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Ruthenium-catalyzed dealkenative *N*-silylation of amines by substituted vinylsilanes

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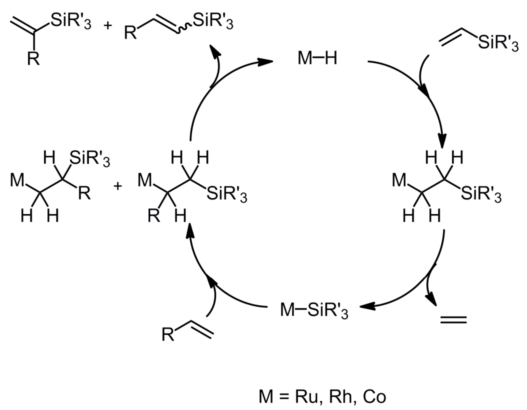
The ruthenium hydride complex-catalyzed *N*-silylation of primary and secondary amines with substituted vinylsilanes of the general formula $R^1CH{=}CHSiR'_3$ (where R^1 = H, Ph, *n*-Bu, $Si(OEt)_3$) leading to formation of Si-N bond with evolution of olefin is described. Vinylsilane acts as a silylative reagent and hydrogen acceptor. Under optimum conditions, the reaction offers an attractive route for the synthesis of silylamines. Preliminary mechanistic view of this novel general silylation reaction based on catalytic and deuterium labeling experiments using NMR and GC-MS methods confirm the synthetic observations.

Introduction

In the last decades we have developed a new type of TM-catalyzed reaction of vinyl-substituted organosilicon compounds with a variety of olefins, called the silylative coupling (SC) which proceeds through the activation of the =C-H bond of olefins and =C-Si bond of organosilicon compounds, occurring in the presence of complexes containing M-H and M-Si bonds (Scheme 1) (for review see 1,2)



Scheme 1 Silylative coupling of olefins with vinylsilanes

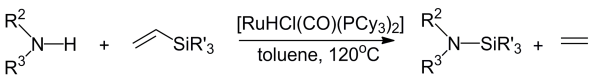
The silylative coupling of olefins with vinyl-substituted organosilicon compounds has been recently successfully extended to catalytic activation of other sp^2 carbons i.e. $=C_{aryl}$-H bonds[3] and sp-hybridized carbon-hydrogen bonds[4] as well as the O-H bonds of silanols,[5] alcohols[6] and boronic acids.[7]
The mechanism of this new general reaction in which vinyl metalloid compounds act as metalation agents and hydrogen acceptors to involve the insertion of a vinyl metalloid compound into the TM-H bond (where TM = Ru, Rh, Ir or Co) and *β*-metalloid transfer to the transition metal with elimination of ethylene and generation of a TM-E (E = Si, Ge, B) bond. In the next step, migratory insertion of a coupling substrate (alkene, alkyne) into the TM-E bond or oxidative addition of a compound containing an -OH group followed by *β*-hydride transfer to the metal (or reductive elimination) eliminates the metalated product.[1,2]
In view of our recent reports on the successful use of vinylsilanes as new hydrogen acceptors for the *O*-silylation of silanols,[5a] the aim of this work was to explore the reactivity of vinylsilanes in catalytic coupling with amines leading to formation of Si-N bond, which can be useful in the synthesis of silylamines as well as in silylation strategy of organometallic materials.
Silylamines are important silicon compounds that have been used as silylating and coupling agents, ligands

for organometallic compounds and precursors for ceramic materials.[8] Conventional approach to silylamines involves reaction of chlorosilanes with amines proceeding with elimination of stoichiometric amounts of HCl.[9] Catalytic dehydrocoupling of amines and hydrosilanes offers a complementary synthetic approach to Si-N bond formation. Several catalytic systems including transition metal carbonyls,[10] early transition metals,[11] f-element complexes,[12] magnesium complexes,[13] tethered ruthenium complex[14] and the metal-free $B(C_6F_5)_3$[15] have been successfully employed for catalytic Si–N coupling reactions. However, the control of selectivity for Si–N coupling has proved to be problematic because the reactions can lead to oligomeric derivatives of silazanes. Moreover, some of these processes are restricted by the necessity of removal of corrosive or explosive stoichiometric by-products and by the instability of silicon substrates toward moisture. On the other hand, Yi and co-workers in their studies on dehydrogenative coupling of amines with alkenes observed catalytic activation of N-H bond of cyclic amines (pyrrolidine and azepane) by vinyltriethoxysilane (used in 10 - fold excess) to give *N*-silylation products.[16]

