DALTON
FULL PAPER

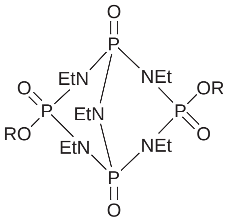
Synthesis, reactivity and structural characterisation of bicyclic tetraphosphapentazanes

Natesan Thirupathi, Setharampattu S. Krishnamurthy *,† and Munirathinam Nethaji

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

The diphenoxy bicyclic tetraphosphapentazane derivatives $(EtN)_5P_4(OPh)_2$ **2** and its monoxide $(EtN)_5P_4(O)(OPh)_2$ **3** have been prepared. Both **2** and **3** exist as a mixture of two isomers. One isomer of $(EtN)_5P_4(O)(OPh)_2$ **3a** has been isolated and its reaction with tetrachloro-1,2-benzoquinone yielded $(EtN)_5P_4(O)(OPh)_2(O_2C_6Cl_4)$ **5** in which the junction phosphorus atom becomes five-co-ordinated. Treatment of **2** or **3a** with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene, bicyclo[2.2.1]hepta-2,5-diene), on the other hand, yielded the chelate complex $[Mo(CO)_4\{(EtN)_5P_4(O)_n(OPh)_2\}]$ ($n = 0$ or 1; **6** or **7**) in which the peripheral phosphorus atoms are bonded to the metal. The structures of **3a** and **5**–**7** have been confirmed by single-crystal X-ray diffraction studies. The two P_3N_3 rings in **3a** and **5** adopt twist/twist and irregular/twist conformations respectively; the phenoxy substituents occupy the 'pseudo axial' positions. However, an ideal chair conformation is observed for the P_3N_3 rings in **6** and **7** with the phenoxy substituents taking up the 'pseudo equatorial' positions. The NMR spectroscopic data for the compounds are discussed.

The chemistry of cyclophospha*zanes* has received considerably less attention than that of cyclophospha*zenes*.[1,2] Earlier we had reported on the synthesis and structures of several aryloxy-λ^3-cyclotriphosphazanes as well as a bicyclic tetraphosphapentazane tetroxide, $(EtN)_5P_4(O)_4(OC_6H_3Me_2\text{-}2,6)_2$ **1**.[3–5] Conformations of the P–N rings and the structural data can be explained in terms of 'negative hyperconjugation' involving nitrogen lone pairs and P–O or P–N σ* orbitals.[3–5] In this paper, we report the results of our investigations on the bicyclic tetraphosphapentazane (P_4N_5) ring system. The bicyclic phosphazane $(EtN)_5P_4(OPh)_2$ and its monoxide as well as their molybdenum tetracarbonyl complexes have been synthesised and structurally characterised. The reaction of the monoxide with tetrachloro-1,2-benzoquinone (TCB) results in the retention of the ring skeleton with the junction λ^3-phosphorus atom undergoing oxidative addition to give a five-co-ordinated λ^5-phosphorus centre.



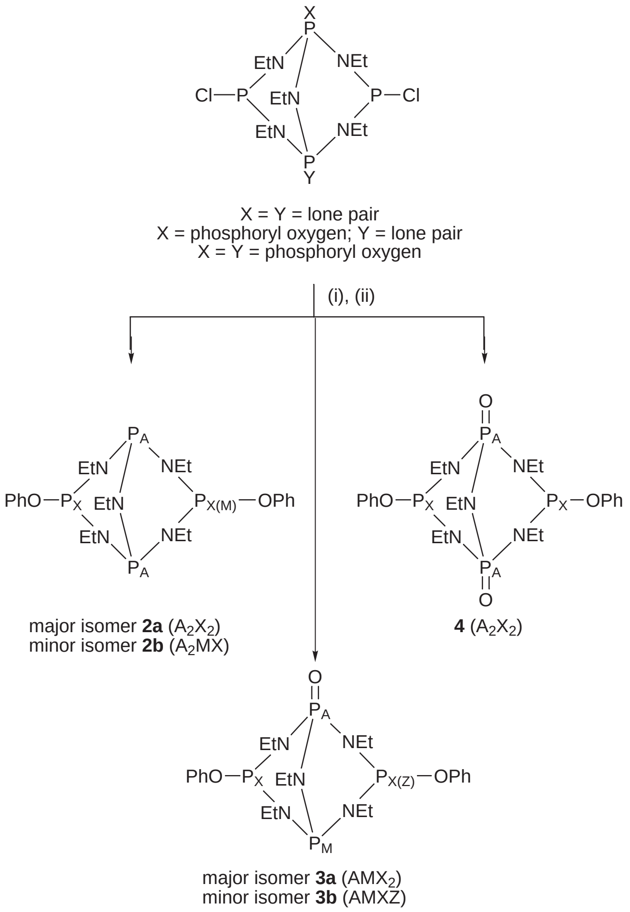
R = $C_6H_3Me_2$–2,6

1

Results and Discussion

Synthesis

Reaction of the chlorobicyclophosphazanes $(EtN)_5P_4(O)_nCl_2$ ($n = 0$–2) with NaOPh in tetrahydrofuran (thf) yields the diphenoxy derivatives $(EtN)_5P_4(O)_n(OPh)_2$ **2**–**4** as shown in Scheme 1. Both **2** and **3** exist as two isomers in solution as shown by ^{31}P NMR spectroscopy. Isomers of **2** could not be separated; the major isomer of **3** could be isolated in a pure state by fractional crystallisation from light petroleum.

