Silylenoids, R₃SiX (X = halogen, M = alkali metal), are important intermediates in many reactions.¹ Yet, in contrast to the extensively studied analogous carbenoids, R₂CX₂M,² they have been little studied. Due to their high reactivity via self-condensation³ or α-elimination of MX producing reactive silylenes,⁴ very little is known about their molecular structure. Such structural information is important for understanding the intriguing multiple reactivity of halosilylenoids toward nucleophiles,⁵,⁶ electrophiles,⁷ and silylene trapping agents.⁸,⁹ An X-ray molecular structure is available only for a dimeric form of a methoxysilylenoid. ³b Other known stable silylenoids include thio-¹⁰ and halosilylenoids,¹¹ for which, however, there is no structural data.

In this paper we report the synthesis, the molecular and electronic structure, and several reactions of the first isolated fluorosilylenoid ¹, exhibiting a tricoordinate silicon. Analogous stable carbenoids have not been reported.

The fluorosilylenoid ¹ was prepared in 40% yield by reaction of fluorobromosilane ² with silyllithium ³ in THF (eq 1).⁶

\[
\text{(R}_3\text{Si)}_2\text{SiFBr} + \text{THF} \rightarrow \text{(R}_3\text{Si)}_2\text{SiFLi} + 3\text{THF}
\]

R₃Si = t-Bu₂MeSi

crystallizes at −30 °C from a 1:2 THF/hexane solution as yellow crystals, and its molecular structure as determined by X-ray crystallography is shown in Figure 1.¹⁷

The X-ray molecular structure reveals that ¹ is a silylenoid with a tricoordinate silicon and a lithium atom bonded to fluorine. The Si1···Li distance is 3.21 Å, significantly longer than that in THF solvated lithiosilanes (2.64–2.77 Å),⁸ indicating weak or no Si···Li bonding. Si1 in ¹ is strongly pyramidal; the sum of the bond angles around Si1 is 307.6°, indicating a weaker Si–F bond in ¹ than that in fluorosilanes.⁸ The Si1–F distance 1.70 Å is relatively long,⁹ indicating a weaker Si–F bond in ¹ than that in fluorosilanes.

Silylenoid ¹ was studied computationally¹⁰ using density functional theory (DFT).¹⁰b The calculated structure of ¹ (see Supporting Information) is similar in its general shape to the experimental structure, but there are significant differences in r(Si–F) (1.70 Å (exptl), 1.84 Å (theor))¹¹ and r(F–Li) (1.77 Å (exptl), 1.82 Å (theor)). The calculations show that the carbene silylenoid ¹ is by 4.8 kcal/mol lower in energy than the tetracoordinate isomer (R₂Si₃SiF₂Br)₁₂ (R₂Si = t-Bu₂MeSi), ⁴,¹¹b in which r(Si–F) = 1.75 Å and r(Si–Li) = 2.76 Å.

The NMR δ²⁹Si(¹) chemical shift of ¹ (107 ppm) is shifted significantly downfield compared with (t-Bu₂MeSi)(HSiF)₂ (22.5 ppm),¹³,¹⁴ (t-Bu₂MeSi)₂SiH₂ (−120 ppm), and (t-Bu₂MeSi)₂HSiLi·3THF (−190 ppm).¹⁵ The measured δ²⁹Si(¹) of ¹ is in very good agreement with the calculated¹⁰a δ²⁹Si (102 ppm using the X-ray coordinates¹⁸a) indicating that the silylenoid structure probably persists in THF solution.¹⁶b

The calculated charge distribution (NPA¹⁷b) of ¹ shows that which is overall neutral, is highly polarized; the positive charge (0.88 el.) is located on the Li₃THF fragment, while most of the negative charge resides on F (−0.74 el.) with −0.14 el. residing on the R₂Si fragment (charge on Si₁ = +0.14 el.). The NPA charge distribution in the tetracoordinate isomer ⁴ is similar: q(R₂Si₁) = −0.22; q(F) = −0.69; and q(Li₃THF) = +0.88. The calculated Si–F, Si–Li, and F–Li Wiberg bond orders (WBO)¹⁹b of ¹ are 0.38, 0.06, and 0.02, respectively, reflecting a covalent Si–F bond (although weaker than that in (H₃Si)₃SiF (WBO = 0.55, r(Si–F) = 1.66 Å, at B3LYP/6-311+G(d,p)) and no covalent bonding between Si–Li (or F–Li). In ¹, the Si–F, Si–Li, and F–Li Wiberg bond orders are 0.43, 0.13, and 0.0, respectively, reflecting a higher covalency in the Si–F and Si–Li bonds in comparison to ¹. The charge distribution and the WBOs in ¹ point to a structure with an R₂SiF⁺ anion attracted to a (Li₃THF)− cation.

