

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/221882078>

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

ARTICLE *in* ANGEWANDTE CHEMIE INTERNATIONAL EDITION · APRIL 2012

Impact Factor: 11.26 · DOI: 10.1002/anie.201200060 · Source: PubMed

CITATIONS

23

READS

35

5 AUTHORS, INCLUDING:



Jesse R Mcatee

Johnson Matthey, West Detpford, New Jersey

8 PUBLICATIONS 123 CITATIONS

SEE PROFILE



Derek T. Ahneman

Princeton University

4 PUBLICATIONS 108 CITATIONS

SEE PROFILE

Published in final edited form as:

Angew Chem Int Ed Engl. 2012 April 10; 51(15): 3663–3667. doi:10.1002/anie.201200060.

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

Jesse R. McAtee, Sara E. S. Martin, Derek T. Ahneman, Keywan A. Johnson, and Prof. Donald A. Watson

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716 (USA)

Donald A. Watson: dawatson@udel.edu

Abstract

A high-yielding protocol for the palladium-catalyzed silylation of terminal alkenes using silyl halides is reported. This method allows facile conversion of styrenes to *E*- β -silyl styrenes using either TMSI or TMSCl/LiI. Terminal allyl silanes with good *E*:*Z* ratios are also readily accessed from α -olefins by this method. When combined with existing technology, this transformation provides a powerful strategy to selectively functionalize the vinyl or allylic position of terminal alkenes.

Keywords

allyl silane; vinyl silane; Heck reaction

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, often making the synthesis of unsaturated organosilanes challenging. For example, many current methods require highly reactive reagents (i.e., addition of carbon nucleophiles to electrophilic silanes), indirect introduction of the silicon atom through C–C bond-forming reactions (i.e., 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 (i.e., alkyne hydrosilylation and metal-catalyzed allyl substitution). Notably, methods to directly attach silyl groups to alkenes to produce allyl or vinyl silanes have received little attention.^{[6],[7],[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 useful entry into either allyl or vinyl silanes, depending upon the site of β -hydride elimination (Figure 1).^[10] We anticipated this reaction manifold would have

**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); Mr. David Plastino and the ACS SURF Program (DTA); HHMI Grant 52006947 to UD and the UD NUCLEUS Program (KAJ). Data were acquired on instruments obtained via NSF and NIH funding (NSF MIR 0421224 & CRIF MU CHE0840401, NIH P20 RR017716).

Correspondence to: Donald A. Watson, dawatson@udel.edu.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

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 to 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 suggested that such a process might be possible,^{[11],[12]} but to date no synthetically viable silyl-Heck reactions of alkenes have been described.

Herein, we report the first high-yielding silyl-Heck reaction to prepare allyl and vinyl silanes from alkenes. We have identified *t*BuPPh₂ 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; terminal olefins bearing allylic hydrogens preferentially give terminal *E*-allyl silanes. This method enables the conversion of simple alkenes into potent nucleophiles capable of reacting with a wide variety of electrophiles, thus allowing 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 reported a three-component coupling of terminal alkynes, iodotrimethylsilane (TMSI) and organostannanes catalyzed by Pd(PPh₃)₄.^[12] Presumably, this reaction proceeds via a Heck-type mechanism, but the use of alkenes as coupling partners was not described. In the same year, Tanaka reported that styrenes give *E*-β-silyl styrenes upon treatment with TMSI and catalytic PdCl₂(PEt₃)₂.^[11] However, the reported conditions of this latter reaction required a large excess of alkene (4 equiv), were harsh (120 °C, 72 h in Et₃N), and were low yielding (3 examples reported: 44–54% based on TMSI; 11–14% based on styrene). From this vantage, it was unclear that a synthetically viable alkene silyl-Heck reaction was possible.

Our effort to develop such a reaction began by examining the silylation of 4-*tert*-butyl styrene using TMSI. Our initial studies were conducted at 80 °C in toluene using the alkene as the limiting reagent. To systematically evaluate the use of various phosphine ligands, (COD)Pd(CH₂TMS)₂^[13] was selected as the palladium precatalyst.^[14] Under these conditions, neither Ph₃P nor Et₃P (the ligands used by Murai and Tanaka, respectively) provided more than trace yield of desired silyl styrene **1** (Table 1, entries 1–2).^[15] Bisphosphines were also ineffective in the reaction (entries 3–4).

