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Bi- and Tricyclic Penta- and Hexacoordinated Phosphoranes with Varying Ring Sizes: Synthesis, Structures, and Reactivity

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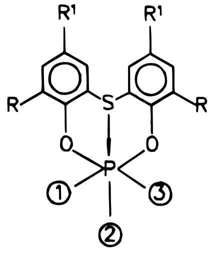
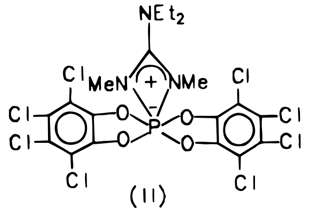
Abstract: New tricyclic hexacoordinated phosphoranes **1**−**6** with internal N→P coordination containing ring sizes varying from five to eight membered have been synthesized by oxidative addition of a quinone or a diol to a cyclic phosphite. The bicyclic phosphorane $\mathrm{(NC_9H_6O)P(O_2(3,5\text{-}t\text{-}Bu)_2C_6H_2)((O\text{-}2,4\text{-}(t\text{-}Bu)_2C_6H_2)_2CH_2)\cdot{}^1/_2H_2O}$ ($\mathbf{7}\cdot{}^1/_2\mathrm{H_2O}$) has been synthesized by adding the 3,5-di-tert-butyl-*o*-benzoquinone to the cyclic phosphite. The compound $\mathrm{(NC_9H_6O)P(2,2'\text{-}OC_6H_4C_6H_4O)_2}$ (**6**) results from a novel ring exchange reaction of a *phosphorinane* by a *phosphepin* in two ways: (a) by treating $\mathrm{(OCH_2CMe_2CH_2O)P((OC_9H_6N)}$ with 2,2′-biphenol/*N*-chlorodiisopropylamine and (b) by treating $\mathrm{(Et_2N)P(OCH_2CMe_2CH_2O)(2,2'\text{-}OC_6H_4C_6H_4O)}$ with 8-hydroxyquinoline. Treatment of the aminophosphorane $\mathrm{(Et_2N)P(OCH_2CMe_2CH_2O)(O_2C_{14}H_8)}$ with 2,4,6-trimethylbenzoic acid led to the unique ester $\mathrm{(OCH_2CMe_2\text{-}CH_2O)P(O)\{OC_{14}H_8O(C(O)\text{-}2,4,6\text{-}Me_3C_6H_2)\}}$ (**10**). ^{31}P NMR data for the new compounds are discussed with respect to the differing ring sizes and coordination number on phosphorus. X-ray analysis shows hexacoordination in **2**, **4**, and **6** with an N→P bond and pentacoordination in **7** without an N→P bond. The coordinating nitrogen is *trans* to an oxygen of the six-membered ring in **2** and of the seven-membered ring in **4**. The eight-membered ring in **7** spans a diequatorial position in a trigonal bipyramidal arrangement.

Introduction

In addition to a sizeable number of oxyphosphoranes with six and higher membered rings,[1] several neutral hexacoordinated phosphoranes with an S→P coordination have been structurally characterized by Holmes and co-workers recently.[2] In these compounds, a sulfur atom in a formal eight-membered phosphocin ring internally forms a donor−acceptor S→P bond leading to two fused five-membered rings with hexacoordination on the phosphorus (**I**). Several cyclic anionic, neutral, and zwitterionic hexacoordinated compounds, primarily with four- or five-membered rings, are also known;[3] in this context the recent X-ray study on the unique hexacoordinated phosphoranes **II** and **III** containing (4 + 5 + 5) and (4 + 5 + 7) ring systems by Schmutzler and co-workers is noteworthy.[4]



(I)



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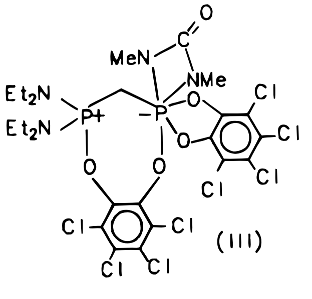

(III)

We have been interested in studying the synthesis, structure, and reactivity of the penta- and hexacoordinated phosphoranes with mainly, six and higher membered rings. Wherever feasible, an extension to arsenic systems has been attempted.[5−7] In

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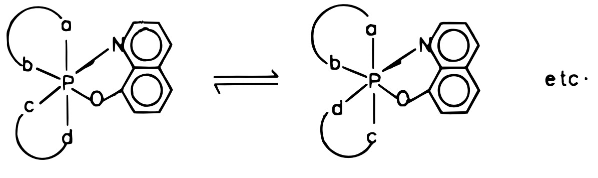
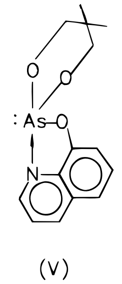
addition to new reaction chemistry, these systems are expected to throw light on the conformational preferences for different ring sizes and, where the 1,3,2-dioxaphosphorinane ring is involved, the nature of the transition state in the action of cyclic AMP.[8]

For the present study, we have chosen two systems. The first one involves a series of hexacoordinated compounds with ring sizes ranging from five to eight. We have selected oxinate as one of the substituents on phosphorus, as its nitrogen can provide the sixth coordination site by means of a donor–acceptor bond[3c,f,g] (as in **IV** or **IVa**) to form a chelate five-membered ring. This study was prompted by our earlier results obtained in analogous arsenic systems wherein the novel tetra- and hexacoordinated arsenanes V and VI respectively, with N→As bonds could be structurally characterized.[7] The use of rings of varying sizes at positions a–d in IV makes such a system attractive to study the possibility of isomers besides providing a larger variety of ring systems than the fused S→P systems mentioned above.



(IV) (IVa)



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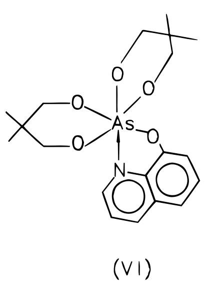
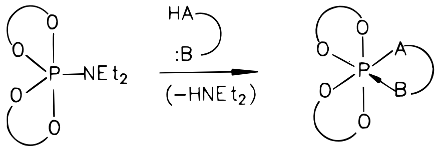


(VI)

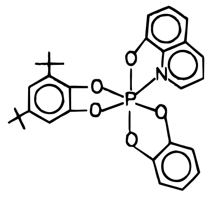
The second system involves the use of an amino functionality on a pentacoordinated phosphorus to achieve hexacoordination (eq 1).



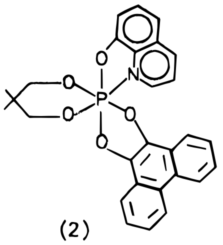
→ (1)

(VII) (VIII)

Herein we report the synthesis and characterization of compounds **1**–**7**. X-ray structures have been determined for **2**·CH_2Cl_2, **4**·CH_2Cl_2, **6**·$^1/_6Et_2O$, and **7**·$^1/_2H_2O$. Compounds **2**, **4**, and **6** represent the first examples of structurally characterized hexacoordinated phosphoranes with nonfused (6 + 5 + 5), (7 + 5 + 5), and (7 + 7 + 5) ring systems. Synthesis of **6** has been achieved by a novel ring exchange reaction. Compound **7** is a new addition to the unique family of phosphoranes containing an eight-membered ring spanning diequatorial site in a trigonal bipyramidal arrangement.[1i]



(1)



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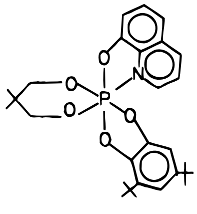

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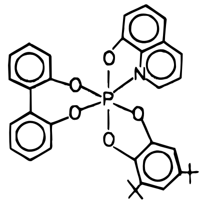

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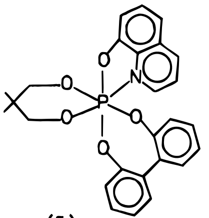

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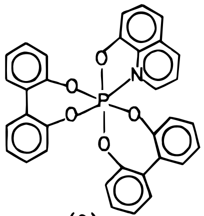

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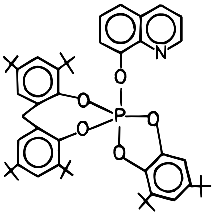
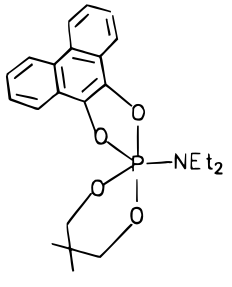


(7)

Also reported here are the synthesis of **8** and **9** and their reactivity toward 8-hydroxyquinoline and carboxylic acids (note that the carboxylate can act as a chelate toward phosphorus, leading to hexacoordination). Compound **8** reacted with 2,4,6-trimethylbenzoic acid in a rather surprising manner to give the rearranged ester **10**; characterization of this compound is also described here.



