

# Silicon–Fluorine and Silicon–Carbon Bond Cleavage in Organofluorosilicates: A Molecular Orbital Study

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The mechanism of silicon–fluorine and silicon–carbon bond cleavage in organofluorosilanes and -silicates is analyzed with the aid of molecular orbital calculations. The optimized geometries of reactants and intermediates are calculated, and these calculations support the view that cleavage of Si–F bonds occurs by way of fluorine-bridged Si–F–Si intermediates. Cleavage of a Si–C bond in PhSiF<sub>3</sub> takes place in the presence of fluoride ion and oxidizing agents, and the calculations are in agreement with the formation of PhSiF<sub>4</sub><sup>−</sup> and PhSiF<sub>5</sub><sup>2−</sup>, followed by oxidation to a radical anion PhSiF<sub>5</sub><sup>•−</sup>. The latter species, however, is predicted to decompose rapidly to give anionic SiF<sub>5</sub><sup>−</sup>, and phenyl radicals. These calculations and the proposed mechanisms of bond cleavage are in agreement with experimental data, where available.

## Introduction

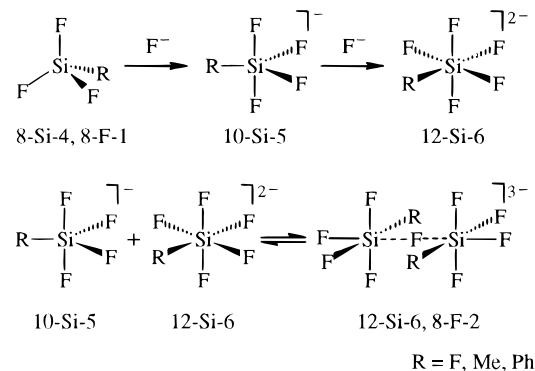
The bond energies of Si–F and Si–C bonds are quite high, on the order of 565 and 318 kJ mol<sup>−1</sup>, respectively,<sup>1</sup> yet these bonds in organofluorosilanes and -silicates may be cleaved under mild conditions in the presence of fluoride ion. A mechanism which accounts for the cleavage of Si–F bonds in typical fluorosilicates such as RSiF<sub>4</sub><sup>−</sup> and RSiF<sub>5</sub><sup>2−</sup>, and involves a fluorine-bridged intermediate<sup>2</sup> is shown in Scheme 1. In this mechanism the N–X–L notation of Perkins *et al.*<sup>3</sup> is used to specify the valence electron count (N) and coordination number (L) of elements (X) silicon and fluorine.

Evidence that fluorine-bridged intermediates are involved in the cleavage of Si–F bonds is based on NMR studies of rapid fluorine exchange in four-, five-, and six-coordinate silicon fluorides,<sup>4</sup> synthesis of new fluorosilicates,<sup>4</sup> and the X-ray structure determination of three fluorine-bridged silicate anions, *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub>F<sup>−</sup> (**6**), *o*-C<sub>6</sub>H<sub>4</sub>(SiPh<sub>2</sub>F)(SiF<sub>3</sub>)F<sup>−</sup>, and *o*-C<sub>6</sub>H<sub>4</sub>(SiPh<sub>2</sub>F)(SiPhF<sub>2</sub>)F<sup>−</sup>.<sup>5,6</sup>

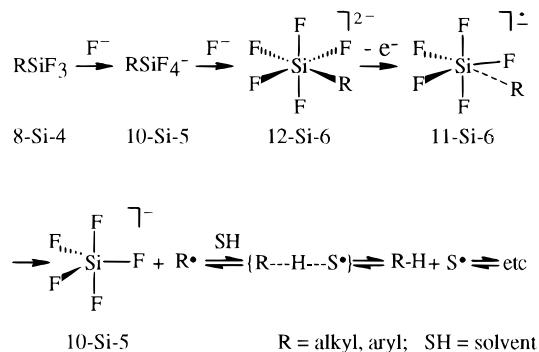
The fluoride-catalyzed cleavage of Si–C bonds is a more complex process, and a mechanism is given in Scheme 2. This mechanism agrees with the proposal of Kumada and co-workers;<sup>7</sup> however, details of the electron-transfer step are not specified since they depend on the choice of oxidizing agent.

