Polycondensation vs. Cyclization of Divinylsubstituted Silicon Compounds Catalyzed by Transition Metal Complexes

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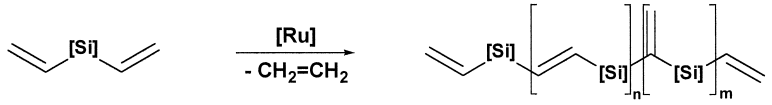
SUMMARY: In the presence of ruthenium complexes divinyldiorganosilicon compounds undergo de-ethenated coupling polycondensation yielding under optimum conditions *trans-tactic* polysilylene(siloxylene, silazanylene)vinylenes and poly(silylene-arylene-vinylenes). Rhodium- ($[RhX(cod)]_2$ X = Cl, $OSiMe_3$) catalyzed ring closure of oligomeric (dimeric, trimeric) products of intermolecular condensation opens a new route to synthesizing organosilicon exo-cyclic methylenes. In the presence of Ru-complexes the cross-coupling (poly)condensation of di- and trivinylsilicon monomers with organic dienes allows syntheses of a series of linear and dendrimeric poly(arylene-silylene-vinylene)s.

Although Cyclic Diene Metathesis (ADMET) Polymerization of dialkenylsilanes occurs efficiently in the presence of highly active metallacarbenes (W, Mo, Ru), vinylderivatives of organosilicon compounds, which are of fundamental industrial importance, are completely inert to productive homometathesis-polymerization presumably due to steric hindrance of silyl groups stimulating non-productive cleavage of disilylmetallacyclobutene [1,2]. However, divinyldiorganosilicon compounds in the presence of ruthenium complexes undergo intermolecular polycondensation under the optimum conditions yielding linear unsaturated polymers according to the following scheme (eq.1) [3-5]:



(1)

where [Si] = $-Si(CH_3)_2-$ (I) or $-(H_3C)_2Si-O-Si(CH_3)_2-$ (II) or $-(H_3C)_2Si-NH-Si(CH_3)_2-$ (III)

(**I**) catalyst $RuCl_2(PPh_3)_3$, 130°C, 120h., M_w = 1510, M_w/M_n = 1.19, DP = 17,

(**II**) catalyst $RuCl_2(PPh_3)_3$, 130°C, 72h, M_w = 1815, M_w/M_n = 1.16, DP = 10,

(**III**) catalyst $RuHCl(CO)(PPh_3)_3$, 130°C, 1 week, M_w = 2385, M_w/M_n = 1.21, DP = 15,

When rhodium complexes $[RhCl(cod)]_2$ [6] or $[Rh(OSiMe_3)(cod)]_2$ [7] are used as a catalyst, two divinyltetramethyldisiloxane molecules undergo competitive ring closure to yield 2,2,4,4,6,6,8,8-octamethylenecyclooctane (**IV**, 30%) as follows (eq.2):

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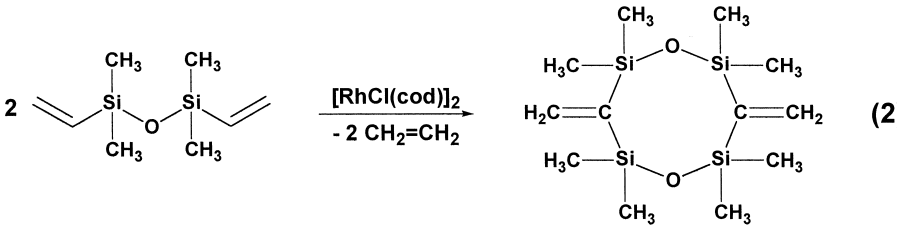


IV

The product (**IV**) was isolated and characterized by spectroscopic methods and its X-ray determined structure was reported revealing the molecule in a close to boat conformation (Fig.1.) [8]:

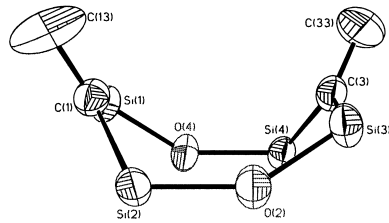
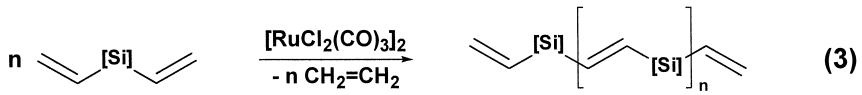


Figure 1.

