(B) invokes a dyotropic[10] rearrangement of two aryl groups, that is, a concerted intramolecular migration of these two σ-bonded groups across the silicon–silicon double bond. The transition state might be linear (**5a**) or 1,3-disilabicyclobutane-like (**5b**). The stereochemical demands of these two mechanisms are quite different. The dyotropic mechanism implies stereoselectivity in the **12** to **33** rearrangement in which only a single isomer should be formed. In contrast, free rotation about the Si–Si bond in the silylsilylene should result in the loss of stereoselectivity. The fact that one isomer is formed preferentially is consistent with pathway B. Analysis is, however, complicated by the concurrent cis/trans isomerization of (*Z*)-**33** and (*E*)-**33**.[2a,11] Experiments are in progress to further elucidate the mechanism and generality of this rearrangement.

Acknowledgment. This work was supported in part by the U.S. Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract F49620-86-C-0010 and the National Science Foundation under Grant CHE-8318820-01.

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Synthon for the Silicon–Silicon Triple Bond

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The recent surge of interest in multiply bonded silicon compounds has resulted in reports of transient species or stable compounds containing Si=C,[1] Si=Si,[2] Si=N,[3] Si=O,[4] and Si=P[5] double bonds.[6] However, no experimental evidence is yet available for species containing a silicon–silicon triple bond,[7] and theoretical calculations on the parent disilyne suggest that the linear triple bond familiar from carbon chemistry may not exist in the silicon series.[8] In this paper evidence is presented for a thermolysis reaction providing the synthetic equivalent of dimethyldisilyne ($MeSi{\equiv}SiMe$).

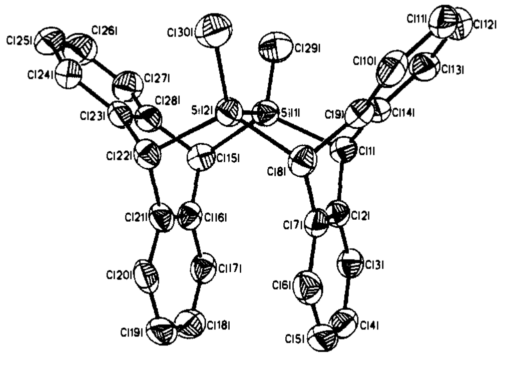
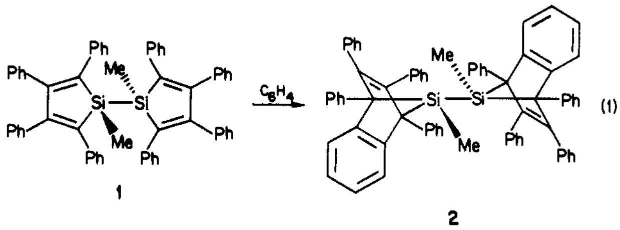


Figure 1. Crystal structure of **4**. Bond lengths (pm); 232.3 [Si(1)–Si(2)], 192.1 [Si(1)–C(1)], 192.5 [Si(1)–C(15)], 185.9 [Si(1)–C(29)], 192.1 [Si(2)–C(8)], 193.0 [Si(2)–C(22)], 186.6 [Si(2)–C(30)]. Torsion angle (deg) of Me–Si–Si–Me, 7.5°.

To synthesize the precursor molecule **2**, bisilole **1**,[9] obtained from 1,2-dimethyltetrachlorodisilane and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, was allowed to react with benzyne by using a modification of the method of Neumann[10,11] (eq 1). A mixture of **2** (1.85 mmol), anthracene (4.17 mmol), and benzene (ca. 1.5 g) was heated in a sealed tube at 350 °C for 2 h, producing 1,2,3,4-tetraphenylnaphthalene (**3**) (1139 mg, 71%), as well as 258 mg (32%) of the formal adduct of dimethyldisilyne **4**: mp >300 °C; ^1H NMR (200 MHz, $CDCl_3$) δ -0.03 (s, 6 H, SiMe), 3.86 (s, 4 H, Ar CH), 6.58–6.70 (m, 4 H, Ar H), 6.70–6.81 (m, 4 H, Ar H), 6.88–7.06 (m, 8 H, Ar H); ^{13}C NMR ($CDCl_3$) δ -10.5 (q), 43.8 (d), 125.1 (d), 125.8 (d), 126.2 (d), 126.5 (d), 137.4 (s), 141.1 (s); ^{29}Si NMR ($CDCl_3$) 12.5 ppm; high-resolution mass (EI, 30 eV), *m/z* 442.1597 (calcd for $C_{30}H_{26}Si_2$ 442.1573). Formation of **4** takes place stereospecifically to give exclusively the cis isomer. The crystal structure of **4** is shown in Figure 1.[12]



