Electrochemical synthesis of bis(2-thienyl)silanes, 2-thienylchlorosilanes, bis[5-(2-bromothienyl)]silanes, and 5-(2-bromothienyl)dimethylchlorosilane, precursors of poly[(silanylene)thiophene]s

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Abstract

Bis(2-thienyl)silanes and bis[5-(2-bromothienyl)]silanes were synthesized by electrochemical reduction of monohalothiophenes (Br,Cl) and 2,5-dibromothiophene respectively in the presence of a dichlorosilane in THF or DME, using an undivided cell, a sacrificial Mg or Al anode, a constant current density and tetrabutylammonium bromide as the supporting electrolyte. In addition, when dichlorosilanes were used in large excess, halothiophenes underwent solely a monocoupling reaction leading selectively to thienylchlorosilanes, which reveals the versatility of the electrochemical method.

Keywords: Silicon; Thienylsilanes; Synthesis; Electrochemical synthesis; Poly[(silanylene)thiophene] precursors; Halide

1. Introduction

Organosilicon polymers containing a regular alternating arrangement of silanylene or polysilanylene units and a carbon π-electron system in the main chain, such as mono-, di-, trithienylene [1–10], phenylene, ethenylene, ethynylene, diethynylene, enynylene, diynylene, napthylene and furylene sequences, have received increasing attention [7–10] because these polymers can be used as functional materials [11] such as photoresists [1,12], semiconducting materials [2–4,7,13] and precursors of silicon carbide [14,15].

Several routes to these materials, and particularly to polymers with alternating silylene and thienylene units, have been described. They generaly involve the sodium condensation of bis(chlorosilyl)-substituted compounds possessing a π-electron system [1] or the coupling reactions of dilithioderivatives of these systems with dichlorosilanes or dichlorodisilanes. The latter method leads to linear poly[2,5-(silyl)thiophenylene] when hex-

ane is the solvent whereas the formation of a cyclic oligomer containing four thiophene units is preferential in THF, limiting the scope of the reaction [2–4]. The use of the dilithium salts of Me_2SiTh_2 (Th = 2-thienyl) or $ThMe_2SiSiMe_2Th$ were preferred to the dilithium salt of thiophene in the polycondensation reaction with dichlorosilanes [16]. The advantage is that the higher molar weights of the monomers enable a better control of the stoichiometry and consequently higher average molecular weights of the final products. The key products Me_2SiTh_2 and $ThMe_2SiSiMe_2Th$ were themselves obtained by condensation of 2-thienyllithium with dichlorodimethylsilane and 1,2-dichlorotetramethyldisilane respectively. The dilithium salts of Me_2SiTh_2 and $ThMe_2SiSiMe_2Th$ were revealed to be good precursors for alternating (thienylene–arylene–thienylene–silylene) polymers by polycondensation with aromatic dibromides using the palladium-catalyzed coupling of zinc derivatives [3,4]. More recently, Me_2SiTh_2, $ThMe_2SiSiMe_2Th$, Ph_2SiTh_2 and 2,5-bis(trimethylsilylthiophene) were found to undergo electrochemical polymerization leading to conducting polymer films similar to those prepared from thiophene [5,17].

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Bis(2-bromothienyl)-substituted mono-, di- and trisilanes constitute another important class of precursors of mono-, di-, and trisilanylenedithienylene polymers by dehalogenation with magnesium in the presence of a nickel(II) catalyst [9]. These monomers were prepared by condensation of dichloromono-, di-, or trisilane on 2-bromo-5-lithiothiophene resulting itself from the monolithiation of 2,5-dibromothiophene.

Following our results in the selective electrochemical trimethylsilylation of arenes, chloroarenes [18,19], mono- and polyhalothiophenes [20], here we report the electrochemical synthesis of a series of both classes of the key products previously mentioned: bis(2-thienyl)silanes and bis(2-bromothienylsilanes). The method involves the cathodic reduction of a mixture of a monohalothiophene (Br,Cl) or 2,5-dibromothiophene and a dichlorosilane. The inexpensive, industrially feasible sacrificial anode technique (massive metallic Al, Mg bar) involving an undivided cell, a cylindrical stainless steel grid as the cathode and a constant current density [21], offers a competitive route to these precursors.

2. Results and discussion

Electrolyses were carried out at room temperature under constant current density ($i = 0.1$ A, $j = 0.1 \pm 0.05$ A dm^{-2}) using a 70 ml:10 ml THF–HMPA solvent and Bu$_4$NBr as the supporting electrolyte at a low concentration (0.02 M) compared with that of the engaged substrate (0.3 M). The structures of the new products obtained were established, or confirmed for the others, by ^{1}H, ^{13}C, ^{29}Si NMR, IR, and mass spectroscopies. Elemental analyses are also provided for the new compounds.

2.1. Electrochemical synthesis of bis(2-thienyl)silanes and 2-thienylchlorosilanes

After passage of 2.2 F mol^{-1} of 2-BrTh, the products of the electroreductive coupling with dichlorodimethyl-
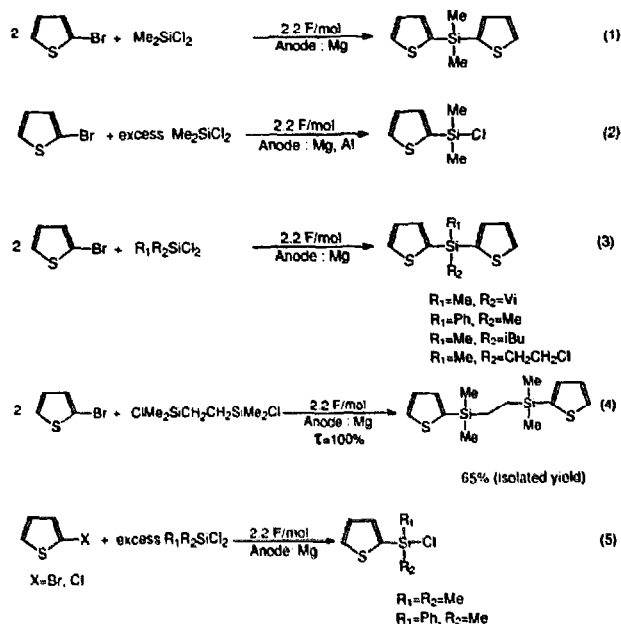
Scheme 1.

silane were essentially dependent upon the molar ratio of the engaged reagents.

