

Synthesis, Molecular Structure, and Reactivity of the Isolable Silylenoid with a Tricoordinate Silicon

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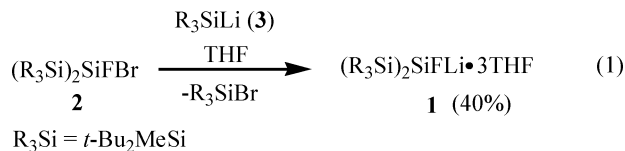
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Silylenoids, R_2SiXM (X = halogen, M = alkali metal), are important intermediates in many reactions.¹ Yet, in contrast to the extensively studied analogous carbenoids, R_2CXM ,² they have been little studied. Due to their high reactivity via self-condensation³ 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,^{3,5} electrophiles,^{3,5} and silylene trapping agents.^{4,5} An X-ray molecular structure is available only for a dimeric form of a methoxysilylenoid.^{3b} Other known stable silylenoids include thio-^{4a} and halosilylenoids,⁵ 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 **1**



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 1.⁷

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

Silylenoid **1** was studied computationally^{10a} 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 $r(Si\text{--}F)$ (1.70 \AA (exptl), 1.84 \AA (theor))^{11a} and $r(F\text{--}Li)$ (1.77 \AA (exptl), 1.82 \AA (theor)). The calculations show that the tricoordinate silylenoid **1** is by 4.8 kcal/mol lower in energy than its tetracoordinate isomer $(R_3Si)_2FSiLi \cdot 3THF$ ($R_3Si = t\text{-Bu}_2\text{MeSi}$), **4**,^{11b} in which $r(Si\text{--}F) = 1.75 \text{ \AA}$ and $r(Si\text{--}Li) = 2.76 \text{ \AA}$.¹²

The NMR $\delta(^{29}Si1)$ chemical shift of **1** (107 ppm)⁶ is shifted significantly downfield compared with $(t\text{-Bu}_2\text{MeSi})_2HSiF$ (22.5 ppm),^{13,14} $(t\text{-Bu}_2\text{MeSi})_2SiH_2$ (-120 ppm), and $(t\text{-Bu}_2\text{MeSi})_2HSiLi \cdot 3THF$ (-190 ppm).¹⁵ The measured $\delta(^{29}Si1)$ of **1** is in very good

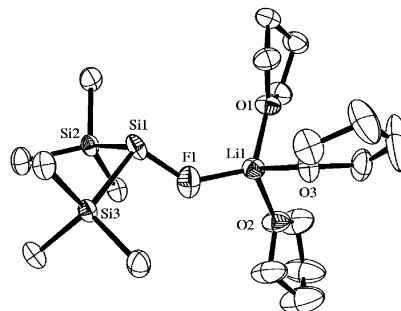


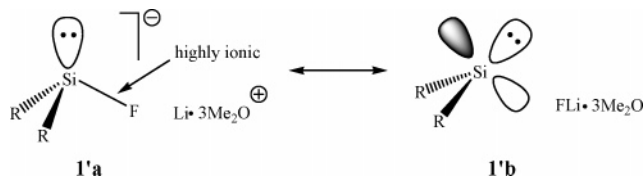
Figure 1. ORTEP drawing of **1**. Hydrogen atoms and CH_3 groups on $t\text{-Bu}$ are omitted for clarity. Selected bond lengths (\AA): $Si1\text{--}F$ $1.698(3)$, $F\text{--}Li$ $1.773(7)$, $Si1\text{--}Si2$ $2.412(14)$, $Si1\text{--}Si3$ $2.402(14)$. Selected bond and dihedral angles (deg): $Si2\text{--}Si1\text{--}Si3$ $104.5(5)$, $Si2\text{--}Si1\text{--}F$ $100.8(10)$, $Si3\text{--}Si1\text{--}F$ $102.3(12)$, $Si1\text{--}F\text{--}Li$ $135.2(3)$, $Si2\text{--}Si1\text{--}F\text{--}Li$ 110.8 , $Si3\text{--}Si1\text{--}F\text{--}Li$ 141.7 .

agreement with the calculated^{10a} $\delta(^{29}Si1)$ (102 ppm using the X-ray coordinates^{16a}) indicating that the silylenoid structure probably persists in THF solution.^{16b}

