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Comparison of Phosphorus and Silicon: Hypervalency, Stereochemistry, and Reactivity

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I. Introduction

Nucleophilic displacement reactions at tetracoordinated phosphorus[1−9] and silicon[9−13] are commonly discussed in terms of mechanisms involving pentacoordinated activated states. However, there is a growing body of evidence, particularly with silicon, that concerns the greater reactivity of isolatable pentacoordinated members which undergo reactions via proposed hexacoordinated states.[3,11,14−23]

It is the purpose of the present review to examine the structural basis for hexacoordinated phosphorus and silicon and how it relates to the pentacoordinated state. In so doing, it is necessary to include recent work on selected examples showing aspects of silicon pentacoordination that are useful in formulating model intermediates. In addition, comparisons between pentacoordinate phosphorus and silicon will be made with *ab initio* calculations on preferred ground-state structures and their accompanying energies.[24,25] Some suggested applications of hypervalent coordination of phosphorus in enzyme systems are then presented on the basis of the above analysis.

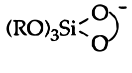
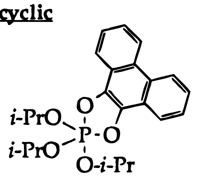
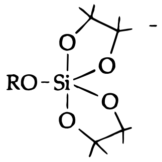
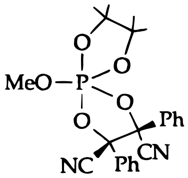
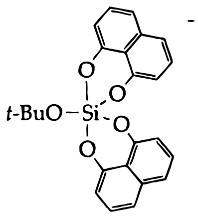
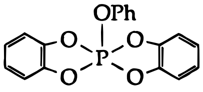
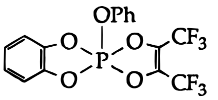
Robert R. Holmes was born in Chicago, IL. He received the B.S. degree in 1950 at the Illinois Institute of Technology, Chicago, and the Ph.D. in 1953 with H. C. Brown at Purdue University. He taught at the Carnegie Institute of Technology before joining the technical staff at Bell Laboratories, Murray Hill, NJ, in 1962. He assumed his present position in 1966 at the University of Massachusetts, Amherst, as Professor of Inorganic Chemistry. His publications number over 200 and include two invited ACS monographs, Nos. 175 and 176, on pentacoordinated phosphorus. His wife, Joan, is a chemist who is a coauthor on many of his publications. Currently, he is Editor-in-Chief of *Phosphorus, Sulfur, and Silicon and the Related Elements* and Consultant Editor of *Main Group Chemistry News*.

At the outset, it should be stated that pentacoordinated silicon compounds are more reactive than comparable isoelectronic pentacoordinated phosphorus compounds. Table 1 illustrates this feature for representative members of acyclic and cyclic compositions of these two elements.[14,26−47] The principal reason for the enhanced reactivity attributed to hypervalent silicon may be simply stated as a result of the lower nuclear charge on silicon compared to that for phosphorus.[24,25] This effect is expected to cause a general loosening of bonds to silicon with concomitant increased ease of cleavage in nucleophilic displacement reactions.

In this review, the terms intermediate, transition state, and activated state are in general used as conventionally found in the literature. In most cases cited these represent proposed formulations in reaction mechanisms which have not been isolated as tractable entities. On this basis, one could refer to all of these terms as activated states. Boldface numbers refer to isolated compounds, whereas letters refer to proposed activated states. Also superscript numbers to formula numbers represent reference citations.

0009-2665/96/0796-0927$25.00/0

Table 1. Comparative Stability of Pentaoxy Silicates and Pentaoxy Phosphoranes

Ref.					Ref.
		Acyclic			
26	$Si(OR)_5^-$	detected but not isolated	$P(OPh)_5$	X-ray	27
		Monocyclic			
		no known examples		X-ray (many other examples) with rings from 5 to 8 membered	28, 29 30-34
		Bicyclic			
26, 35		A few examples studied by X-ray		X-ray (many others with rings from 5 to 8 membered	36, 37 33, 38-45
14		unstable (X-ray of Ph in place of O-*t*-Bu)		X-ray	46
				X-ray	47

All Si are K,$^+$18–crown–6 salts.

II. Structural Characterization

A. Hexacoordinated Phosphorus

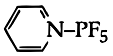
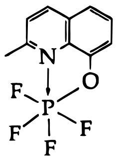
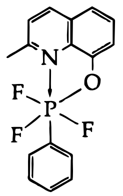
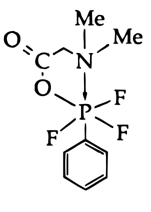
1. Via Nitrogen and Oxygen Donation

The literature provides a number of examples of Lewis acid–base interactions leading to neutral hexacoordinate phosphorus via nitrogen donor atoms. Some of these (**1**–**5**) are listed in Table 2.[48–52] Here the P–N bond length is not too different from the sum of the covalent radii, 1.85 Å.[53] For the last two entries containing the same type of acyclic ligands and a five-membered ring, it is seen that as the P–N length increases, the opposite P–C length decreases, in keeping with that generally observed with other main group elements, *e.g.*, pentacoordinated silicon complexes experiencing Si–O donor action.[54-56] This behavior is consistent with these complexes as models for nucleophilic displacement reactions where the incoming group causes a weakening of the bond to the opposite group undergoing displacement.

The structures of hexacoordinated phosphorus exhibiting cationic and anionic formulations as well as additional neutral species with oxygen and nitrogen ligands also are known, *e.g.*, **6**–**14** (Chart 1).[57–66]

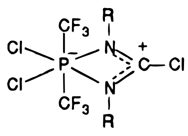
However, only recently have structural studies revealed sulfur capable of inducing hexacoordination for phosphorus. This aspect is discussed in the next section.

Table 2. Some Hexacoordinated Phosphorus Structures

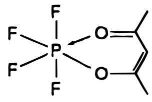
No.		P–N, Å	P–C, Å	Ref.
1		1.885(4)		48
2	$H_3N{-}PF_5$	1.842(2)		49
3		1.911(4)		50
4		1.980(3)	1.833(4)	51
5		2.013(4)	1.814(5)	52
P–N covalent		1.85		

There are quite a few NMR studies that support hexacoordinated phosphorus representations.[63,67-103] The main criterion for establishing the presence of hexacoordination is the observance of an upfield shift in the ^{31}P NMR signal relative to analogous pentacoordinated structures. Some of the formulations are shown in Chart 2 (**15**–**21**).[69,72,74,88,89,101,102]

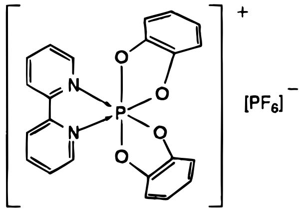
Chart 1



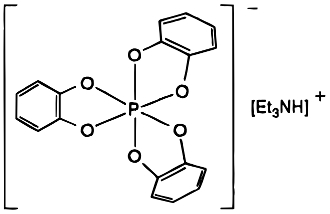
6[57-59]



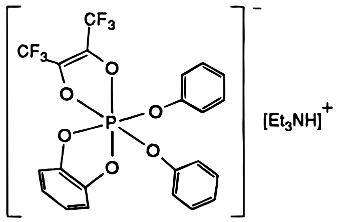
7[60]



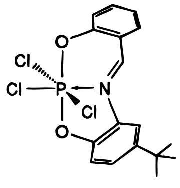
8[61]



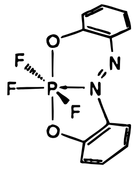
9[62]



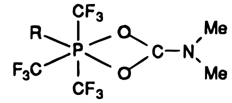
10[63]



11[64]



12[64]



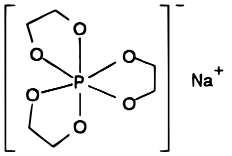
13 (R = Me)[65]; **14** (R = F)[66]

Chart 2

$[(MeO)_6P]^-K^+$

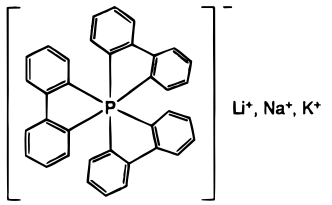
^{31}P, −145 ppm

15[101]

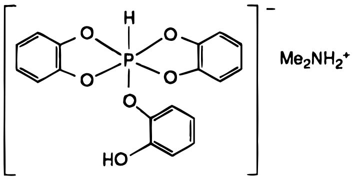


^{31}P, −89 ppm

16[72]

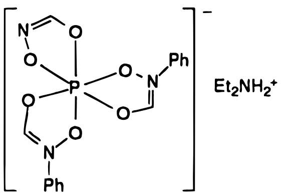


17[88,89]



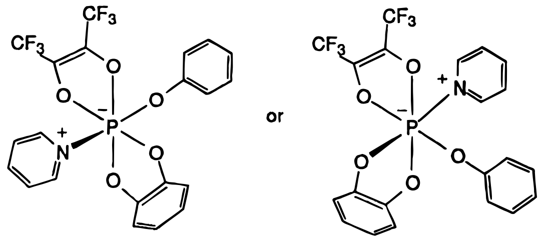
^{31}P, −99 ppm

18[74]

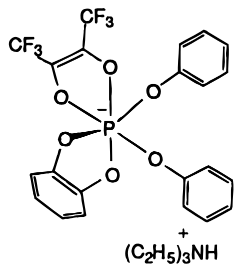


^{31}P, −77 ppm

19[102]

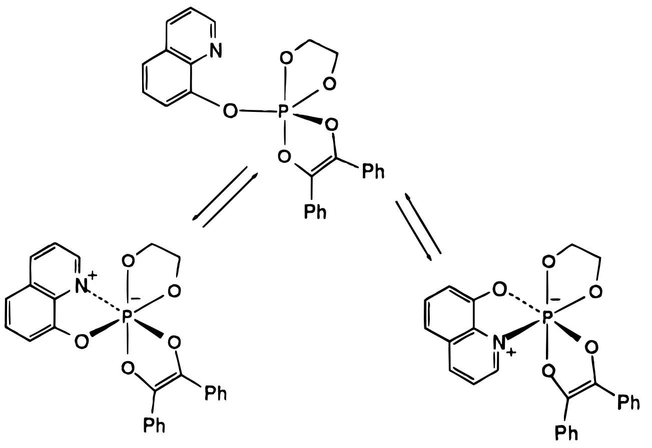


20[69]



21[69]

Munoz and co-workers[103] isolated a number of hexacoordinated compounds, all of a similar kind, which in some cases were found to equilibrate with pentacoordinate forms, *e.g.*, **22**.



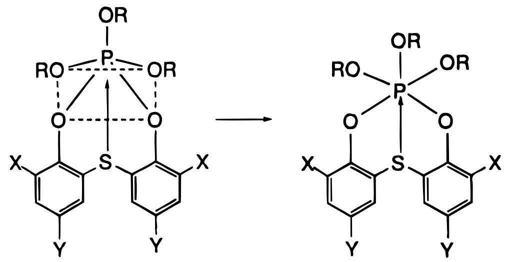
22a[103] **22b**[103]

2. Via Sulfur Donation

Work in our laboratory resulted in a series of pentaoxyphosphoranes (**23**−**27**) containing sulfur as part of a cyclic component which showed P−S coordination with bond distances varying over one-half an angstrom from 2.88 to 2.36Å (Table 3).[32,104−107] Recently Cavell[64] extended this range to 2.33Å in a related phosphorane having the same type of sulfur ring system but with the use of chlorine ligands in place of OR groups.

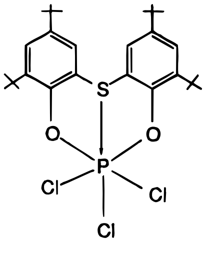
Accompanying the change in donor distance, the X−ray structures of **23**−**27** were displaced from a square-pyramidal geometry toward an octahedron from 44% to 70%, respectively. Figure 1 displays a representative member (**27** [104]) of this series. The disposition of the ring in this type of geometry is contrasted with that in an analogous formulation **29**[32] exhibiting a trigonal-bipyramidal (TBP) geometry with the ring located in diequatorial sites, Figure 2. When two such rings were incorporated in an analo-

Table 3. Selected Parameters for Pentaoxyphosphoranes with Sulfur Containing Eight−Membered Rings



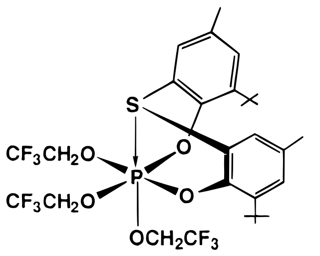
no.[a]	X	Y	R	% octa[b]	P−S, Å
23[105]	Me	Me	Ph	44.1	2.880(1)
24[105]	*t*-Bu	Me	Ph	56.8	2.744(2)
25[105]	*t*-Bu	*t*-Bu	Ph	60.8	2.640(2)
26[32]	*t*-Bu	*t*-Bu	CH_2CF_3	64.5	2.504(3)
27[104]	*t*-Bu	Me	CH_2CF_3	69.4	2.362(2)

[a] Reference numbers are shown as superscripts. [b] Percent displacement from an ideal square pyramid to an octahedron.



P–S = 2.331(1)Å

28[64]



P–S = 2.362(2)Å

P–S Σ cov radii = 2.14Å

Σ van der Waals' radii = 3.75Å

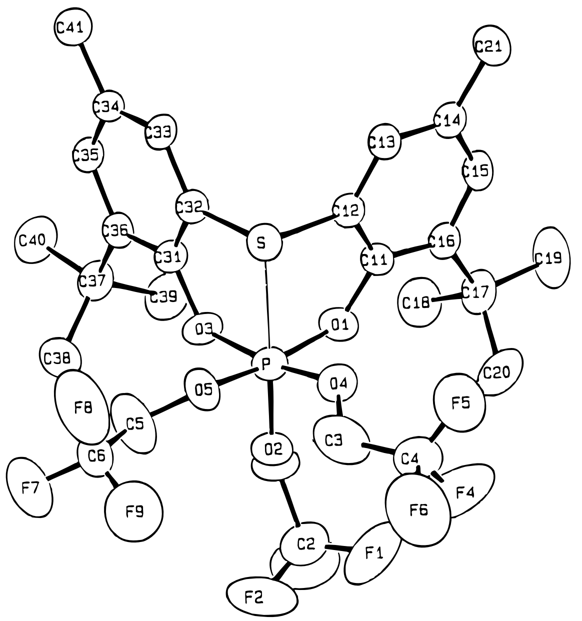
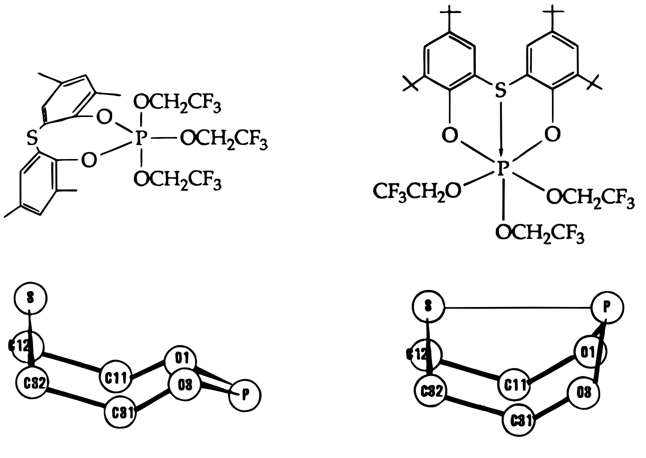


Figure 1. Octahedral X-ray structure of **27**.



