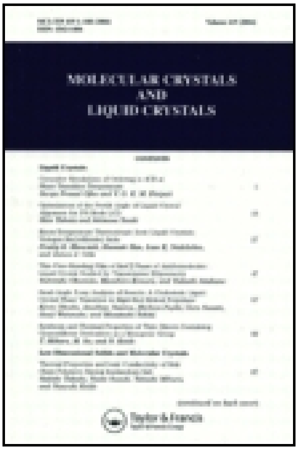

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Synthesis and Properties of Novel Unsaturated Organosilicon Starburst and Polymer Materials via Ruthenium Catalyzed Reactions

Bogdan Marciniec [a], Yujiro Itami [a] & Mariusz Majchrzak [a]
[a] Adam Mickiewicz University, Poznan, Poland

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SYNTHESIS AND PROPERTIES OF NOVEL UNSATURATED ORGANOSILICON STARBURST AND POLYMER MATERIALS VIA RUTHENIUM CATALYZED REACTIONS

Bogdan Marciniec, Yujiro Itami, and Mariusz Majchrzak
Faculty of Chemistry, Adam Mickiewicz University,
60-780 Poznan, Poland

The paper reports methods for synthesis of molecular and macromolecular organosilicon compounds containing arylene-silylene-vinylene sequence. The methods based on silylative coupling condensation and polycondensation catalyzed by ruthenium complexes containing or generating Ru-H bond lead to stereo and regio-selective synthesis of polymers and copolymers – poly(arylene-vinylene-silylene)s as well as starburst derivatives with silicon-bridged π-conjugated fragments. Also functionalization of cyclosiloxanes and cyclosilazanes with styrene furnish new monomers for ROP giving potentially products with silylene-vinylene-phenylenes.

Keywords: silylative coupling reaction; trans-stereoregular polymers and dendrimers; ruthenium complexes

INTRODUCTION

Well-defined unsaturated organosilicon polymers can be prepared either by Ring Opening Metathesis Polymerization (ROMP) of silacycloalkenes or predominantly by Acyclic Diene Metathesis Polymerization (ADMET) of siladienes both reactions catalyzed by W, Mo, Ru, homogeneous (W, Mo, Ru-carbenes) or heterogeneous (e.g. $Re_2O_7/Al_2O_3 + SnR_3$) catalytic systems. In view of the inactivity of metallacarbenes in ADMET polymerization of divinylsilicon compounds, the latter can undergo effective Silylative Coupling (SC) (Poly)condensation to yield in the presence of ruthenium containing or generating RuH/ and/or Ru/Si bonds linear polymers

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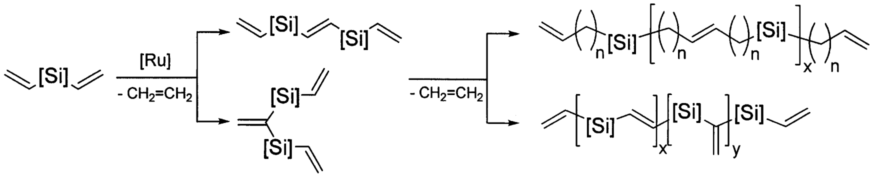
Address correspondence to Bogdan Marciniec, Faculty of Chemistry, Adam Mickiewicz University, Poznan, 60-780, Poland. E-mail: marcinb@amu.edu.pl

according to the following equation:

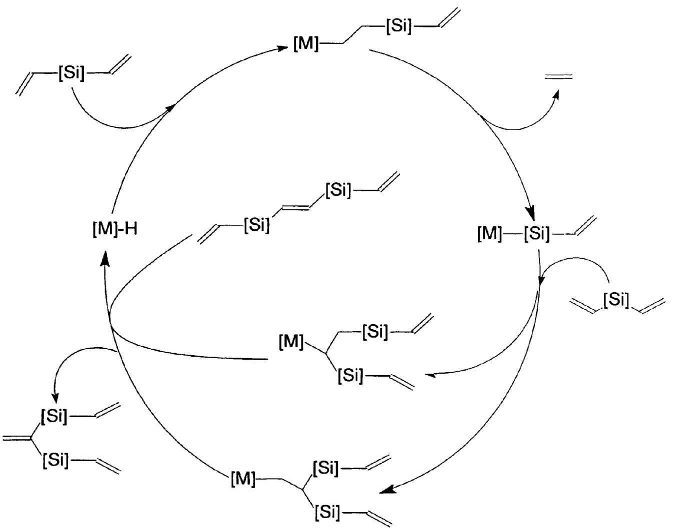


where [Si] = $-SiMe_2-$, $-Me_2Si-O-SiMe_2-$, $-Me_2Si-NH-SiMe_2-$, $-Me_2Si-(CH_2)_m-SiMe_2-$ m = 1 - 4

(1)

The mechanistic pathways for SC of monovinylsilanes are well-established [1–3] and the general catalytic scheme for condensation (dimerization) of divinylsubstituted silicon compounds (as a particular example of the oligomerization) has been reported previously.

