Inorg. Chem. **2004**, *43*, 7403–7411

Phosphorus–Nitrogen Donor Interaction Leading to Atrane Formation in Phosphate and Oxyphosphorane Compositions. Implications for Phosphoryl Transfer Enzymes[1]

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

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003-9336

Received May 20, 2004

Reaction of aminotriphenols, tris(2-hydroxy-3,5-dimethylbenzyl)amine (**E**) and tris(2- hydroxy-3-*tert*-butyl-5-methylbenzyl)amine (**F**), with triphenylphosphite, tris(*p*-methoxyphenyl)phosphite, or phenyldiphenoxyphosphane in the presence of *N*-chlorodiisopropylamine led to the isolation of tetraoxyphosphorane **1**, pentaoxyphosphorane **3**, phosphate-atrane **2**, hexacoordinated pentaoxyphosphorane-atrane **4,** and the first hexacoordinated tetraoxyphosphorane-atrane **5**. X-ray analysis of **1**–**3** and **5** were obtained. NMR data is reported and supports that the atrane **4** has the same hexacoordinated structure as **5**. Phosphate **2** reveals weak phosphorus–nitrogen donor action whereas the hexacoordinated atranes **4** and **5** have pronounced P–N coordination. The results are used to support amino acid donor action occurring at active sites of phosphoryl transfer enzymes. Increased strength of donor action in the higher-coordinate model activated state compared to that in the substrate phosphate composition should serve as a factor in enhancing enzyme reaction rates.

Introduction

We have proposed that residues at active sites of phosphoryl transfer enzymes are capable of entering into donor interaction at the phosphorus atom and as a consequence assist in nucleophilic attack.[2] We have recently outlined our studies on higher-valent phosphorus chemistry that reasonably may be utilized by biochemists in refining their current proposals concerning mechanistic models of nucleophilic displacements at active sites of phosphoryl transfer enzymes.[3] The major factors studied include substrate and transition or intermediate state anionicity and hydrogen bonding,[4,5] packing effects,[1b] i.e., van der Waals forces, the ease of formation of hexacoordinate phosphorus from lower-coordinate states,[6] and the pseudorotation problem common to nonrigid pentacoordinate phosphorus.[7,8] Recent work on enzyme promiscuity[9−12] and moonlighting activities[13−16] also has been considered.

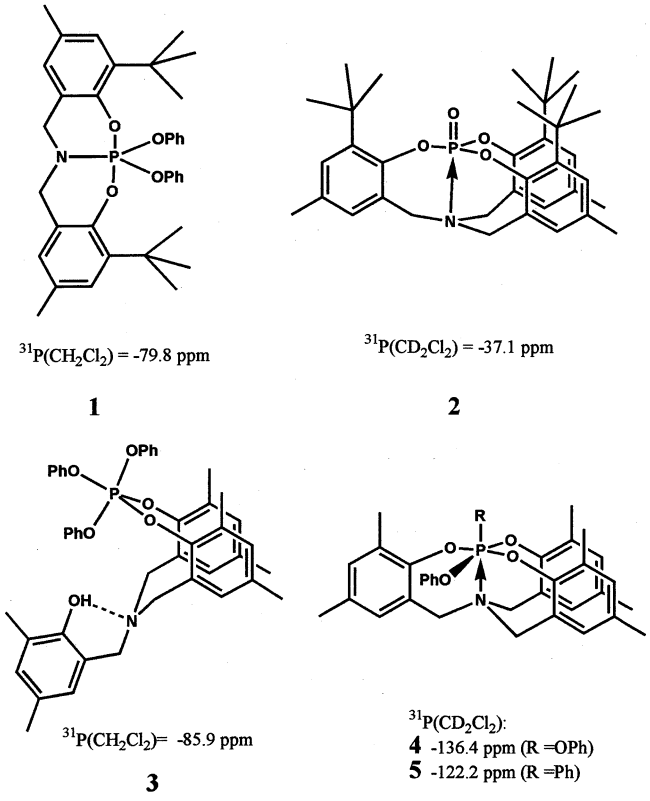
The present work is concerned with nitrogen donor interaction at phosphorus in atrane−phosphate and oxyphosphorane formations **1**−**5**.

Reaction schemes leading to these compositions are outlined. The structural information on these compositions

* Author to whom correspondence should be addressed. E-mail: rrh@chem.umass.edu.

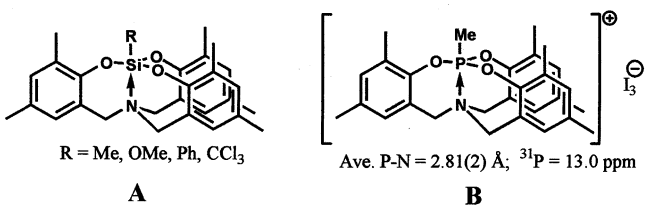
(1) (a) Pentacoordinated Molecules 139. (b) Part 138: Chandrasekaran, A.; Timosheva, N. V.; Day, R O.; Holmes, R. R. *Inorg. Chem.* **2003**, *42*, 3285−3292.
(2) Holmes, R. R. *Acc. Chem. Res.* **1998**, *31*, 535−542 and references therein.
(3) Holmes, R. R. *Acc. Chem. Res.* **2004**, *37*. In press.
(4) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2001**, *40*, 6229−6238.
(5) . Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2002**, *41*, 1645−1651.
(6) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 7035−7040.
(7) Holmes, R. R. *Pentacoordinated Phosphorus − Structure and Spectroscopy*, Volume I, ACS Monograph 175; American Chemical Society: Washington, DC, 1980; p 479.
(8) Holmes, R. R. *Pentacoordinated Phosphorus − Reaction Mechanisms*, Vol. II, ACS Monograph 176, American Chemical Society: Washington, DC, 1980; p 237.
(9) O'Brien, P. J.; Herschlag, D. *Chem. Biol.* **1999**, *6*, R91−105.
(10) James, L. C.; Tawfik, D. S. *Protein Sci.* **2001**, *10*, 2600−2607.
(11) Schmidt, D. M. Z.; Mundorff, E. C.; Dojka, M.; Bermundez, E.; Ness, J. E.; Govindarajan, S.; Babbitt, P. C.; Minshull, J.; Gerlt, J. A. *Biochemistry* **2003**, *42*, 8387−8393.
(12) Seffermick, J. L.; Wackett, L. P. *Biochemistry* **2001**, *40*, 12747−12753.
(13) (a) James, L. C.; Roversi, P.; Tawfik, D. S. *Science* **2003**, *299*, 1362−1367. (b) James, L. C.; Tawfik, D. S. *Trends Biochem. Sci.* **2003**, *28*, 361. These two articles describe conformational diversity of enzymes. The latter reference lists a glossary of terms used to describe the ability of a protein to exhibit more than one specificity or perform more than one function.
(14) Copley, S. D. *Curr. Opin. Chem. Biol.* **2003**, *7*, 265−272, also gives examples of four types of catalytic promiscuity.
(15) Jeffrey, C. J. *Trends Biochem. Sci.* **1999**, *24*, 8−11.
(16) Moonlighting proteins, a term coined by Gregory A. Petsko, is discussed: Yarnell, A. *Chem. Eng. News* **2003**, 33.

10.1021/ic040073+ CCC: $27.50 © 2004 American Chemical Society
Published on Web 10/21/2004



is used to show increased strengthening of donor action in the higher-coordinate model activated state compared to that in the substrate phosphate composition. In addition, NMR data on all compounds and X-ray analysis on key members, **1**−**3** and **5**, are provided.

