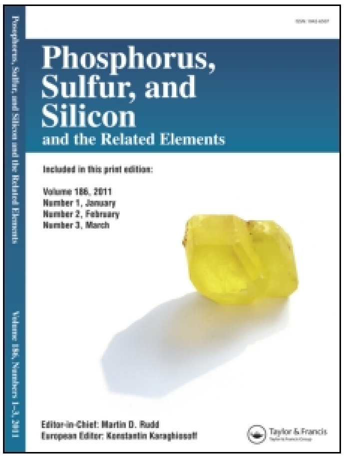

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ENHANCED REACTIVITY OF PENTACOORDINATED SILICON SPECIES. AN AB INITIO APPROACH

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ENHANCED REACTIVITY OF PENTACOORDINATED SILICON SPECIES. AN AB INITIO APPROACH[1]

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Molecular orbital calculations using GAUSSIAN 86 on tetracoordinated silicon species SiH_nF_{4-n} are compared with calculations on the anionic species formed by the addition of fluoride ion $[SiH_nF_{5-n}]^-$. Similar calculations on isoelectronic tetra- and pentacoordinated phosphorus species $[PH_nF_{4-n}]^+$ and PH_nF_{5-n} are also carried out. All bond lengths in the pentacoordinated species are longer than in the related tetracoordinated species, with the greater increase in bond lengths occurring in the axial positions from both the silicon and phosphorus series. Fluoride ion addition results in only slight changes in the positive charge on silicon and phosphorus and in an increase in negative charge on all substituents. These calculations are used to elucidate the enhanced reactivity of pentacoordinated silicon observed in nucleophilic reactions.

INTRODUCTION

Recent work on pentacoordinated silicon species emphasized their enhanced reactivity compared to that observed with related tetracoordinated silicon species.[3–12] We observed[3] that an acetone solution $[Mes_2SiF_3][K,18\text{-crown-6}]$ reacts with water at room temperature in a matter of minutes, whereas Mes_2SiF_2, under similar conditions, is essentially unchanged after 24 h (Mes = mesityl). Corriu and co-workers[4] find that 18-crown-6 potassium salts of anionic organofluorosilicates react more readily with strong nucleophiles (RLi, RMgX, H^-, RO^-) compared to the reactivity of corresponding tetracoordinated derivatives. For example, $MePhSiF_3^-$ undergoes alkylation with *i*-PrMgBr to give MePh(*i*-Pr)SiF more than 150 times faster than the analogous reaction with $MePhSiF_2$. Pentacoordinated silicon dihydrides are markedly more reactive than corresponding tetracoordinated species with alcohols and carboxylic acids.[5] Alkoxy- and (acyloxy)silanes form as a result. With carbonyl compounds, the reaction proceeds without any catalyst to give hydrogenated aldehydes and ketones. In contrast, the related species α-Np(Ph)SiH_2 does not react with aldehydes at room temperature even in the presence of an amine.[5] Similar reductions of carbonyl compounds with pentacoordinated cyclic anionic hydridosilicates have been reported by Kira and co-workers.[9] It is found that silicon–allyl bonds are activated in pentacoordinated silicon species in the presence of nucleophiles such as OMe^- or F^-. A high degree of stereoselectivity

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has been reported in allylation[7,8] and reduction[9] reactions involving anionic pentacoordinated silicate derivatives.

The feature controlling the enhanced reactivity attributed to pentacoordinated silicon is not understood at present, although a greater electropositive character of the pentavalent silicon atom has been suggested[4] to be responsible for the increased reactivity. Some support for this is found in an ab initio calculation by Baybutt[13] employing a relatively small basis set.

In one sense, the experimental results are somewhat unexpected since the pentacoordinated center offers greater steric hindrance to an incoming nucleophile and intuitively should be less electrophilic than a tetracoordinated center having one less fluoride ligand. To address this problem and provide a theoretical basis for the observed increased reactivity of pentacoordinated silicon, we have carried out ab initio calculations on the members of the tetracoordinated silane series SiH_nF_{4-n} and the anionic silicate series $[SiH_nF_{5-n}]^-$ formed by the addition of a fluoride ion. In each of these series, an energy is calculated for the removal of a fluoride ion acting as a model for nucleophilic displacement. Similar conditions are performed on the isoelectronic phosphonium ion series $[PH_nF_{4-n}]^+$ and phosphorane series PH_nF_{5-n} for comparison.

METHOD

The geometry of each tetra- and pentacoordinated silicon and phosphorus species was fully optimized. For the pentacoordinated members, optimization was done at trigonal-bipyramidal minima with apical positions occupied by fluorine atoms where available. Calculations were carried out with the program GAUSSIAN 86[14] at the San Diego Supercomputer Center via the UMass Engineering Computer Services VAX cluster. For the phosphorus molecules, the basis set was 6-31G* (split-level valence with polarization functions on second- and third-row atoms). For the silicon series, neutral, cationic, and anionic species, diffuse orbitals[15] were added to the basis sets for all non-hydrogen atoms, as appropriate for negatively charged species. This basis set is designated 6-31 + G*.

