

Recent Advances in the Hydrosilylation of Alkynes

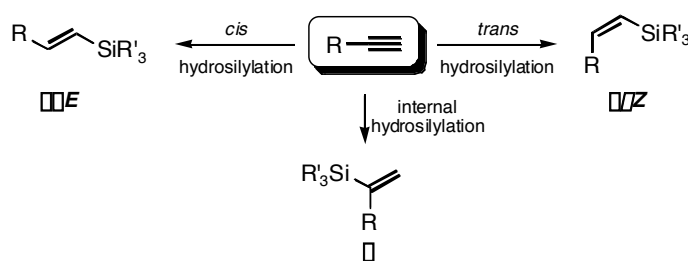
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ABSTRACT



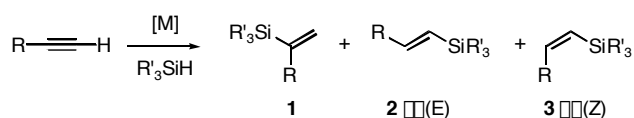
Metal catalyzed hydrosilylation is an efficient and mild method for obtaining vinylsilanes from alkynes. A general mechanistic overview of hydrosilylation is provided along with protocols that selectively prepare *E*, *E*, and *Z* vinylsilanes. Intramolecular variants and tandem reactions are also discussed.

Vinylsilanes have emerged as useful synthetic intermediates in organic synthesis due to their versatility and low toxicity.¹ For example, recent demonstration of Pd catalyzed cross coupling of vinylsilanol with vinyl and aryl halides has provided an alternative to the use of highly toxic organostannanes.² Direct hydrosilylation of alkynes provides the most efficient route to vinylsilanes, but this procedure has been plagued by issues of low stereoselectivity and regioselectivity, rendering the transformation impractical for general use in synthesis. Recent efforts in this area have provided methods for both regioselective and stereoselective hydrosilylation of alkynes. Additionally, intramolecular variants have raised new questions regarding the mechanism of *trans* hydrosilylation of alkynes.

Hydrosilylation of a terminal alkyne can result in three isomeric vinyl silanes, the *β*-silyl product (**1**), and two *α*

stereoisomers, *E* (**2**) and *Z* (**3**) (Scheme 1). The observed selectivity is dependant upon several factors such as the nature of the catalyst, substitution of the alkyne and/or hydrosilane, and the reaction conditions (solvent, temperature and catalyst loading).

Scheme 1



Various catalysts have been employed including, but not limited to, Pt,^{3a} Rh,^{3b} Ru^{3c} and organolanthanide

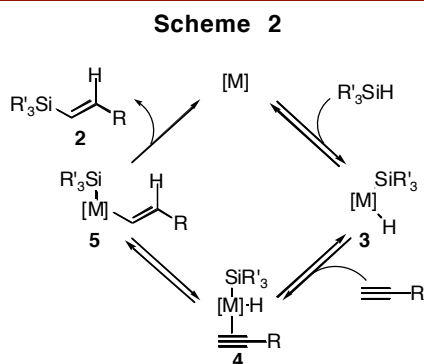
¹ Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, 95, 1375–1408.

² (a) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, 2, 2053–2055. (b) Mowery, E. E.; DeShong, P. J. *Org. Chem.* **1999**, 64, 1684–1688. (c) Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2001**, 123, 6439–6440.

³ (a) Yoshida, J.; Tamao, K.; Takahashi, M.; Kumada, M. *Tetrahedron Lett.* **1978**, 2161–2163. (b) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, 91–95. (c)

complexes.^{3d} The reaction mechanism, and hence the product distribution, is highly dependant not only on the metal used but also the electronic and steric nature of the ligands employed for any given metal.

There are two generally accepted mechanisms for the hydrosilylation of alkenes and alkynes (Schemes 2 and 3). The first mechanism, proposed by Chalk and Harrod in 1965 for the hydrosilylation of alkenes with Pt, is also relevant to the hydrosilylation of alkynes (Scheme 2). Initial oxidative addition of the silane to the catalyst followed by coordination of the alkyne gives rise to **4**, which undergoes alkyne insertion into the metal-hydride bond to furnish vinyl organometallic **5**. Reductive elimination releases the *E*-vinylsilane (**2**) and regenerates the catalyst.⁴ Although this mechanism accounts for Pt catalyzed hydrosilylation,⁵ it does not account for the observed formation of dehydrogenative silylation products (**10**, Scheme 3) and *Z*-vinyl silanes (**3**) from hydrosilylation of alkynes using Ru, Rh, and Ir.



