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Highly stereoselective synthesis of novel *trans*-thiophenylene-silylene-vinylenearylene molecular and macromolecular compounds

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ABSTRACT

Novel stereoregular molecular compounds **8–13** containing thiophenylene-silylene-vinylene-phenylene units have been synthesised *via* highly effective silylative coupling of styrene and 1,4-divinylbenzene (**7**) with respective vinylsilylthiophenes (**3**, **4**) and bis(vinylsilyl)thiophenes (**5**, **6**) catalyzed by RuHClCO ($PCy_3)_2$. Respective copolymers (**14**, **15**) were produced *via* silylative copolycondensation of **5** and **6** with **7**. All products were isolated and characterised by NMR, MS, HRMS and two of them **10** and **11** by X-ray method. Catalytic study as well as stoichiometric reactions of Ru–H (**1**) with 2-(vinylsilyl)thiophene (**3**) and Ru–Si (**16**) with styrene confirmed the mechanism of the silylative coupling olefins with vinylsilicon compounds.

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1. Introduction

Polymeric materials consisting of sulphur-containing heterocycles have not been studied intensively as units in poly(p-phenylenevinylene) PPV. Poly(thienylene-vinylene) is reported to show only very weak red electroluminescence (EL) properties [1]. This type of polymer is really difficult to prepare by precursor routes. In view of their possible applications in electronics, optoelectronics and as non-linear optical materials [2], conjugated polymers have attracted a lot of attention recently. At present, their commercial applications include mainly production of charge dissipations films [3], light-emitting diodes (LED) [4] and electrochromic displays [5]. Conductive polymers are also used as volatile organic gas sensors [6]. Polythiophenes, which are one of the most important conjugated polymer families, have been investigated in terms of spectroscopic and photophysical behaviour by the so-called oligomer approach [7]. Additionally, the study of the properties of poly(thiophene)s appears to be of the great importance in this field [2b, 7-17].

The possibility of synthesis of varied functionalized conjugated oligomers and polymers based on thiophene residues, especially those carrying heteroatoms (phosphorus or silicon) in the side chain or main chain [15,18,19], has considerably increased in recent years. It is achievable to enhance the solubility and processability of the polymer using the chain flexibility owing to silicon atoms. Organosilicon polymers, dendrimers and hyperbranched polymers consisting of silylene-thiophene fragments and saturated carbon bridge $(-CH_2-CH_2-)$ between two silicon atoms have been synthesized *via* hydrosilylation process catalyzed by Pt catalysts, which gave polymeric materials with high polydispersity index (3.71–4.18) and low molecular weight. Moreover, the final product included the colloidal metal [20]. Wang studied the synthesis of unsaturated siliconthiophene derivatives of oligomers from (*p*-(dimethylsilyl)phenyl) acetylene *via* the above mentioned reaction. The products were mostly cross-linked polymers and did not dissolve in organic solvents [21].

The optional and unique as well as convenient and effective way to get this type of unsaturated organosilicon polymers is silylative coupling polycondensation (SCP) reaction of vinylsilanes in the presence of transition metal complexes (e.g. ruthenium and rhodium) containing or generating metal—hydrogen ([M]–H) and metal-silicon ([M]–Si) bonds. The silylative coupling reaction of monovinyl-silanes proceeds through cleavage of the =C–Si bond of the vinylsubstituted silicon compounds and the activation of the = C–H bond of the second vinylsilane molecules [22] (see Scheme 1). The mechanism of this reaction involving β -silyl elimination and insertion of a C=C double bond into the resulting [M]–Si bond has been proved by insertion of ethylene and vinylsilane into [M]–Si (where M = Ru, Rh, Ir, Co) bonds as well as by a series of elaborate mass spectroscopic studies with deuterated styrene and vinylsilanes [23].





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Scheme 1. General scheme of silvlative coupling (SC) reaction.

The evidence for the non-metallacarbene mechanism of monovinylsilane transformation has been reported [23, 26b], but it can be generalized for dimerization of divinyl-substituted silanes [24a, 24b, 25] siloxane [24a, 24b, 25a], silazanes [25b] and bis(vinylsilyl) alkanes [25c] leading subsequently to competitive linear oligomerization [24].

Moreover, the synthesis of homo- and copolymers containing phenylene-silylene-vinylene and copolymers consisting of phenylene-silylene-vinylene-phenylene-vinylene units with well-defined structures [26] has been successfully performed, Scheme 2.

In 2008 we reported the stereoselective synthesis of poly(silylene-thiophene)s and their basic photophysical properties [27].

Therefore, in this paper we would like to describe efficient selective procedures for synthesis of novel stereoregular thiophene (and bithiophene)-silylene-vinylene molecular compounds as well as suitable copolymers with the *trans*-silylene-vinylene-phenylene-silylene bridged structures *via* the respective reaction of bis(vinyldimethylsilyl)thiophene or bithiophene derivatives with 1,4-divinylbenzene.

2. Results and discussion

2.1. Synthesis of substrates

All substrate monomers: 2-(vinyldimethylsilyl)thiophene (**3**), 5-(vinyldimethylsilyl)-2,2'-bithiophene (**4**), 2,5-bis(vinyldimethylsilyl) thiophene (**5**) and 5,5'-bis(vinyldimethylsilyl)-2,2'-bithiophene (**6**) were obtained in 'one pot' by the well known Grignard's reaction of commercially available compounds. Treatment of mono- or dibromothiophene derivatives with magnesium in THF generated 'in situ' the so-called 'Grignard reagent', which in the presence of 10% excess of chlorodimethylvinylsilane at a suitable temperature (from 5 °C to 35 °C, which was controlled all the time), under an argon atmosphere afforded the desirable compounds with good yields (83–93%). All the above mentioned silyl-compounds (**3–6**) are air- and moisturestable, liquids (at room temperature) and were fully characterised by accessible methods.

2.2. Reactivity of vinylsilylthiophene derivatives in the presence of ruthenium-hydride complex

While the mixture of equimolar amounts of 2-(vinyldimethylsilyl) thiophene (**3**) or 5-(vinyldimethylsilyl)-2,2'-bithiophene (**4**) and styrene was treated in toluene with 16-electron ruthenium-hydride catalyst [RuHCl(CO)(PCy₃)₂] (**1**) (2–0.5 mol% in relation to vinyl group of vinylsilane), slow evolution of ethene was observed. Monitoring of the reaction progress *via* GC shows regular conversion of both substrates. Proton NMR analysis of the reaction mixture performed after 6 and 24 h of the reaction course, indicated nearly



Scheme 2. SCP mono- or bis(vinyldimethylsilyl)arenes in the presence of ruthenium complex.

complete conversion of substrates and selective formation of crosscoupling products (**8**, **9**), Scheme 3.

The results obtained are collected in Table 1.

A very similar reactivity was observed when vinyl derivatives **5** and **6** were used as reaction partners, see Scheme 4.

The coupling reactions were examined in the presence of the mononuclear, five-coordinate ruthenium (II) complex **1** checked in the previous system. In each case the reaction led to efficient and selective formation of *E*-isomer of **10** and **11**. The results obtained were collected in Table 2.

A 10% excess of styrene was used to achieve quantitatively or in high yield disubstituted bis(silyl)thiophenes. Very efficient and selective functionalisation was observed.

An analogous system of 1,4-divinylbenzene (**7**) with **3** or **4** in toluene was obtained using **1** as a catalyst, see Scheme 5.

The above mentioned reactions of **7** (DVB) with **3** and **4** performed under the same conditions as above (Tables 1 and 2) lead to not so high conversions of substrates and evolution of ethylene but with good stereo-selectivity. ¹H NMR investigation of the reaction mixtures after 48 h of the reactions course indicated formation of functionalized products **12** and **13**. The results obtained are collected in Tables 3 and 4.

