

ORGANO PHOSPHORUS TAUTOMERS INVOLVING CHANGE OF CO-ORDINATION NUMBER ON PHOSPHORUS

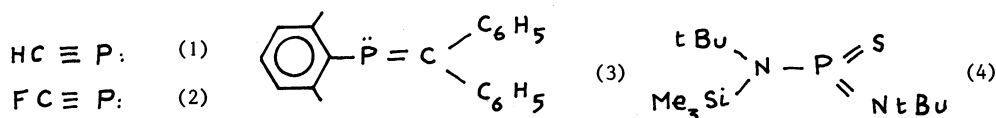
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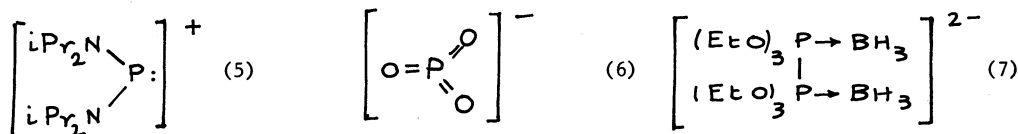
**Abstract** - Numerous hybridization schemes are exhibited by phosphorus and an effort is made to present them in a convenient form. As a result of this complexity a frequent situation occurs : the possibility for a molecule, anion, cation, ... to exist, potentially or actually under two or more structures, involving different co-ordination number on phosphorus. In this direction new results are presented dealing with : electrophilicity of phosphites, tautomerism in bicyclo, hydroxy, and aminophosphoranes ; epimerisation of an hexaco-ordinated phosphorus atom. Closely connected, is the bidentate behaviour of the bicyclo phosphoranes bearing a phosphorus-hydrogen bond.

CONCERNING GENERAL CHEMISTRY OF PHOSPHORUS

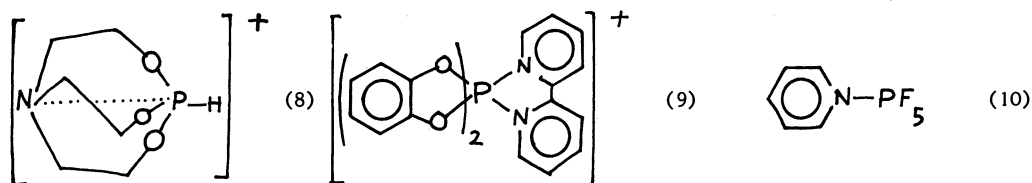
Considering the recent progress during the last two decades a lot of unexpected structures appeared. Among them, we select molecules with co-ordination number at phosphorus, one two and three.



The existence of such compounds was considered during a long time as highly improbable. The formalism used to represent them strongly suggests that simple hybridization scheme which is employed for carbon, nitrogen and oxygen can also be useful in phosphorus chemistry, a point which was not at all evident twenty years ago. Much more, the actual existence or characterisation of entities like :



show that the structural variety observed with neutral structure  $\text{P}^0$  belongs also to the phosphonium  $\text{P}^+$  and phospho-ate  $\text{P}^-$  group. In other words we can write systematically the sets of typical compounds even if a lot of them are forbidden for energetic reasons. A convenient representation appears in figure 1a. The three faces of the cube belong respectively to  $\text{P}^0$ , cations  $\text{P}^+$ , and anions  $\text{P}^-$ . Edges represent either co-ordination numbers or the number of electrons the phosphorus introduce in the bonding pool. These three sets do not cover all the aspects of the chemistry of this element. In particular the phosphonium and neutral structures :  $\text{P}^+$  and  $\text{P}^0$  still exhibit well characterised electrophilicity exemplified by the known X-ray structures of the three following derivatives :



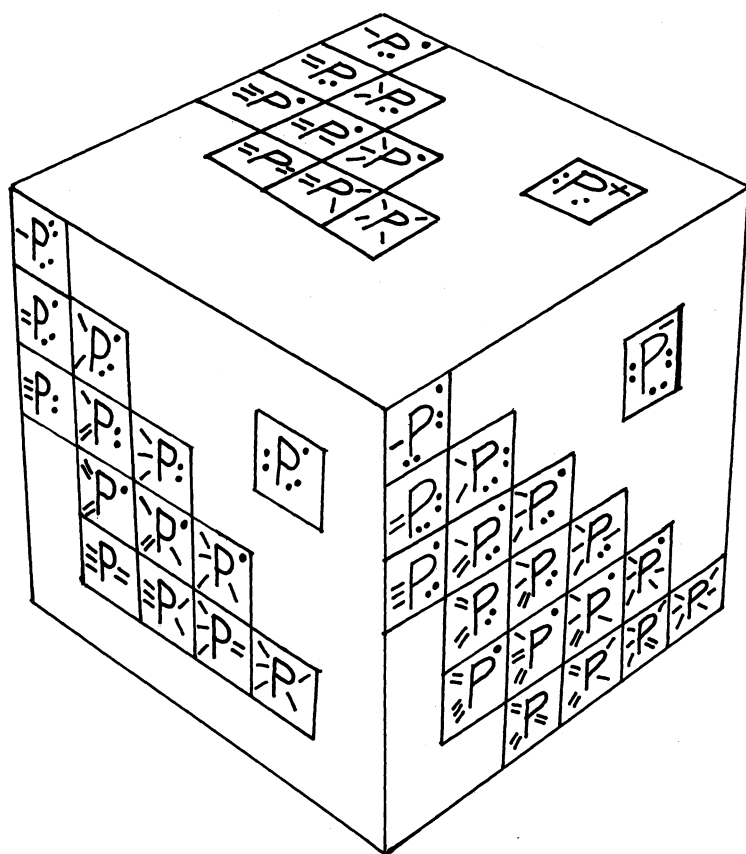


Figure 1a

represents simple hybridization schemes which are available with  $P^+$ ,  $P^0$  and  $P^-$ . Edges represent either co-ordination number or the number of electrons the phosphorus gives to the bonding system. The large majority of these typical species are known.