The mechanism of catalysis involves the insertion of vinyl-silicon dienes into Ru-H and Ru-Si bonds followed by β-Si and β-H elimination to yield ethene and two isomeric trans- and gem-bis(vinylsilyl)ethene, respectively [4]. However, in the presence of $[RuCl_2(CO)_3]_2$ (**I**) catalyst the polycondensation of divinylsubstituted siloxanes [5], silazanes [6] and carbosilanes proceeds stereo-and regio-selectively to give *trans*-tactic polymers.



where [Si] = $-SiMe_2-$, $-Me_2Si-O-SiMe_2-$, $-Me_2Si-NH-SiMe_2-$

SCHEME 1

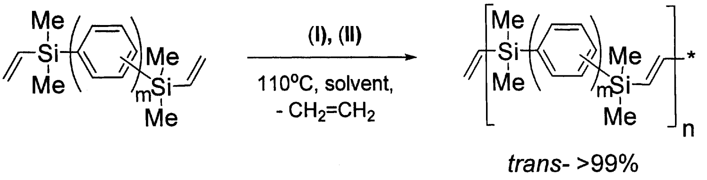
Polymers and starburst compounds containing phenylene-silylene-vinylene units being of great interest as optoelectronic materials, are synthesized by Pt- and Rh-catalyzed hydrosilylation but a mixture of *gem-* as *cis*-1,2- and *trans*-1,2-isomeric fragments is usually yielded. Our preliminary communications on polycondensation of 1,4-bis(dimethylvinylsilyl)benzene [7] and its copolymerization with 1,4-divinylbenzene [8] as well as on the reaction of 1,3,5-tris(dimethylvinylsilyl)benzene with 1,4-divinylbenzene [9] have shown that these reactions can be applied as efficient methods for highly stereo- and regio-selective synthesis of phenylene-silylene-vinylene polymers and starburst compounds.

This paper presents an overview of the synthetic methods for molecular and macromolecular organosilicon compounds containing arylene-silylene-vinylene sequence.

SYNTHESIS AND PROPERTIES OF WELL-DEFINED ARYLENE-SILYLENE-VINYLENE POLYMERS

Silylative Coupling Polycondensation (SC) of bis(dimethylvinylsilyl)arylenes Derivatives

In order to obtain homopolymers the model reaction – silylative *homo*-coupling of vinyldimethylphenylsilane (whose structure is similar to the fragments of polymers chains) catalyzed by ruthenium catalysts–$[RuCl_2(CO)_3]_2$ (**I**), $[Ru(H)(Cl)(CO)(PCy_3)_2]$ (**II**) has been tested in order to establish the optimum conditions for selective synthesis of a well-defined *trans*-tactic polymers. The polycondensation process runs according to the following general equation:



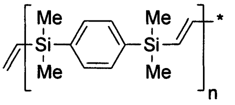
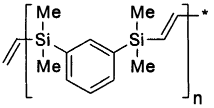
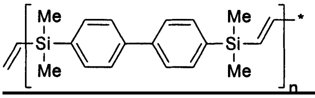
(2)

where: m = 1 or 2

Both catalysts **I** and **II** gave only *trans*-regular isomers fragments (>99%). We used **II** as a catalyst for a long-time reaction to obtain polymers of rather high average molecular weight and low polydispersity index (Table 1).