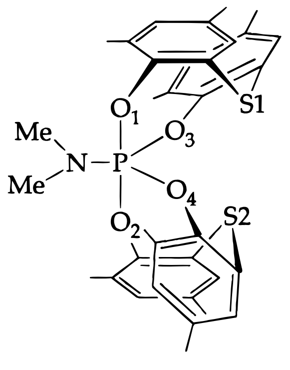
29[32] **26**[32]

P–S distance is 3.504(3)Å P–S distance is 2.504(3)Å

Figure 2. Comparison of diequatorial ring in a TBP (**29**) with ring formation in an octahedron (**26**).

gous formulation (**30**[108]) with a dimethylamino group located in an equatorial site of a TBP, P−S donor action was insignificant (Figure 3). It is suggested that P−N π back-bonding reduced the electrophilicity of phosphorus sufficient to prevent additional coordination.

In an effort to determine if the eight-membered ring containing the sulfur atom was responsible for the formation of the hexacoordinated geometries listed in Table 3, an *ab initio* calculation based on Gaussian 92 was performed on the acyclic system, sulfide−PF_5.[109] This served as a model system for the cyclic series in that it contained five comparable electronegative ligands and a donor atom. The results showed that as the sulfide was brought toward the phosphorus atom starting at an infinite separation, the TBP geometry changed to square pyramidal and then became nearly octahedral on closer approach. The minimum energy structure using a 6-31+G* basis set had a P−S distance of 2.12 Å (which coincidentally is the sum of the covalent bond radii).[53] This compares with the shortest P−S distance found from X-ray structural studies for the phosphoranes listed in Table 3 and that found for **28**. The fact that the calculated reaction trajectory mimics that found for sulfur donor actions in cyclic pentaoxyphosphoranes where X-ray studies[32,104−107] show a range of geometries toward increasing octahedral character from a square pyramid as the P−S interaction increases suggests that inclusion of the donor atom as part of a cyclic system does not control the observed geometrical changes on going from five- to six-coordinate phosphorus.



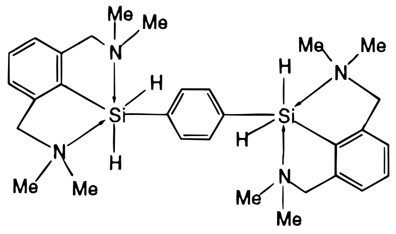
P–S1 = 3.652(3)Å P–S2 = 3.485(4)Å

30[108]

Figure 3. Schematic of the X-ray structure of **30**.

B. Hexacoordinated Silicon

In contrast to phosphorus, structural studies of hexacoordinated silicon compounds are very limited. In addition to about 15 examples cited in the review of Chuit et al.,[11] more recent structural studies reveal hexacoordination for silicon in [Si(cat)$_2$]·2THF (**31**),[110] Li$_2$[Si(catecholate)$_3$]·3.5dme (dme = 1,2-dimethyloxyethane) (**32**),[110] R$_2$Si(tropolonate)$_2$ (R = Ph, Me) (**33**),[111] and [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$SiH$_2$]$_2$C$_6$H$_4$ (**34**).[112] The THF molecules are coordinated in a *trans* fashion around the planar dicatecholate in [Si(cat)$_2$]·2THF, whereas in the R$_2$Si(tropolonate)$_2$ molecules, the R groups have a *cis* orientation. A *cis* orientation also prevails for the hydrogen atoms of the bis(dihydrosilylbenzene) derivative **34**. However, the aforementioned silylcatecholates **31** and **32**[110] and tropolonates **33**[111] have octahedral structures while the dihydrosilane **34** is best described as a bicapped tetrahedron where the NMe$_2$ groups cap two faces of the tetrahedron.[112] Thus, weak Si–N coordination is indicated.



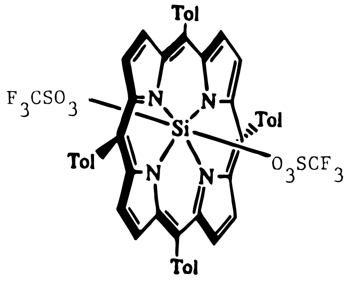
Si–N = 2.681(2)Å, 3.008(2)Å

34[112]

Of some simple acid–base adducts, SiCl$_4$·2PMe$_3$ (**35**),[113] SiF$_4$·2Py (**36**),[114] SiF$_4$·2NMe$_3$ (**37**),[115,116] X-ray diffraction studies favor *trans* orientations of the donor ligands. Chehayber and co-workers[117] performed *ab initio* calculations at a relatively low basis set, STO-6G. Their results agreed with a *trans* orientation for SiF$_4$·2NH$_3$. They conclude that steric effects are absent in controlling the geometry on octahedral complexes containing larger donor groups to silicon, *i.e.*, Py and Me$_3$N. The Si–N distance computed for SiF$_4$·2NH$_3$ is 2.041 Å.

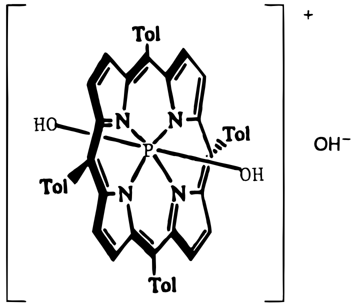
Voronkov and coworkers[118] present an excellent coverage of additional theoretical studies on penta- and hexacoordinate silicon as well as an exposition of structural and dynamic features gleaned from NMR studies appearing in the literature before 1986.

Reactions with macrocyclic ligands have led to the formation of hexacoordinated silicon metalloporphyrin complexes, (OEP)SiX$_2$ (X = Me, Ph, OMe, OPh) (**38**)[119–121] and TTPSiX$_2$ (X = Cl, F, O$_3$SCF$_3$) (**39**).[122] OEP is the dianion of octaethylporphyrin and TTP is the dianion of tetra-*p*-tolylporphyrin. An X-ray structure of (TTP)Si(O$_3$SCF$_3$)$_2$, which is a purple solid unreactive to water, reveals a distorted octahedron with the triflates in *trans* positions and the porphyrin ring in a saddle shape arrangement. The structural parameters compare closely with those of the analogous phosphorus porphyrin complex, [(TTP)P(OH)$_2$]$^+$ OH$^-$ (**40**).[123]



Ave. Si–N = 1.87Å Si–O = 1.842(4)Å

39[122]



Ave. P–N = 1.89Å

40[123]

Like **39**, the porphyrin group of the phosphorus complex **40** has a ruffled conformation. The same kind of porphyrin conformation was found in the recent X-ray structural characterization of [(TPP)P(OCH$_2$CH$_2$CH$_2$OH)$_2$]OH (**41**).[124] The average deviation of the meso carbon atoms from the N$_4$ plane is ±0.79 for **39** and ±0.83 for **40**. With larger main group elements, *e.g.*, in the tin complex, [(TPP)Sn(H$_2$O)$_2$]$^{2+}$(O$_3$SCF$_3$$^-$)$_2$, the porphyrin ring becomes planar.[125] Further developments of this interesting area, leading to the formation of hexacoordinated silicon having restricted geometries due to the presence of macrocyclic ligands, may be anticipated. Some additional examples (**42**–**45**) involving Si–N hexacoordination are shown in Figure 4.[126–129] The anionic ones, **42**[126] and **43**[127] that are nearly octahedral with Si–N distances near the sum of the

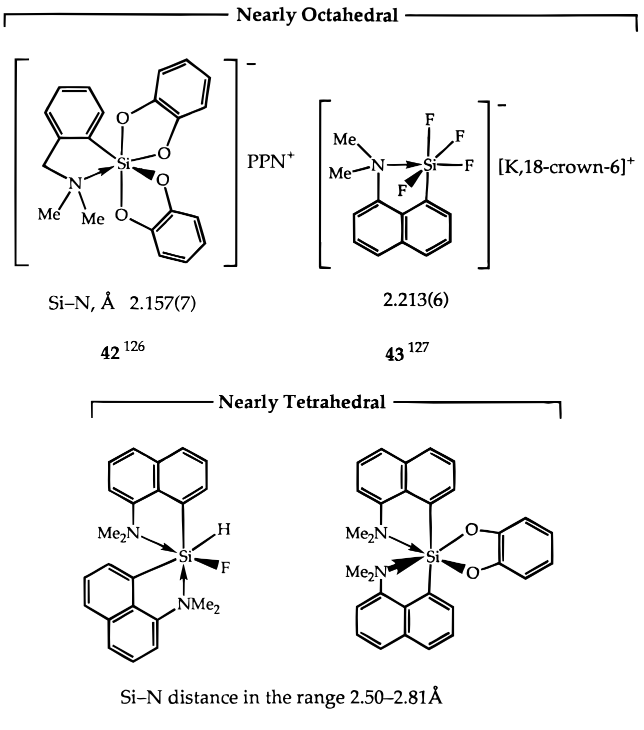
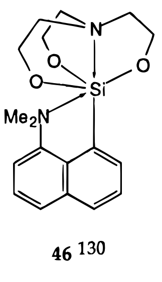


Figure 4. Some hexacoordinated silicon structures via nitrogen coordination.

covalent radii of 1.93Å[53] are isoelectronic with the cyclic pentaoxyphosphoranes **23**−**27** (Table 3) that attained octahedral geometries via sulfur induced coordination. The neutral pair in Figure 4, **44**,[128] **45**[129] however, are nearly tetrahedral with respect to the silane geometry and have achieved hexacoordinate states as a consequence of rather long Si−N coordinate distances. Similar to **44** and **45**, the X-ray structure of the silatrane **46**[130] shows hexacoordination induced by weak coordination of the nitrogen atom of the NMe$_2$ group (the Si−NMe$_2$ distance is 2.952(7)Å). The geometry of the silatrane framework excluding the nitrogen interaction is represented by a displacement from a TBP toward a tetrahedron. Apparently, the penetration of the coordination sphere of silicon by nitrogen in these neutral entities is insufficient to cause any appreciable electronic rearrangement to an octahedral geometry.



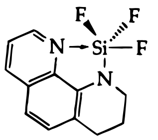
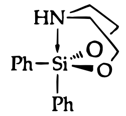
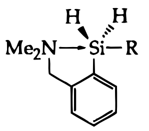
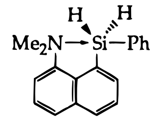
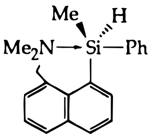
46 [130]

C. Pentacoordinated Silicon

1. Via Nitrogen and Oxygen Donation

In view of the limited information on hexacoordinated silicon, it is of interest to assess the ability of silicon to undergo donor action leading to pentacoordination. Silane structures that have attained pentacoordination via nitrogen (**47**−**51**[131−134]) or oxygen (**52**−**59**[55,56,135−138]) donor action are listed in Tables 4 and 5, respectively. Here also, as mentioned in discussing the entries of Table 2 that list phosphorus compounds, increasing Si−O distance for members of Table 5 with common acyclic groups, **54**−**58**, respectively, is accompanied by a decrease in the opposite Si−Cl distance. In all the examples of Tables 4 and 5, the structures consist of TBP geometries with oxygen or nitrogen donor action occurring at an axial site.

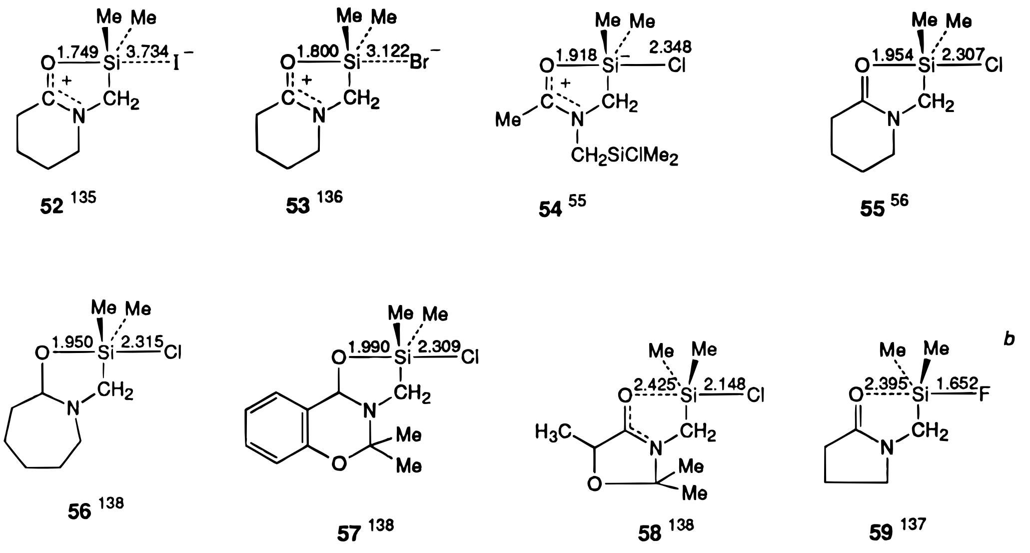
Table 4. Nitrogen-Induced Pentacoordination

No.		Si–N$_{ax}$ (Å)	Si–C$_{ax}$ (Å)
47 [131]		1.969(4)	
48 [132]		2.301(6)	1.901(6)
49 [133]	 R = αNp	2.44(1)	1.92(2)
50 [134]		2.584(3)	1.893(4)
51 [134]		2.66(1)	1.91(1)

Over the whole range of pentacoordinate silicon compounds in Table 5, the axial Si−O distance increases continuously from 1.749 Å for **52**[135] to 2.395 Å for **59**[137] as the opposite axial halogen distance decreases from close to a van der Waals value for **52** to close to a single bond covalent value for **59**. The geometry at silicon in this series is initially distorted from a tetrahedron toward a TBP with the silicon atom displaced from the C$_3$ equatorial plane toward the apical oxygen atom, *i.e.*, for **52**. As the series is traversed[138] toward **59**, the geometry progresses to the TBP and then continues toward an inverted tetrahedron, *i.e.*, for **59**, relative to that for **52**. Thus, this series serves as an excellent model for a nucleophilic displacement reaction at silicon, especially one proceeding by an inversion mechanism where incoming and outgoing groups do so from apical positions of a TBP, the same as found in phosphorus chemistry.[2,4−7,9,10]

Some related pentacoordinated silicon structures containing Si−O donor-induced coordination are **60**,[139] **61**,[54] and **62**.[140]

Table 5. Oxygen-Induced Pentacoordination[a]

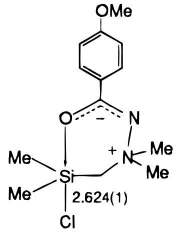


52[135] **53**[136] **54**[55] **55**[56]

56[138] **57**[138] **58**[138] **59**[137]

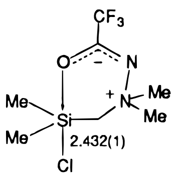
a. From ref. 138.

b. Ave. of 4 independent molecules/unit cell.