RESULTS

Bond lengths, charge densities, and bond overlap populations (Mulliken) for each silicon species are shown in Table I. Table II shows the symmetry point group, minimum energy, and bond angles for each of the neutral silanes and silicate anions. Figure 1 displays the Si–F bond lengths in the SiH_xF_{4-x} series and Si–F bond lengths in the respective anionic silicates that result from the addition of a fluoride ion, while Figure 2 compares the atomic charges resulting from a Mulliken population analysis for the two series. Entirely analogous information is listed in Tables III and IV and shown in Figures 3 and 4 for the phosphonium and phosphorane series $[PH_nF_{4-n}]^+$ and PH_nF_{5-n}, respectively.

TABLE I

Calculated Bond Lengths, Charge Densities, and Bond Overlaps in SiH_nF_{4-n} and $[SiH_nF_{5-n}]^{-}$[a]

	SiH_4[b]	SiH_3F[c]	SiH_2F_2	$SiHF_3$	SiF_4[d]
Bond Lengths, Å					
Si–F		1.6048	1.5887	1.5737	1.5603
Si–H	1.4746	1.4680	1.4589	1.4465	
Charge Density, q					
Si	0.575	0.876	1.151	1.314	1.568
F		−0.447	−0.436	−0.399	−0.392
H	−0.144	−0.143	−0.139	−0.116	
Bond Overlap (Mulliken)					
Si–F		0.189	0.235	0.242	0.356
Si–H	0.386	0.399	0.408	0.470	
	$[SiH_4F]^-$	$[SiH_3F_2]^-$	$[SiH_2F_3]^-$	$[SiHF_4]^-$	$[SiF_5]^-$
Bond Lengths, Å					
$Si–F_{ap}$	1.7656	1.7464	1.7134	1.6854	1.6614[e]
$Si–F_{eq}$			1.6404	1.6313	1.6237[e]
$Si–H_{ap}$	1.5902				
$Si–H_{eq}$	1.5045	1.4933	1.4878	1.4810	
Charge Density, q					
Si	0.521	0.789	1.020	1.319	1.792
F_{ap}	−0.509	−0.531	−0.516	−0.516	−0.539
F_{eq}			−0.519	−0.534	−0.571
H_{ap}	−0.301				
H_{eq}	−0.237	−0.242	−0.234	−0.218	
Bond Overlap (Mulliken)					
$Si–F_{ap}$	−0.165	0.025	0.066	0.111	0.231
$Si–F_{eq}$			0.199	0.235	0.279
$Si–H_{ap}$	0.321				
$Si–H_{eq}$	0.443	0.446	0.474	0.523	

[a] Calculated at the 6-31+G* level. [b] The experimental value of the Si–H bond length for SiH_4 from ref 25a is 1.480 Å. [c] Experimental values of bond lengths for SiH_3F from ref 25a are Si–F = 1.594 Å and Si–H = 1.474 Å. [d] The experimental Si–F bond length in SiF_4 is 1.56 Å from ref 25b. [e] These Si–F bond lengths compare with a $Si–F_{ap}$ value of 1.646 Å and $Si–F_{eq}$ values of 1.602 and 1.579 Å obtained from an X-ray structure of $[PhCH_2NMe_3][SiF_5]$.[24] Mean values corrected for thermal motion are $Si–F_{ap}$ = 1.660 Å and $Si–F_{eq}$ = 1.622 Å.

DISCUSSION

Figure 2 shows that addition of fluoride ion to any of the members of the silane series SiH_nF_{4-n} results in very small decreases in the positive charge at silicon except for SiF_5^-, where a modest increase is observed. Similar behavior is seen in Figure 4 on forming the fluorophosphoranes from the phosphonium salts. In both the silicon and phosphorus series, the average change in silicon charge amounts of 0.1 electron on going from the tetracoordinate to the pentacoordinate state.

More significantly, the bond lengths in the trigonal bipyramids, particularly the apical bond lengths, are considerably longer than those in the tetracoordinated silicon and phosphorus members as shown in Figures 1 and 3, respectively. The

TABLE II

Calculated Angles and Minimum Energy in $[SiH_nF_{3-n}]^+$, SiH_nF_{4-n}, and $[SiH_nF_{5-n}]^-$ [a]

	symmetry		angle, deg	energy, au
SiH_3^+	D_{3h}	H–Si–H	120	−290.329 322
SiH_2F^+	C_{2v}	F–Si–H	116.3	−389.247 062
$SiHF_2^+$	C_{2v}	F–Si–H	121.6	−488.162 492
SiF_3^+	D_{3h}	F–Si–F	120	−587.064 209
SiH_4	T_d	H–Si–H	109.5	−291.226 298
SiH_3F	C_{3v}	F–Si–H	109.3152	−390.155 386
SiH_2F_2	C_{2v}	F–Si–F	107.4	−489.092 536
		F–Si–H	108.7	
$SiHF_3$	C_{3v}	F–Si–H	110.9278	−588.031 975
SiF_4	T_d	F–Si–F	109.5	−686.965 847
$[SiH_4F]^-$	C_{3v}	F_{as}–Si–H_{eq}	89.137	−390.697 818
$[SiH_3F_2]^-$	D_{3h}	reg TP		−489.655 768
$[SiH_2F_3]^-$	C_{2v}	F_{as}–Si–F_{eq}	90.4	−588.605 358
		F_{eq}–Si–H_{eq}	117.7	
$[SiHF_4]^-$	C_{2v}	F_{as}–Si–H_{eq}	89.7458	−687.556 027
		F_{eq}–Si–H_{eq}	122.1217	
SiF_5^-	D_{3h}	reg TP		−786.504 074
F^-				−99.418 586

