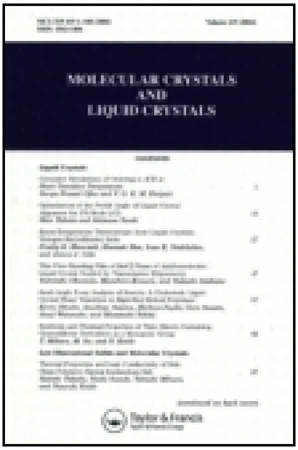

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# New Unsaturated Organosilicon Oligomers Via Catalytic Polycondensation of Divinylsubstituted Silicon Compounds

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# New Unsaturated Organosilicon Oligomers Via Catalytic Polycondensation of Divinylsubstituted Silicon Compounds

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New efficient route for preparation of organosilicon linear and cyclic oligomers containing C=C bond and silicon-atom in the chain, based on the catalytic polymerization of divinylsubstituted organosilicon compounds (i.e. divinyl-silanes, -siloxanes and -silazanes), is overviewed. The oligocondensation yields linear silylene (siloxylene, silazanylene)-vinylene oligomers or cyclic dimers (trimers) when using ruthenium and rhodium complexes, respectively. In the presence of Ru and Rh complexes diallyldiorganosilane and allylvinyldimethylsilane undergo prior isomerization followed by oligocondensation yielding respective silylene-propylene and silylene-propylene-vinylene oligomers.

*Keywords:* Acycled Diene Oligo-Condensation; Ring Closing; divinyldiorgano-silane; divinyltetramethyldisiloxane; divinyltetramethyldisilazane; diallyldimethylsilane; allylvinyldimethylsilane; rhodium and ruthenium catalysts

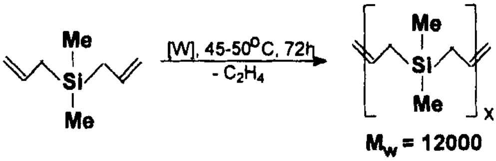
## INTRODUCTION

Unsaturated organosilicon oligomers and polymers have found wide application as adhesives, membranes, materials of special electrophysical, optical and thermal properties as well as precursors for ceramics, graftpolymers and thermosetted and self-cured materials[1].

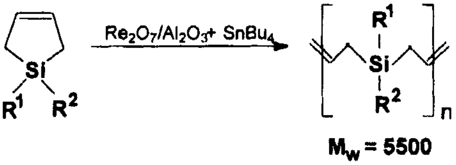
Polymers and oligomers containing C=C bond and silicon atom in the chain can be synthesized either by polyhydrosilylation of respective silylacetylenes[2] or by olefin (diene) metathesis[3].

The polyhydrosilylation of diorganosilanes with diorganoethynylsilanes[4] or intermolecular hydrosilylation of diorganoethynylsilanes[5], both catalyzed by $H_2PtCl_6$-based precursors are the best examples of the first route.

Acyclic Diene Metathesis (ADMET) Polymerization (e.g. dialkyldiorgano-silanes[6-8] or Ring Opening Metathesis Polymerization (ROMP) of silacycloalkenes[9] occur efficiently in the presence of highly active metallacarbenes (W, Mo, Ru) or heterogeneous $Re_2O_7/Al_2O_3$ + $SnR_4$ ($PbR_4$) system according to the following exemplary reaction equations: (1a) (1b):



(1a)



(1b)

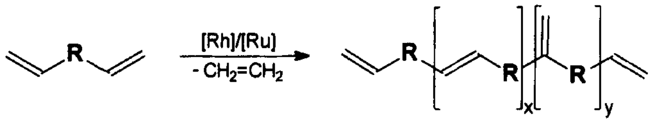
ADMET Polymerization of dialkenyl-silanes - disilanes and -disiloxanes occurring the presence of rhenium catalysts is usually accompanied by intramolecular cyclization of monomer[8,10].

