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Review

Catalysis by transition metal complexes of alkene silylation – recent progress and mechanistic implications

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Contents

Abstract

Many efficient stereo- and regio-selective methodologies for synthesis of substituted vinylsilanes have been reported, involving mostly classical stoichiometric routes as well as, more recently, transition metal catalyzed transformations, in particular, hydrosilylation of alkynes and hydrogenation of silylalkynes.

In the last two decades, two new reactions based on transformations of silicon derivatives catalyzed by transition metal complexes have been developed to provide universal routes for synthesis of well-defined molecular and macromolecular compounds with vinyl-silicon functionality commonly used in organic and polymer synthesis. These are the reactions of silylation of alkenes by hydrosilanes and by vinylsilanes. Since the synthetic aspects of these reactions have been recently discussed, this review is focused on the mechanism of homogeneous catalysis, i.e., the way of activation of C_{vinyl}—H bond of alkenes as well as $\equiv$Si—H and/or $\equiv$Si—C_{vinyl} of silicon derivatives by late transition metal complexes both leading to vinyl-silicon containing compounds. The two reactions occur via the same active intermediates, i.e., late TM complexes involving M—H and M—Si bonds (where M is representative at iron- and cobalt-triades: for silylation by hydrosilane also nickel-triad).

On the basis of experimental and theoretical studies of the reactivity, structure and catalytic activity of late transition metal complexes in the above mentioned reactions, particularly those reported in the last decade, generalized schemes for catalysis of both reactions have been proposed. The common crucial step of the two reactions catalyzed by complexes containing initially M—H and/or M—Si bond is an insertion of alkene into M—Si bonds followed by β-H transfer to metal with elimination of substituted vinylsilane. In this case, a formation of M—Si bond proceeds either via oxidative addition of hydrosilane (silylation by hydrosilane) or via insertion of vinylsilane into M—H bond followed by β-Si transfer with evolution of ethylene (silylation by vinylsilane). Yet, if the catalysts contain initially no M—H and M—Si bond, their formation occurs via oxidative addition of hydrosilane (silylation by hydrosilane) or via preliminary oxidative addition of C_{vinyl}—H of alkene

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to get M—H bond, followed by insertion of vinylsilane to this bond and next β-Si transfer to metal with elimination of ethylene (silylation by vinylsilane).

Keywords: Catalysis; Silylation; Late TM (ruthenium, rhodium, iron, cobalt, nickel and palladium) complexes; Vinylsilanes; Hydrosilanes; M—H bond; M—Si bond

1. Introduction

Like other organometalloids (boron, germanium and arsenic), organosilicon compounds also belong to the class of organometallic ones and the Si–C bond has been the basis of organosilicon monomers and polymers of great industrial application [1,2].

On the other hand, if such metalloids (p-block) replace the carbon atom in the metal–carbon bonding, then they form the real metal–nonmetal bond. Such compounds are a subject of a new field of study called sometimes "inorganometallic chemistry" [3] In particular, the compounds containing d-block–p-block element bonds, which although closely related to organometallics yet distinctly differ from them, can play a significant role as intermediates in transformations of p-block compounds. Silicon is the most common and useful element among p-block elements, so silicometallic (or silaorganometallic) compounds include the derivatives with a metal–silicon bond.

While the making and breaking of the metal–carbon bonds play a fundamental role in catalysis of organic compounds, the reactivity of silicometallic species, particularly those involving a transition metal (TM)–silicon bond, is a key point in most conversions of silicon derivatives catalyzed by metal complexes. The triangle (Fig. 1) illustrates the relation between the organometallic, organosilicon and silicometallic compounds.

Therefore, although in catalytic conversions of (organo) silicon compounds only hydrosilylation reactions are well-known processes of industrial importance [4–8], in the last two decades other reactions of silicon compounds catalyzed by TM complexes have been revealed and spectacularly developed [8–17]. They include double (bis)silylation, dehydrogenative coupling of hydrosilanes, coupling of olefins with hydrosilanes and with vinylsilanes, silylcarbonylation, silyl(hydro)formylation and metathesis of silicon-containing olefins. All of them, except metathesis, occur via intermediates involving metal–silicon (silicometallics) and metal–hydrogen bonds, only occasionally accompanied (or sided) by metal–carbon bonds (organometallics).

Many reviews concerning these processes from the point of view of catalysis [6–9,13,14], coordination chemistry [18–20] and the synthesis of new monomeric and polymeric

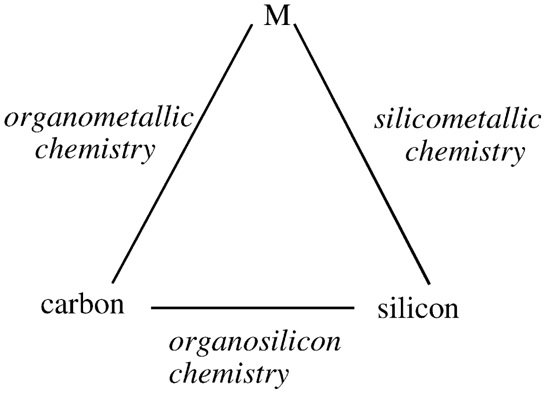
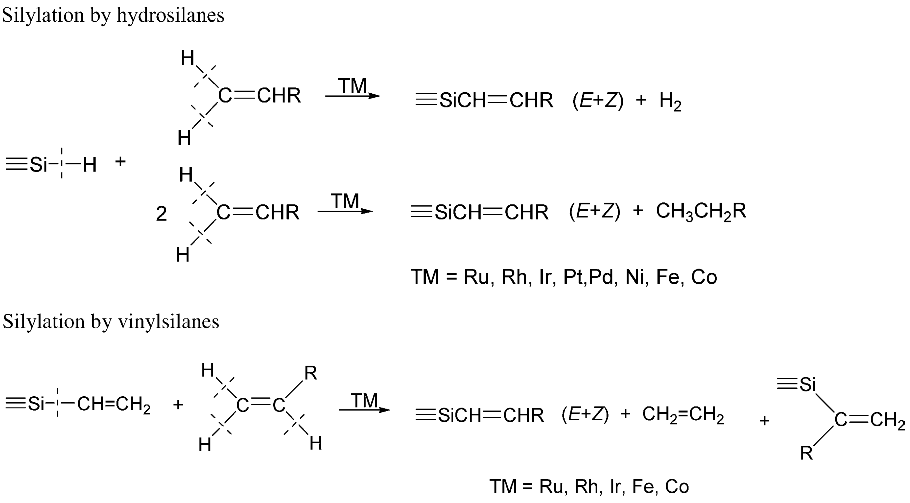
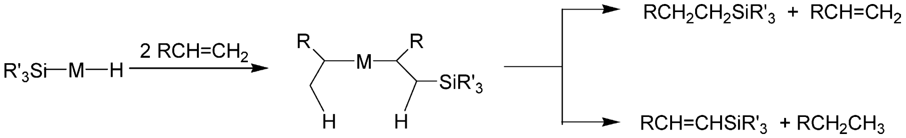


Fig. 1.



Scheme 1. TM catalyzed silylation of alkenes by hydro- and vinylsilane.



Scheme 2. Competitive hydrosilylation and dehydrogenative silylation of alkenes.

compounds [1,11,12,15,16] have provided evidence justifying great interest in the development of new highly efficient routes to organosilicon compounds.

Molecular and polymer compounds of vinyl-silicon functionality constitute a class of organosilicon reagents commonly used in organic synthesis [21–24] and a group of functionalized polymers being precursors of optoelectronic materials [25–27]. Therefore, the aim of this work is to overview recent achievement in two reactions of silicon derivatives with alkenes catalyzed by TM complexes involving M–H and/or M–Si bonds, leading to substituted vinylsilanes and other compounds of vinyl-silicon functionality. In contrast to the other reviews presented in the last decade, this paper is focused on the mechanistic aspects of catalysis and coordination chemistry of two reactions of alkene silylation by hydrosilanes and by vinylsilanes occurring according to the following equations (Scheme 1).

The efficiency and mechanisms of both catalytic methods have been discussed against a background of other catalytic transformations of alkenes with silicon compounds yielding vinylsilane, i.e., cross-metathesis (mostly Ru and Mo catalysts) (for reviews see [15,16,25]) and cross-coupling (Pd catalysts) (for review see [22] and examples [29,30]).

2. Silylation of olefins by hydrosilanes catalyzed by TM complexes

The hydrosilylation of alkenes catalyzed by TM complexes is often accompanied by side reactions such as isomerization, oligomerization, polymerization and hydrogenation of alkenes as well as redistribution and dehydrogenation of silicon hydrides and reactions in which both substrates take part, e.g., dehydrogenative silylation [7]. The latter reaction, which under some conditions permits direct production of unsaturated silyl compounds, has been a subject of separate extensive study in the past two decades. In most cases, group R (Scheme 1) depicts an electronegative substituent in such olefins as, e.g., styrene and substituted styrenes [28,31] trifluoropropene [32] and vinyltri-substituted silanes [33]. Complexes of iron and cobalt triads have appeared as extremely favored catalysts for the dehydrogenative silylation but Ni, Pd and Pt complexes have also recently been reported as active catalysts of these olefin conversions (for reviews see [4,7–10]).

