

CATALYSIS OF HYDROSILYLATION

VII *. CATALYSIS OF HYDROSILYLATION OF C=C BONDS BY RUTHENIUM PHOSPHINE COMPLEXES

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Summary

A full account of the catalysis of hydrosilylation of the C=C bond in olefins, their derivatives with functional groups as well as in vinyl-trisubstituted silanes by ruthenium(II) and ruthenium(III) phosphine precursors is given. The ruthenium complexes are far more efficient catalysts for the hydrosilylation of 1-alkenes and vinyl-substituted silanes than for the substituted olefins and unsaturated esters. General features characterizing all hydrosilylation reactions catalyzed by the above catalysts are as follows: the reaction proceeds with alkoxy-substituted silanes (also with vinylsilanes) in the absence of solvent, and is enhanced (for Ru^{II} and olefins occurs exclusively) in the presence of molecular oxygen. Two general mechanisms are proposed for hydrosilylation of olefins and of vinylsilanes, respectively, which account for most of the experimental observations.

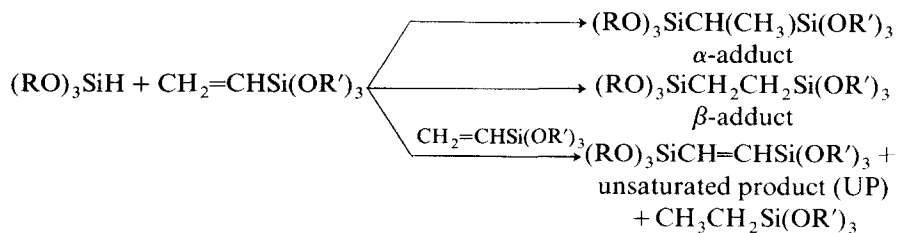
Introduction

In a short communication [1] we reported previously the results of our preliminary examinations carried out on the hydrosilylation of C=C bonds in 1-alkenes in the presence of RuCl₂(PPh₃)₃ as the ruthenium(II) homogeneous catalyst which has not yet been involved in the catalysis of the addition of trisubstituted silanes to a C=C bond. It was found, however, that the reaction only takes place for alkoxy-substituted silanes in the absence of solvent and in the presence of small amounts of molecular oxygen. The identification of an isolated ruthenium dioxygen silyl phosphine complex and its high activity as intermediate in the hydrosilylation of 1-hexene by triethoxysilane accounts for the role of oxygen in this process.

On the other hand, addition of trialkoxysilane to vinyltrialkoxysilanes catalyzed by various transition metal (Pt, Rh, Ru, Ni) complexes proceeds according to the

* For Part VI see ref. 28.

following reaction [2]:



The main product is usually the β -adduct but in the presence of ruthenium complexes, in contrast to the other catalysts examined, the reaction between vinyltriethoxysilane and triethoxysilane leads also to an unsaturated product and no α -adduct is observed. Speier's predictions of the possibility of dehydrogenative double hydrosilylation resulting in formation of an unsaturated product [3] were recently confirmed also in the reaction catalyzed by pentacarbonyl iron(0) [4].

In this paper we give a full account of the catalytic aspects of the addition of trialkoxysilanes to organic and organosilicon olefins in the presence of various ruthenium(II) and ruthenium(III) complexes as precursors of homogeneous catalysts.

Results and discussion

Addition of trialkoxysilanes and methyl(dialkoxy)silanes to alkenes catalyzed by ruthenium(II) precursor complexes

The application of $\text{RuCl}_2(\text{PPh}_3)_3$, a well-known homogeneous catalyst of the hydrosilylation of C=O bonds [5], to the addition of trisubstituted silanes to a C=C bond did not give the expected results when the reaction was carried out in argon and in the benzene solutions [6]. It appears that elimination of solvent and introduction of molecular oxygen required to make this catalyst effective in the addition of trialkoxysilanes to 1-alkenes [1]. Preliminary examinations, reported previously, also showed that chloro-substituted silanes as well as alkylsilanes do not react with olefins under a range of reaction conditions. The hydrosilylation proceeds only in the case of alkoxy-substituted silanes. The main product is usually the adduct with the terminal silyl group (β -adduct). The yield of the β -adduct in the hydrosilylation of 1-hexene drops from 66–68% for trimethoxy- and triethoxy-silanes to 15%, 5% and traces for tripropoxy-, tributoxy- and triisopropoxysilanes, respectively. This appears to be a consequence not only of inductive effects and small steric effects but predominantly of conjugation of oxygen ($d-p$) π in the methoxy- and the ethoxy-substituted silanes, which is supported by the high yield, 48%, of the reaction of methyldiethoxysilane with 1-hexene [1]. The effect of the nature of the alkene is illustrated by the results given in Table 1.

Apparently, 2-alkenes are not directly active in this reaction. The formation of the β -adduct on hydrosilylation of 2-pentene may be accounted for by the mechanism of olefin isomerization via the catalytic center with the metal-silicon bond [7]. The effects of temperature and reaction time, illustrated also in Table 1, showed that 80°C and 2 h are usually effective enough for the reaction of the examined substrates.

