The Stereochemistry of Nucleophilic Substitution at Tetracoordinated Silicon

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Contents

I. Introduction

During the past decade experimental work, largely through the efforts of Corriu[1,2a–c] and co-workers, has greatly expanded the reaction chemistry of tetracoordinated silicon compounds that had its initial basis arising from the pioneering work of Sommer[2d] and co-workers. A large body of the results are interpretable in terms of reaction mechanisms involving pentacoordinated species. This has given rise to some proposed pathways for nucleophilic displacement that complement those in phosphorus chemistry.[3] These are illustrated in Figure 1 for (a) an inversion process proceeding by way of nucleophilic attack at a tetrahedral face resulting in the formation of a transient trigonal bipyramid with the entering and leaving groups in apical positions and (b) a retention process governed again by facial attack by the nucleophile, only this time yielding a transient trigonal bipyramid with the leaving group in an adjacent equatorial position. For departure to occur from an apical position, as postulated in phosphorus chemistry,[3,4] pseudorotation is envisioned to occur.

A reaction pathway for nucleophilic displacement, not widely considered in phosphorus chemistry, involving edge attack at tetrahedral silicon has been advanced by Corriu.[1] This is shown in Figure 1c and leads to a trigonal bipyramid with the incoming nucleophile situated equatorially. Apical departure of the leaving group in this process results in retention of configuration for chiral derivatives.

Recently, considerable attention, from both a theoretical and a structural point of view, has been directed toward the isolation and characterization of five-coordinated anionic silicon species that serve as models in nucleophilic substitution reactions at silicon centers. This has resulted in the formation of a large variety of new pentacoordinated derivatives along with a study of their stability, structural variations, and dynamic NMR behavior. As a consequence, sufficient data are available to make meaningful comparisons with the more comprehensive studies performed on related phosphorane derivatives.[5]

It is the purpose of this review to assess the present state of knowledge in this area with a view toward defining the role that pentacoordination assumes in nucleophilic substitution reactions at silicon. Much of the literature on reaction kinetics and product formation has been the subject of reviews by Corriu and co-workers.[1,2a–c,6–8] However, recent advances[9–11] have shown new features of silicon pentacoordination revealing its heightened reactivity compared to that of tetracoordinated silicon. The impact of this interesting finding will be examined here. Of greater concern is the integration of knowledge from experimental, structural, and theoretical aspects that has not been treated before. Recent theoretical studies[10–17] have given added insight into the stereochemical transformations encountered in nucleophilic displacement reactions. This area has provided results from a range of computational methods that have focused attention on the stability of pentacoordinated molecules and ions. Fortunately, for the

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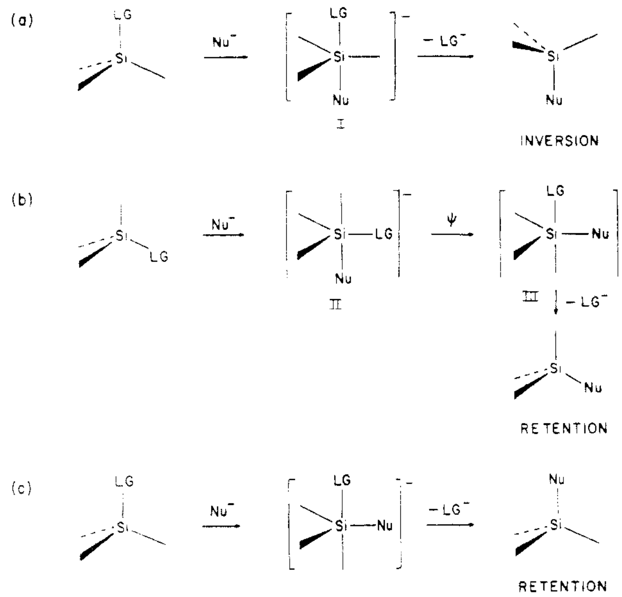


Figure 1. Mechanisms for nucleophilic substitution reactions of silicon: (a) inversion; (b) retention involving axial attack and pseudorotation to give axial departure; (c) retention involving equatorial attack and axial departure. ψ symbolizes a pseudorotational process.

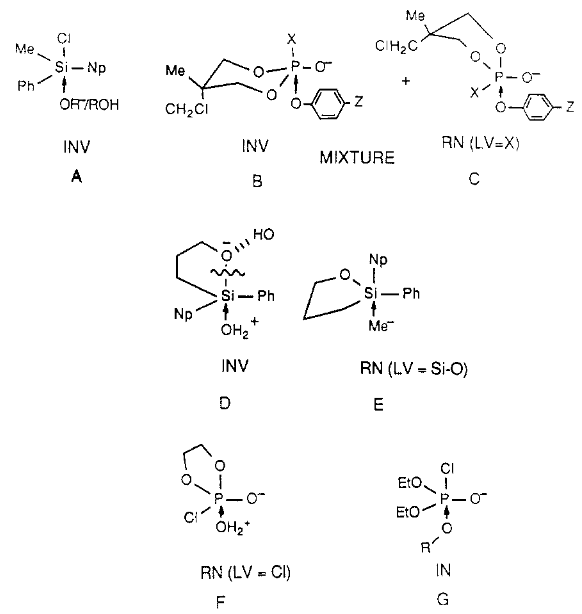


Figure 2. Possible activated states in nucleophilic substitution reactions at tetracoordinate silicon and phosphorus.

purposes of this review, much of this material has been summarized.[17] The overview presented here takes advantage of the existing knowledge from phosphorus chemistry in an effort to assess results from recent structural and theoretical studies on pentacoordinated silicon relative to their usefulness in advancing our understanding of mechanistic features of nucleophilic substitution reactions at silicon.

II. Mechanisms

A. Experimental Basis

1. Kinetics and Product Formation

In this section, sufficient experimental information[1,6,7] is presented to indicate the range of systems studied and the conclusions concerning mechanistic pathways that have been advanced.

When the leaving group at a chiral silicon center is chlorine, inversion of configuration invariably occurs. Fluorine is a poorer leaving group. Si–F bond cleavage may lead to inversion, retention, or a mixture of products, depending on the system and nucleophile entering into the displacement process. Si–H bond cleavage occurs primarily with retention of configuration. A more extensive series showing decreasing leaving group ability and increasing degree of retention toward the right is (INV) Cl, Br, OAc > F, SR > OMe, H (RN). This is a similar order to that found in phosphorus chemistry.

Examples of some representative intermediates appearing in S_N2 solvolysis, hydrolysis, and alkylation reactions[7] may take the forms in Figure 2 if we are to have agreement with the mechanistic schemes shown in Figure 1a,b; i.e., the entering nucleophile and leaving group do so at apical positions in accord with Westheimer's proposal.[4] These intermediates are a result of facial attack at tetrahedral silicon and phosphorus reactants. To accommodate the Westheimer proposal, cleavage of the P–X bond in C,[2b] the Si–O bond in E,[18] or the P–Cl bond in F[2c,19] would require pseudorotation of the intermediate to bring the departing group to an apical position. In the case of the phenoxide reaction in B and C, a mixture of isomers is obtained,[2b] showing more retention when X = F as the departing group compared to when X = Cl. Corriu[7] states that since fluorine is more apicophilic than chlorine, inversion should be more favorable when X = F compared to when X = Cl, and hence these results could not be predicted with Westheimer's concepts. On the basis of calculations,[10b] we have shown that chlorine is more apicophilic than fluorine except when highly electronegative ligands are present, i.e., in the PCl_nF_{5-n} series. In the intermediates B and C, considerable negative charge resides on the equatorial phosphoryl oxygen, making it a group of low electronegativity,[20] comparable to that of a hydrogen atom. Thus, it may be that no "rules" are violated in interpreting the greater cleavage of P–Cl bonds by an inversion route compared to cleavage of P–F bonds.

That the two forms B and C might arise in competition with each other in the first place most likely rests with a balance of relief of a certain degree of ring strain for the six-membered form favoring intermediate C. As Marsi[21,22] has shown in the alkaline cleavage of cyclic phosphonium salts varying in ring size from five to seven membered, the stereochemistry goes from 100% retention for reaction of a five-membered-ring cis phosphonium salt, to about 50% retention for reaction of the corresponding six-membered-ring cis phosphonium salt, and to 0% retention for reaction of the seven-membered-ring salt, all with cleavage of the poor leaving group, benzyl.

Activated-state E may result as a kinetically favored initial intermediate if we assume that the α-naphthyl group is of sufficient size to sterically block the approach of the nucleophile opposite the endocyclic Si–O bond undergoing cleavage.[10b] Pseudorotation then brings the Si–O bond to a departing apical position. Intermediate D may gain relative stability to E with the use of a softer nucleophile.[10b] In addition to the relief of ring strain, hydrogen bonding may assist in the

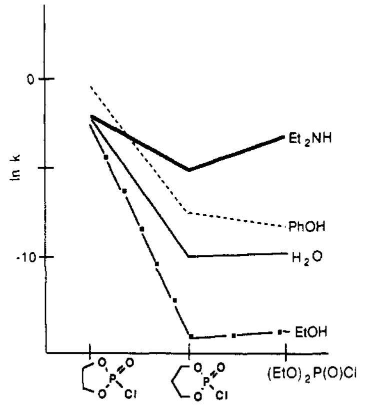
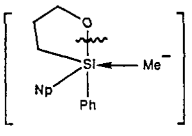


Figure 3. Changes in rates of solvolysis (P–Cl bond cleavage) of chlorophosphates as a function of nucleophile.

cleavage process as indicated in D. The above discussion relative to Figure 2 is given to indicate possible uniformity with the principal inversion–retention schemes, Figure 1a,b, previously discussed in connection with phosphorus reaction stereochemistry.[3]

In contrast to the above, Corriu[7] concludes that the inversion stereochemistry and high hydrolysis and methanolysis rates of Si–O ring cleavage associated with the formation of D in the case of five-membered rings are attributable to the symmetry of the intermediate, i.e., that these effects result when an oxygen displaces another oxygen at silicon. In the case of organometallics as nucleophiles (RLi, RMgX), the retention stereochemistry and reduced rate of Si–O ring bond cleavage are attributed to a lack of symmetry associated with the incoming alkyl nucleophile relative to the leaving oxygen group.[7] Here, equatorial entry, depicted in Figure 1c, and axial departure are proposed,[7] as shown in H.



