

Hydroformylation and related reactions of vinylsilanes catalyzed by siloxide complexes of rhodium(I) and iridium(I)

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Abstract

Rhodium(I) and iridium(I) complexes of the formula [(cod)Rh(OSiMe₃)(PPh₃)] (**1**), [(cod)Rh(OSiMe₃)(PCy₃)] (**2**), [(cod)Rh(OSiMe₃)₂] (**3**), [(cod)Ir(OSiMe₃)(PCy₃)] (**4**), and [(cod)Ir(OSiMe₃)₂] (**5**), used as catalysts of hydroformylation of the vinylsilanes Me₃SiCH=CH₂, Me₂PhSiCH=CH₂, (MeO)₃SiCH=CH₂, and Me₂PhSiCH=CHPh at 80 °C and 10 atm of H₂/CO (H₂:CO = 1), produced aldehydes (*n* + iso) as the main products with yields of up to 100%. In the presence of the iridium complexes (**4**) and (**5**), some amounts of ethylsilanes, up to 40%, were obtained, besides aldehydes as a result of hydrogenation of the substrates. In the presence of the rhodium complexes (**1**) and (**2**), isomerization of iso-aldehydes to 1-siloxyprenes was observed under the reaction conditions. Under 10 atm of H₂, the rhodium complexes appeared to be very effective catalysts of vinylsilanes hydrogenation. The hydrogenation reaction products, in addition to ethylsilanes, also included products of homocoupling of vinylsilanes (hydrogenated and non-hydrogenated).

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1. Introduction

Silylaldehydes, potential building blocks for organic synthesis, can be synthesized by hydroformylation of vinylsilanes catalyzed by transition metal complexes [1]. This process has only scarcely been studied till now, and catalytic activity of some rhodium and iridium complexes has been reported [2–4]. Therefore, it was reasonable to search for new catalysts that would be easy to obtain and relatively stable to ensure high reaction selectivity towards aldehydes. Catalysts showing high activity in the presence of a small excess of free phosphorus ligands are, additionally, attractive as environmentally friendly catalytic systems. This paper presents the results of studies of Rh(I) and Ir(I) siloxide complexes used as catalysts in hydroformylation of vinylsilanes. The com-

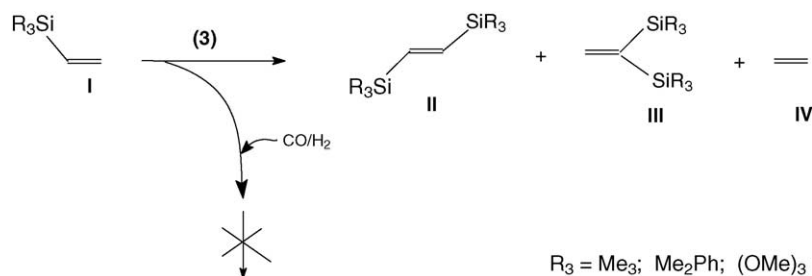
plexes had previously been tested as catalysts of vinylsilane disproportionation [5], silylative coupling [6,7], and hydrosilylation [8]. Their high catalytic activity, particularly in the silylative coupling reactions, warranted the expectation that they would also show significant activity in other reactions of vinylsilanes, especially the hydroformylation reaction. It is also important to recognize and understand the catalytic reactivity of siloxide complexes towards vinylsilanes in the presence of H₂/CO or H₂ and compare it with their previously studied reactivity in an N₂ atmosphere [9,10].

2. Results and discussion

2.1. Hydroformylation of vinylsilanes

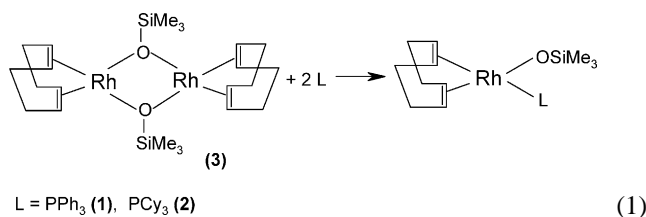
Rhodium(I) and iridium(I) complexes of the formula [(cod)Rh(OSiMe₃)(PPh₃)] (**1**), [(cod)Rh(OSiMe₃)(PCy₃)]

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Scheme 1.

(2), [(cod)Rh(OSiMe₃)₂] (3), [(cod)Ir(OSiMe₃)(PCy₃)] (4), and [(cod)Ir(OSiMe₃)₂] (5) were tested as catalysts in the hydroformylation of vinylsilanes, CH₂=CHSiR₃ (I) (R₃ = Me₃, Me₂Ph, and (MeO)₃). The complexes were used in the form of isolated compounds and only complex (1) was used as obtained in situ from stoichiometric amounts of substrates, i.e., the dimer (3) and PPh₃ ([PPh₃]:[Rh] = 1) (Eq. (1)).



