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# SYNTHESIS AND ELECTRONIC SPECTRA OF 2,5-BIS-(2-ARYLETHENYL)SILOLES*

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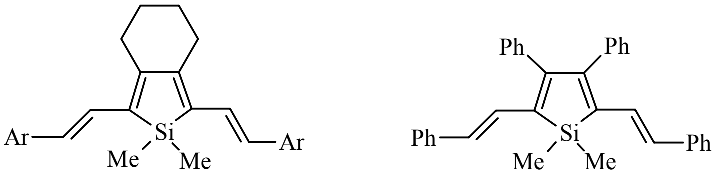
*A new series of 2,5-bis(arylethenyl)siloles **1a-d** was prepared by the reaction of the corresponding zirconacyclopentadienes with $H_2SiCl_2$ in $CH_2Cl_2$. Absorption maxima of siloles **1a-d** were observed in the significantly longer wavelength region compared to those of distyryl-substituted benzenes and heteroles. The emission spectrum of distyrylsilole **1a** showed a large Stokes shift compared with distyrylsilole **2**.*

**Keywords:** 2,5-divinylsilole, silacyclopentadiene, silole, zirconacyclopentadiene, absorption spectrum, emission spectrum.

Much attention has been focused on siloles (silacyclopentadienes) in the field of material science, due to their unique electronic properties [1-7]. Since siloles among various heteroles have exceptionally low-lying LUMO levels due to effective σ*–π* interaction [8], the incorporation of silole units into π-conjugated molecules is expected to cause significant lowering of the LUMO levels, hence narrowing their band gaps [9-13].

Herein we report a novel synthetic method for a series of 2,5-bis(arylethenyl)siloles **1a-d** and their electronic spectra. Although vinyl-substituted siloles should be useful models for silole-containing conjugated polyenes, there have been very few studies of the synthesis of this type of siloles reported so far, with the exception of a study of the synthesis of 3,4-diphenyl-2,5-distyrylsilole (**2**) by Tamao and co-workers [14].



**1a–d** **2**

**1** **a** Ar = Ph, **b** Ar = 4-MeOC$_6$H$_4$, **c** Ar = 4-ClC$_6$H$_4$, **d** Ar = 2-Thienyl

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* Dedicated to Professor E. Lukevics on the occasion of his 65th birthday.

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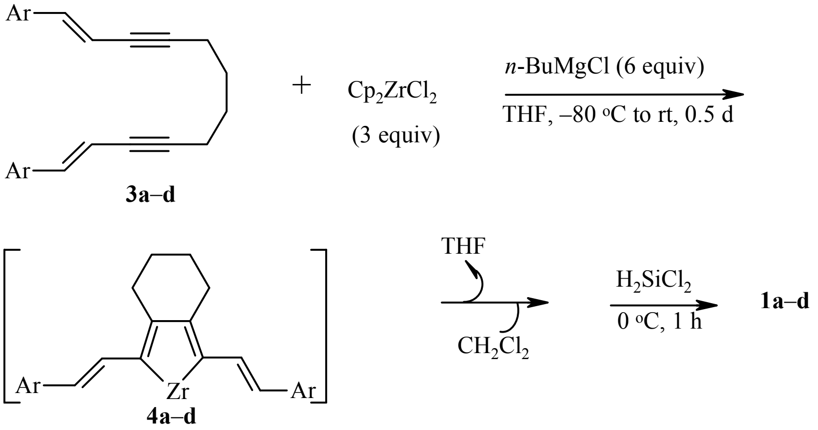
## Results and Discussion

**Synthesis of 2,5-bis(2-arylethenyl)siloles.** We have recently found that the direct reactions of zirconacyclopentadienes with sterically unhindered halosilanes afford a convenient and useful method for the synthesis of siloles [15]. This method was found to be applicable for the synthesis of a series of 2,5-bis(2-arylethenyl)siloles **1a-d** (Scheme 1). Bis-enynes **3a-d** as precursors were prepared by the Sonogashira coupling reactions [16, 17] of 1,7-octadiyne with the corresponding (*E*)-1-bromo-2-arylethylenes in good yields. The reactions of the enynes with 3 equivalents of $Cp_2ZrBu_2$ gave the corresponding zirconacyclopentadienes **4a-d** [18-22]. Without isolation, the zirconacycles were treated with $H_2SiCl_2$ in $CH_2Cl_2$ to afford the corresponding siloles in moderate yields (43-50%).

