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Dehydrocondensation of organylsilanes giving Si – Si bonds

V B Pukhnarevich, M G Voronkov, L I Kopylova

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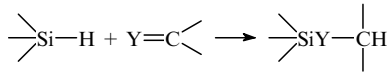
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Abstract. The data on catalytic dehydrocondensation of organylsilanes with the formation of Si – Si bonds are systematised and generalised. The mechanism and general features (the effects of the nature of the reactants and the catalyst, the solvent and the reaction conditions) of these reactions catalysed by cyclopentadienyl complexes of transition metals are considered. Electrochemical and other procedures for the dehydrocondensation of organylsilanes are discussed. The bibliography includes 220 references.

I. Introduction

Organosilicon compounds with Si – H bonds, in particular, organylsilanes of the $R_{4-n}SiH_n$ type ($n = 1-3$), are highly reactive substances.[1] In this connection, these compounds are of considerable theoretical and practical interest.

Thus addition of silanes to unsaturated substrates containing the C=C, C=N, N=N, C=O, C≡C or N≡N bonds, *viz.*, hydrosilylation,[2] is one of the most important procedures for the synthesis of various organosilicon compounds.[1–8] This unique reaction makes it possible to form Si – C bonds as well as Si – O – C and Si – N – C groups in one stage.



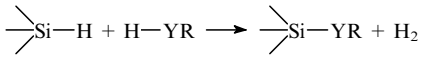
Y = R_2C, O, HN *etc.*

Organylsilanes, unlike their formal analogues, *viz.*, hydrocarbons, readily enter into dehydrocondensation reactions with OH, NH, SH and CH acids. Dehydrocondensation reactions with different compounds, such as water, alcohols, phenols, inorganic and carboxylic acids, amines, thiols, *etc.*, have been well studied.

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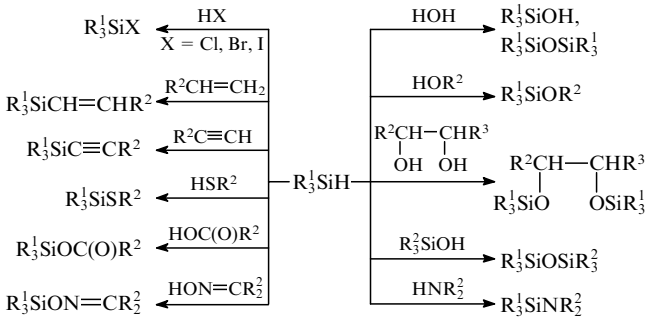
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Y = O, S, NH; R = H, Alk, Ar, Ac *etc.*

Hydrosilylation and dehydrocondensation are most often catalysed by transition metal compounds and nucleophiles. Examples of the use of dehydrocondensation of organylsilanes for the preparation of organosilicon compounds are shown in Scheme 1.

Scheme 1

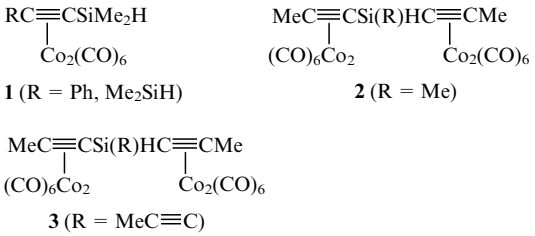


Synthetic applications of dehydrocondensation of silanes with hydroxy-containing organic compounds and the mechanism of this reaction have been adequately surveyed in the reviews.[1,9–14] Of more recent investigations, studies on alcoholysis of mono-, di- and trisubstituted silanes with saturated and unsaturated primary and secondary alcohols and diols in the presence of complexes of copper $\{[Ph_3PCuH]_6\}$,[15] titanium [16] and manganese $\{[Mn(CO)_4Br]_2\}$ [17] as well as in the presence of soluble platinum, palladium, nickel, ruthenium and rhodium complexes fixed on silica gel,[18–20] and studies on alcoholysis of disilanes in the presence of tetrabutylammonium fluoride [21] are worthy of note.

Dehydrocondensation of silanes with phenols, ammonia, amines, thiols and carboxylic acids are less well understood.[11] Of the recent advances, phenolysis catalysed by potassium fluoride [22,23] and ammonolysis (with ammonia or hydrazines) of phenylmethyl-, diphenylmethyl- and methyldichlorosilanes in the presence of dimethyltitanocene [24–27] should be mentioned. The synthesis of quaternary ammonium difluorosilicates by the reactions of $R^1_2R^2SiH$ with $R^3_2R^4N^+HF_2^-$ was reported.[28] The reactions of unsaturated organic acids with dimethylchlorosilane followed by intramolecular hydrosilylation of the resulting β,γ-unsaturated acyloxysilanes catalysed by Pt(II) 1,5-cyclooctadiene (COD) complexes afford silaoxacyclopentanones. The latter can

be converted into esters of hydroxycarboxylic acids. This method was used in the stereoselective synthesis of methyl ester of (2*S*,3*R*)-3-hydroxy-*N*-Boc-proline.[29] Products of hydrosilylation of styrene, 1-octyne and phenylacetylene with phenyl- and diphenylsilane enter into dehydrocondensation reactions with arenethiols ArSH (Ar = Ph, 4-MeC_6H_4 or 4-$MeOC_6H_4$) in the presence of rhodium tris(triphenylphosphine) chloride.[30]

Dehydrocondensation of octacarbonyldicobalt complexes of mono-, di- and triethynylsilanes (**1**–**3**) in the absence of nucleophilic or metal complex catalysts occurs through interactions between the Si–H bond and water, alcohols, carboxylic acids, primary amines, *etc.*[31,32]

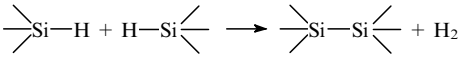


1 (R = Ph, Me_2SiH) **2** (R = Me)

3 (R = MeC≡C)

Dehydrocondensation of silanes with CH acids (alkanes, alkenes, alkynes and their derivatives) has been studied in sufficient detail.[11,33–39]

Dehydrocondensation of organosilicon compounds containing Si–H bonds to form disilanes has remained poorly studied for a long time and attracted considerable attention only recently.



Organosilicon compounds containing Si–Si bonds have attracted growing interest because they can be used as starting compounds in the synthesis of organic and inorganic derivatives of oligo- and polysilanes possessing specific structural, electronic, optical and chemical properties.[40,41] These oligo- and polysilanes find use in the production of ceramic materials,[42–64] semiconductors,[4,42,48,49,65–69] photoresistors,[42,44,46,48,49,70–77] photoinitiators of polymerisation of alkenes, *etc.*[42]

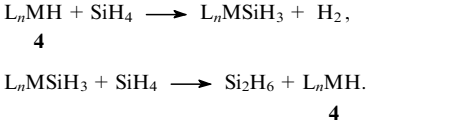
In this review, studies on dehydrocondensation of organylsilanes (which is sometimes wrongly called 'dehydropolymerisation'[42]) accompanied by the formation of Si–Si bonds are surveyed.

II. Catalytic dehydrocondensation of organylhydrosilanes

1. Catalysis by compounds of Group IIIB elements

The data on the use of complex compounds of Group IIIB elements as catalysts of dehydrocondensation of silanes are scarce.

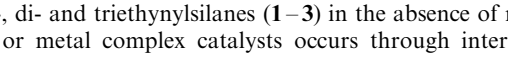
The activation energies and the enthalpies of dehydrocondensation of monosilane in the presence of complexes of lanthanides M (M = Sc, Y, La, Lu or Sm), which were calculated in a study,[78] indicate that this reaction can in principle proceed. It is believed that the first stage of the process involves silylation of intermediate **4**. The second stage leads to the formation of disilane and regeneration of intermediate **4**.



Of Group IIIB elements, only derivatives of lanthanides and actinides, as far as is known, are active in dehydrocondensation.[78–80] Thus $PhSiH_3$ in the presence of $Cp^*_2NdCH(SiMe_3)_2$ ($Cp^* = \eta^5$-C_5Me_5) was converted into oily polyphenylsilane with a molecular weight (*M*) of 600 at 80 °C during two days.[80]

The dimeric hydride complex of lanthanocene $[Cp^*_2LaH]_2$ is also an active catalyst of dehydrocondensation of phenylsilane.[80,81] In this case, a mixture of $PhSiH_2SiH_2Ph$ and $(PhSiH_2)_2SiHPh$ was formed from $PhSiH_3$.

Cyclopentadienyl complexes of actinides also catalyse dehydrocondensation of organylsilanes. Thus cyclopentadienyl derivatives of dimethyluranium and dimethylthorium converted phenylsilane into 1,2-diphenyldisilane (M = Th) or an oligomer (M = U) in 70% and 30% yields, respectively, even at room temperature during 6 h.[82]



M = U, Th.

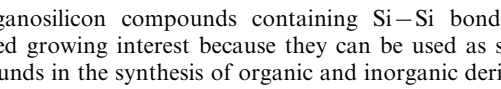
Dimethylmetallocenes, which are actinide derivatives, rank below isostructural titanocenes and zirconocenes in the catalytic activity.[82]

Dehydrocondensation of silanes of the $Si_aH_bR^1_c$ type [R^1 = Alk, Ar, alkenyl, AlkO, Hal or NHR^2; $a \geqslant 2$; $b \geqslant 1$; $(b + c) = (2a + 2)$] occurs under an inert atmosphere in the presence of $Cp_2MR^3_2$ (M = Th or U).[83–85]

2. Catalysis by compounds of Group IVB elements

a. Catalysis by alkyl- and arylmetallocenes $CpMR_3$, Cp_2MR_2 and Cp_2MPh_2

Dehydrocondensation of silanes, such as $PhSiH_3$, $MeSiH(OR)_2$ and $HSi(OR)_3$, in the presence of dimethyltitanocene was first reported by Harrod and coworkers in 1984.[86] The above-mentioned silanes react with dimethyltitanocene in a hydrocarbon solvent or without a solvent at room temperature to give the titanium hydride complex and the corresponding disilane derivatives.



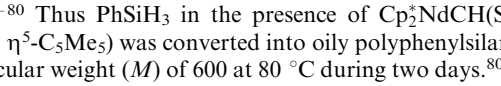
Trialkyl- and triarylsilanes as well as chlorosilanes do not undergo dehydrocondensation even at 80–120 °C.[82,86,87]

More recently, Harrod and coworkers published a series of studies[82,88–100] on dehydrocondensation of monosubstituted silanes ($RSiH_3$, where R = Ph, Bn or C_6H_{13}), disubstituted silanes ($R^1R^2SiH_2$, where $R^1 = R^2$ = Ph or R^1 = Ph and R^2 = Bu), trialkoxysilanes $(RO)_3SiH$ (R = Me or Et), $Me(EtO)_2SiH$ and 1,3,5,7-tetramethylcyclotetrasilane catalysed by dialkyltitanocenes Cp_2MR_2 (M = Ti or Zr; R = Me or Bn but not Ph). Later on, the series of catalysts of dehydrocondensation of silanes was substantially extended. It was demonstrated[82,89–91] that mono(cyclopentadienyl)trialkyl and di(cyclopentadienyl)dialkyl derivatives of Group IVB metals (Ti, Zr and Hf) exhibit a high catalytic activity in this reaction.

The most important advantage of the above catalysts over inorganic compounds,[24,29,101–107] complex and organometallic compounds[108,109] is their ability to catalyse the formation of oligomers containing 10–20 silicon atoms in the chains under rather mild conditions (Table. 1).

The catalytic activity of sterically hindered (cyclopentadienyl)trimethyltitanium as well as of its zirconium analogue in dehydrocondensation of phenylsilane is low.[82] Attempts to perform dehydrocondensation of phenylsilane in the presence of Cp_2HfMe_2 at 20 or 90 °C (12 h) were unsuccessful.