All tables demonstrate good or very high yields of corresponding products obtained *via* silylative coupling reaction. The procedures applied for isolation of products from the reaction mixture are very simple and useful. Each molecular compound (**8–13**) was isolated (the crude product obtained was purified by column chromatography (silica gel/hexane), in practically quantitative yield (80–99%)), and fully characterised spectroscopically, which allowed to confirm expected structures.

2.3. X-ray study

The structures of **10** and **11** were confirmed by crystallographic method analysis. Molecular compounds **10** and **11** proved to be solid ones and gave crystals amenable to X-ray crystal structure determination. To the best of our knowledge, this is the first structural characterisation of thionyl-silyl-substituted aromatic compounds containing heteroaryl group.

In **10** the planes of the terminal phenyl rings are almost perpendicular to the central thiophene ring; the dihedral angles are $74.1(2)^{\circ}$ and $85.8(2)^{\circ}$. The double bond is in *trans* disposition, the appropriate torsion angles are Si6–C9–C10–C11 –176.4(5)° and Si18–C21–C22–C23 –175.3(4)°. The molecular dimensions are typical, see Fig. 1.

In **11**, the planes of central thiophene rings are inclined by 25.7 (2)°, and the terminal phenyl rings are also significantly twisted, by $54.06(8)^{\circ}$ and 76.4596° , which leads to the almost perpendicular disposition of the phenyl rings ($75.22(7)^{\circ}$). The double bonds are also in the *trans* disposition, the Si–C=C–C dihedral angles are 176.87(15) and $-178.74(16)^{\circ}$, see Fig. 2.

In both structures there are practically no specific, directional intermolecular interactions (one can list some weak $C-H\cdots$ S contacts), so the packing is probably determined by the van der Waals interactions and close packing requirements. The crystal data are collected in Table 5, please see supporting materials.



Scheme 3. SC of dimethylvinylsilylthiophene derivatives with styrene.

Table 1
Silvlative coupling of dimethylvinylsilvlthiophene derivatives with styrene.

Vinylsilane	Molar ratio [ViSi]: [Styrene]:[RuH]	Time (h)	Conversion of vinylsilane (%) ^a	Yield (%) ^b
Mo	1:1:0.015	3	>99	>99 (99) ^c
Mie	1:1:0.010	3	87	87
		6	95	95
Me	1:1:0.005	3	70	70
		6	88	88
		18	94	94
	1.1.0.020	3	85	85
	1.1.0.020	6	98	98 (95) ^c
	1:1:0.015	3	57	57
		6	94	94
Me //		18	99	99
∠ y Si	1:1:0.010	3	30	30
S´ S´ I		6	47	47
We		18	79	79
		24	86	86
	1:1:0.005	3	13	13
		6	36	36
		18	59	59
		24	73	73

Reaction conditions: T = 83-85 °C, toluene (1 M solution).

^a Conversion of silane was calculated from GC chromatogram (decane, 5% the total volume).

^b Yield was calculated from GC chromatogram (decane, 5% the total volume)

 $^{\rm c}$ Isolated yield; argon; selectivity of the reaction = 100% isomer trans-(¹H NMR calculation).

When DVB was used as a substrate, the coupling reaction required longer time (48 h). DVB is less reactive than styrene in SC reaction but could be very active in radical polymerization particularly in high concentration solution and temperature. Furthermore, vinylsilyl part at thiophene derivatives is definitely less reactive than at typical alkyl- or aryl- substituted silanes. Conceivably, this fact comes from a strongly drawn out heterocyclic fragment of the substrate.

2.4. Proposed of silylative coupling mechanism and stoichiometric studies

As we have reported earlier, ruthenium-hydride complexes effectively catalyse silylative coupling of olefins with vinylsilicon compounds (for review see ref. 22b). This reaction proceeds according to the non-metalacarbene mechanism involving insertion of vinylsilylthiophene into [Ru–H] bond ((\mathbf{a}) \rightarrow (\mathbf{b}) \rightarrow (\mathbf{c})) followed by evolution of ethylene (β -Si transfer) to get [Ru–Si] intermediate (\mathbf{d}). The insertion of styrene (also 1,4-divinylbenzene) into [Ru–Si] bond ((\mathbf{d}) \rightarrow (\mathbf{e}) \rightarrow (\mathbf{f})) leads to complex (\mathbf{f}). The final step of the product formation (β -H transfer) occurs *via* reductive elimination of product regenerating complex (\mathbf{a}), see Scheme 6.

In order to confirm this mechanism, we mixed a more stable complex [Ru–H] with triphenylphosphine {RuHCl(CO)(PPh₃)₃} with **3** at 100–110 $^{\circ}$ C for 22 h and new thionyl-silyl species Ru (SiMe₂C₄H₃S)Cl(CO)(PPh₃)₂ (**16**) was prepared according to Scheme 7.

The NMR spectroscopic analysis evidently showed the typical silyl-ruthenium catalysis structure. Afterwards, **16** was tested in equimolar reaction in the presence of excess of fresh distilled



Scheme 4. SC of bis(dimethylvinylsilyl)thiophene derivatives with styrene.

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	Silylative	coupling of	of bis(dime	thylvinylsil	yl)thiophenes	with styrene
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Vinylsilane	Molar ratio	Time	Conversion	Yield (%) ^b	
	[ViSi]:[Styrene]: [RuH]	(h)	of vinylsilane (%) ^a	A	B (10 v 11)
	1.2 1.0 015	3	97	20	77
Me // Me //	1.2.1.0.015	6	>99	_	>99 (92) ^c
Śi/ ``Śi	1:2.1:0.010	3	>99	20	80
		6		_	>99
ivie ivie	1:2.1:0.005	3	99	9	90
		6	>99	3	97
		12		_	99
		3		63	33
		6	06	48	52
Me // Me //	1:2.1:0.015	12	> 00	35	65
Śi-{{ }}-Śi-		18	>99	24	76
		24		1	99 (96) ^c
ivie ivie	1:2.1:0.010	3	91	51	40
		6	>99	46	53
		12		39	60
		18		32	68

Reaction conditions: T = 83-85 °C, toluene (1 M solution).

^a Conversion of silane was calculated from GC chromatogram (decane, 5% the total volume).

^b Yield was calculated from GC chromatogram (decane, 5% the total volume)

 $^{\rm c}$ Isolated yield; argon; selectivity of the reaction $>\!99\%$ isomer trans-(^1H NMR calculation).

styrene. The progress was controlled by GCMS and NMR methods. ¹H NMR examination confirmed the formation of the [Ru–H] complex – trace amount (signal – dt, at –5.82 ppm) providing a convenient test for insertion of the olefin into Ru–SiMe₂(C₄H₃S) bond and next β -H transfer with elimination of 2-silylthionylstyrene, according to Scheme 8.

Careful analysis of GCMS chromatogram and spectrum revealed the formation of **8** after 24 h and free triphenylphosphine as a result of decoordination from complex **16** (see Figs. 3 and 4 in the supporting material). Analysis of full MS(EI) spectrum gave us clear proof that the catalytic process occurs according to the silylative coupling reaction. Only one product shows a very high chemoselectivity of reaction.

2.5. Synthesis of polymeric materials

A preliminary study allowed us to optimise highly stereoselective synthesis of well-defined *trans*-cooligomers. Application of **1** as catalyst for silylative-coupling copolycondensation of **5** and **6** with **7** gave exclusively linear oligomers **14** and **15** containing *trans*-vinylene bond between silicon–carbon atoms with medium average molecular weight $\overline{M_w} = 4313-6065$ and low polydispersity index PDI = 1.31–1.41, see Scheme 9.

The new polymer products obtained were purified by precipitation two times from alcohol at room temperature.

3. Conclusion

Novel stereoregular *trans*-thiophenylene-silylene-vinylene-arylene molecular derivatives have been easily synthesized *via*



Scheme 5. SC of dimethylvinylsilylthiophene derivatives with 7.

 Table 3
 Silylative coupling of 2-dimethylvinylsilylthiophenes with 7.

