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Isomerization of (Z)-alkenylsilanes to (E)-isomers with hydrosilane and RhI(PPh3)3

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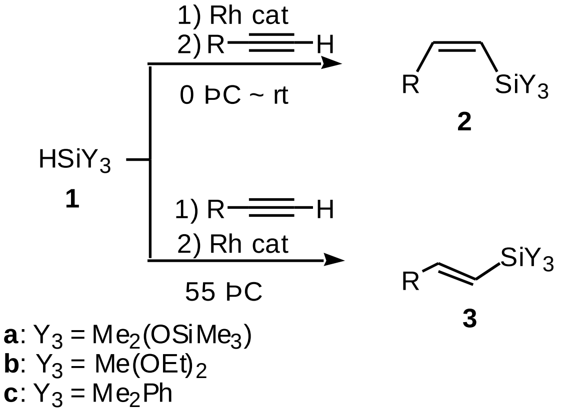
Abstract

Isomerization of (*E*)-2-phenylethenylsilanes to the (*Z*)-isomers is found to easily take place at 60 ˚C within 1 h using 20-100 mol% of a hydrosilane and 0.1 mol % of RhI(PPh$_3$)$_3$ and is understood in terms of insertion of alkenylsilanes to hydridorhodium followed by β-hydride elimination.

Key words: hydrosilylation, isomerization, RhI(PPh$_3$)$_3$, alkenylsilane, hydrosilane

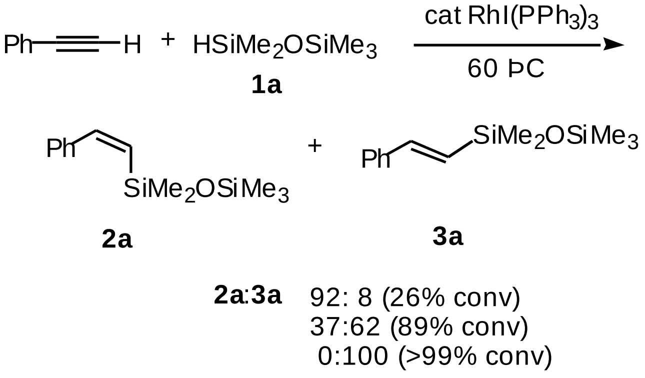
Regio- and stereoselective hydrosilylation of terminal alkynes leading to alkenylsilanes is a significant reaction in organic synthesis as well as organometallic chemistry.[1] Among a number of transition metal catalysts endowed with a variety of features, rhodium complexes show high activity as well as characteristic selectivities. We recently disclosed that rhodium-catalyzed hydrosilylation of terminal alkynes using a hetereoatom-substituted hydrosilane (*e.g.*, **1a** and **1b**) produced (*Z*)-alkenylsilanes (**2**) or (*E*)-alkenylsilanes (**3**) depending on the reaction procedure as shown in Scheme 1.[2]

Meanwhile, we observed that (*E*)-alkenylsilanes **3** were obtained through isomerization of initially produced (*Z*)-isomers **2**. This observation suggests that the hydrosilylation might have occurred through *trans*-addition of a hydrosilane to give **2** followed by isomerization to *cis*-adduct **3**. This isomerization is unusual in view of stereochemistry of hydrosilylation.[3,4] We report here that the isomerization of **2** to **3** is promoted by the presence of a hydrosilane and RhI(PPh$_3$)$_3$. We also discuss mechanistic aspect of the isomerization.



Scheme 1

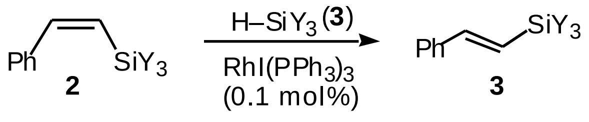
When a mixture of phenylacetylene and pentamethyldisiloxane (**1a**) was heated at 60 ˚C in the presence of 0.1 mol % of RhI(PPh$_3$)$_3$, the reaction leading to (*E*)-2-phenylethenylsilane **3a** proceeded highly selectively.[1] At 26% conversion, ratio of resulting (*Z*)-2-phenylethenylsilane (**2a**) and (*E*)-isomer (**3a**) was 92 : 8. The isomer ratio gradually changed in favor of **3a** as the reaction proceeded. At 89% conversion, the ratio was 37 : 62; at >99% conversion, 0 : 100 (Scheme 2).



