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# Effects of Polar Substituents on Carbon-Silicon Multiple Bonds

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# Effects of Polar Substituents on Carbon-Silicon Multiple Bonds<sup>1</sup>

Mark S. Gordon

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**Abstract:** The results of ab initio calculations on the effects of fluorine and lithium substitution on silaethyne and silaethylene and their isomers are presented. It is found that fluorine has a strong stabilizing effect when attached to silicon. This results in the predictions (a) that a distorted 1-fluoro-1-silaethyne is the most stable structure of HCSiF and (b) that 1,1-difluoro-1-silaethylene is much lower in energy than 1,2-difluoromethylsilylene. Approximate correlation corrections are added to study the  $\text{HC}\equiv\text{SiF} \rightarrow \text{FHC}=\text{Si}$  and  $\text{HC}\equiv\text{SiLi} \rightarrow \text{LiHC}=\text{Si}$  potential energy surfaces.

## I. Introduction

There has in recent years been a great deal of interest in multiple bonds to silicon. Experimentally,  $\text{C}=\text{Si}^2$  and  $\text{Si}=\text{Si}^3$  moieties have now been isolated, while both experimental and theoretical interest has centered around the nature of such bonding<sup>4-11</sup> and on the relative stabilities of the formal multiple bonds vs. their silylene counterparts.<sup>12-23</sup>

While double bonds to silicon are apparently not prohibitively unstable, triple bonds containing silicon have yet to be detected experimentally. Gordon and Koob<sup>23</sup> have predicted  $\text{C}\equiv\text{Si}$  bond to be much less stable than  $\text{C}=\text{Si}$  bonds relative to their hydrocarbon counterparts. In fact, while two ethynes are predicted to be comparable in stability to tetrahedrane,<sup>24</sup> ethyne + silaethyne is much higher in energy than silatetrahedrane.<sup>25</sup> Similarly, the

(1) Supported in part by National Science Foundation Grant CHE77-16362 and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Table I. Geometries of Silaethyne Isomers<sup>a</sup>

molecule	X	Y	$R_{\text{CSi}}$	$R_1$	$R_2$	$\alpha$	$\beta$
HC≡SiH	H	H	1.590	1.055	1.448	180.0	180.0
HC≡SiF	H	F	1.567	1.054	1.614	180.0	180.0
FC≡SiH	F	H	1.581	1.312	1.442	180.0	180.0
HC≡SiLi	H	Li	1.627	1.062	2.409	180.0	180.0
LiC≡SiH	Li	H	1.648	1.915	1.463	180.0	180.0
FC≡SiF	F	F	1.552	1.320	1.617	180.0	180.0
LiC≡SiF	Li	F	1.640	1.882	1.627	180.0	180.0
FC≡SiLi	F	Li	1.630	1.318	2.391	180.0	180.0
HC≡SiCH <sub>3</sub>	H	CH <sub>3</sub>	1.589	1.056	1.892	180.0	180.0
H <sub>3</sub> CC≡SiH	CH <sub>3</sub>	H	1.594	1.468	1.448	180.0	180.0
H <sub>3</sub> C=Si	H	H	1.730	1.080	1.080	123.19	123.19
FHC=Si	F	H	1.761	1.383	1.078	123.16	125.01
LiHC=Si	Li	H	1.674	2.038	1.074	97.07	156.67
F <sub>2</sub> C=Si	F	F	1.792	1.347	1.347	125.17	125.17
FLiC=Si	F	Li	1.674	1.363	2.085	166.77	94.18
H <sub>3</sub> CCH=Si	CH <sub>3</sub>	H	1.739	1.521	1.084	128.84	117.56
C=SiH <sub>2</sub>	H	H	1.796	1.476	1.476	120.49	120.49
C=SiHF	F	H	1.802	1.629	1.467	122.35	126.58
C=SiLiH <sup>b</sup>	Li	H	1.767	1.973	1.536	171.61	92.79
C=SiF <sub>2</sub>	F	F	1.824	1.611	1.611	127.01	127.01
C=SiFLi	F	Li	1.796	1.655	2.466	117.94	115.60
C=Si(H)CH <sub>3</sub>	CH <sub>3</sub>	H	1.796	1.909	1.481	124.28	117.33

<sup>a</sup> Bond lengths in Å; angles in deg. <sup>b</sup> This molecule rearranges with no barrier to nonlinear HSiClLi. The latter structure is the one quoted here.

relative stabilities of ethyne and vinylidene<sup>26</sup> are dramatically reversed when one carbon is replaced by a silicon.<sup>22</sup> In view of the interest in isolating a carbon-silicon triple bond, it is important to consider the possibility of stabilizing this moiety with some substituent. From a computational point of view, the simplest approach is to investigate single polar substituents, such as F or Li. Fluorine is a particularly appealing possibility because of the strength of Si-F bonds. Both substituents are considered in the present work.

Most recent calculations predict silaethylene and its isomer methylsilylene to be very close in energy.<sup>13,17</sup> Since both isomers are primary products in the vacuum UV photolyses of alkylsilanes,<sup>5</sup> once again, it is of interest to consider substituents that might stabilize one isomer or the other. Nagase and Morokuma<sup>21</sup> have found dimethyl substitution strongly stabilizes silaethylene relative to methylsilylene. This is not surprising since monomethyl substitution occurs preferentially at the silicon in both isomers.<sup>23</sup> In the present work the effect of mono- and difluoro substitution on the relative energies of these isomers is investigated.

