Cyclic Three-, Four-, Five-, and Six-Coordinate Nitrogen-Containing Phosphorus Compounds Varying in Ring Size from Five- to Ten-Membered. P−N Donor Action[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

Received June 15, 1998

New nitrogen-containing phosphorus compounds **1** and **3**−**5** were prepared by the reaction of a nitrogen-containing phenol with $PhPCl_2$. Hydrolysis of **1** gave an acyclic anionic phosphinate hydrogen bonded to an ammonium component (**2**). Use of a nitrogen-containing diol with $P(OPh)_3$ resulted in oxidative addition to give hexacoordinate pentaoxyphosphorus compound **6** exhibiting P−N donor action. X-ray analyses performed on all six phosphorus compounds revealed a variety of geometries extending from three- to six-coordinate with ring sizes varying from five- to ten-membered. The structure of **3** is displaced toward a trigonal bipyramid (TBP) as a result of weak P−N donor action. As a consequence of N−C bond cleavage, **1** forms as a bicyclic phosphorane with the nitrogen atom located at an equatorial site of a TBP. In the formation of the tetracoordinate cyclic phosphinate **5**, a P−C bond is formed at the expense of O−C bond cleavage of the reactant diol. ^{1}H and ^{31}P NMR spectra indicated that the basic coordination structures were retained in solution. It is concluded that the more elusive donor action found for nitrogen relative to sulfur and oxygen is a consequence of bond cleavage reactions. However, with sufficient phosphorus electrophilicity in higher valent states, P−N donor action is achievable as found in the pentaoxyphosphorane (**6**) in this study while more modest donor action takes place in the lower coordinate state present in **3**.

Introduction

While series of oxyphosphorane compounds recently have been structurally characterized that exhibit varying degrees of donor atom interaction arising from sulfur[2−12] and oxygen[12−14] atom coordination, little is known about analogous compounds of phosphorus showing P−N coordination from nitrogen ligands. Structures **A**−**H** (Chart 1) are representative examples that show increased coordination leading to penta- and hexacoordinate formulations as a result of sulfur[2,5,15] and oxygen[1b,13−15] donor action.

Corriu and co-workers have reported P−N donor action in the phosphonate **I**[16] (Chart 2) to give a trigonal bipyramid (TBP) and in the phosphine **J**[17] to give a pseudo-TBP where the nitrogen occupies an axial position. Other workers[18−22] have used nitrogen in small-membered rings as a coordinating agent where the remainder of the ligands primarily have been fluorine atoms to form hexacoordinate structures with strong P−N coordination, e.g., **K** and **L**.

In the present work, we examine reactions that potentially should lead to an increase in coordination as a result of nitrogen donor action. The resultant products **1**−**6** were characterized by X-ray diffraction and NMR studies. Higher coordination occurred in the reaction leading to hexacoordinate **6** and pentacoordinate **3**, while bond cleavage reactions were encountered in the case of the formations **1**, **2**, and **5**. This leads to interesting mechanistic features that take precedence in controlling the course of these reactions and provides an opportunity to explore the use of flexible large-membered rings in promoting hypervalent coordination.

Experimental Section

2,4-Dimethylphenol, 2-*tert*-butyl-4-methylphenol, dichlorophenylphosphine (Fluka), methylamine, benzylamine, and hexamethylenetet-

---

(1) (a) Pentacoordinated Molecules. 123. (b) Part 122: Timosheva, N. V.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3862−3867.

(2) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1998**, *37*, 3747−3752.

(3) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913−1920.

(4) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391−3397.

(5) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1993**, *115*, 2690−2695.

(6) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, Silicon* **1993**, *75*, 249−252.

(7) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360−4367.

(8) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317−1322.

(9) Sherlock, D. J.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1998**, *37*, 93−101.

(10) Sood, P.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 5730−5734.

(11) Wong, C. Y.; McDonald, R.; Cavell, R. G. *Inorg. Chem*. **1996**, *35*, 325−334.

(12) Holmes, R. R. *Chem. Rev*. **1996**, *96*, 927−950 and references therein.

(13) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc*. **1997**, *119*, 11434−11441.

(14) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem*. **1997**, *36*, 2578−2585.

(15) Sood, P.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. Unpublished work.

(16) Carre, F.; Chuit, C.; Corriu, R. J. P.; Monforte, P.; Nayyar, N. K.; Reye, C. *J. Organomet. Chem*. **1995**, *499*, 147−154.

(17) Chuit, C.; Corriu, R. J. P.; Monforte, P.; Reye, C.; Declercq, J.-P.; Dubourg, A. *J. Organomet. Chem*. **1996**, *511*, 171−175 and references cited therein.

(18) Sheldrick, W. S. *J. Chem. Soc., Dalton Trans*. **1974**, 1402.

(19) Storzer, W.; Schomburg, D.; Röschenthaler, G.-V.; Schmutzler, R. *Chem. Ber*. **1983**, *116*, 367.

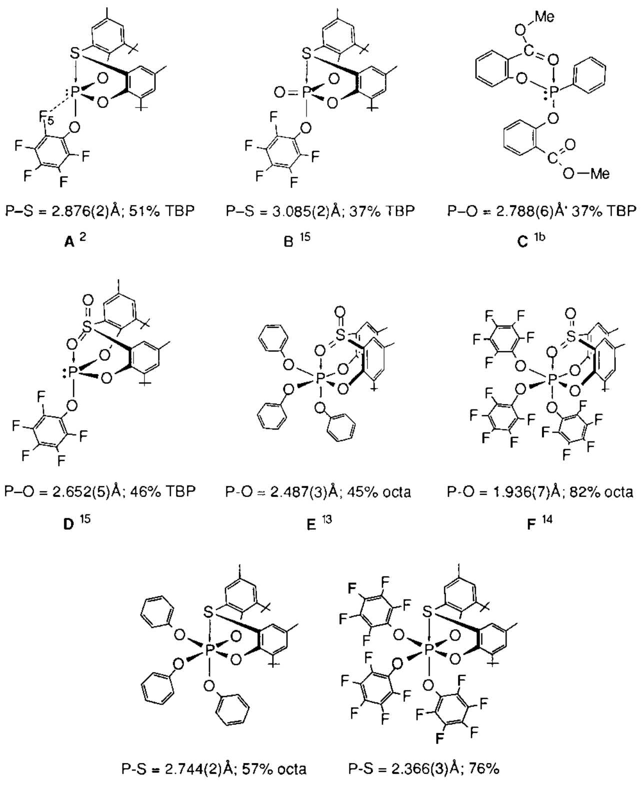
(20) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans*. **1974**, 1841.

(21) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 2466.

(22) Krebs, R.; Schmutzler, R.; Schomburg, D. *Polyhedron* **1989**, *8*, 731.