All polymeric materials were characterized by a linear structure with consecutive arylene-silylene-vinylene linkage. The structures of polymers were characterized and determined by ^{1}H, ^{13}C and ^{29}Si NMR as well as

TABLE 1 Results of Silylation Coupling Polycondensation

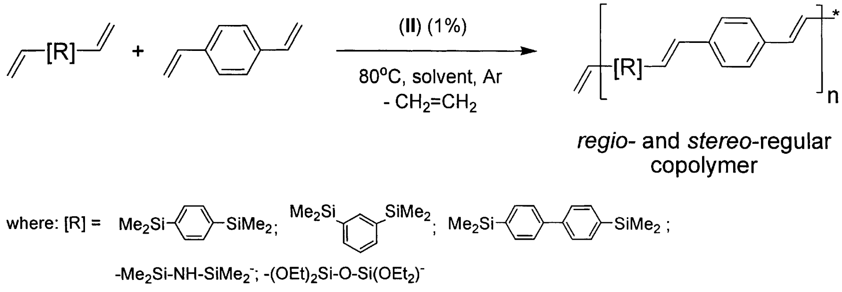
Homopolymer structure	$M_w{}^a$	$M_n{}^a$	M_w/M_n(PDI)	Yield (%)^c	Ref.
	16300	10190	1.6	89	10
	16400	9650	1.7	85	10
	34800	13920	2.5	92	10

^{a,b}calculated from GPC chromatogram (M_w and M_n relative to polystyrenes).
^{c}yield after isolation.

IR and Raman spectroscopy. The absence of quaternary fragments was also revealed by DEPT spectroscopic analysis [10].

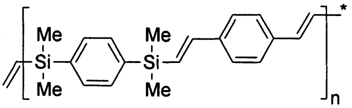
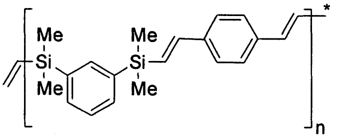
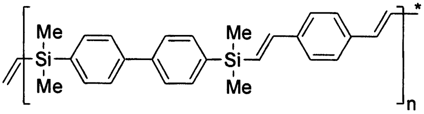
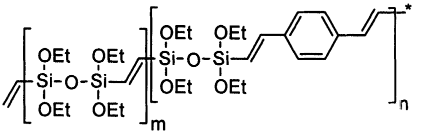
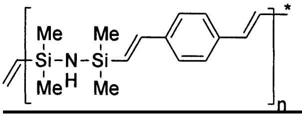
Silylative Coupling Copolycondensation (SC) vs. ADMET copolymerization of divinyl-substituted silicon compounds with 1,4-divinylbenzene (DVB)

The same catalytic procedure was applied for synthesis of copolymers containing 1,4-divinylbenzene (DVB) fragment in the main chain. The model reaction was used to establish the optimum conditions for effective copolycondensation of various bis(vinylsilyl)arylene monomers with 1,4-divinylbenzene [10,11]. A few novel copolymers (derivatives of divinylbenzene) whose structures are presented in Table 2, were synthesized according to the Scheme 2:



SCHEME 2

TABLE 2 Results of Silylative Coupling Copolycondensation

Copolymer structure	$M_w{}^a$	$M_n{}^a$	M_w/M_n (PDI)	Yield (%)^c	Ref.
	16300	10190	1.6	89	10
	16400	9650	1.7	85	10
	34800	13920	2.5	92	10
	12100	3780	3.2	69^d	11
	9150	3380	2.7	82	10

^{a,b} calculated from GPC chromatogram (M_w and M_n relative to polystyrenes).
^{c} yield after isolation.
^{d} m:n = 1:20.

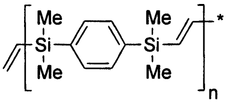
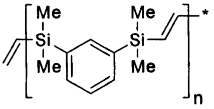
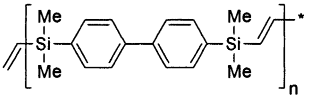
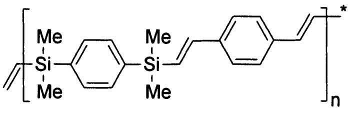
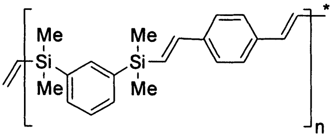
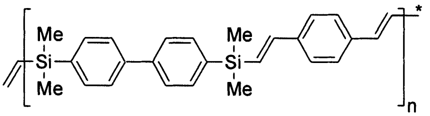
Photophysical Properties of Polymeric Materials

In order to study basic photophysical properties of all polymers we prepared molecular references whose structures referred to proper main chains' fragments of these polymers. The most interesting parameters are collected in Table 3 [12].

