Formation of a Silafluorene from an Intramolecular Ring-Closure Reaction

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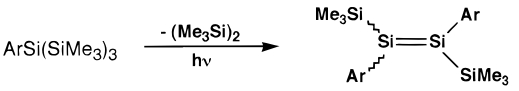
Summary: Trichloro- and trifluoro-2,4,6-triphenylphenylsilanes, ***3a*** *and* ***3b****, yield the highly crystalline 1,3-diphenyl-9,9-bis(trimethylsilyl)-9-silafluorene,* **7***, when treated with lithium metal and chlorotrimethylsilane in THF. The X-ray structure of the silafluorene is reported along with* ^1H*,* ^{13}C*, and* ^{29}Si *NMR data.*

It is now well-established that disilenes, compounds containing silicon−silicon double bonds, can be stabilized by the presence of bulky substituents on silicon.[1] Earlier, we reported the synthesis of silyl-substituted disilenes **2** obtained by the photolysis of 2,4,6-triisopropylphenyltetrasilane **1** (eq 1).[2]



(1)

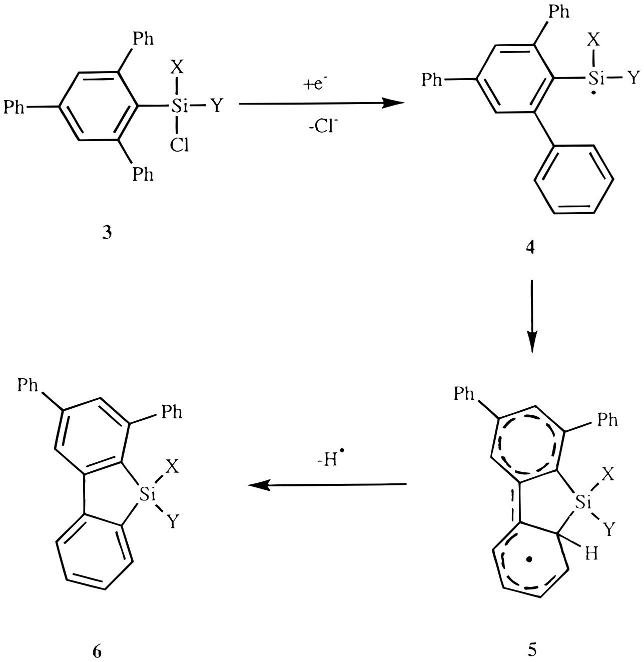
1 2

Ar = 2,4,6-triisopropylphenyl

In order to obtain a second example of this class, we sought to synthesize a tetrasilane analogous to **1** but with 2,4,6-triphenylphenyl as the aryl substituent. Accordingly, trichloro-2,4,6-triphenylphenylsilane **3a** and the corresponding trifluorosilane **3b** were prepared from the aryllithium compound and the tetrahalosilane and then treated with lithium and chlorotrimethylsilane under standard conditions for reductive silyl coupling.[3] To our surprise, the product was silafluorene **7** arising from ring closure to the *ortho*-position of one of the phenyl rings.

The formation of main-group-substituted fluorenes appears to be quite favored in general. Similar ring closures to metallafluorenes have been observed, albeit under different conditions, for other main-group compounds.[4] The pathway leading to formation of **7** is not known, but a possible mechanism leading to the ring closure is shown in Scheme 1. The proposed mechanism begins with reduction and loss of chloride from **3** to give silyl radical **4**. This intermediate silyl radical could add to one of the *ortho*-phenyl rings to provide a delocalized radical **5**, which could then lose a hydrogen atom to give a silafluorene **6**. A pathway involving a silyl anion with loss of hydride is also possible. It is not known whether ring closure takes place before or after reductive coupling with chlorotrimethylsilane.

Scheme 1. Possible Mechanism for Ring Closure of 3[a]



[a] X, Y = chlorine or trimethylsilyl.