Here, we present a general catalytic coupling reaction that involves activation of the N-H bond in primary and secondary amines by vinylsilanes, proceeding in the presence of ruthenium-hydride catalyst, yielding silylamines with elimination of olefins. The *N*-silylation of amines by vinylsilanes with the formation of the olefin as a single by-product could be very attractive since the starting materials for this process are often commercially available and inexpensive. The volatile alkene can be easily removed from the reaction mixture.

Results and discussion

The silylation reaction was examined in the presence of $[RuHCl(CO)(PCy_3)_2]$ **1** (3-5 mol%), which is well-known to be active in silylative coupling of vinylsilanes with olefins and activation of O-H bonds in silanols,[5] in an open or closed (Schlenk bomb flask fitted with a plug valve) systems in toluene (100-120°C), under argon atmosphere (Scheme 2). At first, we investigated the reaction of $(n\text{-Bu})_2NH$ and vinyltriethoxysilane as reagents. After several attempts we found that the reaction of equimolar amounts of $(n\text{-Bu})_2NH$ and vinyltriethoxysilane in the presence of 3 mol% of **1** performed in toluene in a closed system at 120°C afforded selectively *N*-silylation product (AS) after 24h (Table 1, entry 1). The formation of ethylene was observed by ^1H NMR analysis. The competitive *homo*-coupling of vinyltriethoxysilane (HC) brought only a slight contribution (1%) under these conditions.



Scheme 2 *N*-silylation of amines by vinylsilanes (AS)

Table 1 Catalytic *N*-silylation of amines by vinylsilanes

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Entry	Amine	SiR'_3	Time [h]	AS\HC [%]	Yield[a] AS (isolated) %
1	$(n\text{-Bu})_2NH$	$Si(OEt)_3$	24	99/1	95 (90)
2		$SiMe(OEt)_2$	72	99/1	95
3		$Si(OMe)_3$	24	99/1	90 (86)
4		$Si(OSiMe_3)_3$	72	43/57	38
5		$SiMe(OSiMe_3)_2$	72	68/32	65
6		$SiMe_3$	24	79/21	75
7		$C_{30}H_{69}O_{13}Si_9$•	48	100/0	100 (91)
8		$C_{28}H_{63}O_{12}Si_8$•	48	100/0	100 (92)
9	Et_2NH	$Si(OEt)_3$	36	93/7	82 (78)
10		$Si(OMe)_3$	36	99/1	90
11	piperidine	$Si(OEt)_3$	36	95/5	88
12	C_6H_5NHEt	$Si(OEt)_3$	60	90/10	88
13	carbazole	$Si(OEt)_3$	140	90/10	48[b]
14	$C_6H_5NH_2$	$Si(OEt)_3$	60	94/6	90
15		$Si(OMe)_3$	60	99/1	92 (87)
16		$SiMe_3$	36	93/7	89
17		$SiMe_2Ph$	56	62/38	57
18	$i\text{-PrNH}_2$	$Si(OEt)_3$	24	93/7	93 (80)
19		$Si(OMe)_3$	26	99/1	89
20	$t\text{-Bu-NH}_2$	$Si(OEt)_3$	36	90/10	62 (56)
21	2-ethylhexylamine	$Si(OEt)_3$	36	93/7	90