S0020-1669(98)00660-0 CCC: $15.00

Chart 1



P–S = 2.876(2)Å; 51% TBP
A[2]

P–S = 3.085(2)Å; 37% TBP
B[15]

P–O = 2.788(6)Å; 37% TBP
C[1b]

P–O = 2.652(5)Å; 46% TBP
D[15]

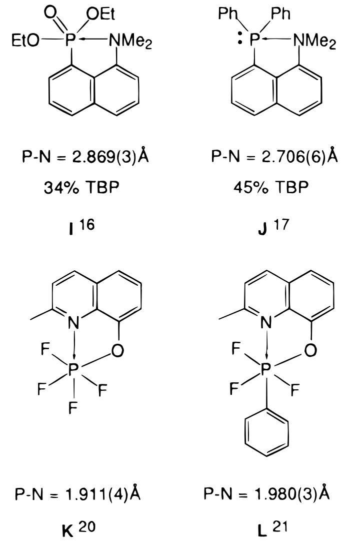
P-O = 2.487(3)Å; 45% octa
E[13]

P-O = 1.936(7)Å; 82% octa
F[14]

P-S = 2.744(2)Å; 57% octa
G[5]

P-S = 2.366(3)Å; 76%
H[2]

Chart 2



P-N = 2.869(3)Å
34% TBP
I[16]

P-N = 2.706(6)Å
45% TBP
J[17]

P-N = 1.911(4)Å
K[20]

P-N = 1.980(3)Å
L[21]

ramine (Aldrich) were used as supplied. The diols **7**−**10** were synthesized by following a procedure used to synthesize methylamino-*N,N*-bis(1-methylene-2-naphthol).[23] Triethylamine was distilled over KOH pellets. Solvents were purified according to standard procedures.[24] Light petroleum fractions are referred to as Skelly-C (88−99 °C) or Skelly-F (35−60 °C). All phosphorus reactions were carried out in a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Phosphorus-31 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 unless otherwise mentioned. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane (for ^{1}H) or 85% H_3PO_4 (for ^{31}P). All were recorded around 23 °C. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. Methylamino-*N,N*-bis(2-methylene-4,6-dimethylphenol), $[Me_2C_6H_2(OH)CH_2]_2NMe$ (7). To a solution of 2,4-dimethylphenol (48.0 mL, 0.40 mol) in methanol (130 mL) was added aqueous formaldehyde (37%, 32 mL, 0.39 mol) and methylamine (40%, 17.2 mL, 0.22 mol) with stirring. The solution was stirred for 20 h at about 25 °C and refluxed for 3 h. The two-layer system was left in a freezer for 2 days by which time the oil at the bottom solidified. The mother liquor was decanted off and the solid washed with a mixture of 2-propanol−methanol (1:1, 100 mL) and air-dried. The washings on cooling gave more diol, mp 118−121 °C (lit. 127 °C[25]) (yield 47.7 g, 81%). ^{1}H NMR: 2.21 (s, 12 H, aryl-*Me*), 2.22 (s, 3 H, N*Me*), 3.64 (s, 4 H, N*CH₂*), 6.73 (s, 2 H, aryl), 6.87 (s, 2 H, aryl).

Methylamino-*N,N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol), $[(t\text{-}Bu)MeC_6H_2(OH)CH_2]_2NMe$ (8). To a solution of aqueous formaldehyde (37%, 7.5 mL, 93 mmol) and *p*-toluenesulfonic acid (100 mg) in methanol (100 mL) was added aqueous methylamine (40%, 4.3 mL, 56 mmol) and the solution stirred for 2 h. Then 2-*tert*-butyl-4-methylphenol (16.5 g, 100 mmol) was added. The solution was stirred for 6 h at room temperature and refluxed for 15 h. Methanol was decanted off from the two-layer system. Skelly-F (100 mL) was added to the residual oil. Crystals formed while in the refrigerator. The crystals were washed with methanol and dried, mp 100−103 °C (yield 15.9 g, 90%). ^{1}H NMR: 1.40 (s, 18 H, *t*-Bu), 2.25 (s, 6 H, aryl-*Me*), 2.30 (s, 3 H, N*Me*), 3.60 (s, 4 H, NCH_2), 6.75 (d, 2.0 Hz, 2 H, aryl), 7.02 (s, 2 H, aryl).

Benzylamino-*N,N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol), $[(t\text{-}Bu)MeC_6H_2(OH)CH_2]_2NCH_2(C_6H_5)$ (9). A procedure similar to that for **8** was used. Benzylamine (5.50 mL, 50.3 mmol) replaced methylamine. Crystallization was difficult. (2-Pyridylmethyl)amino-*N,N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol) crystals were used as seeds, mp 152−155 °C (yield 5.6 g, 26%). ^{1}H NMR: 1.38 (s, 18 H, *t*-Bu), 2.22 (s, 6 H, aryl-*Me*), 3.53 (s, 2 H, NCH_2Ph), 3.59 (s, 4 H, NCH_2), 6.75 (d, 2.0 Hz, 2 H, aryl), 6.98 (s, 2 H, aryl), 7.33 (m, 5 H, Ph).

$(Me_2C_6H_2OCH_2)[Me_2C_6H_2(OH)CH_2]N(CH_2)_2$ (10). A mixture of aqueous formaldehyde (37%, 3.2 mL, 40 mmol), *p*-toluenesulfonic acid (100 mg), hexamethylenetetramine (0.93 g, 6.6 mmol), and 2,4-dimethylphenol (10 mL, 83 mmol) was stirred and heated by an oil bath. The oil bath was slowly heated to 110 °C and maintained there for 6 h. The resultant yellow oil was dissolved in hot methanol (50 mL) and kept overnight. Crystals that formed were washed with methanol and dried, mp 97−99 °C (yield 5.5 g, 70%). ^{1}H NMR: 2.18 (s, 3 H, aryl-*Me*), 2.19 (s, 3 H, aryl-*Me*), 2.22 (s, 6 H, aryl-*Me*), 3.97 (s, 2 H, NCH_2), 4.02 (s, 2 H, NCH_2), 4.88 (s, 2 H, OCH_2), 6.58 (s, 1 H, aryl), 6.60 (s, 1 H, aryl), 6.85 (s, 1 H, aryl), 6.90 (s, 1 H, aryl), 9.70 (s, 1 H, OH).

$MeN[(t\text{-}Bu)MeC_6H_2OCH_2]_2PPh$ (1). To a solution of dichlorophenylphosphine (1.00 mL, 7.37 mmol) in dichloromethane (200 mL) was added a solution of diol **8** (2.80 g, 7.30 mmol) and triethylamine (2.10 mL, 15.1 mmol) in dichloromethane (70 mL) dropwise over a period of 35 min. The reaction mixture was stirred at 25 °C for a further period of 72 h. Dichloromethane was removed completely under vacuum and the resulting solid extracted with diethyl ether (250 mL). The amine hydrochloride was filtered off, and the filtrate was left under a nitrogen flow. Crystals and an oil formed. The oil was quickly washed with diethyl ether (20 mL). The crystals were dried under vacuum, mp 190−192 °C (dec) (yield 1.60 g, 44.5%).

