Fluorinated Organosilicon Cations: A Comparison of Potential Energy Surfaces for $SiC_2X_n^+$ where X Is H or F and n = 1, 3, and 5

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Ab initio molecular orbital calculations are reported for ions SiC_2F^+, $SiC_2H_2F^+$, $SiC_2HF_2^+$, $SiC_2F_3^+$, and $SiC_2F_5^+$. Structure optimizations were performed for several minima at both HF/6-31G(d,p) and MP2(full)/6-31G(d,p). For the $SiC_2H_2F^+$ and $SiC_2HF_2^+$ potential energy surfaces transition structures for interconversion between ions were optimized at HF/6-31G(d,p) and profiles for interconversion between various isomers are given. The $SiC_2F_5^+$ potential energy surface is remarkably flat and has been examined at both HF/6-31G(d,p) and MP2(full)/6-31G(d,p) levels. The five potential energy surfaces reported here are compared with those of the analogous ions in which the fluorine atoms are replaced by hydrogens.

Introduction

Silicon is much more electropositive than carbon, and replacement of a carbon atom in a hydrocarbon by silicon has a profound effect on the relative stabilities of isomers. In general, for unsaturated organosilicon compounds the isomers with the best energies have the hydrogen atoms attached to the carbon atoms; for example, methylsilylene, CH_3SiH, is only slightly higher in energy than silaethylene, $H_2Si{=}CH_2$,[1−12] with the highest level calculations giving differences of 4.1 kcal mol^{-1} at G1[11] and 8.1 kcal mol^{-1} at MP4(SDTQ)/6-31G(d,p) followed by bond additivity corrections.[12] Silavinylidene, $H_2C{=}Si$, is at the global minimum, approximately 50 kcal mol^{-1} below trans-bent silaacetylene, HSiCH.[13−17]

In organosilicon cations, the charge is mainly located on the silicon atom and frequently the silicon has a coordination number that is less than 4. For example, silavinylidene protonates at carbon to produce H_3CSi^+, an ion in which the silicon atom is monovalent.[18] Similarly, in ions of formula $SiC_2H_n^+$ (n = 1 and 3), the structures at the global minima for these highly unsaturated ions each have a monocoordinate silicon atom that formally carries the positive charge.[19] For radical cations $SiC_2H_n^{+\bullet}$ (n = 2 and 4), the structures at the global minima are three-membered rings in which the silicon atom is two-coordinate. On each potential energy surface, however, the structure with the next lowest energy has a monocoordinate silicon atom.[20]

There have been numerous theoretical studies of fluorosilanes.[21,31] Si−F bonds are much stronger than C−F bonds, while C−H bonds are stronger than Si−H bonds.[17,32] Consequently, from experimental dissociation energies, the isodesmic reaction in eq 1 is endothermic by 52 kcal mol^{-1}.

$$SiH_3F + CH_4 \rightarrow CH_3F + SiH_4 \qquad (1)$$

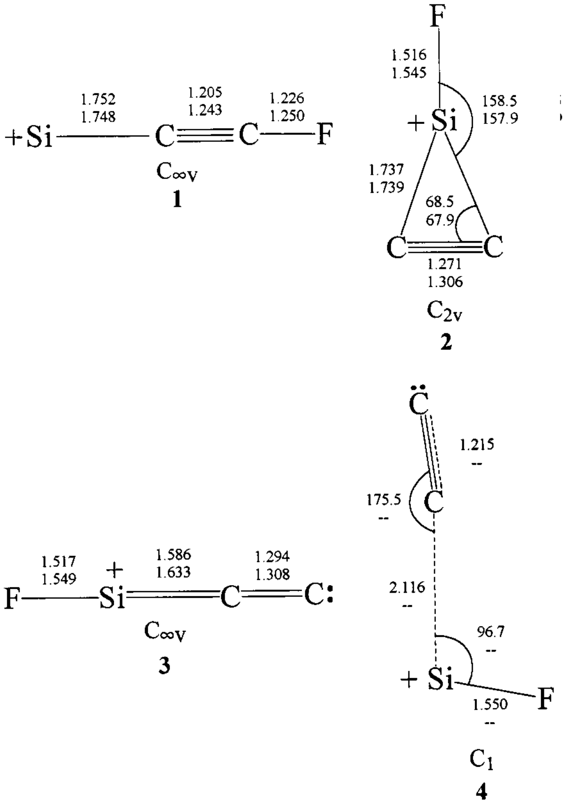

Figure 1. Optimized structures for isomers of SiC_2F^+. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G(d,p). All bond lengths are in angstroms, and angles are in degrees.

TABLE 1: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1}) of SiC_2F^+ Isomers

ion	RHF/6-31G(d,p)	ZPE[a]	HF energy rel. to **1**[b]	MP2/6-31G(d,p)	MP2 energy rel. to **1**[b]
1	−463.69024	7.4	0.0	−464.18618	0.0
2	−463.62415	6.2	+40.3	−464.14424	+24.9
3	−463.60020	5.8	+54.9	−464.09348	+56.6
4	−463.48628	5.1	+125.7		
$SiF^+ + C_2$	−463.46753	3.9	+136.0	−464.03835	+89.0

[a] From RHF/6-31G(d,p) frequency calculations; scaled by 0.89. [b] In kcal mol^{-1}; scaled ZPE included.

Ab initio molecular orbital calculations at MP4SDTQ/6-311++G(2df,p)//HF/6-31++G(d,p) give an enthalpy of 52.7 kcal/mol^{-1} for this reaction,[33,34] in excellent agreement with the experimental value. From these bond dissociation energies, it seems probable that replacing hydrogen atoms by fluorines in organosilicon compounds will tend to favor isomers that contain Si−F bonds. In the current study, we examine potential energy surfaces for ions $SiC_2H_mF_n^+$ (where $m + n$ = 1, 3, and 5) and compare them with those for the corresponding $SiC_2H_{m+n}^+$ ions.

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TABLE 2: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1}) of $SiC_2H_2F^+$ Isomers

ion	RHF/6-31G(d,p)	ZPE^a	HF energy rel. to **5a**^{b}	MP2/6-31G(d,p)	MP2 energy rel. to **5a**^{b}
5a	−464.95739	18.5	0.0	−465.47575	0.0
8a	−464.94383	18.5	+8.5	−465.46285	+8.1
6a	−464.93652	20.5	+15.1	−465.45804	+13.1
SiF^+ + HCCH	−464.91034	16.8	+27.8	−465.45219	+30.0
7a	−464.92135	20.7	+24.8	−465.42743	+32.5
9a	−464.92794	17.7	+17.7	−465.42072	+33.8
7a′	−464.91703	20.7	+27.5	−465.42385	+34.8
7a″	−464.89446	18.8	+39.8	−465.40472	+44.9
6a′	−464.87334	19.0	+53.2	−465.39172	+53.2
5a′	−464.86850	17.4	+54.7	−465.38280	+57.2
8a′	−464.83269	17.5	+77.3	- -	- -
8a″	−464.82442	17.1	+82.0	- -	- -
SiH^+ + FCCH	−464.78338	14.9	+105.6	−465.28464	+116.3

[a] From RHF/6-31G(d,p) frequency calculations; scaled by 0.89. [b] In kcal mol^{-1}; scaled ZPE included.

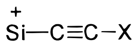
Computational Methods

All molecular orbital calculations were performed using Gaussian 94.[35] Structure optimizations were carried out with the 6-31G(d,p) basis set[36,37] initially at the Hartree−Fock level,[38] then at MP2(full),[39,40] and all structures at critical points were characterized by harmonic frequency calculations.[41] For each transition state, intrinsic reaction coordinate (IRC) calculations[42] were performed to determine the two minima that interconvert through this transition structure.

Results and Discussion

All the computed energies are given in Tables 1−5 and the optimized structures are given in Figures 1−4, 6 and 8. Profiles to interconversion are given in Figures 5, 7, and 10.

