ELSEVIER

Journal of Organometallic Chemistry 570 (1998) 147–154

Journal of Organometallic Chemistry

High-yield electrosynthesis of furylchlorosilanes, silyl and silanylene furans

Carole Moreau, Françoise Serein-Spirau, Michel Bordeau *, Claude Biran

Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux I, F-33405 Talence, France

Received 2 July 1998

Abstract

The intensiostatic sacrificial anode technique proved to be efficient for the silylation of 2-bromo- and 2,5-dibromofurans with trimethylchlorosilane and diorganodichlorosilanes with high selectivity and versatility not accessible by pure chemical routes. Furylsilanes, bromofurylsilanes, bis(furyl)silanes, bis(bromofuryl)silanes, furylchlorosilanes, bis(silyl and chlorosilyl)furans, poly[(silanylene)furylene] oligomers and [1_4]dimethylsila-2,5-furanocalixarene were obtained in good to high yields. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Furylsilanes; Furylchlorosilanes; Bromide; Electrochemical synthesis; Sacrificial anode

1. Introduction

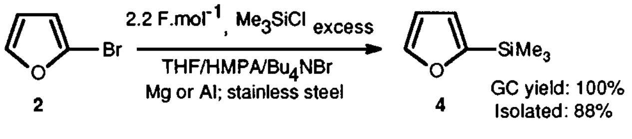
Alkoxysilanes, silylfurans and particularly 2-trimethylsilylfuran have been shown to be useful in obtaining high isotactic polypropylene by Ziegler–Natta catalysed propene polymerization [1]. Trimethylsilylated derivatives of furans are generally obtained in only 50–60% yield from furan either by metallation with *n*-butyllithium [2] or by activation of the 2-C–H bond with calcium [3], followed by reaction with trimethylchlorosilane.

Here we report how the electrochemical sacrificial anode technique enables to prepare various organosilicon derivatives of furan (**1**) from 2-bromo- (**2**), and 2,5-dibromofuran (**3**) not commercially available, but previously prepared by bromination of furan by Br_2 in dimethylformamide (DMF) [4]. The method used involves cathodic reduction of one or two carbon–bromine bonds in the substrate in the presence of a mono- or a dichlorosilane as the electrophile at constant current density ($i = 0.1$ A, $j = 0.1 \pm 0.05$ A dm^{-2}). The electrolysis is carried out at r.t. in an undivided cell using a cylindrical stainless steel grid as the cathode, a massive metallic Mg or Al rod as the anode, tetrahydrofuran/hexamethylphosphoramide (THF/HMPA, 70:10 vol) as the solvent and 0.02 M Bu_4NBr as the supporting electrolyte [5,6].

2. Results and discussion

2.1. Cyclic voltammetry study

A cyclic voltammetry study of the starting furan bromo derivatives was performed under the usual conditions [6], i.e. THF 0.1 M Bu_4NBF_4, at a 1 mm diameter Pt disk (sweep rate, 0.2 V s^{-1}; voltage scan 0/1.0/−2.93/0 V). The measured reduction peak poten-

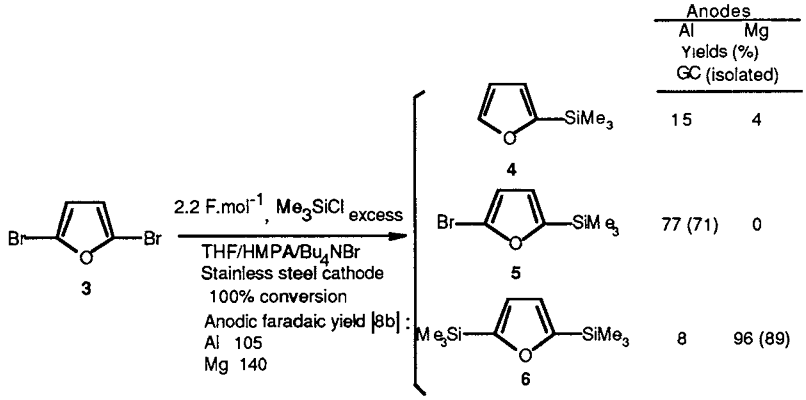


Scheme 1.

---

* Corresponding author. Tel.: +33 556 846281; fax: +33 556 846646.

PII S0022-328X(98)00853-5



Scheme 2.

tials vs. SCE were: −2.10 and −2.60 V for **2** and −1.95, −2.1, and −2.60 V for **3**. For both compounds the last peak recorded at −2.6 V, present as well in the voltammogram of **1** can be assigned to the ring reduction. The first peaks corresponding to reduction of C–Br bonds are less cathodic than the first reduction peak of the mono-and dichlorosilanes used in this work [7]. Thus, furan bromides are expected to be first reduced in the electrochemical process.

2.2. *Reductive electrotrimethylsilylation of bromofurans*

2-Trimethylsilylfuran (**4**) was isolated in 88% yield after the passage of 2.2 F mol^{-1} of charge with either an aluminium or a magnesium anode, using a large excess (20 equivalents) of trimethylchlorosilane compared to engaged **2** (Scheme 1, [8]a).

Under the same conditions, at 2.2 F mol^{-1}, the electrotrimethylsilylation of **3** led, after 100% conversion, to three products which distribution depended on the nature of the anodic metal (Scheme 2).

