The angles at the group 5 elements in the diaryl anions are somewhat larger than those in the corresponding triaryls.[19,20] The larger angle at arsenic compared with phosphorus is somewhat surprising as are the related smaller dihedral angles between the phenyls 11.2° (As) vs. 43.4° (P). It may be that due to the greater electropositive character of carbon relative to arsenic (electronegativity of As > P),[21] the s character of the M–C bond is increased (and as a result the C–M–C angle) in accordance with Bent's rule.[22] An increased angle at the group 5 element also allows closure of the dihedral angle. The normal P–C and As–C bond lengths suggest little or no π-interaction between the phenyl ring and the metalloid atom.

Although the above structural details are of significant interest, the most remarkable feature of **1** and **2** concerns the fact that crown ethers can be used to effect separation of the metal cation and organometalloid anion in both the solid state and in solution. Efforts are under way in this laboratory to extend this technique to the structural characterization of lithium salts of alkyls, aryls, silyls, amides, alkoxides, and thiolates having non-interacting organoanions and crown ether complexed metal ions.

Acknowledgment. We thank the Research Corporation and NSF (CHE-8116355) for generous financial support.

Supplementary Material Available: Listing of atom coordinates, temperature factors, bond distances, and angles of **1** and **2** and a stereoview of **1** (8 pages). Ordering information is given on any current masthead page.

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(19) Trotter, J. *Acta Crystallogr.* **1963**, *16*, 1187–1189; *Can. J. Chem.* **1963**, *41*, 14–17. Springall, H. D.; Brockway, L. O. *J. Am. Chem. Soc.* **1938**, *60*, 996–1000.

(20) Daly, J. J. *J. Chem. Soc. A* **1966**, 1020.

(21) Both the Allred-Rochow and Sanderson electronegativities are significantly greater for arsenic. The Pauling electronegativities for P and As are very nearly equal. Huheey, J. E. "Inorganic Chemistry", 3rd ed.; Harper and Row: New York, 1983; p 146.

(22) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616; *J. Chem. Phys.* **1960**, *33*, 1258–1261; *Chem. Rev.* **1961**, *61*, 275–311. Huheey, J. E. "Inorganic Chemistry", 3rd ed.; Harper and Row: New York, 1983; p 232.

Cis and Trans Isomers of Disilenes: Photochemical and Thermal Interconversions

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The synthesis of tetramesityldisilene (**1**)[1] has opened the way to a new area of organosilicon chemistry.[2] We now report the synthesis of disilenes **2** and **3**, which exist as geometrical isomers, and observation of the facile cis–trans interconversions that they undergo.

Photolysis of 2-*tert*-butyl-2-mesitylhexamethyltrisilane at −80 °C produced more than 95% of the pale yellow disilene **2**, mostly as the trans isomer **2a**.[3,4] Compound **2a** gives a ^{29}Si NMR signal at +90.3 ppm, even more deshielded than the +63.6 ppm resonance for **1**. It exhibits UV maxima at ~400 (sh) and 338 nm (Figure 1). Irradiation at 350 nm leads to a photostationary equilibrium mixture containing 63% of **2a** and 37% of the cis isomer, **2b**.[5] The isomerization can easily be followed by ^{1}H or ^{29}Si NMR; **2b** has its ^{29}Si resonance at +94.7 ppm.

$$\mathrm{Mes(R)Si(SiMe_3)_2} \xrightarrow[\text{pentane}]{h\nu,\ 254\ \mathrm{nm}} \mathrm{Mes(R)Si{=}Si(R)Mes} \quad \begin{array}{l} \mathbf{2},\ \mathrm{R} = tert\text{-butyl} \\ \mathbf{3},\ \mathrm{R} = \mathrm{N(SiMe_3)_2} \end{array}$$

