From Tellurophenes to Siloles. Synthesis, Structures, and Photophysical Properties of 3,4-Unsubstituted 2,5-Diarylsiloles

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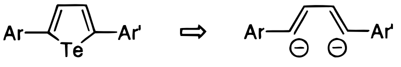
A series of 3,4-unsubstituted 2,5-diarylsiloles have been prepared from the corresponding tellurophenes via the tellurium−lithium exchange reaction. Their crystal structures, UV−vis absorption spectra, and fluorescence spectra have been determined and compared with those of the 3,4-diphenyl and 3,4-dialkyl analogues.

Introduction

Siloles (silacyclopentadienes)[1] having aryl groups at the 2,5-positions generally have a strong fluorescence. We recently reported the application of 3,4-diphenyl-2,5-diarylsiloles as new emissive materials for organic electroluminescent (EL) devices.[2,3] For this application, the elucidation of the intrinsic photophysical properties of the silole π-electron systems, free from the electronic effects of the 3,4-substituents, would give us proper guidelines for further molecular designs. As 3,4-unsubstituted 2,5-diarylsiloles, however, only the 2,5-diphenylsiloles[1a,4] have been reported so far, and there have been no systematic studies on their properties.

For the synthesis of the 3,4-unsubstituted 2,5-diarylsiloles, the most straightforward route may be the reaction of the 1,4-diarylbutadiene 1,4-dianions **1**[5] with dichlorosilanes or related compounds.[6] However, this route has encountered a problem, that is, a poor source of synthetic equivalents for the 1,4-dianions **1**. Considering the wide applicability of the tellurium−lithium exchange reaction,[7] we expected that tellurophenes would be good equivalents for **1**. The tellurium−lithium exchange reaction of tellurophenes has been reported[8] and applied to the synthesis of stannole derivatives.[9] We now report the synthesis of a series of 3,4-unsubstituted 2,5-diarylsiloles **4** and **5** from the corresponding tellurophenes **3**. Their crystal structures and photophysical properties have been investigated. The effects of the 3,4-substituents on their photophysical properties will also be discussed.



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Results and Discussion

Our synthetic route to the 3,4-unsubstituted 2,5-diarylsiloles is shown in Scheme 1, which also includes the synthesis of tellurophenes from 1,3-diynes. 2,5-Diaryltellurophenes[10] were prepared from 1,4-diaryl-1,3-butadiynes using the modified procedure reported by Mack.[11] Thus, lithium telluride, Li_2Te, generated from elemental Te and Li metal in the presence of a catalytic

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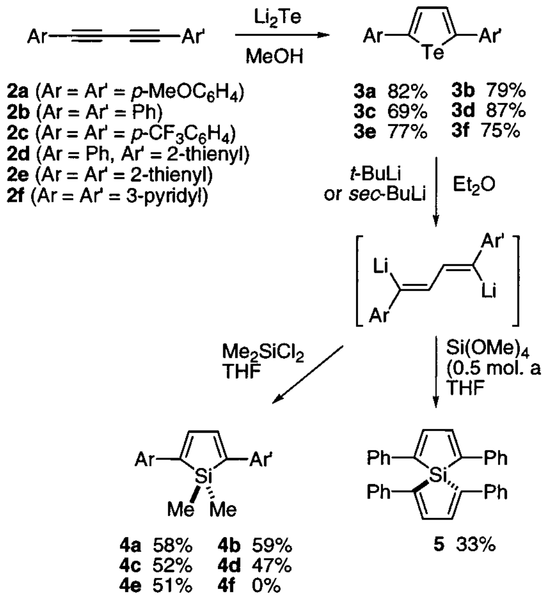
Scheme 1



