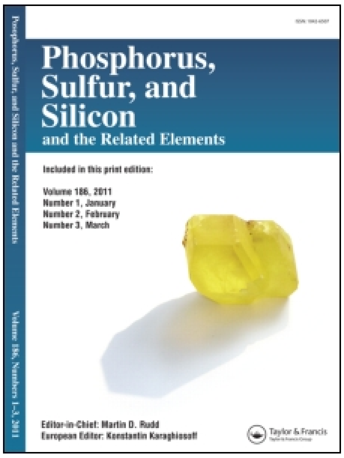


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PATHWAYS FOR NUCLEOPHILIC SUBSTITUTION AT SILICON. A MOLECULAR ORBITAL APPROACH

Joan A. Deiters[a]; Robert R. Holmes[a]
[a] Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Deiters, Joan A. and Holmes, Robert R.(1995) 'PATHWAYS FOR NUCLEOPHILIC SUBSTITUTION AT SILICON. A MOLECULAR ORBITAL APPROACH', Phosphorus, Sulfur, and Silicon and the Related Elements, 99: 1, 33 — 47

To link to this Article: DOI: 10.1080/10426509508031335

URL: http://dx.doi.org/10.1080/10426509508031335

Phosphorus, Sulfur, and Silicon, 1995, Vol. 99, pp. 33–47
Reprints available directly from the publisher
Photocopying permitted by license only

PATHWAYS FOR NUCLEOPHILIC SUBSTITUTION AT SILICON. A MOLECULAR ORBITAL APPROACH[1]

JOAN A. DEITERS[2] and ROBERT R. HOLMES*
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

(Received March 31, 1986)

Minimum strain energy conformations determined by molecular mechanics calculations are used as input structures for a molecular orbital treatment designed to model inversion and retention pathways pertinent to nucleophilic substitution reactions of tetracoordinated silicon compounds. Relative energies along the reaction pathways are compared for the leaving groups, fluorine and chlorine. It is shown that the attacking nucleophile and the leaving group, respectively, prefer axial entry and axial departure over equatorial entry and equatorial departure. Also a retention pathway via pseudorotation is of lower energy than retention occurring via equatorial attack and axial departure. In agreement with experimental results, chlorine is determined to be a better leaving group than fluorine, and chlorine exhibits a strong preference for an inversion pathway over a retention path. In contrast, the inversion and retention routes are more nearly equal in energy when fluorine is the leaving group.

A considerable body of evidence has been accumulated showing that bimolecular displacement reactions at tetracoordinated silicon proceed via a five-coordinated transition state.[3] Unlike carbon chemistry where a similar type of reaction invariably takes place by an inversion process for chiral derivatives, both retention and inversion processes compete with one another for chiral derivatives of silicon. The factors influencing the dominance of one process over the other generally are known, largely from the extensive studies of Corriu[3,4] and co-workers conducted under a variety of experimental conditions in which two principal features were varied, the nature of the attacking nucleophile and the nature of the leaving group. The major conclusions resulting from these studies are that the degree of retention increases along the series of leaving groups in the order OCOR, Br, Cl $<$ SR, F $<$ OR $<$ H and that the use of hard nucleophiles promotes retention of configuration. In the latter class are aryl, phenylethynyl, and alkyl organolithiums, which cause reaction mainly with retention, whereas the softer nucleophiles, allyl, benzyl, and benzhydryl lithiums, react with inversion of configuration.

In many respects, the experimental data on the course of substitution reactions of tetracoordinated silicon parallels related information for the more extensively studied phosphorus compounds. For example, Marsi's studies[5] on the alkaline cleavage of chiral phospholanium salts involving a five-membered ring show increasing retention of configuration as the leaving group is changed according to the series $OSiCl_3 < OCH_3 < CH_2Ph <$ Ph. In another study, that of the alkaline hydrolysis of chiral phosphetanium salts containing a four-membered ring. DeBruin[6] observed retention of configuration increasing in the order of displaced ligands: Cl $< SCH_3 \sim$ OR $\ll Me_2N$. It is seen that retention of configuration in these series for phosphorus, like that for silicon, is inversely related to the axiophilic

---

Reprinted with permission from *J. Am. Chem. Soc.*, **109**, 1686 (1987). Copyright 1987 American Chemical Society.

character of the departing group and that an electronegativity factor is strongly involved. However, other factors enter as well. In the study by DeBruin,[6] a compromise between substituent electronegativity OR > Me_2N ~ Cl > SCH_3 and greater π donor ability of Me_2N[7] and OR[6] compared to that for Cl and SCH_3 was suggested to account for the observed order of retention.

The mechanism generally accepted for the retention process in phosphorus chemistry involves axial entry and axial departure accompanied by pseudorotation of the initially formed five-coordinated intermediate[8,9] (Figure 1). This mechanism shows an adjacent or cis attack, i.e., the relation of the entering group to the group being displaced, with the pseudorotation process taking the initial trigonal bipyramid (TBP) through a square pyramid (SP) to a rearranged trigonal bipyramid. The latter configuration now has the entering nucleophile in an equatorial position and departing group in an axial position.

There is a considerable body of evidence supporting the latter process as the primary retention mechanism for tetracoordinated phosphorus.[10,11] Principal among the evidence is the NMR observance of intramolecular ligand exchange occurring in isolatable phosphoranes[12] and the correlation[13] of solution state and X-ray diffraction structures[14-16] for phosphoranes which follow the Berry pseudorotational coordinate[17] depicted in Figure 1. The latter studies show that a range of phosphoranes[14-16] exist with progressive distortions between the idealized TBP and SP structures. Similar studies have been carried out on isoelectronic members of the series SiX_5^-. Analogous to phosphoranes, the X-ray results show that anionic five-coordinated silicon derivatives are nonrigid and reveal progressive distortions between the TBP and SP.[18-20]

A second mechanism for retention at silicon has been proposed by Corriu[21] in which equatorial attack and axial departure are envisioned (Figure 2). Anh and Minot[22] carried out perturbation studies designed to support the latter adjacent mechanism on the system SiH_3X (X = Cl, F) with H^- as the attacking nucleophile. However, the treatment did not consider the retention scheme in Figure 1 or its

