Cyclic Aminophosphites and -phosphoranes Possessing Six- and Higher-Membered Rings: A Comparative Study of Structure and Reactivity

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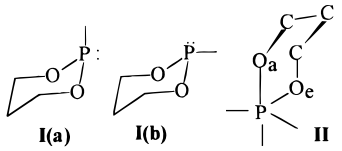
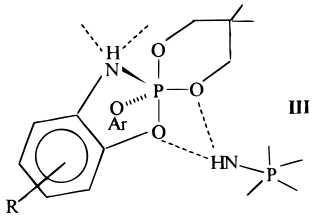
Aminophosphoranes **2** and **4**−**9** with a cyclohexylamino substituent and ring sizes varying from five to eight have been synthesized by oxidative addition reactions of cyclic aminophosphites with diols or 1,2-diketones. The reactivities of these phosphoranes are compared with those of the corresponding cyclic aminophosphites. The difference in hydrolytic pathways between amino- and analogous phenoxyphosphoranes is discussed. X-ray structures of two sets of compounds, (a) $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)$ (**1**) and $(C_6H_{11}NH)P(OCH_2CMe_2CH_2O)(1,2\text{-}O_2C_6Cl_4)$ (**2**) and (b) $(C_6H_{11}NH)P\{O\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2\}$ (**3**) and $(C_6H_{11}NH)P\{(O\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2\}(1,2\text{-}O_2C_6H_4)\cdot{}^1/_2Et_2O$ (**4**$\cdot{}^1/_2Et_2O$) have been determined and geometrical parameters compared between the P(III) and the corresponding P(V) compounds. In **1**, the six-membered ring has a chair conformation with the amino group axial; in **2**, the six-membered ring is located apical-equatorial in a trigonal bipyramidal geometry and has a boat conformation. The eight-membered ring has a boat-chair conformation in **3**, whereas the same ring has a tub conformation in **4**.

Introduction

Cyclic oxyphosphoranes in which the pentacoordinated phosphorus is part of a six- or higher-membered ring have been the subject of intensive structural investigations during the past few years.[1−5] Structural studies on the corresponding cyclic phosphites, particularly those with a 1,3,2-dioxaphosphorinane ring, have been mainly limited to the solution state,[6] except for one important study by Verkade and co-workers.[7] Normally, a change in conformation occurs for the 1,3,2-dioxaphosphorinane ring from a chair in the tricoordinated cyclic phosphite (**I**, solution state studies[6]) to a boat/twist in the pentacoordinated phosphorane (**II**, solid and solution state studies[1−4]). The



presence of H-bonding as in **III** can reduce the relatively small energy difference between the chair and boat conformations;[5] in fact, when R = H and Ar = $Me_2C_6H_2O$, a chair conformation was observed for the phosphorinane ring.[8] In this connection,



an aspect worth looking into is to introduce H-bonding into the phosphorane *via* an acyclic amino group such as -NHR. Such H-bonded systems may also have some bearing on our understanding of the mechanism of action of cyclo-AMP, which possesses a saturated 1,3,2-dioxaphosphorinane ring.[9]

One account of a comparison of the structures of tri- and pentacoordinated systems given by Holmes et al. relates to the compounds **IV** and **V**, which contain different acyclic groups.[4]

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(8) The other case wherein a chair conformation is found for the dioxaphosphorinane ring occupying an a−e position in a TBP arrangement is $(2,6\text{-}Me_2C_6H_3S)(C_6F_5O)_2P(OCH_2CMe_2CH_2O)$. Such an observation has been ascribed to a combination of an electronegativity effect and a steric effect: Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3132.
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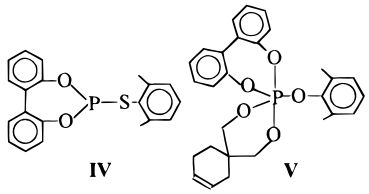
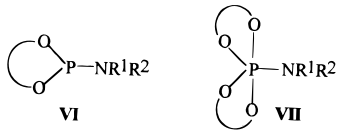
However, no conformational change was observed for the 1,3,2-dioxaphosphepin ring in this pair.



IV **V**

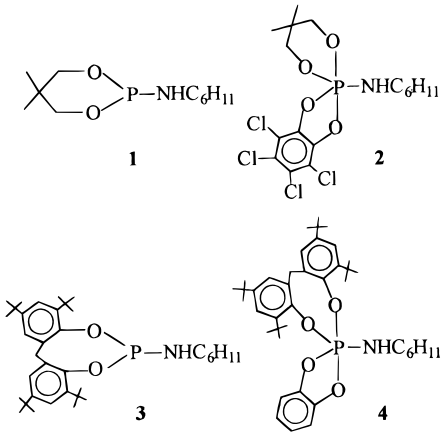
For structural studies as well as for a comparative assessment of the relative reactivity, a pair of substrates such as **VI** and **VII** is very useful because the acyclic amino substituent can lend itself as a replaceable group. Use of aminophosphines as



VI **VII**

precursors for cyclic phosphites is fairly common;[10] however, a knowledge of the relative ease of amino substitution in **VI** and **VII** is not available. This information could be useful for preparing phosphoranes with the desired substituents. Compounds of the type **VII** will also be helpful in assessing the ring size effects on ^{31}P NMR chemical shifts.[11] When R^1 = H, the effects of H-bonding on the structures may be investigated.

In this article, we report the X-ray structures of the pairs **1**, **2** and **3**, **4**·$^1/_2$Et$_2$O); the acyclic cyclo-C$_6$H$_{11}$NH group was chosen to introduce H-bonding. Synthesis and spectra of the



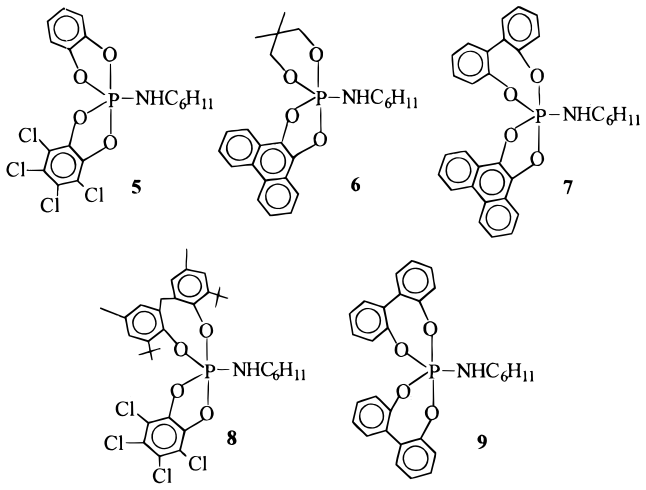
1 **2**

3 **4**

spirocyclic phosphoranes **5**−**9** and identification of related aminophosphoranes is also described; the relative reactivities of selected phosphoranes and their tricoordinated counterparts are compared.