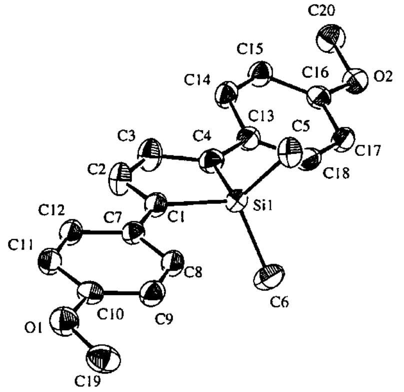


Figure 1. ORTEP drawing of **4a** (50% probability for thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Si1−C1 1.892(1), Si1−C5 1.859(2), C1−C2 1.353(2), C2−C3 1.460(2); C1−Si1−C4 92.92(6), Si1−C1−C2 105.3(1), Si1−C1−C7 129.5(1), C5−Si1−C6 111.44(8), C1−C2−C3 118.2(1).

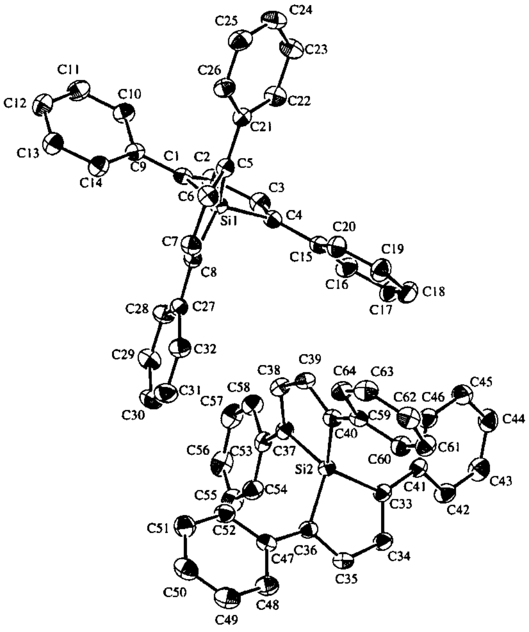


Figure 2. ORTEP drawing of **5** (50% probability for thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Si1−C1 1.880(2), Si1−C5 1.879(3), C1−C2 1.356(4), C2−C3 1.463(3), Si2−C33 1.877(2), Si2−C37 1.883(2), C33−C34 1.357(3), C34−C35 1.456(4); C1−Si1−C4 92.6(1), Si1−C1−C2 106.0(2), Si1−C1−C9 129.3(2), C5−Si1−C8 92.5(1), C1−C2−C3 117.6(2), C33−Si2−C36 93.0(1), Si2−C33−C34 105.7(2), Si2−C33−C41 124.6(2), C37−Si2−C40 92.7(1), C33−C34−C35 117.6(2).

amount of naphthalene in THF, was allowed to react with 1,4-diaryl-1,3-butadiynes **2** in MeOH to give the 2,5-diaryltellurophenes **3** in good yields. In all cases, except for **3e**, the tellurophenes can be isolated by simple reprecipitation. In light of this facile synthesis and isolation as well as their high stability, the tellurophenes **3** would serve as good starting materials for the synthesis of various metalloles and heteroles.

A series of 3,4-unsubstituted 2,5-diarylsiloles **4** were prepared in one pot from the tellurophenes **3** in 47−59% yields (Scheme 1). While the tellurium−lithium exchange reaction successfully proceeded with *sec*-BuLi in ether at low temperature in the case of the 2,5-diphenyltellurophene derivatives **3a**−**c**, the use of *t*-BuLi in place of *sec*-BuLi was necessary for the thienyl group-bound tellurophenes **3d** and **3e** in order to prevent side reactions. In the case of the pyridyl-substituted tellurophene **3f**, unfortunately, the reaction resulted in the formation of a complex mixture. The 1,4-dilithio-1,4-diarylbutadienes thus prepared were treated with Me_2SiCl_2 to give the desired 2,5-diarylsiloles **4a**−**e**. Of special note is that the present method can produce the unsymmetrical 2,5-diarylsiloles **4d**. 2,2′,5,5′-Tetraphenyl-1,1′-spirobisilole, **5**, was also obtained in 33% yield using 0.5 molar amount of $Si(OMe)_4$ instead of Me_2SiCl_2; in contrast, the use of $SiCl_4$ gave **5** in only 3% yield.[4h] All these 2,5-diarylsiloles except for **4b** are new compounds. While the siloles **4a**−**c** containing the substituted phenyl groups are air-stable, the thienylsiloles **4d** and **4e** are rather unstable and hence must be kept in an inert atmosphere at low temperature.