Retention

H

The above stereochemistry for reactions at silicon undergoing endocyclic Si–O bond cleavage by way of postulated intermediates D, E, and H may be compared with similar arguments for the solvolysis of chlorophosphates[7,19] undergoing cleavage of the P–Cl bond containing the better leaving group, chlorine instead of oxygen. Kinetic measurements[19] at 0 °C reveal that the acyclic phosphate $(EtO)_2POCl$ and six-membered-ring phosphate $(OCH_2CH_2CH_2O)POCl$ react slowly with EtOH, 1.2×10^{-6} and 0.55×10^{-6} L mol^{-1} s^{-1}, respectively, but at comparably increasing rates as the nucleophile is changed along the series EtOH < H_2O < PhOH < Et_2NH until at Et_2NH, the rate of solvolysis of the P–Cl bond (0.028 and 0.0038 L mol^{-1} s^{-1}, respectively) approaches to within 1 or 2 orders of magnitude of the rate of cleavage observed for the five-membered-ring phosphate $(OCH_2CH_2O)POCl$ (0.21 L mol^{-1} s^{-1}). In contrast to the variation in rate seen for the acyclic and six-membered-ring phosphate with variation in the nucleophile, little variation is seen for the five-membered-ring compound (Figure 3). Furthermore, there is an expected difference in stereochemistry with the acyclic and six-membered-ring phosphate following an inversion path and the five-membered-ring derivative following a retention route.

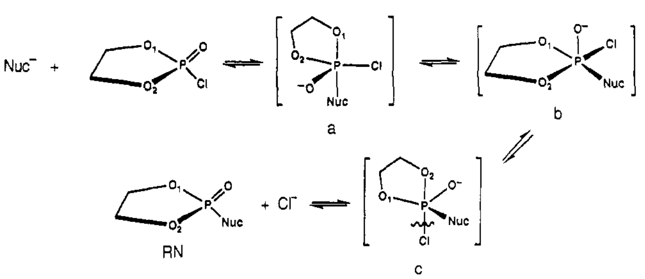
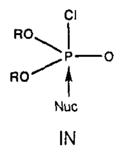


Figure 4. Reaction mechanism for a solvolysis reaction proceeding with pseudorotation according to the retention scheme in Figure 1b.

These results are rationalized[7] in terms of the appearance of activated intermediates I and J postulated for the inversion and retention stereochemistries, respectively. The argument for equatorial entry of the



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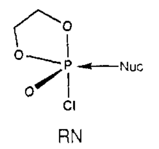


J

nucleophile at 90° to the leaving group is that the reactivity of the apical P–Cl bond should not be influenced to a large degree by variation in the nucleophile,[6] whereas a considerable body of structural[5] and theoretical[23] data support a more direct and heightened influence of the nucleophile when it and the leaving group are both in apical positions of a trigonal bipyramid. These data will be discussed in later sections.

However, instead of following equatorial attack as depicted in Figure 1c leading to the intermediate J, the retention scheme in Figure 1b involving pseudorotation appears equally valid in that the nucleophile and departing chloride ion maintain adjacent positions and are never "in line". This is made clear in Figure 4. Furthermore, we speculate here that the most likely intermediate representing the barrier state is the square pyramid b formed in the pseudorotational process in Figure 4 whose energy may be even less influenced by the type of attacking nucleophile than the initially formed intermediate a or pseudorotated conformer c. The placement of five-membered cyclic ligands in their preferred apical–equatorial positions[3] of a trigonal bipyramid is maintained throughout this scheme. Relief of ring strain accompanying this orientation is expected following Westheimer's work[4] on the hydrolysis of five-membered cyclic esters and is most likely the reason this chlorophosphate exhibits a higher solvolysis rate not reached by any change of nucleophile in the solvolysis of the acyclic and six-membered-ring chlorophosphates.

In general, whether an inversion or retention pathway is followed depends on the energy of the intermediates involved (Figure 1). For the routes conventionally applied in phosphorus chemistry, i.e., Figure 1a,b, Trippett[24] pointed out some time ago that as the apicophilicity of the nucleophile increases, an intermediate like III in Figure 1b or c in Figure 4 will become increasingly less stable. As a consequence, the probability that the reaction will go by an inversion pathway is enhanced. In phosphetane chemistry where placement of four-membered rings in diequatorially positions leads to higher energies compared to five-membered rings,[25] apicophilicity factors have not been sufficient to alter the stereochemical course from the retention route for reactions involving exocyclic cleavage.

In addition to conformational preferences for small-membered rings, steric strain, π bonding, and electronic effects associated with nonreacting substituents all operate to influence the relative energies of activated states postulated for the various pathways in Figure 1. Not all of these factors have received adequate attention to allow a comprehensive correlation of stereochemical results in phosphorus chemistry and less so in silicon chemistry, although an empirical model[26,27] based on energy barriers from NMR studies has offered some predictive value to discriminate among competing pathways in the case of phosphorus reactions. Further, to make comparisons between phosphorus and silicon chemistry on similarities and differences in operational reaction pathways, one must understand how the various terms are altered between the two systems. Corriu and co-workers have done much to provide a thought-provoking basis stemming from their extensive experimental work on these two seemingly closely related chemistries. In the following section, we outline some of the more important structural and theoretical features that lend toward a unified interpretation of nucleophilic substitution reactions.

2. Structural Characterization of Five-Coordinated Species

(*a*) *Solid-State Studies.* It is to be realized that studies of the structural behavior of five-coordinated anionic silicates and comparison with that of isoelectronic phosphoranes provide information useful in establishing structural preferences for activated states in reaction mechanisms that are under thermodynamic control. Approach of a nucleophile to a tetrahedral molecule having sizeable steric properties, for example, may lead to the formation of an initial state that is guided by kinetics. This imposes an additional complication for which there is, at present, no adequate answer. However, much worthwhile information has resulted from work on what might be termed model systems that relate to the thermodynamic stability of proposed activated states.

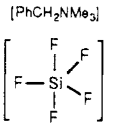
Recent advances in silicon chemistry arise from X-ray studies[28-33] showing that five-coordinated anionic silicon compounds form a series of structures that span the range from trigonal bipyramidal to square pyramidal similar to that found earlier for phosphoranes.[33-35] Most of these silicon compounds are bicyclics wherein ring strain and substituent effects control the degree of distortion from the ideal trigonal bipyramid (TBP) toward the square or rectangular pyramid (RP). A partial tabulation of bond angle data is given in Table I. Formulas of silicon-containing anions represented as salts in Table I and, in general, elsewhere in this review are drawn without charges.

It is useful to plot the values of the trans basal angles θ_{15} and θ_{24} of the RP (which are axial and equatorial angles with reference to the trigonal bipyramid (TBP)) vs the dihedral angle δ_{24}.[34] The latter angle is the dihedral angle formed between normals to the TBP faces 124 and 245 that have the common equatorial edge 24

TABLE I. Axial and Equatorial Angles (θ) and Dihedral Angle (δ) Sums for Pentacoordinated Anionic Silicates (Deg)

compd	δ_{24}	θ_{15}	θ_{24}	%(TBP → RP)[a]	ref[b]
4[c]	59.8	187.5	118.9		40b
2[c]	57.6	181.3	114.8		40b
3	47.8	174.6	121.4	9.0	39
5(B)[d]	41.2	176.6	132.2	25.4	38
5(A)[d]	39.6	176.2	133.7	28.7	38
6	37.0	167.7	127.9	29.5	37
13	35.5	168.4	130.5	33.2	30
8(B)[d]	26.6	168.4	140.7	52.8	28
7	24.7	161.7	136.0	53.3	40a
12	21.9	160.4	137.8	58.7	30
8(A)[d]	18.0	164.0	145.5	68.7	28
9	15.3	159.2	143.6	72.1	29
10	5.5	152.9	147.3	89.8	29
11	1.2	152.1	150.9	97.6	30

[a] Calculated by a dihedral angle method based on unit bond distances.[34] [b] These are references to the X-ray studies. [c] The directions of angular displacement in 2 and 4 are opposite those for the Berry coordinate for both the axial and equatorial angles. This is sometimes referred to as an anti-Berry displacement and is observed occasionally when the structures are close to TBP. [d] Two independent molecules per unit cell.



