Organometallics **2001,** *20,* 3113−3121

Role of Hexacoordinated Silicon Intermediates in the Hydrolysis and Racemization Reactions of Silyl Halides

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Received March 7, 2001

Potential energy surfaces for systems consisting of SiH_3F and SiH_3Cl molecules with addition of two water molecules (as a model for neutral hydrolysis), with one water and one ammonia molecule (base-catalyzed hydrolysis), and with two ammonia molecules (racemization) were investigated by the B3LYP and MP2 methods with 6-31G(d,p) and 6-311+G(d,p) basis sets. It was shown that in addition to global energy minima corresponding to loosely bound complexes with SiO and SiN separations exceeding 2.5 Å, there exist the stationary points for tightly bound, low-entropy complexes with SiO and SiN bonds of length ca. 2.0 Å. Such complexes were predicted earlier by the analysis of experimental data on nucleophile-assisted hydrolysis and racemization. For SiH_3F structures of these complexes are close to octahedral with NH_3 or H_2O in axial positions, while those for silyl chloride are closer to trigonal bipyramidal zwitterions formed by the SiH_3 cation with two nucleophiles and the Cl anion separated from Si by ca. 3 Å. The barriers separating these local minima from collapsing into the global minima (with inversion of configuration) are ca. 10 kcal/mol in systems with two ammonia molecules, However, with substitution of ammonia by water molecules these barriers tend to disappear, and shallow minima at the top of the barrier for inversion of configuration develop into transition states. This tendency is more pronounced for silyl chloride. The barrier for this channel providing inversion of configuration for the $SiH_3Cl + 2H_2O$ system becomes lower than the competing channel leading to the hydrolysis products. This is in keeping with the observed preference of the inversion channel for the neutral hydrolysis of chlorosilanes.

Introduction

Bimolecular nucleophilic displacement of alkyl derivatives with carbon at the center ($S_N2(C)$ reactions) is one of the most studied types of reaction in organic chemistry. The main feature of these reactions is the double-well shape of the potential energy surface with pentacoordinated carbon in the transition state structure. The rather different nature of the S_N2-type reactions at silicon is also well-known due to numerous experimental (see refs 1−5 and references therein) and theoretical[6−25] studies. There are two main experimentally observed differences between displacement reaction at carbon and silicon: (a) the latter are much faster; and (b) two paths, i.e., inversion and retention of configuration, are observed for nucleophilic displacement reactions at silicon, while S_N2 reactions at carbon proceed invariably with the inversion of configuration. These conclusions were drawn from numerous stereochemical studies of such reactions at chiral silicon.

Practically all theoretical studies of the S_N2-type reactions at silicon have been devoted to the anionic systems, where the potential energy surfaces (PES) for

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10.1021/om010181t CCC: $20.00
Publication on Web 06/12/2001

the backside attack of H^-, Hal^-, and OH^- at the SiH_3X were investigated.[6−21] It was shown that the anionic pentacoordinated silicon species, in contrast to similar reactions at carbon, correspond to the minima at the PES of the systems studied. The cleavage of the SiX bond goes with inversion of configuration.

In contrast to this, there are just a few theoretical studies of this type of reaction with neutral molecules. In such reactions the interaction with water, i.e. hydrolysis of silicon compounds, has practical importance, since it is a first step in the sol−gel processes widely used in modern chemical technologies.[26] However, many experimentalists describe its mechanism in terms of textbook $S_N2(C)$ reactions. Although the attack of a hydroxyl anion may be regarded as a model of hydrolysis under highly basic conditions, a more realistic description of neutral hydrolysis should deal with interaction of silanes with water molecule(s). Kudo and Gordon[22] reported a study of the stepwise hydrolysis of $SiCl_3H$ in 1998. At the first step of the sequential cleavage of the three SiCl bonds the minimum for the frontside attack of a water molecule and the transition state for formation of $SiCl_2OH$ were obtained.[22] The analogous minimum and the transition state were found this year for the frontside attack of a water molecule at SiH_3F.[25] Stationary points were also located for the interaction of $MeSi(OMe)(OH)_2$with a water molecule.[23] In all these studies the comparatively low barriers were found only for the retention of configuration channel. The geometry of stationary points for this channel appears to be obvious: formation of a hydrogen bond between the halogen (or oxygen) atom, transition state in which the Si−O bonds begins to form (utilizing the ability of silicon for pentacoordination), and finally formation of a SiO bond with the elimination of the HHal molecule.

It seems more difficult to propose the mechanism for the inversion of configuration under hydrolysis. Experimental results, however, provide evidence that despite the general tendency for a retention channel for silicon, many hydrolysis reactions, especially for R_3SiCl molecules, proceed with inversion of configuration. Although the transition state for hydrolysis with the backside attack at SiH_3F has been found,[25] its barrier height appears to be more than 2 times larger than that of the retention channel. Backside complexes were found to be weakly bound; Si−O separation was optimized to be 2.886 Å [MP2/6-311++G(d,p)] for SiF_4[24] and 2.776 Å [MP2/6-311+G(d,p)] for SiH_3F.[25] One may expect that for halosilanes R_3SiHal with bulky R substituents (hydrolysis of which is usually studied experimentally) such a backside complex will be weaker, if it exists.

Kinetic studies of nucleophilic substitution reactions at the silicon center, and hydrolysis (alcoholysis) reactions particularly, show that these reactions are catalyzed by other nucleophiles.[27−36] To rationalize these experimental observations, it was proposed that the nucleophile forms a hydrogen bond with a water (alcohol) molecule, increasing the nucleophilicity of the attacking molecule.[27−28] However two groups of experiments cannot be explained by this model: (a) the dramatic change from inversion to retention for hydrolysis reactions of chlorosilanes R_3SiCl with addition of nucleophiles and (b) the racemization of halosilanes by nucleohiles. The similarity of the rate laws and the activation parameters leads to the conclusion that a similar mechanism is operative for both reactions. To account for these observations, the model of a hexacoordinated silicon intermediate or transition state was proposed.[32−34] This concept as well as the existence of hexacoordinated silicon compounds has been widely discussed (see refs 37−41 and references therein). However, there are still no theoretical studies of these hexacoordinated molecules, and it is not known whether these intermediates are minima or transition states (the distorted octahedral complex of SiF_4 with two water molecules was found to be the minimum by Ignatov et al.[24]). Thus, the aim of this paper was the systematic study of the hydrolysis reaction of silylhalides (modeled by SiH_3F and SiH_3Cl) with and without the presence of nucleophile (modeled by NH_3). We especially wanted to know whether the qualitative concept of the crucial role of hexacoordinated silicon intermediates in the hydrolysis reactions as well as in their racemization by nucleophiles proposed by Corriu can be understood in terms of the quantum mechanical examination of the PES for these systems.

