatively harsh conditions (3 h at reflux in xylene, Figure 1d).

With this tool in hand, we first examined its sensitivity to the alkyne terminal substituent. Results in Table 1 show that the cyclization takes place in good yields and with total stereo- and regioselectivities, except for the terminal alkyne **1b** that gives a 9:1 mixture of *Z*/*E* isomers (isomerization occurring during column purification). Alkyl-, aryl-, heteroaryl, or alkynes substituted with a haloaryl group are tolerated, (Table 1, entries 4 and 5). Thio-substituted alkyne **1g** transforms efficiently into the matching enol thioether (Table 1, entry 7). The germanylated alkyne **1h** reacts well and affords disilylated-germanylated olefin **2h** exclusively while its trimethylsilyl analogue **1i** gives trisilylated olefin **2i**, albeit with poor conversion (Table 1, entries 8 and 9). Note that the diphenylphosphine substituted alkyne **1j** and chloroalkyne **1k** did not deliver any identifiable product (Table 1, entries 10 and 11). Finally, diyne **1l** was easily converted into the unusual tetrasilylated conjugated diene **2l**.

Table 1: Intramolecular disilylation of alkynes. Influence of the alkyne terminal substituent.[a]



1a-l → **2a-l**

Entry	R	Product	Yield [%][b]
1	Me (**1a**)	**2a**	97
2	H (**1b**)	**2b**	72[c]
3	Ph (**1c**)	**2c**	88
4	4-F-C$_6$H$_4$ (**1d**)	**2d**	93
5	4-Cl-C$_6$H$_4$ (**1e**)	**2e**	53
6	3-Pyr (**1f**)	**2f**	86
7	SMe (**1g**)	**2g**	84
8	GeMe$_3$ (**1h**)	**2h**	74
9	SiMe$_3$ (**1i**)	**2i**	20
10	PPh$_2$ (**1j**)	**2j**	-[d]
11	Cl (**1k**)	**2k**	-[d]
12	diyne (**1l**)	**2l**	84[e]

[a] Typical procedure: aryl disilane **1a–k** (0.5 mmol), Pd(dba)$_2$ (0.025 mmol), P(OEt)$_3$ (0.05 mmol), xylenes (4 mL) under argon at 130°C for 3 h. [b] Isolated yields, based on aryl disilane. All products gave satisfactory analytical data. [c] $Z/E = 9{:}1$ after purification. [d] Degradation. [e] See product **2l** in Figure 2.

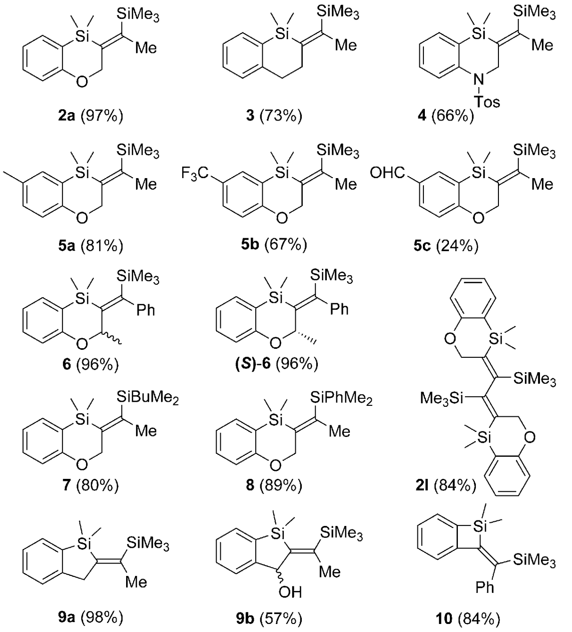
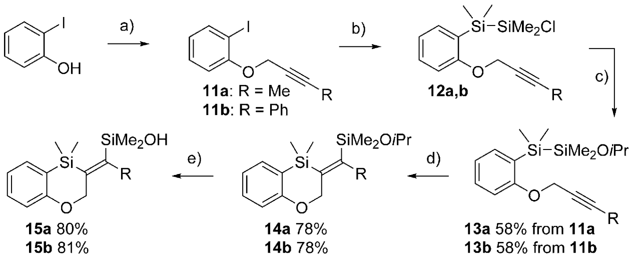


Figure 2. Generalization of the intramolecular disilylation of alkynes.