Unfortunately, vinylderivatives of organosilicon compounds which are of fundamental industrial importance are completely inert to productive homometathesis, (ADMET and ROMP) e.g. vinylalkenyl- and divinyl-derivatives of silanes and siloxanes show inactivity in ADMET Polymerization (and also in intramolecular cyclization) if catalyzed by any metallacarbene catalysts presumably (similar to inactivity of metallacarbenes in self-metathesis of vinylsubstituted silicon compounds) due to steric hindrance of silyl groups stimulating non-productive cleavage of disilylmetallacyclobutane[11].

In this paper, a comprehensive analysis of the new synthetic route to organosilicon polyenes is presented. The method is based on polycondensation of divinylsubstituted (and vinylallylsubstituted) silicon compounds catalyzed by ruthenium and rhodium complexes according to non-metallacarbene mechanism.

## POLYCONDENSATION OF DIVINYLSUBSTITUTED ORGANOSILICON MONOMERS - SYNTHESIS OF LINEAR OLIGOMERS

Intermolecular polycondenastion of divinyldiorganosilane **(1)**[12], divinyltetramethyldisiloxane **(2)**[13] and divinyltetramethyldisilazane **(3)**[14] proceeds in the presence of a variety of ruthenium and rhodium complexes to yield finally a mixture of linear unsaturated oligomers according to the following equation:



(2)

x + y = 2 - 25

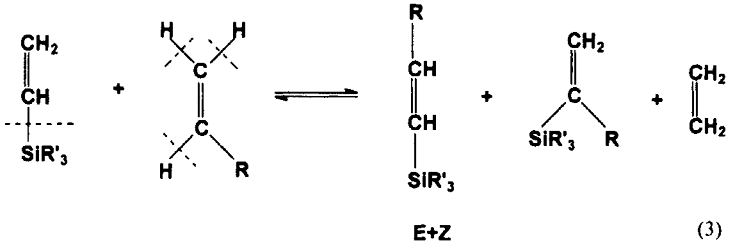
where R = $-SiMe_2$ or $-Me_2Si-O-SiMe_2-$ or $-Me_2Si-NH-SiMe_2-$

**(1)** **(2)** **(3)**

Under the optimum conditions, polycondensation of (1) - (3) gives silylene-vinylene ($RuCl_2(PPh_3)_3$, 130°C; $M_w$=1510; $M_w/M_n$= 1.19; DP≈17 [12]; siloxylene-vinylene: $RuCl_2(PPh_3)_3$, 130°C, 72 h, $M_n$=1815, $M_w/M_n$=1.16, DP≈10 [13]; and silazanylene-vinylene: $RuHCl(CO)(PPh_3)_3$, 130°C, 1 week; Mn=2385, $M_w/M_n$=1.21, DP≈15 [14] oligomers, respectively.

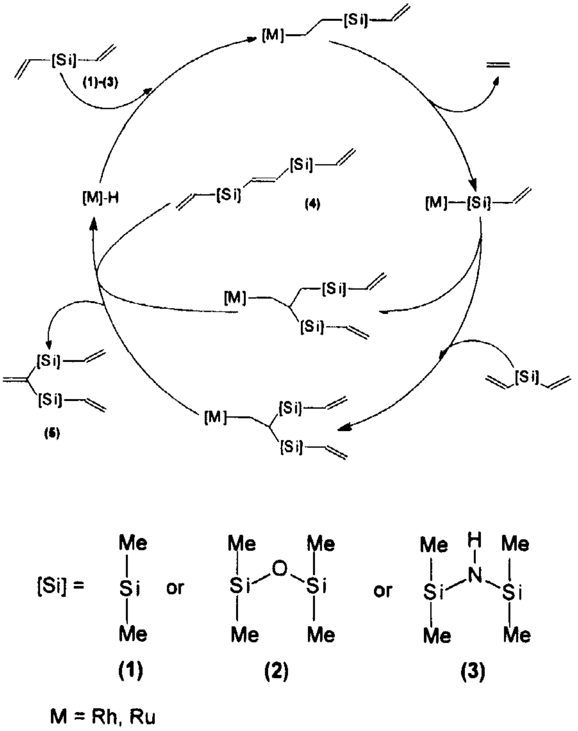
All the oligomers were identified by $^1H$ and $^{13}C$ NMR spectra as well as by the DEPT method to determine a chain with trans-1,2-isomers as well as 1,1-disilyl(disiloxyl, disilazanyl) isomers.