	energy,[a,b] kcal/mol		energy,[a,b] kcal/mol
$SiH_3^+ + F^- \rightarrow SiH_3F$	−255.7	$SiH_4 + F^- \rightarrow SiH_4F^-$	−33.2[c]
$SiH_2F^+ + F^- \rightarrow SiH_2F_2$	−267.8	$SiH_3F + F^- \rightarrow SiH_3F_2^-$	−51.3[d]
$SiHF_2^+ + F^- \rightarrow SiHF_3$	−282.9	$SiH_2F_2 + F^- \rightarrow SiH_2F_3^-$	−59.1
$SiF_3^+ + F^- \rightarrow SiF_4$	−303.1	$SiHF_3 + F^- \rightarrow SiHF_4^-$	−66.2
		$SiF_4 + F^- \rightarrow SiF_5^-$	−75.0

[a] Calculated at the 6-31+G* level. [b] These values are useful to compare with gas-phase work. [c] Ab initio calculations[28b] using the basis set MP2/6-31++G[d,p]//SCF6-31G[d] gave −29.1 kcal/mol for this reaction. At the MP2/6-31+G**//HF/3-21+G* level, a value of −47.8 kcal/mol was obtained.[28a] [d] With use of the basis set in footnote c, −49.4 kcal/mol resulted[28b] for this reaction. Using his best basis set, Baybutt[13] calculated −52.10 kcal/mol for this reaction.

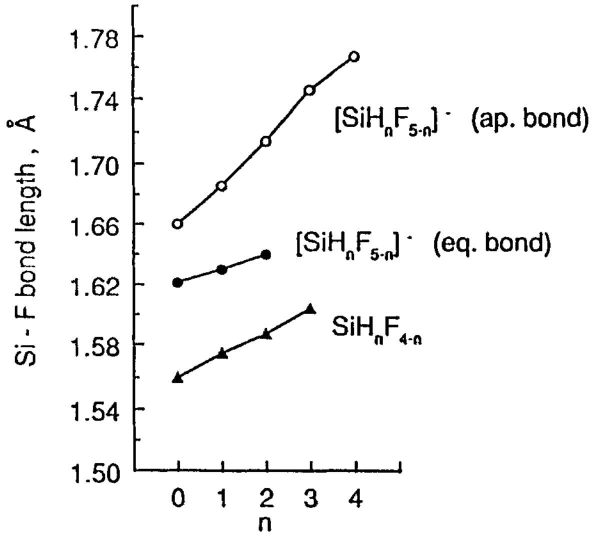


FIGURE 1 Calculated Si–F bond lengths in Si_nF_{4-n} and $[SiH_nF_{5-n}]^-$.

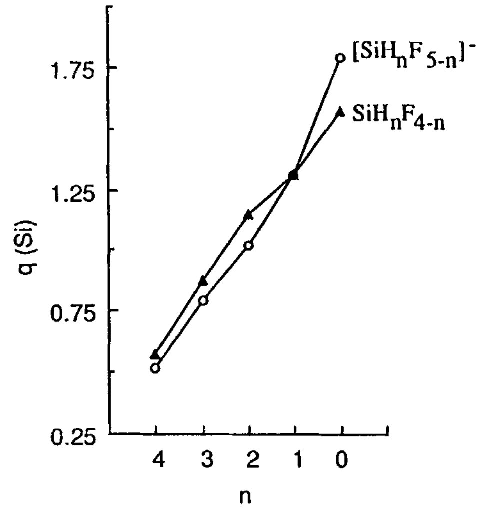


FIGURE 2 Effect of fluorine substitution on the positive charge, q(Si), of the silicon atom on going from SiH_nF_{4-n} (filled triangles) to $[SiH_nF_{5-n}]^-$ (open circles).

TABLE III

Calculated Bond Lengths, Charge Densities, and Bond Overlaps in $[PH_nF_{4-n}]^+$ and PH_nF_{5-n}[a]

	PH_4^+	PH_3F^+	$PH_2F_2^+$	PHF_3^+	PF_4^+
Bond Length, Å					
P–F		1.5227	1.5078	1.4913	1.4795
P–H	1.3795	1.3754	1.3703	1.3641	
Charge Density, q					
P	0.523	1.068	1.470	1.769	2.040
F		−0.351	−0.323	−0.291	−0.260
H	0.119	0.094	0.088	0.105	
Bond Overlap (Mulliken)					
P–F		0.310	0.337	0.358	0.380
P–H	0.367	0.365	0.363	0.371	
	PH_4F	PH_3F_2	PH_2F_3	PHF_4	PF_5[b]
Bond Length, Å					
$P–F_{ap}$	1.6567	1.6375	1.6103	1.5879	1.5679
$P–F_{eq}$			1.5532	1.5424	1.5350
$P–H_{ap}$	1.4395				
$P–H_{eq}$	1.3866	1.3754	1.3708	1.3664	
Charge Density, q					
P	+0.775	1.155	1.488	1.730	1.943
F_{ap}	−0.560	−0.542	−0.500	−0.461	−0.419
F_{eq}			−0.406	−0.386	−0.368
H_{ap}	−0.159				
H_{eq}	−0.019	−0.024	−0.041	−0.037	
Bond Overlap (Mulliken)					
$P–F_{ap}$	0.141	0.197	0.237	0.277	0.320
$P–F_{eq}$			0.325	0.331	0.335
$P–H_{ap}$	0.325				
$P–H_{eq}$	0.387	0.389	0.375	0.371	

[a] Calculated at the 6-31G* level. [b] Experimental values of bond length in PF_5 from electron diffraction[19] are $P–F_{ap}$ = 1.577 Å and $P–F_{eq}$ = 1.534 Å.

