DOI: 10.1002/ange.201200060

Synthetic Methods

Preparation of Allyl and Vinyl Silanes by the Palladium-Catalyzed Silylation of Terminal Olefins: A Silyl-Heck Reaction**

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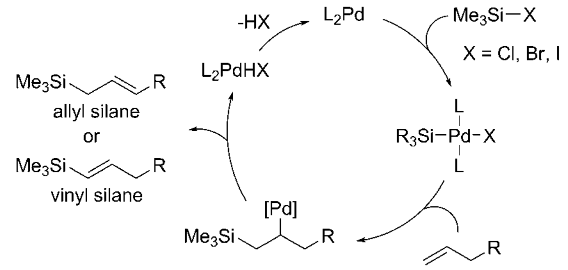
Dedicated to Professor Robert G. Bergman on the occasion of his 70th birthday

Allyl and vinyl silanes are indispensable nucleophiles in organic synthesis.[1] Notable applications include Hiyama cross-coupling reactions[2] and Hosomi-Sakurai-type allylation and crotylation reactions,[3] along with many others.[1c]

Numerous methods are known for the preparation of both allyl and vinyl silanes.[4,5] However, limitations exist with many of the current protocols, which often makes the synthesis of unsaturated organosilanes challenging. For example, many current methods require highly reactive reagents (e.g., the addition of carbon nucleophiles to electrophilic silanes), indirect introduction of the silicon atom through C−C bond-forming reactions (e.g., alkene metathesis, C−C bond-forming cross-coupling reactions, and carbonyl olefination reactions), or reductive processes that decrease the degree of unsaturation of the starting materials (e.g., alkyne hydrosilylation or metal-catalyzed allyl substitution). Notably, methods to directly attach silyl groups to alkenes to produce allyl or vinyl silanes have received little attention.[6–8]

Alkenes are important starting materials in organic synthesis, as they are readily accessed and highly stable. We recognized that oxidative addition of a low-valent transition metal to a silicon halide (Si−X) bond[9] and subsequent insertion into an alkene (analogous to the Heck reaction) could provide a useful route to either allyl or vinyl silanes, depending upon the site of β-hydride elimination (Scheme 1).[10] We anticipated that this reaction manifold would have several advantages. Not only would such a reaction convert simple alkenes into more complex nucleophiles, but it would also allow for the formal conversion of a C−H bond into a C−Si bond. In so doing, this reaction would preserve the degree of unsaturation of the alkene starting material, thereby negating the need for more highly oxidized substrates. Finally, as this is a palladium-catalyzed reaction, it would be expected to proceed under mild conditions and, therefore, be complementary to other routes to these unsaturated organosilanes. Hints in the literature suggest that such a process might be possible,[11,12] but to date, no synthetically viable silyl-Heck reactions of alkenes have been described.



Scheme 1. Putative catalytic pathway for the silyl-Heck reaction.

Herein, we report a high-yielding silyl-Heck reaction for the preparation of allyl and vinyl silanes from alkenes. We have identified *t*BuPPh$_2$ as a uniquely effective ligand for this palladium-catalyzed process. We show that the reaction proceeds at low temperatures (RT to 50 °C) in good to excellent yields and is compatible with a range of substrates. Styrenes and related compounds lead to terminal vinyl silanes, whereas terminal olefins that contain allylic hydrogen atoms preferentially give terminal *E*-allyl silanes. This method enables the conversion of simple alkenes into potent nucleophiles that are capable of reacting with a wide variety of electrophiles, thus, this process allows the facile and selective functionalization of the allylic or vinylic C−H bonds of terminal olefins with a wide array of functional groups.

In 1991, Murai and co-workers reported a three-component coupling of terminal alkynes, iodotrimethylsilane (TMSI), and organostannanes catalyzed by [Pd(PPh$_3$)$_4$].[12] Presumably, this reaction proceeds by a Heck-type mechanism, but the use of alkenes as coupling partners was not described. In the same year, Tanaka and co-workers reported that styrenes give *E*-β-silyl styrenes upon treatment with TMSI and a catalytic amount of [PdCl$_2$(PEt$_3$)$_2$].[11] However, the reported conditions for this reaction require a large excess of alkene (4 equiv), are harsh (120 °C for 72 h in Et$_3$N), and are low yielding (three examples reported: 44–54 % based on TMSI; 11–14 % based on styrene). From this vantage point, it was unclear that a synthetically viable alkene silyl-Heck reaction was possible.