The presence of the latter confirms a non-metallacarbene mechanism for the polycondensation and similar to disproportionation of monovinyl substituted silicon compounds is further evidence for the insertion-elimination mechanism. The reaction proceeds through cleavage of the =C-Si bond of the vinylsubstituted silicon compound and the =C-H bond of the olefin (diene) according to the following equation:



(3)

The evidence for the mechanism pathways of monovinylsilanes has been reported previously[15-19], but the general catalytic scheme for dimerization of divinylsubstituted silicon compounds (as an example of its oligomerization) is given below.

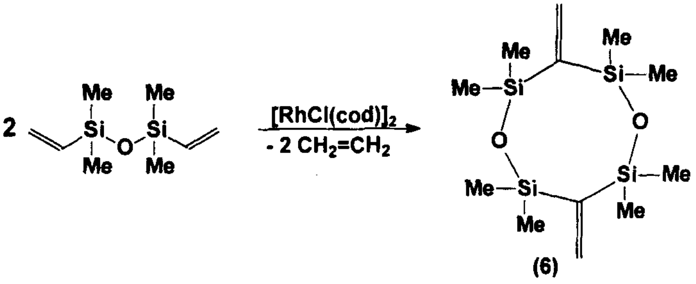


SCHEME 1. Dimerization of divinylsubstituted silicon compounds catalyzed by Rh and Ru complexes

The mechanism of catalysis involves the insertion of the diene into M-Si bond and that of the vinylsilane into M-H bond, followed by β-H and β-Si elimination, giving two isomeric bis(vinylsilyl)ethenes (**4**) and (**5**) and ethene, respectively,. The work has been continued to find the optimum conditions for preparation of the higher molecular weight polymers via the above method.

## INTERMOLECULAR CYCLIZATION OF DIVINYLSUBSTITUTED SILICON COMPOUNDS

Divinyltetramethyldisiloxane (**2**) in the presence of ruthenium complexes (under mild conditions) undergoes condensation of two molecules according to the pathways presented in Scheme 1 providing a facile route to linear carbotetrasiloxanes (**4**) if $RuCl_2(PPh_3)_3$ or $RuHCO(PPh_3)_2$ was used or (**5**) if $RuCl_2(CO)_3$ catalyst was applied [20]. However, when using $[RhCl(cod)]_2$ as a catalyst a ring closure of two monomers of (**2**) takes place to yield 2,2,4,4,6,6,8,8,-octadimethylenecyclooctane (**6**) [20] as follows:



(4)

The products (**4**)-(**6**) were isolated and characterized by $^1H$ NMR and $^{13}C$ NMR and $^{29}Si$ NMR spectroscopy [20, 21] and the X-ray structure of cyclocarbosiloxane (**6**) was reported [21] showing the molecule to be close to boat conformation (Fig.1).