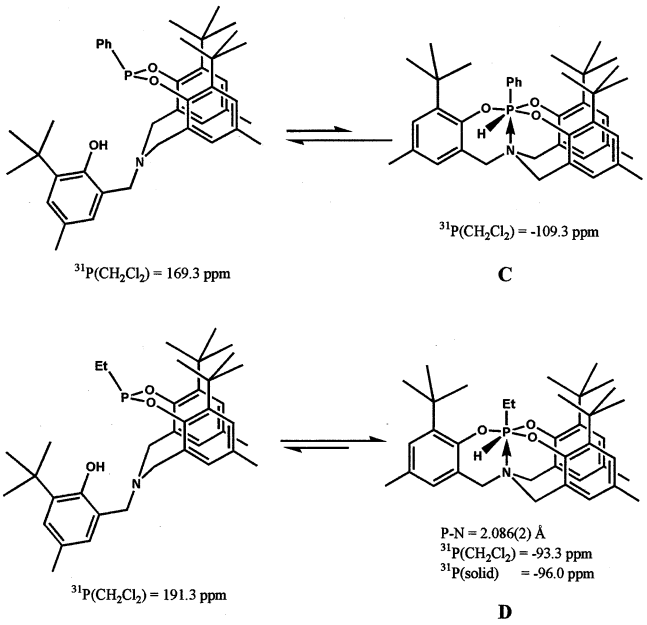
In earlier work in this area, we reported the synthesis and structure of a new class of atranes involving all six-membered rings with silicon (**A**)[17−19] or phosphorus (**B**)[20] as central atoms in pentacoordinate geometries. Also, we reported new phosphorane−atranes[6] that were the first examples of a conversion of three-coordinate to six-coordinate phosphorus on going from the solid to the solution state and the existence of these two disparate geometries in equilibrium with one another in solution (Scheme 1).



Experimental Section

Phosphorus trichloride (Aldrich), *P*,*P*-dichlorophenylphosphine (Fluka), and triphenylphosphite (Eastman) were used as supplied. Aminotriphenols, tris(2-hydroxy-3,5-dimethylbenzyl)amine (**E**)[17]

Scheme 1



and tris(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)amine (**F**),[19] were synthesized according to literature methods. Triethylamine was distilled over KOH pellets. *N*-Chlorodiisopropylamine was synthesized according to a literature method.[21] Solvents were purified according to standard procedures.[22] All reactions were carried out in an argon atmosphere. The NMR spectra were recorded on a Bruker DPX300 FT-NMR spectrometer. Solution phosphorus NMR spectra were recorded in sweep-off mode. Unless mentioned otherwise, all ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 and the solution ^{31}P NMR spectra were recorded in CH_2Cl_2. Chemical shifts are reported in ppm, downfield positive, and relative to tetramethylsilane for ^1H and ^{13}C NMR or 85% H_3PO_4 for ^{31}P NMR. All spectra were recorded at around 23 °C. For ^{13}C NMR, the numbers in parentheses refer to coupling constants or the number of carbons derived by comparing the integrations of signals for carbons with identical connectivities. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. N[CH_2(Me(*t*-Bu)C_6H_2)O]$_2$P(OPh)$_2$ (1). Compound **F** (2.10 g, 3.85 mmol), triphenyl phosphite (1.00 mL, 3.82 mmol), and *N*-chlorodiisopropylamine (0.70 mL, 4.75 mmol) were mixed in 150 mL of diethyl ether. The reaction mixture was stirred for 24 h. The amine−hydrochloride was filtered off. The filtrate was left under a flow of argon for crystallization. Yield 1.20 g (53%); mp 203−205 °C (dec). ^{31}P NMR: −79.8 ppm. ^1H NMR($CDCl_3$): 1.08 (s, 18H), 2.23 (s, 6H), 4.35 (d, 4H, 13.7 Hz), 6.78 (d, 2H, 1.4 Hz), 6.8−7.0 (m, br, 8H), 7.16 (m, 4H). ^{13}C NMR ($CDCl_3$): 21.0 (s, 2C), 30.2 (s, 6C), 34.3 (s, 2C), 55.0 (d, 4.7 Hz, 2C), 121.4 (d, 5.0 Hz), 123.0 (d, 2.2 Hz), 123.5 (d, 2.2 Hz), 126.7 (d, 7.6 Hz), 126.9 (s), 128.7(d, 1.6 Hz), 130.2 (d, 1.6 Hz), 138.7 (d, 4.0 Hz), 151.4 (d, 11.9 Hz, 2C), 155.2 (d, 14.6 Hz, 2C). Anal. Calcd for $C_{36}H_{42}NO_4P$: C, 74.08; H, 7.25; N, 2.40. Found: C, 74.12; H, 7.36; N, 2.34.

N[CH_2(Me(*t*-Bu)C_6H_2)O]$_3$PO (2). A solution of triethylamine (1.90 mL, 13.6 mmol) in dichloromethane (30 mL) was added to

(17) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 1066−1072.
(18) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O. Holmes, R. R. *Organometallics* **2000**, *19*, 5614−5622.
(19) Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **2001**, *20*, 2331−2337.
(20) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **2000**, *39*, 5683−5689.
(21) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 2578−2585.
(22) (a) Riddick, J. A., Bunger, W. B., Eds.; Organic Solvents. In *Physical Methods in Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry;* Longman: London, 1978.

Table 1. Crystallographic Data for Compounds **1**−**3** and **5**

compound	**1**	**2A**	**2B**	**3**	**5**
formula	$C_{36}H_{42}NO_4P$	$C_{36}H_{48}NO_4P\cdot{}^1/_2C_7H_{16}$	$C_{36}H_{48}NO_4P\cdot1^3/_4\ CH_2Cl_2$	$C_{45}H_{46}NO_6P$	$C_{39}H_{40}NO_5P\cdot C_4H_{10}O$
formula weight	583.68	639.82	738.34	727.80	691.81
srystal system	monoclinic	triclinic	trigonal	triclinic	monoclinic
space group	$P2(l)/n$	$P\bar{1}$	$P3c1$	$P\bar{1}$	$P2_1/c$
crystal size, mm	0.60 × 0.60 × 0.50	1.00 × 0.75 × 0.50	0.75 × 0.50 × 0.25	0.50 × 0.50 × 0.25	1.10 × 0.25 × 0.25
a (Å)	18.5856(3)	9.3964(1)	14.7853(2)	10.7003(1)	20.9836(5)
b (Å)	9.0854(1)	13.3153(1)	14.7853(2)	13.1917(1)	17.5040(4)
c (Å)	19.1390(4)	16.0433(2)	25.1806(5)	14.5801(2)	9.7610(2)
α (deg)	90.00	75.1675(5)	90.00	85.5690(5)	90.00
β (deg)	91.7146(6)	84.1853(5)	90.00	84.1928(5)	101.529(1)
γ (deg)	90.00	76.6118(8)	120.00	71.5345(5)	90.00
V (Å^3)	3230.32(9)	1885.77(3)	4767.1(1)	1939.85(4)	3512.8(1)
Z	4	2	4	2	4
D_{calc} (g/cm^3)	1.200	1.127	1.029	1.246	1.308
$\mu_{Mo\ K\alpha}$ (cm^{-1})	1.24	1.11	2.85	1.21	1.27
total reflns	5621	6501	2795	8847	6099
reflns with $I > 2\sigma_I$	4256	5271	1907	6418	4445
R^a	0.0503	0.0498	0.0911	0.0483	0.0582
$R_w{}^b$	0.1241	0.1354	0.2715	0.1144	0.1324