Generally, dehydrocondensation of silanes $RSiH_3$ catalysed by dimethyltitanocene or dimethylzirconocene affords a mixture of linear and cyclic oligomers the ratio of which depends on the nature of the initial silane and the reaction conditions.[92,93,112]



Thus phenylsilane forms predominantly linear oligomers, whereas hexylsilane produces a mixture of linear and cyclic oligomers. In the presence of dimethyltitanocene, benzylsilane was converted predominantly into hexabenzylcyclohexasilane (the yield was ~ 35%).[92]

Table 1. Comparative catalytic activities of metallocenes of derivatives of Groups IV – VII elements in dehydrocondensation of organylhydrosilanes $RSiH_3$ and R_2SiH_2.

$R_{4-n}SiH_n$	Catalyst	T /°C	t /h	Reaction products	Yield (%)	Average molecular weight		Ref.
						M_n	M_w	
$PhSiH_3$	$(MeCp)_2TiMe_2$	20	6	$H(SiHPh)_nH$	85	–	–	82
	$(MeCp)_2ZrMe_2$	20	6	$H(SiHPh)_nH$	100	–	–	82
	$CpCp^*TiMe_2$	20	40	$H(SiHPh)_nH$	80	–	–	82
	$[CpCp^*ZrH_2]_2$	23	0.25	$H(SiHPh)_nH$	11	2430	8360	48
	$[CpCp^*ZrH_2]_2$	23	15	$H(SiHPh)_nH$	14	2300	11 950	48
	$CpCp^*ZrMe_2$	20	40	$H(SiHPh)_nH$	100	–	–	82
	$CpCp^*ZrMe_2$	23	24	$H(SiHPh)_nH$	–	1700	6100	48
	$CpCp^*ZrMe_2$	23	54	$H(SiHPh)_nH$	–	2340	8250	48
	Cp_2TiMe_2	20	168	$H(SiHPh)_{10}H$ [a]	88			110
	Cp_2TiPh_2	110	24	$H(SiHPh)_{160}H$ [b]	83	730	960	49
	Cp_2TiPh_2	110	24	$H(SiHPh)_{30}H$ [b]	99	620	700	49
	Cp_2TiPh_2	110	24	$H(SiHPh)_{40}H$ [b,c]	40	620	780	49
	$Cp_2Ti(OPh)_2$	20	24	$H(SiHPh)_nH$	25	–	2400	110
	$Cp_2Ti(OC_6H_4OMe\text{-}4)_2$	20	48	$H(SiHPh)_nH$	25	–	3100	110
	$Cp_2Ti(OC_6H_4Cl\text{-}4)_2$	25	72	$H(SiHPh)_nH$	30	–	2200	110
	$Cp_2Ti(OC_6H_4CN\text{-}4)_2$	25	72	$H(SiHPh)_nH$	30	–	2200	110
	$Cp_2Ti(OC_6H_4Me\text{-}4)_2$	25	72	$H(SiHPh)_nH$	30	–	2300	110
	Cp_2TiMe_2	20	15	$H(SiHPh)_nH$	25	–	2700	110
	$Cp_2Zr(OPh)_2$	20	72	$H(SiHPh)_nH$	10	–	3200	110
	$CpCp^*Zr[Si(SiMe_3)_3]Me$	23	0.4	$H(SiHPh)_nH$	–	1720	4750	48
	$CpCp^*Zr[Si(SiMe_3)_3]Me$	23	24	$H(SiHPh)_nH$	–	1990	7660	48
	$CpCp^*Zr[Si(SiMe_3)_3]Me$	23	48	$H(SiHPh)_nH$	–	2240	10 150	48
	$Cp^*(C_5H_4Me)Zr[Si(SiMe)_3]_3Me$	23	48	$H(SiHPh)_nH$	–	1560	6110	48
	$(\eta^5\text{-}C_5H_4SiMe_3)_2ZrMe_2$	23	24	$H(SiHPh)_nH$	–	1270	3080	48
	$Cp^*(\eta^5\text{-}C_6H_4SiMe_3)ZrH_2$	23	14	$H(SiHPh)_nH$	–	1660	8630	48
	$CpSiMe_2CpZr[Si(SiMe_3)_3]Me$	23	24	$H(SiHPh)_nH$	–	1910	5090	48
	$CpSiMe_2CpZr[Si(SiMe_3)_3]Me$	23	48	$H(SiHPh)_nH$	–	1730	5250	48
	$CpSiMe_2CpZrMe_2$	23	3	$H(SiHPh)_nH$	–	1880	3770	48
	$CpSiMe_2CpZrMe_2$	23	48	$H(SiHPh)_nH$	–	1570	3890	48
	Cp_2V	100 – 120	40	$H(SiHPh)_2H$,	40			82
				$H(SiHPh)_3H$	20			
	Cp_2VMe_2	100 – 120	40	$H(SiHPh)_2H$,	40			82
				$H(SiHPh)_3H$	20			
Ph_2SiH_2	Cp_2TiMe_2	25	29	$[Ph_2SiH]_4$	100			111
9,10-Dihydro-9-sila-anthracene (**5a**)	Cp_2ZrMe_2	90	10	dimer,	12			111
				trimer	87			
10,11-Dihydro-5*H*-dibenzo[*b*,*f*]silepine (**5b**)	Cp_2ZrMe_2	105	72	dimer	20 [d]			111
Ph_2SiH_2	Cp_2TiPh_2	110	24	$[Ph_2SiH]_2$	72			49
	Cp_2TiPh_2	110	24	$[Ph_2SiH]_2$	66 [e]			49
	Cp_2TiPh_2	110	24	$[Ph_2SiH]_2$	72 [c]			49
	$Cp_2Ti(OPh)_2$	80	5	$[Ph_2SiH]_2$	10			110
$MePhSiH_2$	Cp_2TiPh_2	110	24	$(MePhSiH)_2$,	14			49
				$H(MePhSi)_3H$	32			
	Cp_2TiPh_2	110	24	$(MePhSiH)_2$,	15 [e]			49
				$H(MePhSi)_3H$	23 [c]			
	Cp_2TiPh_2	110	24	$(MePhSiH)_2$,	7			49
				$H(MePhSi)_3H$	88			

[a] In the presence of a hydrogen acceptor; [b] the highest degree of polymerisation; [c] in the presence of cyclooctene; [d] 52% of unidentified oligomers; [e] in the presence of dec-1-ene.

The reactivity of $RSiH_3$ upon catalysis by dimethyltitanocene decreases in the following series (the relative reaction rates at 20 °C are given in parentheses): Ph (13) > Bn (1) = C_6H_{13} (1). In the reactions catalysed by dimethylzirconocene, the reactivity changes in the following order: Ph (100) > Bn (15) > C_6H_{13} (5).[91]

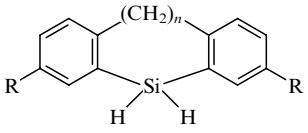
Zirconocenes catalyse dehydrocondensation of substituted phenylsilanes $XC_6H_4SiH_3$ containing the fluoroalkyl, alkoxy, aryloxy, acyloxy, hydroxy or alkylamino groups in the benzene ring.[110] Thus a polymer with the molecular weight of 1330 was prepared from 4-(dimethylamino)phenylsilane.[110]

The only convenient procedure for the synthesis of polymethylsilane involves dehydrocondensation of methylsilane catalysed by dimethyltitanocene or dimethylzirconocene at 50 °C and 10 atm.[92] The molecular weight of the resulting cross-linked polymethylsilane is rather high ($\sim$ 10 000).

Disubstituted silanes, such as $MeSiH_2Ph$ and Ph_2SiH_2, are less reactive than $RSiH_3$. In the presence of dimethyltitanocene or

dimethylzirconocene at 60–80 °C, these silanes form predominantly dimers and trimers, *viz.*, RH_2SiSiH_2R and $(R_2SiH)_2$.SiHR.[91,92] The catalytic activity of metallocenes Cp_2MMe_2 in this reaction decreases in the series Zr > Ti ≫ Hf.[89,91,92] When zirconocene, which was prepared *in situ* by the reaction of Cp_2ZrCl_2 with BuLi, was used as a catalyst, methylphenylsilane was converted into the linear $H(MePhSi)_nH$ oligomer, where $n = 5$ or 6.[113] Unlike methylphenylsilane, butylmethylsilane[91,92] as well as other silanes R_3SiH (see Ref. 42) remained unchanged in the presence of dimethyltitanocene or dimethylzirconocene even at 100 °C.

Dehydrocondensation of dibenzosilaheterocycles **5a–d** was studied.[112]



5a–d

R = H: n = 1 (**a**), 2 (**b**), 0 (**c**);
R = Bu^t, n = 0 (**d**).

Dehydrocondensation of 9,10-dihydro-9-silaanthracene **5a** in the presence of dimethyltitanocene at 20 °C does not occur. In the reaction catalysed by dimethylzirconocene at 90 °C, the corresponding trimer is formed in high yield. Under analogous conditions in the presence of the same catalysts, 10,11-dihydro-5*H*-dibenzo[*b*,*f*]silepine (**5b**) remains unchanged. Silafluorene (**5c**) is converted into a pentamer, which is insoluble in the usual organic solvents, upon catalysis by dimethyltitanocene in toluene in the absence of oxygen for 29 h.

Titanium and zirconium complexes with the [2-(diisopropylamino)ethyl]cyclopentadienyl ligand, *viz.*, $[Cp(CH_2)_2NPr^i_2]_2MMe_2$ (M = Ti or Zr), $[Cp(CH_2)_2NPr^i_2]_2TiBr_2$ and $[Cp(CH_2)_2.NPr^i_2]_2Ti(OPh)_2$, were suggested as efficient catalysts of dehydrocondensation of phenylsilane.[114]

Binary mixtures of dimethyltitanocene with one equivalent of trialkyl- or alkylarylphosphine are used as catalysts of dehydrocondensation of $PhSiH_3$, $MePhSiH_2$, Ph_2SiH_2 and $BnSiH_3$.[97–99] In these cases, microcrystalline products are formed.

Nakano and coworkers[49] succeeded in performing dehydrocondensation of triphenyl-, diphenyl- and methylphenylsilanes in the presence of Cp_2TiPh_2 (under an argon atmosphere, 110 °C, 24 h). In this case, 1,1,2,2-tetraphenyldisilane (72%) formed from diphenylsilane, whereas 1,2,3-trimethyl-1,2,3-triphenyltrisilane (32%) and 1,2-dimethyl-1,2-diphenyldisilane (14%) were obtained from methylphenylsilane. When cyclooctene was used as an acceptor of hydrogen, which was eliminated upon dehydrocondensation, the yield of trisilane was increased to 80%. Dehydrocondensation of phenylsilane under analogous conditions proceeds more readily to yield polyphenylsilanes containing terminal hydrogen atoms (M = 340–17 300). The reaction of phenylsilane in the presence of Cp_2TiPh_2 at 140 °C for 3 h afforded a cyclic six-membered silane.[115] Under analogous conditions, triethylsilane generates hexaethyldisilane in insignificant yield (0.6%).

Dehydrocondensation of 1,2-diphenyldisilane catalysed by dimethyltitanocene or dimethylzirconocene proceeds very rapidly. Thus the $H(PhSiH)_4$ tetramer was obtained in 40% yield after 30 min.[91] Apparently, the presence of $PhSiH_3$ and $H(PhHSi)_2.SiH_2Ph$ among the reaction products results from competitive disproportionation of the initial 1,2-diphenyldisilane

$$2\,PhH_2SiSiH_2Ph \longrightarrow PhSiH_3 + H(PhHSi)_2SiH_2Ph.$$

The enhanced reactivity of 1,2-diphenyldisilane is determined by the lower energy of the Si–H bonds in the $-H_2Si-SiH_2-$ fragment compared to their energy in the SiH_3 group.