To account for the formation of these products, an alternate mechanism for metal catalyzed hydrosilylation invoking silyl migration instead of hydride migration to the coordinated alkyne has been proposed (4 \rightleftharpoons **6**, Scheme 3).⁶ This insertion orients the metal and silyl groups *cis* on vinyl organometallic **6**. Direct reductive elimination from **6** would give the *E*-vinylsilane **2** and regenerate the catalyst. Alternatively, vinyl organometallic **6** could undergo metal assisted isomerization to **9** via a zwitterionic carbene-like intermediate **7**, which is stabilized by the σ -silyl group,⁷ or an η^2 -vinyl complex **8**.⁸ The driving force for this isomerization, which leads to the thermodynamically less stable *Z*-vinyl silane **3**, is the relief of steric strain between the metal and the adjacent silane.

Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics*, **1993**, *12*, 2377–2379. (d) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570–4575.

⁴ Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16–21.

⁵ Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510–9524.

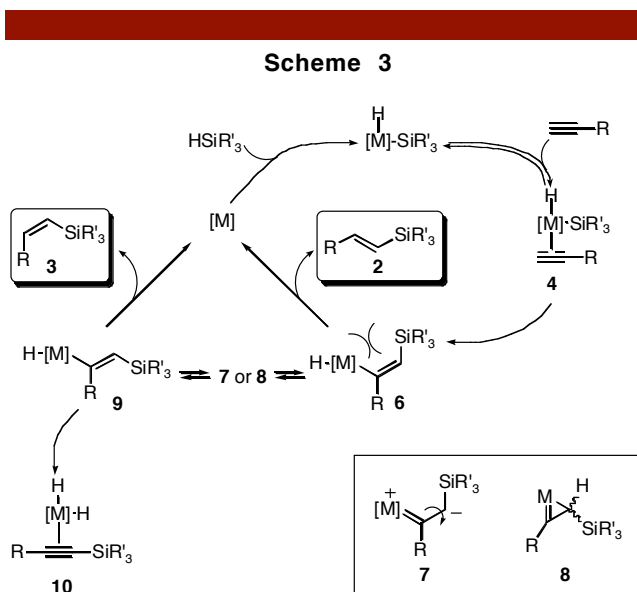
⁶ Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345–358.

⁷ Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127–3133.

⁸ Tanke, R. S.; Crabtree, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 7984–7989.

This mechanism also explains the formation of dehydrogenative hydrosilylation products **10** by β -H elimination from **9**.

Insight provided by the mechanism depicted in Scheme 3 has allowed researchers to alter the ratio of *E* to *Z* products by manipulating the solvent,⁹ silane electronics,⁷ or the bulk of the “R” group on the alkyne.¹⁰ While these changes can result in selectivity for specific applications, they were not generally applicable to a wide scope of substrates.



Recent developments in catalyst design have allowed for the selective production of β (**1**), β -*E* (**2**), or β -*Z* (**3**) vinylsilanes from a wider range of substrates. An important feature of several new methods is the ability to use silanes bearing oxygen ligands. Denmark recently provided evidence that an oxygen substituent on silicon was necessary for rapid transmetalation in Pd-catalyzed cross couplings; thus, the ability to selectively produce vinylsilanol and vinylsilyl ethers is an increasingly important endeavor.¹¹ An overview of recent methods for the production of vinylsilanes and vinylsilanol is provided in the following discussion.

Selective formation of β -*E* vinylsilanes.

Production of *E* vinylsilanes has been widely investigated with Pt, although some researchers have provided selective methods utilizing other metal complexes. The earliest examples of platinum catalyzed *cis* hydrosilylation used Speier's catalyst¹² (H_2PtCl_6), however, recent reports indicate that higher levels of reactivity and regioselectivity can be obtained with *t*-Bu₃P and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane

⁹ Takeuchi, R.; Tanouchi, N. *J. Chem. Soc. Perkin Trans. 1*, **1994**, 2909–2913.

