48 *Organometallics* **2006,** *25,* 48−53

Articles

Palladium-Catalyzed Reactions of 4,4,5,5-Tetramethyl-2,7-bis(trimethylsilyl)dithieno[3,2-*c*:2′,3′-*e*]disilacyclohexadiene with Alkynes

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Received May 11, 2005

The reactions of the dithienodisilacyclohexadiene derivative (**1**) with diphenylacetylene, dimethyl acetylenedicarboxylate, and phenylacetylene in the presence of a palladium catalyst at 150 °C afforded the respective adducts **2**−**4**, arising from insertion of a triple bond of the alkynes into the silicon−silicon bond of **1**, together with a small amount of the oxygen-insertion product **5**, derived from oxidation of the silicon−silicon bond of **1** by molecular oxygen. The oxidation reaction of **1** with trimethylamine *N*-oxide cleanly produced **5** in high yield. The absorption and emission maxima of **2**−**5** were markedly blue-shifted from those of **1**. The optical band gaps taken from the absorption spectra of **2**−**5** agreed very closely with the HOMO−LUMO energy gaps of the model compounds (**6**−**8**) derived from MO calculations, at the level of B3LYP/6-31+G(dp). The structures of adducts **2** and **3** were determined by single-crystal X-ray crystallography.

Introduction

Many papers concerning the addition of a silicon−silicon σ-bond in acyclic and cyclic disilane to unsaturated organic compounds in the presence of transition-metal catalysts have been reported.[1,2] Recently we have found that the platinum-catalyzed thermal reactions of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with 1-phenyl-1-propyne proceed to afford stereospecifically the respective *cis*- and *trans*-1,2,4-trimethyl-1,3,4-triphenyl-1,4-disilacyclooct-2-ene. Both conformations of the eight-membered cyclic skeletons of these adducts were suggested to be pseudo twist boat.[3] The crystal structures of cycloheptene systems containing two silicon atoms in the ring from the palladium-catalyzed reactions of 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentanes with diphenylacetylene have been reported recently.[4] The molecular structures of 1,4-dimetallacyclooctatrienes containing two germanium atoms or two silicon atoms have also been reported.[5,6]

As an extension of our study concerning the chemistry of 2,7-bis(trimethylsilyl)dithienodisilacyclohexadiene[7] (**1**), we have investigated the chemical behavior of **1** toward alkynes in the presence of a catalytic amount of the transition-metal complexes and optical properties of the adducts obtained from these reactions. In this paper we report the reactions of **1** with diphenylacetylene, dimethyl acetylenedicarboxylate, and phenylacetylene in the presence of a tetrakis(triphenylphosphine)palladium(0) catalyst and the crystal structures of the resulting adducts **2** and **3**, along with optical properties of the adducts **2**−**5** in comparison with those of 5,5′-bis(trimethylsilyl)-2,2′-bithiophene reported previously.[8] We also report that the reaction of **1** with trimethylamine *N*-oxide gives the oxidation product,

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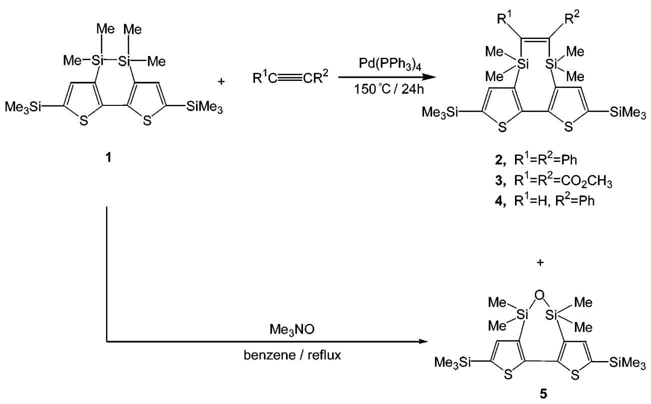
Scheme 1



the oxadithienodisilacycloheptadiene derivative **5**, in quantitative yield and detail its optical and electrochemical properties.