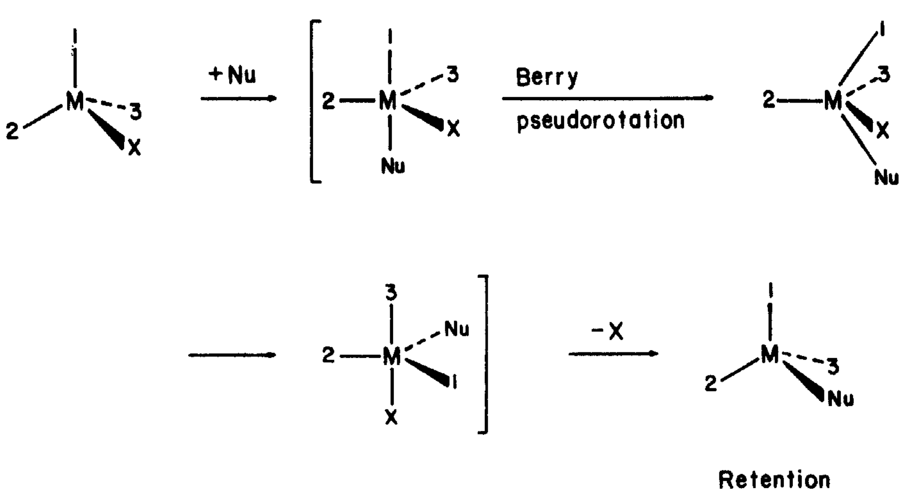


FIGURE 1 Mechanism for retention of configuration in nucleophilic substitution involving equatorial attack and axial departure.

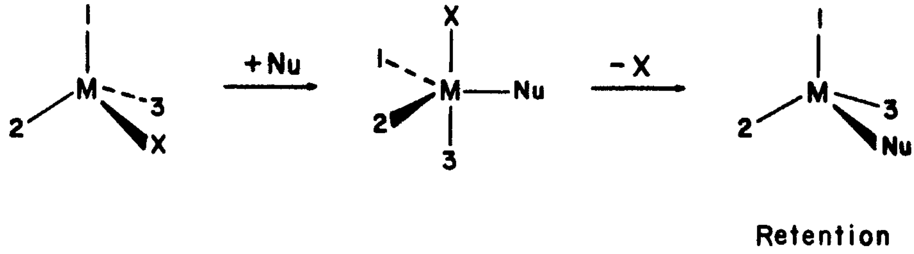


FIGURE 2 Mechanism for retention of configuration in nucleophilic substitution involving equatorial attack and axial departure.

relative merits. Further, the molecular orbital calculations were concerned with fixed geometries, either a tetrahedron or a D_{3h} trigonal bipyramid, employing standard bond parameters.

CALCULATIONS

To gain insight into competitive inversion and retention pathways encountered in nucleophilic substitution reactions of tetracoordinate silicon compounds, we report here molecular orbital calculations on the system

$$SiH_3X + H^- \rightarrow [HSiH_3X]^- \rightarrow SiH_3H + X^-(X = Cl, F)$$

employing GAUSSIAN 82 with STO-3G, STO-6G*, and 6-31+G* basis sets.[23a] The latter includes diffuse orbitals for anionic species.[23b]

The calculations of Anh and Minot[22] were carried out at the STO-3G level. Since this work has been used by Corriu[3,4] to support retention via equatorial attack, we decided to ascertain if this same level of calculation could be extended to support retention via axial attack and pseudorotation. Second, since we were concerned with the relative merits of competing inversion and retention pathways involving energy difference comparisons rather than absolute energies, we felt this objective could be reached more expeditiously by performing calculations at points along the proposed reaction paths using the simpler basis set. Thus, the number of higher order calculations needed to establish the validity of this approach could be reduced.

For this purpose, we carried out calculations with large basis sets on the trigonal bipyramidal system $[SiH_4X]^-$ with X = F_{ax}, F_{eq}, Cl_{ax}, Cl_{eq} to see if the same trends which are evident at the STO-3G level calculations are still evident at a higher level calculation. The two larger basis sets which were used are STO-6G* (includes d orbitals) and 6-31+G* (includes more diffuse orbitals for anionic species[23b]). The results from the latter calculations verified the trends obtained with the simple basis set. Even so, the results should be viewed as indicative since we are relying on potential energy profiles. No attempt is made in this approach to ascertain kinetic features which may exert some importance in evaluating the relative merits of competing reaction coordinates. However, the general agreement with experimental data imparts a measure of confidence to the treatment presented here.

The treatment compares the leaving groups, fluorine and chlorine, and computes the total energy of the system for points along the reaction path defined by the decreasing bond length of the entering group, H^-. To provide more realistic pathways, a geometry associated with a minimum strain energy conformation is determined at each point of approach of H^- by a molecular mechanics calculation employing our adaptation[24] of MMI.[25] The adaptation was formulated specifically for nonrigid phosphorane molecules[24,26] and modified to include the isoelectronic silicon species.[27] The advantage of this type of calculation is that it allows for relaxation from ideal geometry and does not assume standard angles at the silicon center. It has been demonstrated[24,26] that this program reproduces nonrigid five-coordinated geometries that lie along a Berry displacement coordinate[17] (pseudorotational coordinate[14]) between a trigonal bipyramid and a square pyramid and accordingly appears to be a preferable course to use here when dealing with nonrigid entities.

Computed Inversion and Retention Pathways

To compare the relative energies of chlorine and fluorine as leaving groups in inversion and retention processes, four pathways are investigated. These are considered to result from approach of the nucleophile, H^-, at a face or an edge of the tetrahedral molecule, SiH_3X (X = Cl, F), forming trigonal bipyramids. Hydride ion approach at the H-H-H face places the leaving group X in an axial position of a trigonal bipyramid, thus simulating inversion of configuration. Approach of H^- at an H-H-X face results in an adjacent attack with the entering group axial and leaving group at an equatorial site, a retention process. Pseudorotation of this intermediate followed by axial departure models the retention scheme shown in Figure 1.

In contrast to attack at a tetrahedral face which results in the nucleophilic positioned axially, edge attack results in equatorial entry. Both attack at a H-X edge and attack at an H-H edge may be considered adjacent processes. In the former case, the leaving group is situated axially, whereas in the latter, X is located at an equatorial site. The retention process favored by Corriu,[21] i.e., equatorial attack and axial departure (Figure 2), corresponds to the former process.

RESULTS AND DISCUSSION

Pathway Geometries and Energies

Total energies obtained from the molecular orbital calculations on "optimized" geometries for inversion and retention pathways are listed in Table I. These geometries are considered unstable intermediates on the way to products directly or via pseudorotational processes.[10] The optimized geometries resulting from the application of molecular mechanics[24] for the preferred pathways are given in Table SI (supplementary material) as a function of the distance of approach of the hydride ion nucleophile to the silicon center. Parts a and b in Figure 3 graphically portray the relative energies of hydride attack resulting in inversion and retention processes for the leaving groups, fluorine and chlorine, respectively.