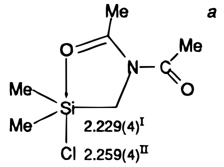
Si–O = 1.788(1)Å

60[139]



Si–O = 1.879(1)Å

61[54]

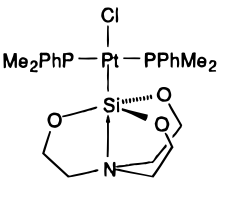


a. Two independent molc./unit cell (I and II).

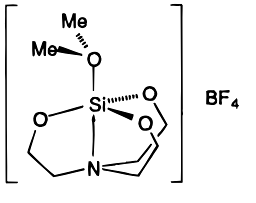
Si–O = 2.077(6)^{I}, 2.027(6)^{II}

62[140]

Silatranes also form a class of pentacoordinate molecules which exhibit TBP geometries.[141] Extensive studies by Voronkov and coworkers exist in this area.[142–145] Si–N$_{ax}$ bond distances have been found to range from 2.89(1) Å for **63**[146a] to 1.965(5) Å for **64**.[146b] The short Si–N$_{ax}$ distance for **64** is not significantly different from that of **47** [131] (Table 4), both of which have highly electronegative ligands, the Me_2O^+ group and the fluorine atom, respectively. Edema et al.[147] formed a pentacoordinated pseudoatom silicon compound $C_5H_3N(CH_2CR_2O)_2SiMe_2$ (RR = adamantyl) with a pyridine-based ligand.



63[146a]



64[146b]

Pentacoordinated neutral adducts are known that exhibit P→Si coordination. For example, Bassindale and coworkers[148] were able to form a 1:1 molecular adduct of $MeHSi(OTf)_2$ (**65**) with HMPA. With NMI (*N*-methylimidazole) ionic products are attainable as well as a 1:1 neutral adduct. Thus, $[Me_2SiH(NMI)_2]^+ Cl^-$ (**66**) has been prepared[149] and its X-ray structure obtained.[150] Spectroscopic studies of $SiF_4 \cdot NH_3$ (**67**)[151] and $SiF_4 \cdot NMe_3$ (**68**)[115,116] support TBP geometries with an axial donor group. *Ab initio* calculations[117] using a low basis set, STO-6G, agree with this geometry for $SiF_4 \cdot NH_3$ (**67**) with a computed Si–N distance of 2.392 Å.

2. Via Sulfur Donation

We recently have studied the use of sulfur as a potential donor with oxysilanes employing the same type of eight-membered ring system that we found effective in promoting increased coordination with pentaoxyphosphoranes. This led to the disiloxane, **69**,[152] whose ORTEP plot is shown in Figure 5 along with a schematic representation.

^{29}Si NMR chemical shifts of −107.8 ppm and −99.4 ppm were obtained in the solid state consistent with the two kinds of silicon atoms present in the X-ray structure.[152] On the basis of angle displacements and observed Si–S bond distances, the disiloxane is displaced approximately halfway from a tetrahedron toward a TBP. Similar to nitrogen and oxygen donation, the sulfur atom is located in an axial position. This geometry is also found in the related silanes **70**–**71**[152] and **72**–**74**,[153] shown in Figure 6 where ^{29}Si chemical shifts are displayed. The Si–S bond distances for these three cyclic dioxysilanes, **73**, **74**, and **71**, are 3.286(1) (av), 3.074(1), and 2.978(4) Å, respectively. Table 6 lists ^{29}Si chemical shifts for specific examples of silicon compounds, **75**–**82**,[14,26,35,154,155] having various coordination numbers.

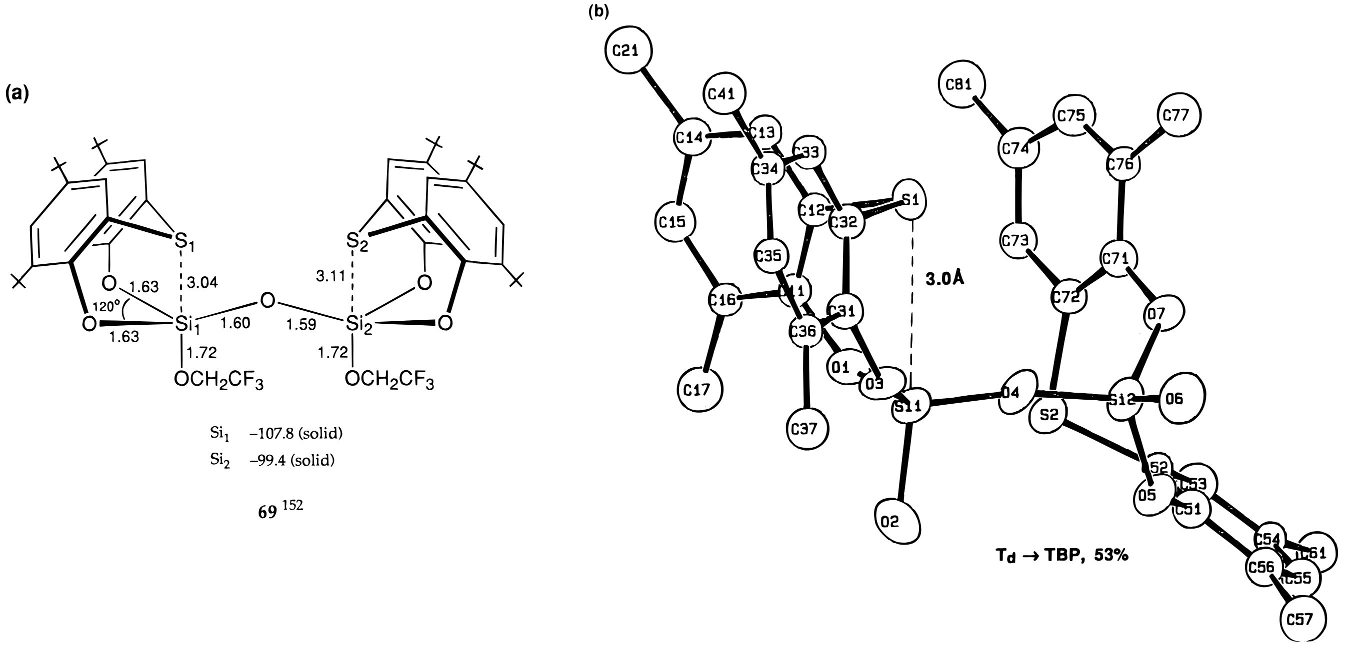
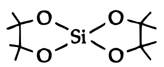
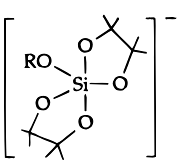
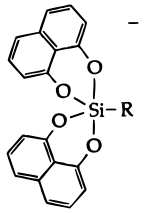
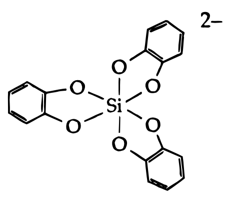
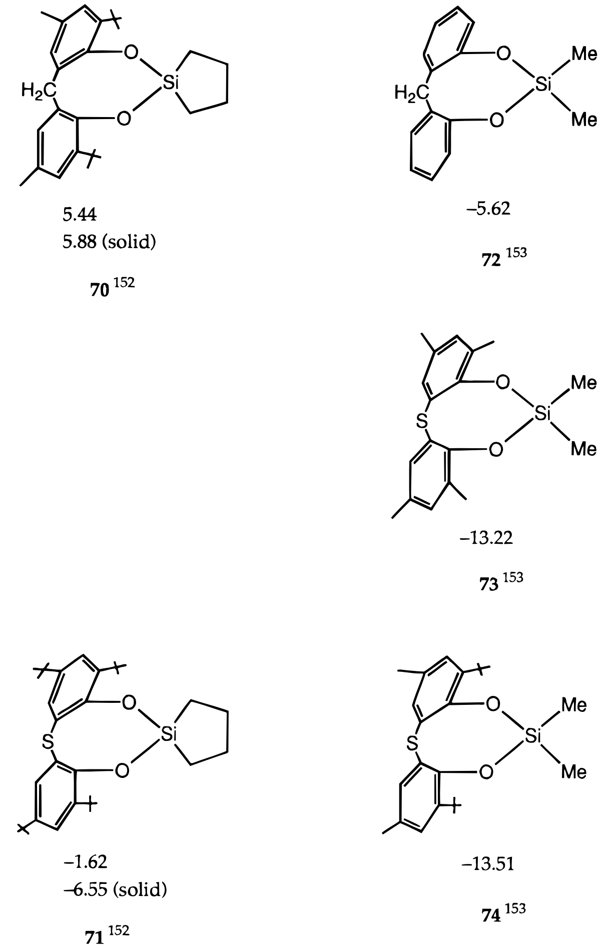


Figure 5. (a) Structural representation and (b) ORTEP plot of disiloxane **69**. The values under the figure in a are ^{29}Si chemical shifts in ppm.

Table 6. ^{29}Si Chemical Shifts (ppm) of Silicates

No.				Ref.
			4-Coordinate	
		$Si(OEt)_4$	−82.4 (toluene)	26
75			−45.1 ($CDCl_3$)	26
			5-Coordinate[a]	
76		$Si(OEt)_5^-$	−131.1 (toluene)	26
77		$PhSi(OEt)_4^-$	−117.3 (toluene)	26
	R			
78	*t*-Bu		−111.8 ($CDCl_3$)	35
79	*i*-Pr		−110.8 ($CDCl_3$) −108.2 (toluene)	26
	R			
80	O-*t*-Bu		−125.8 (CH_2Cl_2)	14
81	Ph		−132.4 ($CDCl_3$)	14
			6-Coordinate[a]	
82			−140.7 (toluene) −143.4 (CD_3OD)	154 155

[a] All cations are K^+,18-crown-6.



5.44
5.88 (solid)
70[152]

−5.62
72[153]

−13.22
73[153]

−1.62
−6.55 (solid)
71[152]

−13.51
74[153]

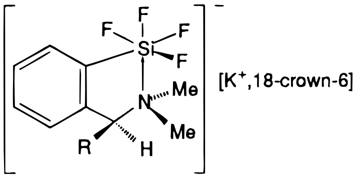
Figure 6. Silicon-29 chemical shifts (ppm) of cyclic silanes.

It is clear that from the comparisons in Figure 6 and Table 6 that increased shielding at silicon accompanies sulfur atom donation.[153] The disiloxane **69**[152] which is monocyclic with respect to each silicon center would be expected to have a ^{29}Si chemical shift of about −64 ppm, *i.e.*, the average of the first two entries of Table 6, if it were only tetracoordinated by way of the four attached oxygen atoms. Its much higher value then is likely a consequence of sulfur base donation.

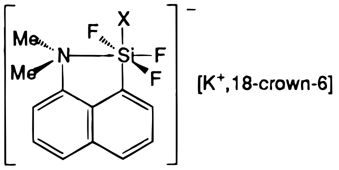
The common structural feature found for donor action by nitrogen, oxygen, and sulfur, that of the incipient formation of TBP geometries with the incoming donor atom seated in an axial position, supports the mechanistic approach whereby displacement reactions of four coordinate silicon[10,11] do so via entering nucleophiles at axial sites of TBP intermediates. Although the structural studies refer to thermodynamically favored geometries and the mechanistic studies to kinetic factors, there often is a parallel between the two.

D. Stereoisomerization

While examples of stereoisomerization of pentacoordinate phosphorus,[6,9,67] and to a lesser degree, pentacoordinated silicon,[10,11] are well known and have been amply discussed via the favored[156] intramolecular pseudorotational mechanism (Berry process[157]), studies of stereoisomerization of both hexacoordinate phosphorus and silicon are in the embryonic stage. In the case of hexacoordinate silicon, mechanistic interpretations concerning ligand exchange phenomena have been advanced largely through the work of Corriu and coworkers.[126,127,158] For example, in the interpretation of the ^{29}Si, ^{19}F, and ^{1}H VT NMR solution spectra of **83**−**86**, it is suggested[127] that intramolecular permutation of fluorine atoms occurs through a mechanism, such as the Bailar twist[159] or Ray−Dutt twist[160] without cleavage of either Si−N or Si−F bonds. Thus, Si−F coupling is retained for **84** as the four fluorine coupled signals become equivalent with increasing temperature. Since $\Delta G_F{}^{\ddagger}$ of 11 kcal/mol from coalescence of fluorine signals in the ^{19}F NMR spectrum of **84** is lower than $\Delta G_H{}^{\ddagger}$ of 14 kcal/mol from coalescence in the ^{1}H NMR spectrum of the signals belonging to the two N−Me groups, which are diastereotopic due to chirality at the α-carbon, it is reasoned that fluorine site exchange takes place without Si−N bond breakage.