SiC_2X^+ Potential Energy Surfaces. On the SiC_2X^+ (X = H and F) potential energy surfaces, the same three structures, **1**−**3**, are at minima. The relative energies of these three isomers are in the same order, but when X = F, the differences are smaller than when X = H, and this is attributed to the fact that structures **2** and **3** have the stabilizing feature of having F attached to Si. We also located a fourth isomer on the SiC_2F^+ surface, $SiF^+\cdots C_2$(singlet), but this is only 10.3 kcal mol^{-1} lower than the dissociation products SiF^+ and C_2 at the Hartree−Fock level and was therefore not investigated at higher levels of theory.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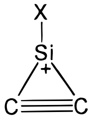
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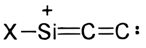
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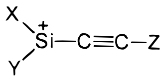
The C_2Si frameworks of ions **1**−**3** have geometries that are largely independent of whether X is H or F. The C_2SiF^+ ions generally have slightly shorter Si−C and C−C bond distances (the C−C distance in **2** is an exception to this generalization as it is 0.004 Å longer in *c*-C_2SiF^+).

$SiC_2H_{(3-n)}F_n^+$ Potential Energy Surfaces. On the $SiC_2H_3^+$ potential energy surface there are three structures at minima, ions **5**, **6,** and **7** (each with X = Y = Z = H). The relative energies of these isomers appear to be dictated by the location of the hydrogen atoms with structures containing the stronger C−H bonds being favored over those with the weaker Si−H bonds. Thus, the structure at the global minimum, ion **7**, has no hydrogens attached to silicon. Ions **5** and **6** are 10.8 and 13.9 kcal mol^{-1}, respectively, above **7**. Gordon et al., using bond separation reactions, concluded that the silacyclopropenyl cation, ion **6**, is slightly destabilized by the presence of two π-electrons and that the structure is best represented by a π-system localized on the two carbon atoms.[43]

TABLE 3: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1}) of $SiC_2HF_2^+$ Isomers and Transition Structures

ion	RHF/6-31G(d,p)	ZPE^a	HF energy rel. to **5b**^{b}	MP2/6-31G(d,p)	MP2 energy rel. to **5b**^{b}
5b	−563.86697	15.6	0.0	−564.55696	0.0
5b′	−563.78317	14.8	+51.8	−564.46983	+53.9
6b	−563.77096	16.3	+61.0	−564.46326	+59.5
8b	−563.76504	14.6	+62.9	−564.45525	+62.8
8b′	−563.76087	14.4	+65.3	−564.45042	+65.6
7b	−563.77486	16.4	+58.6	−564.44748	+69.5
8b″	−563.74574	14.4	+74.8	−564.43183	+77.3
9b	−563.73998	14.5	+78.6	−564.41501	+88.0
SiF^+ + FCCH	−563.73371	15.0	+83.0	−564.41388	+89.2
9b′	−563.73946	14.5	+78.9	−564.41111	+90.4
7b′	−563.73515	16.1	+83.3	−564.40912	+93.3
7b″	−563.72986	16.3	+86.7	−564.40353	+97.0
TS **9b′** → **8b**	−563.72300	12.7	+87.4		
TS **9b** → **9b′**	−563.70348	16.0	+102.9		
6b′	−563.70140	14.9	+103.1	−564.38898	+104.7
TS **8b′** → **9b**	−563.68186	13.0	+113.6		
TS **5b** → **8b″**	−563.64689	13.5	+136.0		
TS **5b′** → **8b**	−563.63332	11.4	+142.4		
SiH^+ + FCCF	−563.59724	10.9	+164.6	−564.26277	+179.9

[a] From RHF/6-31G(d,p) frequency calculations; scaled by 0.89. [b] In kcal mol^{-1}; scaled ZPE included.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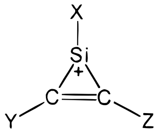
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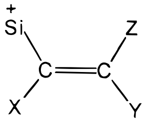
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Ions $SiC_2H_2F^+$. Eleven minima have been located on the $SiC_2H_2F^+$ surface, and the structures of the ions at these minima are given in Figure 2. There are five basic structures, ions **5**−**9**, and their relative energies depend heavily on the location of the fluorine atom. We have chosen to label the monofluoro-substituted ions by adding an "a" to the structure number.

Replacement of one H by F results in the same three types of structures, **5**−**7**, being at minima. The best three structures on this surface have the F atom attached to Si and the α-silapropargyl ion **5a** (X = F) is at the global minimum. Ion **6a**, with X = F, is 13.1 kcal mol^{-1} above **5a** and this compares with a difference of only 3.1 kcal mol^{-1} on the $SiC_2H_3^+$ surface. We have previously shown that π-donating substituents destabilize the cyclopropenyl cation, *c*-$C_3H_3^+$, relative to the propargyl cation[44] and that the destabilization caused by one F atom is 11.4 kcal mol^{-1} (at HF/6-31G(d)). The destabilization of **6a** relative to **5a** by 10 kcal mol^{-1} then is almost identical to that in the $C_3H_2X^+$ system.

The silapropargyl cation substituted by F at the γ-carbon (**5a′** with Z = F) is 57.2 kcal mol^{-1} above the global minimum; this is higher than all other covalently bound structures, and the propargyl cation, **5**, is clearly more sensitive to the location of the F substituent than isomers **6** and **7**. For example, from the MP2 calculations on **6a** and **6a′** (Table 2), F-substitution at silicon in the silacyclopropenyl cation is only 40.1 kcal mol^{-1} better than substitution at carbon.

Structure **7** suffers from having no Si−F bonds and the best isomer (**7a**, Z = F) lies 32.5 kcal mol^{-1} above the global minimum. The other two variations of **7**, ions **7a′** and **7a″**, in which X and Y, respectively, are the fluorine atom, are 12.4

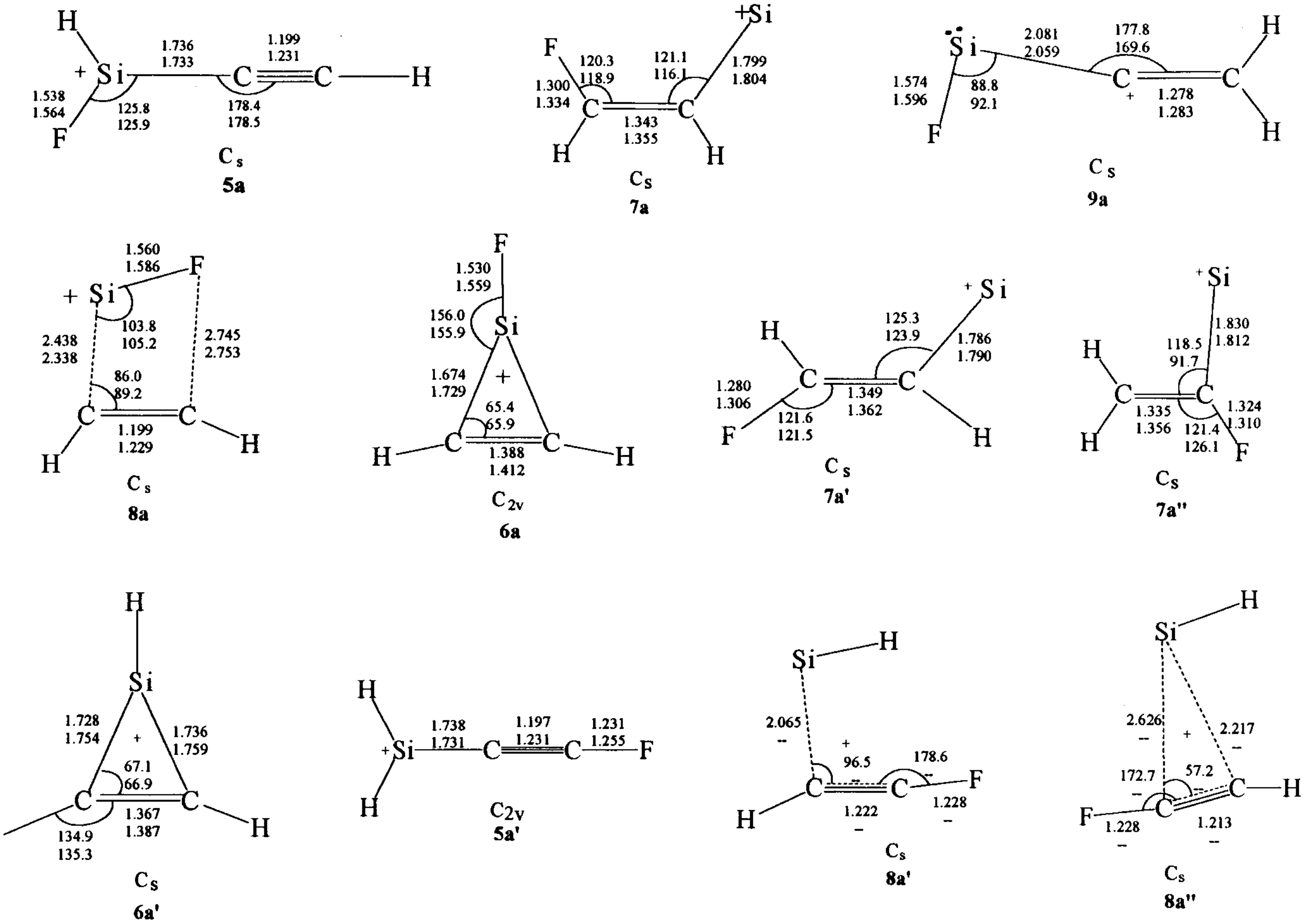


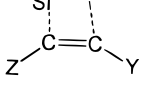
Figure 2. Optimized structures for isomers of $SiC_2H_2F^+$. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G-(d,p). All bond lengths are in angstroms, and angles are in degrees.