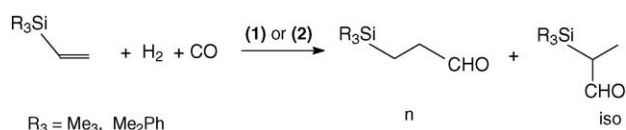
In our earlier studies complex (3) was found to be an active catalyst of vinylsilane disproportionation in which two molecules of bis(silyl)ethenes (II, III) and ethylene (IV) are produced from two molecules of vinylsilanes (Scheme 1) [5].

However, under the hydroformylation reaction conditions, in an H₂/CO atmosphere, the above reaction (Scheme 1) is totally restrained. In the presence of (3), none of the three vinylsilanes studied undergo disproportionation or hydroformylation. It can be explained as a result of total replacement of cod in complex (3) by CO and the formation of a less active, carbonyl complex.

The iridium complex (5), an analogue of the rhodium complex (3), is much more active and in the presence of H₂/CO (10 atm) produces 25–28% of aldehydes and 72–75% of ethylsilanes in a parallel hydrogenation reaction (Table 1). Total conversion of substrates, such as Me₃SiCH=CH₂ and Me₂PhSiCH=CH₂ with complex (5) was obtained after just 1 h of reaction. This is interesting because usually complexes without phosphorus ligands do not catalyze hydroformylation of olefins under such mild conditions.

A slight modification of the structure of complex (3) by inserting phosphine (PPh₃, PCy₃) into the coordination sphere of rhodium(I) to form the complexes [(cod)Rh(OSiMe₃)L] (L = PPh₃ (1), PCy₃ (2)) (Eq. (1)) results in the appearance of catalytic activity in the hydroformylation reaction.

The only products of hydroformylation of the vinylsilanes Me₃SiCH=CH₂ and Me₂PhSiCH=CH₂ with complexes (1)



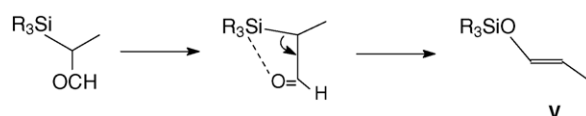
Scheme 2.

and (2), identified after ca. 1 h of reaction, when the conversion of the substrate was almost 100%, are *n*- and iso-aldehydes (Scheme 2) (Table 1). In the hydroformylation reaction products of Me₃SiCH=CH₂, the *n*/*iso* ratio is ca. 1.1 for both catalyst precursors, whereas in the hydroformylation of Me₂PhSiCH=CH₂ the yield of *n*-aldehyde is slightly higher, amounting to *n*/*iso* 1.7 (Table 1). The yield of *n*-aldehyde increases when free PPh₃ phosphine is added and at its four-fold excess relative to (1), the *n*/*iso* ratio is ca. 8 (Table 1).

Prolongation of the hydroformylation reaction time causes the appearance of new products, 1-siloxypropenes (R₃SiOCH=CHCH₃, V), as a result of rearrangement of branched aldehydes via 1,3-silicon shift from carbon to oxygen (Scheme 3) [11,12]. These compounds were identified in the reaction mixture by IR and ¹H NMR measurements. For quantitative analysis, particularly useful were ¹H NMR signals at δ = 4.6 and 6.2 ppm, derived from hydrogen atoms bounded to olefinic carbon atoms (Fig. 1). Over the reaction time, the intensity of those signals increased with a decrease in the signal at δ = 9.68 ppm assigned to the aldehyde group proton of branched aldehyde.

Conversion of branched aldehyde to 1-siloxypropene (V) was monitored by IR measurements, which revealed a decrease in the ν(CO) band at 1696 cm⁻¹ deriving from iso-aldehyde and the appearance of a ν(C=C) band at 1669 cm⁻¹ and ν(C–O) in the Si–O–C group at 1062 cm⁻¹, characteristic for 1-siloxypropene (Fig. 2).

Both in hydroformylation of Me₃SiCH=CH₂ as well as in Me₂PhSiCH=CH₂, 1-siloxypropenes were obtained with the yield higher for catalyst (1) than that for catalyst (2).



Scheme 3.

Table 1

The products of $R_3SiCH=CH_2$ ($R_3 = Me_3, Me_2Ph, (MeO)_3$) and $Me_2PhSiCH=CH_2$ hydroformylation catalyzed by $[(cod)Rh(OSiMe_3)(PPh_3)]$ (1), $[(cod)Rh(OSiMe_3)(PCy_3)]$ (2), $[(cod)Ir(PCy_3)(OSiMe_3)]$ (4), and $[(cod)Ir(OSiMe_3)_2]$ (5)