The next section summarizes the computational methodology used. This is followed by consideration of silaethynes in section

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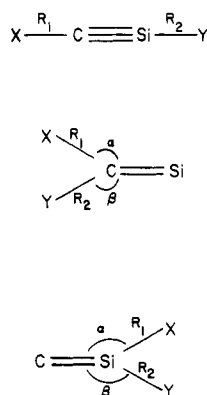


Figure 1. Schematic for silaethynes and isomers.

Table II. Energies and Relative Energies of Silaethyne Isomers<sup>a</sup>

molecule	3-21G//3-21G		6-31G*//3-21G	
	<i>E</i>	$\Delta E$	<i>E</i>	$\Delta E$
H <sub>2</sub> C=Si	-326.14318	0.0	-327.85455	0.0
HC≡SiH	-326.04868	59.3	-327.76488	56.3
C=SiH <sub>2</sub>	-325.98842	97.1	-327.72069	84.0
FHC=Si	-424.43625	0.0	-426.68093	0.0
HC≡SiF	-424.38627	31.4	-426.64668	21.5
C=SiHF	-424.36164	46.8	-426.62870	32.8
FC≡SiH	-424.33939	60.8	-426.58975	57.2
LiHC=Si	-332.97532	0.0	-334.73122	0.0
HC≡SiLi	-332.93721	23.9	-334.69047	25.6
C=SiLiH	-332.89210	52.2	-334.65421	48.3
LiC≡SiH	-332.88235	58.3	-334.63819	58.4
F <sub>2</sub> C=Si	-522.75528	0.0	-525.53288	0.0
C=SiF <sub>2</sub>	-522.74145	8.7	-525.54316	-6.4
FC≡SiF	-522.66491	56.7	-525.46185	44.6
FLiC=Si	-431.27130	0.0	-433.55911	0.0
LiC≡SiF	-431.23365	23.6	-433.53216	16.9
FC=SiLi	-431.24224	18.2	-433.52689	20.2
C=SiFLi	-431.22667	28.0	-433.52392	22.1
H <sub>3</sub> CCH=Si	-364.96106	0.0	-366.88824	0.0
HC≡SiCH <sub>3</sub>	-364.88945	44.9	-366.81486	46.0
H <sub>3</sub> CC≡SiH	-364.87597	53.4	-366.80789	50.4
C=Si(H)CH <sub>3</sub>	-364.82844	83.8	-366.76886	74.9

<sup>a</sup> Energies in hartrees; relative energies in kcal/mol.

## III and silaethylenes in section IV.

## II. Computational Methodology

The geometry optimizations were carried out with the split-valence 3-21G basis set.<sup>27</sup> For all isomers these optimizations were performed with the analytical gradient routines developed for HONDO by King and Dupuis.<sup>28</sup> A similar, numerical, approach<sup>29</sup> was used for constrained optimizations needed for the study of potential energy surfaces. All geometry optimizations were followed by single-point 6-31G\*<sup>30</sup> calculations (denoted 6-31G\*//3-21G). For the isomerization surfaces, the latter SCF calculations were augmented by second-order Moller-Plesset perturbation theory (MP2) correlation corrections.<sup>31</sup>

## III. Silaethynes

A schematic key for the structures of substituted silaethynes and their isomers is given in Figure 1. Initially, the formal ethyne

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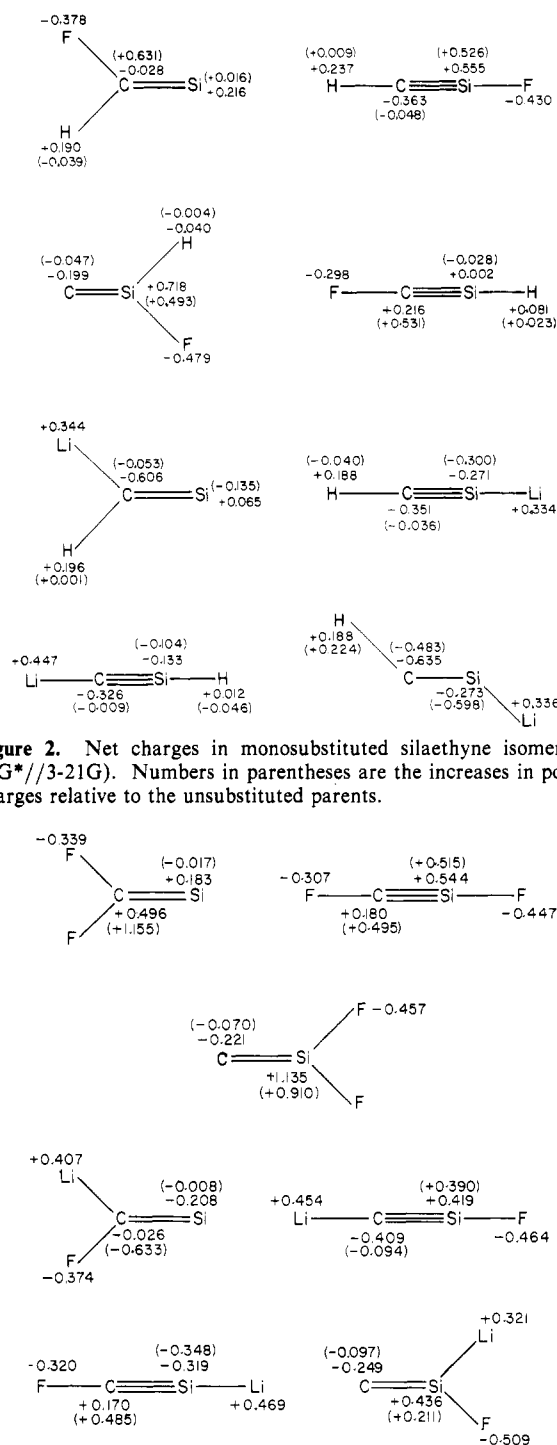


Figure 2. Net charges in monosubstituted silaethyne isomers (6-31G\*//3-21G). Numbers in parentheses are the increases in positive charges relative to the unsubstituted parents.