Theoretical Methods

The computational methods employed in this work included electron correlation. These were the hybrid DFT method with Becke's three-parameter exchange functional[42] and the LYP correlation functional[43] (B3LYP) and second-order Moller−Plesset perturbation theory (MP2).[44] The basis sets were the standard 6-31G(d,p) and 6-311+G(d,p) sets. The frozen core approximation was used with the MP2 method. Both these methods and the 6-31G(d,p) and 6-311+G(d,p) basis set were employed as they are implemented in the GAUSSIAN 94 program.[45] Vibrational frequencies were evaluated for all stationary points at all theory levels. Zero-point vibrational energy (ZPVE) corrections, thermal corrections, and entropies cited in the tables refer to those obtained by the MP2/6-311+G-(d,p) method.

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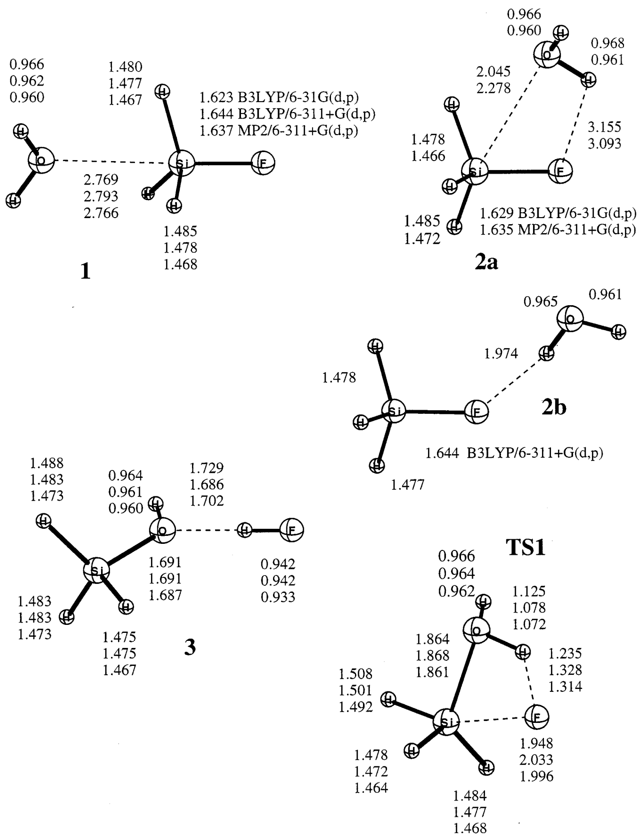

Figure 1. Equilibrium structures (bond lengths in Å) of stationary points for the $SiH_3F + H_2O$ system.

Results and Discussion

A. Interaction of Silyl Halides with One Water Molecule. Attempts to find energy minima for different directions of attack of a water molecule were carried out. These include the attack at the H_3Si face, at the FH_2Si face, and at the HH and HF edges of the H_3SiF tetrahedron. Only two minima (**1** and **2**, Figure 1) corresponding to the well-known backside and frontside attack complexes were found. The backside attack complex **1** is characterized by a substantially large Si−O separation and small perturbation of the H_3SiF geometry. The Si−O bonding within the B3LYP method decreases with the addition of diffuse functions to the basis set, but the MP2 optimized geometry indicates the strengthening of this bond compared to that from B3LYP.

While the optimized geometry of **1** is similar for all three methods employed, the equilibrium geometry of the frontside complex obtained with B3LYP/6-311+G(d,p) (**2b**) is quite different from that optimized with the two other methods (**2a**). The former is characterized by the large Si−O separation (4.19 Å) and a hydrogen bond between the water molecule and the fluorine atom. Geometries optimized with the other two methods show a weaker hydrogen bond but substantially shorter Si−O distances. Both complexes are very shallow minima (Table 1): complex **1** is 3.5 kcal/mol deep and **2** is bound by only 2.7 kcal/mol [ΔH_{298} with MP2/6-311+G(d,p)].

The structure of the transition state **TS1** which connects **2** with the product complex (**3**, Figure 1) shows no significant deviations among the methods employed. The barrier for this pathway was predicted to be 28.4 kcal/mol above reactants. Note that the second path, found in the previous study,[25] which connects **1** with **3**, has too high a barrier to surpass and will not be discussed in the present work. There is a certain difference in the equilibrium structures of the complex **3** between those obtained with the B3LYP and MP2 methods employing the 6-311+G(d,p) basis set and that from B3LYP/6-31G(d,p). The latter has no symmetry and the HF moiety is oriented toward the one lone pair of oxygen, while the two other structures are of C_s symmetry with HF lying in the symmetry plane (**3**, Figure 1). This difference reflects the equilibrium SiH bond lengths: the C_s structures have two elongated SiH bonds (both with *trans*-orientation toward the oxygen lone pairs), while the asymmetric B3LYP/6-31G(d,p) structure exhibits the maximum elongation of the SiH bond, which is in the *trans*-position toward the lone pair involved in the hydrogen bonding.

Similar stationary points were found for the $SiH_3Cl + H_2O$ system (**4**−**6**, Figure 2). However, there is no discrepancy in the equilibrium geometry between the methods employed for the frontside complex **5**. All three methods predict a more loosely bound structure than in the fluorine analogue **2**. The substantially longer H···Cl interatomic distance (2.91 Å at the MP2 level) and equal O−H bond lengths in the water molecule evidence the absence of the hydrogen bond between SiH_3Cl and a water molecule in the frontside complex.

