

⊕~~~~~ = Dioctadecyldimethylammonium cation

Figure 6. An idealized model for CdS-sensitized photoreduction of water by PhSH in aqueous DODAC or DODAB vesicles. The position of the colloid is assumed to be similar to that in anionic DHP vesicles.²⁷

20 h of irradiation were found to be slightly higher in the two than in the one-step preparation (Table I).

The exact position of the CdS/Rh particles with respect to the membrane cannot be assessed with certainty from the present data.

However, due to the efficient fluorescence quenching and electron transfer achieved by PhSH, the semiconductor particle is probably in direct contact with the hydrophobic part of the membrane. This hypothesis is supported by the low quenching efficiency of externally adsorbed cations such as methylviologen or Rh³⁺ for CdS in negatively charged vesicles.²⁷ Figure 6 is an idealized model of CdS-sensitized water reduction by visible light in the presence of PhSH as a sacrificial electron donor.

Conclusion

A number of significant results have been reported in the present work. Specifically, (i) in situ formation of rhodium-coated CdS particles could be accomplished in positively charged vesicles upon complexation with EDTA; (ii) formation of CdS particles outside of the vesicles is at least as efficient as that distributed on both sides; and (iii) catalyst coating can be achieved by visible light irradiation in the presence of a suitable electron donor. These observations substantially simplify the required procedures for artificial photosynthesis by surfactant vesicle entrapped, catalyst-coated, colloidal semiconductors.

Acknowledgment. Support of this work by the Department of Energy is gratefully acknowledged. F.N. gratefully acknowledges CNPq Brazil for a fellowship.

Registry No. H₂, 1333-74-0; DODAC, 107-64-2; DODAB, 3700-67-2; EDTA, 60-00-4; MVCl₂, 1910-42-5; CdS, 1306-23-6; Rh, 7440-16-6; PhSH, 108-98-5.

SiH₂ + SiH₃F → Si₂H₅F. An ab Initio Study of Silylene Insertion into a Silicon-Fluorine Bond

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Reactants, cluster, transition structure, and product were optimized at HF/3-21G and HF/6-31G*; relative energies have been calculated at MP4SDQ/6-31G* and zero point energies at HF/3-21G. When silylene approaches silyl fluoride, a stable complex (23 kJ mol⁻¹ lower than reactants) is formed with the fluorine lone pairs donating to the silylene empty p orbital. The transition structure lies ca. 16 kJ mol⁻¹ above the reactants. Improvements in the basis set and inclusion of triple excitations in the MP4 energy may reduce the barrier to 10 kJ mol⁻¹. The barrier to insertion is predicted to be 0-5 kJ mol⁻¹ lower than the SiH₂ + HF reaction. The transition structure can be viewed equally well as a SiH₂ insertion or a [1,2] fluorine shift in Si₂H₅F. In both the cluster and the transition state, the SiH₃ group is fairly free to rotate.

Introduction

Silylene insertion reactions have received considerable attention in recent years, experimentally as well as theoretically. Silylenes arise as reactive intermediates in organosilicon chemistry and in the pyrolysis of substituted silanes.¹ They are also thought to be important in chemical vapor deposition of silicon films² and in the etching of silicon surfaces.³

Silylene insertions into single bonds have been observed for hydrogen molecule; X-H bonds, where X = N, O, F, Si, P, S, Cl; C-O; Si-O and Si-Si; but not for C-C or C-Si bonds.¹ There appears to be no barrier for insertion into Si-H, while a 23 kJ mol⁻¹ barrier has been obtained⁴ for SiH₂ + H₂ and 88 kJ mol⁻¹ reported⁵ for SiH₂ + CH₄. For molecules with lone pairs, the insertion is proposed to proceed via a zwitterionic or ylid-like intermediate followed by a rearrangement.¹

To date, theoretical studies of silylene insertions have been concentrated on H₂ and on hydrides of first- and second-row atoms.