Catalyst	Reaction time (min)	Yield (%)			
		Aldehydes			
$R_3SiCH=CHR$		$R_3SiCH_2CHR'CHO$	$R_3SiCH(CH_2R')CHO$	$R_3SiOCH=CHCH_2R$	$R_3SiCH_2CH_2R$
Substrate: $R_3 = Me_3, R' = H$					
(1)	15	45	40	–	–
	30	48	51	–	–
	60	47	19	34	–
(2)	60	51	46	3	–
	120	51	38	9	–
(4)	60	16	3	–	10
	120	17	5	–	11
	270	38	12	–	44
(5)	60	14	11	0.3	75
Substrate: $R_3 = Me_2Ph, R' = H$					
(1)	30	52	29	–	–
	60	58	11	31	–
(1) + 2 PPh ₃	60	74	3	23	–
(1) + 4 PPh ₃	60	89	7	4	–
(2)	60	63	37	–	–
	120	61	34	4	–
(4)	120	28	4	–	25
	270	52	9	–	34
(5)	60	18	10	–	72
Substrate: $R_3 = (MeO)_3, R' = H$					
(1)	60	74	26	–	–
	60 ^a	16	14	–	–
	120 ^a	35	50	–	–
(2)	60	49	37	–	–
Substrate: $R_3 = Me_2Ph, R' = Ph$					
(2)	120	36	10	1.3	–
	240 ^b	72	24	4	–

Reaction conditions: 80 °C.

^a 60 °C, 10 atm H₂/CO (1:1), [Rh], [Ir] = 6.7×10^{-3} M, [R₃SiCH=CH₂]:[Rh] = 390.

^b The reaction was carried out with only half of reagents normally used.

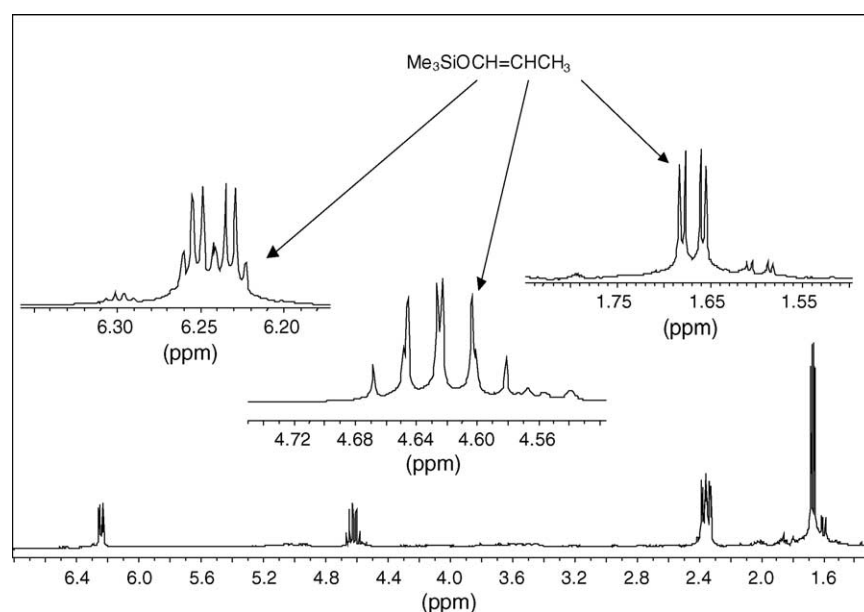


Fig. 1. ¹H NMR spectrum of $Me_3SiOCH=CHCH_3$ in the post-reaction mixture after hydroformylation of $Me_3SiCH=CH_2$ with (1).

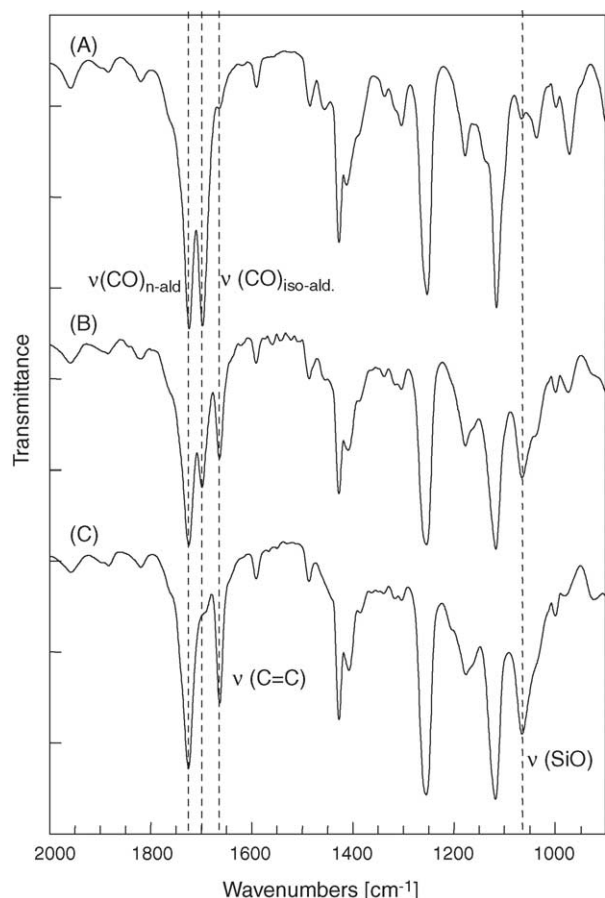


Fig. 2. IR spectra measured during isomerization reaction of $\text{Me}_3\text{SiCH}(\text{CH}_3)\text{CHO}$ at presence of $[(\text{cod})\text{Rh}(\text{OSiMe}_3)(\text{PCy}_3)]$ (**2**) complex in N_2 atmosphere, 80°C . (A) $t = 0$ min (the spectrum of post-hydroformylation reaction mixture); (B) $t = 20$ min; (C) $t = 50$ min. $\nu(\text{C}=\text{O})$ $1725, 1696\text{ cm}^{-1}$, $\nu(\text{C}=\text{C})$ 1668 cm^{-1} , $\nu(\text{Si}-\text{O})$ 1062 cm^{-1} .