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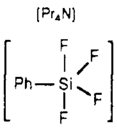

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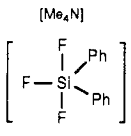

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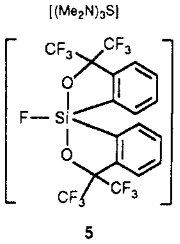

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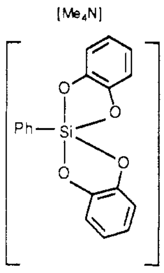

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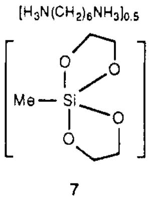

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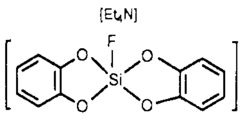

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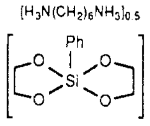

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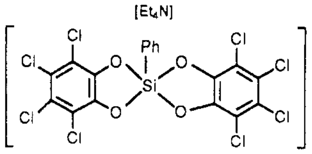

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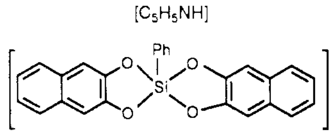

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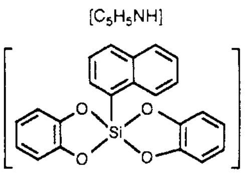

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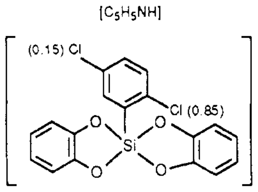

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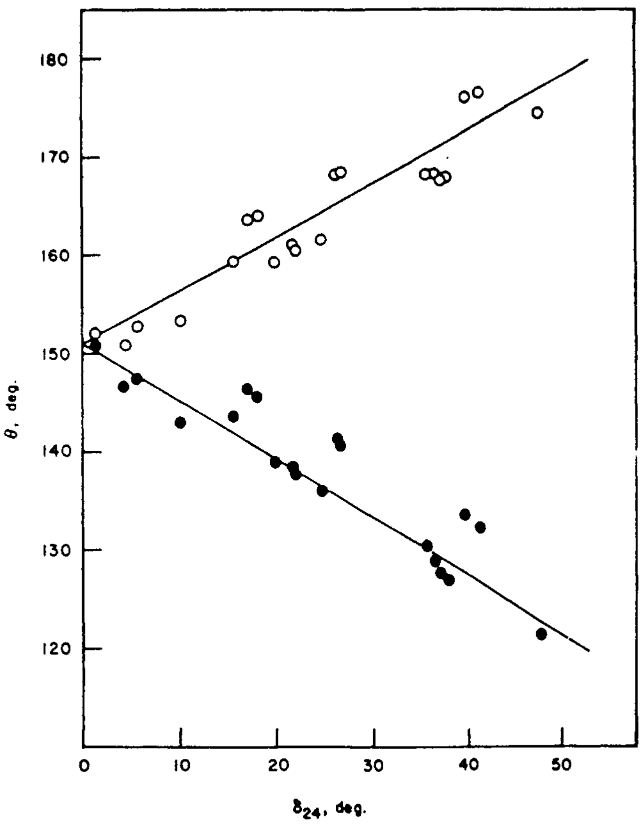
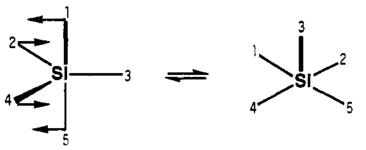


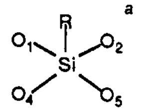
Figure 5. Variations of the axial angle, θ_{15} (open circles), and equatorial angle, θ_{24} (filled circles), vs the dihedral angle, δ_{24}, as structural distortion for pentacoordinated silicon(IV) compounds listed in Table VII of ref 31 and in Table IV of ref 29 proceeds along the Berry coordinate from a rectangular pyramid toward a trigonal bipyramid. The least-squares lines $\theta_{15} = 0.5697\delta_{24} + 150.0$ and $\theta_{24} = -0.5778\delta_{24} + 151.9$ give an average value of 151.0° for the trans basal angle of the "limiting" rectangular pyramid. The solid lines were determined by the values of 180 and 120° for the ideal trigonal bipyramid, $\delta_{24} = 53.1°$, and 151.0° at $\delta_{24} = 0°$.

and is the one most intimately associated with the Berry exchange coordinate.[36] This dihedral angle has a value of 53.1° for an idealized TBP but becomes 0° as edge 24 disappears on forming the RP. Figure 5 represents a θ vs δ_{24} plot for most of the known pentacoordinate silicon compounds that have been structurally characterized by X-ray analysis.[28-32,37-40] It is seen that the Berry coordinate is well followed and leads to a "limiting" RP structure, i.e., as δ_{24} goes to zero, with a θ angle of 151°. Comparison with a similar plot for the more extensively studied phosphoranes[34,35] shows approximately the same scatter from the Berry coordinate and a similar value for the trans basal angle of the RP.



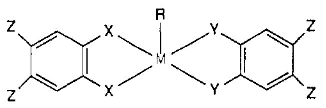
As with phosphoranes,[35,41] reduced ring strain achieved by axial–equatorial placement in a TBP takes preference to the location of the most electronegative element in the axial position; cf. 5 and 8. Also, as observed with phosphoranes,[35,41] the RP geometry is approached when unsaturated five-membered rings contain like atoms in any one ring directly bonded to the central atom and two such rings are present. Lesser factors that favor the RP[35] are the presence of electron-withdrawing ring substituents, Z, and a sterically large acyclic ligand of low electronegativity in the fifth position, R.

TABLE II. Ring Si-O Bond Lengths for Pentacoordinated Anionic Cyclic Silicates



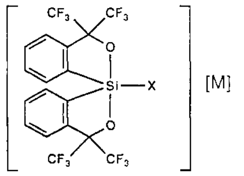
entry	δ_{24}[e]	Si-O_{ax}[b]	Si-O_{eq}[b]	ref
5(A)[c]	39.6	(1) 1.792 (5) 1.787		38
5(B)[c]	41.2	(1) 1.806 (5) (1.782)		38
6[d]	37.0	(1),(5) 1.794	(2),(4) 1.700	37
7	24.7	(1) 1.769* (5) 1.749*	(2) 1.711 (4) 1.735*	40a
8(A)[c]	18.0	(1) 1.742 (5) 1.736	(2) 1.704 (4) 1.706	28
8(B)[c]	26.6	(1) 1.741 (5) 1.738	(2) 1.699 (4) 1.701	28
9	15.3	(1) 1.738* (5) 1.757*	(2) 1.717* (4) 1.685	29
10	5.5	(1) 1.759 (5) 1.753	(2) 1.746 (4) 1.757	29
11	1.2	(1) 1.750* (5) 1.733	(2) 1.734 (4) 1.759*	30
12	21.9	(1) 1.734 (5) 1.772*	(2) 1.742* (4) 1.722	30
13	35.5	(1) 1.820* (5) 1.751	(2) 1.71 (4) 1.698	30

[a] The numbering of the ring oxygen atoms is shown in parentheses. [b] Si-O bond lengths superscripted with an asterisk refer to the involvement of these oxygen atoms in hydrogen bonding. Hydrogen bonding was considered only for X-H···Y distances <2.75 Å. [c] Two independent molecules per unit cell. [d] Contains a crystallographic twofold axis collinear with the equatorial phenyl group. [e] The dihedral angle δ_{24} is the one between triangular faces 124 and 245 containing the common equatorial edge 24.



For the anionic silicates, occasionally lattice effects[28] or intermolecular hydrogen bonding[30,31] influences the expected structural distortion based on the above factors.

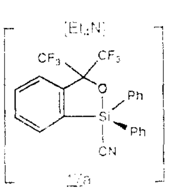
Table II lists Si-O bond lengths. A more extensive compilation including some of these values shows that the ideal trigonal bipyramid has an estimated[30] 1.78-Å distance for the axial Si-O bond length and 1.68 Å for the equatorial Si-O length. As apparent in Table II, there is a general convergence in these lengths in terms of the difference between axial and equatorial Si-O bond distances as δ_{24} goes from 53.1° (for the TBP) to 0° (for the RP). Si-O bonds that are lengthened as a result of hydrogen bonding were not included in this trend. Anionic silicates related to 5 of Table I are known where fluorine is replaced by a phenyl group in a Me_4N^+ salt[42a] and by a cyclohexyl group in a Et_4N^+ salt,[42b] i.e.



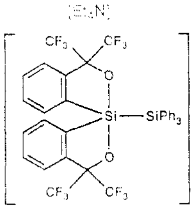
X = F (5), M = $(Me_2N)_3S^+$; X = Ph, M = Me_4N^+; and X = C_6H_{11}, M = Et_4N^+. The Si–O_{ax} bond lengths progressively increase over the series as less electronegative groups are introduced, from 1.792 Å (F)[38] to 1.815 Å (Ph)[42a] to 1.839 Å (C_6H_{11}),[42b] in accord with VSEPR theory. These are average Si–O_{ax} bond lengths, and, in the case of the fluoro and phenyl derivatives, two independent molecules per unit cell are present. The structural distortions of all three derivatives are very similar to each other and as indicated for **5** in Table I approximately 25% displaced from the trigonal bipyramid.

The relative ease of distortion from the TBP toward the RP provided by modest variations in substituents of the anionic silicon derivatives largely composed of oxygen-containing bicyclic ring systems, similar to that studied for phosphoranes, suggests that the energy differences between those two geometries are relatively small and somewhat comparable between the two series of compounds. Most nonrigid phosphoranes have activation energies[26,27] for ligand exchange obtained from NMR studies ranging from 5 kcal/mol for acyclic derivatives to 25 kcal/mol for derivatives containing cyclic ligands exhibiting steric effects. These values most likely reflect the energy differences between the two five-coordinated geometries. From ^{31}P NMR measurements on phosphoranes, it was concluded[43] that the structures observed in the solid state were retained in solution.

The structures of two additional classes of anionic silicates have been studied by X-ray diffraction, cyclic pentaoxysilicates[44] and acyclic fluorosilicates.[45,46] Also the X-ray structure of the first five-coordinated cyanosilicate (**17a**) was reported by Dixon and co-workers[47] and the first silylsilicate by Kiro and co-workers (**17b**). The latter (**17b**) exhibits a very long Si–O bond, 1.838 (5) Å, approaching the longest one known, 1.855 Å, that for the cyclohexyl derivative[42b] referred to above.