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

a solution of *p*-methoxyphenol (1.70 g, 13.7 mmol) and phosphorus trichloride (0.40 mL, 4.58 mmol) in dichloromethane (150 mL) while stirring at room temperature over a period of 5 min. The reaction mixture was stirred further for 20 h. Aminotriphenol **F** (2.50 g, 4.58 mmol) and *N*-chlorodiisopropylamine (0.70 mL, 4.75 mmol) were added, and the solution was stirred for a further period of 24 h. The solvent was removed, and the residue was extracted with diethyl ether (150 mL). The ether solution was left under a flow of argon. The oily material was dissolved in dichloromethane−heptane 2:1 (120 mL). It formed mostly oil and some crystals consisting of a mixture of amine−hydrochloride and compound **2**. These crystals were found to be of the crystalline form **2A**. The mixture was washed with ethanol (3 × 50 mL) to remove the oil and amine−hydrochloride, and the remaining few crystals were air-dried (20 mg). These crystals were recrystallized from dichloromethane−heptane 1:1 (10 mL) by slow evaporation. The crystals that formed early were of the form **2B**, but in the end all crystals were of the form **2A** (see X-ray Studies for more information). The crystals of **2B** become powdery above 100 °C (most likely due to loss of solvent) and melted in the range 189−192 °C. ^{31}P NMR (CD_2Cl_2): −37.1. ^{1}H NMR: 1.51 (s, 27H), 2.26 (s, 9H), 3.52 (s, br, 6H), 6.85 (s, 3H), 7.20 (s, 3H). ^{13}C NMR: 20.9 (s, 3C), 31.0 (s, 9C), 35.5 (s, 3C), 55.0 (s, 3C), 129.2 (s, 3C), 130.1 (d, 1.6 Hz, 3C), 131.4 (d, 2.9 Hz, 3C), 134.9 (d, 1.6 Hz, 3C), 143.2 (d, 4.4 Hz, 3C), 147.8 (d, 13.7 Hz, 3C); the solvent heptane showed singlet peaks at 14.3, 23.1, 29.4, 32.3 ppm (in 2:2:1:2 ratio).

$[HO(Me_2C_6H_2)CH_2]N[CH_2(Me_2C_6H_2)O]_2P(OPh)_3$ (3) and $N[CH_2(Me_2C_6H_2)O]_3P(OPh)_2$ (4). A procedure similar to that for **1** was followed, but dichloromethane (150 mL) was used as the solvent. The quantities were as follows: **E** (2.40 g, 5.72 mmol), *N*-chlorodiisopropylamine (1.00 mL, 6.78 mmol), triphenylphosphite (1.50 mL, 5.72 mmol). The solvent was removed, and the residue was extracted with ether. Heptane (20 mL) was added, and the solution was kept under a flow of argon to yield crystalline product **3**. The crystals were washed with heptane and dried. Yield 0.75 g (18%); mp 127−130 °C. ^{31}P NMR: 85.9 ppm. ^{1}H NMR: 2.19 (s, 6H), 2.28 (s, 6H), 2.53 (2, 6H), 3.70 (s, 4H), 3.77 (s, 2H), 6.57 (s, 2H), 6.8−7.1 (m, br, 19H). ^{13}C NMR: 15.8 (s, 1C), 18.7 (s, 2C), 20.6 (s, 1C), 20.8 (s, 2C), 50.4 (s, 2C), 58.2 (s, 1C), 121.3 (d, 4.9 Hz), 121.6 (s), 124.9 (s), 127.7 (s), 128.0 (s), 128.4 (d, 4.8 Hz), 129.2 (s), 130.9 (d, 4.3 Hz), 131.1 (s), 134.3 (d, 2.5 Hz), 151.0 (d, 15.6 Hz, 2C), 154.1 (s, 1C). Anal. Calcd for $C_{45}H_{46}NO_6P$: C, 74.26; H, 6.37; N, 1.92. Found: C, 74.28; H, 6.58; N, 1.83.

Compound **3** (either isolated or in situ) undergoes an elimination reaction in a day to give phosphorane−atrane **4**. If it is stored in the refrigerator and treated with a mixture of heptane and a little dichloromethane, it results mostly in an oily material or a powdery solid. Isolated yield of the powder: 70 mg; mp 140−147 °C. ^{31}P NMR: −136.4 ppm. ^{1}H NMR: 2.13 (s, 12H), 2.19 (s, 6H), 3.94 (dd, 14.1, 5.4 Hz, 2H), 4.03 (d, 10.2 Hz, 2H), 4.23 (dd, 14.1, 5.4 Hz), 6.4−7.5 (m, 16H). ^{13}C NMR (used **3** in CD_2Cl_2 after 24 h, after verifying ^{31}P NMR): 15.5 (s, 1C), 16.8 (s, 2C), 20.5 (s, 1C), 20.6 (s, 2C), 60.7 (s, 1C), 63.6 (s, 2C), 119.3 (d, 7.1 Hz), 121.0 (s), 121.3 (d, 6.6 Hz), 122.0 (s), 122.4 (d, 5.5 Hz), 123.1 (d, 5.5 Hz), 125.9 (d, 2.2 Hz), 126.6 (d, 2.2 Hz), 128.2 (d, 9.3 Hz), 128.3 (s), 128.9 (s), 129.1 (d, 9.3 Hz), 130.3 (s), 130.6 (d, 2.2 Hz), 131.1 (d, 2.2 Hz), 131.2 (s), 131.7 (s), 150.9 (d, 14.8 Hz, 1C), 151.3 (d, 14.3 Hz, 2C), 156.3 (d, 15.9 Hz, 1C), 156.7 (d, 12.6 Hz, 1C). The phenol byproduct showed singlet peaks at 115.6, 120.7, 129.9, 156.2 ppm in a 2:1:2:1 ratio. Anal. Calcd for $C_{39}H_{40}NO_5P$: C, 73.90; H, 6.26; N, 2.20. Found: C, 73.71; H, 6.56; N, 2.14.

Alternately, when $P(OPh)_3$ made in situ is used (made from PCl_3 (1.00 mL, 11.46 mmol) and phenol (3.30 g, 34.36 mmol) in the presence of triethylamine (4.8 mL, 34.44 mmol) over 20 h in dichloromethane), the reaction with aminotriphenol **E** (4.80 g, 11.44 mmol) and *N*-chlorodiisopropylamine (1.75 mL, 11.87 mmol) leads to compound **4** in about 1 h. As such, it is rather difficult to observe the intermediate **3**.

For comparison purposes, ^{13}C NMR was recorded for the aminotriphenol **E** ($CDCl_3$): 15.9 (s, 3C), 20.4 (s, 3C), 56.5 (s, 3C), 121.7 (s, 3C), 124.6 (s, 3C), 128.8 (s, 3C), 129.1 (s, 3C), 131.3 (s, 3C), 151.1 (s, 3C).

$N[CH_2(Me_2C_6H_2)O]_3PPh(OPh)$ (5). A solution of triethylamine (2.00 mL, 14.4 mmol) in dichioromethane (50 mL) was added to a solution of phenol (1.40 g, 14.9 mmol) and dichlorophenylphosphine (1.00 mL, 7.37 mmol) in dichloromethane (120 mL) while stirring at room temperature over a period of 5 min. The reaction mixture was stirred further for 20 h. Aminotriphenol **E** (3.10 g, 7.39 mmol) and *N*-chlorodiisopropylamine (1.10 mL, 7.46 mmol) were added, and the solution was stirred for a further period of 20 h. The solvent was removed, and the residue was extracted with diethyl ether (150 mL). The ether solution was left under a flow of argon that gave needle crystals of **5**. When the solvent was reduced to about 20 mL, the solution was decanted off and the residue washed with 1:1 mixture of heptane−ether (100 mL) and dried under vacuum. The crystals became powdery on losing solvent and