This warrants the assumption that the isomerization reaction proceeds with the participation of the rhodium(I) complex and is not only thermally initiated. This is also confirmed by the lack of 1-siloxyprenes in the products of reactions catalyzed by the iridium(I) complexes (**4**) and (**5**).

It was interesting to find that the formation of 1-siloxyprenes was also observed in the presence of free PPh_3 (Table 1).

To better understand the process of 1-siloxyprene formation in the reaction under studies, the experiments were conducted in N_2 instead of an H_2/CO atmosphere. The mixtures containing ($n + \text{iso}$) aldehydes, obtained in the hydroformylation of $\text{Me}_2\text{PhSiCH}=\text{CH}_2$ catalyzed by (**1**), (**2**), and $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ during 15–30 min, were used as the iso-aldehyde source for isomerization. After that time the cooled-down autoclave was degassed, then filled with N_2 (1 atm) and warmed up. Samples for analysis were collected every 20 min. The results of ^1H NMR analysis shown in Table 2 suggest that a decrease in the branched aldehyde amount is accompanied by the appearance of the same amount of 1-dimethylphenylsiloxyprene ($\text{Me}_2\text{PhSiOCH}=\text{CHCH}_3$). It is worth noting that as previously (Table 1), the yield of 1-dimethylphenylsiloxyprene is highest in reaction with complex (**1**) (36%), which is equivalent to the total conversion of branched aldehyde (Scheme 3). Total conversion of $\text{Me}_2\text{PhSiCH}(\text{CHO})\text{CH}_3$ was also obtained in reaction catalyzed by $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ (23%). However, during a comparable reaction time (50 min), in reaction catalyzed by complex (**2**), 24% of $\text{Me}_2\text{PhSiOCH}=\text{CHCH}_3$ was obtained, which corresponds to the conversion of 57% of branched aldehyde used for the reaction. The obtained yield is higher than that obtained in reactions conducted in an H_2/CO atmosphere (Table 1). It is worth noting that other authors have not observed

Table 2

The yield of 1-siloxyprenes ($\text{R}_3\text{SiOCH}=\text{CHCH}_3$) formed by isomerization of iso-aldehydes obtained in hydroformylation of $\text{Me}_2\text{SiCH}=\text{CH}_2$ and $\text{Me}_2\text{PhSiCH}=\text{CH}_2$ catalyzed by $[(\text{cod})\text{Rh}(\text{OSiMe}_3)(\text{PPh}_3)]$ (**1**), $[(\text{cod})\text{Rh}(\text{OSiMe}_3)(\text{PCy}_3)]$ (**2**), and $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$

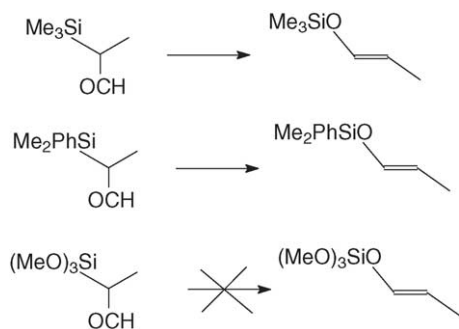
Catalyst	Reaction time (min)	Yield (%)		
		Aldehydes		$\text{R}_3\text{SiOCH}=\text{CHCH}_3$
		$\text{R}_3\text{SiCH}_2\text{CH}_2\text{CHO}$	$\text{R}_3\text{SiCH}(\text{CH}_3)\text{CHO}$	
Substrate: $\text{Me}_3\text{SiCH}=\text{CH}_2$				
(1)	0 ^a	49	50	–
	20	49	8	41
	40	49	6	45
	60	50	–	50
Substrate: $\text{Me}_2\text{PhSiCH}=\text{CH}_2$				
(1)	0 ^b	56	36	–
	50	56	–	36
(2)	0 ^a	58	42	–
	40	58	18	24
$[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$	0 ^c	77	21	2
	50	77	–	23

Reaction conditions: 80°C , 1 atm N_2 .

^a The reaction mixture obtained in hydroformylation reaction carried out at 80°C , 10 atm H_2/CO (1:1) during –30 min.

^b The reaction mixture obtained in hydroformylation reaction carried out at 80°C , 10 atm H_2/CO (1:1) during –15 min.

^c The reaction mixture obtained in hydroformylation reaction carried out at 80°C , 10 atm H_2/CO (1:1) during –20 min.