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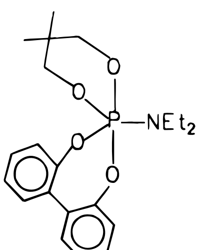

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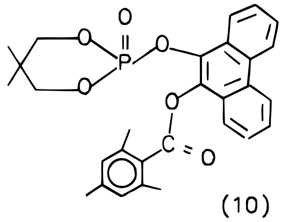

(10)

Experimental Section

Chemicals were procured from Aldrich, Fluka, or the local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[9] All reactions, unless stated otherwise, were performed under dry nitrogen atmosphere. ^1H, ^{13}C and $^{31}P\{^1H\}$ 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_3PO_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.

Compounds $(NC_9H_6O)P(1,2\text{-}O_2C_6H_4)$ (**11**: mp 83 °C; ^{31}P NMR 124.9),[3c] $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (**12**), $(NC_9H_6O)P(2,2'\text{-}OC_6H_4C_6H_2O)$ (**13**), and $(NC_9H_6O)P\{(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2\}$ (**14**)

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[8] Holmes, R. R.; Deiters, J. A. *Inorg. Chem.* **1994**, *33*, 3235.

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Table 1. Crystal Data of **2**, **4**, **6**, and **7**

	2	**4**	**6**	**7**
empirical formula	$C_{28}H_{24}NO_5P{\cdot}CH_2Cl_2$	$C_{35}H_{34}NO_5P{\cdot}CH_2Cl_2$	$C_{33}H_{22}NO_5P{\cdot}{}^1/_6Et_2O$	$C_{52}H_{68}NO_5P{\cdot}{}^1/_2H_2O$
formula weight	570.38	664.53	555.84	827.05
crystal system	monoclinic	orthorhombic	rhombohedral	triclinic
space group	$P2_1/c$	$Pna2_1$	$R\bar{3}$	$P\bar{1}$
a (Å)	10.582(1)	17.463(5)	36.021(2)	10.988(3)
b (Å)	27.900(3)	12.558(2)	36.021(2)	21.980(5)
c (Å)	9.255(1)	30.426(7)	10.646(2)	22.108(5)
α (deg)	90	90	90	110.05(1)
β (deg)	106.57(1)	90	90	101.77(2)
γ (deg)	90	90	120	92.94(1)
V (Å^3)	2619.0(5)	6672(3)	11963(2)	4868(2)
Z	4	8	18	4
D_x (Mg/m^3)	1.447	1.323	1.389	1.129
μ (mm^{-1})	0.351	0.286	0.150	0.103
F(000)	1184	2784	5202	1784
cryst size (mm)	0.5 × 0.8 × 0.9	0.3 × 0.6 × 0.6	0.5 × 0.5 × 0.5	0.6 × 0.7 × 0.8
2θ range	8 − 50	4 − 45	7 − 45	7 − 50
reflect. collect.	5991	9105	6273	17857
indep. reflect.	4612	8723	3498	17492
R_{int}	0.0172	0.0301	0.0290	0.3520
data	4612	8711	3498	17477
parameters	365	824	381	1213
restraints	25	1	7	399
S	1.019	1.069	1.030	1.020
R_1 ($I > 2\sigma(I)$)	0.0420	0.0461	0.0410	0.0732
wR_2 (all data)	0.1011	0.1141	0.0989	0.2256
extinction coeff	0.0020(5)			
Flack x		0.52(8)		
largest diff peak [e Å^{-3}]	0.257	0.351	0.272	0.871
largest diff hole [e Å^{-3}]	−0.271	−0.424	−0.268	−0.448

were synthesized by reacting their respective chloro precursors[6] with 8-hydroxyquinoline in toluene or diethyl ether in yields of 60−80%. Selected physical data are given below.

12 (purified by distillation at 220 °C/0.5 mm): Mp: 50 °C. ^1H NMR: 0.67 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 3.36 (t, 2H, CH_2 (A)), 4.40 (dd, 2H, CH_2(B)), 7.20−8.90 (m, 6H, H (Ar)). $^{31}P\{^1H\}$ NMR: 113.5. Anal. Calcd for $C_{14}H_{16}NO_3P$: C, 60.65; H, 5.78; N, 5.05. Found: C, 60.38; H, 5.65; N, 5.00.

13 (crystallized from CH_2Cl_2 + hexane): Mp: 145−148 °C. ^1H NMR: 7.20−9.16 (m, H(Ar)). ^{31}P NMR: 139.6. Anal. Calcd for $C_{21}H_{14}NO_3P$: 70.19; H, 3.90; N, 3.90. Found: C, 70.10; H, 3.85; N, 3.70.

14 (crystallized from Et_2O + hexane): Mp: 85 °C. ^1H NMR: 1.30 (s, 18H, t-Bu-H), 1.32 (s, 18H, t-Bu-H), 3.58 (d, 1H, ^2J(H−H) = 14.0 Hz, CH_AH_B), 4.49 (dd, J = 4.0 Hz, 14.0 Hz, 1H, CH_AH_B), 7.28−9.05 (m, 10H, H(Ar)). ^{31}P NMR: 131.2. Anal. Calcd for $C_{38}H_{48}NO_3P$: C, 76.38, H, 8.04; N, 2.34. Found: C, 76.45; H, 7.96; N, 2.45.

The aminophosphites $(Et_2N)P(OCH_2CMe_2CH_2O)$ (**15**)[6] and $(Et_2N)P$-(2,2′-$OC_6H_4C_6H_4O$) (**16**) [$\delta(^{31}P)$ = 149.6 ppm] were prepared by reacting their respective chloro precursors[6] with diethylamine.

Synthesis of compounds **1**−**7** was accomplished by the oxidative addition of a diol (in the presence of N-chlorodiisopropylamine) or a quinone to the phosphite. Only typical procedures are given.

(a) Preparation of the Phosphorane $(NC_9H_6O)P(1,2\text{-}O_2C_6H_4)(1,2\text{-}O_2\text{-}3,5(t\text{-}Bu)_2C_6H_2)$ (1). 3,5-Di-*tert*-butylbenzoquinone (0.43 g, 1.95 mmol) was added to **11** (0.55 g, 1.95 mmol) in dry toluene (5 mL). The mixture was heated under reflux for 10 min, solvent was removed *in vacuo*, and the residue crystallized from CH_2Cl_2−n-heptane. Yield: 0.6 g (61%). Mp: 198 °C. ^1H NMR: 1.25 (s, 18H, CH_3), 6.75−9.08 (m, 12H, H(Ar)). ^{31}P NMR: −88.3 (lit. ^{31}P NMR-88[3c]). Anal. Calcd for $C_{29}H_{30}NO_5P$: C, 69.18; H, 5.96; N, 2.78. Found: C, 69.05; H, 5.76; N, 2.70. (This compound has been reported earlier[3c] without melting point data; the carbon analysis was also not correct.)

(b) Preparation of $(NC_9H_6O)P(9,10\text{-}O_2C_{14}H_8)(OCH_2CMe_2CH_2O)$ (2). 9,10-Phenanthrenequinone (0.45 g, 2.18 mmol) was added to **12** (0.60 g, 2.18 mmol) in dry p-xylene (5 mL) and the mixture heated to reflux for 10 min. Solvent was removed *in vacuo* and the residue crystallized from CH_2Cl_2−hexane (1:5) to obtain **2** as red crystals. Yield: 0.6 g (57%). Mp: 265 °C. ^1H NMR: 1.14 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 4.09 (d, 4H, ^3J(P−H) = 17.6 Hz, OCH_2), 5.30 (variable intensity, CH_2Cl$_2$), 7.15−8.68 (m, 14H, H(Ar)). ^{31}P NMR: −100.5. Anal. Calcd (after powdering and drying in a vacuum) for $C_{28}H_{24}NO_5P$: C, 69.28, H, 4.95; N, 2.89. Found: C, 69.05; H, 4.80; N, 2.65.