Gordon⁶ found a 36 kJ mol⁻¹ barrier to SiH₂ insertion into H₂ (HF/3-21G optimization followed by single-point calculations at MP2/6-31G**). Schaefer et al.⁷ performed optimizations with MCSCF calculations with a DZ + P basis set followed by multireference CISD and obtained a smaller barrier. Binkley and Frisch⁸ report that the barrier disappears if very large basis sets are used and correlation energy is taken into account. Sosa and

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* Fellow of the Alfred P. Sloan Foundation, 1981-1983.

TABLE I: Total and Relative Energies^a

level	reactants	complex		transition structures			product
		A	B	C	D	E	
Total Energies							
HF/3-21G	-676.558 34	-676.584 97	-676.546 07	-676.546 07	-676.543 17	-676.546 43	-676.625 17
HF/6-31G*	-680.148 18	-680.156 78	-680.156 61	-680.124 15	-680.127 64	-680.127 87	-680.225 84
MP2/6-31G*	-680.466 78	-680.480 17	-680.479 63	-680.463 08	-680.469 97	-680.469 59	-680.554 87
MP3/6-31G*	-680.494 67	-680.507 29	-680.506 78	-680.487 15	-680.493 01	-680.492 85	-680.579 93
MP4/6-31G*	-680.507 35	-680.519 95	-680.519 43	-680.499 86	-680.505 97	-680.505 73	-680.591 19
ZPE/3-21G	107.2	117.4	117.3	118.6	118.6	119.6	122.6
Relative Energies							
HF/3-21G	0	-70.0	-69.9	32.2	39.8	31.3	-175.4
HF/6-31G*	0	-22.6	-22.1	63.1	53.9	53.3	-203.9
MP2/6-31G*	0	-35.1	-33.7	9.7	-8.4	-7.4	-231.3
MP3/6-31G*	0	-33.1	-31.8	19.7	4.4	4.8	-223.9
MP4/6-31G*	0	-33.1	-31.7	19.7	3.6	4.3	-220.1
ΔZPE/3-21G	0	10.2	11.4	11.4	11.4	12.4	15.4
MP4/6-31G* + ΔZPE	0	-22.9	-21.6	31.1	15.0	16.7	-204.7

^aTotal energies in au, 1 au = 2625.5 kJ mol⁻¹; zero point energies and relative energies in kJ mol⁻¹.

Schlegel⁹ found that fluorine substitution of silylene increases the H₂ insertion barrier by 80–140 kJ mol⁻¹ per fluorine. In a study on SiH₂ + H₂O, Raghavachari et al.¹⁰ found a relatively tightly bound complex prior to the transition state and a large barrier for the rearrangement of this complex to products. These calculations led to a larger investigation of SiH₂ + XH_n, X = N, O, F, P, S, Cl by Raghavachari, Chandrasekhar, Gordon, and Dykema.¹¹ In each case, stable complexes are found in which the lone pair on the heteroatom interacts with the empty p_π orbital on SiH₂. Rearrangement of the complex to the product in general was found to have a sizeable activation energy. By comparison SiH₂ + CH₄ and SiH₂ + SiH₄ do not appear to form complexes and only the former has a barrier to insertion.¹²

In the present paper we report the first ab initio calculation on silylene insertion into a two heavy atom covalent bond. Our study focuses on the Si–F bond in SiH₃F and serves as a model for insertion into SiF₄ or into an Si–F bond on a silicon surface. Insertion of SiH₂ into an Si–H bond in SiH₃F is also possible and will be the subject of a separate study.