Scheme 1



**1 a** Ar = Ph (42%); **b** Ar = 4-$MeOC_6H_4$ (43%); **c** Ar = 4-$ClC_6H_4$ (50%); **d** Ar = 2-Thienyl (46%)
(yields based on the starting bis-enyne)

Since $Cp_2ZrBu_2$ is known to decompose at room temperature [18], an excess amount of $Cp_2ZrBu_2$ is required to afford siloles **1a-d** in reasonable yields. When one equivalent of $Cp_2ZrBu_2$ was employed in the reactions with bis-enynes **3a-d**, the isolated yields of **1a-d** were significantly decreased to ca. 10% with ca. 40% recovery of the bis-enynes.

We have recently observed the Pd-catalyzed chlorination of the Si–H functions of siloles [23]. Application of this method ($PdCl_2$, allyl chloride, room temperature, 12 h) to the functionalization of **1a** failed, however, to give a complex product mixture.

## Absorption and Emission Spectra

The absorption and emission spectral data of siloles **1a-d** in $CH_2Cl_2$ at room temperature are shown in Table 1. The absorption maxima of **1a-d** were observed at around 440-470 nm and their extinction coefficients were more than 30,000. The emission maxima appeared at around 580-620 nm with quantum yields of 0.01-0.17 [24, 25]. While the aromatic substituent effects on the electronic spectra of **1a-c** were not remarkable, thienyl-substituted silole **1d** showed absorption and emission maxima at much longer wavelengths than those of **1a-c**.

TABLE 1. Absorption and emission spectral data of bis(2-arylethenyl)-siloles **1a-d** in $CH_2Cl_2$ at room temperature

| Silole | Ar | Absorption | | Emission | |
|---|---|---|---|---|---|
| | | $\lambda_{max}$, nm | $\varepsilon$, $cm^{-1}\cdot M^{-1}$ | $\lambda_{max}$, nm | $\Phi_f$ |
| **1a** | Ph | 444 | 35500 | 578 | 0.17 |
| **1b** | 4-$MeOC_6H_4$ | 456 | 31900 | 589 | 0.09 |
| **1c** | 4-$ClC_6H_4$ | 449 | 33600 | 582 | 0.15 |
| **1d** | 2-Thienyl | 465 | 36300 | 624 | 0.01 |

The absorption maxima of siloles **1a-d** were observed at much longer wavelengths compared to those of *p*-distyryl-substituted benzene [26] and heteroles [27, 28]. The results indicate that the incorporation of silole units into vinylene-linked $\pi$-conjugated molecules decreases their HOMO-LUMO gaps effectively due to the $\sigma^*$–$\pi^*$ interaction in siloles.

The absorption and emission maxima of silole **1a** showed the red-shift of 9 and 51 nm, respectively, from those of **2**. The larger Stokes shift of **1a** is suggestive of the more significant conformational difference between the ground and the excited states of **1a**, while further work should be required to elucidate the origin of the difference between the geometric and electronic structure of **1a** and **2**.

## EXPERIMENTAL

**General.** All reactions were carried out under an argon atmosphere in dry solvents and in anhydrous conditions unless otherwise noted. $^1H$ (300 MHz), $^{13}C$ (75.4 MHz), and $^{29}Si$ (59.6 MHz) NMR spectra were recorded on a Bruker AC300P spectrometer. Chemical shifts are based on the residual solvent resonances. Mass spectra and high-resolution mass spectra were obtained in JEOL JMS-600W and JEOL JMS D-300 mass spectrometers. UV spectra were measured by a Hewlett Packard G1103A (8453E) spectrometer or a Milton Roy MR-3000 spectrometer. Emission spectra were recorded on a Hitachi Fluorescence Spectrophotometer 850. GC analyses were done using a SHIMADZU GC-8A packed with SE-30 (5 and 15% in 5-mm glass columns). Silica gel column chromatography was carried out using Merck silica gel 60 (particle size 63-200 μm) or Wakosil C-300 (particle size 40-64 μm). Thin-layer chromatography was carried out using Merck silica gel plate 60 G-254.

