

Silylation of silanols with vinylsilanes catalyzed by a ruthenium complex

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Abstract

A new ruthenium complex-catalyzed O-silylation of silanols with vinylsilanes leading to siloxane bond formation with the evolution of ethylene is described. A maximum conversion of silanol is reached using an excess of vinylsilane to also yield the product of the *homo*-coupling of the latter. Under the optimum conditions, when vinylsilane with at least one ethoxy substituent is used, the reaction gives exclusively unsymmetrical siloxanes.

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The silylative coupling of olefins with vinyl-substituted organosilicon compounds, which we have developed in the last two decades as a new effective catalytic activation of the =C–H bond of olefins and =C–Si bond of organosilicon compounds (generally occurring in the presence of complexes containing M–H and M–Si bonds) appears to be a valuable synthetic tool in the preparation of vinyl-substituted organosilicon reagents and polymers.¹ This mode of catalytic reactivity has also been extended to vinylsilicon compounds of other sp,² that is, =C_{aryl}–H bonds² and sp-hybridized carbon–hydrogen bonds³ as well as O–H bonds of alcohols.⁴ The mechanism of this new general reaction in which vinylsilicon compounds function as silylating agents and hydrogen acceptors has been proved to involve the insertion of the vinyl–Si bond into the TM–H bond (where TM = Ru, Rh, Ir or Co) and β-Si transfer to the metal with the elimination of ethylene and generation of a TM–Si bond. Next migratory insertion of an alkene (or alkyne) into the TM–Si bond and β-H transfer to the metal eliminate the substituted silylethene (or silylethyne), respectively.⁵

When rhodium and ruthenium complexes (e.g., RhCl(PPh₃)₃, Ru₃(CO)₁₂, [Rh(cod)(OSiMe₃)₂]) are used as catalysts, the initiating process involves an oxidative

addition of alkene⁶ or benzyl alcohol⁴ to the metal centre followed by the insertion of vinylsilicon compounds into a new M–H bond, forming M–Si bonds with the elimination of ethylene. The final step is the elimination of the silylation product and regeneration of the precursor. Very recently, this mode of vinylsilane reactivity was applied in [RhCl(cod)₂]-catalyzed silylation of hydrogen chloride affording a chlorosilane.⁷

The aim of this work is to use the new role of vinylsilanes as hydrogen acceptors in O-silylation of silanols, which has a great potential in the hydrophobization strategy of inorganic (and organometallic) materials as well as in the synthesis of siloxane derivatives.

Conventional approaches to unsymmetrical siloxanes involve condensation of silanols with chloro-, amino-, acyloxy- or alkoxysilanes, co-hydrolysis of two chloro- or alkoxysilanes and the reaction of silanolates with halosilanes.⁸ Not only stoichiometric reactions, but also catalytic methods such as rhodium(I)-catalyzed dehydrocoupling of silanols with hydrosilanes,⁹ or dealkylative coupling of hydrosilanes with alkoxysilanes¹⁰ were reported for disiloxane bond formation. Unsymmetrical siloxanes were also obtained from silanols and hydrosilanes using a phase transfer catalytic system.¹¹ However, some of these processes are restricted by the necessity of the removal of corrosive HCl, H₂O or explosive (H₂) stoichiometric by-products and by the instability of the silicon substrates

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towards moisture. Besides, non-symmetric disiloxanes cannot be produced effectively using some of these methods.

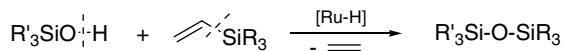
Herein, we present a new catalytic reaction that involves activation of the O–H bond in silanols by vinylsilanes occurring in the presence of a ruthenium–hydride catalyst yielding siloxanes via the elimination of ethylene (Scheme 1).

Since the vinylsilane has to be used in excess, the unsymmetrical siloxanes can be accompanied by the products of vinylsilane *homo*-coupling (Scheme 2).