With an aluminium anode, the main product, as expected for this charge, is 2-bromo-5-trimethylsilylfuran (**5**) (71% isolated) in spite of 15% of protonated product **4**, and 8% of bis(trimethylsilyl)furan (**6**). With a magnesium anode, the disilylated product **6** was mainly obtained (89% isolated), likely due to a chemical reductive role of the anodically scoured magnesium revealed by the abnormally high anodic faradaic yield (140%). Chemical routes only enabled the preparation of **4** in 57% yield from furan using BuLi/Me$_3$SiCl at low temperature and the synthesis of **6** from **4** in 31% yield by the same reaction ([2]b).

When pursuing the electrolysis of **3** with an Al anode from 2.2 up to 4.4 F mol^{-1}, **3** was exhausted and the reduction of the C–Br bond of **5** in the presence of Me$_3$SiCl in excess was expected to give rise to **6**. In fact, **6** was not the final product and the major formation of **4** (Table 1) was assigned to further reduction of one C$_{\text{furyl}}$–Si bond of **6**. Similarly, using a Mg anode, **6** previously formed quantitatively at 2.2 F mol^{-1}, was partially transformed in **4** at 4.4 F mol^{-1}. This ability of C$_{\text{furyl}}$–Si bonds to be reduced was confirmed by cyclic voltammetry measurements under the above conditions. Peaks were effectively observed at −2.47 V for **5** and −2.55 V vs. SCE for **6**.

Thus, under these conditions, the cleavage of the C$_{\text{furyl}}$–Si bond is favoured relative to the reductive silylation of the furyl ring that is in agreement with the good leaving group ability of the furyl anion in nucleophilic substitutions [9]. The reductive cleavage of carbon–silicon bonds was yet pointed out in the electrochemical reduction of 2,5-dibromothiophene in the presence of dimethyldichlorosilane [10]. Taking into account that Me$_3$SiH was isolated and characterized and that protonation can occur from the solvent or the supporting electrolyte, the proposed mechanism for the formation of **4** is depicted in Scheme 3.

2.3. *Electroreductive coupling of bromofurans with dichlorosilanes*

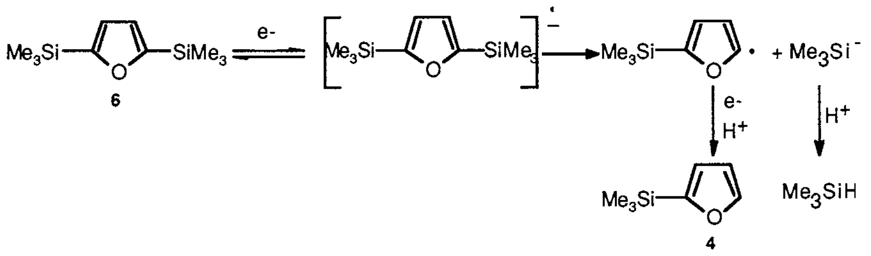
The use of dichlorodiorganosilanes as silylating agents enables the access to furylchlorosilanes and to compounds containing regularly alternated 2-furylene/diorganosilylene units.

2.3.1. *Electroreductive coupling of 2-bromofuran with diorganodichlorosilanes*

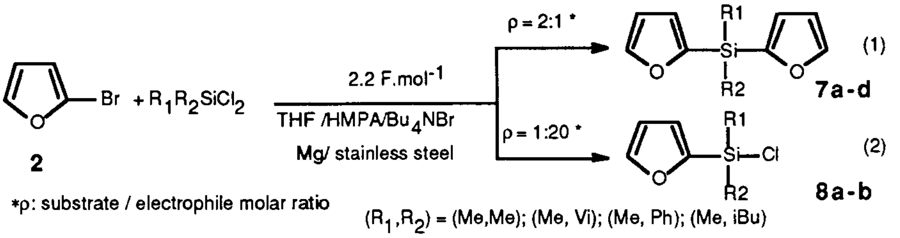
After passage of 2.2 F mol^{-1} of **2**, using a magnesium anode, the products of the electroreductive cou-

Table 1
Influence of the anode nature on the electrotrimethylsilylation of 2,5-dibromofuran after having passed 4.4 F mol^{-1}

Anodes	**4** Yield (%)		**5** Yield (%)	**6** Yield (%)	
	GC	Isolated	GC	GC	Isolated
Al	52	41	20	28	—
Mg	48	37	—	52	43



Scheme 3.



Scheme 4.

Table 2
Electrochemical preparation of bis(2-furyl)silanes and (2-furyl)chlorosilanes

$R_1R_2SiCl_2$	Substrate/electrophile molar ratio	Product obtained		Yields (%)	
				GC	Isolated
Me_2SiCl_2	2:1	Bis(2-furyl)dimethylsilane	**7a**	100	98
	1:20	(2-Furyl)dimethylchlorosilane	**8a**	96	87
$MeViSiCl_2$	2:1	Bis(2-furyl)methylvinylsilane	**7b**	100	96
$PhMeSiCl_2$	2:1	Bis(2-furyl)methylphenylsilane	**7c**	100	94
	1:20	(2-Furyl)methylphenylchlorosilane	**8b**	98	85
$^iBuMeSiCl_2$	2:1	Bis(2-furyl)methylisobutylsilane	**7d**	100	95

pling with dichlorodiorganosilanes were dependent upon the molar ratio of the engaged reagents.

First, 2:1 substrate/$R_1R_2SiCl_2$ molar ratio led to the expected bis(2-furyl)diorganosilanes (**7a**–**d**) (Scheme 4, Eq. 1) with a complete conversion of **2** and an excellent yield of isolated product (Table 2). Chemical routes involved addition of dimethyldichlorosilane on furyllithium at − 10°C to obtain 45% yield of **7a** [2]b. Thus, under these conditions a variety of bis(2-furyl)silanes **7a**–**d** were prepared in 95–98% yields, including new compounds.