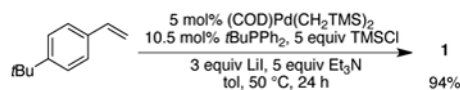
From the outset, we suspected that a sterically demanding, electron-rich ligand would be required to effect the desired reaction in high yield. Such ligands have proven effective in a variety of challenging palladium-catalyzed transformations as they allow the formation of highly reactive, low-valent palladium intermediates, which can aid in both oxidative addition and ligand exchange processes.^[16] Surprisingly, however, neither the use of *t*Bu₃P (Tolman Angle, θ = 182°)^[17] nor Cy₃P (θ = 170°)^[17] provided significant amounts of the desired product (entries 5–6).

Consideration of the intermediates in the proposed catalytic cycle (Figure 1) suggested that the reason for the failure of these all-alkyl ligands might be related to the large steric demand of the trimethylsilyl (TMS) group. We reasoned that large, electron-rich all-alkyl ligands, while providing 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 containing both phenyl groups and large alkyl groups. Although these ligands are less commonly used in catalysis, we reasoned that they might provide sufficient electronic donation and size to support low-valent palladium

complexes, while providing sufficient space around the resulting Pd(II) center to accommodate the sterically demanding TMS group. In accord with this hypothesis, the use of Cy₂PPh ($\theta = 161^\circ$)^[17] significantly increased the yield of the desired product (27%, entry 7). *This result is particularly remarkable given the failure of both Ph₃P and Cy₃P, which contain only a single type of phosphine substituent.* The silyl-Heck reaction was further improved by switching to the slightly smaller CyPPh₂ ($\theta = 153^\circ$)^[17] which provided **1** in 65% yield (entry 8). Ultimately, *t*BuPPh₂ ($\theta = 157^\circ$)^[17] proved to be the most effective ligand to date, providing **1** in 80% yield under the assay conditions (entry 9). After optimization (most significantly by lowering the temperature to 50 °C and decreasing the concentration), vinyl silane **1** was obtained in 98% GC yield after 24 h (entry 10).

A wide variety of styrene substrates participate in the silyl-Heck reaction to provide vinyl silanes in good yield (Table 2). Under preparative conditions (ca. 1 mmol scale), vinyl silane **1** was isolated in 97% yield.^[18] Unsubstituted styrene was also an excellent substrate, giving rise to **3** in 95% isolated yield. Both electron-rich and electron-poor substrates proved viable in the reaction; compounds **4** and **8** could be prepared in 96% and 81% yield, respectively. Good functional group tolerance was also observed, with substrates incorporating aryl ethers, esters, chlorides, fluorides, and ketones all providing products in high yield.^[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 with increased substitution on the alkene, such as in α - or β -methyl styrene, so far have failed to participate in the silylation. Although the formation of highly Lewis basic products, such as pyridine **11**, was possible, yields in these reactions were diminished. Increased steric demand about the Lewis basic site, such as in picoline **12**, greatly improved the reaction, suggesting that the low yield for compound **11** may be due to ligation of the pyridyl group to the palladium catalyst. Finally, other electron-rich alkenes lacking allylic hydrogen atoms also participated 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 observed (¹H NMR and GC). It is worth noting that the reactions are operationally simple to conduct; all preparative reactions were set up using standard bench-top techniques, and both the palladium precatalyst **2** and *t*BuPPh₂ were stored and handled under air.^[20]

We were cognizant that TMSI is more expensive than chlorotrimethylsilane (TMSCl) and that a procedure employing TMSCl would be highly attractive. However, the oxidative addition of transition metal complexes to Si–Cl bonds is known to be challenging due to its bond strength (ca. 97 kcal/mol vs. ca. 57 kcal/mol for Si–I).^[21] It was not surprising, therefore, that no reaction was observed when TMSCl was used in place of TMSI. However, TMSI can be prepared *in situ* from TMSCl using iodide salts.^[22] After optimization, we identified conditions employing LiI as an additive that allow the direct use of TMSCl in the silyl-Heck reaction of styrenes. In most cases, similar yields are obtained using this procedure compared 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 having allylic hydrogen atoms. Silyl-Heck reactions to prepare allyl silanes from terminal alkenes have not been previously reported.^{[25],[26]}