The silylation of silanols by vinylsilanes with the formation of ethylene as a by-product could be very attractive since the starting materials for this process are often commercially available and inexpensive and ethylene can be easily removed from the reaction mixture.

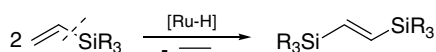
The silylation reactions were examined in the presence of a ruthenium–hydride catalyst: RuHCl(CO)(PCy₃)₂ (2 mol %)—known to be active in silylative coupling of vinylsilanes with olefins and alkynes,⁵ in an open or closed (sealed ampoules) system in toluene (110–120 °C), under argon.

Since the equimolar reaction of vinyldimethylphenylsilane with selected silanols (Table 1, entries 1–2) proceeded



R, R' = alkyl, aryl, siloxy, alkoxy

Scheme 1.



R = alkyl, aryl, siloxy

Scheme 2.

with maximum 90% conversion of the respective silanol to yield a mixture of siloxane and 1,2-bis(dimethylphenylsilyl)-ethene as a result of *homo*-coupling of vinyldimethylphenylsilane (Scheme 2), a two- or fourfold excess of vinylsilane was necessary to achieve complete conversion of the silanol. Although the excess of vinylsilane in the presence of a ruthenium–hydride complex facilitates competitive formation of the vinylsilane *homo*-coupling product, its use also enables quantitative conversion of the silanol to the silylation product. Moreover, the accompanying bis(silyl)ethenes can be easily separated by column chromatography or simple evaporation from the reaction mixture (when vinyltrimethylsilane is used as a silylating agent and volatile 1,2-bis(trimethylsilyl)ethene is formed).

Most of the reactions examined proceeded in good yield to give unsymmetrical siloxanes accompanied by 1,2-bis(silyl)ethene.¹² However, the reaction required a longer time (24–48 h) than the previously reported silylation of alkenes⁵ or alkynes.³ While vinyltrimethylsilane and vinyldimethylphenylsilane reacted efficiently in this process, the silylation of silanols by vinyl(siloxy)silanes was less effective (Table 1, entries 12–13). It is worth noting that the process described led to exclusive formation of unsymmetrical siloxanes (without vinylsilane *homo*-coupling products), when a vinylsilane with at least one ethoxy substituent was used (Table 1, entries 8–10).

Regardless of the substrate ratio, the silylation reaction between bulky vinyltris(trimethylsiloxy)silane and tris(trimethylsiloxy)silanol (Table 1 entry 14) did not occur. Most of the siloxane products were isolated and characterized spectroscopically.¹³

On the basis of the results obtained and our previous reports on the silylation of alkenes and alkynes by vinylsilanes,⁵ an insertion–elimination mechanism is postulated for this process. The reversible insertion of vinylsilane into a ruthenium–hydride bond was previously reported by Wakatsuki et al.¹⁴ to provide evidence for one half of the

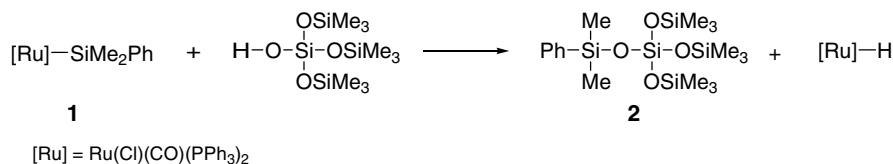
Table 1
Silylation of silanols (HOSiR'₃) by vinylsilanes catalyzed by RuHCl(CO)(PCy₃)₂