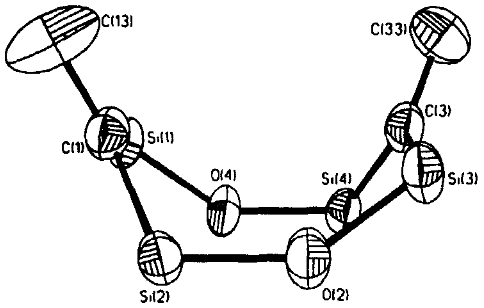
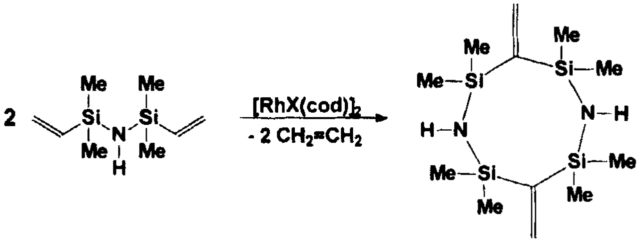
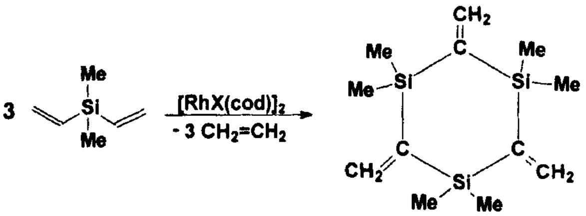


FIGURE.1. X-ray structure of (**6**)

Divinyldimethylsilane (**1**) and divinyltetramethyldisilazane (**3**) also undergo condensation particularly in the presence of [RhCl(cod)$_2$] and [Rh(OSiMe$_3$)(cod)]$_2$ catalysts to give products according to the following equations:



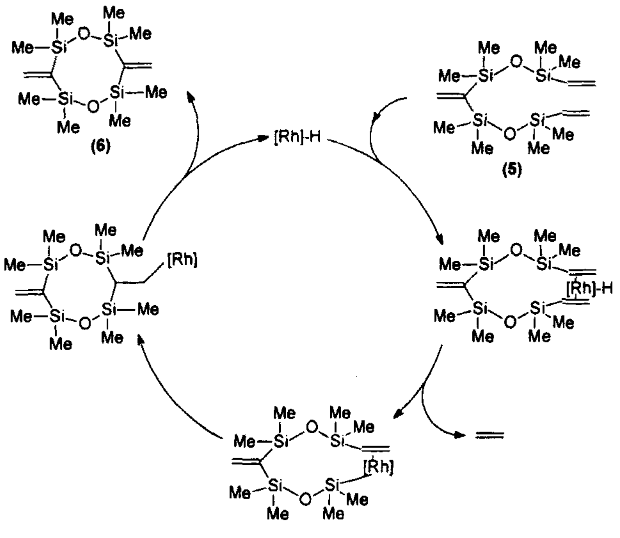
(5)



(6)

The products were isolated and the structures were determined on the basis of NMR spectra and GC-MS analysis [22]

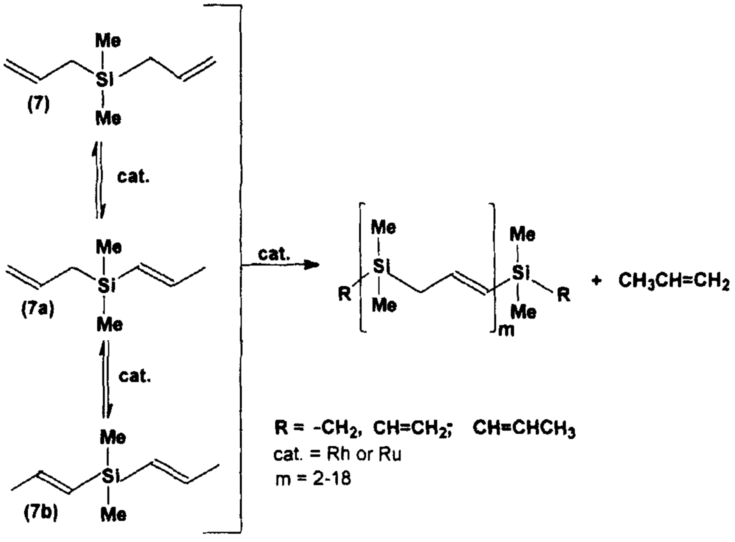
It is worth noting that contrary to ring closing olefin metathesis, which has recently become a very efficient method for preparation of endocyclic organic (also organosilicon) unsaturated compounds, the intermolecular condensation of examplary (**1**)-(**3**) opens an original route to synthesizing organosilicon compounds containing exo-cyclic methylidenes. Such cyclic monomers can make a basis for subsequent ring opening polymerization yielding finally new linear polymers. The catalytic cycle describing formation of (**6**) from (**5**) catalyzed preferably by rhodium complexes is given below.



