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Metathesis of silicon-containing olefins

X. Metathesis of vinyltrimethylsilane catalyzed by ruthenium complexes *

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Abstract

Self metathesis of vinyltrimethylsilane in the presence of an oxygenated benzene solution of $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$ follows an unusual course and yields two products, 1,2-bis(silyl)ethene (E) and 1,1-bis(silyl)ethene, with products of dimerization, namely 1,4-bis(silyl)butenes-2 ($E + Z$) and butenylsilanes as well as hexamethyldisiloxane. Gaseous ethylene and traces of ethane were also detected. It is proposed that vinylsilane is inserted into the Ru-Si bond (via *ortho*-metallation of the ruthenium triphenylphosphine complex) in competition with pathways involving metal-carbene species. Complexes of ruthenium containing no phenylphosphine give stereoselectively only the (E)-product of metathesis (even in the absence of oxygen and hydrosilane co-catalysts) accompanied by traces of the same by-products.

Key words: Silicon; Ruthenium; Metathesis; Olefin

1. Introduction

Recent advances in the study of catalysis by ruthenium complexes of metathetical activity of vinyltrisubstituted silanes have shown that this reaction can be a very attractive, useful and versatile tool for synthesizing olefins containing silicon and with an internal C=C bond [1]. Traditional tungsten and molybdenum catalysts appeared to be quite inactive in the metathesis of vinylsilanes [2]. Only heterogenous catalysts Re_2O_7/Al_2O_3 and MoO_3/Al_2O_3 were reported to convert vinyltrimethylsilane to bis(silyl)ethene, but only with minor (10–13%) yields [3]. On the other hand, the dehydrogenative silylation of vinylsilane observed in the presence of Ru^0 and Ru^{II} complexes has opened new mechanistic possibilities for the transformation of vinylsilane into bis(silyl)ethene [1e,4].

Ru–H complexes have been considered as [1a,b,e,g,i] as catalytically active species in all Ru-catalyzed metatheses of vinyltrisubstituted silanes. A mechanism for the insertion of alkenes (vinylsilanes) into the metal–silicon bond was discussed [5] in connection with the dehydrogenative silylation of alkenes under hydrosilylation conditions and it was proposed to account for metathesis (disproportionation) of vinylsilane, but only in the presence of a Ru–H initial catalyst [$RuCl(CO)H(PPh_3)_3$] [1i] or with silicon hydride as co-catalyst [1e]. The former was the initial catalytic system which provided the evidence for an addition of vinylsilane and β-Si-elimination which permitted isolation of the air stable complex, $RuCl(CO)(PPh_3)_2SiMe_2R$ (R = Me, OEt). Reversible insertion of ethylene into Ru–Si was also observed. In the catalyzed disproportionation of CH_2=$CHSiMe_3$ (140°C, 14 h) a yield of 38% of bis(silyl)ethene ($E/Z = 44/56$) was achieved [1e,i].

Contrary to the findings of Seki *et al.* [1e] and Wakatsuki *et al.* [1i], our experiments on the metathetical activity of vinyl substituted silanes (but not of vinyltrimethylsilane) and siloxanes have shown a high effectiveness not only in the presence of direct ruthenium hydrides (or with hydride co-catalyst) but also in

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the presence of many non-hydride Ru^0 and Ru^{II} complexes *e.g.* $RuCl_2(PPh_3)_3$, $RuCl_3 \cdot nH_2O$, $Ru_3(CO)_{12}$ and $[RuCl_2(CO)_3]_2$. The reaction is promoted by dioxygen and peroxides, and also by hydrides, and is inhibited by all the reaction solvents tested [1a–d]. In this paper we report for the first time an unusual course of self-metathesis of vinyltrimethylsilane in the presence of $RuCl_2(PPh_3)_3$ and of other ruthenium complexes.

2. Experimental section

$RuCl_2(PPh_3)_3$ was prepared by the standard procedure. $[RuCl_2(CO)_3]_2$, and $Ru_3(CO)_{12}$ were purchased from Strem Chemicals and $RuH_2(PPh_3)_4$ from Alfa Products. Vinyltrimethylsilane was purchased from ABCR. Benzene (POCh) was dried and distilled before use. $N_2{=}CHSi(CH_3)_3$ was purchased from Aldrich and used without additional purification.

Triethoxysilane and tetraethoxysilane were obtained by alcoholysis of $SiHCl_3$ and $SiCl_4$ respectively, according to standard procedures.