17a

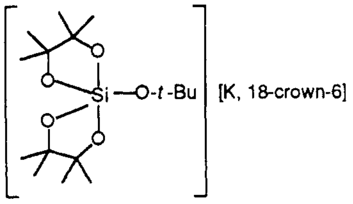


17b

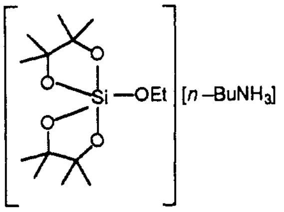
TABLE III. Pesudorotational Parameters for Pentaoxy Anionic Silicates[44]

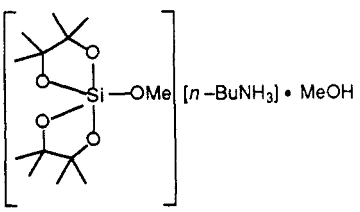
compd	θ_{15},[a] deg	θ_{24},[b] deg	δ_{24} (unit)[c]	%(TBP → RP) (unit)[d]
14	170.9 (2)	127.6 (2)	38.9 (40.4)	24.6 (24.1)
15	169.0 (2)	134.0 (2)	31.6 (33.1)	39.3 (38.9)
16	161.2 (2)	144.6 (2)	15.4 (16.2)	71.5 (71.2)

[a] θ_{12} represents the O_{ax}–Si–O_{ax} angle. [b] θ_{24} represents the O_{eq}–Si–O_{eq} angle. [c] δ_{24} is the dihedral angle between polyhedral faces 1, 2, 4 and 2, 4, 5, where the numbers identify the atom positions. [d] The percent displacement from the TBP to the RP is calculated by a dihedral angle method.[34] The values in parentheses refer to the use of unit Si–O bond lengths.



14





15 **16**

The spirobispinacolate derivatives $[(Me_4C_2O_2)_2SiO\text{-}t\text{-}Bu][K,18\text{-}crown\text{-}6]$ (**14**), $[(Me_4C_2O_2)_2SiOEt][n\text{-}BuNH_3]$ (**15**), and $[(Me_4C_2O_2)_2SiOMe][n\text{-}BuNH_3]\cdot CH_3OH$ (**16**) provided the first structural characterization of cyclic pentaoxysilicates[44] and suggests that a similar study of the more easily hydrolyzable acyclic pentaoxysilicates that closely model proposed intermediates[14,49] in the sol–gel process may be possible. Thus far, however, the isolation of crystalline derivatives has been elusive, although NMR data have established their existence (see section on NMR). The characterization of the pinacolate derivatives **14**–**16**[44] was based on variations of synthetic methods reported earlier by Frye,[50] who formed **16** in addition to other members of this class. In terms of structural displacement from the TBP toward the RP, **15** is 38.9% displaced, **16** is 71.2% displaced, and **14** is 24.1% displaced (Table III). All of these derivatives lie along the Berry pseudorotational coordinate. Hydrogen bonding provided by the n-$BuNH_3^+$ cation is implicated in accounting for the greater structural displacements of **15** and **16**.[44]

Schomburg[39] obtained the first accurate X-ray structure of an acyclic anionic pentacoordinated silicon compound, i.e., $[PhSiF_4][NPr_4]$ (**3**). Schomburg and Krebs[40b] also reported the structures for the pentafluorosilicate $[SiF_5][PhCH_2NMe_3]$ (**2**) and the related diphenyl derivative $[Ph_2SiF_3][Me_4N]$ (**4**). The X-ray analysis of additional members of the series $R_nSiF_{5-n}^-$ is now available[45,46] with ligands of increasing steric bulk. All of these derivatives (**17**–**24**) are listed in Table IV, which records their Si–ligand bond lengths. A distortion parameter Δ is included which is calculated[51] as the sum of the displacements of the bond angles, F_{ax}–Si–F_{ax} and F_{eq}–Si–F_{eq}, from 180° and 120°, respectively, for the ideal TBP structure.

There is an approximate linear relation between an increase in the Si–C bond lengths with increasing angular distortion.[51] This type of correlation is less apparent in the Si–F bond lengths,[51] although the longest apical Si–F bonds reside with the derivatives containing the bulkiest ligands, 1-Np, Mes, Xyl, and t-Bu. To relieve steric crowding the apical and equatorial F–Si–F bond angles undergo ready deformation, giving rise to the increasing value of Δ down the series in Table IV. The F_{ax}–Si–F_{ax} angle in all of these silicates is involved in the low-energy pseudorotational motion.

The longest Si–F bond in five-coordinated anionic silicates is found in the mesityl derivative $[Mes_2SiF_3][K,18\text{-}crown\text{-}6]\cdot CH_2Cl_2$[11] for the Si–$F_{ax}$ bond, 1.729 (6) Å. The shortest one is an equatorial Si–F bond of 1.579 (2) Å observed in $[SiF_5][BzNMe_3]$.[40b] Relative to the isoelectronic phosphoranes, a comparable range of distances are present. P–F bond lengths extend from

TABLE IV. Si–C Bond Lengths (Å) and the Distortion Parameter Δ (Deg) for Anionic Fluorosilicates[a]

compd	Si–F_{ax}	Si–F_{eq}	Si–C	Δ	ref
SiF_5^- (**2**)	1.646	1.579 1.602		3.1	40b
$PhSiF_4^-$ (**3**)	1.668 1.670	1.597 1.604	1.871	6.8	39
$PhMeSiF_3^-$ (**17**)	1.689 1.701	1.621	1.882 (Ph) 1.845 (Me)	7.2	51
$Ph_2SiF_3^-$ (**4**)	1.688	1.648	1.893	8.7	40b
1-$NpPh_2SiF_2^-$ (**18**)	1.720		1.915 (Ph) 1.925 (1-Np)	9.4	51
(*o*-Tol)$_2SiF_3^-$ (**19**)	1.706 1.695	1.640	1.904 1.886	9.9	46
$Mes_2SiF_3^-$ (**20**)	1.729 1.678	1.641	1.915 1.872	11.4	11
$Xyl_2SiF_3^-$ (**21**)	1.703 1.725	1.652	1.919 1.925	11.8	46
t-$BuPhSiF_3^-$ (**22**)	1.682 1.718	1.639	1.902 (Ph) 1.897 (*t*-Bu)	12.4	46
$MesSiF_4^-$ (**23**)	1.672[b]	1.606[b]	1.902	12.5	45
(TTBP)SiF_4^-[c] (**24**)	1.696 1.657	1.613 1.630	1.942	15.0	45

[a] All are K^+, 18-crown-6 salts except $[SiF_5][PhCH_2NMe_3]$ (**2**), $[PhSiF_4][Pr_4N]$ (**3**), $[Ph_2SiF_3][Me_4N]$ (**4**), $[PhMeSiF_3][n\text{-}Bu_4N]$ (**17**), and $[1\text{-}NpPh_2SiF_2][(NMe_2)_3S]$ (**18**). [b] Average values are listed due to disorder. [c] TTBP = 2,4,6-tri-*tert*-butylphenyl.

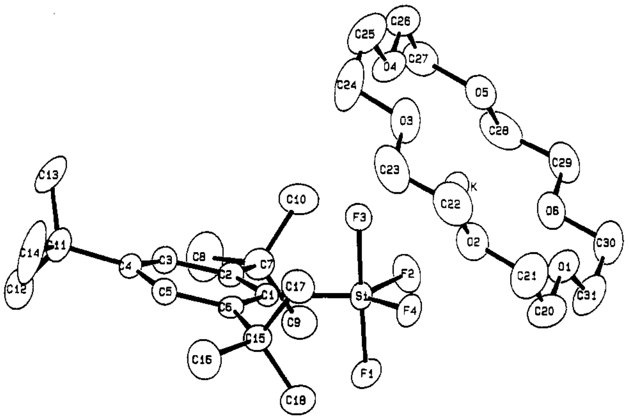


Figure 6. ORTEP plot of the cation–anion pair in $[(t\text{-}Bu)_3C_6H_2SiF_4][K,18\text{-crown-}6]\cdot CH_2Cl_2$ (**24**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

the shortest, 1.534 ± 0.004 Å for the P–F_{eq} bond in PF_5,[52a] to 1.685 (1) Å reported for the P–F_{ax} bond length in Me_3PF_2.[52b] Both of these structures were obtained on the gaseous state by electron diffraction.

Detailed examination[45] of $[(t\text{-}Bu)_3C_6H_2SiF_4][K,18\text{-crown-}6]$ reveals the extreme steric crowding in the molecule. The F_{eq}–Si–F_{eq} angle of 107.1° is very small and the phenyl group is not rotated out of the equatorial plane as normally occurs but is tipped up out of it (Figure 6).

The compounds in Table IV include both steric and electronic effects in their influence on bond parameters. In an effort to separate these terms, two distinct correlations[51] of bond parameter variations encountered in each of the two series $MePhSiF_3^-$, $Ph_2SiF_3^-$, *t*-$BuPhSiF_3^-$, $Xyl_2SiF_3^-$, where the number of fluorine atoms is held constant, and SiF_5^-, $PhSiF_4^-$, $Ph_2SiF_3^-$, $NpPh_2SiF_2^-$, where the number of fluorine atoms is successively diminished, show progressively increasing Si–F and Si–C bond lengths along these series. The first series presumably is controlled primarily by increasing steric effects, whereas the second series shows bond length increases primarily reflecting the insertion of less electronegative ligands in place of fluorine atoms.[53]

TABLE V. Energy Barriers (kcal/mol) for Intramolecular Exchange in $[RR'SiF_3][K,18\text{-crown-}6]$[a] and Ph_2PF_3[b]

compd	R	R′	$\Delta G^{\ddagger}$
25	*p*-Tol	*p*-Tol	12.2
19	*o*-Tol	*o*-Tol	10.6
26	*p*-NO_2Ph	*p*-NO_2Ph	10.8
27	1-Np	1-Np	10.2
28	Ph	Xyl	10.2
22	Ph	*t*-Bu	9.0
21	Xyl	Xyl	>14.5
4	Ph	Ph	11.7
17	Ph	Me	9.9
29	$(CH_2)_5$[c]		9.1
Ph_2PF_3			18.7

[a] Reference 56 except compound **29**, which is from ref 46 and 57. [b] Reference 58a. [c] $(CH_2)_5$ forms a six-membered ring with silicon.

