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The Synthesis and Molecular Structure of a Disilacyclopropanimine

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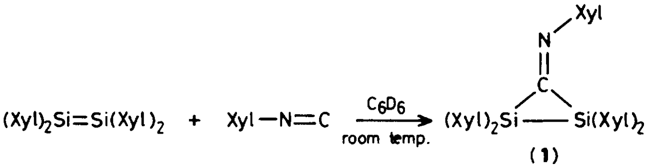
Tetra(2,6-dimethylphenyl)disilene reacts with (2,6-dimethylphenyl)isocyanide in benzene solution at room temperature to form disilacyclopropanimine (**1**), a bright red crystalline compound with λ_{max} = 510 nm, whose structure was established by *X*-ray crystallography.

The reactions of disilenes[1] lead to many new classes of silicon compounds, including several three- and four-membered rings which present novel problems in chemical bonding.[2] We report here the reaction of a disilene with an isonitrile to form the first disilacyclopropanimine, (**1**).

The addition of the colourless 2,6-dimethylphenylisocyanide (57 mg) to a yellow solution of tetra(2,6-dimethylphenyl)disilene (200 mg) in 2 ml of benzene at room temperature, resulted in an immediate colour change to deep red. Upon standing, crystals of (**1**) suitable for *X*-ray crystallographic analysis were obtained from this reaction mixture (Scheme 1).† The compound decolourizes slowly, both in solution and in the solid state, on exposure to air.

The reaction leading to (**1**) may be viewed as a [2 + 1] addition of the carbene-like carbon of the isonitrile to the disilene, and represents the first clear example of such a reaction. In contrast, similar reactivity is not observed for alkenes, but strained cyclic or electron-rich alkynes are reported to react with isonitriles in benzene solution to form cyclopropenimines.[3,4]

Figure 1 shows an ORTEP diagram of (**1**).‡ The plane of the disilacyclopropane ring and that of the exocyclic C–N double bond, defined by N(1), C(1) and C(34), are nearly coplanar with a dihedral angle of ~13°. It is noteworthy that the mean plane of the *N*-xylyl group is orthogonal to the plane of the C–N double bond. As the result of a slight pyramidalization at C(1),§ N(1) lies 17.5 pm out of the plane of the disilacyclopro-



(**1**)

Scheme 1. Mes = 2,4,6-trimethylphenyl; Xyl = 2,6-dimethylphenyl.

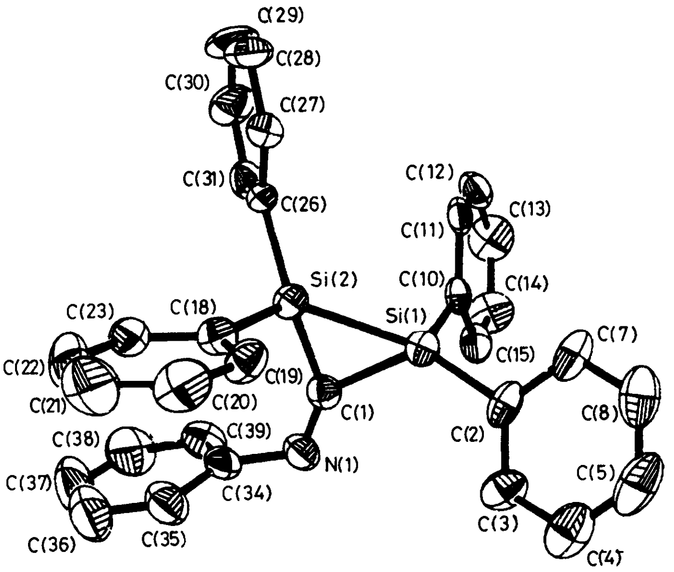


Figure 1. Molecular structure of (**1**). (Methyl groups have been omitted for clarity.) Bond lengths (pm): Si(1)–Si(2) 232.8(3), Si(1)–C(1) 190.1(7), Si(2)–C(1) 194.6(6), C(1)–N(1) 126.1(8). Bond angles (degrees): Si(1)–Si(2)–C(1) 53.6(2), Si(2)–Si(1)–C(1) 51.9(2), Si(1)–C(1)–Si(2) 74.5(2), C(1)–N(1)–C(34) 122.1(6).

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† *Spectral data* for (**1**): m.p.: 171—173 °C; ^{1}H n.m.r. (270 MHz, C_6D_6) δ 1.67 (s, 6 H), 1.8—2.7 (br. m, 24 H), 6.7—7.1 p.p.m. (m, 15 H); ^{13}C n.m.r. (125 MHz, C_6D_6) δ 214.0 p.p.m. (>C=N–); ^{29}Si n.m.r. (71.5 MHz, C_6D_6) δ +37.2 p.p.m., i.r.; (KBr, cm^{-1}) 1585, 1560, 1450; u.v. (C_6D_6) λ_{max} (ε) = 510 nm (176); mass spectrum (30 eV) calculated for $C_{41}H_{45}Si_2N$ *m/z* 607.3090, found *m/z* 607.3073.