Experimental Section

Chemicals were procured from Aldrich/Fluka or from the local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[12] All reactions, unless stated otherwise, were performed under dry nitrogen atmosphere. ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker 200 MHz spectrometer in CDCl$_3$ solutions (unless stated otherwise), with shifts referenced to SiMe$_4$ ($\delta = 0$) or 85% H$_3$PO$_4$ ($\delta = 0$). IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer.



5 **6** **7**

8 **9**

The cyclic compounds (C$_6$H$_{11}$NH)P(OCH$_2$CMe$_2$CH$_2$O) (**1**), (C$_6$H$_{11}$NH)P{(O-(*t*-Bu)$_2$C$_6$H$_2$)$_2$CH$_2$} (**3**), (C$_6$H$_{11}$NH)P(1,2-O$_2$C$_6$H$_4$) (**10**), (C$_6$H$_{11}$NH)P(2,2′-OC$_6$H$_4$-C$_6$H$_4$O) (**11**), and (2,6-Me$_2$C$_6$H$_3$O) P(OCH$_2$CMe$_2$CH$_2$O)(1,2-O$_2$C$_6$Cl$_4$) (**X**) were prepared as described before.[13] The compound (C$_6$H$_{11}$NH)P{(O-(2-*t*-Bu)(4-Me)C$_6$H$_2$)$_2$CH$_2$} (**12**) was also prepared similarly. More physical data for **1** and **3** are described below; data for other compounds are given as Supporting Information.

1 (sublimed product used as such for X-ray crystallography): mp 78 °C (bp 136 °C/0.5 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.92 (s, 3H, C*H*$_3$), 1.02 (s, 3H, C*H*$_3$), 1.00−2.10 (m, 10H, cyclohexyl-*H*), 2.95 (br, 1H, N*H*), 3.20 (br, 1H, N-C*H*), 3.60−3.85 (m, 4H, OC*H*$_2$); ^{13}C NMR δ 21.94, 22.81 (two s, *C*H$_3$), 25.4, 25.6 (s each, C*C*H$_2$), 32.75 (d, ^3J = 6.5 Hz, *C*Me$_2$), 37.30 (d, J = 3.5 Hz, NC*C*H$_2$), 49.65 (d, ^2J = 15.5 Hz, N*C*H), 72.07 (s, O*C*H$_2$); ^{31}P NMR δ 132.1. Anal. Calcd for C$_{11}$H$_{22}$NO$_2$P: C, 57.14; H, 9.52; N, 6.06. Found: C, 57.01; H, 9.50; N, 6.51.

The unsublimed but recrystallized (from *n*-hexane) product showed essentially the same ^{1}H and ^{31}P NMR spectra [δ_P of 118.8 ppm reported earlier[13] is incorrect]. Even in toluene-d_8, we could not effect clear-cut separation of the peaks for calculating the coupling constants.

3 (recrystallized from hexane for X-ray work): mp 212 °C; ^{1}H NMR δ 1.32 (s, 18H, *t*-Bu-*H*), 1.45 (s, 18H, *t*-Bu-*H*), 1.10−2.25 (m, 10H, cyclohexyl-*H*), 2.90 (dd, $^2J \approx 25$ Hz, $^3J \approx 11$ Hz, 1H, N*H*), 3.42 (d, $^2J \approx 14$ Hz, 1H, C*H*$_A$H$_B$), 3.75 (br, 1H, N-C*H*), 4.42 (dd, $^2J \approx 14$ Hz, J(*P*−*H*) ≈ 3 Hz), 7.20−7.40 (m, 4H, Ar-*H*); ^{31}P NMR δ 140.9. Anal. Calcd for C$_{35}$H$_{54}$NO$_2$P: C, 76.22; H, 9.80; N, 2.54. Found: C, 76.10: H, 9.65; N, 2.54.

The phosphoranes **2** and **4**−**9** were prepared by oxidative addition reactions of quinones (procedure a) or diols (procedure b) to the phosphites; only typical procedures are given.

(i) Preparation of (C$_6$H$_{11}$NH)P(OCH$_2$CMe$_2$CH$_2$O)(1,2-O$_2$C$_6$Cl$_4$) (2) (Procedure a). Tetrachloro-*o*-benzoquinone (0.3 g, 1.58 mmol) was added to **1** (0.36 g, 1.58 mmol) in dry toluene (5 mL). The mixture was stirred for 10 min, solvent removed *in vacuo*, and the residue crystallized from dichloromethane−hexane mixture (1:2). Yield: 0.45 g (60%); mp 127 °C; ^{1}H NMR δ 0.90−2.10 (m, 10H, cyclohexyl-*H*), 1.00 (s, 3H, C*H*$_3$), 1.05 (s, 3H, C*H*$_3$) 3.03 (br dd, 1H, N*H*), 3.32 (br, 1H, NC*H*), 3.94 (d, $J \approx 20$ Hz, 4H, OC*H*$_2$); ^{31}P NMR δ −45.7. Anal. Calcd for C$_{17}$H$_{22}$Cl$_4$NO$_4$P: C, 42.78; H, 4.61; N, 2.94. Found: C, 42.61; H, 4.60; N, 3.00.

(ii) Preparation of (C$_6$H$_{11}$NH)P{(O-*t*-Bu)$_2$C$_6$H$_2$)$_2$CH$_2$}(1,2-O$_2$C$_6$H$_4$)·$^1/_2$Et$_2$O (4·$^1/_2$Et$_2$O) (Procedure b). To a mixture of **10** (1.25 g, 5.28 mmol) and CH$_2$[(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ (2.24 g, 5.28 mmol) in dry ether (40 mL) maintained at −60 °C was added *N*-chlorodiisopropylamine (0.72

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g, 5.28 mmol) in ether (30 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30 °C, stirred overnight, and filtered. The product was crystallized from a mixture of dichloromethane−hexane (1:2). Yield: 2.5 g (72%); mp 173−5 °C; IR (cm^{-1}) 3440 (ν (N−H)); ^{1}H NMR δ 1.03−2.03 (m, 46H, cyclohexyl-*H* + *t*-Bu-*H*), 3.32−3.52 (br, 2H, N*H* + NC*H*), 4.07 (br d, 1H, CH_AH_B), 4.60 (br d, 1H, CH$_A$*H*$_B$), 6.72−7.35 (m, 8 H, Ar-*H*); ^{31}P NMR δ −56.3, −56.8 (these values were too close to ascertain the exact shift for the crystal chosen for X-ray). Anal. Calcd for $C_{41}H_{58}NO_4P$ (after evacuating at 0.3 mmHg for 3 h): C, 74.60; H, 8.80; N, 2.12. Found: C, 73.93; H, 9.05; N, 2.10.

