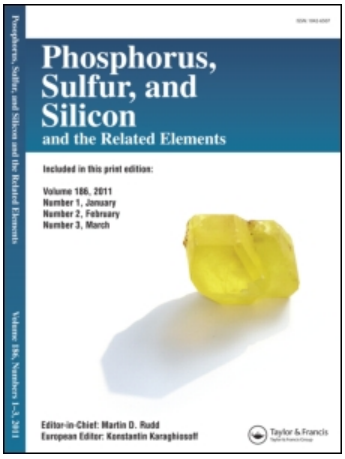

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Donor Action Leading to Higher Coordination in Cyclic Phosphorus Compounds

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DONOR ACTION LEADING TO HIGHER COORDINATION IN CYCLIC PHOSPHORUS COMPOUNDS

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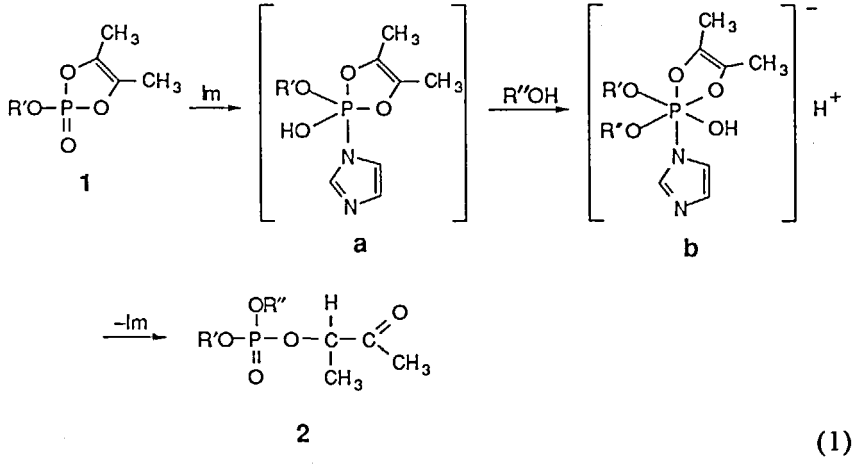
Sulfur, oxygen, and nitrogen ligands, prominent at enzyme active sites, are incorporated in flexible ring systems and exhibit donor action at phosphorus centers. X-ray studies reveal an increase in coordination geometry for phosphorus atoms in phosphites, phosphates, and oxyphosphoranes that model substrates and enzyme activated complexes. The increase in coordination results in trigonal bipyramids for the tri- and tetra-coordinated phosphorus compounds and octahedral geometries for the pentacoordinated ones. Using sulfur as an example, the degree of coordination as measured by the displacement toward the more highly coordinated geometry follows the order: oxyphosphoranes > phosphites > phosphates. With the use of an oxygen donor in place of sulfur in flexible ring systems, a lesser degree of coordination is indicated by the smaller displacement toward the more highly coordinated geometry. Nitrogen donor systems are also illustrated. The possible role of donor atom coordination from nearby residues at active site environments of phosphoryl transfer enzymes in enhancing substrate reaction rate is discussed.

Keywords cyclic oxyphosphoranes; phosphates; donor coordination.

INTRODUCTION

It has been recognized for some time now that hexacoordinate phosphorus may appear as an important intermediate in the course of

nucleophilic substitution reactions. Such intermediates or activated states have been proposed in connection with the reactivity of pentacoordinate phosphorus as well as that for tetracoordinate phosphorus.[1] The latter type of displacement mechanism has been referred to as a nucleophilic assisted nucleophilic attack. For example, in the phosphorylation of alcohols by alkyl cyclic enediol phosphates with imidazole as a catalyst in aprotic solvents, a mechanism in terms of both five- and six-coordinate phosphorus has been proposed by Ramirez et al,[2] eq 1.



(1)

What is needed at this stage is an exploration of the tendency of phosphorus to add nucleophiles or donor atoms that cause an increase in coordination geometry and to determine the requirements in terms of substituent effects and ligand constitution that stabilize hexacoordinate phosphorus. Recent reviews have summarized much of the information known about hypervalent phosphorus.[1,3,4] We have embarked on an extensive structural program to provide a quantitative description leading to the formation of higher coordinate geometries via donor action on tri-, tetra- and pentacoordinate phosphorus. In examining nucleophilic displacement reactions, it is necessary to know the relative ability of phosphorus to add a nucleophile in its various coordination states. Thus in eq 1 a knowledge of the strength of coordination by the imidazole catalyst in the pentacoordinate state a relative to that in the hexacoordinate state b would be important in ascertaining the driving force for the phosphorylation reaction.