Second, when dichlorodiorganosilanes were used in large excess (20 equivalents), **2** underwent solely and quantitatively a monocoupling reaction leading selectively to the corresponding diorganofurylchlorosilanes (**8a**–**b**) (Scheme 4, Eq. 2), showing that these products result from the first step of the previous reaction, as expected. **8a**–**b** were thus isolated in high yield (85–87%, Table 2). These compounds are particularly sought after to reach bicyclopropylidene derivatives which undergo clean intramolecular Diels–Alder reactions with complete *endo*-diastereoselectivities under suitable experimental conditions [11]. **8a** was previously chemically synthetised by the usual method in only 60% yield [11], while **8b** was not yet described.

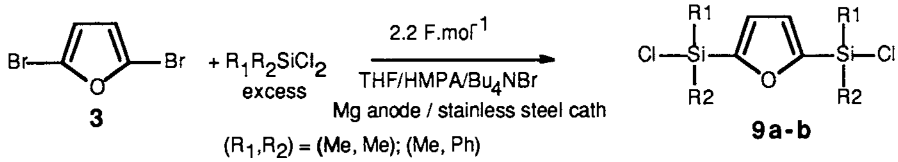
2.3.2. Electroreductive coupling of 2,5-dibromofuran with diorganodichlorosilanes

As electrotrimethylsilylation of **3** led directly to disilylated **6** for only 2.2 F mol^{-1} of charge using a Mg anode, we got bis(diorganochlorosilyl)furans (**9a**–**b**) with excellent selectivities and isolated yields under the same conditions: 2.2 F per mole of **3**, diorganodichlorosilanes in large excess (20 equivalents) (Scheme 5 and Table 3). The anodic faradaic yield of 165% revealed a chemical participation of the anodic metal inducing reduction of the two C–Br bonds of **3**.

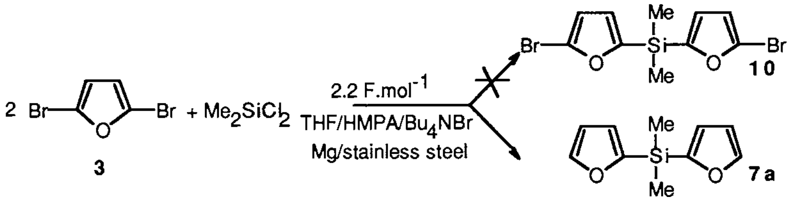
These results constitute a real improvement of the common chemical routes involving two steps and the use of expensive (Pd catalysts) [24] or dangerous reagents as benzoyle peroxide [23]. The yields are better and our electrochemical technique is a good alternative to prepare these compounds which are key intermediates in the synthesis of highly conducting poly[2,5-bis-

Table 3
Electrochemical reduction of 2,5-dibromofuran in the presence of a large excess of dichlorosilane after having passed 2.2 F mol^{-1} of substrate

$R_1R_2SiCl_2$	Product obtained		Yield (%)		Chemical route (%)
			GC	Isolated	
Me_2SiCl_2	2,5-Bis(dimethylchlorosilyl)furan	**9a**	98	76	29 [23]
$PhMeSiCl_2$	2,5-Bis(methylphenylchlorosilyl)furan	**9b**	96	64	52 [24]



Scheme 5.



Scheme 6.

(dimethylsilyl)]furan and poly[2,5-bis(methylphenylsilyl)]furan films ($\sigma = 0.057$ S cm^{-1}) [24] after treatment with antimony pentafluoride vapor.

In order to synthesize longer oligomers regularly alternating furylene and dimethylsilanylene units, the electrocoupling of **3** with Me_2SiCl_2 in a substrate/electrophile molar ratio of 2:1 was envisaged. Under the same other electrolytic conditions, using a magnesium anode, the sole product was, after 2.2 F mol^{-1} of charge passed, not the expected bis[5-(2-bromofuryl)]dimethyl silane (**10**), but the corresponding hydrogenated compound **7a** in quantitative GC and 75% isolated yields (Scheme 6).

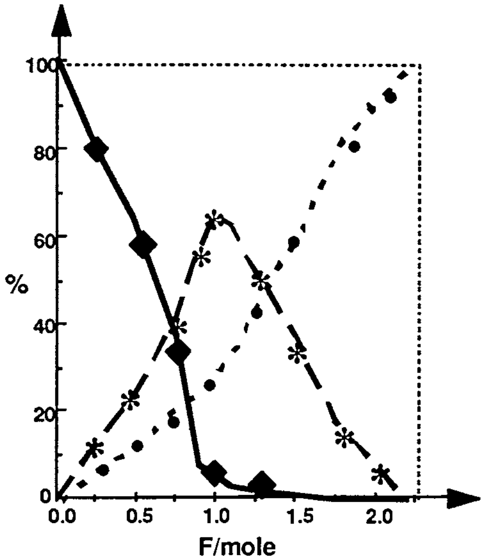


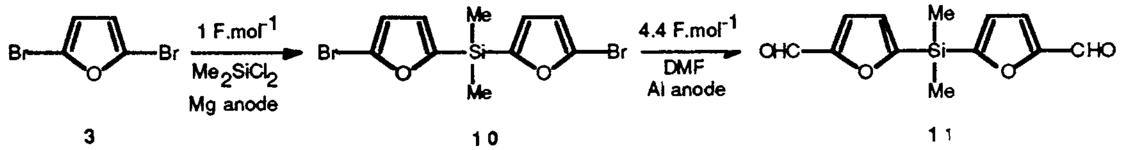
Fig. 1. Dynamic GC analysis of 2,5-dibromofuran (**3**) and Me_2SiCl_2 electrocoupling.