TABLE 1

EFFECT OF ALKENE, REACTION TIME AND TEMPERATURE ON THE YIELD OF THE β -ADDUCT IN THE REACTION WITH TRIETHOXSILANE IN THE PRESENCE OF $\text{RuCl}_2(\text{PPh}_3)_3^a$

Alkene	Yield of β -adduct ^b (%)	Temp. (°C)	Time (h)	Yield of hexyltriethoxysi- lane ^c (%)
1-pentene	48	60	2	6
2-pentene	26	60	6	48
1-hexene	68	80	2	66
2-hexene	trace	80	6	65
1-heptene	53	120	2	65
1-octene	72	120	6	68
1-dodecene	15	reflux	5	63
c-octene	0			

^a In glass ampoules; $[\equiv\text{SiH}]:[\text{alkene}]:[\text{catalyst}] = 1:1:2 \times 10^{-4}$. ^b 120°C, 6 h, in air. ^c In air.

The results presented in Table 2 indicate that catalytic activity does not change in the comparatively wide, 10^{-4} – $10^{-3}M$, catalyst concentration range. Varying the ratio of substrates gives unexpected results (Table 2), since a ten-fold excess of an olefin completely stops its hydrosilylation whereas the respective excess of a silane only slightly decreases the optimal substrate conversion.

Identification of all the products of the reaction of triethoxysilane with 1-hexene revealed that besides the product $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}_2\text{C}_4\text{H}_9$, formed according to the anti-Markownikov rule, the following products were also formed: $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}(\text{CH}_3)\text{C}_4\text{H}_9$ (α -adduct), $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (the product of redistribution of $\text{HSi}(\text{OC}_2\text{H}_5)_3$), 2-hexene (the olefin isomerization product) and $[(\text{C}_2\text{H}_5\text{O})_3\text{Si}]_2\text{O}$ (the silane oxygenation and further condensation product). The total yield of all these by-products never exceeded 5% in all the reaction systems examined.

As mentioned above, the isolation of the active species obtained by treatment of triethoxysilane with $\text{RuCl}_2(\text{PPh}_3)_2$ in dry air without any solvent, and its identifi-

TABLE 2

EFFECT OF CATALYST CONCENTRATION AND OF SUBSTRATE RATIO ON THE YIELD OF PRODUCT (SUBSTRATE CONVERSION) IN THE REACTION OF TRIETHOXSILANE WITH 1-HEXENE IN THE PRESENCE OF $\text{RuCl}_2(\text{PPh}_3)_3^a$

$\frac{[\text{catalyst}]}{[\equiv\text{SiH}]}$	Yield of β -adduct ^b (%)	$\frac{[\text{alkene}]}{[\equiv\text{SiH}]}$	Substrate conver- sion ^c (%)
5×10^{-5}	10	10	0
10^{-4}	59	5	28
2×10^{-4}	66	1.5	59
5×10^{-4}	64	1	66
10^{-3}	60	0.66	56
		0.2	50
		0.1	54

^a 80°C, 2 h, air, glass ampoules. ^b $[\equiv\text{SiH}]/[\text{alkene}] = 1$. ^c Conversion of minor substrate; $[\text{catalyst}]/[\equiv\text{SiH}] = 2 \times 10^{-4}$.

TABLE 3

YIELD OF β -ADDUCTS IN THE REACTION OF TRIETHOXYSILANE WITH 1-HEXENE IN THE PRESENCE OF PHOSPHINE COMPLEXES OF RUTHENIUM(II) ^a

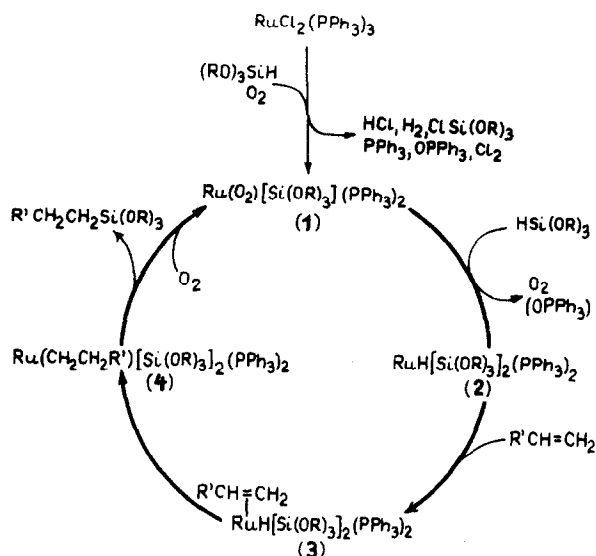
Complex	Yield (%)
RuCl ₂ (PPh ₃) ₃	68 (68 ^b)
A	75 (74 ^b)
RuH[Si(OC ₂ H ₅) ₃](PPh ₃) ₂	5 (5 ^b)
B	5 (4 ^b)
RuCl ₂ (CO) ₂ (PPh ₃) ₂	15
RuCl ₃ (NO)(PPh ₃) ₂	28
RuH(acac)(PPh ₃) ₃	24
RuHCl(PPh ₃) ₃	16
RuH ₂ (PPh ₃) ₄	16

^a 120°C, 6 h, air, glass ampoules; [≡SiH]:[1-hexene]:[catalyst] = 1:1:2 × 10⁻⁴. ^b 80°C, 2 h.

cation as a mixture of Ru(O₂)[Si(OC₂H₅)₃](PPh₃)_n and RuH[Si(OC₂H₅)₃]₂(PPh₃)_n (complex A) indicate the role that the oxygen molecule plays in the catalysis of hydrosilylation by ruthenium(II) precursor complexes [1]. The activity of complex A is compared with that of some ruthenium(II) precursor phosphine complexes in Table 3. The table contains also the activity data for complex B, which was previously isolated from the mixture of RuCl₂(PPh₃)₃ with triethoxysilane under oxygen-free conditions and identified as RuH[Si(OR)₃](PPh₃)_n [1]. Such a complex (with n = 2) was also prepared under similar conditions using the method given by Kono et al. [8].