B. Interaction of Halosilanes with One and Two Ammonia Molecules. A Model for Nucleophile-Assisted Racemization. Kinetic studies of nucleo-

Table 1. Energy E_e, E_0, and E_{298} Values (hartrees) for the Reactants in the $SiH_3X + H_2O$ (X = F, Cl) Systems and Relative Values (with respect to reactants, kcal/mol) of These Energetic Quantities for the Other Stationary Points

	B3LYP		MP2		
	6-31G(d,p)	6-311+G(d,p)	6-311+G(d,p)		
stationary points	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_0(\Delta H_0)$	$E_{298}(\Delta H_{298})$
$SiH_3F + H_2O$	−467.60358	−467.70566	−466.79528	−466.74519	−466.73727
1	−5.5	−3.9	−5.0	−3.4	−3.5
2	−6.1	−3.5	−4.1	−2.6	−2.7
TS1	23.0	27.4	28.9	30.0	28.4
3	−4.3	−3.5	−1.9	−0.2	−0.7
$SiH_3OH + HF$	15.1	9.7	8.3	7.6	7.7
$SiH_3Cl + H_2O$	−827.95404	−828.04743	−826.75264	−826.70358	−826.69550
4	−5.9	−3.5	−4.5	−3.2	−3.1
5	−4.8	−2.2	−3.8	−2.6	−2.5
TS2	16.4	22.0	24.2	26.2	24.7
6	−6.0	−2.9	−4.2	−4.1	−4.5
$SiH_3OH + HCl$	0.7	3.6	2.9	1.3	1.3

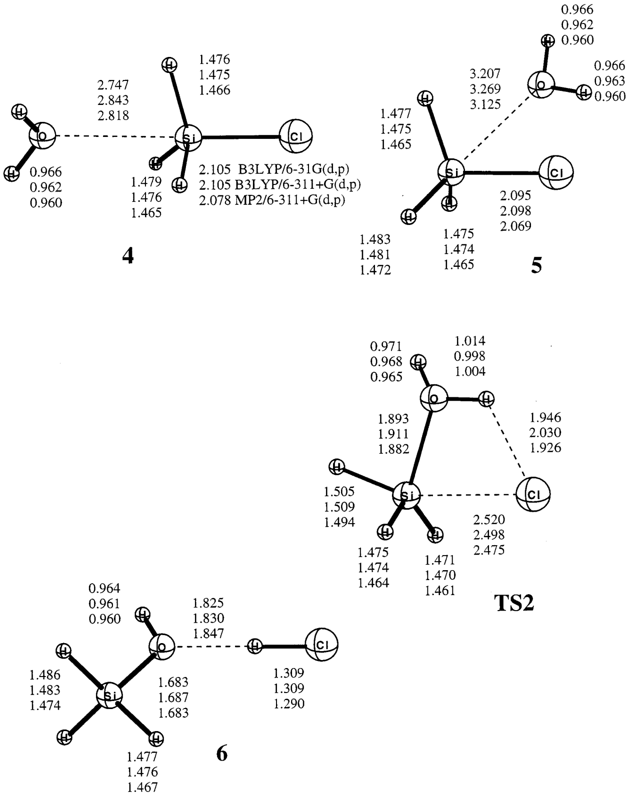

Figure 2. Equilibrium structures (bond lengths in Å) of stationary points for the $SiH_3Cl + H_2O$ system.

phile-assisted racemization of halosilanes have shown that it is a second-order process with respect to nucleophile. These reactions are also characterized by small enthalpies of activation (0−4 kcal/mol) and large and negative entropies of activation (from −55 to −70 cal/mol·K).[46−47] To account for these observations Corriu[46] proposed a model of the octahedral $SiR_3Hal·2Nu$ intermediate (or transition state) with two nucleophile molecules in the axial positions. The attack of the first nucleophile molecule at the chiral SiR_3Hal leads to the formation of the pentacoordinated intermediate. The second slow (rate-determining) step in the racemization reaction is the attack by a second nucleophile at the R−Hal edge and the formation of the octahedral intermediate. Dissociation of this intermediate results in the inversion of the configuration of SiR_3Hal. Note that kinetic studies cannot provide evidence whether the activation complex is an intermediate or a transition state.

In the present study we model these processes with SiH_3Hal (Hal = F, Cl) and NH_3 as a nucleophile. Although the formation of the stable pentacoordinated complexes between SiH_3Hal (Hal = F, Cl),[48] SiH_4,[48,49] and SiH_4[49−51] was predicted by semiempirical and ab initio methods earlier, here we report equilibrium geometries of complexes between SiH_3F, SiH_3Cl, and NH_3. In keeping with the above consideration of the H_2O attack at the SiH_3F molecules, we have studied the backside (at the H_3 face of the SiH_3F tetrahedron) and the frontside (at the HF edge) attacks by NH_3 (the frontside attack complex was not reported earlier). Both directions of attack produce energy minima (**7** and **8**, Figure 3); however the complex formed by the backside attack is more stable by 3 kcal/mol (Table 2).

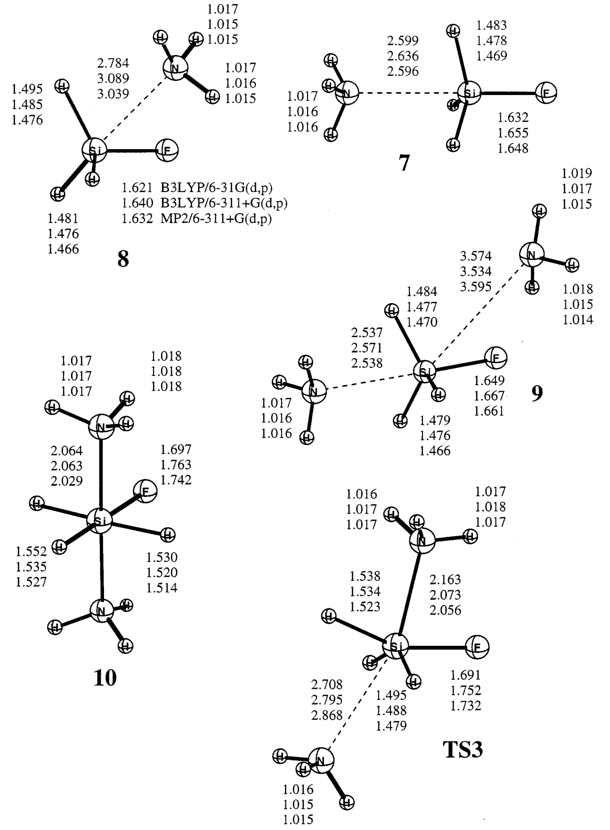

Figure 3. Equilibrium structures (bond lengths in Å) of minima for the interaction of the SiH_3F molecule with one (**7** and **8**) and two (**9** and **10**) ammonia molecules and the transition state **TS3** for inversion of configuration of SiH_3F.

The attack of two ammonia molecules from both directions leads to the barrierless formation of complex **9**, stable at all levels of theory employed. It may be regarded as a backside complex with an additional ammonia molecule coordinated through the HF edge, since the backside Si−N separation is even shorter than in **7** and the frontside separation is longer than in **8** (Figure 3). Note the coordination of the second ammonia molecule stabilizes the backside complex **7** by 2 kcal/mol (Table 2).