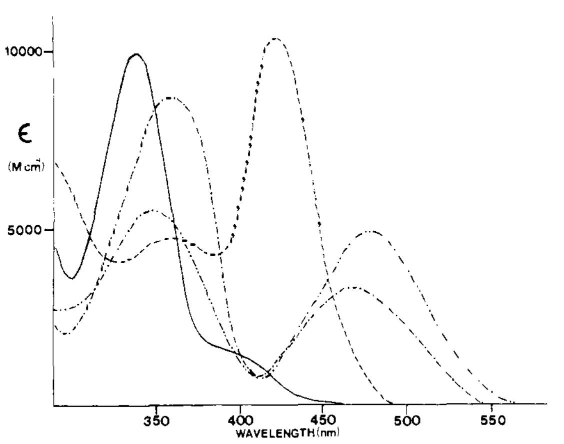
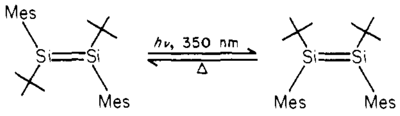


Figure 1. Electronic spectra of stable disilenes (in C_6H_6): (a) **2a** (—), (b) Mes_4Si_2 (---), (c) **3b** (-·····-), (d) **3a** (-··-··-).



2a 2b

The cis isomer **2b** is thermodynamically unstable, reverting back to the equilibrium mixture of **2a**–**2b**. At 25 °C in benzene this mixture contains 98% **2a** and 2% **2b**; the half-life for equilibration under these conditions is 570 ± 30 h.

Similar photolysis of 2-mesityl-2-(bis(trimethylsilyl)amino)-hexamethyltrisilane in pentane at −60 °C gives disilene **3** in 95% yield, mainly as the *unstable* isomer **3b**. Pure solid **3b** was obtained by evaporation of solvent and subsequent recrystallization from pentane at −78 °C. At 25 °C in benzene **3b** isomerized to the equilibrium mixture **3a**:**3b** = 94:6, with a half-time of 40 ± 3 h. Isomers **3a** and **3b** show ^{29}Si resonances at +61.9 and +6.8 ppm and +49.4 and +6.2 ppm, respectively.[6] The isomers cannot be identified decisively at this time, but by analogy with the behavior of **2a**, **2b** we tentatively assign **3a** as trans and **3b** as cis. The more rapid cis–trans interconversion in **3a**–**3b** may reflect weakening of the Si–Si π bond by electron donation from nitrogen, as is observed also for C–C double bonds substituted with π-electron-donating atoms.[7]

Disilenes **1**, **2**, and **3** all show distinctively different properties. Compound **1** is bright yellow and reversibly thermochromic, undergoing transformation to a red color when heated as a solid.

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† University of Utah.

(1) (a) West, R.; Fink, M. J.; Michl, J. *Science* (*Washington, D.C.*) **1981**, *214*, 1343. (b) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992. (c) Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *Ibid.* **1982**, *104*, 1150. (d) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (e) Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464.

(2) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. Zilm, K. W.; Grant, D. M.; Michl, J.; Fink, M. J.; West, R. *Organometallics* **1983**, *2*, 193.

(3) **2a**: ^{1}H NMR (C_6D_6) δ 1.13 (s, 18 H, *t*-Bu), 2.13 (s, 6H, para CH_3), 2.88 (s, 12 H, ortho CH_3), 6.90 (s, 4 H, ArH); MS, 408 (M^+, 52%), 351 (M − *t*-B, 10%). Exact mass for $C_{26}H_{40}Si_2$ calcd *m/e* 408.2658, found *m/e* 408.2671.

(4) The trans structure for **2a** was established by X-ray crystallography: Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics*, submitted for publication.

(5) **2b**: ^{1}H NMR (C_6D_6) δ 1.40 (s, 18 H, *t*-Bu), 1.88 (s, 6 H, para CH_3), 2.71 (s, 12 H, ortho CH_3), 6.65 (s, 4 H, ArH). A UV spectrum of the mixture of **2a** and **2b** shows a slight shift of the principal absorption band to shorter wavelength, indicating that **2b** has λ_{max} ~ 332 nm.

