Molecular Interactions of Polysilane and Unsaturated Nitrogen Compounds. Photochemical Addition of Disilene *versus* Silylene to Azobenzene

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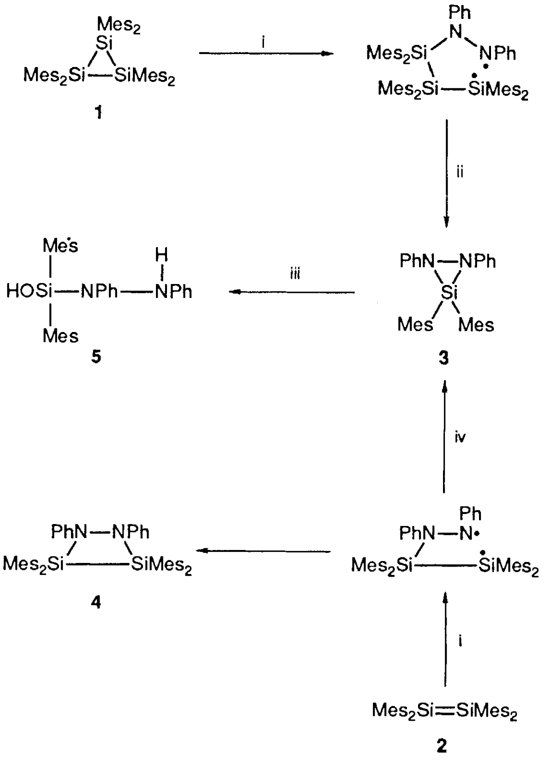
Photochemical reaction of hexamesitylcyclotrisilane **1** or tetramesityldisilene **2** with azobenzene produces silanol **5** *via* hydrolysis of diazasilacyclopropane **3** and/or 1,2-diaza-3,4-disilacyclobutane **4**; the structure of **4** has been confirmed by variable temperature ^{1}H NMR spectroscopy and single-crystal X-ray diffraction, the existence of an Si_2N_2 ring system is demonstrated.

There has been great interest in the chemistry of stable disilenes[1] and cyclotrisilanes[2] for the synthesis of novel heterocyclic organosilanes. Recently, the thermal addition and insertion reactions of stabilized disilenes and cyclotrisilanes with bulky ligands have been studied. Nevertheless, little is known about their photochemical behaviour with unsaturated nitrogen compounds. Our previous studies showed that the insertion of cyclotetrasilane and cyclotetragermane with azo compounds is thermally unreactive but extremely labile photochemically (> 300 nm irradiation).[3] This prompted us to examine the photochemical reactivity of azobenzene towards other polysilanes such as cyclotrisilane and disilene. Now we report that the photochemical reaction of hexamesitylcyclotrisilane **1** or tetramesityldisilene **2**, formed on photolysis of **1**, with azobenzene affords diazasilacyclopropane **3**[4] and/or the first 1,2-diaza-3,4-disilacyclobutane system **4**.

A benzene solution of hexamesitylcyclotrisilane **1** (0.125 mmol) and azobenzene (0.188 mmol) was irradiated with a high-pressure mercury lamp using a phenanthrene filter solution (cut off 360 nm) for 3 h. After loss of the colours due to azobenzene, preparative HPLC was used to separate and purify the reaction mixture, yielding silanol **5** (33%)[†] and 1,1,3,3-tetramesityl-1,3-cyclodisiloxane (12%). It is reasonable to suggest that the silanol **5** may be derived from the hydrolysis of the diazasilacyclopropane intermediate **3** and 1,3-cyclodisiloxane was obtained by oxidation of disilene,[1a] where the photochemical deoligomerization of cyclotrisilane **1** induced by azobenzene yielded diazasilacyclopropane **3** and disilene **2**, shown in Scheme 1. If visible light (>360 nm) is used, the direct photolysis of cyclotrisilanes leading to silylene and disilene cannot be considered.