Our initial investigations focused on 1-decene as a model substrate. Under the reaction conditions optimized for the silylation of styrenes, modest amounts (33%, GC) of silylated products were observed. These products were determined to be almost exclusively allyl silane products **14** in an approximate 85:15 *E:Z* ratio (Table 3, entry 1). However, significant amounts of alkene isomers of decene were also observed (GC/MS), indicating non-productive consumption of the starting material. In an attempt to favor formation of allyl silanes, we undertook a survey of reaction solvents. Although most solvents, such as dioxane, hexanes and acetonitrile, provided inferior results compared to toluene (entries 2–4), the use of 1,2-dichloroethane (DCE) led to slightly less isomerization of the starting material, while providing similar yield of the desired product (entry 5). Based upon these observations, we examined the use of other halogenated solvents. With fluorobenzene, increased yield of the desired product was observed (entry 6). Lowering the reaction temperature from 50 °C to RT further improved the yield (entry 7). Ultimately, we found that α,α,α -trifluorotoluene was most effective (entry 8). Using this solvent, allyl silane **14** was observed in 68% yield (GC) after 24 h at RT, with nearly complete consumption of the starting alkene (GC).^[27] Isomerized starting material accounted for the mass balance.

Under preparative conditions, **14** was isolated in 60% yield as an 83:17 mixture of *E:Z* allyl silanes (Table 4). The product was readily separable from isomerized starting material by simple vacuum distillation. These reaction conditions proved applicable to the preparation of other terminal allyl silanes, and on preparative scale (9–15 mmol, ca. 3 g), the catalyst loading could often be lowered to 2.5 mol% palladium without erosion 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 benzene gave rise to allyl silane **15** in 57% isolated yield. In this case, high (>95:5) *E:Z* selectivity was observed. While the silylation was equally effective using 4-phenylbutene, a small amount (ca. 3%) of the homoallyl silane was also observed in this reaction, likely due to 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 (e.g., **19**). Substrates bearing pivalate-protected alcohols could 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 observed (only starting material was observed in the crude reaction mixture by GC). The origins of this phenomenon are not clear at this point. Notably, allyl trimethylsilane was also an effective substrate for the silylation reaction, leading to 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; **22** was isolated as an approximate 2:1 mixture of *E*-allyl to *E*-vinyl silanes. Presumably, increased substitution at the homoallylic position disfavors β -hydride elimination leading 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. In order to highlight the utility of this process, we have examined the reactivity of the silylated products in a number of previously reported reaction types. For example, allyl silanes are well known to participate in allyl transfer reactions and proceed with good scope.^[1] Treatment of allyl silane **19** with benzaldehyde dimethylacetal and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ results in the formation of methyl ether **23** in 70% isolated yield as an 84:16 mixture of diastereomers (Scheme 1).^[3a] As the reactivity of allyl silanes is orthogonal to non-silated alkenes, crotylation reactions can often be carried out without purification of the intermediate allyl silane. For example, silylation of 4-phenylbutene followed by treatment of the crude product with butyraldehyde and TiCl_4 provided homoallyl alcohol **24** in 59%

isolated yield as a 95:5 mixture of diastereomers based on the starting alkene (Scheme 1).^{[3a, 30],[31]} Finally, branched allylic alcohols can be prepared via the oxidation of allyl silanes without purification of the intermediate allyl silane. Silylation of decene followed by treatment of the crude product with *m*-CPBA and then TBAF produced allyl alcohol **25** in 54% overall yield (Scheme 1).^[32] Overall, this method provides a highly flexible route for allylic functionalization, which complements existing direct allylic functionalization reactions.^[33]

In summary, we have demonstrated the first high-yielding protocol for the silyl-Heck reaction of alkenes. Key to this discovery is the identification of *t*BuPPh₂ 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 trimethylsilyl group. The disclosed method allows for the direct silylation of monosubstituted alkenes. In the case of substrates lacking allylic hydrogen atoms, such as styrenes, high yields of *E*-vinyl silanes result. Conditions employing both TMSI, as well as the less expensive TMSCl, have been developed. Substrates bearing allylic hydrogen atoms are transformed to terminal allyl silanes in good yield and with good levels of *E:Z* stereocontrol. When combined with existing methods, the conversion of α -olefins to allyl silanes allows for the facile and selective functionalization of the allylic position, resulting in a rapid increase of molecular complexity from simple starting materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