**Materials.** Reagents and spectral grade solvents were purchased and used without further purification unless otherwise noted. Anhydrous tetrahydrofuran (THF) was obtained by distillation from sodium benzophenone, or as a commercial source (KANTO Chemical). Dichloromethane ($CH_2Cl_2$) was dried by distillation from phosphorous oxide followed by distillation from calcium hydride. Hexane and toluene were distilled from sodium under argon. (*E*)-1-Bromo-2-(4-methoxyphenyl)ethylene [29] and 1-bromo-2-(2-thienyl)ethylene [30, 31] were prepared by the literature methods.

**Synthesis of (*E*)-1-Bromo-2-(4-chlorophenyl)ethylene.** To a 100 ml three-necked flask with a condenser, 4-chloro-β,β-dibromostyrene [15] (11.07 g, 37.3 mmol), diethyl phosphite (10.38 g, 75.2 mmol), and triethylamine (7.92 g, 78.2 mmol) were added and stirred at 50°C for 12 h [31]. After cooled to room temperature, the mixture was diluted with ether. White precipitate formed and was removed by filtration. The filtrate was concentrated and purified by flash chromatography to afford colorless crystals (7.63 g). $^1H$ NMR analysis of the crystals revealed that the *E/Z* ratio was 91/9. The crystals were further purified by crystallization from EtOH to afford pure *E*-isomer of the title compound (6.07 g, 75%). The spectral data were consistent with the literature values [33].

**General Procedure for the Synthesis of 1,12-Diaryldoceca-1,11-dien-3,9-diynes 3a-d. Synthesis of 3a (Ar = Ph).** Typically, in a 50 ml two-necked flask, a mixture of $Pd(PPh_3)_4$ (1.15 g, 0.995 mmol), β-bromostyrene (mixture of isomers, *E/Z* = 9/1, 8.15 g, 40.1 mmol of *E*-isomer), and 1,7-octadiyne in 40 ml of pyrrolidine was stirred at room temperature overnight. At this time, a fluffy precipitate formed. The suspension was treated with ice-cooled saturated aq. $NH_4Cl$ and extracted with ether (in the case of **3b** and **3c**, $CHCl_3$ was used instead of ether for extraction). The organic layer was washed with water, saturated aq. $NaHCO_3$, and brine, and then dried over anhydrous $Na_2SO_4$. After removal of the solvent, the residue was subjected to flash chromatography (hexane:toluene = 5:1 to 4:1) to afford a yellow solid. Pure **3a** was obtained by recrystallization from ethanol as colorless crystals (3.96 g, 64% yield).

**3a.** Yield 64%; mp 76-77°C. $^1H$ NMR ($CDCl_3$): 7.39-7.21 (10H, m); 6.87 (2H, d, *J* = 16 Hz); 6.14 (2H, dt, *J* = 16, 2 Hz); 2.49-2.35 (4H, m); 1.79-1.64 ppm (4H, m). $^{13}C$ NMR ($CDCl_3$): 140.2, 136.5, 128.6, 128.2, 126.0, 108.8, 92.3, 80.1, 27.9, 19.2 ppm. MS (70 eV), *m/z* (%): 310 ($M^+$, 80), 267 (40), 219 (67), 191 (51), 156 (33), 141 (46), 128 (31), 115 (100), 91 (40). Found, %: C 92.79; H 7.15. $C_{24}H_{22}$. Calculated, %: C 92.86; H 7.14.

**3b.** Yield 82%; mp 117-119°C. $^1H$ NMR ($CDCl_3$): 7.28 (4H, dt, *J* = 9, 3 Hz); 6.83 (4H, dt, *J* = 9, 3 Hz); 6.81 (2H, d, *J* = 16 Hz); 6.00 (2H, dt, *J* = 16, 2 Hz); 3.79 (6H, s); 2.45-2.40 (4H, m); 1.74-1.65 ppm (4H, m). $^{13}C$ NMR ($CDCl_3$): 159.8, 139.7, 129.4, 127.3, 114.1, 106.4, 91.5, 80.3, 55.3, 28.0, 19.2 ppm. MS (70 eV), *m/z* (%): 370 ($M^+$, 84), 249 (22), 141 (39), 129 (23), 128 (100), 127 (27), 121 (67), 115 (37). Found, %: C 84.03; H 7.16. $C_{26}H_{26}O_2$. Calculated, %: C 84.29; H 7.07.