This compound hydrolyzed in solution in the presence of moisture to afford **23** (see also i(iii) below).

(c) Preparation of $(NC_9H_6O)P(1,2\text{-}O_2\text{-}3,5\text{-}(t\text{-}Bu)_2C_6H_2)(OCH_2CMe_2CH_2O)$ (3). The procedure was similar to that given for **1** using similar molar quantities. Crystallization was done from CH_2Cl_2−n-heptane. Yield: 50%. Mp: 172 °C. ^1H NMR: 1.05 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.21 (s, 9H, t-Bu-H), 1.46 (s, 9H, t-Bu-H), 3.80−4.40 (m, 4H, OCH_2), 6.60−8.60 (m, 8H, H(Ar)). ^{31}P NMR: −101.0. Anal. Calcd for $C_{28}H_{36}NO_5P$: C, 67.60; H, 7.24; N, 2.82. Found: C, 67.35; H, 7.10; N, 2.58.

(d) Preparation of $(NC_9H_6O)P(1,2\text{-}O_2\text{-}3,5\text{-}(t\text{-}Bu)_2C_6H_2)(2,2'\text{-}OC_6H_4C_6H_4O)$ (4). The procedure was similar to that for **1** using similar molar quantities. Recrystallization was done using a CH_2Cl_2−hexane (1:5) mixture. Yield: 41%. Mp: 246−248 °C. ^1H NMR: 1.26 (s, 9H, t-Bu-H), 1.43 (s, 9H, t-Bu-H), 5.30 (s, variable intensity, CH_2Cl$_2$), 6.48−8.84 (m, 16H, H(Ar)). ^{31}P NMR: −89.3. Anal. Calcd (after removal of solvent of crystallization) for $C_{35}H_{34}NO_5P$: C, 72.54; H, 5.87; N, 2.42. Found: C, 72.33; H, 5.56; N, 2.15.

(e) Preparation of $(NC_9H_6O)P(OCH_2CMe_2CH_2O)(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)$ (5) and $(NC_9H_6O)P[2,2'\text{-}OC_6H_4C_6H_4O]_2{\cdot}{}^1/_6Et_2O$ ($6{\cdot}{}^1/_6Et_2O$). To a mixture of **2** (1.87 g, 6.74 mmol) and biphenol (1.26 g, 6.74 mmol) in dry ether (40 mL) maintained at −60 °C was added N-chlorodiisoproylamine (0.91 g, 6.74 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.

Product **5** was fractionally crystallized from the precipitate (which also contained diisopropylamine hydrochloride) using a CH_2Cl_2−n-heptane mixture. Yield: 1.5 g (48%). Mp: 155 °C. ^1H NMR: 0.97 (br s, 3H, CH_3), 1.35 (br s, 3H, CH_3), 3.50−4.60 (br m, 4H, CH_2), 6.55−8.82 (m, 14H, H(Ar)). ^{31}P NMR: −107.4. Anal. Calcd for $C_{26}H_{24}NO_5P$: C, 67.68; H, 5.21; N, 3.04. Found: C, 67.89; H, 5.14; N, 2.98.

Compound **6** was isolated by evaporating the solvent from the filtrate and crystallizing the residue from an ether−hexane (1:3) mixture. Yield: 0.12 g (6.6%). The yield of **6** could be significantly improved when a 1:2 molar ratio of **2** to 2,2′-biphenyl was used; thus, by using 1.21 g (4.35 mmol) of **2** and 1.62 g (8.71 mmol) of 2,2′-biphenol, 0.7 g (29%) of **6** was obtained. (For an alternative route, see below.) Mp: 251−253 °C. ^1H NMR: 5.40−8.83 (H(Ar)). ^{31}P NMR: −94.8. Anal.

Calcd for $C_{33}H_{22}NO_5P$ (after drying in a vacuum to remove solvent of crystallization): C, 72.93; H, 4.05; N, 2.58. Found: C, 73.14; H, 4.18; N, 2.40.

(f) Preparation of $(NC_9H_6O)P(O_2(3,5\text{-t-bu})_2C_6H_2)((O\text{-}2,4\text{-}(t\text{-bu})_2C_6H_2)_2CH_2)$ (7). The procedure was essentially the same as that for **1** using 0.63 mmol of the reactants. Yield: 58%. Mp: 142 °C. ^1H NMR: 0.29 (s, 9H, t-bu-*H*), 1.11 (s, 18H, t-bu-*H*), 1.25 (s, 9H, t-bu-*H*), 1.29 (s, 18H, t-bu-*H*), 3.45 (d, J = 15.0 Hz, 1H, CH_2-(A)), 4.55 (dd, $J \approx 3$ Hz, 15.0 Hz, 1H, CH_2(B)), 6.15−9.05 (m, 12 H, *H*(Ar)). ^{31}P NMR: −56.9. Anal. Calcd for $C_{52}H_{68}NO_5P$: C, 76.38; H, 8.32; N, 1.71. Found: C, 76.32; H, 8.25; N, 1.65.

(g) Preparation of $(Et_2N)P(OCH_2CMe_2CH_2O)(O_2C_{14}H_8)$ (8). This compound was prepared by mixing $(Et_2N)P(OCH_2CMe_2CH_2O)$ (2.93 g, 14.26 mmol) and 9,10-phenanthrenequinone (2.97 g, 14.26 mmol) and crystallizing the ensuing solid using CH_2Cl_2−hexane (1:5). Mp: 155 °C. ^1H NMR: 1.02 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.13 (t, ^3J(H−H) = 6.8 Hz, 6H, CH_2CH_3), 3.25 (m, J 13.6, 6.8 Hz, 4H, NCH_2), 3.97 (m, $J \approx 18.4$ Hz. 4H, OCH_2), 7.42−8.76 (m, 8H, *H*(Ar)). ^{31}P NMR: −40.6. A second signal for NCH_2 at *ca.* 2.85 ppm slowly developed over a period of time. Anal. Calcd for $C_{23}H_{28}O_4NP$: C, 66.83; H, 6.78; N, 3.39. Found: C, 66.52; H, 6.50; N, 3.45.

(h) Preparation of $(Et_2N)P(2,2'\text{-}OC_6H_4C_6H_4O)(OCH_2CMe_2CH_2O)$ (9). This compound was prepared by treating **15** (2.95 g, 14.38 mmol) with 2,2′-biphenol (2.68 g, 14.38 mmol) and ClN-i-Pr_2 (1.95 g, 14.38 mmol) as in procedure e above. Compound **9** was obtained after evaporating the solvent from the filtrate. Although the ^{31}P NMR spectrum showed the material to be essentially pure (>95%), a good solid could not be obtained. ^1H NMR: 0.90−1.40 (many lines, 12H, CH_3), 3.15−3.30 (m, 4H, NCH_2), 3.60−3.80 (m, $J \approx 18.0$ Hz, 4H, OCH_2), 7.10−7.65 (m, 8H, *H*(Ar)). A second NCH_2 signal (q) was also observed at 2.65 ppm over a period of time. ^{31}P NMR: −50.1. Anal. Calcd for $C_{21}H_{28}O_4NP$: C, 64.78; H, 7.20; N, 3.6. Found: C, 65.32; H, 7.46; N, 2.91.

(i) Reactions of 8. (i) With 8-Hydroxyquinoline: A mixture of **8** (0.43 g, 1.05 mmol) and 8-hydroxyquinoline (0.15 g, 1.05 mmol) was refluxed in dry toluene (10 mL) overnight. After removal of the solvent, **2** could be crystallized from CH_2Cl_2−hexane (1:1). NMR and melting point data were identical to that given above in b.