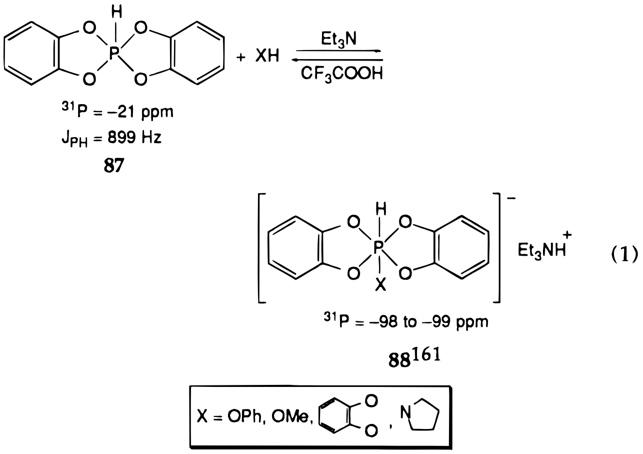
83, R = H **84**, R = Me



85, X = F **86**, X = Ph

Much of the work on hexacoordinated phosphorus that might involve stereoisomerization centers on equilibria between pentacoordinate and hexacoordinate structures has been established by NMR investigations.[67] In the case of ^{31}P NMR, hexacoordinated derivatives give signals shifted upfield about 50−60 ppm from those of analogous pentacoordinated derivatives, at least for pentaoxyphosphoranes. Two examples are provided here to illustrate this area of investigation. Others are summarized in the recent review by Burgada and Setton.[67]

The first evidence for the presence of a penta-hexacoordinate equilibrium subject to acid−base control was provided by the reaction of the hydrido spirophosphorane **87** in basic media which forms the anionic hexacoordinated compound **88**[161] (eq 1). In a reversible reaction with a sufficiently strong acid, *e.g.*, CF_3CO_2H, the spirophosphorane is regenerated.



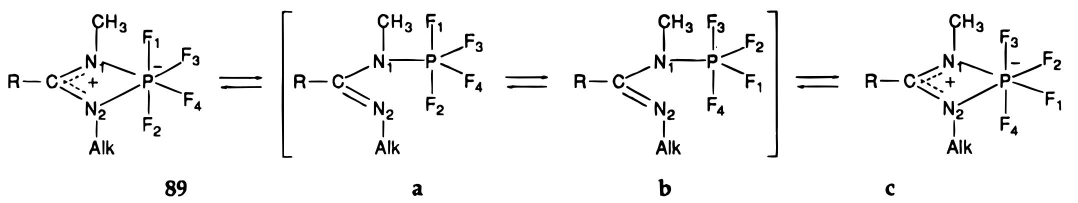
In dealing with mechanistic considerations involving hexacoordinated phosphorus compounds, like that for hexacoordinated silicon compounds,[127] one should expect that they are likely to undergo stereomutations.

Negrebetskii and coworkers[162] established hexacoordinate formulations for a series of amidinium fluorophosphorus compounds by VT NMR, *e.g.*, **89**. Their results showed that ligand exchange was consistent with a mechanism of irregular permutational isomerism.[163] In this process dissociation of a P−N bond of **89** is postulated with intramolecular ligand exchange (pseudorotation) occurring in a proposed pentacoordinated intermediate, **a** → **b**, to allow equivalence of fluorine atoms from their individual environments observed at reduced temperatures (Scheme 1).[162]

In a related system[162] where two of the fluorine atoms were replaced by a catecholate ligand, *i.e.*, in **90**, a higher activation energy ($\Delta G^{\ddagger}_{388K}$) = 19.8 kcal/mol) for equivalence of two types of *N*-methyl groups present at 30°C from ^{1}H NMR spectra resulted compared to that ($\Delta G^{\ddagger}_{375K}$) = 18.6 kcal/mol) obtained for equivalence of the two kinds of fluorine atoms present at 30 °C from the ^{31}P NMR spectra. However, unlike the Bailar twist mechanism postulated as the intramolecular exchange mechanism for the hexacoordinated silicon complexes **83**−**86**[127] exhibiting similar NMR behavior regarding relative activation energies for N-methyl groups and fluorine atoms, a more conventional exchange process was advanced. It is proposed[162] that the *N*-methyl groups equilibrate by route **90**−**d**−**e**−**f** and the fluorine atoms by route **90**−**g**−**h**−**i** where both routes involve intermediate trigonal bipyramids (Scheme 2).

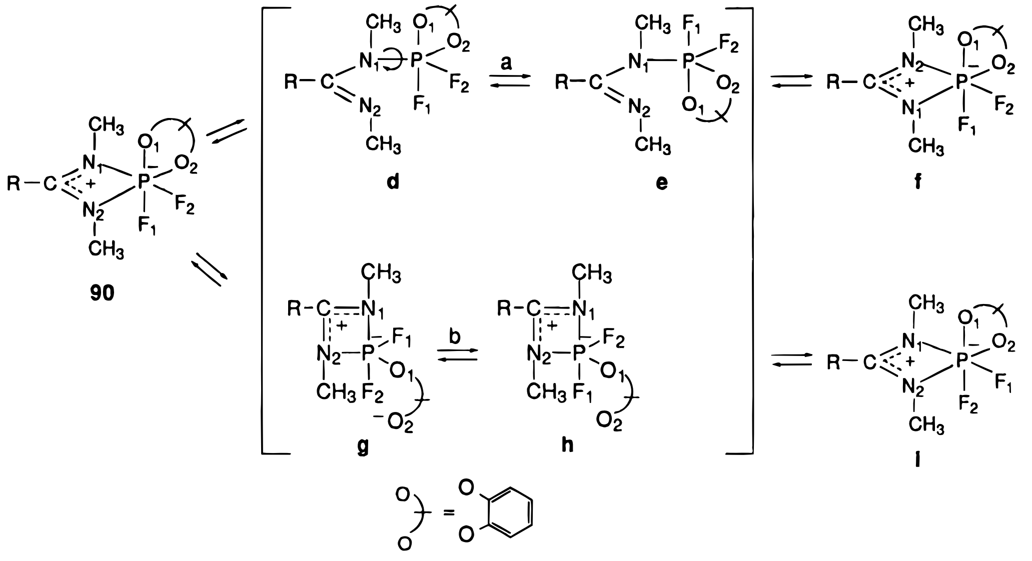
One can argue that the simple method each used to obtain activation energies in each study, *i.e.*, coalescence temperature and line separation, has sufficient uncertainty that the activation energies from two different kinds of NMR nuclei are within experimental deviation from each other. This is certainly the case in the phosphorus study and not

Scheme 1[162]



(*e.g.* for **89** with R = CF_3, Alk = Me, ^{31}P = –137.4 ppm)

Scheme 2[162]

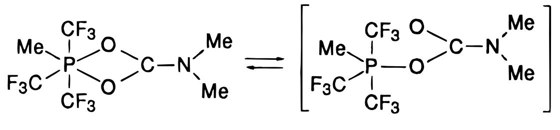


R = C_6H_5

a = rotation relative to P–N bond
b = exchange of positions of fluorine atoms

unreasonable in the silicon study.[164] If so, then the exchange mechanism in both studies would be a conventional one, *i.e.*, central atom–nitrogen bond rupture accompanied by pseudorotation of the pentacoordinate intermediate as proposed by Negrebetskii and coworkers[162] in the case of the amidinium tetrafluorophosphorus compounds, *e.g.*, **89** in Scheme 1.

In a similar vein, Cavell and Vande Griend[166] observed fluxional behavior of **91** from VT NMR. The two types of fluorine environments present at reduced temperatures became equivalent near room temperature. The barrier energy of 13.5 ± 0.7 kcal/mol obtained from line shape analysis is stated[166] as typical of that found for CF_3 permutations on a five-coordinate center in related systems. The exchange mechanism, consistent with this fact, involves transformation of the carbamate to a monodentate ligand followed by a Berry pseudorotation process to bring about equivalency of the CF_3 groups. Thus, complete line shape analysis exhibits a ±0.7 kcal/mol uncertainty on a related mechanism whereby hexacoordinate phosphorus undergoes intramolecular ligand exchange in a pentacoordinate intermediate.



91

Although anionic hexacoordinate silicon and hexacoordinate phosphorus are isoelectronic and a study of their dynamic systems offers a more direct way of comparing stereoisomerization mechanisms, it is also instructive to look at neutral hexacoordinate silicon compounds that give evidence for stereochemical change. In one such study, Corriu and coworkers[168] examined permutational isomerization of the hexacoordinate silicon compounds **44** as well as some related ones. The X-ray structure of **44**[128] is shown in Figure 4 where long Si–N lengths are indicated for a silane geometry which is essentially tetrahedral. The ^1H NMR data at low temperature display signals indicative of four types of N–Me groups and two kinds of naphthyl groups which at higher temperatures coalesce to two N–Me signals and one set of naphthyl signals. A nondissociative isomerization mechanism is proposed without cleavage of the weak Si–N bonds. An isomerization generally reserved for an ideal octahedral geometry, *i.e.*, a Bailar twist,[159] Ray–Dutt twist,[160] or Springer–Siever twist, is suggested, even though the basic silane geometry is nearly tetrahedral. ^{29}Si NMR chemical shifts are very similar for this class of neutral compounds containing Si–N coordination whether they are tetra-, penta-, or hexacoordinate, and hence cannot be used to establish coordination geometry.[168] However, it is pointed out that the larger Si–H coupling constants for hexacoordinated members containing Si–H bonds, 216.4 to 285.5 Hz, compared to tetracoordination, 197.7 Hz for dinaphthylsilane, are a reliable indication of hexacoordination in $CDCl_3$ solution.[133]

In keeping with the solid-state tetrahedral structure for **44** and related members,[128] we might suggest a more conventional mechanism, whereby Si−N dissociation occurs and is accompanied by correlated rotation of the two naphthyl groups about the respective Si−C bonds. However, due to possible steric interference, rotation and inversion at the nitrogen atoms is assumed to be precluded.

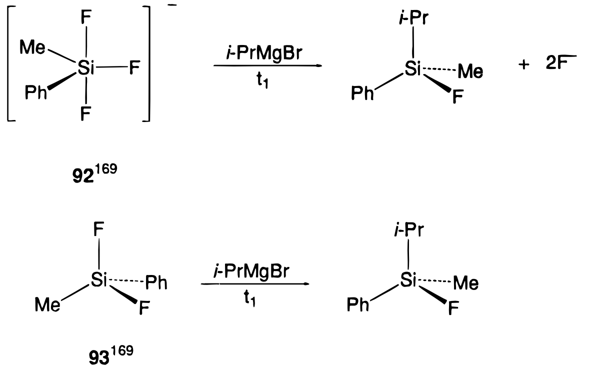
III. Reactivity

A. Pentacoordinated Silicon

Much of the greater reactivity associated with hypervalent states relates to silicon.[10,11,169] Corriu and coworkers,[169b] for example, have shown that the pentacoordinate anionic methylphenyltrifluorosilicate **92** pictured in Figure 7 reacts with a Grignard reagent 150 times faster than the related tetracoordinate fluorosilane **93**. There is a host of other pentacoordinate organosilicon compounds described in the literature[10,11] that accelerate organic reactions. Some of these are postulated to take place via hexacoordinated states.[11,14−22]

The available kinetic data, for example, in hydrolysis and alcoholysis of tetracoordinate chlorosilanes, support the involvement of two molecules of nucleophilic reagent.[22a,170] The formation of an initial pentacoordinate intermediate is consistent with the acceleration in rate observed in the presence of a nucleophilic catalyst. In this context, the rate-determining step is the formation of a hexacoordinate intermediate or transition state by attack of the second nucleophile on the pentacoordinate silicon atom.

Theoretical calculations have shown that the charge on silicon in the anionic five-coordinated series $[SiH_nF_{5-n}]^-$ is not significantly different from that in the related tetracoordinated series SiH_nF_{4-n} other than when $n = 0$.[24b] For this most highly fluorinated member SiF_5^-, the positive charge at silicon is found to be higher than that for SiF_4. Other calculations support an increase in the silicon atom positive charge.[171] The calculations show, in agreement with experimental results, increased bond lengths in the pentacoordinated species compared to those in the related tetracoordinated members, with a greater increase occurring in axial positions of the trigonal-bipyramidal geometry.[24] It is suggested that this axial bond length increase imparts a greater leaving ability to the reactive ligand and that this feature plays a dominant role in causing enhanced reactivity of pentacoordinated silicon.

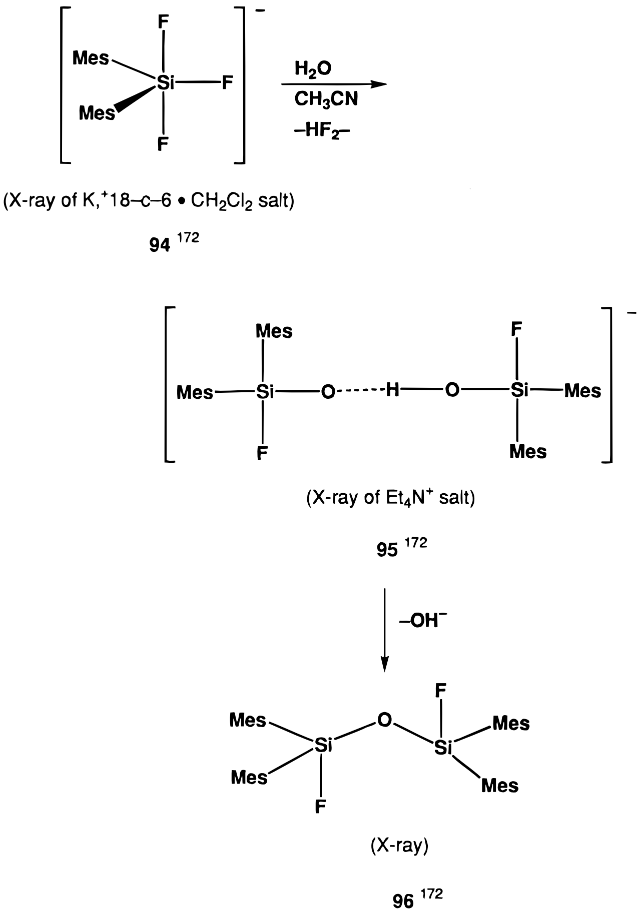


92[169]

93[169]

$t_2/t_1 > 150$ (t = half reaction time)

Figure 7. Half-reaction times of five- and related four-coordinated silicon compounds, **92** and **93**, respectively.