All the analytical and catalytic data obtained suggest the mechanism for the olefin hydrosilylation catalyzed by RuCl₂(PPh₃)₃ as the ruthenium(II) precursor complex given in Scheme 1.

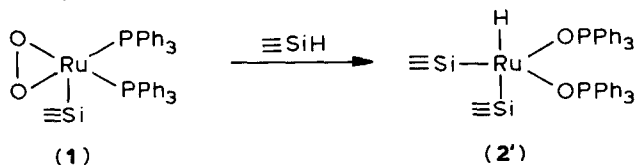
SCHEME 1



The initial formation of the active species **1** (a form of complex A) under the hydrosilylation conditions is the result of complex reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{HSi}(\text{OR})_3$ and oxygen dehalogenation with evolution of HCl , Cl_2 and $\text{ClSi}(\text{OR})_3$, reduction with H_2 (possibly accompanied by HO_2 evolution) and oxygenation by O_2 with oxidation as well as elimination of PPh_3 . It is difficult to determine the real oxidative step of this species **1** and to characterize the ruthenium–oxygen bond but the paramagnetism found for complex A practically excludes a ruthenium(II) species (which are diamagnetic) and suggests rather peroxide bonding to the ruthenium(III) center. The addition of trialkoxysilane to the center with the simultaneous elimination of molecular oxygen or the oxygenation of phosphines to phosphine oxides gives rise to formation of another ruthenium(III) species complex **2**. The next step is the olefin coordination to this ruthenium(III) complex followed by rearrangement of the π -complex **3** to the σ -complex **4** according to the general mechanism of Chalk and Harrod [7]. Fast decomposition of the intermediate **4** gives the β -adduct and regenerates, in the oxygen atmosphere, the active complex **1**.

The results of Kono [8], Hetflejs [6] and their coworkers show clearly an effect of solvents on the composition and structure of complexes formed in the reaction of chlororuthenium(II) phosphine complexes with trisubstituted silanes. When the reaction proceeds in solvents (benzene, toluene, nitrobenzene, CH_2Cl_2 , hexane) five-, and sometimes six-coordinated phosphine complexes are formed, e.g. a mixture of $\text{Ru}[\text{Si}(\text{OC}_2\text{H}_5)_2(\text{PPh}_3)_3]$ and $\text{RuHCl}(\text{PPh}_3)_3$ in the case of triethoxysilane as a reagent. But when the reaction occurs in the absence of a solvent mostly four-coordinated complexes of general formula $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_2$ [8], where $\text{R}_3 = \text{Cl}_3, \text{Cl}_2\text{CH}_3, (\text{OC}_2\text{H}_5)_3, (\text{OCH}_3)_3$, are observed. The electron-donating character of alkyl substituents reduces the possibility of forming trialkoxysilylruthenium complexes [8–10], which also explains the inactivity of the Ru^{II} complexes in the hydrosilylation by trialkylsilanes. On the other hand, the inactivity of chlorosubstituted silanes may be accounted for by their high stability as well as by migration of the chlorine atom from the silyl ligand to ruthenium, followed by the cleavage of the Si–Ru bond in the silylruthenium hydrides [8]. Four-coordinated trialkoxysilylhydridobis(triphenylphosphine)ruthenium(II) complexes are apparently also too stable and since, as we found, they do not add to olefins, they are not efficient catalysts of hydrosilylation, either. Thus, the only active ruthenium species is the complex **1** formed by the reaction of Ru^{II} complex with a trialkoxysilane in the absence of solvent but in an oxygen atmosphere. This complex is therefore presumably a ruthenium(III) intermediate involving dioxygen as a ligand which is however labile enough in the reaction with trialkoxysilane leading to the complex **2**. The latter as a ruthenium(III) trialkoxysilyl hydride adds directly to the olefins.

Phosphine oxide, found as a byproduct in the reaction mixture is the result of the oxygenation of complex **1** to **2'**, which is a well-known process for ruthenium phosphine complexes [11,12]:



This reaction can be followed by the elimination of OPPh_3 or the exchange of

OPPh₃ for PPh₃ in the coordination sphere of the Ru^{III} intermediate, as well as its dimerization [12]. Addition of excess PPh₃ or OPPh₃ to the reaction mixture in the ratio [P]/[catalyst] = 3/1 does not influence the reaction course. However, deactivation of the catalyst observed if one stops the addition of oxygen during the reaction, regardless of the excess OPPh₃ present, may indicate that the Ru(O₂)^{III} intermediate is still necessary for the catalytic cycle. Deactivation of the catalyst in excess olefin may be explained by the olefin also acting as solvent, when inactive complexes of Ru^{II} can be only formed. Thus, coordination of the olefin to the active species **1** prior to the oxidative addition step is less probable unless the olefin ratio is low. On the other hand, the great sensitivity of ruthenium intermediates of low coordination number is demonstrated by the complete deactivation of the catalyst on adding acrylonitrile which coordinates readily to such ruthenium complexes [13,14] (in the ratio [acrylonitrile]/[catalyst] = 3/1) to the reaction mixture.

Addition of trialkoxysilanes to alkenes catalyzed by ruthenium(III) precursor complexes

The above mechanistic considerations demonstrate that ruthenium(III) complexes are involved in the hydrosilylation of 1-alkenes by trialkoxysilanes in the presence of ruthenium(II) phosphine precursors and molecular oxygen. Therefore, we have tried to apply ruthenium(III) phosphine precursors to this reaction both in oxygen and oxygen-free atmospheres.