These results show that **2**, upon thermolysis, serves as a dimethyldisilyne synthon and raise the question of a mechanism for transfer of the $(MeSi)_2$ unit to the anthracene molecules. Because

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(9) The bisilole, bi(1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadien-1-yl), was prepared as a yellow-green solid, mp >300 °C in 33% yield by the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with 1,2-dimethyl-1,1,2,2-tetrachlorodisilane in THF. ^1H NMR ($CDCl_3$) δ 0.18 (s, 6 H), 6.59–7.10 (m, 40 H); HRMS (EI, 30 eV), *m/z* 798.3157 (calcd for $C_{58}H_{46}Si_2$, 798.3138).

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(11) A solution of 5.01 mmol of **1** and 30.1 mmol of *o*-bromofluorobenzene in 1 L of hot THF was added to excess activated magnesium in THF. Upon workup **2** was isolated as a white solid (4.47 g, 94%); the pure compound was obtained by recrystallization from hexane/benzene or acetone/benzene. Of the two possible isomers, only a single product was obtained, to which the anti structure is tentatively assigned. Mp 284–285 °C dec; ^1H NMR ($CDCl_3$) δ 0.53 (s, 6 H, SiMe), 6.19–6.34 (m, 10 H, Ar H), 6.65–6.78 (m, 10 H, Ar H), 6.78–7.19 (m, 28 H, Ar H); ^{13}C NMR ($CDCl_3$) δ 1.31, 60.3, 123.1, 124.0, 125.4, 125.8, 127.2, 127.6, 128.3, 131.1, 136.7, 138.3, 148.2, 149.8; ^{29}Si NMR ($CDCl_3$) 58.2 ppm; HRMS (FAB, $M^+ + 1$) 951.3806 (calcd for $C_{70}H_{55}Si_2$, 951.3828).

(12) A crystal of $C_{30}H_{26}Si_2$ (**4**), $M = 442$, 0.15 mm × 0.2 mm × 0.5 mm, was found to be orthorhombic with $a = 10.147$ (4) Å, $b = 17.267$ (7) Å, $c = 26.645$ (11) Å, $U = 4668$ Å^3, space group P_{bca}, $Z = 4$, $\mu(\text{Mo K}\alpha) = 1.6$ cm^{-1}, $D_c = 1.26$ g cm^{-3}. Data were collected on a Nicolet $P_{3/F}$ diffractometer with Mo Kα X-radiation using θ–2θ scans. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to $R = 0.093$ for 5269 observed reflections ($|F_o| > 3\sigma|F_o|$, $2\theta \leq 54.9°$).

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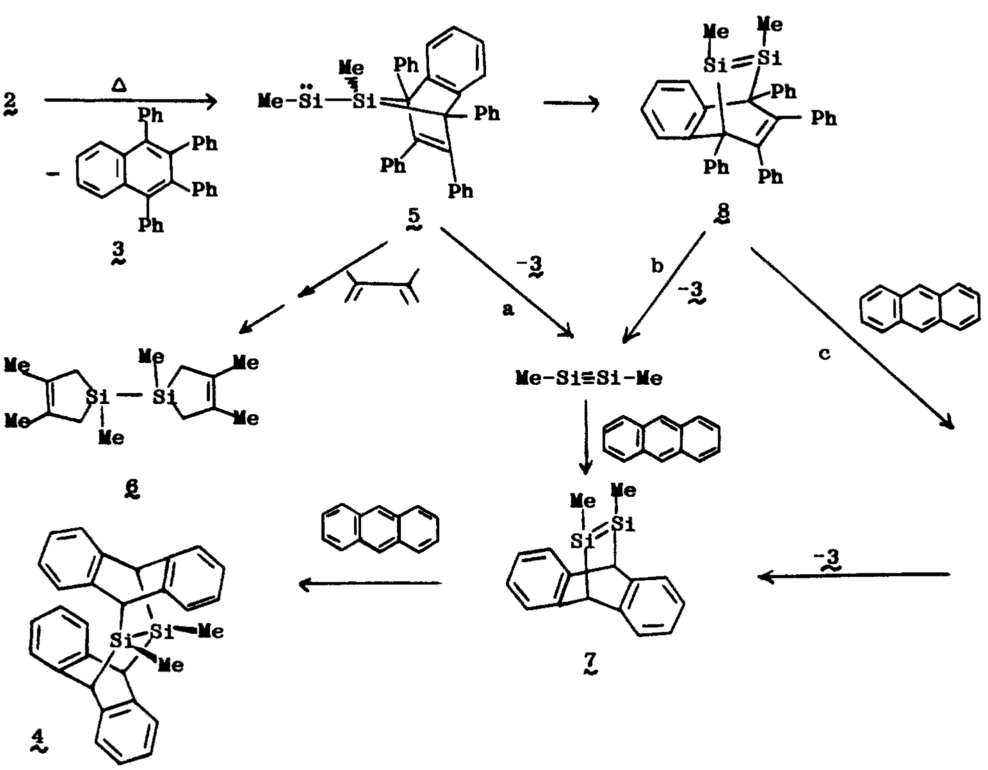
Scheme I