TABLE 4: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1}) of $SiC_2F_3^+$ Isomers and Transition Structures

ion	RHF/6-31G(d,p)	ZPE[a]	HF energy rel. to **5c**[b]	MP2/6-31G(d,p)	MP2 energy rel. to **5c**[b]
5c	−662.69272	11.9	0.0	−663.55099	0.0
6c	−662.59968	12.2	+58.7	−663.46250	+55.8
10	−662.59436	10.0	+59.8		
9c	−662.57698	10.6	+71.3	−663.43049	+74.3
TS **7c** → **9c**	−662.56733	10.8	+77.5		
8c	−662.56016	10.2	+81.5	−663.41977	+80.6
7c	−662.58218	11.9	+69.4	−663.42177	+81.1
SiF^+ + FCCF	−662.54757	10.5	+89.7	−663.39201	+98.4
TS **7c** → **8c**	−662.53979	10.4	+94.4		
TS **8c** → **6c**	−662.51577	9.9	+109.1		
11	−662.50717	10.8	+115.3		
TS **5c** → **8c**	−662.46586	9.6	+140.0		

[a] From RHF/6-31G(d,p) frequency calculations; scaled by 0.89. [b] In kcal mol^{-1}; scaled ZPE included.

and 2.3 kcal mol^{-1} higher in energy than **7a**.



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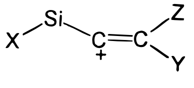

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On all $SiC_2H_nF_{(3-n)}^+$ potential energy surfaces, where $n = 0-2$, there are two additional types of isomers, structures **8** and **9**, for which no corresponding structures were found on the $SiC_2H_3^+$ surface. The existence and stability of these ions is attributable to the strength of the Si−F bond. **8a** is essentially an SiF^+ ion stabilized by interaction with the π-system of acetylene. On the $SiC_2H_2F^+$ surface ion **8a** is very low lying, only 8.1 kcal mol^{-1} above the global minimum. Dissociation into SiF^+ and C_2H_2 requires 21.9 kcal mol^{-1}, and these dissociation products are at lower energy than *all* the isomers of $SiC_2H_2F^+$ in which F is attached to carbon.

TABLE 5: Total Energies (hartrees) and Zero-Point Energies (kcal mol^{-1}) of $SiC_2F_5^+$ Isomers and Transition Structures

ion	RHF/6-31G(d,p)	ZPE[a]	HF energy rel. to **12**[b]	MP2/6-31G(d,p)	MP2 energy rel. to **12**[b]
12	−861.59634	16.2	0.0	−862.80044	0.0
14	−861.58083	16.0	+9.5	−862.79690	+2.0
15	−861.59151	15.1	+1.9	−862.79510	+2.2
TS **12** → **14**	−861.57853	15.9	+10.9	−862.78806	+7.5
TS **14** → **15**	−861.57694	15.2	+11.2	−862.78671	+7.6
16	−861.50672	15.0	+55.1	−862.71360	+53.3
SiF_3^+ + FC≡CF				−862.72278	+46.0[c]
SiF^+ + F_2CCF_2	−861.50417	14.8	+56.4	−862.69442	+65.1
17	−861.43482	15.5	+98.4		

[a] From RHF/6-31G(d,p) frequency calculations; scaled by 0.89. [b] In kcal mol^{-1}; scaled ZPE included. [c] Zero-point energy at MP2 is 13.5 kcal mol^{-1}.

Two other structures of type **8**, ions **8a′** and **8a″**, in which SiH^+ is stabilized by interaction with the π-orbitals of fluoroacetylene, are at the highest minima that we located on this surface. The dissociation energies of these ions at the Hartree−Fock level are calculated to be approximately 25 kcal mol^{-1} and, as these structures are at very high energies, they were not investigated at MP2.

Isomer **9a** is the highest energy isomer containing an Si−F bond (33.8 kcal mol^{-1} above **5a**) and is above one structure (ion **7a**) in which there is a C−F bond. **9a** has a long C−Si

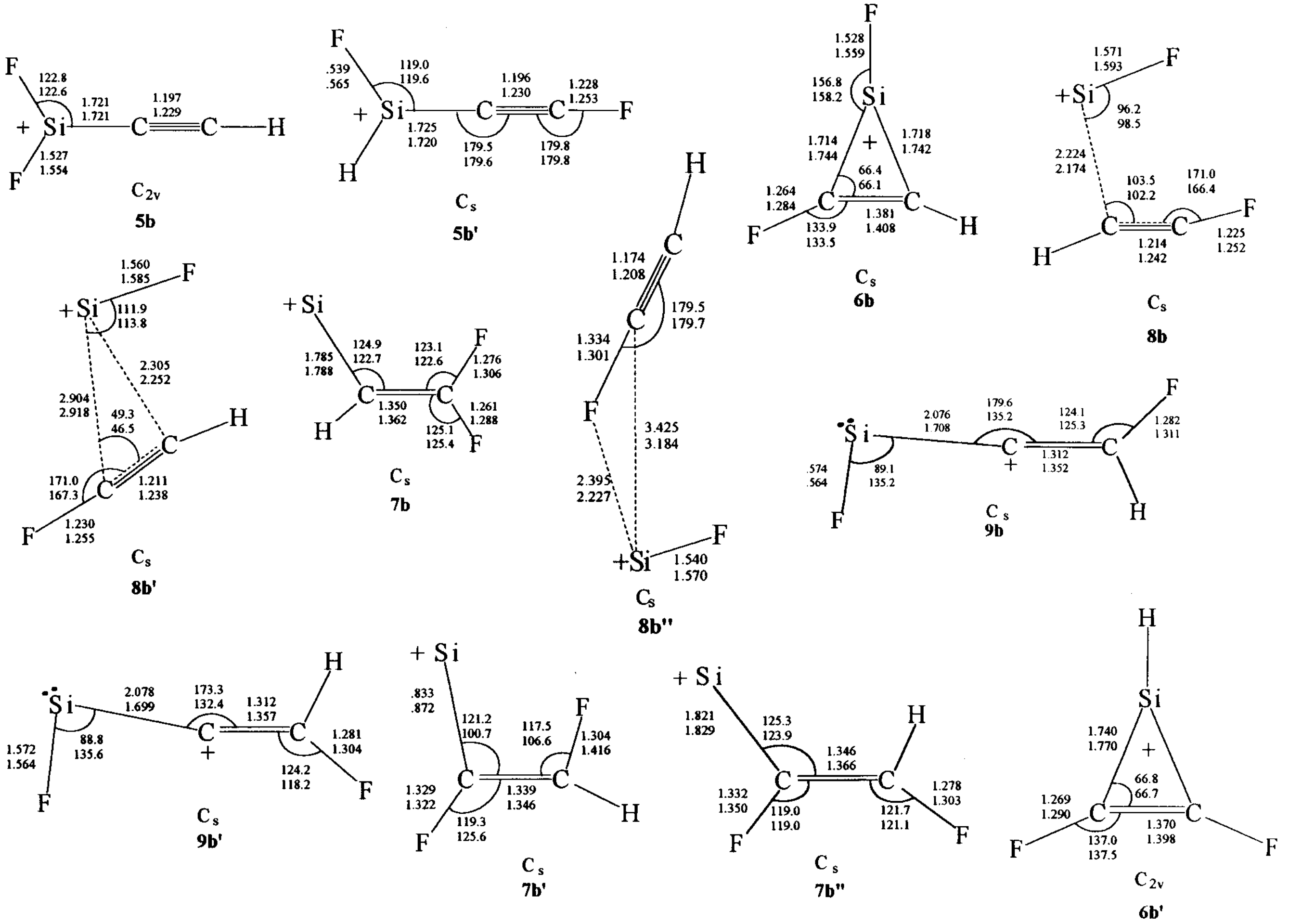


Figure 3. Optimized structures for isomers of $SiC_2HF_2^+$. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G-(d,p). All bond lengths are in angstroms, and angles are in degrees.

