J. Am. Chem. Soc. **1994,** *116,* 11715−11722 11715

Oligosiloles: First Synthesis Based on a Novel *Endo−Endo* Mode Intramolecular Reductive Cyclization of Diethynylsilanes

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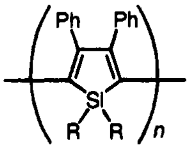
Received July 5, 1994[⊗]

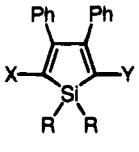
Abstract: A general and versatile synthesis of 2,5-difunctional siloles and their conversion into oligosiloles are described. Diethynylsilanes undergo intramolecular reductive cyclization in an *endo−endo* mode upon treatment with lithium naphthalenide to form 2,5-dilithiosiloles. The 2,5-dilithiosiloles are converted into various 2,5-difunctional siloles by treatment with electrophiles. The resulting 2,5-dibromosilole is further converted into several highly functionalized siloles via palladium-catalyzed cross-coupling reaction or selective mono-lithiation using *n*-butyllithium in ether. Oligosiloles, from bisiloles to quatersilole, are prepared from certain functional siloles. Oxidative coupling of 2,5-dilithiosilole by use of an Fe(III) complex affords 2,2′-bisilole as yellow crystals. Difunctional oligosiloles, 5,5′-dibromo-2,2′-bisilole and 5,5‴-dibromo-2,2′:5′,2″:5″,2‴-quatersilole, are prepared by oxidative coupling via higher order cyanocuprate of 2-bromo-5-lithiosilole and 5-bromo-5′-lithio-2,2′-bisilole, respectively. X-ray crystal structures of these bisiloles show highly twisted arrangements between two silole rings with 62−64° of torsion angle. ^{1}H NMR studies on bisiloles show a rapid equilibration between non-coplanar conformers in solution. In UV-visible spectra, nevertheless, all of the oligosiloles have unusually long absorption maxima.

Introduction

π-Conjugated polymers containing silole (silacyclopentadiene) rings have recently been highlighted as a promising candidate for novel π-electronic materials, because of their anticipated properties such as conductivity, thermochromism, and nonlinear optical properties.[1−6] Whereas thiophene−silole copolymers have recently been reported as only one example of the synthesis of silole-containing π-conjugated polymers,[1,7] polysiloles, silole 2,5-linked homopolymers, have still remained to be a center of target. Some theoretical approaches to polysiloles have predicted interesting properties,[4−6] including small bandgaps for coplanar polysiloles[5] and, alternatively, non-coplanar arrangement as the most stable conformer.[6] Experimentally, however, the well-characterized polysilole has not ever been obtained despite some attempts, as exemplified by polymerization of diethynylsilanes.[2] Although the most straightforward route to polysiloles would be the direct coupling of silole monomers at 2,5-positions, there had been a great difficulty for introduction of the requisite functional groups, such as Li, Br, SnR_3, into the 2,5-positions of silole ring by conventional methods.[8] Therefore, we commenced to develop a new methodology for the synthesis of 2,5-difunctional siloles. Herein we describe the first general and versatile synthesis of various 2,5-difunctional siloles via a conceptually new intramolecular reductive cyclization of diethynylsilanes and the first synthesis of oligosiloles as models of polysiloles by use of functional siloles in hand.



Polysilole



2,5-Difunctional Silole
(X = Li, Br, SnR_3 *etc.*)

Results and Discussions

Intramolecular Reductive Cyclization of Diethynylsilanes. We have found that diethynylsilanes undergo intramolecular reductive cyclization in an *endo−endo* mode upon treatment with lithium naphthalenide (LiNp) to form 2,5-dilithiosiloles, as shown in Scheme 1, which could not be prepared by conventional methods for the synthesis of siloles.[8]

Thus, reductive cyclization of bis(phenylethynyl)dialkylsilane **1** was carried out by dropwise addition of a THF solution of **1** into 4 equiv of LiNp in THF at ambient temperature under an argon atmosphere to afford 2,5-dilithiosilole **2** exclusively. Lithium 4,4′-di-*tert*-butyl-2,2′-biphenylide (LDBB)[9] or lithium (*N,N*-dimethylamino)naphthalenide (LDMAN)[10] instead of LiNp as a reductant was also effective for the present reductive cyclization. The key point to attain high yield is the dropwise

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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(7) Polymers involving only the silicon atom of the silole ring in the main chain have recently been prepared: (a) Corriu, R. J. P.; Douglas, W. E.; Yang, Z.-X.; Garnier, F.; Yassar, A. *J. Organomet. Chem.* **1991,** *417,* C50. (b) Corriu, R. J. P.; Douglas, W. E.; Yang, Z.-X. *J. Organomet. Chem.* **1993,** *456,* 35.

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(10) Cohen, T.; Sherbine, J. P.; Matz, J. R.; Hutchins, R. R.; McHenry, B. M.; Willey, P. R. *J. Am. Chem. Soc.* **1984,** *106,* 3245.

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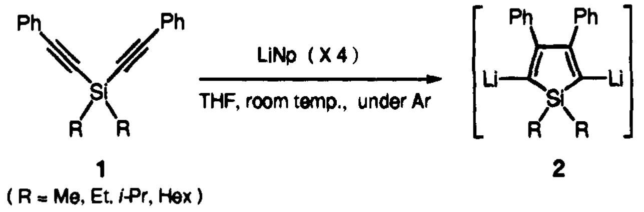
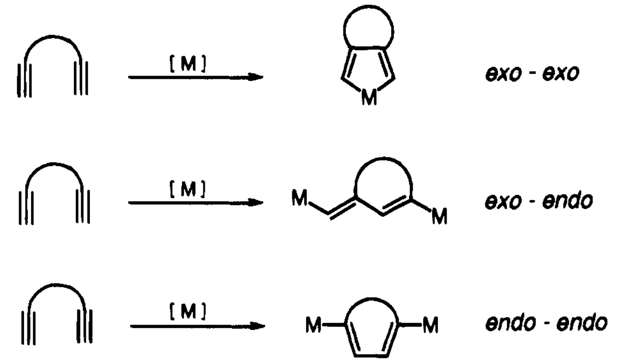
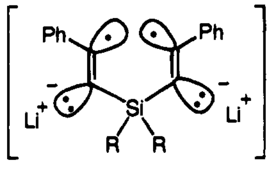
Scheme 1



Scheme 2



addition of diethynylsilane into an "electron pool" consisting of an excess amount of reductant, and thereby both acetylene moieties are reduced *simultaneously* to form a bis(anion radical) intermediate **3** that undergoes radical coupling to form the 3,4-carbon–carbon bond with leaving anions at the 2,5-positions. The use of a stoichiometric amount of reductant lowered the yield of dilithiosilole significantly, together with the formation of a lithium phenylacetylide as a byproduct via cleavage of the carbon–silicon bond. Thus, it appears that a mono(anion radical) arising from less efficient stepwise reduction under the electron deficiency is prone to undergo cleavage of the carbon–silicon bond prior to the formation of the di(anion radical). The phenyl group at the terminal position of acetylene is also essential for obtaining the dilithiosiloles: A complex mixture was obtained in the case of an alkyl- or a silyl-substituted ethynyl group. The phenyl groups may thus act as a stabilizer of the crucial bis(anion radical) species **3**.