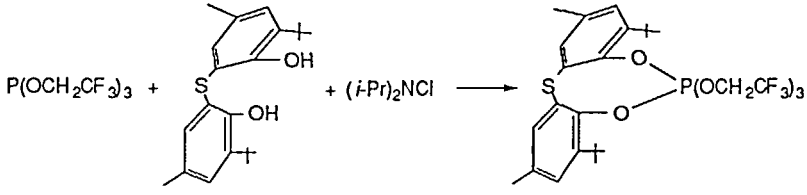
DONOR COORDINATION

Although there is some structural information available on nitrogen donor coordination at phosphorus,[1] less is known about oxygen coordination and none about sulfur donor action until our recent work.[4] Since these three donor atoms exist in residues at active sites of phosphoryl transfer enzymes, a study of their coordination may have implications for enzyme mechanisms as well as those for non enzymatic reactions.

The work reported here centers on sulfur and oxygen coordination at phosphorus.

Synthesis

The donor atom is incorporated in a flexible eight-membered cyclic system that allows for ring conformations which move the donor atom out toward the Van der Waals distance if donor coordination does not take place. This ring flexibility provides for a gradation in the degree of donor interaction which reflects the strength of the coordination and its effect on the local geometry at phosphorus. In the process, many new compounds were synthesized, usually by oxidative addition reactions of a donor containing diol to a phosphite in forming the hexacoordinate state or by a condensation reaction of a donor containing diol with a tri- or tetracoordinate phosphorus compound in forming pentacoordinate dervatives. These processes are illustrated in eqs 2 and 3, respectively.

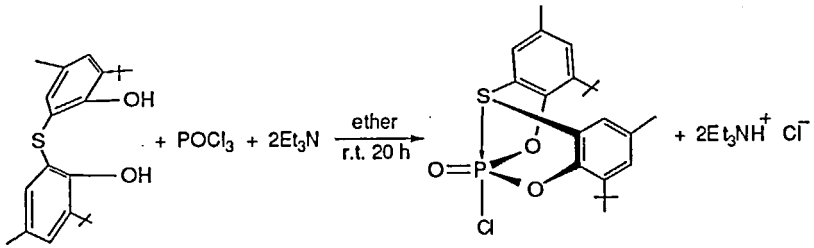


^{31}P ($CDCl_3$) -82.25 ppm, 76% yield

3

+ $(i\text{-Pr})_2NH_2^+$ Cl

(2)



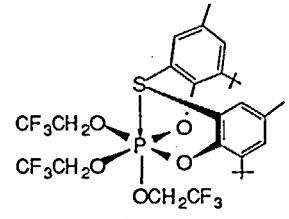
^{31}P, -9.49 ppm, 37% yield

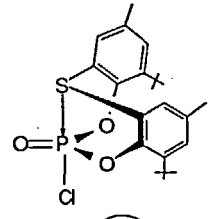
4

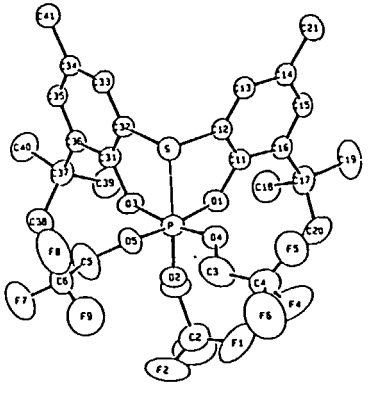
(3)

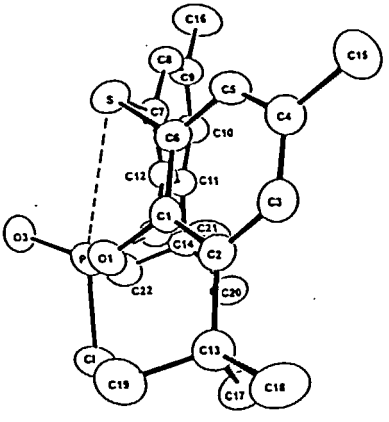
Sulfur Cordination. Structure

The X-ray structures of 3 and 4 are shown in the following plots.