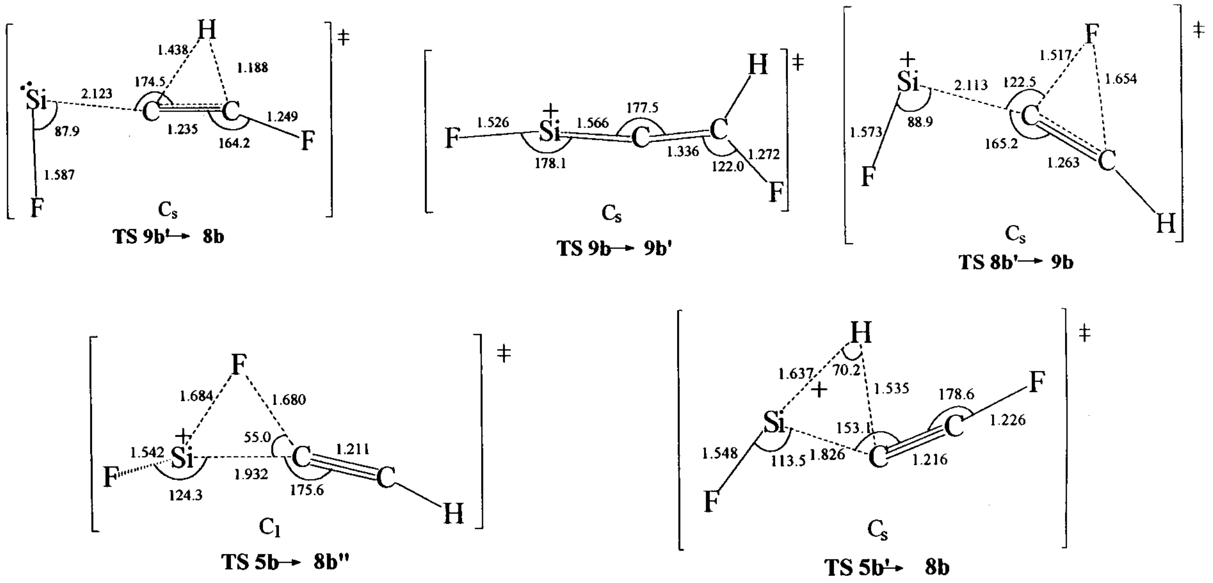


Figure 4. Transition structures on the $SiC_2HF_2^+$ potential energy surface. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G(d,p). All bond lengths are in angstroms, and angles are in degrees.

distance (2.059 Å) and is probably best described as an SiF^+ ion stabilized by lone pair donation from vinylidene carbene.

Finally, silicon is noted for its reluctance to form multiple bonds with carbon and it is interesting to note that in all five types of structures on the $SiC_2H_2F^+$ surface, silicon is involved in only *single* bonds, i.e., even in these heavily unsaturated ions there are no multiple C−Si bonds.

Ions $SiC_2HF_2^+$. Replacement of two hydrogen atoms of $SiC_2H_3^+$ by fluorine atoms illustrates the powerful stabilizing effect of the Si−F bond. The α-silapropargyl ion **5b** in which

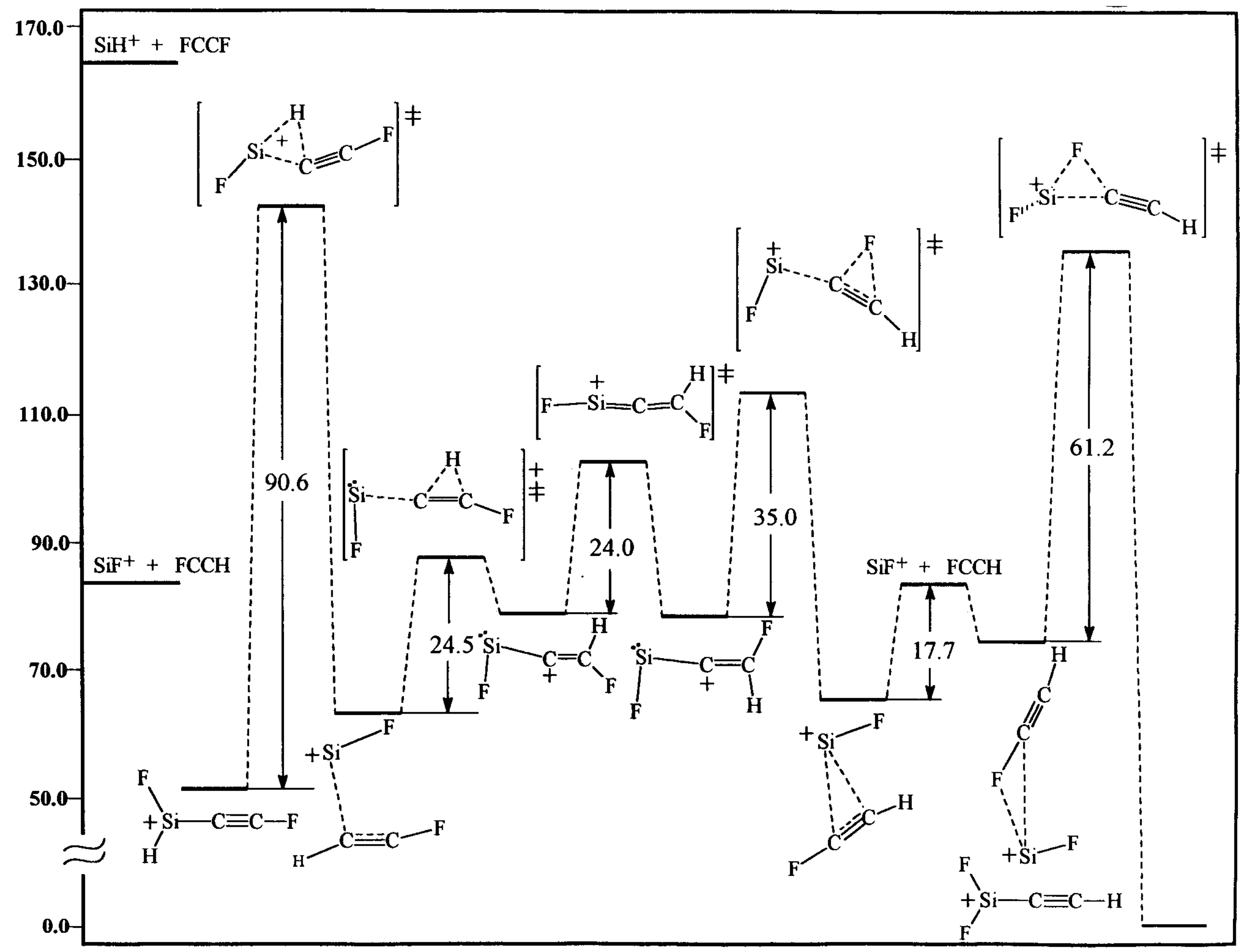


Figure 5. Profile for interconversion of the two lowest energy isomers, ions **5b** and **5b′**, on the $SiC_2HF_2^+$ potential energy surface as calculated at HF/6-31G(d,p). Relative energies are given in kcal mol^{-1}.

both fluorine atoms are attached to the silicon (**5** in which X = Y = F) is at the global minimum and is more than 50 kcal mol^{-1} better in energy than all the other structures. (Structures at minima are given in Figure 3 and transition structures for their interconversion are in Figure 4). The structure with the next best energy is the other α-silapropargyl ion, **5b′**, in which there is one fluorine atom on silicon and one on carbon (**5** with X = Z = F).