Diaryltrisilanes often photolyze to give silylenes, which may dimerize to stable disilenes when the aryl groups are large. The photolysis of **7** for 24 h at −60 °C in pentane solution, however, led only to recovery of the starting material. When **7** was photolyzed at 77 K in 3-methylpentane glass, intense phosphoresence ($t_{1/2}$ = 5−6 s) of **7** was observed. Similar behavior had previously been noted in the photolysis of another 9,9-bis(trimethylsilyl)-9-silafluorene.[5]

The molecular structure and selected bond lengths and angles of **7** are shown in Figure 1. The fluorene substructure of trisilane **7** is similar to that of other silafluorenes,[6] particularly with regard to the acute endocyclic bond angle about the central silicon atom; C(1)−Si(1)−C(12) is 90.2(1)° for **7**. Both the reluctance of the biphenyl moiety to distort and the geometrical constraints imposed by the length the of carbon−silicon

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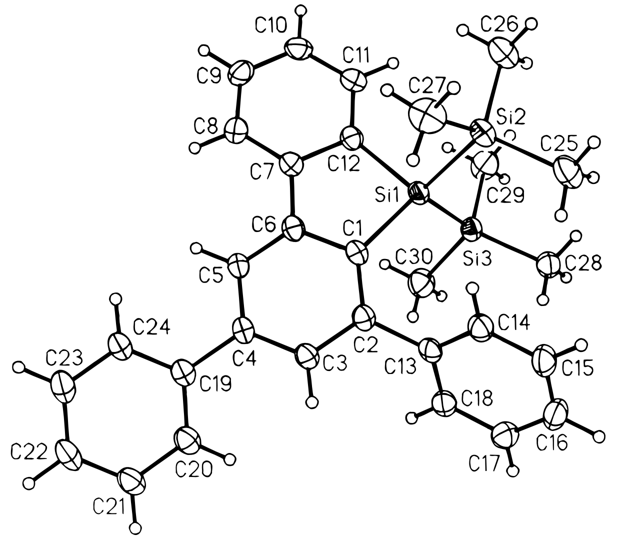

Figure 1. Thermal ellipsoid drawing of silafluorene **7**. Selected bond lengths (pm) and angles (deg): Si(1)−Si(2) 236.1(1), Si(1)−C(1) 189.0(3), C(6)−C(7) 148.5(4), C(7)−C(12) 141.4(4), Si(1)−Si(3) 235.0(1), Si(1)−C(12) 189.4(3), C(1)−C(6) 141.4(4); Si(2)−Si(1)−Si(3) 116.7(1), Si(3)−Si(1)−C(1) 111.4(1), Si(3)−Si(1)−C(12) 110.7(1), Si(2)−Si(1)−C(1) 118.3(1), Si(2)−Si(1)−C(12) 105.8(1), C(1)−Si(1)−C(12) 90.2(1), Si(1)−C(1)−C(6) 109.8(2), Si(1)−C(12)−C(7) 109.8(2).

bonds account for this structural feature. The five-membered ring is nearly planar. The biphenyl moiety is slightly distorted with endocyclic bond angles C(1)−C(6)−C(7) and C(6)−C(7)−C(12) of about 115°.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon or nitrogen using Schlenk techniques. Solvents were distilled from Na/K and benzophenone. Silicon tetrachloride and trimethylchlorosilane were distilled from potassium carbonate under an atmosphere of dry nitrogen. Silicon tetrafluoride was purchased from Matheson Gas Products and used without further purification.

The ^{1}H NMR spectra were obtained on a Bruker WP-270 NMR spectrometer. Proton chemical shifts were referenced to an internal standard of tetramethylsilane. The ^{29}Si NMR spectra were obtained on a Bruker AM-500 NMR spectrometer using a proton-decoupled refocused INEPT (ERNST) pulse sequence and referenced to an external tetramethylsilane standard.

1-Lithio-2,4,6-triphenylbenzene. A solution of 1-bromo-2,4,6-triphenylbenzene[7] (3.75 g, 10.0 mmol) in 50 mL of THF was cooled to −78 °C. To this solution was added *n*-butyllithium (6.8 mL, 1.5 M, 10.2 mmol) with stirring. After 1 h, an aliquot of the solution was quenched with water, extracted with hexane, and analyzed by GC as >99% 2,4,6-triphenylbenzene. The solvent was removed under vacuum, and the sticky green residue was dissolved in 100 mL of dry hexane for use in subsequent reactions.

Trichloro-2,4,6-triphenylphenylsilane (3a). To a solution of 10 mmol of 1-lithio-2,4,6-triphenylbenzene in 50 mL of THF at −78 °C was slowly added silicon tetrachloride (2.5 g, 1.7 mL, 15 mmol) with stirring. The mixture was allowed to warm slowly to 25 °C and stirred for 12 h. Analysis of the reaction by GC indicated 90% of **3a** and 10% of 1,3,5-triphenylbenzene. The THF was removed, and the oil and salts were extracted with toluene. The toluene was removed under vacuum. In the case of the trichlorosilane, the residue was crystallized from hexane at −20 °C, yielding colorless crystals of **3a** (3.2g, 72%); mp 137−139 °C. ^{29}Si NMR (C_6D_6): δ −4.74. HRMS exact mass for $C_{24}H_{17}Cl_3Si$ calcd: *m*/*e* 438.0165. Found: *m*/*e* 438.0182.