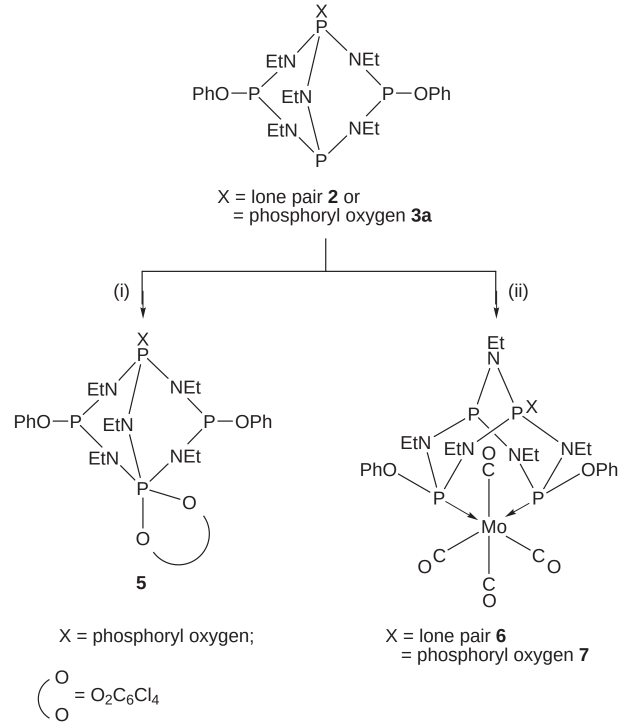


Scheme 1 (i) NaOPh–thf; (ii) chromatographic separation over silica gel, eluent light petroleum (b.p. 60–80 °C)–ethyl acetate (95:5, v/v)

Treatment of **3a** with TCB gives $(EtN)_5P_4(O)(OPh)_2(O_2C_6Cl_4)$ **5** in nearly quantitative yield (see Scheme 2). Other diones such as benzil or acenaphthenequinone do not react with **3a**; in both cases **3a** can be quantitatively recovered. During this reaction, the junction phosphorus atom undergoes oxidative addition as it is a better donor than the peripheral

---

† E-Mail: ipcssk@ipc.iisc.ernet.in



Scheme 2 (i) Tetrachloro-1,2-benzoquinone, benzene, 0 °C; (ii) $[Mo(CO)_4(nbd)]$, light petroleum, 50–60 °C

phosphorus atoms. The mechanism of the reaction involves the donation of the phosphorus lone pair to the dione and hence a strong electrophilic dione such as TCB reacts readily. It may be noted that λ^3-cyclotriphosphazanes react with TCB by an unusual pathway resulting in ring contraction–rearrangement to give λ^5-cyclodiphosphazanes with an aminophosphite moiety as the exocyclic unit.[6] However, in the reaction of **3a** with TCB, no such rearrangement is observed and the P_4N_5 skeleton remains intact.

Treatment of bicyclic phosphazanes **2** or **3a** with $[Mo(CO)_4(nbd)]$ in light petroleum yields the chelate complexes, $[Mo(CO)_4\{(EtN)_5P_4(O)_n(OPh)_2\}]$ ($n = 0$ or 1; **6** or **7**) in which the two peripheral phosphorus atoms are co-ordinated to the metal (see Scheme 2). The preferential co-ordination of peripheral phosphorus centres is due to their greater π-acceptor character as compared to the junction phosphorus centres. Furthermore, chelation would favour the formation of **6** and **7**.

Spectroscopic data

The bicyclic phosphazanes have been characterised by elemental analysis, IR and NMR spectroscopy. The IR spectra of **3a**, **5** and **7** each show a strong peak at 1238, 1240 and 1207 cm^{-1} respectively due to the presence of a P=O group. The chelate complexes **6** and **7** show four intense peaks in the metal carbonyl region ($\nu_{C=O}$, cm^{-1}; 2025, 1933, 1918 and 1893 **6**; 2028, 1943, 1919 and 1907 **7**) indicating the presence of a $Mo(CO)_4$ moiety. The slightly higher values of ν_{CO} for **7** indicates that **3a** is a less effective π-acceptor ligand than **2**.

The ^{31}P NMR spectrum of **2** shows the presence of two isomers (3 : 1 ratio) giving rise to an A_2X_2 and an A_2MX pattern. The junction phosphorus nuclei resonate upfield in comparison to peripheral phosphorus nuclei. The spectrum of **3a** represents an AMX_2 spin system while the minor isomer, **3b** gives rise to an AMXZ type spin system. The major isomer in each case can be assigned the 'bbff' (boat/boat; flagpole/flagpole disposition of the substituents) conformation while the minor isomer is likely to have the 'bcfa' (boat/chair; flagpole/axial disposition) conformation (see ref. 7 for a description of these conformations). In the solid state, **3a** exhibits a conformation close to 'bbff'. The ^{31}P NMR spectrum of **3a** remains unchanged even after the sample is heated in boiling benzene for 12 h suggesting that the barrier to interconversion of isomers of **3** is high. This observation is in accord with the earlier experimental and theoretical studies on λ^3-cyclotriphosphazanes for which axial ⟶ equatorial conversion at phosphorus has a large activation barrier.[3] Unlike **2** and **3**, the dioxide **4** exists as a single isomer which gives rise to an A_2X_2 pattern. The ^{31}P chemical shifts and P–P coupling constants are comparable with those for the chloro precursors[7] and also for the *N*-methyl derivatives, $(MeN)_5P_4(OR)_2$ (R = Ph or Bu^t).[8]

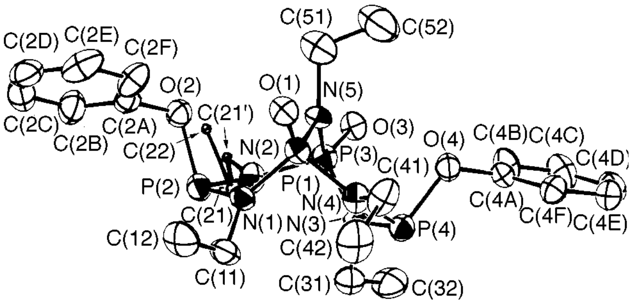


Fig. 1 Molecular structure of compound **3a**. 'Statistical disorder' of ethyl group at N(2) and oxygen atom at P(1) and P(3) are shown

Compound **5** represents the first example of a P–N ring system containing $\lambda^3\sigma^3$-, $\lambda^5\sigma^4$- and $\lambda^5\sigma^5$-phosphorus centres and its ^{31}P NMR spectrum displays the expected AMX_2 pattern. The peripheral λ^3-phosphorus nuclei are shielded while the junction four-co-ordinated phosphorus is deshielded in comparison to the corresponding values for the monoxide **3a**.