Molar ratio [ViSi]:[DVB]:[RuH]	Sol. con. (M)/temperature (°C)	Time (h)	Conversion (%) ^a		Selectivity (%) ^b	
			ViSi	DVB	A	B (12)
2:1:0.030	1 M/100 °C	3	8	55	8	_
	0.5 M/100 °C	3	30	44	30	_
		6	42	60	45	20
		24	83	>99	15	75
		48	99		1	99
2:1:0.020	1 M/100 °C	3	21	42	21	_
	0.5/100 °C	24	98	>99	2	87
		3	24	26	24	_
		24	79	>99	13	72
		48	99		2	98

^a Conversions of substrates were calculated from GC chromatogram (decane, 5% the total volume).

^b Selectivity of the reaction >99% isomer *trans*-(GC–MS and ¹H NMR calculations); argon.

silylative coupling of 2-vinyldimethylsilylthiophene (**3**) and 5vinyldimethylsilyl-2,2'-bithiophene (**4**) with styrene and 1,4divinylbenzene (**7**) to yield respective new products **8–13**. The structures of **10** and **11** were solved by X-ray crystal structure method. The compounds 2,5-bis(vinyldimethylsilyl)thiophene (**5**) and 5,5'-bis(vinyldimethylsilyl)-2,2'-bithiophene (**6**) react effectively with styrene to yield respective compounds **12** and **13**. Compounds **5** and **6** undergo silylative coupling copolycondensation with **7** (DVB) to get exclusively linear oligomers **14** and **15** of low molecular weight and low polydispersity index 1.31–1.41. Catalytic results and stoichiometric reactions of ruthenium-hydride (**2**) with **3** and ruthenium-silyl (**16**) complex with styrene confirm a general catalytic scheme of the silylative coupling of olefins with vinylsilanes.

4. Experimental

4.1. Instruments

¹H NMR (300 MHz), ¹³C NMR (75 MHz) and ²⁹Si NMR (60 MHz) and DEPT spectra were recorded on a Varian XL 300 MHz spectrometer in CDCl₃ solution. Chemical shifts are reported in *d* (ppm) with reference to the residue solvent (CD₃Cl) peak for ¹H, ¹³C and to TMS for ²⁹Si. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GCMS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m)) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. Gel permeation

Table 4

Silylative coupling of 5-dimethylvinylsilylbithiophene with 7.

chromatography (GPC) analysis was performed using an Agilent HPLC system equipped with UV absorbance detector and RI detector (analysis conditions: mobile phase – CH₂Cl₂; flow rate – 0.80 mL/min; temperature – 20 °C; injection volume – 17 μ L). The number-average molecular weight ($\overline{M_n}$), weight-average molecular weight ($\overline{M_w}$) and polydispersity index (PDI) were determined by polystyrene standard calibration curve. Thin-layer chromatography (TLC) was made on plates coated with 250 μ m thick silica gel (Aldrich and Merck), and column chromatography was conducted with silica gel 60 (70–230 mesh, Fluka).

4.2. Materials

The chemicals were obtained from the following sources: toluene, diethyl ether, THF, pentane and hexane, were purchased from Fluka, CDCl₃, from Dr Glaser A.G. Basel, styrene, 2,5-dibromothiophene, 5,5'-dibromo-2,2'-bithiophene from Avocado, 2bromothiophene, 5-bromo-2,2'-bithiophene, magnesium sulphate, calcium hydride (CaH₂), sodium hydride (NaH), 1,2-dibromoethane, ethanol, methanol, from Aldrich and chlorodimethylvinylsilane from Gelest. Tetrahydrofuran (THF), toluene and diethyl ether were distilled from sodium and hexane from calcium hydride under argon. The above mentioned solvents were stored over molecular sieves type 4 Å. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the syntheses of monomers, polymeric materials and catalytic tests were carried out under an inert argon atmosphere. The ruthenium complexes $RuHCl(CO)(PCv_3)_2(1)$ and RuHCl(CO)(PPh₃)₃(**2**) were prepared according to the literature procedure [28,29].

Molar Ratio [ViSi]:[DVB]:[RuH]	uH] Sol. con. (M)/temperature (°C) Time (h) Conversion (%) ^a		Selectivity (%) ^b			
			ViSi	DVB	A	B (13)
2:1:0.040	0.5 M/100 °C	3	3	5	3	_
		6	15	16	15	_
		24	44	49	44	trace
		48	80	>99	35	62
2:1:0.030	0.5 M/100 °C	3	7	8	7	_
		6	14	17	14	_
		24	32	60	53	5
		48	49	87	43	27
2:1:0.020	0.5 M/100 °C	3	1	6	_	_
		6	17	21	17	_
		24	30	66	54	3
		48	39	70	62	8

^a Conversions of substrates were calculated from GC chromatogram (decane, 5% the total volume).

^b Selectivity of the reaction >99% isomer *trans*-(GC–MS and ¹H NMR calculations); argon.



Fig. 1. A perspective view of **10** with labelling scheme. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

4.3. Syntheses of organosilicon and organic compounds

2-(*Vinyldimethylsilyl*)*thiophene* (**3**): In a two-neck flask equipped with magnetic stirrer, under Argon atmosphere, a suspension of Mg (0.6 g, 24.7 mmol, whose surface was activated by the use of 1,2-dibromoethane, 0.2 mL) and chlorodimethylvinylsilane (3.1 mL, 22.7 mmol) in 6 mL of THF was prepared. A solution of 2-bromothiophene (3.37 g, 20.6 mmol) in 14 mL of THF was added dropwise to the suspension and the reaction mixture was refluxed. Progress of the reaction was controlled by GC analysis. Then, the mixture was cooled to room temperature, excess of organic solvent was evaporated and the product was isolated by extraction with hexane/water solvents. The organic layer was separated, dried under magnesium sulphate and filtered. Then, the solvent was evaporated, and the residue was separated with silica gel column (hexane, $R_f = 0.45$) to afford (**3**) as a colourless liquid. Yield: 2.9 g (84%).

¹H NMR (CDCl₃, δ (ppm)): 0.43 (s, 6H, -CH₃), 5.81 (dd, 1H, *J_{HH}* = 3.8, 20.0 Hz, -HC=CH₂), 6.08 (dd, 1H, *J_{HH}* = 3.7, 14.7 Hz, -HC=CH₂), 6.32 (dd, 1H, *J_{HH}* = 14.6, 20.4 Hz, -HC=CH₂), 7.22 (dd, 1H, *J_{HH}* = 3.3, 4.7 Hz, -SCH=CH-CH=C- from -C₄H₃S), 7.30 (d, 1H, *J_{HH}* = 3.3 Hz, -SCH=CH-CH=C- from -C₄H₃S), 7.64 (d, 1H, *J_{HH}* = 4.7 Hz, -SCH=CH-CH=C- from -C₄H₃S), 7.64 (d, 1H, *J_{HH}* = 4.7 Hz, -SCH=CH-CH=C- from -C₄H₃S), 130.8 (-CH=CH-S- from -C₄H₃S), 130.8 (-CH=CH-S- from -C₄H₃S), 133.0 (-HC=CH₂), 134.6 (-CH=C-S from -C₄H₃S), 137.5 (-HC=CH₂), 137.7 (Si-C<). ²⁹Si NMR (CDCl₃, δ (ppm)): -11,43. MS (EI): *m/z* (rel. intensity – %): 168 (40), 153 (100), 141 (27), 138 (3), 127 (19), 115 (3), 101 (8), 85 (12). HRMS (*m/z*) Calcd. for C₈H₁₂SSi: 168.04290, found 168.04278.

5-(*Vinyldimethylsilyl*)-2,2'-thiophene (**4**): In a two-neck flask equipped with magnetic stirrer, under Argon atmosphere, a suspension of Mg (0.14 g, 5.7 mmol, whose surface was activated by 1,2-dibromoethane, 0.2 mL) and chlorodimethylvinylsilane (0.67 mL, 4.9 mmol) in 6 mL of THF was prepared. A solution of



Fig. 2. A perspective view of 11 with labelling scheme. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.