First, a 1:0.5 2-BrTh–Me$_2$SiCl$_2$ molar ratio led to the expected bis(2-thienyl)dimethylsilane (Me$_2$SiTh$_2$, Scheme 1, Eq. (1)) with a complete conversion of 2-BrTh and an excellent yield of isolated product (87%) when a magnesium rod was used as the anode (Table 1). This result constitutes a real improvement of the common chemical route involving the coupling reaction of dichlorodimethylsilane with monolithiothiophene, which occurs only in 50–60% yields, due to side reactions such as the formation of dilithiothiophene and disubstituted thiophenes [6]. In addition, the electrochemical method is simple, easy to control, the consumption of massive magnesium is less expensive, and the use of lithioderivatives is avoided.

As a comparison, under the same conditions, with an aluminium anode, the conversion rate (60%) and the isolated yield (30%) were significantly lower (Table 1).

Table 1
Influence of the reagents proportions and of the anode nature on the coupling reaction of 2-BrTh and Me$_2$SiCl$_2$ after passing 2.2 F mol^{-1} of 2-BrTh

Anodes	2-BrTh–Me$_2$SiCl$_2$ [a]	2-BrTh r(%) [b]	Anodic faradaic yield (%)	Me$_2$SiThCl yield (%)		Me$_2$SiTh$_2$ yield (%)	
				GC [d]	isolated	GC [d]	isolated
Al	1/20	100	115	96	88	4	
	1/10	100	110	60	51	40	30
	1/0.5	60	110	0		45	30
	1/0.5 [c]	100	115	0		65	55
Mg	1/20	100	120	95	88	5	
	1/0.5	100	145	0		98	87

[a] Molar ratio. [b] r: conversion rate. [c] $Q = 3$ F mol^{-1}. [d] GC: gas chromatography.

Table 2

Synthesis of a variety of bis(2-thienyl)silanes in stoichiometric conditions

$R_1R_2SiCl_2$	2-BrTh conversion $\tau(\%)$	$R_1R_2SiTh_2$ yield (%)		Chemical routes	
		GC	isolated	Yield (%)	Ref.
Me_2SiCl_2	100	98	87	67	[6]
$ViMeSiCl_2$	100	96	52		[4] [c]
$PhMeSiCl_2$	100	96	58	50–60	[6]
Ph_2SiCl_2	0 [a]	0	0 [a]		[4] [c]
$^iBuMeSiCl_2$	100	97	61		
$ClCH_2CH_2MeSiCl_2$	100	96	42 [b]		

[a] Under these cond.tions, no reaction proceeded with 2-BrTh, but formation of polysilane resulting from the electrochemical reduction of Ph_2SiCl_2 [22] was observed. Ph_2SiTh_2 can be obtained from 2,5-dibromothiophene (see below, Scheme 2). [b] An elimination reaction occurred after exposure to daylight giving $ViMeSiTh_2$. [c] Yield not mentioned.

The different conversion rates with Mg and Al were in good agreement with the observed anodic faradaic yields (amount of consumed metal compared with charge passed); these were almost theoretical for Al (110%, Table 1) and abnormally high for Mg (145%, Table 1), showing that a chemical reduction also occurred at the anodically scoured Mg. Thus, for Mg, we can assume that the chemical participation compensates for the possible loss in cathodic current efficiency observed for Al due to exhaustion of the substrate at the end of the electrolysis. It must be pointed out, however, that after having passed 3 F mol^{-1} of electricity with an aluminium anode the conversion rate was quantitative but the final yield only slightly improved (55%).

Second, when dichlorodimethylsilane was used in large excess, 2-BrTh underwent solely a monocoupling reaction leading selectively to dimethylthienylchlorosilane (Scheme 1, Eq. (2)), showing that this product results from the first step of the previous reaction, as expected. Thus, with a magnesium or aluminium anode and a 1 : 20 2-BrTh–Me_2SiCl_2 molar ratio, the 2-BrTh

conversion was quantitative and the yield of isolated $Me_2Si(Th)Cl$ high (88%, Table 1). Table 1 also shows that a lower selectivity was obtained with a lower excess of Me_2SiCl_2 (1 : 10 molar ratio).

The coupling of 2-BrTh was extended to various dichlorosilanes using a Mg anode. Thus, in stoichiometric conditions, a variety of bis(2-thienyl)silanes were prepared in 42–87% yields, including several new ones (Scheme 1, Eq. (3), Table 2). Stoichiometric reaction with 1,2-bis(dimethylchlorosilyl)ethane also afforded 1,2-bis(dimethylthienyl)ethane in fairly good yield (65%) (Scheme 1, Eq. (4)).

The influence of the nature of the halogen of the 2-halothiophene was also investigated. Thus, the coupling with Me_2SiCl_2 or $PhMeSiCl_2$ was shown to proceed with the less expensive 2-ClTh as well as with 2-BrTh, providing the corresponding bis(2-thienyl)silanes and (2-thienyl)chlorosilanes (Scheme 1, Eq. (5) and Table 3).

Differences in isolated yields are essentially due to a loss of product during liquid chromatographic purification. Conversion rates and GC yields were excellent.