Dehydrocondensation of silanes of the $Si_aH_bR_c$ type [R = Alk, Ar, alkenyl, AlkO, Hal or NR_2; $a \geqslant 2$; $b \geqslant 1$; $(b + c) = (2a + 2)$] catalysed by dialkylmetallocenes Cp_2MAlk_2 (M = Ti, Zr or Hf) afforded liquid linear polymers containing from three to seven monomer units.[83–85]

Dehydrocondensation of phenylsilane with 1,2-dimethyldisilane in the presence of Cp_2MMe_2 (M = Ti or Zr) yielded the $H[(MeSiH)_x(PhSiH)_y]_nH$ oligomer.[116]

The reaction of $Me_2HSiSiH_2Me$ with 1,2-dimethyldisilane afforded the $H[(MeSi)_x(Me_2Si)_y]_nH$ oligomer. The structures of these oligomers were established by GLC-mass spectrometry.[116]

b. Catalysis by alkoxy- and aryloxymetallocenes and titanium alkoxides

Dehydrocondensation of phenyl-, diphenyl- and dibutylsilane catalysed by dialkoxy-, diphenoxytitanocene, its derivatives $Cp_2Ti(OR)_2$ (R = Alk, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4 or 4-CNC_6H_4) or diphenoxyzirconocene $Cp_2Zr(OPh)_2$ was studied.[117–120] Dehydrocondensation of $PhSiH_3$ afforded a mixture of linear and cyclic oligomers (15 min, 50 °C, the total yield was 25%). In this case, the reaction rate and the compositions of the resulting oligomers are comparable with those observed in the reactions with the use of Cp_2TiMe_2 (see Ref. 87) or the Cp_2TiCl_2–2 BuLi binary mixture[113] as catalysts.

In the presence of $Cp_2Ti(OPh)_2$ at 100 °C, diphenylsilane formed the $Ph_2SiHSiHPh_2$ dimer in 10% yield.[111] In the presence of 5 mol. % of $Cp_2Ti(OPh)_2$ at 110 °C, dibutylsilane gave mono- and diphenoxy derivatives due to the interaction with the catalyst.

$$Bu_2SiH_2 + Cp_2Ti(OPh)_2 \longrightarrow$$
$$\longrightarrow Bu_2SiH(OPh) + Bu_2Si(OPh)_2 + Bu_2HSiSiHBu_2 + Cp_2TiH_2$$

For the reaction to start, preliminary heating of the reaction mixture is required. In this case, an induction period from 15 to 120 min was observed. Probably, the reduction of the Ti–OPh bonds in the catalyst to form an intermediate hydride complex occurs in one of the initial stages.[119] Diphenoxytitanocene derivatives containing substituents in the benzene ring, *viz.*, $Cp_2Ti(OC_6H_4X\text{-}4)_2$ (X = Me, Cl, CN or OMe), exhibit higher catalytic activity. In the presence of these complexes even at 20 °C, phenylsilane yielded products identical to those obtained at 50 °C in the presence of diphenoxytitanocene (see Table 1).[119]

Dehydrocondensation of diphenylsilane catalysed by diphenoxyzirconocene occurs at 20 °C with elimination of hydrogen. However, an induction period was also observed and prior heating (50 °C, 15 min) of the reaction mixture is required. In this case, the amount of cyclic oligomers among the reaction products is smaller than that obtained with the use of diphenoxytitanocene.[119]

Dehydrocondensation of phenylsilane in the presence of dicyclopentadienylzirconium dimethoxide as a catalyst was reported.[121]

Dehydrocondensation of 1,4-disilapentane catalysed by diphenoxytitanocene was described.[119] The rate of this reaction is smaller than that in the case of phenylsilane and is close to that observed with the use of dimethyltitanocene or the Cp_2TiCl_2–2 BuLi system as catalysts.[122] Initially, the catalyst was activated at 0 °C and then the reaction was performed at 20 °C. In this case, exclusively SiH_3 groups reacted resulting in a linear oligomer containing the $SiMeH_2$ fragments. This oligomer was converted into an insoluble cross-linked polymer upon heating.[119]

$$n\,MeSiH_2CH_2CH_2SiH_3 \longrightarrow$$
$$\longrightarrow H(MeSiHCH_2CH_2SiH_2)_nH + (n-1)\,H_2$$

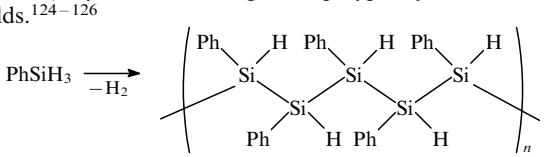
Alkoxy derivatives of titanium, which do not contain cyclopentadienyl ligands, such as $Ti(OPr^i)_4$ or $MeTi(OPr^i)_3$, were also used as catalysts of dehydrocondensation of alkyl- and arylsilanes.[117]

c. Catalysis by metallocene chlorides and the Cp_2MHal_2–RLi(RMgX) systems

Metallocene dichlorides Cp_2MCl_2 are similar to Cp_2MMe_2 (M = Ti or Zr) in catalytic activity.[90,123] The activity of Cp_2HfCl_2 is substantially lower than that of Cp_2HfMe_2, but it can be enhanced by adding MeLi in a molecular ratio of 1 : 2. In this case, both chlorine atoms are apparently completely replaced by

the methyl groups. Dehydrocondensation of phenylsilane in the presence of a mixture of Cp_2HfCl_2 and MeLi afforded cyclophenylsilanes in 15% yield.[90] When the reagents were taken in a ratio of 1 : 3 or 1 : 4, the yield of $(PhSiH)_n$ was only 25%; the molecular weights of the resulting phenylcyclosilanes were larger than those obtained with the use of dimethyltitanocene or dimethylzirconocene as a catalyst.[90] When a mixture of [1,2-bis(tetrahydroindenyl)ethane]dichlorozirconium with MeLi taken in a ratio of 1 : 2 was used, cyclophenylsilanes were formed in 42% yield.[123]

Dehydrocondensation of phenylsilane catalysed by zirconocene derivatives of the $Cp_2ZrX(Y)$ type (X = H or Cl and Y = Cl or Alk) yields stereoregular polyphenylsilane in good yields.[124–126]



It was expected[90] that dehydrocondensation of phenylsilane catalysed by Zr complexes containing ethylenebis(tetrahydroindenyl) or -indenyl ligands would also afford stereoregular polyphenylsilanes, unlike the reactions catalysed by biscyclopentadienyl complexes of Ti and Zr, which yield atactic polymers. According to the data of ^1H NMR spectroscopy and gel-permeation chromatography, this reaction afforded a mixture of linear and cyclic oligomers, which hindered the interpretation of the microstructure of the resulting polymer. It should be remembered that, for example, nine stereoisomers of hexaphenylcyclohexasilane possessing 23 chiral centres can exist.[90]

Dehydrocondensation of hydrosilanes $RSiH_3$ (R = Bu^n, C_6H_{13} or Ph) catalysed by the Cp_2MCl_2 – 2 BuLi system (M = Ti, Zr or Hf) was studied in detail.[127–130] The course of the reaction was monitored by gas chromatography and GLC-mass spectrometry. Dehydrocondensation of phenylsilane afforded linear oligomers with M = 1775 and 614 ($M_w : M_n$ = 1.17 and 1.01, respectively, when Cp_2ZrCl_2 was used) and M = 1308 and 600 ($M_w : M_n$ = 1.09 and 1.03, respectively, when Cp_2TiCl was used). Therefore, the molecular weight of the dehydrocondensation products of phenylsilane is affected by the nature of the catalyst. The molecular weight increases in the series Hf ≪ Ti ≪ Zr, as in the case of the use of individual metallocenes.[82] Dehydrocondensation of diphenylsilane catalysed by the Cp_2HfCl_2 – 2 BuLi system at 20 °C for 1 h yielded only 1,1,2,2-tetraphenyldisilane. When the temperature was increased to 50 °C, higher oligomers up to decaphenylpentasilane (the yield was 17%) were also obtained after 5 h. Under analogous conditions, butylsilane in the presence of the Cp_2MCl_2 – 2 BuLi system (M = Ti or Zr) was converted into a mixture of linear and cyclic oligomers containing up to 11 silicon atoms. Two individual diastereomers of tetrabutyltetrasilane were isolated from this mixture. It is remarkable that the ratio of the diastereomers remained unchanged in the course of the reaction if M = Ti, whereas in the case of M = Zr, the diastereomers were formed at different rates.

Hexylsilane in the presence of the Cp_2ZrCl_2 – 2 BuLi system forms linear and cyclic tetra- and heptamers.[127]

Dehydrocondensation of $R^1R^2SiH_2$ (R^1 = Ph and R^2 = Me; $R^1 = R^2$ = Ph; or R^1 = 3-MeC_6H_4 and R^2 = Me) and dibenzosilaheterocycles **5a**,**b**,**d** in the presence of the Cp_2MCl_2 – 2 BuLi system (M = Ti, Zr or Hf) was studied.[113] In the case of dehydrocondensation of $MePhSiH_2$ (90 °C, 24 h), the activity of these catalysts increases in the series Hf < Ti < Zr. Linear oligomers containing from 2 to 8 silicon atoms are the major reaction products. At 20–90 °C, more sterically hindered diphenylsilane yields only tetraphenyldisilane. Silafluorene (**5d**) reacted analogously to give (after 2 h) the corresponding disilane in 82% yield. Dehydrocondensation of 9,10-dihydro-9-silaanthracene (**5a**) in the presence of the binary catalyst proceeds substantially more slowly than the reaction with the use of dimethyltitanocene.

Dibenzosilepine (**5b**) remained unchanged at 90 °C in the presence of any catalytic system based on zirconium. The use of ethyl-, isopropyl- or butylmagnesium chlorides instead of BuLi (90 °C, 24 h, toluene) led to a substantial decrease in the proportion of tri- and tetramers. The binary Cp_2ZrCl_2 – BuLi system is an efficient catalyst of dehydrocondensation of diorganylsilanes, but its use, unlike dimethyltitanocene, leads predominantly to the formation of short-chain oligomers.[113]

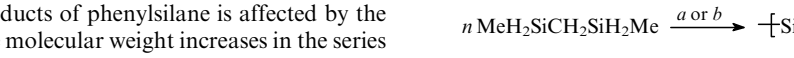
Syndiotactic polyphenylsilanes with high M_w (> 10 000) were prepared by dehydrocondensation of phenylsilane in the presence of a mixture of the zirconium complex {Cp*[$Cp(CH_2)_n$.NMe_2]$ZrCl_2$ (n = 2 or 3) or Cp*[$Cp(CH_2)_nCHMe_2$]$ZrCl_2$ (n = 1 or 2)} with two equivalents of BuLi.[131, 132]

The catalytic activity of pure dimethyltitanocene as well as of its mixture with butyllithium decreases substantially in the presence of atmospheric oxygen.[122]

Dehydrocondensation of silanes [both symmetrical, *viz.*, $H(PhMeSi)_2H$ and $H(BuMeSi)_2H$, and unsymmetrical, *viz.*, $HPh_2SiSiPhMeH$, $HPhMeSiSiMe_2H$, $HPhMeSiSiPrMeH$ and $HPh_2SiSiPhH_2$] catalysed by the Cp_2MCl_2 – 2 BuLi system (M = Ti or Zr) in the presence of cyclooctene was studied.[133, 134] When the disilane : cyclooctene : Cp_2MCl_2 ratio was 30 : (> 30) : 1, trisilanes were rapidly formed from $HPh_2SiSiPhMeH$ and $HPhMeSiSiMe_2H$. The products were identified by GLC-mass spectrometry. Dehydrocondensation of $HPh_2SiSiPhH_2$ afforded Ph_2SiH_2 and $PhSiH_3$, which were subsequently converted into a mixture of linear and cyclic polysilanes. These data indicate that dehydrocondensation is accompanied by the cleavage of the Si – Si bond in the initial disilane.