TM complexes can catalyze both dehydrogenative silylation and hydrosilylation competitively. The decisive step of the two alternative reactions is actually a competitive β-H transfer from the two ligands (σ-alkyl and σ-silylalkyl) of the complex formed during the reaction (as illustrated in Scheme 2).

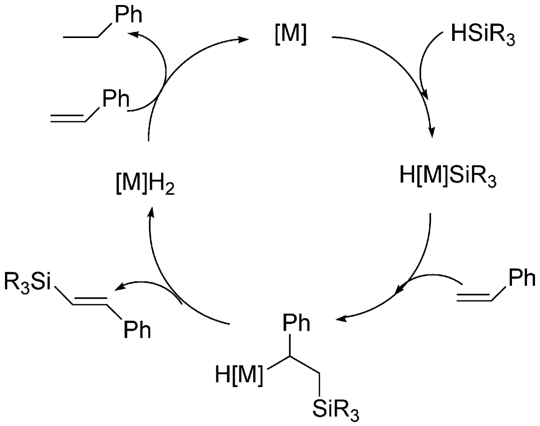
The migratory insertion of an alkene into a M–Si bond (silyl migration) is a key step in the dehydrogenative silylation catalyzed by transition metal complexes but a theoretical study of the hydrosilylation of ethylene has confirmed the preference of rhodium over platinum complexes as catalysts in this reaction [34].

The first convincing argument for a mechanistic pathway was presented by Wrighton group on the basis of the photocatalyzed reaction of alkenes with hydrosilanes catalyzed by $M_3(CO)_{12}$ (where M = Fe, Ru and Os) [35] and $(CO)_4CoSiR_3$ [36] yielding a mixture of alkyl- and vinylsilanes.

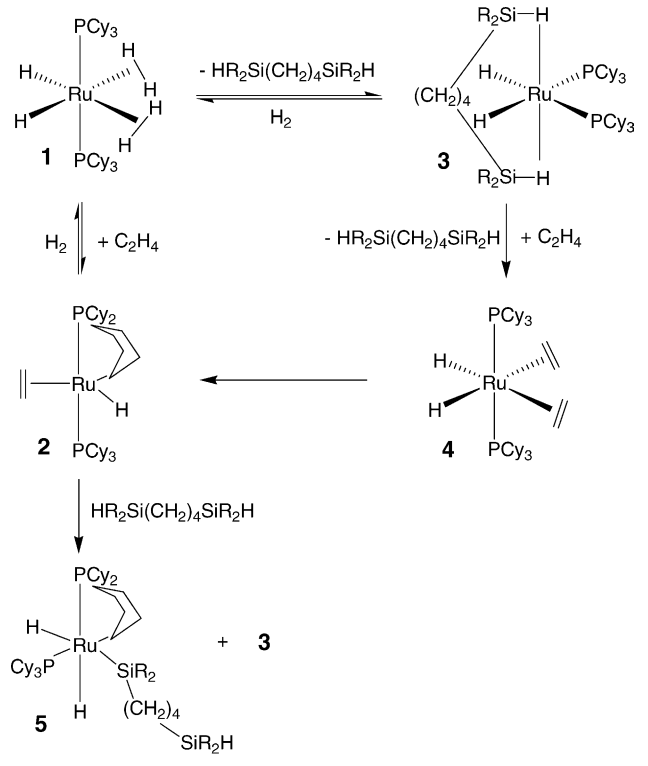
A general scheme of the catalysis of the dehydrogenative silylation of exemplary styrene by late TM complexes is given in Scheme 3.

Although much data on such competitive reactions have been reported, the number of examples of selective dehydrogenative silylation remains limited.

In the past decade, the study has been focused on the search for new selective catalysts of dehydrogenative silylation ensuring efficient generation of vinylsilanes and other vinylsilicon compounds as well as on mechanistic implications of TM complexes as real intermediates of these complicated processes. Dehydrogenative silylation has become a useful method for synthesis of vinylsilanes although its drawback is a formation of a mixture of products. The formation of vinylsilane is promoted by a high alkene to silane ratio.



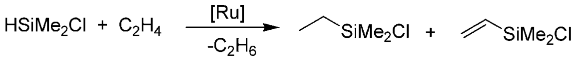
Scheme 3. Catalysis of the dehydrogenative silylation of styrene.



Scheme 4. Effect of the order of substrate addition on catalytic pathways.

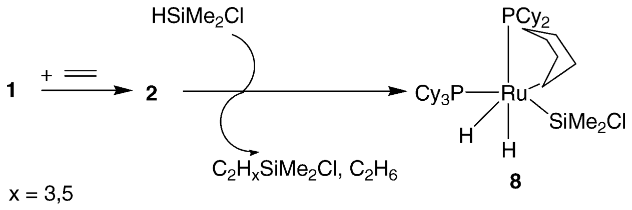
The bis-dihydrogenruthenium complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and the ethylene complex $RuH(C_2H_4)[P(\eta^3\text{-}C_6H_8)Cy_2](PCy_3)$ (**2**) obtained by the addition of ethylene to the former one are precursors to very efficient catalysts for selective synthesis of vinyltriethylsilane [38–40]. If these complexes are used as catalysts of ethylene silylation by disilane $HSiMe_2SiMe_2H$ and by bis(hydrosilyl)alkanes, $HSiMe_2(CH_2)_nSiMe_2H$, (where $n = 2–4$) competitive dehydrogenative silylation, hydrosilylation and cyclization to exo-cyclic compounds is observed [41]. The stoichiometric studies have shown that different complexes are involved in the catalytic process depending on the order of addition of ethylene and dihydrosilylalkane (see Scheme 4). The complex **1** reacts with ethylene to produce **2** which further can react with silane giving ruthenium(IV) species but the addition of bis-silylethene to **1** results in the formation complex of **3** which in ethylene presence gives **4**. The latter can be transformed into **2** in the absence of disilane.

Hydrogen complexes **1** and **2** as well as the chloro complex $RuHCl(\eta^2\text{-}H_2)(PCy_3)_2$ (**6**) were also tested as catalysts in the following reaction:



(1)

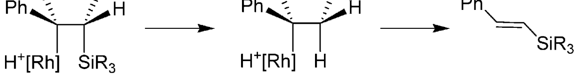
In contrast to the results on triethylsilane, in the case of chlorodimethylsilane, vinylsilane was favored as a product with a low pressure of ethylene. Stoichiometric study of the initial complexes with $HSiMe_2Cl$ (2–10-fold excess) revealed a mixture of three silicon-containing complexes of which two were formulated as σ-silane complexes but the third one results from Si–Cl breaking and formation of the respective chlororuthenium complex $RuCl(\eta^2\text{-}H_2)(SiMe_2Cl)(PCy_3)_2$ (**7**). When complex **1** was subjected to the reaction with ethylene, the ethylene complex was produced and then after addition of $HSiMe_2Cl$ to **2** the formation of vinylsilane, and a new complex **8** was observed. The new complex **8** was fully characterized by multinuclear NMR and X-ray data [42]. An activation of the corresponding complexes by $HSiEt_3$ and bis(hydrosilyl)ethane was formulated as a result of oxidative addition of silane to get dihydro(silyl)ruthenium(IV) complexes [43]. However, in the case of $HSiMe_2Cl$ complex **8** is considered as an intermediate between the Ru(II) and Ru(IV) structure (Scheme 5).



Scheme 5. An intermediate formation in the process catalyzed by **1**.

The cationic complex $[Rh(cod)_2]BF_4/2\ PPh_3$ (**9**) appeared an efficient catalyst for the reaction of styrene with tri-substituted silanes [37]. Although dehydrogenative silylation was competitive with hydrosilylation, the selectivity was strongly dependent on the molar ratio of the substrates, the reaction temperature and the nature of the hydrosilane and phosphine ligands used. Vinylsilanes were obtained exclusively in 81% when tri-isopropylsilane, PPh_3 and diethyl ketone were used as initial compound as a ligand and as a solvent, respectively. The mechanism of dehydrogenative silylation of styrene involves the insertion of alkene into the silicon–rhodium bond [37].

The steric effect of hydrosilane is reasonably explained by the steric repulsion between the silyl group and cationic rhodium species which forces a bond rotation by about 120° to bring a hydrogen into the *syn* periplanar arrangement [37].



(2)

On the other hand, the dehydrogenative silylation of 1,5-dienes with hydrosilanes using $RhCl(PPh_3)_3$ as a catalyst gives 1-silyl-1,5-dienes instead of the usual hydrosilylation products [45]. In the presence of rhodium(I) complexes, very selective dehydrogenative silylation of divinylsilanes occurs to give 1,2-bis(silyl)ethene and ethylvinylsilane derivatives in equimolar amounts according to the following equation [44].