Results and Discussion

Reactions of Dithienodisilacyclohexadiene (1) with Alkynes and Trimethylamine *N*-Oxide. 4,4,5,5-Tetramethyl-2,7-bis(trimethylsilyl)dithieno[3,2-*c*:2′,3′-*e*]disilacyclohexadiene (**1**) was readily prepared by treating 3,3′-dilithio-5,5′-bis(trimethylsilyl)-2,2′-bithiophene with 1,2-dichlorotetramethyldisilane. All spectral data for **1** were identical with those of the authentic sample obtained from the method reported previously.[7] To obtain more information about the reactivity of the tetramethyldisilanylene-bridged bithiophene (**1**) toward substituted acetylene, we first carried out the reaction of **1** with diphenylacetylene, in the presence of ethylenebis(triphenylphosphine)platinum(0) in a sealed tube at 150 °C. However, no adduct was detected in the reaction mixture, but the starting compound **1** was recovered unchanged. In contrast to the platinum-catalyzed reaction, treatment of **1** with a 3-fold excess of diphenylacetylene in the presence of tetrakis(triphenylphosphine)palladium(0) under the same conditions produced 4,4,7,7-tetramethyl-5,6-diphenyl-2,9-bis(trimethylsilyl)dithieno[3,2-*c*:2′,3′-*g*]-4,7-disilacyclooctatriene (**2**) in 51% isolated yield as white crystals, in addition to a small amount of 4,4,6,6-tetramethyl-2,8-bis(trimethylsilyl)-5-oxadithieno[3,2-*c*:2′,3′-*f*]-4,6-disilacycloheptadiene (**5**) (Scheme 1). The production of **2** may be best explained in terms of insertion of palladium species into a silicon−silicon bond in **1**, followed by insertion of a triple bond in diphenylacetylene into a palladium−silicon bond in the palladium complex and then reductive elimination of the palladium species from the insertion product. Such a mechanism is well-known for the insertion reactions of alkynes into the silicon−silicon bond in the presence of a transition-metal catalyst.[1,4] The formation of **5**, however, may be due to the oxidation reaction[9] of the silicon−silicon bond of **1** with a trace of molecular oxygen, which we were unable to remove from the reaction system.

The palladium-catalyzed reactions of **1** with dimethyl acetylenedicarboxylate under the same conditions afforded the insertion product **3** in 47% yield, as ivory crystals. A similar reaction of **1** with phenylacetylene gave the adduct **4** in 45% yield, as ivory semisolids. In both reactions, a small amount of the oxidation product **5** was also obtained.

Table 1. Properties of Dithieno-4,7-disilacyclooctatrienes 2−4 and 5-Oxadithieno-4,6-disilacycloheptadiene 5

compd	λ_{max}/nm[a] UV	λ_{max}/nm[a] emissn	CV oxidn peak potential/V	mp/°C	λ_{ae}/nm[c]	ΔE_g/eV[d]
2[e]	291	407		250−252	332	3.7
3[e]	289	399		192−194	335	3.7
4[e]	293	406		*f*	332	3.7
5	324	404	1.02[b]	130−132	370	3.4
1	350	419	0.82[b]	85−86	388	3.2

[a] In $CHCl_3$. [b] Versus Ag/Ag^+. [c] Absorption edge. [d] Optical band gap taken from the absorption spectra. [e] No CV measurement possible due to low solubility. [f] Semisolids.

Next, we carried out the reaction of **1** with trimethylamine *N*-oxide.[10] Thus, treatment of a mixture of **1** and trimethylamine *N*-oxide in refluxing benzene produced the oxadithienodisilacycloheptadiene derivative **5** in 91% yield. The use of trimethylamine *N*-oxide as an oxidizing agent for the preparation of **5** led to a better result than that of *m*-chloroperoxybenzoic acid (MCPBA),[4,11] which is known to react readily with an Si−Si bond, giving the Si−O−Si bond. All spectral data for **5** were identical with those of the oxidation product obtained from the reaction of **1** with the alkynes in the presence of the palladium catalyst.

^1H and ^{13}C NMR spectra for the alkyne-insertion products **2**−**4** indicate that two methyl groups on a silicon atom in the disilacyclooctatriene ring are nonequivalent, whereas two methyl groups on the silicon atom in the oxygen-insertion product **5** are equivalent. To get more information about the anomalous behavior of the Me_2Si groups in the disilacyclooctatriene ring, we examined the behavior of compounds **3** and **5** in detail, by variable-temperature NMR techniques. In the ^1H NMR spectrum for the disilacyclooctatriene derivative **3**, two nonequivalent methyl protons on the silicon atom did not coalesce up to 60 °C in $CDCl_3$. However, for compound **5**, two methyl protons on the silicon atom in the oxadithienodisilacycloheptadiene ring were observed as a singlet at −60 °C in $CDCl_3$ and even at −100 °C in CD_2Cl_2. It is likely that nonequivalence of the methyl groups on the ring silicon atom in compounds **2**−**4** may be ascribed to the disilacyclooctatriene ring, which is significantly twisted. In fact, the twisting angle of the disilacyclooctatriene ring in **3** is observed as 59.32° by X-ray crystallographic analysis. On the other hand, a single resonance attributed to two methyl protons on the ring silicon atom in compound **5** is presumably due to rapid interconversion through ring flipping. The oxadithienodisilacycloheptadiene ring is structurally less twisted than the disilacyclooctatriene ring, and therefore the former ring is probably more flexible than the latter. Indeed, it has been reported that compounds with seven-membered ring have a very low barrier for ring flipping, and these compounds are generally inaccessible by variable-temperature NMR studies.[12]