Dehydrocondensation of $RSiH_3$ and RH_2SiSiH_2R, where the R substituent is the $Cp(CO)_2Fe$ metallocene group, was performed in the presence of the Cp_2MCl_2 – BuLi system (M = Ti or Zr). Dehydrocondensation of $Cp(CO)_2FeSiH_3$ and $Cp(CO)_2$.$FeSiH_2SiH_2Fe(CO)_2Cp$ gave organometallic oligosilanes characterised by spectroscopic and chromatographic methods.[135]

Dehydrocondensation of 2,4-disilapentane catalysed by the Cp_2ZrCl_2 – 2 BuLi or Cp_2TiCl_2 – 2 MeLi system afforded new poly(silacarbo)silanes containing the $SiCH_2Si$ fragments in the main chain.[43, 128]

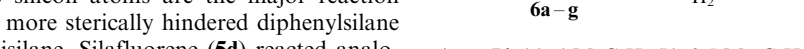


(*a*) Cp_2ZrCl_2 – 2 BuLi; (*b*) Cp_2ZrCl_2 – 2 MeLi.

This reaction yielded predominantly oligomers (50% – 80%), while di- and trimeric products were formed in insignificant amounts. The yields of oligomers depend substantially on the nature of the metal atom in the metallocene, the duration of the reaction and the concentration of the monomer. The Cp_2ZrCl_2 – 2 BuLi catalytic system is more efficient than the Cp_2TiCl_2 – 2 MeLi system (the yields of oligomers are 80% and 50%, respectively). The degree of condensation of these monomers is somewhat higher than that of $PhMeSiH_2$; the resulting polymers are characterised by moderate M values, which indicates that they are partially cross-linked.[86, 89, 113] The higher reactivity of 2,4-disilapentane compared to phenylmethylsilane is attributable to the favourable steric factors.

d. Catalysis by the Cp_2MCl_2 – Al system

Dehydrocondensation of 3-arylpropylsilanes **6a**–**g** as well as of 2-phenyl-1,3-disilapropane [$H_3SiCH_2CH(Ph)CH_2SiH_3$, **7**] catalysed by the Cp_2MCl_2 – Al system (M = Ti or Hf) was performed.[44, 45]



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 2,5-$Me_2C_6H_3$ (**c**), ClC_6H_4 (**d**, mixture of isomers), 4-MeC_6H_3Cl (**e**, mixture of isomers), $PhOC_6H_4$ (**f**, mixture of isomers), $C_{10}H_7$ (**g**, mixture of isomers).

Substituted polysilanes **8a–g** prepared from compounds **6a–g** have predominantly linear structures and molecular weights from 800 to 1028 (the degree of polymerisation is 3–7, M = Hf) and from 800 to 1300 (the degree of polymerisation is 6–16, M = Ti), *i.e.*, the molecular weights are higher than those of the analogous polyarylalkylsilanes synthesised in the presence of other catalytic systems.[42,46] The catalytic activity of the Cp_2HfCl_2–Al system is lower than that of its titanium analogue (the yields of polysilanes are 31%–84% and 79%–99%, respectively).

The reaction rate increases both as the concentration of the catalyst increases [from 0.5 mol. % to 10 mol. % (M = Ti) or from 1.0 mol. % to 6.5 mol. % (M = Hf)] and as the reaction temperature increases to 90 °C. Dehydrocondensation of compound **7** catalysed by the Cp_2TiCl_2–Al system proceeded smoothly and the total yield of polysilanes reached 90%.[44] Two polymeric reaction products were isolated from the resulting mixture by column chromatography. One of these products is a viscous weakly cross-linked soluble polysilane (M_w = 1046, M_n = 819, n = 11) and the second product is a completely cross-linked insoluble white solid polymer.

Dehydrocondensation of organylsilanes **6b** and **6d**, **6b** and **6f** or **6d** and **6f** catalysed by the Cp_2TiCl_2–Al system afforded the corresponding cooligomers (the yields were 51%–86%) with M_w = 678–994 and M_n = 405–538 (the degree of copolymerisation was 7).[44]

e. Catalysis by the ternary Cp_2MCl_2–RLi–$B(C_6F_5)_3$ system and by the cationic bis(cyclopentadienyl) complexes of zirconium and hafnium

Dehydrocondensation of phenylsilanes in the presence of the ternary Cp_2MCl_2 ($CpCp^*MCl_2$)–2 BuLi–$B(C_6F_5)_3$ catalytic system (M = Ti, Zr or Hf) afforded polyphenylsilanes with M = 10 910–13 790.[47,95,96] It is remarkable that when the reaction was performed in the presence of only $B(C_6F_5)_3$ at 20 °C for 10 days, the molecular weight of the resulting polyphenylsilane reached only 2450. In both cases, the ratio between linear and cyclic polymers remained the same.[47] The addition of $B(C_6F_5)_3$ to the Cp_2MCl_2–BuLi catalytic system changes the ratio between the cyclic and linear dehydrocondensation products from 45 : 55 to 15 : 85. The catalytic activity of zirconocenes both in the presence of $B(C_6F_5)_3$ and in its absence increases in the series $Cp^*_2Zr \ll Cp_2Zr \approx (MeC_5H_4)_2Zr < CpCp^*Zr$ (*cf.* Ref. 136). The Cp_2TiMe_2–$B(C_6F_5)_3$ and $[Cp_2ZrMe(THF)](BPh_4)$ systems, which are successfully used for the polymerisation of alkenes,[137] do not catalyse dehydrocondensation of phenylsilane.[47]

Dehydrocondensation of organylsilanes in the presence of the ternary catalytic system, which contains Group IVB metallocene, a trimethylsilyl derivative of alkali metal and THF, has been described.[138] Thus a polymer with M = 6800 was prepared from phenylsilane in the presence of the Cp_2HfCl_2–Me_3SiLi–THF system.

Dehydrocondensation of phenylsilane in the presence of cationic bis(cyclopentadienyl) complexes of Zr and Hf was studied. These complexes were prepared *in situ* by the reactions of Cp_2MMe_2 (M = Zr or Hf) with $[Bu_3NH]^+[B(3,5\text{-}Me_2C_6H_3)_4]^-$ or $[PhMe_2NH]^+[B(C_6F_5)_4]^-$.[48] The activity of these catalysts appeared to be low. The total yield of cyclophenylsilanes at 23 °C is no higher than 13%. Dehydrocondensation with the use of the $CpCp^*ZrMe_2$–$[Bu_3NH]^+$.$[B(3,5\text{-}Me_2C_6H_3)_4]^-$ system as a catalyst (23 °C, 1 h) affords linear and cyclic polyphenylsilanes with rather low M values (up to 2810). In this case, variations in the anion and the metal atom in the metallocene (Zr or Hf) have no substantial effect on the course of the process.[48]

f. Catalysis by metallocenes containing organosilicon groups at the metal atom

Metallocenes (Ti, Zr or Hf) containing organosilicon groups at the metal atom were also suggested as catalysts of dehydrocondensation of organosilanes. In the presence of these catalysts, di- and trisubstituted silanes form linear (at $\leqslant$ 60 °C) or cyclic (at $\geqslant$ 80 °C) polysilanes.[48,65,91,94,100,139–147] For example, dehydrocondensation of phenylsilane catalysed by $Cp_2Ti(CH_2SiMe_3)_2$ afforded linear polysilane (92%, M = 1890) and cyclic oligophenylsilane (95%, M = 738) at 30 °C (24 h) and 80 °C, respectively.[139]

Dehydrocondensation of arylsilanes $RC_6H_4SiH_3$ (R = H, 4-Me, 3-Me, 2-Me, 4-CF_3, 3-CF_3 or 2-CF_3) in the presence of $Cp_2Zr[Si(SiMe_3)_3]Me$ yielded poly(trifluoromethylphenyl)-, poly(methylphenyl)silanes and polyphenylsilane.[65] In the dehydrocondensation process, the reactivity of $RC_6H_4SiH_3$ decreases depending on the radical R in the series (the relative reaction rates are given in parentheses) 4-CF_3 (1.34) $\approx$ 3-CF_3 (1.33) > H (1.00) > 4-Me (0.95) $\approx$ 3-Me (0.93) $\gg$ 2-Me (0.18) $\approx$ 2-CF_3 (0.14). These data indicate that the reaction rate is influenced both by the electronic and steric effects of the substituents in the aromatic core. 2-Substituted phenylsilanes exhibit the lowest activities. The molecular weights of poly(trifluoromethyl)phenylsilanes and polyphenylsilanes obtained under analogous conditions are much the same.

Silyl complexes of zirconocene and hafnocene of the $CpCp'M(SiR^1_3)R^2$ type (Cp′ = Cp or Cp*; M = Zr or Hf; R^1 = Me, Ph or $SiMe_3$; R^2 = Alk, $SiMe_3$ or Cl) are also efficient catalysts of dehydrocondensation of arylsilanes. In these cases, the molecular weights of linear and cyclic polymers vary over wide ranges depending on the nature of the catalyst and the reaction conditions.[48,140–142]

Phenylsilane in the presence of $Cp_2Zr[Si(SiMe_3)_3]Me$ or $Cp_2Zr[Si(SiMe_3)_3]Cl$ formed polymers with M = 990 and polymers with M = 1240 containing from 10 to 20 SiHPh monomer units after 15 min and 7 h, respectively. Phenylcyclosilane (containing from 5 to 8 silicon atoms) was identified among these polymers.[14,48] It should be noted that polyphenylsilane with M_n = 560 was obtained upon catalysis by dimethylzirconocene during 24 h. Zirconocenes with mixed cyclopentadienyl ligands (nonsubstituted or partially or completely methylated) appeared to be more active catalysts in these reactions. The molecular weight of the linear polymer $H(PhHSi)_nH$ formed in the presence of $CpCp^*Zr[Si(SiMe_3)_3]Me$ reached 3000 and 5260 after 15 min and 48 h, respectively. Linear and cyclic polymers contain about 70 silicon atoms in the polysilane chains (see Table 1).[48]

Dehydrocondensation of methylphenyl- and diphenylsilanes catalysed by alkyne zirconocene and titanocene complexes of the $Cp_2M(L)(RC{\equiv}CSiMe_3)$ type (M = Ti or Zr; L = THF or Py) affords oligomers. Under these conditions, phenylsilane forms polymers.[148,149]

The catalytic activities of the zirconium and titanium complexes, *viz.*, $(\eta^5\text{-}C_5H_4SiMe_3)_2Zr[Si(SiMe_3)_3]Cl$ (**9**) and $Cp_2Ti[Si(SiMe_3)_3]Cl$ (**10**), respectively, in dehydrocondensation of phenylsilane and dibutylstannane were studied.[143] According to the data of GLC-mass spectrometry, a viscous mixture of linear $H(PhHSi)_nH$ and cyclic $(PhSiH)_n$ (n = 5 or 6) oligomers (M_n = 900, M_w = 1810) was formed from phenylsilane in the presence of the complex **9** after 24 h. Under analogous conditions, a mixture of linear and cyclic polysilanes with M_n = 1870 and M_w = 3280 was formed upon catalysis by the $CpCp^*Zr[Si(SiMe_3)_3]Cl$ complex, which does not contain the trimethylsilyl group in the cyclopentadienyl ring. Dehydrocondensation of dibutylstannane in the presence of the complex **9** affords polybutylstannanes with a broad molecular weight distribution spectrum (M_w = 4800, M_n = 1420). The reaction of the complex **10** with an equivalent amount of phenylsilane in C_6D_6 gave a mixture of the metathesis product **11** and the reductive elimination product **12** in a ratio of 2 : 1 in quantitative yield.[143]

$$\underset{\mathbf{10}}{Cp_2Ti[Si(SnMe_3)_3]Cl} + PhSiH_3 \longrightarrow \underset{\mathbf{11}}{HSi(SnMe_3)_3} + \underset{\mathbf{12}}{ClSi(SnMe_3)_3}$$

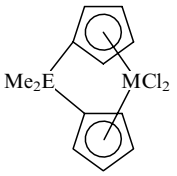
Dehydrocondensation of 1,4-$RH_2SiC_6H_4SiH_2R$ (R = Me, Et or C_6H_{13}) catalysed by $CpCp^*Zr[Si(SiMe_3)_3]Me$ under mild

conditions (20 °C) afforded linear oligomers $RH_2Si(C_6H_4SiHR.SiHR)_nC_6H_4SiH_2R$.[150] Further heating of the resulting mixture of oligomers (R = Me or Et) led to an increase in the molecular weight due to partial cross-linking of the polymer chains through free Si – H groups. Thermolysis of the insoluble cross-linked polymer $EtH_2Si(C_6H_4SiHEtSiHEt)_nC_6H_4SiH_2Et$ at 1100 °C afforded ceramics in higher yield (67%) than that with the use of the corresponding low-molecular-weight oligomers (35%).[150]

It was reported that the $Cp_2Zr(OMe)_2 – (Me_3Si)_3SiLi – 3\,THF$ ternary system was used as a catalyst of dehydrocondensation of phenylsilane.[121]

g. Catalysis by ansa-metallocenes

Dehydrocondensation of phenyl- and methylphenylsilane catalysed by ansa-metallocenes (**13a – f**),[144, 145, 151, 152] which are used for the preparation of iso- and syndiotactic polypropylenes, was studied.[153, 154]



13a – f

E = Si: M = Ti (**a**), Zr (**b**), Hf (**c**);
E = C: M = Ti (**d**), Zr (**e**), Hf (**f**).