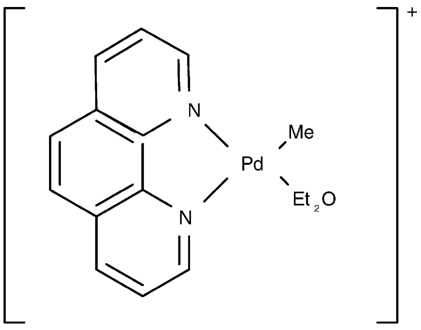


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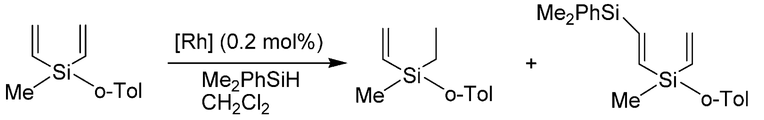
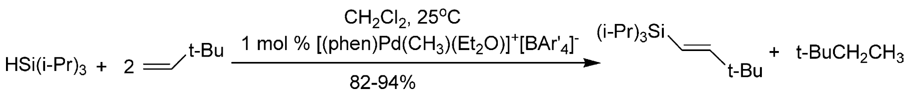
Fig. 2.



[Rh] = [Rh(dppb)(cod)]ClO$_4$, RhCl(PPh$_3$)$_3$, 1/2[RhCl(cod)]$_2$, Rh(CO)$_2$(acac), RhCl$_3$ x 3 H$_2$O;
[Rh(L*)(cod)]ClO$_4$, L* = (*S*,*S*)-DIOP, ee. = 5-15%, conv. 100% (3)

Very interesting variation and extension of the dehydrogenative silylation have been reported by Brookhart and co-workers, with the cationic palladium complex **10** (Fig. 2) catalyzed reaction [46] yielding, under optimum conditions, exclusively vinyl *t*-butylsilane and *trans*-silylstyrene (see Eq. (4)).



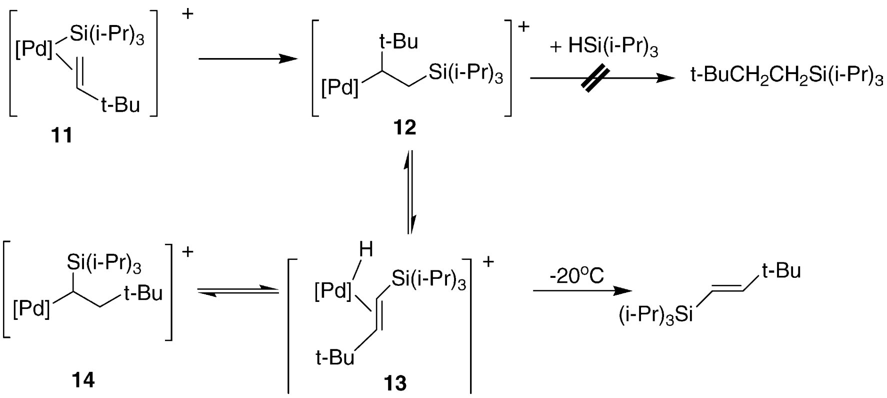
(4)

Similar to the reactions catalyzed by iron and cobalt triads, highly electrophilic cationic Pd(II) complexes catalyze the dehydrogenative silylation (as well as the hydrosilylation) via migratory insertion of the alkene into Pd–Si bond [46]. Independent study by Hayashi and co-workers [47] on the catalysis by π-allyl Pd complex PdCl(π-C_3H_5)$_2$] supports this observation.

The results of low-temperature NMR studies, kinetics experiments and deuterium labeling studies have provided evidence supporting the mechanistic scheme proposed by Brookhart and co-workers [46]. The key features of this mechanism are the rapid reversible silyl migration to alkene, isomerization of the alkyl complexes as intermediates and, finally, a cleavage of the alkyl complex by HSi-(*i*-Pr)$_3$. The catalyst resting state is the η^2-alkene complex **11** (Scheme 6).

If the ligands in intermediate **12**, **13** and/or the silane are too bulky, the cleavage of Pd-C in **12** by triorganosilane is unfavorable, so a dissociation of *t*-BuCH=CHSi(*i*-Pr)$_3$ occurs both in the presence or absence of HSi(*i*-Pr)$_3$ when no hydrosilylation is observed. The proposed mechanism of styrene dehydrogenative silylation and hydrosilylation is similar to the above presented for alkene silylation, but the difference is that in the styrene silylation the catalyst resting state are the π-benzyl complexes rather than η^2-alkene (**11**). The stability of the π-benzyl complexes (**15** and **16**) is responsible for a slow reaction with HSiEt$_3$, which is predominantly competitive with displacement of vinylsilane (see Scheme 7).

Nickel complexes such as Ni(acac)$_2$, Ni(cod)$_2$ and Ni analogue of Karstedt's catalyst are very efficient catalytic precursors in the dehydrogenative silylation of vinylsilanes [48,49], styrene [50,51] and other alkenes [50].

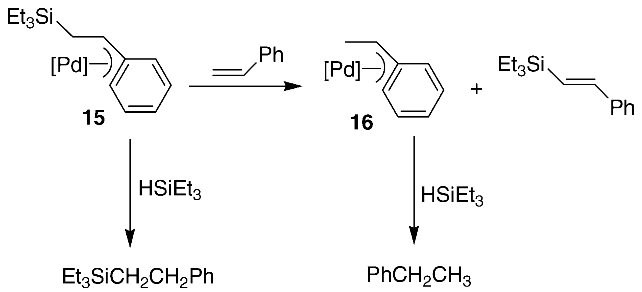


Scheme 6. Mechanism of Pd(II) complex catalyzed dehydrogenative silylation.

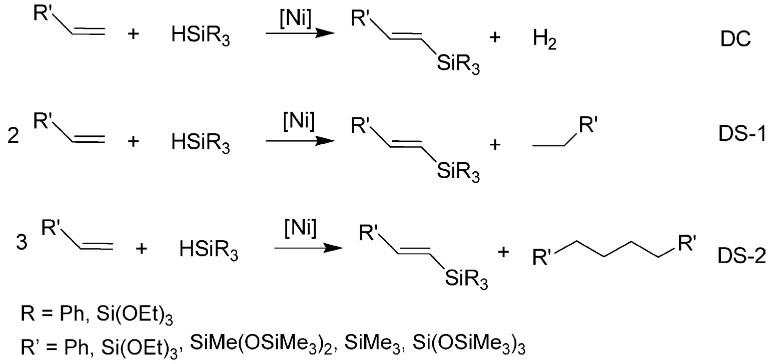
The unsaturated product of the dehydrogenative process is formed via three parallel steps also yielding products of direct dehydrogenation (DC), alkene hydrogenation (DS-1) and hydrogenative dimerization (DS-2) according to the following equations (Scheme 8).

The reaction can be accompanied by side hydrosilylation reaction (H).

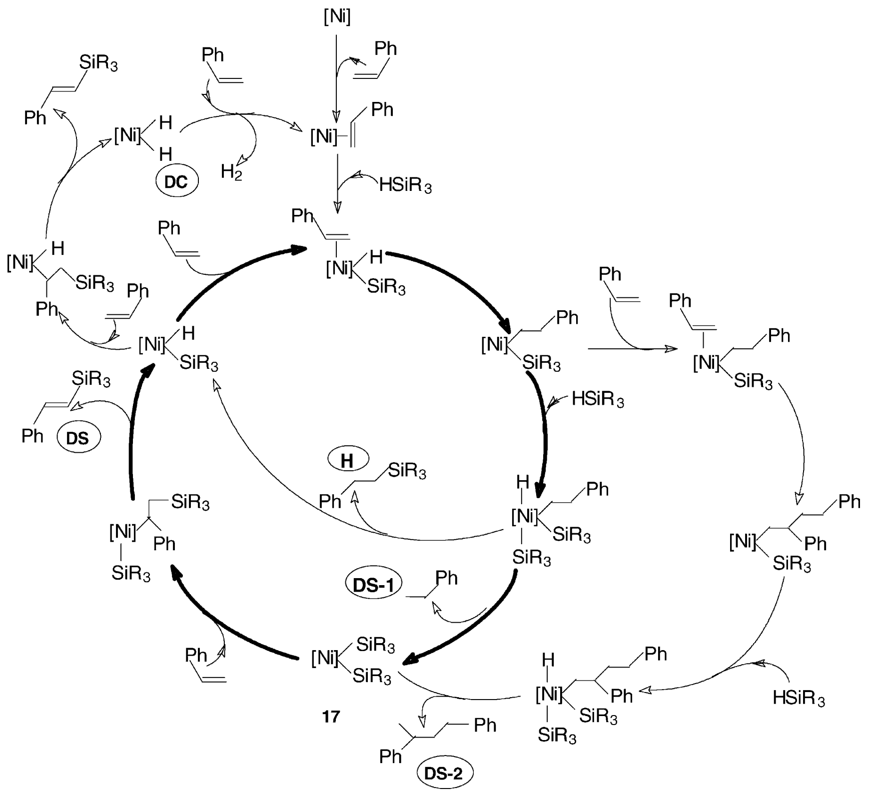
Stoichiometric reactions of the nickel analogue of Karstedt's catalyst with substrates (HSi(OEt)$_3$ and styrene), particularly synthesis of bis(triethoxysilyl)(divinyltetramethyldisiloxane)nickel complex (**17**) and the first documented insertion of alkene(styrene) into Ni–Si bond



Scheme 7. π-Benzyl complexes as intermediates of the competitive hydrosilylation and dehydrogenative silylation.



Scheme 8. Catalytic pathways of the dehydrogenative silylation of alkenes catalyzed by nickel complexes.



