The first 1,2,4-thiadisiletane ring compound: synthesis from an overcrowded silylene and carbon disulfide

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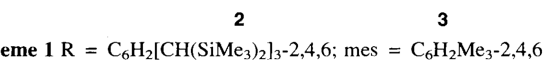
Treatment of an extremely hindered disilene, (*Z*)-R(mes)Si=Si(mes)R (R = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, mes = mesityl) with carbon disulfide in THF at 60 °C gives a novel 1,2,4-thiadisiletane-3-thione derivative, the formation of which is most likely interpreted in terms of a stepwise 2 : 1 addition reaction of the thermally generated overcrowded silylene R(mes)Si: to CS_2 followed by a skeletal rearrangement of the resulting 3,3′-spirobi[1,2-thiasilirane] intermediate.

Divalent silicon species (silylenes) are among important reactive intermediates in organosilicon chemistry.[1] Much interest has been focused on their reactivities such as additions to olefins,[2] heteroatom-containing multiple-bond compounds,[3,4] and a transition-metal complex[5] in connection with the reactivities of carbenes. Several methods have been reported for generating silylenes (photolysis of cyclic or linear trisilane, pyrolysis of silanorbornadiene derivatives, thermolysis of silacyclopropane derivatives, and so on).[1] There is, however, a severe limitation in a study on the reactivities of silylenes using these methods since almost all of these reactions are carried out either at high temperature or under irradiation conditions.

Meanwhile, we recently reported the synthesis and structural analysis of extremely hindered, air-stable disilenes R(mes) Si=Si(mes)R **1** [(*Z*)-**1**: *cis*-form; (*E*)-**1**: *trans*-form; mes = mesityl] kinetically stabilized by a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (R), and their facile thermal dissociation into the corresponding overcrowded silylene R(mes)Si: **2** under very mild conditions (*ca.* 70 °C).[6] Since this method for the generation of a silylene is very mild and clean, one can anticipate that it would be possible to isolate reaction products of a silylene which are unstable under the reaction conditions of the conventional methods. Here, we present a novel reaction of the overcrowded diarylsilylene, R(mes)Si: **2**, with carbon disulfide leading to the formation of a new cyclic thiocarbonyl compound, 1,2,4-thiadisiletane-3-thione **3**.

When a mixture of disilene (*Z*)-**1** (76 mg, 0.041 mmol) and carbon disulfide (0.04 ml, 0.67 mmol) dissolved in 3 ml of dry degassed THF was heated at 60 °C for 2 days, the characteristic yellow colour of (*Z*)-**1** disappeared and the chromatographic separation of the reaction mixture afforded the 1,2,4-thiadisiletane-3-thione **3** as greenish yellow crystals (72 mg, 90%; mp 267–269 °C)[†] (Scheme 1). Compound **3** is the first example not only of a 1,2,4-thiadisiletane ring[7] but also of a stable disilylthioketone derivative.[8] Although there has been observed an inevitable disorder with regard to the geometry of the thiocarbonyl unit and the ring sulfur atom, the molecular structure of **3** was determined by X-ray crystallographic analysis as shown in Fig. 1.[‡] It is intriguing that **3** has *cis* geometry and the 1,2,4-thiadisiletane ring showed a large fold angle of 35.5° with regard to two C–Si–S planes, while the two mesityl groups facing each other are almost parallel with the dihedral angle between these two aromatic rings being 4.6°. The unique geometry of **3** can be explained in terms of smaller steric repulsion between two bulky R groups in the folded *cis*-form than in a *trans*-form which is expected to be planar.



Scheme 1 R = $C_6H_2[CH(SiMe_3)_2]_3$-2,4,6; mes = $C_6H_2Me_3$-2,4,6

Only one example has been reported for the synthesis of a disilylthioketone [*i.e.* bis(trimethylsilyl) thioketone],[8] which is too labile to be purified by distillation or chromatography on Florisil. By contrast, compound **3** is very stable not only toward moisture and oxygen but also toward heating up to its melting point (267 °C), most likely owing to the presence of the effective steric protection groups. Although compound **3** exhibits a ^1H NMR spectrum too complicated to be assigned because of great steric congestion around the silicon atoms, **3** shows ^{13}C NMR and UV–VIS spectra characteristic of the thiocarbonyl group. The chemical shift of δ_c 340.54 (C=S) is much downfield shifted from those of usual thiocarbonyl compounds[9] and, to the best of our knowledge, is the most deshielded carbon ever observed in neutral molecules.[9] The absorption maximum at 795 nm (ε 50 dm^3 mol^{-1} cm^{-1}) in hexane is assignable to the n–π^* transition of a disilylthioketone unit of **3**, whereas the previously reported bis(trimethylsilyl)thioketone showed quite a different spectral data [δ_c 267 (C=S) λ_{max} 530 nm].[8]

The formation of **3** can be reasonably explained as shown in Scheme 2. Silylene **2** generated by dissociation of disilene (*Z*)-**1** reacts with carbon disulfide to form a 1 : 1 adduct, a silathiiranethione **4**. The second addition of silylene **2** occurs toward the resulting C–S double bond of **4** to produce 3,3′-spirobi[1,2-thiasilirane] intermediate **5**, which eventually undergoes skeletal rearrangement to give **3**. A similar reaction has been reported for silicocene Si(η^5-C_5Me_5)$_2$ by Jutzi and Möhrke,[10]

