

Silylene Dimers: Highly Fluxional Molecules with Unusual Structures

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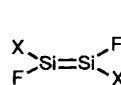
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The bridged structures, $\text{HSi}(\mu\text{-F})_2\text{SiH}$ and $\text{FSi}(\mu\text{-H})_2\text{SiF}$ are minima on the $\text{Si}_2\text{H}_2\text{F}_2$ potential energy surface and are less than 10 kcal mol^{-1} higher in energy than the classical disilene, $\text{HFSi}=\text{SiHF}$ (MP3/6-31G**//6-31G*), suggesting that the species observed recently by Jutzi *et al.* at low temperature by ^{29}Si NMR is the bridged $(\text{C}_5\text{Me}_5)\text{Si}(\mu\text{-F})_2\text{Si}(\text{C}_5\text{Me}_5)$ rather than the suggested $\text{F}(\text{C}_5\text{Me}_5)\text{Si}=\text{Si}(\text{C}_5\text{Me}_5)\text{F}$.

The last decade has witnessed the isolation of the first compounds with doubly bonded silicon.¹⁻³ Theoretical studies of these novel molecules have consistently added important insights into their properties.⁴ Disilenes, bearing alkyl, aryl, and bis(trimethylsilyl)amino substituents have been isolated and characterized,¹ but the properties of disilenes substituted with other heteroatoms, such as oxygen or fluorine, are still unknown. The first claim for a spectroscopic detection of a fluorine-substituted disilene comes from recent interesting studies by Jutzi *et al.* on the reactions of $(\text{C}_5\text{Me}_5)_2\text{Si}$ with HBF_4 .⁵ These authors suggested that the reaction follows the path shown in Scheme 1, in which disproportionation occurs to yield the silylene $(\text{C}_5\text{Me}_5)\text{FSi}$, which dimerizes to form the transient disilene (**1a**). Compound (**1a**) dimerizes to the tetrasilane (**2**), which was isolated and characterized by *X*-ray crystallography. The evidence presented for the transient disilene (**1a**) was a low temperature ^{29}Si NMR spectrum which showed a single ^{29}Si resonance, split into a triplet ($J_{\text{Si-F}}$ 341 Hz; it was suggested that $^1J_{\text{Si-F}} = 2J_{\text{Si-F}}$).⁵

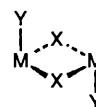
We were attracted to this problem by the indication from the calculations that the potential energy surfaces (PES) of the isoelectronic C_2H_4 and Si_2H_4 molecules differ dramatically

and that unusual bridged-structures may be important in the chemistry of disilenes. Thus, at HF/6-31G**//6-31G**† ethylene lies in a very deep well and is more stable than two singlet carbenes and the non-classical bridged structure (**3a**) by 179.6



(1)

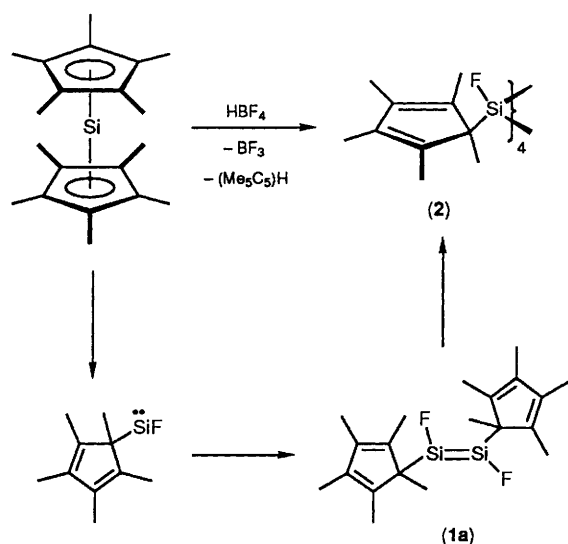
- a; X = (C_5Me_5)
- b; X = F
- c; X = H
- d; X = Me



(3)

- a; M = C, X = Y = H
- b; M = Si, X = Y = H
- c; M = Si, X = Y = F
- d; M = Si, X = OH, Y = H
- e; M = Si, X = H, Y = F
- f; M = Si, X = F, Y = H
- g; M = Si, X = Me, Y = F
- h; M = Si, X = F, Y = Me
- i; M = Si, X = F, Y = (C_5Me_5)
- j; M = Si, X = (C_5Me_5) , Y = F

† The Gaussian 82 series of programs⁶ was used.