Methylphenylsilane in the presence of ansa-metallocenes with a BuLi cocatalyst (the ratio is 22 : 1 : 2) in toluene at 90 °C formed low-molecular-weight oligomers, *viz*., the corresponding di-, tri- and tetrasilanes. In this case, tetramers existed in the reaction mixture in insignificant amounts (1.8% – 5.5% according to the GLC data). In the presence of ansa-hafnocene, tetrasilane is not formed at all. The activity of ansa-metallocenes, which was estimated from the yield of disilane after 24 h, decreases in the series Ti > Hf > Zr.

Catalyst	**13a**	**13c**	**13b**	**13d**	**13f**	**13e**
Yield of disilane according to GLC (%)	36	30	22	58	37	25

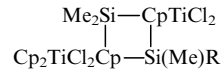
The activity of metallocene dichlorides in dehydrocondensation of methylphenylsilane decreases in the series Hf (37) > Ti (32) > Zr (15) (the yields of disilane according to the GLC data are given in parentheses). 1,2-Dimethyl-1,2-diphenyldisilane and 1,2,3-trimethyl-1,2,3-triphenyltrisilane prepared from methylphenylsilane exist as mixtures of diastereomers. Dehydrocondensation of phenylsilane catalysed by ansa-metallocenes (Ti, Zr or Hf) in the absence of a solvent affords a mixture of linear and cyclic polyphenylsilanes. In this case, the molecular weight of the linear polymer increases in the series Ti < Zr < Hf.[144] Under analogous conditions (the silane : complex : BuLi ratio is 24 : 1 : 2, 13 – 24 h, 20 °C), the molecular weight of polyphenylsilanes prepared in the absence of ansa-metallocenes is always lower than that obtained with the use of usual metallocenes.

e. Catalysis by binuclear titanium and zirconium complexes

Dehydrocondensation of phenyl-, benzyl-, hexyl- and diphenylsilanes catalysed by the binuclear titanium complexes $Cp_2Ti(\mu\text{-}HSiHPh)_2TiCp_2$ and $Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2$ generally affords oligomers.[100] Alkenes, the activating action of which increases in the series cyclohexene < 2-pentene < 1-pentene ~ norbornene ~ styrene, are used as cocatalysts, which substantially enhance the rate of this reaction.

It was reported [146] that binuclear titanocene complexes can be used as catalysts of dehydrocondensation of phenylsilane, for example

$CpTiCl_2CpSi(Me)(R)CpTiCl_2Cp$ (R = H, Me, Ph),
$CpTiCl_2CpSiMe_2(CH_2)_nSiMe_2CpTiCl_2Cp$,



(a mixture of *cis* and *trans* isomers)

These reactions give mixtures of linear and cyclic polyphenylsilanes;[146] BuLi is used as a cocatalyst.

3. Catalysis by compounds of Group VB – VIIB elements

The data on the use of compounds of Group VB – VIIB metals as catalysts of dehydrocondensation of organylsilanes are scarce. Vanadocene Cp_2V and dimethylvanadocene Cp_2VMe_2 do not catalyse this reaction at 20 °C.[82] However, phenylsilane in boiling toluene in the presence of these compounds was converted into a mixture of the PhH_2SiSiH_2Ph dimer (40%) and the $(PhSiH_2)_2.SiHPh$ trimer (20%). Under analogous conditions (100 – 120 °C, 123 h), higher metallocenes Cp_2M (M = Nb or Ta) do not catalyse dehydrocondensation of phenylsilane. Neither at high temperature (115 – 120 °C) nor upon UV irradiation is this reaction catalysed by hydride complexes of niobium or tantalum Cp_2MH_3 (M = Nb or Ta),[82] whereas phenylsilane actively undergoes dimerisation in the presence of trimethylsilyl derivatives of tantalocene $Cp^*Ta(SiMe_3)Cl_3$. In this case, reduction products of the catalyst, *viz*., trimethylsilane and the tantalum hydride complex $[Cp^*TaHCl_3]_n$, are formed along with 1,2-diphenyldisilane.[46]

Cyclopentadienyl complexes of chromium, molybdenum and tungsten, *viz*., Cp_2Cr, Cp_2MoH_2 and Cp_2WH_2, do not catalyse dehydrocondensation of $PhSiH_3$ at room temperature as well as under irradiation.[82] Cyclopentadienyl chromium complexes, such as $(\eta^6\text{-}H_3SiC_6H_5)Cr(CO)_3$, act as catalysts of dehydrocondensation of silanes. In this case, the corresponding polysilanes containing chromium carbonyls in the side chain are formed.[155]

Some binary carbonyl complexes of manganese catalyse dehydrocondensation of phenylsilane at 100 °C.[68]

4. Catalysis by compounds of Group VIIIB elements

The use of platinum complexes as catalysts of dehydrocondensation of pentamethyldisilane and symmetrical tetramethyldisilane was reported for the first time in 1970.[156] Later on, these reactions were described as disproportionations catalysed by phosphine complexes of platinum metals.[157]

It was found that penta- and tetramethyldisilanes were converted into the $(Me_3SiSiMe_2)_2$ dimer or a mixture of $H(Me_2Si.SiMe_2)_nH$ oligomers ($n = 2 – 6$), respectively, in the presence of platinum bis(triethylphosphine) dichloride at 90 °C (18 h).[156 – 158]

$$RMe_2SiSiMe_2H \xrightarrow{cat} R(Me_2Si)_nH$$

R = H, Me; $n = 2 – 6$; cat = *trans*-$[PtCl_2(PEt_3)_2]$, $[NiCl_2(PEt_3)_2]$ *etc*.

The ethylenebisphosphine complex of platinum $[C_2H_4Pt(PPh_3)_2]$ at room temperature does not induce dehydrocondensation of silanes, such as Ph_3SiH, Me_2PhSiH, Et_3SiH and $(EtO)_3SiH$.[109, 112] However, $MePhSiH_2$ and Et_2SiH_2 in the presence of this complex were converted into the corresponding dimers in 27% and 95% yields, respectively.[109] It is remarkable that in the case of Et_2SiH_2, dehydrocondensation occurs more readily than hydrosilylation of 1-hexene. In attempting to perform hydrosilylation of 1-hexene with a mixture of Et_3SiH and Et_2SiH_2, only dehydrocondensation products $Et_2HSiSiHEt_2$ and $Et_2HSi – SiEt_3$ were obtained in a ratio 7 : 1. In this case, hexaethyldisilane was not formed. The dehydrocondensation product, *viz*., tetraethyldisilane, was also not detected upon hydrosilylation of 1-hexene with diethyldisilane in the presence of H_2PtCl_6 (Spier's catalyst) or Ph_2PtCl_2.[109]

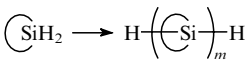
Dehydrocondensation of acyclic and cyclic disubstituted silanes $R^1R^2SiH_2$ [R^1 and R^2 = Alk, $(CH_2)_n$ ($n = 3 – 5$) or 1,2-C_6H_4] catalysed by the $Pt(COD)_2$ or $Me_2Pt(COD)$ complexes affords polysilanes with high molecular weights (M_w up to 40 000; M_n up to 39 000) in 60% – 95% yields.[159]

Dehydrocondensation of dimethylphenylsilane in the presence of platinum complexes with different phosphine ligands was

studied.[160] Their catalytic activities are rather low. The exception is the $Pt(PPhMe_2)_4$ complex in the presence of which the yield of 1,1,2,2-tetramethyl-1,2-diphenyldisilane reaches 50%. Methyldiphenylsilane in the presence of $Pt(PPhMe_2)_4$ forms 1,2-dimethyltetraphenyldisilane in low yield.[160] Platinum black as well as PtO_2, $H_2PtCl_6 \cdot 6H_2O$ and $(PhCN)_2PtCl_2$ do not catalyse dehydrocondensation of dimethylphenylsilane.[160]

A procedure for the dehydrocondensation of substituted oligosilanes of the general formula $H_aSi_bR_c$ [R = Alk, Ar, alkenyl, AlkO, Hal or R_2N; $a \geqslant 1$; $b \geqslant 2$; $(a + c) = (2b + 2)$] in the presence of dialkyldicyclopentadienyl Pt or Rh complexes was covered by a patent.[83]

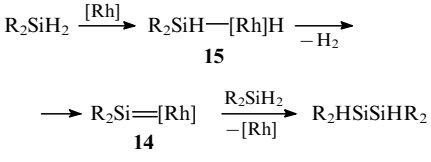
In 1973, $(Ph_3P)_3RhCl$ (Wilkinson's complex) was suggested as a catalyst of dehydrocondensation of hydrosilanes.[108] In its presence, methylphenylsilane was converted into a mixture of 1,2-dimethyl-1,2-diphenyldisilane (14%) and 1,2,3-trimethyl-1,2,3-triphenyltrisilane (30%) at 70 °C for 1 h. Under analogous conditions, 1,1,2,2-tetraphenyldisilane was formed from diphenylsilane in 38% yield. 1,2-Diphenylsilane and 1,2,3-triphenyltrisilane were obtained from phenylsilane. 1,1,2,2-Tetraethyldisilane and 1,1,2,2,3,3-hexaethyltrisilane were obtained from diethylsilane. Dehydrocondensation of dibenzosilaheterocycles **5a–d** in the presence of $(Ph_3P)_3RhCl$ proceeds according to the following scheme [108, 112, 161]



m = 2, 3.

The drawback of Wilkinson's catalyst is the fact that it promotes oxidation of Si–Si bonds to Si–O–Si groups when the reaction is performed in air.[109, 113]

The possible reaction mechanism involves the formation of the silylene rhodium(II) complex **14** as an intermediate, which appears as a result of β-elimination of the hydrogen molecule from the rhodium(I) complex **15**.