(ii) With 2,4,6-Trimethylbenzoic Acid. A mixture of **8** (0.55 g, 1.34 mmol) and 2,4,6-trimethylbenzoic acid (0.22g, 1.34 mmol) was heated in dry *p*-xylene (5 mL) overnight, the solvent removed completely, and the residue crystallized from CH_2Cl_2−hexane (1:2) to give $(OCH_2CMe_2CH_2O)P(O)(O\text{-}(2,4,6\text{-}Me_3\text{-}C_6H_2C(O)O)C_{14}H_8)$ (**10**). Yield: 0.4 g (59%). Mp: 160 °C. IR: 1742 (ν(C=O), of the ester) [ν(C=O) for the parent carboxylic acid observed at 1686 cm^{-1}], 1607 cm^{-1} (no OH band observed). ^1H NMR: 0.73 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 2.40 (s, 3H, CH_3(Ar)), 2.75 (s, 6H, CH_3(Ar)), 3.85 (dd, 2H, CH_2(A)), 4.20 (d, 2H, CH_2(B)), 7.06−8.80 (m, 10H, *H*(Ar)). ^{31}P NMR: −14.4. Anal. Calcd for $C_{29}H_{29}O_6P$: C, 69.05; H, 5.75. Found: C, 68.45; H, 5.81.

(iii) With Benzoic Acid. The procedure was same as i.ii above. The known compound $(OCH_2CMe_2CH_2O)P(O)(O(OH)C_{14}H_8)$ (**23**)[10] was isolated. Mp: 157−160 °C (lit. mp 162−164 °C[10]). ^1H NMR: 1.00 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 4.05 (dd, 2H, OCH_2), 4.50 (d, 2H, OCH_2), 7.50−8.70 (m, 8H, *H*(Ar), 9.50 (br, 1H, O*H*). ^{31}P NMR: −10.2 (above data are not reported before).

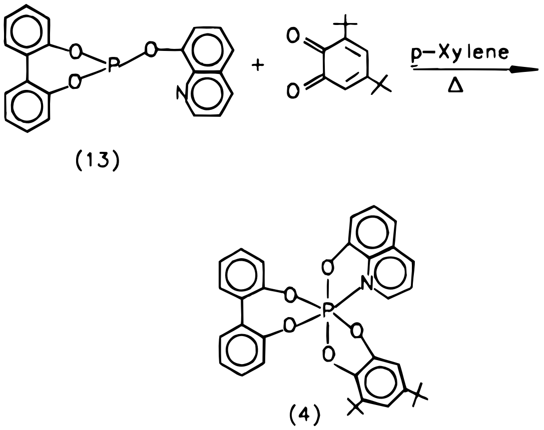
(j) Reaction of 9 with 8-Hydroxyquinoline. Compound **9** (0.70 g, 1.80 mmol) and 8-hydroxyquinoline (0.23g, 1.62 mmol) were heated to reflux in xylene (5 mL) for 12 h. Solvent was removed and the residue crystallized from ether−heptane (1:1) to afford **5**. Yield: 0.2 g (23% based on 8-hydroxyquinoline) (Physical data are given above in e). The ^{31}P NMR of the mother liquor after removal of **5** showed a large number of peaks in the tetracoordinated region [10 to −20 ppm].

X-ray Crystallography Experimental Section. Crystal data for **2**, **4**, **6**, and **7** are summarized in Table 1. All data were collected at −120 °C on a Stoe-Siemens-AED-diffractometer with monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods.[11] All nonhydrogen atoms were refined anisotropically with the exception of the Et_2O molecule in structure **6**.[12] For the hydrogen atoms the riding model was used. 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 $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$.

In structure **2** the CH_2Cl_2 molecule and in structure **6** the Et_2O are disordered. They are refined with distance restraints and restraints for the displacement parameters. In structure **4** the two independent molecules are related by a pseudoinversion center at −0.123, 0, 0.1685. A transformation to a centrosymmetric space group was not possible. The structure is refined as a racemic twin with a twin parameter of 0.52(8).[13] In structure **7** one *tert*-butyl group in each of the two independent molecules is disordered. The anisotropic displacement parameters of the carbon atoms lying opposite to each other are fixed to the same values. Also, distance restraints were used. Additionally the quinoline ring in one molecule is disordered and refined with distance restraints and restraints for the anisotropic displacement parameters. There is still some high residual density in the neighborhood of this quinoline ring that might be explained as a further disorder. At the end of the data collection there were some problems with icing leading to the high value of R_{int}.

Results and Discussion

Syntheses. The oxinate compounds **1**−**4** and **7** as well as the (diethylamino)phosphorane **8** were prepared by the oxidative addition of a quinone to the cyclic phosphite in isolated yields of 40−60%. A typical synthesis is illustrated in eq 2 for the formation of **4**. For introducing a six or a higher membered ring on cyclic phosphites the route in eq 2 is not feasible. Therefore, for synthesizing the tricyclic derivative **5** we employed the reaction of the cyclic phosphite **12** with 2,2′-biphenol in the presence of *N*-chlorodiisopropylamine in ether at −60 °C. By careful fractional crystallization of the precipitate from a dichloromethane−heptane mixture we could isolate **5** in yields of about 50%. However the crystalline solid **6** which came out from the ether filtrate as the etherate in 6−7% yield *was a surprise*. This compound containing two 2,2′-biphenoxy units *must* arise from the exchange of the six-membered *phosphorinane* ring by the seven-membered *phosphepin* ring; the yield of **6**•Et_2O could be significantly enhanced (to 30%) by using a 1:2 molar ratio of cyclic phosphite to 2,2′-biphenol. These reactions are illustrated in eq 3.



(13)

(4)

(2)

The above exchange leading to **6** is unique because when either 2,6-dimethyl phenoxy or 2,4,6-trimethyl phenoxy or diethylamino group was used in place of oxinate, no such phenomenon was observed (eq 4).

What is perhaps more puzzling is the reaction of **9** with 8-hydroxyquinoline to yield **6** (eq 5). It can be noted that *even though no 2,2′-biphenol has been added, the reorganization still takes place*. To our knowledge, such a reaction in phosphorane chemistry is unknown to date.