Most of the examinations of the hydrosilylation of alkenes occurring in the presence of RuCl₃(PPh₃)₃ under the same conditions as for RuCl₂(PPh₃)₃ lead to the same observations, i.e.:

- deactivation of the catalyst in the presence of any solvent (benzene, acetone, hexane, tetraethoxysilane, as well as 1-hexene);
- inactivity of the chloro-, alkyl- and alkylchloro-substituted silanes and the high activity of trialkoxysilanes;
- reaction of 2-pentene and 1-pentene with triethoxysilane yielding a product of hydrosilylation having terminal silyl groups in 26 and 52% yields, respectively;
- complete lack of reaction under a ten-fold excess of 1-hexene relative to triethoxysilane and a slight decrease of 1-hexene conversion under a ten-fold excess of triethoxysilane.

However, the most significant difference is not only the greater catalytic activity of RuCl₃(PPh₃)₃ in air but above all, in contrast to RuCl₂(PPh₃)₃, its observed activity in oxygen-free conditions. The characteristic feature is however, that a replacement of the phenyl-substituted phosphine by the others with electron-donating substituents, e.g. butyl or ethyl, in the Ru^{III} complex causes deactivation of the catalyst in argon. All the reliable results for the ruthenium(III) phosphine precursor-catalyzed hydrosilylation of 1-hexene are presented in Table 4.

The results show the highest activity for the catalyst prepared "in situ" in air containing equimolar amounts of RuCl₃ and PPh₃; addition of one equivalent of ligand, as well as its replacement by OPPh₃ decrease the activity slightly. However, if formation of the catalyst occurs in an oxygen-free atmosphere, then a little higher activity is noticed for phosphine oxide complex than for the phosphine one. The decrease of RuCl₃ activity is caused by its greater sensitivity to oxygenation.

By analogy to the ruthenium(II) precursors and complexes A and B, we prepared and isolated the complexes C and D as the products of treatment of RuCl₃(PPh₃)₃ with triethoxysilane in air and argon, respectively. Complex C, in contrast to

TABLE 4

EFFECT OF ATMOSPHERE ON THE YIELD IN THE ADDITION OF TRIETHOXSILANE TO 1-HEXENE IN THE PRESENCE OF RuCl_3 AND VARIOUS Ru^{III} PHOSPHINE COMPLEXES^a

Ru^{III} compound	Yield of β -adduct (%)	
	air	argon
RuCl_3	77	60
$\text{RuCl}_3 + \text{PPh}_3$ (1:1)	96	63
$\text{RuCl}_3 + \text{PPh}_3$ (1:2)	86	—
$\text{RuCl}_3 + \text{PPh}_3$ (1:3)	89	—
$\text{RuCl}_3 + \text{PPh}_3$ (1:10)	89	—
$\text{RuCl}_3 + \text{OPPh}_3$ (1:1)	81	68
$\text{RuCl}_3(\text{PPh}_3)_3$	86	52
$\text{RuCl}_3(\text{PPh}_3)_2 \cdot \text{CH}_3\text{OH}$	85	45
$\text{RuCl}_3[\text{P}(\text{C}_2\text{H}_5)_3]_3$	24	0
$\text{RuCl}_3[\text{P}(\text{C}_4\text{H}_9)_3]_3$	69	0
Complex C	0	0
Complex D	44	52

^a 120°C, 6 h, glass ampoules; $[\equiv\text{SiH}]:[1\text{-hexene}]:[\text{catalyst}] = 1:1:2 \times 10^{-4}$.

complex A, is an inorganic derivative of ruthenium, e.g. an oxygenated product of ruthenium, (presumably a chlororuthenium oxide [15] or silicate) and it is undoubtedly not an intermediate of the reaction. Complex D gives irreversibly complex C when heated in the silane solution in air and also when exposed to air at room temperature. Complex D is so sensitive to traces of oxygen in the air that it remains not fully characterized. This property of the complex D is presumably the reason why in the mass spectrum a peak at m/z 297, 100% relative intensity, which we attributed to the $[\text{Ru}(\text{O}_2)\text{Si}(\text{OC}_2\text{H}_5)_3]^+$ species (see catalyst A [1]) was found. However, in contrast to catalyst A, further exposure of complex C to air results in oxygenation and decomposition.

Since, in contrast to ruthenium(II) phosphine complexes, there is little known on the reaction of ruthenium(III) phosphine complexes with trialkoxysilanes in particular and since we have not found any active intermediates, the mechanistic discussions must be very limited. However, the double role of oxygen in catalysis by the Ru^{III} precursor seems to be similar to that for the Ru^{II} ones, i.e. stabilizing Ru^{III} complexes, e.g. via formation of $\text{Ru}(\text{O}_2)$ species under the reaction conditions and oxidizing phosphines to phosphine oxides, which releases ligand molecules from the coordination site of the catalyst. Both roles ensure essentially the high catalytic activity of the catalyst in oxygen atmosphere but as the Ru^{III} complexes are more sensitive to air, the intermediates can release all the phosphine ligands. It is interesting that the 77% yields of β -adduct are identical when RuCl_3 (at standard 1:1 substrate ratio) and $\text{RuCl}_3(\text{PPh}_3)_3$ (at the silane:1-hexene 10:1 ratio) are used as precursors, suggesting that the reaction occurs in air via the same intermediates. Oxidation of the phosphines followed by their complete release and decomposition of the complex is apparently enhanced by an excess of the silane. In conclusion, the relative higher activity of ruthenium(III) precursor in air (86% adduct) against 68% of ruthenium(II) can be accounted for by the higher concentration of the intermediate **1** (see Scheme 1) in the former case and by the incomplete substitution of

chlorine by silyl ligands in this intermediate (what makes it more sensitive to oxidation of phosphines and addition of silanes).