Synthesis and Properties of Unsaturated Organosilicon Starburst Compounds

Kim *et al.* have synthesized π-conjugated carbosilane dendrimers having vinylene chains (dendron). They started from tetrakis(phenylethynyl)-silane and constructed dendrimers up to G3 via repeated sequences of hydrosilylation with dichloromethylsilane and subsequent alkynylation with

TABLE 3 Photophysical Properties of Arylene-Silylene-Vinylene Polymers

Polymer structure	UV-Vis λ_{max} (nm)	Fluorescence λ_{max} (nm)	ε^{a} (dm^3 mol^{-1} cm^{-1})
	≈260	310	20 000
	≈260	—	20 100
	268	322	27 200
	302	354	27 900
	301	349	25 900
	268 302	350	42 900

[a] calculated per one mer.

lithium phenylacetylene, forming silylene-vinylene repeating structure [13]. The hydrosilylation process occurred in regio-selective manner in the presence of a heterogeneous Pt/C catalyst.

The authors also reported similar ethynylsilane dendrimers having 1,3,5-tris(dimethylsilyl)benzene [14] as a core, although it is not totally "π-conjugated" since it includes partially aliphatic chains (Fig. 1).

We have applied the silylative coupling SC reaction catalyzed by ruthenium complexes to synthesize novel starburst derivatives with the silicon-bridged π-conjugation structure of the expected potential optoelectronic properties. The silylative coupling reaction of 1,3,5-tris(dimethylvinylsilyl)benzene with p-substituted styrenes catalyzed by **II** leads to the respective products with high yield and selectivity.

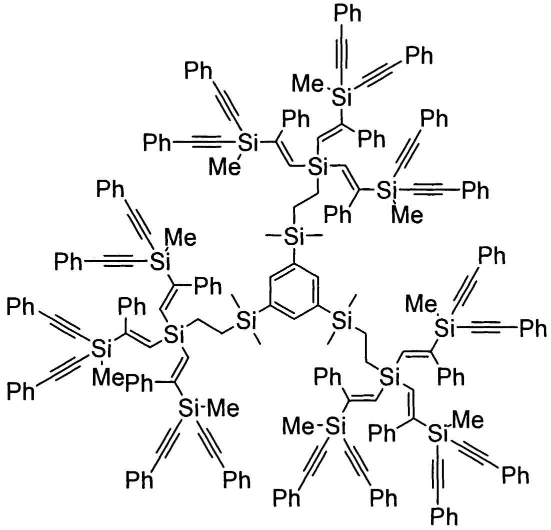
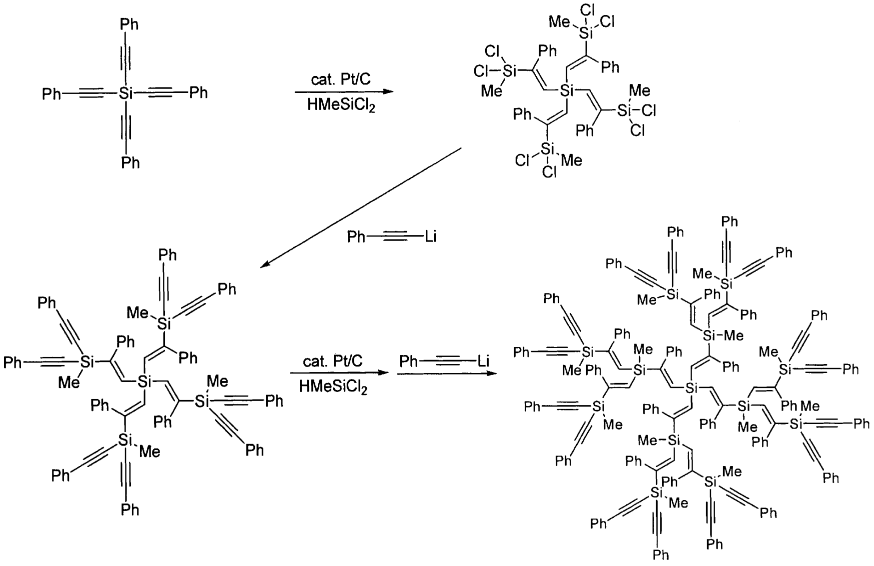
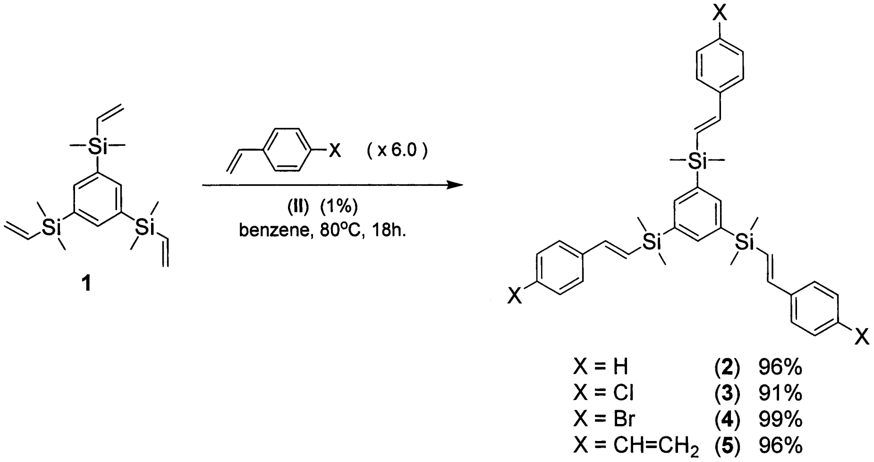