Scheme 6. Proposed SC of mechanism of vinylsilylthiophene derivatives with styrene.

5-bromo-2,2'-bithiophene (1 g, 4.1 mmol) in 2.5 mL of THF was added dropwise to the suspension and the reaction mixture was refluxed. The reaction progress was controlled by GC analysis. Then, the mixture was cooled to room temperature, excess of organic solvent was evaporated and the product was isolated by extraction with hexane/water solvents. The organic layer was separated, dried under magnesium sulphate and filtered. Then, the solvent was evaporated, and the residue was separated with silica gel column (hexane, $R_f = 0.33$) to afford (**4**) as a green liquid. Yield: 0.87 g (83%).

¹H NMR (CDCl₃, δ (ppm)): 0.42 (s, 6H, $-CH_3$), 5.83 (dd, 1H, $J_{HH} = 3.8$, 20.0 Hz, $-HC=CH_2$), 6.09 (dd, 1H, $J_{HH} = 3.8$, 14.6 Hz, -HC=CH₂), 6.34 (dd, 1H, J_{HH} = 14.6, 20.0 Hz, -HC=CH₂), 7.02 (dd, 1H, J_{HH} = 3.7, 5.0 Hz, -SCH=CH-CH=C- from -C₄H₃S), 7.16 (d, 1H, *J*_{HH} = 3.3 Hz, -S-C=CH-CH=C- from -C₄H₂S-), 7.20 (d, 1H, J_{HH} = 3.7 Hz, -SCH=CH-CH=C- from -C₄H₃S), 7.21 (d, 1H, $J_{HH} = 5.0$ Hz, -SCH=CH-CH=C- from $-C_4H_3S$), 7.24 (d, 1H, $J_{HH} = 3.6 \text{ Hz}, -S-C=CH-CH=C- \text{ from } -C_4H_2S-$). ¹³C NMR (CDCl₃, δ (ppm)): -1.7 (-CH₃), 123.8 (-S-C=CH- from -C₄H₃S), 124.4 $(-S-C=CH-from -C_4H_3S)$, 125.0 (-S-C=CH-CH=C-Si)from -C₄H₂S-), 127.7 (=CH- from -C₄H₃S), 133.2 (-HC=CH₂), 135.4 (-S-C=CH-CH=C-Si from -C₄H₂S-), 137.1 (-S-C= CH-CH=C-Si- from -C4H2S-), 137.2 (-S-C=CH-CH=C-Sifrom -C₄H₂S-), 137.3 (-HC=CH₂), 142.8 (Si-C<). ²⁹Si NMR (CDCl₃, δ (ppm)): –11.49. MS (EI): m/z (rel. intensity – %): 250^{•+} (80), 235 (100), 223 (15), 209 (38), 183 (10), 160 (14), 133 (12), 115 (15), 89 (17), 75 (18). HRMS (*m*/*z*) Calcd. for C₁₂H₁₄S₂Si: 250.03062, found 250.03025.

2,5-*bis*(*Vinyldimethylsilyl*)*thiophene* (**5**): A solution of 2,5dibromothiophene (6.45 g, 26.7 mmol) in 15 mL of THF was added slowly dropwise to a suspension of Mg (1.62 g, 66.75 mmol, whose surface was activated by 1,2-dibromoethane, 0.3 mL) and chlorodimethylvinylsilane (8.25 mL, 60.15 mmol) in 15 mL of THF (the mixture was slightly warmed, 20–30 °C). After the addition was completed, the reaction mixture was refluxed. The reaction progress was controlled by GC analysis. Then the mixture was cooled to



Scheme 7. Stoichiometric reaction of [Ru-H] (2) with 3.



Scheme 8. Stoichiometric coupling reaction of [Ru–Si] (16) with styrene.

room temperature, excess of organic solvent was evaporated and the product was extracted with hexane/water solvents. The organic layer was separated, dried under magnesium sulphate and filtered. Then the solvent was evaporated, and the residue was distilled under reduced pressure to afford the crude product (**5**) as a colourless liquid (collected fraction 66–70 °C/0.6 mmHg). Yield: 6.26 g (93%).

¹H NMR (CDCl₃, δ (ppm)): 0.41 (s, 12H, $-CH_3$), 5.80 (dd, 2H, $J_{HH} = 3.9$, 20.1 Hz, $-HC=CH_2$), 6.06 (dd, 2H, $J_{HH} = 3.9$, 14.7 Hz, $-HC=CH_2$), 6.31 (dd, 2H, $J_{HH} = 19.5$, 20.4 Hz, $-HC=CH_2$), 7.35 (s, 2H, =CH- from $-C_4H_2S-$). ¹³C NMR (CDCl₃, δ (ppm)): -1.45 ($-CH_3$), 132.90 ($-HC=CH_2$), 135.72 (=CH- from $-C_4H_2S-$), 137.50 ($-HC=CH_2$), 147.97 (Si-C<, from $-C_4H_2S-$). ²⁹Si NMR (CDCl₃, δ (ppm)): -11.82. MS (EI): m/z (rel. intensity - %): 252^{•+} (24), 237 (100), 212 (50), 167 (16), 148 (24), 133 (9), 85 (73), 75 (18). HRMS (m/z) Calcd. for $C_{12}H_{20}Si_2$: 252,08242, found 252.08239.

5,5'-bis(Vinyldimethylsilyl)-2,2'-bithiophene (**6**): A solution of 5,5'-dibromo-2,2'-bithiophene (5.83 g, 7.5 mmol) in 25 mL of THF was added slowly dropwise to a suspension of Mg (0.45 g, 18.45 mmol, whose surface was activated by 1,2-dibromoethane, 0.15 mL) and chlorodimethylvinylsilane (2.33 mL, 16.95 mmol) in 8 mL of THF (the mixture was slightly warmed, 20-30 °C). After the

 $(C_i-C_i, -C_8H_4S_2-)$, 137.16 $(C_i, 5-C_4H_2S-)$, 142.71 $(-HC=CH_2)$. ²⁹Si NMR (CDCl₃, δ (ppm)): -11.32. MS (EI): *m/z* (rel. intensity – %): 334^{•+} (100), 319 (73), 307(17), 293 (22), 275 (5), 261 (10), 244 (25), 229 (16), 207 (8), 154 (6), 127 (9), 115 (14), 101 (10), 85 (23), 73 (14), 59 (26). HRMS (*m/z*) Calcd. for C₁₆H₂₂S₂Si₂: 334.07015, found 334.07012.

1,4-*Divinylbenzene* (**DVB**) (**7**): The synthesis of olefin consists of two steps. We completed the two-stage synthesis of 1,4-divinylbenzene (**7**) using classical Wittig's reaction (yield 85%, pure >98.5% GC). In our recent studies we observed that this reaction occurred even more efficiently when conducted in toluene (1 M and 0.5 M solution) with lower catalyst loading (1 mol%), however, it required longer time 48 h.

The first step, synthesis of methylenetriphenylphosphane:

$$(Ph_3PCH_3)J + t-BuOK \xrightarrow{Et_2O} (Ph_3P=CH_2) + KJ + t-BuOH$$

Reaction mixture of methyltriphenylphosphane iodide (Ph₃PCH₃) I (15 g, 37.1 mmol) and potassium butylate (4.37 g, 38.9 mmol) in 140 mL of diethyl ether was stirred at room temperature for 2 h and then the mixture was heated at 35 °C. After 12 h the reaction mixture was cooled at room temperature and filtered with cannula. The organic solvent was evaporated to afford methylenetriphenyl-phosphane as yellow crystals (10.19 g, yield: 99%).