P-S = 2.362(2)Å ΣP-S cov = 2.12Å P-S = 3.114(2)Å

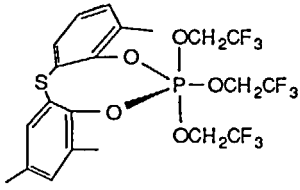
ΣP-S vdw = 3.65Å

3 **4**

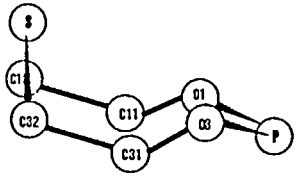
(hydrogen atoms have been omitted for clarity)

It is apparent that the degree of sulfur donor coordination for the pentaoxyphosphorane **3** is much greater than that for the phosphate **4** based on the comparison of the relative P-S distances. For **3** this distance approaches the sum of the covalent radii of 2.12Å[5] whereas for **4**, the P-S distance is closer to the van der Waals' sum of 3.65Å.[6] The octahedral geometry exhibited for **3** and the trigonal bipyramidal (TBP) geometry for **4** have the associated rings in *syn*-boat conformations. For the phosphate **4**, the sulfur atom occupies an axial site. When donor atom coordination does not take place, as in the pentaoxyphosphorane **5**, the ring usually assumes an *anti*-chair conformation as shown below. This ring conformation is compared with the *syn*-boat conformation found for the octahedral geometry associate with **6**. The latter has the same type of ring conformation as that for the structurally and compositionally related pentaoxyphosphorane **3**.

TBP, (e-e) ring

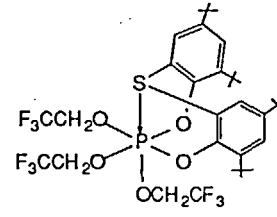


P-S = 3.504(3)Å
^{31}P, -77.3 ppm

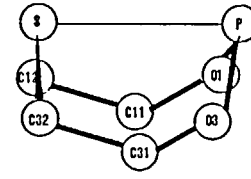


5

Octahedron



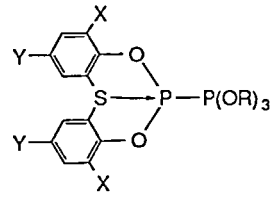
P-S = 2.504(3)Å
^{31}P, -82.4 ppm



6

A study of a series of monocyclic pentaoxyphosphoranes[1,7] has led to a variation in the phosphorus-sulfur donor distance that reflects ligand effects. This series is listed in Table 1. A method has been applied to the local bond parameters at phosphorus that yields the percent displacement toward an octahedral geometry. Over a 0.5Å variation in the P-S distance resulted from the X-ray studies on this series.

TABLE 1 Selected parameters for monocyclic pentaoxyphosphoranes with sulfur containing eight-membered rings.[a]

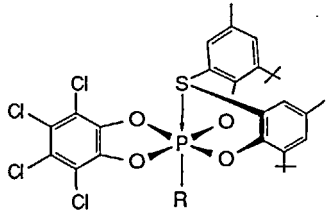


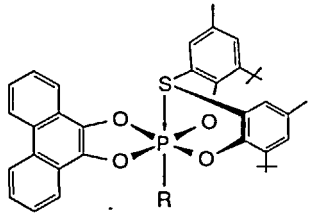
X	Y	R	% octa.[b]	P-S, Å
Me	Me	Ph	44.1	2.880(1)
t-Bu	Me	Ph	56.8	2.744(2)
t-Bu	*t*-Bu	Ph	60.8	2.640(2)
t-Bu	*t*-Bu	CH_2CF_3	64.5	2.504(3)
t-Bu	Me	CH_2CF_3	69.4	2.362(2)
t-Bu	Me	OC_6F_5	76.3	2.366(3)

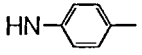
[a] All data are cited in reference 1 except the last entry which is reference 7.
[b] Percent displacement from an ideal square pyramid to an octahedron.

In a series of bicyclic tetraoxyphosphoranes, a similar variation in P-S distance resulted primarily by varying the ligand in the fifth position, Table 2.[8]

TABLE 2 Hexacoordination via sulfur donor action in nitrogen and chlorine bonded bicyclic tetraoxyphosphoranes[8]





7	8	9	10	11
R = Cl		NMe_2	R = Cl	$HNCH_2Ph$

Bond distances, Å

compd	P-S	% octa[a]
11 (R = N)	3.041(3)	23.8
9 (R = N)	2.731(2)	37.1
8 (R = N)	2.665(2)	47.4
10 (R = Cl)	2.581(2)	62.9
7 (R = Cl)	2.479(2)	70.8

[a] The degree of structural displacement from a square pyramid toward an octahedron.