From the results of the energy calculations (Table I), several observations can be made for both cases, i.e., when X = F and X = Cl, edge attack is higher in

TABLE I

Total energy, *E*(RHF) (au), for minimum strain energy conformations of the system H^- + SiH_3

	d(Si-H), Å					
point of attack	∞	3.08	2.37	1.81	1.58	1.50
			X = F			
H-H-H face[a]	−385.540	−385.561	−385.612	−385.690	−385.710	−385.711[e]
X-H-H face[b]	−385.540	−385.553	−385.602	−385.684	−385.707	−385.709[f]
H-H edge[c]	−385.540	−385.548	−385.584	−385.671	−385.703	−385.709[f]
H-X edge[d]	−385.540	−385.546	−385.595	−385.681	−385.708	−385.711[e]
			X = Cl			
H-H-H face[a]	−742.127	−742.160	−742.221	−742.315	−742.344	−742.348[e]
X-H-H face[b]	−742.127	−742.143	−742.198	−742.290	−742.321	−742.325[f]
H-H edge[c]	−742.127	−742.145	−742.189	−742.285	−742.319	−742.324[f]
H-X edge[d]	−742.127	−742.130	−742.197	−742.305	−742.340	−742.346[e]

[a] Inversion path, axial entry, and axial departure. [b] Retention path via pseudorotation, axial entry, and axial departure. [c] Retention path, equatorial entry, and axial departure. [d] Retention path, equatorial entry, and equatorial departure. [e] X is in axial position of TBP. [f] X is in equatorial position of TBP.

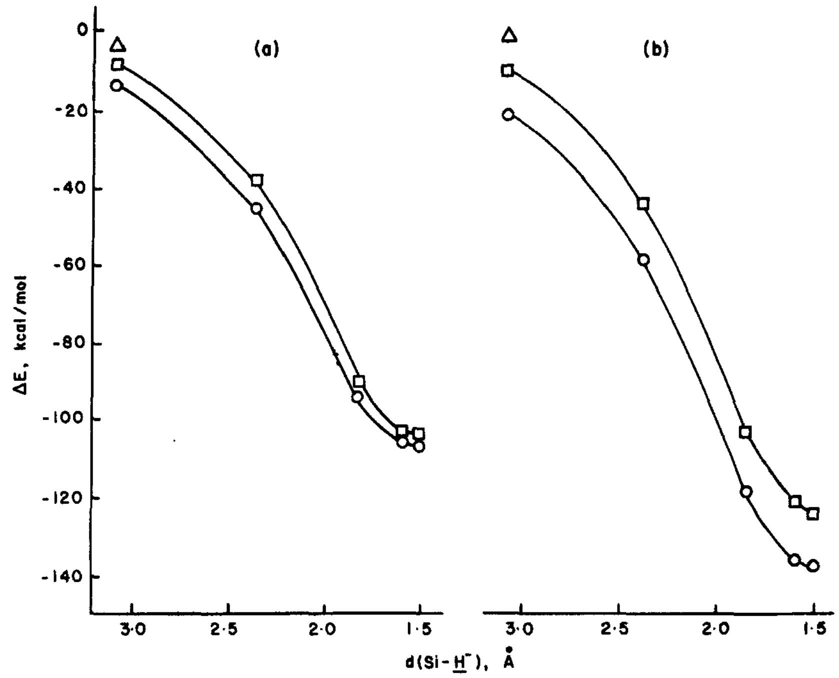


FIGURE 3 Relative molecular orbital energies for minimum strain energy conformations for the system H^- + SiH_3X as the Si-H distance decreases to 1.50 Å from infinity: (a) X = F, (b) X = Cl. Circles refer to the inversion path involving H-H-H face attack and the squares to the retention path involving X-H-H face attack. The triangles refer to the relative energy of the retention path proceeding by way of H-X edge attack.

energy than face attack in the initial approach of H^-. For example, with X = F and d(Si-H) = 3.08 Å, attack by H^- at either the H-H edge or the H-F edge of SiH_3F is higher in energy than attack at the H-H-H or F-H-H face: (−385.546, −385.548) vs. (−385.561, −385.553) au, respectively. This is shown by the triangles in Figure 3 corresponding to H-X edge attack (for both F and Cl), i.e., equatorial entry of H^-, relative to the two facial attack pathways. It seems not at all surprising that entry of H^- into the middle of a tetrahedral face is energetically favored over entry directly between two ligands. As the edge attack continues and the Si—*H* bond forms, a rearrangement occurs such that the edge track pathways eventually lead to conformations identical with face attack. However, until they do so, the edge displacements remain higher in energy than facial attacks. The two ligands which form the tetrahedral edge open out to become axial ligands (see Figure 2). For attack at the H-X edge, a conformation results which is equivalent to that formed in H-H-H face attack within the context of our calculations. Since edge attack (equatorial entry) is higher in energy than face attack (axial entry), these calculations support the case for axial entry vs equatorial entry for both leaving groups, F and Cl. What is likely to occur, since edge attack is not a local energy minimum, is that the incoming nucleophile slips over to a lower energy tetrahedral face approach and follows the course of axial entry.

With regard to the relative importance of the inversion and retention routes resulting from face attack, Figure 3 shows that the two routes have energies closer to one another for fluorine as the departing group compared to those energies for the departure of chlorine. In both cases, the inversion route is lower in energy. For X = F, an average energy advantage for the inversion route of 4 kcal/mol is obtained from the data in Table I. When X = Cl, this energy advantage is much greater, about 14 kcal/mol.

Hence, one may conclude from this level of calculation that the inversion pathway clearly is preferred for X = Cl. For X = F, the closeness in energy makes the inversion and retention routes more competitive. The latter is in agreement with experimental findings of Corriu[3,4] and co-workers about the effect of the leaving group showing that fluorine has a considerably greater tendency to cause retention of configuration compared to chlorine.

Pseudorotation Pathway for Retention

Since, as we show in the section on overlap populations, equatorial departure is not a likely displacement mechanism, nor has it seriously been considered, then one must investigate the occurrence of pseudorotation (Figure 1) to allow axial departure of the leaving group in the favored retention pathway. Actually, this is what we find in carrying out geometry minimization using the molecular mechanics program. In either of the two pathways which lead to retention (attack at the X-H-H face and at the H-H edge) at short Si-Nu distances, a molecular mechanics minimization will actually move the atoms through a Berry pseudorotation to yield the preferred TBP with X axial and the nucleophile equatorial. The pseudorotation process provides a connecting pathway between the lower energy TBP with X axial and the higher energy TBP with X equatorial.