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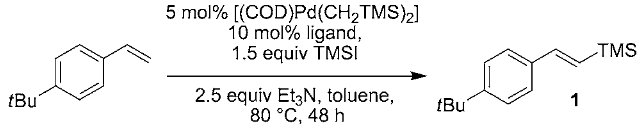
[**] We acknowledge the University of Delaware (UD) for research support and the following sources for fellowships: NIH/NIGMS CBI Program (5T32 GM 08550-16, SESM); David Plastino and the ACS SURF Program (DTA); HHMI Grant 52006947 to the University of Delaware, and the UD NUCLEUS Program (KAJ). Data were acquired on instruments obtained through NSF and NIH funding (NSF MIR 0421224 & CRIF MU CHE0840401, NIH P20 RR017716).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200060.

Our effort to develop such a reaction began by examining the silylation of 4-*tert*-butylstyrene using TMSI. Our initial studies were conducted at 80 °C in toluene with the alkene as the limiting reagent. To systematically evaluate the use of various phosphine ligands, [(COD)Pd(CH$_2$TMS)$_2$][13] (**2**) was selected as the palladium precatalyst.[14] Under these conditions, neither Ph$_3$P nor Et$_3$P (the ligands used by Murai and Tanaka, respectively) provided more than trace yield of the desired silyl styrene **1** (Table 1, entries 1 and 2).[15] Bisphosphines were also ineffective in the reaction (Table 1, entries 3 and 4).

Table 1: Identification of the catalyst for the silyl-Heck reaction.[a]

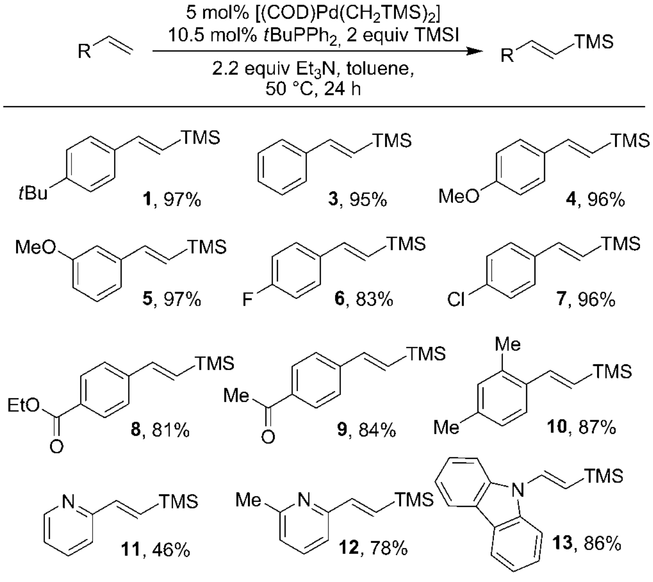


Entry	Ligand	Yield [%][b]	Entry	Ligand	Yield [%][b]
1	Et$_3$P	6	6	Cy$_3$P	4
2	Ph$_3$P	4	7	Cy$_2$PPh	27
3	dppe	0	8	CyPPh$_2$	65
4	dcpe	1	9	*t*BuPPh$_2$	80
5	*t*Bu$_3$P	1	10[c]	*t*BuPPh$_2$	98

[a] Conc. of substrate = 2 M. [b] Determined by GC. [c] 2 equiv TMSI, 2.2 equiv Et$_3$N, tol, conc. = 1 M, 24 h, 50 °C.