The other energy minimum was also found in the $SiH_3F + 2NH_3$ system. It corresponds to the octahedral tightly bound complex **10** (Figure 3). All methods predict that it lies 3−6 kcal/mol higher than reactants (Table 2). This complex has a C_{2v} symmetry with the in-plane hydrogens of ammonia slightly elongated. This indicates weak hydrogen bonding between SiH_3F and NH_3. The SiH_3F moiety becomes planar with elongated SiF and SiH bonds. Analysis of the molecular orbitals shows a substantial increase in participation of the silicon d orbitals in **10** compared to the loosely bound complex **9**.

The two minima on the PES of the $SiH_3F + 2NH_3$ system are connected by the transition state **TS3**

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Table 2. Energy E_e, E_0, and E_{298} Values (hartrees) and Entropy (S, cal/mol·K) for the Reactants in the $SiH_3Hal + nNH_3$ (Hal = F, Cl, n = 1, 2) Systems and Relative Values (with respect to reactants) of Energies (kcal/mol) and Entropies (ΔS) for the Other Stationary Points

	B3LYP	B3LYP	MP2			
	6-31G(d,p)	6-311+G(d,p)	6-311+G(d,p)			
stationary points	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_0(\Delta H_0)$	$E_{298}(\Delta H_{298})$	$S(\Delta S)$
$SiH_3F + NH_3$	−447.74161	−447.82984	−446.93587	−446.87265	−446.86470	102.9
7	−7.7	−6.2	−7.2	−5.1	−5.5	−26.6
8	−4.8	−2.8	−4.0	−2.6	−2.7	−22.0
$SiH_3F + 2NH_3$	−504.29938	−504.41248	−503.35118	−503.25315	−503.24139	148.9
9	−11.9	−8.7	−10.6	−7.1	−7.4	−48.1
TS3	7.3	12.8	11.0	15.0	13.9	−54.9
10	3.6	5.8	1.7	8.2	6.3	−65.6
$SiH_3Cl + NH_3$	−827.95404	−828.04743	−826.75264	−826.70358	−826.69550	104.8
11	−8.4	−5.4	−6.4	−4.5	−4.7	−25.5
12	−3.9	−2.1	−3.9	−2.6	−2.6	−21.7
$SiH_3Cl + 2NH_3$	−864.64984	−864.75425	−863.30854	−863.21154	−863.19962	151.7
13	−11.9	−7.3	−9.8	−6.6	−6.6	47.4
TS4	7.1	12.4	11.0	15.4	14.2	−57.1
14	−6.6	0.1	−2.0	5.0	3.1	−67.6

(Figure 3). This structure belongs to the C_s point group and is characterized by the nonequivalence of SiN bonds: one bond is almost as short as in **10**, while the length of the other is close to that of the backside complex **9**. The SiH_3F moiety is close to becoming planar with the in-plane HSiF bond angle of 161.4° and the HSiH angle in the orthogonal plane of 136.7° (MP2 values). The barrier height associated with **TS3** varies with the method, but with the more reliable MP2 method the ΔH_{298} value is 14 kcal/mol above the reactants.

Similar stationary points were found on the potential energy surfaces of the $SiH_3Cl + NH_3$ and $SiH_3Cl + 2NH_3$ systems. Front- and backside orientations of the ammonia attack at chlorosilane give two minima (**12** and **11** with slightly longer SiN separations than those for fluorosilanes (Figure 4). However, the energy gain of this complexation does not differ significantly, and the frontside complex **12** is also less stable than the backside complex **11** by 3 kcal/mol (Table 2).

The structure of complex **13** formed by the attack of two NH_3 molecules differs slightly from the fluorine analogue **9** in the orientation of the loosely bound ammonia due to increase of repulsive interactions between the electron densities of ammonia and chlorine (Figure 4), but the energy of complexation is nearly the same for the two complexes.

More significant differences may be found between the structures of the tightly bound "orthogonal" complexes **10** and **14**. While that with fluorine is nearly orthogonal (HSiH and HSiF angles are close to 90°), the chlorine complex is closer to the trigonal bipyramidal structure with HSiH = 104.2° and HSiCl = 75.8°. This and the extremely long Si−Cl distance allow one to describe the structure of **14** as a doubly coordinated SiH_3^+ cation with a Cl^- counterion. Although the C_{2v} symmetry is still maintained in **14** the N−Si−N angle is not close to 180°, as in the case with the fluorine analogue **10**, but rather is 156.5°.

In contrast to the loosely bound pair (**9** and **13**) the tight Cl complex **14** is substantially more stable than its fluorine analogue **10**. Both B3LYP/6-31G(d,p) and MP2/6-311+G(d,p) predict the energy of this complex to be lower than the reactants. However, with the ZPVE and thermal corrections ΔH_{298} becomes 3 kcal/mol higher than the reactants (Table 2).

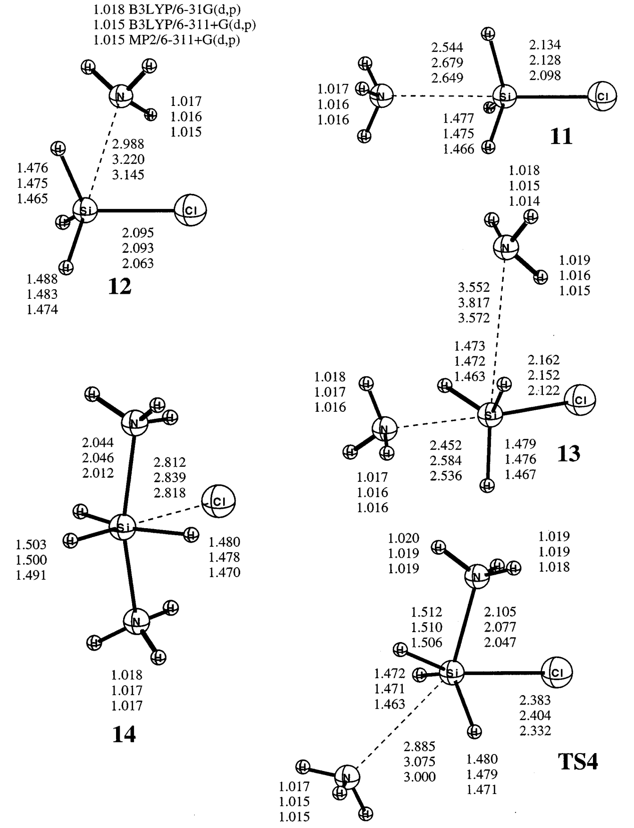

Figure 4. Equilibrium structures (bond lengths in Å) of minima for the interaction of the SiH_3Cl molecule with one (**11** and **12**) and two (**13** and **14**) ammonia molecules and the transition state **TS4** for inversion of configuration of SiH_3F.