The ^{31}P chemical shift vs the percent octahedral character is plotted in Figure 1.

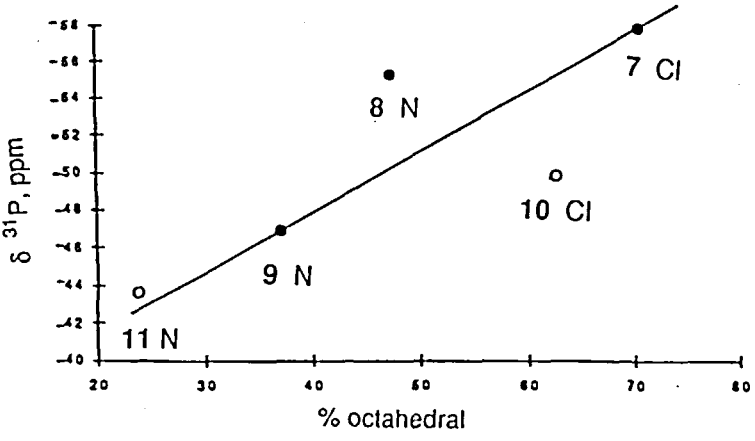


FIGURE 1 Variation of displacement toward an octahedron vs ^{31}P chemical shift.[8]

Increased ^{31}P NMR shielding accompanied the chloro derivatives **7** and **10** while increased π P-N back-bonding resulted in the least shielded members **9** and **11** containing the less electronegative nitrogen atom. These changes in ^{31}P chemical shift correlate with the extent of octahedral character where the more shielded phosphorus atom has the greater octahedral character.

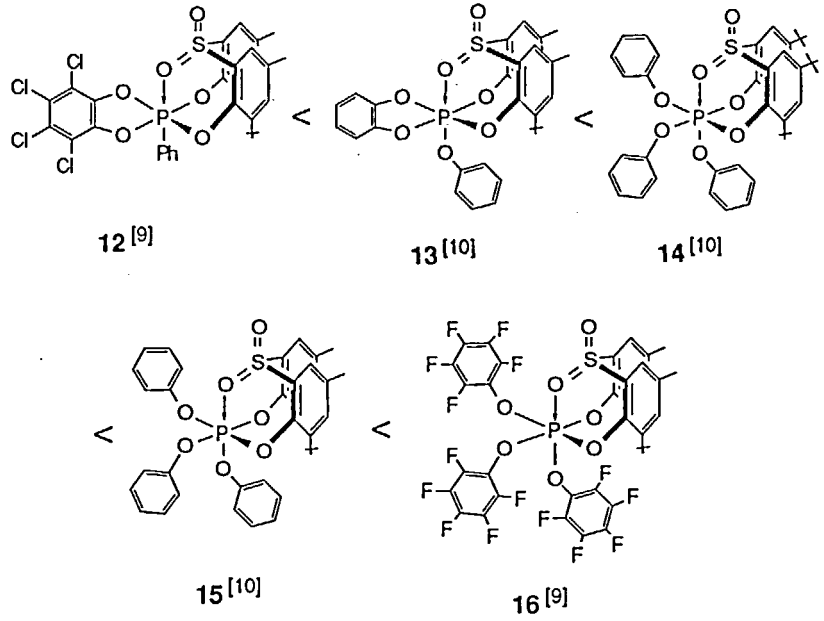
Oxygen Coordination. Structural

A series of oxyphosphoranes was recently synthesized using the oxygen atom of the sulfonyl group as the donor atom in place of sulfur as part of the same type of flexible cyclic system.[9,10] Synthesis followed a similar route as that with sulfur containing diols. Table 3 lists the oxyphosphoranes having oxygen coordination. The P-O distance decreases over 0.7Å toward the sum of the covalent radii of 1.83Å as the percent octahedral character increases to 82% for **16**. The latter oxyphosphorane has the shortest P-O distance in the series attributable to the presence of the three electronegative pentafluorophenyl ligands which increases the electrophilicity at phosphorus to the greatest degree.