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

	Bond Lengths		
P−O(l)	1.688(1)	P−O(2)	1.681(1)
P−O(3)	1.607(1)	P−O(4)	1.607(1)
P−N	1.639(2)		
	Bond Angles		
O(1)−P−O(2)	172.96(7)	O(4)−P−N	121.38(9)
O(1)−P−O(3)	87.31(7)	C(l)−O(1)−P	121.7(1)
O(1)−P−O(4)	88.91(7)	C(14)−O(2)−P	122.8(1)
O(1)−P−N	93.39(7)	C(15)−O(3)−P	130.2(1)
O2)−P−O(3)	89.11(7)	C(21)−O(4)−P	130.2(1)
O(2)−P−O(4)	87.40(7)	C(7)−N−P	123.8(1)
O(2)−P−N	93.65(7)	C(8)−N−P	124.4(1)
O(3)−P−0(4)	117.85(9)	C(8)−N−C(7)	111.8(2)
O(3)−P−N	120.77(9)		

melted in the range 132−135 °C. Yield 1.80 g (40%). ^{31}P NMR (CD_2Cl_2): −122.2. ^{1}H NMR: 1.81 (s, 3H), 1.88 (s, 3H), 1.96 (s, 6H), 2.16 (s, 6H), 3.22 (dd, 13.6, 8.6 Hz, 2H), 3.85 (d, 6.2 Hz, 2H), 4.98 (dd, 13.6, 3.3 Hz, 2H), 6.01 (s, 1H), 6.51 (s, 1H), 6.68 (m, 7H), 6.92 (m, 2H), 7.31 (m, 3H), 8.20 (m, 2H). ^{13}C NMR: 17.0 (s, 2C), 17.4 (s, 1C), 20.3 (s, 1C), 20.4 (s, 2C), 61.5 (s, 1C), 65.0 (s, 2C), 120.0 (d, 6.0 Hz), 120.6 (s), 121.4 (d, 7.1 Hz), 124.9 (d, 2.4 Hz), 125.3 (d, 8.4 Hz), 126.3 (s), 126.6 (s), 126.8(s), 127.5 (d, 10.0 Hz), 127.7 (d, 3.5 Hz), 128.1 (d, 12.0 Hz), 128.8 (s), 129.7 (s), 129.9 (s), 130.8 (s), 131.0 (d, 2.7 Hz), 131.3 (s), 133.6 (d, 8.2 Hz), 147.7 (s), 151.3 (d, 18.7 Hz, 1C), 151.6 (s), 152.7 (d, 18.6 Hz, 2C), 157.9 (d, 13.8 Hz, 1C). Anal. Calcd for $C_{39}H_{40}NO_4P$: C, 75.83; H, 6.53; N, 2.27. Found: C, 75.86; H, 6.52; N, 2.20.

X-ray Studies. The X-ray crystallographic studies were performed using a Nonius-Kappa CCD diffractometer and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected at 23 ± 2 °C for $\theta_{\text{Mo K}\alpha} \leq 25°$ except the data were collected at 100 K for **5** and $\theta_{\text{Mo K}\alpha} \leq 27.5°$ for **3**. 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 2.6 GHz Pentium 4 computer using SHELXS-86 for solution[23] and SHELXL-97 for refinement.[24] All of the non-hydrogen atoms were refined anisotropically. The hydroxyl hydrogen atom in **3** was located from difference Fourier and refined isotropically. Other hydrogen atoms were included in the refinement as isotropic scatterers riding either in ideal positions or with torsional refinement (in the case of methyl and hydroxyl hydrogen atoms) on the bonded atoms. No hydrogen atoms for the solvents (in **2** and **5**) were included in the calculations. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

The crystals of **2A** were slightly sensitive and were coated with epoxy. The crystals of **2B** were so extremely sensitive (they crack and turn to powder very quickly) that they cannot be exposed to air even for a few seconds. The crystals were directly taken into epoxy from mother liquor (within epoxy they were stable for few days). There were disordered solvent molecules in both the crystals. The crystals **2A** had 0.5 M heptane, whereas **2B** had about 1.75 equiv of dichloromethane. It appears that the form **2B** is preferred when the solution contains more dichloromethane, and form **2A** is preferred when there is much less dichloromethane. Attempted low-temperature X-ray studies at 173 K made no improvement to **2A** and made the solvent more complicated and unresolvable for **2B**, so only the data at ambient temperature are reported. There was also a disordered ether solvent molecule in the crystal lattice of **5**. It could not be clearly identified. It resides in a channel, which allows the solvent to occupy random positions and also easily escape, causing crystal decay. The positions and their occupancies for this solvent molecule are based on difference Fourier peaks and the peak heights.

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

2A			
	Bond Lengths		
P−O(1)	1.573(1)	P−O(3)	1.578(1)
P−O(2)	1.576(1)	P−O(4)	1.455(1)
P−N	2.980(1)		
	Bond Angles		
O(1)−P−O(2)	107.31(7)	O(2)−P−N	68.72(6)
O(1)−P−O(3)	107.76(7)	O(3)−P−N	68.35(5)
O(1)−P−O(4)	111.50(8)	O(4)−P−N	178.28(7)
O(2)−P−O(3)	108.73(7)	C(1)−O(1)−P	132.6(1)
O(3)−P−O(4)	111.20(8)	C(14)−O(2)−P	131.5(1)
O(3)−P−O(4)	110.21(8)	C(21)−O(3)−P	134.1(1)
O(1)−P−N	70.04(5)		
2B			
	Bond Lengths		
P−O(1)	1.572(3)	P−O(2)	1.442(5)
P−N	2.947(5)		
	Bond Angles		
O(1)−P−O(2)	110.5(1)	O(1)−P−O(1)[a]	108.5(1)
O(1)−P−N	69.5(1)	O(2)−P−N	180.0(1)
C(1)−O(1)−P	133.7(2)	C(7)−N−C(7)[a]	112.7(2)
C(7)−N−P	106.0(2)		

[a] Atoms were generated by $1 - y, x - y, z$.

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

	Bond Lengths		
P−O(1)	1.606(1)	P−O(2)	1.608(1)
P−O(4)	1.604(1)	P−O(5)	1.660(1)
P−O(6)	1.660(1)		
	Bond Angles		
O(1)−P−O(2)	122.55(6)	O(4)−P−O(6)	88.19(6)
O(1)−P−O(4)	124.76(6)	O(5)−P−O(6)	177.05(6)
O(1)−P−O(5)	88.57(6)	C(1)−O(1)−P	130.2(1)
O(1)−P−O(6)	88.81(6)	C(14)−0(2)−P	125.8(1)
O(2)−P−O(4)	112.63(6)	C(28)−O(4)−P	129.8(1)
O(2)−P−O(5)	92.01(6)	C(34)−0(5)−P	133.6(1)
O(2)−P−O(6)	90.55(6)	C(40)−0(6)−P	131.9(1)
O(4)−P−O(5)	92.18(6) 30		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **5**

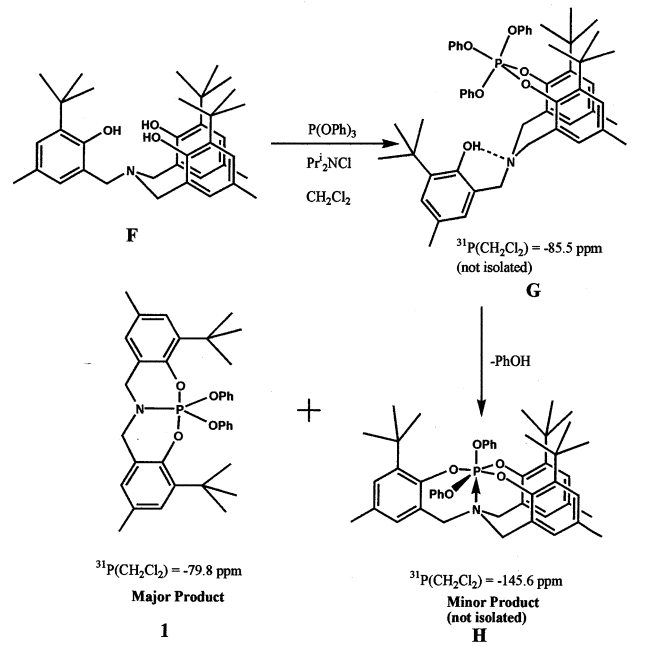
	Bond Lengths		
P−O(1)	1.690(2)	P−O(4)	1.686(2)
P−O(2)	1.688(2)	P−C(34)	1.843(3)
P−O(3)	1.709(2)	P−N	2.161(2)
	Bond Angles		
O(1)−P−O(2)	177.43(9)	O(1)−P−N	90.40(8)
O(1)−P−O(3)	87.95(9)	O(2)−P−N	87.41(8)
O(1)−P−O(4)	90.95(9)	O(3)−P−N	86.08(8)
O(2)−P−O(3)	90.55(9)	O(4)−P−N	80.63(8)
O(2)−P−O(4)	90.03(9)	C(34)−P−N	176.6(1)
O(3)−P−O(4)	166.66(9)	C(1)−O(1)−P	129.3(2)
O(1)−P−C(34)	92.8(1)	C(14)−O(2)−P	136.7(2)
O(2)−P−C(34)	89.4(1)	C(21)−O(3)−P	120.5(2)
O(3)−P−C(34)	95.1(1)	C(28)−O(4)−P	129.5(2)
O(4)−P−C(34)	98.2(1)		

