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Hydrosilylation of alkynes catalyzed by ruthenium carbene complexes

Sarah V. Maifeld, Michael N. Tran and Daesung Lee*

Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

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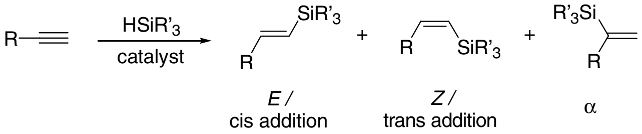
Abstract—Hydrosilylation of terminal alkynes with a variety of silanes catalyzed by $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) affords mainly the *Z*-isomer via *trans* addition in excellent yields. The presence of a hydroxyl group in close proximity to the triple bond was observed to exert a strong directing effect, resulting in the highly selective formation of the α-isomer. Intramolecular hydrosilylation of a homopropargylic silyl ether was demonstrated to give the *cis* addition product.

The significant growth in olefin metathesis chemistry can primarily be attributed to the development of new and effective metathesis catalysts.[1] In particular, Grubbs' ruthenium complexes, $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**)[2a–c] and $Cl_2(PCy_3)(NHC)Ru{=}CHPh$ (**2**),[2d,e] have demonstrated remarkable reactivity in the presence of a variety of functional groups. Additionally, complexes **1** and **2** have been employed as catalysts for a variety of transformations,[3] including an intramolecular [3 + 2] cycloaddition of alkynylidenecyclopropanes[4] as well as the dehydrogenative condensation of alcohols and the hydrosilylation of carbonyls.[5] Our studies now show that the utility of **1** can further be extended to include the stereoselective hydrosilylation of a variety of alkynes in the presence of various silanes.

Organosilanes play an important and diverse role in organic chemistry.[6] In particular, vinylsilanes have attracted considerable attention due to their versatility in both laboratory and industrial applications. The transition metal-catalyzed hydrosilylation of alkynes offers a simple and direct means of producing vinylsilanes.[7] One important issue regards the selectivity of such a process, since the primary products of the reaction may contain a mixture of three isomeric vinylsilanes, including the branched α-isomer as well as the *E*- and *Z*-vinylsilanes resulting from respective *cis* and *trans* additions across the alkyne (Scheme 1).



Scheme 1. Isomeric vinylsilanes formed from the hydrosilylation of alkynes.

To ensure the synthetic utility of alkyne hydrosilylation, both the regio- and stereoselectivity of this process must be addressed. A variety of factors including the choice of substrate, solvent, and temperature have been shown to affect the regio- and stereoselectivity of alkyne hydrosilylation. In particular, the choice of transition metal catalyst significantly influences the outcome of the reaction. Rhodium catalysts have been employed for the selective generation of both *E*-[8] and *Z*-vinylsilanes.[8b,9] The *Z*-isomer has also been successfully generated from iridium[9a,10] and ruthenium[11] catalysts. In addition, ruthenium[12] as well as platinum[13] catalysts have been employed for the selective formation of the α-isomer.

In previous work from our group in the area of silyl ether-mediated metathesis reactions,[14,15] Grubbs' carbene catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**), could effectively catalyze the activation of silanes to form silyl ethers in excellent yields via dehydrogenative condensation with alcohols and hydrosilylation of carbonyls.[5] Thus we anticipated the activation of silanes by **1** could also be

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Keywords: Hydrosilylation; Alkyne; Vinylsilane; Ruthenium; Catalysis.

* Corresponding author. Tel.: +1 608 265 8431; fax: +1 608 265 4534; e-mail: dlee@chem.wisc.edu

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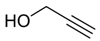
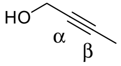
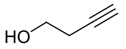
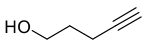
Table 1. Hydrosilylation of alkynyl alcohols catalyzed by **1**

Entry	Alkyne	Silane	*T* (°C)/h	(*Z*)/(*E*)/(α)[a]	Yield[b] (%)
1		Me_2PhSiH	60/13	0:1:3.5	60
2		Me_2PhSiH	60/4	1.2:0:1	80[c]
3		Ph_2SiH_2	70/12	—	NR[d]
4		Me_2PhSiH	60/4	1:2:10	82
5		Ph_2SiH_2	70/12	—	NR[d]
6		Me_2PhSiH	60/4	3:1.5:1	68

[a] Ratio of isomers was determined by ^1H NMR.

[b] Combined % yield of hydrosilylated alcohols.

[c] *Z*-Stereochemistry for both regioisomers was determined by NOE.