(X-ray of $K,^+18\text{-}c\text{-}6 \bullet CH_2Cl_2$ salt)

94 [172]

(X-ray of Et_4N^+ salt)

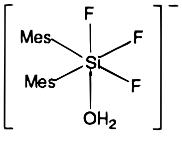
95 [172]

(X-ray)

96 [172]

Figure 8. Rapid hydrolysis of Si−F bonds of **94**.

In our own work, we studied the hydrolysis of $Mes_2SiF_3^-$ (**94**) in comparison with Mes_2SiF_2 in acetone solution (Mes = mesityl).[172] Whereas ^{19}F NMR spectra showed that Mes_2SiF_2 remained almost unchanged after 24 h after the addition of a 2:1 molar ratio of water to silane, nearly complete hydrolysis occurred within 15 min for a comparable treatment of hypervalent $Mes_2SiF_3^-$ with water. Products that were isolated from the same type of reaction in acetonitrile and studied by X-ray diffraction revealed the formation of a hydrogen bisilonate, $[Mes_2Si(F)O{-}H{-}OSi(F)Mes_2]^-$ (**95**) and a disiloxane, $(Mes_2SiF)_2O$ (**96**) pictured in Figure 8.[172] Initial nucleophilic attack by H_2O with formation of the anionic hexacoordinate silicate



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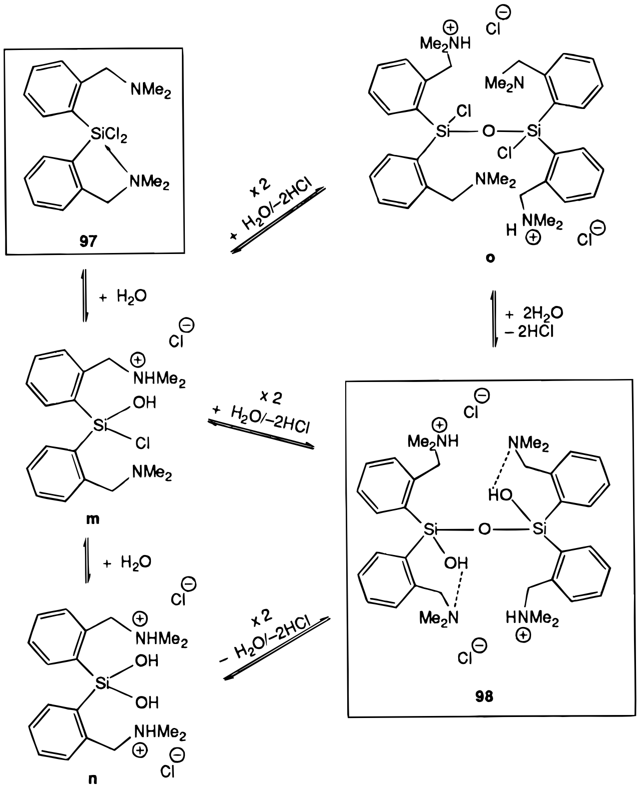
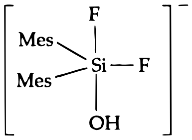
is consistent with that discussed in the previous

Scheme 3[173]

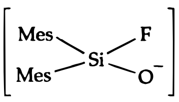


section. Successive loss of HF leads to



k

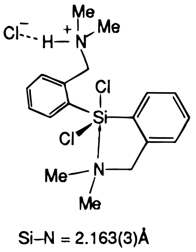
and



l

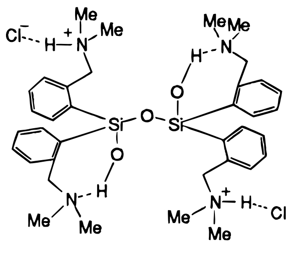
as intermediates which may combine to yield the hydrogen bisilonate with concurrent loss of fluoride ion.

Somewhat related to the hydrolysis of $Mes_2SiF_3^-$, **94**, Auner and coworkers[173] studied the controlled hydrolysis of the dichlorosilane **97** which resulted in the formation of the 1,3-siloxanediol **98**. An X-ray structure of the protonated salt of **97**, *i.e.*, **99**, and that of the product **98** suggested a reaction mechanism incorporating N → Si donor action (Scheme 3).[173] The structure of the pentacoordinate silane **97**



Si–N = 2.163(3)Å

99



98

containing two aromatic and three electronegative components may be compared to a similar ligand constitution for anionic $Mes_2SiF_3^-$ (**94**).[172] Likewise, the X-ray structures of the hydrolysis products, the siloxanediol **98** and the siloxane **96**, are comparable.

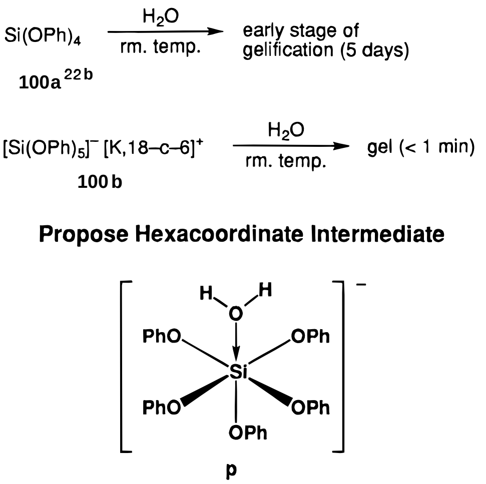


Figure 9. Rapid gel formation of $Si(OPh)_5^-$ (**100a**) relative to $Si(OPh)_4$ (**100b**).

Although not indicated by the authors,[173] at least the initial step in the hydrolysis may proceed by nucleophilic attack of water to give a hexacoordinated activated state similar to that proposed, *i.e.* **j**, for the hydrolysis of $[Mes_2SiF_3]^-$ (**94**).[172]

In another hydrolysis process, Corriu and coworkers[22b] proposed the hexacoordinate silicate intermediate **p** (Figure 9) to account for the rapid hydrolysis of pentacoordinate $[Si(OPh)_5]^-$ (**100b**), which gels in less than 1 min compared to that for the tetracoordinate silane, $Si(OPh)_4$ (**100a**). The latter hydrolysis proceeds only to an early stage of gel formation after 5 days.

Hydrolytic instability is common for pentaoxysilicates to such an extent that isolation is a considerable problem. Acyclic anionic pentaoxysilicates like $Si(OR)_5^-$ have only been detected in solution by NMR measurements[26] and in the gas phase by negative ion ionization,[174] *e.g.*, $Si(OMe)_5^-$ (**101**,[26] $^{29}Si = -127.5$ ppm) and $HSi(OEt)_4^-$ (**102**,[23a,175] $^{29}Si = -88.1$ ppm) in solution and $Si(OMe)_5^-$, $HSi(OMe)_4^-$ (**103**), and $H_2Si(OMe)_3^-$ (**104**), in the gas phase.[174] The same is true for members of the classes $PhSi(OR)_4^-$ and $Ph_nSi(OCH_2CF_3)_{4-n}$ ($n = 1-3$) other than the K^+,18-crown-6 salt of $PhSi(OCH_2CF_3)_4^-$ (**105**), which was obtained as a crystalline material.[26] Solids have been isolated in the hydrido series $HSi(OR)_4^-$ (**106**) as K^+ salts (R = Et, *i*-Pr, Ph).[23a,175] In the case of $K^+[H_2Si(OR)_3]^-$ (**107**, R = *i*-Pr, C_6H_{11}, or *s*-Bu), solids are also obtained.[23b] In solution ligand exchange is indicated[176] for the latter, whereas site exchange in the presumably more fluxional series, $Si(OR)_5^-$ and $RSi(OR)_4^-$, has not been identified.[26]

In gas-phase ionization studies under flowing afterglow conditions, Squires and coworkers[177] report the formation of pentacoordinate silicon hydride anions, *e.g.*, SiH_5^- (**108**), *n*-$C_5H_{11}SiH_4^-$ (**109**), $Et_3SiH_2^-$ (**110**), *n*-$BuSiH_3F^-$ (**111**), $Et_2SiH_2OCH_3^-$ (**112**), and $CF_3SiH_4^-$ (**113**). This adds to the extensive series of siliconate anions of the forms, H_3SiXY^- and Me_3SiXY^- generated in a combined experimental and theoretical study by Damrauer, Burggraf, Davis, and Gordon.[178] No monocyclic anionic pentaoxy silicates have been isolated. However, several anionic pentaoxy bicyclic silicates have had their structures

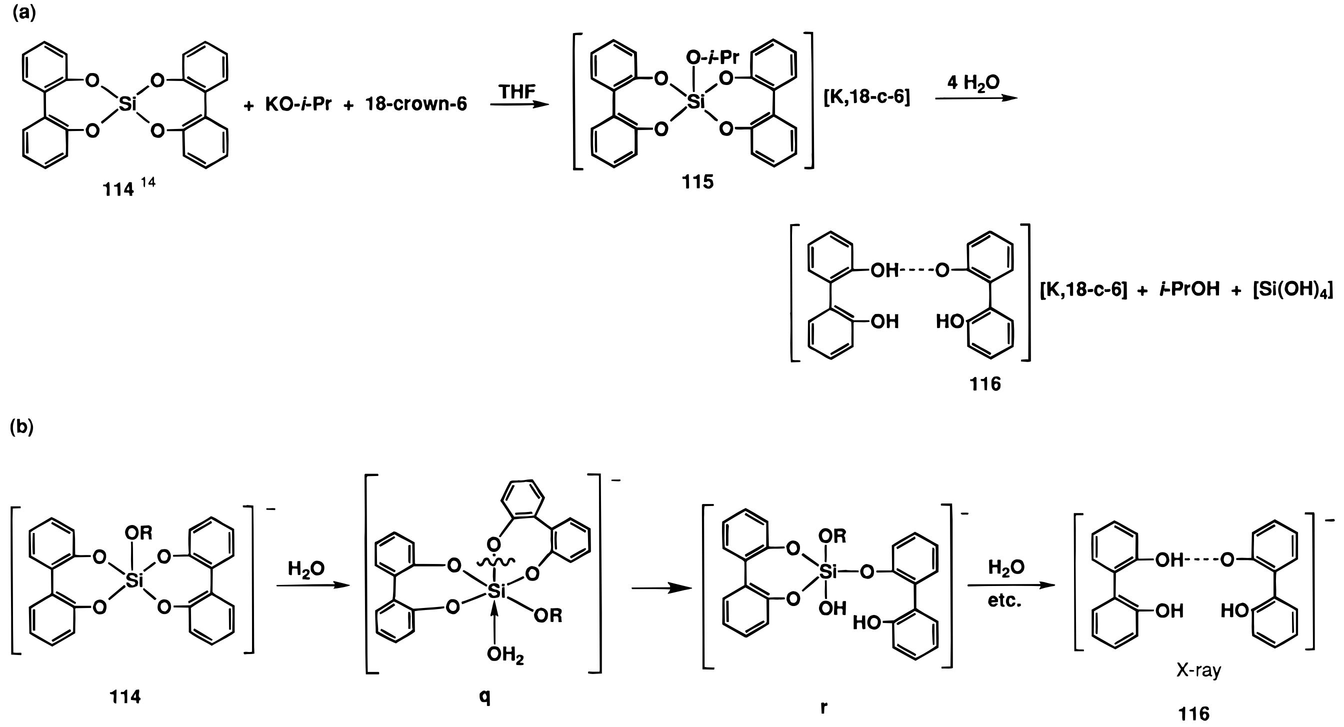


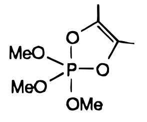
Figure 10. (a) Hydrolytic instability of pentaoxy silicates with seven-membered rings, *e.g.* **114**, and (b) proposed mechanism via hexacoordinated state.

established by X-ray diffraction, primarily those with five-membered rings, *e.g.*, **78**[35] and **79**[26] in Table 6. The only X-ray study of a bicyclic tetraoxy silicate with a six-membered ring was obtained on a derivative which has a phenyl group in the fifth position, **81**[14] (Table 6). Pentacoordinated anionic bicyclic pentaoxy silicates with seven-membered rings have been isolated and identified only by elemental analysis and NMR spectral data.[14] Hydrolysis of one of these (**115**, Figure 10a) has yielded a biphenolate, **116**, characterized by an X-ray study.[14] The hydrolysis mechanism again is proposed[14] to proceed by an initial nucleophilic attack by water with the formation of a hexacoordinated state **q**. Successive stages then should result in cleavage of all five Si–O bonds and yield the hydrogen bonded biphenolate anion, **116**, Figure 10b.

B. Pentacoordinated Phosphorus[179]

As discussed in the Introduction and highlighted in the previous section, the reactivity of pentacoordinated phosphorus appears lower compared to related pentacoordinated silicon compounds. For example, we mentioned the high reactivity of $R_2SiF_3^-$ complexes in hydrolysis.[172] The analogous isoelectronic R_2PF_3 compounds hydrolyze at a considerably slower rate.[181]

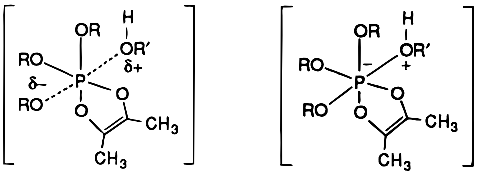
Similar to silicon chemistry, nucleophilic substitution reactions of pentacoordinated phosphorus have been the subject of a variety of studies mostly centered on oxyphosphoranes. Like silicon, rate laws and mechanistic considerations suggest the importance of hexacoordinate intermediates (or transition states) as controlling features. Thus, in the reaction of trimethoxyphospholene **117** with benzyl alcohol, which proceeds without ring opening, hexacoordinate activated states are invoked.[182]



^{31}P, –48.9 ppm

117

A possible transition state in a concerted displacement of methanol at phosphorus (**s**) or an intermediate (**t**) in a stepwise substitution of methanol are considered.

