RhCl(PPh$_3$)$_3$/NaI Catalyst System for Hydrosilylation of 1-Alkynes: Stereodivergent Syntheses of *E*- and *Z*-Alkenylsilanes with Heteroatom Substituents on Silicon

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Both (*E*)- and (*Z*)-alkenylsilanes are synthesized by the reaction of hydrosilanes and 1-alkynes catalyzed by RhCl(PPh$_3$)$_3$/NaI or RhI(PPh$_3$)$_3$ highly selectively.

We herewith disclose that the addition of sodium iodide to a system of the RhCl(PPh$_3$)$_3$-catalyzed hydrosilylation of 1-alkynes i) enhances the reaction rate, ii) controls regio- and stereochemistry of the resulting alkenylsilanes, and iii) suppresses undesirable polymerization when 1-arylalkynes is used as a substrate.

Hydrosilylation of alkynes has increased its importance[1] since the resulting alkenylsilanes serve as versatile intermediates for the synthesis of various heteroatom substituted alkenes[2] as well as for the construction of organic framework through carbon-carbon bond formation.[3] To achieve these transformations successfully, the silicon atom of the alkenylsilanes should be substituted with one or more heteroatom(s) as represented by fluoro or alkoxy group.

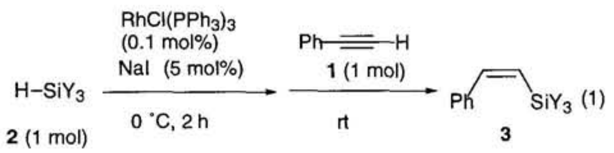
Although platinum catalysts are effective for the stereocontrolled hydrosilylation of 1-alkynes using halosilanes to give the corresponding (*E*)-alkenyl(halo)silanes, the reaction with trialkyl- or alkoxysilanes decreases the (*E*)-selectivity.[4]

Rhodium catalysts, on the other hand, are stereochemically divergent to give (*E*)- or (*Z*)-alkenylsilanes. For example, the reaction using a cationic rhodium complex furnishes (*E*)-alkenylsilanes,[5] whereas a neutral rhodium species such as RhCl(PPh$_3$)$_3$ affords (*Z*)-products.[6] However, these characters are highly dependent on the species of catalyst, substrate and hydrosilane and mainly observed by use of trialkylsilanes, which considerably limit possibilities of further transformations of the resulting carbon-silicon bond. In addition, these rhodium catalyzed hydrosilylations are not effective for 1-arylalkynes, since the rhodium complexes are reported to initiate the polymerization of the alkynes.[7]

Hence, an efficient stereoselective preparation of the alkenylsilanes bearing a heteroatom substituent on silicon, has been a major concern in the field of organic and organometallic chemistry.[3]

During the course of our studies on the synthesis of alkenylsilanols via hydrosilylation of cyclic hydridosiloxanes,[8] we found that the rate of hydrosilylation of phenylacetylene (**1**) with pentamethyldisiloxane (**2a**) was accelerated by the addition of sodium iodide to RhCl(PPh$_3$)$_3$ with the undesirable polymerization of **1** being suppressed.[7, 9] Further studies have revealed that the reaction is highly stereoselective to give the corresponding (*Z*)-alkenylsilanes.

When the hydrosilylation was carried out by the addition of **1** to the premixed 0.1 mol% of RhCl(PPh$_3$)$_3$, 5 mol% of NaI, and **2a**, the corresponding (*Z*)-alkenylsiloxane (**3a**) and its (*E*)-isomer (**4a**) was obtained in a ratio of 97:3.[10] The regioisomer, (1-phenylethenyl)pentamethyldisiloxane (α-adduct), was not obtained. Such high selectivity and reactivity were not observed in the reaction catalyzed by RhCl(PPh$_3$)$_3$ to give the corresponding products in 30% yield (**3a**:**4a**=ca. 1:1) along with a trace amount of the α-adduct.



a: SiY$_3$=SiMe$_2$OSiMe$_3$, **b**: SiY$_3$=SiMe$_2$OEt,
c: SiY$_3$=SiMe(OEt)$_2$, **d**: SiY$_3$=Si(OEt)$_3$

The highly effective catalyst system, generated in situ from RhCl(PPh$_3$)$_3$ and NaI, is considered to be a rhodium(I) iodide species, a resultant of the substitution of chlorine with iodine. Indeed, the hydrosilylation of **1** with **2a** in the presence of 0.1 mol% of RhI(PPh$_3$)$_3$[11] also gave **3a** predominantly in >95% yield.

The use of ethoxydimethylsilane (**2b**) and diethoxymethylsilane (**2c**) similarly afforded the corresponding (*Z*)-alkenylsilanes **3b** and **3c** with (*Z*)-selectivities of 90% and 93%, respectively. However, the catalyst was less effective to triethoxysilane (**2d**) (ca. 20% conv, **3d**:**4d**=60:40).

Several terminal alkynes substituted with an aryl or alkyl group such as (4-methylphenyl)ethyne (**5**), (4-methoxyphenyl)ethyne (**6**), (4-acetylphenyl)ethyne (**7**), 3-ethynylquinoline (**8**), and 1-octyne (**9**) are transformed to the corresponding (*Z*)-alkenylsilanes with high selectivities. The results are summarized in Table 1.