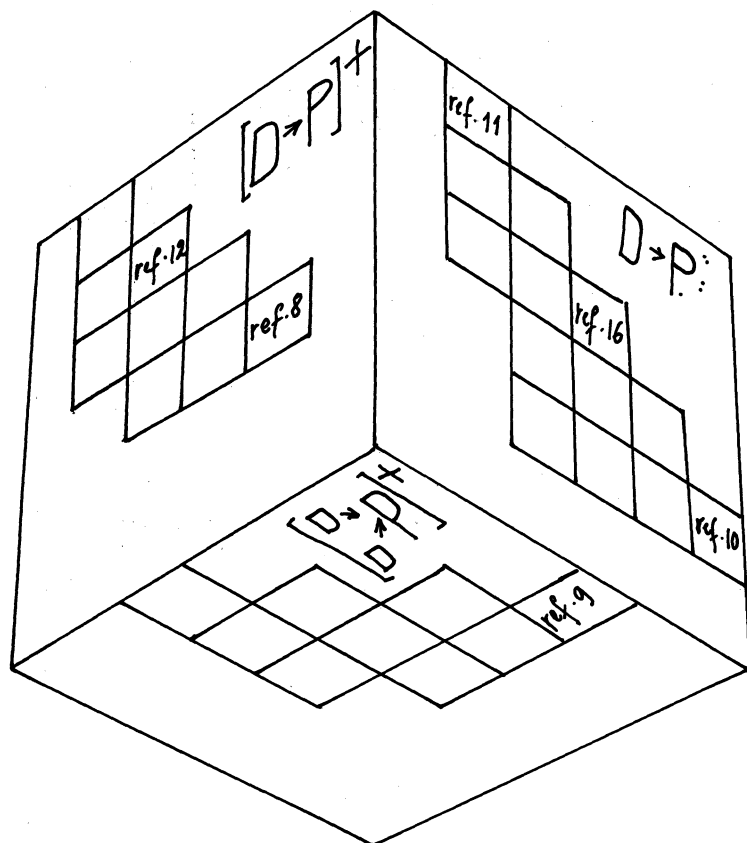
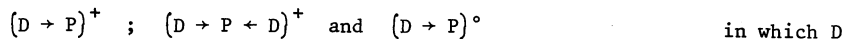


Figure 1b

As both neutral molecules and cationic species still have Lewis acid properties, the figure represent the corresponding adducts. Several possibilities are known (see references) some not yet explored. The surrounding of phosphorus is of major importance for adduct formation. When coloured for teaching purpose the cubes look like Vasarely's "Tridim"

Here the co-ordinations around phosphorus are respectively five, six and six, each one being symbolized by :



is the donor molecule lone pair. Not only the species  $(P)^+$  and  $(P)^\circ$  behave here as Lewis acids, but it is interesting to point out that  $(P)^+$  can play two times this role to reach respectively penta and hexacoordination. These Lewis properties lead to three new sets which are represented on figure 1b. In these new sets the elementary hybridization schemes are the same, we introduce only a displacement of abscissa due to the change of coordination number by one or two units. Several exotic species of type  $(D \rightarrow P)^\circ$  or  $(D \rightarrow P)^+$  actually exist as  $Me_3P \rightarrow \ddot{P}-CF_3$  (11) and  $(Me_2N)_3P \rightarrow \ddot{P}(NMe_2)_2$  (12).

The presentation 1a - 1b needs some explanations :

a) When the double bond appears in an hybridization scheme it covers the cases in which the phosphorus is donor : as an example  $\overset{\ominus}{P} =$  contains both the phosphoric esters  $(RO)_3P = O$  and the phosphino boranes  $R_3P \rightarrow BH_3$

b) The "allene = acetylen" correspondance must be considered. For example  $\equiv P <$  only appears in the figure but  $\overset{\ominus}{P} -$  is implicit.

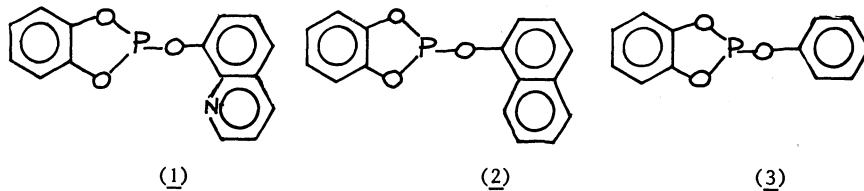
c) All the compounds in which the phosphorus has a co-ordination number higher than the number of electrons in the bonding system are not considered ; for example : in the carboranes a phosphorus which keeps its electron pair and is surrounded with five boron atoms is not considered. Also it's the case of the hexacoordinated radicals with eleven electrons from KABACHNIK et al. (13)

d) The exceptional multi-charged phosphorus moiety like  $(PF_3, 3 \text{ Pyridine})^{2+}$  (14) or  $PCl_6^{2-}$  (15) do not appear and very likely I have missed some evident possibilities. Any way for the moment the aim of this presentation is to underline the diversity of the hybridization schemes exhibited by phosphorus and the simple connections between them. It is easy to observe that the "elementary cubes" are related by simple entities : one electron, one anion or cation, a base ...etc. Each time a compound is bearing such an entity on one of its substituant leads to a structural ambiguity. As a consequence many structural problems are dealing with the possibility for a molecule to exist, potentially, or actually, as two or more structures involving a different co-ordination number on phosphorus. We are now presenting recent results obtained in this direction.