Scheme 2

In the presence of 0.1 mol% of RhI(PPh$_3$)$_3$ only, **2a** did not isomerize at 60 ˚C in 24 h (see: Table 1, entry 1), whereas the isomerization started to take place rapidly when 10 mol % of pentamethyldisiloxane (**1a**) was added to the mixture, and after 1 h a 65 : 35 mixture of (*Z*)-isomer **2a** and (*E*)-isomer **3a** resulted. The ratio did not change 1 h thereafter, while most of **1a** was consumed.[5,6] Addition of **1a** (0.6 mol) to the reaction mixture reinitiated the isomerization to complete the transformation to (*E*)-isomer **3a** within 1 h. Use of larger amount of **1a** more accelerated the isomerization (entries 4-6). Thus, the isomerization appears to be competitive with the consumption of hydrosilane **1a**, both presumably being catalyzed by the rhodium complex. (*Z*)-Isomer **2b** with a *p*-tolyl group isomerized faster than **2a** to give (*E*)-isomer **3b** exclusively using 20 mol% of **1a** in 1 h at 60 ˚C (entry 8). Isomerization of (*Z*)-isomer **2c** to (*E*)-isomer **3c** also occurred similarly in the presence of diethoxy(methyl)silane (**1b**).[7]

Table 1. Isomerization of (*Z*)-alkenylsilanes[a]



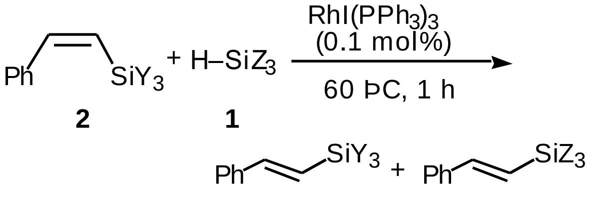
entry	**2** (% Z)	H–SiY$_3$, mol		time/h	**2** : **3**[b]
1	**2a** (99)		none	24	97:3
2		**1a**	0.1	1	65:35
3				2	61:39
4			+0.6[c)]	1	0:100
5			0.2	1	24:76
6			0.3	1	0:100
7	**2b** (95)		0.1	1	27:73
8			0.2	1	0:100
9	**2c** (93)	**1b**	0.2	1	2:98

[a] All reactions were carried out using 0.1 mol% of RhI(PPh$_3$)$_3$ at 60 ÞC.[b] The ratio was determined by ^{1}H NMR. [c] Additional 0.6 mol of hydrosilane was added to the product mixture resulting from the experiment in entry 3.

Table 2 shows scrambling experiments using an equimolar mixture of (*Z*)-2-phenylethenylsilane **2** and hydrosilane **1** with a different silyl group SiY$_3$ or SiZ$_3$. Scrambling of a silyl group was at best 6% after isomerization at 60 ˚C for 1 h. These results show that the silyl exchange does not occur extensively during the isomerization to the corresponding (*Z*)-silane **3**.

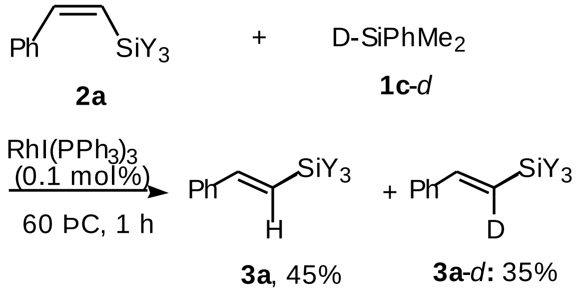
On the other hand, the scrambling experiments using DSiMe$_2$Ph (**1c**-*d*) revealed that a fair amount of deuterium was incorporated into the product. For example, as illustrated in Scheme 3, when the isomerization was carried out starting with an equimolar mixture of **1c**-*d* and (*Z*)-2-phenylethenylsilane **2a**, a 1.3 : 1 mixture of (*E*)-isomer **3a** and 1-deuterio-2-phenylethenyllsilane **3a**-*d* resulted.[8]

Table 2. Isomerization of *Z*-alkenylsilanes using hydrosilane with different substituents



