Molecular Structures of Three-, Four-, and Five-Coordinate Phosphorus Compounds Containing Salicylate Ligands[1]

Natalya V. Timosheva, A. Chandrasekaran, Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003-4510

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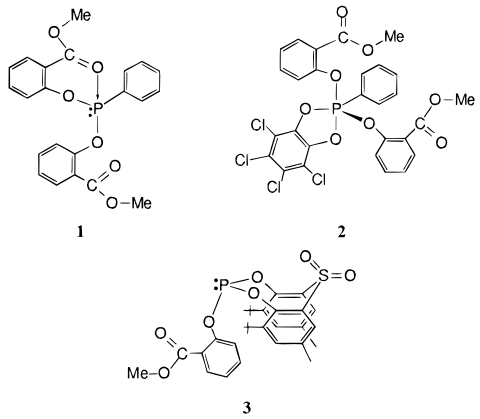
The new cyclic compound 2,2′-sulfurylbis(4-methyl-6-*tert*-butylphenyl) methyl 2-benzoate phosphite, $O_2S[(t\text{-}Bu)MeC_6H_4O]_2(OC_6H_4CO_2Me)P$ (**3**), containing a salicylate ligand was synthesized from 2,2′-sulfurylbis(4-methyl-6-*tert*-butylphenyl) chlorophosphite and methyl salicylate in the presence of triethylamine in ether solution. X-ray analyses of bis(methyl salicylate-*O*)phenylphosphine, $(OC_6H_4CO_2Me)_2PPh$ (**1**), and bis(methylsalicylato-*O*)phenyl-(tetrachlorophenylene-1,2-dioxy)phosphorane, $(O_2C_6Cl_4)(OC_6H_4CO_2Me)_2PPh$ (**2**), as well as that for **3** were obtained. The phosphane **1** has a pseudo trigonal bipyramidal (TBP) structure due to coordination of a carbonyl oxygen atom at an axial site. The cyclic phosphorane **2** and the phosphite **3** lack any coordination from salicylate ligands. This results in a TBP geometry and a pyramidal geometry respectively for **2** and **3**. Comparisons with X-ray structures for carboxylate-containing phosphorus compounds exhibiting oxygen coordination show the formation of four- and five-membered cyclic systems. Thus, **1** appears to be the first example of formation of a six-membered ring via carbonyl oxygen coordination. Reference is made to the tyrosyl-tRNA synthetase system where it is proposed that carbonyl oxygen atom coordination is a likely occurrence in the transition state on the basis of the analysis presented in this work.

Introduction

Recent work in our laboratory has involved the use of ring systems with sulfur,[1−12] oxygen,[12−14] and nitrogen[15] ligands as potential donor groups in causing an increase in coordination geometry for cyclic phosphorus compounds. This has resulted in the formation of a series of phosphates,[2] phosphites,[1,2] and oxyphosphoranes[3−12] for which P−S donor interaction was found to increase in the latter order. Use of an oxygen atom of a sulfonyl group[12−14] present as part of a similar cyclic system was found to result in decreased donor action compared to that for the corresponding sulfur-containing oxyphosphoranes.[14] Nitrogen donor action has been studied to a more limited extent, but available results support the latter conclusion with sulfur that phosphorus atom donor action increases with an increase in coordination geometry.[16] Some examples illustrating these effects are shown in Chart 1 with respect to oxygen and sulfur donation.

The ligands exhibiting donor action at phosphorus, i.e., sulfur, oxygen, and nitrogen, are the ones present at active sites of phosphoryl transfer enzymes[17,18] and in enzyme action involving cAMP.[17] To broaden the scope of the study of donor interaction, the present work focuses on the carbonyl oxygen atom as a potential donor. The systems chosen for study contain salicylate ligands attached to phosphorus in tri- and pentacoordinate phosphorus compounds, **1**−**3**. If donor action takes place via the carbonyl function, a six-membered cyclic system would result.