TABLE 3 Increasing octahedral character for sulfonyl containing cyclic oxyphosphoranes as the electrophilicity of phosphorus increases from 12 to 16

compd [a]	P-O, Å	% octa [a]
12	2.646(5)	27.9
13	2.606(5)	32.4
14	2.546(9)	39.6
15	2.487(3)	44.5
16	1.936(7)	82.2

[a] Percent displacement from an ideal square pyramid toward an octahedron.



Comparison of Sulfur vs Oxygen Donor Action

By comparing pentaoxyphosphoranes with similar compositions, other than the presence of the donor atom, it is found that sulfur is a stronger donor atom than the oxygen atom of the sulfonyl group.[9] Figure 2 shows this comparison where the sulfur containing systems 17, 3, and 6

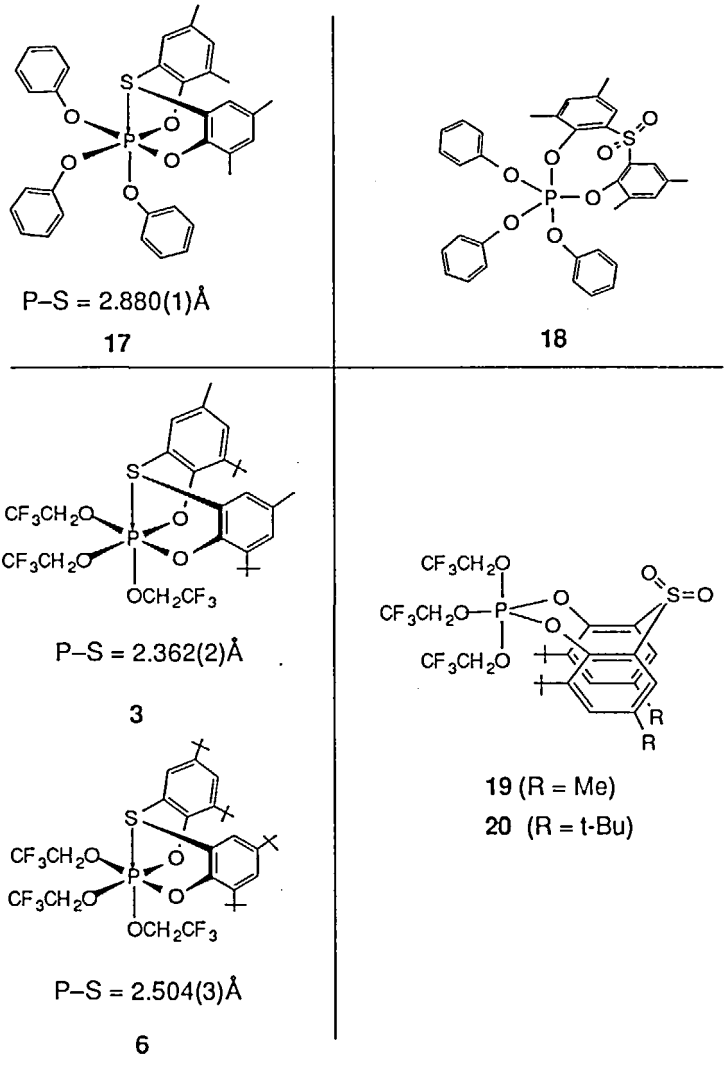


FIGURE 2 With similar ligands sulfur donors provide hexacoordination, whereas pentacoordination is retained for pentaoxyphosphoranes with sulfone groups.[9]

are hexacoordinate while the analogous sulfonyl systems **18-20** are TBP. This may provide a rationale for the existence of isomers for some of the sulfonyl systems, *e.g.*, **19** and **20**, whereas none are known for the sulfur systems.[10] Presumably the other isomer is the octahedral

form for **19** and **20** where the energy difference between the two isomers is lower for the sulfonyl containing oxyphosphoranes relative to those for the sulfur systems.

Relative Donor Action vs Coordination Geometry

In comparison to oxyphosphoranes, sulfur coordination in phosphites and phosphates is implied to be weaker by the longer P-S distances observed in the X-ray study of a series of these derivatives.[7,11] Table 4 lists the values of P-S distances for phosphites and phosphates while Figure 3 shows the range of P-S distances observed for phosphates relative to phosphites. The weaker sulfur coordination expressed by phosphites relative to that for oxyphosphoranes is emphasized in a comparison of the similar ligated compounds **21** and **22** where the pentaoxyphosphorane **21** shows a much shorter P-S distance than that for the phosphite **22**.[7]