3

Metal (M)-promoted intramolecular reductive cyclization of diynes is formally classified into three types with respect to the orientations of acetylene moieties to the newly formed ring, as shown in Scheme 2.[11] Whereas the *exo–exo* mode of reductive cyclization has been well known to proceed with various transition-metal two-electron reductants such as Zr(II), Ti(II), Co(I), Rh(I), Ni(0), Pd(0),[12] the *exo–endo* mode reductive cyclization has been very rare[13] and the *endo–endo* mode reductive cyclization has been unknown, to our best knowledge.[14] The reductive cyclization by use of the one-electron reductant lithium reagent described herein is the first example of the last type of cyclization. The present reductive cyclization may also be regarded as an anion analogue of Bergman cyclization, a neutral thermal cyclization of enediynes in the *endo–endo* mode,[18] and as an intramolecular version of intermolecular coupling of diphenylacetylene with lithium to afford dilithiobutadiene.[19]

Synthesis of Various 2,5-Difunctional Siloles. By trapping with various electrophiles such as trimethylchlorosilane, *n*-tributylstannyl chloride, phenylselenenyl chloride, and bromine, 2,5-dilithiosiloles were transformed into the corresponding 2,5-difunctional siloles, 2,5-disilylsilole **4** (86%), distannylsilole **5** (49%), diselenenylsilole **6** (73%), and dibromosilole **7** (44–72%), respectively, as shown in Scheme 3: In the synthesis of dibromosilole **7**, the excess LiNp should be quenched with bulky triphenylchlorosilane, *tert*-butyldiphenylchlorosilane, or triisopropylchlorosilane before treatment with bromine. The chlorosilane is converted into the corresponding disilane.

Dibromosilole **7** was converted into the extended π-conjugated compounds, dithienylsilole **8** and diethynylsilole **9**, via palladium-catalyzed cross-coupling reaction with (2-thienyl)stannane and (phenylethynyl)stannane, respectively.[20] Furthermore, dibromosilole **7** was selectively monolithiated by *n*-butyllithium in ether at −78–0 °C to afford 2-bromo-5-lithiosilole **10**. This selective mono-lithiation of **7** was attained only in dry ether: Lithiation in dry THF by use of *n*-butyllithium (1 equiv) or *tert*-butyllithium (2 equiv) resulted in the predominant formation of a 2-bromosilole **11** via H-abstraction. The monolithiosilole **10** was trapped with water, trimethylchlorosilane, and *n*-tributylstannyl chloride to give the corresponding unsymmetrical functional siloles, 2-bromosilole **11**, 2-bromo-5-silylsilole **12**, and 2-bromo-5-stannylsilole **13**, respectively, in 79–82% isolated yields (Scheme 3). Monobromosiloles **11**–**13**, especially **11**, gradually decompose in the air under light and should be stored in a freezer in the dark under an argon atmosphere.

All of the functional siloles obtained in this study, except **4**, are new compounds barely accessible by traditional methods which have allowed to introduce only a limited number of inactive groups, such as alkyl, aryl, and silyl groups, to the 2,5-positions.[8,21] It may be noted that some of the new compounds

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(11) A recent review on acetylene oligomerization: Gleiter, R.; Kratz, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 842.

(12) For example: (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, p 1129. (b) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, p 1163.

(13) Reductive cyclizations of macrocyclic acetylenic compounds using Li metal or Na/NH$_3$ have already been reported: In these cases, the intramolecuclar cyclizations proceed in the *exo–endo* mode, but result in the partial or exhaustive hydrogenation. (a) Youngs, W. J.; Djebli, A.; Tessier, C. A. *Organometallics* **1991**, *10*, 2089. (b) Bradshaw, J. D.; Solooki, D.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 3177. (c) Behr, O. M.; Eglinton, G.; Raphael, R. A. *Chem. Ind.* **1959**, 699. (d) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614.

(14) Except for reductive cyclization, a few examples of the *exo–endo* mode or *endo–endo* mode intramolecular cyclizations of diynes have been reported. See, for example, refs 15–17.

(15) Molybdenum- or tungsten-catalyzed polymerization of diynes to polyacetylene derivatives formally belongs to the *exo–endo* mode cyclization: (a) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelmann, H.; Kaplan, S.; Harbour, J.; Yang, X.-Q.; Tanner, D. B.; Pochan, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4417. (b) Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1988**, 1149. See also ref 2b.

(16) Iodine-promoted oxidative cyclization of a macrocyclic acetylenic compounds has recently been reported to proceed in the *exo–endo* mode: Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294.

(17) Acidic cyclization of bis(stannylethynyl)silanes may fall into the *endo–endo* category: (a) Wrackmeyer, B. *J. Chem. Soc., Chem. Commun.* **1986**, 397. (b) Wrackmeyer, B. *J. Organomet. Chem.* **1986**, *310*, 151.

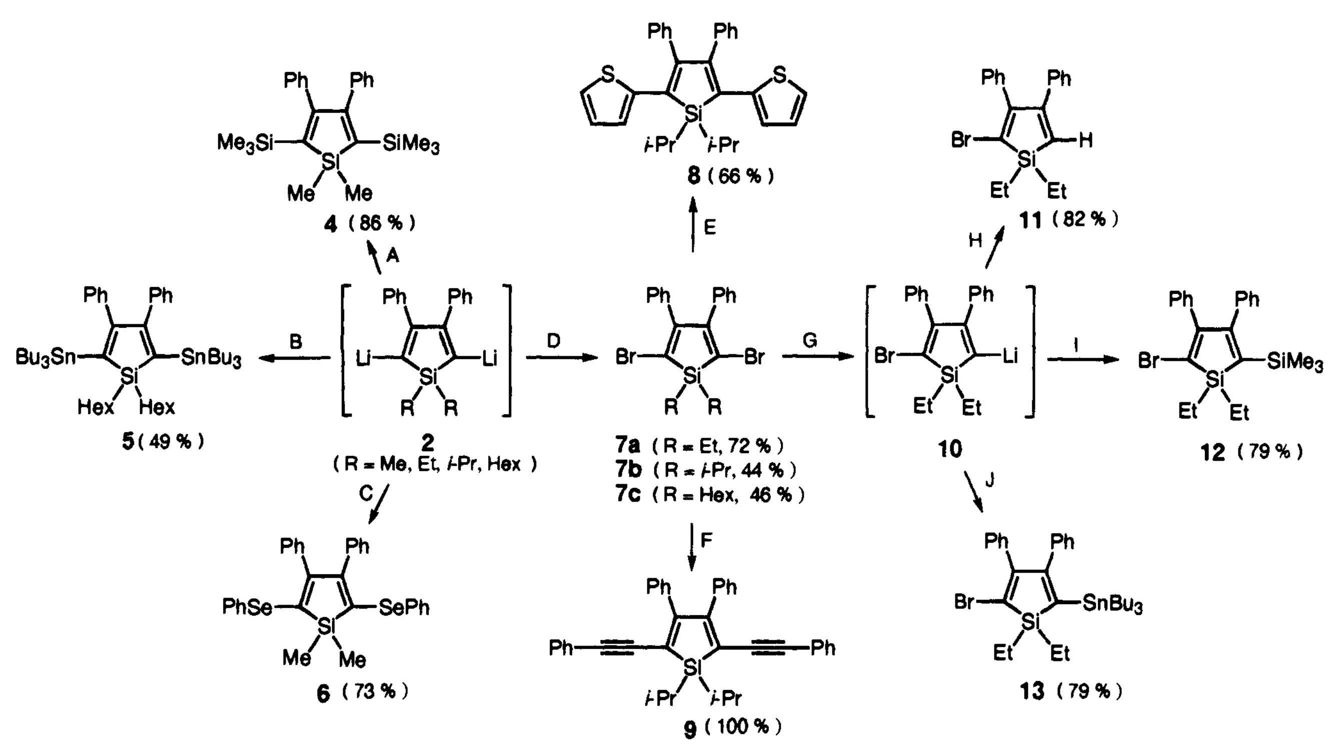
(18) (a) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. (b) Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 3120.