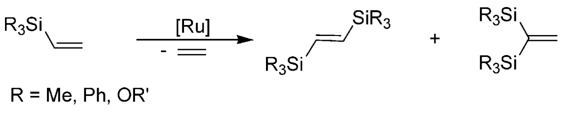
Scheme 9. Mechanism of dehydrogenative silylation vs. hydrosilylation of styrene catalyzed by Ni(0) complex.

of complex (**17**) as well as all catalytic data, permitted proposing the following mechanism of catalysis (Scheme 9).

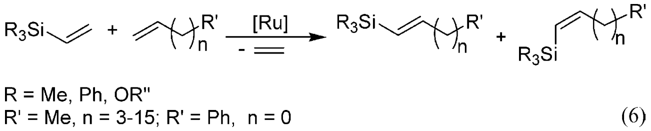
This scheme shows that all the above-mentioned reactions (DC, DS-1, DS-2 and H) occur as a consequence of the insertion of styrene into the Ni–Si, Ni–H and Ni–C bonds [51]. Some platinum complexes have been reported to promote dehydrogenative silylation, e.g.,the reaction of olefins and dienes with *o*-bis(dimethylsilyl)benzene [52,53].

3. Silylation of alkenes by vinylsilanes (silylative coupling, silyl group transfer) catalyzed by TM complexes containing M–H and/or M–Si bond

In 1984, we reported the first very effective example of disproportionation of vinyl-substituted silicon compounds, which could be catalyzed by Ru and Rh complexes [54]. It opened a new route of great synthetic importance and allowed us to synthesize a series of unsaturated silicon compounds with yields much higher than 70%. Numerous reports on vinylsilanes disproportionations (Eq. (5)) and their co-disproportionation (Eq. (6)) have been published in the first decade since 1984 (for previous review see [7]).



(5)

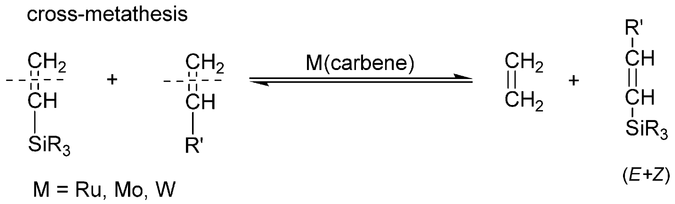


(6)

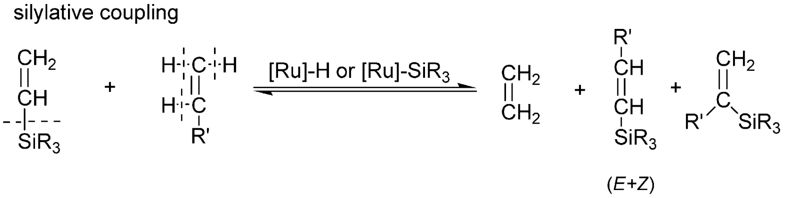
The following ruthenium complexes were active in this reaction: $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, $[RuCl_2(CO)_3]_2$, $Ru_3(CO)_{12}$, $[RuCl_2(p\text{-cymene})]_2$, $RuCl_3 \times nH_2O$ with $HSiEt_3$, $HSi(OEt)_3$, $RhCl(PPh_3)_3 + HSiPh_3$ as well as $LiAlH_4$ used as co-catalysts.

However, at that time the results obtained did not permit a distinction between the reaction mechanisms involving ruthenium–carbene complexes responsible for the olefin metathesis (well-defined ruthenium–carbenes complexes had not been revealed yet) and/or non-metallocarbene mechanisms.

Co-catalysis of all ruthenium and rhodium complexes by $HSiR_3$ and $LiAlH_4$ as well as catalysis by ruthenium hydride complexes indicated that formation of Ru–H bond is a crucial stage for the initiation of catalytic process. However, spectacular evidence for migratory insertion of ethylene into Ru–Si bond given by Wakatsuki et al. [55] as well as of vinylsilane [56] into Ru–Si bond (reported by us) yielding vinylsilane and two bis(silyl)ethane-regioisomers (*E*-1,2- and 1,1-bis(silyl)ethene), respectively, has shown that in the reaction referred to as the “metathesis” of vinylsilanes and their “cross-metathesis” with alkenes, instead of C=C bond cleavage, formally characterizing alkene metathesis (Eq. (7)), a different type of alkene conversion occurs that is a silylative coupling of alkenes with vinylsilanes (Eq. (8)).



(7)



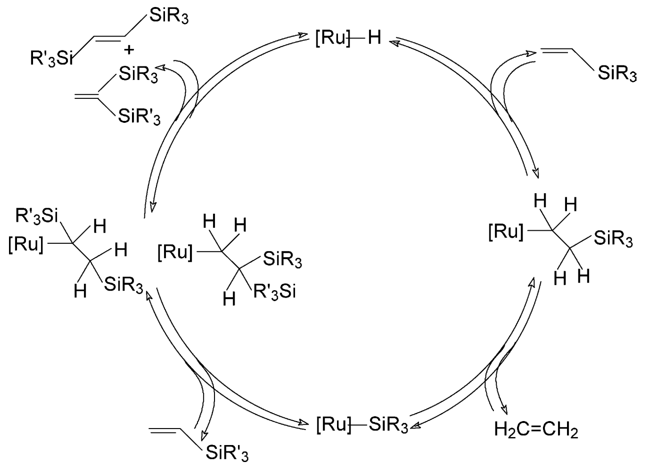
(8)

For the homocoupling of vinylsilanes a mechanistic scheme involves the insertion of vinylsilane into Ru–Si bond and into Ru–H bond followed by β-H and β-silicon transfer to metal, respectively, to yield 1,1- and 1,2-bis(silyl)ethene and ethylene (Scheme 10).

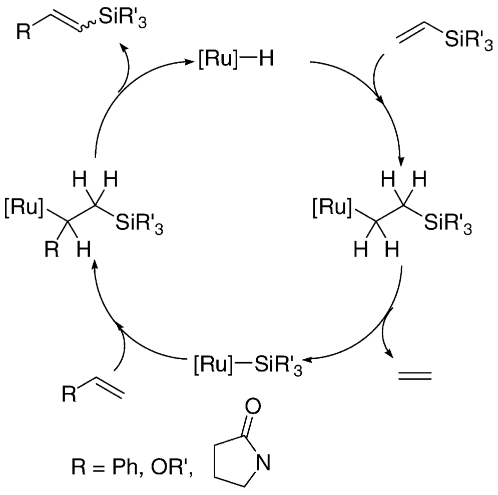
The most synthetically effective results have been compiled in refs. [16,23,25].

The detailed mechanism of silylative coupling of functionalized alkenes, such as styrene [57], vinyl alkyl ethers [58], vinylamides [60] and vinylboronates [61] catalyzed by ruthenium complexes containing Ru–H or Ru–Si bond ($RuHCl(CO)(PPh_3)_3$ (**18**), $RuHCl(CO)(PCy_3)_2$ (**19**), $RuHCl(CO)(PCy_3)_2 + CuCl$ (1:3) (**20**), $RuCl(SiMe_3)(CO)(PPh_3)_2$ (**21**) and $RuCl(SiMe_2Ph)(CO)(PPh_3)_2$ (**22**)), has also been subsequently presented.

Stoichiometric reactions of alkene with Ru–Si and Ru–H bonds have demonstrated the insertion–elimination mechanisms of catalysis.

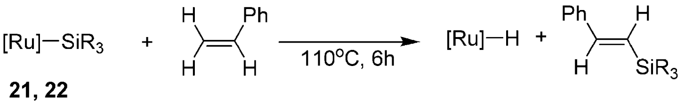


Scheme 10. Catalysis of vinylsilane homocoupling by ruthenium complexes.

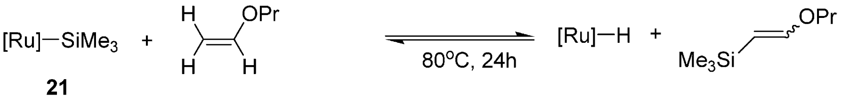


Scheme 11. Catalysis of alkene silylation with vinylsilanes by ruthenium complexes.

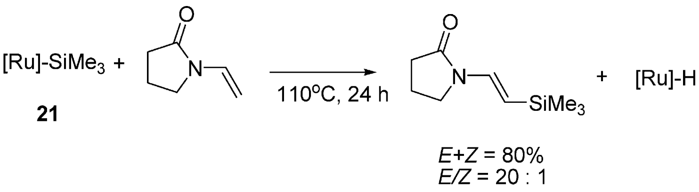
Exemplary reactions are given below (Eqs. (9)–(13)).



