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

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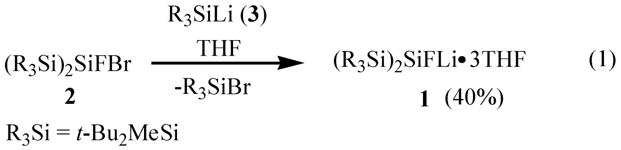
Silylenoids, R_2SiXM (X = halogen, M = alkali metal), are important intermediates in many reactions.[1] Yet, in contrast to the extensively studied analogous carbenoids, R_2CXM,[2] they have been little studied. Due to their high reactivity via self-condensation[3] or α-elimination of MX producing reactive 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**



$$\underset{\mathbf{2}}{(R_3Si)_2SiFBr} \xrightarrow[\text{-}R_3SiBr]{R_3SiLi\ (\mathbf{3})\ \ \text{THF}} \underset{\mathbf{1}\ (40\%)}{(R_3Si)_2SiFLi\bullet 3THF} \qquad (1)$$

$R_3Si = t\text{-}Bu_2MeSi$

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···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°, which is similar to that in THF solvated lithiosilanes.[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 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−F) (1.70 Å (exptl), 1.84 Å (theor))[11a] and r(F−Li) (1.77 Å (exptl), 1.82 Å (theor)). The calculations show that the tricoordinate silylenoid **1** is by 4.8 kcal/mol lower in energy than its tetracoordinate isomer $(R_3Si)_2FSiLi\cdot 3THF$ ($R_3Si = t\text{-}Bu_2MeSi$), **4**,[11b] in which r(Si−F) = 1.75 Å and r(Si−Li) = 2.76 Å.[12]

The NMR $\delta(^{29}\text{Si1})$ chemical shift of **1** (107 ppm)[6] is shifted significantly downfield compared with $(t\text{-}Bu_2MeSi)_2HSiF$ (22.5 ppm),[13,14] $(t\text{-}Bu_2MeSi)_2SiH_2$ (−120 ppm), and $(t\text{-}Bu_2MeSi)_2HSiLi\cdot 3THF$ (−190 ppm).[15] The measured $\delta(^{29}\text{Si1})$ of **1** is in very good agreement with the calculated[10a] $\delta(^{29}\text{Si1})$ (102 ppm using the X-ray coordinates[16a]) indicating that the silylenoid structure probably persists in THF solution.[16b]

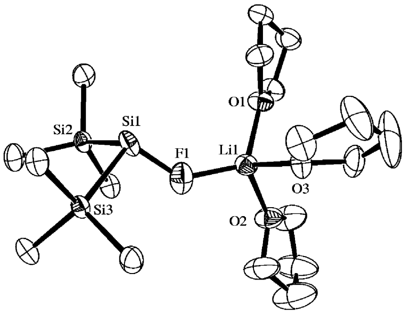


Figure 1. ORTEP drawing of **1**. Hydrogen atoms and CH_3 groups on t-Bu are omitted for clarity. Selected bond lengths (Å): Si1−F 1.698(3), F−Li 1.773(7), Si1−Si2 2.412(14), si1−Si3 2.402(14). Selected bond and dihedral angles (deg): Si2−Si1−Si3 104.5(5), Si2−Si1−F 100.8(10), Si3−Si1−F 102.3(12), Si1−F−Li 135.2(3), Si2−Si1−F−Li 110.8, Si3−Si1−F−Li 141.7.

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•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 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−F, Si−Li, and F−Li Wiberg bond orders (WBO)[19a,b] in **1** are 0.38, 0.06, and 0.02, respectively, reflecting a covalent Si−F bond (although weaker than that in $(H_3Si)_3SiF$ (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 **4**, the Si−F, Si−Li, and F−Li WBOs 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 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−F) = 1.84 Å), 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−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[19e] 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

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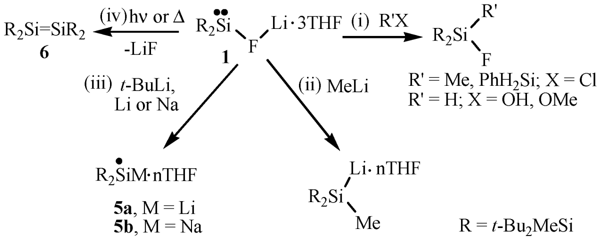
on the calculations, **1** is best described by RS **1′a** with a minor contribution of **1′b**.[21]

The calculated energy for the dissociation of **1** to R_2Si: and FLi·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 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:.