(19) Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1941**, *63*, 1184.

(20) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(21) Only one example of synthesis of functional siloles, 2,5-distannyl-3-borylsiloles, has been reported.[17]

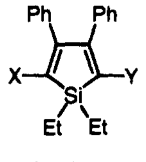
Scheme 3



[a] Reagents and Conditions: A: Me_3SiCl (4 equiv), room temp. B: *n*-Bu_3SnCl (4 equiv), room temp. C: PhSeCl (4 equiv), room temp. D: (1) Ph_3SiCl (2 equiv), −78 °C; (2) Br_2 (2 equiv), −78 °C to room temp. E: (2-Thienyl)tributylstannane (3 equiv), $PdCl_2(PPh_3)_2$ (10 mol %), THF, reflux, 2 days. F: (Phenylethynyl)trimethylstannane (2 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), THF, reflux, 12 h. G: *n*-BuLi (1.1 equiv), ether, −78 to 0 °C, 3 h. H: H_2O, 0 °C. I: Me_3SiCl, 0 °C to room temp, 3 h. J: *n*-Bu_3SnCl, 0 °C to room temp, 3 h.

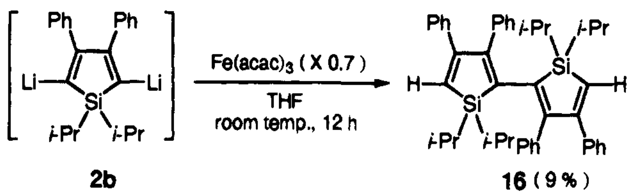
exhibit interesting properties: For example, diselenenylsilole **6** and diethynylsilole **9** are yellow crystals and have considerably long λ_{max} at 386 and 430 nm, respectively.

Synthesis of Oligosiloles. By use of the functional siloles **2**, **5**, and **7** and additional 2,5-dimetalated siloles **14** and **15** generated in situ from **2** with $MgBr_2{\cdot}OEt_2$ and $ZnCl_2{\cdot}TMEDA$, respectively, we have tried to prepare polysiloles under a variety of conditions, which include homocoupling of 2,5-dilithiosilole **2** with Fe(III), Ni(II), Cu(II) etc.,[22] homocoupling of 2,5-dibromosilole **7**, and cross-coupling of **7** with tin reagent **5**, magnesium reagent **14**, and zinc reagent **15** in the presence of nickel or palladium catalyst,[23] but none of them afforded characterizable polysiloles. Large steric hindrance due to the phenyl groups at the 3,4-positions of silole and an inherent low reactivity at the 2,5-positions of siloles may be responsible for these failures.[24]


14 (X = Y = MgBr)
15 (X = Y = ZnCl)

We ultimately, however, succeeded in preparation of oligosiloles by oxidative coupling of lithiosiloles. In an attempted preparation of polysilole by oxidative coupling of 2,5-dilithiosilole **2** with tris(acetylacetonato)iron(III), 2,2′-bisilole **16** was isolated as yellow crystals in 9% yield, together with uncharacterizable polymeric materials, as shown in Scheme 4.[22a-c] A two-step oxidative coupling of lithiosiloles via higher order cyanocuprate was most effective.[25] Thus, 2-bromo-5-lithiosilole **10** was treated with 0.5 equiv of copper cyanide to form the higher order cyanocuprate **17** which was subsequently treated with an excess amount of *p*-dinitrobenzene (5 equiv relative to **7**) as an oxidant to produce 5,5′-dibromo-2,2′-bisilole **18** as yellow crystals in 77% yield, as shown in Scheme 5, the whole transformation being performed in one pot. The butyl bromide produced during the initial lithiation must be removed *in vacuo* prior to the treatment of monolithiosilole **10** with copper cyanide to avoid its reaction with the higher order cuprate. A large excess amount of *p*-dinitrobenzene is essential to the efficient oxidation of the higher order cuprate smoothly: The use of a slightly excess amount (1.5 equiv) of dinitrobenzene or a molecular oxygen as an oxidant lowered the yield of bisilole **18** considerably down to 46 and 39% yield, respectively. Under

Scheme 4



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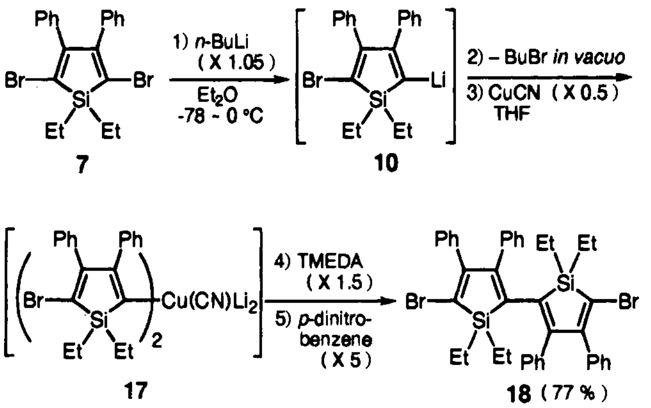
(22) (a) Artz, S. P.; Cram, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 2160. (b) Katz, H. E.; Cram, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 4977. (c) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214. (d) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379. (e) Tamura, M.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3063.

(23) Pertinent references: Ni(0) catalyzed homocoupling: (a) Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80. Ni(0) or Pd(0) catalyzed cross-coupling, Mg: (b) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347. Zn: (c) Negishi, E.; Luo, F. T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117. (d) Minato, A.; Suzuki, K.; Tamao, K.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 511. Sn: (e) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359. (f) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. See also ref 20.

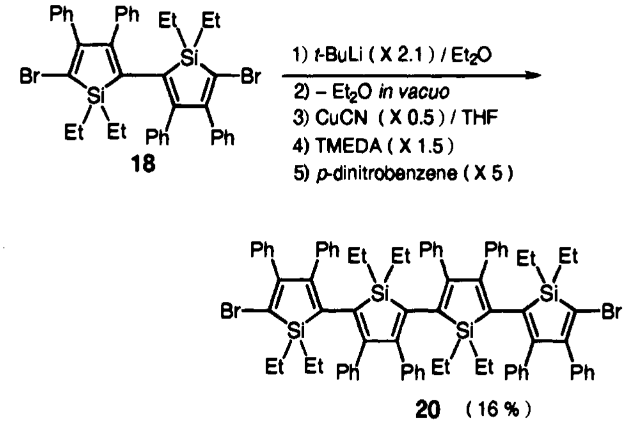
(24) The low reactivity at the 2,5-positions of silole may be exemplified by the fact that silyl groups thereon could not be desilylated by a variety of electrophiles: (a) Tamao, K.; Yamaguchi, S., unpublished data. (b) Kurita, J.; Ishii, M.; Yasuike, S.; Tsuchiya, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1309.

(25) Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, *115*, 9276.