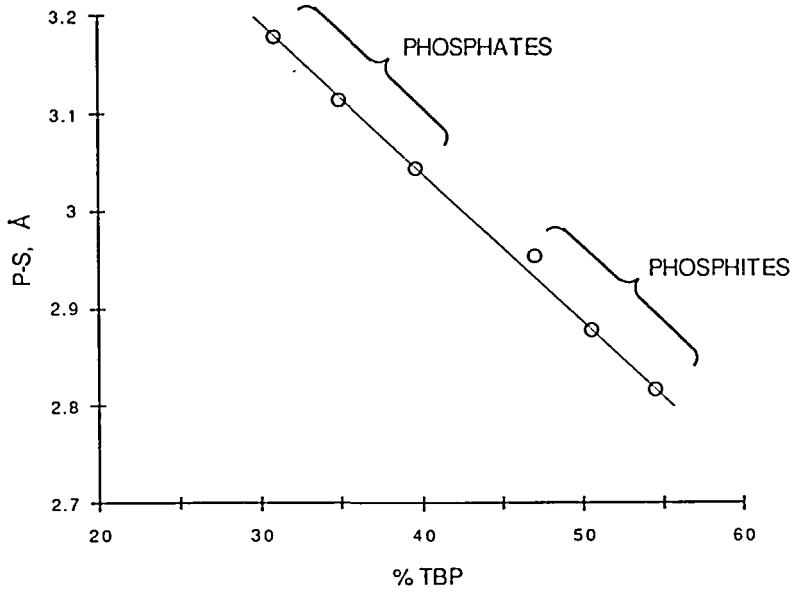
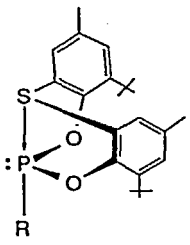
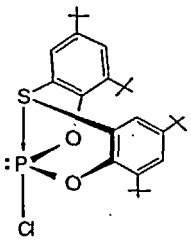
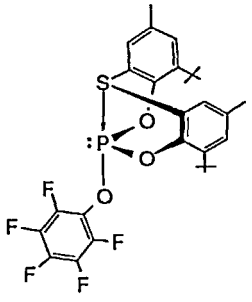


FIGURE 3 Variation of the P-S distance with percent TBP character for phosphates and phosphites.

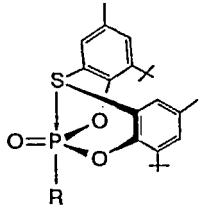
TABLE 4 Sulfur donor action in tri- and tetracoordinated phosphorus compounds [a]

Phosphite pseudo trigonal bipyramids

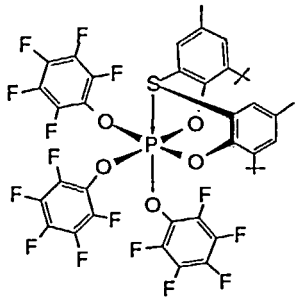
R	Cl	NMe_2		
P-S, Å	2.816(2)	2.952(9)	3.043(2)	2.876(2)
% TBP	54.5	47.1	39.7	50.6

Phosphate trigonal bipyramids



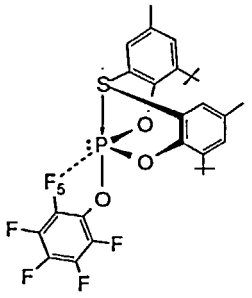
R	Cl	
P-S, Å	3.114(2)	3.177(2)
% TBP	35.0	30.9

[a] All are from reference 11 excet the phosphite with the pentafluorophenoxy ligand which is from reference 7.



21

P-S = 2.366(3)Å



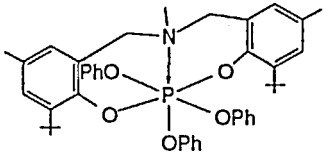
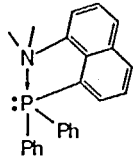
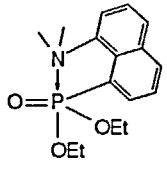
22

P-S = 2.876(2)Å

The same order of donor strength is indicated for coordination by nitrogen atoms from recent structural work displayed in Table 5.[12,13,14]

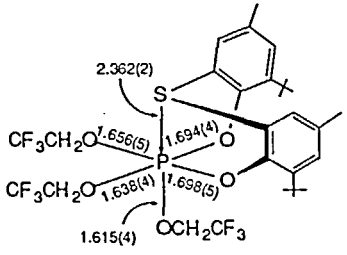
TABLE 5 Indicated strength of nitrogen donor coordination

Phosphorane > phosphite > phosphate

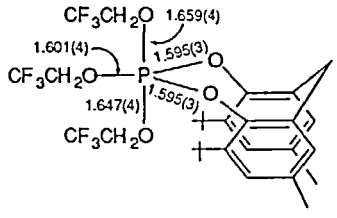
compound	P-N, Å
	2.143(3) [a]
	2.706(6) [b]
	2.869(3) [c]

[a] Reference 12. [b] Reference 13. [c] Reference 14.