The experimental evidence that supports a radical anion intermediate in Scheme 2 is the finding that typical one-electron oxidizing agents such as Hg(I/II), Sb(III), Pb(IV), Bi(III), Ag(I), Cu(I/II), Pd(II), NBS, halogens, etc., bring about rapid cleavage of Si–C bonds in RSiF<sub>5</sub><sup>2−</sup>.<sup>7,8</sup> Furthermore, if an

## Scheme 1



## Scheme 2



electron acceptor such as tetracyanoethylene (TCNE) is added to RSiF<sub>5</sub><sup>2−</sup>, the radical anion TCNE<sup>•−</sup> can be observed by ESR, and TCNE is alkylated.<sup>7</sup> Spin trapping of alkyl radical intermediates has been reported,<sup>9</sup> and electron transfer from RSiF<sub>5</sub><sup>2−</sup> to TCNE also occurs in the solid state.<sup>10</sup> Electrolysis of PhSiF<sub>5</sub><sup>2−</sup> gives benzene, while MeSiF<sub>5</sub><sup>2−</sup> gives methane and ethane.<sup>8</sup> Benzene is also detected in samples of PhSiF<sub>5</sub><sup>2−</sup> after several weeks in dichloromethane solution.<sup>11</sup> In the presence of fluoride ion, the Si–C bond in silatranes is cleaved by

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**Table 1.** Experimental and Calculated Si-F Bond Lengths (pm), and Average Lengthening<sup>a</sup> of Bonds (%) Relative to SiF<sub>4</sub>

	SiF <sub>4</sub>	SiF <sub>5</sub> <sup>-</sup>		SiF <sub>6</sub> <sup>2-</sup>	PhSiF <sub>4</sub>	PhSiF <sub>4</sub> <sup>-</sup>		PhSiF <sub>5</sub> <sup>2-</sup>		{Ph--SiF <sub>5</sub> <sup>-</sup> }	
experimental	155.98 <sup>34</sup>	166.0 ax (5.2%)	162.2 eq <sup>35</sup> (9.4%)	170.6 <sup>36</sup> (9.4%)	157.2 <sup>35,37</sup>	169.1 ax (6.3%)	162.6 eq <sup>35</sup>				
6-31+G*	156.0	166.1 ax (5.3%)	162.4 eq (9.6%)	170.9							
6-31G*	155.7	165.3 ax (4.9%)	161.8 eq (9.0%)	170.0	157.4	167.1 ax (5.7%)	162.7 eq (8.8%)	168.9 ax (8.8%)	169.8–170.4 eq	165.1 ax	161.7–162.2 eq <sup>b</sup>
3-21G*	155.7	164.2 ax (4.3%)	161.2 eq (7.7%)	168.0	157.2	165.9 ax (5.0%)	161.8 eq (7.4%)	166.6 ax (7.4%)	167.4–168.5 eq	163.8 ax	160.9–162.1 eq <sup>b</sup>
STO-3G*	152.1	160.8 ax (2.1%)	157.6 eq (5.5%)	164.6	152.4	159.8 ax (1.6%)	157.3 eq (4.0%)	162.0 ax (4.0%)	162.3–162.4 eq	160.7 ax	157.5–157.7 eq <sup>b</sup>

<sup>a</sup> For compounds having nonequivalent fluorines, an average of the axial and equatorial bond lengths is used for estimating % lengthening of bonds; ax = axial, eq = equatorial fluorines. <sup>b</sup> Note similarity to SiF<sub>5</sub><sup>-</sup> in third column.

**Table 2.** Experimental and Calculated Si--F--Si Bridging Bond Lengths (pm) and Lengthening<sup>a</sup> of the Bridging Bond (%) Relative to SiF<sub>4</sub>