¹⁰ Jun, C.-H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177–187.

¹¹ Denmark, S. E.; Sweis, R. F. *Acc. Chem. Res.* **2002**, *35*, 835–846.

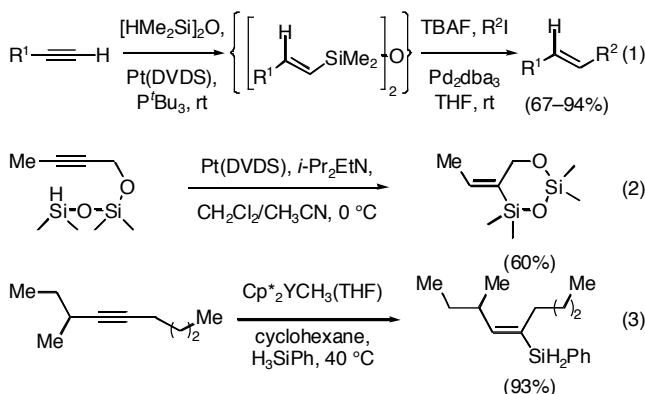
¹² Speier, J. L.; Webster, J. A.; Bernes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974–979.

[Pt(DVDS)].¹³ Denmark reported that *t*-Bu₃P-Pt(DVDS) was the most active and regioselective catalyst for a one-pot hydrosilylation/cross-coupling of 1-heptyne with aryl and alkenyl halides (Scheme 4, eq 1).¹⁴ This catalyst system was also used for an intramolecular hydrosilylation with a disiloxane tethered to a propargylic alcohol (eq 2).¹⁵ Limitations of this procedure are the problematic formation of the disiloxanes, which require a large excess of tetramethyldisiloxane, and the highly reactive nature of the propargyl disiloxane silyl ether, which can oligomerize under the hydrosilylation conditions giving lower yields.

Takeuchi¹⁶ and Molander have provided exceptions to the general use of platinum for *cis* hydrosilylation.^{3d} Takeuchi demonstrated that the cationic [Rh(COD)₂]BF₄/2PPh₃ complex promotes fast reductive elimination due to its electron-poor nature, therefore eliminating the metal-assisted isomerization pathway shown in Scheme 3. This catalyst was competent for the hydrosilylation of a variety of terminal alkynes with Et₃SiH, including those with unprotected hydroxyl functionality.

Molander employed an organoyttrium complex to catalyze the selective hydrosilylation of internal alkynes with phenylsilane. Organolanthanide catalysts of this type are believed to operate through the Chalk-Harrod mechanism. It was found that branching at the β -position of the alkyne provided enough steric bias to direct regioselective *cis* hydrosilylation (Scheme 1, eq. 3).¹⁷

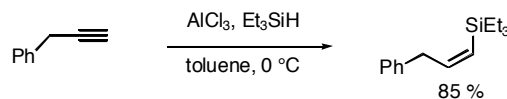
Scheme 4



Selective formation of β -Z vinylsilanes. The selective formation of *Z*-vinylsilanes can be accomplished by both Lewis acid and metal catalyzed hydrosilylation of alkynes. Yamamoto has demonstrated that Lewis acid-

catalyzed hydrosilylation can be used to prepare *cis* vinylsilanes efficiently from unactivated alkynes (Scheme 5).¹⁸ Unfortunately, (EtO)₃SiH was unsuccessful in the reaction. Although this transformation is highly selective, it is limited to alkynes bearing functional groups that are stable to strong Lewis acid conditions. Thus this procedure may not be amenable to complex molecule synthesis.