References

1. a) Brook, MA. Silicon in Organic, Organometallic, and Polymer Chemistry. Wiley; Chichester: 2000. b) Fleming I, Barbero A, Walter D. Chem Rev. 1997; 97:2063–2192. [PubMed: 11848898] c) Fleming, I.; Dunoguès, J.; Smithers, R. Organic Reactions. John Wiley & Sons, Inc; New York: 2004. p. 57-575.
2. a) Nakao Y, Hiyama T. Chem Soc Rev. 2011; 40:4893–4901. [PubMed: 21755089] b) Denmark SE, Liu JHC. Angew Chem Int Ed. 2010; 49:2978–2986.
3. a) Hosomi A, Endo M, Sakurai H. Chem Lett. 1976; 5:941–942. b) Masse CE, Panek JS. Chem Rev. 1995; 95:1293–1316. c) Denmark SE, Fu J. Chem Rev. 2003; 103:2763–2793. [PubMed: 12914480]
4. a) Oshima, K. Science of Synthesis. Fleming, I., editor. Vol. 4. Thieme; Stuttgart: 2001. p. 713-75. b) Sarkar, TK. Science of Synthesis. Fleming, I., editor. Vol. 4. Thieme; Stuttgart: 2001. p. 837-924.
5. For recent advances in the preparation of allyl and vinyl silanes see: Trost BM, Ball ZT. J Am Chem Soc. 2005; 127:17644–17655. [PubMed: 16351094] Ohmiya H, Yorimitsu H, Oshima K. Org Lett. 2006; 8:3093–3096. [PubMed: 16805560] Hayashi S, Hirano K, Yorimitsu H, Oshima K. J Am Chem Soc. 2007; 129:12650–12651. [PubMed: 17902673] Berthon-Gelloz G, Schumers JM, De Bo G, Markó IE. J Org Chem. 2008; 73:4190–4197. [PubMed: 18476744] Nakamura S, Yonehara M, Uchiyama M. Chem Eur J. 2008; 14:1068–1078. [PubMed: 18034443] Murakami K, Yorimitsu H, Oshima K. J Org Chem. 2009; 74:1415–1417. [PubMed: 19108632] Rooke DA, Ferreira EM. J Am Chem Soc. 2010; 132:11926–11928. [PubMed: 20690689] Lim DSW, Anderson EA. Org Lett. 2011; 13:4806–4809. [PubMed: 21838273] For additional references, see the Supporting Information.
6. For reactions involving low-valent zirconium catalysts see: Terao J, Torii K, Saito K, Kambe N, Baba A, Sonoda N. Angew Chem Int Ed. 1998; 37:2653–2656. Terao J, Jin Y, Torii K, Kambe N. Tetrahedron. 2004; 60:1301–1308.
7. For an elegant method for the direct silylation of alkenes using silacyclobutanes see: Hirano K, Yorimitsu H, Oshima K. J Am Chem Soc. 2007; 129:6094–6095. [PubMed: 17441723]