Results and Discussion

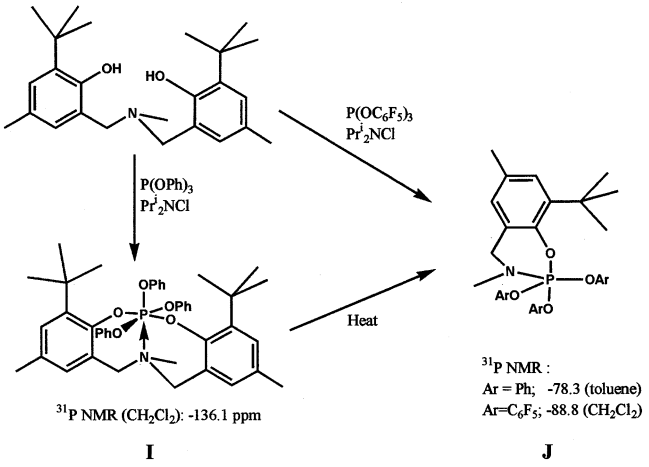
The atom-labeling schemes for **1**, **2A**, **2B**, **3,** and **5** are given in the ORTEP plots of Figures for **1**−**5**, respectively. These figures were made using the ORTEP-III for Windows

(23) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(24) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*, University of Gottingen, 1997.

Scheme 2



Scheme 3

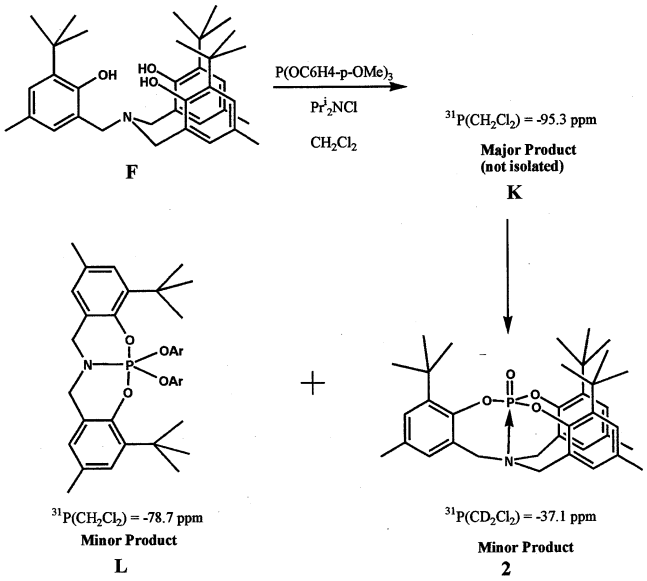


program.[25] The hydrogen atoms and solvent molecule (in the case of **2**) are omitted for clarity The thermal ellipsoids are shown at the 50% probability level. Selected bond parameters are given in Tables 2−5.

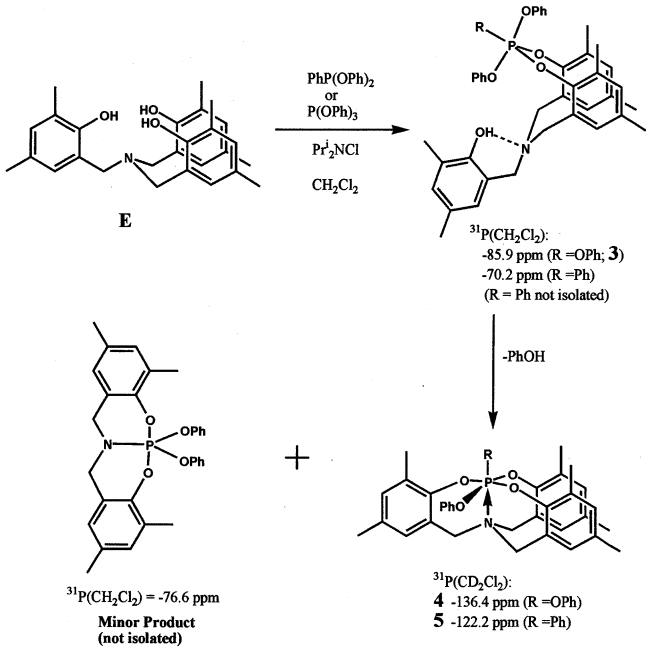
Syntheses and Reaction Schemes. Phosphorane **1** was obtained as the major product in the reaction of aminotriphenol **F** with triphenylphosphite in the presence of *N*-chlorodiisopropylamine as shown in Scheme 2. The phosphorane−atrane **H**, observed by way of its ^{31}P NMR chemical shift in solution, could not be isolated in the solid state. The formation of **1** which results from P−O and N−C bond cleavage from **H** is a process we have observed in other reactions. For example, the hexacoordinated phosphorane **I** on heating resulted in pentacoordinated phosphorane **J,** and the analogous reaction with $P(OC_6F_5)_3$ resulted directly in pentacoordinated phosphorane formation (Scheme 3). The structural representation shown for **G** has support from the

(25) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Scheme 4



Scheme 5



isolation and characterization of pentaoxyphosphorane **3** formed by an entirely analogous reaction sequence with the sterically unencumbered aminotriphenol **E**, represented in Scheme 5.

In view of the comparison of the products obtained in the reactions with the phenoxy and pentafluorophenoxy groups (Scheme 3), perhaps the employment of an electron-donating group might slow or stop the N−C bond cleavage reaction. Hence the reaction with *p*-methoxyphenol was attempted. It went as expected with the formation of **2** as a minor product that crystallized after several attempts. (Scheme 4). The major product had a ^{31}P NMR value of −95.3 ppm. It is suggested that its formulation is similar to **3** in the analogous reaction depicted in Scheme 5. The formation of phosphorane **L** by P−O and N−C bond cleavage is obtained as a minor product as well.

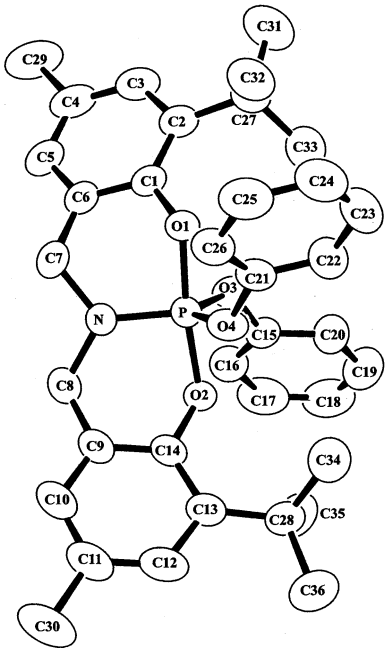


Figure 1. ORTEP diagram of **1**.