Recent literature on carbonyl donor action has demonstrated the formation of four-[19−21] and five-membered[22−24] ring systems.

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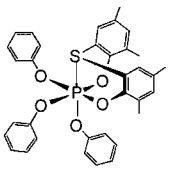
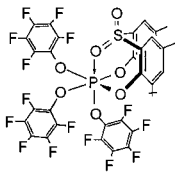
Chart 1

Pentaoxyphosphorus Octahedra



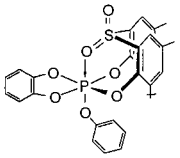
P-S = 2.880(1)Å; 44.1% octa

A [5]



P-O = 1.936(7)Å; 82.2% octa

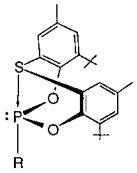
B [14]



Ave. P-OSO = 2.606(5)Å; 32.4% octa

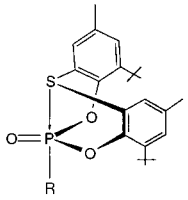
C [13]

Phosphite Pseudo Trigonal Bipyramids



R	Cl	NMe_2
P-S, Å	2.816(2)	2.952(9)
% TBP	54.5	47.1
	D [2]	E [2]

Phosphate Trigonal Bipyramids



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

With the inclusion of OR groups, a wider variety of donor−acceptor interactions is known giving similar size rings.[21,25−30] Some examples are shown in Chart 2, which includes three examples[31−33] with potential for donor−acceptor interactions but whose X-ray structures give excessively long P−O distances. Of the ones that form small-membered ring systems, they are by necessity rigid compared to that for the conformationally more flexible six-membered cyclic systems employed in the present study. As a consequence, if coordination occurs in the present study, it does so at the expense of the appearance of other conformations. For the smaller ring formations (shown in Chart 2) resulting from donor action, the rigidity of the ring components places the donor oxygen atom in near proximity to the phosphorus atom whether coordination takes place or not.

Herein are reported the synthesis of the cyclic phosphite **3**. Both the syntheses of **1** and **2** have been reported previously.[34] The X-ray structures of **1**−**3** are obtained and the results compared with existing X-ray data illustrating the ability of the carbonyl moiety to function as a donor group in increasing the coordination geometry of phosphorus. These results are then used to focus attention on the possible existence of such an interaction in the tyrosyl-tRNA synthetase mechanism.[35]

Experimental Section

Phosphorus trichloride, methyl salicylate, tetrachlorobenzoquinone (all from Aldrich) and dichlorophenylphosphine (Fluka) were used as supplied. Sulfurylbis[2-(4-methyl-6-*tert*-butylphenol)] (**4**) was synthesized according to a literature method.[36] Triethylamine was distilled over KOH pellets. Solvents were purified according to standard procedures.[37] Light petroleum (88−99 °C) is referred to as Skelly-C. All the reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. ^{31}P NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All ^{1}H NMR spectra were recorded in $CDCl_3$, and all the ^{31}P NMR spectra were recorded in CH_2Cl_2 in the sweep-off mode. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane or 85% H_3PO_4 at 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. $(OC_6H_4CO_2Me)_2PPh$ (1). Compound **1** was synthesized using a procedure modified from the literature.[34] Diethyl ether was used as a solvent instead of THF. The reaction time was 27 h. The amine hydrochloride was filtered, and the solution was left under a nitrogen flow. Large colorless crystals resulted that were suitable for an X-ray study: yield 74%; mp 86−88 °C (lit. mp 95.5−97.5 °C).[34]

$(O_2C_6Cl_4)(OC_6H_4CO_2Me)_2PPh$ (2). Compound **2** was synthesized by a procedure modified from the literature.[34] Compound **1** and tetrachlorobenzoquinone were mixed in diethyl ether. The solvent was removed after 24 h. The residue was recrystallized from a mixture of 1:1 dichloromethane and Skelly-C by slow evaporation under a nitrogen flow. Large colorless crystals resulted that were suitable for an X-ray study.

