5 (0.64 mmol, 90 μL) was added. After a reaction time of 2 h (the same results were obtained after stirring overnight), the brown-green solution was evaporated to dryness and the residue washed several times with diethyl ether until the filtrate was colorless. We were unable to obtain a pure complex after several attempts at recrystallization. A mixture of different species was always obtained, from which the two complexes [Cp*Ru($\eta^6$-*p*-$MeOC_6H_4OH$)]($CF_3SO_3$) (7) and [Cp*Ru($\eta^6$-*p*-$MeOC_6H_4OMe$)]($CF_3SO_3$) (8) were identified by comparison to an authentic sample (see below).

**Reaction of Cp*Ru$^+$ with 4-Methoxyphenol.** $CF_3SO_3H$ (0.28 mmol, 25 μL) was added to a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (from 0.28 mmol (86 mg) of (Cp*$RuCl_2$)$_n$). After 10 min of stirring, $MeOC_6H_4OH$ (0.28 mmol, 35 mg) was added. After it was stirred overnight, the mixture was evaporated to dryness. The residue was washed several times with diethyl ether until the filtrate was colorless. The precipitate was recrystallized from $CH_2Cl_2/Et_2O$, affording [Cp*Ru($\eta^6$-*p*-$MeOC_6H_4OH$)] ($CF_3SO_3$) (7) as greenish crystals (yield ca. 80%). Anal. Calcd for $C_{18}H_{23}O_5F_3SRu$: C, 42.44; H, 4.52. Found: C, 42.05; H, 4.65. $^1H$ NMR (($CD_3$)$_2$CO): $\delta$ 2.11 (s, 15 H, $C_5(CH_3)_5$), 3.93 (s, 3 H, $OCH_3$), 5.90 and 6.05 (AA′BB′, 4 H, $J_{app}$ = 6.6 Hz, $C_6H_4$). $^{13}C$ NMR (($CD_3$)$_2$CO): $\delta$ 9.7 (q, $J_{C-H}$ = 128 Hz, $C_5(CH_3)_5$), 56.7 (q, $J_{C-H}$ = 146 Hz, $OCH_3$), 74.4 (d, $J_{C-H}$ = 177 Hz, $C_6H_4$), 75.6 (d, $J_{C-H}$ = 176 Hz, $C_6H_4$), 128.2 (s, $C_6H_4$), 130.0 (s, $C_6H_4$), 95.3 (s, $C_5(CH_3)_5$).

**Reaction of Cp*Ru$^+$ with 1,4-Dimethoxybenzene.** The same procedure as above was used with $CF_3SO_3H$ (0.49 mmol, 45 μL), (Cp*$RuCl_2$)$_n$ (0.49 mmol, 150 mg) and $C_6H_4(OMe)_2$ (0.48 mmol, 66 mg). [Cp*Ru($C_6H_4(OMe)_2$)]($CF_3SO_3$) (8) was obtained as a gray powder (yield ca. 80%). Anal. Calcd for $C_{19}H_{25}O_5F_3SRu$: C, 43.59; H, 4.78. Found: C, 43.51; H, 4.78. $^1H$ NMR (($CD_3$)$_2$CO): $\delta$ 2.13 (s, 15 H, $C_5(CH_3)_5$), 3.95 (s, 6 H, $OCH_3$), 6.12 (s, 4 H, $C_6H_4$).

**Reaction of Cp*Ru$^+$ with 3,3,6,6-Tetramethoxy-1,4-cyclohexadiene (6).** The same procedure as above was used with $CF_3SO_3H$ (0.65 mmol, 57 μL), (Cp*$RuCl_2$)$_n$ (0.65 mmol, 200 mg), and 6 (0.64 mmol, 127 mg). [Cp*Ru($\eta^6$-1,2,4-$(MeO)_3C_6H_3$)]($CF_3SO_3$) (9) was obtained as a gray powder (yield ca. 60%). Anal. Calcd for $C_{20}H_{27}O_6F_3SRu$: C, 43.40; H, 4.88. Found: C, 43.08; H, 4.83. $^1H$ NMR (($CD_3$)$_2$CO): $\delta$ 2.10 (s, 15 H, $C_5(CH_3)_5$), 3.97 (s, 3 H, $OCH_3$), 4.00 (s, 3 H, $OCH_3$), 4.06 (s, 3 H, $OCH_3$), 5.90 (dd, 1 H, $J_{H_3-H_5}$ = 1.7 Hz, $J_{H_5-H_6}$ = 6.4 Hz, $H_5$), 6.32 (d, 1 H, $J_{H_5-H_6}$ = 6.4 Hz, $H_6$), 6.43 (d, 1 H, $J_{H_3-H_5}$ = 1.7 Hz, $H_3$). $^{13}C$ NMR (($CD_3$)$_2$CO): $\delta$ 9.8 (q, $J_{C-H}$ = 128 Hz, $C_5(CH_3)_5$), 57.1 (q, $J_{C-H}$ = 147 Hz, $OCH_3$), 57.3 (q, $J_{C-H}$ = 147 Hz, $OCH_3$), 57.4 (s, $J_{C-H}$ = 147 Hz, $OCH_3$), 65.3 (d, $J_{C-H}$ = 179 Hz, $C_5$), 70.9 (d, $J_{C-H}$ = 179 Hz, $C_6$), 72.3 (d, $J_{C-H}$ = 174 Hz, $C_3$), 121.3 (s, $C_{1\,or\,2\,or\,4}$), 122.7 (s, $C_{2\,or\,1\,or\,4}$), 128.9 (s, $C_{4\,or\,2\,or\,1}$).