7-silanorbornadienes are known thermal precursors to silylenes,[13] a likely first step is fragmentation to give silylene **5** (Scheme I). Evidence for the intermediacy of **5** was obtained by thermolyzing **2** in the presence of 2,3-dimethylbutadiene, which afforded the five-membered ring compound bi(1,3,4-trimethyl-1-sila-3-cyclopenten-1-yl) (**6**) as final product in 13% yield.[14]

Several pathways are conceivable leading from **5** to the final product **4**. Silylene **5** might lose tetraphenylnaphthalene **3** according to pathway a to give dimethyldisilyne, which could add to anthracene successively to give **7** followed by **4**. Alternatively **5** could undergo ring expansion to disilene **8**.[15] The latter might fragment to give MeSi≡SiMe (pathway b) or might add anthracene to give the mixed compound **9**, which upon loss of **3** could produce **7** and ultimately **4** (pathway c).[16] Because of the possible involvement of the disilyne, the mechanism of this transformation is now of considerable interest.

The anthracene adduct **4** is also a possible dimethyldisilyne precursor or synthon. In this connection the mass spectrum of **4** (EI, 30 eV) is suggestive; peaks are observed at *m/e* 442 (M^+, relative intensity 35), 264 (M^+ – anthracene 100), 249 (M^+ – anthracene – Me, 36), 178 (anthracene$^+$, 50). In addition to these, a peak with relative intensity 15 is found at *m/e* 86. The exact mass and isotope ratios of this peak show that it has composition $C_2H_6Si_2^+$.[17]

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[14] ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 6 H, SiMe), 1.34 (d, J = 17.5 Hz, 4 H, ring proton), 1.53 (d, J = 17.5 Hz, 4 H, ring proton), 1.68 (br s, 12 H, C=CMe); HRMS (EI, 30 eV), *m/z* 250.1588 (calcd for $C_{14}H_{26}Si_2$, 250.1573). This compound was independently prepared from the reaction of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane with 2,3-dimethylbutadiene and Mg in HMPA.

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[16] An additional pathway might be considered involving addition of silylene **5** to anthracene to form a dibenzosilanorborandiene, which could undergo loss of tetraphenylnaphthalene followed by ring expansion to give **7**. However, this mechanism seems less likely because there is no precedent for 9,10-addition of silylenes to anthracene.

[17] HRMS for 86 peak 85.9995 (calcd for $^{12}C_2{}^1H_6{}^{28}Si_2$, 86.0008), 86.9980 (calcd for $^{12}C_2{}^1H_6{}^{28}Si^{29}Si$, 87.0004), 87.9969 (calcd for $^{12}C_2{}^1H_6{}^{29}Si_2$, 87.9976). The relative intensity of these peaks was 100:14:7, in agreement with the calculated ratio, 100:13:7.

Second-Order Effects in Two-Dimensional Cross-Relaxation Spectra of Proteins: Investigation of Glycine Spin Systems

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The use of two-dimensional (2-D) nuclear Overhauser effect spectroscopy (NOESY) for biomolecule structure determination is becoming increasingly frequent.[1-3] In principle, the well-known $1/r^6$ distance dependence of the intensity of cross-relaxation peaks

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