$O_2S[(t\text{-}Bu)MeC_6H_2O]_2(OC_6H_4CO_2Me)P$ (3). To a solution of PCl_3 (1.00 mL, 11.5 mmol) in diethyl ether (250 mL) that was stirred was added a solution of sulfuryl diol (4.47 g, 11.4 mmol) and NEt_3 (3.20 mL, 22.9 mmol) in diethyl ether (100 mL) over a period of 30 min. The reaction mixture was stirred for an additional 24 h. The amine hydrochloride was filtered off. Methyl salicylate (1.50 mL, 11.4 mmol) and NEt_3 (1.60 mL, 11.5 mmol) were added to the filtrate, and the mixture was stirred for 24 h. It was filtered and the solvent removed from the filtrate. The residue was washed with Skelly-F and dissolved in hot toluene. On cooling of the solution to 0 °C, crystals formed: yield 3.2 g (50%); mp 206−209 °C. ^{1}H NMR: 1.34 (s, 18 H, *t*-Bu),

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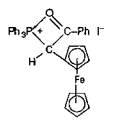
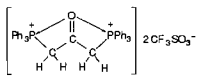
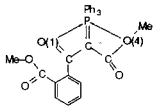
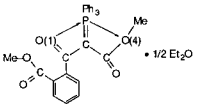
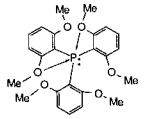
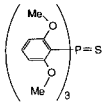
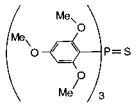
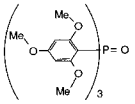
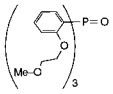
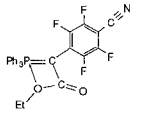
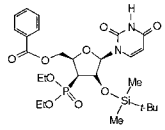
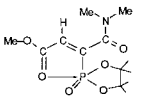
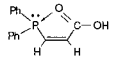
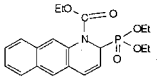
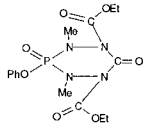
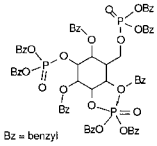
Chart 2

No.	Compound	P–O donor distance, Å
	Four-membered ring systems	
H [19]		3.184(6)
I [20]		2.959
J [21]		2.786 (P–O1) 3.063 (P–O4)
K [21]		2.733 (P–O1) 3.060 (P–O4)
L [25]		2.743 2.816
M [26]		2.805
N [26]		2.863
O [27]		2.784(4) [a] 2.823(4) [a]
P [28]		2.876(2)
Q [29]		2.811
R [31]		3.846
	Five-Membered Ring Systems	
S [22]		2.941(3)
T [23]		2.823(2)
U [24]		2.669(3)
V [32]		3.794
W [33]		3.767 3.859
X [30]		3.113

[a] Two molecules per unit cell.

2.36 (s, 6 H, aryl-*Me*), 3.89 (s, 3 H, OMe), 7.19 (t, 7.6 Hz, 1 H, aryl), 7.41 (d, 2.2 Hz, 2 H, aryl), 7.54 (t, 8 Hz, 1 H, aryl), 7.77 (br, 2 H, aryl), 7.88 (d, 7.6 Hz, 1 H, aryl), 8.04 (d, 7.3 Hz, 1 H, aryl). ^{31}P NMR: 123.2. Due to ready decomposition of the compound, satisfactory elemental analyses could not be obtained.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Details of the experimental procedures have been described previously.[38]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. The crystals of **1** and **2** were extremely sensitive to X-rays, and the data were collected using four crystals each. Data were collected using the $\theta-2\theta$ scan mode with $3° \le 2\theta_{\mathrm{MoK}\bar{\alpha}} \le 43°$ at 23 ± 2 °C. No correction was made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[39] and SHELXL-93 for refinement.[40] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded atoms. The final agreement factors are based on reflections with $I \ge 2\sigma_I$.