	SiF <sub>4</sub> Si-F	F <sub>4</sub> Si--F--SiF <sub>4</sub> <sup>-</sup> (1) Si--F--Si	MeF <sub>3</sub> Si--F--SiF <sub>3</sub> Me <sup>-</sup> (2) Si--F--Si	F <sub>5</sub> Si--F--SiF <sub>5</sub> <sup>3-</sup> (3) Si--F--Si	C <sub>2</sub> H <sub>2</sub> (SiMeF <sub>2</sub> ) <sub>2</sub> F <sup>-</sup> (4) Si--F--Si	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SiMeF <sub>2</sub> ) <sub>2</sub> F <sup>-</sup> (5) Si--F--Si	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SiPhF <sub>2</sub> ) <sub>2</sub> F <sup>-</sup> (6) Si--F--Si
experimental	155.98 <sup>34</sup>						189.8–206.5 <sup>5,6</sup> (21.7–32.4%)
6-31G*	155.7	184.5 <sup>g</sup> (18.3%)	189.8 <sup>g</sup> (21.7%)	188.4 <sup>g</sup> (20.8%)	191.4, <sup>b,e,g</sup> 190. <sup>c</sup> (22.7%)		
3-21G*	155.7	180.5 (15.7%)	184.2 (18.1%)	182.6 (17.1%)	185.1, <sup>b,f</sup> 185.3 <sup>c</sup> (18.7%)	184.9, <sup>b,d,g,h</sup> 184.4 <sup>c</sup> (18.5%)	
STO-3G*	152.1	175.1 (12.3%)	174.9 (12.1%)	176.5 (13.2%)	174.6 <sup>c</sup> (11.9%)	174.1 <sup>b</sup> (11.6%)	

<sup>a</sup> For compounds having nonequivalent fluorines, an average of the axial and equatorial bond lengths is used for estimating % lengthening of bonds. <sup>b</sup> Methyl groups have *trans* configuration. <sup>c</sup> Methyl groups have *cis* configuration. <sup>d</sup> *Trans* isomer is more stable than *cis* isomer by 1.7 kJ mol<sup>-1</sup>. <sup>e</sup> *Trans* isomer is more stable than *cis* isomer by 1.9 kJ mol<sup>-1</sup>. <sup>f</sup> *Trans* isomer is more stable than *cis* isomer by 2.4 kJ mol<sup>-1</sup>. <sup>g</sup> With second derivative calculations and full optimization. <sup>h</sup> Geometry of benzene ring relaxed.

Hg(II), Pb(IV), Sb(III), and Bi(III),<sup>8,12</sup> and the Si-C bond in hexacoordinate diorgano(phthalocyaninato)silicon compounds is cleaved by NBS, halogens and Cu(II).<sup>13</sup> Radical anions have been observed in silicon catecholates.<sup>14</sup>

The possibility that the pentacoordinate anion RSiF<sub>4</sub><sup>-</sup>, rather than the hexacoordinate dianion RSiF<sub>5</sub><sup>2-</sup>, is responsible for Si-C bond cleavage is unlikely in view of the finding that MeSiF<sub>4</sub><sup>-</sup> reacts with Ag(I) salts only in the presence of added fluoride ion.<sup>8</sup> In the absence of oxidizing agents, organopentafluorosilicates RSiF<sub>5</sub><sup>2-</sup> are stable, even in aqueous solution,<sup>7,8</sup> and can be conveniently identified by their AB<sub>4</sub> fluorine NMR spectra.<sup>11,15</sup>

A three-stage method of analyzing reaction mechanisms has been proposed recently.<sup>2,16,17</sup> This method requires, first, the construction of a reaction pathway P(X,C) which defines each elementary step of a reaction mechanism and specifies the connectivity of atoms along that pathway, taking into account their coordination number and electron count. Second, the pathway P(X,C) is tested by carrying out molecular orbital calculations of all postulated intermediates, and that is the subject of this paper with regard to the mechanisms of Schemes 1 and 2. Finally, kinetic simulations of the proposed pathways P(X,C) may be carried out by associating elementary rate constants with the four elementary steps of a reaction, *i.e.*, +C, -C, +C<sup>c</sup>, -C<sup>c</sup>, as illustrated previously for the BF<sub>3</sub>-base system.<sup>17</sup>

## Calculations

All *ab initio* molecular orbital calculations were performed with the GAUSSIAN86 and GAUSSIAN92 system of programs,<sup>18</sup> and geometrical parameters were fully optimized with analytical gradient methods by the Hartree-Fock method. Interacting molecules and ions are treated as one large system.<sup>19</sup> Standard literature values were used for the geometries of methyl and phenyl substituents, except for some calculations in Table 3 where the geometry of the phenyl group was relaxed. The basis sets STO-3G\*, 3-21G\*, 6-31G\*, and 6-31+G\* were used in the calculations, and the optimized geometries were compared with experimental data, where available. Second-derivative calculations were carried out for structures 1, 2, and 5, and polarization functions (6-31G\*\*\*) were used for the hydrogen-bonded structure 7. Frequency calculations were carried out for all fully optimized fluorine-bridged intermediates 1–5, and it was found that all the frequencies are real from second-derivative calculations. Hence these final structures correspond to minima on the potential surfaces.