Reaction conditions: [amine]:[CH2=CHSiR`3] = 1;1, toluene, 120°C. Catalyst **1** loading 3 mol% (entry 1-3, 6, 9-11) and 5 mol% (entry 4, 5, 7, 8, 12-21);
[a] calculated by GC-MS, [b] 60% conversion of carbazole

The optimum reaction conditions were applied to other secondary amines (Table 1, entry 9-13). Many reactions examined with vinyltriethoxysilane proceeded within 36h in good yield to give *N*-silylated amines accompanied only by small amounts of bis(silyl)ethene isomers (1-10%). However, for *N*-ethylaniline and carbazole the reaction required a longer time (60-140h) and higher catalyst loading (5 mol%) to achieve a full conversion of vinyltriethoxysilane (Table 1, entry 12-13). We found that *N*-silylation occurred efficiently also when primary aliphatic or aromatic amines were applied

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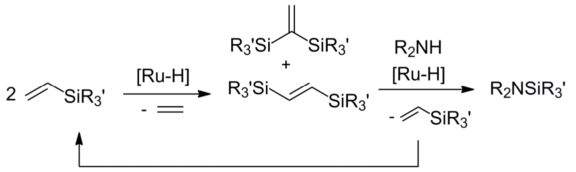
as coupling substrates (Table 1, entry 14-19). The reactions with primary amines proceeded selectively to give monosilylated products $RHNSi(OEt)_3$, while the formation of bis(silyl)amine was not observed under the conditions applied. Selected products were isolated and characterized spectroscopically. Other vinylsilanes were also tested as potential silylating agents for the synthesis of *N*-silylamines. Vinyltrimethylsilane and simple vinylsiloxanes showed a similar reactivity in the silylation of secondary amines as vinyltrialkoxysilanes, however, the reactions occurred with lower selectivity (Table 1, entry 4-6). The lower selectivity in the reaction with vinylsiloxanes is caused by their competitive *homo*-coupling, which produces the significant amounts of geminal bis(siloxy)ethenes.[17] Reaction of mono-vinylsilsesquioxane (Si_8O_{12}(*i*-Bu)$_7$($CH=CH_2$)) and monovinyl-spherosilicate (Si_8O_{12}(*i*-Bu)$_7$($OSiMe_2CH=CH_2$)) with $(Bu)_2NH$ proceeded with higher selectivity to give exclusively silylamine derivatives (Table 1, entry 7-8).

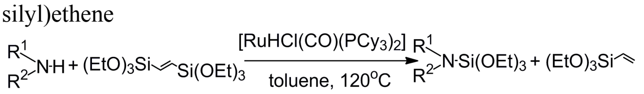
Detailed monitoring of the reaction progress (using GC-MS method) revealed that in the first stage of the process only *homo*-coupling of vinylsilane occurred to give isomeric bis(silyl)ethenes (*E/gem* > 9/1). The obtained *(E)*-1,2-bis(silyl)-ethene is then reacted readily with an amine to yield silylamine and vinylsilane, which in the presence of ruthenium-hydride catalyst was reconverted to bis(silyl)ethene, whereas geminal isomer of bis(silyl)ethene was unreactive under these conditions (Scheme 3).



Scheme 3 Consecutive silylative homo-coupling (HC) and *N*-silylation of amines by vinylsilanes (AS).

This phenomenon was confirmed in the catalytic reaction of $(n\text{-}Bu)_2NH$ with *(E)*-1,2-bis(triethoxysilyl)ethene. We found that the reaction proceeded faster (17h) with a full conversion of *(E)*-1,2-bis(triethoxysilyl)ethene and the identified silicon-containing by-product was a geminal bis(silyl)ethene.