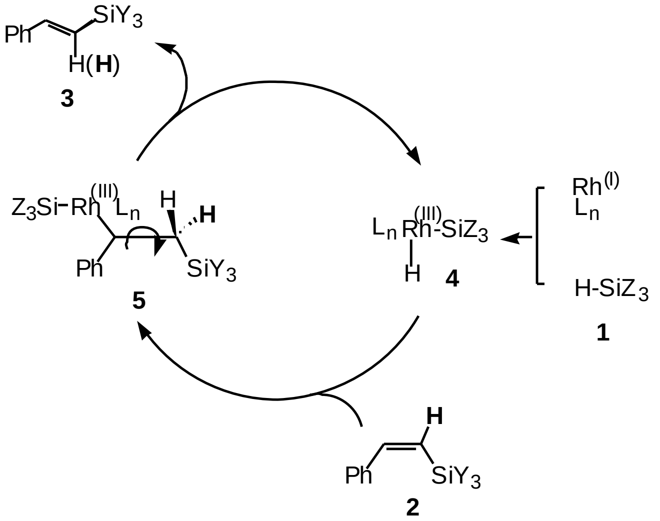
entry	**2**	**1**	Products[a]	
			–SiY$_3$	–SiZ$_3$
1	**2b**	**1a**	86%	0%
2	**2a**	**1b**	87%	6%
3	**2a**	**1c**	80%	0%

[a] Yields determined by ^{1}H NMR.



Scheme 3

Above observations lead to a mechanism shown in Scheme 4: Oxidative addition of HSiZ$_3$ to Rh(I)L$_n$ followed by insertion of (*Z*)-alkenylsilane **2** to the resulting Rh(III) species **4** would furnish intermediate **5**. The scrambling experiments shown in Table 2 and Scheme 3 suggest that the insertion occurs at a Rh(III)-H bond in **4** rather than a Rh(III)-Si bond. The results contrast sharply to the fact that insertion of a carbon-carbon triple bond towards a H-Rh(III)-SiZ$_3$ species is considered to occur at a rhodium-silicon bond.[3] Thus, the isomerization proceeds via an insertion–β-elimination mechanism, which is rarely considered for alkenylsilane isomerization though often discussed in olefin isomerization.[8] The regiochemistry is controlled to give **5** so that the rhodium atom is located at β–position of SiY$_3$. Successive β-elimination leading to (*E*)-alkenylsilanes **3** would occur after C-C bond rotation to induce *syn*-periplanar conformation of a Rh-C-C-H moiety.



Scheme 4

We have found that the rhodium-catalyzed isomerization of (*Z*)-2-phenylethenylsilane **2** to (*E*)-isomers **3** takes place in the presence of a catalytic amount of hydrosilane and a rhodium catalyst. Since hydrosilylation of 1-alkynes also proceeds in a similar stereochemical manner, it would be reasonable to assume that similar isomerization pathway is invoved in these cases also. In addition, the isomerization was demonstrated to proceed through insertion–β-elimination of a hydridorhodium H-Rh(III)-Si to alkenylsilane in contrast to the reaction of the species with a triple bond which has been considered to insert at the rhodium–silicon bond.

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† This paper is dedicated to Professor Victor Snieckus on the occasion of his 64th birthday.

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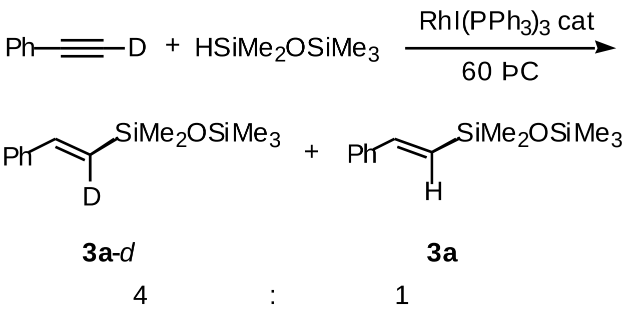
8 Typical experimental procedure: To a screw capped glass tube were added a (*Z*)-2-phenylethenylsilane **2** (1.0 mmol), a hydrosilane (0.1-0.3 mmol) and $RhI(PPh_3)_3$ (0.1 mol %, 1 mg). The resulting mixture was heated at 60 ˚C for 1 h. The isomerization was monitored by taking aliquot of the solution and measuring ^{1}H NMR spectra in a $CDCl_3$ solution. After the isomerization was completed, the corresponding (*E*)-silane **3** was isolated by bulb-to-bulb distillation.

9 The major product of the following equation showed ^{1}H NMR spectrum identical to the deuterated product in Scheme 3. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.92 (t, *J* = 2.7 Hz, 1 H, PhC$\underline{H}$=CDSi) for **3a**-*d*; 6.95 (d, *J* = 19.2 Hz, 1 H, PhC$\underline{H}$=CHSi) for **3a**.



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