The X-ray crystal structures of **4a** and **5** have been determined; their ORTEP drawings are shown in Figures 1 and 2, respectively.[12] 2,5-Bis(*p*-methoxyphenyl)silole **4a** has a highly coplanar arrangement of three rings, apparently due to the lack of the 3,4-substituents. Thus, the dihedral angles between the mean plane of the central silole ring and the mean planes of the two benzene rings at the 2,5-positions are 5.9 and 18.1°, which are smaller than those for 2,3,4,5-tetraphenyl-1,1-dimethylsilole, **6** (36.4−52.5°).[13] On the other hand, 1,1′-spirobisilole **5** crystallized in two crystallographically independent forms. The dihedral angles between the silole rings and the outer benzene rings vary in the range 21.6−29.7°. It is interesting here that the two silole rings are arranged not exactly perpendicular but slightly twisted. The dihedral angles between the two silole mean planes are 95.1 and 95.4° for the two forms.

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(12) For the 3,4-unsubstituted 2,5-diphenylsilole derivatives, only the crystal structure of a charge-transfer complex of 1,1-dimethyl-2,5-diphenylsilole with tetrafluoroquinone has been reported: Kyushin, S.; Ohkura, Y.; Nakadaira, Y.; Ohashi, M.; Yasui, M.; Iwasaki, F. *Chem. Lett.* **1991**, 883.

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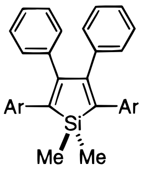
Table 1. UV−Vis Absorption and Fluorescence Spectral Data for 2,5-Diarylsiloles

compd	UV−vis[a] λ_{max}/nm (log ϵ)	fluorescence[a,b] λ_{max}/nm (Φ_f)[c]
4a	395 (4.31)	488 (0.18)
4b	376 (4.24)	463 (0.29)
4c	371 (4.01)	461 (0.71)
4d	398 (4.37)	495 (0.018)
4e	415 (4.22)	505 (0.039)
5	387 (4.33)	489 (0.038)
6[d]	359 (4.31)	467 (0.0014)
7[e]	418 (4.28)	515 (0.0014)
8[e]	409 (4.38)	492 (0.054)

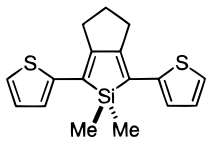
[a] In chloroform. [b] Excited at 366 nm. [c] Relative quantum yields with respect to quinine sulfate (Φ_{366} = 0.55). [d] Reference 14. [e] Reference 15.

For both **4a** and **5**, the bond lengths and bond angles of the silole rings themselves are in the normal range.

The UV−vis absorption and fluorescence spectral data for the 2,5-diarylsiloles are summarized in Table 1, together with those for compounds **6**−**8** as a comparison.[14−16] All the siloles have strong absorption and fluorescence in the visible region with relatively large Stokes shifts (90−100 nm). The following points are noteworthy. (1) 2,5-Diphenylsilole **4b** has a 17 nm longer absorption maximum than 2,3,4,5-tetraphenylsilole, **6**, probably due to the more effective π-conjugation in the more coplanar conformation of **4b**, while their emission maxima are comparable. (2) From the comparison among **4a**−**c**, while the electron-donating OMe group causes significant bathochromic shifts of both the absorption and emission maxima, the electron-withdrawing CF_3 group only induces a subtle blue shift. (3) According to the data for **4b**, **4d**, and **4e**, the successive replacement of one phenyl group by one thienyl group induces about a 20 nm red shift in the absorption maxima. (4) There are significant differences in their quantum yields. In a series of 2,5-bis(*p*-substituted phenyl)siloles **4a**−**c**, the CF_3-substituted **4c** has a much higher quantum yield. In the thiophene-substituted series **4b**, **4d**, and **4e**, the unsymmetrical **4d** has the lowest quantum yield. (5) As for the spirobisilole **5**, its absorption and emission maxima are red-shifted in comparison with those of 2,5-diphenylsilole **4b**, by about 10 and 20 nm, respectively. A notable feature of the spiro skeleton is the much lower quantum yield relative to that of **4b**.