In order to understand the respective role of the reagents in the coupling reaction, a comparison can be made with the electrochemical reaction of 2-BrTh or 2-ClTh with Me_3SiCl we previously studied under the same conditions [20]. In this case, Me_3SiCl is known to be very cathodically reducible (at a potential inferior to -3 V vs. SCE [22,23]), that is less readily than all organic halides. 2-BrTh or 2-ClTh are therefore reduced first and the anion formed is trapped by Me_3SiCl acting as the electrophile. Knowing that the reduction potentials of 2-BrTh and $R_1R_2SiCl_2$ are of the same order, the respective roles of the reagents in this coupling reaction are not clear. (Several voltammetric measurements have been made for both series but in different conditions of solvent, supporting electrolyte and electrode, so a fine comparison cannot be effected at the present time [20,22].) Nevertheless, several arguments issued from the synthesis allow clarification of the

Table 3

Influence of the nature of the halogen of the substrate on the synthesis of bis(2-thienyl)silanes and (2-thienyl)chlorosilanes (Mg anode, 2.2 F mol^{-1}) [a]
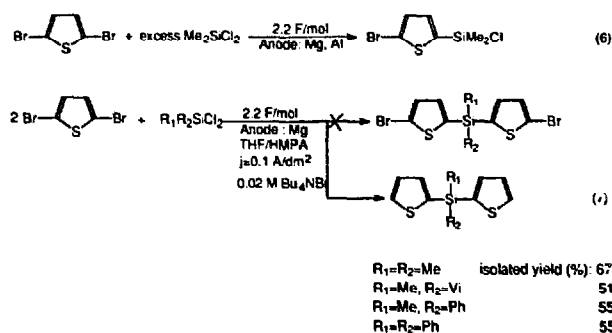
2-XTh	$R_1R_2SiCl_2$	2-BrTh–$R_1R_2SiCl_2$ [b]	$R_1R_2SiThCl$ yield (%)		$R_1R_2SiTh_2$ yield (%)	
			GC	isolated	GC	isolated
2-BrTh	Me_2SiCl_2	1/0.5	0		98	87
		1/20	95	88	5	
	$PhMeSiCl_2$	1/0.5	0		96	58
		1/20	95	64	5	
2-ClTh	Me_2SiCl_2	1/0.5	0		97	84
		1/20	94	85	5	
	$PhMeSiCl_2$	1/0.5	0		96	55
		1/20	94	63	4	

[a] Conversion was always 100%. [b] Molar ratio.

process: (i) no deposition of polydimethylsilane (PDMS) occurred with 2-BrTh or 2-ClTh, even when Me_2SiCl_2 was used in large excess, while the cathode was coated with PDMS in the absence of halothiophene [22,24] or in the presence of PhBr, which is less readily reduced than halothiophenes [25]. Knowing that halothiophenes are less electrophilic than chlorosilanes, this means that Me_2SiCl_2 or $PhMeSiCl_2$ are not the reduced substrate; (ii) after having passed 2.2 F mol^{-1} of 2-XTh (X = Br, Cl) in the presence of an excess of Me_2SiCl_2 or $PhMeSiCl_2$, the halothiophene is quantitatively consumed (anode Mg, Al). So, we can conclude that the halothiophene is reduced first and Me_2SiCl_2 acts as the electrophile; (iii) this conclusion is also available for the other dichlorosilanes studied, except Ph_2SiCl_2 which is much more easily reduced [22,23]; this shows the preferential formation of polysilanes, under the same conditions, with the halothiophene being recovered. In this case, Ph_2SiCl_2 is indeed reduced first and also acts as the electrophile.

2.2. Electrochemical synthesis of bis[5-(2-bromothienyl)]silanes and 5-(2-bromothienyl)dimethylchlorosilane

As for the previous reaction, the electrolysis of 2,5-dibromothiophene (2,5-Br$_2$T) with an excess (20 molar equivalents) of Me_2SiCl_2 using a Mg or Al anode under the conditions mentioned above ($i = 0.1$ A, $j = 0.1 \pm 0.05$ A dm^{-2}, 70 ml : 10 ml THF–HMPA, 0.02 M

R$_1$=R$_2$=Me   isolated yield (%): 67
R$_1$=Me, R$_2$=Vi   51
R$_1$=Me, R$_2$=Ph   55
R$_1$=R$_2$=Ph   55

Scheme 2.

Bu_4NBr) with up to 2.2 F mol^{-1} of dibromothiophene led to 5-(2-bromothienyl)dimethylchlorosilane, $Me_2Si(TBr)Cl$, with a good yield (80%, Scheme 2, Eq. (6), Table 4).

When 2,5-dibromothiophene (1 molar equivalent) was electrolyzed with 0.5 molar equivalents of $R_1R_2SiCl_2$, using a Mg anode, under the same conditions until 2.2 F mol^{-1} of dihalothiophene was consumed, the sole product formed was not the expected bis[5-(2-bromothienyl)]silane, $R_1R_2Si(TBr)_2$, but the corresponding hydrogenated compound $R_1R_2SiTh_2$ with quantitative GC yields (isolated yields after purification by liquid chromatography are shown in Scheme 2, Eq. (7), and Table 4). In order to limit this undesired reaction, an extensive study was carried out with Me_2SiCl_2 as a model. Different parameters were investigated: nature

Table 4
Electrolysis of 2,5-dibromothiophene and Me_2SiCl_2 after the passage of up to 2.2 F mol^{-1}: influence of the reagents proportions and of the nature of the anode [a]

Anode	2,5-Br$_2$T–Me$_2$SiCl$_2$ [b]	2,5-Br$_2$T r(%) [c]	Anodic faradaic yield (%)	Me$_2$Si(TBr)Cl yield (%)		Me$_2$Si(TBr)$_2$ yield (%)		Me$_2$Si(Th)$_2$ yield (%)	
				GC	isolated	GC	isolated	GC	isolated
Al	1/0.5	60 [c]	105	0	—	45	30	3	—
	1/0.5 [d]	100 [c]	115	0	—	65	49	16	—
	1/20	100	110	94	79	6	—	0	—
Mg	1/0.5	100	140	0	—	0	—	96	67
	1/20	100	130	96	82	0	—	0	—

[a] THF–HMPA solvent, $j = 0.1 \pm 0.05$ A dm^{-2}, Bu$_4$NBr: 0.02 M. [b] Molar ratio. [c] Conversion rate. [d] $Q = 3$ F mol^{-1}. [e] Several unidentified by-products were formed.