The barriers on both sides of the local minima (**TS3** for **10** in the F system; **TS4** and **14** for Cl) increase their height on going from SiH_3F to SiH_3Cl and become 11 kcal/mol above the minimum (**TS4**, Table 4). The motion through this bump (**TS4**−**14**−**Ts4**) with subsequent detachment of ammonia inverts the configuration of the SiH_3Cl molecule and in the case of the chiral molecule $R_1R_2R_3SiCl$ leads to its racemization. Our estimate of the entropy difference between reactants and tight structures **10** and **14** is ca. 67cal/mol·K (Table 2). This is in good agreement with values derived from the racemization kinetic studies (from −55 to −70 cal/mol·K),[46−47] although Δ*S* values for **TS1** also fall in this range.

Thus, answering the question posed by experimentalists whether the tightly bound species postulated are intermediates or transition states, we may say that for the systems with two nucleophiles the metastable intermediate may exist at the top of a bump, but the overall barrier is determined by the transition states **TS1**. Our predictions of these barrier heights exceed those estimated from the kinetic data. However, the system studied experimentally contained much more bulky substituents than H. Below we will see that substitution of ammonia in the axial positions by water leads to the disappearance of the minimum at the top.

C. Interaction of Halosilanes with One Water and One Ammonia Molecule. A Model for Nucleophile-Assisted Hydrolysis. Nucleophilic substitutions at silicon and particularly hydrolysis reactions of halosilanes have been found experimentally to be catalyzed by the presence of other nucleophiles.[27−36] These reactions proceed with retention of configuration even with chlorosilanes, where inversion of configuration is preferable in the absence of the nucleophilic catalyst. Nucleophile-assisted hydrolysis involves activation parameters similar to nucleophile-assisted racemization, but the former is first order in the nucleophile. These observations allowed Corriu[32−34] to propose similar models of the hexacoordinated activated complex for the racemization and hydrolysis reactions. The explanation of the difference in stereochemistry between the nucleophile-catalyzed hydrolysis of chlorosilanes and the neutral one is obvious. In the former case the nucleophile blocks one axial position in the octahedron, allowing the water in the other axial position to react with the SiH_3Cl moiety only in a retentive way, while the symmetric octahedral complex of SiH_3Cl and two water molecules may dissociate either by inversion or by retention.

As in the previous case, our modeling of the catalyzed hydrolysis starts with SiH_3F interacting with NH_3 as a nucleophile. Now we have two plausible forms of the complexes originating from the simultaneous attack of a water molecule and an ammonia molecule. The structure in which ammonia takes the backside position and the water molecule is in the frontside position, **15**, Figure 5), is more stable by 4 kcal/mol than the complex with the water molecule in the backside position (**16**). Both complexes are similar to complex **13** in the $SiH_3F + 2NH_3$ system, in that the molecule in the backside position has stronger bonding to silicon than that in the frontside position. However, in **15** attraction between SiH_3F and H_2O is provided by H-bonding. The latter structure is similar to **2b**, Figure 1, with addition of NH_3 in the backside position. Addition of NH_3 stabilizes **2** by 6.6 kcal/mol (Tables 1 and 3). Complex **16** may be regarded as a variant of complex **1** (Figure 1) with addition of NH_3 in the frontside position. In this case stabilization enthalpy that results from the addition of ammonia is less than 2 kcal/mol.

The third energy minimum (**17**, Figure 5) in the $SiH_3F + H_2O + NH_3$ system corresponds to the structure with hexacoordinated silicon and comparatively short SiO and SiN bonds. This local minimum is predicted to lie 10.6 kcal/mol (ΔE_e, MP2, Table 3) above reactants. Thermal corrections at 298 K raise its value to 15.0 kcal/mol, and at this temperature it is separated from the more stable loosely bound complex **15** by a very low barrier **TS5** (Figure 5). The height of this barrier decreases with the theory level, reaching only 0.6 kcal/mol at MP2 (ΔH_{298}, Table 3). The second channel for the rearrangement of the octahedral complex **17** is the elimination of HF, leading through **TS6** to the exit complex **18**, dissociation of which gives the final product of hydrolysis, i.e., methanol and HF.

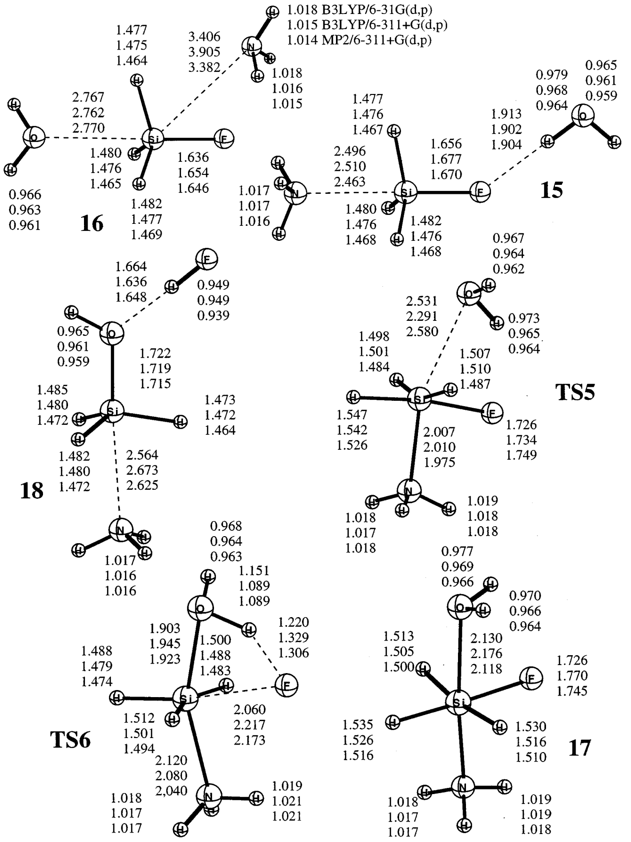

Figure 5. Equilibrium structures (bond lengths in Å) of stationary points for the $SiH_3F + H_2O + NH_3$ system.