6 (Ar = Ph)
7 (Ar = 2-thienyl)



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The electronic effects on the properties of the 2,5-diarylsiloles exerted by the 3,4-substituents have now become clear by comparisons of the data for the series of 2,5-dithienylsiloles **4e**, **7**, and **8**. Since these three 2,5-dithienylsiloles have coplanar arrangements of three thiophene−silole−thiophene rings in their crystal structures,[17] the differences in the UV−vis absorption and fluorescence spectra may be directly attributed to the electronic effects of the 3,4-substituents. Thus, the data shown in Table 1 clearly demonstrate that the 3,4-diphenyl- and the 3,4-dialkyl-substitutions induce a red shift and a blue shift, respectively, in both of the absorption and fluorescence spectra. It is also noted that while the phenyl groups at the 3,4-positions significantly reduce the quantum yield, the bicyclic skeleton in **8** does not affect the quantum yield in comparison with the 3,4-unsubstituted **4e**. The present fundamental data will be helpful for the further molecular design of silole-based optoelectronic materials.

Experimental Section

General Considerations. ^{1}H NMR spectra were measured using a JEOL EX-270 (270 MHz) or JEOL JMN-AL400 (400 MHz, only for **4d**) spectrometer. ^{13}C and ^{29}Si NMR spectra were measured using a JEOL EX-270 (67.8 MHz for ^{13}C and 53.5 MHz for ^{29}Si) spectrometer. Chemical shifts are reported in δ (ppm) with reference to the residual proton-solvent peak, i.e., $CHCl_3$, for ^{1}H and ^{13}C and to TMS for ^{29}Si, respectively. Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick 60F-254 silica gel (Merck). Column chromatography was performed using Kieselgel 60 (70−230 mesh; Merck). High-performance liquid chromatography (HPLC) was performed using a 20 mm × 250 mm Wakosil 5Sil column (Wako).

Materials. THF and Et_2O were distilled under nitrogen from sodium benzophenone ketyl. Dimethyldichlorosilane and tetramethoxysilane were purchased from commercial sources and distilled prior to use. 1,4-Diaryl-1,3-butadiynes **2** were prepared by the procedures reported in the literature.[18] All reactions were carried out under an inert atmosphere.

A Typical Procedure for the Preparation of 2,5-Diaryltellurophenes: 2,5-Bis(*p*-(trifluoromethyl)phenyl)tellurophene (3c). Lithium telluride was generated as follows. A mixture of Te (5.1 g, 40 mmol), granular Li (0.828 g, 119 mmol), and naphthalene (0.1 g, 0.78 mmol) in 60 mL of THF was stirred under argon for 70 h. The resulting Li_2Te suspension was transferred to another flask through cannular in order to remove the excess Li metal. After removal of the solvent in vacuo, Li_2Te was dissolved in 60 mL of methanol. A THF (50 mL) solution of 1,4-bis(*p*-(trifluoromethyl)phenyl)-1,3-butadiyne, **2c** (6.76 g, 20 mmol), was added to the Li_2Te suspension at room temperature. The reaction mixture was stirred for 5 h. After addition of 200 mL of methanol to the mixture, the precipitated tellurophene was collected by filtration. The crude tellurophene was dissolved again in THF, and the insoluble tellurium powder was filtered off. Concentration of the filtrate gave almost pure tellurophene **3c** (6.46 g, 13.8 mmol) in 69% yield. Mp: 238−240 °C. ^{1}H NMR ($CDCl_3$): δ 7.55−7.63 (m, 8H, Ph), 7.93 (s, 2H, tellurophene). ^{13}C NMR ($CDCl_3$): δ 122.06, 126.03 (q, J = 3.5 Hz), 126.90, 129.49 (q, J = 40.2 Hz), 135.54, 143.68, 147.98. MS (EI) *m/e* (relative intensity): 468/470 (M^+ 93/100), 340 (58), 271 (87), 202 (54).