(iii) Preparation of (C$_6$H$_{11}$NH)P(1,2-O$_2$C$_6$H$_4$)(1,2-O$_2$C$_6$Cl$_4$) (5) (Procedure a). Quantities used: phosphite **10**, 0.90 g, 3.79 mmol; tetrachloro-1,2-benzoquinone, 0.93 g, 3.79 mmol. Yield: 1.1 g (60%, after recrystallization from dichloromethane−hexane (1:2)); mp 182 °C; IR (cm^{-1}) 3368 (sharp); ^{1}H NMR δ 1.05−1.95 (m, 10H, cyclohexyl-*H*), 3.10−3.35 (m, 2H, N*H* and NC*H*), 6.80−7.30 (m, 4H, Ar-*H*); ^{31}P NMR δ −29.4. Anal. Calcd for $C_{18}H_{16}Cl_4NO_4P$: C, 44.74; H, 3.31; N, 2.90. Found: C, 44.53; H, 3.29; N, 3.76.

(iv) Preparation of (C$_6$H$_{11}$NH)P(OCH$_2$CMe$_2$CH$_2$O)(9,10-O$_2$C$_{14}$H$_8$) (6) (Procedure a). Quantities used: phosphite **1**, 0.76 g, 3.31 mmol; 9,10-phenanthrenequinone, 0.69 g, 331 mmol. Yield: 0.9 g (62%); mp 158 °C; IR (cm^{-1}) 3350 (sharp); ^{1}H NMR δ 1.03, 1.08 (two s, 6H, 2CH_3), 1.00−2.20 (m, 10H, cyclohexyl-*H*), 3.12 (dd, 1H, N*H*), 3.21 (m, 1H, NC*H*), 3.90−4.20 (m (AB), 4H, OCH_2), 7.40−8.65 (m, 8H, Ar-*H*); ^{31}P NMR δ −46.2. Anal. Calcd for $C_{25}H_{30}NO_4P$: C, 68.34; H, 6.83; N, 3.20. Found: C, 68.21; H, 6.75; N, 3.50.

(v) Preparation of (C$_6$H$_{11}$NH)P(2,2′-OC$_6$H$_4$-C$_6$H$_4$O)(9,10-O$_2$C$_{14}$H$_8$) (7) (Procedure a). Quantities used: phosphite **11**, 03.2 g, 10.51 mmol; 9,10-phenanthrenequinone, 2.19 g, 10.51 mmol. Yield (after recrystallization from dichloromethane−hexane (1:2)): 3.5 g (64%); mp 185 °C; IR (cm^{-1}) 3381, 3450 (ν (N−H)); ^{1}H NMR δ 0.90−2.20 (m, 10H, cyclohexyl-*H*), 3.25−3.60 (m, 2H, N*H* and NC*H*), 7.22−8.72 (m, 16H, Ar-*H*); ^{31}P NMR δ −34.4. Anal. Calcd for $C_{32}H_{28}NO_4P$: C, 73.70; H, 5.37; N, 2.69. Found: C, 73.17; H, 5.46; N, 3.13.

(vi) Preparation of (C$_6$H$_{11}$NH)P{(O-(2-*t*-Bu)(4-Me)C$_6$H$_2$)$_2$CH$_2$}((O$_2$C$_6$Cl$_4$) (8) (Procedure a). Quantities used: phosphite 12, 1.34 g, 2.88 mmol; tetrachloro-*o*-benzoquinone, 0.71 g, 2.88 mmol; and benzene, 5 mL [*Warning:* Benzene is a carcinogen; all operations involving this solvent should be performed inside an efficient hood.] Yield (after crystallization from dichloromethane−hexane mixture (1:2)): 1.1 g (54%); mp 118 °C; IR (cm^{-1}) 3366 (sharp, ν (N−H)); ^{1}H NMR δ 0.72−2.52 (m, 34H, cyclohexyl-*H* + CH_3), 3.25−3.70 (m, 3H, CH_AH$_B$ + N*H* + NC*H*), 4.55 (d, 1H, ^2J = 14 Hz, CH$_A$*H*$_B$), 6.75−7.15 (m, 4H, Ar-*H*); ^{31}P NMR δ −54.6. Anal. Calcd for $C_{35}H_{42}Cl_4NO_4P$: C, 58.92; H, 5.89; N, 1.96. Found: C, 59.05; H, 6.10; N, 1.76.

(vii) Preparation of (C$_6$H$_{11}$NH)P(2,2′-OC$_6$H$_4$C$_6$H$_4$O)$_2$ (9) (Procedure b). Quantities used: phosphite 11, 1.25 g, 3.99 mmol; 2,2′-biphenol, 0.74 g, 3.99 mmol; and *N*-chlorodiisopropylamine, 0.54 g, 3.99 mmol. Yield (after crystallization from dichloromethane−hexane (1:2)): 1.5 g (79%); mp 209−212 °C; ^{1}H NMR δ 0.80−2.10 (br m, 10H, cyclohexyl-*H*), 3.35 (br, 2H, N*H* + NC*H*), 6.90−7.65 (m, 16H, Ar-*H*); ^{31}P NMR δ −39.6. Anal. Calcd for $C_{30}H_{28}NO_4P$: C, 72.43; H, 5.63; N, 2.82. Found: C, 72.42; H, 6.03; N, 2.57.

(viii) Preparation of (C$_6$H$_{11}$NH)P(O)(OCH$_2$CMe$_2$CH$_2$O) (13). This compound was prepared by reacting (OCH$_2$CMe$_2$CH$_2$O)P(O)Cl[14] with 2 mol equiv of cyclohexylamine in diethyl ether: mp 172 °C; ^{1}H NMR δ 0.88 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 0.88−2.12 (m, 10H, cyclohexyl-*H*), 2.72 (m, 1H, N*H*), 3.10 (br, 1H, NC*H*), 3.80 (dd, 2H, OCH_2(A)), 4.30 (dd, 2H, OCH_2(B)); ^{31}P NMR δ 4.4. Anal. Calcd for $C_{11}H_{22}NO_3P$: C, 53.44; H, 8.91, N, 5.67. Found: C, 53.82; H, 9.32; N, 6.48.

(ix) Reaction of 1 with Ethylene Glycol/*N*-Chlorodiisopropylamine (Procedure b). Quantities used: phosphite **1**, 1.55 g, 6.71 mmol; ethylene glycol, 0.42 g, 6.71 mmol; and *N*-chlorodiisopropylamine, 0.91 g, 6.71 mmol. The compounds **13** (0.3 g, 20%) and [(OCH$_2$CH$_2$O)$_2$P]$_2$(OCH$_2$CMe$_2$CH$_2$O) (**14**, 0.2 g, 14%) were isolated by fractional crystallization from the reaction mixture. Compound **14** (very hygroscopic): mp 145 °C; ^{1}H NMR δ 0.93 (s, 6H, CH_3), 3.65−3.95 (m, 20H, OCH_2); ^{31}P NMR δ −28.1. Anal. Calcd for $C_{13}H_{26}O_{10}P_2$: C, 38.61; H, 6.44. Found: C, 40.18; H, 7.11.