TABLE IV

Calculated Angles and Minimum Energy in $[PH_nF_{3-n}]^{2+}$, $[PH_nF_{4-n}]^+$, and PH_nF_{5-n}[a]

symmetry			angle, deg	energy, au
PH_3^{2+}	D_{3h}	H-P-H	120	-341.480 590
PH_2F^{2+}	C_{2v}	F-P-H	115.1	-440.342 196
PHF_2^{2+}	C_{2v}	F-P-H	121.6	-539.200 798
PF_3^{2+}	D_{3h}	F-P-F	120	-638.036 120
PH_4^+	T_d	H-P-H	109.4712	-342.761 578
PH_3F^+	C_{3v}	H-P-F	108.3209	-441.627 475
$PH_2F_2^+$	C_{2v}	H-P-F	108.4125	-540.508 498
		F-P-F	107.9633	
PHF_3^+	C_{3v}	H-P-F	110.8788	-639.394 144
PF_4^+	T_d	F-P-F	109.4712	-738.272 418
PH_4F	C_{3v}	H_{eq}-P-F_{ap}	89.316	-442.430 204
PH_3F_2	D_{3h}	H_{eq}-P-F_{ap}	90.000	-541.348 888
PH_2F_3	C_{2v}	H_{eq}-P-F_{ap}	89.6787	-640.249 851
		H_{eq}-P-F_{eq}	117.549	
PHF_4	C_{2v}	H_{eq}-P-F_{ap}	89.784	-739.152 293
		H_{eq}-P-F_{eq}	121.985	
PF_5	D_{3h}	F_{eq}-P-F_{ap}	90.000	-838.050 724
F^-				-99.350 482

	energy,[a,b] kcal/mol		energy,[a,b] kcal/mol
$PH_3^{2+} + F^- \rightarrow PH_3F^+$	-499.7	$PH_4^+ + F^- \rightarrow PH_4F$	-199.6
$PH_2F^{2+} + F^- \rightarrow PH_2F_2^+$	-511.9	$PH_3F^+ + F^- \rightarrow PH_3F_2$	-232.7
$PHF_2^{2+} + F^- \rightarrow PHF_3^+$	-528.8	$PH_2F_2^+ + F^- \rightarrow PH_2F_3$	-245.3
$PF_3^{2+} + F^- \rightarrow PF_4^+$	-555.8	$PHF_3^+ + F^- \rightarrow PHF_4$	-255.8
		$PF_4^+ + F^- \rightarrow PF_5$	-268.4

[a] Calculated at the 6-31G* level. [b] These values are useful to compare with gas-phase work.

apical Si–F bonds range from 0.10 Å longer in SiF_5^- (compared to that in SiF_4) to 0.15 Å longer in $SiH_3F_2^-$ (compared to SiH_3F). The Si–H bond lengths also experience an increase on going from the tetra- to the pentacoordinate series. In the only case where an apical Si–H bond is present, in SiH_4F^-, the increase in length is 0.12 Å. A similar comparison with the phosphorus series gives a range from 0.09 to 0.12 Å associated with the increase in P–F bond lengths as one goes to the less fluorinated species. Formation of PH_4F from PH_4^+ results in a 0.06-Å increase in the P–H_{ap} bond length, just half that found for the increase in the Si–H_{ap} bond in the related silicon system.

The greater change in bond lengths on going from the tetra- to pentacoordinate species in the silicon series (Figure 1) compared to such changes in the isoelectronic phosphorus series (Figure 3) is a function of the increased effective nuclear charge of phosphorus. As a consequence, pentacoordinated silicon may be regarded as possessing a more loosely bound structure compared to phosphoranes. This difference seems to be followed by experimental behavior. For example, all members of the phosphorus chlorofluoride series PCl_nF_{5-n} have been synthesized[16] in stable molecular forms maintainable at ambient temperatures and their structures examined,[16–21] whereas no corresponding chlorofluorides of anionic silicon have been shown to exist under these conditions.

In agreement with the increase in bond lengths along the series $[SiH_nF_{5-n}]^-$ as n increases, bond overlap populations (listed in Table I) decrease. Comparison of

