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# Novel radial oligothienyl silanes

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**Abstract**—A series of thiophene-based homologues with a silicon core surrounded by mono-, bi-, terthiophene, and their derivatives with alkylsilyl linkages has been prepared using hydrosilylation and Stille coupling methods.


The chemistry of dendrimers containing silicon as the core started in 1989, when the first dendrimer containing 48 silicon atoms was prepared.[1] Hyperbranched compounds with carbosilane, polysilane, alternating silicon–germanium, carbosilazane, and carbosiloxane cores have been obtained in the last decade.[2] Among the various π-conjugated organic materials[3] for which control of the solid-state characteristics is of utmost importance for industrial applications, there are α-conjugated oligothiophenes and polythiophenes.[4] Various thiophene dendrons and dendrimers have been successfully synthesized by metal-mediated coupling reactions using $Ni(dppp)Cl_2$,[5a] $Pd(PPh_3)_4$,[5b] and $Pd(PPh_3)_2Cl_2$[5b] as catalysts. The study of conjugated thiophene based dendrimers has received special attention because of their nonlinear optical and electronic properties.[5] Recently the first dendrimer containing both silicon atoms and thiophene rings was synthesized from tetra(2-thienyl)silane by lithiation with 4 equimolar amounts of *n*-BuLi in ether followed by quenching with an excess of methoxytri(2-thienyl)silane.[6] The formation of C–C bonds using Stille cross-coupling reactions is a very powerful method for the synthesis of polyconjugated systems. The reaction usually involves the cross-coupling of an organic halide and an organotin compound. As a rule, commercially available $(Ph_3P)_4Pd$ has been used to prepare oligothiophenes through the Stille coupling.[7] The present paper presents our preliminary results on the synthetic opportunities of the novel radial oligothienyl silanes.

Tetravinylsilane was chosen as the core of the molecule. It has been shown that in the presence of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) 4 equiv of dimethyl(2-thienyl)silane[8a] and 5-(2,2′-bithienyl)dimethylsilane[8b] react exothermically with tetravinylsilane to yield the corresponding radial precursors tetra[2-((2-thienyl) **1**[9] and -5-(2,2′-bithienyl) **2**[9] dimethylsilyl)ethyl]silane. Attempts to hydrosilylate tetravinylsilane with di-(2-thienyl)methylsilane led to the formation of derivative **3**[9] with eight thiophene rings in low yield (25%). To increase the yield of the target compound **3** an alternative synthetic pathway was used. Tetravinylsilane was quantitatively hydrosilylated using an excess of dichloromethylsilane. Then, after removing the excess chlorosilane the crude product was added to the mixture of 8 M equiv of 2-thienyllithium and the desired compound **3**[10] was obtained in 45% overall yield. Attempts to hydrosilylate tetravinylsilane with di-(5-(2,2′-bithienyl))methylsilane[8b] failed due to steric effects.

Trimethylstannyl substituted radial thienyl silanes **4**[11] and **5**[11] were prepared from silanes **1** and **2** by lithiation with BuLi followed the addition of 4 equiv of trimethyltin chloride. This reaction afforded compounds **4** and **5** in high yields (96%). The total lithiation of tetra[2-(di(2-thienyl)methylsilyl)ethyl]silane **3** was impossible due to the insolubility of the lithium salt in organic solvents (ether, THF, etc.). Stannylated tetrathienyl silanes **4** and **5** reacted with bromothiophenes and bromothiophene-*S*,*S*-dioxide in the presence of $Pd(PPh_3)_4$ to form carbon–carbon bonds in yields up to 85%. Tetra[2-(5-(2,2′:5′,2″-terthienyl)dimethylsilyl)ethyl]silane **6**[12] was synthesized as a yellow powder in moderate yield (56%) from bithienyl derivative **5** by reaction with 2-bromothiophene. The alternative preparation from thienylsilylethyl silane **4** and 5-bromo(2,2′-bithiophene) in the presence of a palladium catalyst led