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(14) Yamaguchi, S.; Endo, T.; Uchida, M.; Ohno, S.; Tamao, K. Manuscript in preparation. The spectral data for the compounds **6** have also been reported: (a) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596. See also ref 16.

(15) Yamaguchi, S.; Itami, Y.; Tamao, K. *Organometallics* **1998**, *17*, 4910.

(16) Fluorescence of **4b**: (a) Hennig, H.; Heckner, K.-H.; Paviov, A. A.; Kuzmin, M. G. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *84*, 1122. (b) Sakurai, H.; Nakamura, A.; Nakadaira, Y. *Organometallics* **1983**, *2*, 1814.

(17) X-ray crystal structure of **7**: Yamaguchi, S.; Goto, T.; Tamao, K. Manuscript in preparation. X-ray crystal structure of **8**: ref 15. In both cases, coplanar arrangements of the three rings have been revealed.

(18) Brandsma, L. *Preparative Acetylene Chemistry*, 2nd ed.; Studies in Organic Chemistry 34; Elsevier: Amsterdam, 1988; Chapter 10.

Anal. Calcd for $C_{18}H_{10}F_6Te$: C, 46.21; H, 2.15. Found: C, 46.21; H, 2.09.

The following tellurophenes were prepared in essentially the same manner as described for **3c**, unless otherwise stated.

2,5-Bis(*p*-methoxyphenyl)tellurophene (3a) was prepared in a similar manner, except the reaction was carried out at 40 °C for 24 h and the crude product was dissolved in hot toluene instead of THF. Yield: 82%. Mp 282−283 °C. ^{1}H NMR (CDCl$_3$): δ 3.83 (s, 6H, OCH$_3$), 6.85−6.88 (m, 4H, Ph), 7.38−7.41 (m, 4H, Ph), 7.65 (s, 2H, tellurophene). ^{13}C NMR (CDCl$_3$): δ 55.38, 114.25, 127.78, 132.76, 132.97, 146.65, 159.23. MS (EI) *m*/*e* (relative intensity): 392/394 (M$^+$ 93/100), 379 (51), 132 (52), 91 (60). Anal. Calcd for $C_{18}H_{16}O_2Te$: C, 55.16; H, 4.11. Found: C, 55.29; H, 4.04.

2,5-Diphenyltellurophene (3b). Yield: 79%. Mp: 225 °C (lit.[19] 225 °C). ^{1}H NMR (CDCl$_3$): δ 7.27−7.38 (m, 6H, Ph), 7.47−7.50 (m, 4H, Ph), 7.82 (s, 2H, tellurophene). MS (EI) *m*/*e* (relative intensity): 332/334 (M$^+$ 61/64), 203 (100), 202 (63), 102 (50), 78 (70).

2-(2-Thienyl)-5-phenyltellurophene (3d). Yield: 87%. Mp: 209−210 °C. ^{1}H NMR (CDCl$_3$): δ 6.97 (dd, 1H, J = 5.1 and 3.5 Hz, thienyl), 7.03 (dd, 1H, J = 3.5 and 1.4 Hz, thienyl), 7.18 (dd, 1H, J = 5.1 Hz and J = 1.4 Hz, thienyl), 7.27−7.37 (m, 3H, Ph), 7.43−7.46 (m, 2H, Ph), 7.66 (d, 1H, J = 4.3 Hz, tellurophene), 7.73 (d, 1H, J = 4.3 Hz, tellurophene). ^{13}C NMR (CDCl$_3$): δ 124.62, 125.10, 126.69, 127.67, 127.80, 128.99, 133.28, 134.21, 137.90, 139.694, 143.94, 147.62. MS (EI) *m*/*e* (relative intensity): 338/340 (M$^+$ 93/100), 210 (88), 209 (73), 165 (49). Anal. Calcd for $C_{14}H_{10}STe$: C, 49.76; H, 2.98. Found: C, 49.69; H, 2.94.