The structure of the transition state **TS6** resembles that for the retention channel in the $SiH_3F + H_2O$ system (**TS1**, Figure 1), and it may be produced by the backside attack of NH_3 at this transition state. Similar to **TS1** in the system with one water molecule, the transition state for HF elimination in the $SiH_3F + H_2O + NH_3$ system is characterized by elongation of the Si−F bond and formation of the H−F bond. The catalytic effect of ammonia is revealed by the fact that the barrier height for this transition state with addition of the NH_3 molecule decreases from 28.4 kcal/mol (Table 1) to 20.9 kcal/mol (ΔH_{298}, MP2).

The downhill motion from the above barrier results in the exit complex **18**, which is similar to the complex between silanol and HF **3** with an ammonia molecule coordinated to the backside of the silanol molecule. This coordination lowers the ΔH_{298} value of the exit complex by 5 kcal/mol.

Similar stationary points are found for the $SiH_3Cl + H_2O + NH_3$ system (Figure 6). The loose complex **19** is connected with the tight “octahedral” complex **21** (better described as trigonal bipyramidal, since as in the $SiH_3Cl + 2NH_3$ system the Si−Cl separation is substantially

Table 3. Energy E_e, E_0, and E_{298} Values (hartrees) and Entropy (S, cal/mol·K) for the Reactants in the $SiH_3Hal + NH_3 + H_2O$ (Hal = F, Cl) Systems and Relative Values (with respect to reactants) of Energies (kcal/mol) and Entropies (ΔS) for the Other Stationary Points

	B3LYP		MP2			
	6-31G(d,p)	6-311+G(d,p)	6-311+G(d,p)			
stationary points	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_0(\Delta H_0)$	$E_{298}(\Delta H_{298})$	$S(\Delta S)$
$SiH_3F + NH_3 + H_2O$	−524.16135	−524.28830	−523.21059	−523.12569	−523.11396	148.0
15	−15.0	−11.3	−12.8	−8.8	−9.3	−46.3
16	−9.8	−6.1	−8.2	−5.4	−5.3	−44.7
TS5	10.2	15.6	12.2	23.0	15.6	−62.1
17	8.7	13.4	10.6	16.8	15.0	−63.3
TS6	15.4	19.9	18.5	23.6	20.9	−70.0
18	−3.5	−6.0	−8.7	−4.9	−5.8	−52.7
$SiH_3Cl + NH_3 + H_2O$	−884.51181	−884.63007	−883.16795	−883.08408	−883.07219	150.7
19	−14.4	−8.7	−10.8	−7.2	−7.5	−48.4
20	−8.8	−5.1	−7.8	−5.2	−5.0	−45.1
TS7	9.8	17.5	17.3	22.2	20.7	60.8
21	−1.6	6.9				
TS8	−1.5					
22	−14.0	−8.2	−10.6	−8.5	−9.2	−51.5

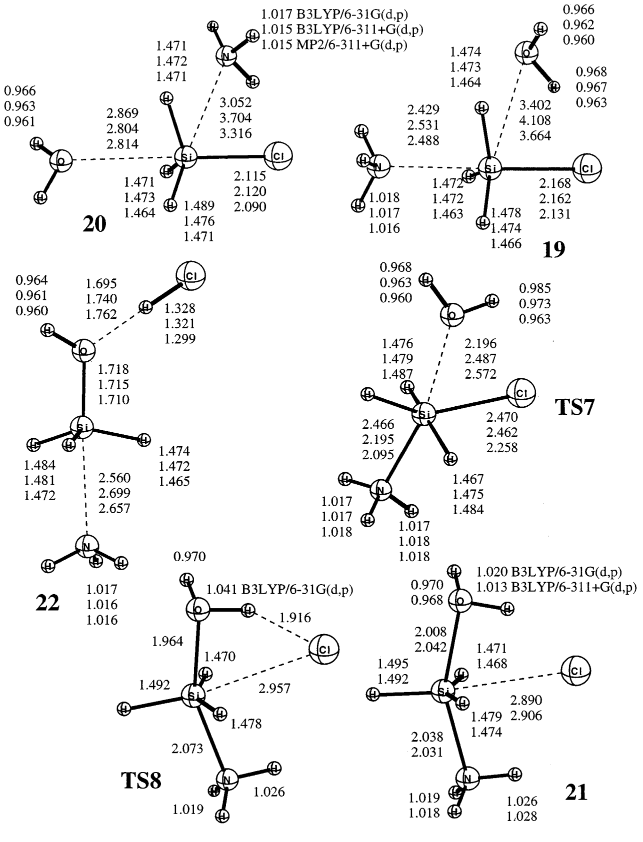

Figure 6. Equilibrium structures (bond lengths in Å) of stationary points for the $SiH_3Cl + H_2O + NH_3$ system.

large) by the transition state **TS7** (Figure 6). However in contrast to the $SiH_3F + H_2O + NH_3$ system, where a distinctive albeit shallow minimum exists at all the theory levels employed, for chlorosilane such a minimum could not be located at the MP2/6-311+G(d,p) level. All attempts to find it resulted in the exit complex **22**. The transition state separating **21** and **22** was located only at the B3LYP/6-31G(d,p) level (**TS8**, Figure 6), but its structure is very close to **21** and the barrier is only 0.1 kcal/mol. Neither B3LYP nor MP2 with the basis set including diffuse functions was able to locate this transition state. Thus, **TS7** is the only transition state in this system, and it connects the loose complex **19** with the product complex **22**. Although the structure of **TS7** deviates from symmetric species (with nearly equal SiO and SiN bond lengths and a planar SiH_3Hal moiety as in **17**), it is tight enough ($\Delta S = 60.8$ cal/mol·K) to be a good candidate for the low-entropy transition state proposed by experimentalists.[32−34] Note that the basis set with and without diffuse functions predicts different structures for this transition state. The B3LYP/6-31G(d,p) gives a SiN separation larger than SiO, while the two other methods predict shorter SiN bonds (**TS7**, Figure 6).

D. Interaction of Halosilanes with Two Water Molecules. A Model for Neutral Hydrolysis. Since it was observed that hydrolysis of chiral chlorosilanes without nucleophile catalysts proceeds mainly with inversion of configuration, we will try to find how our model explains this observation. The prediction of the mechanism of the inversion of configuration for neutral hydrolysis (interaction with water molecules) is a challenging task for theory, since it is difficult to construct a mechanism by which the configuration of chlorosilanes may be inverted in a weakly bound complex (in contrast to the attack of the anion, where the path for this inversion is straightforward). Earlier we found a transition state for the inversion of configuration of SiH_3F,[25] but this barrier was prohibitively high (ca. 80 kcal/mol) and the similar barrier in SiH_3Cl is only 20 kcal/mol lower.