The second step, synthesis of 1,4-divinylbenzene:

2.1 (Ph₃P=CH₂) +
$$H \rightarrow O = H \rightarrow O =$$

addition was completed, the reaction mixture was heated at 40 °C. Progress of the reaction was controlled by GC analysis. Then the mixture was cooled to room temperature, excess of organic solvent was evaporated and the product was extracted with hexane/water solvents. The organic layer was separated, dried under magnesium sulphate and filtered. Then the solvent was evaporated, and the residue was separated by silica gel chromatography, eluting with *n*-hexane ($R_{\rm f} = 0.46$) (2.015 g, yield 90%) to afford the crude product (**6**) as a greenish liquid.

¹H NMR (CDCl₃, δ (ppm)): 0.40 (s, 12H, $-CH_3$), 5.81 (dd, 2H, *J*_{HH} = 3.9, 20.4 Hz, $-HC=CH_2$), 6.07 (dd, 2H, *J*_{HH} = 3.9, 15.0 Hz, $-HC=CH_2$), 6.29 (dd, 2H, *J*_{HH} = 14.7, 20.1 Hz, $-HC=CH_2$), 7.17 (d, 2H, *J*_{HH} = 3.9 Hz, $3-C_4H_2S-$), 7.28 (d, 2H, *J*_{HH} = 4.2 Hz, 4- C_4H_2S-). ¹³C NMR (CDCl₃, δ (ppm)): -1.72 ($-CH_3$), 125.08 (=CH-, $3-C_4H_2S-$), 133.22 ($-HC=CH_2$), 135.42 (=CH-, $4-C_4H_2S-$), 137.43



Scheme 9. SCCP of bis(dimethylvinylsilyl)thiophenes with 7.

Terephthalic aldehyde (2.22 g, 16.5 mmol) was added slowly to a suspension of methylenetriphenylphosphane (10.19 g, 36.7 mmol) in 100 mL diethyl ether at room temperature. The mixture colour changed from yellow to green-blue-violet-bordeaux (deep-red). After the addition was completed, the reaction mixture was heated at 35 °C for 2 h. Then, the synthetic air (20 mL) was injected into the reaction mixture by syringe and cooled to 10 °C, the mixture was filtered with cannula, concentrated to 40 mL and filtered again. The organic solvent was evaporated and the residue was distilled trapto-trap to afford the crude product (**7**) as a white solid ("flowing" at 30 °C) (1.83 g, yield 85%, pure >98.5% GC).

¹H NMR (C₆D₆, δ (ppm)): 5.25 (d, 2H, *J*_{HH} = 9 Hz, -CH=CH₂), 5.68 (d, 2H, *J*_{HH} = 17.4 Hz, -CH=CH₂), 6.57 (dd, 2H, *J*_{HH} = 11.1, 18.0 Hz, -CH=CH₂), 7.19 (s, 4H, -C₆H₄-). ¹³C NMR (C₆D₆, δ (ppm)): 114.12 (-CH=CH₂), 127.25 (-C₆H₄-), 137.36 (-CH=CH₂), 137.96 (>C-CH=CH₂). MS (EI): *m/z* (rel. intensity - %): 130 (M^{+•}) (100), 115 (39), 103 (10), 89 (5), 77 (12), 63 (15), 51 (20). HRMS (*m/z*) Calcd. for C₁₂H₂₀SSi₂: 130.07825, found 130.07838.

4.4. A typical procedure for catalytic examinations

The oven dried 5 mL glass ampoule-reactor equipped with a magnetic stirring bar was charged under argon with toluene (amount depend of total concentration -1 M, 0.5 M), vinylsilane (0.595 mmol), decane (5% of total volume of reaction mixture – internal standard) olefin (styrene or 1,4-divinylbenzene (DVB), the amount depended on the [olefin]:[ViSi] ratio = 1:1 for styrene and

1:2.1 for DVB) and ruthenium-hydride complex RuHCl(CO)(PCy₃)₂ (**1**) (2 mol%, 1.5 mol%, 1 mol%, 0.5 mol%). The system was heated in an oil bath at 80–100 °C for 3–48 h. The reaction progress was monitored by gas chromatography (GC), mass spectroscopic analysis (MS) and ¹H NMR (NMR spectra were measured at room temperature in CDCl₃ solution).

4.5. Isolation procedure of molecular compounds

All molecular compounds were isolated from the best catalytic tests mixtures. After the reaction was completed, solvent was evaporated. The final solution was separated with silica gel column (hexane, $R_{\rm f} = 0.30-0.55$).

4.5.1. Analytical data of molecular compounds

{(E)-1-Phenyl-2-(dimethyl-2-thienylsilyl)}ethene (8): ¹H NMR (CDCl₃, δ (ppm)): 0.51 (s, 6H, -CH₃), 6.60 (d, 1H, $J_{HH} = 18.9$ Hz, Si-CH=CH-C<), 7.00 (d, 1H, J_{HH} = 19.2 Hz, Si-CH=CH-C<), 7.23 (dd, 1H, $J_{HH} = 3.3$, 4.7 Hz, S-CH=CH-CH=C, from -C₄H₃S), 7.30–7.38 (m, 3H, 3,4-C₆H₅), 7.34 (d, 1H, $J_{HH} = 3.3$ Hz, S–CH= CH-CH=C- from $-C_4H_3S$), 7.47 (d, 2H, $J_{HH} = 8.2$ Hz, 2- C_6H_5), 7.60 $(d, 1H, I_{HH} = 4.7 \text{ Hz}, -S-CH=CH-CH=C- \text{ from } -C_4H_3S).$ ¹³C NMR $(CDCl_3, \delta(ppm)): -1.2(-CH_3), 126.5(3-C_6H_5), 126.5(Si-HC=CH-),$ $128.1 (=CH-S \text{ from } -C_4H_3S), 128.2 (4-C_6H_5), 128.4 (2-C_6H_5), 130.8$ $(-CH=CH-S- \text{ from } -C_4H_3S)$, 134.7 $(-CH=C-S \text{ from } -C_4H_3S)$, 145.4 (Si–HC=CH–), 137.9 (C_i from $-C_6H_5$), 137.9 (Si–C<). ²⁹Si NMR (CDCl₃, δ (ppm)) = -10.78. MS(EI) m/z (rel. intensity - %): 244 $(M^{+\bullet})$ (60), 229 - CH₃ (59), 195 (16), 154 - styryl (24), 145 - CH₃ and -C₄H₃S (100), 127 MeSiC₄H₃S (18), 101 (12), 91 (10), 75 (18). HRMS (m/z) Calcd. for C₁₂H₁₄S₂Si: 244.07420, found 244.07412. White powder/solid, yield 99%.



{(E)-1-Phenyl-2-(dimethyl-5-(2,2'-bithiophene)silyl)}ethene (9): ¹H NMR (CDCl₃, δ (ppm)): 0.51 (s, 6H, -CH₃), 6.60 (d, 1H, J_{HH} = 19.1 Hz, Si-CH=CH-C<), 7.00 (d, 1H, J_{HH} = 19.1 Hz, Si-CH=CH-C<), 7.02 (dd, 1H, J_{HH} = 3.6, 5.0 Hz, S-CH=CH-CH=C, from -C₄H₃S), 7.20 (d, 1H, J_{HH} = 3.3 Hz, S-C=CH-CH=C, from -C₄H₂S-), 7.20 (d, 1H, J_{HH} = 3.6 Hz, S-CH=CH-CH=C, from -C₄H₃S), 7.22 (d, 1H, $J_{HH} = 5.0$ Hz, S–CH=CH–CH=C, from –C₄H₃S), 7.28 (d, 1H, $J_{HH} = 3.0$ Hz, S–C=CH–CH=C, from –C₄H₂S–), 7.30–7.38 (m, 3H, 3,4-C₆H₅), 7.5 (d, 2H, J_{HH} = 8.6 Hz, 2-C₆H₅). ¹³C NMR (CDCl₃, δ (ppm)): $-1.3(-CH_3)$, 123.8(S-CH=CH-CH=C from $-C_4H_3S$), 124.4(S-CH= CH-CH=C from -C₄H₃S), 125.0 (=CH-, 3-C₄H₂S-), 126.1 (3-C₆H₅), 126.5 (Si-HC=CH-C<), 127.7 (S-CH=CH-CH=C from -C₄H₃S), 128.3 (4-C₆H₅), 128.5 (2-C₆H₅), 135.5 (=CH-, 4-C₄H₂S-), 137.2 (C_i from -C₄H₃S), 137.6 (C_i, >C-C< from -C₄H₂S-), 137.8 (C_i from -C₆H₅), 142.9 (C_i, >C-Si from -C₄H₂S-) 145.6 (Si-HC= CH–CH<). ²⁹Si NMR (CDCl₃, δ (ppm)): –10.84. HRMS (*m*/*z*) Calcd. for C₁₂H₁₄S₂Si: 326.06192, found 326.06175. White powder, yield 95%.