Optical and Electrochemical Properties of Dithieno-4,7-disilacyclooctatrienes 2−4 and 5-Oxadithieno-4,6-disilacycloheptadiene 5. Table 1 summarizes absorption and emission maxima, melting points, absorption edges, and optical band gaps of **2**−**5** and the oxidation peak potential of **5** in the cyclic voltammogram (CV) in comparison with those of dithienodi-

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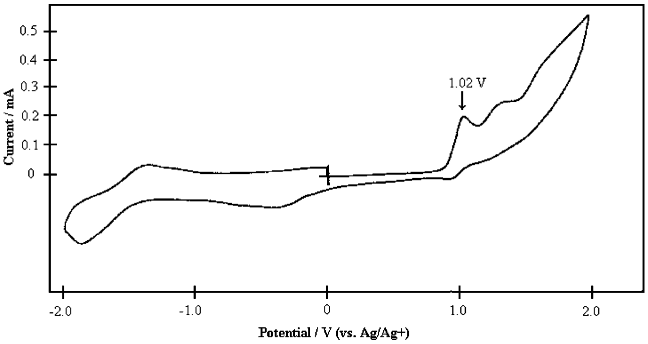
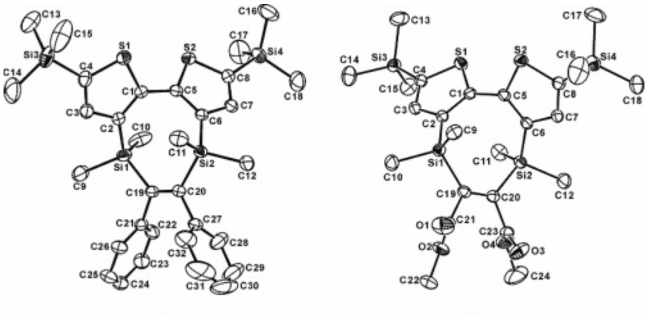


Figure 1. CV profile of compound **5** in acetonitrile on the first scan.



2 **3**

Figure 2. ORTEP diagrams for **2** and **3** showing thermal ellipsoids at the 30% level. Hydrogen atoms are omitted for clarity. Selected torsional angles (deg): **2**, C2−C1−C5−C6 = −50.4(4), C1−C5−C6−Si2 = −12.0(4), C20−Si2−C6−C5 = 87.2(2), C6−Si2−C20−C19 = −35.7(3), Si1−C19−C20−Si2 = −8.0(4), C2−Si1−C19−C20 = −28.2(3), C19−Si1−C2−C1 = 83.7(3), C5−C1−C2−Si1 = −15.4(4); **3**, C2−C1−C5−C6 = 56.5(5), C1−C5−C6−Si2 = 10.1(5), C20−Si2−C6−C5 = −89.5(3), C6−Si2−C20−C19 = 42.2(3), Si1−C19−C20−Si2 = 2.0(5), C2−Si1−C19−C20 = 30.1(4), C19−Si1−C2−C1 = −81.4(3), C5−C1−C2−Si1 = 11.5(5).

silacyclohexadiene **1**. The absorption and emission maxima of **2**−**5** were markedly blue-shifted from those of **1**, indicating that introduction of an ethylene or oxygen moiety to the parent tetramethyldisilanylene-bridged bithiophene **1** leads to large optical band energies. This may be due to the more significant twisting of two thiophene rings, by elongation of the bridging unit.

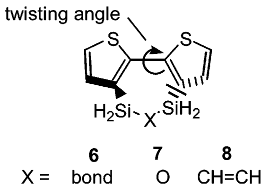
The CV of **5** was measured in acetonitrile. The CV curve of compound **5** on the first scan is depicted in Figure 1, which exhibits an irreversible CV with an oxidation peak appearing at 1.02 V vs Ag/Ag$^+$ as listed in Table 1. The oxidation potential of **5** is slightly higher than that of dithienodisilacyclohexadiene **1**. Assuming that oxidation peak potentials obtained by CV measurements are related to HOMO levels of the compounds, the HOMO level for **5** is suggested to be slightly lower than that of **1** from the results of CV measurements, in good agreement with the theoretical calculations, which predict a slightly lower HOMO level for **7** than that of **6**, as shown in Figure 3.

Crystal Structures of 2 and 3. The crystal structures of compounds **2** and **3** were determined by X-ray single-crystal diffraction strudies. ORTEP diagrams[13] for **2** and **3** are depicted in Figure 2. Cell dimensions and data collection and refinement parameters are given in Table 2, and bond distances and angles are given in Tables 3 and 4 for **2** and **3**, respectively.

Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 2 and 3

	2	3
mol formula	$C_{32}H_{42}S_2Si_4$	$C_{24}H_{38}O_4S_2Si_4$
mol wt	603.14	567.02
cryst syst, space group	triclinic, *P*1	monoclinic, *P*2$_1$/*c*
unit cell dimens		
a, Å	11.395(1)	13.452(4)
b, Å	11.788(1)	20.239(4)
c, Å	14.173(1)	11.850(4)
α, deg	87.39(1)	90
β, deg	72.44(1)	91.19(2)
γ, deg	87.36(1)	90
V, Å^3	1812.1(3)	3225.5(16)
Z	2	4
D_{calcd}, Mg/m^3	1.105	1.168
F_{000}	644	1208
cryst size, mm^3	0.60 × 0.44 × 0.38	0.63 × 0.50 × 0.25
temp, K	298(2)	
wavelength, Å	0.710 69 (Mo Kα)	
monochromator	graphite cryst	
diffractometer	STOE STAI4	
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0534, wR2 = 0.1267	R1 = 0.0600, wR2 = 0.1170
R indices (all data)	R1 = 0.0853, wR2 = 0.1535	R1 = 0.1130, wR2 = 0.1471

Chart 1. Model Compounds for MO Calculations



As can be seen in Figure 2, compounds **2** and **3** have essentially identical dithieno-4,7-disilacyclooctatriene units which involve a significantly twisted bithiophene system with a twisting angle of 54.28° for **2** and 59.32° for **3** between the two thiophene rings. These are in contrast with the crystal structure of **1**, which has the small twisting angle of 20.2°.[7] Similar twisting has been reported previously for a 2,5,7-tribenzo-1,4-disilacyclooctatriene derivative, in which two adjacent benzene rings have turned out to be twisted with an angle of 63.6°.[6] A slightly larger twisting angle for this benzo derivative than for compounds **2** and **3** is presumably due to steric repulsion between the ortho protons of the benzene rings. It is noted that the bond distances of Si−C(sp^2), e.g., Si1−C19 (1.901(3) Å) and Si2−C20 (1.896(3) Å), in the eight-membered-ring compound **3** are slightly longer than those of Si1−C2 (1.878(3) Å) and Si2−C6 (1.874(3) Å). The long bond distances of Si1−C19 and Si2−C20 seem to lessen the ring strain to some extent.

Theoretical Calculations of Model Compounds. We carried out theoretical calculations on the simplified model compounds **6**−**8** (Chart 1) at the level of B3LYP/6-31+G(dp) to see their electronic structures.

The relative energy levels for the model compounds are plotted versus the twisting angles of the bithiophene units of the optimized geometries in Figure 3. The twisting angle of **8** (−56.85°) is comparable to those of the crystal structures of **2** and **3** described above. As shown in Figure 3, the HOMO energy levels are lowered and the HOMO−LUMO energy gaps increase as the twisting angles increase, in the order **6** < **7** < **8**, in accordance with the blue-shifted UV λ_{max} in the same order. This agrees also with the results of CV measurements of the compounds **1** and **5** in Table 1, which suggest a slightly higher HOMO level of **1** as compared to that of **5**. In contrast, no

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[13] Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 3. Selected Distances (Å) and Angles (deg) for Compound 2 with Their Esd's in Parentheses

Si1−C2	1.875(3)	Si1−C19	1.891(3)	Si2−C6	1.878(3)
Si2−C20	1.892(2)	S1−C1	1.731(3)	S1−C4	1.722(3)
S2−C5	1.725(3)	S2−C8	1.726(3)	C1−C2	1.373(3)
C1−C5	1.453(4)	C2−C3	1.434(4)	C3−C4	1.365(4)
C5−C6	1.380(3)	C6−C7	1.434(3)	C7−C8	1.370(4)
C19−C20	1.349(3)				
C2−Si1−C19	115.74(11)	C6−Si2−C20	112.57(11)	C1−S1−C4	93.14(13)
C5−S2−C8	93.04(13)	S1−C1−C2	111.91(19)	S1−C1−C5	121.17(19)
C2−C1−C5	126.9(2)	Si1−C2−C1	124.6(2)	Si1−C2−C3	124.5(2)
C1−C2−C3	109.8(2)	C2−C3−C4	116.4(3)	S1−C4−C3	108.7(2)
S2−C5−C1	120.6(2)	S2−C5−C6	112.07(19)	C1−C5−C6	127.2(2)
Si2−C6−C5	125.40(19)	Si2−C6−C7	124.33(19)	C5−C6−C7	110.0(2)
C6−C7−C8	115.9(2)	S2−C8−C7	109.0(2)	Si1−C19−C20	129.03(18)
Si2−C20−C19	127.47(19)				