In such a situation we can only postulate that when the hydrosilylation reaction proceeds in an oxygen-free atmosphere chloro, silyl and hydride ruthenium complexes (presumably dimers) are the active intermediates involving also ruthenium(III) species with Ru–H bonds in which olefin molecules can be readily inserted forming σ -complexes of type 4 (Scheme 1).

Addition of triethoxysilane to substituted olefins in the presence of $RuCl_2(PPh_3)_3$ and $RuCl_3(PPh_3)_3$

The catalytic activity of ruthenium complexes in hydrosilylation of some substituted organic olefins (vinyl and allyl derivatives) as well as esters of unsaturated acids was examined. The ruthenium complexes were generally not efficient catalysts, e.g. methyl acrylate and methyl methacrylate hydrosilylated by triethoxysilane gave adducts in 15–20% yields together with 10–12% yields of byproducts in the presence of used catalysts. However, under the conditions examined (see Table 4), and only in air, the addition of triethoxysilane to vinyl acetate led, in the presence of the Ru^{II} and Ru^{III} complexes, to 46 and 52%, respectively, of 2-triethoxysilylethyl acetate. The reaction can be applied synthetically. Refluxing the reaction mixture for 6 h followed by distillation gives a 70% yield of the β -adduct (in the presence of rhodium complexes in only 17% [16]). The residue consists of polymeric byproducts. Ruthenium phosphine complexes, similarly to the rhodium ones, do not in general catalyze hydrosilylation of the allyl derivatives. The observed conversion of the silane is sometimes as high as 75% in the case of allyl chloride and allylamine, but the substitution products are usually yielded. Allyl acetate and allyl cyanide do not undergo reaction at all. The hydrosilylation of allyl alcohol by triethoxysilane gives, under the conditions examined (see Table 4), 3-hydroxypropyltriethoxysilane in 20% yield and byproducts (mostly of hydroxy group condensation with silane) are also detected. This is only one example of the catalytic activity of the ruthenium complexes in the hydrosilylation of allyl compounds.

Addition of trialkoxysilanes to vinylsilanes catalyzed by Ru^{II} and Ru^{III} precursor catalysts

The previously reported preliminary examinations of hydrosilylation of vinyltrisubstituted silanes catalyzed by $RuCl_2(PPh_3)_3$ and other metal complexes [2] show general features of catalysis of olefin hydrosilylation by ruthenium complexes as follows:

- the trichlorosilane as well as alkyl(chloro)- and aryl(chloro)-silanes, do not undergo addition to vinyltrisubstituted silanes; catalytic hydrosilylation of vinyltrialkoxysilanes by trialkoxysilanes occurs under the conditions examined only in an atmosphere of molecular oxygen and in absence of any solvent;
- the hydrosilylation of $(RO)_3SiCH=CH_2$ by trialkoxysilanes, $(RO)_3SiH$, gives mostly β -adduct (66–77% for $R = CH_3, C_2H_5$ and C_3H_7 and 6% for $R = iso-C_3H_7$) and small amounts (6% for $R = C_2H_5$ and 10% for $iso-C_3H_7$) of the unsaturated product. A small amount of α -adduct (1%) was found only for trimethoxy-substituted silanes.

Other reliable results for the hydrosilylation of the vinyltrisubstituted silanes in the presence of ruthenium(II) and ruthenium(III) compounds are summarized in Tables 5–7.

TABLE 5

EFFECT OF ATMOSPHERE ON THE YIELD OF β -ADDUCT AND OF UNSATURATED PRODUCT (UP) IN THE HYDROSILYLATION OF VINYLTRIETHOXSILANE BY TRIETHOXSILANE IN THE PRESENCE OF VARIOUS RUTHENIUM(II) AND RUTHENIUM(III) PHOSPHINE COMPLEXES^a

Catalyst	Yield of products (%)			
	air		argon	
	β -adduct	UP	β -adduct	UP
RuCl ₂ (PPh ₃) ₃	66	6	4	0
RuCl ₂ (CO) ₂ (PPh ₃) ₂	71	9	57	14
RuCl ₃ (NO)(PPh ₃) ₂	71	trace	71	12
RuHCl(PPh ₃) ₃	40	0	20	0
RuH(acac)(PPh ₃) ₃	74	7	30	6
RuH ₂ (PPh ₃) ₄	trace	trace	trace	trace
RuCl ₃ (PPh ₃) ₃	75	0	60	3
RuCl ₃ (PPh ₃) ₂ ·CH ₃ OH	77	0	46	trace

^a 120°C, 6 h, glass ampoules; [\equiv SiH]:[CH₂=CHSi \equiv]:[catalyst] = 1 : 1 : 2 × 10⁻⁴.