(*b*) *NMR Studies.* Consistent with the ease of structural distortion along the Berry pseudorotational coordinate found in the solid state,[29,31] NMR studies[11,38,42a,45,46,54–57] of anionic silicates have provided evidence for rapid intramolecular ligand exchange similar to that studied for phosphoranes.[5,26] At low temperatures, exchange is sufficiently slowed in some cases to see the NMR pattern of the ground-state molecule. This area has received attention only recently in supplying activation barriers for ligand exchange processes for silicon, although Klanberg and Muetterties[54] first reported rapid ligand exchange processes for SiF_5^- and $RSiF_4^-$ derivatives some time ago. In the case of $Ph_2SiF_3^-$, exchange was stopped at low temperature as shown by ^{19}F NMR.

All of the data discussed so far have referred to pentacoordinated fluorosilicates. Table V lists the activation barriers for ligand exchange resulting from line shape analysis of ^{19}F NMR spectra obtained by Damrauer and co-workers[56] at various temperatures for members of the series $[RR'SiF_3][K,18\text{-crown-}6]$. Since Si–F spin coupling is seen and the log (k/T) vs $1/T$ plot is linear throughout the temperature range, Damrauer et al.[56a] conclude that the exchange is intramolecular. We have confirmed this conclusion by obtaining the corresponding ^{29}Si NMR spectra, which showed retention of Si–F coupling over the entire temperature region extending from the low-temperature limit of "stopped" exchange up to the fast-exchange region for a number of derivatives, e.g., $Mes_2SiF_3^-$ (**20**)[46] and (TTBP)SiF_4^- (**24**) (TTBP = 2,4,6-tri-*tert*-butylphenyl).[45] This is illustrated in Figure 7 for Mes_2SiF_3 (**20**).

The diphenyl derivatives for phosphorus[58a] and silicon[56a] are the only acyclic ones in common that have had their exchange barriers determined. The considerably lower value for the silicon derivative may be associated with the greater nonrigid character previously implied[30] for pentacoordinated anionic silicates relative to the isoelectronic phosphoranes. The latter is reasonable in terms of a reduction in the inherent difference in energy for the normally higher energy SP relative to the ground-state TBP expected for a "looser" structure implied for silicon with its greater charge dispersal as a result of the lower nuclear charge on silicon. Ab initio calculations performed on the TBP–SP energy difference between PF_5 and SiF_5^- support this conclusion, showing a smaller energy difference for

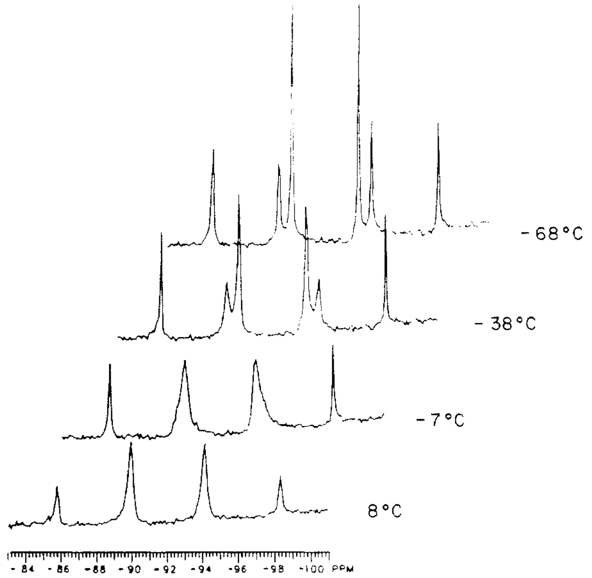


Figure 7. Variable-temperature ^{29}Si NMR spectra of [Mes$_2$SiF$_3$][K,18-crown-6] showing retention of ^{29}Si–^{19}F spin–spin coupling from the "stopped" exchange region, −68 °C, to the fast exchange region, 8 °C.

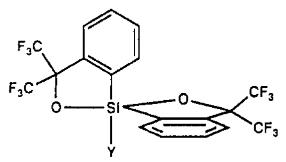
TABLE VI. Energy Barriers (kcal/mol) for Intramolecular Exchange in [(TTBP)SiF$_4$][K,18-crown-6] (24) and Phosphoranes (RPF$_4$)

compd	$\Delta G^{\ddagger}$	ref
$ClPF_4$	4.2	60
Me_2NPF_4	8.8	60
i-Pr_2NPF_4	7.5	61
$(TTBP)SiF_4^-$	12.8	45, 57

the anionic pentafluorosilicate compared to that for PF$_5$.[59]

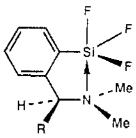
Table VI compares the exchange barrier value of [(TTBP)SiF$_4$][K,18-crown-6] (**24**),[45,57] 12.8 kcal/mol, with values for related isoelectronic RPF$_4$[60,61] derivatives. Consistent with the high degree of steric crowding in the (TTBP)SiF$_4^-$ anion, this is the only example of an RSiF$_4^-$ compound where ligand exchange has been "stopped" on the NMR time scale. Rotational motion of the substituted phenyl group about the Si–C bond (see Figure 6) must accompany the pseudorotation process, and undoubtedly steric hindrance contributes to the slowing of fluorine exchange for this substance. The magnitude of the steric effects required to stop exchange for organotetrafluorosilicates apparently needs to be large. Even the mesityl derivative MesSiF$_4^-$ showed no evidence for significant slowing of fluorine exchange down to −100 °C.[45] The latter behavior is analogous to that observed in a ^{19}F NMR study by Appel and Krieger[62] of (TTBP)PF$_4$ containing the identical ligand, although an activation energy was not obtained. The ^{19}F spectra corresponding to the ground-state structure was reported at −60 °C.

For cyclic derivatives, a phenylphosphorane analogous to the isoelectronic phenyl derivative of silicate **5** (Table I) exhibits a ligand exchange barrier leading to configurational inversion of 28.3 kcal/mol.[42a] Like that observed for the acyclic derivatives Ph$_2$MF$_3$ (M = P, Si$^-$), the exchange barrier is lower for the cyclic phenylsilicate, 26.0 kcal/mol,[42a] compared to the cyclic phenylphosphorane. Energy barriers for inversion of silicates related to **5**,[42a] where the acyclic ligand varies across the series n-Bu, PhCHMe, 4-MeOC$_6$H$_4$, Ph, 3-CF$_3$C$_6$H$_4$, 3,5-(CF$_3$)$_2$C$_6$H$_3$, C$_6$F$_5$, PhO, F,[38] CN, show an excellent linear correlation with Taft σ^* inductive parameters.[42a,55] This trend supports an intramolecular exchange process in which a trigonal bipyramid having a diequatorial ring acts as a close approximation to the barrier state.

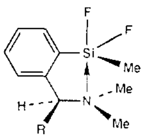


As such, an increase in apicophilicity, i.e., electronegativity of Y in this case, is an accord with a reduction in the exchange barrier. The barrier decreases from 28.6 kcal/mol for Y = n-Bu to 16.8 kcal/mol for Y = CN.[42a]

Working with neutral pentacoordinated silicon compounds **29** and **30**, which contain an intramolecular Si–N coordination bond, Corriu and co-workers[63] established ligand exchange barrier energies from dynamic ^{1}H, ^{19}F, and ^{29}Si NMR measurements. Two independent exchange processes occur: the intramolecular ligand exchange process of the type we have been discussing and exchange via Si–N bond opening accompanied by rotation and inversion at nitrogen. For example, the former process equilibrates fluorine atoms in **29b** but not the methyls of the NMe$_2$ group, whereas the latter process does. In this case, $\Delta G^{\ddagger}$ results as 13.1 kcal/mol for pseudorotation from the ^{19}F spectra and 15.8 kcal/mol for the process involving Si–N bond opening and rearrangement obtained from the ^{1}H NMR data. The corresponding values for **30b** are $\Delta G^{\ddagger}$ = 9.4 and 11.8 kcal/mol, respectively.



29a, R = H
b, R = Me



30a, R = H
b, R = Me

All of the comparisons of NMR data between five-coordinated silicon derivatives and phosphoranes are remarkably similar, and like the similarities in reaction schemes of tetracoordinated derivatives for these two elements undergoing nucleophilic substitution, one is led to the conclusion that a common set of criteria appears to guide the course of both exchange processes and reaction mechanisms.

3. *Application to the Sol–Gel Process*

Acyclic pentaoxy silicon species are of especial interest in modeling condensation reactions of silicic acids in the sol–gel process[49] due to their presumed intermediacy. However, no five-coordinated derivatives of this class have been isolated for structural study by X-ray diffraction. Only recently has X-ray analysis of some cyclic members been reported,[44] as discussed in the preceding section. ^{29}Si NMR measurements have established the existence of members of the classes Si(OR)$_5^-$, PhSi(OR)$_4^-$, Ph$_n$Si(OCH$_2$CF$_3$)$_{4-n}^-$,[42b,64] and HSi(OR)$_4^-$.[65] Powders were isolated in the hydrido series as K$^+$ salts (R = Et, i-Pr, Ph).[65] In the case of the K$^+$,18-crown-6 salt of PhSi(OCH$_2$CF$_3$)$_4^-$, a crystalline material resulted.[42b,64] For the other members,

TABLE VII. ^{29}Si NMR Data for $R'_nSi(OR)_{5-n}^-$ Species[a,b]

species	δ, ppm	species	δ, ppm
$Si(OMe)_5^-$	-127.5	$Ph_2Si(OMe)_3^-$	-97.3
$Si(OEt)_5^-$	-131.1	$Ph_2Si(OEt)_3^-$	-101.3
$Si(OCH_2CF_3)_5^-$	-137.4	$Ph_2Si(OCH_2CF_3)_3^-$	-107.7
$Si(OC_6H_4Me\text{-}p)_5^-$	-144.2	$Ph_3Si(OCH_2CF_3)_2^-$	-101.2
$PhSi(OMe)_4^-$	-112.4	$HSi(OEt)_4^-$	-88.1 (223)[c]
$PhSi(OEt)_4$	-117.3	$HSi(OPh)_4^-$	-111.9 (296)[c]
$PhSi(OCH_2CF_3)_4^-$	-120.1		
$PhSi(OC_6H_4Me\text{-}p)_4^-$	-129.7		

[a] Formed from the reaction $R'_nSi(OR)_{4-n}$ + K(OR) + 18-crown-6 except the $HSi(OR)_4^-$ members, which resulted from $HSi(OR)_3$ + K(OR). [b] References 42b and 64, except for the $HSi(OR)_4^-$ compounds.[65] [c] $J(^1H-^{29}Si)$ in hertz.

comparisons of ^{29}Si NMR data obtained at low temperature with that for related anionic fluorosilicates indicated the presence of pentacoordination. Representative ^{29}Si parameters are listed in Table VII.