According to previous analog results concerning the electrochemical coupling of 2,5-dibromothiophene with Me_2SiCl_2 under exactly the same experimental conditions ([6]c), the electrochemical coupling of **3** was attempted with an aluminium anode to avoid the H-ended product **7a**, but only 7% of **3** were converted.

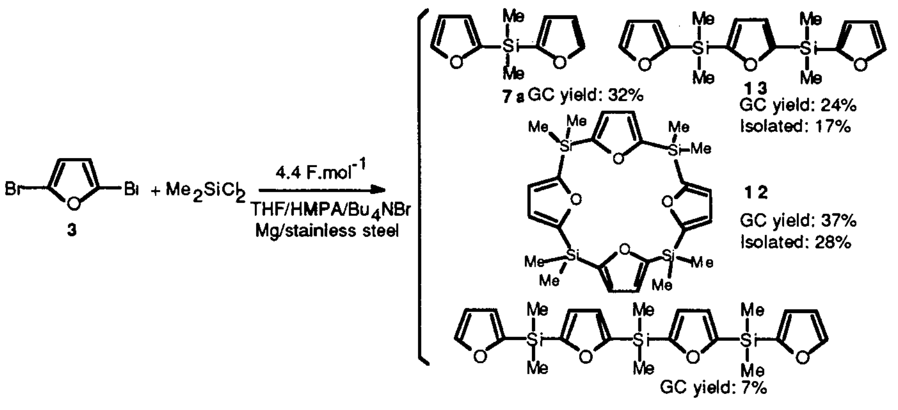
Then, despite the loss of the terminal bromine atoms, the electrochemical reaction involving a sacrificial magnesium anode was studied more precisely by dynamic gas chromatography throughout the electrolysis. Fig. 1 shows that during the passage of 2.2 F mol^{-1} of charge, **10** is effectively formed at the beginning of the electrolysis up to 63% at 1.0 F mol^{-1} to finally lead to **7a**. From the beginning of the reaction, the formation of **10** and **7a** are competitive. For a charge of 1 F per mole of **3**, the substrate conversion was almost 95% and the anodic faradaic yield of 140% revealed the chemical reductive role of the anodically scoured magnesium. At 2.2 F mol^{-1}, the two C–Br bonds of **10** have been reduced to lead to **7a**.

In order to isolate not yet described **10**, the electrolysis was stopped at 1 F mol^{-1} and a yield of 59% in isolated product was obtained.

The reduction of **10** in DMF using an aluminium anode and 4.4 F mol^{-1} of charge gave rise to bis[2-(5-formylfuryl)]dimethylsilane **11** in 83% isolated yield, both C–Br bonds being hydroformylated under conditions described elsewhere ([12], Scheme 7). **11** is sought



Scheme 7.



Scheme 8.

after as an intermediate in the synthesis of macrocycles [13] but chemical routes enable to reach **11** in only 4% isolated yield.

Knowing that at 4.4 F per mol of substrate, with a substrate /Me$_2$SiCl$_2$ molar ratio = 1:1 we succeeded in the synthesis of [1$_4$]dimethylsila-2,5-(1-methyl)pyrrolocalixarene [14], the electrochemical reduction of **3** was envisaged under these operating conditions in order to attempt the synthesis of the analogous cyclic [1$_4$]dimethylsila-2,5-furanocalixarene (**12**). **12** was effectively formed in 37% GC yield and isolated in 28% from a mixture of linear interesting alternating silanylene-furylene unit oligomers which are: **7a** (GC yield 32%), not yet described 2,5-bis[(2′-furyl)-dimethylsilyl)]furan (**13**) (GC yield 24%, isolated 17%) and bis{5-[(2′furyl)dimethylsilyl]2-furylene}dimethylsilane (**14**) (GC yield 7%) identified by GC/MS analysis (Scheme 8).

The sacrificial anode method enabled to greatly improve the preparation of **12** previously synthesized in 2% yield by reaction of dilithiofuran with Me$_2$SiCl$_2$ [15] and optimized only in 16% yield by treatment of **1** with two equivalents of ^{n}BuLi/TMEDA/tBuOK in hexane followed by slow addition of dimethyldichlorosilane [16]. Such sila-macrocyclic oligomer, particularly sought after because of the new binding properties due to the silicon atoms compared to analogous structures having only carbon as bridging element, has proved its efficiency as a receptor for membrane transport of metal ions: compared to other silicon bridged macrocycles, **12** was the most performant and selective to extract Hg^{2+} ions from aqueous solutions [17].

3. Conclusion

We have achieved a successful electrochemical alternative to the use of lithio derivatives to prepare with high selectivities and yields several silylated furyl derivatives. The method also allowed to obtain a variety of bis(2-furyl)silanes, furyl chlorosilanes, bis[5-(2-bromofuryl)]dimethylsilane, and longer linear alternating silanylene-furylene oligomers and to improve bis[(5-formyl-2-furyl)]dimethylsilane and [1$_4$]dimethylsila-2,5-furanocalixarene synthesis.

4. Experimental section

4.1. General methods

Gas chromatography was performed with a temperature-programable Hewlett Packard 5890A apparatus equipped with a 25 m × 0.25 µm CP-Sil 5CB capillary column. ^{1}H-NMR spectra were recorded in CDCl$_3$ at 250 MHz on a Bruker AC 250 spectrometer, using residual CHCl$_3$ ($\delta = 7.27$ ppm) as the internal standard. ^{13}C-NMR spectra were obtained at 62.86 MHz using a Bruker AC 250 using CDCl$_3$ ($\delta = 77.70$ ppm) as the internal standard. ^{29}Si-NMR spectra were recorded in CDCl$_3$ at 39.73 MHz on a Bruker AC 200 spectrometer. Electron impact mass spectra were measured at 70 eV on a VG Micromass 16F mass spectrometer coupled with a gas chromatograph equipped with a 25 m × 0.25 µm CP-Sil 5CB capillary column. IR spectra were recorded with a Perkin-Elmer 1420 Spectrophotometer with pure liquid films (NaCl or KBr plates). Elemental analyses were performed by the Service Central de Microanalyse du CNRS (France).