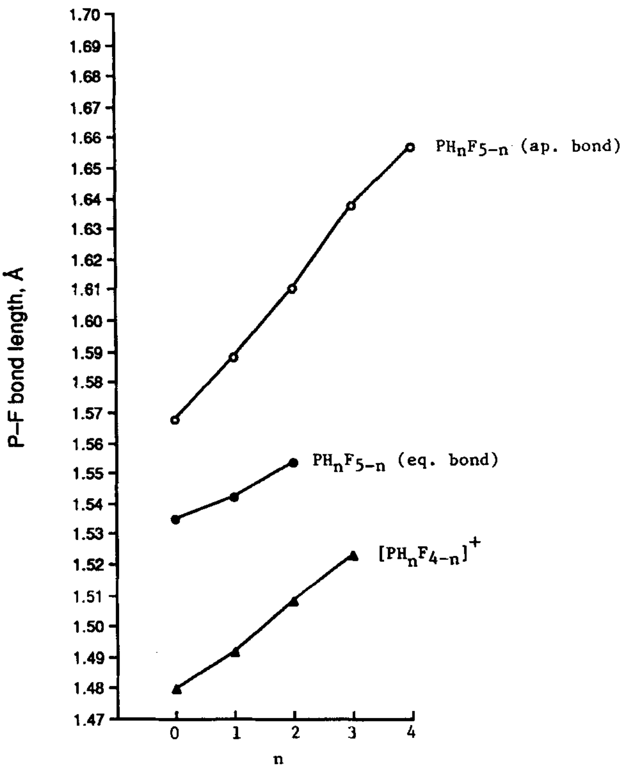


FIGURE 3 Calculated P–F bond lengths in $[PH_nF_{4-n}]^+$ and PH_nF_{5-n}.

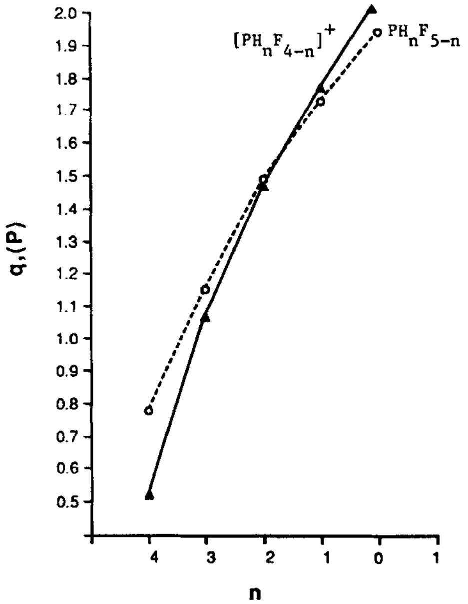


FIGURE 4 Effect of fluorine substitution on the positive charge, q(P), of the phosphorus atom on going from $[PH_nF_{4-n}]^+$ (filled triangles) to PH_nF_{5-n} (open circles).

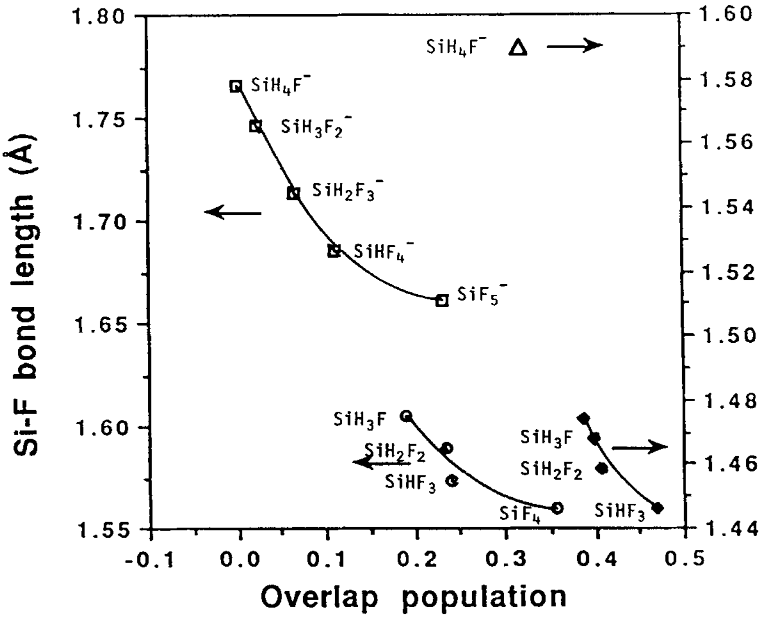


FIGURE 5 Relation between bond lengths (Si–F, left scale: Si–H, right scale) and Mulliken overlap populations on going from SiH_nF_{4-n} to $[SiH_nF_{5-n}]^-$. Only the apical bond lengths are included for the anionic series.

the relationship between apical bond lengths and bond overlaps in the anionic pentacoordinated series (Figure 5) indicates a considerably weaker Si–F or Si–H bond compared to the respective members of the tetracoordinated series. Like in the anionic silicates, overlap populations listed in Table III show similar changes with bond lengths in the phosphoranes PH_nF_{5-n} compared to changes in the phosphonium salts $[PH_nF_{4-n}]^+$. We are led to conclude that enhanced reactivity of pentacoordinated silicon compared to tetracoordinated silicon, discussed in the Introduction, is associated with more loosely held ligands, particularly apical ligands, in the trigonal-bipyramidal species.

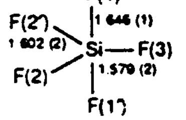
Confirmation of this conclusion is found in that removal of a fluoride ion from members of the tetracoordinated silicon series (Table II) requires a much greater energy than that for this process for corresponding members of the pentacoordinated silicon series. Thus, additional support is provided for the relative ease of nucleophilic displacement observed experimentally for the more highly coordinated anionic silicon series. Phosphorus in its pentacoordinated state shows much greater energy requirements for fluoride removal (Table IV) compared to the analogous silicon series. The latter results confirm pentacoordinate silicon reactivity relative to that found for hypervalent phosphorane molecules. Phosphoranes are not known[16g] to have the enhanced reactivity that is assigned[3–12] to pentacoordinated anionic silicon species.