2,5-Bis(2-thienyl)tellurophene (3e). Yield: 77%. Mp: 187 °C. ^{1}H NMR (CDCl$_3$): δ 6.96 (dd, 2H, J = 4.9 and 3.9 Hz, thienyl), 7.00 (dd, 2H, J = 3.9 and 1.4 Hz, thienyl), 7.18 (dd, 2 H, J = 4.9 and 1.4 Hz, thienyl), 7.55 (s, 2H, tellurophene). ^{13}C NMR (CDCl$_3$): δ 124.69, 125.07, 127.80, 133.55, 137.25, 143.68. MS (EI) *m*/*e* (relative intensity): 344/346 (M$^+$ 69/73), 216 (100), 171 (58), 108 (67). Anal. Calcd for $C_{12}H_8S_2Te$: C, 41.91; H, 2.34. Found: C, 42.08; H, 2.32.

2,5-Bis(3-pyridyl)tellurophene (3f). To a MeOH (60 mL) solution of Li$_2$Te (40 mmol), prepared in the same manner as described for **3a**, was added a solution of 1,4-bis(3-pyridyl)-1,3-butadiyne (4.08 g, 20 mmol) in THF (120 mL) at room temperature. The mixture was stirred for 5 h. After filtration, the filtrate was concentrated by rotary evaporation. The residue was dissolved in ether and washed with water and brine. The organic layer was dried over MgSO$_4$ and concentrated. Recrystallization from a THF/hexane mixed solvent gave 5.02 g of **3f** in 75% yield as brown crystals. Mp: 129 °C. ^{1}H NMR (CDCl$_3$): δ 7.29 (ddd, 2H, J = 7.7, 4.6, and 0.7 Hz, pyridyl), 7.76 (ddd, 2H, J = 7.7, 2.0, and 1.6 Hz, pyridyl), 7.90 (s, 2H, tellurophene), 8.52 (dd, 2H, J = 4.6 and 1.6 Hz, pyridyl), 8.73 (dd, 2H, J = 2.0 and 0.7 Hz, pyridyl). ^{13}C NMR (CDCl$_3$): δ 123.74, 133.53, 135.29, 135.51, 144.89, 147.74, 148.84. MS (EI) *m*/*e* (relative intensity): 336/334 (M$^+$, 69/63), 205 (100), 178 (27). Anal. Calcd for $C_{14}H_{10}N_2Te$: C, 50.37; H, 3.02; N, 8.39. Found: C, 50.55; H, 2.98; N, 8.36.

A Typical Procedure for the Synthesis of 2,5-Diarylsiloles: 2,5-Bis(*p*-(trifluoromethyl)phenyl)-1,1-dimethylsilole (4c). To a suspension of 2,5-bis(*p*-(trifluoromethyl)phenyl)tellurophene, **3c** (2.34 g, 5 mmol), in Et$_2$O (200 mL) was added *sec*-BuLi (1.05 M in cyclohexane, 19.5 mL, 20.5 mmol) dropwise over 5 min at −75 °C. The reaction mixture was allowed to warm to −60 °C and stirred for 2 h. A THF (10 mL) solution of dimethyldichlorosilane (1.94 mL, 16 mmol) was added dropwise to the mixture over 10 min. The reaction mixture was allowed to warm to room temperature with stirring over 12 h. After removal of solvents and volatiles in vacuo, hexane was added to the residue and insoluble salts were filtered off. The filtrate was concentrated, and the residue was recrystallized from ethanol to give 1.05 g of **4c** in 53% yield as yellow crystals. Mp: 171 °C. ^{1}H NMR (CDCl$_3$): δ 0.53 (s, 6H, SiCH$_3$), 7.37 (s, 2H, silole), 7.49−7.60 (m, 8H, Ph). ^{13}C NMR (CDCl$_3$): δ −3.21, 122.25, 126.13 (q, J = 3.7 Hz), 126.33, 128.81 (q, J = 32.9 Hz), 139.89, 142.01, 144.82. ^{29}Si NMR (CDCl$_3$): δ 3.28. MS (EI) *m*/*e* (relative intensity): 298 (M$^+$ 100), 383 (21), 192 (22), 151 (38). Anal. Calcd for $C_{20}H_{16}F_6Si$: C, 60.29; H, 4.05. Found: C, 60.34; H, 3.95.