Scheme 5

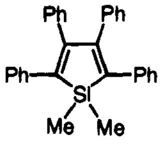


Scheme 6



essentially the same optimum conditions, dibromoquatersilole **20** was also obtained in 16% yield as an orange powder by coupling of 5-bromo-5′-lithio-2,2′-bisilole **19**, prepared in situ from **18** by monolithiation using 2.1 equiv of *tert*-BuLi in ether (Scheme 6). Bisilole **16** is air-stable, but dibromooligosiloles **18** and **20** gradually decompose in the air under the light. The oxidative coupling via higher order cyanocuprate seems to be most promising for the synthesis of higher oligosiloles and polysiloles, since the reaction is little influenced by steric factor, as pointed out by Lipshutz.[25]

Structures of Bisilole 16 and Dibromobisilole 18. Crystal structures of bisilole **16** and dibromobisilole **18** are shown in Figure 1 and their selected bond lengths, bond angles, and torsion angles between two silole least squares planes are listed in Table 1, which contains those data of 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**21**) for comparison.[26] Most of the bond lengths and bond angles for bisiloles **16** and **18** are not largely different from those for tetraphenylsilole **21**, except for Si1−C1 and Si1−C4 bond lengths. Thus, in the bisiloles the Si1−C1 bonds are about 0.04 Å longer than the Si1−C4 bonds. The distortion of the silole rings is probably due to the steric repulsion between the alkyl groups on Si1 and the phenyl group on the adjacent silole C2′. The most interesting and characteristic feature for bisiloles is a highly non-coplanar arrangement between two silole rings with 62.3° (**16**) and 63.7° (**18**) of torsion angles,[27] which are larger than the torsion angle 44.6° between silole and phenyl rings in **21**. The fact that almost the same degrees of torsion angles are observed for **16** (having isopropyl groups on Si) and **18** (having ethyl groups on Si) implies that the twist angles are little influenced by the bulkiness of substituents on silicon atoms.



21

The structures of bisiloles in solution have been analyzed by ^{1}H NMR spectroscopy at room temperature, a part of spectrum of **18** being shown in Figure 2. The spectrum of **18**, showing two six-line patterns at −0.14 and 0.41 ppm and one triplet at 0.77 ppm, provides two significant aspects of the solution structures as follows: (1) The former two resonances and the latter triplet are assignable to the two double quartets of diastereotopic methylene protons and the triplet of enantiotopic methyl protons of the $Si(CH_2CH_3)_2$ moieties, respectively. In other words, the two ethyl groups on each silicon atom are observed enantiotopic and the two methylene protons on each ethyl group are observed diastereotopic. The observation is best explained by racemization of the axial chirality due to atropisomerism, *i.e.* a rapid equilibration between the twisted conformers, occurring at room temperature in solution on the NMR time scale, since, if not, the two ethyl groups on each silicon atom become diastereotopic, so that two resonances for the methyl groups and four resonances for the methylene protons should be observed. (2) The considerable upfield shift observed for one of the two methylene protons (−0.14 ppm) for bisilole **18** may be due to thermodynamically stable twisted conformers, in which one of them is just located over the benzene ring at 3-position of the adjacent silole, as observed by X-ray structural analysis. The spectrum of **16**, not shown herein, also demonstrates similar characteristic structural features in solution.

As discussed above, both the bisiloles, **16** and **18**, have been ascertained to have non-coplanar twisted conformers as the most stable conformation. Despite these experimental results and semiempirical calculations suggesting the non-coplanar arrangement for unsubstituted polysiloles,[6] the origin of the non-coplanarity, whether inherence or steric repulsion, has not yet been clarified. These results, however, must suggest inefficient π-conjugation over two silole rings. Nevertheless, these bisiloles are yellow and have unique optical properties as discussed in the next section.

UV-Visible Absorption Data for Oligosiloles. The UV-visible absorption data for oligosiloles are summarized in Table 2. There are several characteristic features as follows. (1) Bisilole **16** and dibromobisilole **18** have unusually long absorption maxima λ_{max} 398 and 417 nm, respectively, in chloroform. It is surprising, considering their twisted conformation, that these λ_{max} values are the longest of those of nonfused two-ring π-conjugated compounds, as shown by the following data: Compound, λ_{max} (nm): 2,2′-bifuran, 278;[28b] 2,2′-bithiophene, 302;[28] 2,2′-biselenophene, 321;[28b] bicyclopentadiene (isomeric mixture), 333, 352(sh).[29] (2) The same absorption maximum is observed for **18** in solution and in the solid state (KBr pellet).

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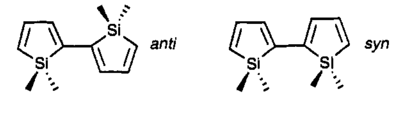
(26) Párkányi, L. *J. Organomet. Chem.* **1981**, *216*, 9.

(27) There are two conformations for coplanar arrangement of bisilole, anti and syn, as shown below. The torsion angle in the text is defined to be the angle between two silole rings out of coplanarity from the anti conformer.



(28) (a) Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B., Jr.; Pham, C. V.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021. (b) Shabana, R.; Galal, A.; Mark, H. B., Jr.; Zimmer, H.; Gronowitz, S.; Hörnfeldt, A.-B. *Phosphorus, Sulfur, Silicon* **1990**, *48*, 239.

(29) Escher, A.; Rutsch, W.; Neuenschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644.

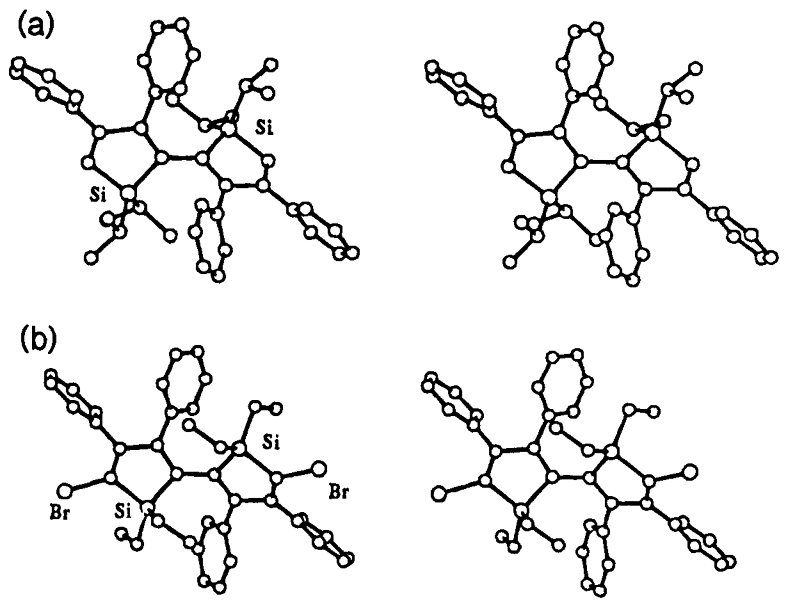
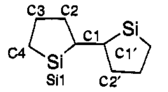
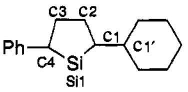


Figure 1. Stereoviews of 2,2′-bisiloles **16** (a) and **18** (b), determined by X-ray crystallography.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Bisilole **16**, Dibromobisilole **18**, and Tetraphenylsilole **21**

	compound		
	bisilole **16**	dibromobisilole **18**	tetraphenylsilole **21**[a]
bonds and angles			
Si1−C1	1.895(3)	1.895(3)	1.868(3)
Si1−C4	1.851(3)	1.860(3)	
C1−C2	1.356(4)	1.366(4)	1.358(2)
C3−C4	1.343(4)	1.336(5)	
C2−C3	1.513(4)	1.510(4)	1.511(2)
C1−C1′	1.484(4)	1.486(4)	1.477(2)
C1−Si1−C4	92.0(1)	90.4(1)	92.7(1)
torsion angle	62.3[b]	63.7[b]	44.6[c]

[a] The data for 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**21**) are cited from ref 26. All values of bond lengths and angles are averaged values. [b] Torsion angle between the two silole least-squares planes. [c] Averaged values of torsion angles between silole least-squares plane and benzene least-squares planes.