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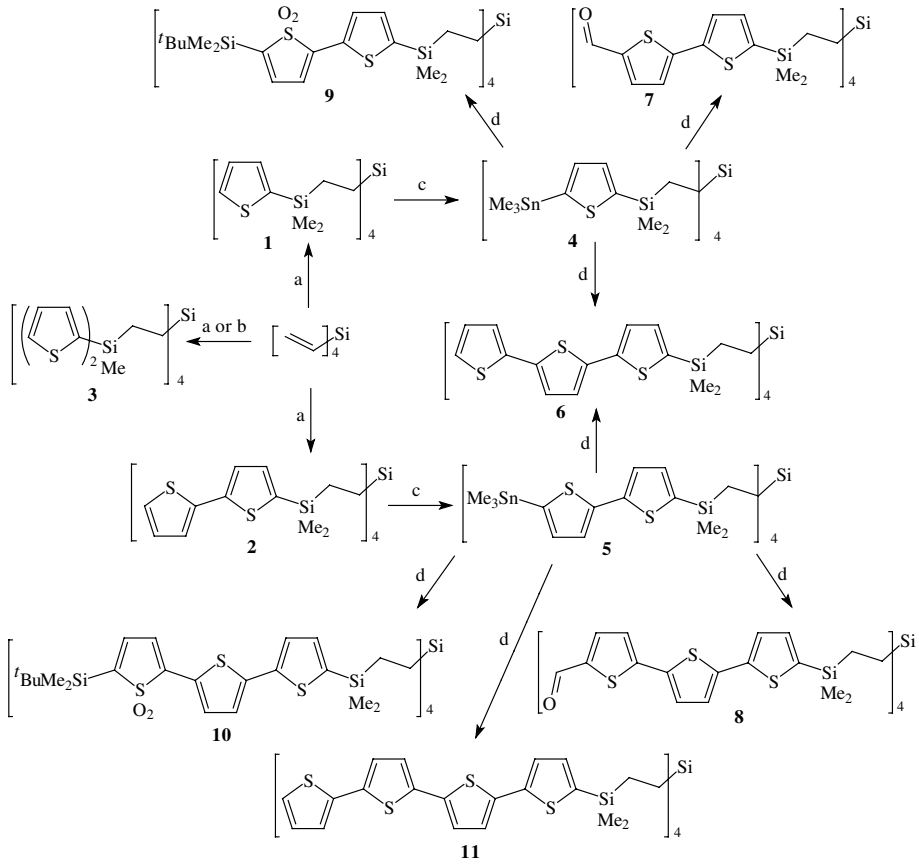

**Scheme 1.** Reagents and conditions: (a) silane, THF, Speier's catalyst; (b) dichloromethylsilane, THF, Speier's catalyst, thienyl lithium; (c) BuLi, THF, −78 °C, $Me_3SnCl$; (d) corresponding bromothiophene, toluene, $Pd(PPh_3)_4$.

to an increased yield up to 64%. Stannyl derivatives **4** and **5** were successfully used for the synthesis of radial formyl bithienyl **7**[12] and terthienyl **8**[12] silanes by Stille coupling with 5-bromo-2-thiophene aldehyde. As shown in Scheme 1, the reaction of 2-bromo-5-*tert*-butyldimethylsilylthiophene-1,1-dioxide and stannanes **4** and **5** allowed the insertion of thiophene 1,1-dioxide units at the terminal positions of oligothiophenes. The radial silane with four bithiophene-1,1-dioxide groups **9**[12] was prepared in 51% yield, besides terthiophene-1,1-dioxide derivative **10**,[12] which was obtained in a decreased yield (31%). Similarly the radial silane with quaterthiophene fragments **11** was synthesized as an orange solid in 33% yield. Product **11** exhibited a low level of solubility in THF and dichloromethane.

In summary, we present a new strategy for the preparation of a new type of radial silanes starting from tetravinylsilane. Further studies will be connected with the synthesis and nonlinear optical properties of radial oligothienyl silanes with more branched structures.