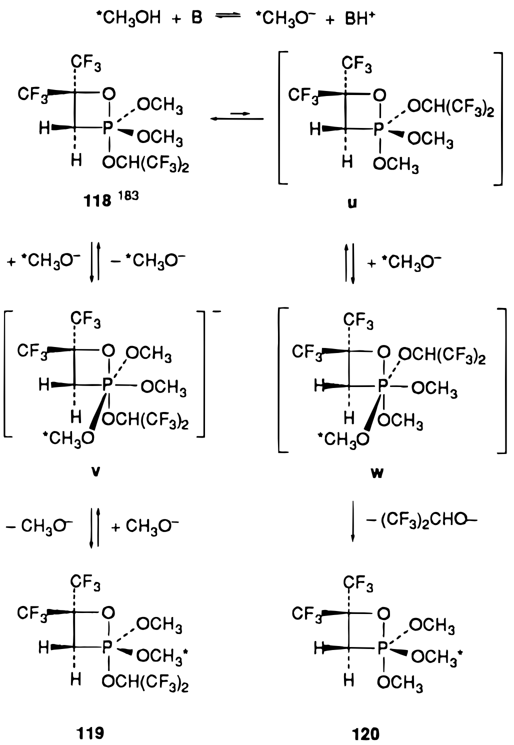


R = CH_3; R′ = $C_6H_5CH_2$

s **t**

In a more detailed base-catalyzed substitution reaction of cyclic oxaphosphetanes with alcohols at 25 °C, hexacoordinate activated states are consistent with the experimental findings.[183] The phosphetane **118**, which does not react with methanol (introduced as CD_3OD) or in the presence of acid, does so on addition of catalytic amounts of Et_3N. This results in the displacement of the hexafluoroisopropoxy group by the methoxy group to give a trimethoxyoxaphosphetane **120**. Both CH_3OD and $(CF_3)_2CHOD$ appear as the reaction proceeds along with the deuterated methoxy group of the product containing the $OCH(CF_3)_2$ group **119**. The increase in $(CF_3)_2$-CHOD is accompanied by an increase in the deuter-

Scheme 4[183]

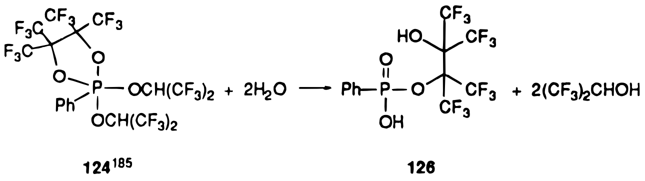


ated trimethoxyphosphetane **120**. These observations[183] are accounted for by the simplified mechanism outlined in Scheme 4 with the qualification that the rate of formation of **119** is faster or at least equal to the rate of pseudorotation of **118** to give **u** which then allows the formation of **120**.

In contrast to these alcohololysis reactions, hydrolysis reactions of cyclic oxyphosphoranes proceed with ring opening. Belskii et al.[184] studied the kinetics of hydrolysis of a variety of phosphoranes of the type **121** which gave (*o*-hydroxybenzyl)phosphonates as initial hydrolysis products, *e.g.*, **122**. The reactions are second order with respect to water in dioxane and DMFA but first order in ethanol. A mechanism is proposed where nucleophilic attack by a water molecule at phosphorus yields an octahedral activated state **x** while a second water molecule cooperatively enters into a proton transfer in the ring-opening process in **y** leading to **122** (Scheme 5).[184]

A similar study of the hydrolysis of pentaphenoxyphosphorane $P(OPh)_5$ (**123**), and the cyclic tetraoxyphosphorane **124** conducted in aqueous dioxane led Queen et al.[185] to propose a hexacoordinate intermediate in a mechanistic sequence leading to the products, $(PhO)_3P{=}O$, **125**, and **126**, respectively. Scheme 6 illustrates the overall reaction for **124**.

Scheme 6[185]



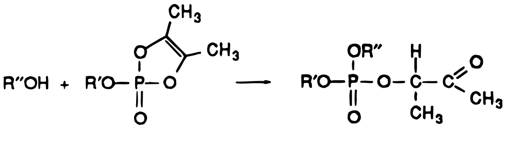
In reactions of chlorophosphoranes, *e.g.* **127**, with trimethylsilyl azide (Me_3SiN_3) or benzyltri-*n*-butylammonium azides, Skowronska and coworkers[186] formulated hexacoordinate complexes incorporating azide substituents (Scheme 7).

The earlier literature covers a number of additional studies of nucleophilic displacement reactions that led investigators to postulate the intermediacy of hexacoordinated phosphorus formulations. Like those already outlined, most of these studies also center on oxyphosphoranes and their derivatives.[72,187–189]

C. Comparison of Tetracoordinated Phosphorus and Silicon via Hexacoordinated States

While most of the mechanisms of nucleophilic displacement reactions of tetracoordinated phosphorus and tetracoordinated silicon have been interpreted in terms of the intermediacy of pentacoordinated activated states, there exist studies of tetracoordinated derivatives for both phosphorus and silicon where postulated hexacoordinated species have been invoked in mechanistic schemes. An example of each is described here.

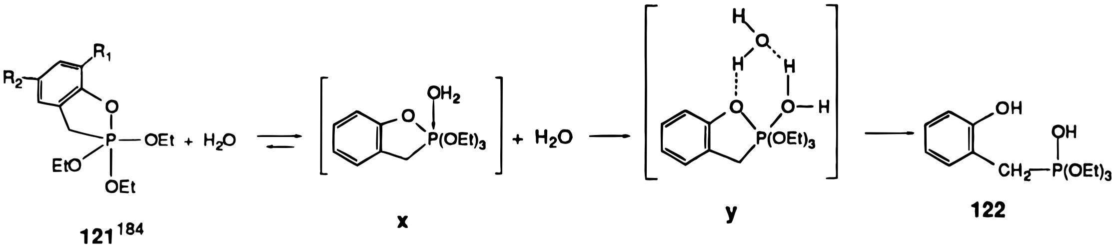
A mechanism of nucleophilic catalysis of the phosphorylation of alcohols by alkyl cyclic enediol phosphates (eq 2) in aprotic solvents has been advanced by Ramirez et al.[190] in terms of penta- and hexacoordinate phosphorus.



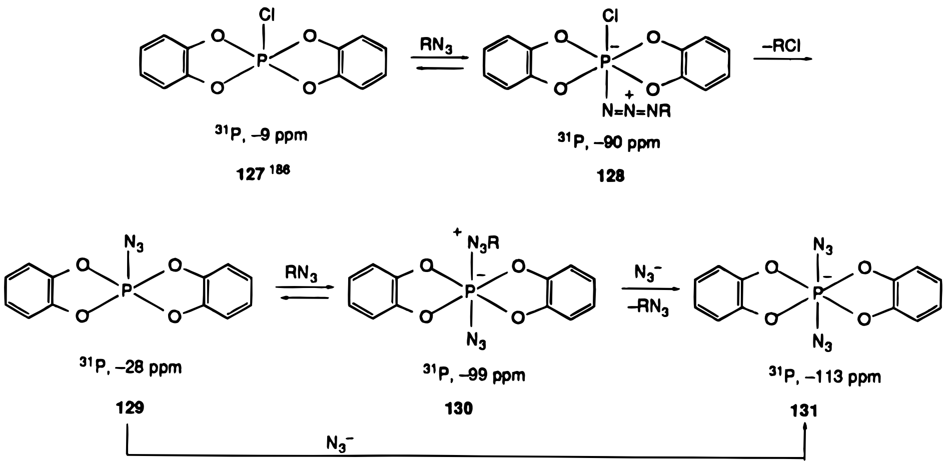
132 **133** (2)

Hydrolysis of the unsymmetrical triester **133** results in the unsymmetrical dialkyl phosphate, (R′O)(R″O)P(O)OH (**134**). With imidazole as a catalyst, **z** and **aa** are proposed to be formed, *i.e.*, **z** is formed initially which can add a second alcohol to give the hexacoordinate intermediate **aa** (Scheme 8).[190]

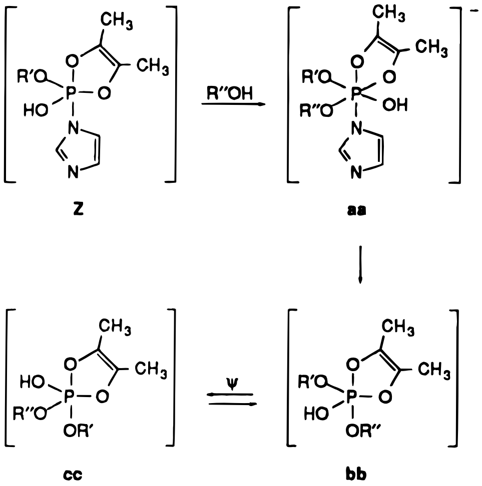
Scheme 5[184]



Scheme 7[186]



Scheme 8[190]



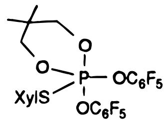
Decomposition of **aa** via loss of imidazole leads to ring opening from the resultant pentacoordinate states **bb** and **cc**. Alternatively, an alcohol can be displaced from the apical position of **cc** giving a product with ring retention. The formation of the phosphorane **z** is considered rate controlling. Addition of alcohol to produce the hexacoordinate intermediate **aa** is assumed to be relatively rapid. The catalysis is due to the greater nucleophilicity of imidazole compared to the alcohol. With other bases, it is found that Et_3N is a poorer catalyst than imidazole even though it is a stronger base. Steric requirements are implicated in the penta- and hexacoordinate intermediates. Use of quinuclidine, for example, with less of a steric effect than Et_3N acts as a better catalyst, comparable to imidazole.

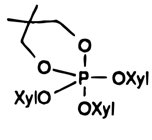
On the basis of this and related studies,[190−193] it is suggested[190] that the possible intervention of hexacoordinate species in mechanisms of biological phosphoryl group transfer,[194−201] particularly those that involve histidine and lysine residues[200−201] in catalytic activity, should be considered in future interpretations.

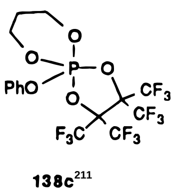
Corriu and co-workers[202−207] have studied silicon phosphorus analogies in nucleophilic displacement reactions. In a study of relative rates and the stereochemistry of product formation for alcoholysis of halogen-containing tetracoordinated dioxaphosphorinanes, *e.g.*, **135**, a mechanism involving initial formation of a fluorophosphate **136** is proposed[202] followed by reaction with additional fluoride to give a reactive pentacoordinated phosphoranoxide anion with a symmetrical structure **dd**, *i.e.*, with the two fluorine ligands in apical positions of a TBP. Reaction of this transient state with an alcohol yields the phosphate product **137** with release of a fluoride ion (Scheme 9).[202]

Presumably the displacement of fluoride by an alcohol in the last step would involve the intervention of a hexacoordinate formulation following the precedence for hexacoordination in nucleophilic activation proposed earlier by Ramirez and coworkers.[182,183,187,190−193] An example was discussed for the base-catalyzed alcoholysis of cyclic oxaphosphetanes, **118**, in Scheme 4.[183]

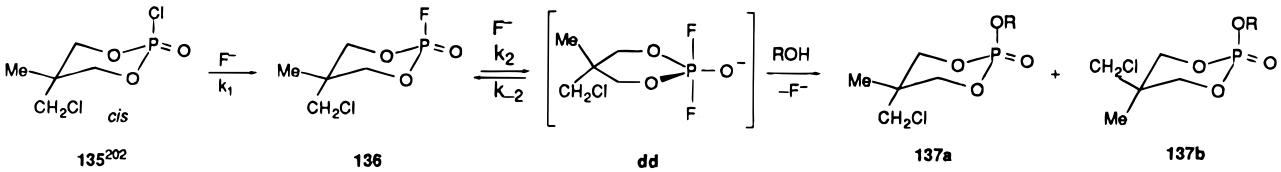
On the basis of current literature showing that the dioxaphosphorinane ring is only found in axial-equatorial positions of a TBP,[8,30,38−41,44,208−211] usually in a boat or twist-boat conformation, in the presence of unconstrained electronegative ligands, *e.g.*, **138a**,[34] **138b**,[30] and **138c**,[211] it appears that a better model for the proposed[202] pentacoordinated intermediate in Scheme 9 would be **ee** rather than **dd**. Pseudorotation of this type of geometry to **ff** is facile[6,9] and could yield two hexacoordinated activated states **gg** and **hh**


138a[34]

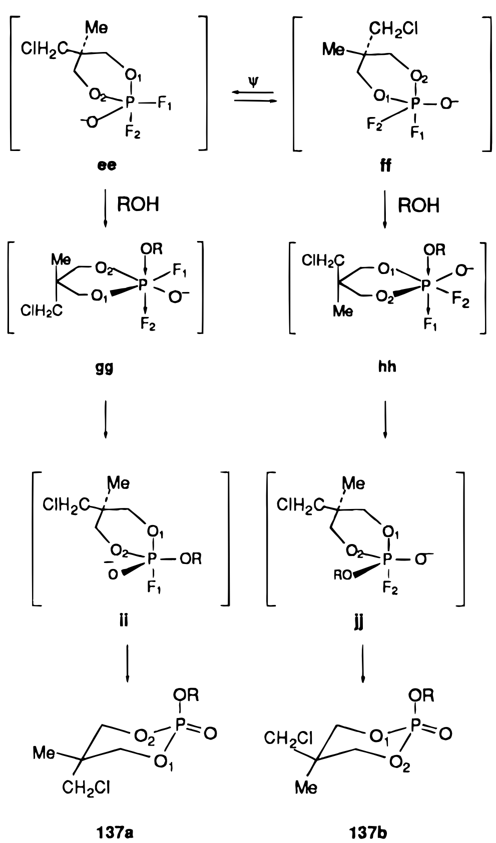

138b[30]


138c[211]

Scheme 9[202]



Scheme 10

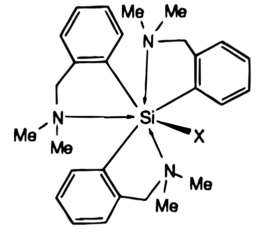


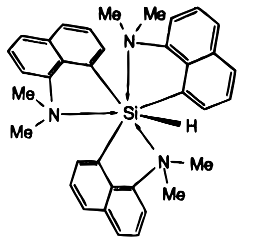
of similar energy whose decomposition to **ii** and **jj** would give the observed isomeric phosphates (Scheme 10). The proviso is that in forming the activated hexacoordinate states the entering alcohol does so to cause a departure of the opposite fluoride ion. This is similar to that proposed by Ramirez[182] in the reaction of dioxaphospholenes with alcohols.