The results of dehydrocondensation of disubstituted silanes in the presence of $(Ph_3P)_3RhCl$ are given in Table 2.[112] The conversion of R_2SiH_2 decreases in the series **5c**,**d** (100%) > **5a** (83%) > Ph_2SiH_2 (59%) > **5b** (10%).[113] The addition of cyclohexene as an acceptor of hydrogen does not affect the activity of silanes. In attempting to perform dehydrocondensation of dihydrosilaanthracene (**5a**) in the presence of the $[Rh(COD)(PPh_3)_2]PF_6$ complex (37 °C, 25 h), only the corresponding disiloxane was isolated in 33% yield.[112]

Dehydrocondensation of methylphenylsilane catalysed by different rhodium complexes has been studied. In these reactions, a dimer and a trimer were obtained as by-products (Table 3).[50]

Table 2. Dehydrocondensation of diorganylsilanes in the presence of Wilkinson's catalyst (0.4 mol. %, 10 h, 25 °C).[112]

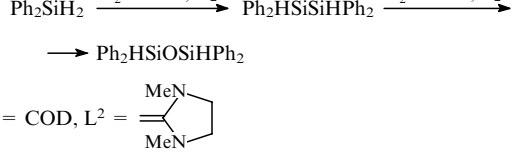
R_2SiH_2	Yield of the reaction products (%)				
	R_2SiH_2	dimer	trimer	disiloxane	other products
Ph_2SiH_2	41	48			11% (Ph_3SiH)
5a	17	38	42	3	
5b	90	10			
5c					oligomer
5d					oligomer

Table 3. Dehydrocondensation of methylphenylsilane in the presence of rhodium complexes (0.1 mol. %).[50]

Catalysts	Cocatalyst	t/h	T/°C	Yield (%)		
				$MePhSiH_2$	dimer	trimer
$RhCl(PPh_3)_3$		1	80	65.5	16.3	3.9
	PPh_3	1.5	90	29.3	15.4	6.9
$RhH(PPh_3)_4$		2	100	58.5	14.3	4.0
	PPh_3	2	100	29.3	10.3	4.1
	PPh_2Me	2	100	19.2	16.7	3.7
$Rh_2(OAc)_4$		2	100	69.0	3.3	0
$[RhCl_4(H_2O)_2]^-X^+$ (see [a])		2	100	31.2	25.8	8.8

[a] $X = NH(C_8H_{13})_3$.

Dehydrocondensation of diphenylsilane catalysed by carbene rhodium complexes (20 °C, 18 h) afforded predominantly 1,1,2,2-tetraphenyldisilane.[162] The reaction was monitored by GLC. It was demonstrated that the disilane $Ph_2HSiSiHPh_2$, which was initially formed, was then oxidised by atmospheric oxygen to the corresponding disiloxane.



Hydrosilylation with diethylsilane catalysed by complexes of Group VIII metals involves the dimerisation of diethylsilane as a competitive process. The relative rate constants of dehydrocondensation of diethylsilane (18 °C, 75 h) depending on the catalyst were determined.[109] These constants change in the following order (k_{rel} are given in parentheses):

$(Ph_3P)_3RhCl$ (31) > $[Pd(\eta^3\text{-}C_3H_5)Cl_2]$ (12) > $[Rh(CO)_2Cl]_2$ (5) > > $(Ph_3P)_2Pt(C_2H_4)$ (1) ~ $[Rh(COD)Cl]_2$ (1) > $Pt(COD)Cl_2$ (0.7) > > $RhCl_3$ (0.3) > $CpRh(C_2H_4)$ (0.2) ~ $[Ir(COD)Cl]_2$ (0.2) > > H_2PtCl_6 (0.1) ~ $(Ph_3P)_2PtCl_2$ (0.1).

The reactivity of silanes in dehydrocondensation decreases in the series $RSiH_3 > R_2SiH_2 \gg R_3SiH$. Dimethylphenylsilane in the presence of platinum complexes undergoes only dimerisation.

Dehydrocondensation of compounds of the $A(SiH_3)_2$ type [A = CH_2, $Alk(CH_2)_n$, $Me_3Si(CH_2)_n$ (n = 2–7) or $Me_3Si(CH_2)_m$ (m = 3–8)] catalysed by $HRh(CO)(PPh_3)_3$ was studied. The reactions afforded polysilanes, which were further converted into silicon carbide.[163]

Dehydrocondensation of 1,4-bis(trihydrosilyl)benzene in the presence of $RuCl_2[P(C_6H_4Me\text{-}4)_3]_3$ afforded a white polymer (M = 1170) containing alternating $SiH_2C_6H_4$ groups.[164, 165]

5. Reaction mechanism

Dehydrocondensation of organylsilanes is a promising procedure for the formation of Si–Si bonds. This procedure is suitable for the preparation of polyorganylsilanes with the controlled chain length. However, the majority of the published studies generally dealt with the preparative aspects of this reaction. The difference in the reaction conditions and sometimes the contradictory results do not allow one to propose the mechanism of catalytic dehydrocondensation of organylhydrosilanes with assurance.

Presently, three rather justified schemes of the process proceeding in stages are available. These schemes are interrelated and complement each other.

1. Harrod's mechanism involves oxidative addition of organylsilanes to complex-forming metal followed by α-elimination of

the RH molecule (R = Alk or Ar) to form a silylene complex of the $Cp_2M=SiHR$ type (M = Ti or Zr) as an active catalytic intermediate. The latter forms polyorganylsilanes through a series of successive conversions with the participation of organylsilane.

2. Tilley's mechanism is based on the metathesis of the σ-bond. The reaction proceeds through a four-centre transition state containing the M – H, M – Si, Si – H and Si – Si bonds followed by the metathesis of the M – Si σ-bond and the formation of dehydrocondensation products $H(SiHR)_nH$.

3. Hengge's mechanism involves silylene Me_2Si:, which is formed in a four-centre transition state according to a β-elimination reaction of a new type, as an active catalytic intermediate. Dimethylsilylene is then inserted into the Si – H or Si – Si bonds to form linear or branched oligomers, respectively.

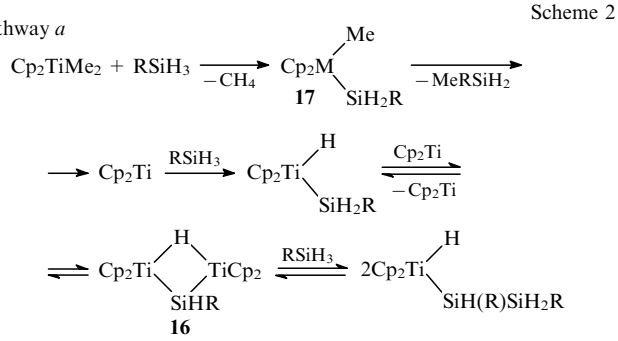
Let us consider these mechanisms in more detail.

Harrod and coworkers [68, 87, 89, 93] suggested two schemes of the dehydrocondensation mechanism for organylsilanes (Scheme 2).

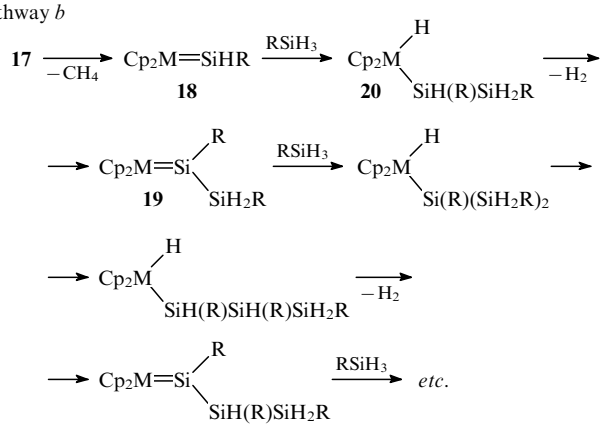
One of the schemes [87] assumes that the bridging hydride complex **16** is formed as an active catalytic intermediate. This scheme involves oxidative addition of silane to metallocene to form the complex **17** followed by α-elimination of $MeRSiH_2$. The resulting Cp_2Ti reacts with silane to give the complex **16**, which accomplishes the chain growth (Scheme 2, pathway *a*).

Scheme 2

Pathway *a*



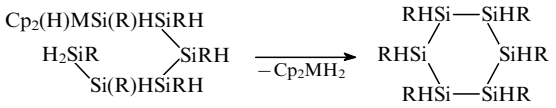
Pathway *b*



However, the high catalytic activity of possible intermediates of dehydrocondensation, *viz*., the Ti and Zr complexes of type **17** containing μ-H and μ-Si bonds, was not confirmed.[87, 89, 91, 94, 100]

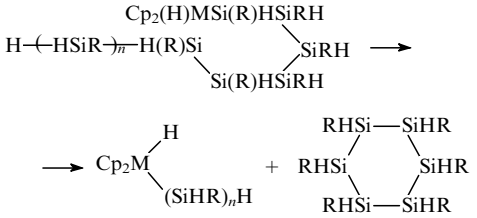
Later on, Harrod and coworkers[93] suggested that the silylene complexes **18** and **19** are intermediates in dehydrocondensation. The complex **19** can be formed upon elimination of hydrogen from the hydride complex **20**. The chain growth occurs through the repeated insertion of the newly formed silylene complex into the M – Si bond (Scheme 2, pathway *b*). This scheme adequately describes the formation of the linear polyphenylsilanes $H(PhSiH)_nH$ and $H(Ph_2Si)_2H$ from $PhSiH_3$ and Ph_2SiH_2, respectively.

The formation of cyclic products upon dehydrocondensation of $PhSiH_3$ and $PhCH_2SiH_3$ in the presence of dimethyltitanocene or dimethylzirconocene proceeds through the intermolecular metathesis of the terminal SiH_2 group and the M – Si bond of the growing terminus of the chain.[68] This process is most probable when the chain contains six Si atoms.



M = Ti, Zr.

The second pathway, which involves the cleavage of the Si – Si bond by a particular reactive intermediate and intermolecular metathesis, is also possible.



M = Ti, Zr.

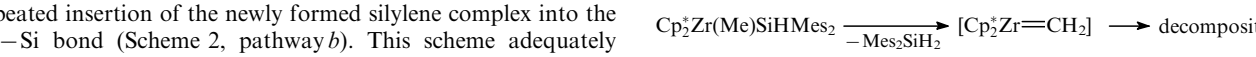
The scheme proposed by Harrod does not explain why only tetraorganyldisilanes rather than higher oligomers are formed from diorganyldisilane.

An alternative reaction mechanism was proposed [112] to account for the formation of cyclic oligomers, for example, of 1,2,3-triphenyltrisilane from Ph_2SiH_2 in the presence of titanocene or zirconocene complexes. This mechanism involves either dehydrocondensation of Ph_2SiH_2 with the resulting $Ph_2SiHSiHPh_2$ (which is formed, probably, through a silylene complex) or disproportionation of 1,1,2,2-tetraphenyldisilane.

However, it was established [161] that the dimeric product of dehydrocondensation of 9,10-dihydro-9-silaanthracene in the presence of Wilkinson's catalyst formed the corresponding trimer only in 7% yield, *i.e*., disproportionation is not the major process.

Silylene complexes of type **18** or **19** are very attractive compounds for explaining the mechanism of dehydrocondensation of silanes. These compounds have been extensively studied in the last decade.[166] Base-stabilised silylene complexes of transition metals, which are used in different catalytic (hydrosilylation [108]) and photochemical [167] reactions, are known.

Nevertheless, it is believed [46] that silylene metal complexes cannot be intermediates of dehydrocondensation for two reasons. First, during catalytic dehydrocondensation of organylsilanes, complexes of the $CpCp^*M[Si(SiMe_3)_3]Cl$ type are quantitatively converted into the corresponding polymeric complexes $[CpCp^*MHCl]_n$.[142] Only one σ-bond of complex-forming metal is used in the course of dehydrocondensation. At the same time, the participation of at least two σ-bonds is necessary for the formation of the silylene complex followed by its reaction. Second, the formation of silylene complexes through α-elimination of the RH molecule should result in complexes of the $M(SiHR^1R^2)R^3$ type (R^1, R^2 and R^3 = H or Alk). Several mixed alkylsilyl complexes containing Si – H bonds were isolated. However, the latter do not undergo decomposition with α-elimination of substituents at the silicon atom. Only one instance where decomposition proceeds through α-elimination of the hydrogen atom from the alkyl group at the silicon atom is known.[168] This reaction afforded dimesitylsilane in quantitative yield along with an unidentified zirconium-containing compound. Methane was not detected among the reaction products.