[d] Formation of a small amount of silyl ether was noted followed by significant decomposition of the alkyne in the presence of unreacted diphenylsilane.

employed for the hydrosilylation of alkynes. Since the selectivity between *O*-silylation and *C*-silylation remains unclear in many examples of transition metal catalysis, we commenced our investigation with molecules containing both alcohol and alkyne functionalities.

In general, alkynyl alcohols, in the presence of silanes and **1** (1 mol%) and in the absence of solvent, underwent faster hydrosilylation at the triple bond rather than dehydrogenative condensation at the hydroxyl group (Table 1).[16,17] Hydrosilylation of propargylic and homopropargylic alcohols by dimethylphenylsilane favored formation of the α-isomer, most likely due to the chelation effect of the hydroxyl group.[11] This effect was strongest for propargyl alcohol and 3-butyn-1-ol (entries 1 and 4) but decreased significantly as the distance between the hydroxyl group and the triple bond increased (entry 6).

Hydrosilylation of an internal alkyne yielded two regioisomers, both possessing *Z*-stereochemistry, following silylation of the α- and β-carbons (entry 2). Surprisingly, the alkynyl alcohols in entries 3 and 5 were remarkably resistant toward hydrosilylation by Ph_2SiH_2 even under extended reaction times and elevated temperatures, yielding only small amounts of the corresponding silyl ethers. This is in stark contrast to our previous observation that Ph_2SiH_2 in the presence of **1** is extremely reactive toward the hydroxyl functionality.[5]

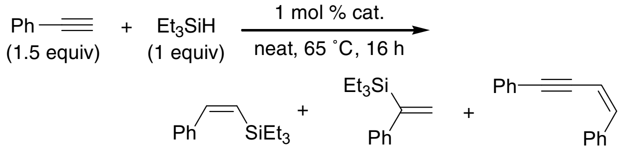
With the entries in Table 1 confirming the viability of alkyne hydrosilylation promoted by **1**, we proceeded to compare the reactivity of **1** with ruthenium carbene catalysts **2**–**4** that are similar in structure and also known to effectively promote metathesis chemistry (Fig. 1). While catalysts **2**–**4** either contain an imidazolin-2-ylidene[2d,e] or imidazol-2-ylidene[18] ligand with the benzylidene group, only catalyst **4**[18c,19] replaces the benzylidene with a 3-phenylindenylid-1-ene moiety.

In the reaction between phenylacetylene, triethylsilane, and 1 mol% of catalyst at 65 °C, catalysts **1**–**4** showed a strong propensity to favor the formation of the *Z*-isomer **5a**, while the α-isomer **5b** formed in minor amounts (Table 2).

In all cases, the alkyne was completely consumed after heating for 16 h. Hydrosilylation was achieved in 90% yield when catalyst **1** was employed. Interestingly, reactions catalyzed by **2**–**4** suffered due to the appearance of significant amounts of tail-to-tail phenylacetylene dimer **6**.[20]

After completing a cursory investigation of catalysts, further investigation revealed that **1** efficiently catalyzes the hydrosilylation of various terminal alkynes with a variety of silanes. In the presence of 1 mol% of **1**, nearly all reactions gave complete conversion of the substrate alkynes to the corresponding vinylsilanes (Table 3). Hydrosilylation of terminal alkynes generates mainly linear vinylsilanes with *Z*-stereochemistry, accompanied by varying amount of the α-isomer in high combined yields. The use of more sterically demanding silanes resulted in higher ratios of *Z*- and *E*-stereoisomers. Diphenyl-(−)-menthoxysilane, derived from the condensation catalyzed by **1** between diphenylsilane and (−)-menthol, offered high degrees of *Z*-isomer selectivity (entries 1 and 7). In particular, hydrosilylation of phenylacetylene by triphenylsilane resulted exclusively in the *Z*-isomer at

Table 2. Comparison of catalysts **1**–**4**



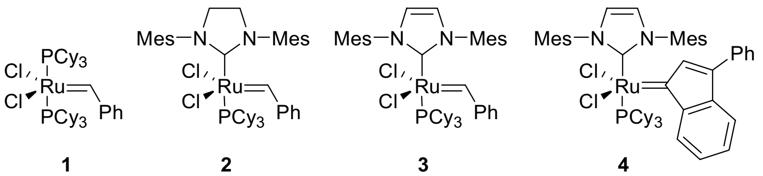
5a **5b** **6**

Catalyst	(*Z*)/(*E*)/(α)[a]	% Conversion of **5a,b**[b]
1	1:0:Trace	90[c]
2	19:0:1	40
3	14.5:0:1	53
4	16.7:0:1	31

[a] Ratio of isomers was determined by ^1H NMR.

[b] % Conversion was determined by ^1H NMR of the crude reaction mixture.