Since pseudorotation of the initially formed intermediate proceeds by a simultaneous bending of axial and equatorial angles, Nu-M-**1** and **3**-M-X, respectively (Figure 1), with ligand **2** as the pivotal group, and allows the structure to pass through a square pyramidal state on the way to the rearranged trigonal bipyramid, calculation of the energy associated with the SP should indicate the relative ease of this process.

The total energies for the system $[\mathit{H}SiH_3X]^-$ (X = F, Cl) in each of the ideal geometries corresponding to their appearance along the pseudorotational coordinate, TBP (X equatorial), SP (X basal), TBP (X axial), are listed in Table II in

TABLE II

Energy of $[SiH_3X\text{-}H]^-$ in trigonal bipyramidal and square pyramidal conformations (au)[a]

	TBP X_{eq}	SP X_{basal}	TBP X_{ax}
X = F	−385.711	−385.707	−385.716
X = Cl	−742.323	−742.327	−742.343

[a] Calculated at Si–*H* distance of 1.50 Å.

au. The barrier for X = F, $E_{SP} - E_{TBP(Xeq)}$, is only 0.004 au (2.5 kcal/mol) and should act as no hindrance to the occurrence of retention of configuration by this mechanism. For Cl as the leaving group, the SP is calculated to be more stable than the TBP with Cl equatorial by 2.5 kcal/mol. However, TBP (Cl_{eq}) is so much higher in energy, 12.6 kcal/mol, than TBP (Cl_{ax}) that competitively a strong preference should exist favoring the formation of TBP (Cl_{ax}) as the initial activated state with subsequent inversion of configuration implied. Support for this was shown in the preceding section where the competitive inversion process is found to be a much more favorable pathway for the departure of chlorine, maintaining a considerably lower energy profile than the retention route via pseudorotation.

This conclusion may be viewed with some skepticism since the STO-3G basis set reportedly does not describe negative ion species all that well.[28] However, our conclusions are based on energy differences and not absolute energies. Hence, some reasonable assurance exists that the same trends will be maintained at a

TABLE III

Energy, charge density, and bond overlap for trigonal bipyramidal conformations of $[SiH_4X]^-$

	$X = F_{ax}$			$X = F_{eq}$		
	STO-3G	STO-6G*	6-31+G*	STO-3G	STO-6G*	6-31+G*
$d(Si\text{-}H_{ax})$, Å	1.50	1.50	1.60[a]	1.50	1.50	1.57[a]
$d(Si\text{-}H_{eq})$, Å	1.50	1.50	1.50	1.50	1.50	1.50
$d(Si\text{-}X)$, Å[b]	1.70[a]	1.61[a]	1.76[a]	1.67[a]	1.58[a]	1.68[a]
$E(RHF)$, au	−385.7231	−389.1297	−390.6977	−385.7149	−389.1221	−390.6795
$\Delta E(F_{ax}-F_{eq})$,[c] kcal/mol	5.2	4.8	11.4			
charge density						
$q(Si)$	0.828	0.495	0.517	0.859	0.518	0.683
$-q(H_{ax})$	0.391	0.316	0.304	0.396	0.324	0.330
$-q(H_{eq})$	0.312	0.274	0.236	0.316	0.277	0.257
$-q(X)$	0.502	0.354	0.504	0.435	0.315	0.508
bond overlap						
$Si\text{-}H_{ax}$	0.269	0.338	0.323	0.250	0.330	0.371
$Si\text{-}H_{eq}$	0.287	0.338	0.444	0.296	0.341	0.373
	$X = Cl_{ax}$			$X = Cl_{eq}$		
	STO-3G	STO-6G*	6-31+G*	STO-3G	STO-6G*	6-31+G*
$d(Si\text{-}H_{ax})$, Å	1.50	1.50	1.57[a]	1.50	1.50	1.53[a]
$d(Si\text{-}H_{eq})$, Å	1.50	1.50	1.50	1.50	1.50	1.50
$d(Si\text{-}X)$, Å	2.42	2.25	2.62	2.26	2.14	2.28[a]
$E(RHF)$, au	−742.3865	−748.1985	−750.7527	−742.3464	−748.1760	−750.7209
$\Delta E(Cl_{ax}-Cl_{eq})$,[c] kcal/mol	25.2	14.1	20.0			
charge density						
$q(Si)$	0.743	0.569	0.515	0.813	0.603	0.566
$-q(H_{ax})$	0.338	0.294	0.266	0.304	0.269	0.271
$-q(H_{eq})$	0.212	0.207	0.171	0.283	0.250	0.243
$-q(X)$	0.772	0.655	0.737	0.638	0.566	0.538
bond overlap						
$Si\text{-}H_{ax}$	0.284	0.338	0.334	0.288	0.347	0.395
$Si\text{-}H_{eq}$	0.326	0.357	0.415	0.304	0.345	0.360

[a] Distance optimized. [b] Estimates from structural data on anionic fluorosilicates[34] suggest values of 1.73 Å for the axial Si–F bond length and 1.67 Å for the Si–F equatorial bond for an anionic five-coordinated silicate containing four ligands of low electronegativity. This indicates that the simpler STO-3G and 6-31+G*, which includes more diffuse orbitals, provide Si–F bonds lengths in approximately equally good agreement with projections from experimental data, whereas the Si–F values from the STO-6G* level are unreasonably short. [c] These energy differences reflect the relative apicophilicities of the halogen atoms calculated at the three basis set levels.

higher level. To verify this to some extent, we performed calculations at the 6-31+G* level which includes more diffuse orbitals to describe anionic species. This level of calculation served to magnify the energy differences even more. For Cl as the leaving group, TBP (Cl_{eq}) is 20.0 kcal/mol higher in energy than TBP (Cl_{ax}), whereas for F, this difference 11.4 kcal/mol (Table III). Thus, inversion is again highly favored when Cl is the leaving group compared to F.

The higher level calculations appear to more accurately reflect experimental observations in indicating that hydride has a tendency to displace F^- with inversion.[4] This is further in accord with the ability of hydride to act as a soft nucleophile. Later we show[29] that by extending the calculations to a series of nucleophiles of increasing hardness, the conclusion is verified that F^- maintains its greater tendency toward retention compared to Cl^- in nucleophilic displacement and the use of harder nucleophiles favors a greater tendency toward a retention process.