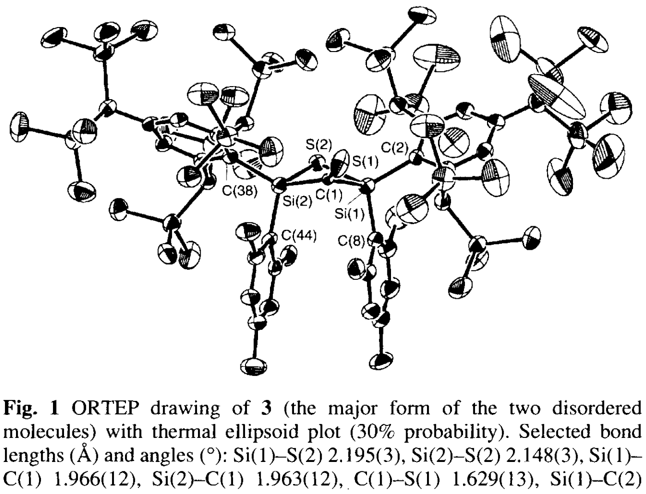
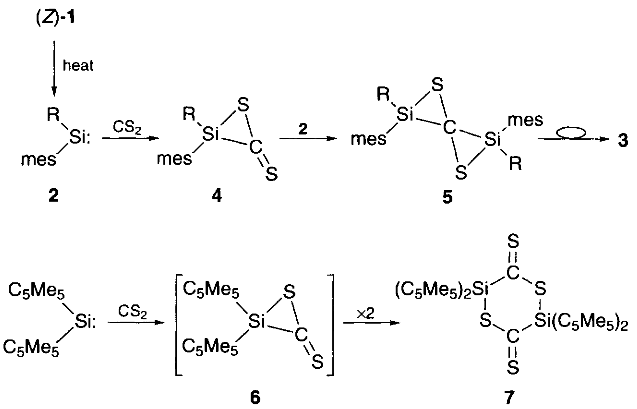


Fig. 1 ORTEP drawing of **3** (the major form of the two disordered molecules) with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°): Si(1)–S(2) 2.195(3), Si(2)–S(2) 2.148(3), Si(1)–C(1) 1.966(12), Si(2)–C(1) 1.963(12), C(1)–S(1) 1.629(13), Si(1)–C(2) 1.926(6), Si(1)–C(8) 1.903(6), Si(2)–C(38) 1.935(6), Si(2)–C(44) 1.893(6); S(1)–C(1)–Si(1) 122.9(7), S(1)–C(1)–Si(2) 137.9(7), C(1)–Si(1)–S(2) 81.3(4), C(1)–Si(2)–S(2) 82.6(4), Si(1)–S(2)–Si(2) 86.0(1), C(2)–Si(1)–C(8) 110.7(3), C(38)–Si(2)–C(44) 109.8(3).



Scheme 2

but, in that case, the intermediary silathiiranethione **6** reportedly undergoes a ready dimerization to afford the cyclic thioester **7** as shown in Scheme 2.

The successful isolation of 1,2,4-thiadisiletane-3-thione **3** and the lack of any dimerization products of the intermediary silathiiranethione **4** in this reaction suggest effective steric protection due to the combination of R and mes groups. It is noteworthy that the unique reactivity of the sterically hindered silylene **2** with carbon disulfide here described is quite different from those of the analogously hindered germylene and stannylene, $R(C_6H_2Pr^i_3\text{-}2,4,6)M$: (M = Ge, Sn) toward carbon disulfide.[11]

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Footnotes

† Compound **3**: High-resolution FAB-MS: observed m/z 1472.7185; Calc. for $C_{73}H_{140}S_2Si_{14}$ 1472.7166. Found: C, 58.30; H, 9.43; S, 4.73. Calc. for $C_{73}H_{140}S_2Si_{14}\cdot H_2O$: C, 58.72; H, 9.58; N, 4.29%.

‡ *Crystallographic data* for **3**: $C_{73}H_{140}S_2Si_{14}$, M = 1475.23, monoclinic, space group $P2_1/c$, a = 17.969(4), b = 21.709(5), c = 24.273(3) Å; β = 93.19(1)°; U = 9454(2) Å^3; Z = 4; D_c = 1.036 g cm^{-3}; μ(Mo-Kα) = 2.68 cm^{-1}. The intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and an empirical absorption correction using the program DIFABS (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158) was applied resulting in transmission factors ranging from 0.95 to 1.04. The structure was solved by direct methods and expanded using Fourier techniques. Since there has been observed an inevitable disorder with regard to the geometry of the thiocarbonyl unit and the ring sulfur atom, these atoms are refined with two sets of disordered positions (the population ratio was 7:3). The non-hydrogen atoms except for S(2), S(2*), C(1) and C(1*) [isotropic treatment for the former three atoms and fixed positional and thermal parameters for C(1*)] were refined anisotropically, while all hydrogen atoms were located in calculated positions. The final cycle of full-matrix least-squares refinement was based on 7600 observed reflections [$I > 2.00\sigma(I)$ and 805 variable parameters with $R(R_w)$ = 0.077(0.036). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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