### Table I. Some Physical Properties of New Compounds

- **3b**: mp 239-241 °C; mass spectrum (rel intensity) M<sup>+</sup> 552 (100); NMR δ (CCl<sub>4</sub>) 0.20 (3 H, s, CH<sub>3</sub>), 6.4–7.7 (29 H, m, Ph)
- 4d: bp 77 °C (20 mmHg); mass spectrum (rel intensity) M<sup>+</sup> 220 (4.9), *m/e* 73 (100); NMR δ (CCl<sub>4</sub>) 0.12 (18 H, s), 0.34 (3 H, s), 3.34 (3 H, s)
- 4e: bp 63 °C (0.5 mmHg); mass spectrum (rel intensity) M<sup>+</sup> 278 (1.5), *m/e* 73 (100); NMR δ (CCl<sub>4</sub>) 0.14 (27 H, s), 3.35 (3 H, s)
- 6d: bp 160-180 °C (0.2 mmHg); mass spectrum (rel intensity) M<sup>+</sup> 410 (24.9), m/e 232 (100); NMR δ (CCl<sub>4</sub>), trans, -0.07 (6 H, s), -0.12 (18 H, s), 4.08 (2 H, s), 7.0-7.2 (8 H, m, arom), and cis, -0.26 (6 H, s), 0.00 (18 H, s), 4.10 (2 H, s), 7.0-7.2 (8 H, m, arom)
- 6e: mp 275 °C; mass spectrum (rel intensity) M<sup>+</sup> 526 (4.3), m/e 348 (100); NMR δ (CCl<sub>4</sub>) 0.06 (36 H, s) 4.27 (2 H, s), 6.8-7.2 (8 H, m, arom)





is also not reactive enough to be susceptible to silvlene insertion. Therefore, we favor the mechanism shown in Scheme I.

Methoxypolysilanes are also well-defined silylene generators<sup>9</sup> and, indeed, the dimethylsilylene generated from 4a afforded **6a** by reaction with anthracene. The yield of **6a** from 4a was highly temperature dependent. Thus, at 300 °C, no adduct was found in the thermolyzed mixture of 4a and anthracene, but 6a was obtained as a trace at 350 °C and in 6.2% yield at 390 °C. Methyl(trimethylsilyl)silylene (2d) and the bis(trimethylsilyl)silylene (2e), more bulky silylenes, generated from 4d and 4e, gave the corresponding adducts 6d (72% yield, 350 °C, 4 h) and 6e (48% yield, 250 °C, 3 h), respectively, in higher yields. These results indicate that dimerization of silylenes competes with insertion into the Si-OMe bond of the precursor.<sup>10</sup> Some physical properties of new compounds are summarized in Table I.11

Interestingly, an  $\sim 1:1$  mixture of trans and cis isomers of 6b was obtained from 4b (350 °C). Since cis- and trans-1,2diphenyl-1,2-dimethyldisilene are configurationally stable under these conditions,<sup>12</sup> the result implies no stereochemical preference in the dimerization of the phenylmethylsilylene. However, 4d gave two isomers of 6d in the ratio 3:1 at 250 °C. Therefore, the methyl(trimethylsilyl)silylene dimerized stereoselectively to the disilenes in favor of one isomer which was tentatively assigned to be trans.

2 Me<sub>z</sub>SiSiMe  $\overset{\mathrm{ld}}{\leadsto}$ trans-2d cis-2d

Very recently, Wulff, Goure, and Barton<sup>13</sup> reported that tetramethyldisilene (2a) isomerizes to 1d and that 1d also isomerizes to 2a to some extent in vapor phase.



However, in our experimental conditions, there is no indication of such a rearrangement. In fact, we generated 1d in the hope of obtaining 2a which has been known to be trapped by anthracene,<sup>4</sup> but no **6a** was detected. The discrepancy between these experiments may arise from the different experimental conditions, but we reserve the explanation until new experimental results are available.

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# trans- and cis-1,2-Dimethyl-1,2-diphenyldisilene. Is Si=Si a True Double Bond?<sup>1</sup>

### Sir:

Although disilenes, the silicon-silicon double-bonded species, have been recognized as intermediates in certain reactions,<sup>2</sup> no experimental knowledge has been obtained on the double-bond properties such as geometrical isomerism of the Si=Si bond.<sup>3</sup> We report in this communication the first evidence of the geometrical isomerism of the silicon-silicon double bond.

The reaction of 1,4-dilithio-1,4-diphenylbutadiene<sup>4</sup> with 1,2-difluoro-1,2-dimethyl-1,2-diphenyldisilane in THF gave a mixture of *trans*- and *cis*-1,2-dimethyl-1,2-diphenyl-1,2disilacyclohexadiene which was separated into each isomer by silica gel chromatography.5

The stereochemical assignment of trans (1a) and cis isomers (1b) is not easy from the NMR results only, but can be accomplished unequivocally by examination of the NMR signals due to Si-Me groups of products of the next step (2a and 2b).

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The trans isomer la gave trans-2,3-benzo-1,4,7,8-tetraphenyl-7,8-dimethyl-7,8-disilabicyclo[2.2.2]octadiene (2a)<sup>6</sup> quantitatively by the reaction with benzyne generated from benzenediazonium 2-carboxylate in THF at 70 °C. Similarly 1b afforded the corresponding cis isomer 2b.7 Two Si-Me signals appeared in the spectrum of 2a, whereas only one appeared in that of 2b; therefore the stereochemical assignment is obvious. Only a single product was obtained in the reaction of 1b with benzyne and, for steric reasons, the structure of 2b was tentatively assigned to that product. However, the conclusion obtained in the following text is not affected by the stereochemical assignment of 2b.