Reactivity of Cyclic Phosphites and Phosphoranes. (i) Hydrolysis. Compound **2** (0.085 g) was dissolved in THF (5 mL) and kept in open air until all the solvent evaporated (*ca.* 24 h). Analysis of the product mixture by ^{31}P and ^{1}H NMR, after completely evaporating the solvent *in vacuo*, showed that it contained **13** (δ_P 4.2; 40%) and other unidentified products [δ_P −2.5 *ca.* 45%), −8.6 (*ca.* 10%), −7.5 (*ca.* 3%)]; the compound (OCH$_2$CMe$_2$CH$_2$O)P(HOC$_6$Cl$_4$O) (**15**) was not detected.

Under identical conditions using similar molar quantities, **1** hydrolyzed to HOCH$_2$CMe$_2$CH$_2$OP(O)(H)(O)$^-$(H$_3$NC$_6$H$_{11}$)$^+$ (**IX**) quantitatively, whereas **6** and **7** were recovered unchanged. The compound **X**[13] gave **15** (50%): mp 215 °C; ^{1}H NMR δ 0.99 (s, 3H, CH$_3$), 1.38 (s, 3H, CH$_3$), 4.08 (dd, J = 11.0, 23.6 Hz, 2H, OCH_2(A)), 4.60 (d, J = 11.0 Hz, OCH_2 (B)); ^{31}P NMR δ −11.4. Anal. Calcd for $C_{11}H_{11}Cl_4O_5P$: C, 33.33; H, 2.77. Found: C, 33.64; H, 2.90. The same compound **15** was obtained as a major isolable product (50%) when (PhO)P(OCH$_2$CMe$_2$CH$_2$O) was reacted with *o*-chloranil.

(ii) Reaction with 8-Hydroxyquinoline. A mixture of **1** (0.19 g, 0.83 mmol) and 8-hydroxyquinoline (0.12 g, 0.83 mmol) in toluene (10 mL) was heated under reflux for 5 h. The compound (NC$_9$H$_6$O)P(OCH$_2$CMe$_2$CH$_2$O) (**XI**) [δ_P 113.8;[15] isolated] was obtained quantitatively.

Under identical conditions, **6** and **13** did not react.

Compound **11** reacted with 8-hydroxyquinoline (1.67 mmol each) in refluxing *p*-xylene (20 mL, 10 h) to give (NC$_9$H$_6$O)P(2,2′-OC$_6$H$_4$-C$_6$H$_4$O) (**XII**) (15%, δ_P 140.1), **11** (80%), and another product (5%) with δ_P of 11.6 ppm. The pentacoordinated derivatives **7** and **17** did not react under identical conditions.

X-ray Crystallography Experimental Section. Crystal data for **1**−**3** and **4**·$^1/_2$Et$_2$O are summarized in Table 1. Data for **1**, **2**, and **4**·$^1/_2$Et$_2$O were collected at −120 °C on a Stoe-Siemens-Huber diffractometer and for **3** at −80 °C on a Stoe-Siemens-AED diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods.[16] All non-hydrogen atoms were refined anisotropically.[17] For the hydrogen atoms bonded to carbon atoms, the riding model was used. The hydrogens bonded to nitrogen were refined with distance restraints. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$, with $P = (F_o^2 + 2F_c^2)/3$. The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$.

In structures **3** and **4**·$^1/_2$Et$_2$O, one *tert*-butyl group is disordered. The anisotropic displacement parameters of the carbon atoms opposite to each other are fixed to the same values. Also, distance restraints were used. Additionally, in structure **4**·$^1/_2$Et$_2$O, the ether molecule is severely disordered. It is refined with distance restraints and restraints for the displacement parameters. In structure **1**, there are four independent molecules in the asymmetric unit. Each two of them are related by a pseudoinversion center at −0.118, 0, −0.106. A transformation to a centrosymmetric space group was not possible.

Results and Discussion

Synthesis, Reactivity, and Spectra. The pentacoordinated compounds **2** and **4**−**9** are readily synthesized by oxidative addition reaction of the cyclic phosphite with a quinone (**2**, **5**−**8**) or a diol (**4**, **9**). The reaction using diol is illustrated for the synthesis of **4** (eq 1). However, when (C$_6$H$_{11}$NH)P(OCH$_2$CMe$_2$-CH$_2$O) (**1**) was reacted with ethylene glycol/ClN(*i*-Pr)$_2$, we could not isolate the expected phosphorane, (C$_6$H$_{11}$NH)P(OCH$_2$CMe$_2$-CH$_2$O)(OCH$_2$CH$_2$O) (**VIII**); instead, the phosphoramidate **13** and a diphosphorane formulated as [(OCH$_2$CH$_2$O)$_2$]$_2$P(OCH$_2$-CH$_2$O) (**14**) were isolated as crystalline solids (eq 2). It can be noted that δ_P for **14** is close to that of the monophosphorane

(14) Zwierzak, A. *Can. J. Chem.* **1954**, *37*, 1498.

(15) Said, M. A.; Pülm, M.; Irmer, R. H.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **1996**, *118*, 9841.

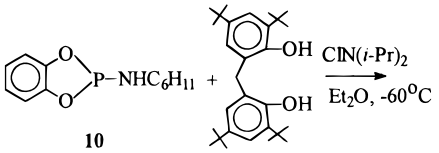
(16) Sheldrick, G. M. SHELXS-90. *Acta Crystallogr.* **1990**, *A46*, 467.

(17) Sheldrick, G. M. SHELXS-93, University of Göttingen, 1993.

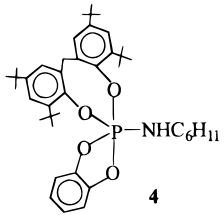
Table 1. Crystal Data for **1**−**4**

	1	**2**	**3**	**4**·$^1/_2$Et$_2$O
empirical formula	$C_{11}H_{22}NO_2P$	$C_{17}H_{22}Cl_4NO_4P$	$C_{35}H_{54}NO_2P$	$C_{41}H_{58}NO_4P$·0.5$(CH_3CH_2)_2O$
formula weight	231.27	477.13	551.76	696.91
crystal system	orthorhombic	monoclinic	triclinic	monoclinic
space group	*Pna*2$_1$	*P*2$_1$/*c*	*P*$\bar{1}$	*P*2$_1$/n
a/Å	18.287(2)	9.845(1)	9.676(3)	9.499(1)
b/Å	15.157(1)	17.923(4)	13.060(3)	18.971(1)
c/Å	18.541(3)	12.344(2)	13.969(4)	23.478(2)
α/deg	90	90	96.97(2)	90
β/deg	90	107.47(1)	103.96(2)	95.93(1)
γ/deg	90	90	96.53(2)	90
V/Å^3	5139(1)	2077.7(6)	1681.6(8)	4208.2(6)
Z	16	4	2	4
D_{calc}/g cm^{-3}	1.196	1.525	1.090	1.100
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73
T/°C	−120	−120	−80	−120
μ/cm^{-1}	1.98	6.70	1.11	1.05
F(000)	2016	984	604	1516
cryst size/(mm^3)	0.5 × 0.4 × 0.2	0.6 × 0.4 × 0.4	0.6 × 0.4 × 0.4	0.6 × 0.5 × 0.4
2*θ* range	7−45	4−50	5−45	7−50
reflect coll	8219	4945	4941	9259
indep reflect	6689	3681	4406	7458
R_{int}	0.0395	0.0205	0.0669	0.0599
data	6658	3672	4403	7453
parameters	561	249	375	537
restraints	7	1	31	240
S	1.021	1.052	1.027	1.028
R_1 [I > 2*σ*(I)][a]	0.0584	0.0382	0.0585	0.0634
wR_2)all data)[a]	0.1210	0.1107	0.1639	0.1864
Flack *x*[18]	0.0(1)			
largest diff peak/eÅ^{-3}	0.241	0.440	0.398	0.669
largest diff hole/eÅ^{-3}	−0.210	−0.355	−0.297	−0.406