2,5-*bis*{((*E*)-2-*Phenylethenyldimethylsily*]}*thiophene* (**10**): ¹H NMR (CDCl₃, δ (ppm)): 0.51 (s, 12H, *CH*₃), 6.61 (d, 2H, *J_{HH}* = 18.6 Hz, Si–CH= *CH*–), 7.01 (d, 2H, *J_{HH}* = 18.6 Hz, Si–*HC*=CH–), 7.28–7.38 (m, 6H, 3, 4-C₆H₅), 7.43 (=*CH*– z C₄H₂S), 7.48 (d, 4H, *J_{HH}* = 7.8 Hz, 2-C₆H₅). ¹³C NMR (CDCl₃, δ (ppm)): -1.25 (–*C*H₃), 126.48 (3-C₆H₅), 128.16 (4-C₆H₅), 128.41 (2-C₆H₅), 135.82 (Si–HC=CH–), 137.87 (*C_i* from *C*₆H₅), 144.26 (*C_i* from C₄H₂S), 145.25 (Si–HC=CH–). ²⁹Si NMR (CDCl₃, δ (ppm)): -11.43. MS (EI): *m/z* (rel. intensity – %): 404 (M^{+•}), 389, 315, 301, 286, 219, 195, 161, 145, 105, 73. HRMS (*m/z*) Calcd. for C₂₄H₂₈SSi₂: 404.14502, found 404.14499. White powder, yield 92%.



5,5'-*b*is{((*E*)-2-*P*henylethenyldimethylsilyl)}-2,2'-*b*ithiophene (**11**): ¹H NMR (CDCl₃, δ (ppm)): 0.51 (s, 12H, -CH₃), 6.59 (d, 2H, *J*_{HH} = 19.2 Hz, Si-HC=CH-), 7.01 (d, 2H, *J*_{HH} = 19.2 Hz, Si-HC=CH-), 7.20 (d, 2H, *J*_{HH} = 3.9 Hz, 3-C₄H₂S-), 7.28 (d, 2H, *J*_{HH} = 3.2 Hz, 4-C₄H₂S-), 7.31-7.38 (m, 6H, 3,4-C₆H₅), 7.48 (d, 4H, *J*_{HH} = 7.8 Hz, 2-C₆H₅). ¹³C NMR (CDCl₃, δ (ppm)): -1.30 (-CH₃), 125.13 (=CH-, 3-C₄H₂S-), 126.11 (3-C₆H₅), 126.50 (Si-HC=CH-), 128.24 (4-C₆H₅), 128.42 (2-C₆H₅), 135.51 (=CH-, 4-C₄H₂S-), 137.68 (*C_i*-*C_i*, from -C₈H₄S₂-), 137.80 (*C_i* from -C₆H₅), 142.78 (*C_i* from 5-C₄H₂S-), 145.59 (Si-HC=CH-). ²⁹Si NMR (CDCl₃, δ (ppm)): -10.67. MS (EI): *m/z* (rel. intensity - %): 487 (M^{+•}), 472, 457, 397, 382, 370, 327, 307, 282, 238, 207, 162, 147, 137, 115, 105, 73. HRMS (*m/z*) Calcd. for C₂₈H₃₀S₂Si₂: 486.13275, found 486.13268. White powder, yield 96%.



1,4-*bis*{((*E*)-2-*Ethenyldimethyl*-2-*thienylsilyl*)}*benzene* (**12**): ¹H NMR (CDCl₃, δ (ppm)): 0.48 (s, 12H, –CH₃), 6.58 (d, 2H, *J_{HH}* = 18.9 Hz, Si–CH=CH–C<), 6.95 (d, 2H, *J_{HH}* = 19.2 Hz, Si–CH=CH–C<), 7.22 (dd, 2H, *J_{HH}* = 3.3, 4.7 Hz, S–CH=CH–CH=C), 7.33 (d, 2H, *J_{HH}* = 3.3 Hz, S–CH=CH–CH=C), 7.42 (s, 4H, –C₆H₄–), 7.64 (d, 2H, *J_{HH}* = 4.7 Hz, S–CH=CH–CH=C). ¹³C NMR (CDCl₃, δ (ppm)): –1.2 (–CH₃), 126.8 (Si–CH=CH–C<), 128.1 (S–CH=from –C₄H₃S), 128.7 (=CH–from –C₆H₄–), 130.9 (S–CH=CH–CH=C from –C₄H₃S), 134.7 (S–CH=CH–CH=C from –C₄H₃S), 137.8 (*C_i* from –C₄H₃S), 140.2 (*C_i* from –C₆H₄–), 144.9 (Si–CH=CH<). ²⁹Si NMR (CDCl₃, δ (ppm)): –10.78. HRMS (*m*/*z*) Calcd. for C₁₂H₁₄S₂Si: 410.10145, found 410.10126. White powder, yield 95%.



1,4-bis{((E)-2-Ethenyldimethyl-5-(2,2'-bithiophene)silyl)}benzene (**13**): ¹H NMR (CDCl₃, δ (ppm)): 0.51 (s, 12H, $-CH_3$), 6.57 (d, 2H, *J*_{HH} = 18.9 Hz, Si–CH=CH–C<), 7.00 (d, 2H, *J*_{HH} = 19.1 Hz, Si–CH= CH–C<), 7.03 (dd, 2H, J_{HH} = 3.6, 5.0 Hz, Si–C=CH–CH=C–, from C₄H₂S), 7.10 (d, 2H, J_{HH} = 3.0 Hz, -C=CH-CH=C-, from C₄H₃S), 7.21 (d, 2H, J_{HH} = 3.6 Hz, S-CH=CH-CH=C, from C₄H₃S), 7.32 (d, 2H, $J_{HH} = 5.0$ Hz, C-CH=CH-CH=C, from C₄H₃S), 7.62 (s, 4H, from $-C_6H_4-$), 7.64 (d, 2H, $J_{HH}=$ 4.7 Hz, C-CH=CH=C-, from C_4H_2S). ¹³C NMR (CDCl₃, δ (ppm)): -1.29 (-CH₃), 123.7 (=CH- from ndash; C_4H_3S), 124.6 (=CH- from $-C_4H_3S$), 126.8 (Si-HC=CH-C<), $125.3 (=CH- \text{ from } -C_4H_3S), 128.7 (=CH- \text{ from } -C_6H_4-), 135.7 (=$ CH-, 4-C₄H₂S-), 136.9 (=CH-, 4-C₄H₂S-), 136.7 (C_i from $-C_4$ H₃S), 137.6 (C_i , >C-C< from -C₄H₂S-), 140.2 (C_i from -C₆H₄-), 142.7 $(C_i, >C-Si \text{ from } -C_4H_2S-), 145.2 (Si-HC=CH-CH<).$ ²⁹Si NMR (CDCl₃) $\delta = -10.85$. HRMS (*m*/*z*) Calcd. for C₁₂H₁₄S₂Si: 486.13275, found 486.13268. White powder, yield 80%.