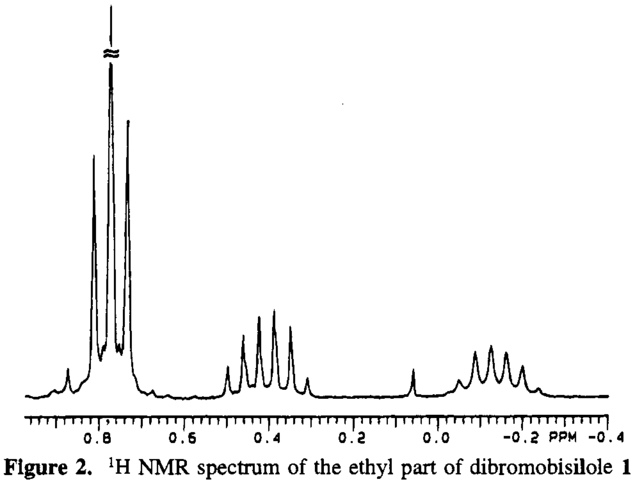


Figure 2. ^1H NMR spectrum of the ethyl part of dibromobisilole **18** in $CDCl_3$ at room temperature.

This result is well consistent with the twisted conformation both in solution and in the solid state proved by NMR and X-ray analysis. (3) Dibromoquatersilole **20** (λ_{max} 443 nm) exhibits only 26 nm red shift compared with the bisilole **18**. This rather small red shift considering a change from two to four π-ring systems is probably due to the noneffective π-conjugation mentioned above, because much larger red shift would be expected for coplanar π-conjugated systems, as exemplified by about 90 nm red shift for quaterthiophene (λ_{max} 390 nm) in comparison with bithiophene (λ_{max} 302 nm).[28a,30] (4) Most noticeably, there is a considerably large bathochromic shift, more than 90 nm, upon changing from monosilole **7** to bisilole **18**, suggesting the development of a unique π-electronic structure by combination of two silole rings. Bisilole might be regarded as a silyl-substituted *transoid*-bis(*cisoid*-butadiene),[5a] where silicon atoms may act merely as fixatives of the labile tetraene skeleton. This hypothesis, however, would not be able to fully explain the long absorptions for bisiloles, because their carbon analogue, bicyclopentadiene (isomeric mixture), has its absorption maxima up to 352 nm at most, as mentioned above.[29] The silicon atom in silole may thus play a more crucial role in the π-electronic structure of bisilole.

Table 2. UV-Visible Absorption Data for Oligosiloles[a]

compound	λ_{max} (nm)	$\log \epsilon$
dibromosilole **7**	326	3.64
bisilole **16**	398	3.71
dibromobisilole **18**	417 416 (in solid state)[b]	4.05
dibromoquatersilole **20**	443	4.21

[a] In chloroform, unless otherwise stated. [b] KBr pellet.

Summary and Conclusions

In the course of our research on polysilole chemistry, the first general and versatile method for the synthesis of 2,5-difunctional siloles has been developed based on the novel *endo—endo* mode intramolecular reductive cyclization of diethynylsilanes. This *endo—endo* mode reductive cyclization of diyne derivatives may become an attractive tool in organic synthesis, not confining to the silole synthesis, as a new type of annulation with $C_{sp^2}-C_{sp^2}$ bond formation. A study on its scope and limitations are under way in our laboratory.

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(30) Coplanarity of oligothiophenes: (a) van Bolhuis, F.; Wijnberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. J. *Synth. Metals* **1989**, *30*, 381. (b) Hotta, S.; Waragai, K. *J. Mater. Chem.* **1991**, *1*, 835. (c) Herrema, J. K.; Wildeman, J.; van Bolhuis, F.; Hadziioannou, G. *Synth. Metals* **1993**, *60*, 239. (d) Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *Adv. Mater.* **1993**, *5*, 834.

With the various functional siloles in hand, we have tried to synthesize well-defined polysiloles under a variety of conditions without success. We eventually, however, succeeded in preparation of oligosiloles, from bisilole to quatersilole, for the first time. The present investigation on oligosiloles as models of polysiloles have enhanced our interests in the still veiled fascinating polysiloles. Thus, the oligosiloles show unusually long absorption maxima in the visible region in spite of the non-coplanar arrangement along the main chain. Furthermore, a large bathochromic shift observed for changing from dibromosilole to dibromobisilole suggests the development of a unique π-electronic structure by combination of two silole rings. The present results thus strongly suggest that the introduction of the oligosilole skeleton, especially bisilole skeleton, into the π-conjugated chain is one of the promising routes to novel π-electronic materials. The projects aiming at such new materials as well as the elucidation of the origin of the unique optical properties observed for oligosiloles are also now in progress.

Experimental Section

General. Melting point (mp) determinations were performed by using a Yanaco MP-S3 instrument and are uncorrected. ^{1}H NMR spectra were measured with a Varian VXR-200 (200 MHz) spectrometer in $CDCl_3$. ^{13}C NMR were obtained with a Varian VXR-200 (50 MHz) spectrometer. Chemical shifts are reported in δ (ppm). Mass spectra were recorded on a JEOL JMS-DX-300. UV-visible spectra were measured with a JASCO UVIDEC 610B spectrometer in chloroform. UV-visible spectra in the solid state was measured with a Shimadzu UV-2100PC as a pellet form using crystalline KBr. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60F-254 (Merck). Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). High-performance liquid chromatography (HPLC) was done by using a 20 mm × 250 mm Wakosil 5Sil column (Wako).

Materials. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were freshly distilled before use from lithium aluminum hydride and sodium benzophenone ketyl, respectively. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was freshly distilled before use from *n*-butyllithium. Lithium metal (granular) was purchased from Metallgesellschaft AG. Dialkylbis(phenylethynyl)silanes **1** were prepared by coupling of the corresponding dialkyldichlorosilanes with phenylethynyllithium. (2-Thienyl)tributylstannane and (phenylethynyl)trimethylstannane were prepared by the reaction of the corresponding organolithiums with the trialkylstannyl chlorides. Dichlorobis(triphenylphosphine)palladium(II) was prepared according to the literature.[31] Tris(acetylacetonato)iron(III), copper cyanide, *p*-dinitrobenzene, $MgBr_2{\cdot}OEt_2$, and $ZnCl_2{\cdot}$TMEDA were purchased from commercial sources and used without further purification. All reactions were conducted under an atmosphere of argon.

A Typical Procedure for the Preparation of 2,5-Dilithiosilole (2). A solution of lithium naphthalenide was prepared by stirring a mixture of naphthalene (256 mg, 2 mmol) and lithium (14 mg, 2 mmol) in dry THF (2 mL) for 3 h at room temperature under an argon atmosphere. To the solution of lithium naphthalenide was added a THF (5 mL) solution of a dialkylbis(phenylethynyl)silane **1** (0.5 mmol) dropwise at room temperature, and then the mixture was stirred for 15 min.