## Results and Discussion

**Silicon-Fluorine Bond Cleavage.** The optimized geometries of silicon fluorides were calculated with the aid of GAUSSIAN86 and GAUSSIAN92 programs. Several basis sets were used for the calculations and the results are compared with experimental data, where available, in Tables 1–3. Structural data for related four-, five-, and six-coordinate silicon fluorides are available,<sup>15</sup> and silicon fluorides have previously been the subject of theoretical analysis.<sup>20</sup>

For the series SiF<sub>4</sub>, SiF<sub>5</sub><sup>-</sup> and SiF<sub>6</sub><sup>2-</sup>, there is an increase in the experimental Si-F bond length of 5.2% in SiF<sub>5</sub><sup>-</sup> and 9.4% in SiF<sub>6</sub><sup>2-</sup>, relative to SiF<sub>4</sub>, as shown in Table 1. This

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**Table 3.** Experimental and Calculated Si–C Bond Lengths (pm), and Lengthening of Si–C Bonds (%) Relative to PhSiF<sub>3</sub>

	PhSiF <sub>3</sub>	PhSiF <sub>4</sub> <sup>-</sup>	PhSiF <sub>5</sub> <sup>2-</sup>	{Ph--SiF <sub>5</sub> <sup>-</sup> }
experimental	182.2 <sup>35,37</sup>	189.6 <sup>35</sup> (4.1%)	193.2 (12.3%)	360.2 (97.7%)
6-31G*	184.0	192.5, <sup>a</sup> 193.2 (5.7%)	204.7 (12.3%)	360.2 (97.7%)
3-21G*	182.5	190.6, <sup>a</sup> 191.3 (4.6%)	202.0, <sup>a</sup> 203.1 (10.9%)	312.6, <sup>a</sup> 312.6 (71.6%)
STO-3G*	184.3	196.1, <sup>a</sup> 196.6 (7.6%)	217.3 (19.3%)	336.3 (84.6%)

<sup>a</sup> Geometry of phenyl ring relaxed.

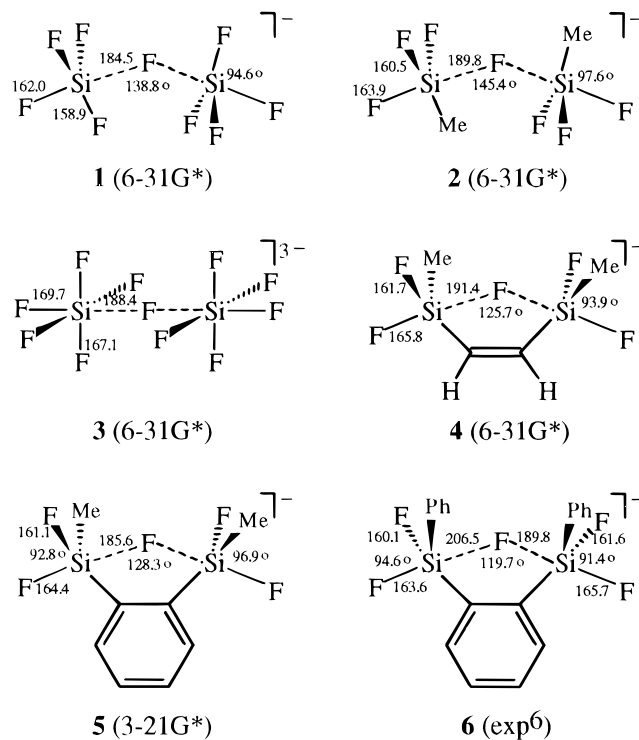
experimental trend is reproduced quite satisfactorily by the higher level calculations, *i.e.*, 5.3% (SiF<sub>5</sub><sup>-</sup>) and 9.6% (SiF<sub>6</sub><sup>2-</sup>) with the 6-31+G\* basis set, and 4.9% (SiF<sub>5</sub><sup>-</sup>) and 9.0% (SiF<sub>6</sub><sup>2-</sup>) with the 6-31G\* basis set. Agreement with the 3-21G\* calculation of 4.3% (SiF<sub>5</sub><sup>-</sup>) and 7.7% (SiF<sub>6</sub><sup>2-</sup>) is less satisfactory, but even the STO-3G\* calculation, although underestimating the Si–F bond lengths, nevertheless provides a useful estimate of the relative lengthening of Si–F bonds of 2.1% (SiF<sub>5</sub><sup>-</sup>) and 5.5% (SiF<sub>6</sub><sup>2-</sup>).