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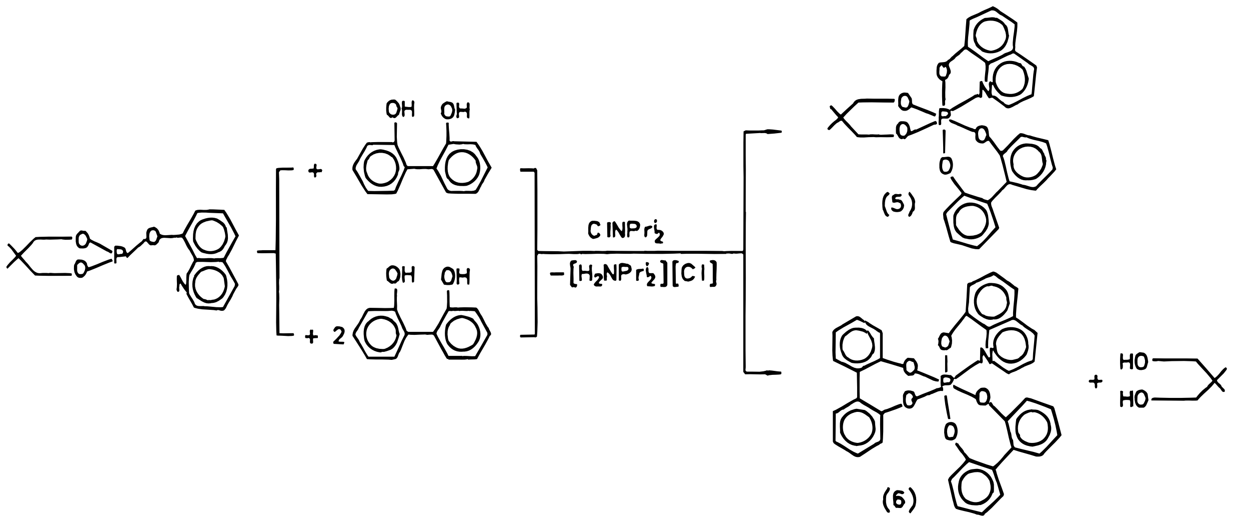
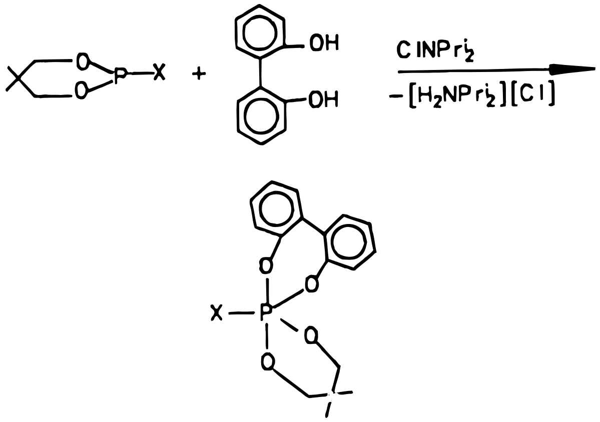
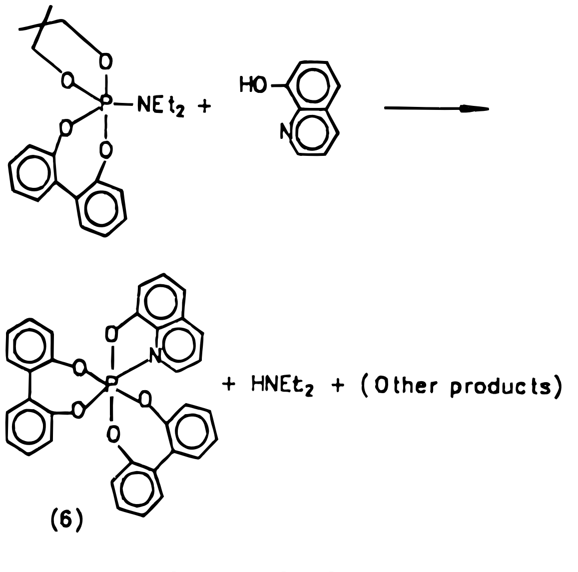


(3)

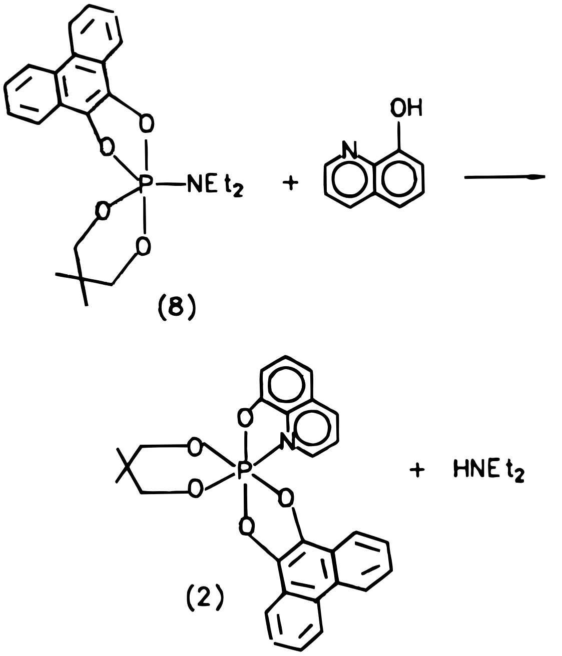


(4)

X = 2,6-$Me_2C_6H_3$[1f]
X = 2,4,6-$Me_3C_6H_2$[12]
X = NEt_2 (**9**)



(5)

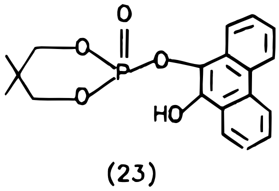


(6)

By contrast, the aminophosphorane **8** upon treatment with 8-hydroxyquinoline afforded the ring-preserved compound **2**, which could be readily isolated (eq 6).

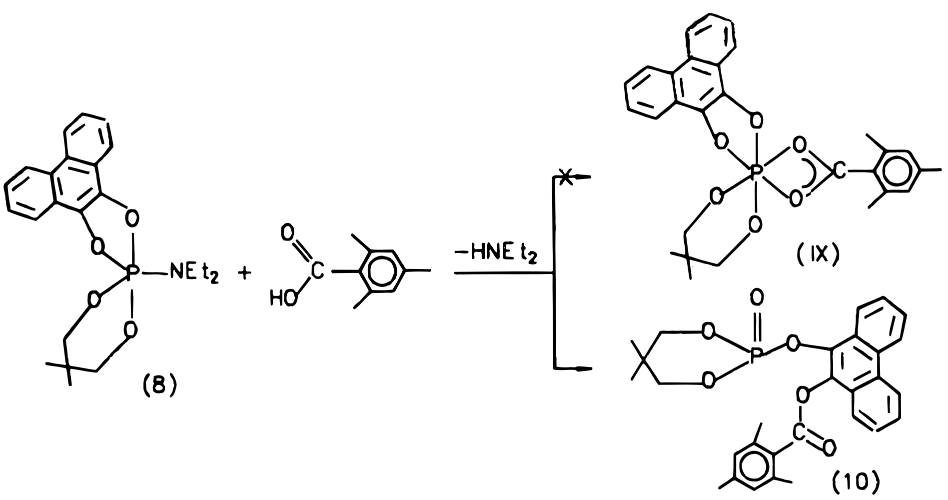
It is difficult to ascertain the reason for the exchange of the six-membered phosphorinane ring by the seven-membered phosphepin ring, thereby leading to the preferential formation of the (7 + 7 + 5) ring compound **6**. Two factors which may be responsible for this are (i) the aromatic residues on the seven-membered 1,3,2-phosphepin rings increase the acidity on phosphorus and hence its ability to form to stronger N→P bond in **6** than in either **2** or **4** as seen by the shortest N→P bond (1.938 Å) in **6** and (ii) the presence of two identical seven-membered rings imparts certain stability to the molecule as it tends to resist any deformation of its bonds and hence the compound does not react further.

We also tried to obtain hexacoordinated phosphoranes with chelating carboxylates of type **IX** in place of oxinate. However, strangely, treatment of **8** with 2,4,6-trimethylbenzoic acid (eq 7) gave the ester **10**, which is a crytalline solid showing a ^{31}P NMR chemical shift of −14.4 ppm; the IR spectrum of this compound showed an ester band at 1742 cm^{-1} (It can be seen that **10** is actually a rearranged product of **IX**). When benzoic acid was used instead of 2,4,6-trimethylbenzoic acid, the only product that we could isolate was the known compound **23**.[10]



(23)

Although this hydrolysis product is essentially similar to the ester **10** (eq 7), transfer of an entire acid residue as observed for the latter, to our knowledge, is unprecedented.



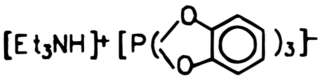
(7)

^{31}P NMR Spectroscopy. The ^{31}P NMR shift values for **1**−**7** along with those for other selected compounds are shown in Table 2. An examination of Table 2 reveals the following features.

(a) The ^{31}P NMR chemical shifts for **2**, **4**, **6**, and **7** show that the hexacoordinated structures observed for **2**, **4**, and **6** and the pentacoordinated structure observed for **7** in the solid state, as shown by X-ray, are retained in solution.

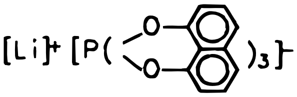
(b) The hexacoordinated derivatives experience an upfield shift of 48−60 ppm when compared to their close pentacoordinated analogues [e.g. entries 6 and 18, $\Delta\delta = 49.7$ ppm].