**Acknowledgment.** We warmly thank Klaus Bechgaard and his group in Copenhagen for a generous gift of DMTCNQ and DETCNQ and Johnson-Matthey for a gift of $RuCl_3 \cdot 3H_2O$. X.-D.H. thanks the CNRS, PICS France-Venezuela, for financial support.

**Supplementary Material Available:** Tables of atomic positional parameters, thermal parameters, bond lengths and angles, root-mean-square amplitudes of thermal vibration, and torsion angles (11 pages). Ordering information is given on any current masthead page.

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# Theoretical Study of Ligand Substitution Reactions in Pentacoordinated Silicon Species

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*Received April 6, 1992*

Ab initio MO calculations have been carried out to study the reactions of pentacoordinated silicon species $SiH_3F_2^-$ and $SiH_2F_3^-$ with $H^-$ and $F^-$. The possibility of ligand displacements taking place via hexacoordinated intermediates has been discussed by locating the transition state on the potential energy surface. The difference in mechanisms between the reaction of silicon species and the biomolecular nucleophilic substitution reaction of carbon compounds has been clarified by applying the orbital interaction scheme.

## Introduction

The chemistry of penta- and hexacoordinated silicon species is developing rapidly.[1-9] For instance, pentacoordinated species have been suggested to be the intermediates in nucleophilic displacements at silicon centers.[10-12] Hexacoordinated silicon species are now also assumed to intervene in the reactions of organosilicon

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compounds.[13-20] The racemization of halosilanes in the base-catalyzed fluorine displacements of $SiF_5^-$ in polar solvents and the intramolecular rearrangements of silicon peroxides promoted by $F^-$ have all been interpreted by proposing hexacoordinated transition states or reaction intermediates.[13,19,20] The synthetic applications of hexacoordinated organosilicates are becoming more and more important.

A number of theoretical calculations have been carried out on pentacoordinated silicon species in order to reveal the nature of hypervalent bonds.[21-30] Qualitatively, the concept of three-center, four-electron bonds represented by a combination of a doubly occupied bonding MO and a nonbonding MO seems to be accepted.[31,32] The difference between a silicon center and a carbon center in the trend of forming pentacoordinated species has been ascribed to the existence of a low-lying unoccupied MO in the silicon species.[33] In this paper, we report the results of our MO calculations on the reaction models of pentacoordinated halosilanes to yield hexacoordinated species.

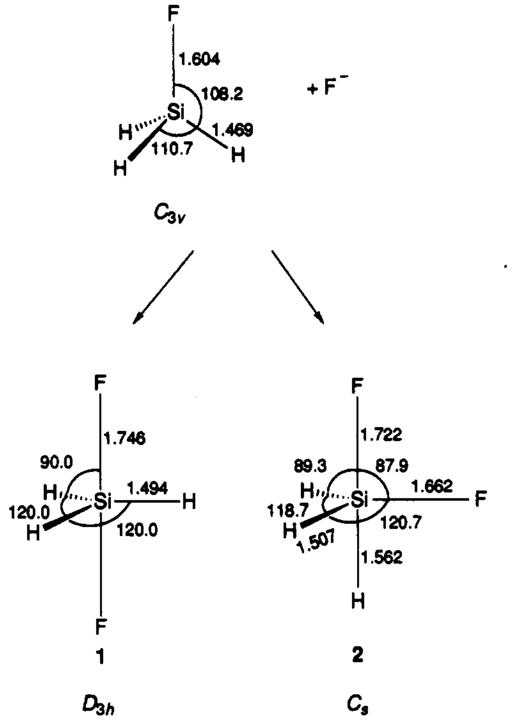


Figure 1. Stable structures of pentacoordinated silicon species 1 and 2. Bond lengths are given in Å and bond angles in degrees.

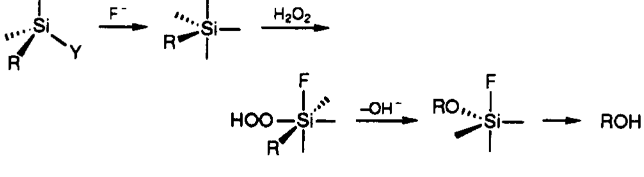
Table I. Total Energies and Activation Barriers of TS1, TS2, and TS3

| | TS1 | TS2 | TS3 |
|---|---|---|---|
| total energy, hartrees | | | |
| *a* | −490.39569 | −490.39970 | −490.39621 |
| *b* | −490.52085 | −490.52398 | −490.51915 |
| *c* | −490.54011 | −490.54317 | −490.53855 |
| activation energy, kcal/mol | | | |
| *a* | 88.965 | 83.516 | 86.704 |
| *b* | 92.257 | 81.026 | 84.055 |
| *c* | 92.671 | 81.409 | 84.306 |
| product | 4 | 3 | 3 |

[a] MP2/6-31G**//RHF/3-21G*. [b] MP2/6-31++G**//RHF/6-31++G**. [c] MP4SDTQ/6-31++G**//RHF/6-31++G**.