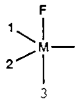
The spectral characterization, particularly of the class $Si(OR)_5^-$, provides strong support for the presence of pentacoordinated species in the polymerization of silicic acid. Further evidence was supplied by Liebau,[66] who analyzed data from 15 crystal structures that contained C, N, F, or Cl ligands attached to silicon in addition to oxygen. He found a continuous change from an SiA_4 tetrahedron to an SiO_5 trigonal bipyramid. On the basis of a Dunitz reaction path concept,[67] it is suggested[66] that this observation reflects a mechanism involving SiO_5 intermediates that occur during reactions of silicates.

Further modeling results from a study of the hydrolysis of dimesityldifluorosilane.[11] Reaction of Mes_2SiF_2 with $Et_4NF{\cdot}2H_2O$ in acetonitrile resulted in the formation of the five-coordinated complex $[Et_4N][Mes_2SiF_3]$, the hydrogen bisilonate $[Mes_2Si(F)O]_2[H][Et_4N]$, and the disiloxane $(Mes_2SiF)_2O$. Each of these products was isolated and characterized by solution-state ^1H, ^{19}F, and ^{29}Si NMR spectroscopy and X-ray analysis.[11] The hydrolysis pathway suggested by this study involving the intermediates $Mes_2SiF_3^-$ and $Mes_2Si(F){-}O{-}H{-}OSi(F)Mes_2^-$ on the way to the disiloxane is used as a model (Figure 8) for the initial hydrolysis of silicic acid. Ab initio calculations[11] show that this model which results in the formation of the disiloxane $(HO)_3Si{-}O{-}Si(OH)_3$ is one of low energy and points to the importance of anionic pentacoordinate silicon in the hydrolytic sequence.

B. Theoretical Basis

1. Apicophilicity

A useful concept in discussing nucleophilic substitution reactions and one that can be put on a quantitative basis via ab initio molecular orbital calculations is provided by the expression for apicophilicity. It is defined as the change in energy when an apical and an equatorial substituent exchange positions in a trigonal bipyramid. For example, the isomer energy difference $E_{II} - E_I$ is the apicophilicity of fluorine relative to hydrogen, $A(F_H)$. The expression written this way will give a positive value for the apicophilicity when structure I with the fluorine axial is more stable than II.



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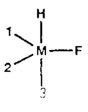

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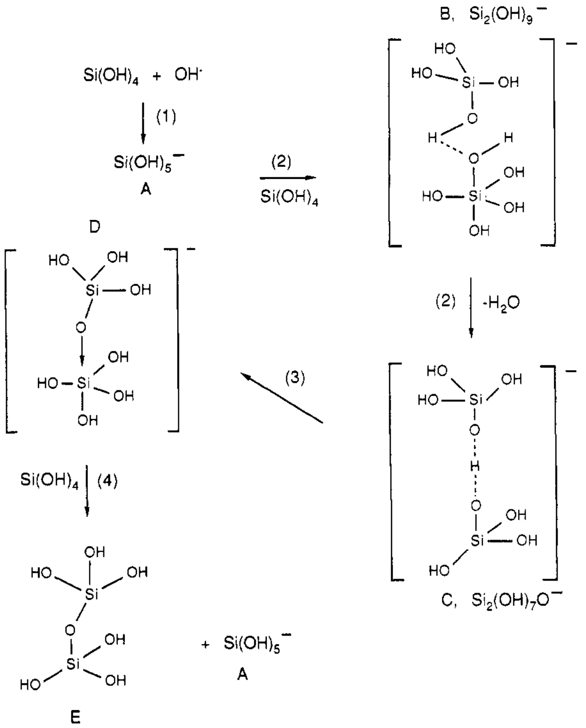


Figure 8. Possible mechanism for initial stages of silicic acid hydrolysis.

Thus, this energy difference measures the degree to which the fluorine atom "prefers" the axial site compared to the hydrogen atom. For acyclic derivatives having simple ligands, apicophilicity integrates a number of factors including electronegativity, inductive effects, and π-bonding contributions. If small-ring systems or sterically encumbered groups are present, then changes in strain energies as the substituents involved move between apical and equatorial positions, e.g., in pseudorotational processes, are additional factors that will contribute to isomer energy differences.[24,27] As discussed in section II.B.2., apicophilicity is found to parallel leaving group ability. Hence, these terms are used somewhat synonymously.

Ab initio calculations utilizing supercomputers on well-developed programs, such as the GAUSSIAN package of programs,[68] are able to give meaningful energies as long as a sufficiently advanced basis set is used. However, the system must be kept within reasonable limits relative to available computational time. Since a calculation of apicophilicity for minimum-energy trigonal bipyramids refers to an isomer energy difference and not an absolute energy, some enhancement in the level of confidence in the results is expected. Variation in the apicophilicity of a particular leaving group can be studied as a function of the "attacking" nucleophile or changes in nonreacting substituents. Calculations of this type have been carried out recently for a series of leaving groups. This allows an order of leaving groups to be obtained and examined for changes in ordering that may result from substituent variations.

It was found that computed apicophilicities, in general, agree with the order experimentally established by Corriu and co-workers.[1,6] For example, GAUSSIAN 82 calculations employing a 6-31+G* basis set, which includes both diffuse orbitals that are important for anionic species and d orbitals for improvement of energies,[68b] gave an order of apicophilicities Cl > SH > F

> OH for the series H_3SiXY, where Y = H represents the nucleophile and X the variable leaving group, both occupying apical positions of a TBP.[13] This order correlates with the experimental leaving group order (IN) Cl > SH, F > OH > H (RN).[1,6] Also for $[H_3Si(LG)(Nuc)]^-$, the overlap population for the Si–(LG) bond increases in the order Cl < F ~ SH < OH < H[13] for the three series where the nucleophile is varied from H to F to Cl, again in agreement with the experimental order showing an increase in retention of configuration from chlorine to hydrogen as leaving groups.

2. *Effect of Nucleophile on Apicophilicity of Leaving Group*

For a given leaving group, experimentally, variation in the nucleophile may shift the reaction toward a retention or inversion process.[69] This shift is also reflected in the above type of calculations by a change in the overlap population of the bond between silicon and the leaving group and by a change in the apicophilicity of the leaving group. For a given leaving group, variation in the nucleophile is accompanied by a sizable change in the apicophilicity of the leaving group. This variation correlates linearly with the difference between the equatorial and axial overlap population of the LG, that is, when the LG is moved from an axial to an equatorial position (with the nucleophile in an axial position). This population difference Δl(Si–LG) may be an expression of the relative tendency to form the initial transition states in the retention and inversion processes in Figure 1, b and a, respectively, if the reaction is regarded as under thermodynamic control.

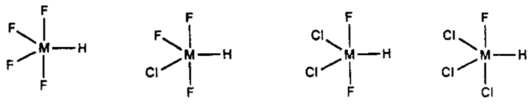
For a given leaving group, such as Cl^-, the apicophilicity of Cl^- is found to decrease with nucleophile in the order $Cl^- > H^- > SH^- > F^- > OH^-$. The same order is observed for F^- as the LG: $H^- > SH^- > F^-, OH^-$.

Corriu[70] has noted that for a given LG, softer nucleophiles tend to promote an inversion process and harder nucleophiles tend toward retention of configuration.[71] This finding agrees with the general trend calculated for variations in apicophilicity; that is, for the computed series, the softer nucleophiles, H^- and SH^-, result in a greater apicophilicity of the LG compared to harder nucleophiles, F^- and OH^-.[72]

In a more extensive study,[10b] comparative ab initio molecular orbital calculations on pentacoordinated phosphorus and silicon model states have been used to establish apicophilicities in a series of trigonal-bipyramidal molecules composed of all combinations of the ligand atoms, hydrogen, chlorine, and fluorine. In agreement with experimental observations, chlorine is found in general to be more apicophilic than fluorine except when the collective electronegativity of equatorial atoms is increased sufficiently, e.g., as in the PCl_nF_{5-n} series. The crossover in halogen apicophilicity for silicon has an even greater electronegativity requirement in equatorial sites than that for phosphorus and may be responsible for some differences observed between the reaction chemistries of the two systems. Further, as applied in nucleophilic substitution reactions, the apicophilicity of the leaving group is diminished by the compositions of equatorial ligands in the order Cl > F > H. As an example, substitution in MHF_4 illustrates these trends, showing the magnitude of the changes in apicophilicity for the phosphorus series compared to the silicon series (Chart I). In contrast, the apicophilicity of the leaving group is enhanced by the opposite apical atom in this same order, Cl > F > H, in all cases except that in which the equatorial atoms are of very low electronegativity. Here, the order becomes Cl > H > F. Further, it is found that when equatorial substituents are altered, the calculated apicophilicity correlates directly with ligand charges obtained from a Mulliken population analysis; i.e., the apicophilicity decreases as the difference of the sums of the apical and equatorial ligand atom charges, $\sum q_{eq} - \sum q_{ap}$, decreases.[10b]

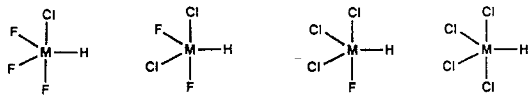
CHART I[a]

a. $A(F_H)$ (kcal/mol)



M = P:	5.82	4.23	2.85	6.08
M = Si[b]:	4.11	2.21	0.42	4.55

b. $A(Cl_H)$ (kcal/mol)



M = P:	3.00	0.25	-2.04	0.69
M = Si[b]:	5.57	2.37	-0.52	3.97

[a] Reference 10b. [b] It is understood that when M = Si, the formulations have a negative charge.