Tilley [136] suggested an alternative mechanism of dehydrocondensation of organylsilanes, which was called the metathesis of the σ-bond. This mechanism was confirmed by the kinetic data obtained by monitoring the process by ^1H NMR spectroscopy in C_6D_6.[46, 48, 142, 169] In this case, the cyclopentadienyl tris(trimethylsilyl) hafnium complex **21**, which exhibits lower reactivity and higher stability compared to the isostructural titanium and zirconium complexes, was used as a catalyst.

$$CpCp^*Hf[Si(SiMe_3)_3]Cl + PhSiH_3 \longrightarrow \underset{\mathbf{21}}{} \longrightarrow CpCp^*Hf(SiH_2Ph)Cl + HSi(SiMe_3)_3$$

These authors also synthesised and studied the behaviour of other silylated cyclopentadienyl hafnium complexes, *viz*., $CpCp^*Hf(SiHR^1R^2)Cl$ (R^1 = H and R^2 = Ph, 4-MeC_6H_4, Mes, Bn or *cyclo*-C_6H_{11}; $R^1 = R^2$ = Ph; or R^1 = Me and R^2 = Ph), in dehydrocondensation of $PhSiH_3$.[141, 170] The general second order of the reaction, first order with respect both to the catalyst and the organylsilane, were established. The activation parameters of the process ($\Delta H^{\neq} = 68.5$ kJ mol^{-1}, $\Delta S^{\neq} = -27$ kJ mol^{-1} K^{-1}) and the kinetic isotopic effect ($k_H/k_D = 2.5$) correspond to the values observed for the reactions of hydrocarbons proceeding through the metathesis of the σ-bond.[170, 171]

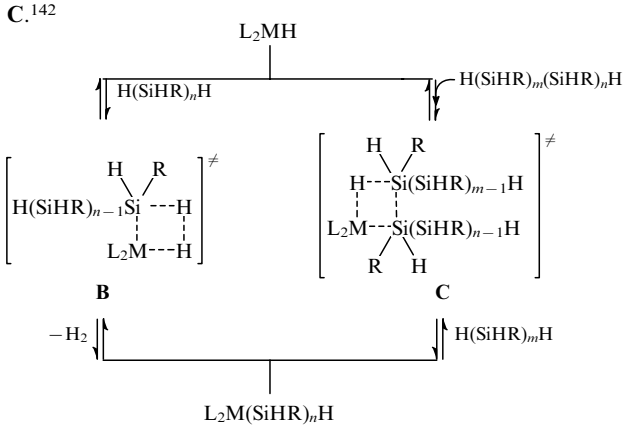
$$L_nMR^1 + HR^2 \longrightarrow \left[\begin{array}{c} \overset{\delta-}{R^2}\cdots\overset{\delta+}{H} \\ L_nM\cdots R^1 \end{array}\right]^{\neq} \longrightarrow L_nMR^2 + HR^1$$

R^1, R^2 = H, Alk, Ar;
L_nM = Cp^*_2Sc, Cp^*_2Y, Cp^*_2Lu, $[(Me_3Si)_2N]_3U$, *etc*.

The kinetics of thermal decomposition of CpCp*.Hf(SiH_2Ph)Cl, which obeys a second-order equation with $\Delta H^{\neq} = 81.5$ kJ mol^{-1} and $S^{\neq} = -21$ kJ mol^{-1} K^{-1}, was studied.[142] The four-centre transition state **A** was suggested for the dehydrocondensation process.

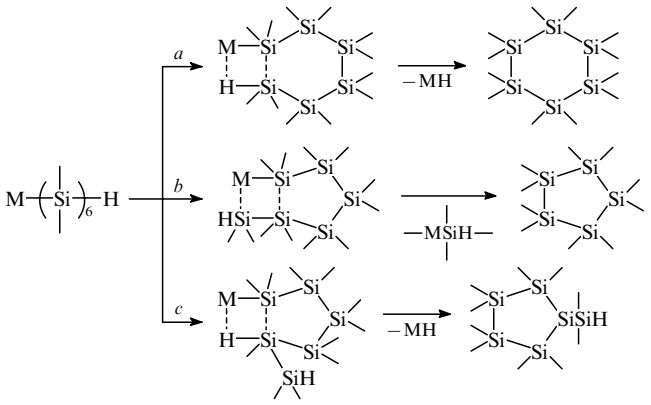
$$2\,HfSiH_2Ph \longrightarrow \left[\begin{array}{c} H\cdots Si(M)PhH \\ Hf\cdots SiH_2Ph \end{array}\right]^{\neq} \xrightarrow[-HfH]{HfSiH_2Ph} \underset{\mathbf{A}}{} \longrightarrow HfSi(Ph)HSiH_2Ph \xrightarrow[-HfH]{HfSiH_2Ph} Hf(SiHPh)_2SiH_2Ph, \textit{etc}.$$

Decomposition of the hafnium complex was performed in the presence of efficient traps of silylene, such as Et_3SiH, (cyclo-$C_6H_{11})_3SiH$, Ph_2SiH_2 or $MePhSiH_2$, which had no effect on the reaction rate. It is suggested that a hydride complex, which reacts predominantly with the sterically most accessible terminal SiH_2R group of the polysilane chain, is an active catalytic species in the reaction. This leads to the appearance of the polysilyl group in the coordination sphere about the metal atom. The formation of the Si–Si bonds (chain growth) occurs through the two-stage metathesis of the σ-bond *via* the four-centre transition states **B** and **C**.[142]



Slow oligomerisation of phenylsilane catalysed by CpCp*.Hf(SiH_2Ph)Cl was used as a model reaction. In this process, intermediates of dehydrocondensation, for example, $CpCp^*Hf(SiHPhSiH_2Ph)Cl$, were identified. This complex was prepared by independent synthesis from $CpCp^*Hf[Si(SiMe_3)_3]Cl$ as two diastereomers, which were detected in the course of the reaction by ^{1}H NMR spectroscopy. The addition of two equivalents of phenylsilane to $CpCp^*Hf(SiH_2Ph)Cl$ afforded (after 24 h) $[CpCp^*HfHCl]_n$ (33%) and a mixture of $CpCp^*Hf[SiH(Ph)SiH_2Ph]Cl$, PhH_2SiSiH_2Ph and PhH_2Si–$SiH(Ph)SiH_2Ph$ in a ratio of 3 : 2 : 3. Dehydrocondensation of $PhSiH_3$ catalysed by Cp^*HfH_2 afforded also free oligophenylsilanes. Due to steric hindrance, this hafnium hydride reacts with the Si–H bond very slowly, which makes it possible to observe the conversion of phenylsilane into 1,2-diphenyldisilane. The latter is even more slowly converted into 1,2,3-triphenyltrisilane, and apparently, finally into 1,2,3,4-tetraphenyltetrasilane. The correlation between the concentration of the silane and the reaction time indicates that the cleavage of the Si–Si bond is an important stage of the process. Within the framework of this mechanism, the formation of cyclic oligomers is attributed to the intramolecular metathesis of $R(RSiH)_nH$, where n = 5 (Scheme 3).[127] The metathesis with the participation of the terminal Si–H (pathway *a*) or Si–Si (pathway *b*) bonds affords five- or six-membered rings. The metathesis with the participation of the exocyclic Si–H bonds (pathway *c*) can lead to rings containing organosilicon substituents.

Scheme 3



The suggested multistage mechanism of dehydrocondensation of organylsilanes can serve as the basis for the design of new catalysts, *viz*., coordinatively unsaturated electrophilic metal hydride complexes, which can participate in the concerted process of metathesis of the σ-bond.

The proposed mechanism explains many aspects of dehydrocondensation, including steric requirements imposed on the catalyst and the substrate as well as the formation of rather short polymer chains. However, this mechanism inadequately explains the difference in the behaviour of, on the one hand, the silyl complexes of zirconium and hafnium and, on the other hand, of the titanium complexes.

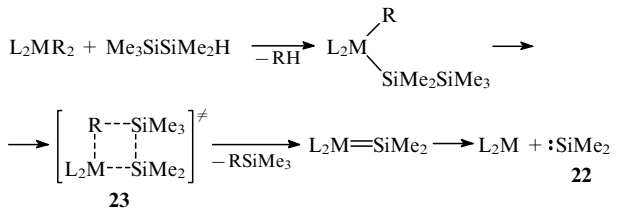
The mechanism of metathesis of the σ-bond was also used for the explanation of the regularities of other dehydrocondensation reactions, *viz*., the reaction of $RSiH_3$ catalysed by the Cp_2MCl_2–2BuLi binary system or Cp_2MMe_2,[129] the reaction of $R^1R^2SiH_2$ in the presence of Wilkinson's complex[112] and the reaction of 2,4-disilapentane in the presence of titanocene or zirconocene.[43]

Hengge and Weinberger[172] suggested yet another mechanism of dehydrocondensation of organylsilanes in the presence of dimethylzirconocene with the use of autocondensation of 1,2,3-trimethyltrisilane and a mixture of diastereomers of 1,2,3,4-tetramethyltetrasilane as a model reaction. The conversions of these oligomers cannot be explained in the context of Harrod's mechanism[87, 89] because α-elimination should be accompanied by evolution of CH_4.

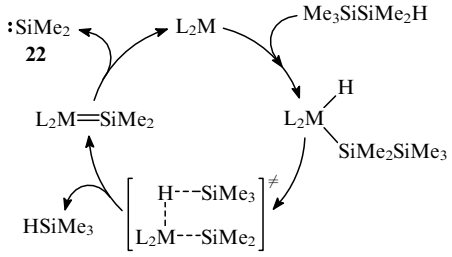
Dimethylsilylene Me_2Si**:** was suggested as an intermediate in dehydrocondensation of $Me_3SiSiMe_2H$ and $HMe_2SiSiMe_2H$ in the presence of Cp_2ZrMe_2 (**22**, Scheme 4). This intermediate is formed from the intermediate silyl metal complex **23** as a result of β-elimination. This process is not the classical elimination of an organic substituent at the β position with respect to the metal atom. This mechanism can more likely be considered as β-bonding

Scheme 4

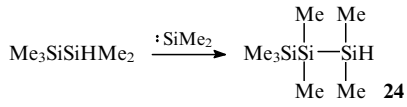
Pathway *a*. Formation of the active catalytic L_2M molecule



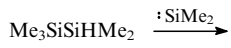
Pathway *b*. Dehydrocondensation



Pathway *c*. Insertion of silylene into the Si–H bond



Pathway *d*. Insertion of silylene into the Si–Si bond

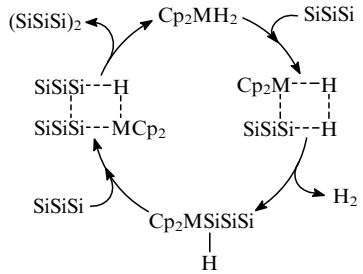


upon destruction of a four-centre transition state accompanied by elimination of the resulting residue, *viz*., the so-called elimination of the β-bond (Scheme 4, pathways *a*,*b*). The resulting dimethylsilylene can be inserted both into the Si–H bond (Scheme 4, pathway *c*) and into the Si–Si bond (Scheme 4, pathway *d*) of the initial pentamethyldisilane to form the heptamethyltrisilane **24**.

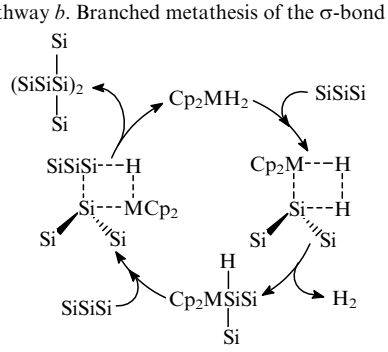
Two pathways of dehydrocondensation of diorganylsilanes and higher silanes are possible, *viz*., the metathesis of the σ-bond resulting in the formation of linear polymers with evolution of H_2

Scheme 5

Pathway *a*. Linear metathesis of the σ-bond of $H(MeHSi)_3H$



Pathway *b*. Branched metathesis of the σ-bond of $H(MeHSi)_3H$



(Scheme 5, pathway *a*) or the β-elimination with evolution of $MeSiH_3$ (Scheme 5, pathway *b*) to form a branched polymer.