## Results and Discussion

**Structures of Penta- and Hexacoordinated Silicon Species.** The following mechanism involving the participation of penta- and hexacoordinated silicon anions has been suggested for the reaction of $R_{4-n}SiY_n$ ($n$ = 1–3 and Y = F, Cl, OR, $NR_2$, etc.) with hydrogen peroxide to yield alcohols:[34]



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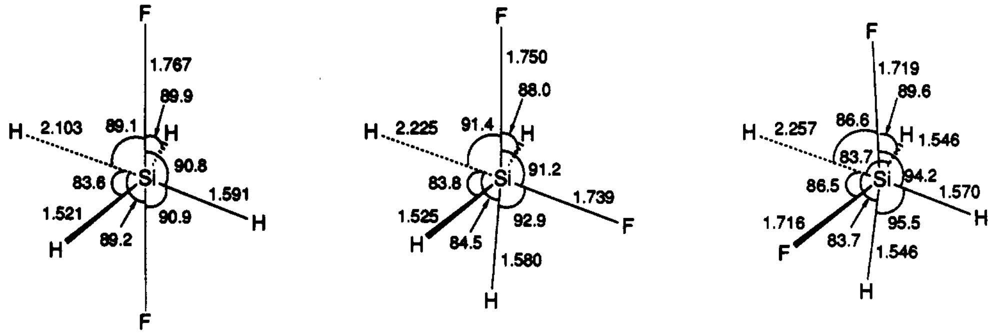
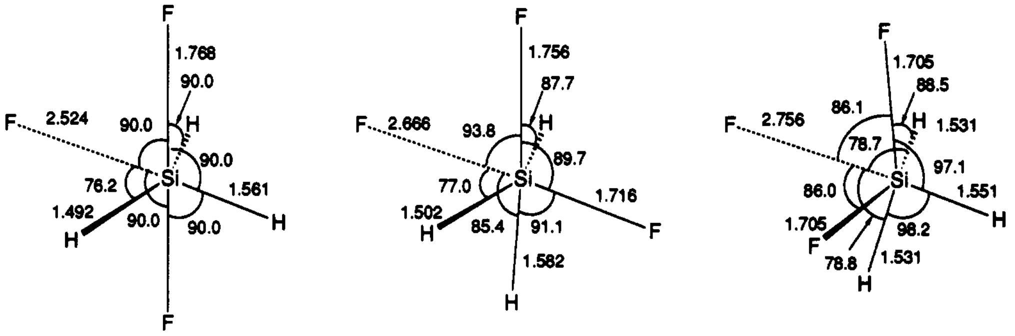


**TS1** , 753.4*i* **TS2** , 658.8*i* **TS3** , 675.0*i*

**Figure 2.** Structures of **TS1**, **TS2**, and **TS3**.



**TS4** , 178.8*i* **TS5** , 158.1*i* **TS6** , 147.9*i*

**Figure 3.** Structures of **TS4**, **TS5**, and **TS6**.

With a view to determining a basic aspect of the reaction, we study here the simplest reaction models. The reaction of $SiH_3F$ and of $SiH_2F_2$ with a fluoride ion gives rise to pentacoordinated species, $SiH_3F_2^-$ and $SiH_2F_3^-$, respectively. The pentacoordinated species are assumed then to react further with a hydride ion or a fluoride ion to yield hexacoordinated species. Several different transition states appear in these processes, depending on the structure of the pentacoordinated species and on the direction of attack of the anion.

In experiments, silicate anions and, probably, dianions are produced in the presence of fluorides of alkali metals. Accordingly, the anionic species should be stabilized in solutions by releasing the excess electronic charge over the counterions and solvent molecules.[35] However, to use the MO scheme, it is assumed in the present study that the penta- and hexacoordinated species have a formal charge of −1 and −2, respectively. We report in this paper the structures of the anionic silicon species and of the transition states that appear on the way in going from the pentacoordinated species to the hexacoordinated species. An adequate description of the energetics of anions requires the addition of diffuse functions to the basis set.[36] In this study, the MO calculations were performed within the RHF/6-31++G** scheme[37] and the energy of the silicon species has been evaluated at the MP2 and MP4/6-31++G** levels[38,39] by applying GAUSSIAN 82, 86, and 90 programs.[40–42]

The optimized structures of the pentacoordinated anion $SiH_3F_2^-$, produced in the first stage of the reaction of $SiH_3F$ with a fluoride ion, are illustrated in Figure 1. The anion 1, having two fluoride ligands at the apical positions, is shown to be 9.27 kcal/mol more stable at the MP2/RHF 6-31++G** level than its structural isomer 2, in accordance with the calculations reported so far.[26b] At higher levels of theory, 2 may not be a stable structure but may be a transition state.[26f] For the present, we will study the attack of X ($X = H^-, F^-$) at the silicon center of 1 and 2 from the backside of a Si–Y bond (Y = H, F) of the pentacoordinated species in the equatorial plane. The transition-state structures are shown in Figures 2 and 3, together with the imaginary frequency of vibration along the reaction coordinate. The Si–X bond being formed between the silicon center and the attacking anion is seen to be 1.4–1.6 times longer than the corresponding bond in the