From the outset, we suspected that a sterically demanding, electron-rich ligand would be required to effect the desired reaction in high yield. Such ligands have proven effective in a variety of challenging palladium-catalyzed transformations, as they allow the formation of highly reactive, low-valent palladium intermediates, which can aid in both oxidative addition and ligand-exchange processes.[16] Surprisingly, however, neither the use of *t*Bu$_3$P (Tolman Angle, $\theta = 182°$)[17] nor Cy$_3$P ($\theta = 170°$)[17] provided significant amounts of the desired product (Table 1, entries 5 and 6).

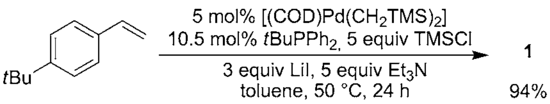
Consideration of the intermediates in the proposed catalytic cycle (Scheme 1) suggested that the reason for the failure of these all-alkyl ligands might be related to the large steric demand of the TMS group. We reasoned that large, electron-rich, all-alkyl ligands, which provide an electronic benefit to the reaction, might sterically disfavor oxidative addition of Pd^0 to the TMS–I bond. To address the apparent dichotomy between steric and electronic factors, we examined ligands that contain both phenyl groups and large alkyl groups. Although these ligands are less commonly used in catalysis, we reasoned that they might be sufficiently electron-donating and large enough to support low-valent palladium complexes, and also provide sufficient space around the resulting Pd^{II} center to accommodate the sterically demanding TMS group. In accordance with this hypothesis, the use of Cy$_2$PPh ($\theta = 161°$)[17] significantly increased the yield of the desired product (27 %, Table 1, entry 7). This result is particularly remarkable given the failure of both Ph$_3$P and Cy$_3$P, which contain only a single type of phosphine substituent. The silyl-Heck reaction was further improved by switching to the slightly smaller CyPPh$_2$ ($\theta = 153°$),[17] which provided **1** in 65 % yield (Table 1, entry 8). Ultimately, *t*BuPPh$_2$ ($\theta = 157°$)[17] proved to be the most effective ligand and provided **1** in 80 % yield under the assay conditions (Table 1, entry 9). After optimization (most significantly by lowering the temperature to 50 °C and decreasing the concentration), vinyl silane **1** was obtained in 98 % yield after 24 h, as assessed by GC (Table 1, entry 10).



Scheme 2. Scope of the silyl-Heck reaction for substrates that lack allylic hydrogen atoms. Conc. of substrate = 1 M. For **8**, **11**, and **12**: [(COD)Pd(CH$_2$TMS)$_2$] (10 mol%), *t*BuPPh$_2$ (21 mol%), solvent = PhCF$_3$. For **9**: [(COD)Pd(CH$_2$TMS)$_2$] (10 mol%), *t*BuPPh$_2$ (21 mol%), solvent = PhCF$_3$, TMSI (4 equiv), Et$_3$N (4.4 equiv), conc. = 0.5 M, after cleavage of the silyl enol ether, 48 h. For **10** and **13**: [(COD)Pd(CH$_2$TMS)$_2$] (10 mol%), *t*BuPPh$_2$ (21 mol%),TMSI (3 equiv) Et$_3$N (3.5 equiv), 48 h.

A wide variety of styrene substrates participate in the silyl-Heck reaction to provide vinyl silanes in high yields (Scheme 2). Under preparative conditions (ca. 1 mmol scale), vinyl silane **1** was isolated in 97 % yield.[18] Unsubstituted styrene was also an excellent substrate and gave a 95 % yield of isolated **3**. Both electron-rich and electron-poor substrates proved viable in the reaction; compounds **4** and **8** were prepared in 96 % and 81 % yield, respectively. The reaction also tolerates functional groups well, with substrates that contain aryl ethers, esters, chlorides, fluorides, and ketones all providing products in high yields.[19] Steric hindrance on the arene of the styrene was also tolerated; compound **10**, which contains a methyl group *ortho* to the alkene, was isolated in 87 % yield. However, substrates that have increased substitution on the alkene, such as in α- or β-methyl styrene, failed to react in the silylation. Although the formation of highly Lewis-basic products, such as pyridine derivative **11**, was possible, the yields in these reactions were diminished. Increased steric demand around the site of the Lewis base, such as in picoline derivative **12**, greatly improved the reaction, which suggests that the low yield for **11** may be a result of ligation of the pyridyl group to the palladium catalyst. Finally, other electron-rich alkenes that lack allylic hydrogen atoms are also viable substrates in the reaction. For example, the use of vinyl carbazole gave rise to silane **13** in 86 % yield. In all cases, only the *E* isomer of the vinyl silane was detected (by ^{1}H NMR spectroscopy and GC). It is worth noting that the reactions are operationally simple to conduct; all preparative reactions were set up by using standard benchtop techniques, and both **2** and *t*BuPPh$_2$ were stored and handled in air.[20]