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9. A mixture of the corresponding hydrosilane (0.01 mol), tetravinylsilane (0.01 mol), and $10^{-4}$ M% of Speier's catalyst ($H_2PtCl_6 \times 6H_2O$) were stirred for 0.5–1 h in a Wheaton vial at room temperature. Products were chromatographed on silica gel using dichloromethane/hexanes mixture (1:15) as eluent. Tetra[2-((2-thienyl)dimethylsilyl)ethyl]silane **1**, yield 84%, $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.28 (s, 24H), 0.44–0.50 (m, 16H), 7.18 (dd, $J = 4.2$ Hz, $J = 4.6$ Hz, 4H), 7.22 (d, $J = 4.2$ Hz, 4H), 7.56 (d, $J = 4.6$ Hz, 4H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −2.4, 2.5, 8.7, 128.0, 130.4, 134.2, 138.8; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −3.9, 10.0; Anal. Calcd for $C_{32}H_{52}S_4Si_5$: C, 54.48; H, 7.43; S, 18.18. Found: C, 54.32; H, 7.38; S, 18.26. Tetra[2-((5-(2,2′-bithienyl))dimethylsilyl)ethyl]silane **2**, yield 79%, mp = 79 °C, $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.27 (s, 24H), 0.50–0.52 (m, 16H), 6.91 (dd, $J = 3.4$ Hz, $J = 3.6$ Hz, 4H), 7.06 (d, $J = 3.6$ Hz, 4H), 7.11–7.20 (m, 12H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −2.5, 2.6, 8.6, 123.7, 124.3, 125.0, 127.8, 135.0, 137.4, 138.4, 142.4; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −21.9, −3.8; Anal. Calcd for $C_{48}H_{60}S_8Si_5$: C, 55.76; H, 5.85; S, 24.81. Found: C, 55.67; H, 5.81; S, 24.88. Tetra[2-(di(2-thienyl)methylsilyl)ethyl]silane **3**, yield 25%, mp = 107–110 °C, $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.58 (s, 12H), 0.71–0.77 (m, 16H), 7.16 (dd, $J = 3.2$ Hz, $J = 4.4$ Hz, 8H), 7.26 (dd, $J = 1.0$ Hz, $J = 3.2$ Hz, 8H), 7.59 (dd, $J = 1.0$ Hz, $J = 4.4$ Hz, 8H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −2.7, 2.5, 8.7, 128.1, 131.3, 135.7, 136.4; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −12.6, 11.2; Anal. Calcd for $C_{44}H_{52}S_8Si_5$: C, 54.05; H, 5.36; S, 26.23. Found: C, 53.98; H, 5.32; S, 26.28.
10. Tetra[2-(di(2-thienyl)methylsilyl)ethyl]silane **3**. Tetra-2-(dichloromethylsilyl)ethylsilane prepared from tetravinylsilane and methyldichlorosilane was treated with 8 equiv of 2-thienyllithium. After workup compound **3** was chromatographed on silica gel using dichloromethane/hexanes mixture (1:15) as eluent. Yield 45%.
11. A mixture of **1** or **2** (5 mmol) in dry THF was treated with 4 equiv of BuLi at rt. After 1 h, 4 equiv of trimethyltin chloride were added dropwise to the reaction mixture. Stannyl derivatives **4** and **5** were obtained after usual workup and purification on silica gel using dichloromethane/hexanes (1:25) as eluent. Tetra[2-(2-(5-trimethylstannylthienyl)dimethylsilyl) ethyl]silane **4**. Yield 96%, mp = 112–113 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.26 (s, 24H), 0.35 (s, 12H), 0.49–0.53 (m, 16H), 7.27 (d, $J = 3.2$ Hz, 4H), 7.35 (d, $J = 3.2$ Hz, 4H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −8.2, −2.2, 2.8, 8.8, 135.1, 136.0, 143.0, 144.9; $^{29}$Si NMR: −3.7; 7.9; $^{119}$Sn NMR (39.74 MHz, $CDCl_3$, 298 K): −25.4; Anal. Calcd for $C_{44}H_{84}S_4Si_5Sn_4$: C, 38.95; H, 6.24; S, 9.45. Found: C, 39.06; H, 6.31; S, 9.42%. Tetra[2-((5-(5′-trimethylstannyl-2,2′-bithienyl))dimethylsilyl)ethyl]silane **5**. Yield 96%, mp = 107–110 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.26 (s, 24H), 0.36 (s, 12H), 0.42–0.52 (m, 16H), 7.05 (dd, $J = 3.4$ Hz, $J = 3.8$ Hz, 4H), 7.16 (d, $J = 3.4$ Hz, 4H), 7.21–7.24 (m, 8H, arom); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −8.2, −2.5, 2.6, 8.6, 124.8, 125.0, 135.1, 135.9, 137.2, 138.1, 142.5, 142.9; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −21.9, −3.9; $^{119}$Sn NMR: −26.5; Anal. Calcd for $C_{60}H_{92}S_8Si_5Sn_4$: C, 42.76; H, 5.50; S, 15.22. Found: C, 42.71; H, 5.47; S, 15.25.