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$.

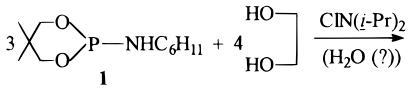


10

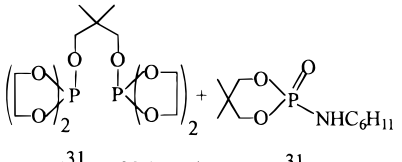


4 (1)

(EtO)P[OCH$_2$CH$_2$O]$_2$ (δ_P −27.0 ppm[19]). Compound **14** is very sensitive to moisture.

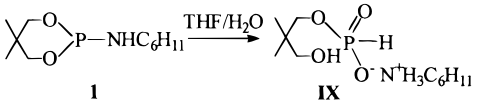


1

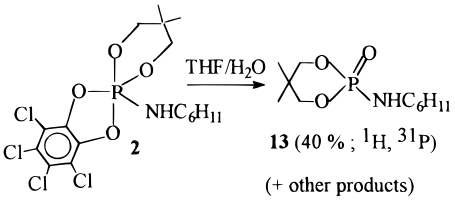


14 (^{31}P: -28.1 ppm) **13** (^{31}P: 4.2 ppm) (2)

Hydrolytically, **1** is much less stable than **2**, **6**, or **13**. As reported by us before,[13] the ring-opened product **IX** is obtained upon treating **1** with THF/water; even exposing a THF solution of **1** to air for 24 h leads to **IX** quantitatively (eq 3). The pentacoordinated **2** hydrolyzed to give **13** as one of the major products (eq 4); the identity of **13** is confirmed by an

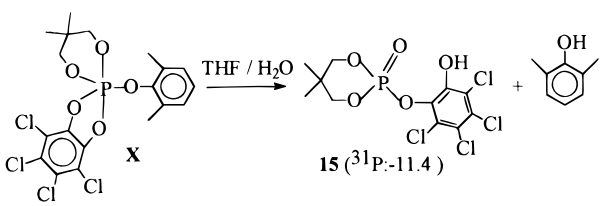


1 **IX** (3)



2 (4)

independent synthesis. This reaction is interesting because, when the (2,6-dimethylphenoxy)phosphorane **X**[13] is hydrolyzed, the crystalline product obtained, **15**, has the five-membered ring residue connected to phosphorus (eq 5); this latter product is *not detected* in the hydrolysis of **2** (^{31}P NMR). The rationale



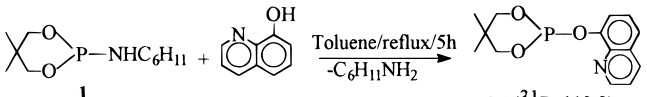
X **15** (^{31}P:-11.4) (5)

for the difference in the hydrolysis of **2** and **X** may lie in the relative apicophilicities of the NHC_6H_{11} and OPh groups in a trigonal bipyramidal environment.

As can be expected,[10] the cyclohexylamino group in **1** can be readily replaced by an aryloxy group (eq 6). By contrast,

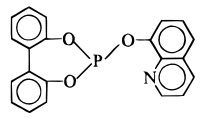
(18) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
(19) Chang, B. C.; Conrad, W. E.; Denney, D. B.; Denney, D. Z.; Edelman, R.; Powell, R. L.; White, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 4004.

both **13** and the aminophosphorane **2** do not undergo replacement of the NHC_6H_{11} group under similar experimental conditions. The replacement of the amino group in **11** is not as facile



(6)

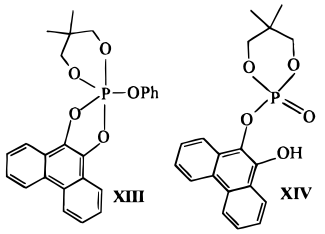
as it is in **1**, and the product **XII** is formed in 15% yield after refluxing **11** with 8-hydroxyquinoline for 10 h in *p*-xylene. The



XII (^{31}P: 140.1)

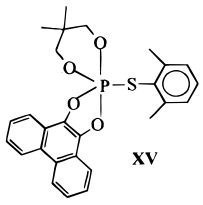
corresponding pentacoordinated derivative **7** does not react; both the eight-membered ring compounds **3** and **4** are also unreactive, probably due to steric factors.

The difference in reactivity between the tri- and pentacoordinated amino compounds cannot be simply due to steric factors, because the pentacoordinated phenoxy derivative **XIII**[20] is readily hydrolyzed[21] in THF solution to the ring-opened product **XIV**, whereas the corresponding amino compound **6** is resistant

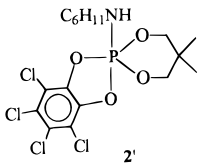


to hydrolysis under these conditions; thus, there does not appear to be severe hindrance for nucleophilic attack. At this point, we can only say that both lability and strength of the P−N bond may contribute to the difference. In fact, it can be noted that the P−N bond is longer in the phosphites **1** and **3**, *albeit marginally*, than in the phosphoranes **2** and **4**, respectively (see X-ray section).

The OCH_2 region in the ^{1}H NMR spectrum (24 °C) of **6** is similar to that observed for **XV**; **2** shows a broad doublet



[^3J(P−H) = 20 Hz] for the OCH_2 protons, which is analogous to the high-temperature (≥41 °C) spectrum of **XV**. We ascribe these features to the a-e ⇔ e-a processes in a TBP structure as described by Holmes *et al.*,[2a] with the difference that a diequatorial disposition of the six-membered ring as shown in **2′** could contribute to the equivalence of protons in **2**.