The ^{31}P NMR spectra of **6** and **7** display an A_2X_2 and an AMX_2 pattern respectively. As a result of complexation to the $Mo(CO)_4$ moiety, the chemical shift of the junction λ^3-phosphorus nucleus in **7** moves upfield compared to its value for **3a**; on the other hand, the chemical shift of the junction λ^3-phosphorus nuclei in **6** occurs downfield compared to the corresponding value for **2**. The observed changes in the chemical shifts of the junction and the peripheral λ^3-phosphorus nuclei are more marked than the change in chemical shift of the λ^5-phosphorus nucleus.

The ^1H NMR spectrum of **3a** shows the presence of only two types of methyl and methylene protons in 4 : 1 ratio although one would expect three different types of NCH_2CH_3 protons. The ^{13}C NMR spectrum also shows the presence of two types of methyl carbon nuclei (δ 17.20 and 17.45). However, the methylene region of the spectrum shows the presence of three types of methylene carbons in ≈2 : 2 : 1 ratio. The two bond P–C coupling is observed only with λ^3-phosphorus nuclei; coupling to junction λ^5-phosphorus is close to zero as observed for the tetroxide **1**.[5] The ^1H and ^{13}C NMR spectra for **5** are consistent with its structure. Four multiplets are observed at δ 3.10, 3.36, 3.54 and 3.71 (relative intensities 1 : 2 : 1 : 1) for the NCH_2CH_3 protons indicating that different conformations adopted by the two P_3N_3 ring segments in the solid state (see below) are retained in solution. However, the ^{13}C NMR spectrum shows only three kinds of methyl and methylene carbon nuclei. Two bond P–C coupling is observed only between the methylene carbon and λ^3-phosphorus nuclei as in the case of **3a**.

Crystal structures

The molecular structures of **3a** and **5** along with the atom labelling schemes are shown in Figs. 1 and 2 respectively. The structural features of **3a**, **5** and the related tetroxide **1** are compared in Table 1. The two P_3N_3 rings in **3a** exhibit a twist conformation in contrast to the half-chair conformation observed in the tetroxide **1**. However, in **5**, one of the P_3N_3 rings adopts an irregular conformation while the other is in a twist conformation. The extent of distortion of the P_3N_3 ring from an ideal twist conformation can be defined by the asymmetry parameter,[9]

Table 1 Comparison of structural features of bicyclic phosphazanes **3a**, **5** and **1**[a]

Structural feature	**3a**	**5**	**1**
P–N ring conformation			
(a) P_4N_4 ring	saddle	saddle	saddle
(b) P_3N_3 ring	twist/twist	irregular/twist	half-chair/half-chair
asymmetry parameter, ΔC_2	10.7, 8.8/10.4, 10.4	9.8, 3.7[b]	6.9/6.9
Bond parameters[c]			
ave. P_j–N/Å	1.682(5)	at P(1), 1.664(2); at P(3), 1.699(2)	1.654(4)
ave. P_p–N/Å	1.692(5)	1.707(2)	1.661(4)
ave. P–N/Å	1.687(5)	1.690(2)	1.659(4)
P=O/Å	1.397(9)[d]	1.469(2)	1.455(3)[d]
ave. P–O/Å	1.672(5)	1.657(2)	1.591(2)
ave. P_j–N–P_p/°	125.2(3) (123.1–127.3)	at P(1) 120.8(2) (120.7–120.9); at P(3) 125.4(1) (122.1–128.7)	127.0(2) (123.6–130.3)
ave. N–P_j–N/°	102.1(3) (99–104.3)	at P(1) 104.4(1) (100.0–106.7); at P(3) 101.7(1) (94.3–114.8)	103.3(2) (102.4–104.2)
ave. N–P_p–N/°	101.2(3) (100.9–101.4)	102.2(1) (100.0–104.3)	104.9(2)
ave. P–N–P/°	123.4(3)	122.9(1)	124.2(2)
ave. N–P–N/°	101.7(3)	102.8(1)	103.8(2)
Geometry of nitrogen atoms	trigonal planar except N(4) (ΣN angle = 356.5°)	trigonal planar	trigonal planar except N(1) (ΣN angle = 355.3°)
Dihedral angle, φ/°[e]	77.9	71.3	125.0

[a] Ref. 5. [b] ΔC_2 is not defined for irregular conformation. [c] P_j and P_p are junction and peripheral phosphorus atoms. [d] ave. (P=O) distance. [e] Angle between the best least-squares mean plane of two P_3N_3 rings.

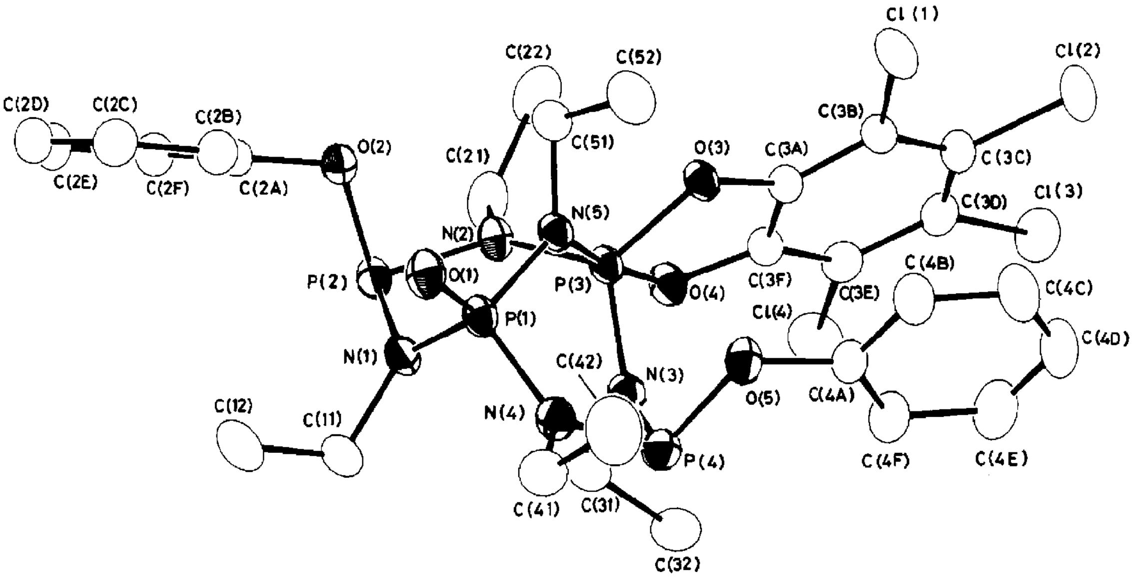


Fig. 2 Molecular structure of compound **5**

ΔC_2, which is slightly larger for **3a** than for **5** (see Table 1). The angle between the mean plane of the two P_3N_3 rings in **3a** and **5** is less than that observed in the tetroxide **1**. The phenoxy groups occupy 'pseudo axial' positions on the respective phosphorus atoms.