Figure 3. Net charges in disubstituted silaethyne isomers (6-31G\*//3-21G). Numbers in parentheses are the increases in positive charges relative to the unsubstituted parents.

and vinylidene and silylidene structures were restricted to *C<sub>2v</sub>* and planar *C<sub>s</sub>* symmetry, respectively. The resultant geometries are listed in Table I, and the corresponding total and relative energies for each set of isomers are compared in Table II. The unsubstituted parents and the methyl-substituted species are included in both tables for comparison. The 6-31G\*//3-21G Mulliken charge densities are shown in Figures 2 and 3.

To the extent that bond energy-bond length relationships are valid, it appears that fluorine substitution strengthens the C≡Si bond, with substitution at Si having a greater effect. Conversely, lithium substitution seems to weaken the triple bond, particularly if the substitution occurs at the carbon. This effect on bond lengths is not an obvious  $\pi$  effect since the net  $\pi$  overlap populations in the four monosubstituted silaethynes are essentially the same. The

**Table III.** Geometries along the HCSiX-HXCSi Isomerization Paths<sup>a</sup>

$\alpha$	$R_{CH}$		$R_{CSi}$		$R_{SiX}$		H-C-Si	
	F	Li	F	Li	F	Li	F	Li
180	1.054	1.062	1.567	1.627	1.614	2.409	180.0	180.0
160	1.061	1.062	1.614	1.629	1.615	2.416	147.77	176.09
140	1.068	1.062	1.674	1.635	1.620	2.427	143.49	173.00
120	1.069	1.064	1.739	1.642	1.629	2.434	151.78	171.98
104.35 <sup>b</sup>	1.070		1.791		1.643		164.02	
100	1.070	1.065	1.802	1.648	1.646	2.425	167.87	187.49
90	1.070		1.816		1.659		181.83	
80 <sup>c</sup>	1.069	1.066	1.807	1.654	1.685	2.423	180.01	188.20
60	1.062	1.068	1.736	1.665	1.825	2.533	180.00	194.32
40	1.064	1.077	1.734	1.678	2.313	2.959	155.13	151.00
$\alpha_{min}^d$	1.078	1.074	1.761	1.674				

<sup>a</sup> Bond lengths in Å; angles in deg. <sup>b</sup> Minimum on 3-21G surface. <sup>c</sup> The structure at  $\alpha = 80^\circ$  was tested for nonplanarity and returned to planar. <sup>d</sup>  $\alpha_{min}$  refers to XHC=Si.

mixed disubstituted compounds both appear to be dominated by the lithium substitution, since the C=Si bond lengthens in both. Methyl substitution has virtually no impact on the bond length.

The effect of substituents on the C=Si bond in silylenes and vinylidenes is just the reverse of that discussed in the preceding paragraph. Here, fluorine substitution results in a longer C=Si bond, while lithium has the opposite effect. As for the silaethynes, methyl substitution has little effect. Here again, the C-Si  $\pi$  overlap populations are quite similar for all of these molecules. One carbene, C=SiLi<sub>2</sub>, is unstable and rearranges to a planar, nonlinear, HSiLi structure.

It is clear from Table II that substitution of fluorine at silicon dramatically lowers the relative energy of the corresponding isomer. Thus, the energy of HC=SiF relative to the more stable silylidene is 45 kcal/mol lower than the unsubstituted analogue. The same is true for the carbene C=SiHF. On the other hand, fluorine substitution at the carbon has a negligible effect. The stabilizing effect of fluorine is certainly due in part to the strength of Si-F bonds. An additional factor is the stabilizing effect of fluorine on C=Si vs. the destabilizing effect on C=Si. The effect of fluorine substitution is the most striking in the case of C=SiF<sub>2</sub>. Relative to the unsubstituted compounds, the normally rather unstable carbene becomes comparable in energy with the isomeric silylidene.

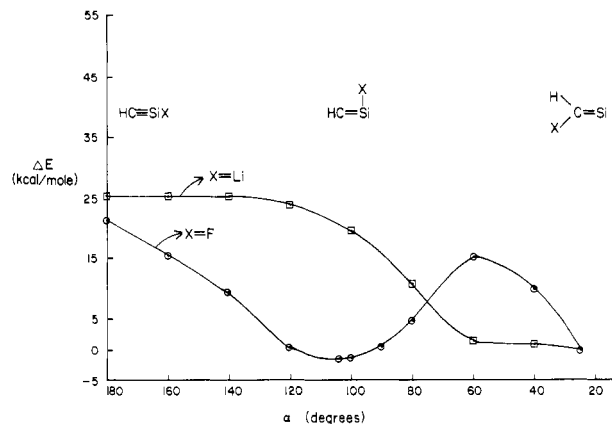
Perhaps more surprising is the stabilizing effect lithium appears to have when it is attached to Si. Since, according to our earlier discussion, Li substitution at the carbon stabilizes C=Si and Li substitution at the silicon destabilizes C=Si, the change in C-Si bonding is opposite to the change in relative stabilities of the silylidene and silaethyne. A possible explanation for the latter is the fact that the Si-Li bond in HC=SiLi is 0.12 Å shorter than in SiH<sub>3</sub>Li, whereas the C-Li bond in LiHC=Si is 0.04 Å longer than in CH<sub>3</sub>Li, according to 3-21G calculations. Thus, the Si-Li bond in the silaethyne appears to be unusually strong, while the C-Li bond in the silylidene is somewhat weaker than "normal".