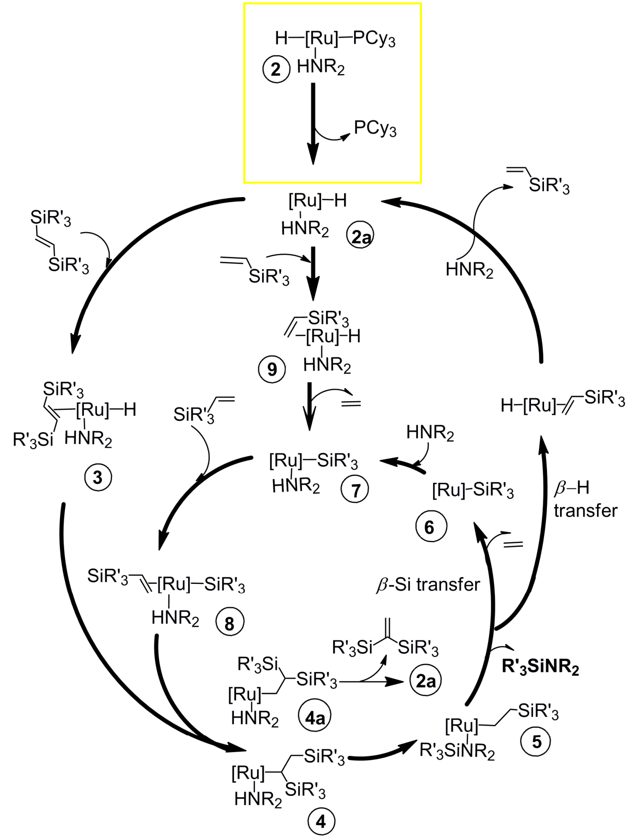
Table 2 Catalytic *N*-silylation of amines by 1,2-bis(triethoxy-silyl)ethene



Entry	Amine	Time [h]	Yield [%][a]
1	$(n\text{-}Bu)_2NH$	17	88
2	Et_2NH	24	86
3	piperidine	24	88
4	C_6H_5NHEt	48	90
5	$C_6H_5NH_2$	48	95
6	$i\text{-}PrNH_2$	17	94
7	$t\text{-}BuNH_2$	24	92

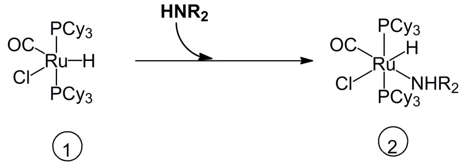
Reaction conditions:[amine]:[$(EtO)_3SiCH=CHSi(OEt)_3$]:[**1**] = 2:1:0.05, toluene, 120°C; [a] calculated by GC-MS

All the catalytic measurements performed were followed by stoichiometric study of complex **1** with substrates using NMR and GC-MS methods to gain mechanistic insights into the catalytic reaction. The proposed mechanism is given in Scheme 4.



Scheme 4 Proposed mechanism of *N*-silylation of amines with vinylsilanes and bis(silyl)ethenes.

The reaction of Et_2NH with *(E)*-1,2-bis(triethoxysilyl)ethene in the presence of 10 mol% of complex $[RuHCl(CO)(PCy_3)_2]$ **1** in toluene-d_8 was monitored by ^1H NMR analysis. Addition of amine (20 equiv. of Et_2NH to 1 equiv. of **1**; room temperature) to the reaction mixture caused the disappearance of the signal at -24.30 ppm, originating from the ruthenium-hydride complex **1,** after only 5 minutes, the color of the reaction mixture changed from pale-yellow to yellow greenish and formation of new ruthenium-hydride peak at -17.29 ppm (t, JPH = 19.1 Hz) was detected by ^{1}H NMR. The peak was assigned to hexacoordinated ruthenium-hydride complex containing diethylamine as a ligand (Scheme 5, complex **2**). After 12h we observed the formation of the second triplet at -17.52 ppm (t, JPH = 18.7 Hz). The peaks were assigned to isomeric hexacoordinated ruthenium-hydride complex containing Et_2NH as a ligand.