Scheme 1. Suggested reaction pathway of $(C_5Me_5)_2Si$ with HBF_4 .⁵

Table 1. Relative energies (kcal mol⁻¹) of bridged and classical Si_2H_4 and $Si_2H_2F_2$ molecules.

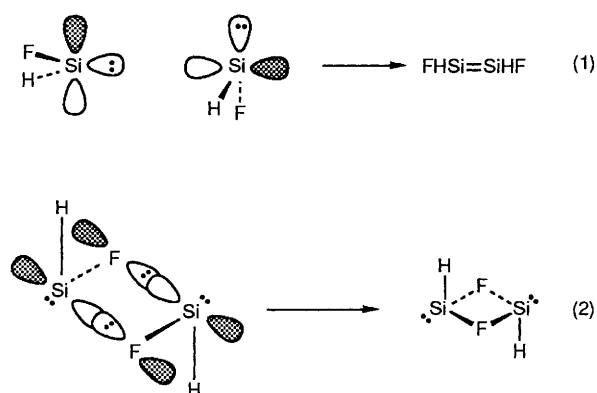
	Relative energy		
	3-21G//3-21G	6-31G*//6-31G*	MP3/6-31G*//6-31G*
$H_2Si=SiH_2$	0.0	0.0	0.0
$HSi(\mu-H)_2SiH$ (3b)	26.0	23.5	25.8
$2 \times H_2Si$: ^a	44.0	48.4	62.4
$HFSi=SiHF$ (1c)	0.0	0.0	0.0
$FSi(\mu-H)_2SiF$ (3e)	2.8	4.8	6.1
$HSi(\mu-F)_2SiH$ (3f)	-29.9	5.0	9.5
$2 \times HFSi$: ^a	15.0	20.9	32.8

^a The energy of two isolated silylenes.

and 172.5 kcal mol⁻¹, respectively. The PES of disilene displays a considerable narrowing of the analogous energy gap; at the same level of theory, two silylenes, H_2Si , are calculated to be only 48.6 kcal mol⁻¹ higher in energy than $H_2Si=SiH_2$. Furthermore, the non-classical bridged structure $HSi(\mu-H)_2SiH$,[‡] (**3b**), is a minimum on the PES and is only 22.8 kcal mol⁻¹ higher in energy than the classical ethylene-type structure (Table 1). Earlier studies, using a compact basis set with diffuse functions, reported an even lower energy gap of 15 kcal mol⁻¹.⁷ We were also aware of the surprising computational result that the classical structure of Si_2F_4 , (**1b**), collapses without a barrier to the bridged (**3c**).⁸

In a systematic computational study of substituted disilenes, we found that groups bearing lone pairs (*e.g.*, NH_2 , OH , and F) further reduce, when compared with the PES of Si_2H_4 , the energy differences between the classical disilene structure, the free silylenes, and the bridged species. In some cases the bridged species (*e.g.*, $HSi[\mu-(OH)]_2SiH$ (**3d**)) are lower in energy than the classical disilene structures. On the PES of $Si_2H_2F_2$, (Table 1), the disilene, (**1c**), is the global minimum at 6-31G*//6-31G*. The bridged structures $FSi(\mu-H)_2SiF$, (**3e**),[‡] and $HSi(\mu-F)_2SiH$, (**3f**),[‡] and two isolated silylenes lie just 4.8,

[‡] The energy differences between the *syn* and *anti* isomers are *ca.* 0.2 kcal mol⁻¹.



Scheme 2. Alternative pathways for the dimerization of fluorosilylene.

5.0, and 20.9 kcal mol⁻¹, respectively, higher in energy. Corrections for electron correlation at MP3/6-31G* stabilize the classical structure (**1c**) by 4.5 kcal mol⁻¹ with respect to (**3f**). We note that smaller basis sets (3-21G//3-21G, 3-21G*//3-21G*) find that (**3f**) is actually more stable than (**1c**) and (**3e**). Substituting H by methyl, a better model of (C_5Me_5) , has little effect on the relative energies of the fluoro-bridged and the classical structures. However, because of the poorer bridging ability of methyl as compared to H, structure (**3g**) with bridging methyls is destabilized relative to (**1d**) and (**3h**).