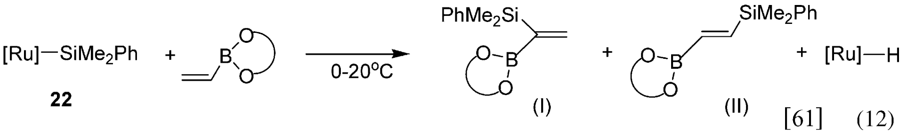
[57] (9)



[58] (10)

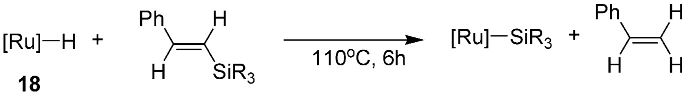


[60] (11)



[61] (12)

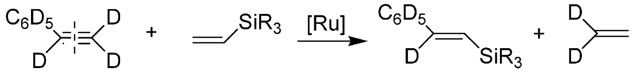
0 °C—exclusively (I); 20 °C – (I) + (II)



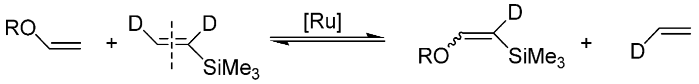
[57] (13)

The mechanisms of catalysis of the heterocoupling reaction could be finally proven by employing a new diagnostic tool, introduced for the first time, i.e., by using mass spectrometry to study the product of deuterated alkene, e.g., styrene, vinyl alkyl ether and/or deuterated vinylsilane [57–61]. The above test is able to distinguish between the two above-mentioned mechanisms, i.e., metathesis (occurring via metal–carbenes) and silylation (proceeding via Ru–H and Ru–Si intermediates).

If the reaction occurs according to the metallocarbene mechanism (cross-metathesis), the processes shown in Eqs. (14)–(16) will take place, to give silylstyrene-d$_6$ or d$_1$ – 1-silyl-2-alkoxyethenes-d$_1$, 1-silyl-2-*N*-amido-ethene-d$_1$, respectively (Eqs. (14)–(16)).



(14)



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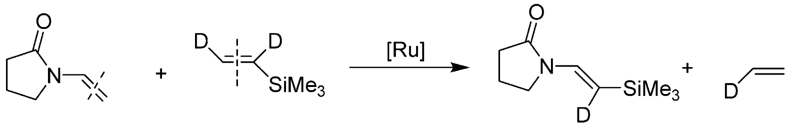
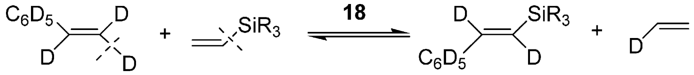


(16)

But if the reaction proceeds via the insertion–elimination mechanism (silylative coupling) than β-silylstyrene-d_7 as well as 1-silyl-2-alkoxy-ethene and 1-silyl-2-*N*-amido-ethene containing no deuterium in the molecule will be yielded (Eqs. (17)–(19)).



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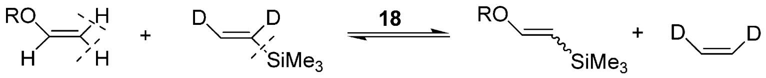
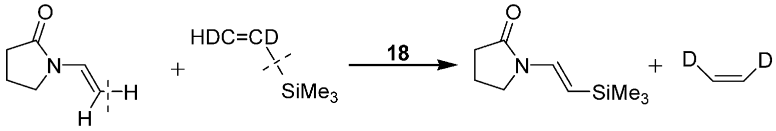


(18)



(19)

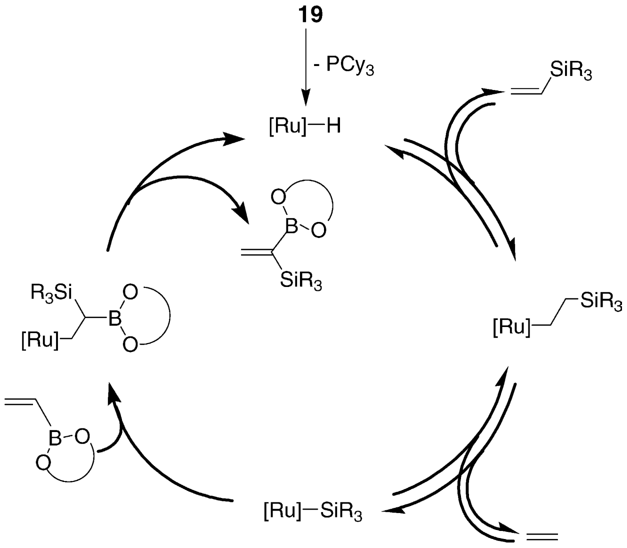
The GC–MS study of the reactions examined in the first stage (10% of the reaction) show exclusive formation of silylation products, which strongly supports the silylative coupling mechanisms given in Scheme 11.

Organodimetallic compounds have attracted a great deal of attention as they can serve as versatile intermediates in organic synthesis [23]; particularly useful starting materials are alkenes bearing both silyl and boryl groups.

Silylation of vinylborane with $H_2C{=}CHSiR_3$ in the presence of the catalytic system $RuHCl(CO)(PCy_3)_2/CuCl$ (**20**) where [Ru]:[Cu] 1:5 at ambient temperature (for $SiR_3 = SiMe_3$) and at 0 °C (for $SiR_3 = SiMe_2Ph$) occurs regioselectively giving exclusively *gem*-product 1-(silyl)-1-(boryl)ethene [61]. Stoichiometric study of ruthenium silyl complex with vinylborane carried out at 0 °C (see Eq. (12)) supplies evidence for the reaction illustrated in Scheme 12.

Screening tests performed at the 1:1 ratio of styrene and dimethylphenylvinylsilane with a variety of ruthenium catalysts have shown that $RuHCl(CO)(PCy_3)_2$ (**19**) appears to be the most active and selective catalyst even at a concentration 0.05 mol%. Cuprous salts (chloride and bromide) have recently been reported to be very good co-catalysts markedly increasing the rate and selectivity of all ruthenium phosphine complexes presumably due to phosphine scavenger [62].

The above silylation reactions have been recently used for synthesis of other types of unsaturated organosilicon compounds, which mostly cannot be obtained by the cross-metathesis procedure. The effective functionalization of 1,3,5-tris(dimethylvinylsilyl)benzene with 1,4-divinylbenzene leads to formation of a dendrimer having a silicon-bridged π-conjugated structure of potential optoelectronic properties [63] (Fig. 3). Organosubstituted octasilsesquioxane can be prepared by cross-metathesis and silylative coupling of octavinylsilsesquioxane with some olefins. The latter reaction occurs in the presence of **19** and **20** [64]. The products illustrated in Fig. 4 can be synthesized



Scheme 12. Catalysis of regioselective silylation of vinylborane with vinylsilanes.

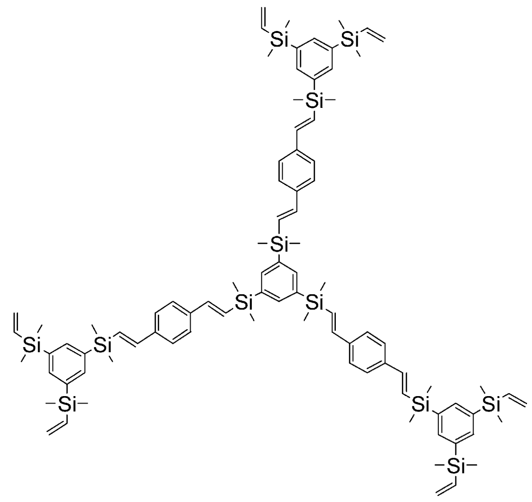


Fig. 3.

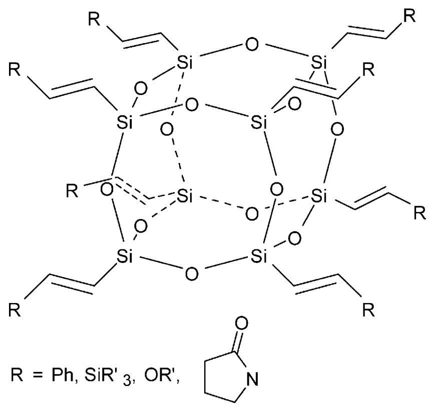
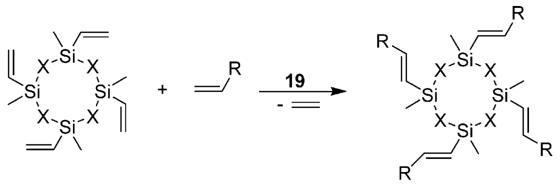


Fig. 4.

exclusively (except styrene derivatives) by catalytic silylation.

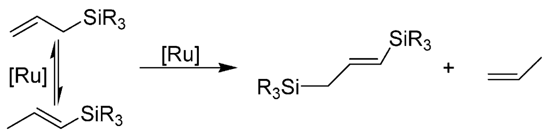
Vinylcyclosiloxanes and vinylcyclosilazanes also undergo efficient catalytic silylation (no cross-metathesis occurs) with styrene and vinyl alkyl ethers to open a new route to functionalized monomers for ring opening polymerization (Eq. (20)) [65].



X = O, NH; R = Ph; OR'

yield = 83-95 %, only *E* (20)

It is noteworthy to say that the complexes containing Ru–H bond catalyze a migration of C=C bond so allyl tri-substituted silanes undergo homocoupling and heterocoupling with other alkenes but via preliminary isomerization to 1-propenyl-tri-substituted silanes followed by heterocoupling with parent allylsilane or alkene, respectively [66,67] (Eqs. (21) and (22)).