Upon attempted recrystallization from a Skelly-C−toluene mixture (2:1, 60 mL), crystals of $MeNH_2[(t\text{-}Bu)MeC_6H_2(OH)CH_2]_2PhPO_2$ (**2**) were obtained, which were a result of hydrolysis, mp 200−201 °C. ^{1}H NMR for **1**: 1.00 (s, 9 H, *t*-Bu), 1.51 (s, 9 H, *t*-Bu), 2.28 (s, 6 H, arylMe), 3.06 (d, 9.4 Hz, 3 H, N−CH_3), 3.55 (d, 9.0 Hz, 1 H, CH_2),

---

[23] Burke, W. J.; Kolbezen, M. J.; Stephens, C. W. *J. Am. Chem. Soc.* **1952**, *74*, 3601.

[24] (a) Riddick, J. A.; Bunger, W. B. Organic Solvents. In *Physical Methods in Organic Chemistry*, 3rd ed.; Weissberger, Ed.; Wiley-Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

[25] Burke, W. J.; Bishop, J. L.; Glennie, E. L. M.; Bauer, W. N., Jr. *J. Org. Chem.* **1965**, *30*, 3423.

3.66 (d, 2.2 Hz, 1 H, CH_2), 4.00 (dd, 14.4 Hz, 19.5 Hz, 1 H, CH_2), 4.34 (dd, 10.5 Hz, 14.4 Hz, 1 H, CH_2), 6.76−7.25 (multiplet, 9 H, aryl). ^{31}P NMR: −26.7. Anal. Calcd for $C_{31}H_{40}NO_2P$: C, 76.04; H, 8.23; N, 2.86. Found: C, 76.01; H, 8.13; N, 2.88. ^{1}H NMR for **2**: 1.32 (s, 9 H, *t*-Bu), 1.40 (s, 9 H, *t*-Bu), 1.72 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.22 (s, 3 H, NMe), 2.99 (d, 14.4 Hz, 2 H, PCH_2), 3.67 (s, 2 H, CH_2), 6.53 (s, 1 H, aryl), 6.76 (s, 1 H, aryl), 6.84 (s, 1 H, aryl), 7.10 (s, 1 H, aryl), 7.33 (m, 3 H, aryl), 7.66 (m, 2 H, aryl). ^{31}P NMR: 32.3. Anal. Calcd for $C_{31}H_{44}NO_4P$: C, 70.83; H, 8.44; N, 2.66. Found: C, 71.27; H, 8.73; N, 2.62.

$MeN[Me_2C_6H_2OCH_2]_2PPh$ (3). To a solution of dichlorophenylphosphine (2.00 mL, 14.7 mmol) in dichloromethane (200 mL) was added a solution of diol (**7**) (4.42 g, 14.7 mmol) and triethylamine (4.20 mL, 30.1 mmol) in dichloromethane (80 mL) dropwise over a period of 45 min. The reaction mixture was stirred at 25 °C for a further period of 65 h. Half of the dichloromethane was removed under vacuum. Then diethyl ether (80 mL) was added, and amine hydrochloride was filtered off. The filtrate was left under a nitrogen flow to give a crystalline product, mp 160−163 °C (yield 4.9 g, 80%). ^{1}H NMR: 1.69 (s, 6 H, Me), 1.99 (s, 3 H, N−Me), 2.23 (s, 6 H, Me), 3.19 (d, 11.9 Hz, 2 H, CH_2), 4.33 (d, 11.5 Hz, 2 H, CH_2), 6.78 (s, 2 H, aryl), 6.80 (s, 2 H, aryl), 7.47 (m, 3 H, aryl), 7.93 (m, 2 H, aryl). ^{31}P NMR (toluene): 168.6. Anal. Calcd for $C_{25}H_{28}NO_2P$: C, 74.05; H, 6.96; N, 3.45. Found: C, 73.06; H, 7.17; N, 3.50.

$C_6H_5NH^+[(t\text{-}Bu)MeC_6H_2(O)CH_2]_2CH_2PPhCl^-$ (4). To a solution of dichlorophenylphosphine (1.00 mL, 7.4 mmol) in dichloromethane (200 mL) was added a solution of diol **9** (3.40 g, 7.4 mmol) and triethylamine (2.10 mL, 15.1 mmol) in dichloromethane (60 mL) dropwise over a period of 30 min. The reaction mixture was stirred at 25 °C for a further period of 68 h. Dichloromethane was completely removed under vacuum, and the residue was extracted with diethyl ether (200 mL). The amine hydrochloride was filtered off, and the filtrate was left under a nitrogen flow. A solid and an oil formed. The solid was dried under vacuum, and the oil was extracted with Skelly-F (50 mL). The phosphorus NMR of the Skelly-F extract showed three peaks at 177.7, 20.2, and 11.5 ppm in a ratio of 60:23:19. Several attempts to crystallize this mixture were not successful, mp 155−159 °C (yield 0.50 g, 11%). ^{1}H NMR: 1.04 (s, 9 H, *t*-Bu), 1.08 (s, 9 H, *t*-Bu), 2.28 (s, 3 H, Me), 2.34 (s, 3 H, Me), 2.95 (t, 10.5 Hz, 1 H, CH_2), 3.99 (d, 11.9 Hz, 1 H, CH_2), 4.33 (d, 11.9 Hz, 1 H, CH_2), 4.61 (d, 14.8 Hz, 1 H, CH_2), 4.86 (t, 11.5 Hz, 1 H, CH_2), 5.30 (dd, 7.3 Hz, 15.2 Hz, 1 H, CH_2), 7.18 (m, 3 H, aryl), 7.44 (m, 7 H, aryl), 7.86 (m, 4 H, aryl). ^{31}P NMR (CH_2Cl_2): 177.8. Anal. Calcd for $C_{37}H_{45}ClNO_2P$: C, 73.79; H, 7.53; N, 2.33. Found: C, 74.28; H, 7.89; N, 2.30.

$[CH_2PO_2Ph(Me_2C_6H_2)CH_2N]CH_2(Me_2C_6H_2OH)$ (5). To a solution of dichlorophenylphosphine (1.00 mL, 7.4 mmol) in dichloromethane (200 mL) was added a solution of **10** (4.40 g, 14.8 mmol) and a slight excess of triethylamine (2.50 mL, 17.9 mmol) in dichloromethane (70 mL) dropwise over a period of 35 min. The reaction mixture was stirred at 25 °C for a further period of 48 h. Dichloromethane was removed completely under vacuum and the resulting solid extracted with diethyl ether (150 mL). The amine hydrochloride was filtered off, and the filtrate was left under a nitrogen flow. Crystals were obtained from a mixture of CH_2Cl_2/Skelly C (1:1, 70 mL), mp 162−167 °C (yield 1.50 g, 48%). ^{1}H NMR: 2.19 (s, 6 H, CH_3), 2.26 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 3.42 (s, 2 H, CH_2), 4.05 (m, 4 H, CH_2), 6.58 (s, 1 H, aryl), 6.69 (s, 1 H, aryl), 6.88 (s, 1 H, aryl), 7.04 (s, 1 H, aryl), 7.49−7.60 (m, 5 H, aryl). ^{31}P NMR: 31.4. Anal. Calcd for $C_{25}H_{28}NO_3P$: C, 71.25; H, 6.70; N, 3.32. Found: C, 71.33; H, 6.90; N, 3.42.