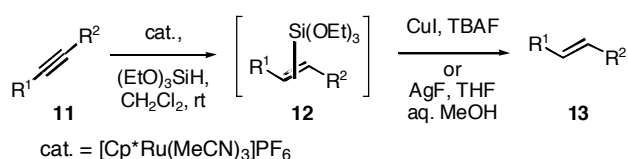
Scheme 5



More mild hydrosilylation conditions can be used with transition metal catalysts such as ruthenium and rhodium. Complexes such as RuHCl(CO)(P^{*i*}Pr)₂,¹⁹ [RhCl(PPh₃)₃],²⁰ [Rh(COD)Cl]₂,²¹ and [RuCl₂(*p*-cymene)]₂²² have all been reported to selectively provide *Z* vinylsilanes with Et₃SiH under a variety of specialized conditions.

Several researchers have expanded the scope and utility of *trans* hydrosilylation by generating vinylsilanols and then incorporating them into tandem reactions. *Trans* hydrosilylation followed by desilylation stereoselectively generates *E* alkenes from alkynes²³ in a more mild fashion than Birch reduction; thus providing a complimentary methodology to Lindlar reduction (Scheme 6).

Scheme 6



Denmark used intramolecular *trans* hydrosilylation followed by Pd-catalyzed cross coupling to stereoselectively prepare trisubstituted homoallylic alcohols (Scheme 7, eq 1). The intramolecular hydrosilylation, catalyzed by [RuCl₂(C₆H₆)₂], proceeds in a 5-*exo*-dig manner, giving the exocyclic vinylsilane product (**15**) of defined *Z*

¹³ Itami, K.; Mitsudo, K.; Nishino, A.; Yoshida, J. *J. Org. Chem.* **2002**, *67*, 2645–2652.

¹⁴ Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073–1076.

¹⁵ Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119–1122.

¹⁶ Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem.* **1995**, *60*, 3045–3051.

¹⁷ For more recent examples of organolanthanide hydrosilylation of alkynes including tandem reactions, see: (a) Molander, G. A.; Knight, E. E. *J. Org. Chem.* **1998**, *63*, 7009–7012. (b) Molander, G. A.; Corrette, C. P. *J. Org. Chem.* **1999**, *64*, 9697–9703.

¹⁸ (a) Sudo, T.; Asao, N.; Gevorgyan, V.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494–2499. (b) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781–6786. (c) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654–7655.

¹⁹ Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics*, **1993**, *12*, 2377–2379.

²⁰ Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1974**, *66*, C14–C16.

²¹ Takeuchi, R.; Tanouchi, N. *J. Chem. Soc. Perkin. Trans. 1* **1994**, 2909–2913.

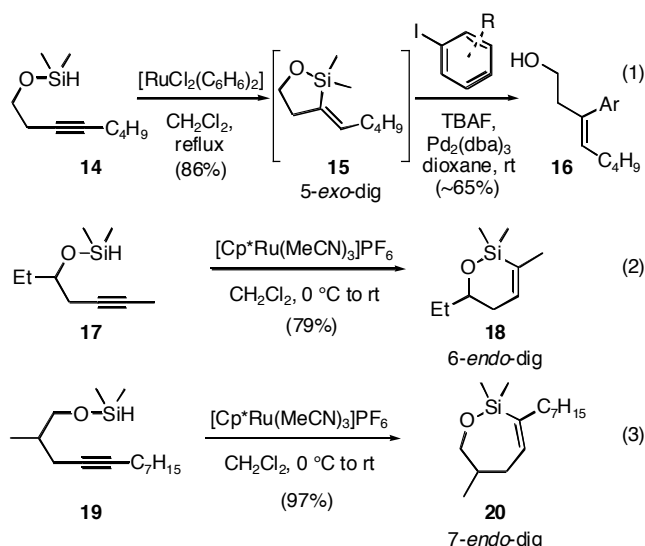
²² Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887–1889.

²³ (a) Trost, B. M.; Ball, Z. T.; Jøge, T. *J. Am. Chem. Soc.* **2002**, *124*, 7922–7923. (b) Fürstner, A.; Radkowski, K. *Chem. Comm.* **2002**, 2182–2183.

configuration from homopropargylic alcohol **14**. Subsequent Pd-catalyzed cross coupling to a variety of aryl and vinyl halides generates homoallylic trisubstituted alkenes in a one-pot procedure.²⁴

Interestingly, Trost reported that hydrosilylation of similar substrate **17** with $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$, provided the 6-*endo*-dig product **18** (Scheme 7, eq 2).²⁵ The bis-homopropargylic alcohol **19** also undergoes *endo*-dig cyclization furnishing the seven-membered ring product **20** (eq 3), even though the *exo*-dig process would form the more favorable six-membered ring. The implication of these results is that a different mechanism may be operating for ruthenium catalyzed *trans* hydrosilylation of alkynes.