Table 5
Influence of the solvent, charge passed, and concentration of the supporting electrolyte [a]

Solvent	Charge passed (F mol^{-1})	Bu$_4$NBr concentration (M)	2,5-Br$_2$T r(%)	Me$_2$Si(TBr)$_2$ GC yield (%)	Me$_2$Si(Th)$_2$ GC yield (%)	Silanylenethiophene oligomers GC yield (%)
THF	0.5	0.02	100	0	35	65
		0.01	69	12	27	30
		0.005	50	7	21	22
	2.0	0.01	100	0	98 [b]	0
DME	0.5	0.01	24	11	12	1
	2.0	0.01	92	12	40	40

[a] Mg anode, HMPA cosolvent, 1/0.5 2,5-Br$_2$T–Me$_2$SiCl$_2$, $j = 0.1 \pm 0.05$ A dm^{-2}. [b] 67% isolated.

Table 6
Influence of current density after 2.0 F mol^{-1} of charge passed [a]

Current density j (A dm^{-2})	2,5-Br$_2$T τ (%)	Me$_2$Si(TBr)$_2$ yield (%)		Me$_2$Si(Th)$_2$ yield (%)		Silanylenethiophene oligomers GC yield (%)
		GC	isolated	GC	isolated	
0.1–0.2	92	12		40		40
0.02–0.05	92	84	73	8		
~0.01	67	60	51	7		

[a] Mg anode, 70 ml:10 ml DME–HMPA solvent, 0.01 M Bu$_4$NBr.

of the anode, supporting electrolyte, solvent, current density.

2.2.1. Nature of the anode

With an Al anode under the previous conditions, Me$_2$Si(TBr)$_2$ was formed with a quasi-theoretical anodic faradaic yield, but medium conversion rate and yields (Table 4). The latter could, however, be increased by increasing the charge passed up to 3 F mol^{-1}. As for the reaction of 2-BrTh (cf. Section 2.1) the complete conversion with a Mg anode for 2.2 F mol^{-1} is associated with a chemical participation of the anodically scoured Mg (high anodic faradaic yield: 140%) allowing the reaction to proceed further.

2.2.2. Supporting electrolyte and charge passed

Me$_2$Si(TBr)$_2$ could also be obtained with a Mg anode in THF–HMPA, but in low yield (12%, Table 5), provided the concentration of Bu$_4$NBr was decreased to 0.01 M, and the charge limited to 0.5 F mol^{-1}.

2.2.3. Solvent and charge passed

For a charge of 2.0 F mol^{-1}, a Mg anode, and a 0.01 M Bu$_4$NBr solution, Me$_2$Si(TBr)$_2$ was recovered in DME–HMPA also in a low amount (12%), but not in THF–HMPA (Table 5). In fact the process of the reaction is complex: silanylenethiophene oligomers were formed at the beginning of the reaction and then disappeared in THF but remained up to 2.0 F mol^{-1} in DME. This point is still under consideration.

2.2.4. Current density

Current density was varied with a 0.1 A constant current intensity using three stainless steel grids with different active surface areas in order to get 0.1–0.2,

0.02–0.05 and 0.01 A dm^{-2}. Table 6 highlights that decreasing current density to 0.02–0.05 A dm^{-2} is the main factor for recovering Me$_2$Si(TBr)$_2$, our desired product, with a convenient yield (73%). Under these conditions, the formation of the hydrogenated product Me$_2$SiTh$_2$ is strongly reduced (8%). From this result, it can be assumed that, during electrolysis using the highest current density, Me$_2$Si(TBr)$_2$ is also reduced in conditions where electrophile chlorosilanes (Me$_2$SiCl$_2$ or Me$_2$Si(TBr)Cl) are exhausted. A proton or an H atom must then be abstracted from the medium.

These experimental conditions being established, we could synthesize a variety of bis[5-(2-bromothienyl)]-silanes with yields equivalent to those of the chemical routes for the known products (Scheme 3, Table 7).

3. Conclusion

In conclusion, we have achieved a successful electrochemical alternative to the use of lithio-compounds for the synthesis of a variety of bis(2-thienyl)silanes and bis[5-(2-bromothienyl)]silanes, precursors of poly-[(silanylene)thiophene]s. The high selectivity of the method also allowed the (2-thienyl)chlorosilanes and 5-(2-bromothienyl)dimethylchlorosilane formed in the first step to be obtained.

4. Experimental details

4.1. General methods

The electrolysis of magnetically stirred solutions was performed under nitrogen, in a previously described [19] undivided cell fitted with a sacrificial magnesium rod as the anode, and a cylindrical stainless steel grid as the
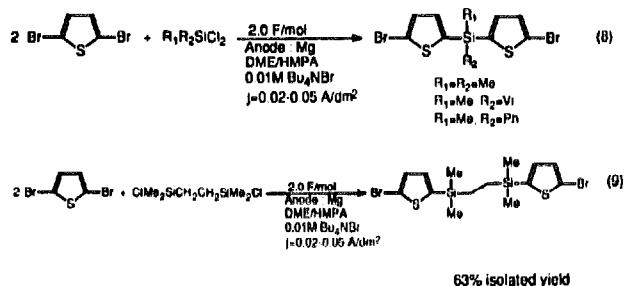
63% isolated yield

Scheme 3.