4.2. Voltammetry

Cyclic voltammetry was carried out under argon in THF (20 ml) solutions containing the substrate (2 mM) and 0.1 M Bu_4NBF_4, using a 1 mm diameter Pt or glassy carbon disk as the working electrode and an aqueous saturated calomel reference electrode (Tacussel XR 110) separated from the medium by a Tacussel AL 120 junction filled with the same electrolytic solution. For measurements with a Pt disk working electrode, ferrocene (10^{-3} M) was used as the internal standard ($E_{pa} = 0.63$ V, $E_{pc} = 0.56$ V). The solution resistance was compensated for with a positive feedback device. The potentiostat used (Sirius) was previously described ([6]a). The sweep rate was 0.2 V s^{-1}, and the voltage scan 0/1.0/−3/0 V.

4.3. General procedure for electrolysis

Electrolysis was performed in an undivided cell (100 ml) described elsewhere ([6]a), equipped with a sacrificial cylindrical aluminium or magnesium bar (1 cm diameter) as the anode and a concentric stainless steel grid or carbon (1.0 ± 0.2 dm^2) as the cathode. A constant current (0.1 A, density 0.1 ± 0.05 A dm^{-2}) was provided by a Sodilec EDL 36-07 regulated dc power supply. To the dried cell, containing a magnetic spin bar, was added Bu_4NBr (0.5 g, 1.6 mmol) as the supporting electrolyte. The cell then was deaerated twice under vacuum and flushed with dry nitrogen. THF (70 ml), HMPA (6 ml), and a minimum excess of trimethylchlorosilane just sufficient for drying the medium (generally between 1 and 1.5 ml) were introduced through a septum by syringe. The solution was degassed by bubbling nitrogen for 10 min. The resulting HCl (from the reaction of Me_3SiCl with traces of water) was removed by pre-electrolyzing the solution ($i = 0.1$ A). The formed Me_6Si_2O is electrochemically inert. When evolution of H_2 had ceased, the substrate (20 mmol) and the suitable chlorosilane (10 mmol) for the synthesis of **7**, **10**, **12**, **13**, and **14**, or 400 mmol for the synthesis of **4**, **5**, **6**, **8** and **9** 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 addition of anhydrous pentane (2 × 50 ml) and subsequent filtration, solvents and excess of di- or trichlorosilane were evaporated. The crude product was analyzed by GC and then distilled under vacuum or eluted with pentane on a silica gel column.

4.4. Materials

Bu_4NBr (Aldrich) was used without purification. THF (SDS) and HMPA (Aldrich) were dried by distillation over sodium benzophenone ketyl and CaH_2, respectively, while dichlorosilanes were distilled over Mg powder just before use. Bromine, furan (Aldrich) and DMF (SDS) were used without any treatment. Brominated derivatives of furan **2** and **3** were preliminary prepared as described in the literature [4].

4.4.1. 2-Trimethylsilylfuran (4)

RN 1578-33-2; Yield 88%; b.p. 58°C/20 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.33 (s, 9H, $SiMe_3$), 6.42 (m, 1H, CH_{furyl}), 6.67 (d, 1H, $^3J = 3.2$, CH_{furyl}), 7.68 (d, 1H, $^3J = 3.2$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ −1.6 ($SiMe_3$), 109.4 (T), 119.5 (T), 146.6 (T), 161.9 (Q); ^{29}Si-NMR ($CDCl_3$): δ −10.58; IR (neat KBr): 2965, 2906, 1257, 1203, 1147, 1106, 1005, 899, 845, 748. The spectral data agree with those reported in the literature [18].

4.4.2. 2-(Trimethylsilyl)-5-bromofuran (5)

RN 119987-27-8; Yield 71%; b.p. 77°C/20 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 6.28 (d, 1H, $^3J = 3.1$, CH_{furyl}), 6.58 (d, 1H, $^3J = 3.1$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ −1.7 ($SiMe_3$), 110.9 (T), 119.2 (Q), 122.1 (T), 164.2 (Q); ^{29}Si-NMR ($CDCl_3$): δ −9.91; MS m/z (rel. intensity, %): 220 (38), 218 (37, M), 205 (99), 203 (100, M-CH_3), 139 (49), 137 (48), 73 (24), 43 (22); IR (neat NaCl): 2960, 2899, 1552, 1456, 1408, 1314, 1251, 1186, 1128, 1090, 1008, 925, 842, 782, 757, 699, 631. The spectral data agree with those reported in the literature [19].

4.4.3. 2,5-Bis(trimethylsilyl)furan (6)

RN 1578-29-6; Yield 89%; b.p. 43°C/1 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.32 (s, 18H, $SiMe_3$), 6.66 (s, 2H, $^3J = 3.1$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ −1.4 ($SiMe_3$), 119.6 (T), 164.9 (Q); ^{29}Si-NMR ($CDCl_3$): δ −10.74; MS m/z (rel. intensity, %): 212 (41, M), 197 (61, M-CH_3), 147 (100), 73 (23); IR (neat NaCl): 2959, 2899, 1538, 1456, 1407, 1295, 1250, 1172, 1126, 1093, 1011, 926, 840, 791, 757, 698, 632. The spectral data agree with those reported in the literature [13,18,20,21].