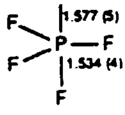
Confidence Level

Regarding the degree of uncertainty in fluoride dissociation energies for the silicon series in Table II attributable to basis set superposition errors (BSSE), we find, for example, that the energy of the fluoride ion in the presence of SiH_4 basis functions (counterpoise calculation[22]) decreased the reaction energy for $SiH_4 + F^- \rightarrow SiH_4F^-$ from −33.2 and −32.8 kcal and from −51.3 to −50.9 kcal for $SiH_3F + F^- \rightarrow SiH_3F_2^-$. Since the counterpoise method, according to Clark,[22] slightly overestimates the BSSE correction, the effect of BSSE on the energies reported in Table II would account for only 1–2% of the reaction energies reported for the silicon reactions. Possible errors at the 6-31+G* level for these reactions due to the neglect of electron correlation also are not considered large as previous calculations have shown (see footnotes *c* and *d* to Table II). Overall, it would appear that relative energy values have an uncertainty of about ±4 kcal/mol.

COMPARISONS WITH THEORY AND EXPERIMENT

Of the members of the pentacoordinated hydridofluoro series for which we have computed geometries,[23] only SiF_5^- and PF_5 have had their structures determined. Schomburg and Krebs[24] determined the structure of the benzyltrimethylammonium salt $[PhCH_2NMe_3][SiF_5]$, and Hansen and Bartell[19] first determined the structure of PF_5 by gas-phase electron diffraction. The pentafluorosilicate anion displays crystallographic C_2 symmetry with the 2-fold axis passing through the silicon and one of the equatorial fluorine atoms, F(3). The angles deviate slightly from the ideal trigonal bipyramid due to solid-state interactions, with the largest deviation occurring at the F(2′)–Si–F(2) angle of 117.5 (1)°. The bond lengths for the computed structures agree with the experimental values to within ±0.025 Å for SiF_5^- and ±0.005 Å for PF_5. Correcting the experimental bond lengths for thermal motion gave a $Si{-}F_{ap}$ value of 1.660 Å and $Si{-}F_{eq}$ value (mean) of 1.622 Å.[24] The comparison for PF_5 is more meaningful since it results from a gas-phase study[19] and implies that the computed parameters for SiF_5^- should be used in preference to the X-ray value for gas-phase studies requiring a knowledge of its structure. Experimentally determined bond lengths for some of the silanes are compared with the computed values in Table I.[25]





A further comparison can be made of Si–F bond lengths resulting from X-ray analysis of the series of anionic silicates showing a continuous decrease in the number of fluorine atoms, $[SiF_5][PhCH_2NMe_3]$,[24] $[PhSiF_4][Pr_4N]$,[26] $[Ph_2SiF_3][Me_4N]$,[24] and $[(1\text{-}Np)Ph_2SiF_2][S(NMe_2)_3]$.[27] Despite the variability in the counterion used, Figure 6 illustrates a linear relation between an increase in the apical Si–F bond length accompanying a decrease in fluorine atom content across the series[27] that parallels a similar trend for calculated apical Si–F bond lengths in the $[SiH_nF_{5-n}]^-$ molecules depicted in Figure 1. Consistent with the knowledge that phenyl groups are more electron withdrawing than protons, the increase in apical bond lengths over the phenyl series (0.06 Å) is less than that in the hydrido series (0.085 Å).

With reference to related work, an earlier calculation by Baybutt[13] on the $SiH_3F-[SiH_3F_2]^-$ system determined bond lengths and charge densities (obtained

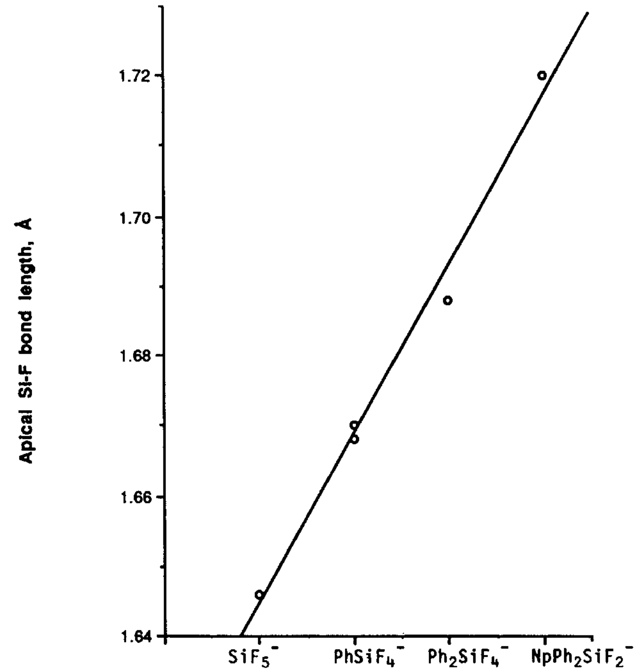
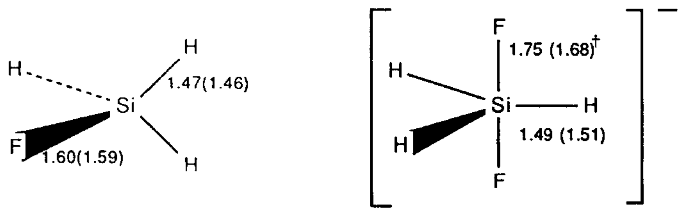


FIGURE 6 Variation in apical Si–F bond length for a series of trigonal-bipyramidal anionic fluorosilicates undergoing decreasing fluorine atom substitution.