1,1-Dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)silole (4). To the solution of 1,1-dimethyl-2,5-dilithiosilole (0.5 mmol) was added trimethylchlorosilane (0.25 mL, 2 mmol) at room temperature. The mixture was stirred for 1 h and then was concentrated under reduced pressure. The resulting mixture was passed through a short silica gel column (hexane) and subjected to HPLC on silica gel (hexane; R_f = 0.67) to afford pure **4** (175 mg, 0.43 mmol) in 86% yield as white crystals: mp 100 °C; ^{1}H NMR δ −0.16 (s, 18H), 0.40 (s, 6H), 6.8–6.87 (m, 4H), 6.98–7.07 (m, 6H); ^{13}C NMR δ −2.86, 0.66, 125.96, 126.90, 128.69, 142.84, 144.73, 168.63. Anal. Calcd for $C_{24}H_{34}Si_3$: C, 70.86; H, 8.42. Found: C, 70.93; H, 8.61.

1,1-Dihexyl-3,4-diphenyl-2,5-bis(tributylstannyl)silole (5). 1,1-Dihexyl-2,5-dilithiosilole (0.5 mmol) prepared according to the procedure described above was trapped with tributylstannyl chloride (0.54 mL, 2 mmol) at room temperature. The purification by HPLC on silica gel (hexane, R_f = 0.70) gave 240 mg (0.245 mmol, 49% yield) of **5** as a colorless viscous oil: ^{1}H NMR δ 0.51–0.66 (m, 12H), 0.76–0.94 (m, 28H), 1.10–1.46 (m, 40H), 6.84–6.91 (m, 4H), 6.98–7.06 (m, 6H); ^{13}C NMR δ 10.49, 13.23, 13.60, 14.16, 22.68, 24.25, 27.48, 29.25, 31.78, 33.41, 125.95, 127.06, 128.43, 145.14, 147.91, 169.80. Anal. Calcd for $C_{52}H_{90}SiSn_2$: C, 63.68; H, 9.25. Found: C, 63.48; H, 9.40.

1,1-Dimethyl-3,4-diphenyl-2,5-bis(phenylselenenyl)silole (6). A solution of phenylselenenyl chloride (401 mg, 2.1 mmol) in dry THF (6 mL) was added dropwise to the solution of 1,1-dimethyl-2,5-dilithiosilole (0.5 mmol) at −78 °C. The reaction mixture was gradually warmed up to room temperature over 6 h. After removal of the solvent, the residue was subjected to column chromatography on silica gel (hexane, R_f = 0.18) to give 213 mg (0.372 mmol, 74% yield) of **6** as yellow crystals: mp 121 °C; ^{1}H NMR δ −0.33 (s, 6H), 6.99–7.06 (m, 4H), 7.12–7.28 (m, 12H), 7.58–7.66 (m, 4H); ^{13}C NMR δ −2.87, 126.94, 127.60, 128.13, 128.71, 129.02, 135.22, 136.19, 139.16, 153.65; UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 247 (4.26), 296 (sh, 3.94), 386 (3.92). Anal. Calcd for $C_{30}H_{26}SiSe_2$: C, 62.94; H, 4.58. Found: C, 63.15; H, 4.67.

2,5-Dibromo-1,1-diethyl-3,4-diphenylsilole (7a). 1,1-Diethyl-2,5-dilithiosilole (10 mmol) was prepared according to the procedures described above starting from lithium naphthalenide (40 mmol), diethylbis(phenylethynyl)silane (2.88 g, 10 mmol), and dry THF (30 mL). The mixture was cooled to −78 °C, followed by dropwise addition of a solution of triphenylchlorosilane (5.9 g, 20 mmol) in dry THF (14 mL) in order to quench the excess lithium naphthalenide. After stirring for 20 min, bromine (1 mL, 20 mmol) was added dropwise to the reaction mixture over 10 min at −78 °C. The resulting yellow-white suspension was gradually warmed up to room temperature over 6 h. After filtration of salts and most part of the hexaphenyldisilane produced, the filtrate was concentrated, followed by addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O. The combined extract was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was heated to 55 °C *in vacuo* (0.5 mmHg) to remove the naphthalene by sublimation. The residue was then recrystallized from hexane several times to afford 3.21 g (7.16 mmol, 72% yield) of **7a** as white crystals: mp 97 °C; ^{1}H NMR δ 0.96–1.06 (m, 4H), 1.06–1.18 (m, 6H), 6.90–6.98 (m, 4H), 7.10–7.18 (m, 6H); ^{13}C NMR δ 1.51, 6.54, 120.82, 127.38, 127.52, 128.98, 137.10, 157.28. Anal. Calcd for $C_{20}H_{20}Br_2Si$: C, 53.59; H, 4.50. Found: C, 53.52; H, 4.50.

2,5-Dibromo-1,1-diisopropyl-3,4-diphenylsilole (7b): 44% yield; mp 126 °C; ^{1}H NMR δ 1.25 (d, J = 7.0 Hz, 12H), 1.47 (sep, J =7.0 Hz, 2H), 6.88–6.98 (m, 4H), 7.10–7.20 (m, 6H); ^{13}C NMR δ 9.82, 17.17, 119.79, 127.32, 127.53, 128.95, 137.30, 157.89. Anal. Calcd for $C_{22}H_{24}SiBr_2$: C, 55.48; *H*, 5.08. Found: C, 55.52; H, 5.02.

2,5-Dibromo-1,1-dihexyl-3,4-diphenylsilole (7c): 46% yield; mp 64 °C; ^{1}H NMR δ 0.85–1.10 (m, 10H), 1.2–1.7 (m, 16H), 6.9–7.0 (m, 4H), 7.1–7.2 (m, 6H); ^{13}C NMR δ 9.73, 14.14, 22.58, 22.88, 31.43, 32.69, 121.86, 127.35, 127.52, 128.96, 137.21, 156.84. Anal. Calcd for $C_{28}H_{36}SiBr_2$: C, 60.00; H, 6.47. Found: C, 60.08; H, 6.53.

Cross-Coupling Reaction of 2,5-Dibromosilole (7b) with (2-Thienyl)stannane or (Phenylethynyl)stannane Catalyzed by a Palladium Complex. 1,1-Diisopropyl-3,4-diphenyl-2,5-bis(2-thienyl)silole (8). To a mixture of **7b** (48 mg, 0.1 mmol) and bis(triphenylphosphine)dichloropalladium(II) (7 mg, 10 μmol) in dry THF (1 mL) was added a THF (1 mL) solution of (2-thienyl)tributylstannane (112 mg, 0.3 mmol). The mixture was refluxed for 2 days. After confirmation of disappearance of **7b** by TLC, the reaction mixture was concentrated under reduced pressure and the residue was subjected to column chromatography on silica gel (hexane, R_f = 0.16) to give pure **8** (32 mg, 0.066 mmol) in 66% yield as yellow crystals: mp 112 °C; ^{1}H NMR δ 1.20 (d, J = 7.3 Hz, 12H), 1.68 (sep, J = 7.3 Hz, 2H), 6.83 (d, J = 2.4 Hz, 2H), 6.84 (d, J = 4.0 Hz, 2H), 6.90–6.97 (m, 4H), 7.00 (dd, J = 2.4 and 4.0 Hz, 2H), 7.09–7.18 (m, 6H); ^{13}C NMR δ 12.41, 17.87, 125.86, 126.98, 127.84, 128.22, 129.90, 139.40, 143.43, 155.21. Anal. Calcd for $C_{30}H_{30}SiS_2$: C, 74.63; H, 6.26. Found: C, 74.46; H, 6.19.