$MeN[(t\text{-}Bu)MeC_6H_2OCH_2]_2P(OPh)_3$ (6). To a stirred solution of diol **8** (3.60 g, 9.4 mmol) and $P(OPh)_3$ (3.00 mL, 11.4 mmol) in ether (200 mL) was added *i*-Pr_2NCl (1.20 mL, 8.2 mmol). The reaction mixture was stirred for 22 h and filtered. The solid was washed with 95% ethanol (70 mL) and air-dried. Single crystals suitable for an X-ray study were obtained from a dichloromethane solution, mp 186−190 °C (d) (yield 4.1 g, 73%). ^{1}H NMR: 1.22 (s, 18 H, *t*-Bu), 2.28 (s, 6 H, aryl-*Me*), 2.88 (d, $^{3}J_{P-H}$ 4.8 Hz, 3 H, NMe), 3.56 (dd, J_{H-H} 13.5, $^{3}J_{PH}$ 12.0 Hz, 2 H, NHC_2), 4.56 (dd, $^{3}J_{H-H}$ 13.2, $^{3}J_{P-H}$ 4.2 Hz, 2 H, NCH_2), 6.62−7.22 (m, 19 H, aryl). The CH_2 protons of NCH_2 group are not equivalent; one pair is axial, and the other pair is equatorial (see Figure 6). On the basis of a larger J_{PH} value, the peak at 3.56 is assigned to the equatorial proton H8A, the C−H bond of which is parallel to the P−N bond. ^{31}P NMR: −136.1. A minor peak at −134.0 also was observed. Anal. Calcd for $C_{43}H_{50}NO_5P$: C, 74.65; H, 7.28; N, 2.02. Found: C, 74.28 H, 7.07, N, 2.09.

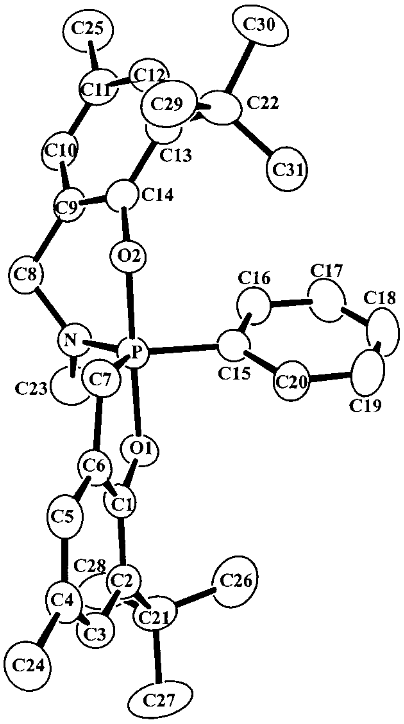


Figure 1. ORTEX diagram of bicyclic phosphorane **1**.

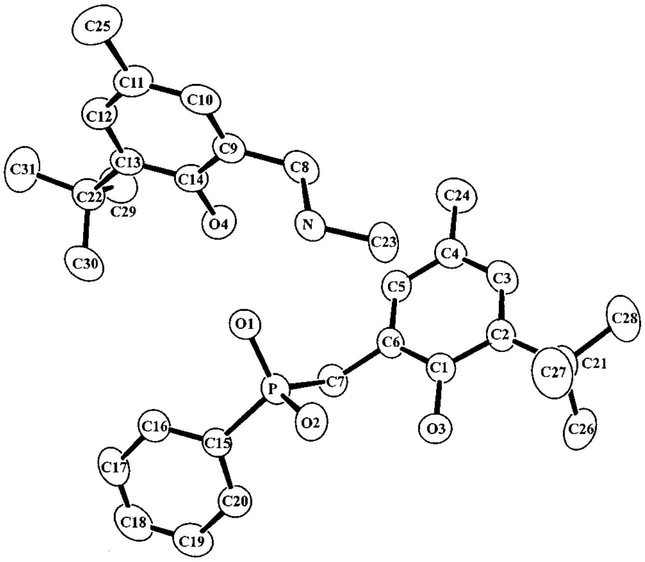


Figure 2. ORTEX diagram of the hydrogen-bonded anion−cation phosphinate **2**.

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.[26]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the $\theta-2\theta$ scan mode with $3° \leq 2\theta_{Mo\,K\bar{\alpha}} \leq 43°$ at 23 ± 2 °C. No corrections were 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

---

(26) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

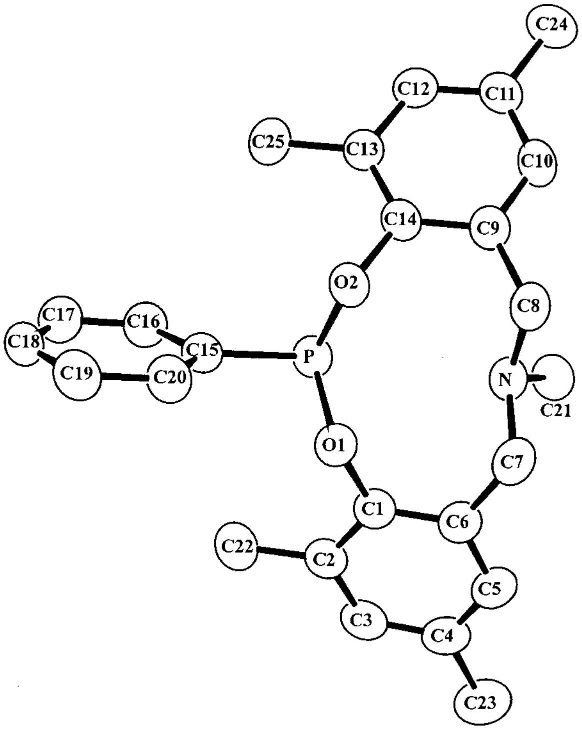


Figure 3. ORTEX diagram of the cyclic nitrogen-containing phenylphosphine **3**.