While the syntheses employing the aminotriphenol **F** composed of bulky *tert*-butyl groups led to unstable intermediates and low yields, similar reactions with the methyl-substituted aminotriphenol **E** proceeded smoothly. By monitoring the reaction with ^{31}P NMR, it was established that the aminotriphenol first reacted just like an aminodiphenol, leading to an unstable hydroxy-containing phosphorane **3**, which slowly underwent an elimination reaction to form the phosphorane−atranes **4** or **5** (Scheme 5). Compound **3** is the first 10-membered ring containing phosphorane while **4** is the first pentaoxyphosphorane−atrane.

Phosphorane **4** was fairly stable. After 2 days in a mixture of $CDCl_3$−water, only 20% had hydrolyzed, but we were unable to obtain a crystalline product. However, the intermediate hydroxy-containing pentaoxyphosphorane **3** could be easily obtained in crystalline form. Though the intermediate was not isolated in the synthesis of **5**, the ^{31}P NMR data of the reaction mixture (checked after 3 h) suggests that it also proceeds through an intermediate similar to **3**, and the phenyl group is expected to be in equatorial position. It is included in Scheme 5 based on these data.

Structure. The X-ray structure of the tetraoxyphosphorane **1** is close to a trigonal bipyramidal geometry (Figure 1) and represents the first example with two fused six-membered rings forming the bicyclic phosphorane. The P−N distance is 1.639(2) Å. The single P−N bond distance is reported as 1.85 Å. As apparent in Table 2, the equatorial bond angles are within 1° or 2° of 120°. The axial angle O(1)−P-O(2) is 172.96°. The establishment of the structure of **1** with a ^{31}P chemical shift of −79.8 ppm adds credence to the related formulations assigned to phosphorane **L** in Scheme 4 with a ^{31}P shift of −78.7 ppm and to phosphorane **M** in Scheme 5 with a ^{31}P shift of −76.6 ppm.

Like **1**, the structure of **3** (Figure 4) shown schematically in Scheme 5 serves to increase the credibility for related

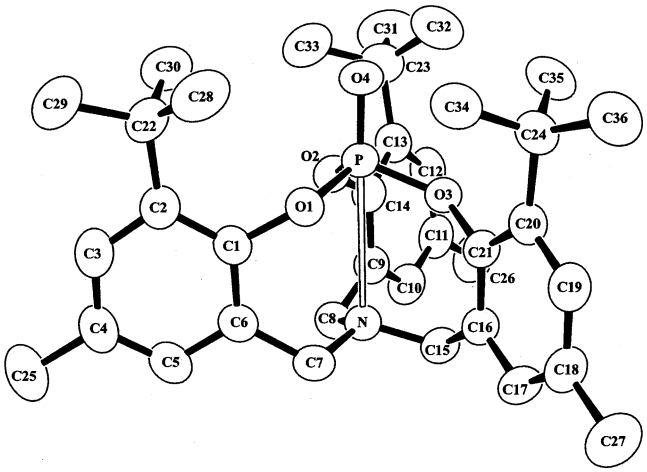


Figure 2. ORTEP diagram of **2A** (solvent molecule omitted).

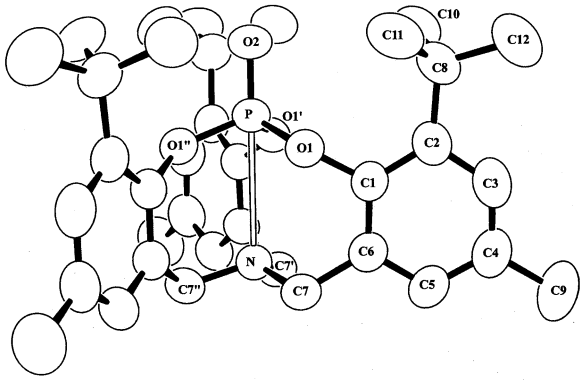


Figure 3. ORTEP diagram of **2B** (solvent molecule omitted). The primed atoms were generated by $1 - y, x - y, z$ and the double primed atoms were generated by $1 - x + y, 1 - x, z$.

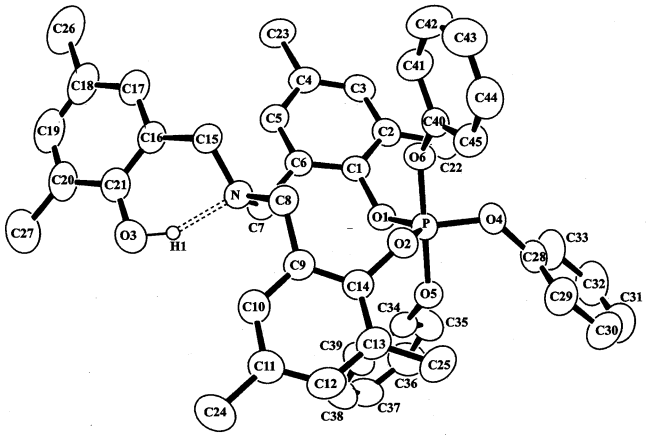
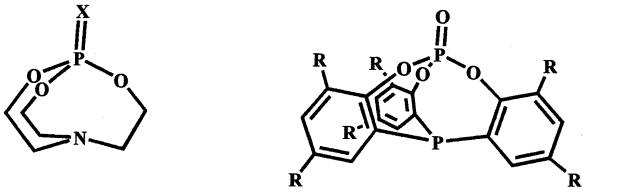


Figure 4. ORTEP diagram of **3**. Hydrogen bonding is shown with a dotted line.

formulations **G** in Scheme 2 and perhaps a related formulation for **K** in Scheme 4. All three have very close solution ^{31}P NMR values, −85.5 ppm for **G**, −95.3 ppm for K, and −85.9 ppm for **3**. The pentaoxyphosphorane **3** acts as an intermediate in the preparative scheme and converts to **4** in solution in a day. It is the only known phosphorane with a ten-membered ring. The geometry is quite close to trigonal bipyramidal as indicated by the bond angles listed in Table 4. The atoms O(1), O(2), and O(4) occupy the equatorial sites with O(5) and O(6) located at the axial sites. In previous

Scheme 6



O (X = S; P--N = 3.132 Å; ^{31}P = 61.0 ppm)
P (X = O; ^{31}P = -6.6 ppm)
reference 35 refers to O and P

Q (P--P = 3.563 Å; ^{31}P = -15.9 ppm; R=H)
R (^{31}P = -20.0 ppm; R=Bu^t)
reference 38 refers to Q and R

studies involving six-, seven-, and eight-membered ring-containing phosphoranes, it has been demonstrated that an axial−equatorial orientation is preferred for up to eight-membered ring systems.[26−30] In the eight-membered ring system, depending on the steric and electronic factors, the ring arrangement may be either diequatorial or axial−equatorial orientation.[31−34] Thus, the diequatorial orientation in **3** is not unexpected.

The X-ray structure of the phosphate−atrane **2** is the most interesting of the four reported in this work. It forms two different crystalline systems, **2A** (Figure 2) and **2B** (Figure 3), but has nearly identical structures in each. The only other related compound structurally analyzed is the thiophosphate−atrane **O**[35] shown in Scheme 6. It has a P−N distance of 3.132 Å. This compares with **2** that exhibits a P−N distance of 2.980 (1) Å for **2A** and 2.947 (5) Å for **2B**. The phosphate−atrane **2** expresses a slight degree of P−N coordination in that the average P−N distance of 2.964 Å is 0.44 Å less than the sum of the van der Waals radii for P−N of 3.40 Å.[36] However, this degree of interaction does not influence the bond angles for **2A** and **2B** to any appreciable extent as they do not deviate by more than 2° or 3° from the tetrahedral value of 109° 28′.