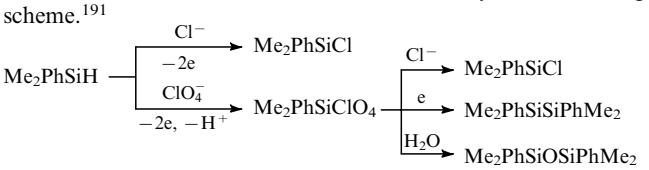
We believe that the mechanism suggested by Tilley,[46] which is based both on the kinetic data and on the identification of the intermediate reaction products, is the most probable one among the above-considered mechanisms of catalytic dehydrocondensation of organylsilanes. The mechanism suggested by Hengge[172] attracts attention because it involves a new type of elimination reactions, *viz*., the elimination of the β-bond.

III. Electrochemical dehydrocondensation of organylhydrosilanes

Electrochemical reactions are used for the synthesis of various organosilicon compounds, including functionally substituted compounds.[173] Methods for the cathodic electroreduction of organylchlorosilanes to form substituted disilanes[174–177] and oligo- and polysilanes[178–182] have been developed. Since organylchlorosilanes are difficult to reduce, cathodic processes with their participation generally require preliminary electrogeneration of carbanions (or other nucleophiles), which then replace the chlorine atoms bound to the silicon atoms.[173] Most of cathodic reactions based on organylchlorosilanes are variations of this process.

Anodic reactions of organosilicon compounds are more diversified, though less well studied, than cathodic reduction processes.[173,183–186]

Electroreduction of mono-, di- and triorganylsilanes $RSiH_3$ (R = Ph or n-C_6H_{13}), $R^1R^2SiH_2$ (R^1 and R^2 = Me or Ph) and R_3SiH (R = Et or EtO) on metallic (Pt, Au or Hg)[187–190] and nonmetallic (glassy-carbon)[191] electrodes was studied. The reactions were performed in acetonitrile in the presence of Bu_4NBF_4 (see Refs 187–190) or $LiClO_4$.[191] Organylsilanes have low oxidation potentials on metallic electrodes (the $E_{Red/Ox}$ value varies from −0.05 to 0.7 V). On the contrary, the oxidation potential of dimethylphenylsilane on a glassy-carbon electrode is rather high ($E_{Red/Ox}$ = 2.2 V). Preparative electrooxidation of Me_2PhSiH in the DME–Bu_4NClO_4 system (DME is dimethoxyethane) in the presence of CuCl or $CuCl_2$ affords a mixture of compounds. The formation of the latter can be described by the following scheme.[191]



Chlorodimethylphenylsilane is formed in a yield from 46% to 95% depending on the degree of oxidation of copper and the quantity of electricity passed. Under these conditions, 1,1,2,2-tetramethyl-1,2-diphenyldisilane is formed in insignificant yield. When the supporting electrolyte was changed for Bu_4NBF_4, fluorodimethylphenylsilane predominantly formed (the yield was 90%). In this case, the exchange reaction of the initially formed $Me_2PhSiCl$ with BF_4^- apparently proceeded.[180,192–194]

The oxidation potentials of the initial monomeric organylsilanes[190] are ~ 200 mV lower than the oxidation potentials of polyorganylsilanes, which hinders oxidation of the latter with the cleavage of the Si–Si bond.[173]

Electrolysis of methylphenyl- and diphenylsilane in the DME–Bu_4NBF_4 system with the use of a platinum cathode and a platinum anode for 5.3 h afforded the corresponding oligomers.[195,196]

$$n\,RPhSiH_2 \longrightarrow H(RPhSi)_nH$$

R = Me: n = 2–6; R = Ph: n = 2–5.

According to GLC data, the dehydrocondensation product of methylphenylsilane, which is characterised by M_n = 454 and the molecular distribution coefficient M_w/M_n = 1.05, is a mixture of at least five compounds. 1,2-Dimethyl-1,2-diphenyldisilane

($n = 2$, $M = 242$, the yield was 10%) and 1,2,3-trimethyl-1,2,3-triphenylsilane ($n = 3$, $M = 362$, the yield was 14%) were identified in the reaction mixture by mass spectrometry. The yields of methylphenyloligosilanes with $n = 4$ and 5 were 16% and 6%, respectively.[185] Under analogous conditions, diphenylsilane was predominantly converted into the dimer, *viz*., 1,1,2,2-tetraphenyldisilane (the conversion was 38%), in 23% yield. Apparently, silyl radical cations are intermediates in this anodic reaction. Then these radical cations attack the corresponding monomers or oligomers to form the Si–Si bond.

Polyorganylsilanes of the $H(RHSi)_nH$ type are formed upon electrolysis of organylsilanes R^1SiH_3 (R^1 = Alk, Ar or $CH_2CH_2R^2$, where R^2 is a perfluoroalkyl group) in an organic solvent containing an appropriate electrolyte. Previously unknown oligo- and polyfluoroalkylsilanes with $M = 200-5000$ were synthesised according to this procedure in high yields.[197]

Electrolysis of organylchlorosilanes $RSiH_nCl_{3-n}$ ($n = 1$ or 2) in the $THF-Bu_4NBF_4$ system in an undivided cell yields two different condensation products depending on the metal of the electrodes.[198] Electrolysis of methylphenylchlorosilane with the use of a stainless steel cathode and a subcritical anode affords predominantly 1,2-dimethyl-1,2-diphenyldisilane, which is formed upon cathodic reduction with elimination of chlorine.

$$2\,MePhSiHCl \xrightarrow[-2\,Cl^-]{e} MePhHSiSiHPhMe$$

When platinum electrodes are used, the cathodic reduction is suppressed and the anodic oxidation becomes the predominant reaction. In this case, the Si–Si bond is formed through the elimination of the proton on an anode.

$$2\,MePhSiHCl \xrightarrow[-2\,H^+]{e} ClMePhSiSiPhMeCl$$

Radical cations formed upon electrochemical oxidation of triorganylsilanes R_3SiH were identified as adducts with tetracyanoethylene[199] or cyclohexene.[188,189,200] The lifetime of the radical cation $Et_3SiH^{+\bullet}$, which was detected by the rotating disk-ring electrode method, is 0.003–0.006 s.[188,189]

In the absence of radical traps, these radical cations decompose with liberation of the hydrogen atom.

$$Et_3SiH \underset{+e}{\overset{-e}{\rightleftharpoons}} [Et_3SiH]^{+\bullet} \longrightarrow Et_3Si^+ + H^\bullet$$

IV. Other reactions

Dehydrocondensation of organylsilanes can also occur under the action of di-*tert*-butyl peroxide.[201–203] Thus the reaction of dimethylcyclopropylsilane with di-*tert*-butyl peroxide afforded tetramethyl-1,2-di(cyclopropyl)disilane in small yield,[202] whereas the reaction of dimethylphenylsilane gave a mixture of $PhMe_2Si-SiMe_2H$ (2%), $PhMe_2SiSiMe_3$ (6%), $Ph_2MeSiSiMe_3$ (3%) and $PhMe_2SiSiMe_2Ph$ (3%) in insignificant yield.[203] Disilane was prepared by the reaction of di-*tert*-butyl peroxide with dimethyl(2-thienyl)silane in noticeable yield (26%).[203]

Recently, it was found that triethylsilane underwent dehydrocondensation to form hexaethyldisilane in the reaction with germanium or tin dihalides.[204–206]

$$Et_3SiH + GeX_2 \xrightarrow{CD_2Cl_2 \text{ or } CD_3CN} Et_3SiSiEt_3 + (GeX)_n + 2\,HX,$$

$$Et_3SiH + SnX_2 \xrightarrow{CD_3CN} Et_3SiSiEt_3 + Sn + 2\,HX$$

X = Cl, I.

The reaction of triethylsilane with tetrachlorogermanium affords a mixture of hexaethyldisilane and triethylchlorosilane in a ratio of 1 : 3.[204,205]

$$4\,Et_3SiH + 2\,GeCl_4 \xrightarrow{CD_3CN} Et_3SiSiEt_3 + 2\,Et_3SiCl + 2/n\,(GeCl)_n + 4\,HCl$$

The reactions of germanium dichloride with Et_3SiH proceed readily in more or less polar solvents (CD_3CN or CD_2Cl_2) but do not proceed in nonpolar solvents (C_6D_6). Tetrachlorogermanium reacts with Et_3SiH only in a polar solvent (CD_3CN). It is believed that electron transfer to form the $[Et_3SiH^{+\bullet}\,GeCl_2^{-\bullet}]$ and $[Et_3SiH^{+\bullet}\,GeCl_4^{-\bullet}]$ radical ion pairs, respectively, is the key stage of these reactions.

Thermal and photochemical decomposition of bis(triorganylsilyl)mercury and -cadmium **22a**,**b** can be considered as a two-stage procedure for the dehydrocondensation of triorganylsilanes to form hexaorganyldisilanes.[207–212] The compounds **22a**,**b** were prepared by the reactions of triorganylsilanes with dialkyl derivatives of mercury and cadmium.[207,209,213]

$$2\,R^1_3SiH + MR^2_2 \xrightarrow[-2R^2H]{} \underset{\mathbf{22a,b}}{R^1_3SiMSiR^1_3} \xrightarrow{\Delta \text{ or } h\nu} R^1_3SiSiR^1_3 + M$$

M = Hg (**a**), Cd (**b**).

The reaction proceeds according to the radical mechanism through intermediate formation of the $R_3Si^\bullet$ radicals.[214–217] The latter not only can undergo recombination but also can react with the solvent (particularly, in a photochemical process).[213,218–220]

$$(Me_3Si)_2Hg \xrightarrow[-Me_3Si^\bullet]{} {}^\bullet HgSiMe_3 \xrightarrow[-Me_3Si^\bullet]{} Hg,$$

$$Me_3Si^\bullet + Hg(SiMe_3)_2 \longrightarrow Hg + Me_3SiSiMe_3 + {}^\bullet SiMe_3\,.$$

Thermolysis of bis(triphenylsilyl)mercury, -zinc and -barium derivatives proceeds with elimination of free metal.[210] Hexaphenyldisilane is formed from the mercury derivative. The barium and zinc compounds give tetraphenylsilane and diphenylsilylene. The latter undergoes subsequent oligomerisation.[212]

$$Ph_3SiMSiPh_3 \xrightarrow[\Delta]{M = Hg} Ph_3SiSiPh_3 + M$$

$$Ph_3SiMSiPh_3 \xrightarrow[\Delta]{M = Ba,\ Zn} 1/n\,(Ph_2Si)_n + SiPh_4 + M$$

Bis(methyldichlorosilyl)- and bis(dimethylchlorosilyl)-mercury, which were prepared under UV irradiation of a mixture of bis(trimethylsilylmethyl)mercury and the corresponding methyldichloro- or dimethylchlo-rosilane, spontaneously decompose above −79 °C with elimination of mercury to form substituted disilanes.[212]

V. Conclusion

To summarise, dehydrocondensation of organosilicon compounds containing Si–H bonds is a promising procedure for the preparation of linear and cyclic oligo- and polyorganylsilanes $H(R^1R^2Si)_nH$ and $-(SiR^1R^2)_n-$, which find use as precursors of ceramics, semiconductors, photoresistors, photoinitiators of polymerisation of alkenes, *etc*.

Group IVB metallocenes Cp_2ML_2 (M = Ti, Zr or Hf; L = H, Alk, OAlk, Ar or Hal) and their binary systems with promoters, such as alkyllithium, triorganylphosphines, aluminium, *etc*., are the most efficient catalysts of dehydrocondensation. These compounds allow one to prepare linear and cyclic polysilanes under rather mild conditions. The catalytic activity of metallocenes decreases in the Zr > Ti ≫ Hf series depending on the nature of the central metal atom. When heteronuclear metallocenes are used, monosilanes $RSiH_3$ are more active than diorganylsilanes R_2SiH_2, while triorganylsilanes R_3SiH do not undergo dehydrocondensation.

As for the mechanism of dehydrocondensation, it is evidently nontrivial and complicated. Apparently, further studies will be aimed at elucidating details of the mechanism, which can allow one to elaborate an approach to the choice of catalysts for the purpose of enhancing the selectivity of a procedure for the preparation of polysilanes with the desired structures.

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