[Ru] = $RuHCl(CO)(PPh_3)_3$, $RuCl_2(PPh_3)_3$
SiR_3 = $SiMe_3$, $Si(OEt)_3$ (21)

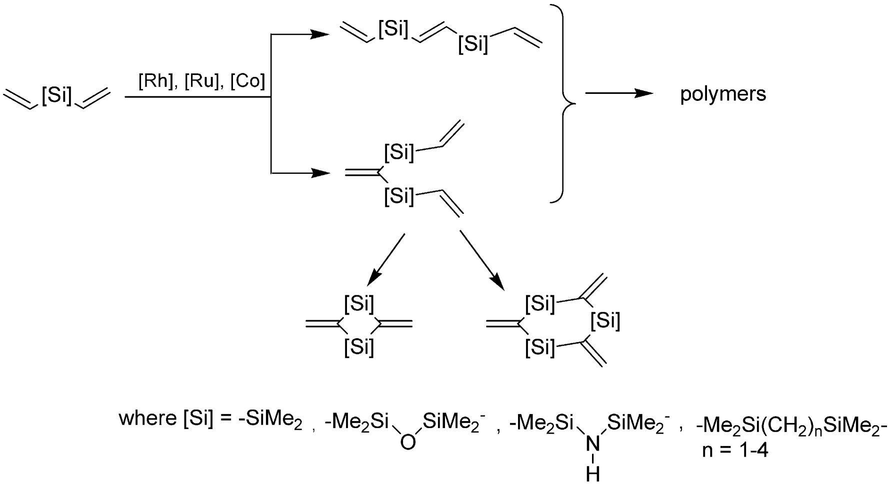
As has been already mentioned, the silylative coupling in the presence of ruthenium complexes containing Ru–H and/or Ru–Si bond is based on the crucial steps involving the insertion of olefin into Ru–Si bond and vinylsilanes into Ru–H bond. The occurrence of the latter process has been the first evidence of β-silyl transfer from carbon to ruthenium followed by ethylene evolution [55]. Therefore, the next step for extending silylative coupling of olefins with vinylsilanes was attempted on searching the respective rhodium and cobalt complexes as catalysts. $RhH(CO)(PPh_3)_3$ (**23**) [68] appeared to be good catalysts and $Co(SiEt_3)(CO)_4$ (**24**) [69] – good photocatalyst for selected reactions of vinylsilanes particularly with styrene. Although the insertion of olefin into Co–Si [36] and Rh–Si [18,70,71] as a step of hydrosilylation and dehydrogenative silylation was documented earlier but in order to provide another evidence for the mechanism of catalytic silylation, we have performed stoichiometric reactions of $RhH(CO)(PPh_3)_3$ with $Me_3SiCH{=}CHSiMe_3$, being the first ever realization of β-transfer of silyl group to the rhodium atom with elimination of vinylsilane [68] (Eq. (22)).

$$\underset{\mathbf{23}}{RhHCO(PPh_3)_3} + Me_3SiCH{=}CHSiMe_3 \longrightarrow Rh(SiMe_3)(CO)(PPh_3)n + CH_2{=}CHSiMe_3$$

$n = 2,3$ (22)

This reaction indicates reversibility of the vinylsilane homocoupling.

Per analogy to ruthenium and rhodium catalyzed reaction, $Co(SiEt_3)(CO)_4$ (**24**) was used as a precursor for silylative coupling of vinylsilanes and divinylsilanes with styrene which appeared to be effective although not as good as ruthenium and rhodium complexes. However, the reaction occurred exclusively if the reactants were exposed to UV irradiation. Nevertheless, this catalytic process has been the first documented realization of β-silyl transfer from carbon to cobalt resulted ethylene evolution [69].



Scheme 13. Silylative coupling polycondensation vs. cyclization of divinyl-substituted silicon compounds.

A similar reaction of homocoupling of vinylsilanes was observed in the presence of catalytic system $Fe(CO)_5 + Et_3SiH$ (**25**) and also under UV irradiation but it was accompanied by other processes which will be discussed in the one of the next part of this review [72].

4. Silylative coupling cyclization versus polycondensation of divinyl-substituted silicon compounds

According to the hitherto knowledge, divinylderivatives of organosilicon compounds which are of fundamental industrial importance, are inert to RCM and ADMET polymerization (see ref. [15,16]).

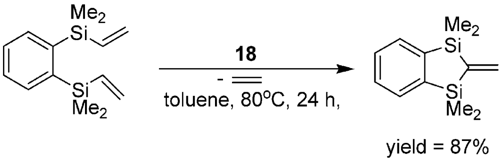
However, divinyl-substituted silanes, siloxanes and silazanes undergo efficient silylative coupling polycondensation to yield a mixture of linear oligomers and cyclic dimers and trimers containing *exo*-cyclic methylene bonds (Scheme 13) [15,16,73–78]. The unique feature of this silylative coupling reaction, distinguishing this reaction from cross-metathesis is the formation of 1,1-bis(silyl)ethene fragment in given conditions.

The mechanism of catalysis involves the insertion of vinylsilicon dienes into M–H and M–Si bonds, followed by β-Si and β-H elimination, to yield ethene and two isomeric *trans* and *gem*-bis(vinylsilyl)ethenes, respectively [75].

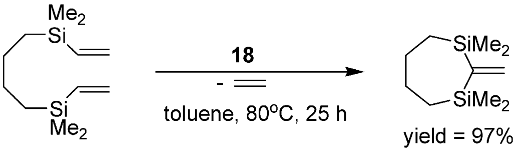
In the presence of $[RuCl_2(CO)_3]_2$ as a catalyst, *trans*-bis(vinylsilyl)ethenes are exclusively formed but $[(cod)RhX]_2$ (where X = Cl, $OSiMe_3$) catalyzes mostly formation of *gem*-dimeric products. Ruthenium phosphine complexes give both products. The *gem*-products subsequently undergo intramolecular ring closure to yield cyclotetrasiloxane, cyclotetrasilazane and cyclohexacarbosilanes [77,79].

The products were isolated and characterized by ^1H, ^{13}C and ^{29}Si NMR spectroscopy and the X-ray structure of cyclocarbosiloxane was reported [79] showing the molecule to assume a close to boat conformation.

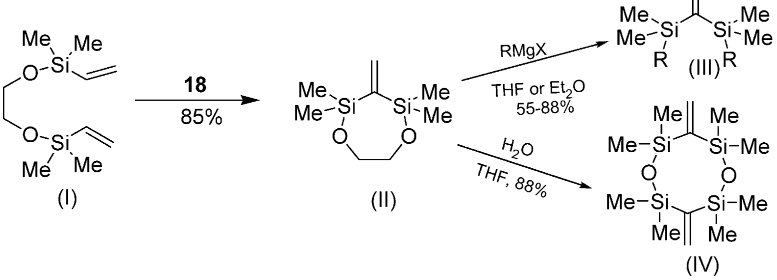
Cyclization has been also reported to furnish cyclocarbosilanes with one exocyclic methylene group (Eqs. (23) and (24)) [76].



(23)



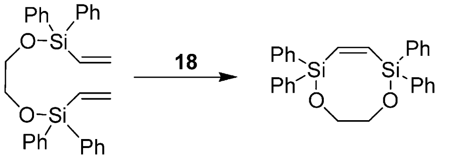
(24)



(25)

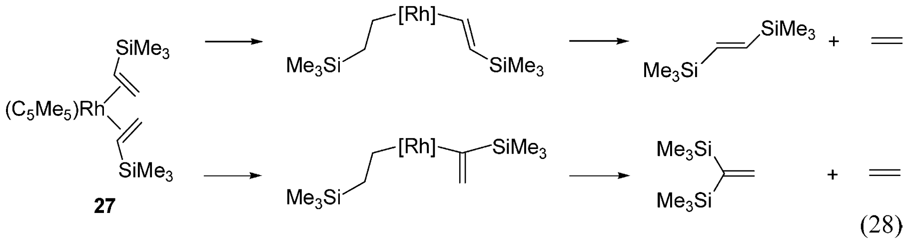
Such a ring closing reaction has also been observed for divinyl disilyl ethers (see Eq. (25)) which can be a good starting material for synthesis of 1,1-bis(silyl)ethenes(III) in moderate to good yields and excellent regioselectivity [80]. Compound(II) was a good starting substrate for the synthesis of cyclic tetrasilacarbosiloxane(IV) containing two exo-methylene bonds between silicon atoms in the molecule.

Contrary to 1,2-bis(dimethylvinylsiloxy)ethane, 1,2-bis(diphenylvinylsiloxy) ethane under similar conditions gives a disilacyclic product containing exclusively *endo* cyclic C=C *cis* bond with perfect regioselectivity [81] (Eq. (26)).



(26)

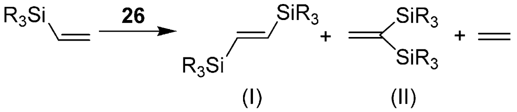
The ruthenium complex-catalyzed silylative coupling polycondensation was used for synthesis of well-defined poly(arylene, silylene, vinylenes) [82–85], poly[alkylene (silylene, siloxylene, silazanylene)vinylenes] [77,78] and others (for recent reviews see [15,16,25]). All the reactions proceed according to the mechanism concerted for monovinyl-silicon compounds, i.e., involving the insertion of vinyl-silicon dienes into M–H (and M–Si bond), followed by β-Si (and β-H) elimination to yield ethene and polymers.