Since the calculations show that structures (**1c**) and (**3f**) are close in energy, we believe it is very likely that the structure observed at low temperature by Jutzi *et al.* is the bridged compound (**3i**). This structure would be fully consistent with the NMR data, since one silicon absorption would be observed, split by two fluorines.[§] This suggestion makes the *ad hoc* assumption made by Jutzi *et al.*, that in (**1a**) $^1J_{Si-F} = ^2J_{Si-F}$, unnecessary. Furthermore, it is difficult to reconcile one- and two-bond coupling constants of the same magnitude, since the few reported $^2J_{Si-F}$ spin-spin coupling constants are significantly smaller than the observed 341 Hz.⁹ On the other hand, the observed value is consistent with known data of $^1J_{Si-F}$.⁹ Data for C-F coupling constants also contradicts the above assumption, as $^1J_{C-F}$ for 1,2-difluoroalkenes are five to eight times greater than $^2J_{C-F}$.¹⁰

How can the bridged (**3i**) be formed in preference to (**1a**)? Calculations show that two $HFSi$ silylenes can dimerize without a barrier to either the bridged or the classical structure. Dimerization of two fluorosilylenes according to mode (1) of Scheme 2 leads to (**1c**). This approach is similar to the one leading from two H_2Si units to disilene.¹¹ Alternatively, two fluorosilylenes can combine as in mode (2) of Scheme 2 in which interactions occur between the fluorine of one molecule and the empty p-orbital of the other, leading with no barrier to (**3f**). Similar interactions were documented in an earlier study of the insertion of H_2Si into the Si-F bond of H_3SiF .¹² Once formed, (**3f**) is kinetically stabilized at low temperatures from interconversion to the more stable (**1c**), since isomerization requires dissociation to two isolated or weakly bound $HFSi$ silylenes.[¶] The barrier is therefore

[§] One may dismiss alternative structures. A stable silylene or a structure with bridging (C_5Me_5) (**3j**), would have a doublet silicon absorption. A fast equilibrium between (**3i**) and (**1a**) is also unlikely because it requires an observed coupling constant which is the average of $^1J_{SiF}$ and $^2J_{SiF}$, which is expected⁹ to be much smaller than 341 Hz. The silylenes, $F(C_5Me_5)_2SiFSi$ or $(C_5Me_5)_2Si(C_5Me_5)Si$, and $F_2Si=Si(C_5Me_5)_2$ would have two silicon resonances.

[¶] Despite considerable effort we could not locate a transition state for the direct interconversion of (**3f**) to (**1c**).

estimated to be as high as 20 kcal mol⁻¹ at MP3/6-31G**/6-31G*.

Other factors may increase the kinetic stability of (**3i**), the experimentally studied system. Substitution of a proton by the bulky (C₅Me₅) group is expected to hinder sterically approaches of type (1) (Scheme 2), thus favouring type (2) (Scheme 2) leading to (**3i**). The experimental conditions (tetrahydrofuran solution) vs. gas phase, may also stabilize the hypovalent structure (**3i**) relative to (**1a**). In support of this suggestion, we find that complexation of a water molecule to (**1c**) leaves only a very weak silicon-silicon bond, as in the case of the water-disilene adduct.¹³

The likelihood of existence of (**3i**) raises the possibility that similar species play a role in other reactions of silylenes and disilenes, for example in the symmetry 'forbidden' [2 + 2] reactions of disilenes.^{5,14} A bridged species similar to (**3**) has been suggested as a possible transition state of the dyatropic rearrangement of asymmetrical disilenes.¹⁵

In conclusion, this study demonstrates that the PESs of isoelectronic doubly-bonded silicon and doubly-bonded carbon compounds are not isomorphic, and that unusual bridged structures like (**3**) can play a role in the chemistry of disilenes and may even exist as isolable compounds. We hope that this preliminary report will promote further experimental efforts to substantiate these theoretical predictions.

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