Methods

Ab initio molecular orbital calculations were performed with the GAUSSIAN 82 system¹³ using split valence (3-21G)¹⁴ and polarization (6-31G*)¹⁵ basis sets. All equilibrium geometries and transition structures were fully optimized with analytical gradient methods¹⁶ at the Hartree–Fock level. Electron correlation energy was estimated from Møller–Plesset perturbation theory up to fourth order, including all single, double, and quadruple excitations (MP4SDQ, frozen core).¹⁷ Vibrational frequencies and zero point energies were obtained from analytical second derivatives¹⁸ calculated at the HF/3-21G level by using the HF/3-21G optimized geometry. Molecular orbitals were plotted on a Printronix MVP

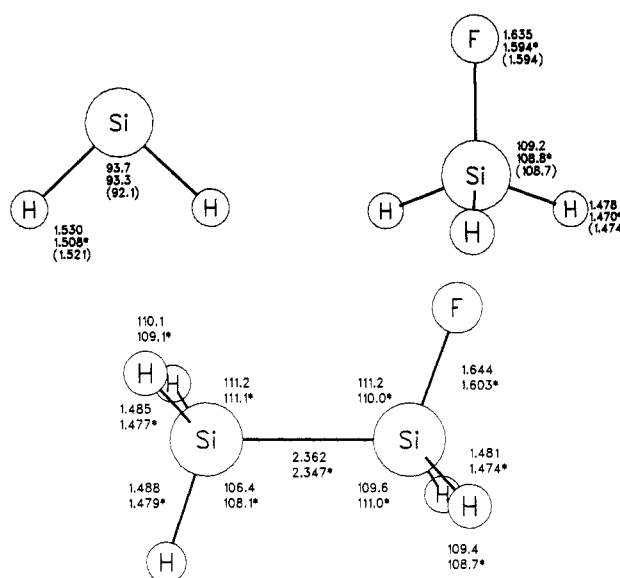


Figure 1. Reactant and product geometries (HF/3-21G optimized, no superscript; HF/6-31G* optimized, asterisks; experimental values in parentheses).

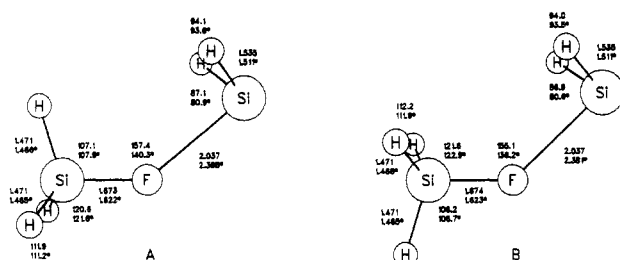


Figure 2. Complex between SiH₂ and SiH₃F. Structure A is the minimum energy conformation, while B is a local maximum with respect to rotation of the SiH₃ group (HF/3-21G optimized, no superscript; HF/6-31G* optimized, asterisk).

dot line printer with a program written by the authors, based on algorithms published by Hehre et al.¹⁹ The contour shells enclose 70% of the electrons.

Results and Discussion

Structures. The optimized geometries for SiH₂ + SiH₃F → Si₂H₅F are collected in Figures 1–3; the corresponding energies are in Table I. The reactants have been published previously but

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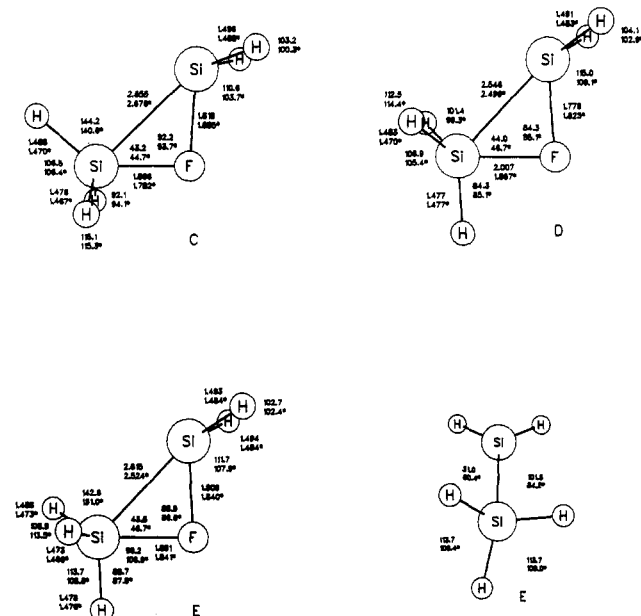