The stable disilene **2** was prepared by the photolysis of cyclohexane solution of cyclotrisilane **1** (0.37 mmol) in a quartz tube with a low-pressure mercury lamp (254 nm) for 5 h, azobenzene (0.75 mmol) was then added. Continued photochemical treatment (>360 nm irradiation) resulted in the isolation of 1,2-diaza-3,4-disilacyclobutane **4**[†] as yellow crystals (7%) together with the silanol **5** (41%). When the stable disilene was treated with an azobenzene in the dark at 70 °C, 1,3-cyclodisiloxane was obtained together with unreacted azobenzene. This result is equally consistent with photochemical deoligomerization of disilene **2** by azobenzene to the diazasilacyclopropane **3** and silylene, while [2 + 2] cycloaddition of the disilene to azobenzene produces diazadisilacyclobutane **4**, shown in Scheme 1. Since the photolysis of 2,2-dimesitylhexamesityltrisilane with azobenzene under low-pressure mercury lamp (254 nm) yielded the silanol **5** (38%), secondary formed silylene in this reaction mechanism can add to azobenzene[5] and double the yield of diazasilacyclopropane **3**.

The structure of **4**, new 1,2-disilacyclobutane system, was established based on variable temperature ^{1}H NMR spectroscopy and an X-ray structure analysis. At low temperature (−30 °C), two sharp and four relatively broad singlets of equal intensity were observed and assigned to the *p*- and *o*-methyl protons on the mesityl ring. At higher temperature (−1 °C), *p*-methyl protons coalesced and five broad singlets were observed (ratio 1 : 2 : 1 : 1 : 1). Evidently the rapid ring inversion on two nitrogen atoms renders the *p*-methyl groups on each ring equivalent. Finally, at 18 °C, *o*-methyl protons also coalesced and one broad singlet was observed in addition to the single *p*-methyl resonance.[†] At this temperature four aryl rings undergo rapid rotation around the Si–C bond such that the eight *o*-methyl groups become equivalent. The energy barrier for ring flipping on nitrogen atoms and hindered rotation of the mesityl rings can be estimated to be 14.3 and



Scheme 1 *Reagents and conditions:* i, *h*ν (>360 mm), PhN=NPh; ii, −**2**; iii, hydrolysis; iv, $-SiMes_2$

[†] *Spectral and Physical data* for **4**: m.p. 181–182 °C; ^{1}H NMR (500 MHz, $CDCl_3$, −30 °C) δ 0.89 (s, 6H, *o*-Me), 1.83 (s, 6H, *o*-Me), 2.09 (s, 6H, *o*-Me), 2.18 (s, 6H, *p*-Me), 2.28 (s, 6H, *p*-Me), 2.77 (s, 6H, *o*-Me), 6.41 (s, 2H, *m*-Mes), 6.55 (d, 4H, 5Hz, *o*-Ph), 6.65 (t, 2H, 5Hz, *p*-Ph), 6.66 (s, 2H, *m*-Mes), 6.69 (s, 2H, *m*-Mes), 6.85 (s, 2H, *m*-Mes), 7.02 (brs, 4H, *m*-Ph); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ 1.90 (brs, 24H, *o*-Me), 2.20 (s, 12H, *p*-Me), 6.55 (d, 4H, 5Hz, *o*-Ph), 6.60 (t, 2H, 5Hz, *p*-Ph), 6.63 (brs, 8H, *m*-Mes), 6.96 (t, 4H, *m*-Ph); ^{13}C NMR (125 MHz, $CDCl_3$, RT–39 °C) δ $\underline{20.97\ (q),\ 24.45\ (q)}$, 115.66 (d), 117.04 (d), 127.91 (d), $\underline{129.79\ (d),\ 139.68\ (s)}$, 147.56 (s). The underlined mesityl carbons are temperature dependent and so broad that two other quaternary carbons cannot be detected; ^{29}Si NMR (18 MHz, $CDCl_3$) δ 10.70; MS (El) *m/z* 714 (M^+).