D. Possible Heptacoordination at Silicon and Phosphorus

Although pentacoordinate silicon exhibits greater reactivity than corresponding pentacoordinate phosphorus compounds,[24,212] we have recently discovered pentaoxyphosphoranes which show sulfur-induced coordination and form isolatable hexacoordinated compounds[32,104–108] that undergo hydrolytic cleavage to yield phosphates.[108] With good leaving groups, as is present in **27** in Figure 11, a cyclic phosphate **139** is formed. With poorer departing groups, *e.g.*, OPh, an acyclic phosphate is formed.[108] In these processes, one might envision nucleophilic attack by water giving an initial seven-coordinated state which would activate P–O bond cleavage.

In this context, Auner and coworkers[213] and Corriu and coworkers[214] have suggested heptacoordination at silicon from X-ray structural studies of silanes, **140a**,[214] **140b**,[213] and **141**,[214] that have a "tricapped tetrahedral" structure as a result of intramolecular coordination by three nitrogen atoms at Si–N distances ranging from 2.88 to 3.49 Å. Further in the case of a tricoordinated phosphane, **142** Corriu and co-workers observe[215] evidence of pseudo heptacoordination at phosphorus composed of the same ligand system as in **141** with the seventh position occupied by a lone electron pair. The pyramidal structure is retained at phosphorus, and P–N distances, 2.805, 2.844, and 2.853 Å, are shorter than the van der Waals' sum (3.4 Å).



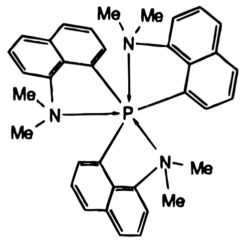


Si---N(ave) Å

3.267(5) **140a** (X = F)[214]

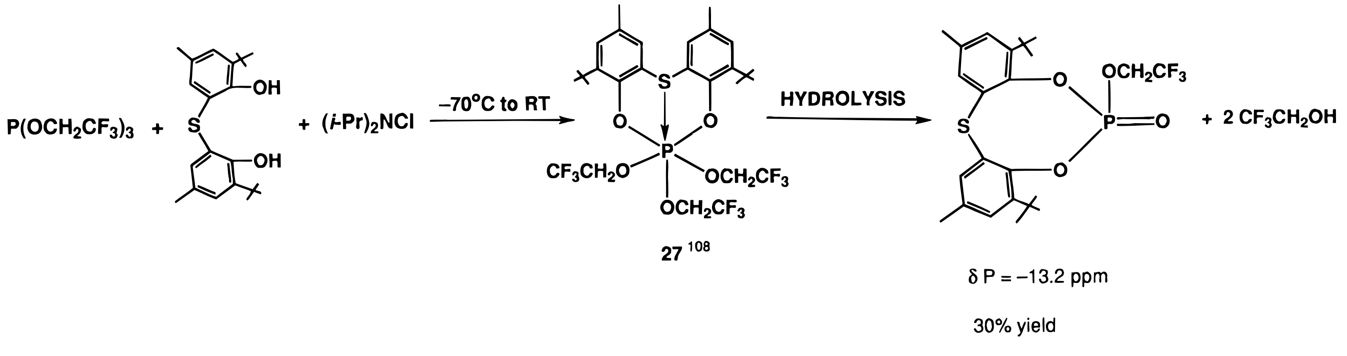
3.012(6) **140b** (X = H)[213]

2.895(7) **141**[214]



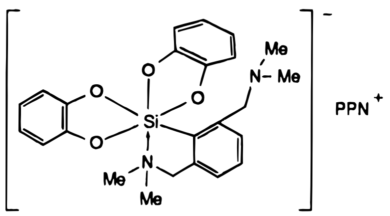
142[215]

When the ligands are sufficiently electronegative, as in the recently reported X-ray structure of **143**[216] which closely resembles **42**[126] of Figure 4, the Si–N distance approaches the covalent sum of 1.93Å.[53] The interesting feature of **143** is the possibility of heptacoordination due to the presence of the additional Me_2N group. ^1H, ^{19}F, and ^{29}Si VT NMR measurements are consistent with dynamic coordination in



139

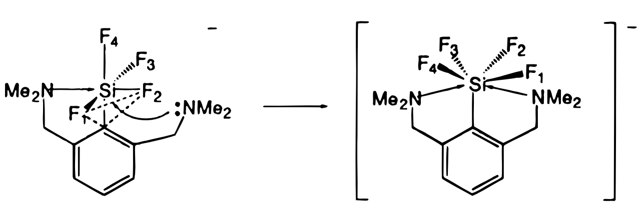
Figure 11. Hydrolysis via **27** leading to cleavage of two acyclic groups.



Si–N, Å 2.173(6) ^{29}Si, –129.8 ppm

143[216]

which the NMe_2 groups displace each other by way of a heptacoordinate transition state.[216] Similar NMR behavior is seen in the analogous anionic tetrafluorosilicate **144** which is postulated[216] to pass through a symmetrical heptacoordinate activated state **kk** (eq 3) to account for the equivalence of all



144 **kk**

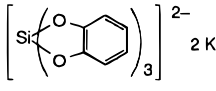
(3)

four fluorine atoms at 273 K compared to the observance of three signals in the ^{19}F NMR spectrum at 193 K. The latter pattern corresponds to an X_2-YZ system. A $\Delta G^{\ddagger}_{183\mathrm{K}}$ of activation from the ^{1}H spectrum of the *N*-methyl signals gave 9.2 kcal/mol for the exchange. This compares with $\Delta G^{\ddagger}_{203\mathrm{K}}$ of 11.1 kcal/mol from coalescence of the *N*-methyl signals and 10.1 kcal/mol from coalescence of the CH_2N signals for the bis-catecholate **143**. For both of these anionic silicates, ^{29}Si–^{19}F coupling is retained throughout the temperature range studied.

Although consistent with a heptacoordinate intermediate (or transition state), the results do not rule out Si–N bond cleavage with accompanying pseudorotation via a five-coordinate activated state for **144** and Si–N coordination to the initial noncoordinating NMe_2 group. It is noted that the structurally characterized silicon compounds that exhibit some measure of heptacoordination, *i.e.*, **140** and **141**,[213,214] retain the main silane tetrahedral geometry. The average deviation of the six angles around the silane framework of **140b**[213] from the tetrahedral angle of 109.5° is 2.3 ± 1.0°. This compares with 2.0 ± 1.0° for the same quantity obtained from the bond angles of the related tetracoordinate molecule, Ph_3SiH.[217] For **141**[214] ($R_w = 0.062$), which did not refine as well as **140b** ($R_w = 0.046$), the angle deviation is 4.0 ± 2.3° while for the fluoride derivative **140a**,[214] it is 1.9 ± 1.6° ($R_w = 0.045$). It might be expected that allowing two NMe_2 groups to enter the coordination sphere of silicon in forming the exchange intermediate **kk** would retain a trigonal bipyramid for the main framework at silicon rather than the pictured square pyramid.

A pseudoheptacoordinate structure has been found for a tris(dithiacarbamato) complex of phosphorus(III), $P[S_2CNMe_2]_3$ (**145**).[218] Six sulfur atoms are attached to phosphorus with three short (2.18–2.20Å) and three long (2.87–3.02 Å) P–S distances along with a phosphorus atom lone pair which gives a geometry described as a distorted capped trigonal antiprism. The S–P–S angles involving the short P–S bonds are near pyramidal, in the range 89.3–91.4°, and those involving the long P–S distances, in the range of 106.1–112.2°. Thus, the structure does not deviate appreciably from the pyramidal PS_3 unit relative to the short P–S linkages.

Concerning application of heptacoordination in mechanistic studies centering on reaction rates of hexacoordinated silicates with nucleophiles, the principal work in this area was performed by Corriu and coworkers[219a] who found that reactivity of silicates toward Grignard reagents decreased in the order **146** > **147** >> **45**. Since increased reactivity is associated with an increase in the number of electronegative Si–O bonds in this series, it is suggested[219a] that the accompanying enhancement in the electrophilicity of the silicon atom implies a heptacoordinate silicon intermediate (or transition state).



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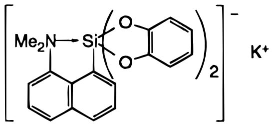
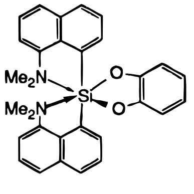
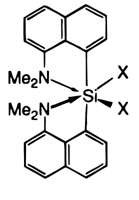


147

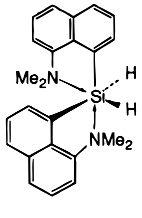


45

As an example of the reactivity of neutral hexacoordinate silicon that shows the possibility of nucleophilic substitution via heptacoordinated intermediates (or transition states), Corriu and coworkers[219b] have found that **148**–**150** react differently.[219b] Silane **148** is inert to nucleophilic reagents of the type, $LiAlH_4$, RM, ROH, and RONa, in contrast to the high reactivity shown by pentafluorosilicates. Silane **150** like **148** is inert toward similar strong nucleophiles, RLi and RMgX, whereas RLi reagents are able to substitute Si–H bonds in tetra- and pentacoordinate silicon compounds. Although silane **149** is very similar to **148**, the Si–Cl bond is easily displaced by $LiAlH_4$, MeONa, MeMgX, and MeLi in high yields. The ready cleavage of the more polarizable Si–Cl bonds compared to Si–F bonds is offered as an explanation. The lack of reactivity of **148** and **150** is taken as a demonstration that silicon is hexacoordinated in solution since any equilibrium with



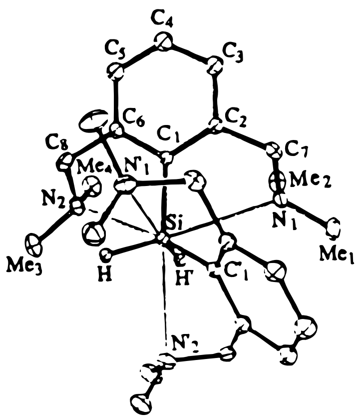
148, X = F
149, X = Cl



150

pentacoordinated silicon by rupture of Si—N bonds should lead to the higher reactivity associated with the pentacoordinated state.

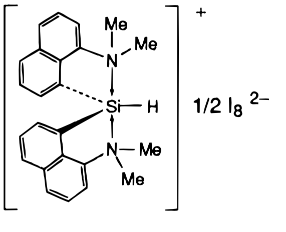
In consideration of reactivity of possibly higher coordinate silicon, Corriu and coworkers reported an X-ray structure of **151**[219c] that maintained a basic tetrahedral geometry for the silane unit with a NMe_2 group entering each of the four tetrahedral faces. A C_2 axis resulted in the presence of two Si—N distances, 2.895(5) and 3.117(6) Å, in the range found for the tricapped tetrahedral silanes, **140** and **141**.

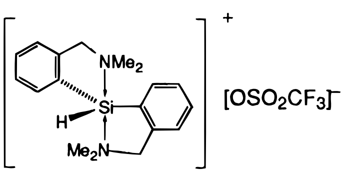


151 [219c]

Enhanced reactivity was exhibited by this hypercoordinated silane with HX (X = Cl, Br) with the loss of H_2 in forming a dication silicon compound. This reaction does not take place with Ph_2SiH_2. NMR, IR, and conductance data are in accord with a hexacoordinated structure for the dication having four Si—N interactions. Similarly, reaction of **151** with Ph_3C^+ BF_4^- resulted in the loss of one hydrogen atom and the formation of a monocation silicon product, indicated to be pentacoordinate via the presence of two Si—N interactions.

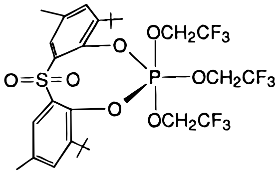
In this connection, the X-ray structures of related silyl cationic compounds have been reported that exhibit TBP structures with Si—N bond lengths in the range 2.05—2.08Å, *i.e.*, quite close to the sum of the covalent radii of 1.93 Å.



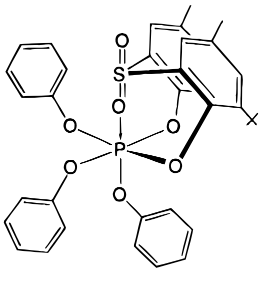


The pseudo-heptacoordinated structures defined so far, **140** and **141**, serve as poor models for such a mechanistic intermediate in that their long Si—N interactions are not capable of supplying sufficient energy[220] to appreciably displace the framework silane structure from its tetrahedral geometry. A more suitable model possibly could be found with the use of electronegative ligands in place of Si—C bonds, *e.g.* by examining SiF_6^{2-}, SiF_4, or $[Si\ cat_3]^{2-}$ for increased coordination with donor molecules. Octahedral structures of $SiCl_4{\cdot}2PMe_3$ (**35**),[113] $SiF_4{\cdot}2Py$ (**36**),[114] and $SiF_4{\cdot}2NMe_3$ (**37**)[115,116] have been reported but other donor molecules could provide additional coordination.

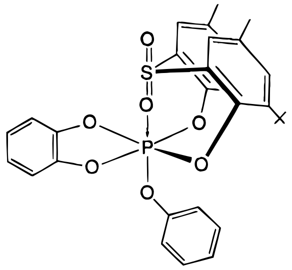
In phosphorus chemistry, we have recently provided the first study of enhanced reactivity of hexacoordinated phosphorus relative to pentacoordinated phosphorus.[221] The study centered on the sulfone-containing cyclic pentaoxyphosphorus compounds **152**—**154**.