Figure 3. Transition structure for SiH_2 insertion into the Si-F and of SiH_3F at the HF/3-21G and HF/6-31G* levels. Structures C and D are local maxima with respect to SiH_3 rotation, and structure E is the transition structure at the Hartree-Fock level. When correlation energy is included at the HF/6-31G* optimized geometry, D is lower in energy than E. (HF/3-21G optimized, no superscript; HF/6-31G* optimized, asterisk).

are reproduced here to facilitate comparisons with the other structures. The product, $\text{Si}_2\text{H}_5\text{F}$, has an Si-F bond that is slightly longer than SiH_3F and an Si-Si bond that is 0.026 Å shorter than Si_2H_6 (HF/6-31G*).

Silylene and SiH_3F form a fairly tightly bound complex characterized by a short $\text{SiH}_3\text{F} \cdots \text{SiH}_2$ distance. The plane of SiH_2 is nearly perpendicular to the $\text{F} \cdots \text{SiH}_2$ bond, and the $\text{SiF} \cdots \text{Si}$ angle is bent away from linear by ca 40°. Four conformations of C₂ symmetry can be envisioned: SiH_2 staggered and eclipsed with SiH_2 , the SiH_2 hydrogens pointing toward SiH_3 (A and B in Figure 2); SiH_3 eclipsed and staggered, SiH_2 pointing away from SiH_3 (not shown). The latter two structures optimize to A and B, respectively, by linear inversion of the $\text{SiF} \cdots \text{Si}$ angle. Of the two rotomers, A is more stable than B by 1.3 kJ mol⁻¹, i.e., essentially free rotation.

Candidates for the transition structure for SiH_2 insertion into the Si-F bond are shown in Figure 3. Akin to other carbene-like insertions, these are on a nonleast motion pathway, with the SiH_2 plane roughly parallel to the Si-F bond. One can construct two structures of C₂ symmetry (C and D, Figure 3), with the SiH bond of SiH_2 syn or anti to the incoming SiH_2 . When fully optimized within the C₂ symmetry the former is lower at HF/3-21G and the latter at HF/6-31G*. However, frequency calculations reveal that neither C nor D is a true transition state, since both have two imaginary frequencies (see below and Table II). Structures C and D are local maxima at the Hartree-Fock level, and the additional imaginary frequency corresponds to rotation of the SiH_3 group. Rotation of the SiH_3 group reduces the symmetry to C₁ and full optimization²⁰ leads to the transition structure E. At the larger basis set, D and E are relatively similar in geometry and energy but HF/3-31G* frequency calculations confirm that D is a local maximum. When correlation energy is added, D becomes slightly more stable than E.

A number of observations can be made from the geometry of the transition state. There are three equivalent structures of type C, three of type D, and six of type E (three enantiomeric pairs). From C through E to D requires only a 60° rotation of the SiH_3

TABLE II: Vibrational Frequencies^a

reactants ^b	complex		transition structure			product
	A	B	C	D	E	
800 (728)	10 a''	24i a''	399i a'	445i a'	424i	106 a''
800 (728)	62 a''	55 a''	123i a''	246i a''	147	164 a'
943 (875)	63 a'	64 a'	283 a''	281 a''	292	390 a''
990 (961)	242 a'	240 a''	392 a'	340 a'	381	406 a'
990 (961)	689 a''	691 a''	580 a'	634 a'	590	568 a'
1107 (1005)'	750 a'	743 a'	684 a''	657 a''	674	665 a''
1132 (991)	774 a''	773 a''	732 a'	702 a''	709	829 a''
2063'	792 a'	792 a'	756 a''	776 a'	774	911 a'
2078 (2022)'	852 a'	993 a''	931 a'	931 a'	861	925 a'
2338 (2209)	994 a'	993 a''	931 a'	931 a'	946	986 a'
2338 (2209)	995 a''	997 a'	1038 a'	1024 a'	1029	995 a''
2353 (2206)	1078 a'	1078 a'	1091 a''	1085 a'	1042	996 a'
	1108 a'	1107 a'	1095 a'	1085 a''	1131	1046 a'
	2021 a''	2023 a''	2253 a''	2253 a''	2238	2279 a'
	2043 a'	2045 a'	2235 a'	2254 a'	2243	2290 a'
	2380 a'	2380 a'	2255 a'	2282 a'	2253	2294 a''
	2385 a'	2385 a''	2335 a''	2308 a''	2322	2324 a''
	2385 a''	2385 a''	2350 a''	2325 a'	2358	2329 a'