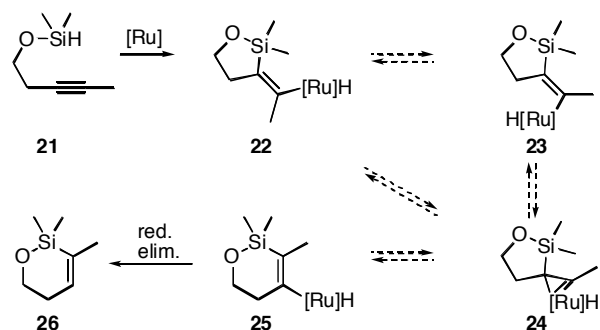
Scheme 7



Although the stereochemistry of the 5-*exo*-dig cyclization (Scheme 7, eq 1) can be explained by the *cis* hydrosilylation/isomerization mechanism shown in Scheme 3, Trost claims that a similar rearrangement mechanism for the formation of *endo*-dig products **18** and **20** from an initial 5-*exo*-dig cyclization is unlikely because of the strained nature of intermediate **24** (Scheme 8).²⁵

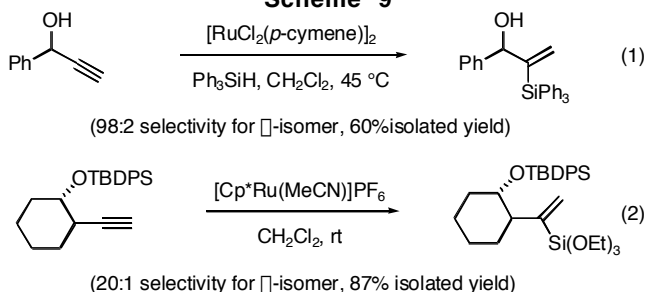
Trost hypothesizes instead that **18** and **20** result from direct *trans* hydrosilylation of the orthogonal π -systems of the alkyne. Alternatively, a polynuclear ruthenium complex could be responsible for the observed products as proposed by Oro and coworkers.²⁶ Although the mechanism of ruthenium catalyzed *trans* hydrosilylation is at present controversial, the methods reported by both Denmark and Trost provide stereoselective and mild approaches to functionalized *Z* vinylsilanes.

Scheme 8



Selective formation of π -vinylsilanes. Very few methods have been developed for the regioselective production of π -vinylsilanes. One method uses propargyl and homopropargyl hydroxyl functionality to direct internal hydrosilylation with $[\text{RuCl}_2(p\text{-cymene})]_2$ (Scheme 9, eq. 1).²² Trost reported selective, non-directed π -hydrosilylation using $[\text{Cp}^*\text{Ru}(\text{MeCN})]\text{PF}_6$. A variety of alkyne substrates gave regioselectivities on the order of 9:1–20:1 in favor of the π -vinylsilane, an example of which is shown in Scheme 9, eq. 2.²⁷ He does not comment as to why this particular Ru complex gives the π -hydrosilylation product instead of the π -*Z* hydrosilylation product, which has been demonstrated with other Ru complexes.^{3c,22}

Scheme 9



In conclusion, improvements in catalyst design have rendered hydrosilylation of alkynes an efficient and mild method for the production of *E*-vinylsilanes, π -vinylsilanes and *Z*-vinyl silanes. Unprotected oxygen functionality is tolerated by many of the new methods, allowing these transformations to be useful with more complex substrates. Areas in this field deserving further investigation are the mechanism of intramolecular *trans* hydrosilylation, and the selective production of *E* vinylsilanes bearing more diverse silicon moieties.

²⁴ Denmark, S. E.; Pan, W. *Org. Lett.* **2002**, *4*, 4163–4166.

²⁵ Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 30–31.

²⁶ Martín, M.; Sola, E.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2002**, *21*, 4027–4029.

²⁷ Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726–12727.