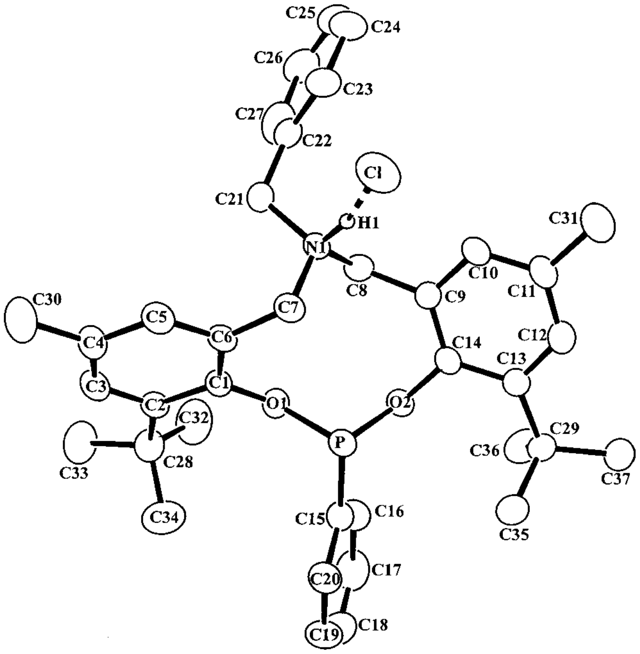


Figure 4. ORTEX diagram of the cyclic nitrogen-containing phenylphosphine hydrochloride **4**.

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[27a] and SHELXL-93 for refinement.[27b] 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 carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

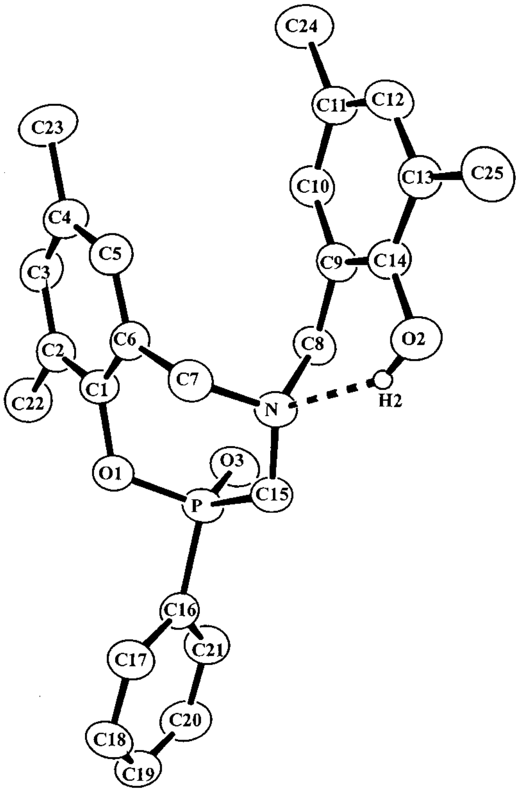


Figure 5. ORTEX diagram of the cyclic phosphinate **5**.

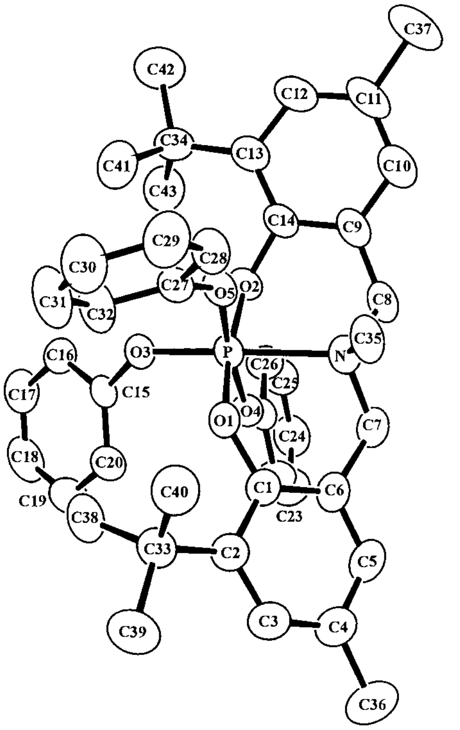


Figure 6. ORTEX diagram of the cyclic hexacoordinate P−N-bonded pentaoxyphosphorane **6**.

Results and Discussion

Tables 2−7 list selected bond parameters for **1**−**6** while Figures 1−6 depict the respective ORTEX[28] plots from the crystallographic studies. The thermal ellipsoids are shown at

---

[27] (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXL-93: program for crystal structure refinement, University of Gottingen, 1993.

[28] McArdle, P. ORTEX 5e, Crystallography Centre, Chemistry Department, University College Galway, Ireland, 1996.

Table 1. Crystallographic Data for Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{31}H_{40}NO_2P$	$C_{31}H_{44}NO_4P$	$C_{25}H_{28}NO_2P$	$C_{37}H_{44}NO_2P.HCl$	$C_{25}H_{28}NO_3P$	$C_{43}H_{50}NO_5P$
fw	489.6	525.6	405.5	602.2	421.5	691.8
cryst system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
cryst size, mm	1.00 × 0.30 × 0.30	0.30 × 0.20 × 0.20	1.00 × 0.40 × 0.27	1.00 × 0.35 × 0.20	1.00 × 0.70 × 0.08	0.45 × 0.35 × 0.25
a (Å)	8.778(2)	13.668(2)	32.018(12)	15.047(5)	5.679(4)	8.905(3)
b (Å)	11.782(3)	12.092(4)	14.626(3)	12.282(3)	9.770(2)	11.249(2)
c (Å)	14.286(3)	18.587(3)	9.666(3)	18.261(5)	20.569(4)	20.291(4)
α (deg)	74.18(2)	90	90	90	83.17(2)	98.19(2)
β (deg)	86.47(2)	90.52(2)	101.09(3)	99.74(3)	84.03(3)	89.99(2)
γ (deg)	81.79(2)	90	90	90	82.650(3)	111.06(2)
V (Å^3)	1406.6(6)	3072(1)	4442(2)	3326(2)	1119.3(8)	1874.8(8)
Z	2	4	8	4	2	2
D_{calc} (g/cm^3)	1.156	1.137	1.213	1.202	1.251	1.225
$\mu_{Mo\ K\alpha}$ (cm^{-1})	1.25	1.23	1.44	1.96	1.49	1.19
tot. reflns	3211	3518	2522	3821	2552	4287
reflns with $I > 2\sigma_I$	2596	2024	1807	2436	2057	2879
R^a	0.0402	0.0469	0.0391	0.0425	0.0451	0.0403
$R_w{}^b$	0.0999	0.1044	0.1033	0.0994	0.1216	0.0921

[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−N	1.648(2)	P−C(15)	1.810(2)
P−O(2)	1.744(2)	P−C(7)	1.828(2)
P−O(1)	1.775(2)		
N−P−O(2)	94.12(9)	O(1)−P−C(7)	88.7(1)
N−P−O(1)	91.59(9)	C(15)−P−C(7)	119.9(1)
O(2)−P−O(1)	173.34(8)	C(1)−O(1)−P	114.9(1)
N−P−C(15)	116.5(1)	C(14)−O(2)−P	125.9(2)
O(2)−P−C(15)	92.86(9)	C(23)−N−C(8)	114.4(2)
O(1)−P−C(15)	87.64(9)	C(23)−N−P	124.6(2)
N−P−C(7)	123.6(1)	C(8)−N−P	120.8(2)
O(2)−P−C(7)	85.3(1)	C(6)−C(7)−P	109.5(2)