2.1. Equipment and analytical measurements

^1H and ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer (300 MHz, $CDCl_3$). The mass spectra of products were determined by GC-MS analysis (Varian 3300 gas chromatograph equipped with a DB-1 30 m capillary column and a Finnigan Mat 700 ion trap detector). GLC analysis was additionally performed on a Varian 3300 gas chromatograph with megabore column DB-1, 30 m.

2.2. General procedures

In a typical catalytic test, a benzene solution of the ruthenium catalyst with or without co-catalyst was placed in a glass ampoule in air (or under argon). Vinyltrimethylsilane was then added (also in air or under argon) and sealed ampoules were heated at 130°C for 48 h.

Liquid products were purified from catalysts using column chromatography (neutral silica gel MN-60) and isolated by vacuum distillation. The products of the reaction were identified by GC-MS and NMR methods by comparing their parameters with those of authentic samples [6–14].

3. Results and discussion

Vinyltrimethylsilane metathesis occurs in the presence of $RuCl_2(PPh_3)_3$ according to the following equation:

$$
\begin{aligned}
CH_2{=}CHSiMe_3 \longrightarrow\ & \underset{\mathbf{1}}{(E)Me_3SiCH{=}CHSiMe_3} \\
& + \underset{\mathbf{2}}{(Me_3Si)_2C{=}CH_2} \\
& + \underset{\mathbf{3}}{(E+Z)Me_3SiCH_2CH{=}CHCH_2SiMe_3} \\
& + \underset{\mathbf{4}}{C_4H_7SiMe_3} + \underset{\mathbf{5}}{Me_3SiOSiMe_3} + \underset{\mathbf{6}}{CH_2{=}CH_2}
\end{aligned}
$$

Catalytic data are presented in Table 1 and show that most Ru^0 and Ru^{II} complexes are effective in the reaction irrespective of the initial Ru–H and of whether or not silicon hydride co-catalyst is present.

TABLE 1. Metathesis of vinyltrimethylsilane catalyzed by ruthenium complexes

Catalyst	Conversion of vinyltrimethylsilane [%]	Ratio of bis(silyl) ethenes **1/2**	Yield [%]				
			1 + 2	**3**	**4**	**5**	**7** [b]
I	75	6/1	58	8	3	4	1
I [a]	trace		trace	0	0	trace	0
I + $HSi(OEt)_3$ (1 : 1)	75	6/1	58	8	3	3	2
I + $HSi(OEt)_3$ (1 : 10)	75	6/1	58	8	3	4	6 [c]
I + $N_2{=}CHCO_2Et$ (1 : 1)	90	6/1	70	10	5	4	trace
I + $N_2{=}CHSi(CH_3)_3$ (1 : 1)	80	6/1	65	8	3	4	trace
II	80	5/1	58	10	4	8	trace
III	60	(*E*)	48	0	trace	5	2
III [a]	58	(*E*)	55	trace	0	1	trace
III + $HSi(OEt)_3$ (1 : 1)	52	(*E*)	50	1	0	trace	1 [c]
IV	68	(*E*)	55	1	2	5	trace
IV [a]	53	(*E*)	50	trace	0	–	trace
IV + $HSi(OEt)_3$ (1 : 1)	58	(*E*)	55	1	0	trace	1 [c]

130°C, 48 h, dry air, ampoules $[CH_2{=}CHSiMe_3]:[Ru]:[benzene] = 100:1:160$ [a] in argon; [b] unidentified products; [c] $EtSiMe_3$ among products I, $RuCl_2(PPh_3)_3$; II, $RuH_2(PPh_3)_4$; III, $[RuCl_2(CO)_3]_2$; IV, $Ru_3(CO)_{12}$.

Results were contradictory to those of the catalytic examination of Wakatsuki *et al.* [1i]. Very high yields were observed of the main products, bis(trimethyl)silylethene, *E*-isomer (**1**) and, unexpectedly, (when the reaction occurs in the presence of phosphine complexes), 1,1-bis(trimethylsilyl)ethene (**2**). These were accompanied by two 1,4-bis(trimethylsilyl)butenes-2 (*Z* + *E*) (**3**), three isomers of butenylsilanes (**4**), hexamethyldisiloxane (**5**) and ethylene (**6**). Traces of ethane were also detected.

All liquid products were recorded, determined and characterized by GLC, GC-MS and ^1H, ^{13}C NMR methods. The spectroscopic data of the products of vinyltrimethylsilane metathesis (experimental and literature reported) are listed in Table 2.

It is worth pointing out that in the presence of non-phosphine complexes of Ru^0 and Ru^{II}, (*E*)-bis(trimethylsilyl)ethene (**1**) is stereoselectively yielded yet accompanied by siloxanes and only traces of bis(silyl)butenes and butenylsilanes. No (*Z*)-isomer (or only a trace) and no 1,1-bis(silyl)ethene were noticed in any of the runs examined.