The important point is the comparison of the structure of **2** (Figures 2 and 3) with that obtained for the first tetraoxyphosphorane−atrane **5** (Figure 5) whose synthesis is represented in Scheme 5. The P−N distance listed in Table 5 for **5** is 2.161(2) Å, only 0.31 Å longer than the single bond value of 1.85 Å[37] and far shorter than the sum of the van der Waals radii for P−N, i.e., 3.40 Å.[36] In terms of these values, the geometry of **5** is displaced 80% of the way from a trigonal bipyramid to an octahedron. The bond angles agree with this interpretation in that most of the adjacent angles are near 90°, and two of the three trans angles are close to 180°. The third one, O(3)−P−O(4) = 166.66(9)° where O(4) as part of a phenoxy ligand, is apparently displaced away from 180° due to the presence of a nonbonding interaction between the phenoxy ligand and the adjacent phenyl group. In terms of the bond angles in Table 5, the residual trigonal bipyramidal character locates O(1) and O(2) in the axial positions with O(3), O(4), and C(34) in the equatorial sites.

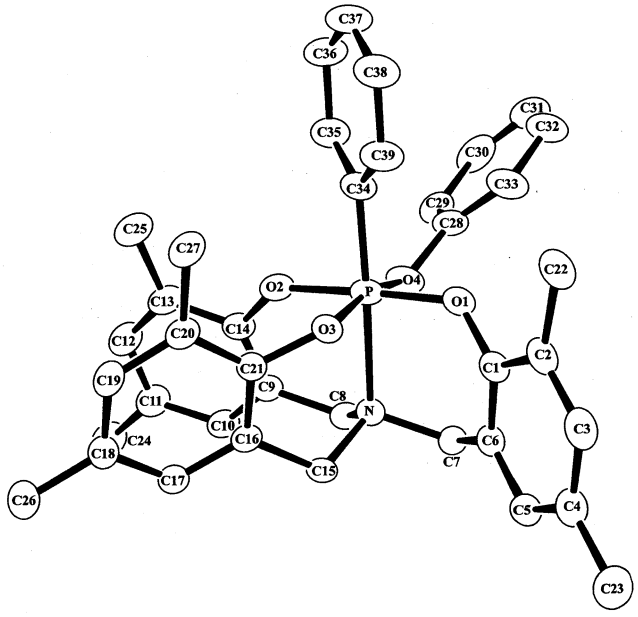


Figure 5. ORTEP diagram of **5** (solvent molecule omitted).

The phosphate structure **2** is representative of substrate composition in a phosphoryl transfer enzyme reaction, and the octahedrally coordinated phosphorane **5** is representative of an activated complex formed by an attacking nucleophile if coordination occurs with a donor atom from a nearby active site residue. The presence of donor interaction would assist the attacking nucleophile in expelling the leaving group in the hexacoordinated state and hence facilitate the reaction.[2,3]

NMR Spectroscopy. The solution state ^{31}P chemical shift for **1** was −79.8 ppm that can be assigned to a pentacoordinate phosphorane. This value is close to that for the quite analogous tetraoxyphosphorane **J** that exhibited a ^{31}P shift of −76.6 ppm. Phosphorane **3** gave a ^{31}P NMR signal at −85.9 ppm that can be unambiguously assigned to a pentacoordinate phosphorane. The nearly 6 ppm difference between **1** and **3** might possibly be attributed to the presence of nitrogen and smaller rings in **1**. In contrast, the phosphoranes **4** and **5** show resonances at −136.4 and −122.2 ppm, respectively, clearly showing that the phosphorus is hexacoordinated, similar to that found for the somewhat similarly structured hexacoorinated **I** (−136.1 ppm) in Scheme 3. Both **4** and **I** are pentaoxyphosphoranes with nitrogen donor

(26) Kumara Swamy, K. C.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6095−6103.
(27) Burton, S. D.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6104−6115.
(28) Holmes, R. R.; Kumara Swamy, K. C.; Holmes, J. M.; Day, R. O. *Inorg. Chem.* **1991**, *30*, 1052−1062.
(29) Yu, J. H.; Sopchik, A. E.; Arif, A. M.; Bentrude, W. G. *J. Org. Chem.* **1990**, *55*, 3444.
(30) Yu, J. H.; Arif, A. M.; Bentrude, W. *G. J. Am. Chem. Soc.* **1990**, *112*, 7451.
(31) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725−726.
(32) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525−4526.
(33) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552−6560.
(34) Said, M. A.; Pulm, M.; Irmer, R. H.; Swamy, K. C. K. J. *Am. Chem. Soc.* **1996**, *118*, 9841−9849; *Inorg. Chem.* **1997**, *36*, 2044−2051.
(35) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607.
(36) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(37) Sutton, L., Ed.; *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publications 11 and 18; The Chemical Society: London, 1958 and 1965.

interaction, making the comparison very reliable. The crystal structure of **5** also provides additional support that **4** has the same type of hexacoordinate structure as **5**.

Additional evidence for the donor interactions in **4** comes from proton NMR data that shows that there is P−H coupling across the P−N bond. The NCH_2 protons appear as three sets of signals for **4** (3.94, 4.03, and 4.23 ppm). The NCH_2 signal at 4.03 is a simple doublet (J_{PNCH} = 10.2 Hz) whereas the other two NCH_2 signals appear as ABX patterns (where X = phosphorus) with an apparent J_{PNCH} value of 5.4 Hz. This coupling is not reliable since the expected couplings should have two different values, depending on the orientation (similar to **5** and **I**). This ABX pattern was found to be unresolvable due to the fact that the X-part lies in the phosphorus region where the phosphorus is involved in coupling with many other protons. Efforts to simplify the pattern by going to higher field (600 MHz) did not show any difference other than some intensity changes. Also irradiation experiments of the **A** or **B** part failed to show any change in the nonirradiated part.

In compound **1**, where there is a P−N covalent bond, the P−H coupling values observed for the NCH_2 protons were 13.7 Hz. Also the equivalence of protons suggests that the six-membered ring is fluxional, similar to one of the rings in **4**. For phosphorane **I**, P−H coupling values were 12.0 and 4.2 Hz for two different orientations. For the ethylhydridophosphorane−atrane **D,** there were also three resonances for the NCH_2 protons, but they were broad with no detectable coupling owing to a rapid interconversion with an equilibrated three-coordinated species (see Scheme 1). The proton resonance values were 3.61, 3.82, and 3.95 ppm, indicative of a downfield shift resulting from electron donation by nitrogen.

Phosphorane−atrane **5** has some unusual chemical shifts that appear to be influenced by aromatic ring currents (anisotropy). This leads to one set of NCH_2 protons at 3.22 ppm presumably shielded by ring currents. Another set is located at 4.98 ppm in a more deshielded region. A third set of NCH_2 protons at 3.85 ppm are in the normal range. Here the J_{PNCH} coupling values are 8.6, 3.3, and 6.2 Hz, respectively. The lower coupling constant (6.2 Hz) and the less deshielded chemical shift (3.85 ppm) of the NCH_2 protons for **5** that are unaffected by anisotropy compared to the corresponding values of(10.2 Hz and 4.03 ppm) for **4** suggest a weaker coordination for **5** as expected for a tetraoxyphosphorane compared to a pentaoxyphosphorane. Here also one of the six-membered rings of **5** is fluxional leading to equivalence of the NCH_2 protons, similar to that observed for **4**.

The phosphate **2** shows a ^{31}P chemical shift of −37.1 ppm that is somewhere between phosphate and pentacoordinate phosphorane, suggesting a partial P−N interaction similar to that indicated from the value of the P−N distance for **2** already discussed. The trihydroxyphenylphosphine-based atrane **Q**[38] (Scheme 6) has a chemical shift of −15.9 ppm with a P−P distance of 3.563 Å that is very close to the sum of the P−P van der Waals radii of 3.70 Å.[36] A similar phosphate with 2,6-dimethylphenyl-derived macrocyclic cryptand that is structurally closer to **2** has a chemical shift of −21.8 ppm.[39] This suggests that about 15 ppm of shielding is associated with P−N donor interaction in **2**. The ring sizes of 8 and 10 are not expected to have much difference in ring strain. Hence most of this chemical-shift difference probably is a result of P−N interaction.