Scheme 4.

the formation of 1-trimethylsiloxypropene in hydroformylation reaction of $\text{Me}_3\text{SiCH}=\text{CH}_2$ catalyzed by different rhodium complexes, including by $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ [3]. Small amounts of the iso-aldehyde transformation product have been reported in hydroformylation reaction of $\text{Et}_3\text{SiCH}=\text{CH}_2$ [2]. Our results show that branched aldehydes undergo transformation to 1-siloxypropenes in reactions catalyzed by the rhodium-siloxide complexes (1) and (2). Higher catalytic activity was found for catalyst (1), which coordinates the less basic and less bulky PPh_3 ligand compared with PCy_3 coordinated in (2).

In contrast to the rhodium complexes, the iridium complexes, (4) and (5), do not catalyze transformation of branched aldehydes, and 1-siloxypropene was not observed even after 270 min of reaction catalyzed by (4) (Table 1). However, it is worth noting that in hydroformylation of $\text{Me}_3\text{SiCH}=\text{CH}_2$ and $\text{Me}_2\text{PhSiCH}=\text{CH}_2$ catalyzed by (4), high values of the n/iso ratio were found from 5.3 to 3.2 and 7.0 to 5.8, respectively (Table 1). In both cases, the n/iso ratio decreased as substrate conversion increased. Under the hydroformylation reaction conditions, the iridium complexes (4) and (5) are active also in hydrogenation of the substrates, leading to the formation of ethylvinylsilanes (34–44%) (Table 1).

As could be expected, hydroformylation of $(\text{MeO})_3\text{SiCH}=\text{CH}_2$ leads to the formation of two main products: 2-trimethoxysilylpropanal and 3-trimethoxysilylpropanal (Table 1), characterized by ^1H NMR signals at 9.77 and 9.71 ppm. Besides those two ^1H NMR signals, a triplet of much lower intensity at 9.72 ppm ($J = 1.3$ Hz) was detected and assigned to unidentified n -aldehyde.

Both catalysts, (1) and (2), made possible a total conversion of the substrate to aldehydes within 1 h. However, when the reaction time was prolonged to 2 h, poorly resolved multiplets at ca. 9.5–9.8 ppm were found in the ^1H NMR spectrum, suggesting the appearance of new aldehydes. Because of the poor quality of the ^1H NMR spectra, these reaction products were not characterized. It may, however, be concluded from the ^1H NMR spectra that 2-trimethoxysilylpropanal does not undergo transformation in contrast to 2-trimethylsilylpropanal and 2-dimethylphenylsilylpropanal (Scheme 4).

Hydroformylation of a silane with an internal double bond, $\text{Me}_2\text{PhSiCH}=\text{CHPh}$, catalyzed by complex (2), was also studied. As expected, the reaction was slower in comparison with that of vinylsilanes, $\text{R}_3\text{SiCH}=\text{CH}_2$, but total conversion of the substrate to two aldehydes, $\text{Me}_2\text{PhSiCH}_2\text{CH}(\text{Ph})\text{CHO}$ (main product) and $\text{Me}_2\text{PhSiCH}(\text{CHO})\text{CH}_2\text{Ph}$, was observed after 4 h (Table 1).

The interactions of Rh-siloxide complexes with CO, very important for the hydroformylation process, were studied using IR spectroscopy. When (3) was heated for 2 h at 80°C under 10 atm of CO, a brown precipitate was formed which presented two strong $\nu(\text{CO})$ bands at 1805 and 2073 cm^{-1} , characteristic for bridging and terminal carbonyl groups, respectively. The spectrum, very similar to that of $\text{Rh}_6(\text{CO})_{16}$, suggested the reduction of Rh(I) to Rh(0) with simultaneous elimination of the siloxide ligand from the coordination sphere. Quite different reactivity was observed for complex (1), which after reaction with CO still contains $-\text{OSiMe}_3$ ligands, as confirmed by the presence of $\nu(\text{SiO})$ at 1040 cm^{-1} . In the region of terminal $\nu(\text{CO})$ groups, four bands were observed at 1944, 1993, 2039, and 2069 cm^{-1} and one bridging $\nu(\text{CO})$ frequency at 1800 cm^{-1} . Complex (1) reacts with CO forming a mixture of Rh-siloxide-carbonyl complexes, which are probably responsible for observed catalytic activity.

2.2. Hydrogenation of vinylsilanes

Complexes (1), (2), and (3) were tested as catalysts of hydrogenation reaction of vinylsilanes at 80°C and 10 atm of H_2 . Under such conditions, all of the complexes that were used catalyzed the reaction, and its main product were ethylsilanes (R_3SiEt ; $\text{R} = \text{Me}_3, \text{Me}_2\text{Ph}, (\text{MeO})_3$) (Scheme 5).

The highest yields of ethylsilane, from 72 to 90%, were found in the hydrogenation reaction of $(\text{MeO})_3\text{SiCH}=\text{CH}_2$. In the two remaining reactions, the yields were ca. 60%. GC-MS analysis of the reaction product mixture led to the identification of four other compounds (Table 3) in the liquid phase and ethane in the gas phase. The results of the analysis made it possible to design the reaction scheme (Scheme 5) according to which, both reactions disproportionation as well as hydrogenation of vinylsilanes, take place in an H_2 atmosphere.