The ^{31}P NMR data for the aminophosphoranes listed according to ring size are shown in Table 2. As observed for tetra-[22] and hexacoordinated phosphoranes,[15] *five*- and *seven*-membered

Table 2. ^{31}P NMR Data for Aminophosphoranes Along with Ring System Assignment

compound no.[a]	ring system	δ_P (ppm)	compound no.[a]	ring system	δ_P (ppm)
5	5 + 5	−29.4	**4**	5 + 8	−56.3, −56.8
16	5 + 5	−28.2	**8**	5 + 8	−54.6
2	5 + 6	−45.5	**18**	6 + 7	−54.2
6	5 + 6	−46.2	**19**	6 + 8	−70.3
7	5 + 7	−34.4	**9**	7 + 7	−39.6
17	5 + 7	−36.6	**20**	7 + 8	−58.8

[a] Compound **17** is pure by ^{31}P NMR but could not be crystallized; **16** and **18**−**20** have been identified by NMR but not isolated in a pure state

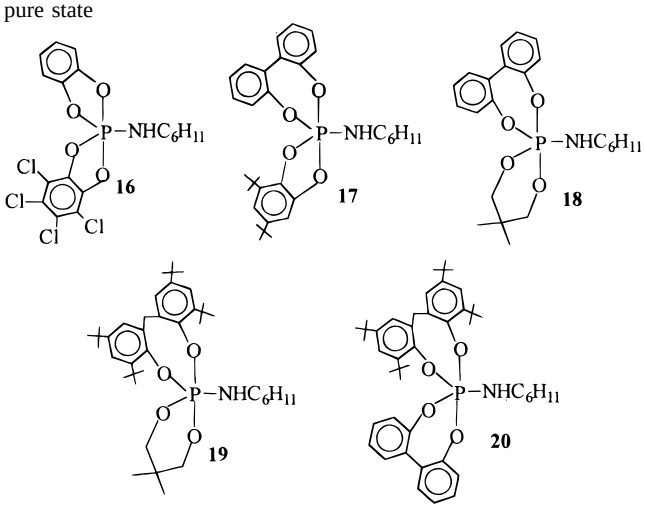


Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

P(1)−O(2)	1.624(5)	P(1)−O(1)	1.642(4)
P(1)−N(1)	1.652(5)	P(2)−O(3)	1.637(4)
P(2)−O(4)	1.638(5)	P(2)−N(2)	1.657(5)
P(3)−O(5)	1.629(5)	P(3)−O(6)	1.636(4)
P(3)−N(3)	1.646(5)	P(4)−O(8)	1.632(5)
P(4)−O(7)	1.638(4)	P(4)−N(4)	1.671(5)
O(2)−P(1)−O(1)	98.6(2)	O(2)−P(1)−N(1)	107.7(3)
O(1)−P(1)−N(1)	101.3(2)	O(3)−P(2)−O(4)	99.3(3)
O(3)−P(2)−N(2)	100.7(2)	O(4)−P(2)−N(2)	106.9(3)
O(5)−P(3)−O(6)	98.9(2)	O(5)−P(3)−N(3)	108.1(3)
O(6)−P(3)−N(3)	100.4(2)	O(8)−P(4)−O(7)	99.7(2)
O(8)−P(4)−N(4)	107.3(3)	O(7)−P(4)−N(4)	100.6(3)

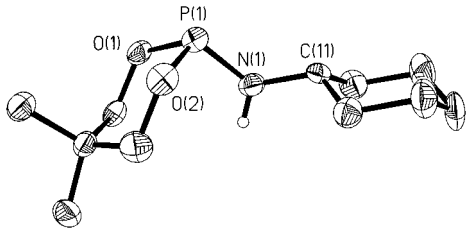


Figure 1. ORTEP plot of **1**. Only phosphorus, nitrogen, oxygen, and the carbon connected to nitrogen are labeled.

(20) Sarma, R.; Ramirez, F.; Mckeever, B.; Marecek, J. F.; Lee, S. *J. Am. Chem. Soc.* **1976**, *98*, 581.

(21) In fact, the hydrolyzed compound was obtained earlier in an attempt to prepare the pentaoxyphosphorane[20] by the oxidative addition of the quinone to the phosphite, see: Gallucci, J. C.; Holmes, R. R. *Inorg. Chem.* **1980**, *19*, 3540.

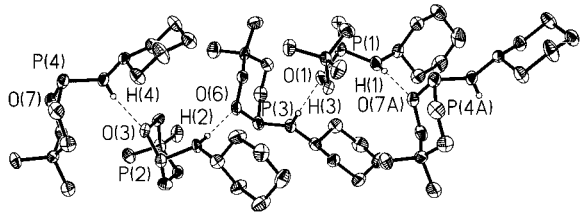


Figure 2. ORTEP plot of **1** showing the H-bonding interactions.

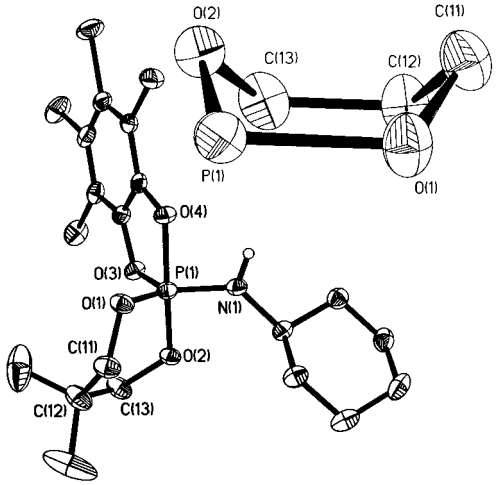
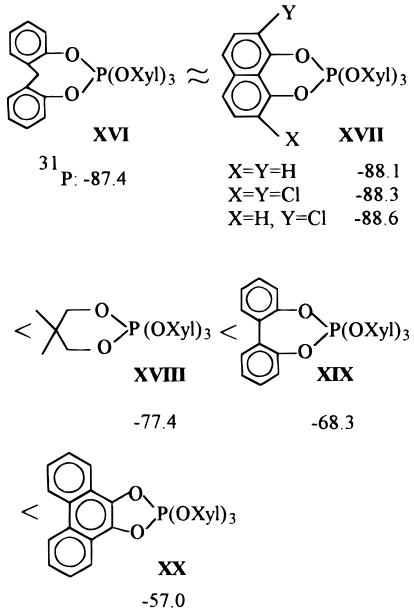


Figure 3. ORTEP plot of **2**. Only the phosphorus atom and those connected to it are labeled. Also shown is the conformation of the 1,3,2-dioxaphosphorinane ring with all the ring atoms labeled.

rings tend to deshield the phosphorus relative to *six*- and *eight*-membered rings. This effect has also been observed for pentaoxyphosphoranes **XVI**−**XX** reported by Holmes *et al.*[3a,11] These data are suggestive of a ring size effect, with five- as well as seven-membered rings deshielding the phosphorus in ^{31}P NMR.