We were cognizant that TMSI is more expensive than chlorotrimethylsilane (TMSCl) and that a procedure that uses TMSCl would be highly attractive. However, the oxidative addition of transition-metal complexes to Si–Cl bonds is known to be challenging because of the Si–Cl bond strength (ca. 97 kcal mol^{-1} versus ca. 57 kcal mol^{-1} for Si–I).[21] It was not surprising, therefore, that no reaction occurred when TMSCl was used in place of TMSI. However, TMSI can be prepared in situ from TMSCl by using iodide salts.[22] After optimization, we identified LiI as an additive that allows the direct use of TMSCl in the silyl-Heck reaction of styrenes. In most cases, similar yields are obtained by using this procedure relative to the TMSI conditions [Eq. (1)].[23,24]

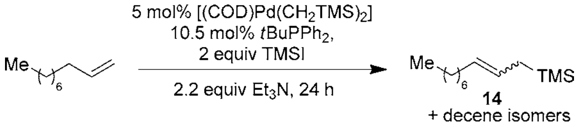


(1)

Having established high-yielding protocols for the silylation of styrenes and related substrates, we turned to terminal alkenes that contain allylic hydrogen atoms. Silyl-Heck reactions to prepare allyl silanes from terminal alkenes have not been reported previously.[25,26]

Our initial investigations focused on 1-decene as a model substrate. Under the optimized reaction conditions for the silylation of styrenes, modest amounts (33 % yield by GC) of silylated products were obtained. These products were almost exclusively allyl silane products **14** in an approximate 85:15 *E*/*Z* ratio (Table 2, entry 1). However, significant amounts of alkene isomers of decene were also obtained (as shown by GC/MS), which indicates nonproductive consumption of the starting material. In an attempt to favor the formation of allyl silanes, we undertook a survey of reaction solvents. Although most solvents, such as dioxane, hexanes, and acetonitrile, gave inferior results relative to toluene (Table 2, entries 2–4), the use of 1,2-dichloroethane (DCE) led to slightly less isomerization of the starting material, but provided a similar yield of the desired product (Table 2, entry 5). Based upon these results, we examined the use of other halogenated solvents. With fluorobenzene, an increased yield of the desired product was obtained (Table 2, entry 6). Lowering the reaction temperature from 50 °C to RT further improved the yield (Table 2, entry 7). Ultimately, we found that α,α,α-trifluorotoluene was most effective (Table 2, entry 8). Using this solvent in the reaction, allyl silane **14** was obtained in 68 % yield after 24 h at RT, with nearly complete consumption of the starting alkene (by GC).[27] Isomerized starting material accounted for the mass balance.

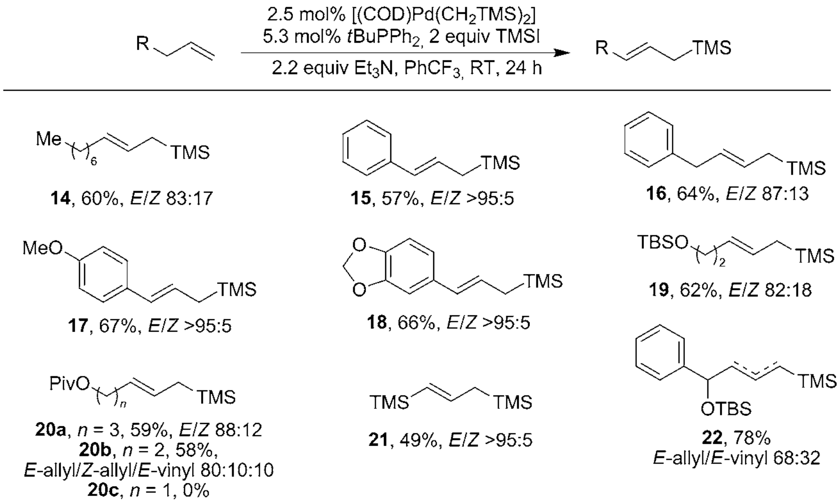
Table 2: Identification of conditions for α-olefin substrates.