Charge Density and Bond Overlap

A graphical display of the changes in overlap populations as the hydride nucleophile enters axially, either at an H-H-H or X-H-H face leading to inversion (X axial) or retention (X equatorial), respectively, is given in Figure 4. For these calculations,

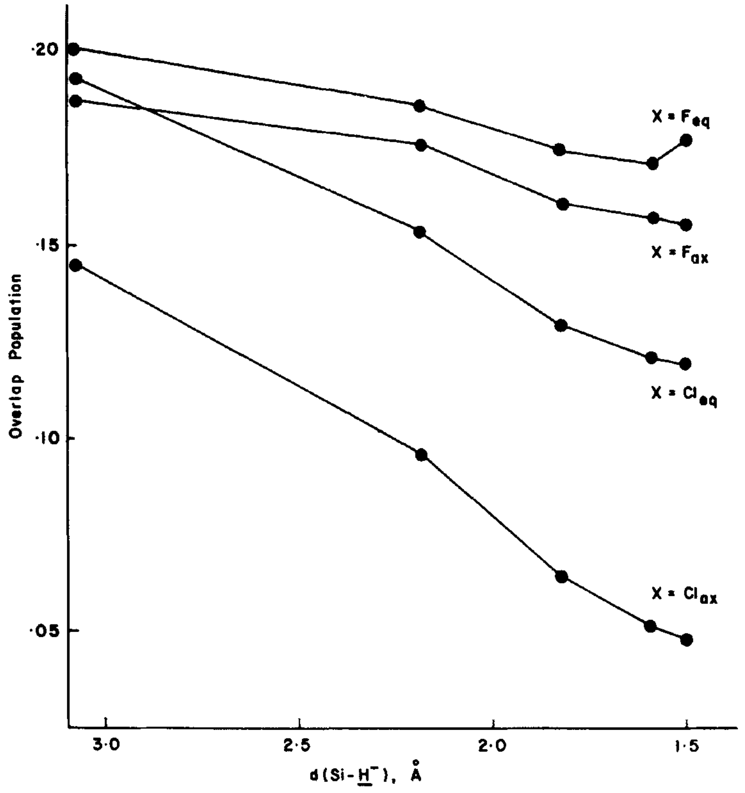


FIGURE 4 MO overlap population for the Si-X bond in the system $[H\text{-SiH}_3X]^-$ corresponding to axial attack at H-H-H and X-H-H faces.

the bond distances (except Si—*H*) were fixed at the following values: Si—H = 1.50 Å; Si—F = 1.58 Å; Si—Cl = 2.00 Å.

As the latter figure shows, for both X = F and Cl, the approach of H^- along the axial direction weakens the SiX_{ax} bond to a greater extent than the Si—X_{eq} bond. Further, this relative bond weakening is much more pronounced for X = Cl consistent with the greater leaving ability of Cl over F found from a consideration of the relative energies of the pathways displayed in Figure 3. In agreement, the charge density for Cl_{ax}, as the intermediate state is reached with Si—*H* distance at 1.50 Å, is appreciably higher, −0.66, than that for F_{ax}, −0.52, and higher than that for these atoms located at equatorial positions, −0.57 for Cl_{eq}, and −0.45 for F_{eq}.

In the case of equatorial edge attack, weakening of Si—X bonds is also observed. When X is in an axial position (i.e., attack at an H-X edge), bond overlap data (Tabel SII) indicate a greater weakening of the Si—X bond than is the case when X is in an equatorial position (i.e., attack at an H-H edge). For example, when X = Cl, and at an Si*H* distance of 1.81 Å, Si—Cl_{ax} overlap is 0.057 as compared to Si—Cl_{eq} overlap of 0.136. Again the relative effect between axial and equatorial positions is more pronounced for Cl over F.

It is concluded here that axial departure is always the preferred route compared to equatorial departure, and this is more pronounced for chlorine compared to fluorine as the departing ligand. Coupled with the discussion of the total energies for pathways listed in Table I, axial entry of H^- is the preferred route compared to equatorial entry.

The above conclusions also receive support from the principle of microscopic reversibility.[30] In the system under discussion which involves an asymmetric reaction coordinate, i.e., the entering and departing groups (X and Y) are different, if equatorial entry of X and Axial Departure of Y is considered a viable process for retention, then axial entry of Y and equatorial departure of X must be considered equally likely.[30c] However, no experimental evidence has been advanced to seriously support the latter process.

Effect of Si—X Bond Stretching

As a nucleophile approaches in an axial position, it is often assumed that the trans axial bond will simultaneously increase in length.[31] Evidence that this is the case is outlined here.

With the other bond lengths and bond angles held constant, we explored the energy of the system $[HSiH_3X]^-$ as a function of the Si—X bond length. Choosing points on the reaction coordinate (see Figure 3a,b), we found the optimum Si—X bond length corresponding to an energy minimum. Results are illustrated in Figure 5 (Table SIII) for the energy pathway corresponding to attack of H^- at the H-H-H face of SiH_3X (X = F, Cl). The results of this calculation show a decided difference between Si—F and Si—Cl bonds.

If the Si—F bond length increases by more than 0.1 Å as hydride ion moves toward the bonding distance of 1.5 Å, the energy of the system increases. The energy gained by a small Si—F stretch (Δd < 0.1 Å) is about 0.01 au (about 6.3 kcal/mol). This result seems to favor a fairly tightly bound pentacoordinated in-