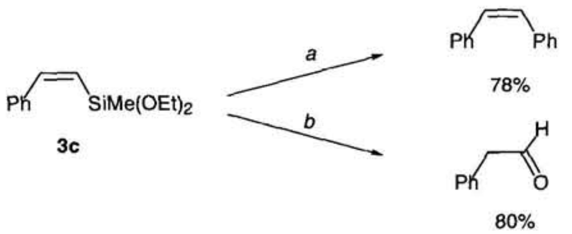
The obtained (*Z*)-alkenylsilane bearing heteroatom substi-

Table 1. Hydrosilylation of alkynes with hydrosilanes (**2**) catalyzed by RhI(PPh$_3$)$_3$[a]

alkyne	hydrosilane	time/h	yield /%[b]	*Z*/*E*
C$_6$H$_5$C≡CH	HSiMe$_2$OSiMe$_3$ (**2a**)	2	>95	>99:1
(**1**)	HSiMe$_2$OEt (**2b**)	2	>95	90:10
	HSiMe(OEt)$_2$ (**2c**)	2	>95	93:7
	HSi(OEt)$_3$ (**2d**)	16	20	60:40
4-MeC$_6$H$_4$C≡CH (**5**)	**2a**	3	>95	>99:1
	2c	16	>95	96:4
4-MeOC$_6$H$_4$C≡CH (**6**)	**2a**	3	>95	96:4
4-MeCOC$_6$H$_4$C≡CH (**7**)	**2a**	16	>95	95:5
3-ethynylquinoline (**8**)	**2a**	48	40	90:10
HexC≡CH (**9**)	**2a**	48	>95	85:15

[a] Reactions were carried out at room temperature using 0.1 mol% of RhI(PPh$_3$)$_3$.
[b] Estimated by ^{1}H NMR.

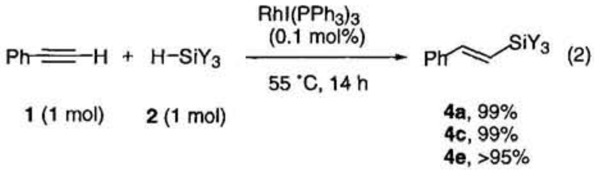
tuent(s) on silicon can be transformed to various molecules. For example, **3c** (Z/E=91:9) was converted to *cis*-stilbene in 78% yield with retention of configuration by the reaction of iodobenzene in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.5 mol%) and Bu_4NF (1.5 mol)[3, 12] and to phenylacetaldehyde in 80% yield by the Tamao oxidation[2b] as shown in Scheme 1.



a: PhI, $[PdCl(\eta^3\text{-}C_3H_5)]_2$, (2.5 mol%), Bu_4NF (1.5 mol), THF, 65 °C
b: H_2O_2-$KHCO_3$, MeOH/THF, rt, 1 h

Scheme 1.

To our surprise, stereochemical outcome was reversed when the reaction was carried out without premixing the rhodium catalyst and hydrosilane. For example, successive addition of **1** and **2a** to 0.1 mol% of $RhI(PPh_3)_3$ followed by stirring the resulting mixture at 55 °C for 14 h afforded **4a** in >99% yield;[13, 14] no (Z)-isomer was observed by ^{1}H NMR measurement. Similar high E-selectivities were achieved in the reactions using hydrosilanes **2c** and **2e** as shown in eq 2.



a: SiY_3=$SiMe_2OSiMe_3$, **c**: SiY_3=$SiMe(OEt)_2$,
e: SiY_3=$SiEt_3$

In summary, the $RhCl(PPh_3)_3$/NaI system or $RhI(PPh_3)_3$ catalyst was found to be effective for the stereodivergent syntheses of (E)- and (Z)-alkenylsilanes by hydrosilylation of 1-alkynes. Since (Z)-alkenylsilanes (**3**) with heteroatom substituents on silicon are not easily accessible by other approaches, the present stereoselective syntheses of the alkenylsilanes opens a wide variety of synthetic applications, taken together with further transformations of **3**.

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9 Our preliminary experiment revealed that the atempted hydrosilylation of phenylacetylene using $[RhCl(cod)]_2$ caused the polymerization even in the presence of a hydrosilane.

10 Pentamethyl[(Z)-2- phenylethenyl]disiloxane (**3a**): Bp 110 °C (0.2 Torr, bath temp). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9H), 0.10 (s, 6H), 5.75 (d, J = 15.5 Hz, 1H), 7.24-7.44 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.0, 2.2, 126.7, 128.3, 128.7, 128.8, 138.3, 144.2. IR (neat) 2959, 1607, 1576, 1495, 1253, 1055, 845 cm^{-1}. HRMS. Calcd for $C_{13}H_{22}OSi_2$: 250.1209 ; Found: 250.1233.

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13 This result is not due to the temperature effect. The reaction at 55 °C under the condition to form the (Z)-product did not exhibit high (E)-selectivity to give (Z)-major product with slightly lower selectivity.

14 Pentamethyl[(E)-2-phenylethenyl]disiloxane (**4a**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.23 (s, 6H), 6.43 (d, J = 19 Hz, 1H), 6.95 (d, J = 19 Hz, 1H), 7.26-7.49 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 1.0, 2.2, 126.7, 128.3, 128.7, 128.8, 138.3, 144.2. IR (neat) 2959, 1593, 1572, 1493, 1253, 1051, 843 cm^{-1}. HRMS. Calcd for $C_{13}H_{22}OSi_2$: 250.1209 ; Found: 250.1223.