^a Harmonic vibrational frequencies in cm⁻¹ calculated with HF/3-21G. ^b SiH_2 modes indicated by a prime; observed (anharmonic) frequencies in parentheses.

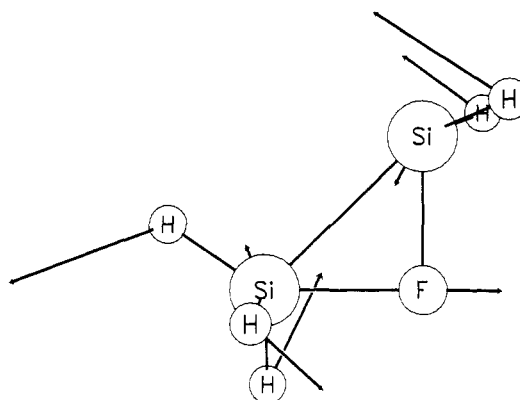
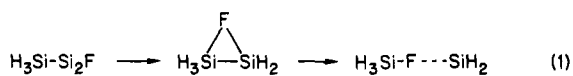
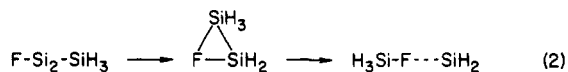


Figure 4. Transition vector for $\text{SiH}_2 + \text{SiH}_3\text{F}$ computed at HF/3-21G for structure E.

group. Hence it is not too surprising that internal rotation is quite facile. Secondly, the two Si-F bonds in the transition structure are nearly equal (structure D or E, HF/6-31G* values in Figure 3) and are ca. 0.35 Å longer than in SiH_3F . The Si-Si bond, however, is only 0.15–0.17 Å longer than in $\text{Si}_2\text{H}_5\text{F}$. Thus, the geometry of the transition structure is more appropriate for a [1,2] fluorine shift. Writing the insertion reaction in reverse, we see that the [1,2] shift and the insertion points of view are quite compatible:



Likewise, the geometry of the transition structure is consistent with an early [1,2] SiH_3 shift transition state



The computed transition vector for structure E is shown in Figure 4. Insertion involves stretching the $\text{SiH}_3\text{-F}$ bond and rotating the SiH_2 about F. The reverse of the [1,2] F shift requires shortening of the $\text{SiH}_2\text{-F}$ bond and lengthening of $\text{SiH}_3\text{-F}$. The SiH_3 [1,2] shift character is more difficult to see because of the large component of SiH_3 rotation. It should be emphasized that the SiH_2 insertion, the [1,2] fluorine shift, and the [1,2] silyl shift are three different ways of describing the *same* transition state for the *same* net reaction.

Frequencies. The harmonic vibrational frequencies for the various structures on the $\text{SiH}_2 + \text{SiH}_3\text{F}$ surface are listed in Table II. The frequencies of the reactants are overestimated by 5–10%,

(20) Because of the flexibility of the structure and the large number of degrees of freedom, these transition structure optimizations were very difficult. The optimizations had to be restarted several times, using the full Hessian computed analytically at the HF/3-21G level.

