Synthesis and Photolysis of a 1,2-Disilathietane

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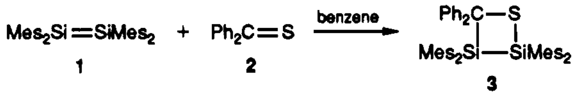
Summary: The reaction of tetramesityldisilene (**1**) with thiobenzophenone (**2**) gave the first disilathietane, 4,4-diphenyl-1,1,2,2-tetramesityl-1,2,3-disilathietane (**3**), as air-stable colorless crystals. An X-ray crystallographic study showed that **3** contains a long silicon–silicon bond (2.443 Å) and a highly distorted four-membered ring. Photolysis of **3** in the presence of ethanol afforded two compounds, dimesityl(diphenylmethyl)ethoxysilane (**5**) and dimesitylethoxysilanethiol (**6**); in the absence of ethanol photolysis gave the silene 1,1-dimesityl-2,2-diphenylsilene (**7**), in moderate yield.

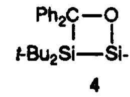
Disilenes[1] undergo cycloaddition reactions with many unsaturated substrates to give novel cyclic compounds containing two silicon atoms.[2] An important example is the reaction of disilenes with aldehydes and ketones to produce 1,2-disilaoxetanes.[3] We now report the [2 + 2] cycloaddition reaction of tetramesityldisilene (1) with thiobenzophenone (2) to yield 4,4-diphenyl-1,1,2,2-tetramesityl-1,2,3-disilathietane (3).[4]



Mes = 2,4,6-$Me_3C_6H_2$

When 0.442 g (0.828 mmol) of 1 was stirred in 35 mL of dried and degassed benzene with 0.240 g (1.21 mmol) of 2 for 24 h at 75 °C, the green solution gradually turned blue. The air-stable compound 3 was isolated as colorless crystals after recrystallization from benzene (0.332 g, 0.454 mmol, 55%).[5] The thermal ellipsoid plot of 3 and selected bond distances and angles are shown in Figure 1.[6]

It is of interest to compare the structure of 3 with that of the related oxygen compound 4,4-diphenyl-1,1,2,2-tetra-*tert*-butyl-1,2,3-disilaoxetane (4).[3b] The silicon–silicon bond length is abnormally long in 4 (2.409 Å) and even longer in 3 (2.443 Å).[7] The silicon–sulfur bond in 3 of 2.177 Å is also one of the longest reported silicon–sulfur bond lengths.[8] In 4 the four-membered ring is nearly planar, whereas in 3 it is highly distorted, with a dihedral angle of 45.6° between the Si(1)–Si(2)–C plane and the Si(1)–S–C plane.



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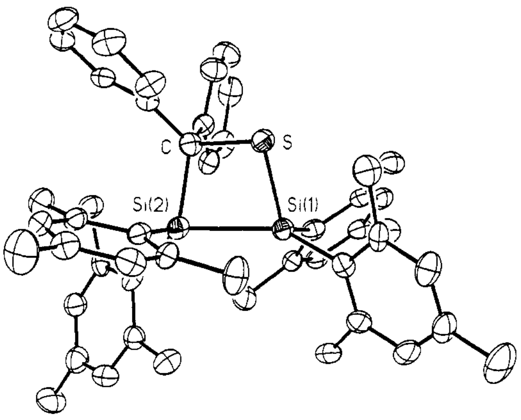
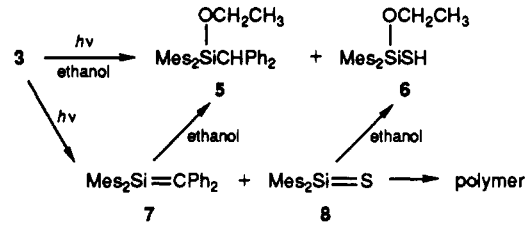


Figure 1. Thermal ellipsoid plot (50% probability) for 3. Selected bond distances (Å) and angles (deg): Si(1)–Si(2) = 2.443 (2), Si(2)–C = 1.994 (6), C–S = 1.870 (6), S–Si(1) = 2.177 (3); Si(1)–Si(2)–C = 81.9 (2), Si(2)–C–S = 93.0 (3), C–S–Si(1) = 92.3 (2), S–Si(1)–Si(2) = 74.5 (1).

Scheme I



The photolysis of 3 at −60 °C in pentane with excess ethanol yielded two compounds, dimesityl(diphenylmethyl)ethoxysilane (5)[9] and dimesitylethoxysilanethiol (6),[10] quantitatively. Photolysis of 3 in the absence of ethanol, on the other hand, gave a bright yellow solution, which showed two main signals at +76.68 and −7.05 ppm in the ^{29}Si NMR spectrum. Addition of ethanol led to simulta-

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[1] West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

[2] West, R.; Gillette, G. R.; Yokelson, H. B.; Millevolte, A. J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 3.

[3] (a) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. (b) Schäfer, A.; Weidenbruch, M. *J. Organomet. Chem.* **1985**, *282*, 305.