Table 7
Synthesis of a variety of bis[5-(2-bromothienyl)]silanes [a]

R$_1$R$_2$SiCl$_2$	R$_1$R$_2$Si(TBr)$_2$ isolated yield (%)	Chemical routes yield (%) [ref]
Me$_2$SiCl$_2$	70	72 [7]
ViMeSiCl$_2$	61	[7] [b]
PhMeSiCl$_2$	64	69 [7]

[a] Mg anode, 70 ml:10 ml DME–HMPA, 0.01 M Bu$_4$NBr, $j = 0.02$–0.05 A dm^{-2}, 2.0 F mol^{-1}. [b] Yield not mentioned.

cathode. Constant current ($i = 0.1$ A, $j = 0.1 \pm 0.05$ A dm^{-2}) was provided by a Sodilec EDL 36-07 regulated d.c. power supply.

Bu$_4$NBr (0.3 g, 1 mmol) was introduced into the previously dried cell. The cell was then deaerated twice under vacuum and then with dry nitrogen gas. THF (70 ml), HMPA (10 ml), and a minimum excess of trimethylchlorosilane just sufficient for drying the medium (generally between 1 to 1.5 ml) were introduced through a septum by syringe. The solution was degassed by bubbling nitrogen for 10 min. The resulting HCl coming from the reaction of Me$_3$SiCl with traces of water was removed by pre-electrolyting the solution ($i = 0.1$ A). The (Me$_3$Si)$_2$O formed is electrochemically inert. When evolution of H$_2$ had ceased, the substrate (20 mmol) and dichlorosilane (10 mmc̣) for the synthesis of R$_1$R$_2$SiTh$_2$, or 400 mmol for the synthesis of R$_1$R$_2$SiThCl were introduced by means of a syringe. The electrolysis ($i = 0.1$ A) was then performed until the theoretically required charge had been passed. The reaction was monitored by gas chromatography. After precipitation of the major part of the salts from the resulting solution by the addition of anhydrous pentane (2 × 50 ml), and subsequent filtration and evaporation of the solvents, the residue was extracted with Et$_2$O (2 × 50 ml), and, when the product was R$_1$R$_2$SiTh$_2$ (but not with R$_1$R$_2$SiThCl), washed with a 10% HCl solution (2 × 20 ml). After drying over MgSO$_4$, Et$_2$O was evaporated. The crude product was analysed by GC, distilled or purified with a silica gel column.

Gas chromatography was performed with a temperature-programmable Hewlett Packard 5890A apparatus equipped with a 25 m × 0.25 µm CP-Sil capillary column. ^{1}H NMR spectra were recorded in CDCl$_3$ at 250 MHz with a Bruker AC 250 spectrometer, using residual CHCl$_3$ ($\delta = 7.27$ ppm) as the internal standard. The signals are designated s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). ^{13}C NMR spectra were obtained at 62.86 MHz with a Bruker AC 250 using CDCl$_3$ ($\delta = 77.70$ ppm) as the internal standard. The signals are designated P (primary carbon), S (secondary), T (tertiary), or Q (quaternary). ^{29}Si NMR spectra were recorded in CDCl$_3$ at 39.73 MHz with a Bruker AC 200 spectrometer. Electron-impact mass spectra were recorded at an ionization voltage of 70 eV with a VG Micromass 16F spectrometer coupled with a gas chromatograph equipped with a 25 m × 0.25 µm CP-Sil capillary column. IR spectra were recorded with a Perkin–Elmer 1420 spectrophotometer in pure liquid films (NaCl or KBr plates). Elemental analyses were performed by the 'Service Central de Microanalyse' of CNRS (B.P.22, 69390 Vernaison, France).

4.2. Materials

THF, DME (Aldrich) were dried by distillation over sodium benzophenone ketyl and HMPA (Aldrich) over

CaH$_2$. Bu$_4$NBr (Aldrich) was used as-received, whereas dichlorosilanes were distilled over Mg powder just before use.

4.2.1. (2-Thienyl)dimethylchlorosilane

Yield, 88%; b.p. 38°C/0.5 mm Hg. ^{1}H NMR (CDCl$_3$): δ 0.80 (s, 6H, SiMe$_2$); 7.27 (dd, 1H, $J^3_{H4H5} =$ 3.5 Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H$_4$); 7.48 (dd, 1H, $J^3_{H5H4} = 3.5$ Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl H$_5$); 7.73 (dd, 1H, $J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl H$_3$). ^{13}C NMR (CDCl$_3$): δ 3.3 (P); 128.5 (T); 132.4 (T); 135.9 (T); 138.3 (Q). MS m/z (rel. intensity, %): 178 (8); 176 (24, M); 163 (45); 162 (14); 161 (100,-CH$_3$); 63 (13). IR (neat): 3079 (w); 3064 (w); 2964 (m); 1497 (w); 1326 (m); 1259 (s); 1216 (m); 1086 (s); 1059 (s); 1003 (s); 856 (m); 835 (s); 809 (s); 793 (s); 750 (s); 714 (m); 495 (s).