4.4.4. Bis(2-furyl)dimethylsilane (7a)

RN 1578-44-5; Yield 98%; b.p. 107°C/20 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.27 (s, 6H, $SiMe_2$), 6.14 (m, 2H, CH_{furyl}), 6.42 (d, 2H, CH_{furyl}),7.39 (s, 2H, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ −3.5 ($SiMe_2$), 109.4 (T), 121.1(T), 147.0 (T), 156.5 (Q); ^{29}Si-NMR ($CDCl_3$): δ −23.79; MS m/z (rel. intensity, %): 192 (55, M), 178 (16), 177 (100, M-CH_3), 151 (20), 149 (42), 95 (12), 45 (15), 43 (17); IR (neat NaCl): 2939, 1541, 1438, 1345, 1248, 1202, 1145, 1106, 1071, 1004, 895, 854, 827, 805, 768, 742, 671. The spectral data agree with those reported in the literature [9]b, [18].

4.4.5. *Bis(2-furyl)methylvinylsilane* (**7b**)

RN 10447-98-0; Yield 96%; b.p. 64°C/0.5 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.38 (s, 3H, SiMe), 5.52-5.98 (m, 3H, SiVi), 6.04 (m, 2H, CH_{furyl}), 6.54 (m, 2H, CH_{furyl}), 7.38 (m, 2H, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.2 (SiMe), 109.4 (T), 124.3 (T), 132.9 (T), 135.5 (S), 147.4 (T), 155.8 (Q); MS m/z (rel. intensity, %): 204 (42, M), 189 (100, M-CH_3), 163 (18), 161 (37); IR (neat NaCl) 2945, 1543, 1450, 1409, 1360, 1251, 1203, 1148, 1109, 1069, 1005, 895, 860, 830, 805, 770, 742, 672. The spectral data agree with those reported in the literature [22].

4.4.6. *Bis(2-furyl)methylphenylsilane* (**7c**)

Yield 94%; b.p. 151°C/3 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.70 (s, 3H, SiMe), 6.22 (m, 2H, CH_{furyl}), 6.63 (d, 2H, $^{3}J = 3.3$, CH_{furyl}), 7.19 (m, 3H, CH_{phenyl}), 7.47 (m, 2H, CH_{phenyl}), 7.53 (d, 2H, $^{3}J = 1.5$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.4 (SiMe), 109.7 (T), 123.1 (T), 128.0 (T), 130.0 (T), 133.9 (Q), 134.7 (T), 147.8 (T), 155.0 (Q); ^{29}Si-NMR ($CDCl_3$): δ -23.79; MS m/z (rel. intensity, %): 254 (96, M), 239 (100, M-CH_3), 213 (16), 211 (12), 178 (11), 165 (12), 115 (12), 105 (25), 55 (11), 45 (14); IR (neat NaCl): 3100, 3059, 3039, 2950, 1551, 1452, 1431, 1364, 1257, 1209, 1151, 1118, 1011, 900, 887, 791, 750, 730, 703, 691. Anal. Found: C, 69.97; H, 5.46; O, 12.46. $C_{15}H_{14}O_2Si$. Calc.: C, 70.86; H, 5.51; O, 12.59%.

4.4.7. *Bis(2-furyl)isobutylmethylsilane* (**7d**)

Yield 95%; b.p. 82°C/1 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.33 (s, 3H, SiMe), 0.72(d, 6H, $(CH_3)_2$), 0.82 (d, 2H, CH_2), 1.70 (m, 1H, CH), 6.11 (m, 2H, CH_{furyl}), 6.27 (d, 2H, $^{3}J = 3.3$, CH_{furyl}), 7.39 (d, 2H, $^{3}J = 1.5$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.5 (SiMe), 23.9 (S), 24.0 (T), 25.9 (P), 109.4 (T), 121.4 (T), 147.0 (T), 156.2 (Q); MS m/z (rel. intensity, %) 234 (27, M), 177 (100, M-^{i}Bu), 163 (11), 152 (41), 95 (16); IR (neat NaCl): 2948, 1541, 1448, 1407, 1250, 1203, 1146, 1107, 1079, 1004, 892, 860, 827, 805, 767, 741, 671. Anal. Found: C, 66.43; H, 7.52; O, 13.54. $C_{13}H_{18}O_2Si$. Calc.: C, 66.66; H, 7.69; O, 13.67%.

4.4.8. *(2-Furyl)dimethylchlorosilane* (**8a**)

Yield 87%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; ^{1}H-NMR ($CDCl_3$): δ 0.70 (s, 6H, $SiMe_2$), 6.22 (m, 1H, CH_{furyl}), 6.63 (d, 1H, $^{3}J = 3.3$, CH_{furyl}), 7.53 (d, 1H, $^{3}J = 1.5$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.4 ($SiMe_2$), 109.7 (T), 123.1 (T),147.8 (T), 155.0 (Q); MS m/z (rel. intensity, %): 162 (8), 160 (24, M), 147 (45), 145 (100, M-CH_3); IR (neat NaCl): 2935, 1540, 1435, 1347, 1244, 1200, 1140, 1111, 1070, 1003, 894, 854, 826, 803, 768, 742, 677. Anal. Found: C, 44.89; H, 5.56; O, 9.86. C_6H_9ClOSi. Calc.: C, 45.0; H, 5.62; O, 10.0%. The spectral data agree with those reported in the literature [11].

