Structure of the THF Solvate of Tetramesityldisilene

Michael Wind, Douglas R. Powell, and Robert West*

Department of Chemistry, University of Wisconsin—Madison, Madison Wisconsin 53706

Received August 30, 1996[⊗]

*Summary: The X-ray crystal structure of $Mes_2Si{=}SiMes_2$·THF (**1**·THF) has been determined. The THF molecule is not coordinated to silicon. The two Mes_2Si units are twisted relative to one another by 13°, while the arrangement at each silicon is coplanar. This conformation differs from that found for **1**·C_7H_8 (12° twist, 18° pyramidalization) and unsolvated **1** (3° twist, 12, 14° pyramidalization).*

Tetramesityldisilene (**1**) was both the first disilene to be synthesized and the first to have its structure determined.[1] The earliest structure was of crystals of the yellow toluene solvate **1**·C_7H_8, grown from warm toluene solution.[2] Later, orange unsolvated crystals of **1** obtained by slow cooling of hexane solutions of the disilene were also studied by X-ray crystallography;[3] The conformations of the disilene molecule are somewhat different in **1** and **1**·C_7H_8.

Quite early **1** was obtained from THF, or THF−hydrocarbon mixtures, as the 1:1 solvate **1**·THF.[4] Several attempts were made over the past decade in our laboratories to obtain crystals of this solvate suitable for X-ray analysis, but only now have these efforts been successful. A key to obtaining suitable crystals was rigorous purification of the THF and exclusion of air; it seems that in this case, rather small amounts of impurities prevent orderly crystal growth.

Experimental Section

Tetramesityldisilene (**1**) was prepared in the usual way by photolysis of $Mes_2Si(SiMe_3)_2$ in pentane−THF solution.[4] The crude disilene was transferred to a drybox and dissolved in THF which had been distilled from sodium benzophenone; this solution was then degassed by 10 chill (−80 °C)−pump−thaw cycles. Slow cooling of a hot saturated solution of **1** in THF so purified produced yellow transparent prisms of **1**·THF.

Results and Discussion

X-ray structure determination was carried out using a Siemens P4 diffractometer at −145 °C. A 50% thermal ellipsoid diagram for **1**·THF is shown in Figure 1, and the structure determination summary is given in Table 1.[5] A comparison of the structures of the three forms of **1** is shown in Table 2. **1**·THF, with space group *Ccca* and crystal symmetry C_2-222, is more symmetric than the other known forms of **1**. The disilene molecule sits on a 222 crystallographic site with the silicon on a 2-fold axis. The THF molecule sits on another 222 site, in a 2-fold disordered position. Only one-fourth of the molecule is crystallographically independent, the positions of the other atoms being determined by symmetry operations. It follows that each of the aromatic rings, helically disposed about the silicon−silicon double bond, must have the same tilt angle to the Si−Si π bond, 62.6°.

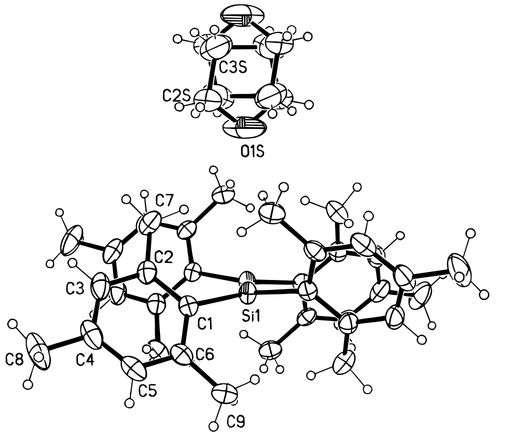

Figure 1. Thermal ellipsoid diagram (50%) for **1**·THF.

Each of the known forms of **1** is somewhat distorted from planarity at the double bond. In unsolvated **1**, the halves of the molecule are twisted relative to one another by 3°, and the two silicon atoms are anti-pyramidalized by 12 and 14°. In **1**·C_7H_8 both the twist angle and pyramidal angles are larger: 12 and 18°, respectively. In **1**·THF, there is a 13° twist angle but no pyramidalization. Perhaps the larger twist angle in **1**·THF offsets the absence of pyramidalization found in the other forms of **1**. In general, however, we believe that the differences in conformation in the three forms of **1** may result from subtle crystal-packing forces. Theoretical calculations on the model disilenes $H_2Si{=}SiH_2$ and $(CH_3)_2Si{=}Si(CH_3)_2$ indicate that the potential energy surface is quite flat both for twisting and for pyramidalization.[6]