Compound **3** had a loosely bound toluene molecule which did not refine well. All the ring atoms were restrained to a regular hexagon, and the methyl group was refined under restraint in two positions with equal occupancy. The toluene molecule was refined isotropically, and the solvent hydrogen atoms were not included in the calculation. Crystallographic data are summarized in Table 1.

Results and Discussion

Selected bond parameters for **1**−**3** are given in Tables 2−4. Figures 1−3 display the respective atom labeling schemes in the ORTEX plots.[41] The thermal ellipsoids are shown at the 40% probability level with hydrogen atoms omitted for clarity.

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Table 1. Crystallographic Data for Compounds **1**−**3**

compd	**1**	**2**	**3**
formula	$C_{22}H_{19}O_6P$	$C_{28}H_{19}Cl_4O_8P$	$C_{30}H_{35}O_7PS{\cdot}C_7H_8$
fw	410.34	656.20	662.74
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst size, mm			0.25 × 0.25 × 1.00
a (Å)	10.221(3)	9.428(6)	12.124(12)
b (Å)	15.979(2)	10.536(4)	12.251(9)
c (Å)	13.239(3)	16.354(6)	13.218(5)
α (deg)	90	73.49(3)	104.16(5)
β (deg)	110.46(2)	79.68(4)	95.81(6)
γ (deg)	90	67.45(4)	106.42(7)
V (Å^3)	2025.8(8)	1434(1)	1795(2)
Z	4	2	2
D_{calc} (g/cm^3)	1.345	1.520	1.226
$\mu_{MoK\alpha}$ (cm^{-1})	1.72	5.18	1.81
tot. reflns	2329	3271	4073
reflns with $I > 2\sigma_I$	1983	2795	3087
R^a	0.0376	0.0304	0.1005
$R_w{}^b$	0.0969	0.0786	0.2797

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

P−O(1)	1.654(4)	P−O(3)	2.788(6)
P−O(2)	1.655(4)	P−O(4)	3.049(6)
P−C(13)	1.821(3)	O(4)−C(20)	1.188(4)
O(3)−C(19)	1.196(4)		
O(1)−P−O(2)	100.11(10)	O(3)−P−O(4)	122.11(7)
O(1)−P−C(13)	95.2(2)	C(1)−O(1)−P	121.0(2)
O(2)−P−C(13)	94.02(12)	C(7)−O(2)−P	118.5(2)
O(1)−P−O(3)	72.20(8)	C(19)−O(3)−P	103.5(2)
O(2)−P−O(3)	172.21(8)	C(20)−O(4)−P	99.1(2)
C(13)−P−O(3)	88.02(11)	C(14)−C(13)−P	122.2(2)
O(1)−P−O(4)	163.16(9)	C(18)−C(13)−P	119.3(2)
O(2)−P−O(4)	65.28(10)	O(6)−C(20)−C(8)	111.4(2)
C(13)−P−O(4)	94.2(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

P−O(2)	1.591(2)	P−O(7)	1.759(2)
P−O(1)	1.642(2)	P−C(13)	1.804(3)
P−O(8)	1.648(2)		
O(2)−P−O(1)	90.6(1)	C(7)−O(2)−P	128.6(2)
O(2)−P−O(8)	120.9(1)	C(19)−O(5)−C(21)	115.9(3)
O(1)−P−O(8)	88.88(9)	C(20)−O(6)−C(22)	117.7(3)
O(2)−P−O(7)	91.02(9)	C(23)−O(7)−P	112.2(2)
O(1)−P−O(7)	176.92(9)	C(28)−O(8)−P	115.1(2)
O(8)−P−O(7)	88.04(9)	C(14)−C(13)−P	120.4(2)
O(2)−P−C(13)	119.3(1)	C(18)−C(13)−P	120.3(2)
O(1)−P−C(13)	90.5(1)	O(7)−C(23)−C(28)	111.6(2)
O(8)−P−C(13)	119.8(1)	O(7)−C(23)−C(24)	128.0(2)
O(7)−P−C(13)	91.0(1)	C(23)−C(28)−O(8)	111.6(2)
C(1)−O(1)−P	126.8(2)	C(27)−C(28)−O(8)	125.3(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