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

P−O(1)	1.505(3)	P−C(7)	1.792(4)
P−O(2)	1.510(3)	P−C(15)	1.793(4)
O(1)−P−O(2)	115.0(2)	O(2)−P−C(15)	109.3(2)
O(1)−P−C(7)	110.0(2)	C(7)−P−C(15)	104.8(2)
O(2)−P−C(7)	107.2(2)	C(6)−C(7)−P	115.7(3)
O(1)−P−C(15)	110.0(2)		

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

P−O(1)	1.651(2)	P−O(2)	1.656(2)
P−C(15)	1.830(3)	P−N	3.152(3)
N−C(7)	1.455(4)	N−C(8)	1.450(4)
N−C(21)	1.452(4)		
O(1)−P−O(2)	100.5(1)	N−P−C(15)	154.0(1)
O(1)−P−C(15)	95.7(1)	C(8)−N−C(21)	112.1(2)
O(2)−P−C(15)	96.1(1)	C(8)−N−C(7)	114.2(2)
C(1)−O(1)−P	121.3(2)	C(21)−N−C(7)	111.8(3)
C(14)−O(2)−P	119.2(2)	N−C(7)−C(6)	110.4(3)
N−P−O(1)	67.38(8)	N−C(8)−C(9)	111.6(2)
N−P−O(2)	69.35(8)		

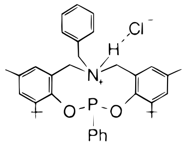
Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

P−O(2)	1.646(3)	P−O(1)	1.661(3)
P−C(15)	1.811(4)	P···N	3.987(3)
N(1)−H(1)	0.91[a]	H(1)···Cl	2.239[a]
N(1)−C(7)	1.508(5)	N(1)−C(8)	1.502(5)
N(1)−C(21)	1.501(5)		
O(2)−P−O(1)	97.9(1)	C(21)−N(1)−C(8)	112.3(3)
O(2)−P−C(15)	97.4(2)	C(21)−N(1)−C(7)	113.0(3)
O(1)−P−C(15)	100.1(2)	C(8)−N(1)−C(7)	112.8(3)
C(1)−O(1)−P	125.1(2)	C(6)−C(7)−N(1)	115.2(3)
C(14)−O(2)−P	120.2(2)	N(1)−C(8)−C(9)	111.8(3)
N(1)−H(1)···Cl	150.0[a]		

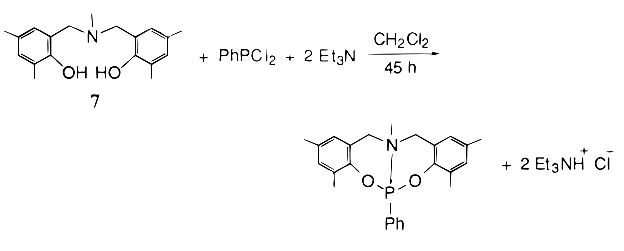
[a] These distances and directions involving H(1) are fixed.

the 40% probability level, and all hydrogen atoms are omitted for clarity. Ring conformations are shown in Figures 7−11 for **1** and **3**−**6**, respectively.

Synthesis. The synthesis of **3** and **4** followed the generally expected route in that a cyclic phenylphosphine formed, although in case of the formation of **4**, the cyclic product resulted as the amine hydrochloride salt. The process is illustrated for the reaction producing **3**, eq 1.



4



7

3 ^{31}P, 168.6 (1)

After the heating of **3** for 30 min at 140 °C in an NMR tube, a ^{31}P spectrum indicated that conversion to a phosphorane ($\delta(^{31}P) = -29$ ppm) and a small amount of phosphate took place. The phosphorane probably has an analogous formulation as **1** as evidence in the next section suggests.

In the formation of **1**, an entirely analogous diol reagent **8** that was employed to form **3** was used. However, the reaction took a different course and N−C bond cleavage occurred accompanied by oxidative addition in giving the bicyclic TBP phosphorane product. It seems reasonable to postulate that the expected product, as in the formation of **3** and **4**, may appear as an intermediate (**11**) in the formation of **1** and that an N−P interaction results to promote the cleavage of the N−C bond and concurrent rearrangement to form a P−C bond. This is expressed in eq 2.

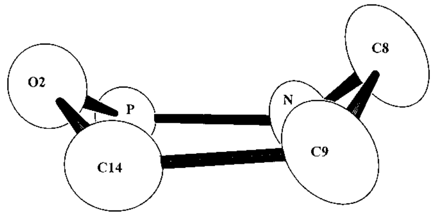


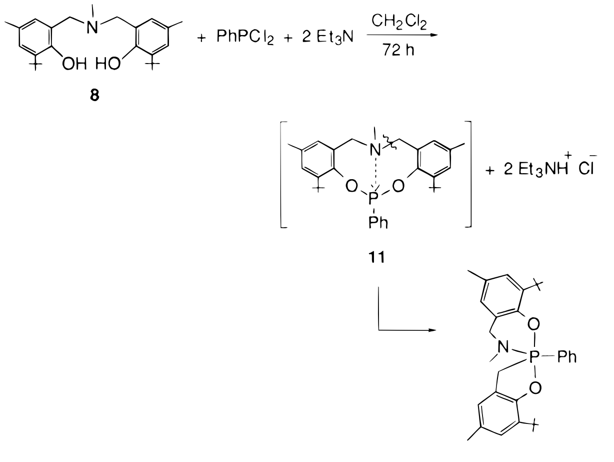
Figure 7. Boat conformation for the nitrogen-containing six-membered ring in **1**.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **5**

P−O(3)	1.479(3)	P−O(1)	1.603(3)
P−C(16)	1.781(4)	P−C(15)	1.816(4)
N−C(7)	1.471(5)	N−C(8)	1.480(5)
N−C(15)	1.459(5)		
O(3)−P−O(1)	114.4(2)	C(15)−N−C(7)	113.5(3)
O(3)−P−C(16)	113.8(2)	C(15)−N−C(8)	113.8(3)
O(1)−P−C(16)	100.2(2)	C(7)−N−C(8)	113.2(3)
O(3)−P−C(15)	114.4(2)	N−C(7)−C(6)	114.8(3)
O(1)−P−C(15)	104.2(2)	N−C(8)−C(9)	111.6(3)
C(16)−P−C(15)	108.5(2)	N−C(15)−P	117.0(3)
C(1)−O(1)−P	120.0(2)		