For the series PhSiF<sub>3</sub>, PhSiF<sub>4</sub><sup>-</sup>, and PhSiF<sub>5</sub><sup>2-</sup>, experimental information is only available for PhSiF<sub>3</sub> and PhSiF<sub>4</sub><sup>-</sup>. The experimental lengthening of the Si–F bond is 6.3% in PhSiF<sub>4</sub><sup>-</sup>, relative to SiF<sub>4</sub>, and this may be compared with the calculated lengthening of 5.0–5.7% (3-21G\* and 6-31G\*). These calculations assume a fixed phenyl ring of standard geometry. The calculations also show a bond lengthening of 7.4–8.8% in PhSiF<sub>5</sub><sup>2-</sup>, relative to SiF<sub>4</sub> (Table 1).

Since it is known from NMR studies of fluorine exchange that no Si–F bond cleavage occurs in purified samples of RSiF<sub>3</sub>, RSiF<sub>4</sub><sup>-</sup>, or RSiF<sub>5</sub><sup>2-</sup> (R = F, Me, Ph),<sup>2,4,21</sup> we must conclude that a bond lengthening of about 5–9% is insufficient to cause Si–F bond cleavage in these compounds under mild thermal conditions.

In order to establish that fluorine bridging leads to more substantial bond lengthening/weakening, the structures of five Si–F–Si-bridged anions **1–5** were calculated, and the results are summarized in Chart 1 and in Table 2.

Two of the anions (**4** and **5**) contain a five-membered ring, and these were chosen so that calculations could be compared with the experimental result that is available for the bridged anion *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub>F<sup>-</sup> (**6**),<sup>5,6</sup> which, in the solid state, has an unsymmetrical Si–F–Si bridge and a *cis* arrangement of phenyl substituents. Calculations of both *cis* and *trans* isomers of **4** and **5** were carried out, and a slightly lower energy of 1.8–1.9 kJ mol<sup>-1</sup> was found for the *trans* isomer, but all calculations show symmetrical Si–F–Si bridges in anions **4** and **5**. The synthesis and stability of cyclic Si–F–Si-bridged anion **6** is undoubtedly favored by a 5-center step,<sup>2</sup> and bridging bonds in related systems, *e.g.* S–F–S<sup>22</sup> and B–F–B,<sup>23</sup> are also part of four- and five-membered ring structures. The experimental Si–F bridging bond length in **6** varies between 189.8 and 206.5 pm in the solid state, which corresponds to a bond lengthening of 21.7–32.4%, relative to SiF<sub>4</sub>. The calculated Si–F bond

**Chart 1**

lengthening in **4–5** is 19–23%, using the 3-21G\* and 6-31G\* basis sets, and 12% according to STO-3G\* calculations.