The mixed substitutions still leave the silylidene as the most stable structure, with the remaining three isomers being similar in energy.

Finally, note that all of the relative energies in Table II are well represented at the split-valence level. The polarization functions only result in a quantitative adjustment.

The charge density distributions in Figures 2 and 3 contain few surprises. Fluorine substitution induces a large positive charge on the attached atom and a small increase in electron density on geminal atoms, while lithium has the reverse effect. Once again, the difluoro compounds are most striking, with the silicon of the carbene isomer predicted to have a positive charge of greater than one.

In a previous paper,<sup>22</sup> it was found that silaethyne rearranges with no barrier to silylidene at the SCF level. Inclusion of correlation corrections introduces an energy barrier separating the two isomers, with silaethyne actually becoming somewhat nonlinear at the silicon end. The analogous potential energy surfaces

**Figure 4.** 6-31G\*/3-21G relative energies (kcal/mol) along the HCSiX → HXCSi surface.**Table IV.** Change in C-Si Bond Length along HCSiX-HXCSi Isomerization Path<sup>a</sup>

$\alpha$	$\Delta R(\text{HC}\equiv\text{SiH})^b$	$\Delta(\Delta E)^c$	$\Delta R(\text{HC}\equiv\text{SiF})^b$	$\Delta R(\text{HC}\equiv\text{SiLi})^b$
180	-0.14	-16.2	-0.19	-0.05
160	-0.13	-17.0	-0.15	-0.05
140	-0.10	-14.9	-0.09	-0.04
120	-0.05	-4.9	-0.02	-0.03
104			0.03	
100	-0.01	5.5	0.04	-0.03
80	0.0	6.9	0.05	-0.02
60	-0.04	-1.5	-0.02	-0.01
40	-0.05	-4.0	-0.03	0.0
$\alpha_{min}^d$	0.0	0.0	0.0	0.0

<sup>a</sup> Bond lengths in Å; energies in kcal/mol. <sup>b</sup>  $\Delta R = R - R(\text{XHC}=\text{Si})$ . <sup>c</sup>  $\Delta(\Delta E) = \Delta E(\text{MP2}) - \Delta E(\text{SCF})$ . <sup>d</sup>  $\alpha_{min}$  corresponds to XHC=Si.

were investigated for the two pairs of monosubstituted species. Because distortions from planarity were not found to be important in the previous work,<sup>22</sup> C<sub>v</sub> symmetry was maintained throughout, and the H-Si-C angle, hereafter referred to as  $\alpha$ , was chosen to be the reaction coordinate.

The structures of the two systems along the reaction path are listed in Table III, and the SCF energies relative to the silylidene are plotted in Figure 4. The lithium curve looks very much like that of the unsubstituted parent,<sup>22</sup> with no apparent barrier to rearrangement from the ethyne to the silylidene structure. With the 3-21G basis set, the linear structure actually has a positive definite force constant matrix, indicating the existence of a true minimum at this geometry and a small (1 kcal/mol) barrier to isomerization. Refinement of the geometries with 6-31G\* might yield the same result since the 6-31G\*/3-21G potential energy curve is nearly linear between  $\alpha = 180^\circ$  and  $\alpha = 140^\circ$ .

In contrast to the results for X = H and Li, the fluoro-substituted system already displays a minimum at a rather distorted silaethyne geometry at the SCF level. In fact, this distorted structure is predicted to be slightly (1.5 kcal/mol) lower in energy than the silylidene and to be separated from the latter by a 16.8 kcal/mol barrier. Thus, fluorine substitution not only stabilizes the formal triple-bond structure relative to the silylidene isomer but also results in a very distorted structure whose stability is comparable to that of the silylidene.

For the isomerization path of the unsubstituted species, it was noted<sup>22</sup> that much of the change in relative energies is due to the change in the correlation correction in the C-Si bond. A simple way of predicting the qualitative effect of correlation on the shape of the potential energy curve is therefore to assume that the correlation correction will diminish as the bond lengthens. That this is roughly correct is illustrated in Table IV, where the change in  $R_{CSi}$  is compared with the change in  $\Delta E$ . Extending this result to the fluoro compounds, one would expect both the minimum at  $\alpha = 104^\circ$  and the barrier at  $\alpha = 60^\circ$  to shift to larger angles when correlation corrections are added. For lithium, one expects

Table V. Total and Relative Energies for Fluoro-Substituted Silaethylene Isomers<sup>a</sup>