A distorted trigonal bipyramidal geometry is observed for the five-co-ordinated phosphorus P(3) in **5** and this distortion follows a non-Berry coordinate[10] due to ring strain. The six-membered P_3N_3 rings and the five-membered PO_2C_2 ring each span one apical and one equatorial site while the eight-membered P_4N_4 ring spans two equatorial sites at P(3). The five-membered PO_2C_2 ring assumes an envelope conformation. The apical P–N and P–O bonds are longer than the corresponding equatorial bonds. The P–N distances lie in the range 1.660–1.703 Å and 1.647–1.742 Å for **3a** and **5** respectively. The average P–N bond lengths decrease in the following order: $\lambda^5\sigma^5$ P–N > $\lambda^3\sigma^3$ P–N > $\lambda^5\sigma^4$ P–N. The average P–O distance in **3a** and **5** is longer than that observed in tetroxide **1** while the P=O distance in **3a** is much shorter than that observed in **5** or the tetroxide **1**. The geometry around the nitrogen atoms in **3a** and **5** is trigonal planar; only the nitrogen atom N(4) in **3a** deviates slightly from planarity. The observed structural features arise as a result of 'negative hyperconjugation' which involves the interaction of nitrogen lone pairs with adjacent P–X (X = O or N) σ* orbitals. As noted earlier,[3,4] a C–N–P–X torsion angle of 90° would result in maximum 'negative hyperconjugation' while any departure from this value would reduce this interaction. In general, the lone pairs of electrons on the nitrogen atoms orient parallel to P–X bonds as observed for other cyclophosphazanes.[5,11] However, the lone pair at N(1) in **5** orients parallel to the P=O bond. An additional point of interest in the structure of **5** is the π-stacking interaction observed between the aromatic rings of the catecholate unit and phenoxy group bonded to P(4).

There are four molecules in the unit cell of **6**; the asymmetric part consists of two different half-molecules. In both the mole-

Table 2 Comparison of structural features of compounds **6**, **7** and (MeN)$_6$P$_4$S$_2$[a]

	Compound			
	6		**7**	(MeN)$_6$P$_4$S$_2$
Structural feature	Molecule 1	Molecule 2		
P$_3$N$_3$ ring conformation	chair/chair	chair/chair	chair/chair	chair/chair
Asymmetry parameters,[9]				
ΔC_2	1.1, 2.4, 1.4	0.4, 0.8, 0.7	0.2, 1.8, 1.7	2.1, 1.9, 2.2/2.2, 1.3, 1.2
ΔC_s	0.9, 1.6, 1.7	0.5, 0.7, 0.5	0.9, 1.6, 0.9	0.7, 1.7, 2.3/0.9, 1.4, 1.6
P–N distances[b]/Å				
P$_j$–NP$_j$	1.705(4)	1.707(4)	1.672(6)	1.70(1)[c]
ave. P$_j$–NP$_p$X	1.727(6)	1.730(5)	1.695(9)	1.73(1)
ave. XP$_p$–NP$_j$	1.696(5)	1.692(5)	1.710(9)	1.67(1)
ave. P–N	1.710(5)	1.710(5)	1.696(8)	1.697(7)
XP$_p$–MP$_p$X	2.439(2)	2.446(2)	2.433(3)	1.692(4)[c]
P–N–P angles/°				
ave. P$_j$–N–P$_p$X	121.5(3)	121.7(3)	120.7(5)	121.7(2)
XP$_p$–M–P$_p$X	77.9(8)	77.8(8)	77.6(1)	119.4(2)[c]
ave. P–N–P	122.1(4)	122.0(3)	120.5(5)	121.5(2)
N–P–N angles/°				
ave. N–P$_j$–N	102.1(2)	101.2(2)	104.3(4)	101.4(2)
ave. N–P$_p$X–N	102.5(3)	102.7(3)	101.8(4)	104.2(2)
ave. N–P–N	101.5(2)	101.9(2)	103.7(4)	102.8(2)
Dihedral angle, φ/°[d]	73.5	74.1	73.8	101.7
ΣN$_b$ angle[e]/°	355.4	354.7	354.0	355.5
ΣN$_p$ angle[e]/°	348.1, 352.5	351.6, 351.9	342.3, 348.6	348.8, 348.0/353.6, 355.1

[a] Parameters calculated from ref. 12. [b] X = OPh, M = Mo (in **6** and **7**); X = S, M = N [in (MeN)$_6$P$_4$S$_2$]; P$_j$ and P$_p$ are junction and peripheral phosphorus atoms. [c] Average value. [d] Angle between the best least-squares mean plane of two P$_3$N$_3$ rings. [e] N$_b$ and N$_p$ are bridging and peripheral nitrogen atoms.