(c) Among the oxinate hexacoordinated compounds investigated, the deshielding effect of ring size is in the order five > seven > six ≈ four > eight. A comparable effect is discernible in anionic hexacoordinated phosphates (**XII**−**XIV**) also.[19,20] A similar trend has been noted by Holmes and co-workers in pentaoxyphosphoranes.[21]



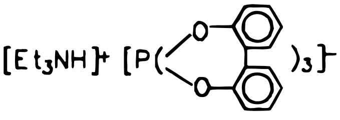
(XII)

^{31}P: −84.0



(XIII)

^{31}P: −168.0



(XIV)

^{31}P: −93.2

The trends observed in the oxinate system suggest that phosphorus experiences more deshielding in compounds with *odd*-membered rings as compared to those with *even*-membered rings. It may be worthwhile to examine a few more examples containing seven-membered (those more flexible than the 2,2′-biphenoxy system) and nine-membered rings to understand these effects more clearly.

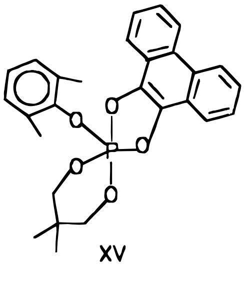
(d) When saturated 1,3,2-dioxaphosphorinane (entry no. 16) or phospholane (entry no. 13) rings are present, the nitrogen of the oxinate refuses to form a coordinate bond, thus leaving the phosphorus pentacoordinated. It is likely that in these cases phosphorus does not become sufficiently acidic to accept the lone pair of electrons from the oxinate nitrogen.

The presence of N→P coordination in the eight-membered ring compounds containing the 2,2′-methylene bis(4-chlorophenoxy) group (entries 9 and 11) and its absence in those containing the 2,2′-methylene bis(4,6-di(t-butyl)phenoxy) group (entries 14 and 15) is noteworthy; steric factors may be partly responsible for the absence of N→P coordination in the latter case. The ^{31}P NMR chemical shift values for these compounds (entries 14 and 15) are comparable to those in which there is no possibility of internal coordination (entries 22 and 23).

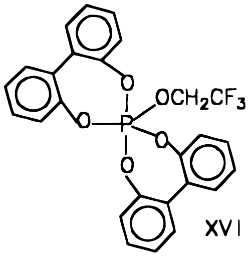
Structural Aspects

The molecular geometry along with atom labeling scheme for **2**, **4**, **6**, and **7** is shown in Figures 1−4, respectively. Selected bond lengths and bond angles are given in Tables 3−6. Other details including atomic coordinates and a full list of bond lengths and bond angles are provided as supporting information.

In compounds **2**, **4**, and **6**, the phosphorus atoms are octahedrally coordinated by cyclic ligands; the coordinating nitrogen is *trans* to an oxygen of the six-membered ring in **2** and of the seven-membered ring in **4**. The three structures are quite similar in terms of the geometry at the central phosphorus atom. The endocyclic O−P−N angles lie between 84.0° and 85.9°. The greatest deviation from 90° are exhibited by the six-membered ring system in **2** [99.90(8)°]; this is possibly due to ring strain. The strain in the seven-membered rings is less; therefore, the O−P−O angles are closer to 90° [92.79(8)° for **6** and 95.9(2)° and 95.5(2)° for **4**]. Such a feature is also discernible in the closely analogous pentacoordinated structures **XV**[1h] and **XVI**[17] in which the O−P−O angle for the six-



XV



XVI

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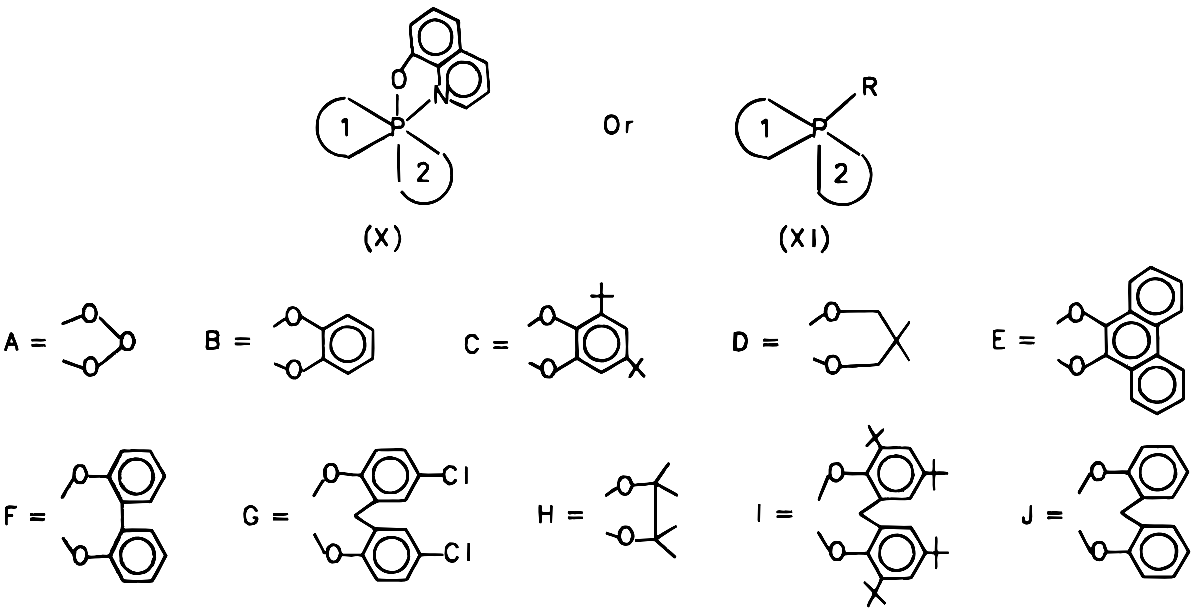
Table 2. ^{31}P NMR Data for Selected Penta- and Hexacoordinated Compounds with Oxinate/Aryloxy/Alkoxy Groups



no.	ring 1[a]	ring 2[a]	$\delta(^{31}P)$, ppm	ring system assignment (compd no.)[b]	method of preparation[c]	ref
				Structure **X**		
1	A	$(OPh)_2$	−123.0	0 + 4 + 5	i	3d
2	A	B	−102.0	5 + 4 + 5	i	3d
3	B	C	−88.3 (−88)	5 + 5 + 5 (**1**)	i	this work; 3c
4	B	B	−89.5[d]	5 + 5 + 5 (**17**)	ii	this work
5	D	B	−102.3	6 + 5 + 5 (**18**)	ii[e]	this work
6	D	C	−101.0	6 + 5 + 5 (**3**)	i	this work
7	D	E	−100.8	6 + 5 + 5 (**2**)	i	this work
8	F	C	−89.3	7 + 5 + 5 (**4**)	i	this work
9	G	B	−106.7	8 + 5 + 5 (**19**)	ii	this work
10	D	F	−107.5	7 + 6 + 5 (**5**)	ii	this work
11	D	G	−127.1	8 + 6 + 5 (**20**)	ii	this work
12	F	F	−94.8	7 + 7 + 5 (**6**)	ii	this work
				Structure **XI**		
13	D	H ($R = OC_9H_6N$)[f]	−57.5	6 + 5 + 0 (**21**)	ii	this work
14	C	I ($R = OC_9H_5N$)	−56.9	8 + 5 + 0 (**7**)	i	this work
15	E	I ($R = OC_9H_6N$)	−56.1	8 + 5 + 0 (**22**)	i	this work
16	D	D ($R = OC_9H_6N$)	−67.0	6 + 6 + 0	ii	7
17	B	B (R = OPh)	−30.2	5 + 5 + 0	g	14
18	C	D ($R = 2,6\text{-}Me_2C_6H_2O$)	−51.3	6 + 5 + 0	i	15
19	D	D ($R = 2,6\text{-}Me_2C_6H_2O$)	−68.8, −66.9[h]	6 + 6 + 0	ii	16
20	D	F ($R = 2,6\text{-}Me_2C_6H_2O$)	−60.0	7 + 6 + 0	ii	4
21	F	F ($R = CF_3CH_2O$)	−47.3	7 + 7 + 0	ii	17
22	C	I ($R = 2,6\text{-}Me_2C_6H_2O$)	−54.5	8 + 5 + 0	i	18
23	D	J ($R = 2,6\text{-}Me_2C_6H_2O$)	−69.0	8 + 6 + 0	ii	18

[a] Ring types are pictured below the structures of **X** and **XI**. [b] Compounds **17**−**22** identified mainly by ^{31}P NMR spectroscopy. [c] Method i: Oxidative addition of ozone/quinone to the phosphite. Method ii: Oxidative addition of diol to phosphite in the presence of *N*-chlorodiisopropylamine. [d] Another peak observed at −84.8 ppm ascribed to a $[P(O_2C_6H_4)_3]^-$ anion.[19] [e] The reaction was conducted two ways either by starting with $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ or $(NC_9H_6O)P(O_2C_6H_4)$. [f] NC_9H_6O = quinolin-8-yloxy. [g] Different route by starting with PCl_5. [h] Two peaks observed; possibly two different conformers.