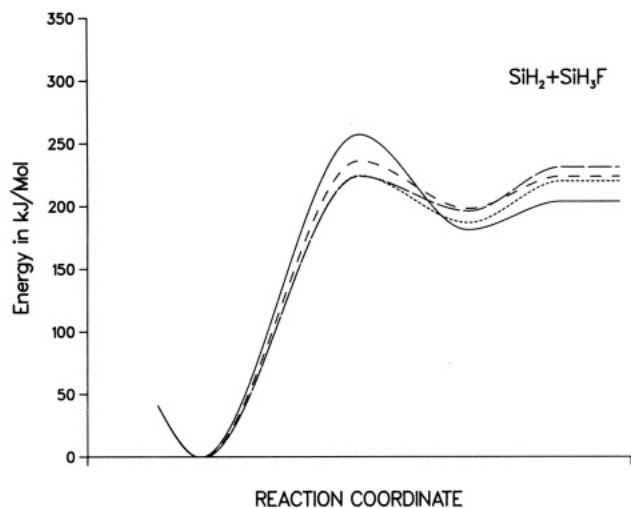


Figure 5. Energy profile along reaction path for insertion: HF/6-31G* (solid line), MP2/6-31G* (long dashes), MP3/6-31G* (medium dashes), MP4/6-31G* (short dashes).

primarily because vibrational anharmonicity and electron correlation were not taken into account in the HF/3-21G frequency calculations.²¹ The vibrational frequencies of the SiH₂ + SiH₃F complex (A) are approximately the same as the monomers, plus six low-frequency modes for the relative motion of the monomers. The additional modes are SiH₃ torsion (10 cm⁻¹), --SiH₂ torsion (62 cm⁻¹), Si-F--Si bend (63 cm⁻¹), Si--F stretch (242 cm⁻¹), and F--SiH₂ bend (689, 750 cm⁻¹). Some of these modes, particularly the Si--F stretch, are probably too high because the well depth for the complex is overestimated by a factor of two at the HF/3-21G level. Complexation also shifts some of the monomer vibrational levels. The Si-H stretches are the simplest to interpret. Complexation involves donation of electron density from SiH₃F to SiH₂, weakening the SiH₂ bonds, and lowering the stretching frequency. In SiH₃F, the lone pair on F is antibonding to the SiH₃ group, and removal of electron density from F strengthens the SiH₃ bonds and increases their vibrational frequency.²² Complex B differs from A only in that it has an imaginary frequency for the SiH₃ torsion mode, indicating that it is a transition state to SiH₃ rotation. It should be noted that the low-frequency modes are associated with large-amplitude motions and nearly free rotations. Harmonic frequencies, calculated by the usual Wilson FG method, probably do not represent these motions adequately.

The vibrational frequencies for the transition structure to insertion and the associated local maxima are also listed in Table II (structures C, D, and E). The local maxima (C and D) have two imaginary frequencies; in each case the first is predominantly the SiH₂F insertion mode and the second is SiH₃ rotation. The transition (E) structure has only one imaginary frequency, with a normal mode corresponding to SiH₂ insertion or [1,2] fluorine shift, strongly mixed with SiH₃ rotation as shown in Figure 4. The remaining frequencies of the transition structure, for the most part, lie between the frequencies of the reactants or complex and the frequencies of the products.

Energetics. The relative energies are collected in Table I and are summarized in Figure 4. The results are compared with SiH₂

(21) The apparently better agreement with experiment for vibrational frequencies of molecules containing second-row atoms (cf. 10–12% overestimation if only first-row atom are involved) is an artifact of the basis set. At the HF/3-21G level, the Si-F bond lengths are overestimated by ca. 0.04 Å, leading to lower Si-F stretching and bending frequencies, and better agreement with experiment.

(22) An alternative explanation can be put forward that does not involve orbital interactions. For a normal covalent bond, the nuclear-nuclear contribution to the stretching force constant is large and positive; the electronic contribution is smaller and negative. If the electron density is increased (e.g., by donation from SiH₃F to SiH₂ during complexation), the electronic contribution becomes larger in magnitude, i.e., more negative, and the force constant becomes smaller. Analogously, charge withdrawal increases the force constant.