The calculations of the linearly-bridged anions, **1–3**, show a lengthening of 18–22% (6-31G\*) and 16–18% (3-21G\*), which is nearly identical to that of the cyclic anions **4–5**. Anion **3** has an eclipsed (*D*<sub>4h</sub>) geometry, with a lengthening of 21% (6-31G\*) or 17% (3-21G\*) for the bridge bond, relative to SiF<sub>4</sub>. For the isoelectronic anion P<sub>2</sub>F<sub>11</sub><sup>-</sup>, the calculated lengthening of the bridging bond is 18%, relative to PF<sub>5</sub>, and the energy of the staggered (*D*<sub>4d</sub>) conformation is only 0.59 kJ mol<sup>-1</sup> lower than the eclipsed (*D*<sub>4h</sub>), implying virtually free rotation about the bridging bond.<sup>24</sup> The calculations therefore support the view that substantial bond lengthening/weakening occurs as a consequence of the formation of Si–F–Si intermediates; hence, these bridged intermediates can provide a pathway for rapid cleavage of silicon–fluorine bonds in fluorosilanes and -silicates, as well as related fluoro compounds. Although the experimental and calculated Si–F bridging bonds of **1–6** are in the range 174–207 pm, these are still less than the sum of the van der Waals radii of 360–370 pm.<sup>25</sup>

A crude estimate of the experimentally determined strength of these silicon–fluorine bridging bonds may be obtained from dynamic NMR studies of fluorine exchange, which show energy barriers of about 21 kJ mol<sup>-1</sup> for the SiF<sub>5</sub><sup>-</sup>–SiF<sub>6</sub><sup>2-</sup> system,<sup>4</sup> 23 kJ mol<sup>-1</sup> for the MeSiF<sub>3</sub>–MeSiF<sub>4</sub><sup>-</sup> system,<sup>4</sup> and 38 kJ mol<sup>-1</sup> for **6**.<sup>5</sup>

**Silicon–Carbon Bond Cleavage.** Since NMR studies of fluorine exchange in organosilicon fluorides and in related main group compounds of tin,<sup>26</sup> phosphorus,<sup>27</sup> and tellurium<sup>28</sup> have demonstrated that rapid cleavage of element–fluorine bonds is not accompanied by cleavage of element–carbon bonds, the

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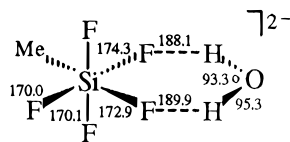
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pathway by which Si-C bonds are weakened must therefore differ significantly from that of Si-F bonds, as postulated in Scheme 2.

The calculated Si-C bond lengths for the series PhSiF<sub>3</sub>, PhSiF<sub>4</sub><sup>-</sup>, and PhSiF<sub>5</sub><sup>2-</sup> are shown in Table 3, and these are compared with experimental data for PhSiF<sub>3</sub> and PhSiF<sub>4</sub><sup>-</sup>. For some calculations in Table 3, the geometry of the phenyl ring was relaxed, and this reduced the Si-C bond length slightly. There is moderate lengthening/weakening of the Si-C bond with increasing fluoride content, for example, the experimental lengthening of the Si-C bond is 4.1% in PhSiF<sub>4</sub><sup>-</sup>, relative to PhSiF<sub>3</sub>, and this may be compared with the calculated bond lengthening of 4.6–5.7% (3-21G\* and 6-31G\*). The calculations show greater bond lengthening of 11–14% in PhSiF<sub>5</sub><sup>2-</sup> (3-21G\* and 6-31G\*), relative to PhSiF<sub>3</sub>. These calculations are in agreement with IR studies which indicate that the force constant of the Si-C bond, as well as of the Si-F bond, in MeSiF<sub>5</sub><sup>2-</sup>, is smaller than that in MeSiF<sub>3</sub>.<sup>29</sup> Since NMR studies have shown that Si-C bond cleavage does not occur in these purified compounds under mild conditions, we may therefore conclude that a bond lengthening of about 4–12% is insufficient to cause Si-C bond cleavage in PhSiF<sub>4</sub><sup>-</sup> or PhSiF<sub>5</sub><sup>2-</sup> under mild thermal conditions.