Entry	Vinylsilane SiR ₃	Silanol HOSiR' ₃	Molar ratio [CH ₂ =CHSiR ₃]/[HOSiR' ₃]	Silanol conversion (%) ^b	Time (h)	Yield ^b (isolated) (%)
1 ^a	SiMe ₂ Ph	HOSi(OSiMe ₃) ₃	1:1	89	24	89 (58)
2 ^a	SiMe ₂ Ph	HOSi(<i>i</i> -Pr) ₃	1:1	90	24	90 (60)
3 ^a	SiMe ₂ Ph	HOSi(OSiMe ₃) ₃	2:1	99	24	99 (69)
4 ^a	SiMe ₂ Ph	HOSi(<i>i</i> -Pr) ₃	2:1	99	24	99 (67)
5	SiMe ₃	HOSi(OSiMe ₃) ₃	4:1	100	24	99 (78)
6	SiMe ₃	HOSi(<i>i</i> -Pr) ₃	4:1	100	24	98 (86)
7	SiMe ₃	HOSiMe ₂ Ph	4:1	100	24	99 (83)
8	Si(OEt)Me ₂	HOSi(OSiMe ₃) ₃	2:1	100	48	99 (79)
9	Si(OEt) ₂ Me	HOSi(OSiMe ₃) ₃	2:1	100	48	99 (67)
10	Si(OEt) ₂ Me	HOSiMe ₂ Ph	2:1	100	48	98
11	SiMe ₂ (OSiMe ₃)	HOSiMe ₂ Ph	2:1	100	48	99
12	SiMe ₂ (OSiMe ₃)	HOSi(<i>i</i> -Pr) ₃	2:1	49	48	49
13	SiMe(OSiMe ₃) ₂	HOSiMe ₂ Ph	2:1	78	48	78
14	Si(OSiMe ₃) ₃	HOSi(OSiMe ₃) ₃	2:1	0	48	0

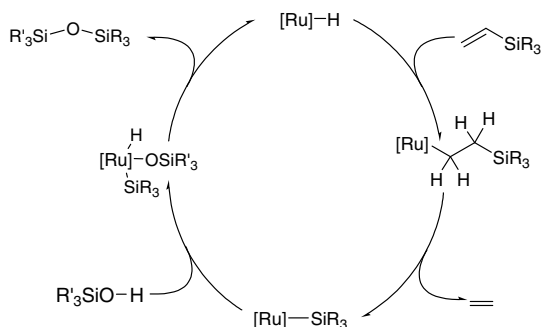
Reaction conditions: toluene, 110–120 °C, [Silanol]/[Catalyst] = 1:2 × 10⁻² mol.

^a Reaction carried out in an open system.

^b Calculated by GC.



Scheme 3.



Scheme 4. Mechanism of the O-silylation of silanols with vinylsilanes.

catalytic cycle. To supply evidence for the second half, the stoichiometric reaction of silanol with a Ru–Si complex was examined (Scheme 3).

Therefore, the reaction of equimolar amounts of the ruthenium–silyl complex $\text{Ru}(\text{SiMe}_2\text{Ph})(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ **1** and tris(trimethylsiloxy)silanol was carried out at room temperature and the reaction progress was monitored by ^1H NMR and GCMS.¹⁵

Analysis of the reaction mixture by GCMS revealed the formation of unsymmetrical siloxane **2** after 0.5 h (Scheme 3) and free triphenylphosphine as a result of decoordination of the starting ruthenium–silyl complex **1**. As in the previously reported reaction of a ruthenium–silyl complex with silylacetylene,³ ^1H NMR examination confirmed the formation of a complex containing the Ru–H bond (dt signals at -5.43 ppm). Although only trace amounts of the ruthenium–hydride complex were observed by ^1H NMR spectroscopy in this stoichiometric test, the above experiment provides convincing evidence for the oxidative addition of the silanol into the Ru–Si bond. The proposed mechanism (omitting the competitive vinylsilane homo-coupling process) is given in Scheme 4.

In conclusion, we have developed a new catalytic route for efficient O-silylation of silanols with vinylsilanes, in which vinylsilane acts as a silylating agent and hydrogen acceptor to form a disiloxane bond with the evolution of ethylene. Further application of this protocol to the synthesis of polysiloxanes as well as hydrophobization of silica surfaces is currently under study.