These new efficient routes for preparation of organosilicon linear and cyclic oligomers have been recently overviewed [9].

In this paper, however, the highly stereo- and regioselective polycondensation of divinyl- and trivinylsubstituted silicon compounds catalyzed by ruthenium (and rhodium) complexes is presented to yield *trans-tactic* silylene(siloxylene, silazanylene)vinylene as well as silylene-phenylene-vinylene polymers under the optimum conditions.

$[RuCl_2(CO)_3]_2$ catalyzes the polycondensation of divinylsubstituted silanes, siloxanes and silazanes to give linear polymers according to the following scheme (eq.3):



where [Si] = $-Si(CH_3)_2-$ (V) or $-(H_3C)_2Si-O-Si(CH_3)_2-$ (VI) or

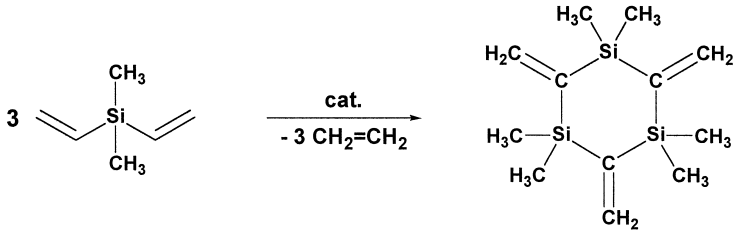
$-(H_3C)_2Si-NH-Si(CH_3)_2-$ (VII) or $-(C_2H_5O)_2Si-O-Si(OC_2H_5)_2-$ (VIII)

Reaction conditions:

[monomer]:[catalyst] = 100:1, 90°C, 10 days,

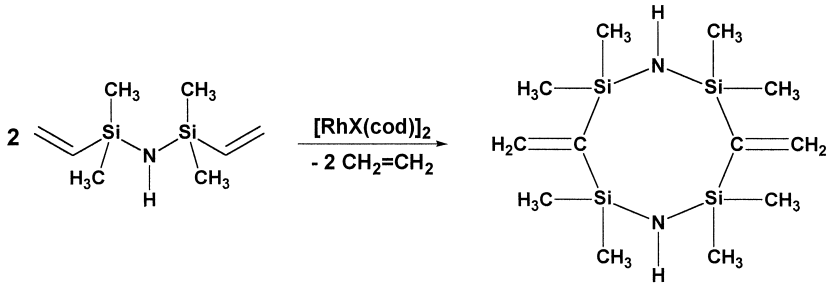
The polymers were identified by ^{1}H NMR, ^{13}C NMR spectra as well as by the DEPT method and characterized by GPC analysis.

However, divinyldimethylsilane and divinyltetramethyldisilazane in the presence of other catalysts, e.g. $[RhX(cod)]_2$ where X = Cl or $OSiMe_3$ undergo predominantly condensation and ring closure of dimeric (trimeric) linear products to yield a respective cyclocarbosilane (**IX**) (eq.4) and cyclocarbosilazane (**X**) (eq.5):



(4)

IX



(5)

X

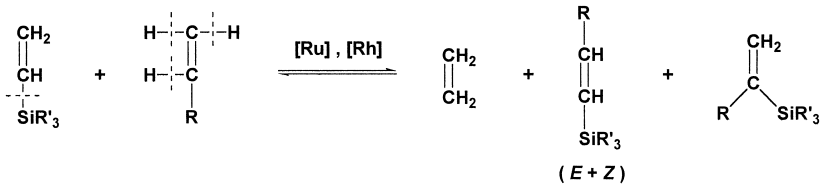
Reaction conditions:

[monomer]:[$[RhCl(cod)]_2$] = 100:1, 130°C, 4 weeks, autoclave.