4.2.2. (2-Thienyl)methylphenylchlorosilane

Yield, 64%; b.p. 131°C/1 mm Hg. ^{1}H NMR (CDCl$_3$): δ 1.09 (s, 3H, SiMe); 7.33 (dd, 1H, $J^3_{H4H5} =$ 3.5 Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H$_4$); 7.52 (m, 5H, thienyl and phenyl protons); 7.79 (m, 2H, thienyl and phenyl protons). ^{13}C NMR (CDCl$_3$): δ 3.2 (P); 128.6 (T); 128.8 (T); 129.1 (T); 130.9 (T); 133.1 (T); 135.3 (T); 136.8 (Q); 139.1 (Q). ^{29}Si NMR (CDCl$_3$): δ 5.2. MS m/z (rel. intensity, %): 240 (8); 238 (24, M); 225 (50); 224 (16); 223 (100, -CH$_3$). IR (neat): 3060 (w); 3040 (w); 2945 (w); 1496 (m); 1401 (m); 1322 (w); 1249 (m); 1211 (m); 1107 (m); 1069 (m); 997 (m); 980 (w); 951 (w); 791 (s); 775 (s); 751 (s); 742 (s); 709 (m); 496 (s).

4.2.3. Bis(2-thienyl)dimethylsilane

Yield, 87%; b.p. 75–85°C/1 mm Hg. ^{1}H NMR (CDCl$_3$): δ 0.64 (s, 6H, SiMe$_2$); 7.18 (dd, 2H, $J^3_{H4H5} =$ 3.5 Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H$_4$); 7.33 (dd, 2H, $J^3_{H5H4} = 3.5$ Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl H$_5$); 7.61 (dd, 2H, $J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl H$_3$). ^{13}C NMR (CDCl$_3$): δ 0.1 (P); 128.0 (T); 130.3 (T); 133.9 (T); 139.9 (Q). ^{29}Si NMR (CDCl$_3$): δ -14.66. MS m/z (rel. intensity, %): 224 (34, M); 209 (100, M -CH$_3$). IR (neat): 3090 (w); 3060 (w); 3052 (w); 2944 (s); 2892 (w); 1493 (m); 1401 (s); 1322 (m); 1247 (s); 1205 (s); 1102 (s); 998 (s); 847 (m); 823 (s); 809 (s); 785 (s); 750 (m); 703 (s); 657 (m). The spectral ^{1}H NMR data are in good agreement with those reported in the literature [6].

4.2.4. Bis(2-thienyl)methylvinylsilane

Yield, 52%: this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; ^{1}H NMR (CDCl$_3$): δ 0.89 (s, 3H, SiMe); 6.02–6.59 (m, 3H, vinyl protons); 7.35 (dd, 2H, $J^3_{H4H5} = 3.5$ Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H$_4$); 7.52 (dd, 2H, $J^3_{H5H4} =$ 3.5 Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl H$_5$); 7.77 (dd, 2H,

$J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl H_3). ^{13}C NMR (CDCl$_3$): δ -1.4 (P); 128.5 (S); 128.6 (T); 132.0 (T); 135.3 (T); 135.9 (T); 136.5 (Q). ^{29}Si NMR (CDCl$_3$): δ -22.43. MS m/z (rel.intensity, %): 236 (56, M); 221 (100, M $-$ CH$_3$,); 209 (28); 195 (24); 152 (11); 127 (15); 111 (22); 75 (17); 51 (14); 39 (11). IR (neat): 3098 (w); 3041 (m); 2943 (s); 2908 (m); 2844 (w); 1597 (w); 1496 (m); 1402 (s); 1325 (m); 1253 (s); 1213 (s); 1083 (s); 1002 (s); 998 (m); 902 (m); 848 (m); 830 (m); 796 (s); 768 (s); 731 (s); 709 (s); 663 (m).

4.2.5. Bis(2-thienyl)methylphenylsilane

Yield, 58%; b.p. 105–110 °C/0.1 mm Hg. ^1H NMR (CDCl$_3$): δ 1.01 (s, 3H, SiMe); 7.29 (dd, 2H, $J^3_{H4H5} = 3.5$ Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H_4); 7.45 (m, 6H, thienyl and phenyl protons); 7.74 (m, 3H, thienyl and phenyl protons). ^{13}C NMR (CDCl$_3$): δ -0.8 (P); 128.0 (T); 128.1 (T); 128.4 (T); 130 (T); 132.8 (T); 134.8 (T); 135.5 (Q); 137.7 (Q). ^{29}Si NMR (CDCl$_3$): δ -19.48. MS m/z (rel. intensity, %): 286 (46, M); 271 (100, M $-$ CH$_3$). IR (neat): 3058 (w); 3040 (w); 2947 (w); 1498 (w); 1438 (m); 1403 (m); 1326 (w); 1254 (m); 1214 (m); 1109 (m); 1073 (m); 999 (m); 978 (w); 849 (w); 793 (s); 776 (s); 758 (s); 743 (s); 709 (m). The spectral ^1H NMR data are in good agreement with those reported in the literature [6].

4.2.6. Bis(2-thienyl)diphenylsilane

Yield, 55%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^1H NMR (CDCl$_3$): δ 7.31 (m, 1H, thienyl and phenyl protons); 7.39 (m, 1H, thienyl and phenyl protons); 7.51 (m, 8H, thienyl and phenyl protons); 7.81 (m, 8H, thienyl and phenyl protons). ^{13}C NMR (CDCl$_3$): δ 128.1 (T); 128.6 (T); 130.3 (T); 132.7 (T); 134.6 (T); 136.0 (T); 137.8 (Q); 138.7 (Q). ^{29}Si NMR (CDCl$_3$): δ -24.87. MS m/z (rel. intensity, %): 350 (15); 349 (26); 348 (100, M); 273 (11); 272 (19); 271 (82); 265 (12); 188 (16); 187 (11); 173 (12); 137 (14); 111 (12); 105 (22); 77 (16). IR (neat): 3061 (w); 3038 (w); 2943 (w); 1497 (m); 1401 (m); 1253 (m); 1211 (m); 1087 (m); 1003 (m); 969 (m); 847 (w); 797 (s); 761 (s); 749 (s); 710 (m).