2,5-Bis(*p*-methoxyphenyl)-1,1-dimethylsilole (4a) was prepared in essentially the same manner as described for **4c**. Recrystallization from hexane gave **4a** in 58% yield as yellow crystals. Mp: 164−166 °C. ^{1}H NMR (CDCl$_3$): δ 0.49 (s, 6H, SiCH$_3$), 3.82 (s, 6H, OCH$_3$), 6.86−6.89 (m, 4H, Ph), 7.36−7.39 (m, 4H, Ph), 7.16 (s, 2H, silole). ^{13}C NMR (CDCl$_3$): δ −2.71, 55.31, 114.20, 127.21, 131.79, 136.10, 142.95, 158.62. ^{29}Si NMR (CDCl$_3$): δ 1.70. MS (EI) *m*/*e* (relative intensity): 322 (M$^+$ 100), 307 (28), 178 (40), 149 (71), 135 (26). Anal. Calcd for $C_{20}H_{22}O_2Si$: C, 74.49; H, 6.88. Found: C, 74.41; H, 6.77.

2,5-Diphenyl-1,1-dimethylsilole (4b) was prepared in essentially the same manner as described for **4c**. Recrystallization from hexane gave **4b** in 59% yield as yellow crystals. Mp: 131 °C (lit.[4f] 133 °C). ^{1}H NMR (CDCl$_3$): δ 0.53 (s, 6H, SiCH$_3$), 7.20−7.46 (m, 12H, Ph and silole). MS (EI) *m*/*e* (relative intensity): 262 (M$^+$ 100), 247 (29), 84 (63).

2,5-Bis(2-thienyl)-1,1-dimethylsilole (4e) was prepared in essentially the same manner as described for **4c**, except for the use of *t*-BuLi (in pentane, 2.05 molar amount) instead of *sec*-BuLi. After the usual aqueous workup, the resulting mixture was subjected to column chromatography on silica gel (hexane/EtOAc = 20/1, R_f = 0.45) to give **4e** in 51% yield. Mp: 73−75 °C dec. ^{1}H NMR (CDCl$_3$): δ 0.51 (s, 6H, SiCH$_3$), 6.93 (d, 2H, J = 3.5 Hz, thienyl), 6.99 (dd, 2H, J = 5.1 and 3.5 Hz, thienyl), 7.05 (s, 2H, silole), 7.17 (d, 2H, J = 5.1 Hz, thienyl). ^{13}C NMR (CDCl$_3$): δ −3.05, 124.03, 124.47, 127.66, 136.86, 137.08, 144.08. ^{29}Si NMR (CDCl$_3$): δ 4.51. MS (EI) *m*/*e* (relative intensity): 274 (M$^+$ 100), 259 (14). Anal. Calcd for $C_{14}H_{14}S_2Si$: C, 61.26; H, 5.14. Found: C, 61.00; H, 5.12.