There is only one type of loosely bound complex of halosilanes with two water molecules (**23**, **26**) where the waters occupy two plausible positions (back- and frontside). The addition of the second water to **1** or **2** strengthens the Si−O and F−H bonds between fluorosilane and water and lowers the energy of this complex by ca. 5 kcal/mol (addition of ammonia exceeds this effect by 2−3 kcal/mol). Similar to the case of one water molecule, the water in the frontside position has a channel for HF elimination through the transition state **TS10**, Figure 7). This is a retention of configuration channel with comparatively low barrier discussed above. An analogous transition state was found for SiH_3Cl (**TS12**, Figure 8). The catalytic effect of the second water in lowering this barrier is small (ca. 2 kcal/mol). The descent from this barrier gives the product complexes **25** and **28**.

Table 4. Energy E_e, E_0, and E_{298} Values (hartrees) and Entropy (S, cal/mol·K) for the Reactants in the $SiH_3Hal + NH_3 + H_2O$ (Hal = F, Cl) Systems and Relative Values (with respect to reactants) of Energies (kcal/mol) and Entropies (ΔS) for the Other Stationary Points

	B3LYP		MP2			
	6-31G(d,p)	6-311+G(d,p)	6-311+G(d,p)			
stationary points	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_e(\Delta E_e)$	$E_0(\Delta H_0)$	$E_{298}(\Delta H_{298})$	$S(\Delta S)$
$SiH_3F + 2H_2O$	−544.02332	−544.16412	−543.07000	−542.99823	−542.98653	147.1
23	−12.4	−8.3	−9.7	−6.7	−6.7	−40.7
TS9	18.8	23.5	23.6	29.2	27.0	−6.2
24	16.4		21.3	27.2	25.4	−64.6
TS10	18.8	25.0	25.4	28.2	26.7	−58.6
25	−1.6	−4.0	−6.7	−3.5	−4.0	−48.8
$SiH_3Cl + 2H_2O$	−904.37378	−904.50589	−903.02736	−902.95662	−902.94476	149.6
26	−11.4	−6.1	−8.2	−5.6	−5.4	−42.3
TS11	5.8	16.4	16.2	22.7	20.0	−69.8
27	5.6					
TS12	11.4	19.4	20.1	23.7	22.5	−55.4
28	−11.8	−6.4	−8.8	−7.2	−7.6	−47.4

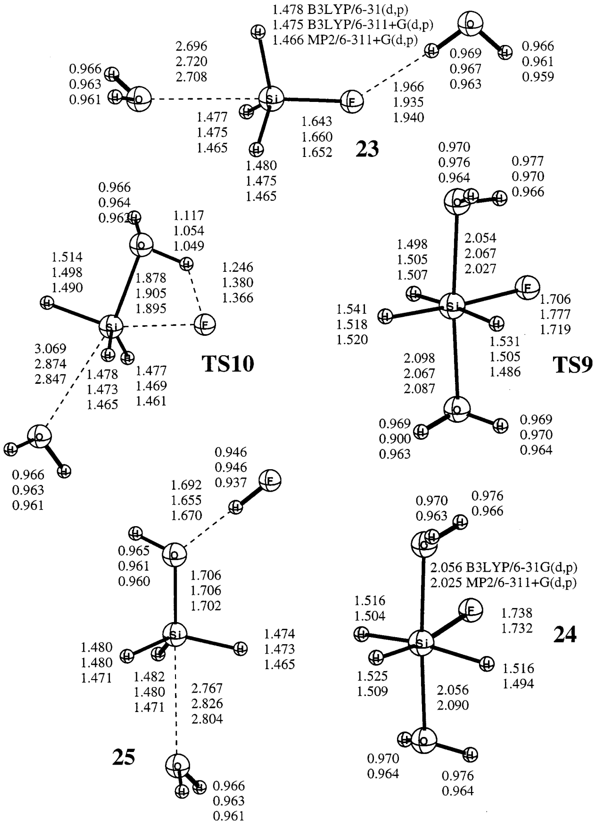

Figure 7. Equilibrium structures (bond lengths in Å) of stationary points for the inversion of configuration (**23**−**TS9**−**24**−**TS9**−**23**) and hydrolysis (**23**−**TS10**−**25**) channels in the $SiH_3F + 2H_2O$ system.

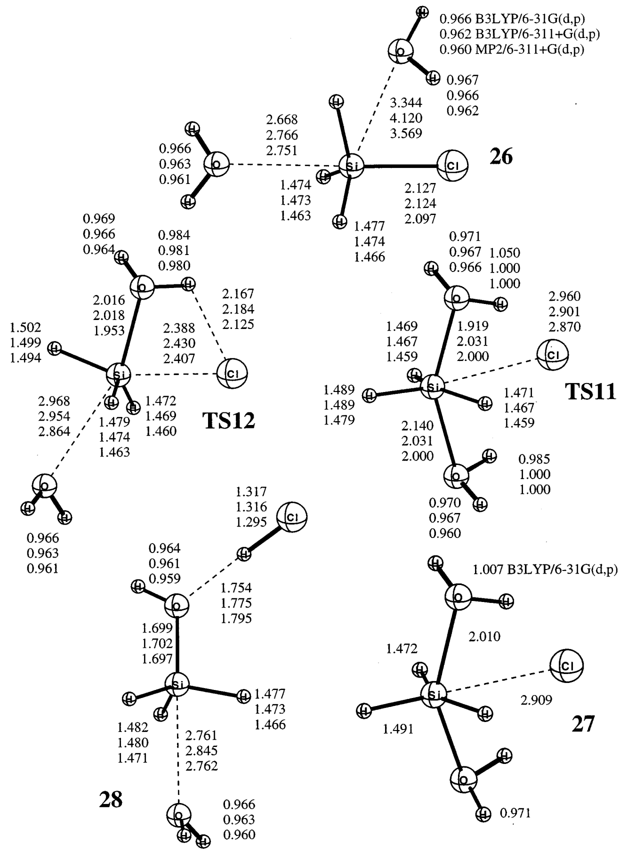

Figure 8. Equilibrium structures (bond lengths in Å) of stationary points for the inversion of configuration (**26**−**TS11**−**27**−**TS11**−**23**) and hydrolysis (**26**−**TS12**−**28**) channels in the $SiH_3Cl + 2H_2O$ system.