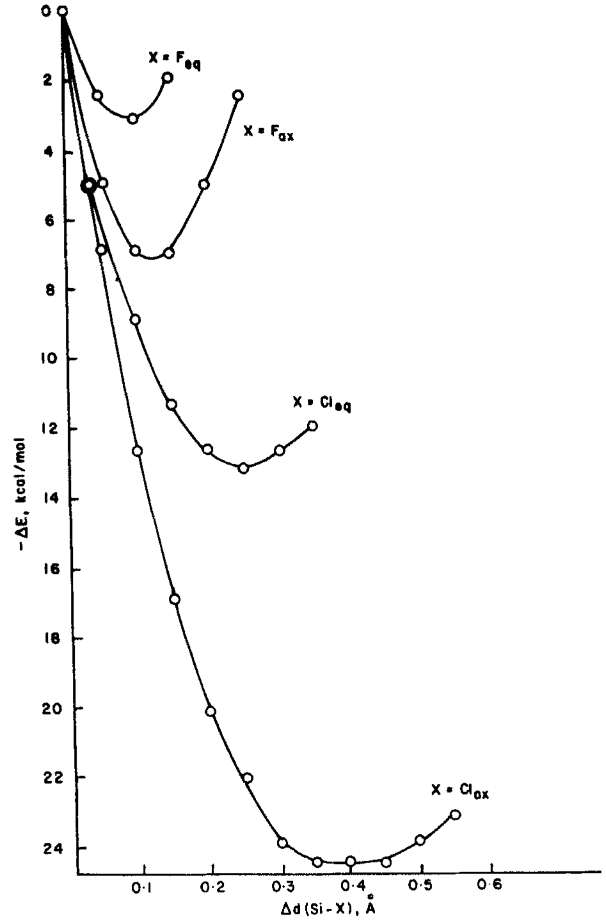
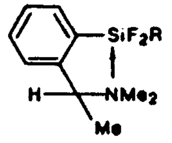


FIGURE 5 Minimized MO energies of $[\mathit{H}\text{—}SiH_3]^-$ with respect to the Si—X bond length for H^- attack at the H-H-H face and an X-H-H face. The ΔE values are differences between energies for d(Si—X) and d'(Si—X) listed in Table SIII.

termediate. On the other hand, a lengthening of the Si—Cl bond is energetically favored for a given Si—*H* bond length. For example, in the H^- approach to the H-H-H face of SiH_3Cl (compare Figures 4 and 5), the energy of the system decreases by 0.04 au (~25.1 kcal/mol) when the Si—*H* distance reaches 1.5 Å. At this point the Si—Cl optimum bond length is 2.42 Å (a stretch of 0.4 Å from the Si—Cl bond length in SiH_3Cl). The fact that no five-coordinated anionic silicon compound exists containing an axial chlorine atom, apparently even at low temperature,[32] may reflect the validity of this calculation. A spirocyclic silicon structure displaced about 60% toward the SP and containing an axial fluorine atom is known[33] as are the anionic fluorosilicates $[Ph_nSiF_{5-n}]^-$, where $n = 0 \rightarrow 2$.[34]

A difference in the two pathways, attack at the H-H-H face vs. attack at the X-H-H face, also is evident from these results. In both cases, when X is in the axial position of the TBP, the Si—X bond is more easily stretched and the energy gain is greater than when X is equatorial (Figure 5). This also supports the conclusion, based on bond overlap data, that the leaving group prefers to exit from an axial position. When the leaving group is chlorine, if the Si—Cl_{ax} bond stretches as the Si—H_{ax} bond forms, an inversion mechanism is favored. In the case of fluorine, a tightly bound intermediate is favored and, as indicated by the total energy calculations shown in Table I, attack at either H-H-H (inversion) or F-H-H face (retention) is competitive. In the event of F-H-H face attack, the presence of a tightly bound intermediate would favor pseudorotation to put X into a leaving axial position by the retention pathway outlined in Figure 1.

An example of the occurrence of a pseudorotational process is found in the NMR behavior of the intramolecularly formed nonrigid five-coordinated silicon derivatives.[35] More pertinent to the present treatment, members of the anionic series $[R_nSiF_{5-n}]^-$ (R = Me, Ph) show rapid intramolecular ligand exchange behavior.[36] For example, $[(n\text{-}C_3H_7)_4][MeSiF_4]$ and $[(n\text{-}C_3H_7)_4][SiF_5]$ show one fluorine environment in the low-temperature ^{19}F NMR spectra with Si—F spin coupling retained. For the tetrafluoro derivative, F—CH_3 coupling also is present. Recently, Damrauer and Danahey[37] reported exchange barriers from ^{19}F NMR for $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^{-38}$ anions consistent with the pseudorotational exchange mechanism.



R = F, Me

Effect of Inclusion of d Orbitals and Diffuse Orbitals

Table III shows the results of including d orbitals (STO-6G*) and more diffuse orbitals (6-31 + G*) for comparison to results with the simple basis set (STO-3G). The calculations were carried out at the three levels mentioned above for the trigonal bipyramidal conformation of $[SiH_4X]^-$ with X = F_{ax}, F_{eq}, Cl_{ax}, and Cl_{eq}. As expected, the energy of all species decreases as the level of the calculation increases. However, the important point remains that at the 6-31 + G* level calculation as compared to the STO-3G level, the energy difference, ΔE ($X_{ax} - X_{eq}$), is significantly greater when X = Cl than when X = F, and it shows quite clearly the same trend which is predicted at the STO-3G level.

Comparison with Previous Results

Anh and Minot[22] calculated the total MO energy of the system $SiH_3X + H^-$ (X = F, Cl) at the STO-3G level with SiH_3X fixed in a tetrahedral geometry while H^- approach the H-H-H face, or the X-H-H face. The energies corresponded to optimum SiH distances for this fixed configuration. It was assumed that this calculation modeled an initial reaction stage in nucleophilic displacement.[39] We have reproduced their results from our calculations.

In order to obtain more realistic geometries at these Si—H distances for approach of the H^- nucleophile and to compare energies from our treatment with those of

Anh and Minot,[22] we employed our molecular mechanics program[24] to obtain minimum energy geometries for the four $[H\text{—SiH}_3\text{X}]^-$ systems considered by Anh and Minot. Following this, the STO-3G energies were calculated. Our results are compared with those of Anh and Minot[22] in Table IV and in Figure 6. At the Si—H distances used by Anh and Minot[22] for hydride ion approach, our computed structures show the geometries to be nearly trigonal bipyramidal. Thus, the assumed tetrahedral geometry is not a good model at this stage of the reaction. Further, H^- attack trans to the leaving group and cis to the leaving group show the same energy difference for X = F and Cl. Hence, use of the closeness in energy between the two paths for X = F compared to X = Cl obtained by Anh and Minot[22] in support of a preferred retention scheme for F over Cl at these Si—H distances is not sustained.

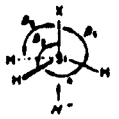
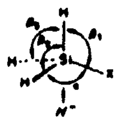
These authors also used a frontier orbital approach[22] in which the major interaction leading to discrimination between inversion and retention is considered to involve the HOMO of the nucleophile with the LUMO of the tetracoordinated silicon species in an edge attack process, i.e., equatorial entry and axial departure. Although the arguments are admittedly complex involving a decision of the relative importance of several factors, it is concluded[22] that equatorial entry, i.e., retention, is more favorable for fluorine relative to chlorine as the leaving group. Our results (Table I) show that edge attack leading to retention is a high-energy process.