^{13}C NMR. Since there is an abundance of carbon resonances, only those close to the phosphorus atom are discussed (namely POC-aryl and NCH_2 carbons). Interestingly, none of the phenoxy carbons were observed for phosphorane **3**, while all other carbons were observed as normal sharp peaks. This may be due to different rates of fluxional processes for the phenoxy groups and the ring arrangements.

In general, two, three, and four bond P− C couplings are observed with distinct ranges (11.9−15.6 Hz for $^2J_{POC}$, 2.9−5.5 Hz in **1**−**3** and 5.5−9.3 Hz in **4**, for $^3J_{POCC}$ and 1.6−2.2 Hz for $^4J_{POCCC}$). The unsubstituted phenoxy C−O carbons resonate around 155 ppm while the substituted aryloxy C−O carbons resonate in the range 147−154 ppm (far from the remaining aryl carbons, which resonate in the region 120−140 ppm). This makes it easier to identify the carbons that are closest to phosphorus. The aryl methyl carbons also show differences about their aromatic ring orientations. Though most of the carbons show small chemical-shift differences compared to the free starting material (such as **3** or **4** vs **E**), the NCH_2 carbons show the maximum chemical-shift difference.

The NCH_2 carbon appears in the region 50−58 ppm for **1**−**3** and **E**. However, the NCH_2 carbons appear above 60 ppm in **4** (as two signals with an integral ratio of 2:1). This is a downfield shift of about 4 and 7 ppm compared to that of **E** and 2.5 and 10.3 ppm compared to that of **3**. This may indicate that there is an appreciable reduction in electron density at nitrogen for **4** compared to that of **E** and **3**. The aryloxy carbons show four distinct resonances in the case of **4** (with an integral ratio of 2:1:1:1). Both phenoxy C−O carbons are different, and the three aryloxy C−O carbons have two different orientations as illustrated in Scheme 5. This is similar to the structure we have solved for the first phosphorane−atrane **D** (depicted in Scheme 1).

Thus, for the pentaoxyphosphorane−atrane **4**, the highly shielded phosphorus NMR signal, the number and ratio of NCH_2 proton resonances and carbon resonances (and their deshielding), and the number and ratio of aryloxy ipso carbon signals and aryl-CH_3 carbon signals are all consistent with the schematic in Scheme 5, confirming that the structure of **4** is highly similar to that determined for the related phosphorane−atrane **5** (which also has a similar NMR spectral pattern as **4**).

Nitrogen Donor Interaction in Phosphorus Atranes. The first six entries in Table 7 are hexacoordinated phos-

(38) Bolm, C.; Davis, W. M.; Halterman, R. L.; Sharpless, K. B. *Angew. Chem., Int. Ed Engl.* **1988**, *27*, 835.

(39) Bauer, I.; Habicher, W. D. *Phosphorus, Sulfur Silicon Related. Elem.* **1997**, *130*, 89−105.

Table 6. ^{13}C NMR Data (ppm) for Phosphorane and Atrane Compositions[a]

compound	aryl-CH_3	NCH_2	aryl-CH_3	NCH_2	(aryl)C−O−P	(Ph)C−O−P
1[b]	2.23	4.35	21.0	55.0 (4.7)	151.4 (11.9)	155.2 (14.6)
2	2.26	3.52 (br)	20.9	55.1	147.8 (13.7.)	
3	2.19, 2.28, 2.53 (6:6:6)[c]	3.70, 3.77 (4:2)	15.8, 18.7[d], 20.6, 20.8[d]	50.4,[d] 58.2	151.0 (15.6),[d] 154.1	not seen
4	2.13, 2.19 (12:6)[c]	3.94, 4.03, 4.23	15.5, 16.8[d], 20.5, 20.6[d]	60.7, 63.6[d]	150.9 (14.8), 151.3 (14.3)[d]	156.3 (15.9), 156.7 (12.6)
5	1.81, 1.88, 1.96, 2.16 (3:3:6:6)	3.22, 3.85, 4.98	17.0[d], 17.4, 20.3, 20.4[d]	61.5, 65.0[d]	151.3 (18.7), 152.7 (18.6)[d]	157.9 (13.8)
E[b]	2.21	3.63	15.9;20.4	56.5	151.1	156.2[e]

[a] Chemical shifts are in ppm and coupling values given in parentheses are in Hz. [b] Data in $CDCl_3$ (others in CD_2Cl_2). [c] Some peaks coincide accidentally. [d] Two carbons. [e] For free PhOH.

Table 7. P−N Distances (Å) and ^{31}P Chemical Shifts (ppm) for Phosphorus−Atranes

compdound[a]	P−N distance[b]	δ ^{31}P	comments[c]
D (F)	2.086(2)	−96.0	Et, H
H(F)		−145.6	
I (F)	2.143(3)	−136.1	
4 (E)		−136.4	
5 (E)	2.161(2)	−122.2	Ph
N (E)		−90.4	Ph, H
B (E)	2.81(2)	13.0	cationic, Me
2 (F)	2.964(5) ave.	−37.1	phosphate
O	3.132	61.0	thiophosphate, S
P		−6.6	phosphate
Q	3.563 (P−P)	−15.9	phosphate
R		-20.0	phosphate

[a] The compound designation is followed by the type of triphenol used in its preparation defined in the Experimental Section. [b] The compounds are arranged according to increasing P−N distance that was obtained from the X-ray analysis. [c] All compounds have the atrane composition and are hexacoordinate except the phosphates that are noted. These phosphate formulations are interpreted as modestly displaced toward the trigonal bipyramid from the tetrahedron to varying degrees. Also listed are groups other than oxygen and nitrogen attached to phosphorus.

phorane−atranes that have P−N distances where obtained that show a narrow range not too far from the sum of the covalent radii for a P−N bond, 1.85 Å.[37] The corresponding ^{31}P chemical shifts for the pentaoxyphosphoranes, entries **2**, **3**, and **4**, again show a narrow range upfield from the others having either fewer electronegative groups attached to the phosphorus atom or lower coordination number. This is as expected for the most electrophilic atranes. The phosphate atranes by contrast, the last five entries of Table 7, have much lower ^{31}P chemical shifts and P−N distances that tend toward the van der Waals sum of 3.40 Å.[36] Studies with sulfur as the donor atom in flexible eight-membered rings showing little strain, earlier reported,[40] revealed a similar finding in that phosphate compositions had P−S distances near 3.14 Å whereas bicyclic oxyphosphoranes dispiayed an average P−S distance of 2.53 Å. The van der Waals value for the sum of the radii is 3.65 Å, and the sum of the covalent radii is 2.12 Å.

The phosphate structure **2** reported here is representative of a substrate composition in a phosphoryl transfer enzyme reaction, and the octahedrally coordinated phosphorane **5**, also structurally characterized in this work, is representative of an activated complex formed by an attacking nucleophile if coordination occurs with a donor atom from a nearby active site residue. From the correlation in Table 6, it is apparent that donor coordination would be enhanced in the more electrophilic hexacoordinated state than in the phosphate substrate. The presence of donor interaction would assist the attacking nucleophile in expelling the leaving group in the hexacoordinated state and hence facilitate the reaction.[2,3]

Acknowledgment. The support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly acknowledged as is the X-ray Structural Characterization Laboratory at the Department of Chemistry supported by the University of Massachusetts and the National Science Foundation (CHE-9974648). We also acknowledge Dr. L. Charles Dickinson for checking the high field ^1H NMR spectrum and irradiation experiments for compound **4**.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**−**3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC040073+

(40) (a) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552−6560, and references therein. (b) Said, M. A.; Pulm, M.; Irmer, RPH.; Swamy, K. C. K. *J. Am. Chem. Soc.* **1996**, *118*, 9841−9849; *Inorg. Chem.* **1997**, *36*, 2044−2051.