Entry	*T* [°C]	Solvent	Conversion [%][a]	Yield [%][a]
1	50	toluene	72	33
2	50	dioxane	34	18
3	50	hexanes	46	20
4	50	MeCN	2	0
5	50	DCE	63	29
6	50	PhF	73	41
7	RT	PhF	80	55
8	RT	PhCF$_3$	93	68

[a] Determined by GC.

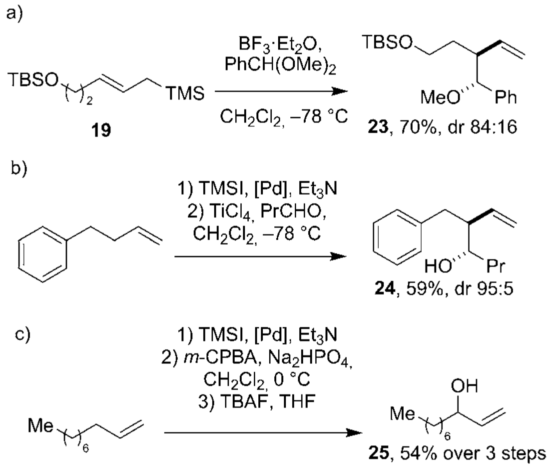
Under preparative conditions, **14** was isolated in 60 % yield as an 83:17 mixture of *E*/*Z* allyl silanes (Scheme 3). The product was readily separable from the isomerized starting material by simple vacuum distillation. These reaction conditions proved applicable to the preparation of other terminal allyl silanes. On a preparative scale (9–15 mmol, ca. 3 g) the catalyst loading could often be lowered to 2.5 mol % palladium without a loss of yield. In general, the selectivity for allyl over vinyl silane was greater than 93:7, and often better than 95:5.[28] For example, allyl silane **15** was isolated in 57 % yield from the reaction with allyl benzene. In this case, high (greater than 95:5) *E*/*Z* selectivity was obtained.



Scheme 3. Substrate scope for formation of allyl silanes. For **14** and **22**: [(COD)Pd(CH$_2$TMS)$_2$] (5 mol %), *t*BuPPh$_2$ (10.5 mol %). For **15**: 35 °C, 48 h. For **20 a, b,** and **c**: [(COD)Pd(CH$_2$TMS)$_2$] (10 mol %), *t*BuPPh$_2$ (21 mol %). For **21**: 50 °C, 48 h, solvent = PhH.

Although the silylation was equally effective with 4-phenylbutene, a small amount (ca. 3%) of the homoallyl silane was also produced in this reaction, likely as a result of isomerization of the alkene of **16** into conjugation with the arene. Ethers were well tolerated in this reaction; silanes **17** and **18** were isolated in 67% and 66% yield, respectively. In the aliphatic series, silyl ethers were compatible with the reaction conditions (for example, **19**). Substrates that contain pivalate-protected alcohols can also be used. Interestingly, the proximity of the pivalate to the alkene had a remarkable effect on the reaction. Whereas **20a** and **20b** were produced in good yields (58–59%), the product derived from 3-buten-1-ol (**20c**) was not obtained (the crude reaction mixture only contained starting material by GC). The origins of this phenomenon are not clear at this point. Notably, allyltrimethylsilane was also an effective substrate for the silylation reaction and gave disilane **21** in 49% yield.[29] Finally, we note that the ratio of allyl to vinyl silane products appears to be dependent upon the degree of substitution at the homoallyl position in the starting material, with increased substitution at this position partially eroding selectivity for the allyl silane; for example, **22** was isolated as an approximate 2:1 mixture of *E*-allyl to *E*-vinyl silanes. Presumably, increased substitution at the homoallylic position disfavors the β-hydride elimination that leads to the allyl product, thereby making the pathway to the vinyl silane more competitive.