Other substitution patterns have also been studied (Figure 2). First, the tether linking the aryl to the triple bond was revealed to be properly flexible; the sila tetrahydronaphthalene **3** and quinoline **4** were obtained in the same experimental conditions, from the corresponding all-carbon and nitrogenated alkynes. Electron-donating and -accepting groups on the aromatic ring were tolerated, as shown by the *meta* (to silicon) methyl (**5a**: 81%) or trifluoromethyl (**5b**: 67%) substituents. A free aldehyde is also fully compatible with the cyclization, even if it seems to interfere with the catalytic process and decelerates the reaction (**5c**: 24% after 24 h, 100% based on starting material recovery).[21] A substituent on the propargylic position is equally compatible with the silapalladation process, as shown in the case of **6**, which was recovered in excellent yield. This reaction is respectful of a propargylic asymmetric center, as demonstrated using the chiral non-racemic substrate (*ee* > 99%), leading to (*S*)-**6** with a similarly high *ee*. Varying the trimethylsilyl group has little impact: an alkyl, aryl, or alkoxy substituent (see **13** and **14**, Scheme 1) were introduced on the terminal silicon with a minor effect on the yield. Finally, if the tether cannot be lengthened[22] it can be shortened, as shown in the case of compounds **9** and **10**. Thus, benzosiloles are within reach of this method—even



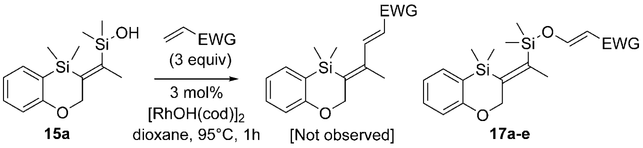
Scheme 1. Synthesis of silanols **15**. Reaction conditions: a) Ref [23]; b) *n*BuLi (R = Me) or *n*BuMgBr (R = Ph) then ClSiMe$_2$-SiMe$_2$Cl; c) *i*PrOH, DMAP, imidazole; d) Pd(OAc)$_2$, PCy$_3$, xylenes, 130°C; e) acetate buffer (pH 5.0), MeCN, 50°C.

when the propargylic position is functionalized (**9b**). The four-membered benzosiletane **10**, prepared previously by Matsuda, is also obtained in good yield.

To further increase the synthetic potential of these disilylated synthons, we decided to alter the oxidation state of the exocyclic silicon atom and to evaluate the corresponding silanols. With this aim in mind, we prepared the new disilanes monoether **13** through a revised procedure in which *o*-iodophenol is first *O*-propargylated into **11**,[23] reacted with commercially available $ClSiMe_2$-$SiMe_2Cl$ and then treated with isopropanol in basic conditions (Scheme 1). Regrettably, the conditions described above for the cyclization did not apply to this substrate and we had to reoptimize the catalytic system to access **14** in 78% yield.[24] A pH-controlled hydrolysis of **14** ultimately afforded silanols **15** in 80% yield.

To evaluate substrates **15** in non-fluorinated, non-basic conditions,[25] we turned our attention to the rhodium-catalyzed Heck-type coupling of arylsilanediols reported by Mori.[26] Applied to **15**, this reaction was expected to provide attractive new dienes (Table 2). To our surprise, adjusting conditions led instead, and for the first time, to a fully selective oxa-Heck coupling, affording the corresponding silylenol ether (Table 2).

Table 2: Rhodium-catalyzed oxa-Heck reaction with silanol **15a**.

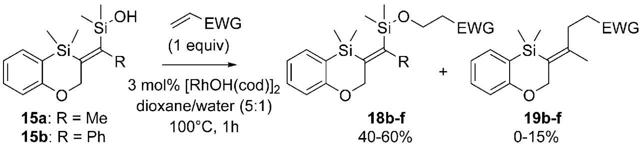


Entry	EWG	Product	Yield [%]
1	CO_2Bu	**17a**	84
2	CO_2Bn	**17b**	76
3	CO_2Ph	**17c**	65
4	$CONMe_2$	**17d**	85
5	CN[b]	**17e**	57
6	COEt	**18a**[c]	57

[a] Electron-withdrawing group (EWG). [b] Reaction run at 70°C for 24 h. [c] See structure of **18** in Scheme 2.

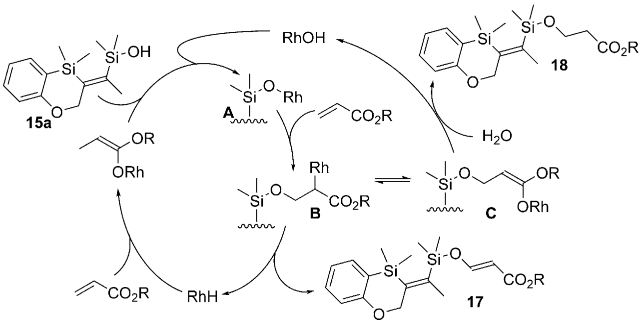
This reaction was successfully extended to more sensitive substrates, such as benzyl or phenyl acrylates, as well as to dimethylacrylamide and acrylonitrile. The yields are decent to good considering the products sensitive functions. Note that the reaction does not work with electron-rich olefins (styrene), or with α- or β-substituted esters such as ethyl methacrylate or crotonate. The particular case of ethyl vinyl ketone also deserves comment since a selective oxa-Michael addition was observed this time, leading to silylether **18** in moderate yield. When it comes to these competing reactions, the diverging behavior of methyl vinyl ketone (or ethyl vinyl ketone) with respect to acrylates has been reported before by Mori[26] and others,[27] and can be understood on the basis of the mechanism proposed below.