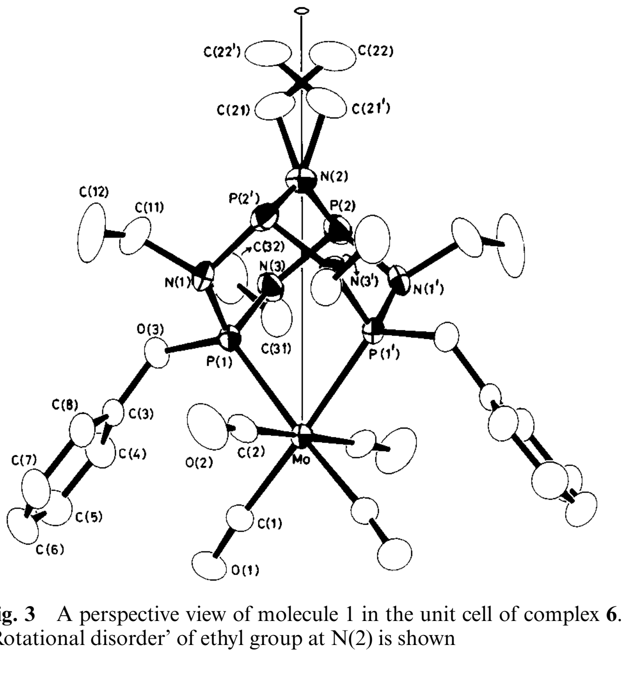


Fig. 3 A perspective view of molecule 1 in the unit cell of complex **6**. 'Rotational disorder' of ethyl group at N(2) is shown

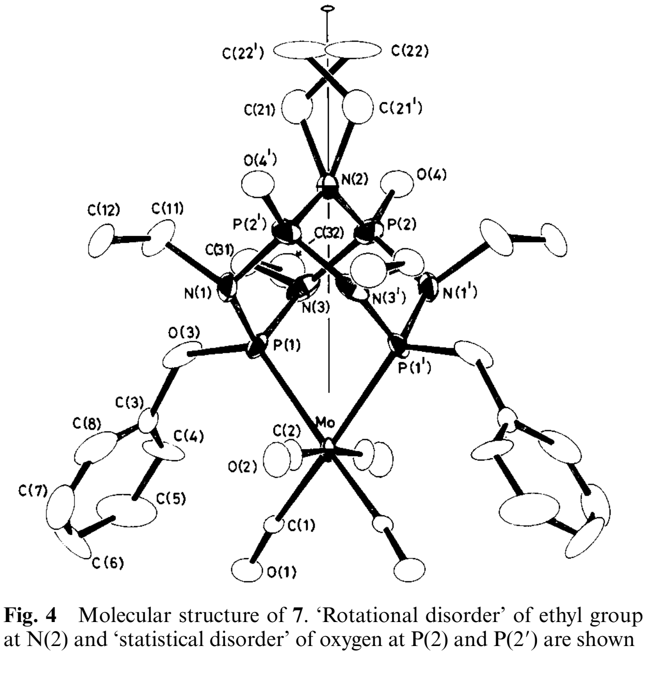


Fig. 4 Molecular structure of **7**. 'Rotational disorder' of ethyl group at N(2) and 'statistical disorder' of oxygen at P(2) and P(2') are shown

cules, the P–N–Mo core has an adamantane-like cage structure but the orientations of the ethyl groups at N(1) and N(3) are different. The structure of one of the molecules along with atom labelling is shown in Fig. 3. The molecular structure of **7** with the atom labelling is shown in Fig. 4. The structural features of **6**, **7** and the related cage compound (MeN)$_6$P$_4$S$_2$[12] are summarised in Table 2. The structural features of **6** and **7** are essentially the same. The geometry around the molybdenum atom is distorted octahedral. The P$_4$N$_5$Mo skeleton is made up of four six-membered rings each adopting a chair conformation. The two nitrogen atoms N(1') and N(3') attached to the phosphorus atoms P(2) and P(2') occupy 'pseudo axial' positions while the phenoxy group at P(1) or P(1') occupies a 'pseudo equatorial' position.

The conformation of **2a** is likely to be the same as that observed for the monoxide **3a**.[3] Two changes occur upon complexation in both cases: the conformations of the P$_3$N$_3$ rings change to chair/chair and the phenoxy groups occupy 'pseudo equatorial' positions. In the resulting arrangement, as the lone pair of electrons on either N(1) or N(3) cannot orient itself parallel to the P–O σ* orbitals, the 'negative hyperconjugative' interaction is decreased and the geometry around N(1) and N(3) deviates from planarity leading to subtle changes in P–N and P–O distances.[13] The differences in P–N bond lengths between the two molecules in the unit cell of **6** arise as a result of different C–N–P–N torsion angles adopted by the ethyl groups attached to N(1) and N(3).

In conclusion, the structural data on bicyclic tetraphosphapentazanes and their metal complexes bring out factors governing the P–N ring conformations and important points relating to P–N bonding.

Experimental

General

All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk-line techniques.[14] Solvents were purified by standard procedures and freshly distilled prior to use.[15] Tetrachloro-1,2-benzoquinone (Aldrich) and ethylamine hydrochloride (Fluka) were used as purchased. The ^{1}H, ^{13}C ($SiMe_4$, internal standard) and ^{31}P (85% H_3PO_4, external standard) NMR spectra were recorded in $CDCl_3$ employing a Bruker AMX 400 or ACF 200 spectrometer. Chemical shifts downfield from the standard were assigned positive values. Mass spectra were recorded on a JEOL MS-DX 303 spectrometer. The FAB mass spectrum was recorded on a Finnigan Mat 8230 mass spectrometer.

Synthesis and characterisation of bicyclic phosphazanes 2–4

The reaction of PCl_3 and ethylamine hydrochloride carried out as described by Keat and co-workers[7] gave a complex mixture containing chlorobicyclophosphazanes, $(EtN)_5P_4(O)_nCl_2$ (n = 0–2), chlorocyclotriphosphazane, $(EtNPCl)_3$ and unidentified impurities as shown by the ^{31}P NMR spectrum of the reaction mixture. Distillation of the reaction mixture at reduced pressure [200–250 °C, 0.01 mm Hg (1 mmHg = 133.322 Pa)] gave a fraction rich in the chlorobicyclophosphazane $(EtN)_5P_4Cl_2$ (≈70%) admixed with its monoxide $(EtN)_5P_4(O)Cl_2$ (≈15%), traces of the dioxide $(EtN)_5P_4(O)_2Cl_2$ and the chlorocyclotriphosphazane $(EtNPCl)_3$ (≈15%) as shown by ^{31}P NMR spectroscopy. The relative amount of $(EtN)_5P_4Cl_2$ and its monoxide $(EtN)_5P_4(O)Cl_2$ in the distilled product varied from batch to batch because of the extreme sensitivity of $(EtN)_5P_4Cl_2$ to air and moisture as also noted by previous workers.[7] Separation of the individual components proved difficult and hence the reaction mixture was used as such for phenoxylation.