Insofar as apicophility as determined in the above type of calculations can be related to nucleophilic substitution reactions, the principal conclusion[10b] reached that might relate to the influence of an entering group in enhancing the reactivity of an electronegative leaving group is that the reactivity should be increased when the equatorial positions are occupied by ligands of low electronegativity and, of the atoms studied, the opposite apical position is occupied by an electronegative atom, where Cl > F in enhancing the apicophilicity of the opposite apical group.

However, since Cl > F in leaving group ability, one would probably not be able to observe experimentally the behavior of fluorine as a leaving group with chlorine in the opposite apical position. Experimentally, one observes that with Cl^- as a leaving group, the nucleophilic enhancement of apicophilicity is in the order $Cl^- > F^-$, whereas with fluorine as a leaving group, one observes that F^- enhances the apicophilicity. This could be attributed to a "like apical atom" effect as suggested by Corriu,[7] but as the calculations have shown,[10b] it is only a part of a more general effect, namely, $Cl^- > F^- > H^-$ in enhancing the apicophilicity of the opposite apical position. Further, this apicophilicity advantage is maintained as the equatorial hydrogen atoms are substituted by the more electronegative chlorine and fluorine atoms in both the phosphorus and silicon series. For a symmetry-related enhancement, the apicophilicity should be greatest whenever the apical positions are occupied by a fluorine atom opposite a fluorine atom or whenever a chlorine atom is opposite a chlorine atom. This is not indicated in the calculations,[10b] at least in the model systems referred to.

3. *Model Calculations*

To gain insight into competitive inversion and re-

TABLE VIII. Energy Barriers to Retention for $[\mathrm{NucSiH_3(LG)}]^-$ (kcal/mol)[13]

Nuc[a]	LG[b]	apicophilicity of LG (ΔE_{12})[c]	pseudorotation barrier (ΔE_{13})[c]	apicophilicity of Nuc (ΔE_{14})[c]
H	Cl	25.6[d]	12.2	
	F	5.6	6.4[d]	
	SH	9.7	12.1[d]	
	OH	4.3	11.7[d]	
	H		7.2[d]	
F	Cl	20.6[d]	12.2	3.7
	F	1.9	4.3[d]	1.9
	SH	7.5	11.5[d]	3.4
OH	Cl	19.9[d]	18.6	6.0
	F	1.9	10.0[d]	2.6
SH	Cl	24.8[d]	24.7	10.2
	F	3.4	11.5[d]	7.5

[a] Nuc = nucleophile. [b] LG = leaving group. [c] ΔE_{12}, ΔE_{13}, and ΔE_{14} are defined in reference to structures **1**, **2**, **3**, and **4**. These structures are as follows: (1) TBP, LG, Nuc(axial); (2) TBP, Nuc(axial), LG(equatorial); (3) SP, LG, Nuc(cis basal); (4) TBP, Nuc(equatorial), LG(axial). [d] Determines total barrier height for retention mechanism 1b of Figure 1.

tention pathways encountered in nucleophilic substitution reactions of tetracoordinate silicon compounds, molecular orbital calculations on the model system $\mathrm{SiH_3X} + H^- \rightarrow [H\mathrm{SiH_3X}]^- \rightarrow \mathrm{SiH_3}H + \mathrm{X}^-$ (X = Cl, F) have been conducted.[12] Anh and Minot[73a] calculated the total MO energy of the system $\mathrm{SiH_3X} + \mathrm{H}^-$ (X = F, Cl) at the STO-3G level with Si–$\mathrm{H_3X}$ fixed in a geometry while H^- approached the H–H–H face, or the X–H–H face, until an optimum Si–H distance was obtained.[73b]

These authors used a frontier orbital approach[73a] 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 a frontside 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[73a] that equatorial entry, i.e., retention, is more favorable for fluorine relative to chlorine as the leaving group. However, the theory does not propose a role for pseudorotation. Further, in more extensive ab initio calculations[13] based on minimization of energies for ideal trigonal-bipyramidal (TBP) and square-pyramidal (SP) geometries for which optimized bond lengths were obtained, equatorial entry and apical departure prove to be a high-energy process. In this treatment,[13] the system $[\mathrm{SiH_3XY}]^-$ included X = H and Y = H, OH, SH, Cl, F; X = Cl, F, OH, SH and Y = F. The basis set employed was STO-3G but supported by a limited number of higher level calculations (6-31+G*) employing diffuse orbitals and d functions.

In considering the relative merits of the retention pathways[13] of Figure 1b (axial entry orthogonal to the LG, pseudorotation, and axial departure of the LG) vs that of Figure 1c (equatorial entry of the nucleophile and apical departure of the LG), one must compare the apicophilicity of the LG (ΔE_{12}), the pseudorotational barrier (ΔE_{13}), and the apicophilicity of the Nuc (ΔE_{14}) (Table VIII). The barrier to retention by the process in Figure 1b is related to the energy difference between structures **1** and **2** or **1** and **3** (depending on whether **2** or **3** is higher in energy), i.e., to ΔE_{12} or ΔE_{13}. The barrier for mechanism b of Figure 1 may be considered in two components: the barrier to attack orthogonal to the LG (as compared to attack by the nucleophile trans to the LG), i.e., ΔE_{12}; and the energy barrier encountered in Berry pseudorotation, ΔE_{13}. The first component of the barrier, ΔE_{12}, is really a measure of the apicophilicity of the leaving group.

Table VIII lists these barrier heights for both retention mechanisms. For example, in the system $\mathrm{SiH_3F} + \mathrm{OH}^- \rightarrow [\mathrm{SiH_3FOH}]^-$, the barrier for retention mechanism b of Figure 1 is 10.0 kcal/mol; i.e., $\Delta E_{13} > \Delta E_{12}$. The barrier consists of two parts: the apicophilicity of F, 1.9 kcal/mol, and the additional barrier to pseudorotation of 8.1 kcal/mol. In the system $\mathrm{SiH_3Cl} + \mathrm{OH}^- \rightarrow [\mathrm{SiH_3ClOH}]^-$, the barrier for retention mechanism b is 19.9 kcal/mol; i.e., $\Delta E_{12} > \Delta E_{13}$. Here the SP (structure **3**) encountered in the pseudorotational process is 1.3 kcal/mol lower in energy relative to the TBP (structure **2**), which is the initial activated state. The LG order predicted by this calculation of retention barriers (mechanism b of Figure 1) with H^- as the nucleophile is

$$\mathrm{IN}\ \xrightarrow{\mathrm{Cl^-} > \mathrm{SH^-} \sim \mathrm{OH^-} > \mathrm{H^-},\ \mathrm{F^-}}\ \mathrm{RN}$$

which, with the exception of fluorine, is the same as the order determined experimentally. A similar conclusion is reached with other nucleophiles.

The order determined by the apicophilicity of the LG, ΔE_{12}, is with one exception (LG = OH^-, Nuc = H^-) the same as the order determined by the total barrier height. It is seen that the calculated apicophilicity of the LG correlates with the experimentally determined tendency toward retention; i.e., groups with low apicophilicity are poor leaving groups and tend toward the retention processes. It is to be appreciated that the order of apicophilicities, e.g., with H^- as the nucleophile, $\mathrm{Cl}^- > \mathrm{SH}^- > \mathrm{F}^- > \mathrm{OH}^- > \mathrm{H}^-$, does not follow that expected from the relative electronegativities of these elements. In the case of chloride as the LG, experimental data show that nucleophilic substitution proceeds invariably with inversion. The high apicophilicity and LG ability of chlorine surmised from the calculations[13] support this process.

If the mechanism under consideration is c of Figure 1, then one needs to consider ΔE_{14}, the apicophilicity of the nucleophile, as well as the energy expenditure for edge attack.[74] The edge attack pathway was shown[12] to be a high-energy process and hence is not considered to be a serious possibility. In addition, there is little correlation between the apicophilicity of the nucleophile and the tendency toward inversion or retention for the edge attack process. For example,[13] compare Cl^- and F^- as leaving groups when F^- is the attacking nucleophile (Table VIII). If mechanism c of Figure 1 were the mechanism for retention, one might expect to see a sizable difference in the apicophilicity of the nucleophile; i.e., when F^- is the leaving group, a low apicophilicity for the nucleophile F^- would promote retention, whereas when Cl^- is the leaving group, one might expect, since experimentally inversion predominates for Cl^-, that the apicophilicity of the nucleophile might be much larger than in the case of F^- as leaving group. However, the difference in apicophilicity amounts to only 1.8 kcal/mol. This compares with a difference in barrier heights of 16.3 kcal/mol for these same groups proceeding by retention mechanism b. Comparisons with other nucleophiles and leaving groups in Table VIII lead to the same conclusion.

Further insight into mechanistic features of S_N2 displacement processes for tetracoordinate silicon comes from calculations for the addition of hydride or fluoride to silane.[17] For example, high-level ab initio calculations by Reed and Schleyer[75] show that H^- ion attack on a tetrahedral face of SiH_4 is predicted to occur without activation, in agreement with a gas-phase kinetic study,[76a] which results in an activation energy of ~0.3 kcal/mol.[76b] Formation of SiH_4F^- also occurs without activation according to calculations of Davis et al.[16] Activationless potential energy surfaces for formation of SiH_4X^- were calculated by Dewar and Healy[77] for X = F, Cl, Br, OMe. For both SiH_5^- [17,75] and SiH_4F^-,[16] calculations involving removal of H^- from an equatorial position of a TBP first involved a change of geometry to give a TBP with the hydride in an apical position.