The silacyclopropenyl cation **6b** in which one fluorine atom is attached to silicon (**6** with X = Y = F) is the next highest structure, 59.5 kcal mol^{-1} above the global minimum. This compares with an energy of 104.7 kcal mol^{-1} for difluorocyclopropenyl cation **6b′** in which both fluorines are on carbon atoms (**6** with Y = Z = F).

On this potential energy surface, ions **7** are even higher in energy relative to the difluorosilapropargyl ion than is the situation for the similar structures on the $SiC_2H_2F^+$ surface. Here again the preferred location for the fluorine atoms is on the carbon atom that is not attached to silicon. Ion **7b** (ion **7** in which Y = Z = F) is 69.5 kcal mol^{-1} above the global minimum, but is over 20 kcal mol^{-1} better in energy than other variations of **7** in which one fluorine is attached to the same carbon atom as the silicon atom.

There are three structures in which SiF^+ is "solvating" fluoroacetylene. All three ions are planar and the best arrangement has the silicon closest to the carbon of CH with the fluorine on the SiF fragment above the other carbon atom (**8b**, X = Y = F). This is 2.8 kcal mol^{-1} better in energy than the structure **8b′** in which the orientation of the SiF is reversed. For this combination, there is another "solvated" ion, **8b″**, in which the silicon lies above the C−F bond of the fluoroacetylene, but this is 14.5 kcal mol^{-1} above the best solvated ion.

There are two forms of vinyl cation **9**, both of which have Si−F attached to the cationic carbon. They are close in energy to the dissociation products, SiF^+ and C_2HF, but the $Si-C^+$ bonds are short and are remarkably sensitive to the level of theory used in the geometry optimization.

We have explored the $SiC_2HF_2^+$ potential energy surface for interconversion between the two lowest isomers, both silapropargyl cations, one with both fluorines attached to silicon (**5b**, X = Y = F) and the other with one of the fluorines on the terminal carbon atom (**5b′**, X = Z = F). The profile for this rearrangement is given in Figure 5. The two highest transition states on this profile, both very high in energy, involve breaking the silapropargyl cations into "solvated" ions in which SiF^+ is loosely attached to fluoroacetylene, C_2FH. Dissociation into these two fragments requires less energy than proceeding through the central part of the pathway via the vinyl cations and would probably be the pathway followed. Our overall conclusion is that interconversion between these two silapropargyl cations will not occur in the gas phase at room temperature and that both should be very stable ions.

Ions $SiC_2F_3^+$. At HF/6-31G(d,p), we optimized structures at seven minima on the $SiC_2F_3^+$ potential energy surface, the five basic structures that exist for the other $SiC_2H_{(3-n)}F_n^+$ ions and two additional ones, ions **10** and **11** (structures are given in

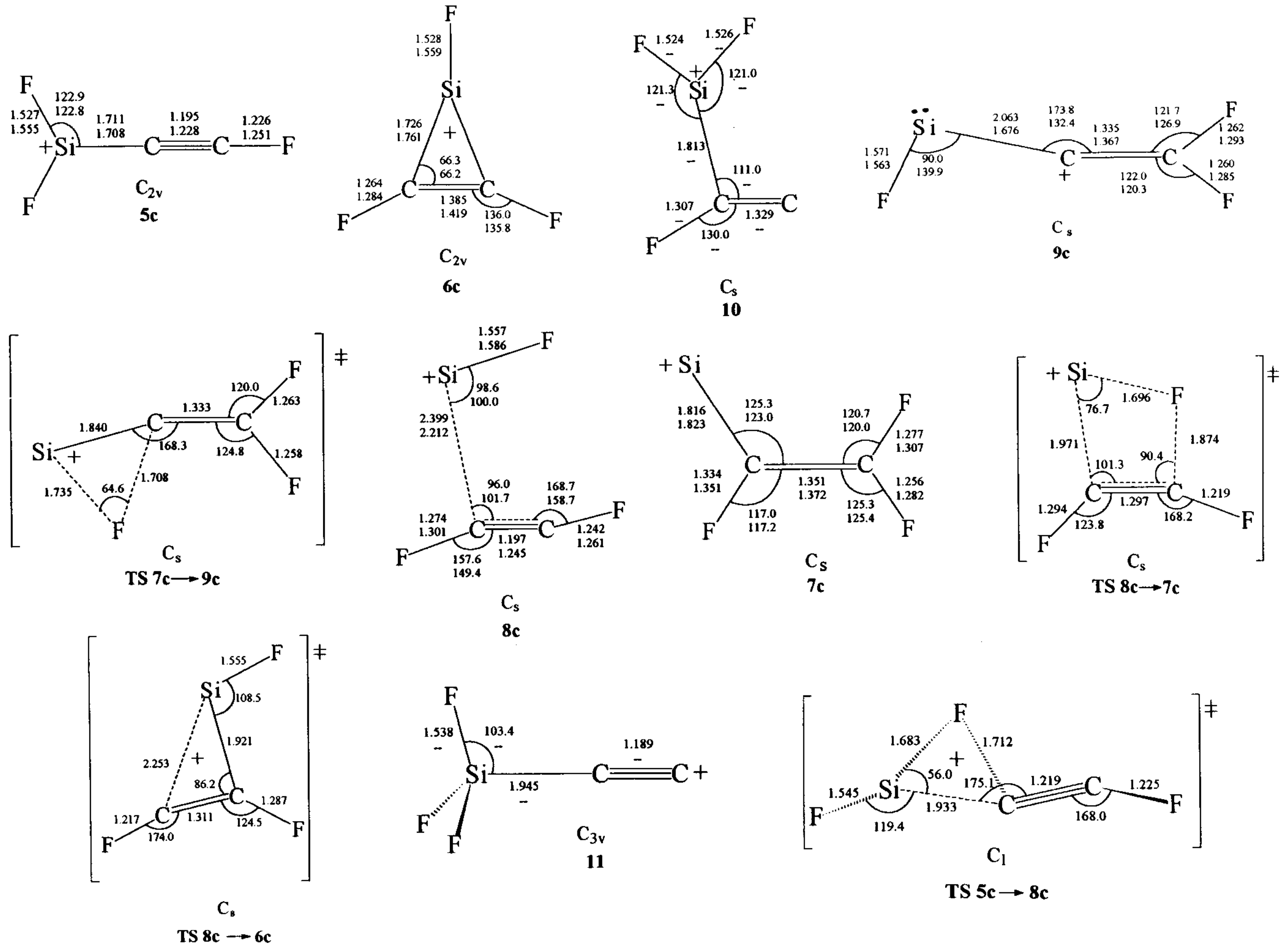
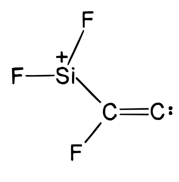
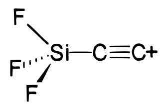


Figure 6. Optimized structures for isomers of $SiC_2F_3^+$. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G(d,p). All bond lengths are in angstroms, and angles are in degrees.

Figure 6). One of these new structures **10**, however, appears to be an artifact of the Hartree−Fock level of theory as it is no longer at a critical point when electron correlation is included and rearranges to **5c** without barrier. Structure **11** is 115 kcal mol^{-1} above **5c** and 25.6 kcal mol^{-1} above the dissociation products SiF^+ and C_2F_2 at HF/6-31G(d,p); consequently, we did not pursue this structure at higher levels of theory.



10



11

The remaining structures are analogous to those found on the $SiC_2H_2F^+$ and $SiC_2HF_2^+$ surfaces. The relative energies of **5c** ≪ **6c** < **9c** < **8c** ≈ **7c** emphasize the stabilizing effect of the Si−F bond. Ion **5c** has two Si−F bonds and is 55.8 kcal mol^{-1} lower in energy than **6c**; by contrast, on the $SiC_2H_3^+$ surface, structure **5** is lower than **6** by only 3.1 kcal mol^{-1}. Ion **7c**, the only structure on the $SiC_2F_3^+$ surface that has no Si−F bonds, is at the highest energy, whereas on the $SiC_2H_3^+$ surface it is at the global minimum.

For ion **5**, replacement of H atoms by F atoms results in a shortening of both the Si−C and C−C distances (by 0.036 and 0.003 Å, respectively). Conversely, in **6** and **7** these distances are both increased by substitution by fluorine. In structure **8c**, the Si−F bond is roughly parallel to the C−C bond of the acetylene and the Si atom is above one of the C atoms and not above the center of the C−C bond as would be expected in a complex in which the π-electrons from the triple bond are donated into the formally vacant p orbital on Si.