The distance between the oxygen of the THF molecule and the center of the Si−Si bond, 444.1 pm, appears to be too great for a coordinating interaction. Lack of coordination is also indicated by the Si−Si bond length in **1**·THF, 214.6 pm, which is insignificantly elongated compared to **1** and actually shorter than the Si−Si distance in **1**·C_7H_8. Thus, **1**·C_7H_8 differs from the THF adducts of compounds with Si=C or Si=N bonds, in

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

[1] For reviews listing known disilene structures, see: Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1995**, *39*, 231. Chaubon, M. A.; Ranaivonjatovo, H.; Escudie, J.; Satge, *J. Main Group Met. Chem.* **1996**, *19*, 145.

[2] Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1994**, *3*, 793.

[3] Shepherd, B. D.; Campana, C. F.; West, R. *Heteroat. Chem.* **1990**, *1*, 1.

[4] Tan, R.; Yokelson, H. B.; Gillette, G. R.; West, R. *Inorg. Synth.* **1992**, *29*, 19.

[5] The hydrogen positions were initially located using geometry and refined using a riding model. Isotropic displacement parameters for the methyl hydrogens were assigned values of 1.4 times the isotropic equivalent displacements of the bonded carbons; other hydrogens were assigned values of 1.2 times the isotropic equivalent displacements of the bonded carbons.

[6] Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 2, pp 129−136.

S0276-7333(96)00753-4 CCC: $12.00

Table 1. Structural Determination Summary for 1·THF

empirical formula	$C_{36}H_{44}Si_2$ (C_4H_8O)
cryst color, habit	yellow transparent prism
cryst size	0.40 × 0.30 × 0.30 mm
crystal syst	orthorhombic
space group	*Ccca*
unit cell dimens	$a = 11.9656(2)$ Å $b = 20.0671(5)$ Å $c = 14.5277(3)$ Å $\alpha = \beta = \gamma = 90°$
V	3488.32(13) Å^3
no. of peaks to determine cell	4492
θ range of cell peaks	3.0−25.5°
temp	133(2) K
wavelength	0.710 73 Å
Z	4
fw	605.00
density calcd)	1.152 Mg/m^3
abs coeff	0.131 mm^{-1}
F(000)	1312
diffractometer	Siemens P4/CCD
θ range for data collection	2.03−26.01°
scan type	ψ-scan frames
no. of reflns collected	6220
no. of indep rflns	1592 ($R_{\text{int}} = 0.0321$)
max and min transmissn	0.905, 0.750
soln	direct methods
refinement method	full-matrix least squares on F^2
weighting scheme	$w = 1/[\sigma^2(F_o{}^2) + (0.293P)^2 + 4.7590P]$, where $P = [F_o{}^2 = 2F_o{}^2]/3$
goodness of fit on F^2	1.293
final R indices ($I > 2\sigma(I)$)	R1 = 0.0460
R indices (all data)	wR2 = 0.1157
no. of obsd data ($I > 2\sigma(I)$)	1377
extinction coeff	0.0012(3)

Table 2. Structures of Various Forms of Tetramesityldisilene

compd	T, °C	space group	site sym	Z	r(Si=Si), pm	twist angle, deg[a]	pyram angle, deg[b]	ring orient, deg[c]	ref
1	−100	$P2_1/c$	C_1-1	4	214.3	3	12, 14	42, 52, 67, 70	3
1·C_7H_8	−85	$I4_1/a$	C_2-2	8	216.0	12	18	35, 35, 78, 78	2
1·THF	−145	*Ccca*	C_2-222	4	214.6	13	0	62.6	

[a] The dihedral angle between the C−Si−C and C′−Si′−C′ planes. [b] The angle between the C−Si−C plane and the Si−Si vector. [c] The dihedral angle between the aromatic ring plane and the C−Si−Si plane.

which the THF is coordinated to the silicon atom.[7,8] Evidently, multiply bonded silicon atoms only acquire Lewis acid character when they are involved in polar double bonds, to electronegative atoms such as carbon or nitrogen.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Supporting Information Available: Tables of atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates with isotropic displacement parameters, and torsion angles (5 pages). Ordering information is given on any current masthead page.

OM960753N

---

(7) Wiberg, N.; Preiner, G.; Scheida, O. *Chem. Ber.* **1981**, *114*, 2087.

(8) Wiberg, N.; Schurz, K. *J. Organomet. Chem.* **1988**, *341*, 145. Walter, S.; Klingebiel, U.; Schmidt-Baese, D. *J. Organomet. Chem.* **1991**, *412*, 319. Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813.