The numerical calculations given by Anh and Minot[22] in support of the conclusion concerning equatorial entry have already been discussed (see Figure 6) and actually refer to axial entry of the nucleophile as the basis of a retention scheme. For this initial step, we have shown that pseudorotation completes the retention process as the preferred low-energy pathway.

The most pertinent experimental data concerning which equatorial nucleophilic

TABLE IV

Energy of $\text{SiH}_3\text{X} + H^-$ at specific Si—H distances

	 attack at H–H–H face		 attack at X–H–H face	
	X = F	X = Cl	X = F	X = Cl
$d(\text{Si}-H)$, Å	1.80	1.68	1.92	1.70
$\beta_1 = \beta_2 = \beta_3 = \alpha$, deg	109.5	109.5	109.5	109.5
$d(\text{Si}-\text{H})$, Å	1.42	1.42	1.42	1.42
$d(\text{Si}-\text{X})$, Å	1.61	2.09	1.61	2.09
$E(\text{RHF})$, au[a]	−385.604	−742.253	−385.590	−742.199
$d(\text{Si}-H)$, Å	1.80	1.68	1.92	1.70
β_1, deg	91.7	92.3	91.9	92.5
$\beta_2 = \beta_3$, deg	91.7	92.3	98.1	92.8
α, deg	119.9	119.8	118.8	118.3
$d(\text{Si}-\text{H})$, Å	1.50	1.50	1.50	1.50
$d(\text{Si}-\text{X})$, Å	1.58	2.01	1.57	2.01
$E(\text{RHF})$, au[b]	−385.691	−742.333	−385.668	−742.307

[a] Calculated by Anh and Minot; see ref 22. [b] This work.

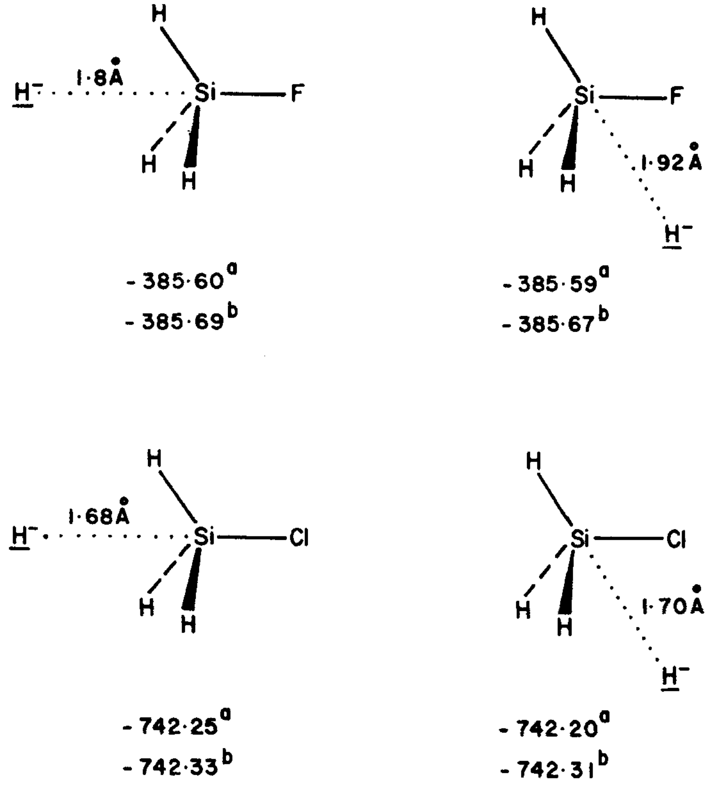
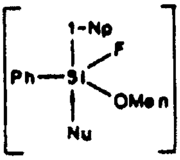


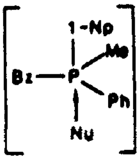
FIGURE 6 Total MO energies (au) of H-H-H and X-H-H face attack. H^- + SiH_3X, for the specific Si—*H* distances used in ref 22. Superscripted *a* values are from ref 22 corresponding to a fixed tetrahedron, and *b* values are from *this work* corresponding to minimized geometries.

attack has been invoked to rationalize retention of configuration center on displacement reactions of silicon containing the relatively large 1-naphthyl group,[3,4] e.g., the competitive cleavage of Si—F and Si—OMen bonds (Men = menthyl) of 1-NpPhSiFOMen with alkyl lithiums.[40] An increasing percentage of product having the larger OMen group cleaved is obtained as the steric bulk of the attacking nucleophile is increased. All reactions in this series proceed with dominant retention. With MeLi, a 99% yield (96% retention) of 1-NpPhSi(Me)OMen is obtained, whereas with neopentyllithium, a 90% yield (85% retention) of 1-Np-PhSi(neopentyl)F results.

There is ample demonstration[41] in related phosphorus reactions that the use of nondeparting groups of increasing steric bulk causes a gradual change over from an inversion stereochemistry to one of retention. For example, in the alkaline cleavage of the chiral phosphonium salts $MePhRP^+—CH_2C_6H_5$ to form the phosphine oxides MePhRP═O, loss of the benzyl group occurs with 97% inversion of configuration when R = C_6H_5 while only 28% inversion is obtained when R = 1-Np.[42]

In these reactions in which steric crowding exists, kinetic control is assumed to locate the attacking group at a tetahedral face opposite the largest ligand. In each





case, the results are consistent with axial attack, followed by pseudorotation to bring the departing group to an axial site.

In conclusion, present theoretical and experimental data suggest that pathways for substitution reactions at tetracoordinated silicon that proceed via five-coordinated states bear a close resemblance to pathways advanced for analogous reactions at tetracoordinated phosphorus.[20b]

Summary

On the basis of our treatment, we summarize the following main points.

For both X = F and Cl in the system $H^- + \mathrm{SiH_3X} \rightarrow [H\text{-}\mathrm{SiH_3X}]^-$, axial entry is a lower energy pathway than equatorial entry, axial departure is the preferred route rather than equatorial departure, and retention via pseudorotation is of lower energy than retention via equatorial attack.

For F vs. Cl as the leaving group, retention via pseudorotation is preferred for fluorine because the retention pathway is comparable in energy to the inversion pathway, and fluorine is more tightly bound in the trigonal bipyramidal intermediate, thus enhancing the possibility of ligand rearrangement before departure. For chlorine as the leaving group, inversion is the favored energy pathway.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation (CHE8504737) is gratefully acknowledged. We thank the University of Massachusetts Computing Center for generous allocation of computer time. The authors also express appreciation to Professor John Ragle for many helpful discussions.