Bond Lengths, A



†Optimized geometry using a small basis set.

Charge Density

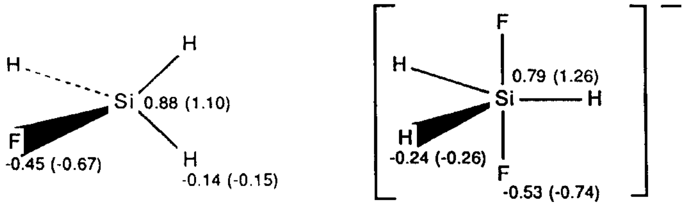


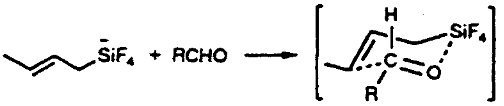
FIGURE 7 Comparison of calculated bond lengths and charge densities between this work (data of Table I) and that in ref 13 (values in parentheses).

by Mulliken population analysis). The calculations optimized the geometry but employed a relatively small basis set. Our computed values are compared in Figure 7 with Baybutt's values, which are listed in parentheses. His computed apical Si–F bond length is decidedly lower than ours. also the charge density at silicon increases on going from the silane SiH_3F to the anion $[SiH_3F_2]^-$, implying a more receptive center for an incoming nucleophile in the pentacoordinate species. We performed a single-point calculation at the Si–F bond values obtained by Baybutt[13] at the higher 6-31+G* level that we have been using to see if geometry had a sufficient influence on causing the increase in charge density from the tetra- to the pentacoordinated species. The calculation resulted in a minor change, giving a charge density at silicon of 0.72 instead of 0.79 that we obtained on our optimized geometry. Hence, the use of a lower level basis set by Baybutt must be responsible for the increased positive charge on silicon that he computed for the anion.

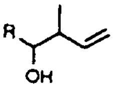
Recently, Streitwieser and co-workers[28a] reported ab initio calculations at the 3-21+G* level on the $SiH_4-[SiH_4F]^-$ system[28b] and employed an integrated projection population analysis (IPP) to obtain charge densities. Their geometries agree well with our values and those we reported earlier[29] for this system where we performed a series of basis set comparisons. The charge they obtained on silicon in the SiH_4 molecule, +2.60, increases to +2.74 on silicon in the $[SiH_4F]^-$ anion. This type of charge density calculation admittedly[28a] emphasizes an ionic model. Regardless of the method used, we view the small changes in charge density on going from tetra- to pentacoordinated species that have been reported with lower level basis sets[13] and that we have obtained over an entire series of minor importance in accounting for the enhanced reactivity of anion pentacoordinated silicon.

MECHANISTIC IMPLICATIONS

For the reactions referred to in the Introduction, although mechanistic details are not known, formation of hexacoordinated intermediates or activated states on reaction of nucleophiles with pentacoordinated silicon is indicated.[7,10–12] In the allylation of aldehydes with allyltrifluorosilane activated by fluoride ion, Kira and co-workers[7] propose an initial formation for a pentacoordinated anionic silicate followed by nucleophilic attack at silicon by the aldehyde oxygen atom resulting in the formation of a six-membered cyclic transition state, which has an enhanced nucleophilicity of the γ-carbon, eq 1. In the latter state, weakening of the allyl Si–C bond is assumed,[7] which upon decomposition leads to the allylated alcohol. The

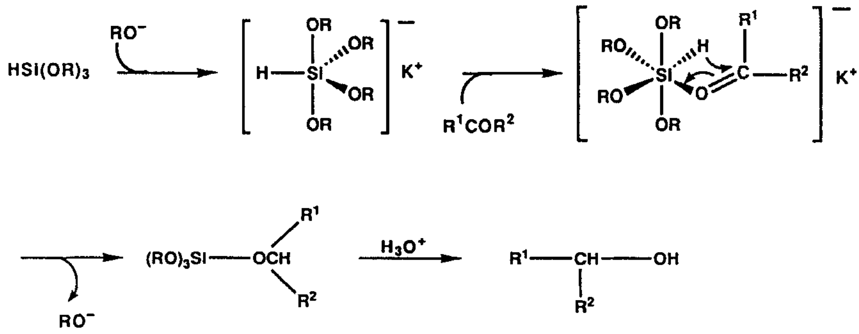


(1)