The cyclization is accompanied by linear polycondensation of respective divinyldimethylsilane and divinyltetramethyldisilazane. In order to synthesize efficiently the cyclic products, the method involves a prolonged polymerization of linear oligomers (3-4 weeks) to isolate products after their separation from catalyst and higher polymers. [10]

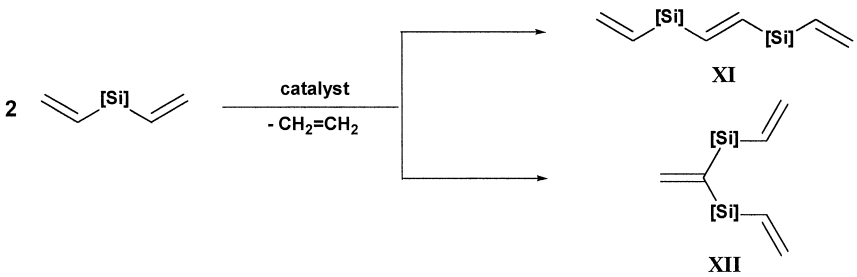
The three cyclic products prepared and characterized are the convincing evidence that this tandem catalytic intermolecular condensation and ring closure reactions can be a very attractive method for preparation of unsaturated organosilicon compounds containing exo-cyclic methylenes which cannot be obtained by ring closing olefin metathesis.

The condensation (silylative coupling) of monovinylsubstituted silicon compounds proceeds through cleavage of the =C-Si bond of the vinylsubstituted silicon compound and the activation of the =C-H bond of the second vinyl(silane) molecule according to the following equation (eq.6):



(6)

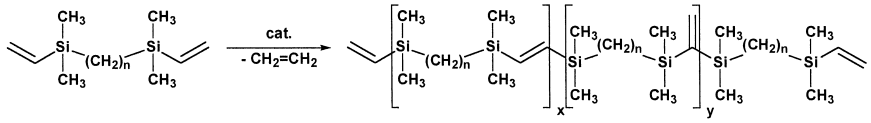
The evidence for the non-metallacarbene mechanism of monovinylsilane transformation has been reported previously [12,13] but it can be generalized for dimerization of divinylsubstituted silicon compounds [6] (see equation 7) leading subsequently to competitive linear oligomerization and ring-closing silylative coupling [9].



(7)

In the presence of $[RuCl_2(CO)_3]_2$ *trans*-dimer (**XI**) is exclusively yielded whereas $[RhX(cod)_2]$, X = Cl or $OSiMe_3$ catalyze preferably a formation of *gem*-product (**XII**) and ruthenium-phosphine complexes ($[RuHCl(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$) furnish both dimeric products (**XI** and **XII**).

This new synthetic route can also be used to synthesize polycarbosilanes particularly if it is based on polycondensation of divinylsubstituted carbosilanes which occurs in the presence of ruthenium and rhodium complexes according to the following general equation (eq.8) [11]:



(8)

cat. = [Ru] or [Rh]

n = 2 - 4

XIII - XV

In the presence of $[RuCl_2(CO)_3]_2$ *trans-tactic* alkylene-silylene-vinylene polymers are exclusively obtained.

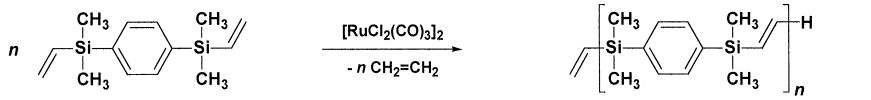
Reaction conditions:

$[RuCl_2(CO)_3]_2$, [monomer]:[catalyst] = 100:1, 90°C, 10 days,

(**XIII**) n = 4, M_w = 8650, M_w/M_n = 1.16; (**XIV**) n = 3, M_w = 7840, M_w/M_n = 1.14; (**XV**) n = 2, M_w = 6350, M_w/M_n = 1.12