12. A mixture of the corresponding stannyl thiophene (5 mmol) and bromothiophene or bromothiophene-*S*,*S*-dioxide (20 mmol) in toluene (2 mL) in the presence of $Pd(PPh_3)_4$ were stirred for 6 h in a Wheaton vial under reflux. Products were chromatographed on silica gel using dichloromethane/hexanes mixture (1:5) as eluent. Tetra[2-((5-(2,2′:5′,2″-terthienyl))dimethylsilyl)ethyl]silane **6**. Yield 56% (from **5**), 64% (from **4**), mp = 122–124 °C (yellow crystals). $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.28 (s, 24H), 0.49–0.54 (m, 16H), 7.0–7.16 (m, 28H, arom); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −2.5, 2.6, 8.7, 123.6, 124.3, 124.9, 127.8, 129.5, 135.1, 136.1, 137.2, 138.6, 142.1; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −21.9, −0.3. Tetra[2-((5-(5′-formyl-2,2′-bithienyl))dimethylsilyl)ethyl]silane **7**. Yield 85%, mp = 84–86 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.29 (s, 24H), 0.51 (m, 16H), 7.11 (dd, $J = 0.8$ Hz, $J = 3.4$ Hz, 4H), 7.41 (d, $J = 4.0$ Hz, 4H), 7.62 (d, $J = 4.0$ Hz, 4H), 7.72 (d, $J = 4.0$ Hz, 4H), 9.91 (s, 4H).$^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −2.6, 2.5, 8.5, 124.5, 126.5, 127.2, 131.9, 135.4, 136.9, 137.4, 141.7, 182.5; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −24.7, −4.1; Anal. Calcd for $C_{52}H_{60}O_4S_8Si_5$: C, 54.50; H, 5.28; S, 22.38. Found: C, 54.58; H, 5.01; S, 22.41. Tetra[2-(5-(5′-formyl-(2,2′:5′,2″-terthienyl))dimethylsilyl)ethyl]silane **8**. Yield 71%, mp = 98–102 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.31 (s, 24H), 0.75 (m, 16H), 7.11–7.21 (m, 8H), 7.44–7.50 (m, 12H), 9.85 (s, 4H). $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −3.2, 7.5, 9.5, 117.5, 126.5, 128.4, 130.9, 135.4, 137.3, 141.1, 147.1, 152.2, 182.8; $^{29}$Si NMR (39.74 MHz, $CDCl_3$, 298 K): −25.1, −4.4. Tetra[2-((5-(5′-*tert*-butyldimethylsilyl-4′,4′-dioxo-2,2′-bithienyl))dimethylsilyl)ethyl]silane **9**. Yield 51%, mp = 186–187 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.28 (s, 24H), 0.33 (s, 24H), 0.46–0.50 (m, 16H), 0.99 (s, 36H), 6.55 (d, $J = 4.6$ Hz, 4H), 6.97 (d, $J = 4.6$ Hz, 4H), 7.20 (d, $J = 3.6$ Hz, 4H), 7.65 (d, $J = 3.6$ Hz, 4H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −6.0, −2.6, 1.0, 2.6, 8.5, 17.2, 26.3, 117.5, 129.7, 134.4, 135.7, 139.1, 140.4, 142.4, 144.1. Tetra[2-(5-(5′-*tert*-butyldimethylsilyl-7′,7′-dioxo-5-5′-formyl-(2,2′:5′,2″-terthienyl))dimethylsilyl)ethyl]silane **10**. Yield 31%, mp = 195–196 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.28 (s, 24H), 0.33 (s, 24H), 0.51 (m, 16H), 1.0 (s, 36H), 6.49 (d, $J = 4.4$ Hz, 4H), 7.09 (dd, $J = 4.4$ Hz, $J = 5.4$ Hz, 8H), 6.97 (d, $J = 4.6$ Hz, 4H), 7.20 (d, $J = 4.0$ Hz, 4H), 7.47 (d, $J = 4.4$ Hz, 4H); $^{13}$C NMR (50.31 MHz, $CDCl_3$, 298 K): −5.9, −2.6, 2.5, 8.5, 17.3, 26.3, 29.7, 116.6, 125.0, 126.3, 128.5, 130.1, 135.3, 139.2, 140.3, 140.6, 140.6, 141.1, 142.3. Tetra[5-((2,2′;5′,2″;5″,2‴-quaterthienyl)dimethylsilyl)ethyl]silane **11**. Yield 33%, mp = 161–163 °C. $^1$H NMR (200 MHz, $CDCl_3$, 298 K): 0.29 (s, 24H), 0.53 (m, 16H), 7.00–7.20 (m, 32H); Anal. Calcd for $C_{80}H_{76}S_{16}Si_5$: C, 56.82; H, 4.53; S, 30.34. Found: C, 56.77; H, 4.48; S, 30.30.