For **5**: 1H NMR (100 MHz, $CDCl_3$) δ 2.20 (s, 12H), 2.22 (s, 6H), 2.31 (s, 1H), 4.01 (s, 1H), 6.50–7.25 (m, 14H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 21.04 (q), 23.86 (q), 110.43 (d), 111.40 (d), 117.14 (d), 118.93 (d), 124.24 (d), 124.79 (d), 129.28 (d), 133.45(s), 138.60 (s), 139.52 (s), 142.77 (s), 144.01 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ −12.34; MS (El) *m/z* 466 (M^+); IR (CCl_4) cm^{-1} 3450 (SiOH), 3380 (NH).

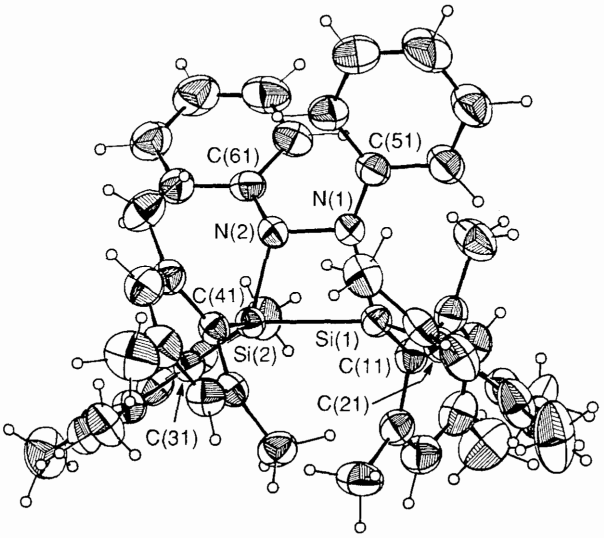


Fig. 1 Perspective ORTEP drawing of **4** showing 50% thermal ellipsoids for non-hydrogen atoms. The molecule contains an approximate C_2 axis which bisects both the Si–Si and N–N bonds. The approxmately equivalent bond lengths (Å) and angles (°) are paired below: Si(1)–Si(2), 2.380(2); N(1)–N(2), 1.477(7); Si(1)–N(1) and Si(2)–N(2), 1.792(5)–1.797(6); Si(1)–C(1) and Si(2)–C(41), 1.890(6)–1.900(6); Si(1)–C(21) and Si(2)–C(31), 1.906(7)–1.910(7); N(1)–C(51) and N(2)–C(52), 1.400(9)–1.417(8); N(1)–Si(1)–Si(2) and N(2)–Si(2)–Si(1), 74.6(2)–74.9(2); N(1)–N(2)–Si(2) and N(2)–N(1)–Si(1), 103.4(4)–103.6(4).

13.3 kcal mol^{-1}, respectively. The molecular structure of **4** was unequivocally confirmed by X-ray crystal analysis as shown in Fig. 1.[‡] Owing to the roughly helical arrangement of four aryl groups attached to each silicon atoms, the crystal structure possesses approximate (not strict) C_2 axis which bisects both the Si–Si and N–N bonds. The Ph_2N_2 fragment has a *trans* conformation so as to minimize the lone pair–lone pair repulsion of two nitrogens. The central Si_2N_2 trapezoidal core deviates from planarity such that Si–N–N–Si torsion angle is 18.20°. This value is comparable with 1,2-digermadioxetane systems (19.5°).[6] Further studies concerning the proposed mechanism and the chemical properties of **4** are in progress.

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[‡] *Crystallographic data:* Compound **4**: $C_{48}H_{54}Si_2N_2$, M_r = 715.15, monoclinic, a = 15.468(6), b = 13.032(2), c = 20.812(7) Å, β = 99.67(1)°, V = 4135.7 Å^3, Z = 4, space group $P2_1/c$, D_c = 1.15 g cm^{-3}. The 4614 independent observed reflections ($2\theta \leqslant 50$ °; $|F_o^2| > 3\sigma|F_o^2|$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo-Kα irradiation and ω-2θ scan. The structure was solved by direct methods and all non-hydrogen atoms were refined anistropically and hydrogen atoms were refined with fixed thermal parameters to R = 0.043 and R_w = 0.044. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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