Calculated barriers for Berry pseudorotations are generally low for the systems treated. For example, calculations by Burggraf and co-workers[17,78] for Me_4SiX (X = H, OMe, OH, and F) gave barriers of 3 kcal/mol or less when methyl was the pivotal (equatorial) ligand. With X as the pivotal ligand, the barriers were larger and increased with increasing ligand softness,[79] F < OH < OMe < H.[17,78]

An interesting trajectory calculation performed by Burggraf and Davis,[17,80] who modeled the dynamics of chloride substitution at chlorosilane, found that the direction of attack was controlled by long-range charge–dipole interactions. Unsymmetrical collisions induced Berry pseudorotational motions. The calculations further suggest that as a result of the latter motion, a strong-ligand bond site (i.e., equatorial site of a TBP) reorients to a weakly binding site (i.e., an apical site) accompanied by a concentration of vibrational energy into the Si–(LG) bond.

All of these data provide further support for the retention pathway in Figure 1b showing it to be one of low energy. Unfortunately, the pentacoordinated silicon anions for which ligand exchange barriers have been calculated are not the same as those measured experimentally, so a direct comparison cannot be made (see section II.A.2.b). However, the following studies give an indication of barrier energies to be expected for simple silicate anions. Tables V and VI show experimental intramolecular exchange barriers for more highly substituted silicon anions, the K,18-crown-6 salts of the series $RR'SiF_3^-$ and $RSiF_4^-$, respectively.

For the SiH_5^- ion, a variety of calculations[81] have been performed on the energies of the TBP (D_{3h}) and SP (C_{4v}) forms. Most of the energy differences lie between 2 and 3 kcal/mol, indicating that the Berry pseudorotational process should be very facile down to low temperatures. Recently, this anion was detected[82] at low pressures in a flowing afterglow apparatus as a metastable species formed by hydride transfer from $Et_3SiH_2^-$ to SiH_4. Quite a few five-coordinated silicon anions have been identified as products of gas-phase ion–molecule reactions.[83-85] More pertinent to solution reaction dynamics is work on the SiF_5^- anion. An early NMR study of $[SiF_5][(n\text{-}Pr)_4N]$ by Klanberg and Muetterties[54] shows only spectroscopic equivalent of fluorine atoms down to −66 °C. This agrees with ab initio results[86] (6-31+G* level) showing a low exchange barrier between the ground-state TBP and SP transition state of 3.6 kcal/mol. A comparative study[59] at the 6-31G* level gives 5.6 kcal/mol for the isomer energy difference in PF_5 and 4.2 kcal/mol for SiF_5^-. In all of these calculations, the SP is always the higher energy form. The lower pseudorotational barrier obtained for SiF_5 compared to PF_5 agrees with other indications of the greater nonrigid character of pentacoordinated silicon over that for phosphorus (vide infra). The greater convergence in energies for isomeric structures encountered for pentacoordinated anionic silicates relative to isoelectronic phosphoranes has been discussed in terms of a relative "looseness" in the silicon five-coordinated structure. In this context, it is interesting that the entire series of chlorofluorophosphoranes PCl_nF_{5-n} exists[52a,86-89] but no chlorofluorides are known for the isoelectronic silicon series, $SiCl_nF_{5-n}^-$.

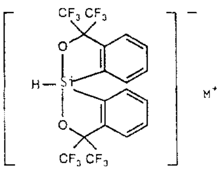
One may conclude that it is necessary to take proper account of the fluxional behavior of the pentacoordinated state in considering the course of nucleophilic substitution reactions. The facile intramolecular isomerizations that may occur in transient states of pentacoordinated species are capable of exerting a profound influence on the course of the reaction.

C. Reactivity of Pentacoordinated Species

Having reviewed both experimental and theoretical aspects of nucleophilic substitution at silicon, we consider in this rather brief section recent studies in which pentacoordinate silicon anions either have been found to be more reactive than their respective tetracoordinate precursors or show interesting catalytic features.

Corriu and co-workers[9a] report that K,18-crown-6 salts of $PhMeSiF_3^-$ and $Ph_3SiF_2^-$ are much more reactive than $PhMeSiF_2$ and Ph_3SiF with RMgBr in ether solution to give PhMe(F)SiR and $Ph_3Si(R)$, respectively. Similar enhanced reactivity is found for reaction of these two anionic silicates with other nucleophiles, $NaBH_4$, $LiAlH_4$, RLi, and OR^-. It is suggested[9a] that the enhanced reactivity might arise from a greater electropositive character of the pentacoordinated silicon atom, as suggested also by calculations.[90] Based on ab initio calculations[10a] on the tetracoordinated series SiH_xF_{4-x} and on the related anionic pentacoordinated series $[SiH_xF_{5-x}]^-$ using GAUSSIAN 86, a small change in charge at silicon between the respective silanes and pentacoordinated silicates is found. However, a general loosening of all bonds in the pentacoordinated state occurs, particularly for the apical Si–F bonds as the number of hydrogen substituents increases. This suggests that enhanced reactivity of pentacoordinated species is primarily associated with the presence of a greater leaving group ability on going from the four- to five-coordinated species.[10a]

Pentacoordinate hydridosilicates have been postulated as reactive species in the reduction of carbonyl compounds with hydrosilanes in the presence of fluoride or alkoxide ion.[91-94] Recently, anionic species of this class, 30 and 31, have been isolated[95,96] and have been

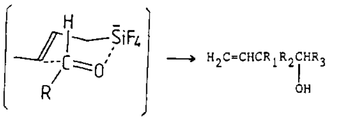


30 M = Li

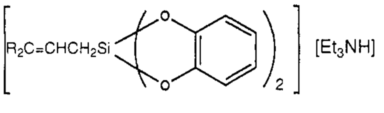
31 M = $Ph_3P{=}N{=}PPh_3$

shown to be the active species in the effective reduction of carbonyl compounds.[95] Also bis(diolato)hydridosilicates prepared in THF solution (but not isolated) reduce carbonyl compounds to the corresponding alcohols chemo- and stereoselectively in high yields without any added catalyst.[93] Further studies on the reactivity of hydridosilicates show that the action of $HSi(OEt)_4^-K^+$, which had been previously isolated,[65] readily causes the reduction of carbonyl compounds to alcohols in the absence of a catalyst at room temperature.[97] Pentacoordinated silicon dihydrides show enhanced reactivity with alcohols and carboxylic acids to form alkoxy- or (acyloxy)silanes compared to reactions of the corresponding tetracoordinated dihydridosilanes.[98]

A further example of the reactivity of five-coordinate silicon is provided by the high specificity in the allylation of aldehydes reported by Kira et al.[9b] A scheme employing allyltrifluorosilane activated by fluoride ion is postulated[9b] to proceed by way of initial formation of a pentacoordinate anionic allylsilicate, $R_1R_2C{=}CHCH_2SiF_4^-$, which is followed by reaction with an aldehyde, R_3CHO, via a six-membered cyclic transition state to give the allylated alcohol:



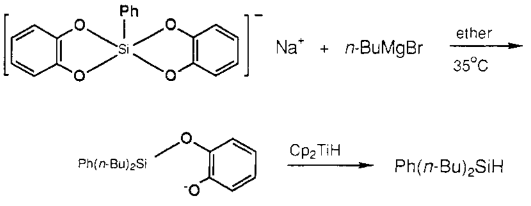
Hosomi and co-workers[99] carried out a similar regiospecific allylation reaction under mild conditions but without the addition of a catalyst. In this case, the allylation agent was triethylammonium bis(pyrocatecholato)allylsilicate **32**.



32

Corriu and co-workers[100] carried out an analogous study with derivatives of **32** and found enhanced reactivity of silicon–allyl bonds in the presence of nucleophiles, e.g., NaOMe, KF, or Bu_4NF. Their results suggest it is possible to selectively transfer an allyl group to an aldehyde in the presence of the less reactive ketones. Interestingly, allylsilatranes do not react under the same conditions.[100]

A one-step synthesis of mono- and dihydrogenosilanes has been provided by Boudin et al.[101] via reaction of anionic hexacoordinated and pentacoordinated silicon compounds, $[(o\text{-}O_2C_6H_4)_3Si]^{2-}$ and $[RSi(o\text{-}O_2C_6H_4)_2]^-$, respectively, toward reducing alkyl Grignard reagents activated by Cp_2TiCl_2. Primary alkyl Grignard reagents give monohydrogenosilane while secondary and tertiary alkyl reagents yield dihydrogenosilanes. This is illustrated for the reaction of $[PhSi(o\text{-}O_2C_6H_4)_2]^-$ with *n*-BuMgBr proceeding by way of the proposed route[101]



A 50% yield results after 3 h of reaction.[102]

The anionic fluorosilicate $[Mes_2SiF_3][K,18\text{-crown-6}]$ reacted[11] rapidly on addition of water to an acetone solution at 25 °C to give the unique hydrogen bisilonate $Mes_2Si(F)O{-}H{-}OSi(F)Mes_2$ and the disiloxane $Mes_2Si(F){-}O{-}Si(F)Mes_2$ as major hydrolysis products. This contrasts to the lack of reaction of Mes_2SiF_2 with water in acetone at 25 °C, showing little change after 24 h.[11]

III. Conclusion and Future Work

It is clear that work is only beginning to appear on the catalytic properties and unique reactivity patterns of pentacoordinated anionic silicon derivatives of diverse composition. The future is very promising for studies utilizing the special properties accorded the pentacoordinated state. The understanding of mechanistic features of these reactions and others, such as those in the sol–gel process[49] and group-transfer polymerizations[103,104] that are dependent on a knowledge of implicated hypervalent species, represents a prime area of investigation. What has been attempted here is to provide an overall view of the complex area of nucleophilic substitution reactions at silicon and to compare their general features, where possible, with similar reactions at phosphorus with the hope of providing a common basis from which future studies may draw. The availability of theoretical studies has provided much needed insight into mechanistic features of the reactions and relative stabilities of pentacoordinated species proposed to take part therein. With the increase in speed continuing to occur in computational chemistry, it should be possible to design models that more closely approximate the actual systems under experimental study.

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Registry No. Si, 7440-21-3.

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