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **6**

P−O(1)	1.678(2)	P−O(4)	1.648(2)
P−O(2)	1.669(2)	P−O(5)	1.660(2)
P−O(3)	1.653(2)	P−N	2.143(3)
N−C(7)	1.492(4)	N−C(8)	1.491(4)
N−C(35)	1.484(4)		
O(4)−P−O(3)	94.5(1)	O(1)−P−N	83.5(1)
O(4)−P−O(5)	173.4(1)	C(1)−O(1)−P	130.2(2)
O(3)−P−O(5)	92.1(1)	C(14)−O(2)−P	125.8(2)
O(4)−P−O(2)	92.8(1)	C(15)−O(3)−P	128.9(2)
O(3)−P−O(2)	93.9(1)	C(21)−O(4)−P	141.7(2)
O(5)−P−O(2)	87.1(1)	C(27)−O(5)−P	132.5(2)
O(4)−P−O(1)	89.6(1)	C(35)−N−C(8)	108.5(3)
O(3)−P−O(1)	94.7(1)	C(35)−N−C(7)	108.9(3)
O(5)−P−O(1)	89.4(1)	C(8)−N−C(7)	106.2(3)
O(2)−P−O(1)	170.8(1)	C(35)−N−P	112.6(2)
O(4)−P−N	85.1(1)	C(8)−N−P	111.2(2)
O(3)−P−N	178.1(1)	C(7)−N−P	109.2(2)
O(5)−P−N	88.3(1)	N−C(7)−C(6)	114.4(3)
O(2)−P−N	87.9(1)	C(9)−C(8)−N	113.2(3)



8

11

1 ^{31}P, -27 (2)

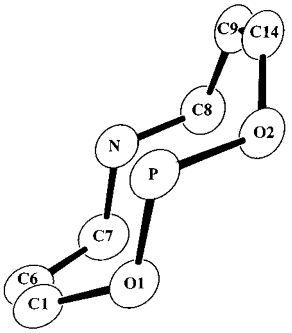


Figure 8. Winglike conformation for the nitrogen-containing ten-membered ring in **3**.

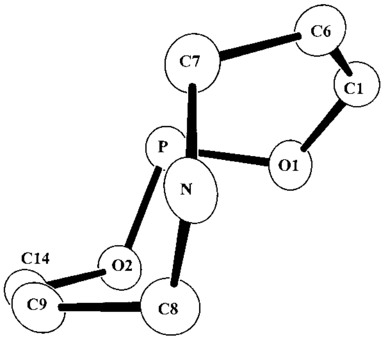
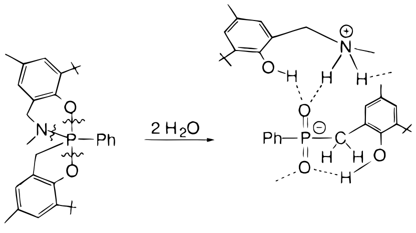


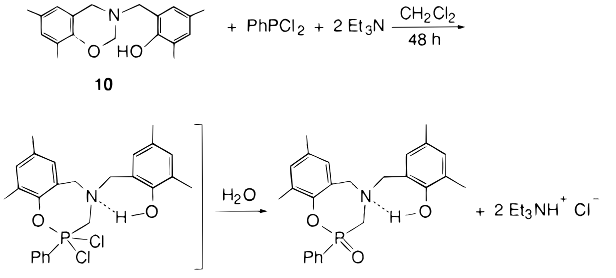
Figure 9. Twisted winglike conformation for the nitrogen-containing ten-membered ring in **4**.

In the hydrolysis of **1** which occurred during recrystallization to give the tetracoordinated acyclic phosphorus compound **2**, both P−O bonds as well as the P−N bond undergo cleavage.[29] The result is that the nitrogen atom of the displaced portion of **1** which lacks a phosphorus atom becomes protonated and this ammonium unit forms a hydrogen-bonded salt with the acyclic phosphorus component. Equation 3 expresses this sequence.



1 **2** ^{31}P, 32.3 (3)

In an attempt to obtain a nitrogen donor interaction in an acyclic three-coordinate phosphorus compound formed from the phenol **10**, a ring-opening reaction occurred with the rupture of the O−CH$_2$ bond. It is postulated that insertion of the phosphorus atom takes place to form the intermediate **12**, which gave the cyclic phosphoryl containing product **5** upon subsequent or concurrent hydrolysis, eq 4. Attempts to isolate **12** were unsuccessful.



10

12 **5**, ^{31}P 31.4 (4)

---

[29] Separately, phosphorane **1** was hydrolyzed directly with water. ^{31}P NMR confirmed that **2** was formed (50% yield) by observance of its chemical shift at 32.3 ppm.

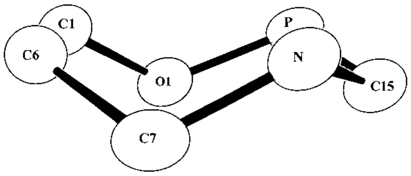


Figure 10. Chairlike conformation for the nitrogen-containing seven-membered ring in **5**.

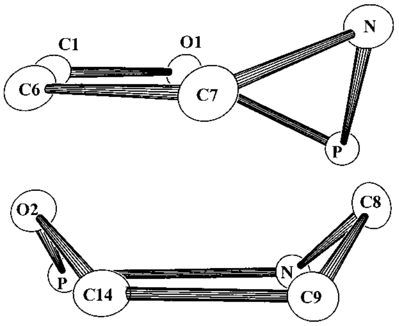
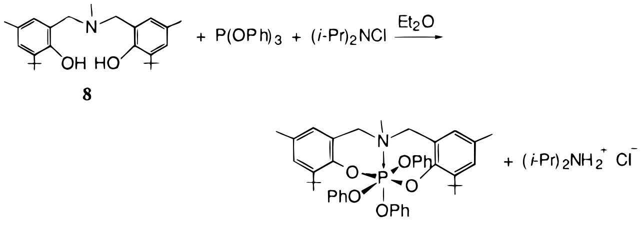


Figure 11. Conformations for the two six-membered rings in **6** resulting from P−N donor action. A twisted form is displayed in the upper part, and a boat form is displayed in the lower part.

In the synthesis of the phosphorane **1**, the formation of a P−C bond takes place while the N−C bond of the diol **8** undergoes cleavage. In the hydrolysis of **1** to give the acyclic derivative **2**, the P−C bond is retained while the other ligands attached to phosphorus are cleaved. The stability of the P−C bond is further indicated in the synthesis of the cyclic phosphinate **5** where a P−C bond is formed while O−C bond cleavage takes place at the reactant diol **10**. Hydrogen bonding also enters to help stabilize **2** and **5**.

In a final synthesis, the diol **8** used in the preparation of **1** was treated with triphenyl phosphite in the presence of *N*-chlorodiisopropylamine, whereupon an oxidative addition reaction took place yielding a pentaoxyphosphorane with P−N coordination, eq 5.