No effect was found of hydrosilane $HSi(OEt)_3$ on the final conversion and yield of silylethenes, examined at its two concentrations. $EtSiMe_3$ as a product of side dehydrogenative silylation of vinylsilanes was detected, particularly at the higher concentration of hydride.

Very recently, certain ruthenium complexes have been reported to be activated towards olefin metathesis by the addition of diazoester as a carbene precursor [15]. It is proposed that this procedure yields the active metal–carbene species *in situ*. In our systems, co-catalysis by both carbene precursors increases the conversion of vinylsilane and the yield of bis(silyl)ethenes as well. This suggests that metal-carbene catalysis plays a significant part in the metathesis of vinyltrimethylsilane. Hexamethyldisiloxane was formed as a by-product in all attempts and this seems to be explained by oxygenation of the Ru–Si bond (under an oxygen-containing atmosphere) followed by reduction, *in situ*, of Ru^{II} to Ru^0. Such a process was documented in the reactions at 80°C of $RuH_2(PPh_3)_4$ with unsaturated trimethylsilyl ethers [16]. The C–O bond in the simple vinyltrimethylsilyl ether was smoothly cleaved by the

TABLE 2. Spectroscopic data of the products of vinyltrimethylsilane metathesis (experimental and reported in the literature)

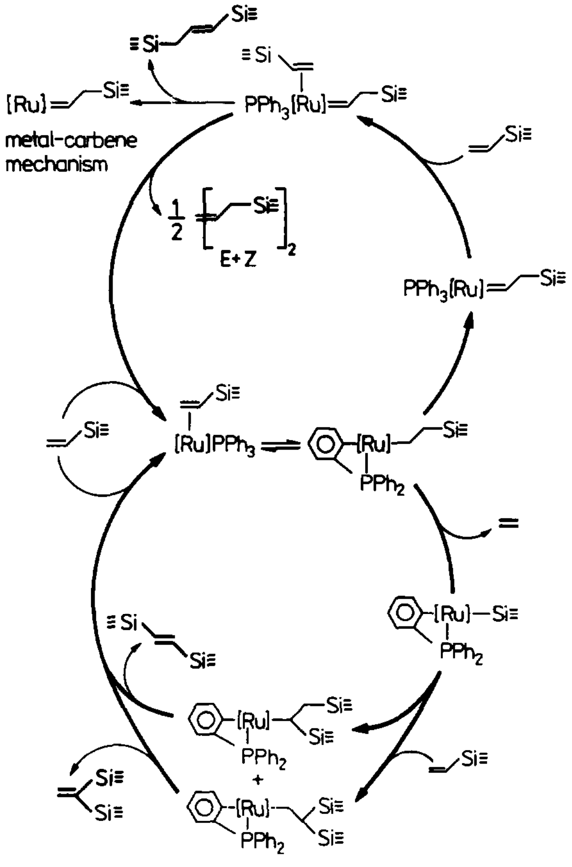
Products		^1H NMR (δ, ppm)				^{13}C NMR (δ, ppm)					MS *m/z* (rel. intensity)	Ref.
		CH_3	=CH	$-CH_2$	Ref.	CH_3	=CH	=C	$=CH_2$	Ref.		
1(*E*)	exp.	0.06 (s, 18H)	6.56 (s, 2H)	–		−1.23	150.65	–	–		172(M, 11), 157(100), 73(30)	
	lit.	0.06 (s, 18H)	6.55 (s, 2H)		[6]	−1.7	150.0	–	–	[7]	172(M, 5), 157(15), 73(100)	[8]
2	exp.	0.07 (s, 18H)	6.27 (s, 2H)	–		0.07	139.84	154.50			172(M, 9), 157(100), 73(38)	
	lit.	0.09 (s, 18H)	6.26 (s, 2H)		[6]	−0.26	139.71	145.03	–	[7]		
						−0.4	139.3	153.5		[9]		
3(*E*)	exp.	0.01 (s, 18H)	5.22 (m, 2H)	1.42–1.37 (m, 4H)		−1.8	124.29	–	22.90		200(M, 8), 185(6), 97(22), 73(100)	
	lit.	−0.02 (s, 9H)	5.3 (m, 2H)	1.5 (d, 4H)	[10]	−1.93	124.33	–	22.83	[11]		
						−1.7	124.7		23.2	[12]		
		−0.04 (s, 9H)	5.15–5.20	1.49–1.55	[11]							
3(*Z*)	exp.	−0.02 (s, 18H)	5.30 (m, 2H)	1.42–1.37 (m, 4H)		−1.5	123.09	–	17.94		200(M, 8), 185(6), 97(42), 73(100)	
	lit.					−1.70	123.12	–	17.81	[11]		
						−1.5	123.5	–	18.2	[12]		
4 (three isomers were observed)	exp.										128(M, 6), 113(21), 85(9), 73(100), 59(21), 55(10) 128(M, 4), 113(33), 85(5) 73(100), 59(21), 55(8), 113(58), 85(20), 73(22), 59(100)	
5	exp.	0.07	–	–	[13]	2.1	–	–	–	[14]	147(100), 146(6), 131(5), 73(5)	[8]
	lit.	0.064				2.4	–	–	–		147(100), 146(1), 131(4), 73(3)	[8]