Trifluoro-2,4,6-triphenylphenylsilane (3b). The same procedure was used as for **3a**. Attempts to purify **3b** resulted in decomposition of the product. Therefore, crude **3b** was used in the next reaction. ^{29}Si NMR (C_6D_6): δ −71.64 (q, ^1J(SiF) = 266 Hz). MS *m*/*e* (relative intensity): 390 (M^+, 100), 289 (10), 208 (12).

Silafluorene 7. To a solution of trichloride **3a** (4.03 g, 9.0 mmol) and trimethylchlorosilane (2.54 g, 20 mmol) in THF (200 mL) was added lithium metal (0.24 g, 34.4 mmol) at 0 °C. After 1 h of stirring, the reaction mixture contained 40% starting material and 40% silafluorene **7** along with other high molecular weight compounds. More lithium metal was cut into the reaction mixture (0.12 g, 17.2 mmol). After an additional hour, 65% of **7** was present and only 3% of **3a** remained. The solution was immediately filtered in order to prevent **7** from reacting further with the lithium, and the solvent was removed under vacuum. The residue was purified by column chromatography and recrystallized from hexane to obtain 0.61 g (35%) of colorless crystals of **7**; mp 146−148 °C. ^{1}H NMR (C_6D_6): δ 0.24 (s, 18 H), 7.2−8.4 (complex, 16 H). ^{29}Si NMR (C_6D_6): δ −13.00, −39.55. ^{13}C NMR (C_6D_6): The quaternary signals were identified through spectral editing by comparing a DEPT 90° spectrum with an NOE ^{1}H-decoupled spectrum (quaternary signals are marked with an asterisk) δ 0.54, 11.8 (br), 126.2−129.9 (br), 133.76 (br), 137.52*, 140.87*, 141.20*, 142.07*, 148.17*, 148.49*, 150.23*. HRMS (the molecular ion could not be observed) exact mass for $C_{29}H_{25}Si_2$ {M − SiMe$_3$} calcd: *m*/*e* 405.1495: Found: *m*/*e* 405.1506. Anal. Calcd for $C_{30}H_{34}Si_3$: C, 75.24; H, 7.16. Found: C, 75.51; H, 6.98. Preparation of the silafluorene from **3b** was essentially the same as described for the trichloride **3a**, except that **3b** was not purified prior to the reaction.

X-ray Crystal Structure Data for Silafluorene 7 ($C_{30}H_{34}Si_3$). Colorless plates were grown by cooling a solution of **7** in hexane. The crystals were triclinic and belonged to the space group *P*1 with a = 9.995(3) Å, b = 11.463(3) Å, c = 13.236(3) Å, α = 103.78(2)°, β = 104.43(2)°, γ = 102.36(2)°, V = 1364.7(5) Å^3, and d_{calcd} = 1.165 g/cm^3 for Z = 2. Data was collected at 154 K on a Siemens P3f diffractometer using Cu Kα radiation (l.541 78 Å). A total of 3894 reflections were collected with 3674 independent reflections (R_{int} = 1.90%) and 3248 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by full-matrix least-squares procedures, using SHELXTL-PLUS software. Hydrogen atoms were added using the riding model. Final *R* indices: R = 3.84%, R_w = 5.59%.

Solution Photolysis of 7 in Pentane. A solution of silafluorene **7** (0.5 g, 1.2 mmol) in 30 mL of pentane was freeze−thaw−degassed 4 times and photolyzed at 254 nm at −60 °C for 24 h. Only unreacted **7** was recovered.

Photolysis of 7 in 3-Methylpentane glass at 77 K. A 3-methylpentane (2.0 mL) solution of silafluorene **7** (5 mg) was placed in a quartz cuvette and freeze−thaw−degassed 4 times. The quartz cuvette was placed in liquid nitrogen in a quartz Dewar equipped with UV windows. The matrix was photolyzed for 45 min with intense phosphoresence ($t_{1/2}$ = 5−6 s). No new UV or visible bands were observed.

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Supporting Information Available: Tables of crystal data, bond lengths, bond angles, atomic coordinates, equivalent isotropic displacement coefficients and occupancies, anisotropic displacement coefficients, and hydrogen atom coordinates and ORTEP diagrams for **5**, **9**, **13**, and **19** (9 pages). Ordering information is given on any current masthead page.

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