Also, on comparison of bond parameters for the pentaoxyphosphorane 3 which is hexacoordinate due to P-S donor action with the related pentaoxyphosphorane 23 which is TBP and lacks donor action, the hexacoordinate molecule 3 has a longer average P-O distance by 0.041Å.[4] Thus, accompanying an increase to the hexacoordinated state, there is an implied loosening of P-O bonds.



3



23

	3	23
Ave. P-O, Å	1.660(4)	1.619(4)

Mechanistic Implication of Donor Action

The results of the above studies may have applicability in enzyme and nonenzyme reactions. For example, in the course of enzymatic hydrolysis of cAMP,[15] the formation of a hexacoordinate activated state due to possible donor action from a nearby residue at the active site may result in a rate enhancement effect[4] (path b in Figure 4) relative to the formation of a pentacoordinate activated state lacking donor atom coordination (path a in Figure 4). In path b, the donor coordination in the phosphate substrate would undergo an increase as the hexacoordinate state is reached. This tigher activated state binding relative to that for the substrate is expected to produce a rate acceleration.[4] Further work is necessary to establish whether this action occurs at cAMP. However, with the knowledge now available, it is a reasonable occurence that may have applicability in certain phosphoryl transfer enzyme systems as well as nucleophilic substitutions that proceed by nonenzymatic routes.

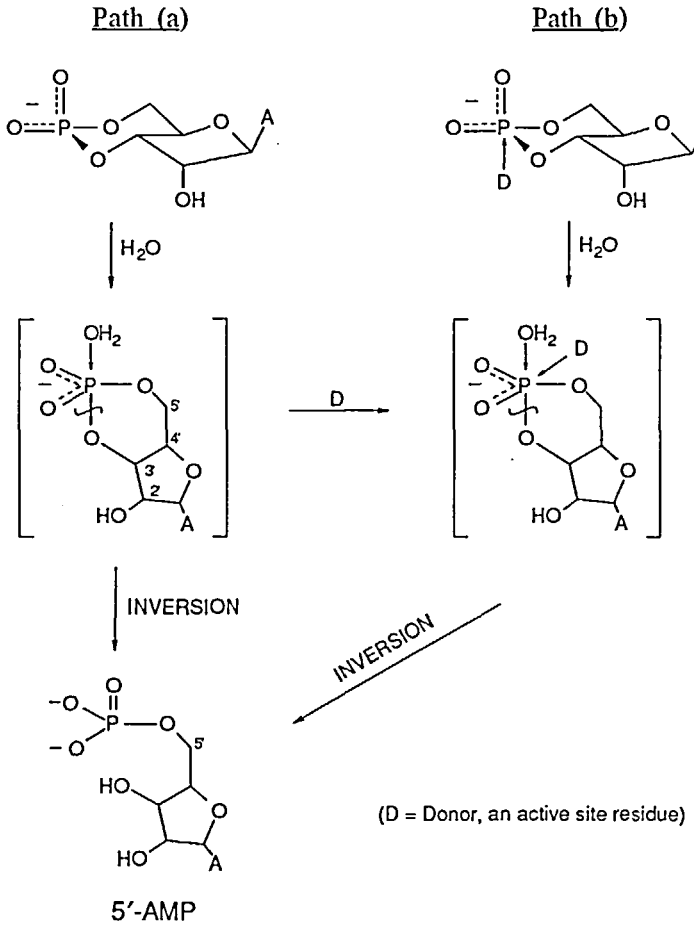


FIGURE 4 Enzymatic hydrolysis of cyclic adenosine monophosphate (cAMP). Path (a): nucleophilic attack by H_2O via pentacoordinate phosphorus[15]; Path (b): nucleophilic assisted nucleophilic attack by H_2O via hexacoordinate phosphorus.[1]

ACKNOWLEDGMENTS

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