Substantially greater changes in Si-C bond lengths accompany a formal change in electron count, as PhSiF<sub>5</sub><sup>2-</sup> is oxidized to Ph--SiF<sub>5</sub><sup>•-</sup>. The calculated Si-C bond in Ph--SiF<sub>5</sub><sup>•-</sup> is in the range 313–360 pm, which corresponds to a lengthening of 72–98%, relative to PhSiF<sub>3</sub>. These calculated bond lengths of 313–360 pm approach the sum of the van der Waals radii of 375 pm,<sup>25</sup> implying that {Ph--SiF<sub>5</sub><sup>•-</sup>} consists essentially of a phenyl radical and anionic SiF<sub>5</sub><sup>-</sup>, and such a view is supported by the calculated Si-F bond lengths of Ph--SiF<sub>5</sub><sup>•-</sup> in Table 2, which are those of anionic SiF<sub>5</sub><sup>-</sup>. We conclude that oxidation of PhSiF<sub>5</sub><sup>2-</sup> to Ph--SiF<sub>5</sub><sup>•-</sup> must be followed by the rapid appearance of phenyl radicals and SiF<sub>5</sub><sup>-</sup>. The experimental result of Kumada and co-workers, who found complete loss of stereospecificity in the Cu(II) cleavage of Si-C bonds in norbornylpentafluorosilicates,<sup>30</sup> is in agreement with the formation of alkyl radicals after an oxidation step.

Organopentafluorosilicates RSiF<sub>5</sub><sup>2-</sup> are known to be stable in aqueous solution,<sup>7,8</sup> and we carried out calculations, with full optimization and using polarization functions (6-31G\*\*), of three water-bonded intermediates. In one intermediate, **7**, water was



**7** (6-31G\*\*)

hydrogen-bonded to two fluorines of MeSiF<sub>5</sub><sup>2-</sup>. In another calculation, only one hydrogen-bond between water and MeSiF<sub>5</sub><sup>2-</sup> was initially assumed, but the optimized geometry of this calculation was essentially that of **7**. In a third calculation, water was treated as a seventh ligand and placed along a pseudo-C<sub>3</sub>

axis of octahedral MeSiF<sub>5</sub><sup>2-</sup>, but this calculation also converged toward the geometry of **7**. Since the hydrogen bonds in **7** remain relatively long, 189.0 pm (average), while the bridging Si-F bond in **7**, 173.6 pm (average), is lengthened by only 11% relative to SiF<sub>4</sub>, we conclude that MeSiF<sub>5</sub><sup>2-</sup> is likely to be stable in water, in agreement with experiment. On the other hand, RSiF<sub>5</sub><sup>2-</sup> is expected to decompose slowly in the H<sub>2</sub>O-HF-glass system because of the release of boron- and silicon-containing Lewis acids from glass in this system.<sup>2</sup>

## Summary

1. The *ab initio* calculations of organofluorosilanes and -silicates support the view that cleavage of Si-F bonds occurs by way of a Si-F-Si-bridged intermediate, while cleavage of Si-C bonds occurs by way of a radical anion RSiF<sub>5</sub><sup>•-</sup>. These intermediates contain, formally, 8-F-2 fluorine and 11-Si-6 silicon, respectively, and the discrete variables of coordination number and electron count,<sup>31</sup> combined with the classification of elementary steps, *i.e.* +C, -C, +C<sup>c</sup>, -C<sup>c</sup>, are helpful for the detailed analysis of multistep reaction pathways.<sup>2</sup> Calculated bond lengths in cyclic and linear Si-F-Si intermediates are very similar, but the preference of cyclic intermediates is ascribed to a favorable ratio of +C<sup>c</sup>/+C, where +C<sup>c</sup> refers to an intramolecular step, and +C to a diffusion-controlled intermolecular step.<sup>2</sup> In the absence of reliable thermodynamic and kinetic data of reactive intermediates, the calculated bond lengths may serve as a simple criterion of bond cleavage, -C, and the generalization "the longer the bond the faster it breaks"<sup>32</sup> is therefore applied to these reactive *intermediates*.

2. The *ab initio* calculations are in agreement with the stability of organopentafluorosilicates RSiF<sub>5</sub><sup>2-</sup> in aqueous solution.

3. Synthetic, mechanistic, and theoretical studies of organofluorosilanes and -silicates agree that fluoride ion in aqueous solution, in combination with common oxidizing agents, can transform organometallic compounds into sources of aryl and alkyl free radicals. This finding has implications for synthetic, as well as environmental,<sup>33</sup> aspects of fluorine and organometallic chemistry.

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**Supporting Information Available:** Lists of optimized structural parameters in the form of **Z**-matrices for all calculated molecules (56 pages). Ordering information is given on any current masthead page.

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