Table 4. Selected Distances (Å) and Angles (deg) for Compound 3 with Their Esd's in Parentheses

Si1−C2	1.878(3)	Si1−C19	1.901(3)	Si2−C6	1.874(3)
Si2−C20	1.896(3)	S1−C1	1.721(3)	S1−C4	1.722(4)
S2−C5	1.724(3)	S2−C8	1.722(3)	C1−C2	1.387(4)
C1−C5	1.459(4)	C2−C3	1.431(4)	C3−C4	1.373(5)
C5−C6	1.377(4)	C6−C7	1.428(4)	C7−C8	1.370(5)
C19−C20	1.346(5)				
C2−Si1−C19	113.19(14)	C6−Si2−C20	109.94(14)	C1−S1−C4	93.41(16)
C5−S2−C8	93.30(16)	S1−C1−C2	111.9(2)	S1−C1−C5	121.8(2)
C2−C1−C5	126.3(3)	Si1−C2−C1	125.5(2)	Si1−C2−C3	124.4(2)
C1−C2−C3	109.8(3)	C2−C3−C4	116.1(3)	S1−C4−C3	108.8(2)
S2−C5−C1	122.3(2)	S2−C5−C6	111.8(2)	C1−C5−C6	126.0(3)
Si2−C6−C5	123.9(2)	Si2−C6−C7	125.6(2)	C5−C6−C7	110.1(3)
C6−C7−C8	116.2(3)	S2−C8−C7	108.6(2)	Si1−C19−C20	130.1(2)
Si2−C20−C19	128.3(2)				

significant changes of the LUMO energy levels are observed on going from **6** to **7**, while introduction of an ethenylene unit leads to simple elevation of the LUMO energy level of **8**, as expected. Presumably, introduction of an electronegative oxygen that would tend to lower the LUMO energy level compensates for the suppressed π-conjugation by twisting in **7**, to make its LUMO lie at almost the same energy as that of **6**.

To know how the silanylene bridges affect the electronic structures, we carried out MO calculations for bithiophenes with different twisting angles, and the results are also shown in Figure 3. In these calculations, the silanylene bridge in the optimized geometries of **6**−**8** was simply replaced with two hydrogen atoms, and the energy calculations were performed without further structure optimization. Interestingly, it is noted that both the HOMO and LUMO energy levels are lowered by introduction of a silanylene bridge. However, the LUMOs are primarily affected by the silanylene bridge, as compared with the HOMOs, leading to smaller HOMO−LUMO energy gaps for **6**−**8** than for the corresponding bithiophene models. Figure 4 depicts the LUMO profiles obtained from the calculations, showing the bonding interaction between the Si orbital and the bithiophene π-orbital. In particular, the LUMO of **7** lies at much lower energy, by about 0.5 eV from that of the corresponding bithiophene, again indicating the influence of the electronegative oxygen atom in the silanylene bridge.

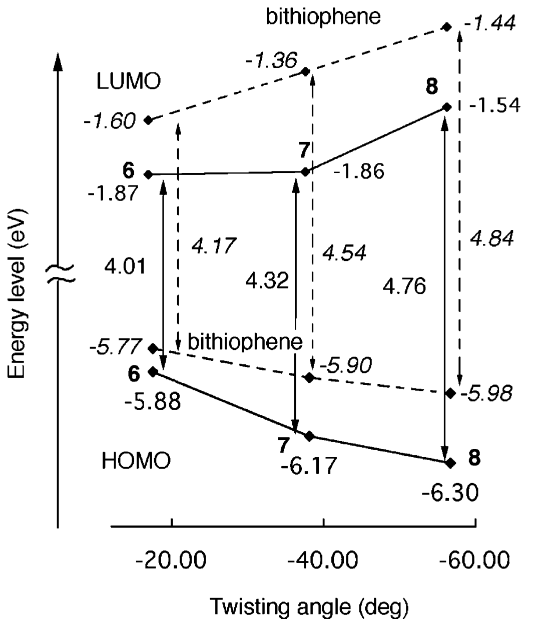
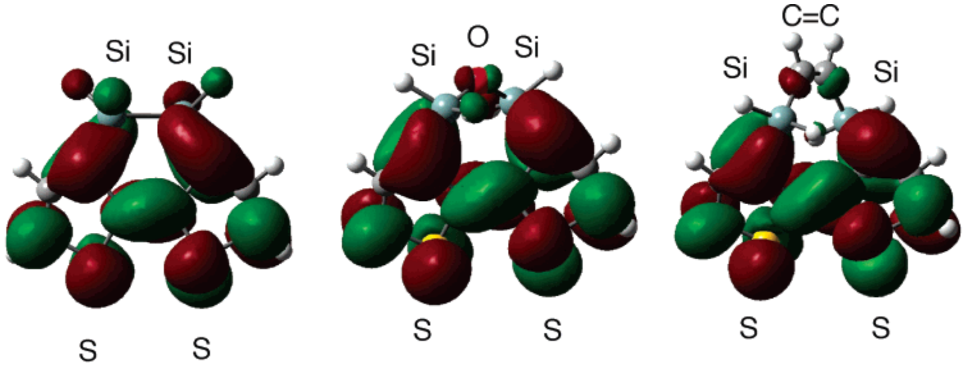