4.6. A general procedure for silylative coupling (SC) copolycondensation

The syntheses were performed under argon using (1) as a catalyst. Reagents and solvent were dried and deoxygenated. A mixture of monomer **4** or **5** (1.5 mmol), DVB (1.5 mmol), complex **1** (0.015–0.075 mmol) and toluene (1.5–6 mL, 1–0.25 M) was placed in a 5–10 mL glass mini-reactor equipped with a magnetic stirring bar and condenser connected to a bubbler. The reaction mixture was stirred and heated at 90–100 °C under an argon flow for 72 h. After the reaction was completed, the excess of solvent was evaporated under vacuum. The resulting polymer was dissolved in THF, isolated and purified by repeated precipitation from methanol. The final polymeric material was filtered off and dried under vacuum for 10–15 min. The isolated yields were as follows: for **14** – 90% and for **15** – 63% (depending on the combination of starting bis(silyl) thiophene derivative monomer).

4.6.1. Analytical data of copolymers

Poly[dimethylsilylene-2,5-thienylene-dimethylsilylene-(E)-vinylene-1,4-phenylene-(E)-vinylene] (14): ¹H NMR (CDCl₃, δ (ppm)): 0.40 (s, 12H, -CH₃ from terminal part), 0.49 (s, 12H, -CH₃ from copolymer), 5.80 (dd, 2H, J_{HH} = 3.9, 20.1 Hz, Si-HC=CH₂, from terminal group), 6.05 (dd, 2H, J_{HH} = 3.9, 14.7 Hz, Si-HC=CH₂, from terminal group), 6.27 (dd, 2H, *J*_{HH} = 19.5, 20.4 Hz, Si-HC=CH₂, from terminal group), 6.84 (s, 2H, Si-HC=CH-Si, traces of homocoupling), 7.40 (s, 2H, =CH- from -C₄H₂S-), 7.41 (s, 4H, from $-C_6H_4$ – DVB). ¹³C NMR (CDCl₃, δ (ppm)): -1.1 (-CH₃ from copolymer), -1.6 (-CH₃ from terminal part), 126.7 (=CHfrom $-C_6H_4$ -), 132.7 (Si-HC=CH₂), 135.8 (=CH- from $-C_4H_2S$ -), $135.9(Si-HC=CH-C<), 137.8(C_i from -C_6H_4-), 144.2(Si-HC=CH_2),$ 144.2 (Ci from C4H2S), 144.7 (Si-HC=CH-C<). ²⁹Si NMR (CDCl₃, δ (ppm)): -11.10, -11.12. Elem. Anal. Calcd. for (C₁₈H₂₂SSi₂)_n: C 66.19, H 6.79; Found C 65.97, H 6.75. GPC: $\overline{M_w} = 4313 \text{ [g mol}^{-1}\text{]}, \overline{M_n} = 3067$ [g mol⁻¹], PDI ($\overline{M_w}/\overline{M_n}$) = 1.406, n = 8. The compound was isolated as white powder.

Poly[dimethylsilylene-5,5'-(2,2'-bithienylene)-dimethylsilylene-(*E*)-vinylene-1,4-phenylene-(*E*)-vinylene] (**15**): ¹H NMR (CDCl₃, δ (ppm)): 0.40 (s, 12H, -CH₃ from terminal part), 0.48 (s, 12H, -CH₃ from copolymer), 5.80 (dd, 2H, $J_{HH} = 3.6$, 20.2 Hz, Si–HC=CH₂, from terminal group), 5.96 (dd, 2H, $J_{HH} = 3.6$, 15.1 Hz, Si–HC=CH₂, from terminal group), 6.16 (dd, 2H, $J_{HH} = 14.7$, 20.1 Hz, Si–HC=CH₂, from terminal group), 6.56 (d, 1H, $J_{HH} = 19.2$ Hz, Si–HC=CH–C<), 6.83 (s, 2H, Si–HC=CH–C) i homo-coupling traces), 6.96 (d, 1H, $J_{HH} = 18.9$ Hz, Si–HC=CH–C<), 7.18 (d, 2H, $J_{HH} = 3.3$ Hz, 3-C₄H₂S–), 7.27 (d, 2H, $J_{HH} = 3.6$ Hz, 4-C₄H₂S–), 7.42 (s, 4H, -C₆H₄–). ¹³C NMR (CDCl₃, δ (ppm)): -1.4 (–CH₃ from copolymer), -1.5 (–CH₃ from terminal part), 126.8 (=CH– from –C₆H₄–), 132.7 (Si–HC=CH₂), 135.8 (=CH– from –C₄H₂S–), 135.9 (Si–HC=CH–C<), 137.9 (*C*_i from –C₆H₄–), 144.2 (Si–HC=CH₂), 144.2 (*C*_i from C₄H₂S), 145.2 (Si–HC=CH–C<). ²⁹Si NMR (CDCl₃, δ (ppm)) = –10.82, -11.49. Elem. Anal. Calcd. for (C₂₂H₂₄S₂Si₂)_n: C 64.65, H 5.92; Found C 63.97, H 5.90. GPC: $\overline{M_w} = 6065$ [g mol⁻¹], $\overline{M_n} = 4626$ [g mol⁻¹], PDI (\overline{M} w/ \overline{M} n) = 1.31, *n* = 11. The compound was isolated as white powder.

4.7. Synthesis of ruthenium—silyl complex Ru(SiMe₂C₄H₃S)Cl(CO) (PPh₃)₂ (II) (**16**)

The title compound was synthesized essentially in a manner similar to that reported in ref. 23, with modifications applied to improve meaningfully the yield of the reaction synthesis.

RuHCl(CO)(PPh₃)₃ (300 mg, 3.15×10^{-4} mol) was refluxed in toluene (10 mL) forming a suspension. Afterwards, **2** (159 mg, 9.45×10^{-4} mol) was added to the mixture, and the final commixture was refluxed for 22h to give a light yellow solution. The excess of solvent was evaporated under reduced pressure, followed by the addition of hexane and gave a yellow precipitate. Next, the latter was filtered ('canula' system), washed with cold hexane (3 × 15 mL) and dried in vacuum (0.18 g, 69% yield).

¹H NMR (C₆D₆, δ (ppm)): 0.97 (s, 6H, $-CH_3$), 7.03–7.11 (m, 18H, $-C_6H_5$), 7.24 (dd, 1H, $J_{HH} = 3.3$, 4.7 Hz, from $-C_4H_3$ S), 7.58 (d, 1H, $J_{HH} = 3.3$ Hz, from $-C_4H_3$ S), 7.68 (d, 1H, $J_{HH} = 4.7$ Hz, from $-C_4H_3$ S). ³¹P NMR (C₆D₆, δ (ppm)): 32.7 (s). IR (KBr, cm⁻¹) 1917 (ν (CO)). Elemental Analysis: calculated C 62.19, H 4.73; found C 62.11, H 4.70.

4.8. Procedure of stoichiometric reaction in NMR tube

In a typical NMR tube, 0.015 g (1.81×10^{-5} mol) of **16** (the tube was deoxygenated), decane (internal standard) and 0.6 mL of C₆D₆ were placed under argon. Then, 2.82 mg (2.71×10^{-5} mol) of styrene was added and the reaction mixture was heated at 35 °C for 1 h, then up to 60 °C. Progress of the catalytic process was monitored by ¹H NMR and MS at room temperature.

4.9. Procedure of GCMS test in glass reactor

In a typical glass reactor (3 mL), 0.010 g (1.21×10^{-5} mol) of **16** (the tube was deoxygenated), and 1 mL of toluene were placed under argon. Then, 7 μ L (3.63×10^{-5} mol) of styrene was added and the reaction mixture was heated at 60 °C for 1 h and 24 h. Progress of the catalytic process was monitored by GC–MS at room temperature.