RuH₂(PPh₃)₄ is inactive in the examined reaction and all other catalysts except RuCl₂(PPh₃)₃ also catalyze the process in an oxygen-free atmosphere, although the observed yields are usually lower (Table 5). Based on the reaction presented in Table 6 the order of reactivity of trisubstituted silanes in the addition to vinylsilanes is as follows:

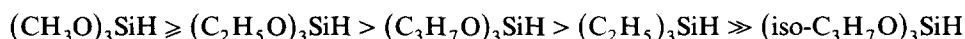


TABLE 6

EFFECT OF SUBSTITUENTS ON SILICON ON THE CATALYTIC ACTIVITY OF RuCl₂(PPh₃)₃ IN THE HYDROSILYLATION OF TRISUBSTITUTED VINYL SILANES (GLC analysis)^a

X ₃	Y ₃	Conversion of CH ₂ =CHSiY ₃ (%)	Yield of β -adduct (%)	Number of products (%)
(CH ₃ O) ₃	(C ₂ H ₅ O) ₃	78	—	8
(C ₂ H ₅ O) ₃	(C ₂ H ₅ O) ₃	72	66	2
(C ₂ H ₅ O) ₃	CH ₃ (C ₂ H ₅ O) ₂	64	62	2
(C ₂ H ₅ O) ₃	(CH ₃) ₂ (C ₂ H ₅ O)	66	60	2
(C ₂ H ₅ O) ₃	(CH ₃) ₃	16	12	2
(C ₂ H ₅ O) ₃	(CH ₃ OC ₂ H ₄ O) ₃	60	34	5
(C ₂ H ₅ O) ₃	(CH ₃ O) ₃	76	—	8
(n-C ₃ H ₇ O) ₃	(C ₂ H ₅ O) ₃	72	66	2
(iso-C ₃ H ₇ O) ₃	(C ₂ H ₅ O) ₃	31	26	2
(C ₂ H ₅) ₃	(C ₂ H ₅ O) ₃	62	—	2
(C ₂ H ₅) ₃	CH ₃ (C ₂ H ₅ O) ₂	20	—	2
(C ₂ H ₅) ₃	(CH ₃) ₂ (C ₂ H ₅ O)	18	—	2
(C ₂ H ₅) ₃	(CH ₃) ₃	34	—	7

^a Glass ampoules; [X₃SiH]:[CH₂=CHSiY₃]:[catalyst] = 1 : 1 : 2 × 10⁻⁴.

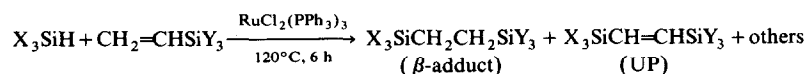


TABLE 7

EFFECT OF SUBSTRATE RATIO ON THE CONVERSION OF SUBSTRATES AND THE PRODUCT RATIO IN THE ADDITION OF TRIETHOXY-SILANE TO VINYLTRIETHOXY-SILANE CATALYZED BY $\text{RuCl}_2(\text{PPh}_3)_3$ AND $\text{RuCl}_3(\text{PPh}_3)_3$ ^a

$\frac{[\text{CH}_2=\text{CHSi}\equiv]}{[\equiv\text{SiH}]}$	Conversion of substrate ^c (%)	β -adduct/UP
<i>RuCl₂(PPh₃)₃</i>		
10	80 (89 ^b)	42/38 (14/75 ^b)
5	68	52/16
2	65	62/ 3
1	72	66/ 6
0.5	66	63/ 3
0.1	24 (13 ^b)	24/trace (13/trace ^b)
<i>RuCl₃(PPh₃)₃</i>		
10	85 (86 ^b)	15/70 (14/72 ^b)
5	76	57/19
1	72	72/trace
0.2	63	63/trace
0.1	25 (15 ^b)	25/traces (15/traces ^b)

^a 120°C, 6h, air, glass ampoules; $[\text{SiH}]:[\text{catalyst}] = 5 \times 10^{-3}$. ^b In argon. ^c Conversion of minor substrate.

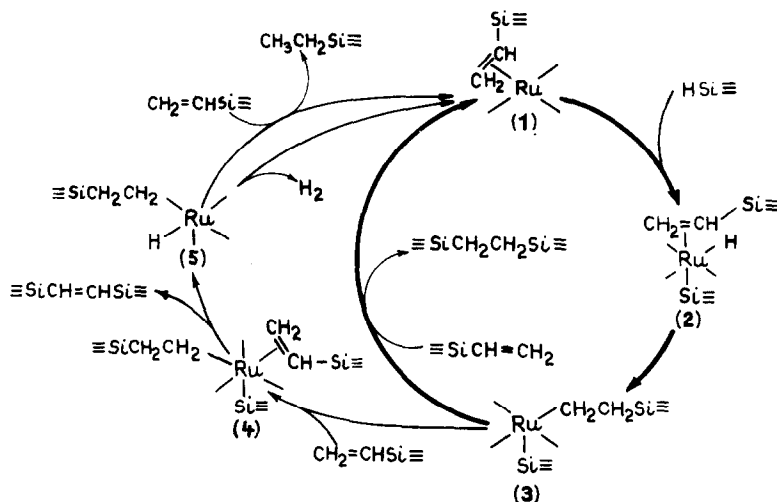
Reactions between trimethoxy- and triethoxy-substituted substrates proceed by exchange of successive alkoxy groups on the silicon of two substrates followed by their hydrosilylation, which leads to at least 8 products (mainly β -adducts). Yet, no net vinyl/hydrogen exchange was observed between the substrates. Such a large number of hydrosilylation products, formed by exchange of alkoxy substituents was also observed in the presence of $\text{Ru}(\text{acac})_3$ as catalyst [2]. The effect of a substituent on silicon in vinylsilanes is illustrated by two series of methyl- and ethoxy-vinylsilanes hydrosilylated by triethoxysilane and triethylsilane, respectively (Table 6). The former shows that only one ethoxy group is necessary for the high reactivity whereas the latter that introduction of only one methyl group strongly retards the addition. Reactions of alkoxy-substituted silanes are influenced by their electronic and $d_\pi-p_\pi$ effects. In the addition of triethoxysilane to the vinylsilane series dative $d_\pi-p_\pi$ bonding seems to be crucial since in triethoxy-substituted silanes only one group forms a $d_\pi-p_\pi$ bond whereas two act solely by their inductive effect [17]. In the second series the electron-withdrawing character of the triethoxy substituents which should stabilize the ruthenium center.