Figure 3. Relative HOMO and LUMO energy levels derived from MO calculations at the B3LYP/6-31+G(dp) level for **6**−**8** (solid lines) and the corresponding bithiophene derivatives with different twisting angles (broken lines).

In conclusion, the palladium-catalyzed reactions of **1** with diphenylacetylene, dimethyl acetylenedicarboxylate, and phenylacetylene afforded the respective adducts **2**−**4**, arising from insertion of a triple bond of the alkynes into the silicon−silicon bond of **1**, together with a small amount of the oxygen-insertion product **5**, derived from oxidation of the silicon−silicon bond of **1** by molecular oxygen. The absorption and emission maxima of **2**−**5** were markedly blue-shifted from those of **1**. This may be due to the singnificantly twisted bithiophene system with a twisting angle of 54.28° for **2** and 59.32° for **3** between the two thiophene rings of the adducts **2** and **3**. These results clearly indicate that introduction of one or two atom(s) into the disilanylene unit of **1** provides a convenient method for fine-tuning of the electronic states of bithiophene derivatives. In particular, introducing an oxygen atom into the disilanylene unit, which affects primarily the HOMO energy level to lower it with the LUMO level almost untouched, seems to be useful to design electron-transporting molecules. Studies to evaluate the utilities of these compounds as carrier-transporting materials are in progress.



6 **7** **8**

Figure 4. LUMO profiles for compounds **6**−**8**, derived from MO calculations.

Experimental Section

General Procedures. All palladium-catalyzed reactions were carried out in a degassed sealed tube (1.0 cm × 15 cm). Yields of the products **2**−**5** were calculated on the basis of the isolated products. The progress of the reaction was checked by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on an HP-1 capillary column (cross-linked 5% methylphenylsilicone, 25 m). NMR spectra were recorded on Bruker Avance 400 and Varian 500 spectrometers. Chemical shifts were given as δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as internal standard. Silicon chemical shifts are referenced to the signal of TMS. Mass spectra were measured on a Shimadzu QP5000 instrument. UV spectra were measured on a JASCO V-530 spectrophotometer, and emission spectra were obtained by a Shimadzu RF-5301PC spectrofluorimeter. Pure adducts **2**−**5** were separated by column chromatography using silica gel and Wakogel C-300 (WAKO). Preparative TLC was performed by using silica gel 60F_{254} (Merck). Elemental analyses were measured on a FISONS EA1106 instrument. Melting points were measured with a Laboratory Devices-MEL-TEMP II apparatus.

Materials. 1,2-Dichlorotetramethyldisilane, 2.5 M *n*-butyllithium hexane solution, phenylacetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate were obtained from Aldrich Chemical Co. and used without further purification. Tetrahydrofuran and ether used as solvents were dried over sodium/benzophenone under a nitrogen atmosphere and distilled before use. Benzene was dried over lithium aluminum hydride and distilled before use.

Preparation of 4,4,5,5-Tetramethyl-2,7-bis(trimethylsilyl)-dithieno[3,2-*c*: 2′,3′-*e*]- disilacyclohexadiene (1). The starting compound **1** was prepared as described previously in the literature.[7] All spectral data for the starting material were identical with those of the authentic sample obtained from the method reported previously.

Palladium-Catalyzed Reaction of 1 with Diphenylacetylene. A mixture of 0.400 g (0.941 mmol) of **1**, 0.563 g (3.16 mmol) of diphenylacetylene, and 0.030 g (0.0260 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. Compound **2** (0.290 g, white crystals, 51%) was isolated by column chromatography (silica gel, hexane) and recrystallized from ethanol, together with a small amount of **5** (17.0 mg, 4%). Then the palladium-catalyzed reaction of **1** with diphenylacetylene was carried out again, in which degassing five times by freeze−vacuum cycles and a more powerful vacuum pump were used in order to remove molecular oxygen completely in the reaction system. No oxygen-insertion product **5** was observed from this catalyzed reaction.