Optimization of ion **9c** gave very different structures at different levels of theory. The Hartree−Fock calculation gave a structure in which C−C−Si is close to linear and has a CSiF angle of 90.0°. While the Si−C distance of 2.063 Å is a bit long for a single bond, this structure is best described as being a vinyl cation with an SiF substituent attached to the cationic carbon. Inclusion of electron correlation resulted in a dramatic shortening of the Si−C distance (to 1.676 Å), an increase in the FSiC angle (to 139.9°), a decrease in the CCSi angle (to 132°), and a lengthening of the C−C distance (from 1.335 to 1.367 Å). These parameters indicate a multiple bond between Si and C, and the structure is more like a 1-silaallene derivative, although the two terminal groups remain coplanar.

Interconversions on the $SiC_2F_3^+$ Surface. The profile for interconversion at the Hartree−Fock level between isomers on the $SiC_2F_3^+$ potential energy surface is given in Figure 7. The transition state for interconversion between isomers **7c** and **9c**

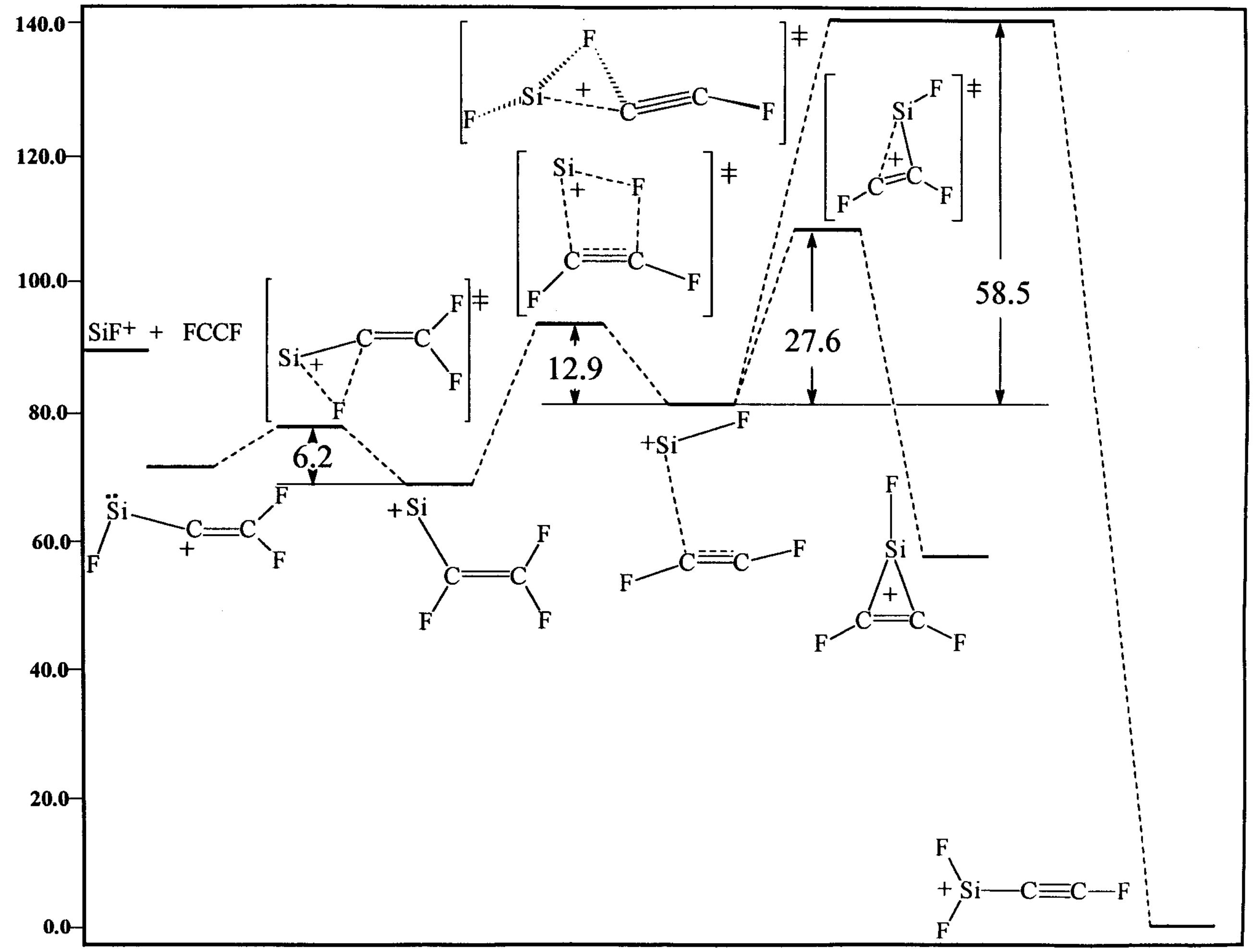


Figure 7. Profile for interconversion of ions on the $SiC_2F_3^+$ potential energy surface as calculated at HF/6-31G(d,p). Relative energies are given in kcal mol^{-1}.

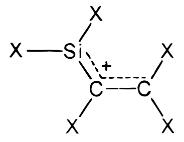
is the only transition state that lies below the energy of the dissociation products, SiF^+ plus C_2F_2.

On the $SiC_2H_3^+$ potential energy surface the highest barrier to rearrangement was found to be from **5** to **7** (68.5 kcal mol^{-1} above **5**). Similarly, on the $SiC_2F_3^+$ surface, the largest barrier is again associated with rearrangement of **5**, but in this case, **5c** is at the global minimum and the product of the rearrangement is the solvated ion **8c**.

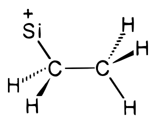
On the $SiC_2F_3^+$ surface cyclic ion **6c** also lies in a deep well, 50.4 kcal mol^{-1} below the transition state for its rearrangement into **8c**. Clearly then, both ions **5c** and **6c** are stable to rearrangement and should be long-lived ions in the gas phase at room temperature.

The remaining ions on the surface interconvert via relatively low-lying transition states and, of these minima, structure **7c** has the lowest energy. To convert **7c** into **6c** the barrier (via **8c**) is 39.7 kcal mol^{-1}, and ion **7c** should therefore be observable in the gas phase at room temperature.

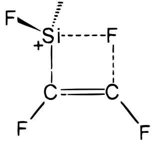
The $SiC_2F_5^+$ Ions. The 1-silaallyl cation **12** is the lowest energy isomer on both the $SiC_2H_5^+$ and $SiC_2F_5^+$ potential energy surfaces. However, there are few other similarities between these two surfaces. For example, for $SiC_2H_5^+$, isomer **13** is only 4.4 kcal mol^{-1} above **12**, but we were unable to locate the corresponding structure on the $SiC_2F_5^+$ surface. This is attributable to the absence of Si−F bonds.



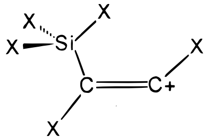
12



13



14



15

There are two isomers of $SiC_2F_5^+$ that have similar energies to **12**; ions **14** and **15** are, respectively, only 2.0 and 2.2 kcal mol^{-1} above **12**. Both of these structures are stabilized by virtue of a large amount of Si−F bonding. (For structures see Figure 8.) Structure **14** has no analogue on the $SiC_2H_5^+$ surface. This ion has a nonclassical structure in which one F atom is shared between the silicon atom and the terminal carbon atom. The C−F distance of 1.497 Å is much longer than a typical C−F