A sample of chlorocyclophosphazane containing ≈70% of $(EtN)_5P_4Cl_2$ (4.13 g) in CH_2Cl_2 (20 cm^3) was slowly added to NaOPh [prepared from PhOH (1.90 g) and sodium (0.5 g) in thf (20 cm^3)] for about 30 min with constant stirring. Stirring was continued for 24 h and the solvent removed under reduced pressure. The ^{31}P NMR spectrum of the reaction mixture showed the presence of bicyclic phosphazane **2**, its monoxide **3** and $[EtNP(OPh)]_3$ in roughly the same ratio as present in the starting material (^{31}P NMR spectroscopic evidence) indicating that the phenoxy derivatives were much less sensitive to aerial oxidation than the chloro precursors. The bicyclic phosphazanes were extracted from the reaction mixture using light petroleum and the mixture was subjected to column chromatography over silica gel using a column of dimensions ≈100 cm length × 2 cm internal diameter and light petroleum (b.p. 60–80 °C)–ethyl acetate (95 : 5, v/v) as the eluent. Two fractions were obtained. The first fraction contained **2** (1.50 g) (two isomers in 3 : 1 ratio) and $[EtNP(OPh)]_3$ in ≈4 : 1 ratio (^{31}P NMR spectroscopic evidence) as an inseparable mixture. This crude product was used for mass spectral studies and to prepare the molybdenum tetracarbonyl complex of **2**. Removal of the solvent from the second fraction followed by crystallisation from light petroleum gave colourless crystals of **3a** (0.25 g). The minor isomer $(EtN)_5P_4(O)(OPh)_2$ **3b** and the dioxide $(EtN)_5P_4(O)_2(OPh)_2$ **4** could not be isolated in a pure state but were identified by ^{31}P NMR spectroscopy. Substantial quantities of **3a** could be obtained by carrying out the phenoxylation with a batch of chlorobicyclophosphazane rich in the monoxide.

$(EtN)_5P_4(OPh)_2$ 2. ^{31}P NMR: **2a**, A_2X_2 pattern, δ_A 63.5, δ_X 111.5. **2b**, A_2MX pattern, δ_A 44.5, δ_M 100.5, δ_X 113.5. Mass spectral data for the crude mixture: m/z 448 $(EtN)_5P_4(O)(OPh)$, 432 $(EtN)_5P_4(OPh)$ (most intense peak), 408 $(EtN)_3P_3(OPh)_2$ and 356 $(EtN)_5P_4(O)$.

$(EtN)_5P_4(O)(OPh)_2$ 3a. M.p. 103–105 °C (Found: C, 47.75; H, 6.59; N, 12.18. $C_{22}H_{35}N_5O_3P_4$ requires C, 48.80; H, 6.47; N, 12.94%). IR (Nujol, cm^{-1}): ν_{PO} 1238vs. ^{31}P NMR: AMX_2 pattern, δ_A −1.6, δ_M 119.1, δ_X 137.8; J_{AX} 24.2, J_{MX} 11.0, J_{AM} 12.0 Hz. ^{1}H NMR: δ 1.24 (t, 12 H, CH_3, $^3J_{HH}$ 7.0), 1.39 (t, 3 H, CH_3, $^3J_{HH}$ 7.2), 3.35 (m br, 8 H, NCH_2), 3.57 (m br, 2 H, NCH_2), 6.83–7.37 (m, 10 H, C_6H_5). ^{13}C NMR: δ 17.20 (s, 2 C, CH_3), 17.45 (s, 1 C, CH_3), 42.10 (d, 2 C, NCH_2, $^2J_{PC}$ 37.0), 42.43 (d, 1 C, NCH_2, $^2J_{PC}$ 30.0), 43.33 (dd, 2 C, NCH_2, $^2J_{PC}$ 38.0, 31.6 Hz), 115.61, 119.58, 121.04, 121.11, 123.40, 129.43, 129.70 (s, 12 C, C_6H_5).

$(EtN)_5P_4(O)(OPh)_2$ 3b. ^{31}P NMR: AMXZ pattern, δ_A −10.6, δ_M 120.0, δ_X 136.1, δ_Z 152.9; J_{AX} 28.5, J_{AZ} 27.0, J_{MX} 8.6, J_{AM} 12.2, J_{MZ} and J_{XZ} 0.0 Hz.

$(EtN)_5P_4(O)_2(OPh)_2$ 4. ^{31}P NMR: A_2X_2 pattern, δ_A 11.8, δ_X 133.1; J_{AX} 38.8 Hz.