FIGURE 1 Dendrimer with terminal ethynylsilyl groups.



SCHEME 3



(4)

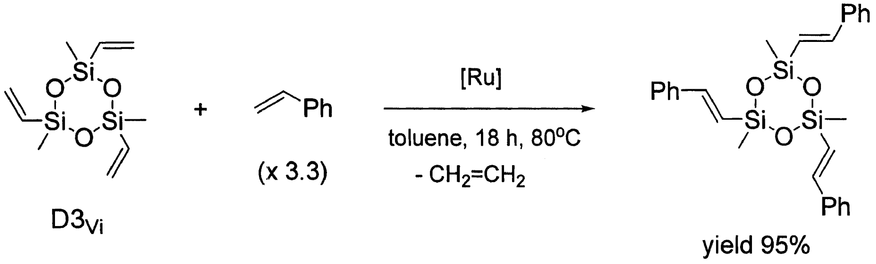
To synthesize the first generation of dendrimer G1 a direct silylation of **5** with **1** was applied using catalyst **II**, equation 3. However, the presence of a terminal vinylsilyl group caused silylative homocoupling of G-1 itself or of G1 with tris(vinylsilyl)-benzene-1 to give a polymeric compounds [9].

Therefore, finally G1 was synthesized via a preliminary formation of an isopropoxydimethylsilyl-terminated precursor (**6**) followed by vinylation with vinyl Grignard reagent and a catalytic amount of CuCN [9].

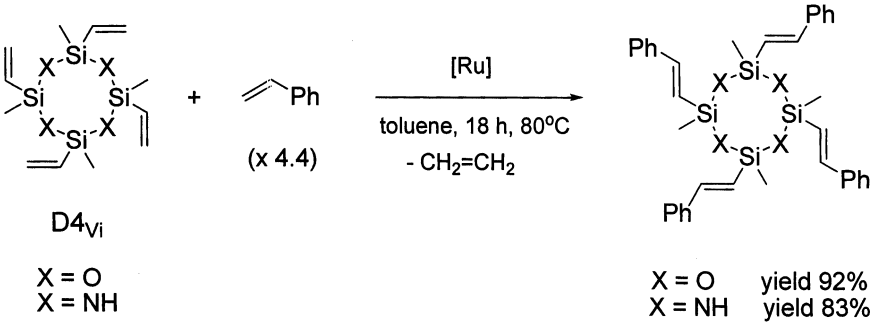
G1 and all the starburst compounds are characterized by longer absorption wavelenghts then the other (**1–5**) and by relatively strong blue-light fluorescence [9].

Synthesis of styryl-cyclosiloxane and -cyclosilazane

Cyclosiloxanes and cyclosilazanes have been used as the basic substrates for anionic and cationic ROM Polymerization (and co-polymerization) to yield respective organofunctional silicon polymers. Besides, vinylaryl-substituted cyclosiloxanes have also been applied recently as a core for the carbosilane dendrimers. Therefore, we have undertaken a study to apply silylative coupling (SC) reaction for synthesis of styryl derivatives of cyclosiloxanes and cyclosilazanes. $[Ru(H)(Cl)(CO)(PCy_3)_2]$ (**II**) was found to be an active and selective catalyst for the reactions of styrene with $D3_{Vi}$ and $D4_{Vi}$ and vinyltetramethylcyclo-tetrasilazane according to the following equations 4 and 5 [15]:



(4)