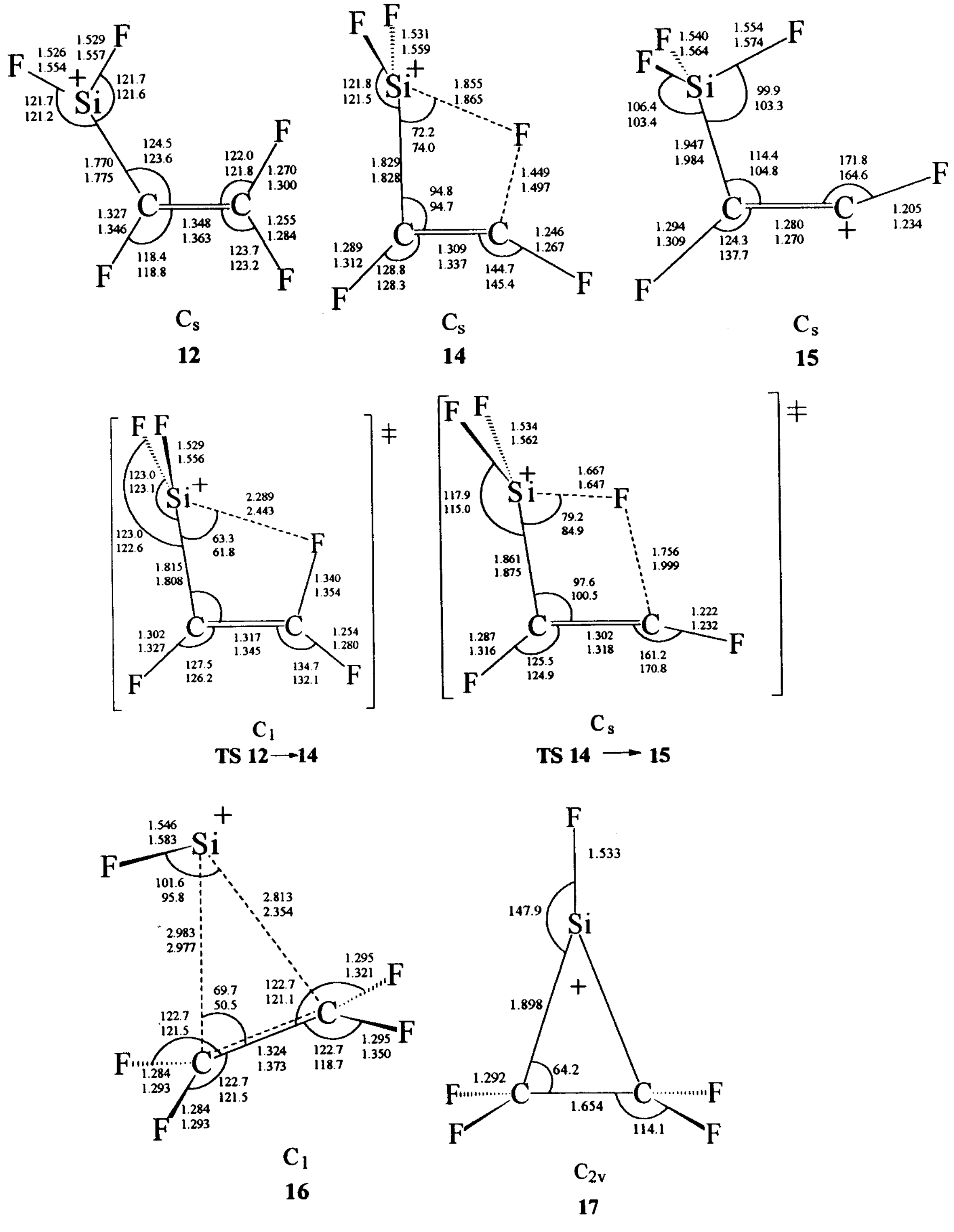


Figure 8. Optimized structures for isomers of $SiC_2F_5^+$. The upper values are from HF/6-31G(d,p) and the lower ones from MP2(full)/6-31G(d,p). All bond lengths are in angstroms, and angles are in degrees.

single bond of around 1.3 Å, and the Si–F distance of 1.865 Å is longer than a typical Si–F single bond of around 1.56 Å.[38] **14** is in a very shallow potential well at the Hartree–Fock level of theory, with a barrier of only 1.4 kcal mol^{-1} preventing it from collapsing into **12**. Inclusion of electron correlation results in stabilization of **14**; at MP2, it is only 2 kcal mol^{-1} above **12**, whereas at the Hartree–Fock level it is 9.5 kcal mol^{-1} higher. Also, at MP2 the barrier to rearrangement is increased to 5.6 kcal mol^{-1}. Mayer bond orders[45] of 0.402 for Si–F and 0.572 for C–F (Figure 9) show the F atom to be more or less equally attached to both centers.

15 bears some resemblance to the cyclic isomer formed by adding SiH_3^+ to C_2H_2, although the latter is almost symmetrically bridged, has very long Si–C distances (around 2.2 Å), and is essentially SiH_3^+ solvated by the π-bond of acetylene (binding energy 39.7 kcal mol^{-1}). By contrast, **15** has a Si–C distance of 1.984 Å (only 0.12 Å longer than the single bond in silaethane), a SiCC bond angle of 104.8°, and a C–C distance of 1.270 Å. The Mayer analysis gives bond orders of 0.478 for the Si–C bond and 1.809 for the C–C bond (Figure 9). These data are consistent with describing **15** as having some vinyl cation character (resonance structure **15a**) and some π-complex

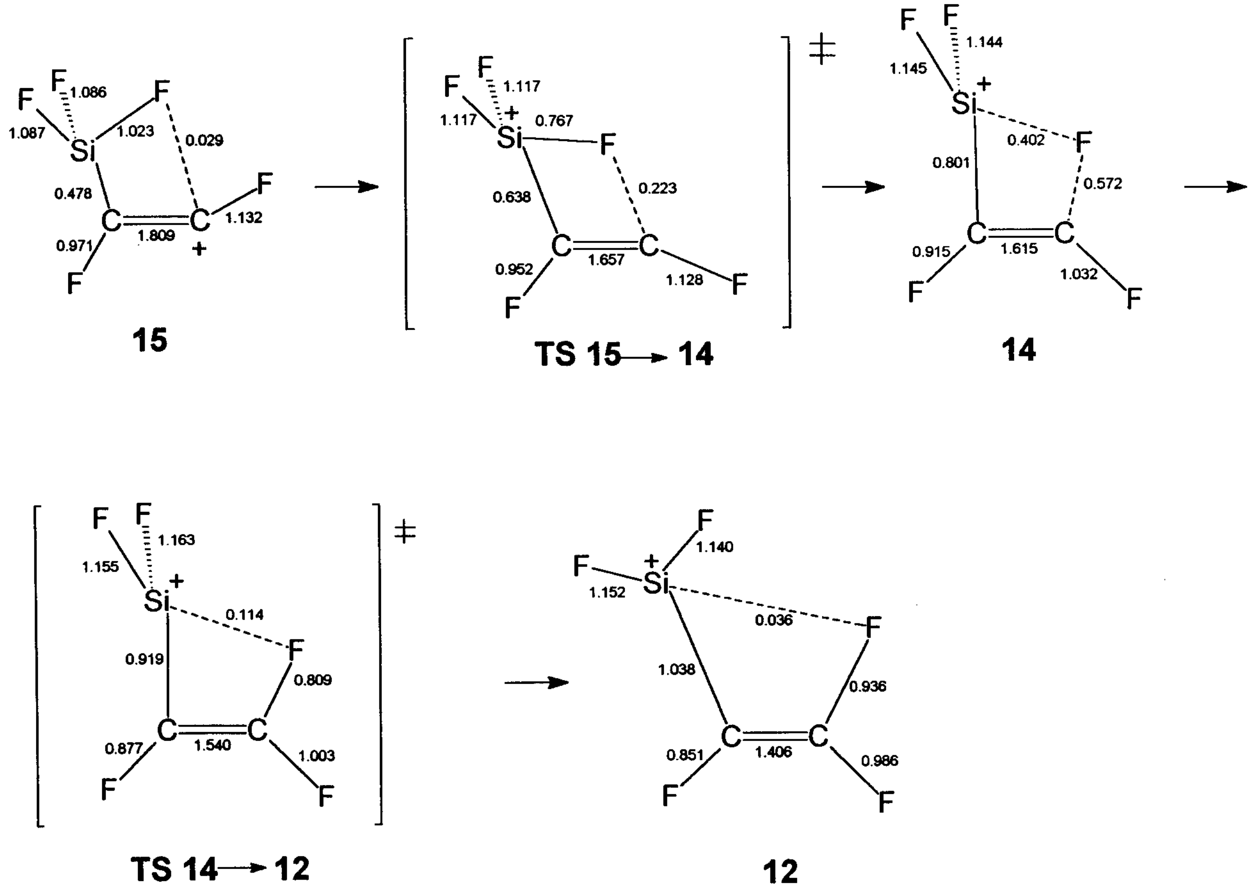
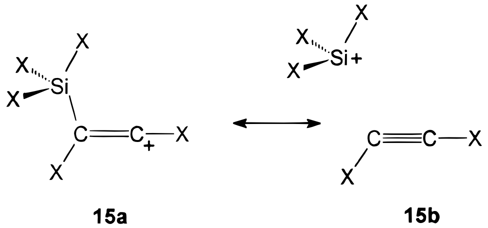


Figure 9. Mayer bond indices as calculated at HF/6-31G(d,p) for structures involved in the rearrangement of **15** into **12** via **14**.