Not only the substrate (vinylsilane I) but also both the unsaturated disproportionation reaction products (bis(silyl)ethenes II, III) and ethylene (IV) undergo hydrogenation to saturated final products (I-H, II-H, III-H, and IV-H). The composition of the reaction products depends on the rate of particular partial reactions. A total amount of 20–28% of unsaturated products (II + III) was obtained in reaction of $\text{Me}_2\text{PhSiCH}=\text{CH}_2$, whereas only 1% was obtained from $(\text{MeO})_3\text{SiCH}=\text{CH}_2$ as the reaction substrate. It is interesting to conclude that in the gas phase of all the reactions studied only ethane was found. This warrants the claim that all the catalysts used are very effective in ethylene hydrogenation.

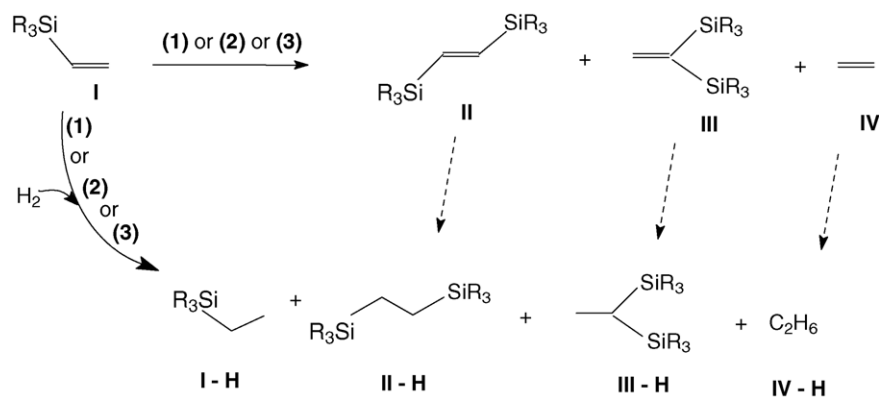


Table 3
The hydrogenation reaction products of $\text{Me}_3\text{SiCH}=\text{CH}_2$, $\text{Me}_2\text{PhSiCH}=\text{CH}_2$, and $(\text{MeO})_3\text{SiCH}=\text{CH}_2$

Catalyst	Yield (%)				
	$\text{R}_3\text{SiEt, I-H}$	$\text{R}_3\text{SiCH}=\text{CHSiR}_3, \text{II}$	$\text{CH}_2=\text{C}(\text{SiR}_3)_2, \text{III}$	$\text{R}_3\text{Si}(\text{CH}_2)_2\text{SiR}_3, \text{II-H}$	$\text{CH}_3\text{CH}(\text{SiR}_3)_2, \text{III-H}$
Substrate: $\text{Me}_3\text{SiCH}=\text{CH}_2$					
(1)	76	–	–	14	10
(2)	55	2	–	23	20
(3)	53	10	14	18	7
Substrate: $\text{Me}_2\text{PhSiCH}=\text{CH}_2$					
(1)	65	13	13	8	2
(2)	60	10	10	12	8
(3)	51	15	23	9	2
(3) ^a	52	18	19	9	2
Substrate: $(\text{MeO})_3\text{SiCH}=\text{CH}_2$					
(1)	90	–	–	9	1
(2)	82	1	–	12	4
(3)	72	–	–	21	7

Reaction conditions: 80 °C, 10 atm., 1.5 h. In all reactions under study, ethane was found in solution as well as in gas-phase; the products abbreviations are as in Scheme 4.

^a 40 min, $[\text{Rh}] = 6.7 \times 10^{-3}$ M, $[\text{R}_3\text{SiCH}=\text{CH}_2]:[\text{Rh}] = 390$.

3. Conclusions

- It was experimentally proved that the catalytic activity of both rhodium(I) (1, 2, 3) and iridium(I) (4, 5) complexes containing siloxide ligands in reactions with vinylsilanes depends on the reaction conditions.
- In the presence of the rhodium(I) complexes (1), (2), and (3) in an H_2 atmosphere, vinylsilanes undergo both disproportionation (like in an N_2 atmosphere) as well as hydrogenation (Scheme 5).
- Under a CO/H_2 atmosphere, only hydroformylation reaction takes place with rhodium complexes, whereas disproportionation and hydrogenation are totally restrained. This is probably caused by the inhibiting effect of CO coordinated to rhodium and the formation of an inactive carbonyl complex.
- The iridium complexes (4) and (5) in a CO/H_2 atmosphere catalyze both hydroformylation and hydrogenation of vinylsilanes.