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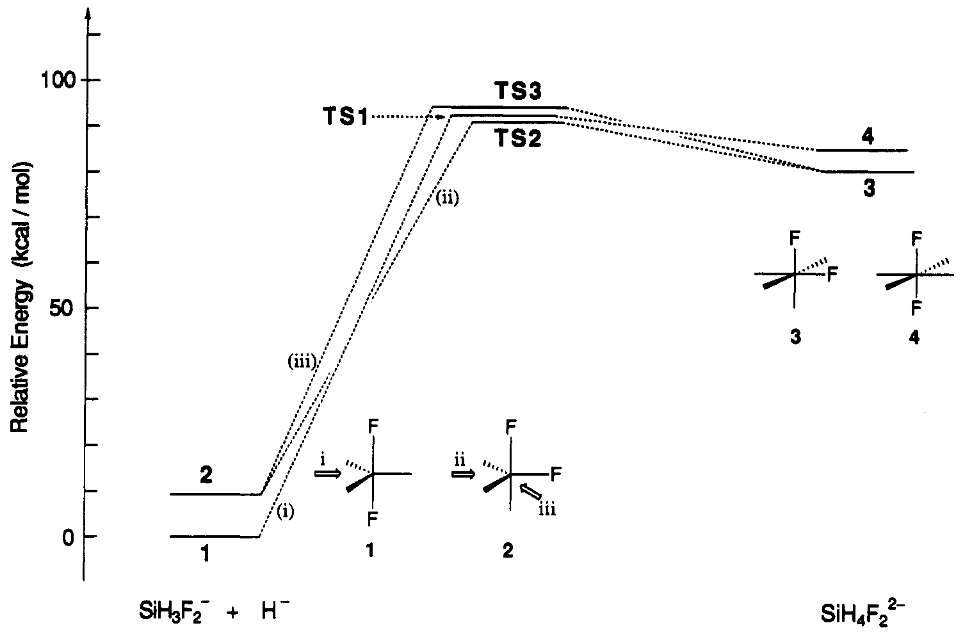


**Figure 4.** Energy profile of the reaction between $SiH_3F_2^-$ and a hydride ion.

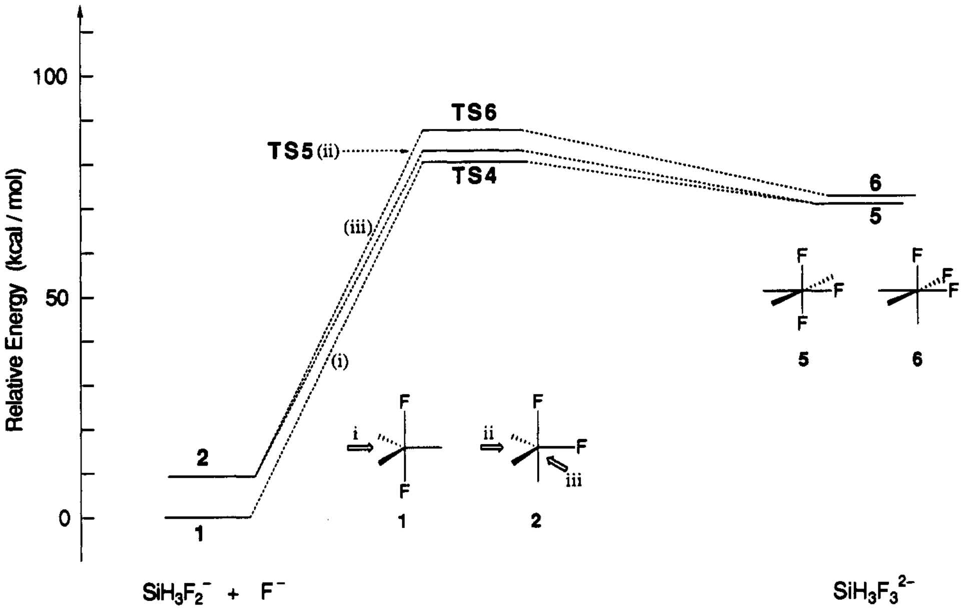


**Figure 5.** Energy profile of the reaction between $SiH_3F_2^-$ and a fluoride ion.

stable structures of pentacoordinated species. In contrast, the Si–Y bond under attack of an anion is shown to be loosened *only slightly*. This result of the calculation implies that the displacement of ligands in a pentacoordinated silicon species does not have to take place in a concerted manner but may proceed via a hexacoordinated transition state or intermediate.