4.10. X-ray structure determination

Diffraction data were collected at room temperature by the ω -scan technique on an Oxford Diffraction SuperNova four-circle diffractometer with Atlas CCD-detector, equipped with Nova microfocus CuK_α radiation source ($\lambda = 1.5418$ Å). The data were corrected for Lorentz-polarization as well as for absorption effects [30]. Accurate unit–cell parameters were determined by the least-squares fit of 4419 (10) and 19387 (11) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [31] and refined with the full-matrix least-squares procedure on F² by SHELXL97 [32]. Scattering factors incorporated

in SHELXL97 were used. The function $\Sigma w(|F_0|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_0)^2 + (A \cdot P)^2 + B \cdot P]$ (P = [Max $(F_0^2, 0) + 2F_c^2]/3$). The final values of A and B are listed in Table 1. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in 10 were found in the difference Fourier maps and isotropically refined, while in 11 they were placed geometrically, in idealized positions, and refined as rigid groups with their U_{iso}'s as 1.2 or 1.5 (methyl) times U_{eq} of the appropriate carrier atom. Relevant crystal data are listed in Table 1, together with refinement details.

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Appendix A. Supplementary material

CCDC numbers 795151 (**10**) and 795152 (**11**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article including GCMS spectra (Fig. 3 and Fig. 4) and summary of crystals data (Table 5). Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.01.020.

References

- D.-H. Hwang, S.-D. Jung, L.-M. Do, T. Ahn, H.-K.T. Zyung, Bull. Korean Chem. Soc. 19 (1988) 332.
- [2] (a) T.A. Skotheim, Handbook of Conducting Polymers. Marcel Dekker, New York, 1986;

(b) J.L. Bredas, R.R. Chance, Conjugated Polymeric Materials: Opportunity in Electronics, Optoelectronics and Molecular Electronics, NATO ASI Series, Series E, Applied Science, vol. 182, Kluwer Academic Publisher, Amsterdam, 1990; (c) J.S. Miller, Adv. Mater. 5 (7–8) (1993) 587;

(d) D.R. Baigent, N.C. Greenham, J. Gruner, R.N. Marks, R.H. Friend, J.C. Moralti, A.B. Holmes, Synth. Met. 67 (1994) 3.

- [3] F. Jonas, G. Heywang, Electrochim. Acta 39 (1994) 1345.
- [4] (a) C.E. Hoyle, J.M. Torkelson (Eds.), ACS Symposium Series, vol. 358, American Chemical Society, Washington, DC, 1987;
 (b) F.M. Winnik, Chem. Rec. 93 (1993) 587;
 - (c) G. Yu, A.J. Heeger, Synth. Met. 85 (1997) 1183.
- [5] (a) I. Schwendeman, J. Hwang, D.M. Welsh, D.B. Tanner, J.R. Reynolds, Adv. Mater. 13 (2001) 634;
 - (b) P. Schotlland, K. Zong, C.L. Gaupp, B.C. Thomas, I. Giurgiu, R. Hickman, K.A. Abboud, J.R. Reynolds, Macromolecules 33 (2000) 7051;

(c) B.C. Thomas, P. Schotlland, K. Zong, J.R. Reynolds, Chem. Mater. 12 (2000) 1563.

- [6] (a) D.T. McQuade, A.E. Pullen, T.M. Swager, Chem. Rev. 100 (2000) 2537;
 (b) J.S. Yang, T.M. Swager, J. Am. Chem. Soc. 120 (1998) 11864;
- (c) G.A. Sotzing, S. Briglin, R.H. Grubbs, N.S. Lewis, Anal. Chem. 72 (2000) 3181.
 [7] R.S. Becker, J. Seixas de Melo, A.L. Macanita, F. Elisei, J. Phys. Chem. 100 (1996) 18683
- [8] R.S. Becker, J. Seixas de Melo, A.L. Macanita, F. Elisei, Pure Appl. Chem. 67 (1995) 9
- [9] A. Yang, M. Kuroda, Y. Shirashi, T. Kobayashi, J. Phys. Chem. B. 102 (1998) 3706.
- [10] D. Beljonne, J. Cornil, R.H. Friend, R.A.J. Janssen, J.L. Bredas, J. Am. Chem. Soc. 118 (1996) 6453.
- [11] R.A. Janssen, L. Smilowitz, N.S. Sarciftci, D. Moses, J. Chem. Phys. 101 (1994) 1787.
- [12] D. Fichou, G. Horowitz, B. Xu, F. Garnier, Synth. Met. 48 (1992) 167.
- [13] P. Ostoja, S. Guerri, S. Rossini, M. Servidori, C. Taliani, R. Zamboni, Synth. Met. 54 (1993) 447.
- [14] H. Heberkern, K.R. Asmis, M. Allan, P. Swiderek, J. Phys. Chem. 5 (2003) 827.
- [15] T.L. Stott, M.O. Wolf, J. Phys. Chem. B. 108 (2004) 18815.
 [16] W. Porzio, S. Destri, U. Giovanella, S.V. Meille, G. Raos, R. Consonni, G. Zotti,
- Chem. Mater. 17 (2005) 242. [17] D. Anestopoulls, M. Fakis, L. Polyzos, G. Tsigaridas, V. Giannetas, J. Phys. Chem.
- B. 109 (2005) 9476. [18] K.-H. Lee, J. Ohshita, K. Kimura, Y.Y. Kunugi, A. Kunai, J. Organomet. Chem. 690
- (2005) 333. [19] H. Usta, G. Lu, A. Facchetti, T.J. Marks, J. Am. Chem. Soc. 128 (2006) 9034.
- [20] Ch. Rim. D.Y. Son. Macromolecules 36 (2003) 5580.
- [21] F. Wang, B.R. Kaafarani, D.C. Neckers, Macromolecules 36 (2003) 8225.
- [22] (a) B. Marciniec, C. Pietraszuk, Curr. Org. Chem. 7 (2003) 691;
- (b) B. Marciniec, C. Pietraszuk, 'Metathesis of Silicon-Containing Olefins'. in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 2. Wiley-VCH, New York, 2003;
 - (c) B. Marciniec, Appl. Organomet. Chem. 14 (2000) 527;
 - Mol. Cryst. Liq. Cryst. 352 (2000) 173; (d) B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374.
- [23] (a) Y. Wakatsuki, H. Yamazaki, N. Nakano, Y. Yamamoto, J. Chem. Soc. Chem. Commun. (1991) 703;
 - (b) B. Marciniec, C. Pietraszuk, J. Chem. Soc. Chem. Commun. (1995) 2003; Organometallics 16 (1997) 4320.
- [24] (a) B. Marciniec, M. Lewandowski, J. Inorg. Organomet. Polym. 5 (1995) 115;
 (b) B. Marciniec, M. Lewandowski, Tetrahedron Lett. 26 (1997) 3777;
 (c) T. Mise, Y. Takaguchi, T. Umem, S. Shimizu, Y. Wakatsuki, Chem. Commun. (1998) 699.
- [25] (a) B. Marciniec, E. Małecka, J. Phys. Org. Chem. 16 (2003) 818;
 (b) B. Marciniec, E. Małecka, Macromol. Rapid Commun. 20 (1999) 475;
 (c) B. Marciniec, E. Małecka, M. Ścibiorek, Macromolecules 36 (2003) 5545.
- [26] (a) M. Majchrzak, Y. Itami, B. Marciniec, P. Pawluc, Tetrahedron Lett. 41 (2000) 10303;
- (b) M. Majchrzak, B. Marciniec, Y. Itami, Adv. Synth. Catal. 347 (2005) 1285.
 [27] M. Majchrzak, M. Ludwiczak, M. Bayda, B. Marciniak, B. Marciniec, J. Polym.
- Sci. Part A: Polym. Chem. 46 (2008) 127.
- [28] C.S. Yi, D.W. Lee, Y. Chen, Organometallics 18 (1999) 2043.
- [29] J.J. Levison, S.D. Robinson, J. Chem. Soc. A. (1970) 2947.
 [30] Oxford Diffraction Crys Alis PRO (Version 1.171.33.36d). Oxford Diffraction Ltd, 2009.
- [31] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, J. Appl. Cryst. 26 (1993) 343.
- [32] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.