4. Experimental

Rhodium(I) complexes: $[(\text{cod})\text{Rh}(\text{OSiMe}_3)_2]$ (3) [13], $[(\text{cod})\text{Rh}(\text{OSiMe}_3)(\text{PCy}_3)]$ (2) [14], $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ [15] as well as iridium(I) complexes: $[(\text{cod})\text{Ir}(\text{OSiMe}_3)_2]$ (5), $[(\text{cod})\text{Ir}(\text{OSiMe}_3)(\text{PCy}_3)]$ (4) [16] were obtained as described in literature. Rhodium(I) complex of formula $[(\text{cod})\text{Rh}(\text{OSiMe}_3)(\text{PPh}_3)]$ (1) was obtained in situ during hydroformylation reaction catalyzed by complex (3) and free PPh_3 ($[\text{PPh}_3]:[\text{Rh}]$ ratio equal to 1).

4.1. Procedures of hydroformylation and hydrogenation of vinylsilanes

Hydroformylation of vinylsilanes was carried out in a thermostated steel autoclave (40 cm^3) with a magnetic stirrer. Reagents were introduced into the autoclave in an N_2 atmosphere.

The catalyst (2×10^{-5} mol) was introduced in a small teflon vessel. Vinylsilane and the solvent (benzene or toluene)

were added in amounts suitable to get a total volume of the solution amounting to 3 cm³ ([silane]/[Rh] = 390). In reactions of (MeO)₃SiCH=CH₂, dioxane was used as an internal standard for ¹H NMR measurements. After the reagents were introduced, the autoclave was twice filled and emptied with H₂ and then filled with a mixture of CO/H₂ (CO:H₂ = 1) to 10 atm. After the reaction was finished, the autoclave was cooled down, then opened, and the samples were taken for ¹H NMR analysis. The amounts of the reaction products: *n*- and iso-aldehydes, 1-siloxypropenes, and ethylsilanes were determined from ¹H NMR spectra.

The hydrogenation reaction procedure was similar to that applied for hydroformylation, except that the autoclave was filled with H₂ only (pH₂ = 10 atm). The reactions were carried out with complex (3) (0.006 g, 2 × 10⁻⁵ mol) or with complex (3) and one of two phosphines: PPh₃ (0.00524 g) or (PCy₃) (0.00566 g) [Rh]/[P] = 1. The amounts of vinylsilanes were identical to those used in hydroformylation. After the reaction was finished, the autoclave was cooled down, opened, and the reaction mixture was passed through the SiO₂ column to separate the catalyst before the samples were suitable for GC–MS.

4.2. Products identification

Products were identified from ¹H NMR spectra: Me₃SiCH₂CH₂CHO, Me₃SiCH(CH₃)CHO [3] Me₂PhSiCH₂CH₂CHO [4]. The ¹H NMR signals reported below have been used for identification of products as well as for quantitative determination of their amounts in post-reaction mixtures. Dioxane has been used as an internal standard.

Me₂PhSiCH(CH₃)CHO: ¹H NMR (CDCl₃): δ (ppm) 0.43 (s, 9H, Si(CH₃)₂), 1.2 (d, 3H, *J* = 6.6 Hz, SiCH(CH₃)CHO), 2.61 (qd, 1H, *J* = 6.6 Hz, 2.1 Hz, SiCH(CH₃)CHO), 9.68 (d, 1H, *J* = 2.1 Hz, CHO).

Me₂PhSiCH₂CH(Ph)CHO: ¹H NMR (CDCl₃): δ (ppm) 0.14 (s, 6H, Si(CH₃)₂), 1.2 (dd, 1H, *J* = 9.5 Hz, 14.9 Hz, CH₂Si), 1.6 (dd, 1H, *J* = 5.7 Hz, 14.9 Hz, CH₂Si), 3.4 (m, 1H, CH(CHO)), 9.4 (s, 1H, CHO).

Me₂PhSiCH(CH₂Ph)CHO: ¹H NMR (CDCl₃): δ (ppm): 0.3 (s, 6H, Si(CH₃)₂), 2.8 (dt, 1H, *J* = 2.6 Hz, 14 Hz, CH₂Ph), 2.6 (dd, 2H, *J* = 2.6 Hz, 14 Hz, CH₂Ph), 3.45 (m, 1H, *J* = 10 Hz, 14 Hz, CH(CHO)Si), 9.57 (d, 1H, *J* = 2.6 Hz, CHO).

(MeO)₃SiCH₂CH₂CHO [3], (MeO)₃SiCH(CH₃)CHO: ¹H NMR (CDCl₃): δ (ppm) 1.29 (d, 3H, *J* = 6.9 Hz, SiCH(CH₃)CHO), 2.6 (qd, 1H, *J* = 6.9 Hz, 1.8 Hz, SiCH(CH₃)CHO), 3.6 (s, 9H, Si(OCH₃)₃) 9.77 (d, 1H, *J* = 1.8 Hz, CHO).

Me₂PhSiOCH=CHCH₃: ¹H NMR (CDCl₃): δ (ppm) 1.68 (dd, Me₂PhSiOCH=CHCH₃, *J* = 6.8 Hz, *J* = 1.8 Hz), 4.6 (qd Me₂PhSiOCH=CHCH₃, *J* = 5.96 Hz, *J* = 6.8 Hz), 6.3 (dq, 1H, Me₂PhSiOCH=CHCH₃, *J* = 1.8 Hz, *J* = 5.96 Hz), Ir: ν(C=C) = 1668 cm⁻¹, ν(Si–O–C) = 1062 cm⁻¹.