(28)

5. Silylation of alkenes with vinylsilanes catalyzed by TM complexes initially not containing M–H and/or M–Si bonds

Rhodium siloxide dimeric complex $[(cod)Rh(\mu\text{-}OSiMe_3)]_2$ (**26**) is active catalyst in homocoupling of vinyl-substituted silanes [86] yielding two *trans-* and *gem*-isomers and in their heterocoupling with styrene.



(27)

[(I) + (II)] was 60–70% (60 °C, 24h) where, $R_3 = Me(OEt)_2$, Me_2Ph, Me_3 and 50% (90 °C, 24h), where $R_3 = Me(OSiMe_3)_2$.

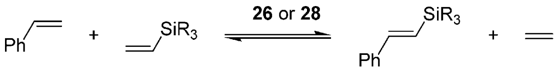
Although rhodium complex is less effective in the disproportionation of vinyltris(trimethylsiloxy)silane than $RuHCl(CO)(PPh_3)_3$ (**18**), the yields of bis(methylsiloxy)ethenes are similar to those reported for ruthenium catalyzed reactions [87], but the relevant reactions can occur effectively at milder conditions (even at 60 °C). Additionally, the transformation of vinylmethylbis(trimethylsiloxy)silane gives almost exclusively *E*-isomer, which can be important for establishing the real conditions for cross-linking of poly(methyl,vinyl)siloxanes via the catalytic disproportionation.

Results of the experiments performed by Brookhart and co-workers [88] using $C_5Me_5Rh(CH_2 = CHSiMe_3)_2$ (**27**) complex under thermolysis conditions (140 °C, cyclohexane-d_{12}) and in the 10-fold excess of vinylsilane provided evidence for hydrovinylation of one of the coordinated molecule of vinylsilane followed by the insertion of the second molecule in the generated Rh–H bond, subsequent elimination of ethylene and reductive elimination of the two types of bis(silyl)ethenes (Eq. (28)) [88].

On the basis of the Brookhart experiment, a catalytic scheme for homocoupling of vinylsilanes was presented [86].

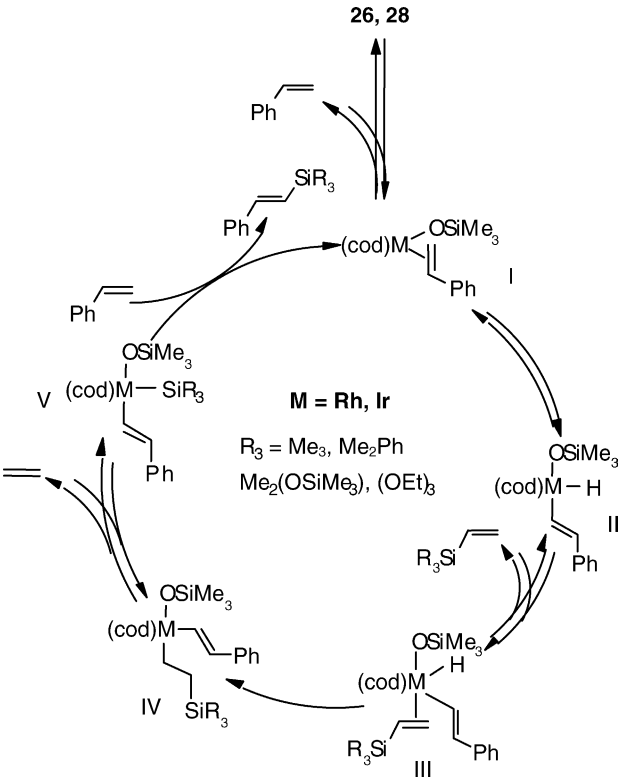
However, in order to find evidence for catalysis by rhodium (**26**) and iridium-siloxide $[(cod)Ir(OSiMe_3)_2]_2$ (**28**) precursors, initially having no M–H or M–Si bond, the reactions of styrene (and *p*-styrenes) with various vinyl-substituted silicon compounds have been tested [89,91].

The reactions occur according to the following equation:



(29)

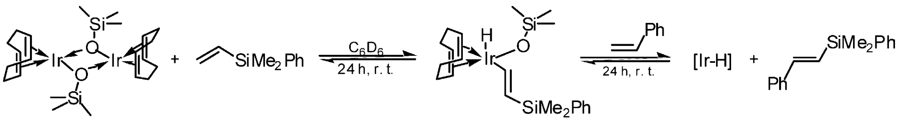
In order to find the mechanism of activation of C_{vinyl}–H in styrene, some experiments with deuterium-labeled reagents were performed. Analysis of the reaction of $H_2C{=}CHSiMe_2Ph$ with styrene-d_8 catalyzed by both **26** and **28** complexes permitted exclusion of the metallocarbene mechanism of the process examined, since the results of GC–MS of the reaction mixtures in a very early stage showed exclusive formation of silylstyrene-d_7 according to the equation given previously for ruthenium catalyst [89] (see the experiments with ruthenium catalysts (Eq. (17)).



Scheme 14. Catalysis of styrene silylation with vinylsilanes by metal (Rh and Ir) siloxide complexes.

Moreover, the reaction between styrene d_0 and styrene d_8 tested in the presence of the catalytic amounts of both complexes yielded a mixture of styrenes (d_0, d_1, d_2, d_3, d_5, d_6 and d_7) whose presence was confirmed by the GC–MS and ^{1}H NMR methods. These experiments clearly showed that H/D exchange had taken place [89].

To characterize the catalytic performance of M–O–$SiMe_3$ complex, a series of pseudostoichiometric reactions between the initial dimeric complexes and both substrates was analyzed [89,90]. In this overview, we present the reaction illustrating experiment of iridium siloxide (**28**) with vinylsilanes followed by introduction of styrene to such a mixture at the next step (Eq. (30)).



28

$[Ir] : [CH_2{=}CHSi{\equiv}] : [styrene] = 1 : 10 : 10$ (30)

A general mechanism of catalysis is summarized in Scheme 14.

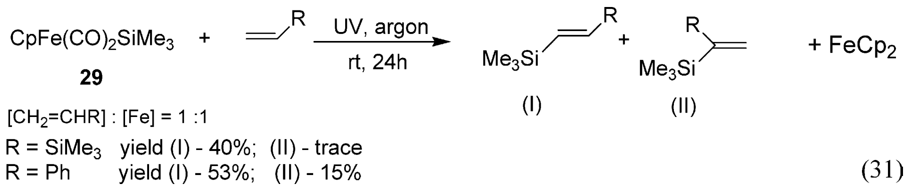
The very fast H/D exchange process occurring between **26** and **28** with styrenes has permitted us to assume that the coordination of styrene to metal is responsible for the cleavage of dimeric metal siloxide complex to form (I) followed by an oxidative addition of C_{vinyl}–H of styrene to the metal. In the presence of vinylsilane as a second substrate, the latter initiates a catalytic process observed by GC–MS. The insertion of vinylsilane into M–H bond of (III) is followed by elimination of ethylene (β-transfer) to give the M–Si intermediate (V). According to the dissociative mechanism, the reductive elimination of (*E*)-silylstyrene takes place, regenerating (in an excess of styrene) complex (I).

Silylation of alkenes in the presence of rhodium(I) and iridium(I) siloxides can be generalized for ruthenium based complexes such $Ru_3(CO)_{12}$ and $[RuCl_2(CO)_3]_2$ [73,92] used effectively in the silylation process. In the presence of those ruthenium complexes containing no Ru–H bond, the homocoupling of vinylsilanes gives only *trans*-1,2-bis(silyl)ethene [93].

6. Competitive silylation of alkenes with vinylsilanes and hydrosilanes catalyzed by ruthenium and iron complexes

In the earlier overview [7], we described the competitive process (catalyzed by $Ru_3(CO)_{12}$) of heterocoupling (dehydrogenative silylation) of vinylsilane with hydrosilane and of homocoupling of vinylsilane which was yet accompanied by some side reactions such as hydrosilylation and hydrogenation of olefins and migration of silyl group. The study led to a conclusion that both competitive reactions as well as hydrosilylation occurred via the same intermediate which was formed by the activation of C_{vinyl}–H and at the same time C_{vinyl}–Si and Si–H bonds, and two catalytic cycles were proposed for explanation of the reactions examined [7].