Structural Aspects. Compound **1** crystallizes in space group $Pna2_1$ with four independent but similar molecules in the asymmetric unit. In Figure 1, the structure and atomic labeling of one of the molecules is shown, while selected bond lengths and angles of all four molecules are listed in Table 3. All molecules are connected by hydrogen bonds [H(1)−O(7A) = 2.22(3), H(2)−O(6) = 2.18(3), H(3)−O(1) = 2.23(3), and H(4)−O(3) = 2.18(3) Å], leading to chains (Figure 2). In the pentacoordinated compound **2** (Figure 3), by contrast, hydrogen

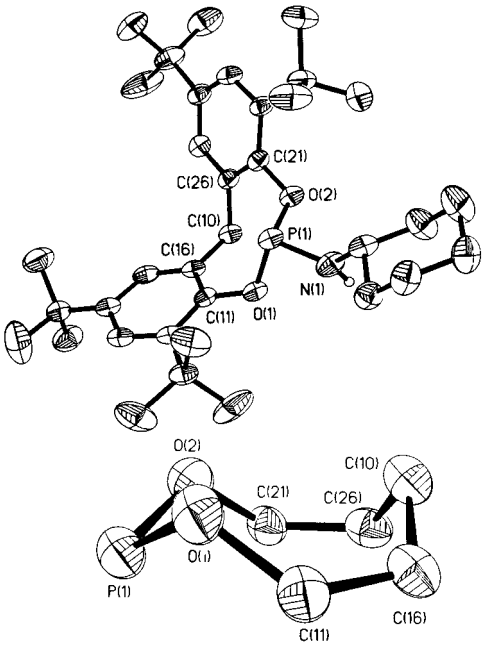


Figure 4. ORTEP plot of **3**. Only the phosphorus, nitrogen, and atoms of the eight-membered ring are labeled. Also shown at the bottom is the conformation of the 1,3,2-dioxaphosphocin ring.

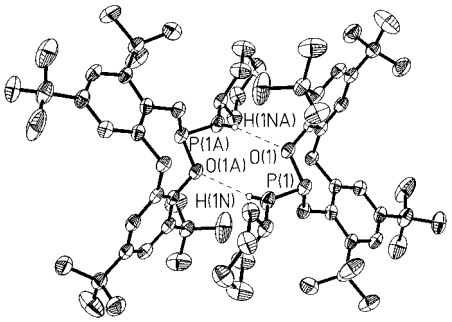


Figure 5. ORTEP plot of **3** showing H-bonding interactions.

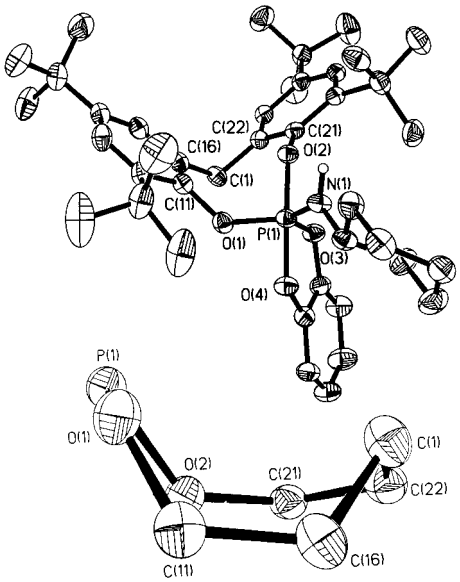


Figure 6. ORTEP plot of **4**. Atoms of the 1,3,2-dioxaphosphocin ring and those connected to phosphorus are labeled. Also shown at the bottom is the conformation of the 1,3,2-dioxaphosphocin ring.

(22) Said, M. A.; Kumara Swamy, K. C.; Chandra Mohan, K.; Venkata Lakshmi, N. *Tetrahedron* **1994**, *50*, 6989.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**

P(1)−O(1)	1.5929(19)	P(1)−N(1)	1.619(2)
P(1)−O(2)	1.6225(18)	P(1)−O(3)	1.6574(19)
P(1)−O(4)	1.7837(18)		
O(1)−P(1)−N(1)	123.81(11)	O(1)−P(1)−O(2)	97.05(10)
N(1)−P(1)−O(2)	92.01(11)	O(1)−P(1)−O(3)	112.45(10)
N(1)−P(1)−O(3)	122.90(11)	O(2)−P(1)−O(3)	90.09(9)
O(1)−P(1)−O(4)	85.34(9)	N(1)−P(1)−O(4)	86.95(10)
O(2)−P(1)−O(4)	177.58(10)	O(3)−P(1)−O(4)	88.65(9)

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **3**

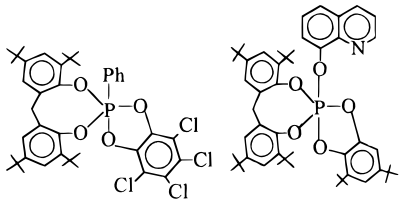
P(1)−N(1)	1.635(3)	P(1)−O(1)	1.662(2)
P(1)−O(2)	1.670(2)		
N(1)−P(1)−O(1)	94.89(13)	N(1)−P(1)−O(2)	100.39(14)
O(1)−P(1)−O(2)	101.56(11)		

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for **4**

P(1)−O(1)	1.606(2)	P(1)−N(1)	1.629(2)
P(1)−O(3)	1.636(2)	P(1)−O(2)	1.669(2)
P(1)−O(4)	1.716(2)		
O(1)−P(1)−N(1)	118.08(12)	O(1)−P(1)−O(3)	116.60(11)
N(1)−P(1)−O(3)	125.18(12)	O(1)−P(1)−O(2)	95.67(10)
N(1)−P(1)−O(2)	89.02(11)	O(3)−P(1)−O(2)	89.40(10)
O(1)−P(1)−O(4)	85.80(10)	N(1)−P(1)−O(4)	90.17(11)
O(3)−P(1)−O(4)	90.06(10)	O(2)−P(1)−O(4)	178.53(11)

bonds are absent. The phosphite **3** forms dimers by weak hydrogen bonds (H(1N)−O(1A) = 2.56(2) Å) (Figures 4 and 5), while there are, again, no hydrogen bonds in the corresponding pentacoordinated structure of **4**·$^1/_2$Et$_2$O (Figure 6). Selected bond lengths and angles for **2**−**4** are given in Tables 4−6.

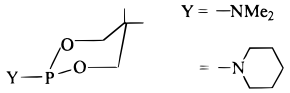
In the tricoordinated structures **1** and **3**, the phosphorus atom has trigonal pyramidal geometry, while in the pentacoordinated compounds **2** and **4** it is trigonal bipyramidal (TBP) with the rings apical-equatorial and the acyclic cyclohexylamino group equatorial. By contrast, in **XXI**[23] and **XXII**,[15] which have the same phosphocin ring as in **4**, the phenyl or the oxinate group is apical. Although oxinate may be expected to be more



XXI **XXII**

apicophilic because of higher electronegativity, the phenyl and the cyclohexylamino groups should have comparable group electronegativities (-Ph, 2.58; -NMe_2, 2.61; -NHC_6H_{11}, data not available) on the Pauling scale.[24] Thus, the preference of -NHC_6H_{11} to be equatorial may be due to the π-interaction involving the lone pair on nitrogen and an unused d orbital on phosphorus in **4**. The sum of the bond angles around N(1) in **4** shows that it is nearly planar and, hence, is possibly involved in π-interaction with phosphorus.