Pyrolysis of a 1:1 mixture of 2a and anthracene in benzene in a sealed tube at 300 °C for 17 h afforded a mixture of 3a (96%) and 3b (4%) in 81% yield.<sup>8</sup> Similar pyrolysis of 2b gave a mixture of 3a (6%) and 3b (94%) in 88% yield. Since 1,2dimethyl-1,2-diphenyldisilene (4) produced by dimerization of PhMeSi: gives rise to a 1:1 mixture of 3a and 3b in the reaction with anthracene,9 the stereospecificity observed in the reaction of 2 is quite remarkable.<sup>10,11</sup>

Thermolysis of 2a and 2b at 350 °C gave slightly less stereospecific results. Thus, 2a afforded 3a (94%) and 3b (6%) in 84% yield, and 2b gave 3a (10%) and 3b (90%) in 85% yield, respectively.



With a seemingly less efficient enephile, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, 2a and 2b gave somewhat less stereospecific Diels-Alder adducts. Thus, at 300 °C for 18 h, three possible adducts, 5a (88%), 5b (8%), and 5b' (4%), were obtained in 82% yield.<sup>12</sup> Since both 5b and 5b' are derived from 4b, 88% retention of configuration is observed in this case. Similar temperature dependency of 2 was also observed in this case. Thus, at 350 °C for 2.5 h, 2a gave 5a (73%), 5b (18%), and 5b' (9%). Thermolysis of 2b in the presence of the silacyclopentadiene at 300 and 350 °C gave 5a (18 and 29%), 5b (56 and 50%), and 5b' (26 and 21%) in 91 and 87% yield, respectively.

These results demonstrate clearly that the  $\pi$  overlap between two 3p orbitals of silicon is effective to retain the configuration; namely, the Si=Si bond is a true double bond like C=C, with slow cis-trans isomerization in the temperature range studied. Related works are in progress.



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- (5) 1a: mp 112-113 °C; mass spectrum (rel intensity) (M+) m/ e 444 (36), 197 (100); NMR δ (CCI<sub>4</sub>) 0.20 (6 H, s, SiMe) 7.0–7.7 (22 H, m, olefinic and aromatic protons); UV λ (*n*-hexane) 235.5 nm (ε 39 700), 305.0 (9850), 354.5 (13 300).
   Ib: mp 114 °C; mass spectrum (rel intensity) (M<sup>+</sup>) m/e 444 (41). 197 (100); NMR δ (CCl<sub>4</sub>) 0.84 (6 H, s, SiMe), 7.0-7.5 (22 H, m, olefinic and aromatic protons); UV  $\lambda$  (*n*-hexane) 228.0 nm ( $\epsilon$  29 000), 299.5 (9070), 356.0 (12 100)
- (6) 2a: mp 199-200 °C; mass spectrum (rel intensity) (M<sup>+</sup>) m/e 520 (12), 240 (100); NMR δ (CCI<sub>4</sub>) 0.24 (3 H, s, SiMe), 0.36 (3 H, s, SiMe), 6.2-7.7 (26 H,
- m, olefinic and aromatic protons). **2b:** mp 192–193 °C; mass spectrum (rel intensity) (M<sup>+</sup>) m/e 520 (9), 240 (100); NMR δ (CCI<sub>4</sub>) 0.45 (6 H, s, SiMe), 6.48 (2 H, s, -CH=CH), 6.5-7.7 (24 H, m, aromatic protons).
- 3a: mp 165 °C; mass spectrum (rel intensity) (M<sup>+</sup>) m/ e 418 (74), 240 (100); NMR  $\delta$  (CCl<sub>4</sub>) 0.37 (6 H, s, SiMe), 4.20 (2 H, s, –CH–Ar), 6.9–7.4 (8 H, m, aromatic protons). **3b:** mp 136–137 °C; mass spectrum (rel intensity) (M<sup>+</sup>) m/ e 418 (60), 240 (100); NMR δ (CCl<sub>4</sub>) 0.31 (6 H, s, SiMe), 4.26 (2 H, s, CH-Ar), 6.9-7.4 (8 H, m, aromatic protons).
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- All of the adducts are thermally stable. For example, no change was ob-(10)served for 3a after heating at 350 °C for 3 h.
- (11)The stereochemistry of 3 is not always unequivocal, the dominant isomer obtained from the trans precursor (2a) being assigned to the trans product (3a). This conclusion is supported by the use of an unsymmetric enephile, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (see text).
- (12)The mixture of these isomers could not be separated, but inspection of the NMR spectra indicated that it contained only three compounds, 5a, 5b, and 5b', In the mass spectrum, the molecular ion corresponding to 5 (502.1945; calcd for  $C_{32}H_{34}S_{13}$ , 502. 1970) was obtained. It is easy to distinguish **5a** from **5b** and **5b'** by NMR. **5b** was tentatively assigned to the abundant isomer. NMR  $\delta$ (CCl<sub>4</sub>): **5a**, -0.19, 0.43, 0.61, 0.79 (3 H, s, SiMe), 6.35 (1 H, d, J = 7.0 Hz, HC=C-), 6.39 (1 H, d, J = 7.0 Hz, HC=C-), 7.0-7.5 (20 H, m, aromatic protons); 5b, - 0.28, 0.50 (3 H, s, SiMe), 0.79 (6 H, s, SiMe) 6.35 (2 H, s, -CH=CH-), 7.0-7.5 (30 H, m, aromatic protons); 5b', · 0.58 (3 H, s, SiMe), 0.80 (6 H, s, SiMe), 6.39 (2 H, s, CH=CH), 7.0-7.5 (20 H, m, aromatic protons)

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