[4] The synthesis of the related monosilathietane (Si–S–C–C) ring compound was recently reported: Boudjouk, P.; Samaraweera, U. *Organometallics* **1990**, *9*, 2205.

[5] **3**: mp 232–236 °C dec; ^{1}H NMR (C_6D_6, δ) 2.03 (s, 6 H, *p*-CH_3), 2.08 (s, 6 H, *p*-CH_3), 2.31 (s, 12 H, *o*-CH_3), 2.53 (s, 12 H, *o*-CH_3), 6.55 (s, 4 H, Mes H), 6.63 (s, 4 H, Mes H), 6.7–6.9 (m, 6 H, Ph H), 7.5–7.7 (m, 4 H, Ph H); ^{29}Si NMR (C_6D_6, δ) −0.21, +7.80, J_{Si-Si} = 98 Hz (by double quantum coherence NMR spectroscopy; see: Yokelson, H. B.; Millevolte, A. J.; Adams, B. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 4116); ^{13}C NMR (C_6D_6, δ) 20.44, 25.74, 26.60, 64.68 (Ph_2C), 125.62, 126.68, 129.55, 129.76, 131.05, 134.92, 136.43, 138.39, 138.50, 143.92, 144.60, 147.46; exact mass (*m*/*e*) calcd for $^{12}C_{40}{}^{1}H_{43}{}^{32}S^{28}Si_2$ 611.2624, found 611.2648. Anal. Calcd for $C_{49}H_{54}SSi_2$: C, 80.49; H, 7.44. Found: C, 80.32; H, 7.41.

[6] A crystal of **3** cocrystallized with benzene ($C_{64}H_{69}SSi_2$, fw 926.4) measuring 0.10 × 0.15 × 0.25 mm was mounted on a Syntex P$\bar{1}$ diffractometer, and cell parameters were determined: triclinic space group $P\bar{1}$ ($Z = 2$), with $a = 11.527$ (4) Å, $b = 12.005$ (4) Å, $c = 20.684$ (7) Å, $\alpha = 101.36$ (3)°, $\beta = 105.02$ (3)°, and $\gamma = 100.04$ (2)°. A total of 4997 reflections with $F > 4.0\sigma(F)$ were measured. Final agreement factors: $R_1 = 7.41\%$, $R_2 = 8.28\%$.

[7] For comparison, in 1,1,2,2-tetramesityldisilane, the two independent Si–Si bond distances are 2.350 and 2.362 Å. See: Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

[8] The normal Si–S bond length for silicon attached to a single sulfur ligand is 2.15–2.16 Å. See: Sibao, R. K.; Keder, N. L.; Eckert, H. *Inorg. Chem.* **1990**, *29*, 4163.

[9] **5**: ^{1}H NMR (C_6D_6, δ) 1.14 (t, J = 7.0 Hz, 3 H, O–C–CH_3), 2.08 (s, 6 H, *p*-CH_3), 2.23 (s, 12 H, *o*-CH_3), 3.70 (q, J = 7.0 Hz, 2 H, O–CH_2–), 4.25 (s, 1 H, Ph_2CH), 6.67 (s, 4 H, Mes H), 6.9–7.1 (m, 6 H, Ph H), 7.3–7.4 (m, 4 H, Ph H); ^{29}Si NMR (C_6D_6, δ) −7.42; ^{13}C NMR (C_6D_6, δ) 18.13, 20.98, 24.27, 49.00 (Ph_2C), 59.80 (O–C), 125.51, 128.08, 129.65, 130.78, 132.87, 138.88, 144.15; exact mass (*m*/*e*) calcd for $^{12}C_{33}{}^{1}H_{37}{}^{16}O^{28}Si$ 477.2614, found 477.2609. Anal. Calcd for $C_{33}H_{38}OSi$: C, 82.79; H, 8.00. Found: C, 82.39; H, 7.72.

[10] **6**: ^{1}H NMR (C_6D_6, δ) 0.64 (s, 1 H, SH), 1.08 (t, J = 7.0 Hz, 3 H, O–C–CH_3), 2.07 (s, 6 H, *p*-CH_3), 2.52 (s, 12 H, *o*-CH_3), 3.68 (q, J = 7.0 Hz, 2 H, O–CH_2–), 6.69 (s, 4 H, Mes H); ^{29}Si NMR (C_6D_6, δ) −5.70; ^{13}C NMR (C_6D_6, δ) 18.06, 21.00, 24.12, 58.61 (O–C), 130.01, 132.14, 139.68, 143.78; exact mass (*m*/*e*) calcd for $^{12}C_{20}{}^{1}H_{28}{}^{16}O^{32}S^{28}Si$ 344.1630, found 344.1623.

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neous decolorization of the yellow solution and disappearance of the ^{29}Si NMR signal at +76.68 ppm, which was replaced by a signal at −7.42 ppm. The resonance at −7.05 ppm remained unchanged throughout. Ethoxysilane **5**, which has a ^{29}Si NMR signal at −7.42 ppm, was isolated from the reaction mixture by preparative TLC (Scheme I).