SCHEME 2. Intramolecular cyclization of (**5**) →(**6**)

## POLYCONDENSATION OF ALLYL(VINYL)DIORGANOSILANES CATALYZED BY RUTHENIUM AND RHODIUM COMPLEXES

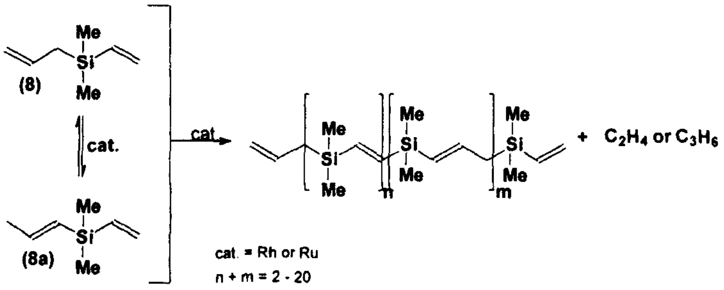
Ruthenium catalysts (e.g. $RuCl_2(PPh_3)_3$, $RuHCl(CO)(PPh_3)_3$ and $RuCl(SiMe_3)(CO)(PPh_3)_2$ appeared to be effective catalysts for oligocondensation of diallyldiorganosilanes (**7**). Surprisingly, the reaction proceeds via preliminary catalytic isomerization of allylsilane to vinylsilane (silyl-1-propene) followed by their co-condensation according to the following equation [23]).



(7)

Under the optimum conditions (5 days, 130°C) the complete conversion of the monomer is observed yielding a mixture of linear silylene-propylene oligomers, but involving only trans-1,2-isomers. GC-MS analysis of the products of diallyldimethylsilane isomerization at the starting point and also of dimers during the reaction (130°C, 12h) suggests that the reactions occur consecutively to give products according to the insertion-elimination mechanism mentioned.

Our recent study on the polycondensation of starting allylvinyldimethylsilane (**8**) in the presence of ruthenium and rhodium complexes allowed finding conditions for effective formation of silylene-vinylene, propylene oligomers which occurs according to the following equation (**8**) [24]



(8)

$^1$H and $^{13}$C NMR measurements as well as GC-MS analysis of the starting substance and dimeric intermediates allow us to conclude that oligocondensation of (**7**) occurs competitively with oligo-co-condensation of (**8**) with the isomer (**8a**) to yield finally oligomers containing both fragments (but not pendant methylidene substituents) as well as to evolve ethylene and propylene.

## CONCLUSIONS

- Divinyl substituted silicon compounds, e.g. divinyldimethylsilane, divinyltetramethyldisiloxane, divinyltetramethyldisilazane - undergo efficient polycondensation to yield linear oligomers (if ruthenium complexes are used as catalysts) or cyclic dimers and trimers (if rhodium catalyst is applied)
- The reaction of oligocondensation opens a new route for synthesizing linear (silyl, siloxyl, silazanyl)ene - vinylene oligomers as well as cyclocarbo-silane - (siloxane and silazane) - containing exo-methylenes. These products of prospective importance as new materials of special applications cannot be synthesized via ADMET Polymerization or Ring Closing Metathesis.
- Diallyldimethylsilane and allylvinyldimethylsilane undergo preliminary isomerization to respective silyl-1-propenes and is followed by their polycocondensation giving poly(silylene-propylene) and poly(silylene-propylene-(vinylene) oligomers, respectively.

**Acknowledgment:** My warmest thanks are due to the talented co-workers whose names appear in the references. Our recent research was partly supported by State Committee for Scientific Research in Poland, Project No 3T09A07413.

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