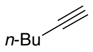
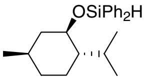
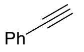
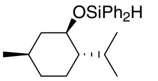
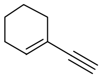
[c] Isolated yield.



1 **2** **3** **4**

Figure 1. Ruthenium carbene catalysts.

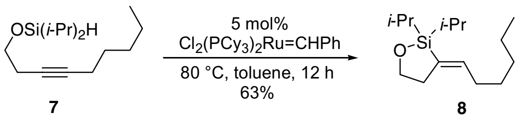
Table 3. Hydrosilylation of terminal alkynes catalyzed by **1**[a]

Entry	Alkyne	Silane	T (°C)/h	$(Z)/(E)/(\alpha)$[b]	Yield[c] (%)
1			70/2	20:1:6	>95[d,e]
2		$MePh_2SiH$	70/2	14:1:4	75
3		Et_3SiH	70/2	9:0:1	86
4		Ph_3SiH	95/2	1:0:0	80
5		$MePh_2SiH$	70/2	20:0:1	95
6		Me_2PhSiH	70/2	9:1:1	72[f]
7			70/4	10:1:0	>95[d,e]
8		Et_3SiH	70/6	1:0:0	93
9		$(EtO)_3SiH$	100/12	1.3:1:0	40[e]
10		$MePh_2SiH$	70/3	21:4:1	70
11		Et_3SiH	70/3	26:17:1	75

[a] Alkyne (1.5 equiv), silane (1 equiv), and **1** (1 mol%) were added to a vial and allowed to react at the specified temperature.
[b] Ratio of isomers determined by ^1H NMR.
[c] Isolated yield.
[d] Product was unstable to silica gel.
[e] % Conversion based upon ^1H NMR of the crude reaction mixture.
[f] At 25 °C, the *trans* isomer was generated as the major product.

95 °C after 2 h, which is comparable to the selectivity achieved by recent examples employing $[RuCl_2(p\text{-cymene})]_2$[11] and $[Cp^*RhCl_2]_2$[8b] as catalysts. The use of higher temperatures also increased the ratio at which the Z-isomer was formed (entry 6). Although **1** effectively promoted alkyne hydrosilylation with aryl- and alkylsilanes at temperatures ranging from 25 to 95 °C, a trialkoxysilane such as triethoxysilane was markedly less reactive even at higher temperatures (entry 9). As in the earlier cases of alkynyl alcohols, terminal alkynes examined in this study did not undergo hydrosilylation with Ph_2SiH_2 in the presence of **1** at elevated temperatures and extended reaction times.

Intramolecular hydrosilylation of triple bonds has been shown to be a useful tool in organic synthesis to control both the regio- and stereochemistry of the resulting double bond.[21,22] Therefore, we further investigated the propensity of **1** to internally deliver silanes across tethered alkynes. Although previous intermolecular hydrosilylation reactions were run under neat conditions, the intramolecular hydrosilylation of homopropargylic silyl ether **7** required a solvent to prevent dehydrogenative condensation between the hydride-bearing silyl ethers. Although the use of toluene as a solvent (0.025 M) slowed reaction rates and required higher temperatures and catalyst loading, the siloxacycle **8** was isolated in 63% yield (Scheme 2).



Scheme 2. Intramolecular hydrosilylation of a homopropargylic alcohol-derived silyl ether.

Previously studied transition metal-catalyzed hydrosilylation reactions suggest that the present hydrosilylation likely proceeds by initial oxidative addition of the silane to the metal center; however, characterization of this initial metal hydride complex by ^1H NMR has been elusive.[23] The increasing Z-stereoselectivity noted at higher temperatures and with more sterically demanding silanes may be explained by the isomerization of an intermediate vinyl complex, as proposed by Crabtree and co-workers[10b,c] and Ojima et al.[9c]

In conclusion, the commercially available complex **1** has been shown to be an effective catalyst for the inter- and intramolecular hydrosilylation of alkynes. A strong directing effect by the hydroxyl group of alkynyl alcohols is suggested to explain the preferential formation of the α-isomer. Additionally, up to complete selectivity for the Z-isomer has been accomplished. Further studies may aid in elucidating the nature of the catalytic species as well as the mechanistic pathways operating in these processes.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.11.025.

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22. For *E*-stereoselective intramolecular hydrosilylation followed by silicon-assisted cross-coupling reactions, see: Denmark, S.; Pan, W. *Org. Lett.* **2001**, *3*, 361.
23. ^{1}H NMR experiments employing a variety of silanes at various temperatures in the absence of alkyne have been attempted to identify this metal hydride intermediate; however, the observation of this complex has been precluded by the formation of silyl byproducts, presumably arising from silyl condensation.