152



153



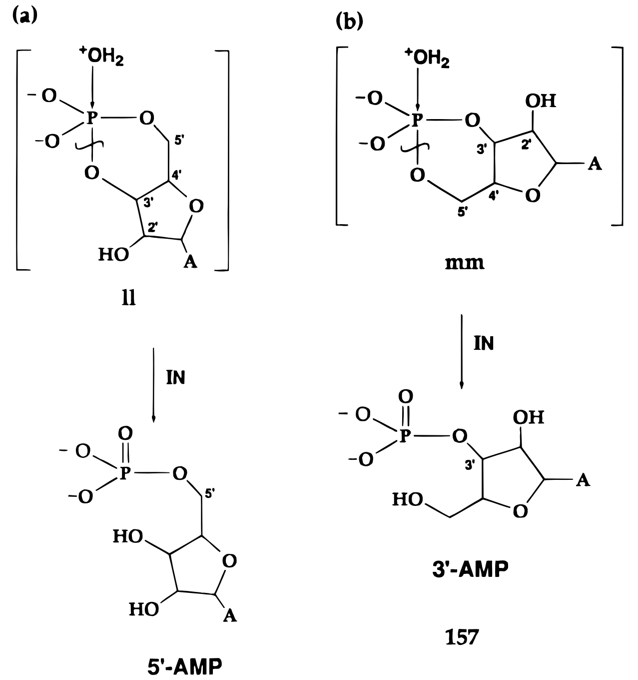
154

X-ray studies reveal that **152** has a trigonal bipyramidal geometry with the diequatorially placed ring in an *anti* conformation, whereas **153** is octahedral due to P—O coordination from the sulfone group. Here the ring is in a *syn* conformation. Phosphorane **152** does not react with catechol in boiling toluene, while **153** reacts readily to give the bicyclic phosphorane **154**. The X-ray structure of the latter phosphorane, like **153**, is an octahedron exhibiting P—O coordination supplied by one of the sulfone oxygen atoms. Thus, one observes increased reactivity of hexacoordinated phosphorus compared to pentacoordinated phosphorus in this series of oxyphosphoranes. Further, the rate of reaction of **153** strongly increases with an increase in catechol concentration or with the use of a stronger nucleophile, 4-nitrocatechol. The demonstrated importance of the attacking nucleophile implies an associative reaction and suggests the appearance of a heptacoordinate activated state along the reaction coordinate.

IV. Application to Enzyme Systems

A. Proposed Pentacoordinated Activated States in cAMP

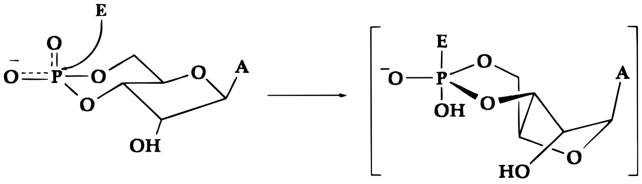
Proposals have appeared in the literature implicating pentacoordinated phosphorus as an important state in the enzymatic hydrolysis of cAMP (**155**) with phosphodiesterases[8,44,45,222—226] and in the activation of protein kinases.[8,224—227] In the former system, a ring-opening reaction ensues with the formation of 5′-AMP (**156**)[222b,c,228—230] while in the latter, activation of protein kinases by cAMP occurs without ring opening. As a consequence, the six-membered ring, which is *trans*-fused to the ribose unit, is proposed in one mechanism[24a,44,226] to be situated in axial—equatorial (a—e) sites of a trigonal bipyramid (TBP) in the case of phosphodiesterase action (**ll** of Figure



157

156

Figure 12. (a) Enzymatic hydrolysis of cAMP. Formation of 5′-AMP with inversion favors in-line attack opposite the 3′-oxygen atom with phosphodiesterases.[231] (b) Nonenzymatic hydrolysis of c-AMP. Formation of 3′-AMP with inversion of configuration favors in-line attack of H_2O opposite the 5′-oxygen atom.[223]



155 **nn**

Figure 13. Proposed intermediate (**nn**) in the activation of protein kinases by c-AMP (**155**).[232]

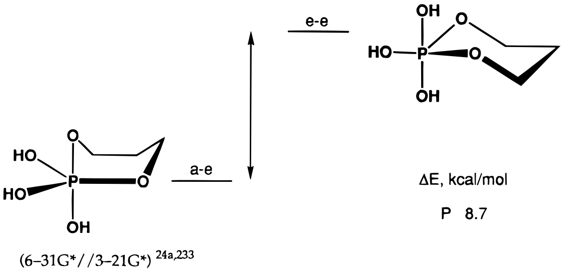
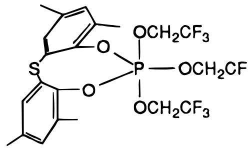


Figure 14. *Ab initio* calculation. Six-membered saturated ring, 6-31G*//3-21G* basis set.[24a,233] The (a−e) ring is in a boat form and the (e−e) ring is a chair.

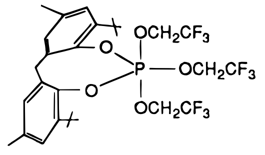
12) and in diequatorial (e−e) sites of a TBP in the case of activation of protein kinases (**nn** of Figure 13).[224−227]

We have carried out *ab initio* calculations on the energy difference between these two ring arrangements[24a,233] and find that the TBP with the (e−e) ring arrangement (chair form) is higher in energy by 8.7 kcal/mol than the (a−e) ring (boat form) for the system at the 6-31G*//3-21G* level shown in Figure 14. To make the calculations more realistic by replacing the equatorial OH by the monoanion O^-, the energy difference at the 6−31+G*//3−21G* level increases to 10.8 kcal/mol.[233] Attachment of a *trans* annelated ribose component to the six-membered ring in the same conformation as in Figure 14 results in a further increase at this same level to 11.9 kcal/mol (Figure 15).[233] However, charge dissipation at the enzyme active site may operate to lower the difference somewhat. Even so, proposal of an intermediate with a (e−e) ring orientation at the active site of a protein kinase-cAMP system based either on these calculations or on experimental work is not favored.[233] Similarly, other mechanisms that have been proposed[222b,c,230b] for the enzymatic hydrolysis of cAMP with phosphodiesterases which invoke diequatorial ring occupancy in TBP geometries of activated states are energetically unfavorable processes. In all of these mechanisms, pseudorotation is required to cause the ring-opening process to take place by P−O bond cleavage at the preferred axial site. Pseudorotation is a process that has not been demonstrated in an enzyme system[234] where nucleophilic substitution occurs at phosphorus. In our theoretical treatment of RNase action on uridylyl-(3′−5′)-adenosine (UpA) using molecular mechanics,[235] calculations on a number of transition state structures connected with pseudorotational processes showed that they were of high energy relative to that for a direct in-line displacement associated with the cyclization step of RNase on the UpA substrate.

Structural work on pentaoxyphosphoranes that might serve as models for mechanistic intermediates in cAMP action so far has invariably shown six-membered rings positioned at (a−e) sites in TBP geometries with the ring in a boat or twist-boat conformation.[8,30,38−41,44,208−211] Extension of the X-ray studies on pentaoxyphosphoranes to larger ring systems[8,31−33,39,40,43,104−108,208,209] revealed an (e−e) ring arrangement only when the ring size reached eight-membered[236] **29**[32] and **158**.[31]

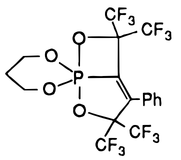


29[32]



158[31]

Bentrude and coworkers[237] provided an example of a six-membered ring located in (e−e) positions of a TBP for a polycyclic tetraoxyphosphorane having a constrained ring system, **160**.



160

Both the experimental observations and theoretical work are in accord in assigning the diequatorial orientation of a saturated six-membered ring in a trigonal-bipyramidal pentaoxyphosphorane a relatively unfavorable energy relative to the axial−equatorial ring orientation. Activation energies from VT NMR studies of oxyphosphoranes with six-membered rings that undergo pseudorotation from

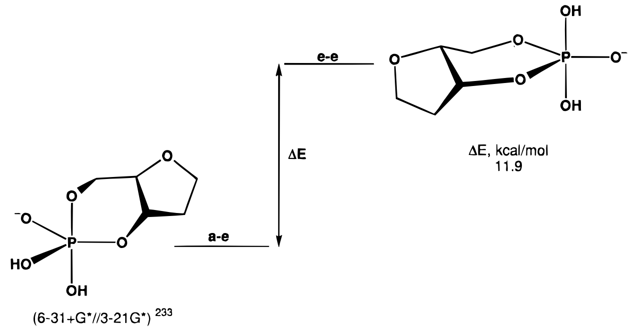
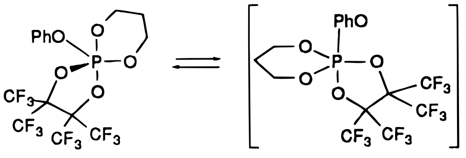
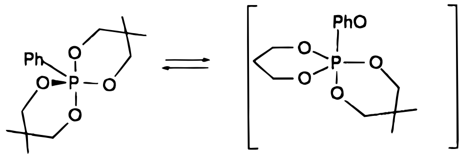


Figure 15. *Ab initio* calculation. Inclusion of *trans*-fused ribose ring, 6-31+G*//3-21G* basis set.[233] The (a−e) ring is in a boat form and the (e−e) ring is a chair.

the ground state (a−e) ring orientation to a (e−e) barrier state ring arrangement have been obtained for **161**[211] and **162**.[238] These values are 6.1 and 11.7 kcal/mol, respectively, which are in accord with results of *ab initio* calculations[24a,233] on related systems as shown in Figures 14 and 15. Of course, it should be recalled that the exchange process involves intervening square pyramids (SP) which more accurately represent the transition states. However, the depicted (e−e) ring locations in TBP geometries are not too different in energy from the SP representations as model calculations have shown.[6,167]


161[211] **oo**


162[238] **pp**

In another approach using an empirical model[6] for approximating energies of pentacoordinate intermediates and transition states, a value of 7 kcal/mol was assigned[167] for the ring strain energy associated with placement of a saturated six-membered ring in (e−e) locations of a TBP relative to an (a−e) orientation.

B. Possible Hexacoordination

The possibility also arises with cAMP−enzyme systems that phosphorus may not be pentacoordinated but intermediate between penta- and hexacoordinated.[104,105,239] Our recent work with P−S coordination[32,104−108] and earlier work in the literature with P−N coordination[48-52,57-59,61,63,64,67,69,103] described in section II.A has shown that hexacoordination at phosphorus is readily attainable. In the presence of an active-site environment containing nitrogen, oxygen (H_2O), or even sulfur amino acid residues, we might speculate[104,105] that a donor molecule may participate in bonding to some degree in forming an activated intermediate. In so doing, the proposed trigonal-bipyramidal intermediate[8,44,45,222−227] may undergo a distortion toward an octahedral structure. It is probable that this proposed additional coordination will not effect the stereochemical outcome due to the somewhat weak coordination supplied by the donor groups under discussion but rather produce a rate enhancement effect as a consequence of the general loosening of bonds associated with higher coordinate structures. However, this would be a proportionate effect depending on the degree of coordination and extent of structural distortion.

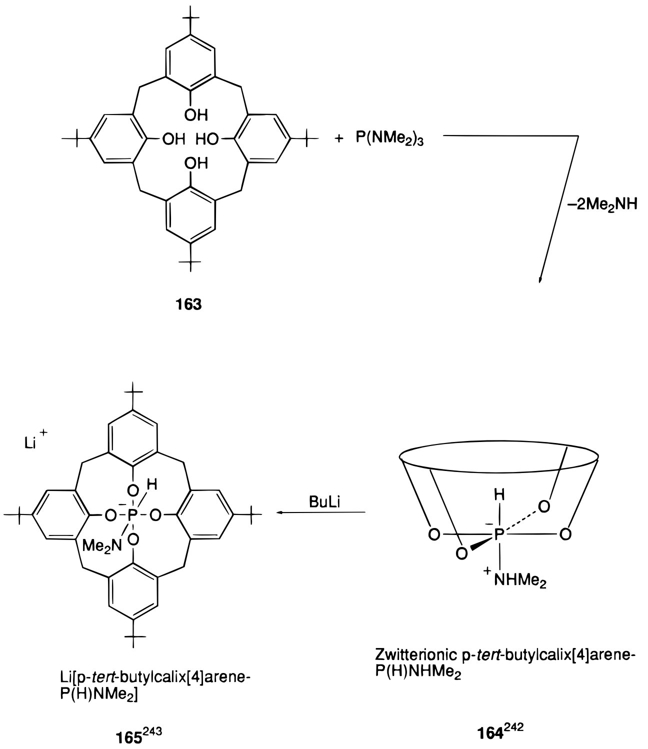


Figure 16. Reaction of *p*-*tert*-butylcalix[4]arene with $P(NMe_2)_3$.

It might be conjectured that such considerations should also apply to active sites of phosphoryl transfer enzymes, as advanced earlier by Ramirez and coworkers,[190] that have appropriate donor groups of sufficient basicity present to cause increased coordination toward hexacoordination. Previously, only pentacoordinated activated states have been proposed at active site environments involving phosphoryl transfer enzymes with the most common geometry proposed being that of a trigonal bipyramid.[1−3,7,240,241] It is realized that this is a speculative notion but on the basis of experimental results on donor induced formation of higher coordinate structures, it is one that deserves consideration and further exploration.

It is interesting in this context that with the use of a calixarene (**163**) Lattman and coworkers[242] entrapped phosphorus as a zwitterionic hexacoordinated species, *p*-*tert*-butylcalix[4]arene $P(H)NHMe_2$ (**164**), rather than the expected pentacoordinate state (Figure 16). An X-ray structural study of the corresponding lithium salt **165**[243] showed retention of hexacoordinated phosphorus. Here, the additional bond formed is via P−N coordination, similar to the examples[48−52] listed in Table 2. This compares with the cyclic pentaoxyphosphoranes in Table 3 which achieved hexacoordination by sulfur donor action.[32,104,105] These results suggest that promotion of phosphorus to the hexacoordinated state by additional donor action may be more common than previously thought. As noted in all of the examples cited, the principal requirement for the formation of hexacoordinated phosphorus is the presence of ligands whose collective electronegativity is high enough to render the phosphorus atom sufficiently electrophilic to be conducive to additional coordination.

V. Conclusion

A great deal of work on the enhanced reactivity of pentacoordinate silicon compounds has appeared in the last decade. However, elucidation of the associated mechanisms is as yet in the embryonic stage. The common assumption is that reactions occur via nucleophilic substitution proceeding by way of hexacoordinated states. Selected phosphorus reactions also appear to be catalyzed at the pentacoordinate stage. Recent work, particularly on donor-induced coordination yielding structural information on pentacoordinated and hexacoordinated silicon and phosphorus compounds, has provided an initial basis on which to judge mechanistic reaction schemes which is applicable to both nonenzymatic and enzymatic environments.

What appears to be most needed at this juncture are studies of related series of hexacoordinate phosphorus and silicon compounds with the aim of learning what are their dominant ligand exchange processes as well as to establish the geometry of structures that could serve as models for the formation and decomposition of hexacoordinate species in mechanistic considerations of nucleophilic substitution, *e.g.*, whether *cis* or *trans* positioning of ligands is more stable.

VI. Acknowledgments

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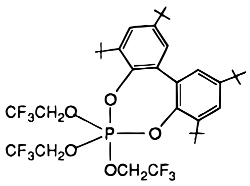

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