#### ELECTROPHILICITY OF PHOSPHITES : $D \rightarrow P(OR)_3$

At the borderline of co-ordination 3 in neutral molecules (symbolized by  $P^{III}$ ) and 4 :  $P^{IV}$ , we found the adducts which result from the interaction of a tricovalent phosphorus molecule and a base. A typical compound in this field is the adduct  $(CH_3)_3N \rightarrow PCl_3$ , studied by vapour pressure and calorimetry by R.R. HOLMES (16). The X-ray structure of the corresponding arsenic analog has been determined (17). Thus, in the following we have explored if the phosphites are sufficiently electron deficient to generate a  $N \dots P$  interaction.

Six phosphites having a phospholane cycle and a lateral chain containing a nitrogen atom has been synthetised (18). The one with pyrocatechyl and 8 hydroxy quinoline (1) is a typical example. It is a solid compound not yet studied by X-ray determination. The  $^{31}P$  NMR spectrum shows without any doubt that the structure belongs to the phosphite field as it is shown :

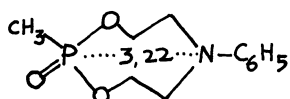


$25^\circ \delta^{31}P^{(a)}$	+ 125	+ 128,5	+ 127
$\Delta\delta \text{ p.p.m./}^\circ T$	- 0,034	- 0,008	- 0,0076

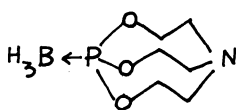
(a) :  $^{31}P$  chemical shifts are in parts per million with positive values downfield from external 85 %  $H_3PO_4$

We have explored the variation of  $\delta^{31}\text{P}$  as a function of temperature in the range  $25^\circ$  to  $-80^\circ$  and observed for (1) (2) and (3) displacement to higher field when temperature is decreasing. The effect is four times larger in the derivative (1) for which an interaction between nitrogen-phosphorus is expected. The effect is really too modest to draw a definite conclusion. Particularly if we compare the  $-0.034 \Delta\delta_{\text{p.p.m.}/^\circ\text{T}}$  with similar results obtained in the literature. For 19 trivalent phosphorus derivatives GORDON and QUIN (19) found values of  $\Delta\delta$  p.p.m./ $^\circ\text{T}$  ranging from  $+0.040$  to  $-0.060$ .

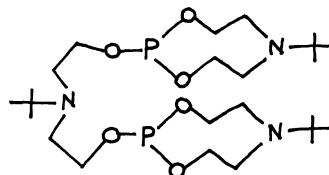
Another approach to detect such a N-P interaction is to include both the phosphite group and the nitrogen atom in an eight-member ring respectively in the 1 and 5 positions. The virtual bicyclo octane structure which can potentially occur is favourable to detect a possible 1 - 5 transannular interaction. This method was used to study the nitrogen... $\text{sp}^2$  carbon interaction (20) and also to study the electrophilicity of Si, Ge.. As.. (21,22). Even in phosphorus chemistry, KALININ *et al.* (23) determined the X-ray structure of an azaphosphocine (4) to establish the eventual occurrence of a short nitrogen phosphorus distance. The intramolecular distance of 3.22 Å was considered as indicating transannular P...N interaction. In (5) the P...N distance is shorter (3.098 (005) Å) (24). NMR spectroscopy is also able to detect such transannular interaction (25).



(4) (ref. 23)



(5) (ref. 24)



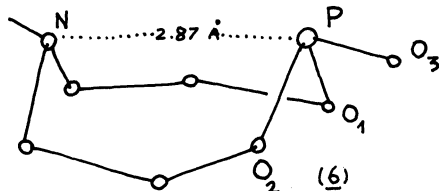
(6) (ref. 26)

Dr F.H. Osman has prepared such a molecule (6) (ref. 26) in order to detect the electrophilicity of phosphite. The synthesis of the compound results from the action of the diethanolamine  $\text{tBuN}(\text{CH}_2\text{-CH}_2\text{OH})_2$  on the trisdimethylamino phosphane  $(\text{Me}_2\text{N})_3\text{P}$ . It is interesting to note that even using 1 : 1 stoichiometry, the diphosphite (6) is obtained exclusively with remaining excess of  $(\text{Me}_2\text{N})_3\text{P}$ . This could be explained by assistance of the  $\text{NtBu}$  group in  $\text{tBuN}(\text{CH}_2\text{-CH}_2\text{O})_2\text{P-NMe}_2$  favouring the leaving of the remaining  $\text{NMe}_2$ . Another remark concerning this experiment : the possible spirophosphorane with two eight membered cycles,  $\text{tBuN}(\text{CH}_2\text{CH}_2\text{O})_2\text{PH}(\text{OCH}_2\text{-CH}_2)_2\text{-NtBu}$  was not detected. The compound (6) which is or "ear-muff"-shape (J.A. Osborn) is a crystalline product and its structure was determined by X-ray (26). The most interesting features of the molecular structure are :

- the conformation of the eight membered ring,
- the geometry around the phosphorus and nitrogen atoms, and
- the transannular P...N interaction.

a) The rings have a boat-chair (BC) conformation. That is, in the present case each ring does not have a mirror plane. Since the entire molecule has a mirror plane, it means that the two rings exist in two enantiomeric forms.

b) The phosphite moiety has slightly distorted  $\text{C}_{3v}$  symmetry (mean lengths of the three P - O bonds are 1.623 Å). The larger OPO angle is the interior (endocyclic) one with  $101.3^\circ$ . The two others angles are nearly identical ( $98^\circ$ ). The three P-O-C angles range from  $119.5^\circ$  to  $123.1^\circ$ . These values do not indicate distortion of the geometry around phosphorus in the direction of a pentacoordinate structure having the lone pair of phosphorus in an equatorial position. Moreover, the geometry around nitrogen supports this conclusion. Indeed, it is remarkable that within the experimental errors, bond angles around the endocyclic nitrogen atom are identical to the corresponding ones around the exocyclic nitrogen.