**3c.** Yield 77%; mp 136°C. $^1H$ NMR ($CDCl_3$): 7.26 (8H, s); 6.79 (2H, d, *J* = 16 Hz); 6.10 (2H, dt, *J* = 16, 2 Hz); 2.44-2.36 (4H, m); 1.74-1.66 ppm (4H, m). $^{13}C$ NMR ($CDCl_3$): 138.8, 135.0, 133.9, 128.8, 127.2, 109.4, 93.0, 79.9, 27.8, 19.2 ppm. MS (70 eV), *m/z* (%): 380 ($M^+$+2, 31), 378 ($M^+$, 38), 265 (24), 253 (23), 218 (20), 204 (21), 203 (30), 202 (21), 175 (28), 165 (39), 153 (42), 152 (38), 151 (32), 149 (52), 141 (29), 149 (54), 139 (100), 127 (28), 125 (34), 115 (37). Found, %: C 75.88; H 5.51. $C_{24}H_{24}Cl_2$. Calculated, %: C 75.99; H 5.31.

**3d.** Yield 48%; mp 68°C. $^1H$ NMR ($CDCl_3$): 7.18-7.09 (2H, m); 7.00-6.89 (4H, m); 6.96 (2H, d, *J* = 16 Hz); 5.96 (2H, dt, *J* = 16, 2 Hz); 2.49-2.30 (4H, m); 1.76-1.60 ppm (4H, m). $^{13}C$ NMR ($CDCl_3$): 141.6, 133.0, 127.6, 126.4, 124.8, 108.0, 92.7, 79.8, 27.8, 19.2 ppm. MS (70 eV), *m/z* (%): 324 ($M^+$+2, 13), 322 ($M^+$, 93), 293 (23), 279 (27), 225 (32), 210 (22), 197 (42), 184 (24), 147 (100), 134 (35), 128 (24), 121 (63), 115 (60), 103 (44), 102 (24), 97 (54), 77 (35), 63 (21). Found, %: C 74.36; H 5.76. $C_{20}H_{18}S_2$. Calculated, %: C 74.49; H 5.63.

**General Procedure for the Synthesis of 2,5-Bis[(*E*)-2-arylethenyl]-3,4-tetramethylenesiloles 1a-d. Synthesis of 1a (Ar = Ph).** Typically, in a Schlenk flask, to a solution of $Cp_2ZrCl_2$ (888 mg, 3.04 mmol) and 1,12-diphenyldodeca-1,11-dien-3,9-diyne (**3a**, 310 mg, 1.00 mmol) in THF (10 ml) was added *n*-BuMgCl (1.17 M THF solution, 5.2 ml, 6.1 mmol) *via* a syringe over 3 min at -80°C and the mixture was slowly warmed to room temperature over 0.5 days with stirring. The solvent was removed *in vacuo* and 20 ml of $CH_2Cl_2$ was added to the residue. $H_2SiCl_2$ (ca. 1 ml at below -10°C) was added to the mixture *via* vacuum transfer and the resulting mixture was stirred at 0°C for 1 h under Ar atmosphere. After removal of the volatiles, the residue was treated with 20 ml of $CH_2Cl_2$ and filtered by a glass filter with Celite. The filtrate was passed through a pad of florisil. Removal of the solvent gave an orange solid contaminated with a significant amount of $Cp_2ZrCl_2$. The residual $Cp_2ZrCl_2$ was removed by passing through a short pad of silica gel (deactivated with 10 wt. % of water; $CH_2Cl_2$ was used as an eluent). Removal of the solvent afforded an orange solid, which was recrystallized from toluene at -20°C to yield the pure title compound (160 mg).

CAUTION: Dichlorosilane is a flammable gas and exposure in air should be avoided.