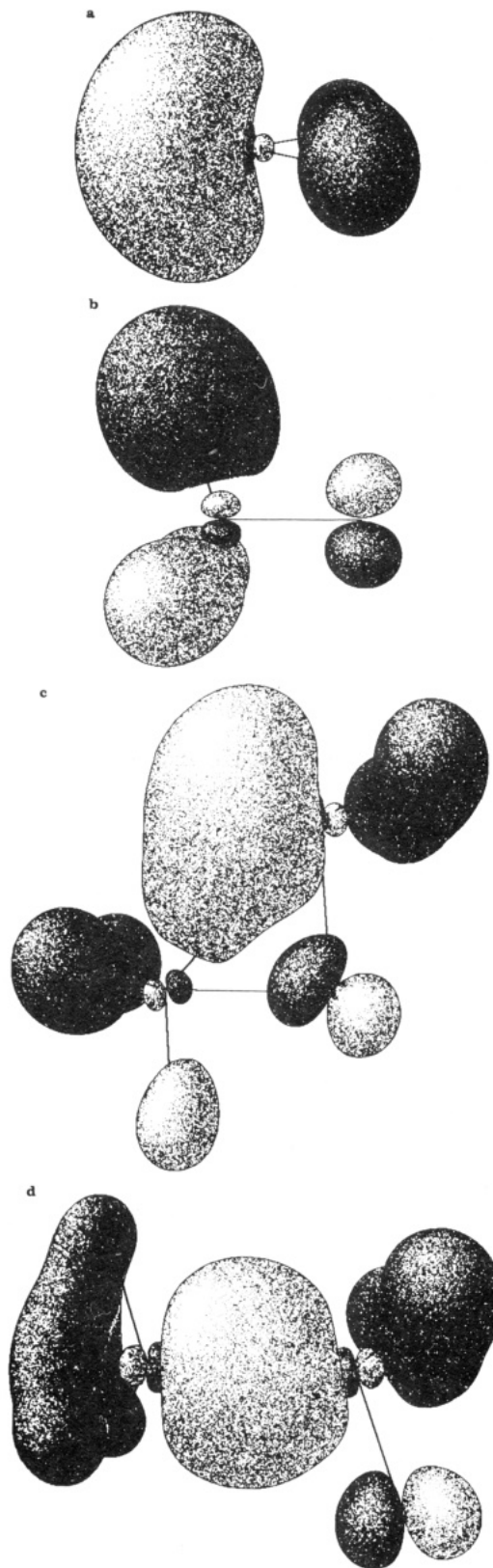


Figure 6. Highest occupied molecular orbitals of (a) SiH₂, (b) SiH₃F, (c) transition state (structure E), and (d) Si₂H₅F at HF/6-31G*. The shell encloses 70% of the electron density.

+ H₂ and SiH₂ + HF in Table III. The SiH₂ + SiH₃F reaction is exothermic by 205 kJ mol⁻¹ at MP4SDQ/6-31G* + ΔZPE. A reliable ΔH_f^o is not available for Si₂H₅F, but bond additivity arguments suggest -200 to -230 kJ mol⁻¹ for the approximate experimental heat of reaction.^{23,24} The agreement with experiment

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TABLE III: Comparison of SiH₂ Insertion into H₂, HF, and SiH₃F^a

	cluster			transition structure			product		
	H ₂	HF ^b	SiH ₃ F	H ₂	HF ^b	SiH ₃ F	H ₂	HF ^b	SiH ₃ F
HF/3-21G	-4		-70	155		31	-209		-175
HF/6-31G*	-2	-28	-23	77	77	53	-259	-383	-204
MP2/6-31G*	-3	-43	-35	35	-6	-7	-252	-397	-231
MP3/6-31G*	-3	-38	-33	35	20	5	-241	-376	-224
MP4/6-31G*	-3	-39	-33	38	12	4	-237	-376	-220
ΔZPE/3-21G		11	10	13	5	12	23	19	15
MP4 + ΔZPE		-28	-23	52	17	16	-214	-357	-205
		(-29)			(11)			(-353)	
exptl				23 ± 4			-204 ± 6		

^a Energies in kJ mol⁻¹ relative to the reactants. ^b From ref 11; numbers in parentheses are MP4SDTQ/6-31G** + ΔZPE.

is similar for SiH₂ + H₂ and SiH₂ + HF.