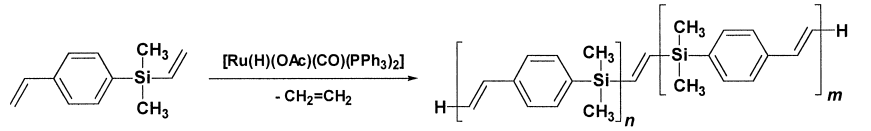
The above mentioned silylative coupling polycondensation procedure has been also used for synthesis of highly stereo- and regio-selective synthesis of silylene-phenylene-vinylene polymers, because of (similar to poly(*p*-phenylene-vinylene)s [14]) their efficient photoluminescence and potentially useful electroluminescence properties. Silicon-containing phenylene-vinylene polymers are expected to have application as blue light emitting polymer materials [15].

Therefore in order to prepare such polymers with phenylene units, the ruthenium-catalyzed homocoupling polycondensation of 1,4-bis(vinyldimethylsilyl)benzene (eq.9) [16] and cross-coupling of (*p*-vinylphenyl)(vinyldimethyl)silane (eq.10) [17] occurring in the presence of ruthenium complexes $[RuCl_2(CO)_3]_2$ and $[RuH(OAc)(CO)(PPh_3)_2]$, respectively, have been tested according to the following scheme:



(9)

XVI



(10)

XVII

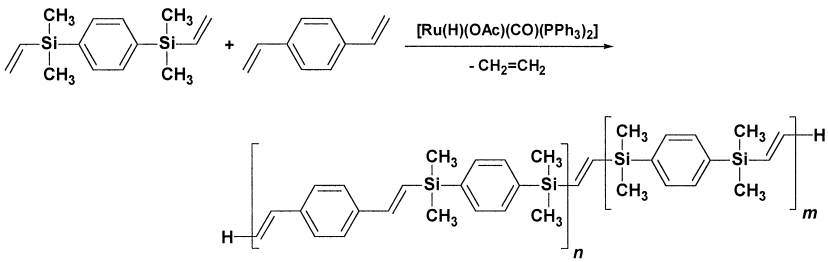
Reaction conditions:

(**XVI**) [monomer]:[catalyst] = 100:1, 110°C, one week, 1M in toluene, under slow flow of argon, yield: 90%, M_w = 7100, M_w/M_n = 1.50, DP = 23

(**XVII**) [monomer]:[catalyst] = 100:1, 80°C, one week, 0.25M in benzene, under slow flow of argon, yield: 88%, M_w = 7600, M_w/M_n = 1.77, DP =26

The products (**XVI** and **XVII**) of homopolycondensation were identified by ^{1}H, ^{13}C, ^{29}Si NMR, IR and Raman spectra as well as by the DEPT method to detect a mixture of well-defined *trans*-tactic polymers. The polycondensation product (**XVII**) is terminated by (*p*-vinylphenyldimethyl)silyl group.

Attempts for co-polycondensation of 1,4-divinylbenzene with 1,4-bis(vinyldimethyl-silyl)benzene have been made to yield respective polymer (**XVIII**) according to the following scheme (eq.11):



(11)

XVIII

Reaction conditions:

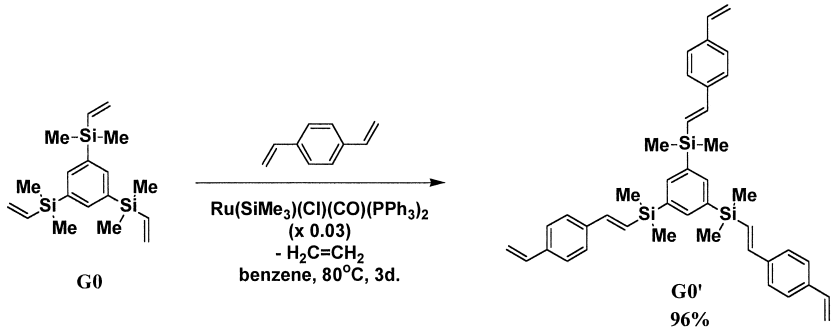
(**XVIII**) [monomers]:[catalyst] = $1:1:10^{-2}$, 80°C, one week, 0.25M in benzene, under slow flow of argon, yield: 83%, M_w = 7900, M_w/M_n = 1.84, DP = 20