Scheme 5 Generation of ruthenium amine hydride complex 2

Addition of 10 equiv. of *(E)*-1,2-bis(triethoxysilyl)ethene and heating at 120°C in an NMR Young tube led to dissociation of cyclohexylphosphine from **2** observed by ^{31}P NMR. Further heating caused a gradual disappearance of the signals of ruthenium amine hydride complexes and after 8h both substrates were consumed and the original signal at -24.30 ppm (t, JPH = 18.2 Hz), characteristic of complex **1**, was regenerated (see supporting information). The formation of the coupling product: $Et_2NSi(OEt)_3$ and ethylene as well as $CH_2{=}CHSi(OEt)_3$ was observed by using ^{1}H NMR (see Scheme 4). The formation of complex **3** occurs via fast coordination of bis(silyl)ethene into pentacoordinated complex **2a.** Complex **3** with coordinated bis(silyl)ethene, initiates the new catalytic reaction via subsequent insertion of olefin into the Ru-H bond (complex **4**) followed by transfer of silyl group to coordinated amine with a simultaneous transfer of hydrogen from amine to *α*-carbon of ligand coordinated to ruthenium atom (Scheme 4) giving a new complex **5**. It is likely that the transfer **4** > **5** occurs with a σ-bond metathesis reaction. ^{1}H NMR analysis of the reaction of complex **1**, *(E)*-1,2-bis(triethoxysilyl)ethene and deuterated diethylamine Et_2ND proved the presence of deuterated vinyltriethoxysilane in the reaction mixture, which confirmed the transfer of deuterium from the nitrogen atom to the *α*-carbon atom (see supporting information). According to the mechanism of silylative coupling[1,2] also complex **4a** can be formed, in which both silyl groups are attached to the *β*-carbon of coordinated ligand. The *β*-H transfer of complex **4a** yields geminal isomer of bis(silyl)ethene which is unreactive under these conditions (see Scheme 3) and leads to regeneration of complex **2a** (silyl-transfer to nitrogen is prevented because both silyl groups are in the *β*-position of ligand coordinated to ruthenium atom). Complex **5** can undergo both *β*-H and *β*-Si transfer. The *β*-H transfer yields finally a terminal vinylsilane which is observed during reaction with bis(silyl)ethene and can be a substrate for its homo-coupling. The *β*-Si transfer from complex **5** leads to formation of complex **6** with evolution of ethylene followed by coordination of amine (complex **7**) and in the presence of vinylsilane leads to formation of complex **8** which can be formed via a direct homo-coupling of terminal vinylsilanes, according to a well-known mechanism of vinylsilane homo-coupling.[1,2] Finally, complex **8** led to direct formation of complex **4** and/or **4a**.

An experiment confirming the regeneration of ruthenium-hydride complex **1** upon heating of the reaction mixture at 120°C for 4h was carried out with the use of deuterated diethylamine Et_2ND (20 equiv.), *(E)*-1,2-bis(triethoxysilyl)-ethene (10 equiv.) and 1 equiv. of complex **1**. ^{1}H NMR analysis confirmed the evolution of deuterated ethylene (triplet 1:1:1 with a coupling constant 1.8 Hz, at 5.24 ppm) (Fig. 1a). Additionally in search of further evidence for the presence of deuterium in ethylene we run a ^{2}H NMR experiment using ^{2}H lockswich unit. This technique also confirmed incorporation of deuterium to the ethylene molecule (a peak at 5.27 ppm; see supporting information) (Fig. 1b).

1a 1b

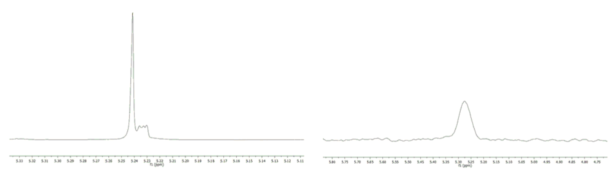
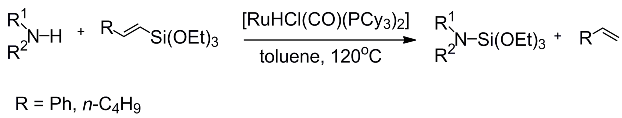


Fig. 1 a) ^{1}H NMR spectra of ethylene and deuterated ethylene b) ^{2}H NMR spectra of deuterated ethylene