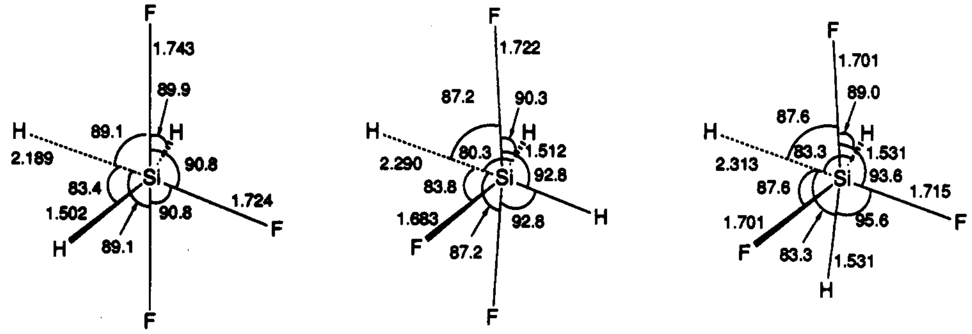
Figure 4 shows the energy profile of the reaction with a hydride ion. The total energy and the barrier height are summarized in Table I. The transition-state structures **TS1**, **TS2**, and **TS3** are almost the same in energy, **TS2** being slightly more stable than **TS1** and **TS3**. One should note here that **TS1** arises from the more stable isomer 1 of $SiH_3F_2^-$, whereas **TS2** and **TS3** come from 2. The activation energy has been estimated to be 92.26, 81.03, and 84.06 kcal/mol for **TS1**, **TS2**, and **TS3**, respectively, by the MP2/6-31++G** level calculation. The MP4 calculations have shown slightly higher values.

A similar result has been obtained for an attack of a fluoride ion as shown in Table II and in Figure 5. The barrier heights of **TS4**, **TS5**, and **TS6** are closer than those for the attack of a hydride ion. In this case, the more stable structure 1 of $SiH_3F_2^-$ leads to **TS4**, which has the lowest potential energy. The activation barrier is calculated to be 80.38 kcal/mol. This barrier height is about 12 kcal/mol lower than that of **TS1** and parallels that of **TS2**. From a comparison of the results given in Tables I and II,

**Table II. Total Energies and Activation Barriers of TS4, TS5, and TS6**

| | TS4 | TS5 | TS6 |
|---|---|---|---|
| total energy, hartrees | | | |
| *a* | -589.50326 | -589.50316 | -589.49710 |
| *b* | -589.66001 | -589.65478 | -589.64909 |
| activation energy, kcal/mol | | | |
| *a* | 79.904 | 77.032 | 80.832 |
| *b* | 80.380 | 74.392 | 77.960 |
| product | 5 | 5 | 6 |

[a] MP2/6-31G**//RHF/3-21G*. [b] MP2/6-31++G**//RHF/6-31++G**.



**TS7**, 698.4*i* **TS8**, 684.7*i* **TS9**, 625.6*i*

**Figure 6.** Structures of **TS7**, **TS8**, and **TS9**.

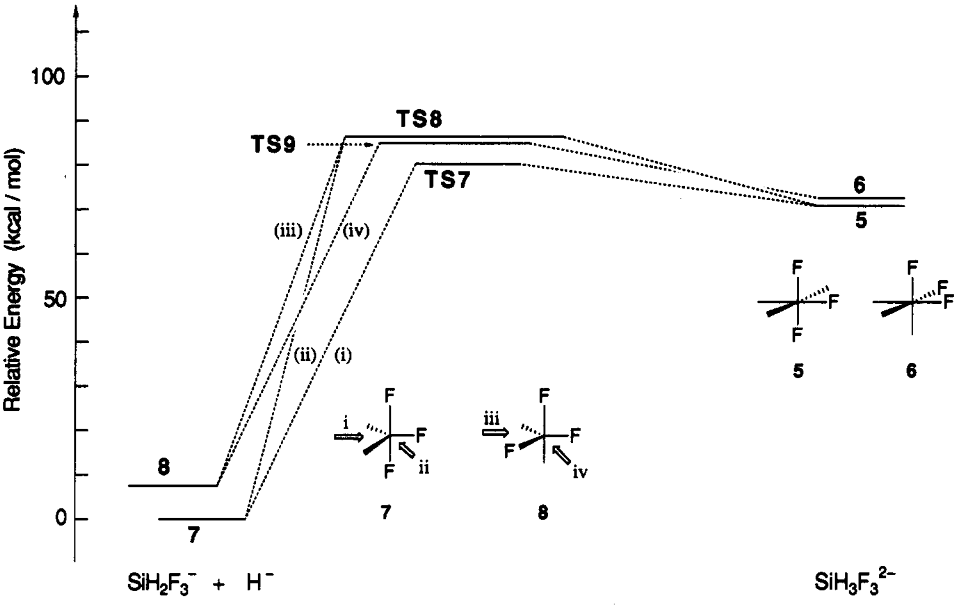


**Figure 7.** Energy profile of the reaction between $SiH_2F_3^-$ and a hydride ion.

a fluoride ion is suggested to be more reactive than a hydride ion. This is related to the nature of the three-center, four-electron bond X–Si–Y that should be stabilized by carrying strongly electronegative atoms or groups X and Y. In the same context, it is more favorable for an anion X to attack a Si–F bond from the backside than to attack a Si–H bond.

Figures 6 and 7 present respectively the transition-state structures and energy profile of the reaction of $SiH_2F_3^-$ with a hydride ion. The total energy and the barrier height are summarized in Table III. The more stable geometrical isomer **7**, which has two fluoride ligands at the apical positions, yields the hexacoordinated dianion **5** via **TS7** and **TS8**. The less stable structure **8** leads to **5** and **6** via **TS8** and **TS9**, respectively.