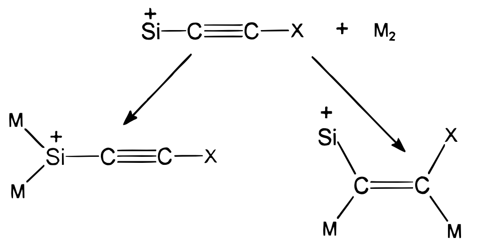
character (resonance structure **15b**).



The only other isomer on the $SiC_2F_5^+$ surface that is below the energy for dissociation into SiF^+ and $F_2C{=}CF_2$ is solvated ion **16** in which the binding energy is 11.8 kcal mol^{-1}. The cyclic structure in which the positive charge is formally on the silicon (ion **17**) is at a minimum at the Hartree−Fock level, but as this was found to be 42 kcal mol^{-1} above the dissociation products, it was not investigated at MP2.

Interconversion between Isomers of $SiC_2F_5^+$ Ions. The transition states on the profile for interconversion of **15** into **14** and **14** into **12** have almost identical energies, and the overall barrier for conversion of **15** into **12** is 5.4 kcal mol^{-1} (Figure 10). On going from **15** to **12**, the five critical points involved show a systematic trend between bond order and bond length. The Si−C distances decrease monotonically from 1.984 to 1.775 Å, and the bond orders increase from 0.478 to 1.038 (Figures 8 and 9). The C−C distances increase from 1.270 to 1.363 Å, and the bond orders decrease from 1.809 to 1.406. For the F atom that migrates in this rearrangement, the Si−F bond order decreases from 1.023 in **15** to 0.036 in **12** and the C−F bond order increases from 0.029 to 0.936.

Hydrogenation and Fluorination. Addition of M_2 to ion **1** can, in principle, occur either across the triple bond or by insertion of the silicon atom, formally the location of a lone pair of electrons, into the M−M bond. Addition of molecular hydrogen occurs at the triple bond. When X = H this product is preferred by 12.5 kcal mol^{-1}, and when M = F it is preferred by 24.7 kcal mol^{-1} (both at MP2/6-31G(d,p)). All of these addition reactions are exothermic, but by relatively modest amounts (20.7−41.3 kcal mol^{-1}, see Table 6). By contrast, addition of molecular fluorine to **1** occurs at silicon and is highly exothermic, by 202.7 and 201.5 kcal mol^{-1} when X is H and F, respectively. Addition of F_2 across the triple bond is much less exothermic; when X is F it is 120.4 kcal mol^{-1} and for X = H it is 105.7 kcal mol^{-1}. These latter values are considerably less than the exothermicity of the reaction of F_2 with difluoroacetylene which is calculated to be 162.5 kcal mol^{-1} at this same level of theory.[46]



Addition of a further F_2 molecule to trifluoropropargyl ion **5c** occurs across the triple bond and is exothermic by 129.3 kcal mol^{-1}. The product is the pentafluoro-1-silaallyl cation, the lowest energy isomer on the $C_2SiF_5^+$ potential energy surface.

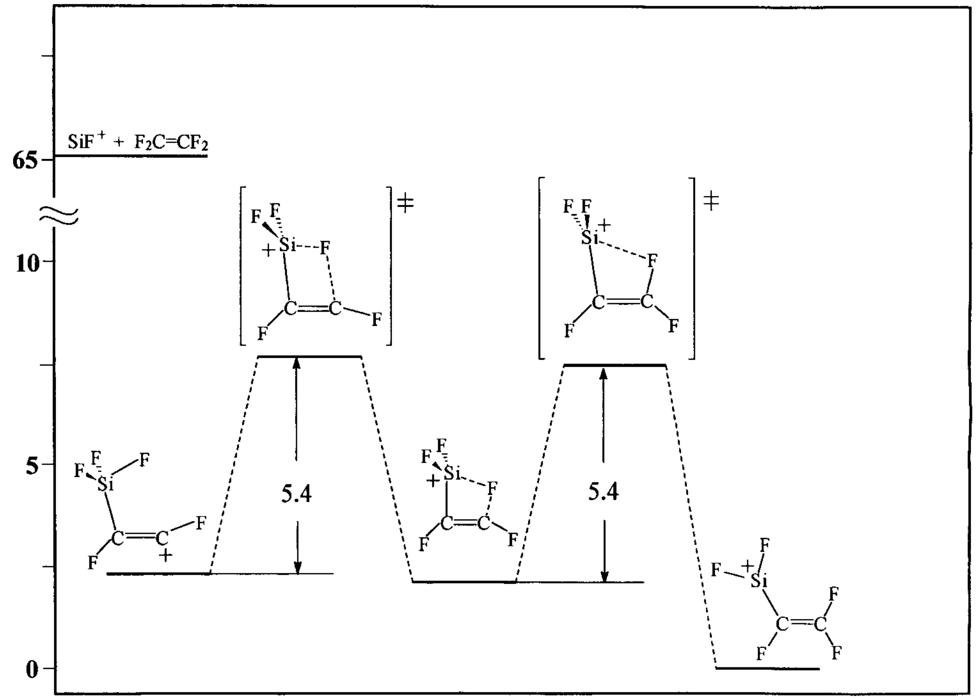
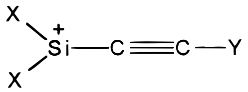
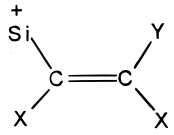


Figure 10. Profile for interconversion of ions on the $SiC_2F_5^+$ potential energy surface as calculated at MP2/6-31G(d,p). Relative energies are given in kcal mol^{-1}.

TABLE 6: $\Delta H°$ (0 K) in kcal mol^{-1} for Reaction of X_2 with $^+Si{-}C{\equiv}C{-}Y$ at MP2(full)/6-31G(d,p)

substituents	 product	 product
X = F, Y = F	−201.5	−120.4
X = H, Y = F	−20.7	−41.3
X = F, Y = H	−202.7	−105.7
X = H, Y = H	−21.8	−34.7

Conclusions

Replacement of the hydrogen atoms in cations $SiC_2H_n^+$ (n = 1, 3, and 5) by fluorines has a dramatic effect on the relative energies of the various isomers. On the SiC_2X^+ surface, the relative energies of the structures are the same, with the linear acetylene-like structure being at the global minimum. Fluorine substitution results in the other two structures, both of which contain Si−F bonds, being much closer in energy to the global minimum than on the SiC_2H^+ surface.

As the number of fluorine atoms in the cation is increased, the preference for structures containing Si−F bonds also increases. Even in $SiC_2H_2F^+$, the presence of fluorine is sufficient to make the fluorosilapropargyl cation the lowest energy isomer, 32.5 kcal mol^{-1} below ion **7**. By contrast, on the SiC_2H^+ surface, **7** is at the global minimum, 10.8 kcal mol^{-1} below the silapropargyl ion. Multiple substitution by fluorine increases this difference and in $SiC_2F_3^+$ the perfluorosilapropargyl cation is 81 kcal mol^{-1} below ion **7c**.

On the $SiC_2F_5^+$ surface the perfluorosilaallyl cation is at the global minimum and in this respect is the same as the $SiC_2H_5^+$ surface. However, the ion with the next best energy on the $SiC_2F_5^+$ surface has a nonclassical structure, only 2.0 kcal mol^{-1} above the global minimum. The equivalent structure does not exist on the $SiC_2H_5^+$ surface. By contrast, the ion with the second best energy on the $SiC_2H_5^+$ surface is essentially an ethane molecule with one of the hydrogen atoms replaced by Si^+, and this lies only 4 kcal mol^{-1} above the global minimum. The equivalent structure does not exist on the $SiC_2F_5^+$ surface.

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