4.2.7. Bis(2-thienyl)isobutylmethylsilane

Yield, 61%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^1H NMR (CDCl$_3$): δ 0.87 (s, 3H, SiMe); 1.12 (d, 6H, $J^3 = 6.5$ Hz, $-(CH_3)_2$); 1.32 (d, 2H, $J^3 = 6.9$ Hz, $-CH_2$); 2.11 (m, 1H, $-CH$); 7.34 (dd, 2H, $J^3_{H4H5} = 3.5$ Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl ring); 7.51 (dd, 2H, $J^3_{H5H4} = 3.5$ Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl ring); 7.75 (dd, 2H, $J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl ring). ^{13}C NMR (CDCl$_3$): 0.9 (P); 25.1 (T); 26.5 (P); 27.3 (S); 128.4 (T); 131.5 (T); 135.8 (T); 137.1 (Q). ^{29}Si (CDCl$_3$): δ -14.02. MS m/z (rel. intensity): 211 (20); 210 (40;

209 (100, $-$isoBu); 195 (10); 183 (12); 182 (42); 127 (16); 111 (10); 75 (19); 44(33); 40 (25). IR (neat): 3086 (w); 3061 (w); 2973 (m); 1485 (w); 1323 (m); 1248 (s); 1201 (s); 995 (s); 843 (m); 827 (s); 803 (s); 787 (s); 758 (m); 701 (s). Anal. Found: C, 58.32; H, 6.83; S, 24.83. C$_{13}$H$_{18}$S$_2$Si. Calc.: C, 58.65; H, 6.77; S, 24.06%.

4.2.8. Bis(2-thienyl)2-chloroethylmethylsilane

Yield, 42%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^1H NMR (CDCl$_3$): δ 0.77 (t, 2H, SiCH$_2$); 1.22 (s, 3H, SiMe); 1.42 (t, 2H, CH$_2$Cl); 7.32 (dd, 2H, $J^3_{H4H5} = 3.5$ Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H_4); 7.47 (dd, 2H, $J^3_{H5H4} = 3.5$ Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl H_5); 7.73 (dd, 2H, $J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl H_3). ^{13}C NMR (CDCl$_3$): δ -2.3 (P); 8.5 (S); 29.9 (S); 128.4 (T); 132.0 (T); 135.5 (T); 136.5 (Q). ^{29}Si NMR (CDCl$_3$): δ -14.92. MS m/z (rel. intensity, %): 274 (6); 272 (16, M); 259 (33); 258 (12); 257 (100, $-$CH$_3$). IR (neat): 3089 (w); 3057 (w); 2963 (m); 1486 (w); 1402 (s); 1321 (m); 1250 (s); 1198 (s); 993 (s); 835 (m); 822 (s); 810 (s); 772 (s); 748 (m); 698 (m). Anal. Found: C, 48.33; H, 4.83; S, 23.21. C$_{11}$H$_{13}$ClS$_2$Si. Calc.: C, 48.45; H, 4.77; S, 23.48%.

4.2.9. 2,2'-Bis(2-thienyldimethylsilyl)ethane

Yield, 65%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^1H NMR (CDCl$_3$): δ 0.31 (s, 12H, SiMe$_2$); 0.74 (s, 4H, SiCH$_2$); 7.17 (dd, 2H, $J^3_{H4H5} = 3.5$ Hz, $J^3_{H4H3} = 4.6$ Hz, thienyl H_4); 7.23 (dd, 2H, $J^3_{H5H4} = 3.5$ Hz, $J^4_{H5H3} = 0.5$ Hz, thienyl H_5); 7.57 (dd, 2H, $J^3_{H3H4} = 4.6$ Hz, $J^4_{H3H5} = 0.5$ Hz, thienyl H_3). ^{13}C NMR (CDCl$_3$): δ -2.1 (P); 8.9 (S); 128.2 (T); 130.6 (T); 134.3 (T); 135.5 (Q). ^{29}Si NMR (CDCl$_3$): δ -3.27. MS m/z (rel. Intensity, %): 310 (16, M); 192 (12); 142 (14); 141 (100, $-$CH$_2$CH$_2$Si(Me$_2$)Th). IR (neat): 3097 (w); 3032 (w); 3027 (w); 2942 (s); 2898 (s); 2781 (w); 1493 (w); 1405 (s); 1323 (w); 1250 (s); 1214 (s); 1136 (s); 1081 (s); 992 (s); 980 (m); 905 (m); 851 (s); 827 (s); 811 (s); 781 (s); 731 (w); 705 (s); 645 (w); 628 (w). Anal. Found: C, 53.88; H, 7.45; S, 22.04. C$_{14}$H$_{22}$S$_2$Si$_2$. Calc.: C, 54.19; H, 7.10; S, 20.65%.

4.2.10. 5-(2-Bromothienyl)dimethylchlorosilane

Yield, 82%; b.p. 73 °C/0.5 mm Hg. ^1H NMR (CDCl$_3$): δ 0.54 (s, 6H, SiMe$_2$); 6.95 (d, 1H, $J^3 = 1.6$ Hz, thienylene proton); 6.98 (d, 1H, $J^3 = 1.6$ Hz, thienylene proton). ^{13}C NMR (CDCl$_3$): δ 3.0 (P); 119.1 (Q); 131.4 (T); 136.1 (T); 139.2 (Q). MS m/z (rel. Intensity, %): 258 (15); 256 (27, M); 254 (24); 243 (37); 242 (10); 241 (100); 239 (76, M $-$ CH$_3$); 179 (19); 159 (18); 157 (26); 135 (46); 96 (10); 93 (13); 65 (10); 53 (14); 46 (15); 45 (31); 44 (20); 42 (11). IR (neat): 3081 (w); 3060 (w); 2975 (m); 1462 (w); 1311 (m); 1264 (s); 1221 (m); 1092 (s); 1063 (s); 1001 (s);

953 (s); 857 (m); 843 (s); 813 (s); 798 (s); 748 (s); 710 (m); 497 (s).