4.4.9. *(2-Furyl)methylphenylchlorosilane* (**8b**)

Yield 85%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; ^{1}H-NMR ($CDCl_3$): δ 0.70 (s, 6H, $SiMe_2$), 6.22 (m, 1H, CH_{furyl}), 6.63 (d, 1H, $^{3}J = 3.3$, CH_{furyl}), 7.21 (m, 3H, CH_{phenyl}) 7.45 (m, 2H, CH_{phenyl}), 7.53 (d, 1H, $^{3}J = 1.5$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.2 (SiMe), 109.9 (T), 123.4 (T), 128.0 (T), 130.2 (T), 133.8 (Q), 134.5 (T), 147.4 (T), 155.1(Q); MS m/z (rel. intensity, %): 224 (13), 222 (31, M), 209 (39), 207 (100, M-CH_3); IR (neat NaCl): 2930, 1541, 1436, 1342, 1250, 1200, 1140, 1109, 1001, 896, 854, 825, 803, 765, 739. Anal. Found: C, 59.32; H, 4.83; O, 7.15. $C_{11}H_{11}ClOSi$. Calc.: C, 59.45; H, 4.95; O, 7.20%.

4.4.10. *2,5-Bis(dimethylchlorosilyl)furan* (**9a**)

RN 125490-59-7; Yield 76%; b.p. 85°C/1 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.70 (s, 12H, $SiMe_2$), 6.22 (s, 2H, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -4.4 ($SiMe_2$), 123.1 (T), 155.0 (Q); ^{29}Si-NMR ($CDCl_3$) δ 9.61; MS m/z (rel. intensity, %): 256 (5), 255 (3), 254 (20), 253 (5), 252 (31, M), 239 (17), 237 (25, M-CH_3); IR (neat NaCl): 2963, 1540, 1454, 1405, 1261, 1175, 1068, 927, 806, 748, 681, 602. The spectral data agree with those reported in the literature [23].

4.4.11. *2,5-Bis(methylphenylchlorosilyl)furan* (**9b**)

RN 129669-64-3; Yield 64%; b.p. 147°C/0.1 mmHg; ^{1}H-NMR ($CDCl_3$): δ 0.90 (s, 6H, $(SiMe)_2$, 6.72 (s, 2H, CH_{furyl}), 7.05–7.72 (m, 10H, CH_{phenyl}); ^{13}C-NMR ($CDCl_3$): δ -4.2 (SiMe), 123.1 (T), 128.1 (T), 130.8 (T), 133.1 (T), 133.2 (Q), 155.3 (Q); IR (neat NaCl): 2960, 1539, 1403, 1259, 1175, 1065, 927, 803, 748, 678, 600. The spectral data agree with those reported in the literature [24].

4.4.12. *Bis[2-(5-bromofuryl)]dimethylsilane* (**10**)

Yield 59%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; ^{1}H-NMR ($CDCl_3$): δ 0.32 (s, 6H, $SiMe_2$), 6.31 (d, 1H, $^{3}J = 3.1$, CH_{furyl}), 6.60 (d, 1H, $^{3}J = 3.1$, CH_{furyl}); ^{13}C-NMR ($CDCl_3$): δ -3.9 ($SiMe_2$) 119.1 (Q), 110.5 (T), 122.2 (T), 157.8 (Q); MS m/z (rel. intensity, %): 352 (15), 350 (44, M), 348 (14), 337 (43), 335 (100), 333 (36, M-CH_3); IR (neat NaCl): 2958, 1550, 1458, 1315, 1250, 1188, 1124, 1090, 1009, 925, 841, 782, 757, 631. Anal. Found: C, 34.33; H, 2.97; O, 9.21. $C_{10}H_{10}Br_2O_2Si$. Calc.: C, 34.28; H, 2.85; O, 9.14%.

4.4.13. *Bis[2-(5-formylfuryl]dimethylsilane* (**11**)

Yield 83%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; F. 53°C; ^{1}H-NMR ($CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 6.72 (d, 2H, $^{3}J = 3.1$, CH_{furyl}), 7.18 (d, 2H, $^{3}J = 3.1$, CH_{furyl}), 9.59 (s, 2H, CHO); ^{13}C-NMR ($CDCl_3$): δ -3.5 ($SiMe_2$), 119.9 (T), 123.6 (T), 157.4

(Q), 161.8 (Q), 178.0 (T); ^{29}Si-NMR (CDCl$_3$): δ -20.5; MS m/z (rel. intensity, %): 248 (100, M); IR (neat NaCl): 2943, 1690, 1538, 1438, 1345, 1248, 1200, 1145, 1003, 894, 854, 827, 811, 757, 743. The spectral data agree with those reported in the literature [13].

4.4.14. *[1$_4$]Dimethylsila-2,5-furanocalixarene* (**12**)

RN 145593-24-4; Yield 37%; F. 115°C; ^{1}H-NMR (CDCl$_3$): δ 0.53 (s, 24H, SiMe$_2$), 6.65 (s, 8H, CH$_{furyl}$); ^{13}C-NMR (CDCl$_3$): δ -3.2 (SiMe$_2$), 120.4 (T), 161.2 (Q); MS m/z (rel. intensity, %): 496 (100, M); IR (neat NaCl): 2941, 1540, 1441, 1343, 1250, 1200, 1105, 1001, 895, 824, 802, 768, 742. The spectral data agree with those reported in the literature [16].