molecule	3-21G//3-21G		6-31G*//3-21G		6-31G*+MP2//3-21G	
	<i>E</i>	$\Delta E$	<i>E</i>	$\Delta E$	<i>E</i>	$\Delta E$
H <sub>2</sub> C=SiH <sub>2</sub>	-327.30167	0.0	-329.03598	0.0	-329.25025	0.0
CH <sub>3</sub> SiH	-327.32543	-14.9	-329.04456	-5.2	-329.24693	2.1
SiH <sub>3</sub> CH	-327.20055	63.4	-328.94935	54.4		
CH <sub>2</sub> =SiHF	-425.68656	0.0	-427.95200	0.0		0.0
CH <sub>3</sub> -SiF	-425.73174	-28.3	-427.98326	-19.6		-9.7 <sup>b</sup>
F- <i>trans</i> -CH <sub>2</sub> FSiH	-425.62627	37.8	-427.88157	44.2		
F- <i>gauche</i> -CH <sub>2</sub> FSiH	-425.62152	40.8				
CHF=SiH <sub>2</sub>	-425.60051	54.0	-427.86611	53.9		
SiH <sub>3</sub> -CF	-425.54298	90.1	-427.81883	83.6		
F- <i>trans</i> -SiH <sub>2</sub> FCH	-425.59301	58.7	-427.87461	48.6		
F- <i>gauche</i> -SiH <sub>2</sub> FCH	-425.59017	60.5				
CH <sub>2</sub> =SiF <sub>2</sub>	-524.07110	0.0	-526.86954	0.0		
<i>trans</i> -CH <sub>2</sub> FSiF	-524.03118	25.0	-526.81698	33.0		
<i>gauche</i> -CH <sub>2</sub> FSiF	-524.02576	28.4				
<i>trans</i> -CHF=SiHF	-523.97794	58.4	-526.77581	58.8		
H- <i>trans</i> -CHF <sub>2</sub> SiH	-523.94801	77.2	-526.73481	84.5		
H- <i>gauche</i> -CHF <sub>2</sub> SiH	-523.94669	78.0				
CF <sub>2</sub> =SiH <sub>2</sub>	-523.91965	95.0	-526.71709	95.7		
H- <i>trans</i> -SiHF <sub>2</sub> CH	-523.99209	49.6	-526.80412	41.0		
H- <i>gauche</i> -SiHF <sub>2</sub> CH	-523.99140	50.0				
H- <i>trans</i> -SiH <sub>2</sub> FCF	-523.93303	86.6	nonconvergent			
H- <i>gauche</i> -SiH <sub>2</sub> FCF	-523.92951	88.8				
CH <sub>2</sub> =Si(H)CH <sub>3</sub>	-366.14165	0.0	-368.08348	0.0		
(CH <sub>3</sub> ) <sub>2</sub> Si	-366.16648	-15.6	-368.09168	-5.1		
CH <sub>3</sub> CH <sub>2</sub> SiH	-366.14132	0.2	-368.07691	4.1		
CH <sub>3</sub> CH=SiH <sub>2</sub>	-366.12028	13.4	-368.06987	8.5		

<sup>a</sup> The *gauche* isomers were obtained by rigid rotation from *trans*; total energies in hartrees; relative energies in kcal/mol. <sup>b</sup> Predicted by using additivity assumption; see text.

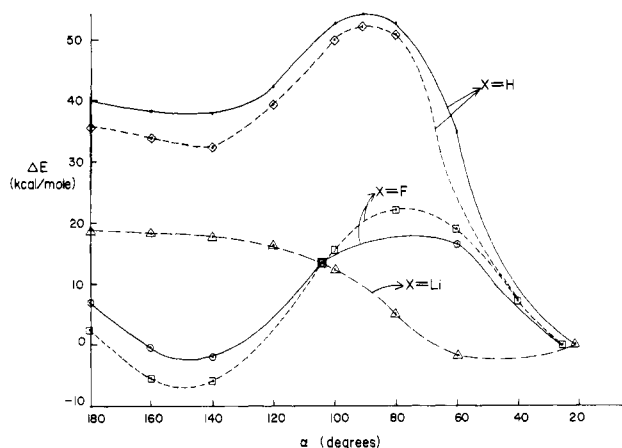


Figure 5. 6-31G\* + MP2//3-21G relative energies (kcal/mol) along the HCSiX → HXCsi surface. Dotted curves are predicted by assuming additivity of polarization function and correlation effects.

a much smaller effect since there is very little change in bond length.

As the number of heavy atoms in a molecule increases, the computer time required to investigate correlation effects increases dramatically for a given basis set. Fortunately, it has been noted recently that the changes in relative energies due to the addition of polarization functions to the basis set and to the addition of correlation corrections are often roughly additive.<sup>32-34</sup> For example, the 6-31G\* + MP2 isomerization energies and barrier heights for the 1,2 hydrogen shifts studied by Pople<sup>35</sup> are predicted to within 15% by assuming additivity.<sup>36</sup> While it is not suggested

(32) M. Dupuis, American Conference on Theoretical Chemistry, Boulder, CO, June 1981.

(33) H. F. Schaeffer III, private communication.

(34) M. L. McKee and W. N. Lipscomb, *J. Am. Chem. Soc.*, **103**, 4673 (1981).

(35) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem.*, **14**, 545 (1978).

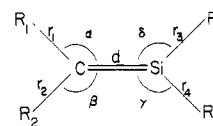


Figure 6. Schematic for geometries of silaethylenes.

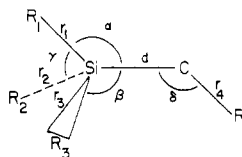
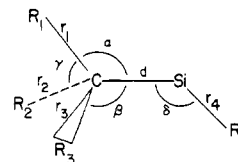


Figure 7. Schematics for geometries of silylenes and carbenes.

that such an approach will always work, it does provide a means of estimating correlation effects at a considerably reduced cost. Figure 5 illustrates the utility of this approach for the potential energy curves of interest in this paper. For the unsubstituted molecules, the predicted curve parallels the actual one, with the absolute deviations being within 15% for all points. For the fluorine-containing compounds, fewer 6-31G\* + MP2 points were actually calculated. The absolute deviations of the predicted  $\Delta E$ 's relative to those actually calculated are larger than those for the unsubstituted system; nonetheless, the general shape of the curve is correctly predicted, as is the shift in the curve relative to that

(36) K. Krogh-Jespersen and M. S. Gordon, unpublished work. 6-31G results rather than 3-21G throughout for additivity predictions to ensure that only polarization effects were being accounted for. However, the two split-valence basis sets predict  $\Delta E$ 's that are virtually identical.