8. For a related silylation of terminal alkenes involving hydrosilylation with sacrificial alkenes see: Marciniak B. *Coord Chem Rev.* 2005; 249:2374–2390. Jiang Y, Blacque O, Fox T, Frech CM, Berke H. *Chem Eur J.* 2009; 15:2121–2128. [PubMed: 19137560] Lu B, Falck J. *J Org Chem.* 2010; 75:1701–1705. [PubMed: 20136153]
9. For studies on oxidative addition of halosilanes to late-metal complexes see: Yamashita H, Hayashi T, Kobayashi T, Tanaka M, Goto M. *J Am Chem Soc.* 1988; 110:4417–4418. Yamashita H, Tanaka M, Goto M. *Organometallics.* 1997; 16:4696–4704. Stöhr F, Sturmayer D, Kickelbick G, Schubert U. *Eur J Inorg Chem.* 2002; 2002:2305–2311. Gatard S, Chen CH, Foxman B, Ozerov O. *Organometallics.* 2008; 27:6257–6263.
10. Migratory insertion may also be reversible in this reaction. See: Tietze LF, Schimpf R. *Angew Chem, Int Ed Engl.* 1994; 33:1089–1091.
11. Yamashita H, Kobayashi T, Hayashi T, Tanaka M. *Chem Lett.* 1991; 20:761–762.
12. a) Chatani N, Amishiro N, Murai S. *J Am Chem Soc.* 1991; 113:7778–7780. b) Chatani N, Amishiro N, Morii T, Yamashita T, Murai S. *J Org Chem.* 1995; 60:1834–1840.
13. Pan Y, Young GB. *J Organomet Chem.* 1999; 577:257–264.
14. This complex readily generates Pd(0) even with sterically demanding phosphines. See: Watson DA, Su M, Teverovskiy G, Zhang Y, Garcia-Fortanet J, Kinzel T, Buchwald SL. *Science.* 2009; 325:1661–1664. [PubMed: 19679769] Sergeev AG, Schulz T, Torborg C, Spannenberg A, Neumann H, Beller M. *Angew Chem Int Ed.* 2009; 48:7595–7599.
15. Pd(PPh₃)₄ and Pd(PEt₃)₂Cl₂ were also ineffective in the reaction under these conditions.
16. a) Littke AF, Dai C, Fu GC. *J Am Chem Soc.* 2000; 122:4020–4028. b) Christmann U, Vilar R. *Angew Chem Int Ed.* 2005; 44:366–374.
17. Tolman CA. *Chem Rev.* 1977; 77:313–348.
18. In a 5 gram scale reaction, vinyl silane **1** was isolated in >99% yield.
19. In the case of ketone **9**, the corresponding silyl enol ether was initially obtained and was subsequently converted to the ketone using mild acid.
20. Other palladium precatalysts, such as Pd(OAc)₂ and Pd₂(dba)₃, were not effective in this transformation.
21. Armitage, DA. *Comprehensive Organometallic Synthesis.* Wilkinson, G.; Stone, FGA.; Abel, EW., editors. Vol. 2. Pergamon; Oxford: 1982. p. 6
22. Olah GA, Narang SC, Gupta BGB, Malhotra R. *J Org Chem.* 1979; 44:1247–1251.
23. See Supporting Information for additional examples and details of reaction optimization.
24. TMSBr and TMSOTf could also be used in the silylation reaction when LiI was employed. In the absence of LiI, both of these reagents gave only trace yields of product.
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 rise to vinyl silanes.
26. For a related nucleophilic process involving silylzincation of alkenes see ref. 5e.
27. The mechanistic underpinnings for the positive effect of the halogenated solvents are currently being investigated.
28. See Supporting Information for exact quantities of vinyl silanes formed.
29. a) Restorp P, Fischer A, Somfai P. *J Am Chem Soc.* 2006; 128:12646–12647. [PubMed: 17002348] b) Nowak A, Bolte O, Schaumann E. *Tetrahedron Lett.* 1998; 39:529–532.
30. Hosomi A, Sakurai H. *Tetrahedron Lett.* 1976; 17:1295–1298.
31. *E* and *Z* isomers of allyl silanes converge to the *erythro* product in TiCl₄ promoted Hosomi-Sakurai reactions. See: Hayashi T, Kabeta K, Hamachi I, Kumada M. *Tetrahedron Lett.* 1983; 24:2865–2868.
32. Fleming I, Lewis JJ. *J Chem Soc, Perkin Trans.* 1992; 1:3267–3275.
33. For recent advances in allylic functionalization see: Lin S, Song CX, Cai GX, Wang WH, Shi ZJ. *J Am Chem Soc.* 2008; 130:12901–12903. [PubMed: 18778061] Campbell AN, White PB, Guzei IA, Stahl SS. *J Am Chem Soc.* 2010; 132:15116–15119. [PubMed: 20929224] Stang EM, White MC. *Angew Chem Int Ed.* 2011; 50:2094–2097. Young AJ, White MC. *Angew Chem Int Ed.* 2011; 50:6824–6827.