This observation suggested that the reaction could be tuned toward an oxa-Heck or oxa-Michael addition by varying the conditions. Inspired again by Mori's work, we were able to favor the reductive conjugate addition by running the reaction in a 5:1 dioxane/water mixture (Scheme 2; Supporting Information, Table S4). The data show that, in these conditions, the reaction is efficient (a conversion of ca. 100%) but not as selective as above. Repeating the reaction with silanol **15b** did not improve the ratios significantly and decreased the reactivity. This drop in selectivity is probably due to water that triggers a competition between the $C(sp^2)$-Si oxidative addition of Rh^I and rhodium alkoxide formation, leading to C−C bond formation through a conjugate addition in the first case (providing **19**) or oxa-Michael product in the second case (providing **18**). In all cases these two additions clearly disfavor oxa-Heck coupling (providing **17**).



Scheme 2. Rhodium-catalyzed oxa-Michael reaction with silanol **15a**.

From a mechanistic point of view, we propose that RhOH first deprotonates **15** to provide rhodium silanolate **A** which adds to the acrylate to afford a σ-alkylrhodium **B** (Scheme 3). At this point **B** can undergo β-elimination of rhodium hydride, leading to the oxa-Heck product **17**. The catalytic cycle continues with the Rh(−1)→Rh(+1) oxidation triggered by a second molecule of acrylate. Alternatively, in the presence of water **B** tautomerizes into the rhodium enolate **C** from which protonation affords the oxa-Michael product **18** and regenerates RhOH.



Scheme 3. Proposed catalytic cycles for the reactivity of **15**.

In conclusion, this paper describes access to original di- and poly-silylated structures. We first report on a catalytic intramolecular silapalladation of alkynes that affords a set of silylated heterocycles in good yields. This transformation adds two silicon atoms on the C≡C triple bond in one single *syn*-selective step. Pushing the investigation further revealed that the resulting vinylic silanols react with activated olefins to provide the oxa-Heck or oxa-Michael products, depending on the reaction conditions. Note that the oxa-Heck sequence converts simple electron-deficient olefins into valuable push–pull building blocks.

Experimental Section

To a solution of aryldisilane **1** (0.5–1 mmol, 1 equiv) in anhydrous xylenes (5 mL) under argon atmosphere was added Pd(dba)$_2$ (0.05 equiv) and triethylphosphite (0.1 equiv). The mixture was stirred for 3 h at 130 °C then hydrolyzed with water. The aqueous layer was extracted with diethyl ether and combined organic layers were washed with brine, dried over anhydrous MgSO$_4$, and concentrated to afford the crude product, which was purified by flash chromatography to give product **2**.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cyclization · disilane · heterocycles · palladium · vinylsilane

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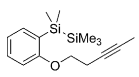
[20] See Tables S1–S2 in the Supporting Information.

[21] The low yield of **5c** is due to the sluggishness of the silapalladation step, since 76% starting material is recovered after 24 h.

[22] Only the starting material is recovered in the case of 1,1,1,2,2-pentamethyl-2-(2-(pent-3-yn-1-yloxy)phenyl)disilane **SI11** (Supporting Information).



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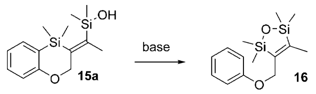
[24] See Table S3 in the Supporting Information.

[25] In basic media, the only product isolated results from a C_{Ar}-Si cleavage and Si—O bond formation, leading, in 60–90% yield, to oxadisilole **16**.



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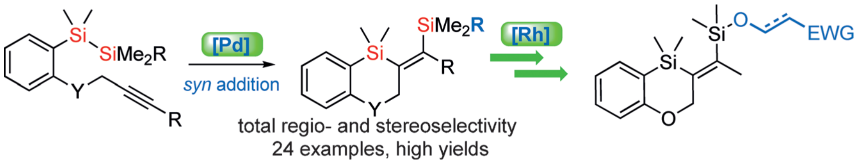
Communications

Silylation Reactions



Disilylated olefins were obtained by a selective Si−Si bond palladium activation followed by intramolecular addition of two silicon atoms to the C≡C triple bond, thereby accessing a family of new silaheterocycles. The reaction affords vinylic silanols that engage in rhodium-catalyzed oxa-Heck or oxa-Michael additions. Tuning of the experimental conditions allows promotion of the preferred addition reaction.