In view of these experiments, an extension of the substrates to *(E)*-styryl(triethoxy)silane and (*E*)-1-hexenyl(triethoxy)-silane was performed to give high yields, indicating that the ruthenium-catalyzed *N*-silylation of amines is a general process and substituted vinylsilanes can be used in it as effective silylating agents (Table 3). GC-MS and ^{1}H NMR analysis of the *N*-silylation of Et_2NH by *(E)*-styryl(triethoxy)silane and (*E*)-1-hexenyl(triethoxy)-silane confirmed the presence of styrene or 1-hexene as a reaction product. The silylation reactions were examined in the presence of a ruthenium-hydride catalyst **1** (5 mol%), in toluene, at 120°C in a Schlenk bomb flask fitted with a plug valve under argon atmosphere. The results of catalytic tests on *N*-silylation reaction using *(E)*-styryl(triethoxy)silane and (*E*)-1-hexenyl(triethoxy)silane as silylating agents with selected primary and secondary amines are collected in Table 3.

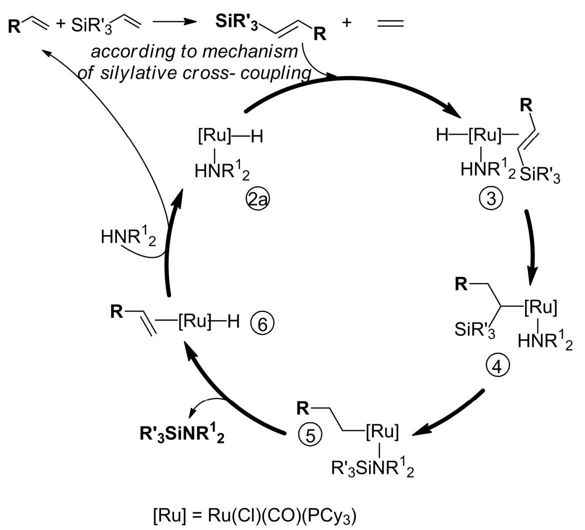
Table 3 Catalytic *N*-silylation of amines by substituted vinyltri-ethoxysilanes



Entry	R	Amine	Time [h]	Yield [%][a]
1	Ph	$(n\text{-Bu})_2NH$	24	90
2	$n\text{-}C_4H_9$		24	90
3	Ph	Et_2NH	24	92
4	$n\text{-}C_4H_9$		56	88
5	Ph	$i\text{-}PrNH_2$	36	95

Reaction conditions: [amine]:[RCH=CHSi(OEt)$_3$]:[1] = 1:1:0.05, toluene, 120^{o}C, [a] calculated by GC-MS

The transfer of deuterium from an amine to the olefin molecule was confirmed by the ^{1}H and ^{2}H NMR monitoring of the reaction of *(E)*-styryl(triethoxy)silane with Et_2ND (molar ratio 1:1) in the presence of 10 mol% **1** in which deuterated styrene was observed (peaks at 5.10 ppm and 5.6 ppm at ^{2}H NMR spectra) after heating the reaction mixture at 120°C for 48h. All the above catalytic and stoichiometric studies allow a generalization of the *N*-silylation reaction mechanism from terminal vinylsilanes to substituted vinylsilanes and permit proposing a general catalytic cycle of this novel reaction (Scheme 6).



Scheme 6 Proposed mechanism of *N*-silylation of amines with (*E*)-alkenyl(triethoxy)silanes

Conclusions

We have developed a catalytic route for the efficient *N*-silylation of aliphatic and aromatic primary and secondary amines with substituted vinylsilanes, in which vinylsilane acts as a silylating agent and hydrogen acceptor to form Si-N bond with evolution of olefin. It is our hope that this novel silylation reaction will provide useful insights into the future possibilities of this aspect of synthetic organic and organosilicon chemistry.

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Notes and references

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† See Supporting Information for experimental procedures and the ^{1}H, ^{13}C and ^{31}P NMR spectra.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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