The binding energy for the complex is overestimated by a factor of two at the HF/3-21G level, and somewhat underestimated at HF/6-31G*. Calculations on SiH₂ + HF by Raghavachari et al.¹¹ yield a similar binding energy. These calculations also indicate that polarization functions on hydrogen (6-31G**) and triple substitutions in the correlation calculation (MP4SDTQ) do not change the well depth. In the complex, the barrier to rotation (A → B) is ca. 1 kJ mol⁻¹, i.e., essentially free rotation. By comparison SiH₂ + H₂ forms a complex that is only weakly bound.⁹

For the transition structures, the Hartree-Fock level significantly overestimates the barrier height for all three reactions (Table II). There is a large drop in the barrier when correlation energy is included. Insertion into SiH₃F appears to have a barrier ca. 10 kJ mol⁻¹ lower than insertion into HF. The more extensive calculations on SiH₂ + HF by Raghavachari et al.¹¹ reveal that triple substitutions at the MP4 level are more important for the transition state than the complex, lowering the barrier by 12 kJ mol⁻¹. They also find that polarization functions on hydrogen raise the barrier by 7 kJ mol⁻¹ (MP4SDQ/6-31G**). Similar improvements can be expected for SiH₂ + SiH₃F, leading to a new lowering of the barrier by 5 kJ mol⁻¹. The zero point energy difference is larger for SiH₃F + SiH₂ than SiH₂ + HF. Thus we estimate that the SiH₂ insertion barrier for SiH₃-F is similar to or ca. 5 kJ mol⁻¹ lower than insertion into HF. The barrier relative to reactants is estimated to be 5-10 kJ mol⁻¹.

Molecular Orbitals. The highest occupied molecular orbitals (HOMO's) of SiH₂, SiH₃F, the transition structure, and the

product are shown in Figure 6. The SiH₂ HOMO is an sp² lone pair; for SiH₃F the HOMO is an antibonding combination of the π-type SiH₃ group orbital and the p_π lone pair on fluorine. Note that the effect of the radial mode of the silicon 3s and 3p orbitals is clearly visible. In the SiH₃F + SiH₂ complex (not shown), the HOMO is the SiH₂ lone pair with a very small contribution from the p_σ on fluorine. The HOMO of the transition state is dominated by the SiH₂ HOMO interacting in an antibonding fashion with the SiH₃F HOMO. The distortion of the SiH₂ lone pair, along with the orientation and phase of fluorine p orbital, indicates a strong contribution from the LUMO of SiH₃F (σ*_{Si-F}). In the product, the HOMO is composed of an Si-Si σ bond and an out-of-phase fluorine p orbital. The evolution of the HOMO from reactants, through the transition state to products, is readily discernible in Figure 6. In the transition structure, the SiH₂ lone pair is already distorted toward an Si-Si σ bond; the fluorine p orbital is rotated half-way to its final position in Si₂H₅F.

Conclusions

In terms of structure and energetics, the insertion of SiH₂ into the Si-F bond of SiH₃F is quite similar to SiH₂ insertion into HF. Both possess a stable complex between SiH₂ and the fluorine lone pair with a binding energy of 20-25 kJ mol⁻¹. The transition structures are reached by a rearrangement of this complex and lie ca. 10 kJ mol⁻¹ above the reactants. The barrier for insertion into Si-F appears to be 0-5 kJ mol⁻¹ lower than insertion into H-F. The transition structure can also be described as [1,2] fluorine shift leading from the products to the complex.

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(24) The overall reaction SiH₂ + SiH₃F → Si₂H₅F can be obtained from SiH₂ + SiH₄ → Si₂H₆ by replacing a single Si-H bond with an Si-F bond in SiH₄ and in Si₂H₆. Since the contribution of an Si-F bond to ΔH^o_f should be similar in SiH₃F and Si₂H₅F, the two reactions should have similar ΔH^o's. For the latter reaction ΔH^o = -200 to -230 kJ mol⁻¹, depending on the ΔH^o_f used for SiH₂.