Analysis of the resonance structures (RS) of the fully optimized (at B3LYP/6-311+G(d)) (Me₃Si)₂SiLi·3MeO⁻ ¹⁺ (a model of ¹, r(Si–F) = 1.84 Å), using NRT¹⁹c calculations, shows that ¹⁺ is the most prominent RS of ¹. The localized NBOs¹⁹d of ¹⁺ show a lone pair orbital on the central Si atom with an occupancy of 1.53 el. and a highly polarized Si–F NBO in which 90% of the charge density resides on F and only 10% resides on Si. A minor contributing RS is ¹⁻ which consists of a silylene fragment and F⁻·3MeO⁺.²⁰ The NRT bond orders¹⁹c of ¹⁺ indicate its high ionicity; i.e., the Si–F BOs are 0.93 (total) and 0.76 (ionic), while the Si–Li and F–Li bonds are entirely ionic. In summary, based...
on the calculations, I is best described by RS \(^{1}a\) with a minor contribution of \(^{1}b\).\(^{21}\)

The calculated energy for the dissociation of I to RSi: and FLi-3THF is \(\Delta G^{298} = 19.5\) kcal/mol (\(\Delta H^{298} = 33.5\) kcal/mol), consistent with the small dissociation of an RS analogous to \(^{1}b\).\(^{22}\)

1 exhibits versatile reactivity, in line with its silylenoid structure. It reacts as a nucleophile with MeCl, PhH\(_{2}\) SiCl, water, and methanol (Scheme 1, path i). It reacts as an electrophile with MeLi (Scheme 1, path ii). With BuLi in THF 1 is a precursor of \(\alpha\)-lithiosilyl radical \(5a^{3}\) (Scheme 1, path iii). The silylenoid type reactivity is revealed when 1 is stirred with lithium or sodium powder in THF to yield \(\alpha\)-lithium (5a) or \(\alpha\)-sodium (5b) radicals, respectively (Scheme 1, path iii).\(^{23}\) When a THF solution of I is kept under sunlight at room temperature for a week or when solid 1 is heated to 120 °C (0.5 h) disilene \(6^{24}\) is formed (Scheme 1, path iv), probably via dimerization of RSi:.

In summary, we have isolated the first fluorosilylenoid, determined its molecular structure by X-ray crystallography and its electronic structure by DFT calculations, and demonstrated its versatile reactivity. We are continuing to explore this interesting new class of reactive intermediates.

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Supporting Information Available: CIF file of the X-ray structure of I, the syntheses and spectroscopic data of I, 1, and 2, and of reaction products of 1 in Scheme 1, calculated structures of I, 1, and 4, and full list of authors of ref 10a. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(6) Experimental details are given in the Supporting Information. NMR (in THF with a DMSO-d6 capillary as external standard, d in ppm): (H) 1: 1.04 (36H, d, t-Bu2MeSi); 0.07 (6H, s, t-Bu2MeSi); 1.0L 0.92 (t-Bu2MeSi); 28.5–27.1 (t-Bu2MeSi); 27.27 (Si); 27.10 (Si, t-Bu2MeSi); 5.60 (2H, d, t-Bu2MeSi). (7) Crystal data of I (180 K): Cs\(_{3}\)H\(_{5}\)F\(_{8}\); Fw 585.04; monoclinic; space group P2\(_{1}\)1/c; a = 11.18(2) Å, b = 18.49(2) Å, c = 19.33(4) Å, \(\beta = 111.40(3)^{\circ}\), \(V = 3721.5\) Å\(^{3}\), \(Z = 8\), \(D_{calcd} = 1.44\) mg/ml, \(R = 0.0681\) (I > 2(I), \(wR_{2} = 0.0206\) (all data), GOF = 0.963.

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