Table VI. Geometries of Silaethylenes<sup>a</sup>

R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	d	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>	α	β	γ	δ
H	H	H	H	1.718	1.074	1.074	1.474	1.474	122.64	122.64	122.19	122.19
H	H	H	F	1.698	1.073	1.074	1.465	1.628	123.15	120.37	127.69	127.99
H	F	H	H	1.730	1.072	1.378	1.471	1.469	125.77	121.87	122.04	118.42
H	H	H	CH <sub>3</sub>	1.716	1.074	1.074	1.482	1.907	122.73	121.91	124.74	120.14
H	CH <sub>3</sub>	H	H	1.725	1.076	1.514	1.477	1.479	120.06	124.56	123.80	120.11
H	H	F	F	1.684	1.072	1.072	1.610	1.610	121.25	121.25	127.61	127.61
F	F	H	H	1.739	1.344	1.344	1.464	1.464	125.14	125.14	117.84	117.84
H	F	H	F	1.712	1.069	1.385	1.459	1.628	126.09	104.50	129.16	106.98

<sup>a</sup> Bond lengths in Å; angles in deg; see Figure 6 for explanation of geometric parameters.

Table VII. Geometries of Silylenes and Carbenes<sup>a</sup>

R <sub>1</sub>	R <sub>2</sub>	R <sub>4</sub>	d	r <sub>1</sub>	r <sub>2</sub>	r <sub>4</sub>	α	β	γ	δ
Silylenes										
H	H	H	1.947	1.082	1.088	1.536	112.88	109.96	108.76	94.81
H	H	F	1.929	1.085	1.089	1.642	110.96	110.76	108.74	98.26
F	H	H	1.952	1.419	1.087	1.538	111.09	110.63	108.79	91.67
H	H	CH <sub>3</sub>	1.953	1.083	1.089	1.953	110.55	111.35	108.43	99.63
CH <sub>3</sub>	H	H	1.951	1.546	1.091	1.538	110.01	114.67	108.40	95.92
F	H	F	1.950	1.419	1.085	1.641	107.44	112.21	109.02	94.53
H	F	H	1.986	1.077	1.392	1.517	117.36	107.40	107.68	92.40
Carbenes										
H	H	H	1.955	1.479	1.494	1.100	111.37	108.85	109.17	110.64
H	H	F	2.002	1.483	1.486	1.357	110.56	107.14	110.88	102.70
F	H	H	1.913	1.630	1.481	1.095	111.04	108.38	108.10	114.56
F	H	F	1.979	1.629	1.475	1.358	110.15	106.56	109.67	100.72
H	F	H	1.919	1.457	1.620	1.091	112.45	109.54	109.40	115.99

<sup>a</sup> Bond lengths in Å; angles in deg; see Figure 7 for explanation of geometric parameters.

in Figure 4. The latter is also consistent with the shift predicted on the basis of the C–Si bond length variations. With the MP2 corrections included, the linear structure is only a few kcal/mol above the silylidene, and the nonlinear silaethyne is still predicted to be the absolute minimum on the curve. For the lithium-containing molecules, additivity was assumed, and, as expected, little change is predicted relative to the SCF curve.

#### IV. Silaethylenes

Figures 6 and 7 contain schematics for the geometrical parameters used in Tables VI and VII to describe the structures of fluoro-substituted ethylenes and silylenes and carbenes, respectively. The corresponding total and relative energies are listed in Table V. Only the most stable structures were optimized, the rotational isomers being obtained by rigid rotation. In general, it is found that fluorine substitution at the silicon shortens the carbon–silicon bond lengths in all three types of molecules, while fluorine substitution at the carbon has the opposite effect. The effect of methyl substitution on these bond lengths is rather small.

As noted earlier for the silaethyne isomers, fluorine substitution at silicon tends to stabilize a structure.<sup>37</sup> This effect appears to be greater for methylsilylene than for silaethylene, since the energy of the former is preferentially lowered on fluorine substitution. Similarly, fluorine substitution at silicon preferentially lowers the carbene relative to silaethylene. It has been noted previously<sup>13,17</sup> that both silicon d functions and correlation corrections preferentially lower the energy of silaethylene relative to methylsilylene. As shown in Table V, the combined effects leave methylsilylene slightly lower in energy. By use of the additivity approximation described in the previous section, a similar result is predicted for fluoro-substituted silaethylene vs. methylsilylene. Here, however, the 6-31G\* SCF  $\Delta E$  is rather large, so the silylene is still much lower in energy after correlation corrections with MP2.

The effect of difluoro substitution is interesting since the second fluorine can be attached to the silicon in silaethylene but obviously not in methylsilylene. Thus, one expects the silaethylene to be preferentially stabilized. Indeed, this is the case, and the effect may be seen to be approximately additive: The first fluorine