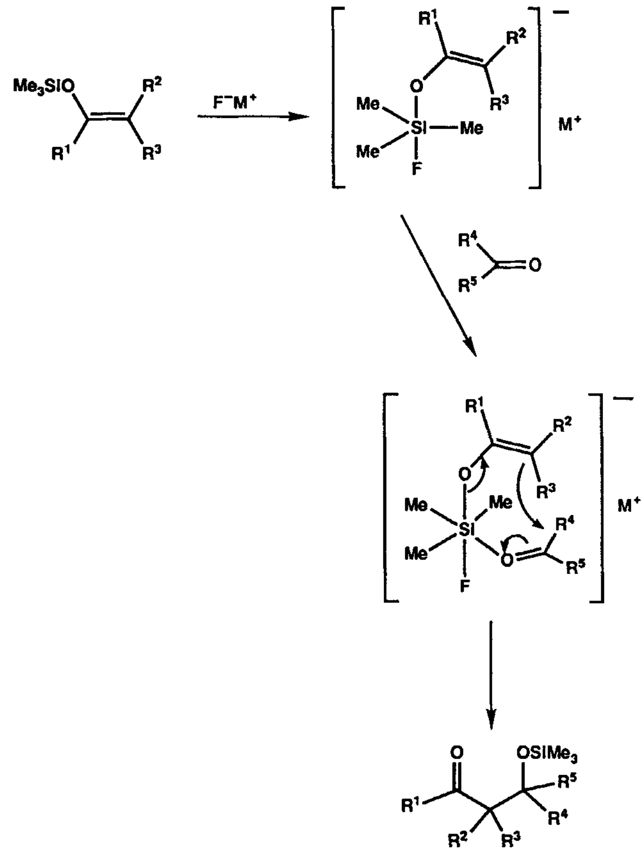


reaction is highly stereospecific, giving the same ratio of diastereomeric products as the ratio of threo and erythro starting crotylsilanes. Somewhat related are mechanistic schemes involving the reaction of initially formed acyclic anionic pentacoordinated silicates that constitute the reactive species. These then react with carbonyl compounds[12] and silyl enol ethers[10] and esters[10] to give alcohols[12] and group transfer[10] products, e.g., Schemes I[12] and II,[10] respectively.

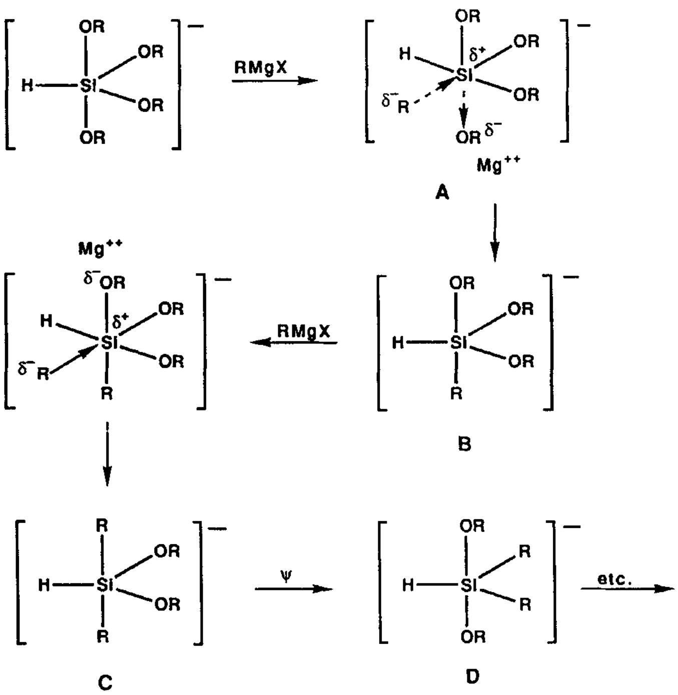
In these mechanistic sequences, the active pentacoordinated anionic silicates are presumed to be susceptible to a further increase in coordination brought about by



SCHEME I



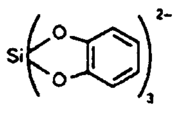
SCHEME II



SCHEME III

an incoming oxygen atom serving as a Lewis base. This type of mechanism is an attractive one that may, in general, be applied to other reactions showing enhanced reactivity by way of pentacoordinated silicon. For example, the ready reaction of tetraethoxydihydridosilicate at low temperature with Grignard reagents[11] may be initiated by attack at a face of the trigonal bipyramid cis to the departing alkoxy group. We envision a concerted displacement of the latter group via the hexacoordinated transition state A depicted in Scheme III leading to an intermediate trigonal bipyramid B. Displacement of the second alkoxy group from its apical position yielding C now requires a pseudorotation process to bring the remaining alkoxy group to the more reactive apical position, as in D, where it undergoes displacement to yield the triorganosilane product.

The conclusion, based on the calculations presented here, that an enhanced reactivity in the pentacoordinated state is attributable to a weakening of silicon–ligand bonds is logically extended to hexacoordinated silicon species. An even greater destabilization of silicon–ligand bonds is projected that should increase as more electronegative groups are displaced by those of lower electronegativity. The latter is consistent with the composition of known compounds of hexacoordinated silicon, which tend to exist only when minimum electronegativity requirements are met. In addition to salts of SiF_6^{2-}[30] and the catecholate[31] adducts of methylhalo-



silanes with 2 mol of pyridine form when at least two halogens are present, e.g., $Me_2SiX_2 \cdot 2Py$, $MeSiX_3 \cdot 2Py$, and $SiX_4 \cdot 2Py$ ($X = Cl, Br$).[32] These compare with a wide range of pentacoordinated silicate derivatives that are now known. In addition to those already mentioned, X-ray structures of the first cyclic pentaoxy anionic silicates[33] and additional members of the organo series, $RSiF_4^-$ [34] and $R_2SiF_3^-$,[35] as well as NMR evidence of acylic pentaoxy anionic derivatives[36] have recently been reported. Their existence provides an experimental basis for the mechanistic considerations presented here.

CONCLUSION

The calculations presented here suggest that the enhanced reactivity of pentacoordinated anionic silicon species relative to tetracoordinated species is associated with an increase in the leaving group ability of the reactive ligand and not with a significant change in the positive character of the silicon center accompanying increased coordination at silicon.

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