Data for **2**: 51% yield; mp 250−252 °C; MS *m*/*z* (relative intensity) 602 (M^+, 8), 587 (7), 512 (100), 73 (43); UV λ_{max} ($CHCl_3$) 291 nm (ϵ = 13 400); ^1H NMR ($CDCl_3$) δ −0.28 (s, 6H, SiMe), −0.07 (s, 6H, SiMe), 0.36 (s, 18H, $SiMe_3$), 6.59 (d, 2H, phenyl ring protons, J = 6.04 Hz), 6.83 (d, 2H, phenyl ring protons, J = 7.04 Hz), 6.88−6.96 (m, 4H, phenyl ring protons), 7.06−7.09 (m, 2H, phenyl ring protons), 7.19 (s, 2H, bithiophene ring protons); ^{13}C NMR ($CDCl_3$) δ −2.67 (MeSi), −0.10 (MeSi), 0.10 (Me_3Si), 124.52, 127.00, 128.44, 140.13, 141.02, 142.64, 145.51, 150.50 (phenyl and bithiophene ring carbons), 158.07 (olefinic carbons); ^{29}Si NMR ($CDCl_3$) δ −16.88 ($SiMe_2$), −6.74 ($SiMe_3$). Anal. Calcd for $C_{32}H_{42}S_2Si_4$: C, 63.72; H, 7.02. Found: C, 64.05; H, 7.20.

Palladium-Catalyzed Reaction of 1 with Dimethyl Acetylenedicarboxylate. A mixture of 0.212 g (0.500 mmol) of **1**, 0.238 g (1.67 mmol) of dimethyl acetylenedicarboxylate, and 0.0162 g (0.0140 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. Compound **3** (0.133 g, ivory crystals, 47%) was isolated by column chromatography (silica gel, hexane:THF = 1:2) and crystallized from ethanol, together with a small amount of **5** (9.00 mg, 4%).

Data for **3**: 47% yield; mp 192−194 °C; MS *m*/*z* (relative intensity) 566 (M^+, 71), 551 (14), 507 (21), 477 (42), 73 (100); UV λ_{max} ($CHCl_3$) 289 nm (ϵ = 12 060); ^1H NMR ($CDCl_3$ at 25 °C) δ −0.30 (s, 6H, SiMe), 0.33 (s, 18H, $SiMe_3$), 0.42 (s, 6H, SiMe), 3.74 (s, 6H, CO_2Me), 7.12 (s, 2H, bithiophene ring protons); ^1H NMR ($CDCl_3$ at 60 °C) δ −0.26 (s, 6H, SiMe), 0.35 (s, 18H, $SiMe_3$), 0.43 (s, 6H, SiMe), 3.73 (s, 6H, CO_2Me), 7.16 (s, 2H, bithiophene ring protons); ^{13}C NMR ($CDCl_3$) δ −3.04 (MeSi), −2.24 (MeSi), −0.04 (Me_3Si), 51.86 (OMe), 138.78, 139.98, 143.42, 150.95 (bithiophene ring carbons), 153.40 (olefinic carbons), 171.71 (C=O); ^{29}Si NMR ($CDCl_3$) δ −15.22 ($SiMe_2$), −6.51 ($SiMe_3$). Anal. Calcd for $C_{24}H_{38}O_4S_2Si_4$: C, 50.84; H, 6.76. Found: C, 51.02; H, 6.88.

Palladium-Catalyzed Reaction of 1 with Phenylacetylene. A mixture of 0.212 g (0.500 mmol) of **1**, 0.153 g (1.50 mmol) of phenylacetylene, and 0.0162 g (0.0140 mmol) of tetrakis(triphenylphosphine)palladium(0) was heated in a degassed sealed tube at 150 °C for 24 h. The palladium species in the resulting mixture was removed by passing through a short silica gel column. Compound **4** (0.118 g, ivory semisolids, 45%) was isolated by a silica gel column with hexane as eluent, together with a small amount of **5** (7.00 mg, 3%).

Data for **4**: 45% yield; MS *m*/*z* (relative intensity) 526 (M^+, 16), 511 (16), 436 (100), 73 (81); UV λ_{max} ($CHCl_3$) 293 nm (ϵ = 12 050); ^1H NMR ($CDCl_3$) δ −0.42 (s, 3H, SiMe), −0.22 (s, 3H, SiMe), 0.18 (s, 3H, SiMe), 0.33 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 0.44 (s, 3H, SiMe), 6.54 (s, 1H, HC=C), 7.08−7.10 (m, 2H, phenyl ring protons), 7.15 (s, 1H, bithiophene ring proton), 7.18 (s, 1H, bithiophene ring proton), 7.20−7.22 (m, 1H, phenyl ring protons), 7.26−7.30 (m, 2H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −2.93 (MeSi), −1.51 (MeSi), −0.64 (MeSi), −0.35 (MeSi), 0.06 (Me_3Si), 125.90, 126.38, 127.87, 139.70, 140.07, 140.16, 140.64, 142.47, 142.58, 148.39, 149.36, 150.04 (phenyl and bithiophene ring carbons), 150.45, 163.32 (olefinic carbons); ^{29}Si NMR ($CDCl_3$) δ −19.47 ($SiMe_2$), −16.03 ($SiMe_2$), −6.77 ($SiMe_3$), −6.75 ($SiMe_3$). Anal. Calcd for $C_{26}H_{38}S_2Si_4$: C, 59.25; H, 7.27. Found: C, 59.35; H, 7.38.