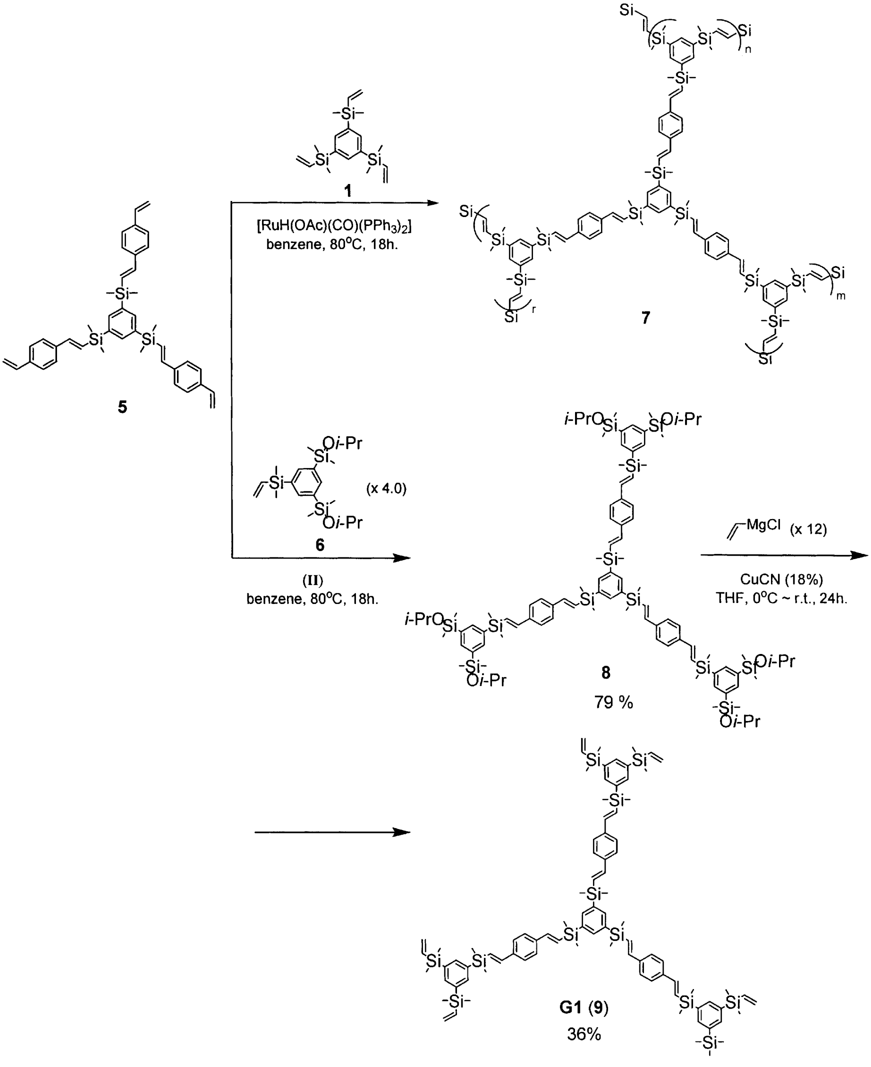
(5)

The reaction occurs stereo- chemo- and regioselectively in contrast to the hydrosilylation processes which always gives a mixture of regio-isomers.

The cross-metathesis of this system with Grubb's catalyst is ineffective presumably due to decomposition of ruthenium carbene species via β-silyl migration in a metathetical intermediate – metallocyclobutane, which occurs in the cross-metathesis of alkenes with vinylsilanes having at least one alkyl group at the silicon atom [16].

CONCLUSIONS

Silylative cross-coupling and polycondensation catalyzed by ruthenium complexes containing or generating Ru-H, e.g. $[Ru(H)(Cl)(CO)(PCy_3)_2]$ (**I**), $[RuCl_2(CO)_3]_2$ (**II**) appeared very attractive routes for stereo- and regio-selective synthesis of well-defined molecular and macromolecular compounds involving arylene-silylene-vinylene sequence. The final polymers and copolymers – poly(arylene-vinylene-silylene)s as well as the respective starburst derivatives with the silicon-bridged π-conjugated



SCHEME 4

structure constitute a group of materials of expected optoelectronic properties. The successful stereo- and regio-selective functionalization of cyclo(tri,tetra)siloxanes and cyclotetrasilazanes with styrene allows to prepare monomers for Ring Opening Polymerization involving silylene-vinylene-phenylene sequences.

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