The 1,3,2-dioxaphosphorinane ring in **1** adopts a chair conformation, which is quite typical for tricoordinated cyclic phosphites.[6,7,25] However, in contrast to Verkade's compounds **XXIII**,[7] the nitrogen in **1** is disposed toward the axial position;



(**XXIII**)

this feature may be due to the presence of H-bonding in **1**. In the corresponding pentacoordinated phosphorane **2**, the same phosphorinane ring adopts a boat conformation, with P(1), O(1), C(13), and C(12) forming the base of the boat (mean deviation, 0.010(1) Å). Atoms O(2) and C(11) are displaced from this plane by 0.592(3) and 0.642(4) Å, respectively. As explained by Trippett[26] and later by Holmes et al.,[27] this is the most favored conformation for this ring located apical-equatorially in a TBP structure. The dihedral angle between the equatorial plane and the endocyclic P−O_{eq}−C bond is 80.7(2)°; this is not too far from 90° and is in the typical range for this kind of structure.[2a] Such a feature allows the lone pair of the equatorial oxygen to approach the equatorial plane, favoring the boat conformation for the phosphorinane ring.[26]

The five-membered rings in **2** and **4** are planar (mean deviation, 0.007(2) Å in **2** and 0.018(2) Å in **4**). Here, the dihedral angles between the equatorial plane and the endocyclic P−O_{eq}−C bond are 87.4(2)° and 83.7(2)°, respectively.

The eight-membered ring adopts a boat-chair conformation[28a] in **3** (Figure 4). This seems to be the typical conformation in cyclic phosphites[28] and in pentacoordinated phosphoranes when the ring spans a diequatorial position (e.g., **XXI** and **XXIII**).[3c,g,15] This ring exhibits a distorted tub conformation when it is located apical-equatorially[3a,d] as in structure **4** (Figure 6). Atoms O(2), C(21), C(11), and C(16) are coplanar to within 0.001(1) Å, while atoms P(1), O(1), C(22), and C(1) depart at the same side from this plane by 1.223(3), 0.977(4), 0.417(5), and 0.978(4) Å, respectively. The dihedral angle between the equatorial plane and the plane containing the endocyclic P−O_{eq}−C bond is 85.2(2)°.

The P−N bond lengths are shortened in the P(V) compounds compared to the P(III) structures [P−N (mean) = 1.657 Å in **1**, P(1)−N(1) = 1.619(2) in **2**, 1.635(3) in **3**, and 1.629(2) Å in **4**]. All of these are shorter than the value of 1.73 Å calculated for a P−N single bond by the modified Schomaker−Stevenson equation.[29]

The P−O bonds differ depending on the ring size.[2a,3b] As expected, the apical bond lengths in the TBP structures are longer than the corresponding equatorial values, and both are shorter than the equivalent bonds in the tricoordinated structures. Because of ring strain, the P−O bonds in the unsaturated five-membered rings are the longest [P−O_{eq} = 1.657(2) Å, P−O_{ap} = 1.784(2) Å in **2**; P−O_{eq} = 1.636(2) Å, P−O_{ap} = 1.716(2) Å in **4**]. The P(1)−O(4) bond in **2** is even 0.11 Å longer than the value of 1.67 Å which is calculated for a P−O single bond by Blom and Haaland.[29] As observed before,[2a] the bond lengths in the six-membered rings are the shortest [P(1)−O_{eq} = 1.593-

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(2) Å, P(1)−O_{ap} = 1.623(2) Å in **2**; P−O (mean) = 1.635 Å in **1**], while the bonds in the eight-membered rings are in a middle range [P(1)−O(2) = 1.670(2) Å, P(1)−O(1) = 1.662(2) Å in **3**; P−O_{eq} = 1.606 Å, P−O_{ap} = 1.669 Å in **4**].

The angles at phosphorus in the tricoordinated structures vary from 98.6(2)° (O(2)−P(1)−O(1)) to 108.1(3)° (O(5)−P(3)−N(3)) in **1** and from 94.9(1)° (N(1)−P(1)−O(1)) to 101.6(1)° (O(1)−P(1)−O(2)) in **3**. The equatorial angles in the trigonal bipyramids are in the range from 112.5(1)° (O(1)−P(1)−O(3)) to 123.8(1)° (O(1)−P(1)−N(1)) in **2** and in the range from 116.6(1)° (O(1)−P(1)−O(3)) to 125.2(1)° (N(1)−P(1)−O(3)) in **4**, while the angles involving the apical atoms are 177.6(1)° in **2** and 178.5(1)° in **4**.

By using the dihedral angle method,[30] the geometry is found to be displaced along the pseudorotational coordinate to an extent of 11.0% for **2** and 10.9% for **4** from the ideal trigonal bipyramid toward the square pyramid, with O(1) as the pivotal atom.

Summary

The hydrolysis of pentaoxyphosphoranes and aminophosphoranes leads to different sets of products. Replacement of the amino group in a phosphite is much more facile than that in the aminophosphoranes studied in this work. The -NH proton of the -HNC_6H_{11} group participates in H-bonding in the phosphites but not in the corresponding pentacoordinated phosphoranes. The amino group in phosphite **1** (which contains the phosphorinane ring) occupies the axial position, possibly because of H-bonding. The change in conformation for a 1,3,2-dioxaphosphorinane ring from chair in cyclic phosphites to boat when this ring is located apical-equatorially in a trigonal bipyramidal arrangement is firmly established by our choice of the same substituents on both the P(III) and P(V) compounds. The uniqueness of the pentacoordinated systems may be appreciated when we recognize that, in both tetracoordinated and hexacoordinated phosphorus[6,15] (and arsenic[31]) compounds, this 1,3,2-dioxaphosphorinane (or 1,3,2-dioxarsenane) ring has a chair conformation. A similar change in conformation from boat-chair in phosphites to tub in phosphoranes is demonstrated for the first time in systems containing the 1,3,2-dioxaphosphocin ring. A generalization that this ring prefers the tub conformation when it is positioned apical-equatorially (three structures) and boat-chair when it is diequatorial (five structures) in a trigonal bipyramidal geometry can, perhaps, be made on the basis of available structures.

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Supporting Information Available: Analytical and spectroscopic data for **10**−**12** and data pertaining to identification of **16**−**20**; atomic coordinates, isotropic displacement parameters, complete listing of bond lengths and angles, and anisotropic displacement parameters for structures of **1**−**4** (20 pages). Four X-ray crystallographic files, in CIF format, are available on the Internet only. Access and ordering information is given on any current masthead page.

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