(6) **3a**: ^{1}H NMR (C_6D_6) δ 0.20 (s, 36 H, $SiMe_3$), 2.10 (s, 6H, para CH_3), 2.80–3.05 (br, 12 H, ortho CH_3), 6.90–6.95 (br, 4 H, Ar H); UV–vis (C_6H_6) λ_{max} = 351, 483 nm. **3b**: ^{1}H NMR (C_6D_6) δ 0.39 (s, 36 H, $SiMe_3$), 1.91 (s, 6 H, para CH_3), 2.58 (s, 12 H, ortho CH_3), 6.62 (s, 4 H, Ar H); UV–vis (C_6H_6) λ_{max} = 362, 468 nm; MS (**3b**) 614 (M^+, 21%), 599 (M − CH_3, 0.7%), 526 (M − $(CH_3)_4Si$, 1.2%), 511 [M − $(CH_3)_4Si$ − CH_3, 9.5%]. Exact Mass for $C_{30}H_{58}N_2Si_6$ calcd *m/e* 614.3200, found *m/e* 614.3214.

(7) Kalinowski, H.-O.; Kessler, H. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1973; Vol. VII, p 310.

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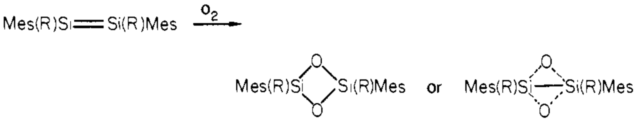
Isomer **2** is a pale yellow and not thermochromic when heated. It does show a reversible decolorization when cooled to −196 °C. **2** is more stable thermally than **1**, decomposing only above 220 °C after melting to a light yellow liquid at 165–173 °C. The nitrogen-substituted disilene isomers, **3a** and **3b**, are orange-red at room temperature (Figure 1). Upon cooling to −196 °C, **3b**, but not **3a**, shows a reversible change to yellow. As solid powders both **1** and **3** react with oxygen rapidly, being converted to their oxidation products upon simple exposure to the atmosphere within a few minutes at room temperature. Solid **2** react much more slowly, with a half-lifetime for oxidaton in air of several hours. Therefore **2** may be transferred from one vessel to another without the protection of an inert atmosphere, although it should be stored under nitrogen or argon. All three compounds oxidize in air to give analogous products, the cyclodisiloxanes **4–6**. The unusual structure of **4** and its implications for chemical bonding are described in the accompanying communication.[8]



4, R = mesityl
5, R = $N(SiMe_3)_2$
6, R = *tert*-butyl

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-82-0067 and by the National Science Foundational Science Foundation under Grant CHE-81-21112.

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(8) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.*, following paper in this issue.

Tetramesitylcyclodisiloxane: A Cyclic Siloxane with an Unusual Structure

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Cyclosiloxanes, $(R_2SiO)_n$, are compounds of considerable commercial importance as precursors to silicone polymers.[1] Although a large number of ring sizes can be obtained by the hydrolysis of difunctional silanes, the first members of this series, the cyclodisiloxanes, are almost unknown.[2] We report herein the unexpected structure of the recently reported tetramesitylcyclodisiloxane (**1**).[3] Compound **1** is produced nearly quantitatively from tetramesityldisilene (**2**) when the latter is simply exposed to atmospheric oxygen.[3] The cyclodisiloxane is a white powder (mp 215 °C) with surprising stability; it survives gas chromatography at 310 °C, prolonged heating in refluxing Decalin, and lengthy photolysis at 254 nm.

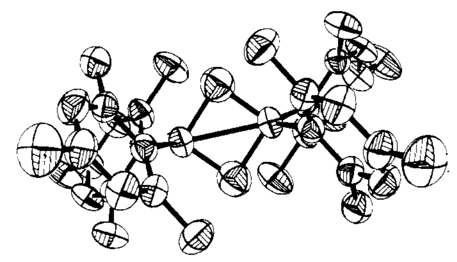

Figure 1. ORTEP drawing of tetramesitylcyclodisiloxane.