4.2.11. Bis[5-(2-bromothienyl)]dimethylsilane

Yield, 70%; b.p. 115 °C/0.1 mm Hg. ^{1}H NMR (CDCl$_3$): δ 0.64 (s, 6H, SiMe$_2$); 7.08 (d, 2H, J^3 = 3.5 Hz, thienylene protons); 7.13 (d, 2H, J^3 = 3.5 Hz, thienylene protons). ^{13}C NMR (CDCl$_3$): 0.0 (P); 118.3 (Q); 131.2 (T); 136.0 (T); 139.4 (Q). ^{29}Si NMR (CDCl$_3$): δ – 15.71. MS m/z (rel. intensity, %): 284 (24); 282 (49); 280 (22, M); 269 (51); 267 (100); 265 (44, M – CH$_3$); 195 (27); 152 (13); 127 (14); 111 (24); 75 (15); 51 (12); 43 (10). IR (neat): 2947 (m); 1501 (w); 1406 (s); 1278 (w); 1257 (s); 1205 (s); 1071 (m); 1008 (m); 951 (s); 902 (s); 831 (m); 799 (s); 781 (s); 738 (s); 677 (w); 650 (m).

4.2.12. Bis[5-(2-bromothienyl)]methylvinylsilane

Yield, 61%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^{1}H NMR (CDCl$_3$): δ 0.72 (s, 3H, SiMe); 5.99–6.43 (m, 3H, vinyl protons); 7.12 (d, 2H, J^3 = 3.5 Hz, thienylene ring); 7.16 (d, 2H, J^3 = 3.5 Hz, thienylene ring). ^{13}C NMR (CDCl$_3$): δ – 1.9 (P); 118.9 (Q); 131.6 (T); 134.0 (S); 136.5 (T); 137.0 (T); 137.6 (Q). ^{29}Si NMR (CDCl$_3$): δ – 23.30. MS m/z (rel. intensity): 396 (28); 394 (47); 392 (23, M); 382 (11); 381 (60); 379 (100); 377 (50, M – CH$_3$); 369 (22); 365 (11); 355 (12); 353 (19); 315 (41); 313 (37); 285 (15); 272 (18); 271 (11); 270 (15); 233 (10); 207 (12); 203 (13); 191 (13); 151 (17); 109 (17); 107 (12); 53 (10). IR (neat): 3093 (w); 3049 (m); 2941 (s); 2911 (m); 2847 (w); 1598 (w); 1494 (m); 1401 (s); 1319 (m); 1251 (s); 1209 (s); 1078 (s); 997 (s); 953 (s); 899 (m); 847 (m); 827 (m); 787 (s); 770 (s); 727 (s); 701 (s); 658 (m).

4.2.13. Bis[5-(2-bromothienyl)]methylphenylsilane

Yield, 65%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^{1}H NMR (CDCl$_3$): δ 0.95 (s, 3H, SiMe); 7.14 (d, 2H, J^3 = 3.5 Hz, thienylene protons); 7.19 (d, 2H, J^3 = 3.5 Hz, thienylene protons); 7.49 (m, 3H, phenyl protons); 7.66 (m, 2H, phenyl protons). ^{13}C NMR (CDCl$_3$): δ – 3.4 (P); 119.2 (Q); 128.3 (T); 130.5 (T); 131.7 (T); 134.6 (T); 134.8 (T); 137.6 (Q); 137.8 (Q). ^{29}Si NMR (CDCl$_3$): δ – 20.31. MS m/z (rel. intensity): 446 (15); 444 (44); 442 (13, M); 431 (43); 429 (100); 427 (35, M – CH$_3$). IR (neat): 3061 (w); 3038 (w); 2949 (w); 1493 (w); 1401 (m); 1321 (w); 1250 (m); 1211 (m); 1101 (m); 1067 (m); 996 (m); 961 (s); 843 (w); 799 (s); 777 (s); 758 (s); 737 (s); 706 (m).

4.2.14. 1,2-Bis[5-(2-bromothienyl)]dimethylsilylethane

Yield, 63%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent. ^{1}H NMR (CDCl$_3$): δ 0.32 (s, 12H, SiMe$_2$); 0.72

(s, 4H, SiCH$_2$); 6.98 (d, 2H, J^3 = 3.5 Hz, thienylene protons); 7.10 (d, 2H, J^3 = 3.5 Hz, thienylene protons). ^{13}C NMR (CDCl$_3$): δ – 2.1 (P); 8.6 (S); 116.9 (Q); 131.1 (T); 134.6 (T); 141.6 (Q). ^{29}Si NMR (CDCl3): δ – 4.94. MS m/z (rel. intensity, %): 470 (1.2); 468 (2.0); 466 (0.8, M); 455 (4); 453 (6); 451 (3, M – CH$_3$); 389 (16); 387 (11); 361 (24); 359 (20); 306 (7); 225 (13); 221 (100); 219 (91); 139 (32); 137 (33); 43 (10); 28 (30). IR (neat): 3094(w); 3029 (w); 2948 (s); 2891 (w); 2779 (w); 1491 (w); 1401 (s); 1321 (w); 1247 (s); 1211 (s); 1129 (s); 1077 (s); 989 (s); 979 (s); 953 (s); 899 (m); 848 (s); 832 (s); 807 (s); 785 (s); 728 (w); 699 (s). Anal. Found: C, 35.97; H, 4.51; S, 13.22. C$_{14}$H$_{20}$Br$_2$S$_2$Si$_2$. Calc.: C, 36.05; H, 4.29; S, 13.46%.

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