**1a.** Yield 47%, red-orange crystals; mp 191-193°C. $^1H$ NMR ($CDCl_3$): 7.48-7.41 (4 H, m); 7.3-7.27 (4H, m); 7.28 (2H, d, *J* = 16 Hz); 7.23-7.16 (2H, m); 6.62 (2H, d, *J* = 16 Hz); 4.67 (2H, s); 2.77-2.63 (4H, m); 1.77-1.63 ppm (4H, m). $^{13}C$ NMR ($CDCl_3$): 156.2, 138.0, 132.1, 129.7, 128.6 127.2, 126.3, 126.2, 27.7, 23.0 ppm. $^{29}Si$ NMR ($CDCl_3$): -44.9 ppm. MS (70 eV), *m/z* (%): 340 ($M^+$, 100), 236 (14), 235 (10), 165 (12), 143 (12), 131 (17), 105 (19), 91 (17).

**1b.** Yield 43%, red-orange crystals; mp 201-203°C. $^1$H NMR (CDCl$_3$): 7.37 (4H, d, $J$ = 9 Hz); 7.13 (2H, d, $J$ = 16 Hz); 6.84 (4H, d, $J$ = 9 Hz); 6.55 (2H, d, $J$ = 16 Hz); 4.63 (2H, s); 3.80 (6H, s); 2.75-2.58 (4H, m); 1.76-1.60 ppm (4H, m). $^{13}$C NMR (CDCl$_3$): 159.0, 155.2, 131.4, 131.0, 129.3, 127.5, 124.4, 114.1, 55.3, 27.7, 23.1 ppm. $^{29}$Si NMR (CDCl$_3$): -45.2 ppm. MS (70 eV), *m/z* (%): 400 (M$^+$, 62), 326 (56), 251 (25), 161 (28), 139 (31), 137 (37), 121 (100), 91 (41), 73 (86), 44 (53), 40 (76). Found, %: C 78.08; H 7.12. $C_{26}H_{28}O_2Si$. Calculated, %: C 77.96; H 7.05.

**1c.** Yield 50%, red-orange crystals; mp 220-222°C. $^1$H NMR (CDCl$_3$): 7.35 (4H, d, $J$ = 9 Hz); 7.26 (4H, d, $J$ = 9 Hz); 7.22 (2H, d, $J$ = 16 Hz); 6.53 (2H, d, $J$ = 16 Hz); 4.62 (2H, s); 2.76-2.62 (4H, m); 1.75-1.64 ppm (4H, m). $^{13}$C NMR (CDCl$_3$): 156.7, 136.5, 132.7, 130.8, 129.7, 128.8, 127.4, 126.7, 27.7, 22.9 ppm. $^{29}$Si NMR (CDCl$_3$): -44.9 ppm. MS (70 eV), *m/z* (%): 412 (M$^+$+4, 18), 410 (M$^+$+2, 92), 408 (M$^+$, 100), 282 (20), 280 (18), 270 (19), 215 (21), 205 (20), 179 (25), 165 (27), 139 (19), 115 (23). Found, %: C 70.65; H 5.58. $C_{24}H_{22}Cl_2Si$. Calculated, %: C 70.41; H 5.42.

**1d.** Yield 46%, red crystals; mp 150-152°C. $^1$H NMR (CDCl$_3$): 7.16-7.10 (2H, m); 7.05 (2H, d, $J$ = 15 Hz); 7.00-6.91 (4H, m); 6.72 (2H, d, $J$ = 15 Hz); 4.60 (2H, s); 2.72-2.57 (4H, m); 1.74-1.59 ppm (4H, m). $^{13}$C NMR (CDCl$_3$): 156.1, 143.7, 129.3, 127.7, 126.2, 125.6, 124.9, 124.1, 27.7, 22.9 ppm. $^{29}$Si NMR (CDCl$_3$): -45.2 ppm. MS (70 eV), *m/z* (%): 354 (M$^+$+2, 17), 352 (M$^+$, 100), 242 (11), 165 (12), 136 (11), 115 (15), 111 (14), 110(13), 97 (42), 91 (11), 84 (14). Found, %: C 68.53; H 5.89. $C_{20}H_{20}S_2Si$. Calculated, %: C 68.13; H 5.72.

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