Synthesis and characterisation of compounds 5–7

$(EtN)_5P_4(O)(OPh)_2(O_2C_6Cl_4)$ 5. A solution of **3a** (0.71 g, 1.32 mmol) in benzene (15 cm^3) was slowly added over a period of 15 min to an ice-cold solution of TCB (0.32 g, 1.32 mmol) in benzene (15 cm^3). The reaction mixture was allowed to attain 25 °C and stirring was continued for 24 h. The solvent was removed under reduced pressure until the volume of the solution was reduced to half; $CHCl_3$ (5 cm^3) was added and the solution set aside at 25 °C for 2–3 d to obtain colourless crystals of **5** (0.95 g, 91%). M.p. 136–138 °C (Found: C, 41.49; H, 4.87; N, 8.09. $C_{28}H_{35}Cl_4N_5O_5P_4$ requires C, 42.70; H, 4.44; N, 8.89%); IR (KBr, cm^{-1}): ν_{PO} 1240vs. ^{31}P NMR: AMX_2 pattern, δ_A −35.0, δ_M 17.0, δ_X 130.7, J_{MX} 23.1, J_{AX} 52.7, J_{AM} 9.0 Hz. ^{1}H NMR: δ 1.15 (t, 6 H, CH_3, $^3J_{HH}$ 6.2), 1.16 (t, 6 H, CH_3, $^3J_{HH}$ 5.4), 1.44 (t, 3 H, CH_3, $^3J_{HH}$ 6.5), 3.10 (m, 2 H, NCH_2), 3.36 (m, 4 H, NCH_2), 3.54 (m, 2 H, NCH_2), 3.71 (m, 2 H, NCH_2), 6.94–7.16 (m, 10 H, C_6H_5). ^{13}C NMR: δ 16.65 (s, 2 C, CH_3), 17.38 (s, 1 C, CH_3), 17.75 (s, 2 C, CH_3), 41.24 (d, 2 C, NCH_2, $^2J_{PC}$ 36.5), 43.68 (s, 1 C, NCH_2), 45.05 (d, 2 C, NCH_2, $^2J_{PC}$ 42.7 Hz), 113.00, 115.00, 120.27, 120.35, 121.50, 123.60, 126.00, 129.60, 138.00, 143.00, 153.33 and 153.41 (s, 18 C, C_6H_5 and $O_2C_6Cl_4$).

$[Mo(CO)_4\{(EtN)_5P_4(OPh)_2\}]$ 6. A solution of $[Mo(CO)_4(nbd)]$[16] (0.22 g) and **2** (0.40 g) in light petroleum (25 cm^3) was gently heated to 50 °C, held at that temperature with stirring for 5–6 h and cooled to 25 °C. Removal of solvent gave an oily product which was passed through a short silica gel column using $CHCl_3$–light petroleum (1 : 1) as the eluent. Evaporation of the solvents under reduced pressure gave an oily residue which was redissolved in light petroleum (5 cm^3). Cooling the solution at 0 °C for 24 h gave pale orange crystals of **6** (0.20 g). M.p. 143 °C (Found: C, 42.67; H, 4.68; N, 9.40. $C_{26}H_{35}MoN_5O_6P_4$ requires C, 42.57; H, 4.77; N, 9.55%); IR (KBr, cm^{-1}): ν_{CO} 2025s, 1933vs, 1918vs, 1893vs. ^{31}P NMR: A_2X_2 pattern, δ_A 121.6, δ_X 157.6; J_{AX} 25.4 Hz. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 12 H, CH_3, $^3J_{HH}$ 7.0), 1.32 (t, 3 H, CH_3, $^3J_{HH}$ 7.1 Hz), 3.24 (m br, 10 H, NCH_2), 3.35 (m br, 2 H, NCH_2), 7.14–7.40 (m, 10 H, C_6H_5).

Table 3 Crystallographic data[a] for compounds **3a** and **5**–**7**

	3a	**5**	**6**	**7**[b]
Chemical formula	$C_{22}H_{35}N_5O_3P_4$	$C_{28}H_{35}Cl_4N_5O_5P_4$	$C_{26}H_{35}MoN_5O_6P_4$	$C_{26}H_{35}MoN_5O_7P_4$
M	541.43	787.29	733.41	749.41
Crystal size/mm	0.35 × 0.35 × 0.15	0.23 × 0.20 × 0.18	0.19 × 0.12 × 0.10	0.60 × 0.30 × 0.14
Space group	$P2_1/c$	$P2_1/c$	$P2/c$	$C2/c$
a/Å	8.668(2)	8.828(4)	17.299(5)	17.356(3)
b/Å	34.879(7)	13.930(5)	12.324(5)	12.179(3)
c/Å	9.784(1)	29.32(1)	17.412(6)	17.301(3)
β/°	107.36(1)	91.20(3)	111.57(2)	111.97(1)
U/Å^3	2823.2(9)	3604(3)	3452(2)	3392(1)
$\rho_{calc.}$/g cm^{-3}	1.274	1.451	1.411	1.468
μ(Mo-Kα)/cm^{-1}	2.99	5.50	6.09	6.23
Index ranges/°	$0 \leq h \leq 10, 0 \leq k \leq 41, -11 \leq l \leq 11$	$0 \leq h \leq 10, 0 \leq k \leq 16, -34 \leq l \leq 34$	$0 \leq h \leq 20, 0 \leq k \leq 14, -20 \leq l \leq 19$	$-17 \leq h \leq 17, -13 \leq k \leq 0, -18 \leq l \leq 0$
Reflections, total	5416	7165	6665	4704
unique	4954	6353	6076	2214
with [$I > 2\sigma(I)$]	2530	4909	4188	1601
Data, restraints, parameters	4949, 30, 318	6351, 0, 420	6074, 12, 403	2214, 20, 203
F(000)	1144	1624	1504	1536
Residual (negative) peak/e Å^{-3}	0.459 (−0.237)	0.281 (−0.328)	0.802 (−1.699)	0.805 (−0.708)
Final $R1$, $wR2$	0.0765, 0.1616	0.0386, 0.0928	0.0644, 0.1588	0.0708, 0.1785
S on F^2	1.105	1.074	1.049	0.994

[a] Details in common: diffractometer, CAD4 (Siemens P4 for **7**); monoclinic; Mo-Kα radiation ($\lambda = 0.7107$ Å); 290 K (158 K for **7**); $Z = 4$; scan method ω (ω–2θ for **6**); 2θ range $2 \leq 2\theta \leq 50°$ ($4 \leq 2\theta \leq 46°$ for **7**). [b] Data was collected in primitive lattice.