Reaction of 1 with Trimethylamine *N*-Oxide. In a 50 mL three-necked flask with a stirrer and reflux condenser was placed a mixture of 0.604 g (1.42 mmol) of **1** and 0.315 g (4.19 mmol) of trimethylamine *N*-oxide in 8 mL of dry benzene.[10] The mixture was heated to reflux for 46 h, the solvent was evaporated off, and the residue was chromatographed on a silica gel column with hexane as eluent to give the product **5** (0.570 g, colorless solids, 91%).

Data for **5**: 91% yield; mp 130−132 °C; MS *m*/*z* (relative intensity) 440 (M^+, 100), 425 (89), 352 (22), 73 (22); UV λ_{max} ($CHCl_3$) 324 nm ($\epsilon = 15\,000$); ^{1}H NMR ($CDCl_3$ at 25 °C) δ 0.27 (s, 12H, SiMe), 0.34 (s, 18H, $SiMe_3$), 7.14 (s, 2H, bithiophene ring protons); ^{1}H NMR ($CDCl_3$ at −60 °C) δ 0.29 (s, 12H, SiMe), 0.33 (s, 18H, $SiMe_3$), 7.14 (s, 2H, bithiophene ring protons); ^{1}H NMR (CD_2Cl_2 at −100 °C) δ 0.13 (s, 12H, SiMe), 0.20 (s, 18H, $SiMe_3$), 7.08 (s, 2H, bithiophene ring protons); ^{13}C NMR ($CDCl_3$) δ 0.05 (Me_3Si), 0.77 (Me_2Si), 139.10, 139.95, 140.97, 150.68 (bithiophene ring carbons); ^{29}Si NMR ($CDCl_3$) δ −6.51 ($SiMe_3$), −0.65 ($SiMe_2$). Anal. Calcd for $C_{18}H_{32}OS_2Si_4$: C, 49.03; H, 7.32. Found: C, 49.13; H, 7.23.

CV Measurements. CV measurements were carried out using a three-electrode system in an acetonitrile solution containing 100 mM of lithium perchlorate as the supporting electrolyte and 2 mM of the substrates **1** and **5**, respectively. Pt wires were used as the working and counter electrodes, and Ag/Ag^+ was used as the reference electrode. The current−voltage curve was recorded at room temperature on a Hokuto Denko HAB-151 potentionstat/galvanostat.

Molecular Orbital Calculations on 6−8 and Bithiophene Derivatives. MO calculations were carried out using the restricted Hartree−Fock (RHF) method at the 6-31G* level within the Gaussian 98 suite of programs (revision 9), attached with a Gauss View interface (Gaussian, Inc., Pittsburgh, PA, 1998). For the calculations of the bithiophene derivatives, the silanylene bridges in the optimized geometries of **6**−**8** were eliminated and hydrogen atoms were placed on the thiophene rings with H−C = 1.07 Å and H−C=C = H−C−C. No structure optimization was applied for the bithiophenes.

X-ray Crystallographic Analysis of 2 and 3. Data were collected on a STOE STADI4 four-circle diffractometer[14] using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) by the $\omega-2\theta$ scan technique at 298(2) K. In each case, unit cell parameters were determined by a least-squares fit of 30 (**2**) and 27 reflections (**3**) having 2θ values in the ranges of 9.5−10.4 (**2**) and 9.5−10.5° (**3**). Intensities of three check reflections were measured after every 1 h during the data collection to monitor the crystal stability. In both cases, there is no significant change in the intensities of the check reflections. A numerical absorption correction for **3** was made,[14] and the transmission factor was 0.9337 (minimum) and 0.9633 (maximum) for **3**. The structures were solved by direct methods[15] and refined on F^2 by full-matrix least-squares procedures.[16] All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model but were not refined. The data collection and structure solution parameters are given in Table 2, together with the standard discrepancy indices R and R_w.

Acknowledgment. This work of "Design and Synthesis of Functional Organosilicon Compounds" was supported by a Korea Research Foundation Grant (No. KRF-2003-015-C00329).

Supporting Information Available: Structure determination parameters, crystal and structure refinement data, atomic coordinates, and anisotropic displacement parameters for **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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