The calculated charge distribution (NPA^{17a,b}) shows that **1**,¹⁸ which is overall neutral, is highly polarized; the positive charge (0.88 el.) is located on the $Li \cdot 3THF$ fragment, while most of the negative charge resides on F (-0.74 el.) with -0.14 el. residing on the R_2Si fragment (charge on $Si1 = +0.14 \text{ el.}$). The NPA charge distribution in the tetracoordinate isomer **4** is similar: $q(R_2Si) = -0.22$; $q(F) = -0.69$; and $q(Li \cdot 3THF) = +0.88$. The calculated $Si\text{--}F$, $Si\text{--}Li$, and $F\text{--}Li$ Wiberg bond orders (WBO)^{19a,b} in **1** are 0.38 , 0.06 , and 0.02 , respectively, reflecting a covalent $Si\text{--}F$ bond (although weaker than that in $(H_3Si)_3SiF$ (WBO = 0.55 , $r(Si\text{--}F) = 1.66 \text{ \AA}$, at B3LYP/6-311+G(d,p)) and no covalent bonding between $Si\text{--}Li$ (or $F\text{--}Li$). In **4**, the $Si\text{--}F$, $Si\text{--}Li$, and $F\text{--}Li$ WBOs are 0.43 , 0.13 , and 0.0 , respectively, reflecting a higher covalency in the $Si\text{--}F$ and $Si\text{--}Li$ bonds in comparison to **1**. The charge distribution and the WBOs in **1** point to a structure with an R_2SiF^- anion attracted to a $(Li \cdot 3THF)^+$ cation.

Analysis of the resonance structures (RS) of the fully optimized (at B3LYP/6-311+G(d)) $(Me_3Si)_2SiFLi \cdot 3Me_2O$ **1'** (a model of **1**, $r(Si\text{--}F) = 1.84 \text{ \AA}$), using NRT^{19c} calculations, shows that **1'a** is the most prominent RS of **1'**. The localized NBOs^{19d} of **1'a** show a lone pair orbital on the central Si atom with an occupancy of 1.53 el. and a highly polarized $Si\text{--}F$ NBO, in which 90% of the charge density resides on F and only 10% resides on Si . A minor contributing RS is **1'b** which consists of a silylene fragment and $FLi \cdot 3Me_2O$.²⁰ The NRT bond orders^{19c} of **1'** indicate its high ionicity; i.e., the $Si\text{--}F$ BOs are 0.93 (total) and 0.76 (ionic), while the $Si\text{--}Li$ and $F\text{--}Li$ bonds are entirely ionic. In summary, based

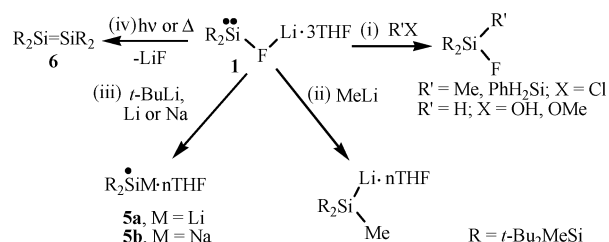
on the calculations, **1** is best described by RS **1'a** with a minor contribution of **1'b**.²¹



The calculated energy for the dissociation of **1** to $R_2Si\cdot$ and $FLi\cdot 3THF$ is $\Delta G^{298} = 19.5$ kcal/mol ($\Delta H^{298} = 33.5$ kcal/mol), consistent with the small contribution 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_2SiCl , water, and methanol (Scheme 1, path i). It reacts as an electrophile with $MeLi$ (Scheme

Scheme 1



1, path ii). With $t-BuLi$ in THF **1** is a precursor of α -lithiosilyl radical **5a**¹⁵ (Scheme 1, path iii). The silylenic-type reactivity is revealed when **1** is stirred with lithium or sodium powder in THF to yield α -lithium (**5a**) or α -sodium (**5b**) radicals, respectively (Scheme 1, path iii).²³ When a THF solution of **1** 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 $R_2Si\cdot$.

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 **1**, the syntheses and spectroscopic data of **1**, **2**, and of reaction products of **1** in Scheme 1, calculated structures of **1**, **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>.

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- (6) Experimental details are given in the Supporting Information. NMR (in THF with a $DMSO-d_6$ capillary as external standard, δ in ppm): 1H 1.04 (36H, d, $t-Bu_2MeSi$); 0.07 (6H, s, $t-Bu_2MeSi$); 7Li 0.92; ^{13}C -1.9 ($t-Bu_2MeSi$); 28.9; -2.71 ($t-Bu_2MeSi$); ^{19}F -277; ^{29}Si 107 (d, $J_{Si-F} = 356.5$ Hz, $SiFLi$), 5.68 (d, $J_{Si-F} = 8.4$ Hz, $t-Bu_2MeSi$).
- (7) Crystal data of **1** (180 K): $C_{30}H_{66}FLiO_3Si_3$; Fw 585.04; monoclinic; space group $P2_1/c$, $a = 11.181(2)$ Å, $b = 18.490(4)$ Å, $c = 19.334(4)$ Å, $\beta = 111.40(3)^\circ$, $V = 3721.5$ Å³, $Z = 4$, $D_{calc} = 1.44$ mg/m³, $R = 0.0681$ ($I > 2\sigma(I)$), $wR2 = 0.2006$ (all data), GOF = 0.963.
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- (14) $\delta^{19}F$ (–277 ppm) in **1** is shifted upfield compared with $\delta^{19}F$ in ($t-Bu_2MeSi$) $_2HSiF$ (–230 ppm); the $\delta^{7}Li$ in **1** (0.9 ppm) is similar to that of other THF-solvated lithiosilanes.⁸
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