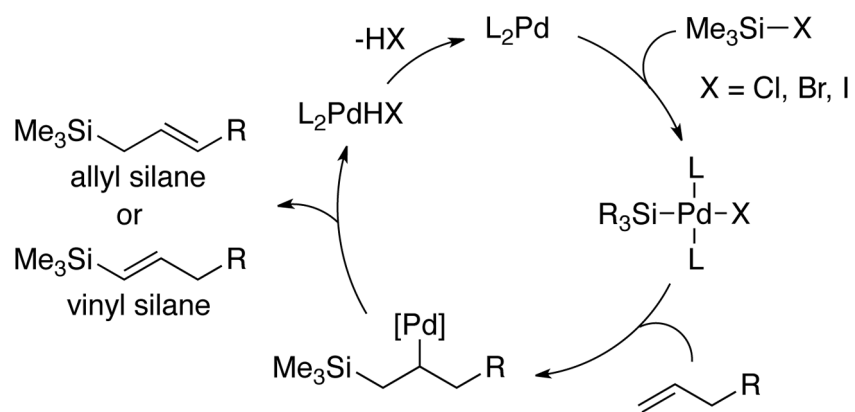
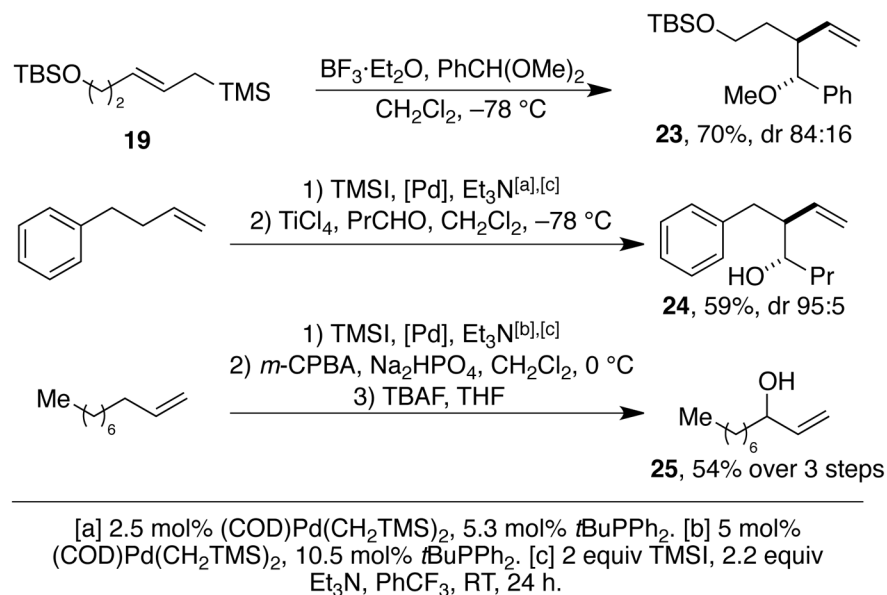


Figure 1.
Putative Catalytic Pathway for the Silyl-Heck Reaction.

**Scheme 1.**

Formal Allylic Functionalization Reactions via Allyl Silanes.

Table 1

Identification of Catalyst for the Silyl-Heck Reaction.

entry	ligand	yield ^[b]
1	Et ₃ P	6
2	Ph ₃ P	4
3	dppe	0
4	dcpe	1
5	<i>t</i> Bu ₃ P	1
6	Cy ₃ P	4
7	Cy ₂ PPh	27
8	CyPPh ₂	65
9	<i>t</i> BuPPh ₂	80
10 ^[c]	<i>t</i> BuPPh ₂	98

^[a] Conc = 2 M.^[b] %, determined by GC.^[c] 2 equiv TMSI, 2.2 equiv Et₃N, toluene, conc = 1 M, 24 h, 50 °C.

Table 2

Scope of the Silyl-Heck Reaction for Substrates Lacking Allylic Hydrogen Atoms.