	distances (Å)	angles ( $^\circ$ )	
$\text{PO}_1$	1,629	$\widehat{\text{O}_1\text{PO}_2}$	101,3
$\text{PO}_2$	1,619	$\widehat{\text{O}_2\text{PO}_3}$	98,2
$\text{PO}_3$	1,621	$\widehat{\text{O}_1\text{PO}_3}$	97,8
P...N	2,870	$\widehat{\text{NPO}_3}$	164,0

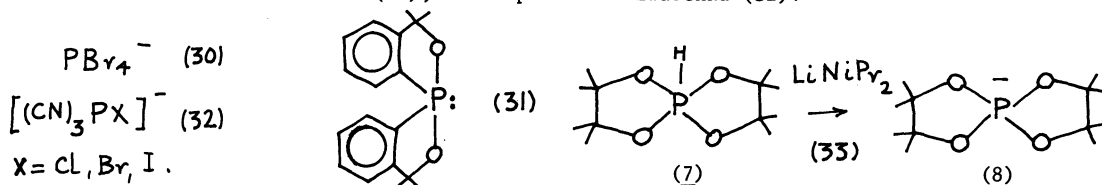
from (26)

c) Concerning the transannular P...N interaction, the P N distance : 2.870 Å is significantly shorter than the one found by Kalinin and al., 3.22 Å (23). The nitrogen atom occupies an apical position at the coordination polyhedron of the phosphorus : the two endocyclic oxygens and the direction attributed to phosphorus lone pair mimic the three equatorial positions - but as we noticed the angles around phosphorus are not significantly different than known phosphite structures. Our finding that the P N distance is 0.5 Å shorter than the Van der Waals radii deserves a careful examination. If we introduce the notion of "one angle radius" (27), that is, the minimal distance between "nonbonded" phosphorus and nitrogen bonded to a common carbon atom, the value can be estimated as

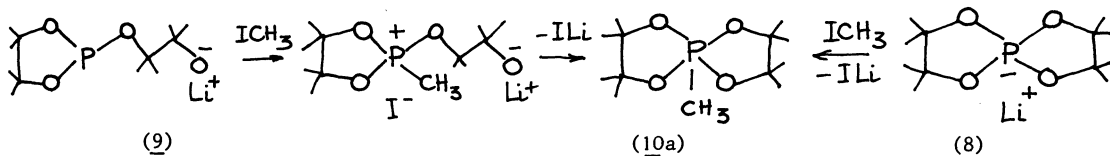
$1.46 + 1.14 \text{ \AA} = 2.60 \text{ \AA}$ , so the bonding interaction is ambiguous. Moreover, the photo electron spectroscopy signals for exo- and endocyclic nitrogens are not distinguishable (28). In brief, we need here to reconcile a short P...N distance which is not accompanied with the expected geometrical distortion at phosphorus. Ab initio calculations performed by Trinquier *et al.* (29) on a very simple model ( $\text{H}_2\text{N} \rightarrow \text{P}(\text{OH})_3$ ) using the geometrical parameters of structure (6) reveal a potential energy well with a depth of about  $1.1 \text{ Kcal mol}^{-1}$  when nitrogen is close to phosphorus in the range  $2.6 - 3 \text{ \AA}$ . The interaction is of electrostatic character and does not involve a donation of electrons from nitrogen to phosphorus. For the moment the conclusion of our investigations concerning the possible interaction between phosphites and bases is clear. In the examples considered, there is no change of the co-ordination number around phosphorus but this does not exclude weak interaction between N and P which would be sufficient to influence chemical reactivity.

PHOSPHORANIDE OR PHOSPHITE PLUS AN ANION

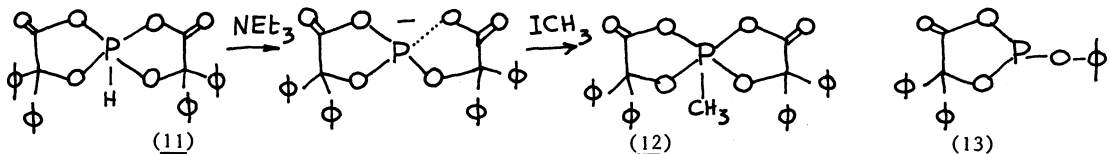
Very close to the border of the system : base + phosphite  $\rightarrow$  [base  $\rightarrow$  phosphite] we just examined, is the corresponding interaction between an anion and phosphite leading to phosphoranide :  $\text{A}^- + (\text{RO})_3\text{P} \rightarrow [\text{A} - \text{P}(\text{OR})_3]^-$  which appear on the  $\text{P}^-$  set of fig. 1a. Such anions are rare and very few, if any, had been investigated between  $\text{PBr}_4^-$  (30) and the very recent results of Granoth and Martin (31), Schmidpeter and Zwaschka (32).