The barrier for pseudorotation in $SiH_5^-$ and $SiH_4F^-$ species has been erported to be about 2.5 and 23 kcal/mol, respectively.[43] These calculations suggest that **2** rearranges to **1** before it reacts with an anion. We note that $[2]/[1] = (q_2/q_1)\exp(-\Delta E/RT)$, in which $q_1$ and $q_2$ signify the partition functions of **1** and **2**, respectively, and $\Delta E$ stands for the energy difference between **1** and **2**. Then, the probabilities of the reaction going through **TS1**, **TS2**, and **TS3** may be estimated. If we assume that **TS1** and

**Table III. Total Energies and Activation Barriers of TS7, TS8, and TS9**

| | TS7 | TS8 | TS9 |
|---|---|---|---|
| total energy, hartrees | | | |
| *a* | −589.51833 | −589.50964 | −589.51384 |
| *b* | −589.65965 | −589.64995 | −589.65181 |
| activation energy, kcal/mol | | | |
| *a* | 84.651 | 90.100<br>(86.438)[c] | 84.036 |
| *b* | 80.525 | 86.607<br>(79.364)[c] | 78.198 |
| product | 5 | 5 | 6 |

[a] MP2/6-31G**//RHF/3-21G*. [b] MP2/6-31++G**//RHF/6-31++G**. [c] Via pentacoordinated species 8.

**Table IV. Thermochemical Data for 1, 2, and $H^-$ and for TS1, TS2, and TS3 (at 1 atm and 298.15 K)[a]**

| | 1 | 2 | $H^-$ |
|---|---|---|---|
| total energy, hartrees | −489.66000 | −489.64838 | −0.48707 |
| thermal energy, hartrees | 0.03542 | 0.03436 | 0.00142 |
| entropy *S*, cal/(mol·K) | 65.855 | 65.538 | 26.014 |
| partition function *q* | 0.00466 | 0.01215 | |
| | **TS1** | **TS2** | **TS3** |
| total energy, hartrees | −490.52085 | −490.52398 | −490.51915 |
| thermal energy, hartrees | 0.03678 | 0.03638 | 0.03612 |
| entropy *S*, cal/(mol·K) | 67.010 | 67.056 | 66.661 |
| Δ*H*, cal/mol | 97851.092 | 88093.575 | 90645.831 |
| Δ*S*, cal/(mol·K) | −24.859 | −24.496 | −24.891 |

[a] Evaluated by the RHF/6-31++G** calculation.

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(43) (a) Gordon, M. S,; Windus, T. L.; Burggraf, L. W.; Davis, L. P. *J. Am. Chem. Soc.* **1990**, *112*, 7167. (b) Windus, T. L.; Gordon, M. S.; Burggraf, L. W.; Davis, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 4356.

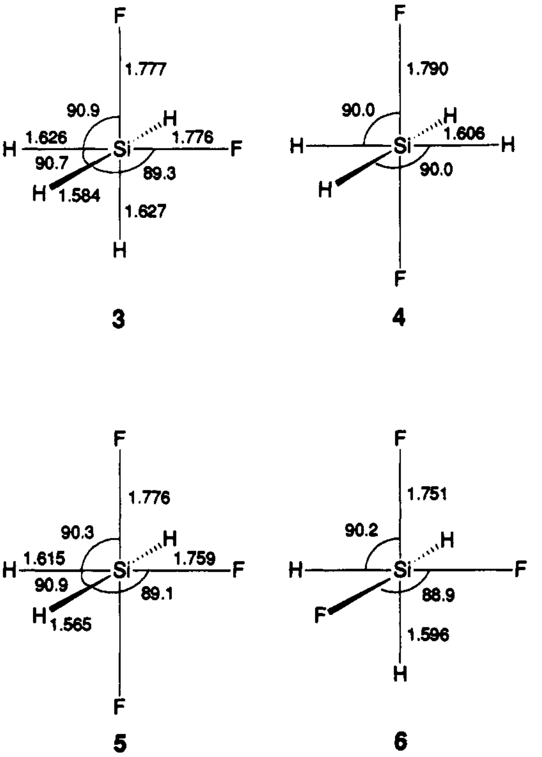

**Figure 8.** Structures of $SiH_4F_2^{2-}$ and $SiH_3F_3^{2-}$.

the pentacoordinated anion 1 are in equilibrium, we obtain $[\mathbf{TS1}]/[\mathbf{1}][H^-] = \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT)$. By utilizing the thermodynamic data presented in Table IV and the ratio of concentrations of the two isomers [**2**]/[**1**] as defined above, we have found that [**TS1**]:[**TS2**]:[**TS3**] = 1:200:2.2 at 298 K. If we use the energy values corrected to the MP2 level, the above ratio is modified to yield a result that shows [**TS1**]:[**TS2**]:[**TS3**] = 1:43:0.27. The reaction path starting from **2**, if it exists, via **TS2** is calculated to be the most favorable. The solvent molecules and counterions will play significant roles when a hexacoordinated species collapses to yield pentacoordinated anions.

As the attacking anion becomes more electronegative and as a pentacoordinated anion is more heavily substituted by electronegative groups, the paths involving less stable pentacoordinated species become unfavorable. The reaction path that goes through the transition state of the lowest potential energy is shown to be the most likely. In the case of the reaction of $SiH_2F_3^-$ with a hydride ion, the path that connects **7** and **5** via **TS7** should predominate.