ruthenium complex to liberate ethylene accompanied by some ethane and methane. $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_3(PPh_3)_2$ were identified among the products.

Our preliminary examination of the ruthenium catalyst ($RuCl_2(PPh_3)_3$ treated with vinyltriethoxysilane in dry air) revealed, similar to the above mentioned process, the presence of Ru–H and Ru(CO) bonds [1d], formed by the well-known process of decarbonylation of organic derivatives on heating in the presence of 5- and 6 coordinated ruthenium phosphine (chloro) complexes, which leads to formation of ruthenium (carbonyl) and/or ruthenium (hydrido, chloro, carbonyl, phosphine) complexes [16].

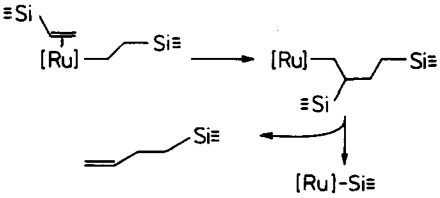
Apparently, complexes containing triphenylphosphine ligands cause marked changes to the stereochemistry of insertion of vinylsilane into Ru–Si. This is proposed to be due to *ortho*-metallation of ruthenium triphenylphosphine complexes which is a well known reversible process occurring particularly at the coordinatively deficient complex – see Scheme 1.

Steric hindrance caused by this *ortho*-metallation enables the insertion of vinyltrimethylsilane (unlike other vinyltrisubstituted silanes with more crowded substituents) in both fashions, to yield 1,1-bis(silyl)ethene as well.



Scheme 1.

On the other hand, a relatively high yield (6–10%) of 1,4-bis(silyl)butenes-2 ($E+Z$) recorded in the presence of Ru phosphine complexes and the increasing amounts of the main product (5–15%) when carbene initiators were added, suggest that pathways involving metal-carbene species are responsible for the metathesis (see Scheme 1). Therefore, Scheme 1 considers both mechanisms although the presence of ($E+Z$) bis(silyl)butenes-2 can be direct evidence for formation of these species but not be necessary for a pathway catalyzed by a metal-carbene species. It is worth emphasizing that a recombination of ruthenium-carbene species to give the products **3** occurs readily with dimeric (polymeric) ruthenium complexes (clusters). Consequently, Scheme 1 involves possible pathways of vinyltrimethylsilane conversion occurring in the presence of ruthenium(II) phosphine complexes assuming initiation by Ru–H species formed *in situ* by the *ortho*-metallation [17]. Butenylsilanes can be formed as products of dimerization of vinylsilanes proceeding via insertion of the vinylsilane molecule into the Ru–C bond according to the following scheme:



Scheme 2.

Several isomers of butenylsilanes are due to the facile migration of the C=C bond, particularly $\alpha \rightarrow \beta$ isomerization of olefins, occurring under the conditions examined [18] as well as an isomerization of butenyl and allylsilane to vinylsilane [19].

When carbonyl complexes which do not contain phosphine have been used, E-isomer and ethylene are the main products accompanied by traces of other products as mentioned above, showing the high efficiency of a "classical" metathetical conversion, which can be explained either as being via metal-carbene species [1f] or by insertion-elimination reactions [1e,i,j] as well as by hydrovinylation by Ru^0 complexes [1j].

It is remarkable that contrary to previous reports [1e] no effect of hydrosilane and oxygen on the final yield of the vinyltrimethylsilane metathesis in the presence of non-phosphine Ru^0 and Ru^{II} complexes has been observed.

Thus, the course (and mechanism) of the reaction is highly dependent upon the presence of ligands, the oxidation state and the coordination number of the ruthenium precursors. For the Ru–PPh_3 system, presence of oxygen also has an important role. Catalysis by Ru-clusters is suggested to be involved in the mechanism, and experimental work along this direction is in progress.

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