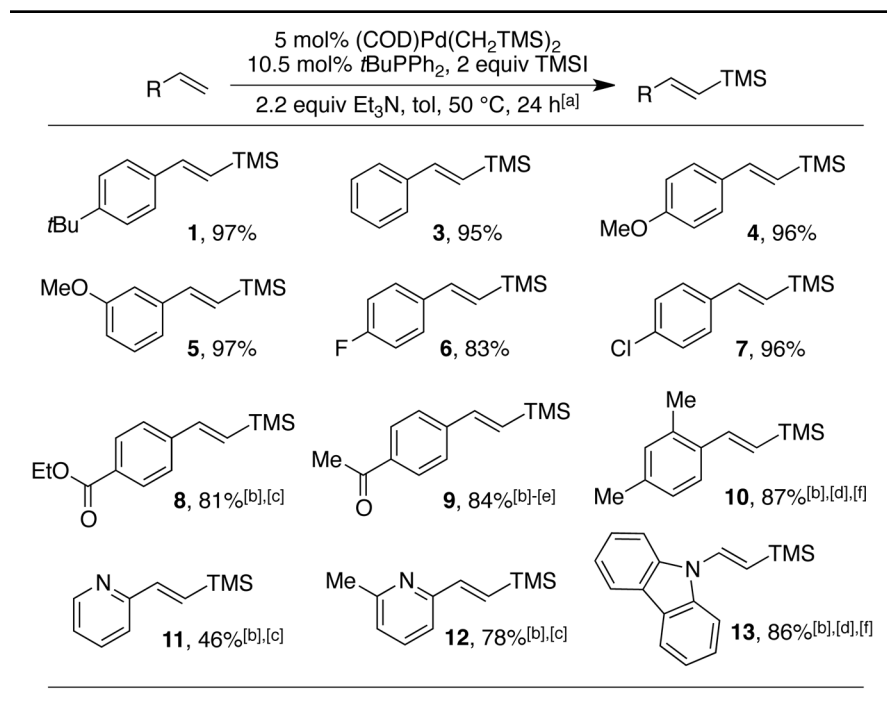
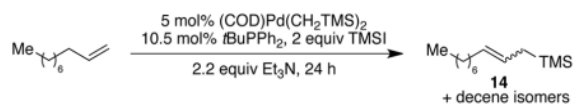
^[a] Conc = 1 M.^[b] 10 mol% (COD)Pd(CH₂TMS)₂, 21 mol% *t*BuPPh₂.^[c] solvent = PhCF₃.^[d] reaction time = 48 h.^[e] 4 equiv TMSI, 4.4 equiv Et₃N, conc = 0.5 M, after cleavage of the silyl enol ether.^[f] 3 equiv TMSI, 3.5 equiv Et₃N.

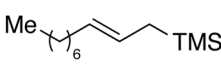
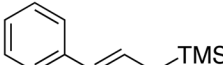
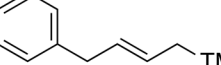
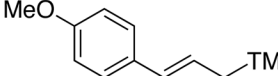
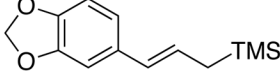
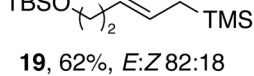
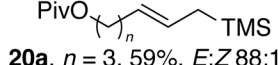
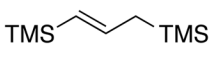
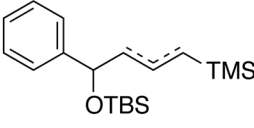
Table 3Identification of Conditions for α -Olefin Substrates.

entry	temp (°C)	solvent	conv ^[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.

Table 4

Substrate Scope for Formation of Allyl Silanes.

$\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[\text{2.2 equiv Et}_3\text{N, PhCF}_3, \text{RT, 24 h}]{\begin{array}{l} \text{2.5 mol\% (COD)Pd(CH}_2\text{TMS)}_2 \\ \text{5.3 mol\% } t\text{BuPPh}_2, \text{2 equiv TMSI} \end{array}} \text{R}-\text{CH}=\text{CH}-\text{CH}_2\text{TMS}$		
 14 , 60%, <i>E:Z</i> 83:17 ^[a]	 15 , 57%, <i>E:Z</i> >95:5 ^[b]	 16 , 64%, <i>E:Z</i> 87:13
 17 , 67%, <i>E:Z</i> >95:5	 18 , 66%, <i>E:Z</i> >95:5	 19 , 62%, <i>E:Z</i> 82:18
 20a , <i>n</i> = 3, 59%, <i>E:Z</i> 88:12 ^[c] 20b , <i>n</i> = 2, 58%, <i>E</i> -allyl: <i>Z</i> -allyl: <i>E</i> -vinyl 80:10:10 ^[c] 20c , <i>n</i> = 1, 0% ^[c]	 21 , 49%, <i>E:Z</i> >95:5 ^[d]	 22 , 78% <i>E</i> -allyl: <i>E</i> -vinyl 68:32 ^[a]

^[a] 5 mol% (COD)Pd(CH₂TMS)₂, 10.5 mol% *t*BuPPh.^[b] Reaction conditions: 35 °C, 48 h.^[c] 10 mol% (COD)Pd(CH₂TMS)₂, 21 mol% *t*BuPPh₂.^[d] Reaction conditions: 50 °C, 48 h, solvent = PhH.