We expect the direct silylation of alkenes to find applications in the synthesis of complex organic molecules. To highlight the utility of this process, we have examined the reactivity of the silylated products in a number of previously reported types of reactions. For example, allyl silanes are well known to participate in allyl transfer reactions and proceed with good scope.[1] Treatment of **19** with benzaldehyde dimethylacetal and $BF_3{\cdot}Et_2O$ gave a 70% yield of isolated methyl ether **23** as a 84:16 mixture of diastereomers (Scheme 4a).[3a] As the reactivity of allyl silanes is orthogonal to nonsilylated alkenes, crotylation reactions can often be carried out without purification of the intermediate allyl silane. For example, silylation of 4-phenylbutene and subsequent treatment of the crude product with butyraldehyde and $TiCl_4$ provided a 59% yield of isolated homoallyl alcohol **24** as a 95:5 mixture of diastereomers, based on the starting alkene (Scheme 4b).[3a,30,31] Finally, branched allylic alcohols can be prepared by the oxidation of allyl silanes without purification of the intermediate allyl silane. Silylation of decene and subsequent treatment of the crude product with *m*-chloroperbenzoic acid and then tetrabutylammonium fluoride produced allyl alcohol **25** in 54% overall yield (Scheme 4c).[32] Overall, this method provides a highly flexible route for allylic functionalization, which complements the existing direct allylic functionalization reactions.[33]



Scheme 4. Formal allylic functionalization reactions via allyl silanes. For b): $[(COD)Pd(CH_2TMS)_2]$ (2.5 mol%), tBuPPh$_2$ (5.3 mol%), TMSI (2 equiv), Et_3N (2.2 equiv), solvent = $PhCF_3$, RT, 24 h. For c): $[(COD)Pd(CH_2TMS)_2]$ (5 mol%), tBuPPh$_2$ (10.5 mol%), TMSI (2 equiv), Et_3N (2.2 equiv), solvent = $PhCF_3$, RT, 24 h.

In summary, we have demonstrated a high-yielding protocol for the silyl-Heck reaction of alkenes. Key to this discovery is the identification of tBuPPh$_2$ as a uniquely effective ligand, which we believe is simultaneously large and electron-rich enough to provide a highly active palladium catalyst, yet small enough to accommodate the bulky TMS group. This method allows the direct silylation of monosubstituted alkenes. In the case of substrates that lack allylic hydrogen atoms, such as styrenes, high yields of *E*-vinyl silanes result. Conditions that use TMSI, as well as the less expensive TMSCl, have been developed. Substrates that contain allylic hydrogen atoms are transformed into terminal allyl silanes in good yields and with good levels of *E*/*Z* stereocontrol. When combined with existing methods, the conversion of α-olefins into allyl silanes allows the facile and selective functionalization of the allylic position, which results in a rapid increase of molecular complexity from simple starting materials.

Received: January 4, 2012
Revised: February 6, 2012

Keywords: alkenes · allyl silanes · Heck reaction · palladium · vinyl silanes

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[18] In a 5 gram scale reaction, vinyl silane **1** was isolated in greater than 99% yield.

[19] In the case of ketone **9**, the corresponding silyl enol ether was initially obtained and was subsequently converted to the ketone by using mild acid.

[20] Other palladium precatalysts, such as $Pd(OAc)_2$ and $[Pd_2(dba)_3]$, were not effective in this transformation.

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[25] Allyl silane was observed in the silylation of allylbenzene in the zirconium catalyzed chemistry described in Ref. [6a]. However, this is not a general process; other aliphatic α-olefins gave vinyl silanes.

[26] For a related nucleophilic process that involves silylzincation of alkenes see ref. [5e].

[27] The mechanistic underpinnings for the positive effect of the halogenated solvents are currently being investigated.

[28] See the Supporting Information for the exact quantities of vinyl silanes formed.

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