4.4.15. *2,5-Bis[(2′-furyl)dimethylsilyl]furan* (**13**)

Yield 17%; this compound was directly purified by silica-gel column chromatography, with pentane as the eluent; ^{1}H-NMR (CDCl$_3$): δ 0.47 (s, 12H, SiMe$_2$), 6.32 (m, 2H, CH$_{furyl}$), 6.63 (m, 4H, CH$_{furyl}$), 7.60 (m, 2H, CH$_{furyl}$); ^{13}C-NMR (CDCl$_3$): δ -3 (SiMe$_2$), 109.7 (T), 119.7 (T), 121.1 (T), 121.3 (T), 146.8 (Q), 147.1 (Q); MS m/z (rel. intensity, %): 316 (39, M), 301 (100, M-CH$_3$), 45 (25), 43 (33); IR (neat NaCl): 2944, 1539, 1425, 1331, 1245, 1201, 1002, 887, 824, 789, 721. Anal. Found: C, 60.82; H, 6.41; O, 15.23. $C_{16}H_{20}O_3Si_2$. Calc.: C, 60.75; H, 6.32; O, 15.18%.

Acknowledgements

C.N.R.S., Ministère de l'Education Nationale and Conseil Régional d'Aquitaine are warmly acknowledged for their financial support.

References

[1] M. Härkonen, J.V. Seppälä, Makromol. Chem. 192 (1991) 2857.

[2] (a) R.A. Benkeser, R.B. Currie, J. Am. Chem. Soc. 7 (1948) 1780. (b) E. Ya. Lukevics, M.G. Voronkov, Khim. Geterotsikl. Soed. 1 (1965) 31.

[3] K. Mochida, K. Kojima, Y. Yoshida, Bull. Chem. Soc. Jpn. 60 (1987) 2255.

[4] M.A. Keegstra, A.J.A. Klomp, L. Brandsma, Synth. Commun. 20 (1990) 3371.

[5] J. Chaussard, J.C. Folest, J.Y. Nédelec, J. Périchon, S. Sibille, M. Troupel, Synthesis 5 (1990) 369.

[6] (a) D. Deffieux, M. Bordeau, C. Biran, J. Dunoguès, Organometallics 13 (1994). 2415. (b) D. Deffieux, D. Bonafou, M. Bordeau, C. Biran, J. Dunogués, Organometallics 15 (1996) 2041. (c) C. Moreau, F. Serein-Spirau, M. Bordeau, C. Biran, J. Donogués, J. Organomet. Chem. 522 (1996) 213.

[7] C. Biran, M. Dordeau, D. Bonafoux, D. Deffieux, C. Duprat, V. Jouikov, M.P. Léger-Lambert, C. Moreau, F. Serein-Spirau, J. Chim. Phys. 93 (1996) 591.

[8] (a) It is well known that 2 F mol^{-1} is the theoretical charge to reduce one carbon–halogen bond. See for example: J.M. Savéant, Bull. Soc. Chim. Fr. (1998) 225. (b) The anodic faradaic yield is the amount of metal consumed compared with charge passed: 100% means a pure faradaic process whereas higher values are the result of metal overconsumption due to a by-chemical process.

[9] (a) G. Stork, Pure Appl. Chem. 61 (1989) 439. (b) V. Gevorgyan, L. Borisova, E. Lukevics, J. Organomet. Chem. 441 (1992) 381. (c) D. Labrecque, K.T. Nwe, T.H. Chan, Organometallics 13 (1994) 332. (D) Y. Landais, D. Planchenault, V. Weber, Tetrehedron Lett. 36 (1995) 2987.

[10] C. Moreau, F. Serein-Spirau, C. Biran, M. Bordeau, P. Gerval, Organometallics (1998) in press.

[11] T. Heiner, S.I. Kozhushkov, M. Noltemeyer, T. Haumann, R. Boese, A. de Meijere, Tetrahedron 52 (1996) 12185.

[12] (a) S. Sibille, J. Périchon, J. Chaussard, Synth. Commun. 19 (1989) 2449. (b) C. Saboureau, S. Sibille, M. Troupel, J. Chem. Soc. Chem. Commun. (1989) 855.

[13] E. Lukevics, N.P. Erchak, I. Castro, S. Rosike, I. Mazika, A.P. Gaukhman, J. Popelis, Zh. Obshch. Kim. 54 (1984) 1315.

[14] C. Moreau, F. Serein-Spirau, M. Bordeau, C. Biran. Synth Commun. (1998) in press.

[15] P. Chicart, R.J.P. Corriu, J.J.E. Moreau, F. Garnier, A. Yassar, Inorganic and Organic Polymers with Special Properties, Kluwer, Dordrecht, 1992, p. 179.

[16] B. König, M. Rödel, P. Bubenitschek, P.G. Jones, Angew. Chem. Int. Ed. Engl. 34 (1995) 661.

[17] B. König, M. Rödel, P. Bubenitschek, J. Org. Chem. 60 (1995) 7406.

[18] F.H. Pinkerton, S.F. Thames, J. Heterocycl. Chem. 7 (1970) 747.

[19] P. Bury, G. Hareau, P. Kocienski, D. Dhanak, Tetrahedron 50 (1994) 8793.

[20] C.S. Carmen, G.F. Koser, J. Org. Chem. 48 (1983) 2534.

[21] E. Lukevicks, V.N. Gevorgyan, Y.S. Golgberg, M.V. Shymanska, J. Organomet. Chem. 294 (1985) 163.

[22] E. Lukevics, L.E. Demicheva, N.P. Yerchak, Y. Popelis, Izv. Akad. Nauk. Ser. Khim. 10 (1993) 1784.

[23] H.H. Hong, W.P. Weber, Polym. Bull. 22 (1989) 363.

[24] J. Oshita, D. Kanaya, M. Ishikawa, T. Yamanaka, Chem. Express 5 (1990) 489.