$\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}_3(\text{PPh}_3)_3$ are both effective catalysts in the hydrosilylations, even at 80°C, and the yield of the reaction is essentially constant in the range 80–120°C and for 2–6 h reaction time as well as in the 5×10^{-5} – 5×10^{-4} mol catalyst/mol silane range of the catalyst concentration.

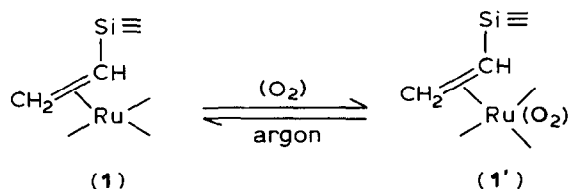
It should be emphasized that the reaction examined can occur in oxygen-free conditions, particularly when the vinyltriethoxysilane is in excess in the reaction mixture regardless of the oxidation state of the ruthenium precursors used (Table 7). Apparently, in contrast to organic olefins, vinylsilanes can effectively stabilize the ruthenium catalytic system by coordination and thus replace one of the roles of molecular oxygen in the active intermediate of the catalytic cycle. Platinum and rhodium phosphine complexes react with vinylsilane to form adducts which can be

isolated [18–20]. Their stabilities are favoured by electron-withdrawing substituents at silicon, e.g. an ethoxy group [19]. Hence, in mechanistic considerations we may postulate a vinylsilane-ruthenium complex as active intermediate **1** (Scheme 2).

SCHEME 2



The formation and reduction of Ru^{II} and Ru^{III} precursors are due to a reaction with hydrosilanes similar to the hydrosilylation of alkenes although in this case they can be stabilized also by vinylsilane complexation. Therefore, we propose the following equilibrium:



which means that in an argon atmosphere the reaction proceeds via complex **1** but in air or oxygen also through the vinyl dioxygen intermediate **1'**. As previously, it is difficult to evaluate the oxidation state of these species, particularly because both Ru^{II} and Ru^{III} precursors catalyze the hydrosilylation of vinylsilanes very similarly.

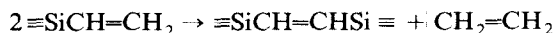
In accordance with the role of the stabilizing ligands and experimental data as well as other ruthenium-catalyzed reaction, e.g. hydrogenation [21], the complex **1** may be a dimeric Ru^I species and the oxidation state of ruthenium in the complex **1'** may be 3 in the case of a monomer or 1 in the case of a dimer. The catalytic cycle involves the oxidative addition of the Si–H bond to the complex **1**, the Ru^I species, as well as possible O₂ elimination or oxidation of phosphine to phosphine oxide of the complex **1'**. The usual route in accordance with the general mechanism [7] leads via the π-(**2**) and σ-intermediates (**3**) to an adduct with a terminal silyl group (see the inner cycle in Scheme 2).

However, we noticed a substantial rise in the yield of the unsaturated product ≡SiCH=CHSi≡, although only a slight increase in the conversion of trisubstituted silane, when an excess of vinylsilane was used (Table 7). Under these conditions, the

alternative pathway (see Scheme 2) involves vinylsilane molecule coordination to the Ru^{III} species **3** followed by dehydrogenation of the complex **4** with σ -ethylsilyl and π -vinylsilane ligands leading to elimination of the unsaturated product and to formation of a hydride σ -intermediate **5**. The latter can competitively eliminate a hydrogen molecule or coordinate a vinylsilane molecule releasing ethyltriethoxysilane. All the cycles go to completion and to recovery of the initial vinyl intermediate **1**. This mechanism essentially explains all the experimental observations.

In the reaction of triethoxysilane with vinyltriethoxysilane catalyzed by RuCl₂(PPh₃)₃ as well as RuCl₃(PPh₃)₃, the following products and by-products were detected (GLC) and identified: 1,2-bis(triethoxysilyl)ethane (β -adduct); 1,2-bis(triethoxysilyl)ethene (*trans*-unsaturated product); as well as ethyltriethoxysilane, tetraethoxysilane (product of triethoxysilane redistribution), divinyltetraethoxydisiloxane and diethyl ether (products of vinyltriethoxysilane condensation) and ethylene.

In both Schemes 1 and 2, we have omitted pathways involving formation of initial catalyst **1**. This stage will involve certain (including redox) reactions similar to those occurring in the ruthenium(II)-catalyzed addition of a C–Cl bond to olefins [22–23]. Most of the experimental data indicate a heterolytic mechanism for the hydrosilylation. However, the mechanism of hydrosilylation of vinylsilane may be incomplete in the view of our recent investigations, which reveal a novel pathway of the vinyltrialkoxysilanes under conditions similar to those for the hydrosilylation, namely metathesis [24] of general formula:



Therefore we cannot state whether the formation of unsaturated product is due to the double dehydrogenation hydrosilylation (Scheme 2) or methathesis (because of the detection of ethylene), or to both pathways, as well as whether both reactions can proceed, at least in the presence of hydrosilanes, via the same intermediates. Further catalytic and analytical investigation of the methathesis of vinylsilanes as well as the kinetics of hydrosilylation and metathesis may give more data supporting our mechanistic propositions.