These results appear to indicate photochemical formation of the yellow silene 1,1-dimesityl-2,2-diphenylsilene (**7**), which is thermally stable at room temperature and has $\delta(^{29}Si) = +76.68$ ppm. The yield of **7** was estimated as 33% from the mesityl methyl proton signals in the ^1H NMR spectrum, but isolation of **7** has so far been unsuccessful. One of the other products of the photolysis is believed to be a derivative of dimesitylsilanethione (**8**). In the presence of ethanol, **8** was trapped to produce **6**. When no trapping agent is present, however, unstable **8** may dimerize or trimerize to give the compound with $\delta = -7.05$ ppm.

As a proof of structure, **5** was synthesized independently by reaction of sodium ethoxide with chlorodimesityl(diphenylmethyl)silane; the latter compound was prepared from dichlorodimesitylsilane and (diphenylmethyl)lithium.[11]

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond lengths and angles and diagrams for **3** (13 pages); a listing of observed and calculated structure factor amplitudes for **3** (24 pages). Ordering information is given on any current masthead page.

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(11) Experimental procedure for **5**: Dichlorodimesitylsilane (1.70 g, 5.03 mmol) was reacted with (diphenylmethyl)lithium tetramethylethylenediamine complex (1.46 g, 5.03 mmol) in benzene at room temperature for 20 h. The formation of chlorodimesityl(diphenylmethyl)silane was followed by ^1H NMR spectroscopy, and the pure sample was separated from the reaction mixture by preparative GC. ^1H NMR (C_6D_6, δ): 2.03 (s, 6 H, *p*-CH_3), 2.21 (s, 12 H, *o*-CH_3), 4.46 (s, 1 H, Ph_2CH), 6.61 (s, 4 H, Mes H), 6.9–7.1 (m, 6 H, Ph H), 7.3–7.4 (m, 4 H, Ph H). Exact mass (*m*/*e*): calcd for $^{12}C_{31}{}^1H_{33}{}^{28}Si$ (product − Cl) 433.2351, found 433.2322. The benzene solvent in the reaction mixture was replaced by toluene, and an ethanol solution of sodium ethoxide (1.02 g, 15.0 mmol) was added to the mixture, which was then heated to 110 °C for 60 h. Compound **5** was isolated in 34% yield by column chromatography (SiO_2; hexane–ethyl acetate).

Synthesis and Structure of Bimetallic Allyl, Alkoxysilyl Complexes $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})M(\eta^3\text{-}2\text{-}RC_3H_4)]$ (M = Pd, Pt; R = H, Me) and of $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnPh_3)]$, a Sn–Pd–Fe–Si Chain Complex with a μ_2-η^2-SiO Bridge

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Summary: The bimetallic allyl, alkoxysilyl complexes $[Fe\{Si(OMe)_3\}(CO)_3(\mu\text{-dppm})M(\eta^3\text{-}2\text{-}RC_3H_4)]$ (M = Pd, R = Me, **2a**; M = Pd, R = H, **2b**; M = Pt, R = H, **3**) have been prepared from the iron metalate $[Fe\{Si(OMe)_3\}(CO)_3(\eta^1\text{-dppm})]^-$, in which the dppm ligand helps in assembling and stabilizing the dinuclear unit. The crystal structure of **2a** was determined by X-ray diffraction (Fe–Pd = 269.94 (7) pm). Reaction of **2a** with $HSnPh_3$ afforded $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})Pd(SnPh_3)]$ (**4a**), the first Sn–Pd–Fe–Si chain complex, in which the presence of an unusual μ_2-η^2-SiO bridge between the Fe and Pd atoms was established by X-ray diffraction (Fe–Pd = 266.55 (5), Sn–Pd = 259.50 (4), Pd–O(4) = 216.5 (2) pm). The lability of the O→Pd bond accounts for the dynamic behavior of the alkoxysilyl ligand, evidenced by variable-temperature ^1H NMR spectroscopy, which renders the methoxy protons equivalent above 313 K ($\Delta G^{\ddagger} \approx 65 \pm 2$ kJ/mol).

Despite numerous studies on the chemistry of silicon-containing transition-metal compounds,[1] there is only one example in the literature where μ_2-η^2-SiO (side-on) coordination for an alkoxysilyl ligand has been established by an X-ray diffraction study.[2] The resulting PdFeSiO four-membered ring in $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})PdCl]$ (dppm = $Ph_2PCH_2PPh_2$) was found to be kinetically labile (^1H NMR evidence) but thermodynamically stable, as typical donor ligands such as CO or PPh_3 would not displace the O→Pd bond under mild conditions. The novel features associated with this μ_2-η^2-SiO bonding, as well as its possible relevance to the stabilization of (i) coordinatively unsaturated, reactive metal complexes or surface species, (ii) silylene complexes,[3] and (iii) metal

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(2) Braunstein, P.; Knorr, M.; Tiripicchio, A.; Tiripicchio Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1361.

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