It is quite obvious that all the products above are extraordinarily well-defined *trans*-tactic polymers and the silylative coupling polycondensation procedure constitutes a novel and efficient method for selective synthesis of phenylene-silylene-vinylene polymers. The polymers of this type are usually synthesized by Pt or Rh-catalyzed hydrosilylation [18] and their polydispersities range between 1.7-3.1 [19] or 2.6-5.5 [20]. Additionally, the polymers occur as a mixture of *gem*- and *cis*-1,2 and *trans*-1,2 isomeric fragments.

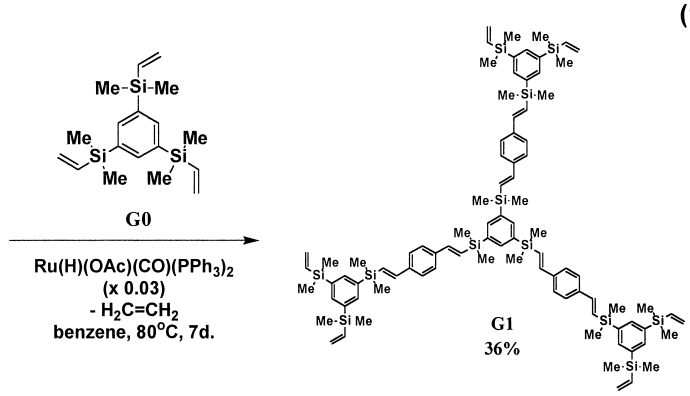
The new process of cross-coupling polycondensation of organic dienes (e.g. divinylbenzene) with divinylsilicon compounds (e.g. 1,4-bis(vinyldimethylsilyl)benzene) can be extended to

the synthesis of novel organosilicon dendrimers,. by the respective reactions of organic dienes with trivinylsubstituted silanes, or otherwise, of organic trienes with divinylsubstituted silicon compounds.

As an exemplary reaction, we have synthesized dendrimeric unit **G0'** by silylative cross-coupling between core **G0** (1,3,5-tris(vinyldimethylsilyl)benzene) and 1,4-divinylbenzene in the presence of $[Ru(SiMe_3)(Cl)(CO)(PPh_3)_2]$ catalyst. The first generation of the dendrimer **G1** was also prepared by a similar reaction between **G0'** and **G0** in the presence of selective $[Ru(H)(OAc)(CO)(PPh_3)_2]$ catalyst, according to the following scheme (eq.12) [19]:



(12)



The above presented unsaturated carbosilane dendrimers seem to have unique properties, though, their synthetic methods had long been limited, to hydrosilylation [20].

Conclusions:

- In the presence of some transition metal complexes (e.g. Ru, Rh and Co), divinyldiorganosilicon compounds undergo intermolecular de-ethenated condensation followed by competitive polycondensation and ring closure

- Under the optimum conditions ($[RuCl_2(CO)_3]_2$) linear *trans-tactic* poly(silylene,siloxylene)vinylenes and poly(alkylene-silylene-vinylenes) [M_w = 6350-8650, M_w/M_n = 1.12-1.16], and poly(silylene-arylene-vinylenes) [M_w = 7100-7900, M_w/M_n = 1.5-1.84] can be synthesized
- Rhodium- ($[RhX(cod)]_2$ X = Cl, $OSiMe_3$) catalyzed intramolecular condensation opens an original route for synthesizing organosilicon compounds containing exo-cyclic methylenes
- Cross-coupling (poly)condensation of di- and tri-vinylsilicon compounds with organic dienes allows syntheses of linear and dendrimeric poly(silylene-vinylene)s.

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