2-(2-Thienyl)-5-phenyl-1,1-dimethylsilole (4d) was prepared in essentially the same manner as described for **4e.** Column chromatography on silica gel using hexane/EtOAc = 20/1 as an eluent (R_f = 0.53) gave **4d** in 47% yield. Mp: 66−68 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.51 (s, 6H, SiCH$_3$), 6.94 (dd, 1H, J = 3.6 and 0.7 Hz, thienyl), 7.00 (dd, 1H, J = 5.1 and 3.6 Hz, thienyl), 7.10 (d, 1H, J = 3.9 Hz, silole), 7.17 (dd, 1H, J = 5.1 and 0.7 Hz, thienyl), 7.18−7.23 (m, 1H, Ph), 7.25 (d, 1H, J = 3.9 Hz, silole), 7.29−7.34 (m, 2H, Ph), 7.40−7.45 (m, 2H, Ph). ^{13}C NMR (CDCl$_3$): δ −2.93, 124.00, 124.62, 126.88, 127.66, 128.77, 136.69, 138.04, 138.15, 138.69, 143.68, 144.15. ^{29}Si NMR (CDCl$_3$): δ 3.36. MS (EI) *m*/*e* (relative intensity): 268 (M$^+$ 100), 253 (21). HRMS(EI) *m*/*e*: calcd, 268.0768; found, 268.0732. A satisfactory elemental analysis was not obtained due to instability.

2,2′,5,5′-Tetraphenyl-1,1′-spirobisilole (5) was prepared in essentially the same manner as described for **4e**, except for the use of Si(OMe)$_4$ (0.5 molar amount) instead of Me$_2$SiCl$_2$. After the usual aqueous workup, recrystallization from a toluene/hexane mixed solvent gave **5** in 33% yield as yellow crystals. Mp: 267 °C. ^{1}H NMR (CDCl$_3$): δ 7.06−7.20 (m, 12H, Ph), 7.35−7.38 (m, 8H, Ph), 7.67 (s, 4H, silole). ^{13}C NMR (CDCl$_3$): δ 126.54, 127.33, 128.68, 137.84, 139.59, 141.28. ^{29}Si NMR: (CDCl$_3$): δ −7.64. MS (EI) *m*/*e* (relative intensity): 436 (M$^+$ 100), 359 (19). Anal. Calcd for $C_{32}H_{24}Si_2$: C, 88.03; H, 5.54. Found: C, 87.87; H, 5.44.

X-ray Crystal Structural Analysis of 4a and 5. Single crystals of **4a** and **5** suitable for X-ray crystal analysis were obtained by recrystallization from benzene. Intensity data were collected at −100 °C on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55°. A total of 15 oscillation images,

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each being oscillated 6° and exposed for 60 min, and a total of 35 images, each being oscillated 4° and exposed for 40 min, were collected for **4a** and **5**, respectively. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were solved by direct methods in SIR92,[20] and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions but not refined. All the calculations were performed using the teXsan crystallographic package from the Molecular Structure Corp. The crystal data and analytical conditions are listed as follows. **4a**: $C_{20}H_{22}O_2Si$, fw = 322.48, crystal size 0.30 × 0.30 × 0.10 mm, monoclinic, $P2_1/c$ (No. 14), $a = 14.3599(5)$ Å, $b = 7.4051(3)$ Å, $c = 16.2752(5)$ Å, $\beta = 95.403(3)°$, $V = 1722.96$ Å^3, $Z = 4$, $D_c = 1.243$ g cm^{-3}, μ(Mo Kα) = 1.43 cm^{-1}, number of unique reflections = 3803, temperature −100 °C, $R = 0.036$, $R_w = 0.054$, GOF = 1.36. **5**: $C_{32}H_{24}Si$, fw = 436.63, crystal size 0.40 × 0.40 × 0.05 mm, triclinic, $P\bar{1}$ (No. 2), $a = 11.1229(4)$ Å, $b = 19.5244(8)$ Å, $c = 11.1150(5)$ Å, $\alpha = 102.705(2)°$, $\beta = 90.064(3)°$, $\gamma = 93.900(2)°$, $V = 2348.94$ Å^3, $Z = 4$, $D_c = 1.235$ g cm^{-3}, μ(Mo Kα) = 1.18 cm^{-1}, number of unique reflections = 8381, temperature −100 °C, $R = 0.049$, $R_w = 0.072$, GOF = 1.28.

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Supporting Information Available: Listings of crystal data, X-ray experimental details, atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **4a** and **5** (10 pages). Ordering information is given on any current masthead page.

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