P−O(3)	1.609(5)	P−O(2)	1.635(5)
P−O(1)	1.645(5)		
O(3)−P−O(2)	97.4(3)	C(1)−O(1)−P	119.2(4)
O(3)−P−O(1)	98.2(3)	C(12)−O(2)−P	119.6(4)
O(2)−P−O(1)	101.4(3)	C(13)−O(3)−P	132.5(5)

Synthesis. Reaction of PCl_3 with the sulfonyl-containing diol in ether solution was followed by the addition of methyl salicylate in situ (eq 1). This afforded **3** in 50% yield.

The ^{1}H NMR spectrum of **3** in $CDCl_3$ solution is consistent with its formulation. In addition to signals assigned to the methyl and *tert*-butyl substituents in the Experimental Section, proton signals for the six independent aromatic protons are present. The signals assigned to the four salicylate ring protons are the two ^3J triplets at 7.19 and 7.54 ppm and the two ^3J doublets at 7.88 and 8.04 ppm. The ^4J doublet at 7.41 ppm and the broad peak at 7.77 ppm are assigned to the equivalent pairs of protons, one pair attached to C(3) and C(10) and the

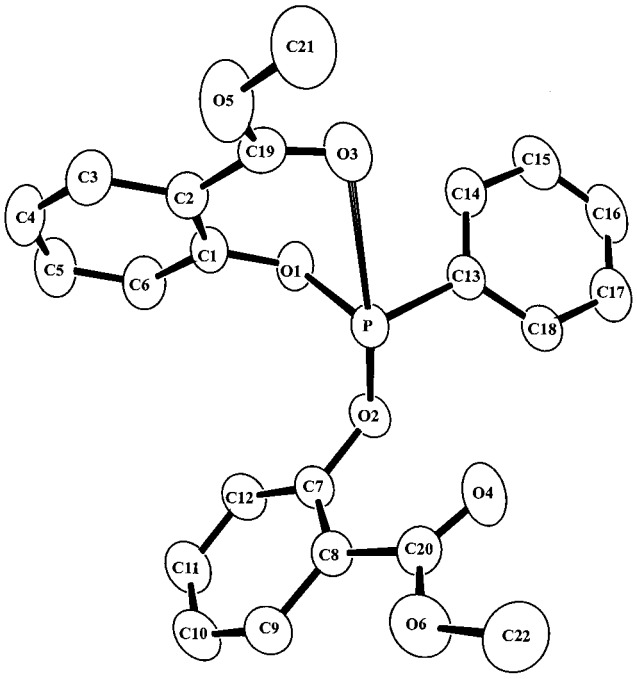


Figure 1. ORTEX diagram of $(OC_6H_4CO_2Me)_2PPh$ (**1**).