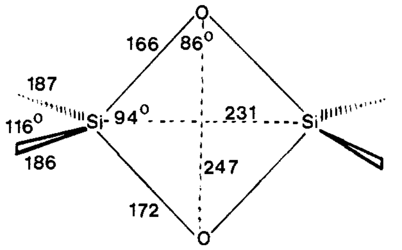

Figure 2. Important bond lengths (pm) and angles in **1**.

$$\underset{\mathbf{2}}{Mes_2Si{=}SiMes_2} \xrightarrow{O_2} \underset{\mathbf{1}}{[Mes_2SiO]_2}$$

Mes = 2,4,6-trimethylphenyl

An X-ray structure determination was undertaken, in order to understand the structural features that contribute to the stability of **1**. Crystals of the toluene solvate of **1** ($C_{36}H_{44}Si_2O_2{\cdot}C_7H_8$, $m = 657.06$) were obtained by slow cooling of a saturated toluene solution of **1** from room temperature to −10 °C. Compound **1** crystallizes in the tetragonal space group ($I4_1/a$) with $a = 1221.2$ pm and $c = 5242.5$ pm (-30 ± 5 °C, $\lambda_{\text{Mo K}\bar{\alpha}} = 71.037$ pm), $D_{\text{calcd}} = 1.12$ g/cm^3, and $z = 8$.[4] Figure 1 is an ORTEP diagram of **1** which shows the silicon–oxygen ring structure. Important bond lengths and angles are displayed in Figure 2. The ring is nearly planar, the dihedral angle between the Si–Si–O three-member planes being 6°. The two independent silicon–oxygen bond lengths are 166 and 172 pm, somewhat longer than those found for other cyclic siloxanes (161–165 pm).[5] The Si–O–Si angle is 86°, highly constrained compared to normal siloxane bond angles of 140–180°.[6] A striking feature of this structure is the silicon–silicon distance of 231 pm, somewhat *shorter* than the normal Si–Si single-bond length of 234 pm. The distance between the oxygen atoms is 247 pm, slightly less than the sum of the Van der Waals radii for oxygen, ~280 pm.

Each silicon is coplanar with the attached carbon atoms and the other silicon atom. A slight twist (11°) about the silicon–silicon axis is observed for the two C–Si–C planes; the siloxane ring is roughly orthogonal to these planes. The molecular structure

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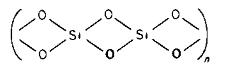
† University of Utah.

(1) Noll, W. "Chemistry and Technology of Silicones"; Academic Press: New York, 1968.

(2) An unstable silica polymorph, orthorombic silica, has been reported to contain the cyclodisiloxane structure unit



It reacts with water at room temperature. Weiss, V. A.; Weiss, A. *Z. Anorg. Allg. Chem.* **1954**, *276*, 93. We are indebted to a referee for pointing out that a disilaoxetane structure has also been proposed by Schwartz, although no structure proof was provided. See: Schwartz, R.; Kuchen, W. *Ibid.* **1955**, *279*, 84.

(3) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. West, R.; Fink, M. J.; Michl, J. *Science* (Washington, D.C.) **1981**, *214*, 1343.

(4) With $z = 8$ there is only $^1/_2$ formula unit per asymmetric unit. This is accommodated by the molecule being located on a 2-fold axis ($^1/_2$, $^1/_4$, z) that relates the two silicon atoms and the two oxygen atoms. The solvent molecule is distorted with the two independent overlapping quarter molecules also located on a 2-fold axis (0, $^1/_4$, z). The structure was solved by direct methods and refined by full-matrix least-squares refinement based on F using the 2292 data with $F_o > 3\sigma(F_o$; $R = 0.079$, GOF = 1.48). Tables of the final atomic coordinates, anisotropic thermal parameters, and selected distances and angles are given as supplementary material.

(5) Kiss, J.; Mencze, G. *Acta Crystallogr., Sect B* 1975, *B31*, 1214.

(6) Examples: $Me_3SiOSiMe_3$, 149°;[7] $(Me_2SiO)_4$, 143°,[8] $(Ph_2SiO)_4$, 160°;[9] $Ph_3SiOSiPh_3$, 180°.[10]

(7) Barrow, M. J.; Ebsworth, E. A. V.; Hardine, M. M. *Acta Crystallogr., Sect. B* 1979, *B35*, 2093.

(8) Steinfink, H.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1955**, *8*, 420.

(9) Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 522.

(10) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 124-128.

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