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1,1-Diisopropyl-3,4-diphenyl-2,5-bis(phenylethynyl)silole (9). By the similar procedure to that used to prepare **8**, the title compound **9** was obtained from **7b** (178 mg, 0.374 mmol), (phenylethynyl)trimethylstannane (199 mg, 0.751 mmol), and bis(triphenylphosphine)dichloropalladium(II) (13 mg, 19 μmol) in dry THF (3 mL) with refluxing for 12 h as yellow crystals (194 mg, 0.374 mmol, 100% yield): mp 121 °C; ^{1}H NMR δ 1.33 (d, $J = 6.8$ Hz, 12H), 1.60 (sep, $J = 6.8$ Hz, 2H), 7.18−7.32 (m, 20H); ^{13}C NMR δ 11.20, 17.79, 91.08, 100.15, 121.40, 124.59, 127.18, 127.32, 127.74, 128.21, 129.38, 137.82, 162.80; UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 238 (4.38), 267 (4.48), 306 (4.29), 430 (4.41); MS *m/e* (relative intensity) 518 (M^+, 100). Anal. Calcd for $C_{38}H_{34}Si$: C, 87.98; H, 6.61. Found: C, 87.58; H, 6.68.

Monolithiation of 2,5-Dibromosilole and Transformation to Unsymmetrical 2,5-Difunctional Siloles. 2-Bromo-1,1-diethyl-3,4-diphenylsilole (11). To a white suspension of 1,1-diethyl-2,5-dibromosilole **7a** (427 mg, 0.95 mmol) in dry Et_2O (10 mL) was added dropwise a hexane solution of *n*-BuLi (1.64 M, 0.7 mL, 1.14 mmol) at −78 °C. The reaction mixture was allowed to warm up to 0 °C over 3 h and quenched with 0.1 mL of water. The resulting mixture was dried over anhydrous Na_2SO_4, filtered, and condensed under reduced pressure. The residue was subjected to column chromatography on silica gel with hexane as an eluent to give a colorless oil of **11** (289 mg, 0.78 mmol) in 82% yield: ^{1}H NMR δ 0.83−0.98 (m, 4H), 1.02−1.12 (m, 6H), 6.09 (s, 1H), 6.92−7.14 (m, 7H), 7.16−7.22 (m, 3H); ^{13}C NMR δ 2.25, 7.16, 125.51, 126.91, 127.07, 127.18, 127.40, 127.51, 127.88, 129.15, 137.61, 140.59, 155.91, 162.35; MS *m/e* (relative intensity) 368 (M^+, 96), 370 (100). The titled compound **11** was unstable and decomposed during drying *in vacuo*. No satisfactory elemental analysis was obtained.

2-Bromo-1,1-diethyl-3,4-diphenyl-5-(trimethylsilyl)silole (12). In essentially the same manner as described for the preparation of **11**, except for the use of trimethylchlorosilane (0.19 mL, 1.5 mmol) instead of water as the quenching agent, the titled compound **12** (351 mg, 0.79 mmol) was prepared from 450 mg (1 mmol) of **7a** in 79% yield as a colorless oil: ^{1}H NMR δ −0.16 (s, 9H), 0.86−1.18 (m, 10H), 6.83−6.93 (m, 4H), 7.02−7.14 (m, 6H); ^{13}C NMR δ 0.70, 3.33, 7.05, 126.67, 126.75, 127.17, 127.40, 128.64, 128.90, 137.57, 138.17, 142.41, 158.91, 169.44. Anal. Calcd for $C_{23}H_{29}BrSi_2$: C, 62.56; H, 6.62. Found: C, 62.80; H, 6.75.

2-Bromo-1,1-diethyl-3,4-diphenyl-5-(tributylstannyl)silole (13). In essentially the same manner as described for the preparation of **11**, except for the use of tributylstannyl chloride (81 μL, 0.3 mmol) instead of water as the quenching agent, the titled compound **13** (114 mg, 0.173 mmol) was prepared from 98.3 mg (0.219 mmol) of **7a** in 79% yield as a colorless oil: ^{1}H NMR δ 0.53−0.63 (m, 6H), 0.78−0.97 (m, 19H), 1.10−1.50 (m, 28H), 6.80−6.88 (m, 2H), 6.88−6.96 (m, 2H), 7.02−7.16 (m, 6H); ^{13}C NMR δ 3.03, 7.08, 10.66, 13.60, 27.36, 29.16, 126.71, 127.36, 128.32, 128.97, 138.47, 141.24, 144.13, 157.93, 169.88. Anal. Calcd for $C_{32}H_{47}BrSi_2Sn$: C, 58.37; H, 7.19. Found: C, 58.23; H, 7.33.

Oxidative Coupling of 2,5-Dilithiosilole by Use of Fe(acac)$_3$. 1,1,1′,1′-Tetraisopropyl-3,3′,4,4′-tetraphenyl-2,2′-bisilole (16). To the THF solution of 1,1-diisopropyl-2,5-dilithiosilole (1 mmol) was added a solution of triphenylchlorosilane (590 mg, 2 mmol) in dry THF (4 mL), and the mixture was stirred for 30 min. To the reaction mixture was added a THF (6 mL) solution of tris(acetylacetonato)iron(III) (494 mg, 1.4 mmol) at room temperature. The resulting yellow-orange suspension was stirred for 12 h at the same temperature and filtered. The filtrate was condensed under reduced pressure and the residue was subjected to column chromatography on silica gel (hexane, $R_f = 0.13$) to give crude **16** (77 mg) as yellow solids. Further purification by recrystallization from hexane/Et_2O mixed solvents afforded pure **16** (30 mg, 47 μmol) in 9% yield as yellow crystals: mp 202 °C; ^{1}H NMR δ 0.2−0.4 (br m, 2H), 0.84 (d, $J = 7.4$ Hz, 6H), 0.90 (d, $J = 7.4$ Hz, 6H), 5.95 (s, 2H), 6.87−6.96 (m, 4H), 7.02−7.14 (m, 6H); ^{13}C NMR δ 11.49, 19.16, 20.03, 126.17, 126.51, 127.21, 127.36, 127.82, 128.39, 130.74, 140.24, 142.30, 145.58, 153.11, 162.96; UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 242 (4.51), 266 (sh, 4.43), 398 (3.71); MS *m/e* (relative intensity) 634 (M^+, 100), 591 (41). Anal. Calcd for $C_{44}H_{50}Si_2$: C, 83.22; H, 7.94. Found: C, 82.95; H, 8.01.