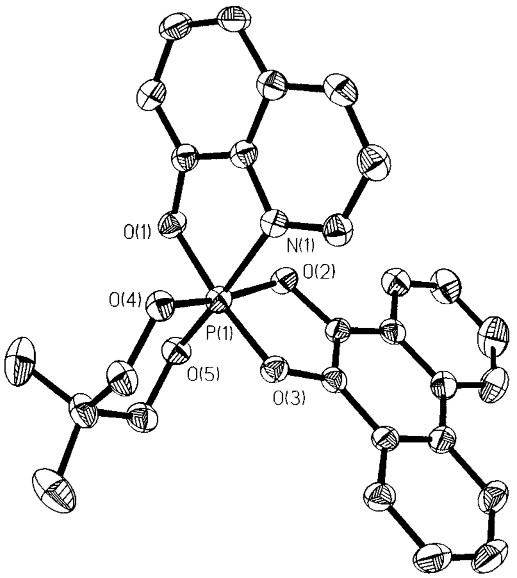


Figure 1. An ORTEP picture of **2**; only the phosphorus atom and those connected to it are labeled. The disordered CH_2Cl_2 molecule of crystallization and all hydrogen atoms have been omitted.

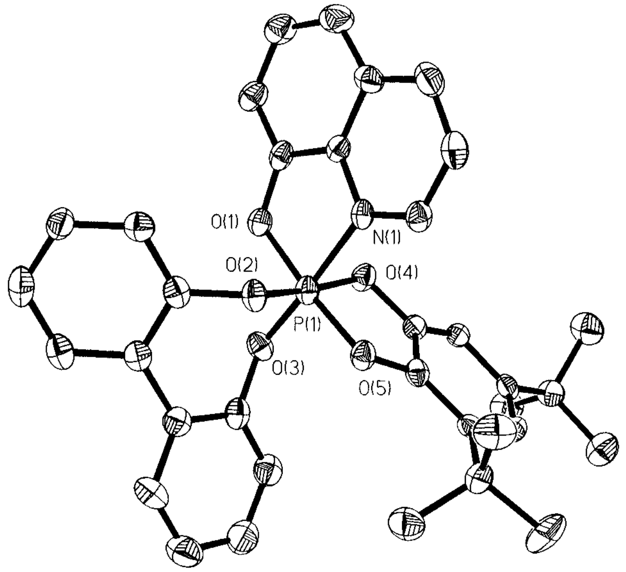


Figure 2. An ORTEP picture of one of the two independent molecules of **4**; only the phosphorus atom and those connected to it are labeled. The CH_2Cl_2 molecule of crystallization and all hydrogen atoms have been omitted.

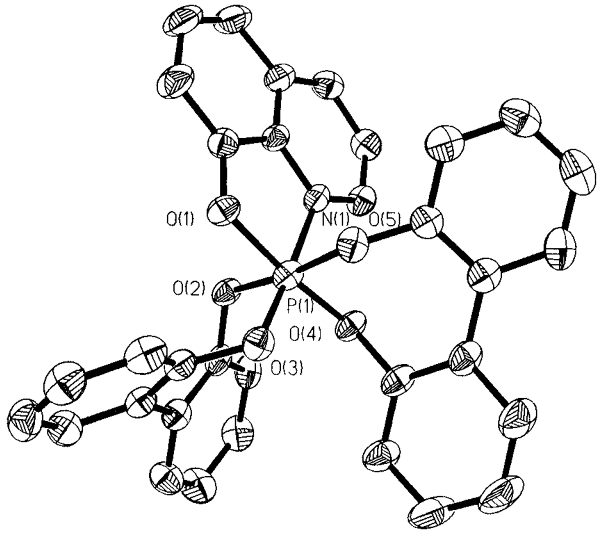


Figure 3. An ORTEP picture of **6**; only the phosphorus atom and those connected to it are labeled. The disordered Et_2O of solvation and all hydrogen atoms have been omitted.

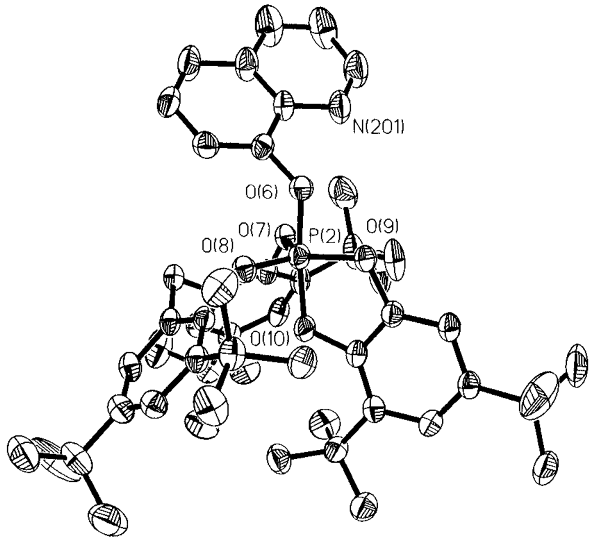


Figure 4. An ORTEP picture of **7** showing the independent molecule in which the oxinate is ordered. Only one set of atoms for the disordered *tert*-butyl group is shown. All hydrogen atoms are omitted and only phosphorus, nitrogen, and those connected to phosphorus are labeled.

membered ring [97.4(1)°] is larger than that observed for the seven-membered ring [94.4(2)° and 93.3(2)°].

The P−O bond lengths differ depending on the ring size. In the five-membered rings the mean P−O distance is 1.709 Å, whereas it is 1.655 Å in the larger rings. The mean P−O bond distances in the 1,3,2-dioxaphosphorinane (1.632 Å) or in the phosphepin (1.660 Å) ring are greater, *albeit marginally*, than those observed in the analogous pentacoordinated structures **XV** (mean 1.613 Å) or **XVI** (mean 1.632 Å) as expected. The P−N distances in **2**, **4**, and **6** are in the range 1.938−1.963 Å; these values are *ca*. 0.2 Å longer than the calculated value for a P−N single bond using a modified Schomaker−Stevenson equation.[22]

The five-membered rings are nearly planar in all three structures. The seven-membered ring in **4** and **6** shows a conformation in between a twist-boat and a boat[23] and is analogous to that in the structures reported by Holmes and coworkers.[1e,f,15,17] The six-membered ring in **2** has a slightly distorted chair conformation (85% chair[24]). By contrast, it can be noted that this ring exhibited mostly a boat/twist-boat conformation in pentaoxyphosphoranes.[1,8] As the only example

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

Bond Lengths			
P(1)−O(5)	1.623 (2)	P(1)−O(4)	1.640 (2)
P(1)−O(3)	1.705 (2)	P(1)−O(1)	1.709 (2)
P(1)−O(2)	1.741 (2)	P(1)−N(1)	1.956 (2)
Bond Angles			
O(5)−P(1)−O(4)	99.90 (8)	O(5)−P(1)−O(1)	89.53 (8)
O(4)−P(1)−O(3)	90.06 (8)	O(3)−P(1)−O(1)	173.23 (8)
O(4)−P(1)−O(1)	91.18 (8)	O(4)−P(1)−O(2)	169.12 (8)
O(5)−P(1)−O(2)	90.85 (8)	O(1)−P(1)−O(2)	87.21 (8)
O(3)−P(1)−O(2)	90.32 (7)	O(4)−P(1)−N(1)	85.11 (8)
O(5)−P(1)−N(1)	172.58 (8)	O(1)−P(1)−N(1)	84.87 (7)
O(3)−P(1)−N(1)	88.61 (7)	C(exo)−N(1)−P(1)	130.4 (2)
O(2)−P(1)−N(1)	84.03 (7)	C(endo)−N(1)−P(1)	110.11 (19)
O(5)−P(1)−O(3)	96.82 (8)		

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[22] Blom, R.; Haaland, *A. J. Mol. Strukt.* **1985**, *128*, 21.