If we examine the reactivity, it appears that several spirophosphoranes with a P - H bond like (7) lose a proton under the action of strong base (33). The intermediate which is formed having the structure (8) or (9) reacts with methyl iodide to give the methyl spirophosphorane (10a). This suggests the intermediate formation of the tetravalent anion (8). Although it is quite possible that the first step of the reaction is the quaternisation of phosphite form, just like as in Arbuzov reaction, followed by an intramolecular cyclisation :



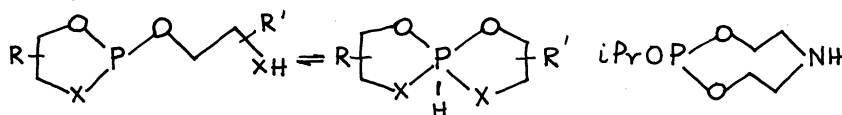
The structure of the entity (8) or (9) in solution was checked by the authors, and undoubtedly it corresponds to (9) with a trivalent phosphorus chemical shift of + 140 p.p.m. (ref. 33). Having in hands spirophosphoranes which we believe are more acidic we explored their behaviour in presence of bases. In DMF, at  $-50^\circ\text{C}$ , it is possible by  $^{31}\text{P}$  NMR to follow the structural change undergone by the spirophosphorane (11) with the regular increase of triethylamine concentration (from 0,1 to 4 equivalent). The essential feature of the  $^{31}\text{P}$  NMR spectrum is the appearance of a unique peak at + 79.4 p.p.m. which increases in intensity as the doublet of the starting product ( $\delta^{31}\text{P} = -47.4$ ,  $^1\text{JH-P} = 980 \text{ hz}$ ) disappears. From the solution a crystalline product having good analytical data for ((11),  $\text{NEt}_3$ ) has been isolated. Also the solution reacts quantitatively with an excess of  $\text{ICH}_3$  giving the corresponding methyl spirophosphorane (12) (34). The observation which is new is that the  $^{31}\text{P}$  chemical shift ( : 79.2 p.p.m. at  $-60^\circ\text{C}$ , 86.4 at  $+90^\circ\text{C}$ ) enable us to exclude that tricoordinated form is the unique structure present (the expected  $\delta$ , measured on the model molecule (13) would be + 128 p.p.m.)



THREE COVALENT OR PENTACOVALENT PHOSPHORUS ?

The transformation of a trivalent phosphorus in neutral molecules in the corresponding pentacoordinated species is controlled by the oxidative addition of an A - B molecule on the

phosphane :  $\text{>P} : + \text{A} - \text{B} \rightarrow \text{>P} \begin{matrix} \text{A} \\ \text{B} \end{matrix}$ . In our previous investigations we have studied the factors which control the ring chain tautomers (35).



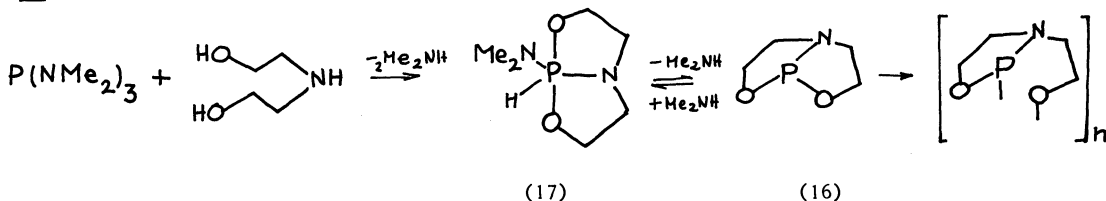
(ref. 35)

X : one of the groups : O, NH, NR

(14)

(15)

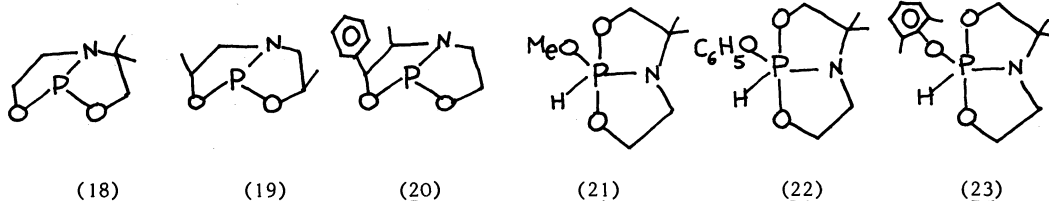
Another facet of this frontier  $\text{P}^{\text{III}} \rightleftharpoons \text{P}^{\text{V}}$  concerns the structures in which a *transannular* oxidative addition can occur. Our first and non published attempt in this field was to prepare a quite simple molecule (14) and (or) (15) in reacting isopropyldichlorophosphite  $\text{iPrOPCl}_2$  with diethanolamine  $(\text{HOCH}_2\text{-CH}_2)_2\text{NH}$ , in presence of triethylamine. In fact the crude mixture examined by  $^{31}\text{P}$  NMR revealed in addition to the expected bicyclic phosphorane numerous different phosphites. We did not succeed in separating a pure product. It appears necessary to envisage more possibilities in such a synthesis and a step by step investigation was needed. We tried to prepare the simplest bicyclic phosphane deriving from diethanolamine (16) which results formally from a reductive elimination of  $\text{iPrOH}$  from (15). In reacting tris(dimethylamino)phosphane  $(\text{Me}_2\text{N})_3\text{P}$  with diethanolamine and following the  $^{31}\text{P}$  NMR of the reaction mixture during the  $\text{Me}_2\text{NH}$  evolution, we learned about two complications. First an oxidative addition of dimethylamine occurs giving the corresponding bicyclic phosphorane (17) ( $\delta = -39$ ; JHP = 826 Hz). This is a reversible process and the intermediate obtained loses again  $\text{Me}_2\text{NH}$  to give the desired aminophosphane (16) ( $\delta^{31}\text{P} = 139$ ). But this monomeric species undergoes an oligomerisation giving rise to a new peak (+134 p.p.m.) which becomes dominant. To summarize, the simplest term in this family of compounds (16), is obtained in pure form only with difficulty.



(17)

(16)

We observed that the oligomerisation is much slower when substituted diethanolamines are used and that oxidative addition remains. This favourable situation enables us to prepare several pure bicyclic phosphoranes (18) (19) (20).