Scheme 1



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.

Acknowledgment. This research was supported by the Israel Science Foundation, administered by the Israel Academy of Sciences and Humanities, the Fund for the Promotion of Research at the Technion, and the Minerva Foundation in Munich. M.B., B.T., and D.B.-Z. are grateful to the Ministry of Immigrant Absorption, State of Israel, for a Kamea scholarship.

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*-Bu₂**MeSi); 0.07 (6H, s, *t*-Bu_2**Me**Si); ^7L 0.92; ^{13}C −1.9 (*t*-Bu_2**Me**Si); 28.9; −2.71 (***t*-Bu₂**MeSi); ^{19}F −277; ^{29}Si 107 (d, $J_{Si-F} = 356.5$ Hz, **Si**FLi), 5.68 (d, $J_{Si-F} = 8.4$ Hz, *t*-Bu_2Me**Si**).

(7) Crystal data of **1** (180 K): $C_{30}H_{66}FLiO_3Si_3$; Fw 585.04; monoclinic; space group $P21/c$, $a = 11.181(2)$ Å, $b = 18.490(4)$ Å, $c = 19.334(4)$ Å, $\beta = 111.40(3)°$, $V = 3721.5$ Å^3, $Z = 4$, $D_{calcd} = 1.44$ mg/m^3, $R = 0.0681$ ($I > 2\sigma(I)$), $wR2 = 0.2006$ (all data), GOF = 0.963.

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(11) (a) The reasons for this large discrepancy are not known. One reason might be the flat potential for Si−F bond stretching. Similar Si−F distances of 1.85 Å (B3LYP/6-31+G(d)) and 1.86 Å (MP2/6-31+G(d)) were calculated for $Me(H_3Si)SiFLi$.[12] (b) The energy difference between **1** and **4** changes only modestly to 1.9 kcal/mol when experimental $r(Si1-F) = 1.7$ Å is used.

(12) A computational study of different isomers of $Me(H_3Si)SiXLi \cdot 3Me_2O$ (X = F, OH, NH_2, PH_3) was reported recently: Flock, M.; Marschner, C. *Chem.—Eur. J.* **2005**, *11*, 4635.

(13) The J_{Si-F} coupling constant in **1** of 356.5 Hz is slightly higher than that in $(t\text{-}Bu_2MeSi)_2SiFR$ (R = H, Me, SiH_2Ph), where it is in the range 323−329 Hz. It is lower, however, than J_{Si-F} of 400 Hz in $(t\text{-}Bu_2MeSi)_2SiFBr$ (**2**).

(14) $\delta^{19}F$ (−277 ppm) in **1** is shifted upfield compared with $\delta(^{19}F)$ in $(t\text{-}Bu_2MeSi)_2HSiF$ (−230 ppm); the $\delta(^7Li)$ in **1** (0.9 ppm) is similar to that of other THF-solvated lithiosilanes.[8]

(15) (a) **5a** can be observed by EPR spectroscopy, and it decays by hydrogen abstraction, producing the corresponding R_2SiHLi. (b) **5a** was recently reported: Bravo-Zhivotovskii, D.; Ruderfer, I.; Melamed, S.; Botoshansky, M.; Tumanskii, B.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 739.

(16) (a) $\delta(^{29}Si1) = 105$ ppm is calculated for the fully optimized structure with only $r(Si-F)$ constrained to the experimental value of 1.698 Å; $\delta(^{29}Si1)$ for a fully optimized **1** ($r(Si-F) = 1.84$ Å) is 152 ppm. (b) The calculated $\delta(^{29}Si1)$ of the fully optimized tetracoordinate isomer **4** is 95 ppm.

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