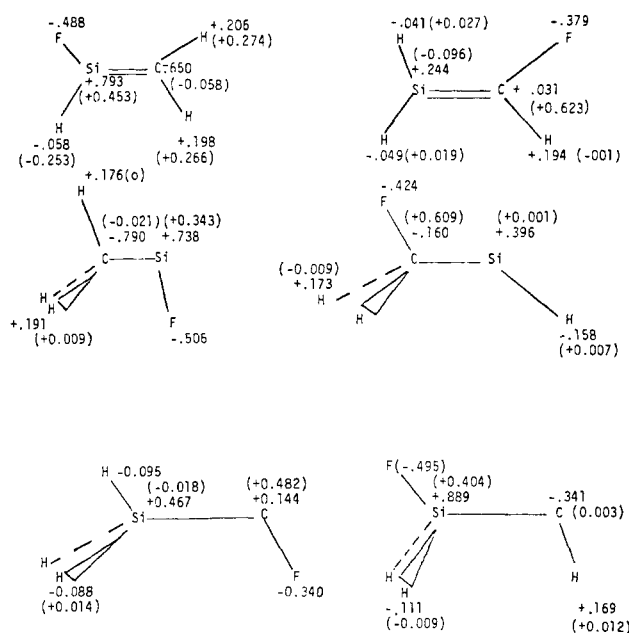
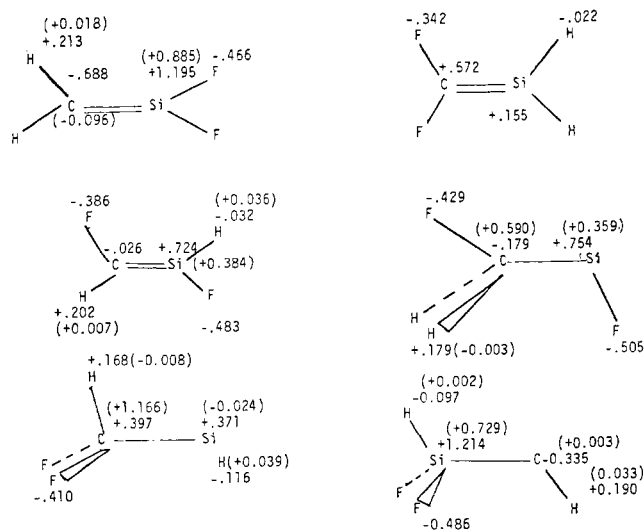


Figure 8. 6-31G\*\*/3-21G charges in monofluoro isomers. Numbers in parentheses are the increases in positive charges relative to unsubstituted parents.

stabilizes CH<sub>3</sub>–SiF relative to CH<sub>2</sub>–SiHF by 14.4 kcal/mol (relative to the unsubstituted species), but destabilizes CH<sub>2</sub>F–SiH relative to CH<sub>2</sub>–SiHF by 49.4 kcal/mol. If the two effects are additive, CH<sub>2</sub>–SiF<sub>2</sub> should be stabilized by 35 kcal/mol relative to CH<sub>2</sub>F–SiF. The actual 6-31G\* calculation results in a predicted stabilization of 38.2 kcal/mol. As noted in the previous section for silaethyne isomers, difluoro substitution at silicon is so stabilizing that a carbene SiHF<sub>2</sub>CH is actually found to be more stable than CHF=SiHF.

The effect of methyl substitution is smaller than that of fluorine, but, as pointed out in earlier papers, substitution is again preferred at silicon. When the additivity arguments of the previous paragraph are used, the effect of dimethyl substitution should be to

(37) This has also been observed by Nagase and Morokuma: S. Nagase, private communication.



**Figure 9.** 6-31G\*/3-21G charges in difluoro isomers. Numbers in parentheses are the increases in positive charges relative to unsubstituted parents.

stabilize 1,1-dimethyl-1-silaethylene by 9.3 kcal/mol relative to methylethylsilylene. While we have not included the dimethylated species in this work, Hanamura, Nagase, and Morokuma<sup>20</sup> do indeed predict the silaethylene to be rather more stable in this case.

The Mulliken charge densities in the fluoro-substituted species are displayed in Figures 8 and 9. As expected, fluorine substitution increases the positive charge of the attached atom and, through  $\pi$  back-bonding, increases the electron density on the geminal heavy atom. Typically, an increase in positive charge on silicon correlates with a stabilized structure and vice versa.

## V. Conclusions

The main conclusions to be drawn from this work are as follows: (a) Fluorine substitution dramatically stabilizes silicon to the degree that normally rather unstable species, such as carbenes, become competitive in stability with their isomers. In the case of silaethyne, a distorted 1-fluoro-1-silaethyne is predicted to be the most stable  $\text{CSiHF}$  structure. Similarly,  $\text{CH}_2=\text{SiF}_2$  is predicted to be much more stable than  $\text{CH}_2\text{F}-\text{SiF}$ . (b) While d orbitals on silicon seem to preferentially stabilize formal triple bonds relative to double bonds and double bonds relative to single bonds, the general effect is quantitative rather than qualitative. Thus, most trends are correctly predicted by the 3-21G basis set. (c) The effects of polarization functions and correlation corrections seem to be approximately additive. While this is certainly not a foolproof approach, it does provide a fast, approximate means for estimating correlation effects.

**Acknowledgment.** I have benefited from stimulating discussions with Professors K. Krogh-Jespersen, R. D. Koob, and P. Boudjouk. The computer time made available by the North Dakota State University Center is gratefully acknowledged.