(18)

(19)

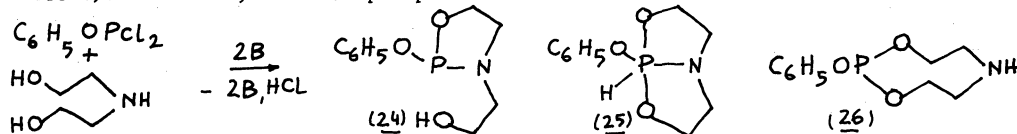
(20)

(21)

(22)

(23)

In particular with (18) the oligomerisation is a stepwise process as in the serie first described by J.B. Robert *et al.* (36). A pure crystalline dimer was characterised by  $^1\text{H}$  NMR spectrum, a unique peak in the  $^{31}\text{P}$  NMR ( $\delta = +149.9$ ) by good analytical data and mass spectroscopy. With pure bicycloaminophosphanes in hands it became easier to investigate equilibria of the type (14)  $\rightleftharpoons$  (15). The oxidative addition of methanol or phenols to (18) is a very clear cut reaction which leads to the bicyclic phosphoranes (21)-(23) without other entities present in the medium. As an indication of the reaction rate, in  $\text{C}_7\text{D}_8$  solution at  $33^\circ\text{C}$ , 70 % of the phosphorane (23) is formed 50 mn after the stoichiometric mixture of 2.6 dimethylphenol and (18). After reaction was completed, the mixture was heated to  $100^\circ$ , no further change occurs, the phenol is not eliminated. These observations focus our attention on the fact that the equilibria between bicyclic phosphoranes +  $\text{R}_2\text{NH}$  or  $\text{ROH}$  and the corresponding bicyclic phosphoranes depend largely of the structures of the reactants. Much more, the study of the reaction of  $\text{C}_6\text{H}_5\text{OPCl}_2$  with diethanolamine shows notable differences probably result from kinetic control. The reaction was conducted in benzene or toluene as solvent in the presence of triethylamine. After the separation of the hydrochloride salt the crude mixture shows essentially in  $^{31}\text{P}$  NMR three peaks which are assigned to oxazaphospholane (24) (145.1) and phosphorane (25) (-39) and the postulated eight membered ring (26) ( $\delta = +133.6$ ). With time, the oxazaphospholane concentration diminishes with concomitant



(24) HO

(25)

(26)

increase of the phosphorane until the former disappears. During this change the + 133 peak remains unchanged. The  $^{31}\text{P}$  NMR spectra registered at higher temperatures show the reductive elimination of phenol leading to the formation of (16) ( $\delta = + 139$ ) which polymerises giving rise to the + 134 p.p.m. absorption, distinct from the 133 one. Due to the complexity of the system we feel that doubt remains about the + 133 peak assignment.

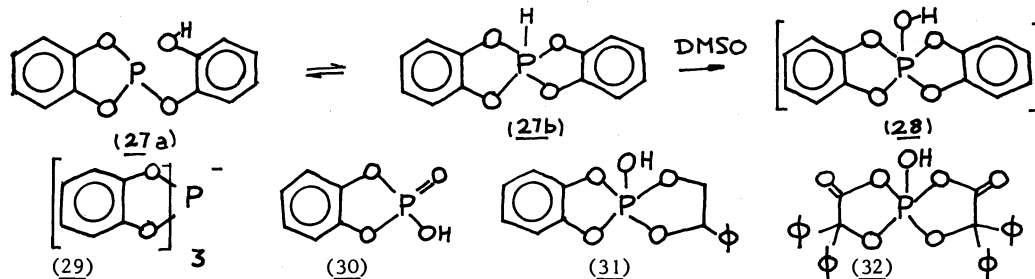
In conclusion, the cyclo - bicyclo systems at the frontier of the coordination  $\text{P}^{\text{III}}$  and  $\text{P}^{\text{V}}$  appear quite versatile. It is clear that further investigations are needed but already now well defined compounds like constrained aminophosphites [(16), (18) - (20)] (37) or bicyclic phosphoranes [(21)-(23)] present interesting properties.

#### HYDROXY-PHOSPHORIC ESTERS AND THE CORRESPONDING HYDROXY-PHOSPHORANES

The fully esterified phosphoric esters  $(\text{RO})_3\text{P} = \text{O}$  containing an hydroxy group in, at least, one of the R substituents can be considered under a tautomeric form resulting from the addition of OH on the phosphoryl bond  $\text{>P} = \text{O}$ ;  $(\text{RO})_2 \text{P}(\text{OH})_2 \rightleftharpoons (\text{RO})_2 \text{P}(\text{OH})(\text{O}^-)$

During a long time it was assumed that the phosphoryl group was a too stable bond to undergo such a chemical reaction. But the progress of our knowledge concerning both the pentaoxyphosphoranes and the nucleophilic substitution on tetracoordinated pentavalent phosphorus, lead the phosphorus chemists to envisage the hydroxyphosphoranes much more as intermediates than transition state.

Recently S.S. SIMONS (38) studying the hydrolysis of diphenyl carboxynorbornyl phosphate tried to detect, unsuccessfully the existence of hydroxyphosphorane by  $^{31}\text{P}$  NMR. We failed also to detect this entity (28) in the first system we investigated (39). It consisted to oxidize by  $\text{Me}_2\text{S} = \text{O}$  (DMSO) the phosphite = phosphorane equilibrium (27a) (27b).