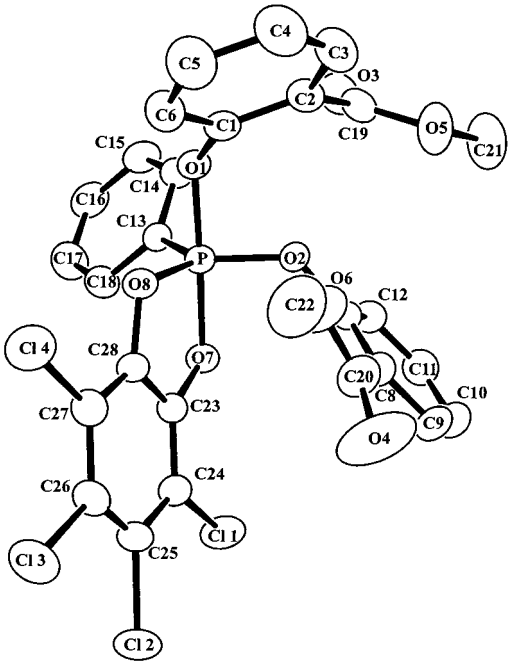
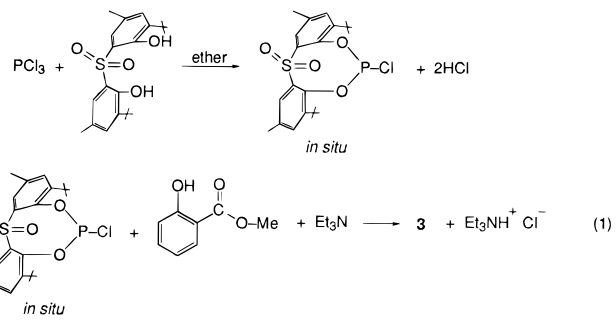


Figure 2. ORTEX diagram of $(O_2C_6Cl_4)(OC_6H_4CO_2Me)_2PPh$ (**2**).



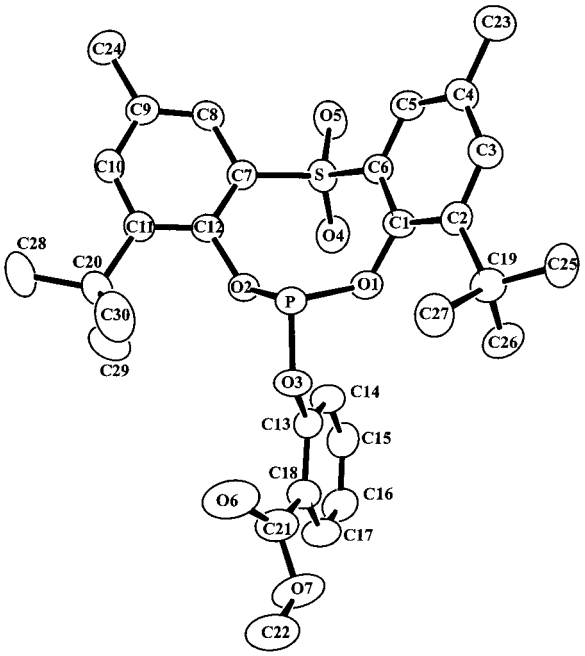


Figure 3. ORTEX diagram of $O_2S[(t\text{-Bu})MeC_6H_2O]_2(OC_6H_4CO_2Me)P$ (**3**). The solvent (toluene) has been omitted for clarity.

other pair attached to C(5) and C(8). The ^{31}P signal at 123.2 ppm is in the range for phosphites.

Basic Structures. The phenyl phosphine **1** may be described as a pseudo trigonal bipyramid (TBP) formed by donor action from a carbonyl oxygen atom that positions itself in an axial site (Figure 1). A lone electron pair is envisioned to occupy the vacant equatorial site. The other two compounds studied by X-ray diffraction **2** and **3** lack any donor action. As a consequence, the tetraoxyphosphorane **2** has a TBP geometry with the cyclic component situated at axial−equatorial sites (Figure 2). As with **1**, the two methyl salicylate groups take up one axial and one equatorial position. In both **1** and **2**, the phenyl group is at an equatorial location and the axial positions are occupied by the more electronegative oxygen atoms in keeping with the electronegativity rule.[42] The phosphite **3** has a pyramidal structure as neither the carbonyl oxygen nor the sulfonyl oxygen atom enter into donor action at phosphorus (Figure 3). The same is true for the methoxy oxygen atom.