[23] Boessenkool, I. K.; Boeyens, J. C. A. *J. Cryst. Mol. Struct.* **1980**, *10*, 11.

[24] Gould, R. O.; Taylor, P. PUCKER Program for the calculation of ring conformations, University of Edinburgh, 1994.

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

Bond Lengths			
P(1)−O(3)	1.652 (4)	P(1)−O(2)	1.655 (3)
P(1)−O(5)	1.692 (3)	P(1)−O(4)	1.696 (3)
P(1)−O(1)	1.710 (4)	P(1)−N(1)	1.959 (4)
Bond Angles			
O(3)−P(1)−O(2)	95.9 (2)	O(3)−P(1)−O(4)	91.5 (2)
O(2)−P(1)−O(5)	87.8 (2)	O(5)−P(1)−O(4)	91.6 (2)
O(2)−P(1)−O(4)	172.6 (2)	O(2)−P(1)−O(1)	93.6 (2)
O(3)−P(1)−O(1)	88.8 (2)	O(4)−P(1)−O(1)	86.2 (2)
O(5)−P(1)−O(1)	173.6 (2)	O(2)−P(1)−N(1)	85.8 (2)
O(3)−P(1)−N(1)	174.5 (2)	O(4)−P(1)−N(1)	86.8 (2)
O(5)−P(1)−N(1)	88.0 (2)	O(8)−P(2)−O(7)	95.5 (2)
O(1)−P(1)−N(1)	85.9 (2)	C(exo)−N(1)−P(1)	132.2 (4)
O(3)−P(1)−O(5)	97.3 (2)	C(endo)−N(1)−P(1)	109.3 (3)

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

Bond Lengths			
P(1)−O(3)	1.637 (2)	P(1)−O(4)	1.662 (2)
P(1)−O(2)	1.673 (2)	P(1)−O(5)	1.681 (2)
P(1)−O(1)	1.725 (2)	P(1)−N(1)	1.938 (2)
Bond Angles			
O(3)−P(1)−O(4)	96.41 (9)	O(3)−P(1)−O(5)	90.15 (9)
O(4)−P(1)−O(2)	91.14 (8)	O(2)−P(1)−O(5)	172.61 (10)
O(4)−P(1)−O(5)	92.79 (9)	O(4)−P(1)−O(1)	171.78 (10)
O(3)−P(1)−O(1)	91.79 (9)	O(5)−P(1)−O(1)	87.67 (9)
O(2)−P(1)−O(1)	87.54 (9)	O(4)−P(1)−N(1)	86.04 (9)
O(3)−P(1)−N(1)	177.39 (9)	O(5)−P(1)−N(1)	90.61 (9)
O(2)−P(1)−N(1)	83.41 (9)	C(exo)−N(1)−P(1)	130.4 (2)
O(1)−P(1)−N(1)	85.75 (9)	C(endo)−N(1)−P(1)	110.0 (2)
O(3)−P(1)−O(2)	95.63 (9)		

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

Bond Lengths			
P(1)−O(3)	1.590 (3)	P(1)−O(2)	1.603 (2)
P(1)−O(4)	1.625 (2)	P(1)−O(1)	1.647 (2)
P(1)−O(5)	1.713 (2)	P(2)−O(8)	1.595 (3)
P(2)−O(7)	1.600 (3)	P(2)−O(9)	1.630 (2)
P(2)−O(6)	1.647 (3)	P(2)−O(10)	1.708 (3)
Bond Angles			
O(3)−P(1)−O(2)	118.50 (13)	O(3)−P(1)−O(4)	123.43 (13)
O(2)−P(1)−O(4)	117.88 (13)	O(3)−P(1)−O(1)	85.35 (13)
O(2)−P(1)−O(1)	91.39 (13)	O(4)−P(1)−O(1)	89.08 (12)
O(3)−P(1)−O(5)	91.51 (12)	O(2)−P(1)−O(5)	93.03 (12)
O(4)−P(1)−O(5)	89.88 (12)	O(1)−P(1)−O(5)	175.43 (13)
O(8)−P(2)−O(7)	117.15 (13)	O(8)−P(2)−O(9)	119.07 (14)
O(7)−P(2)−O(9)	123.55 (14)	O(8)−P(2)−O(6)	91.06 (14)
O(7)−P(2)−O(6)	90.45 (13)	O(9)−P(2)−O(6)	83.87 (13)
O(8)−P(2)−O(10)	92.55 (13)	O(7)−P(2)−O(10)	92.30 (13)
O(9)−P(2)−O(10)	90.05 (13)	O(6)−P(2)−O(10)	173.88 (13)

of a hexacoordinated phosphorane with a saturated ring, **2** is useful for comparing the variation in geometric parameters at phosphorus in compounds with varying coordination numbers ranging from 3 to 6.

There are weak interactions between the solvent and the molecule in structures **2** (O5 is close to a H atom of CH_2Cl_2 at 2.347 Å) and **4** (O3 and O8 are close to H atoms of different CH_2Cl_2 molecules at 2.359 and 2.372 Å, respectively); the oxygen *trans* to the oxinate nitrogen is the one involved in these interactions.

In structure **7** the phosphorus atom has a trigonal bipyramidal geometry. The nonchelating quinoline-8-yloxy substituent is in the axial position, while the 3,5-di-*tert*-butyl-o-quinondiyl substituent is axial−equatorial. The 1,3,2-dioxaphosphocin ring spans a diequatorial position. Four of the five P−O bonds are shorter than single bonds (mean 1.617 Å) while the P2−O10 distance is much longer [1.708(3) Å)].

The P−N distance is 3.853(4) Å for the shown molecule and 3.736(6) and 4.154(7) Å for the disordered second one. A comparison with the sum of van der Waals radii (3.44 Å)[25] shows that there is no interaction between phosphorus and nitrogen. The absence of N→P coordination in **7** is most probably a result of steric factors (see ^{31}P NMR section also).

The equatorial angles lie between 117.15(13)° (O8−P2−O7) and 123.55(14)° (O7−P2−O9). The O6−P2−O10 (O_{ax}−P−O_{ax}) angle has a value of 173.88(13)° and lies in the range observed for analogous phosphoranes.[18] The axial−equatorial angles lie between 83.87(13) (O9−P2−O6) and 92.55(13)° (O8−P2−O10). The eight-membered ring has a boat-chair conformation quite similar to some known structures.[5,6,18]

Summary and Outlook. The presence or absence of N→P coordination in the new phosphoranes with an oxinate group is determined by the nature of the other substituents present, as revealed by X-ray crystallography and (solution state) ^{31}P NMR spectroscopy. The 1,3,2-dioxaphosphorinane ring conformation, which is normally *boat* in non-hydrogen-bonded phosphoranes,[1h,15] becomes *chair* when N→P coordination is present, as in our phosphorane **2**. Furthermore, although no isomerism has been identified so far in the above hexacoordinated systems (Table 1), there is every possibility of obtaining isomers. Amino group replacement reactions on phosphoranes such as those shown by eqs 5−7 may be used to generate new reaction chemistry; for example, the reaction of **8** with *o*-aminothiophenol leads to a crystalline product [$\delta(^{31}P) = -78.9$ ppm] in which the phosphorinane ring appears to have opened and a diethylamino group has been retained (^{1}H NMR). Characterization of this product is in progress.

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Supporting Information Available: Structural diagrams with complete labeling; tables providing X-ray data collection and solution parameters; complete listing of atomic coordinates, bond lengths, and angles; anisotropic displacement parameters; H-atom coordinates and isotropic displacement parameters for structures **2**, **4**, **6**, and **7**, and NMR data pertaining to the identification of compounds **17**−**22** (43 pages). See any current masthead page for ordering and Internet access instructions.

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