[Mo(CO)$_4${(EtN)$_5$P$_4$(O)(OPh)$_2$}] 7. Complex **7** was prepared in 54% yield by a procedure similar to that adopted for **6**. M.p. 182–186 °C (Found: C, 41.80; H, 4.62; N, 9.12. $C_{26}H_{35}MoN_5O_7P_4$ requires C, 41.66; H, 4.67; N, 9.35%). FAB mass spectral data: m/z 751 (M^+), 695 ($M^+ - 2$ CO), 667 ($M^+ - 3$ CO), 639 ($M^+ - 4$ CO); IR (KBr, cm^{-1}): ν_{CO} 2028vs, 1943vs, 1919vs, 1907vs and ν_{PO} 1207vs. ^{31}P NMR: AMX$_2$ pattern, δ_A 10.1, δ_M 71.2, $\delta_X = 169.4$; J_{AM} 7.42, J_{AX} 36.1, J_{MX} 7.35 Hz. ^{1}H NMR: δ 1.22 (t, 6 H, CH$_3$, $^3J_{HH}$ 7.0), 1.26 (t, 6 H, CH$_3$, $^3J_{HH}$ 7.0), 1.31 (t, 3 H, CH$_3$, $^3J_{HH}$ 7.1 Hz), 3.25 (m br, 4 H, NCH$_2$), 3.50 (m br, 4 H, NCH$_2$), 3.53 (m br, 2 H, NCH$_2$), 7.01–7.33 (m, 10 H, C$_6$H$_5$).

Crystallography

The crystals were coated with paraffin oil to protect them from air. A summary of the crystal data for compounds **3a** and **5**–**7** are given in Table 3. A number of crystallographic problems were encountered during the refinement of these structures. When the oxygen atom in **3a** at one of the junction phosphorus atom was refined with a full site occupancy factor (s.o.f.) it showed abnormally high thermal vibrations; also, some residual electron density appeared constantly near the other junction phosphorus in the Fourier-difference map. Hence, an oxygen atom was placed at a bonding distance from each of the junction phosphorus atoms and the structure refined with a s.o.f. of 0.5 for the two atoms O(1) and O(3). This kind of disorder can arise if the molecule is packed in two different ways in the unit cell. In other words, there is a 'statistical disorder' in the packing of the molecules in the unit cell. The ethyl group at N(2) is also 'statistically disordered' over two positions. Hence, the carbon atoms C(21) and C(22) were refined isotropically by assigning a s.o.f. of 0.5 to the two positions [C(21) and C(21′); C(22) and C(22′)].

Intensity data for **6** revealed that the space group could be either $P2/c$ or Pc. The structure was initially solved in the non-centrosymmetric space group Pc. This resulted in erratic bond lengths [for example the P–N bond lengths involving bridging nitrogen atom N(2) varied from 1.50 to 1.90 Å without any trend] and high thermal vibrations for C(21) and C(22). Hence, the structure was redetermined in the centrosymmetric space group $P2/c$. The molecule of **6** would have a two-fold axis passing through the bridging nitrogen N(2) and the Mo atom but for the ethyl group attached to N(2). However, in the crystal, there is a crystallographic two-fold axis passing through N(2) and Mo as a result of 'rotational disorder'. This arises from two positions for carbon atoms C(21) and C(22) with equal s.o.f.s. This model resulted in meaningful bond parameters.

The carbon atoms C(21) and C(22) of **7** were 'rotationally disordered' as observed in **6** and the oxygen atom O(4) was 'statistically disordered' as observed in **3a**. Hence, C(21), C(22) and O(4) were refined anisotropically by assigning a s.o.f. of 0.5 for two positions in each case. The following positionally disordered atoms in the NCH$_2$CH$_3$ and CO components were refined isotropically (the s.o.f. is given in parentheses): C(1)/C(1A) (0.55/0.45), C(11)/C(11A) (0.55/0.45), C(31)/C(31A) (0.55/0.45), O(1)/O(1A) (0.55/0.45), C(12)/C(12A) (0.65/0.35), C(2)/C(2A) (0.50)/(0.50) and O(2)/(O2A) (0.50)/(0.50).

CCDC reference number 186/921.

See http://www.rsc.org/suppdata/dt/1998/1469/ for crystallographic files in .cif format.

Acknowledgements

We thank Professors W. T. Robinson (University of Canterbury, New Zealand) and T. N. Guru Row (Indian Institute of Science, Bangalore) for low-temperature data collection for one of the compounds. We also thank the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore for NMR measurements. N. T. thanks the Council of Scientific and Industrial Research, New Delhi for a Research Fellowship.

References

1 R. Keat, *Top. Curr. Chem.*, 1982, **102**, 89.
2 A. D. Norman and R. M. Hands, *MGCN*, *Main Group Chem. News*, 1996, **4**, 25; S. S. Krishnamurthy, *MGCN*, *Main Group Chem. News*, 1997, **5**, 12.
3 R. Murugavel, S. S. Krishnamurthy, J. Chandrasekhar and M. Nethaji, *Inorg. Chem.*, 1993, **32**, 5447.
4 N. Thirupathi, S. S. Krishnamurthy and M. Nethaji, *Phosphorus, Sulfur, Silicon Relat. Elem.*, in the press.
5 R. Murugavel, S. S. Krishnamurthy and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1993, 2569.
6 N. Thirupathi, S. S. Krishnamurthy and J. Chandrasekhar, *Chem. Commun.*, 1996, 1703.

7 D. A. Harvey, R. Keat and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1983, 425.
8 W. Zeiss and W. Endrass, *Z. Naturforsch., Teil B*, 1979, **34**, 678.
9 W. L. Duax, C. M. Weeks and D. C. Rohrer, *Top. Stereochem.*, 1976, **9**, 279.
10 R. R. Holmes and J. A. Dieters, *J. Am. Chem. Soc.*, 1977, **99**, 3318.
11 R. Murugavel, N. Thirupathi, S. S. Krishnamurthy and M. Nethaji, *Heteroat. Chem.*, 1995, **6**, 63.
12 F. A. Cotton, J. G. Riess, C. E. Rice and B. R. Stults, *Inorg. Chem.*, 1982, **21**, 3123.
13 R. Murugavel, S. S. Krishnamurthy and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1993, 3635; N. Thirupathi, S. S. Krishnamurthy and M. Nethaji, unpublished work.
14 D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, Wiley-Interscience, New York, 2nd edn., 1986.
15 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 3rd edn., 1988.
16 R. B. King, in *Organometallic Syntheses; Transition Metal Compounds*, eds. J. J. Eisch and R. B. King, Academic Press, New York, 1965, vol. 1, p. 122.

Received 19*th February* 1998; *Paper* 8/01443D