6 ^{31}P, -136 (5)

Structural Aspects. The six compounds studied by X-ray diffraction show phosphorus structures varying in coordination number from 3 to 6, all in cyclic formulations except **2**. Correspondingly, the ^{31}P solution chemical shifts vary from 177.8 ppm for **4** to −136 ppm for **6** in agreement with the coordination geometry at phosphorus and the nature of the attached substituents.[30−32] This serves as a good indication that the solid-state structures are retained in solution. In general, this is found to hold true for phosphorus compounds undergoing a change in physical state.[33]

Of the products obtained, P−N donor action was found for the hexacoordinate pentaoxyphosphorus compound **6** (Figure 6) and for **3** which was displaced toward a TBP (Figure 3). From a method previously used,[3,7] it is estimated that the structure of **6** is displaced 74% toward an ideal octahedron on the basis of the displacement of the phosphorus atom from the average plane of the four oxygen atoms that are cis to the nitrogen atom. The P−N distance is 2.143(3) Å which compares with the P−N single bond covalent radius of 1.85 Å.[34] Using the observed P−N value relative to the difference between the covalent sum of 1.85 Å and van der Waals sum of 3.35 Å,[35] a displacement of 80% toward an ideal octahedron is obtained for **6**.

The P−N distances for **3** and **4** whose ORTEX plots are in Figures 3 and 4, are much larger, 3.152(3) and 3.987(3) Å, respectively. The electrophilicity of the phosphorus atom for the pentaoxyphosphorane **6** is expected to be much higher than that for **3**.[36] In the latter lower coordinate compound, a lone pair and a phenyl group replace the electronegative oxygen ligands that are present in **6**. The lower degree of P−N donor action is borne out by comparing the observed P−N distance for **3** relative to the difference between the covalent sum and the van der Waals sum, as with **6**, a displacement of 24% toward a TBP is obtained. Due to the ammonium ion formation for **4**, P−N donor action is precluded. This accounts for the longer P−N distance compared to that for **3**. In compounds containing a more rigid cyclic system, **I**[16] and **J**,[17] shorter P−N distances are present compared to that for **3**, 2.869(3) and 2.706(6) Å, respectively. Interpolation, as above, shows the percent TBP character to be 34% and 45%, respectively, for **I** and **J**. However, due to the planarity restriction on the nitrogen system, it is not obvious to what degree donor action is taking place.

As commented on in the previous section, both the acyclic phosphinate **2** and the cyclic phosphinate **5** receive stabilization from the presence of hydrogen bonding. In the case of **2**, the network is extensive in that a hydrogen-bonded dimeric anion−cation formulation exists. Figure 2 illustrates one anion−cation unit, i.e., one-half of the dimeric unit. Of the hydrogen bonds shown in Figure 2, two of them are indicated to form between the separate halves of the dimer. They are designated as N−H--- and O(2)---. As a result of the presence of hydrogen bonding, each anion−cation has a seven-membered ring within the anion and an eight-membered ring that forms between the anion and cation. For **5**, hydrogen bonding forms a six-membered ring, Figure 5. The hydrogen bond parameters are listed in Table 8.

Ring Conformations. The cyclic systems formed all involve saturated rings. They vary in size from six- for **1** and six- to seven- for **5** to ten-membered for **3** and **4**. These are displayed in Figures 7−11 and indicate the flexibility achieved by employing large-membered rings in fixing structures. The six-membered rings for **1** (Figure 7) and one of these rings for **6** are in boat forms. Near-planarity exists for four of the six atoms involved. The other six-membered ring for **6** (Figure 11) has a twisted conformation which in contrast to the boat form

---

[30] Holmes, R. R. *Pentacoordinated Phosphorus-Structure and Spectroscopy*; ACS Monograph 175, American Chemical Society: Washington, DC, 1980; Vol. 1.

[31] Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur, Silicon* **1993**, *80*, 1−22.

[32] Quin, L. D., Verkade, J. G., Eds. *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; VCH Publishers: New York, 1994.

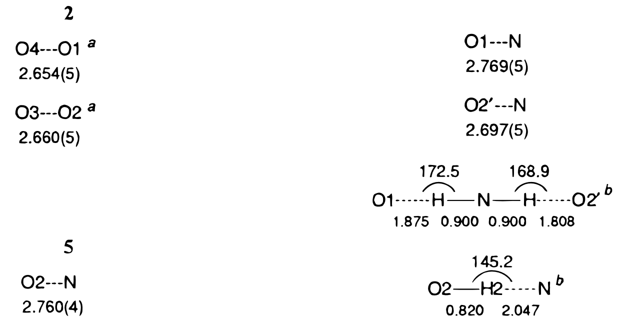
[33] Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230.

[34] *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.

[35] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[36] Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082−5089.

Table 8. Hydrogen Bond Distances (Å) and Angles (deg) for Phosphinates **2** and **5**



2	
O4---O1 [a] 2.654(5)	O1---N 2.769(5)
O3---O2 [a] 2.660(5)	O2′---N 2.697(5)
	172.5 168.9 O1······H—N—H······O2′ [b] 1.875 0.900 0.900 1.808
5	
O2---N 2.760(4)	145.2 O2—H2······N [b] 0.820 2.047

[a] The hydrogen atoms were not located. [b] These hydrogen atoms were placed in fixed positions.

exhibits a different flexibility by having the nitrogen and phosphorus atoms out of the plane of the other four atoms.

The only seven-membered ring is found for **5** (Figure 10), which shows a chairlike conformation. For the ten-membered rings, that for the cyclic phosphine **3** (Figure 8) exists in a winglike conformation. For the cyclic phosphine **4** with an analogous formulation in a salt structure, the ring conformation (Figure 9) is somewhat similar to that of **3** except C(7) has undergone a nearly 90° twist. The result is a less symmetrical arrangement compared to that for **3**. The winglike orientation places the phosphorus and nitrogen atoms adjacent to each other, in a position that is favorable for P—N coordination. In a similar manner, using flexible six- and eight-membered rings as discussed in the Introduction, donor coordination has been observed to take place in related phosphites **A**[2] and **D**,[15] in phosphines, e.g., **C**,[1b] and in phosphates, e.g., **B**,[15] with sulfur and oxygen donor atoms. It is anticipated that increased donor action with nitrogen will occur for tri- and tetracoordinated phosphorus compounds, based on this study, assuming that it is possible to increase the ligand electronegativity relative to that employed for **3**.

Summary and Conclusion

The first examples of phosphorus compounds incorporating ten-membered flexible ring systems that exhibit P—N donor action are reported. It is apparent that use of large flexible ring systems as supports for nitrogen atoms that may serve as potential donor atoms will allow such action to take place if the electrophilicity at phosphorus is sufficiently high. Conditions for strong P—N interaction to take place are found in the pentaoxyphosphorus compound **6** which meets this requirement in that both the higher valent state and the presence of five electronegative ligands are conducive to promoting a sufficiently high Lewis acidity at phosphorus. This is also possible in lower coordinate states if the ligand electronegativity requirement can be met as it has to a more modest extent with **3**, similar to that found for sulfur and oxygen donation to phosphorus in related compounds.[1b,2,15,36]

Acknowledgment. The support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates and *U* values, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1**—**6** (25 pages). Ordering information is given on any current masthead page.

IC980660T