‡ *Crystal data* for (**1**): monoclinic, space group $P2_1/n$, cell dimensions a = 16.664(4), b = 12.471(4), c = 18.766(4) Å, β = 115.133(1)° (T = 293 ± 1 K), λ(Mo-K_α) = 0.71073 Å); U = 3535.6 Å^3, D_c = 1.14 g cm^{-3}, and Z = 4. The structure was solved by direct methods and refined by blocked-cascade least-squares refinement[5] based on F using 2684 data with $F_O > 3\sigma(F_O)$; final discrepancy indices R = 0.083, R_w = 0.082, g.o.f. = 1.23. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The sum of the angles about C(1), Si(1)–C(1)–N(1), Si(2)–C(1)–N(1) and Si(1)–C(1)–Si(2), is 358.5°.

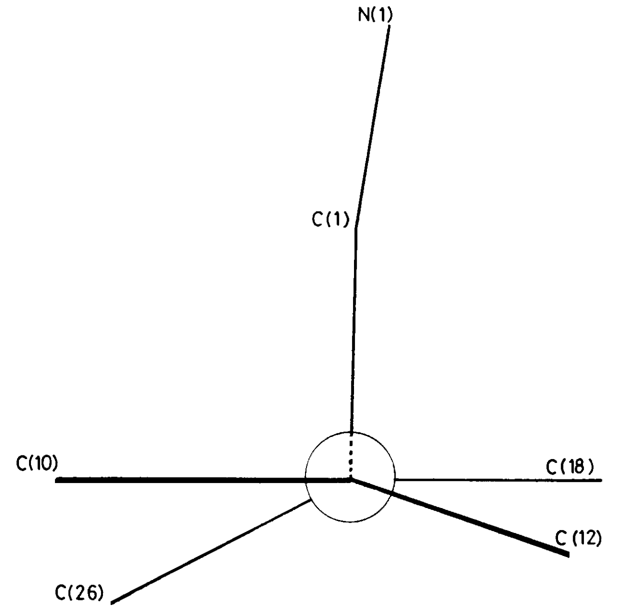
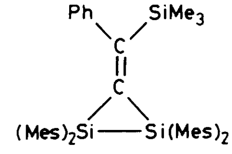


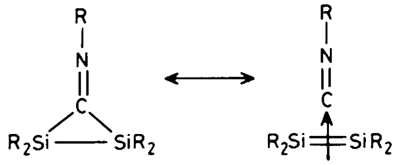
Figure 2. Newman projection of (**1**) along the Si–Si axis showing the twist angles. The numbering scheme is shown in Figure 1; Si(2) is behind Si(1).

pane ring, that is, the C(1)–N(1) vector makes an angle of 9° with the plane of the ring. The two silicon atoms and the four pendant aryl carbons deviate from planarity. The distortion can be described as a moderate *syn*-pyramidalization of the silicons and a slight twisting along the silicon–silicon bond axis. The *cis*-bent geometry of the disilane framework is illustrated in the Newman projection in Figure 2. One silicon atom is distinctly more pyramidalized than the other, and this may provide relief of steric congestion imposed by the *N*-xylyl group.[6]¶

Compound (**1**) is an example of a *C*-disilylimine and its low energy visible absorption band at 510 nm is of considerable interest.†† Electronic absorption bands for both ketones and imines are shifted to longer wavelength by silicon substitution;[7] the longest wavelength absorption lies near 250 nm for *C*-dialkylimines,[8] at 340 nm for *C*-monosilylimines, and at 361 and 406 nm for two *C*-disilylimines recently synthesized by Ito *et al.*[9]§§ The absorption at 510 nm may reflect a sizeable ring-strain effect on the transition energy.¶¶ It is also possible that this band represents a transition not found in the acyclic *C*-disilylimines, such as an intramolecular Si–Si $\sigma \rightarrow \pi^*$ charge transfer absorption.



(**2**)



(**3**)

Only a single signal (δ +37.2) is observed in the ^{29}Si n.m.r. spectrum of (**1**) at 25 °C. This suggests that in solution either the barrier to *syn–anti* inversion at nitrogen is low, or that the geometry at nitrogen is linear, as in (**3**).

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¶ The extent of pyramidalization at the silicons can be gauged by the 16 and 22° angles formed by the C(aryl)–Si–C(aryl) planes and the Si–Si bond axis. The sum of the angles about Si(1), C(2)–Si(1)–Si(2), C(10)–Si(1)–Si(2), and C(2)–Si(1)–C(10) is 357.5, and about Si(2), C(18)–Si(2)–Si(1), C(26)–Si(2)–Si(1) and C(18)–Si(2)–C(26), 354.9°.

Many of the structural features of (**1**) are similar to those of the 3-methylene-1,2-disilacyclopropane (**2**).[6] For example, Si–Si bond lengths of 232.8 pm in (**1**) and 232.7 pm in (**2**) are the same within experimental error. Also, the internal ring angles, 53.6 and 51.9° at Si and 74.5° at C, and Si–C bond distances of 190 and 195 pm, are comparable.

†† The 510 nm band for (**1**) shows a small blue shift (5—10 nm) in a more polar solvent; in tetrahydrofuran, λ_{max} (ε) 235 (5300), 283 sh (4000), 380 sh (700), 505 nm (180).

§§ For the *N*-*o*-tolyl-*C*-bis(dimethylphenylsilyl)imine, λ_{max} = 406 nm (ε = 550); for the *N*-cyclohexyl-*C*,*C'*-bis(dimethylphenylsilyl)imine, λ_{max} = 361 nm (ε = 55).

¶¶ With ketones, the constraint of a three-membered ring results in a red shift relative to acyclic analogues; compare acetone (λ_{max} = 280 nm) with cyclopropanone (λ_{max} = 310, 330 nm).