The structures of **3**–**6** are illustrated in Figure 8. The energy of the highest occupied MO is positive in these species, and therefore, **3**–**6** would spontaneously lose an electron, if they were free in the gas phase. We have assumed here that they are produced in the course of the reaction between the silicon species and hydrides or fluorides of alkali metals. These anions are suggested to be stabilized substantially in the reacting system.

**Table V. Energies of Penta- and Hexacoordinated Silicon Species**

| | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| total energy, hartrees | | | | |
| *a* | −490.00266 | −489.99649 | −588.96190 | −588.96203 |
| *b* | −490.53810 | −490.53089 | −589.67439 | −589.67207 |
| *c* | −490.55682 | −490.54982 | | |
| | **1** | **2** | **7** | **8** |
| total energy, hartrees | | | | |
| *a* | −489.66000 | −489.64838 | −588.60813 | −588.59777 |
| *b* | −490.16434 | −490.14956 | −589.28443 | −589.27288 |
| *c* | −490.17750 | −490.16260 | | |

[a] RHF/6-31++G**//RHF/6-31++G**. [b] MP2/6-31++G**//RHF/6-31++G**. [c] MP4SDTQ/6-31++G**//RHF/6-31++G**.

The relative stabilities of transition states obtained above are summarized in the following manner: (i) we pay attention to the $L_1$–Si–$L_2$ bond ($L_1$ and $L_2$ indicate the ligands that occupy the apical positions in the starting pentacoordinated species) and the X–Si–$L_3$ bond ($L_3$ signifies a ligand in the equatorial plane) that are approximately linear, then (ii) the transition state should be more stable when the number of H–Si–H bonds is smaller, (iii) the transition state should be more stable when the number of F–Si–F bonds is greater, and (iv) the transition state should be more stable when the ligands $L_1$ and $L_2$ are $F^-$. The transition state **TS2** does not have any H–Si–H bond that is almost linear and is shown to be more stable than **TS1** and **TS3**. Among the latter two, **TS1** has a F–Si–F bond, but **TS3** does not. Then, the energy of the transition state is elevated in the order **TS2** < **TS1** < **TS3**. In a similar manner, **TS7** is more stable than **TS9**, which in turn is more stable than **TS8**. In contrast, **TS4**, **TS5**, and **TS6** do not have any H–Si–H bond. Then, **TS4** and **TS5**, each having a F–Si–F bond, are shown to be more stable than **TS6**. The relative stabilities of **TS4** and **TS5** are now ascribed to the location of fluoride ligands. A three-center, four-electron bond is stabilized when it has electronegative ligands. As the silicon species is more heavily fluorinated, the preference of a structure for the other structures will be less significant.

Although the activation barrier as one goes from a pentacoordinated anion to a hexacoordinated dianion calculated above appears to be very high, the energetics of the reactions may be influenced significantly by the environment. The penta- and hexacoordinated anionic species as well as the transition states are supposed to be stabilized by delocalizing a part of the excess electronic charge onto the solvated cations in actual reacting systems.[44] An interesting point to be noted here is that the hexacoordinated species **3**–**6** are not stabilized much relative to the transition states, as indicated in Table V. This signifies that the hexacoordinated silicon species produced in the reaction process tend to liberate one of the ligands or cause rearrangements of ligands to give other pentacoordinated species. This makes a clear-cut difference in mechanisms from the $S_N2$ type substitution reaction of carbon compounds.

Finally, with a view to seeing chemical reactivities of the pentacoordinated silicon species from a chemical bonding viewpoint, we have transformed the MO's calculated at the 3-21G* level of theory for **TS1** into pairs of fragment interacting orbitals.[45,46] The major elements of the bond-order matrix between the two fragment species $H^-$ and

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(44) Tamao, K.; Hayashi, T.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1990**, *112*, 2422.

(45) (a) Fujimoto, H.; Koga, N.; Fukui, K. *J. Am. Chem. Soc.* **1981**, *103*, 7452. (b) Fujimoto, H.; Koga, N.; Yamasaki, T. *J. Am. Chem. Soc.* **1985**, *107*, 6157. (c) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578.

(46) Fujimoto, H. *Acc. Chem. Res.* **1987**, *20*, 448.

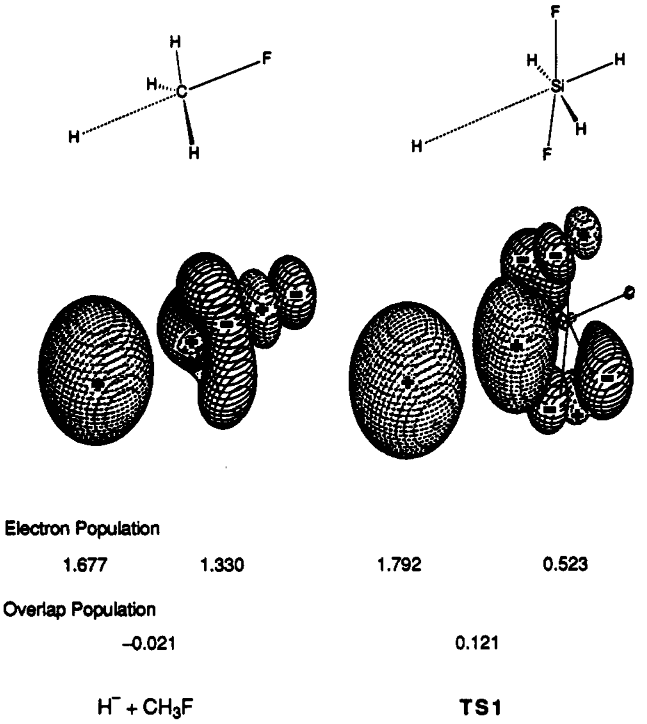

**Figure 9.** Comparison of the interactions in **TS1** and in a model $S_N2$ type reaction in terms of the paired interacting orbitals.