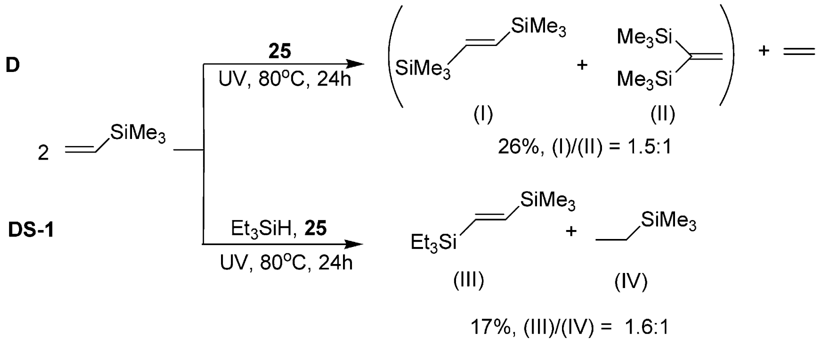
According to Randolph and Wrighton [35], high activity of $Fe(CO)_5$ upon UV irradiation under mild conditions (0–50 °C) in the hydrosilylation of alkenes was due to generation of an active intermediate $H(R_3Si)Fe(CO)_3$ [35] responsible for competitive hydrosilylation and dehydrogenative silylation process. To check the effect of the olefin insertion into Fe–Si bond, the stoichiometric reactions of $CpFe(CO)_2SiMe_3$ (**29**) with a selected olefin (vinyltrimethylsilane, styrene and ethene) were performed to yield olefin derivatives. Also traces of the hydrogenated products (e.g., ethylbenzene and ethyltrimethylsilane) were found [72]. The final iron product (ferrocene) does have not involved Fe–H bond and this is the reason why this catalyst is not active in the silylative coupling reaction (Eq. (31)).



(31)

However, a catalytic system of $Fe(CO)_5 + HSiEt_3$ (**25**) could be selected as a good model for observation of the competitive reaction catalyzed by in situ generated Fe(H)Si complex.

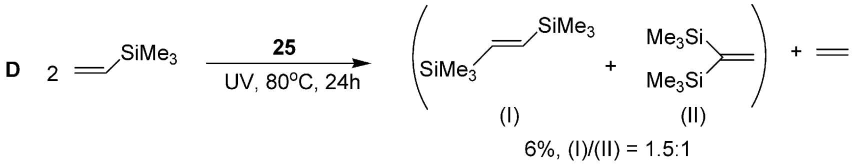
In the case of vinyl–silicon compounds the following reaction can proceed, i.e., homocoupling of vinylsilanes (Eq. (33)) and dehydrogenative silylation of vinylsilane with triethylsilane (Eq. (34)).



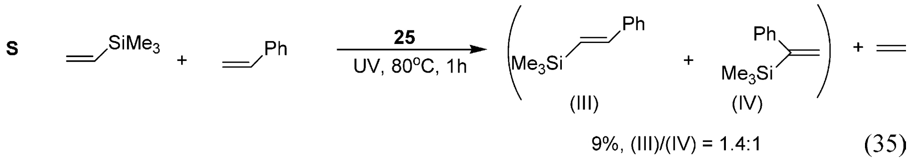
(32)

(33)

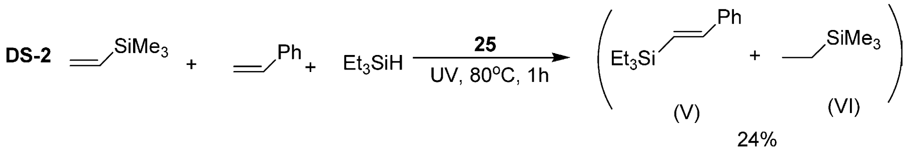
However, if styrene was additionally used in this system, products of the competitive reactions have been detected (see Eqs. (34)–(36)), i.e., silylation of styrene with vinylsilane (S), homocoupling of vinylsilane (D) as well as the process being a combination of the dehydrogenative silylation of styrene and vinylsilane (DS-2).



(34)



(35)

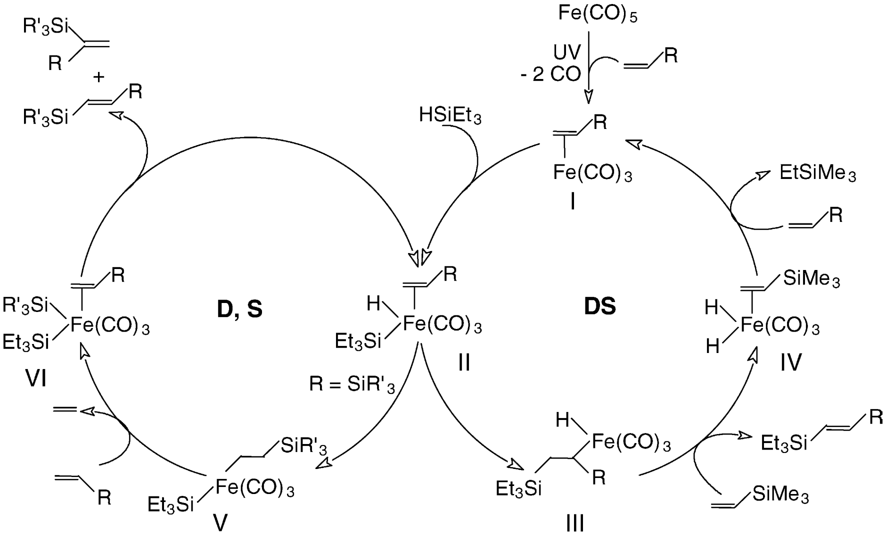


(36)

The complexity of these reactions is illustrated on Scheme 15.

The left hand circle explains a homo and heterocoupling of vinylsilanes according to the mechanism concerted for other complexes involving M–H and M–Si bonds, but the complex (II) (Scheme 15) is a key intermediate in all reactions observed, i.e., also in the dehydrogenative silylation. In the case of two olefins present (styrene and vinylsilane), ethylbenzene is not observed as a product of styrene hydrogenation so apparently the coordination of vinylsilane to $(H)_2Fe(CO)_3$(IV) followed by its hydrogenation occurs more readily than of styrene to get finally $EtSiMe_3$ even in the 10-fold excess of styrene.

The conclusion is that a complex H–Fe–Si (II) catalyzes competitive silylation of olefins (e.g., styrene, vinylsilane) by hydrosilane and by vinylsilane. Although this reaction is the first evidence of β-silyl transfer from carbon to iron followed by ethylene evolution working catalytically in fact it is also a



Scheme 15. Competitive silylation of alkenes with hydro- and vinylsilanes catalyzed by iron complexes.

direct evidence for generation of an intermediate responsible for two reactions of alkene silylation, i.e., by hydrosilanes and vinylsilanes.

It is noteworthy to conclude that while a migratory insertion of alkene into Fe–Si bond (complex II) gives *trans*-adduct as an exclusive product of silylation by hydrosilane, an insertion of alkene into more crowded complex (VI) formed by silylation with vinylsilane can occur according to two different modes giving a mixture of *trans*-product and *gem*-products as well.

7. Conclusions

- Silylation of alkenes with hydrosilanes and vinylsilanes proceeds via the same types of active intermediates, i.e., late TM metal complexes involving M–H and M–Si bonds. In both reactions late TM complexes activate C_{vinyl}–H as well as Si–H and Si–C_{vinyl} bonds, respectively, according to two general equations presented (Scheme 1).
- The common crucial step of the two reactions catalyzed by the complexes containing initially M–H and/or M–Si bond is an insertion of alkene into M–Si bonds followed by β-H transfer to metal with elimination of substituted vinylsilane. In this case, a formation of M–Si bond proceeds either via oxidative addition of hydrosilane (silylation by hydrosilane) or via insertion of vinylsilane into M–H bond, followed by β-Si transfer with evolution of ethylene (silylation by vinylsilane). Yet, if the catalysts contain initially no M–H and M–Si bond, their formation occurs via oxidative addition of hydrosilane (silylation by hydrosilane) or via preliminary oxidative addition of C_{vinyl}–H of alkene to get in situ M–H bond, followed by insertion of vinylsilane to this bond and next β-Si transfer to metal with elimination of ethylene (silylation by vinylsilane). We can conclude that regardless of the way of M–H and M–Si introduction and/or in situ generation a common key step for both reactions, proved by separate stoichiometric experiments is a β-Si transfer versus β-H transfer from β-silyethyl–metal complex to the metal atoms.
- Silylation of alkenes with hydrosilanes is regiospecific due to regioselective insertion of olefins into M–H bond giving products with terminal silyl groups. Since M–H complexes (where M = Ru, Rh) also catalyze *cis* → *trans* isomerization, predominantly *trans*-1,2-products have been isolated stereoselectively. The regioselectivity of alkene silylation by vinylsilane catalyzed by M–H and M–Si bond depends on the way of insertion of olefins into M–Si bond, which is dependent on the structure of the complex, stereoelectronic effects of the ligands as well as bulkiness of alkene. Therefore, homocoupling of vinylsilanes can give *trans*- and *gem*-products.
- If the silylation with vinylsilane occurs according to the mechanism involving preliminary hydrovinylation, i.e., when it is catalyzed by TM complexes containing initially no M–H and M–Si bond, then the regioselectivity of the process depends on the mode of this hydrovinylation stage. On the basis of the experiment reported by Brookhard—also two types disilylethenes (*trans*- and *gem*-) are observed in catalysis by metal(siloxides) of the homocoupling of vinylsilane. However, in the heterocoupling with styrene catalyzed by rhodium and iridium siloxides, as well as by $[RuCl_2(CO)_3]_2$, exclusive formation of silylation product is due to regiospecific hydrovinylation of styrene, followed by regioselective insertion of vinylsilane into Ru–H bond and next β-Si elimination of ethylene and reductive elimination, exclusively, of *trans*-product. There is no olefin insertion into M–Si bond needed in this case as a key step necessary for silylation with vinylsilanes catalyzed by complexes initially containing M–H and M–Si bonds.

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