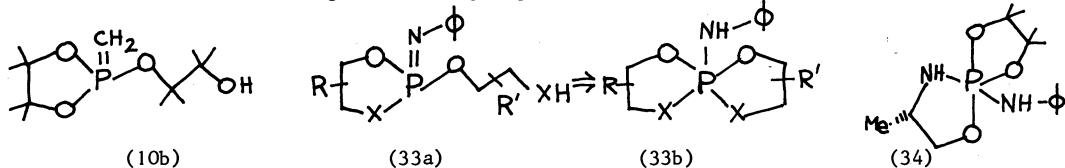


The final products of the reaction were (29) and (30). The results observed, very close of the one of KOIZUMI *et al.* (40) imply the intermediate hydroxyphosphorane (28). It is interesting to underline that this working model was a good choice. Ramirez *et al.* (41) on the same system, but using different experimental conditions, indeed detected in solution the actual existence of (28) in equilibrium with the corresponding phosphoric ester form. In the meantime, we tested such bidentate ligands as to hinder the reaction step following the formation of hydroxyphosphorane that is the pyrocatechyl group transfert. With an analog approach, we clearly observed the conjugate base of the hydroxyphosphorane (31), but here also it is not the unique compound appearing in the oxydation process (42). Finally, using a set of differently substituted  $\alpha$  hydroxyacids as ligands we were able to prepare in solution the conjugate base of hydroxyphosphoranes exclusively. So the compound (32) was prepared from the reaction of  $\text{OPCl}_3$  with benzoic acid and isolated as triethylammonium salt. The oxidation of the spiro phosphorane (11) by DMSO in DMF is also a good synthetic route to obtain the dimethylformamidinium salt of (32). Elemental analysis  $^1\text{H}$  and  $^{31}\text{P}$  NMR ( $\delta = - 48,5$ ) are consistent with the pentaoxyphosphorane structure of the anion. Much more the  $\nu_{\text{C}=\text{O}}$  i.r. absorption at  $1738 \text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  and  $1735 \text{ cm}^{-1}$  in KBr pellet is a good argument in favour of an identical structure both in solution and in the solid state (43) but of course only the X ray determination will bring the decisive proof. Among the recent results obtained by Munoz *et al.* (44) it appears possible to isolate in the solid state, as a pure compound and not as a salt, the hydroxyphosphorane deriving from the acetic acid. This relative stability of the  $\text{>P}(\text{OH})_2$  structure suggest the possibility to detect such an entity in the course of hydrolysis of phosphites, phosphonites, etc... It is the case when water reacts with the bicycloaminophosphite (18) in acetonitrile. In the  $^{31}\text{P}$  NMR spectrum of such a solution (45) the hydroxyphosphorane with a P-H bond ((21) with  $\text{MeO} = \text{OH}$ ) is actually present. It is interesting to notice that during the course of these investigations quite interesting contributions appeared dealing with the same problem (41, 46, 47, 48).

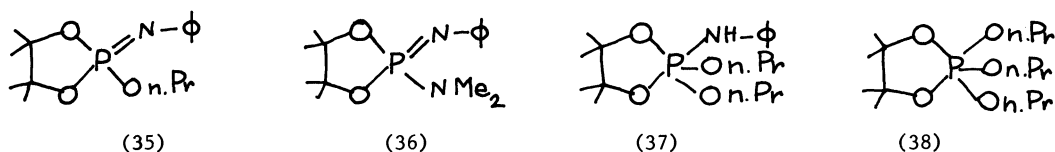
The general conclusion is, that hydroxy phosphoranes exist as isolable entities and in well chosen models this structure prevails over the tautomeric hydroxyphosphoric esters.

## IMINO PHOSPHANES OR AMINO PHOSPHORANES ?

The precedent result can be extended to any molecule: in which the oxygen atom of the phosphoryl group is replaced by another six electrons moiety like (P) = S, (P) = CH<sub>2</sub>,... (P) = GeR<sub>2</sub>. To take only one example of such potentiality the structure (10b) is the tautomeric form of the phosphorane (10a) we already met. Using the Staudinger reaction, that is the action of N<sub>3</sub>C<sub>6</sub>H<sub>5</sub> on the equilibria phosphites  $\rightleftharpoons$  spirophosphoranes already illustrated (ref. 35) we did not detect the tautomers (33a) but isolated only the aminophosphoranes (33b). First obtained on four examples (49) the reaction was extended to eight more new models (50) and among them several are isolated in optically active form like 34 ( $\alpha$ )<sub>546</sub><sup>15</sup>: + 108 for which the absolute configuration of phosphorus must to be confirm.



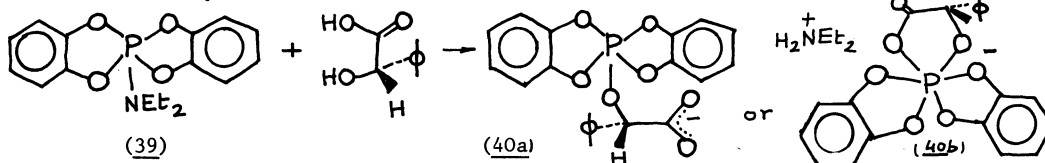
Here, the tautomeric equilibrium observed by Stegmann *et al.* (51) on different models does not occur. The driving force of the intramolecular attack of the nucleophilic fonction XH (X = O, or NH, or NR) on the phosphorus atom is the spirocyclisation. For a better understanding we studied nc<sub>3</sub>H<sub>7</sub>OH alcoylsis of particular iminophosphanes like (35) or (36).



With the former the monocyclic amino phosphorane (37) is observed only in low concentration and move quickly to the more stable pentaoxyspirophosphorane (38). The iminophosphane (36) displays the alcoylsis of NMe<sub>2</sub> moiety before the addition to the phosphazene bond leading first to (35). Interesting publications appeared recently which prove that such a reactions are useful and able to be extend (52 a-b) (53).