General conclusions

1. The electron-withdrawing character of alkoxy groups on silicon on one hand and d_{π} – p_{π} conjugation on the other hand contribute to the predominance of trialkoxy-substituted silanes (and vinylsilane) over trichloro or alkyl-substituted silanes in the formation of the ruthenium-silyl intermediates reactive in the hydrosilylation.
2. The low coordination number of the active ruthenium intermediates in the absence of solvent is required to catalyze the hydrosilylation of the C=C bond.
3. The role of oxygen, the complexation of ruthenium by vinylsilanes and other experimental data indicate that Ru^{III} species are formed in the presence of hydrosilanes. The hydrosilylation of the C=C bond occurs presumably via the Ru^I → Ru^{III} oxidative addition step (although radical pathways cannot be ruled out).
4. Triphenylphosphine ligands are not required to stabilize the transition states. High yields of adducts may be obtained also in presence of RuCl₃ and Ru(acac)₃ precursors, which on treating with silanes and olefins give active complex intermediates.

Experimental

Materials

1-Alkenes, 2-alkenes, triethylsilane, vinyltrimethylsilane, vinylmethyldi(ethoxy)silane, vinyldimethyl(ethoxy)silane and vinyltris(β -methoxyethoxy)silane were commercial products. Trialkoxysilanes and vinyltrialkoxysilanes were obtained by solvolysis of the corresponding chloro-substituted silanes.

Catalysts

Hydrido(triethoxysilyl)bis(triphenylphosphine)ruthenium(II) was prepared according to the published method [8]. Other ruthenium(II) phosphine complexes were purchased from Strem Chemicals and Ventron. Ruthenium(III) complexes, e.g. trichlorotris(triethylphosphine)ruthenium(III), trichlorotris(tributylphosphine)ruthenium(III) and trichlorotris(triphenylphosphine)ruthenium(III) were obtained by treating commercial ruthenium trichloride (Johnson Matthey Ltd) with the appropriate phosphine in an ethanol/HCl medium [25]. Trichlorotris(triphenylphosphine)(methanol)ruthenium(III) was prepared according to the literature [26]. Preparations of complexes A and B were described previously [1].

Synthesis of complex C

0.1 g ($\sim 10^{-4}$ mol) of trichlorotris(triphenylphosphine)ruthenium(III) and 4.5 ml (2.5×10^{-2} mol) of triethoxysilane were placed in a 25 ml round-bottom flask equipped with a condenser. The reaction mixture was warmed up to the reflux temperature (in air) and then was refluxed for 2.5 h. The black solid formed was isolated, washed with n-hexane and dried under vacuum (m.p. $> 360^\circ\text{C}$, Cl: 1.7%, no characteristic bands in IR spectra).

Synthesis of complex D

The complex D was synthesized analogously but under argon atmosphere. The yellow-brown powder was very sensitive to air (m.p. $170\text{--}173^\circ\text{C}$) and changed immediately in air to complex C.

Equipment and analytical measurements

Infrared spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer and ^1H NMR spectra on a Varian EM 360 (60 MHz) spectrometer using TMS as an internal standard. Gas chromatographic analyses were carried out on a Chrom 4 instrument using 2 m steel columns packed with 10% SE-30 on Chromosorb P (with thermal conductivity detector). Other physico-chemical and analytical data were determined by commonly employed methods.

Hydrosilylation tests

Hydrosilylation experiments were carried out in sealed glass ampoules under air or argon without solvent. The reaction mixture (appropriately alkene or vinylsilane, silicon hydride and the catalyst) was warmed up to the reaction temperature and kept at that temperature for 2 to 6 h and then analyzed by gas-liquid chromatography. Standard samples of the hydrosilylation products were prepared in separate series, isolated and identified.

Synthetic procedures

Alkyltriethoxysilanes. A mixture of 9.4 ml (0.05 mol) of triethoxysilane, 6.6 ml (0.05 mol) of 1-alkene and 0.01 g (10^{-5} mol) of dichloro tris(triphenylphosphine)ruthenium(II) as a catalyst was placed into a 50 ml two-necked round-bottom flask equipped with a condenser. The reaction mixture was warmed up to reflux temperature (during 10 minutes) and then kept under reflux for 5 h. The mixture was distilled and the appropriate alkyl(triethoxy)silane was isolated in yield ranged from 50 to 70%.

2-(Triethoxysilyl)ethyl acetate. A mixture of 10.3 ml (0.055 mol) of triethoxysilane, 5.0 ml (0.055 mol) of vinyl acetate and 0.01 g (10^{-5} mol) of dichlorotris(triphenylphosphine)ruthenium(II) as a catalyst were placed into a 50 ml two-necked round-bottom flask equipped with a condenser. The reaction mixture was warmed up to reflux and then refluxed for 6 h. The product was identified as $(C_2H_5O)_3SiCH_2CH_2OCOCH_3$.

Yield: 10.2 g (74%), b.p. 92–95°C (2 mmHg), $n_D^{20} = 1.4112$; lit. b.p. 90.6°C (3 mmHg), $n_D^{20} = 1.4109$ [27]. 1H NMR (CCl_4): δ (ppm) CH_3CH_2O 1.28, t(9H); CH_3CH_2O 3.80, q(6H); $-COCH_3$ 2.12, s, (3H).

The synthesis of 1,2-bis(trialkoxysilyl)ethanes in the presence of $RuCl_2(PPh_3)_3$ was described previously [2].

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