Supplementary Material Available: Angles for minimum strain energy conformations from molecular mechanics for the system $\mathrm{SiH_3X} + H^-$ (Table SI); bond overlap for the Si—X bond for the system $[\mathrm{SiH_3X}—H]^-$ for attack at H-H and H-X edges (Table SII); and energy of $[\mathrm{SiH_3X}—H]^-$ minimized with respect to the length of the Si—X bond (Table SIII) (5 pages). Ordering information is given on any current masthead page.

REFERENCES AND NOTES

1. Presented at the XIX Organosilicon Symposium, L.S.U., Baton Rouge, LA, April 26, 1985.
2. Department of Chemistry, Vassar College, Poughkeepsie, N.Y.
3. Corriu, R. J. P.; and Guerin, C. *J. Organomet. Chem.* **1980,** *198*, 231 and references cited therein.
4. Corriu, R. J. P.; and Guerin, C. *Adv. Organomet. Chem.* **1982,** *20*, 265 and references cited therein.
5. (a) Marsi, K. L. *J. Org. Chem.* **1975,** *40*, 1779 (b) Marsi, K. L. *J. Am. Chem. Soc.* **1969,** *91*, 4724. (c) Egan, W.; Chauviere, G.; Mislow, K.; Clark, R. T.; Marsi, K. L.; *Chem. Commun.* **1970,** 733. (d) Marsi, K. L.; Burns, F. B.; Clark, R. T. *J. Org. Chem.* **1972,** *37*, 238.
6. DeBruin, K. E.; Padilla, A. G.; Campbell, M.-T. *J. Am. Chem. Soc.* **1973,** *95*, 4681.
7. Holmes, R. R. *Pentacoordinated Phosphorus-Reaction Mechanisms*; American Chemical Society: Washington, D.C., **1980,** Vol. II, ACS Monograph No. 176.
8. Reference 7, pp 87-88.
9. Westheimer, F. H. *Acc. Chem. Res.* **1968,** *1*, 70.

10. Reference 7, Chapter 2.
11. Holmes, R. R. *Pentacoordinated Phosphorus–Structure and Spectroscopy*; American Chemical Society: Washington, D.C., 1980; Vol. I, ASC Monograph No. 175.
12. Reference 11, Chapter 3.
13. Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am Chem. Soc.* **1982,** *104*, 230.
14. Holmes, R. R.; Deiters, J. A. *J. Am Chem. Soc.* **1977,** *99*, 3318.
15. Holmes, R. R. *Acc. Chem. Res.* **1979,** *12*, 257.
16. Reference 11, Chapter 2.
17. Berry, R. S. *J. Chem. Phys.* **1960,** *32*, 933.
18. Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984,** *3*, 341.
19. Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Organometallics* **1984,** *3*, 347.
20. (a) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985,** *24*, 2009. (b) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M. *Inorg. Chem.* **1985,** *24*, 2016.
21. Reference 3, pp 295f; Corriu, R. J. P. *Phosphorus Sulfur* **1986,** *27*, 1.
22. Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980,** *102*, 103.
23. (a) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie Mellon University, Pittsburgh, PA. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983,** *4*, 294.
24. Deiters, J. A.; Gallucci, J. C.; Clark, T. E.; Holmes, R. R. *J. Am. Chem. Soc.* **1977,** *99*, 5461.
25 (a) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971,** *93*, 1637. (b) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974,** *30*, 1579.
26. (a) Holmes, R. R.; Deiters, J. A.; Gallucci, J. C. *J. Am. Chem. Soc.* **1978,** *100*, 7393. (b) Deiters, J. A.; Gallucci, J. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1982,** *104*, 5457. (c) Deiters, J. A.; Holmes, R. R. *J Am. Chem. Soc.* **1983,** *105*, 609. (d) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1984;** *106*, 3307.
27. Parameters for the interaction between atoms bonded to silicon were adjusted to bring the angles calculated for the minimum strain energy conformation of SiH_3X ($X = Cl, F$) into agreement to less than an average deviation of 1° with the angles determined by experiment. The experimental values are from the following sources: Sharbaugh, A. H.; Thomas, V. G.; Pritchard, B. S. *Phys. Rev.* **1950,** *78*, 64. McKean, D. C. *J. Mol. Struct.* **1984,** *113*, 251. Bak, B.; Bruhn, J.; Rastrup, J.; Andersen, J. *Acta Chem. Scand.* **1954,** *8*, 367.
28. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons, Inc.: New York, 1986.
29. Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.*, following paper in this issue.
30. (a) Burwell, R. L. Jr.; Pearson, R. G. *J. Phys. Chem.* **1966,** *70*, 300. (b) Tolman, R. C. *Phys. Rev.* **1924,** *23*, 699. (c) Mislow, K. *Acc. Chem. Res.* **1970,** *3*, 321.
31. Experimentally this is documented from inferences made on NMR studies of five-coordinated silicon (ref 3) and from X-ray studies of tin compounds, the latter showing progressive lengthening of a trans axial bond as the acid-base interaction of an axial ligand increases: Swisher, R. G.; Holmes, R. R. *Organometallics* **1984,** *3*, 365. Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981,** *103*, 2971. Further, it is noted that the equatorial bond for examples with common ligands shows little change in the equatorial bond length (Holmes, R. R. unpublished observations).
32. Ault, B. S.; Tandoc, U. *Inorg. Chem.* **1981,** *20*, 1937.
33. Harland, J. J.; Day, R. O.; Vollano, J. F.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1981,** *103*, 5269.
34. (a) Schomburg, D. *J. Organomet. Chem.* **1981,** *221*, 137. (b) Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984,** *23*, 1378.
35. Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G.; Corey, J. Y. *J. Organomet. Chem.* **1984,** *277*, C25.
36. Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968,** *7*, 155.
37. Damrauer, R.; Danahey, S. E. *Organometallics* **1986,** *5*, 1490.
38. Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987,** *26*, 760.
39. Minot, C. *Nouv. J. Chim.* **1981,** *5*, 319.
40. Brelier, C.; Corriu, R.; DeSaxce, A.; Royo, G. *J. Organomet. Chem.* **1979,** *166*, 153.
41. Reference 7, pp 118–123.
42. Luckenbach, R. *Phosphorus* **1972,** *1*, 223.