Me₃SiOCH=CHCH₃: ¹H NMR (CDCl₃): δ (ppm) 1.66 (dd, Me₃SiOCH=CHCH₃, *J* = 6.7 Hz, *J* = 1.8 Hz), 4.6 (qd Me₃SiOCH=CHCH₃, *J* = 5.97 Hz, 6.7 Hz), 6.2 (dq, 1H, Me₃SiOCH=CHCH₃, *J* = 1.8 Hz, 5.97 Hz), Hydrogenation reaction products were identified from ¹H NMR spectra and GC–MS analyses. The reaction yields have been calculated from GC data.

Me₃SiEt: ¹H NMR (CDCl₃): δ (ppm) 1.0 (t, 3H, CH₃CH₂–, *J* = 8 Hz), 0.55 (q, 2H, CH₃CH₂–, *J* = 8 Hz), 0.052, (s, 9H, Si(CH₃)₃).

GC–MS (*m/z*): 87(17), 73(100), 59(50), 43(8), 28(5), 18(4).

Me₃SiCH=CHSiMe₃ [17], (Me₃Si)₂C=CH₂ [17], Me₃SiCH₂CH₂SiMe₃: ¹H NMR (CDCl₃): δ (ppm) 0.45 (s, 4H, CH₂CH₂), 0.06 (s, 18 H, Si(CH₃)₃).

GC–MS (*m/z*): M⁺• 174(6), 159(11), 131(6), 86(29), 73(100), 45(11).

(Me₃Si)₂CHCH₃: ¹H NMR (CDCl₃): δ (ppm) 1.1 (d, 3H, CH₃CH, *J* = 7.6 Hz), 0.09 (s, 18 H, Si(CH₃)₃).

GC–MS (*m/z*): 159(31), 85(39), 73(100), 45(11).

Me₂PhSiEt: ¹H NMR (CDCl₃): δ (ppm) 1.08 (t, 3H, CH₃CH₂–, *J* = 8 Hz), 0.85 (q, 2H, CH₃CH₂–, *J* = 8 Hz), 0.37 (s, 6H, Si(CH₃)₂).

GC–MS (*m/z*): M⁺• 164(6), 135(100), 121(28), 105(10), 43(13).

Me₂PhSiCH=CHSiMe₂Ph: ¹H NMR (CDCl₃): δ (ppm) 7 (s, 2H, CH=CH), 0.47 (s, 12H, Si(CH₃)₂).

GC–MS (*m/z*): M⁺• 296(20), 281(30), 197(30), 135(100), 105(16), 43(20).

(Me₂PhSi)₂C=CH₂: ¹H NMR (CDCl₃): δ (ppm) 6.55 (s, 2H, CH₂=C), 0.38, (s, 12H, Si(CH₃)₂).

GC–MS (*m/z*): M⁺• 296(5), 281(5), 218(60), 197(11), 161(30), 135(100), 105(17), 43(20).

Me₂PhSiCH₂CH₂SiMe₂Ph: ¹H–NMR (CDCl₃): δ (ppm) 0.8, (s, 4H, CH₂CH₂), 0.36, (s, 12 H, Si(CH₃)₂).

GC–MS (*m/z*): M⁺• 298(5), 283(8), 197(11), 135(100), 105(10), 43(11).

(Me₂PhSi)₂CHCH₃: ¹H NMR (CDCl₃): δ (ppm) 1.13, (d, 3H, CH₃CH, *J* = 7.6 Hz), 0.32 (s, 12 H, Si(CH₃)₂).

GC–MS (*m/z*): 283(28), 197(19), 135(100), 105(11), 43(11).

(MeO)₃Si Et: ¹H NMR (CDCl₃): δ (ppm) 1.1 (t, 3H, CH₃CH₂–, *J* = 8 Hz), 0.71 (q, 2H, CH₃CH₂–, *J* = 8 Hz), 3.63, (s, 9H, Si(OCH₃)₃).

GC–MS (*m/z*): M⁺• 150(1), 121(100), 91(61), 59(14), 45(3).

(MeO)₃SiCH₂CH₂Si(OMe)₃: ¹H NMR (CDCl₃): δ (ppm) 0.78 (s, 4H, CH₂CH₂), 3.67 (s, 18 H, Si(OCH₃)₃).

GC–MS (*m/z*): M⁺• 270(5), 238(100), 227(32), 197(46), 167(27), 121(93), 91(64), 61(16), 59(14).

((MeO)₃Si)₂CHCH₃: ¹H NMR (CDCl₃): δ (ppm) 1.25 (d, 3H, CH₃CH, *J* = 7.6 Hz), 3.65 (s, 18H, Si(OCH₃)₃).

GC–MS (*m/z*): M⁺• 270(6), 238(28), 227(48), 197(18), 165(13), 119(67), 90(100), 61(15), 59(19).

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