## PENTA AND HEXACO-ORDINATION BORDERLINE

(\*) Mandelic acid (absolute configuration S) reacts with the pentacoordinated substrate (39) to produce a salt in which the anion can take one of the two tautomeric forms (40a) or (40b). The spectroscopic methods, particularly <sup>31</sup>P NMR shows that the hexacoordinated one (40b) is only present ( $\delta = -90$  in DMSO). The existence in this anion of two chiral centers, the carbon (S) introduced in mandelic acid and the absolute configuration around PVI ( $\Lambda$  or  $\Delta$ ) implies two diastereoisomers which are actually detected in <sup>1</sup>H and <sup>31</sup>P NMR. An optically pure diastereoisomer of (40b) was isolated in crystalline form ( $\alpha$ )<sub>546</sub><sup>18</sup> = 245 (C = 0,343 M in DMSO). In solution it epimerizes due to the lability of the hexacoordinated skeleton. The process was followed both by NMR and polarimetry. With this last method the kinetic parameters of



the P<sup>VI</sup> epimerization were determined in a variety of experimental conditions : seven different solvents, the order of the reaction versus (P<sup>VI</sup>)<sup>-</sup> and (H<sub>2</sub>NEt<sub>2</sub>)<sup>+</sup> concentrations (54,55) To take examples : in DMSO and acetonitrile the apparent rate constants reduces to 20°C are like 1 and 1325 (corresponding  $\Delta G$  in Kcal mole<sup>-1</sup> 21.35 and 17.17) for a salt concentration of 26.10<sup>-3</sup>M. The contrast of the influence on the rate constants of the cations (H<sub>2</sub>NEt<sub>2</sub>)<sup>+</sup> and (NEt<sub>4</sub>)<sup>+</sup> focus our attention on the importance of (H<sup>+</sup>). For the diethylammonium cation influence, the analysis of apparent rate constants emphasize the role of cation in a classical bimolecular process to which the intervention of the proton in a mechanism of acid catalysis must be taken in account. The partial order 0,449 of the cation in the kinetic express the two phenomena (55).

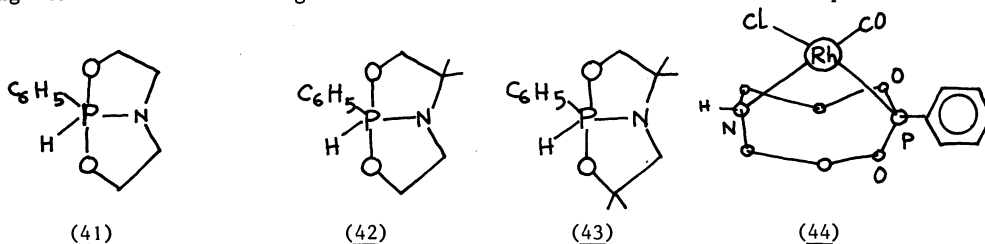
This set of experimental data lead us to propose an isomerization of P<sup>VI</sup> which is going through a change of the coordination number around phosphorus : P<sup>VI</sup>  $\rightarrow$  P<sup>V</sup>  $\rightarrow$  P<sup>VI</sup>. The kinetic b eing controlled by the slow rupture of a phosphorus oxygen bond.



## BICYCLOPHOSPHORANES AS VERSATILE LIGANDS

Till now all the structural problems we have examined are relevant from general phosphorus chemistry. But the results can also have interest in other field of chemistry. If a bicyclo phosphorane with a P - H bond behave in equilibrium with the tricovalent phosphorus form, like (14)  $\rightleftharpoons$  (15), the question arise if (15) containing a tricovalent phosphorus can play a role as ligand in coordination chemistry. Our investigations has been conducted in collaboration with Laboratories of Pr J. Riess (Nice) and Dr Tkatchenko (Villeurbanne). To avoid complications which arise when the reductive elimination or ROH occurs we investigate first the behaviour of organyl bicyclo phosphoranes like (41)-(43). These compounds are formerly in potential equilibrium with phosphonite opened structure. For their synthesis  $C_6H_5P(NMe_2)_2$  is reacting with the corresponding diethanolamine. point of interest concerns the stereochemistry. When the diethanolamine is non symmetric the phosphorane obtained contain a chiral pentacoordinated phosphorus center. This can be easily disclosed on a racemic mixture of (42). The addition of europium optishift I, allows to observe in  $^1H$  NMR (250 Mhz) two different doublet assigned to H-P system. Each one corresponding to a specific diastereoisomer formed in the mixture. Seven compounds of this type, presenting a chiral  $P^V$  atom, has been synthesised (56).

Focusing the interest on the ligand behaviour we have observed several comportements.



When equimolecular amounts of  $Mo(CO)_6$  reacts with (41) (L) the derivative isolated is  $Mo(CO)_4L_2$  plus unreacted  $Mo(CO)_6$ . In the compound obtained L exhibit a monodentate behavior through  $P^{III}$  atom. When  $Mo(CO)_6$  was allowed to react in comparable experimental condition with more sterically hindered phosphorane (43) it gives only the  $Mo(CO)_4L$  compound. On the other hand the bicyclic phosphoranes (41) (42) always behaved as bidentate ligands in their reaction with  $[Rh(CO)_2Cl]_2$  in toluene. The bidentate character of the ligand were assessed by elemental analysis, mass spectra absence of  $\nu_{PH}$ , presence of  $\nu_{NH}$  single  $\nu_{CO}$  ... The bidentate character of the ligand has been further demonstrated by X-ray diffraction (57). The novelty of the compounds obtained when the ligand functions as a bidentate donor is that the metal lies in a cradle to which it is attached by two donor sites of different basicity (44). Reactions of an excess of the phosphorane 42 with  $[Rh(CO)_2Cl]_2$  or  $[Rh(C_2H_4)_2Cl]_2$  proceed differently.  $L_2Rh$  complexes are not observed in the reaction with the first and conversely  $[Rh(C_2H_4)_2Cl]_2$  reacts with two equivalents of 42 to give a yellow cationic complex with two bidentate  $P^{III}-N^{III}$  ligands. A point of interest is that the X ray structure contains a  $C_2$  axis of symmetry and that means that the two ligands possess in the complex the same absolute configuration (58).

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