Oxidative Coupling of Monolithiosilole (10) via Higher Order Cuprate. 5,5′-Dibromo-1,1,1′,1′-tetraethyl-3,3′,4,4′-tetraphenyl-2,2′-bisilole (18). To a suspension of 2,5-dibromo-1,1-diethyl-3,4-diphenylsilole (**7a**, 447 mg, 1 mmol) in Et_2O (6 mL) was added a hexane solution of *n*-BuLi (1.59 M, 0.66 mL, 1.05 mmol) at −78 °C. The reaction mixture was allowed to warm up gradually to 0 °C over 4 h. After removal of the produced butyl bromide together with Et_2O *in vacuo* at 0 °C for 1 h, copper cyanide (45 mg, 0.5 mmol) was added to the mixture as solids under argon flow. After 6 mL of dry THF was injected to the mixture at −78 °C, the reaction mixture was stirred for 5 min and then stirred at −40 to −30 °C for 1 h. The resulting deep-green solution was cooled back down to −78 °C. Dry TMEDA (0.23 mL, 1.5 mmol) was added dropwise to the mixture at −78 °C, and then the mixture was stirred for 20 min at the same temperature. To the resulting deep-green solution was added a THF (12 mL) solution of *p*-dinitrobenzene (840 mg, 5 mmol) via a transfer-tube and the resulting yellow-brown suspension was stirred at −78 °C for 2 h. A 1/1 mixture (4 mL) of a saturated aqueous solution of $NaHSO_3$ and MeOH was added to the mixture via syringe and then the bright yellow suspension was warmed up to room temperature. The mixture was diluted with water and extracted with Et_2O. The combined extract was washed with brine, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The residue was diluted with hexane, and insoluble materials were filtered out. The filtrate was condensed and the residue was subjected to column chromatography on silica gel (hexane/Et_2O = 10/1, $R_f = 0.45$) to afford a slightly impure **18**. Recrystallization from pentane gave 284 mg (0.386 mmol) of pure **18** in 77% yield as yellow crystals: mp 157−159 °C dec; ^{1}H NMR δ −0.14 (dq, $J = 7.8$, 14.8 Hz, 4H), 0.41 (dq, $J = 7.8$, 14.8 Hz, 4H), 0.77 (t, $J = 7.8$ Hz, 12H), 6.87−6.95 (m, 4H), 6.96−7.06 (m, 4H), 7.07−7.18 (m, 12H); ^{13}C NMR δ 2.43, 7.47, 124.71, 126.81, 127.35, 127.85, 129.04, 130.81, 137.97, 139.46, 141.40, 156.39, 157.89; UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 243 (4.52), 278 (4.38), 417 (4.05). Anal. Calcd for $C_{40}H_{40}Br_2Si_2$: C, 65.21; H, 5.47. Found: C, 65.43; H, 5.52.

5,5‴-Dibromo-1,1,1′,1′,1″,1″,1‴,1‴-octaethyl-3,3′,3″,3‴,4,4′,4″,4‴-octaphenyl-2,2′:5′,2″:5″,2‴-quatersilole (20). To a yellow solution of **18** (113 mg, 0.154 mmol) in Et_2O (4 mL) was added a pentane solution of *tert*-BuLi (1.61 M, 210 μL, 0.34 mmol) at −78 °C. The solution was immediately turned to a deep-red suspension and stirred at the same temperature for 1 h. After warmed up to 0 °C with ice/water bath, the solvents were removed *in vacuo* at 0 °C for 10 min. The flask was filled with argon and then copper cyanide (6.9 mg, 0.077 mmol) was added to the mixture as solids under argon flow. The reaction mixture was cooled down to −78 °C and 3 mL of dry THF was injected. The resulting deep-red suspension was warmed up to −40 °C and stirred for 5 min. The mixture was turned to a deep-red solution. Dry TMEDA (70 μL, 0.46 mmol) was added to the mixture at −40 °C. The reaction mixture was stirred at −40 to −20 °C for an additional 1 h and cooled down to −78 °C. A THF (3 mL) solution of *p*-dinitrobenzene (134 mg, 0.8 mmol) was added to the solution via a transfer-tube. The resulting yellow-brown suspension was stirred at the same temperature for 1 h and 2 mL of a 1/1 mixture of a saturated aqueous solution of $NaHSO_3$ and MeOH was added into the mixture via syringe at −78 °C. The resulting yellow-orange suspension was warmed up to room temperature and diluted with 1 N hydrochloric acid. After extraction with Et_2O, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. 1,2-Dichloroethane (5 mL) was added to the residue to form orange precipitates. After filtration and washing with Et_2O, the precipitates were dissolved into *ca.* 3 mL of hexane/CH_2Cl_2 = 1/1 mixed solvent and subjected to column chromatography on Florisil (eluent: hexane/CH_2Cl_2 = 2/1, $R_f = 0.58$) to afford 16.7 mg of **20** (12.7 μmol, 16% yield) as orange solids: mp 287−289 °C dec; ^{1}H NMR δ −1.20 to −0.34 (br m, 8H), −0.05−0.25 (br m, 2H), 0.25−0.70 (m, 24H), 0.82−1.10 (m, 6H), 6.60−7.55 (br m, 40H); UV-vis ($CHCl_3$) λ_{max} nm (log ϵ) 243 (4.75), 282 (4.62), 378 (sh, 3.97), 443 (4.21); FABMS 1310 (M^+), 1312, 1314. Anal. Calcd for $C_{80}H_{80}Br_2Si_4$: C, 73.14; H, 6.14. Found: C, 72.89; H, 6.16.

X-ray Crystal Structure Analysis of 16. Crystal data: $C_{44}H_{50}Si_2$, FW = 635.05, crystal size 0.30 × 0.20 × 0.10 mm, monoclinic, space group $P2_1/c$ (No.14), $a = 14.575(1)$ Å, $b = 11.757(1)$ Å, $c = 22.732(2)$ Å, $\beta = 94.540(9)°$, $V = 3883.3(6)$ Å^3, $Z = 4$, $D_c = 1.086$ g cm^{-3}, μ (Cu Kα) = 10.23 cm^{-1}. Intensity data were measured at 23 °C on a Rigaku AFC5R diffractometer with graphite monochromated Cu Kα

radiation ($\lambda = 1.54178$ Å) using the $\omega - 2\theta$ scan technique to $2\theta_{max} = 120.3°$, and 6115 unique reflections were collected. The structure was solved by the direct method[32] and refined anisotropically by the full-matrix least-squares to $R = 0.045$, $R_w = 0.065$, and $S = 1.71$. Hydrogen atoms were included but not refined.

X-ray Crystal Structure Analysis of 18. Crystal data: $C_{44}H_{50}Si_2Br_2$, FW = 736.73, crystal size 0.35 × 0.30 × 2.00 mm, monoclinic, space group $P2_1/c$ (No.14), $a = 13.259(3)$ Å, $b = 14.361(4)$ Å, $c = 19.890(3)$ Å, $\beta = 108.92(1)°$, $V = 3582(1)$ Å^3, $Z = 4$, $D_c = 1.366$ g cm^{-3}, μ (Cu Kα) = 37.05 cm^{-1}. The general procedure is as described for **16**. The structure was solved for 4729 unique reflections to $R = 0.041$, $R_w = 0.065$, and $S = 1.90$.

Acknowledgment. We thank the Ministry of Education, Science and Culture of Japan for a Grant-in-Aid (No. 04555203) and S.Y. thanks JSPS Fellowships for Japanese Junior Scientists. The authors are indebted to Prof. Y. Ito, Kyoto University, for valuable discussions, and Prof. K. Komatsu of our Institute for measurement of UV-visible spectra in the solid state. Thanks are also due to Shin-etsu Chemical Co., Ltd. for a gift of chlorosilanes.

Supplementary Material Available: X-ray structures, atomic coordinates, anisotropic displacement parameters, and full data of bond distances and angles, least squares planes and their dihedral angles for **16** and **18** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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