The symmetric (with equal SiO bonds) tight structures of C_s and C_2 symmetry were found to be minima at the B3LYP/6-31G(d,p) level **23** in the $SiH_3F + H_2O$ system. However these symmetric structures possess one imaginary vibrational frequency each (ca. 100i cm^{-1}) at two other levels. Attempts to find a minimum for a slightly asymmetric structure succeeded for MP2/6-311+G(d,p), but for B3LYP/6-311+G(d,p) they lead to the global minimum **23**. Corespondingly, the transition state **TS1** was located at the B3LYP/6-31G(d,p) and MP2/6-311+G(d,p) levels, which separate **24** from collapsing to the global minimum **23**. However this barrier is only 1.6 kcal/mol (ΔH_{298}, Table 4).

For $SiH_3Cl + 2H_2O$ the symmetric minimum **27** was found only at the B3LYP/6-31G(d,p) level, and it is divided from the global minimum **26** by a barrier (**TS11**, Figure 8) of only 0.2 kcal/mol. Thus the existence of the minimum at the top of the barrier between two loosely bound complexes with two water molecules (for chiral halosilanes it will be the barrier for racemization) may be (especially for chlorosilanes) an artifact of small basis sets.

Nevertheless, the crossing of the **TS11** barrier may lead to the inversion of configuration of the chlorosilane molecule (similar to the case of two ammonia molecules).

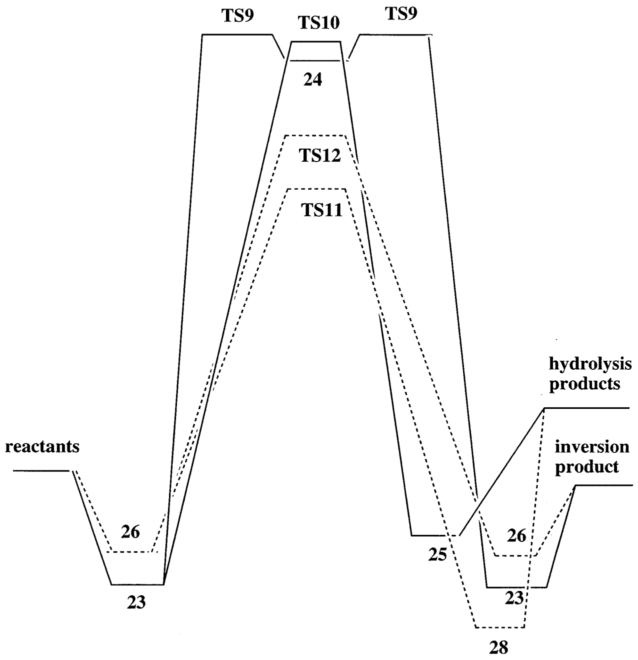

Figure 9. Potential energy diagram for stationary points for the inversion and hydrolysis channels in the SiH_3F + $2H_2O$ and the SiH_3Cl + $2H_2O$ (dashed lines) systems.

The barriers for the systems with two H_2O's are 27 kcal/mol for SiH_3F (**TS9**) and 20 kcal/mol for SiH_3Cl (**TS11**). This process may compete with hydrolysis within the loosely bound complex through **TS10** (for F) and **TS12** (for Cl). The possibility of inversion of configuration before hydrolysis (and the overall observed hydrolysis with inversion of configuration) depends on the relative heights of barriers for inversion of configuration (**TS9** and **TS11**) and hydrolysis (**TS10** and **TS12**). On going from SiH_3F to SiH_3Cl the former barrier decreases by 7 kcal/mol, while the latter decreases only by 4 kcal/mol. Thus for SiH_3Cl in contrast to SiH_3F the inversion transition state **TS11** becomes lower than **TS10**, and inversion of configuration (racemization for chiral molecules) may occur before hydrolysis (Figure 9). Despite the fact that our system substantially differs from those experimentally studied, this may be the rationale for the observed preference of halosilanes for the inversion of configuration hydrolysis without nucleophiles.

Conclusions

1. In the $SiH_3F + 2NH_3$ and $SiH_3Cl + 2NH_3$ systems the global minima correspond to loosely bound structures in which ammonia molecules occupy backside (SiN separations ca. 2.5 Å) and frontside (above 3.5 Å) sites. Addition of the second ammonia stabilizes the systems by ca. 5 kcal/mol. The second energy minimum corresponds to symmetric structures (C_{2v} point group) with comparatively short SiN bonds (ca. 2.0 Å) and a nearly planar configuration of SiH_3Hal molecules. For Hal = F the structure of the heavy atom skeleton in these complexes is close to octahedral, while for Hal = Cl it is closer to trigonal bipyramidal with a large SiCl separation (ca. 3.0 Å). For Hal = F this tight complex is predicted to lie 14 kcal/mol above the global minimum, and for Hal = Cl, 10 kcal/mol. Barriers dividing these local minima from global are 7 and 11 kcal/mol. Crossing these barriers and the minima between them allows halosilane molecules to invert their configuration. The entropy changes found in experimental kinetic studies for activation of the nucleophile-assisted racemization of chlorosilanes are in good agreement with those predicted in our model, while the entropy changes of our model are substantially higher than those obtained from the experiment.

2. The structures with comparatively short SiO bonds and planar arrangement of the SiH_3F moiety were also found as a local minimum in the $SiH_3F + 2H_2O$ system. However, barriers dividing it from the loosely bound global minima are smaller than 2 kcal/mol. In the $SiH_3Cl + 2H_2O$ system the tight complex becomes the transition structure through which inversion of configuration may be realized. The transition state for the elimination of HHal is found in both systems. This is the unique transition state for hydrolysis, and this process proceeds along this pathway with retention of configuration. However, in the $SiH_3Cl + 2H_2O$ system, in contrast to that for SiH_3F, the barrier for inversion of configuration becomes lower than the barrier for hydrolysis, allowing inversion of configuration prior to hydrolysis. This is in keeping with experimental observation of preference of inversion of configuration hydrolysis for chlorosilanes with respect to retention for fluorosilanes.

3. In the $SiH_3Hal + H_2O + NH_3$ systems the ammonia molecule prefers the energetically most favorable backside position. The complex with short SiO and SiN bonds was also found as a local minimum for Hal = F, but on going from F to Cl with higher levels of theory, this stationary point becomes the transition state for hydrolysis with retention of configuration.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE-9815397.

OM010181T