$SiH_3F_2^-$ are then represented practically in terms of an orbital pair that is presented in Figure 9. The interacting orbital of the $SiH_3F_2^-$ fragment shows a large amplitude at the silicon center and overlaps in-phase with the $H^-$ orbital. The electron populations of these orbitals indicate that orbital interactions take place mainly between the occupied MO of $H^-$ and the unoccupied canonical MO's of $SiH_3F_2^-$. A part of the electronic charge has been shifted from $H^-$ to $SiH_3F_2^-$. This forms a marked contrast to the interaction between $CH_3F$ and $H^-$, in which electron delocalization between the occupied MO of $H^-$ and the unoccupied MO's of $CH_3F$ is counterbalanced by the overlap repulsion between the occupied MO's of the two species.

## Conclusion

In experiments, we find various combinations of ligands in silicon species. There may naturally be a variety of reaction mechanisms. The present analysis on a simplified reaction model does not necessarily exclude the concerted mechanism but has revealed an interesting aspect of chemical interactions between pentacoordinated silicon species and nucleophiles. It has been demonstrated that pentacoordinated silicon species have a strong ability to accept the attacking nucleophile without breaking the bond with the leaving group. It seems to be reasonable, therefore, to assume hexacoordinated species as the transition state or reaction intermediate in the ligand substitution reactions of silicon compounds.

**Acknowledgment.** This work was supported in part by a Grant-in-Aid for Scientific Research (No. 03453088) from the Ministry of Education, Science, and Culture of Japan. A part of the calculation was carried out at the Computer Center, Institute for Molecular Science.

OM9201876

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# Sterically Crowded Aryloxide Compounds of Aluminum: Reactions with Main-Group Chlorides

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*Received February 25, 1992*

The interaction of $AlR(BHT)_2$ and $AlR_2(BHT)(OEt_2)$ (R = Me, Et) with main-group chlorides $Me_3SnCl$, $SnCl_2$, $BCl_3$, $AlCl_3$, $InCl_3$, and $ZnCl_2$, in pentane, $Et_2O$, or MeCN, leads to the formation of the aluminum chloride compounds $AlCl(BHT)_2$ (**1**), $AlCl(BHT)_2(OEt_2)$ (**2**), $AlClMe(BHT)(OEt_2)$ (**3**), $AlClEt(BHT)(OEt_2)$ (**4**), $AlCl_2(BHT)(OEt_2)$ (**5**), $[Al(\mu\text{-}Cl)Me(BHT)]_2$ (**6**), and $AlCl(BHT)_2(NCMe)$ (**8**). In contrast, the reaction of $AlMe(BHT)_2$ with $AlCl_3$ in $CH_2Cl_2$ results in Friedel–Crafts alkylation by "$CH_2Cl$" at the 4-position of BHT to give the substituted cyclohexadien-1-one **7**. The kinetics of this reaction have been investigated. The reaction of $AlMe(BHT)_2$ with 2 equiv of 2,6-$Me_2$pyHCl yields the ionic complex $[2,6\text{-}Me_2pyH][AlCl_2(BHT)_2]$ (**9**). The molecular structures of **5**, **6**, and **9** have been determined by X-ray crystallography. Crystal data for **5**: monoclinic, $P2_1/n$, $a$ = 10.796 (2) Å, $b$ = 17.753 (3) Å, $c$ = 11.343 (2) Å, $\beta$ = 97.36 (1)°, $Z$ = 4, $R$ = 0.067, $R_w$ = 0.078. Crystal data for **6**: monoclinic, $P2_1/n$, $a$ = 10.410 (6) Å, $b$ = 9.865 (3) Å, $c$ = 16.42 (1) Å, $\beta$ = 97.20 (5)°, $Z$ = 2, $R$ = 0.069, $R_w$ = 0.088. Crystal data for **9**: triclinic, $P\bar{1}$, $a$ = 9.3799 (8) Å, $b$ = 13.898 (1) Å, $c$ = 14.8255 (14) Å, $\alpha$ = 101.900 (8)°, $\beta$ = 91.080 (7)°, $\gamma$ = 98.050 (7)°, $Z$ = 2, $R$ = 0.050, $R_w$ = 0.062.

## Introduction

The halodealumination of organoaluminum compounds by main-group halides (eq 1) is a class of reaction of industrial significance.[2] The method has been successful

$$MX_n \xrightarrow[-AlXR_2]{AlR_3} MX_{n-1}R \xrightarrow{(n-1)AlR_3} MR_n \qquad (1)$$

for the preparation of organo compounds of, among others, zinc, mercury,[3] boron,[4] gallium,[5] germanium,[6] tin,[7] and lead.[8,9] The aluminum alkyl chloride coproduct formed

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