The P−O(3) donor distance for the axially oriented carbonyl oxygen atom in **1** is 2.788(6) Å. This value is well below the sum of the van der Waals radii of 3.35 Å[43] but greater than the sum of the covalent radii of 1.83 Å.[44] By interpolation of how far the P−O bond distance has decreased relative to the van der Waals sum, it is estimated that the structural displacement toward a TBP is 37%.[2] Other bond parameters for **1** are consistent with this degree of displacement. The equatorial angle O(1)−P−Cl(13) is 95.2°, most likely condensed from the expected 120° due to the presence of the lone pair. For example, in comparison with SF_4, which has a similar TBP structure, the F−S−F equatorial angle is 101.6 ± 0.5° from a microwave study.[45] Also in agreement with a pseudo TBP geometry, the axial O(3)−P−O(2) angle is 172.21(8)°. This compares with 173.06 ± 0.25° for the F_{ax}-S−F_{ax} angle in SF_4. In both of these molecules, the axial atoms are displaced away from the lone pair.

For the TBP geometry for **2**, the rather unusual observation of a shorter axial linkage P−O(1) = 1.642(2) Å compared to 1.648(2) Å for the equatorial P−O(8) bond distance is reasonably associated with a strain effect for the nearly planar five-membered ring. Relief apparently is achieved by a lengthening of both of the P−O ring bonds. This is consistent with the much shorter axial bond distances for attachment of the acyclic salicylate unit, P−O(1) = 1.642(2) Å compared to 1.759(1) Å for the opposite P−O(7) linkage as part of the cyclic component.

No donor interaction is indicated for **2** which might lead toward an octahedral structure similar to examples **A**−**C** in the Introduction. For **2**, the distance from the phosphorus atom to the nearest methoxy oxygen atom is 3.328(3) Å, while the distance to the nearest carbonyl oxygen atom is 3.732(2) Å. These values are just about at or somewhat longer than the van der Waals radius of 3.35 Å.

Phosphite **3** also lacks any donor potential. The P−O distance to the nearest carbonyl oxygen atom is 4.037(8) Å, and that to the nearest sulfonyl oxygen atom is 3.599(5) Å. The sulfonyl group contained in the eight-membered ring system has the capacity to coordinate with phosphorus and increase the coordination geometry as illustrated by pentaoxyphosphoranes in Chart 1. It is known that the sulfonyl group in such a ring is a poorer donor compared to a sulfur atom.[13,14,17] Perhaps if sulfur was present, coordination would occur to give a pseudo TBP similar to **D** and **E** in Chart 1. For these derivatives, like **F** and **G**, the ring arranges to a *syn* boat conformation, whereas in **3** the ring conformation is an *anti* chair arrangement. The latter ring conformation is typical whenever donor interaction is absent.[2,3,13]

Structural Comparisons

A summary of the phosphorus donor interactions illustrated in Chart 2 resulting in four- and five-membered ring systems is presented in Table 5 along with that for **1**. P−O donor distances are listed for interactions that are below the van der Waals value of 3.35 Å. The salicylato phenyl phosphine **1** apparently is the first example of donor action by a carbonyl group resulting in a six-membered ring system.

The shortest donor linkage is that for the diphenyl phosphine **U** (P−O = 2.669(3) Å) which forms a five-membered ring as a consequence of oxygen coordination from the carbonyl group. The shortest carbonyl donation that forms a four-membered ring is that for **K** in Table 5, P−O = 2.733 Å. This compares with the six-membered ring system in **1** formed from carbonyl donor action, P−O = 2.788(6) Å.

For coordination by an alkoxy oxygen atom, most examples in Table 5 give four-membered ring systems. The shortest donor P−O length is 2.743 Å for **L**, which is similar to that found for **K** (2.733 Å) exhibiting a four-membered ring formed by donor action from a carbonyl oxygen atom.