**Registry No.**  $\text{H}_2\text{C}=\text{Si}$ , 65632-07-7;  $\text{HC}\equiv\text{SiH}$ , 59164-06-6;  $\text{C}=\text{SiH}_2$ , 74694-33-0;  $\text{FHC}=\text{Si}$ , 81874-91-1;  $\text{HC}\equiv\text{SiF}$ , 81874-92-2;  $\text{C}=\text{SiHF}$ , 81874-93-3;  $\text{FC}\equiv\text{SiH}$ , 81874-94-4;  $\text{LiHC}=\text{Si}$ , 81874-95-5;  $\text{HC}\equiv\text{SiLi}$ , 81874-96-6;  $\text{C}=\text{SiLiH}$ , 81874-97-7;  $\text{LiC}\equiv\text{SiH}$ , 81874-98-8;  $\text{F}_2\text{C}=\text{Si}$ , 81874-99-9;  $\text{C}=\text{SiF}_2$ , 81875-00-5;  $\text{FC}\equiv\text{SiF}$ , 81875-01-6;  $\text{FLiC}=\text{Si}$ , 81875-02-7;  $\text{LiC}=\text{SiF}$ , 81875-03-8;  $\text{FC}\equiv\text{SiLi}$ , 81875-04-9;  $\text{C}=\text{SiFLi}$ , 81875-05-0;  $\text{H}_3\text{CCH}=\text{Si}$ , 78442-51-0;  $\text{HC}\equiv\text{SiCH}_3$ , 81096-75-8;  $\text{H}_3\text{C}-\text{C}\equiv\text{SiH}$ , 78289-00-6;  $\text{C}=\text{Si}(\text{H})\text{CH}_3$ , 78442-56-5;  $\text{H}_2\text{C}=\text{SiH}_2$ , 51067-84-6;  $\text{CH}_3\text{SiH}$ , 55544-30-4;  $\text{SiH}_3\text{CH}$ , 66605-30-9;  $\text{CH}_2=\text{SiHF}$ , 81875-06-1;  $\text{CH}_3-\text{SiF}$ , 81875-07-2;  $\text{CH}_2\text{FSiH}$ , 81875-08-3;  $\text{CHF}=\text{SiH}_2$ , 81897-63-4;  $\text{SiH}_3-\text{CF}$ , 81875-09-4;  $\text{SiH}_2\text{FCH}$ , 81875-10-7;  $\text{CH}_2=\text{SiF}_2$ , 51675-50-4;  $\text{CH}_2\text{FSiF}$ , 81875-11-8;  $\text{CHF}=\text{SiHF}$ , 81875-12-9;  $\text{CHF}_2-\text{SiH}$ , 81875-13-0;  $\text{CF}_2=\text{SiH}_2$ , 51675-51-5;  $\text{SiHF}_2\text{CH}$ , 81875-14-1;  $\text{SiH}_2\text{FCF}$ , 81875-15-2;  $\text{CH}_2=\text{Si}(\text{H})\text{CH}_3$ , 38063-40-0;  $(\text{CH}_3)_2\text{Si}$ , 6376-86-9;  $\text{CH}_3\text{CH}_2\text{SiH}$ , 81875-16-3;  $\text{CH}_3\text{CH}=\text{SiH}_2$ , 76444-54-7.

## Cytochrome Oxidase Models. 3. Spin Coupling across Imidazolate Bridges in Binuclear Metalloporphyrin Complexes of Iron and Copper<sup>1</sup>

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Contribution from the Department of Chemistry, William Marsh Rice University, Houston, Texas 77001. Received July 27, 1981

**Abstract:** Four new  $\mu$ -imidazolato binuclear metalloporphyrin compounds of  $\text{Fe}^{\text{III}}$  and  $\text{Cu}^{\text{II}}$  or  $\text{Zn}^{\text{II}}$  have been synthesized, isolated, and characterized in the solid state as model systems for the active site of cytochrome *c* oxidase. The compounds have been derived from  $[\text{Fe}^{\text{III}}(\text{TPP})\text{X}]$  ( $\text{X} = \text{Cl}^-$  or  $\text{OSO}_2\text{CF}_3^-$ ) and  $[\text{M}^{\text{II}}(\text{imidH})_2\text{DAP}]^{2+}$  ( $\text{M} = \text{Zn}$  or  $\text{Cu}$ ) to yield species containing the following  $\mu$ -imidazolato cationic cores:  $[\text{ClFe}^{\text{III}}(\text{imid})\text{Zn}^{\text{II}}]^+$  (1),  $[\text{ClFe}^{\text{III}}(\text{imid})\text{Cu}^{\text{II}}]^+$  (2),  $[(\text{OSO}_2\text{CF}_3)-\text{Fe}^{\text{III}}(\text{imid})\text{Zn}^{\text{II}}]^+$  (3), and  $[(\text{OSO}_2\text{CF}_3)-\text{Fe}^{\text{III}}(\text{imid})\text{Cu}^{\text{II}}]^+$  (4). Comparative magnetochemical (15–300 K), Mössbauer (100 K), and EPR (10 K) studies of 1 and 2 are consistent with essentially identical electronic environments about  $\text{Fe}^{\text{III}}$  ( $S = 1/2$ ) with  $-J_{\text{Fe}^{\text{III}}-\text{Cu}^{\text{II}}} \lesssim 15 \text{ cm}^{-1}$  in 2. Similar comparative studies of 3 and 4 are somewhat complicated by the presence of what appears to be two distinct molecular species of  $S = 5/2$  and  $1/2$  coexisting in the same crystalline sample. The magnetic properties and silent EPR behavior of 4 have been rationalized in terms of a ( $S = 0, 2$ ) mixture arising from strong antiferromagnetic coupling between  $\text{Fe}^{\text{III}}$  ( $S = 1/2, 5/2$ ) and  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ), where  $-J_{\text{Fe}^{\text{III}}-\text{Cu}^{\text{II}}} \gtrsim 200 \text{ cm}^{-1}$ . The implication of this result to the possible active-site structure of oxidase has been briefly considered.

Cytochrome oxidase is the respiratory enzyme that catalytically reduces 1 mol of dioxygen to 2 mol of water ( $\text{O}_2 + 4\text{H}^+ + 4e^-$

$\rightarrow 2\text{H}_2\text{O}$ ) with the concomitant release of energy, which is stored in the ADP-ATP cycle.<sup>3</sup> The enzyme contains four metal centers