Acknowledgement

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- Representative experimental procedure*: The glass reactor was charged under argon with dry and deoxygenated silanol (5×10^{-4} mol), vinylsilane (5×10^{-4} – 2×10^{-3} mol), toluene (1 mL) and $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ (1×10^{-5} mol) under the conditions given in Table 1. The reactor was sealed and reaction mixture was heated at 120 °C for 24–48 h. When vinyl dimethyl-phenylsilane was used as the silylating agent, the reaction occurs at 110 °C in an open system under a flow of argon. After the silanol disappearance was confirmed by GC, the solvent was removed, and the crude product was purified by column chromatography (silica gel/hexane) to give the corresponding siloxane.
- Spectroscopic data of selected products: *1,1,1,5,5-Pentamethyl-5-phenyl-3,3-bis(trimethylsiloxy)-trisiloxane* (Table 1, entry 1). ^1H NMR (300 MHz, CDCl_3) δ (ppm): 0.09 (s, 27H, SiCH_3), 0.30 (s, 6H, SiCH_3), 7.21–7.24 (m, 3H, Ph), 7.55–7.60 (m, 2H, Ph). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 0.4 (SiCH_3), 2.2 (SiCH_3), 128.1, 128.3, 129.7, 133.4, (Ph). MS (EI) m/z : 431 (M^+ –15, 50%), 369 (15), 343 (50), 327 (50), 281 (100), 266 (10), 250 (10), 250 (10), 208 (10), 135 (25), 73 (35). Anal. Calcd for $\text{C}_{17}\text{H}_{38}\text{O}_4\text{Si}_5$: C, 45.69; H, 8.57. Found: C, 45.46; H, 8.75.
- 1,1,1-Trisopropyl-3,3,3-trimethyldisiloxane* (Table 1, entry 6). ^1H NMR (300 MHz, CDCl_3) δ (ppm): 0.09 (s, 9H, SiCH_3), 0.92 (m, 21H, $\text{SiCH}(\text{CH}_3)_2$). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 0.4 (SiCH_3), 12.9 ($\text{SiCH}(\text{CH}_3)_2$), 18.2 ($\text{SiCH}(\text{CH}_3)_2$). MS (EI) m/z : 246 (M^+ , 2%), 231 (80), 203 (85), 189 (25), 175 (20), 161 (100), 147 (35), 133 (80), 119 (50), 103 (15), 73 (45). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{OSi}_2$: C, 58.46; H, 12.27. Found: C, 58.71; H, 12.39.
- 1,1-Diethoxy-1,5,5,5-tetramethyl-3,3-bis(trimethylsiloxy)-trisiloxane* (Table 1, entry 9). ^1H NMR (300 MHz, CDCl_3) δ (ppm): 0.11 (s, 30H, SiCH_3), 1.20 (t, 6H, $J = 7$ Hz, OCH_2CH_3), 3.80 (q, 4H, $J = 7$ Hz, OCH_2CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): -5.4 (SiCH_3), 1.6 (OSiCH_3), 18.3 (OCH_2CH_3), 58.0 (OCH_2CH_3) MS (EI)

- m/z*: 429 ($M^+ - 15$, 25%), 399 (30), 342 (100), 325 (45), 267 (20), 73 (75). Anal. Calcd for $C_{14}H_{40}O_6Si_5$: C, 37.80; H, 9.06. Found: C, 37.92; H, 9.19.
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15. In an NMR tube, 0.01 g (1.2×10^{-5} mol) of $Ru(SiMe_2Ph)(Cl)(CO)(PPh_3)_2$, dodecane (internal standard) and 0.5 mL of C_6D_6 were placed under argon. Next, 3.7 mg (1.2×10^{-5} mol) of tris(trimethylsiloxy)silanol was added and the reaction was monitored by 1H NMR and GCMS at room temperature.