Most of the compounds listed in Chart 2 have phenyl groups and oxygen atoms ligated to phosphorus. These substituents apparently provide sufficient electrophilic character at the phosphorus atom for donor coordination to take place. It is surprising in this context that phosphite **3**, which is expected to have a greater Lewis acidity than the phenyl phosphine **1**, lacks donor coordination. It may be that steric interactions due to the larger ring system containing *tert*-butyl groups interferes with the approach of the oxygen atoms of the salicylate group (Figure 3). Some evidence that this might be the correct

(42) Holmes, R. R. *Pentacoordinated Phosphorus-Structure and Spectroscopy*; Vol. I, ACS Monograph 175, American Chemical Society: Washington, DC, 1980; 479 pp and references therein.
(43) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(44) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L., Ed.; Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.
(45) Tolles, W. M.; Gwinn, W. G. *J. Chem. Phys.* **1962**, *39*, 1119.

Table 5. P−O Distances (Å) from Coordinating C═O and OR Groups[a]

Four-membered ring systems					
No.[b]		P←O, Å	No.[b]		P←O, Å
H[19]		3.184	**L**[25]		2.743 2.816
I[20]		2.959	**J**[21]		3.063
J[21]		2.786	**K**[21]		3.060
K[21]		2.733	**M**[26]		2.805
			N[26]		2.863
			O[27]		2.784[c] 2.823[c]
			P[28]		2.876
			Q[29]		2.811
Five-membered ring systems					
No.					
S[22]		2.941	**X**[30]		3.113
T[23]		2.823			
U[24]		2.669			
Six-membered ring system					
1[d]		2.788 3.049			

[a] The complete formulas are shown in Chart 2. [b] References are indicated as superscripts. [c] Two molecules per unit cell. [d] This work.

rationale is found by comparing **3** with the phosphine **U** in Chart 2. The simple composition for **U** implies a lack of a steric interaction and has the shortest P−O donor distance recorded in Table 5, 2.669 Å.

Application to Enzyme Action. In the mechanism describing the activation of tyrosine in the tyrosyl-tRNA synthetase system,[35] the proposed transition-state complex involves formation of an axial P−O bond from the tyrosyl carboxylate group. This leads to cleavage of the opposite P−O linkage from a TBP intermediate. On the basis of the work reported here, it is likely

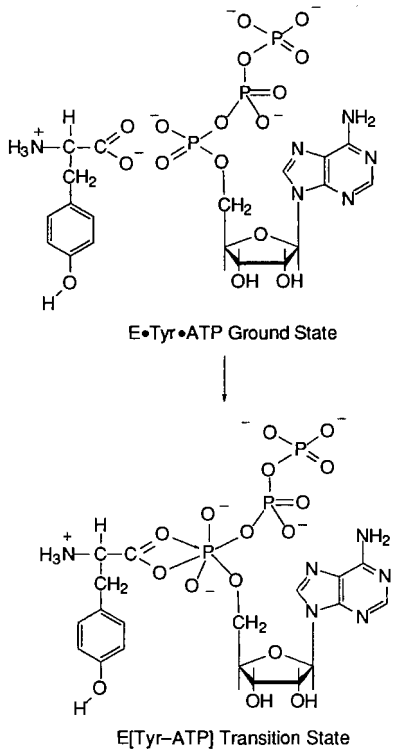


Figure 4. Ground-state complex[35] and proposed hexacoordinate transition state complex in the activation of tyrosine by tyrosyl-tRNA synthetase.

that the carbonyl oxygen atom acts in a donor capacity and forms an additional coordinate bond at phosphorus to give a hexacoordinate formulation as shown in Figure 4. Such added coordination may act as a rate enhancing effect by causing a loosening of the P−O bond undergoing cleavage in forming the enzyme tyrosyl−AMP complex. Recent work[1b,2] in our laboratory has shown that donor coordination is greater in pentaoxyphosphoranes compared to that in phosphates and that the formation of the more highly coordinated oxyphosphoranes shows a general loosening of P−O bonds. The pentaoxyphosphoranes serve as model transition states in active site action of phosphoryl transfer enzymes such as that shown in Figure 4, while the less coordinated phosphates model active site substrates.

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Supporting Information Available: Tables of atomic coordinates and *U* values, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1**−**3** (14 pages). Ordering information is given on any current masthead page.

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