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FORMATION OF STABLE CYCLIC DICOORDINATED PHOSPHORUS COMPOUNDS BY REACTION OF CYCLOPHOSPHAZANES WITH LEWIS ACIDS

C. MALAVAUD,* M.T. BOISDON, Y. CHARBONNEL and J. BARRANS
Laboratoire des Hétérocycles du Phosphore et de l'Azote
Université Paul Sabatier, 118, route de Narbonne, 31077 Toulouse Cédex

Thermal equilibrium between dicoordinated and tricoordinated phosphorus compounds (i.e. benzodiazaphosphole ⇄ cyclotetraphosphazane) has been observed. The dicoordinated compounds have been stabilized by complexing with Lewis acid and isolated.

Only one heterocyclic compound is known in which a dicoordinated phosphorus atom is doubly bonded to a nitrogen atom (1). The N-P-N linkage seems to favour the formation of P=N double bond, so we have studied the action of tris(dimethylamino)phosphine with 2-(N-alkyl)-1-amino-benzene 1.

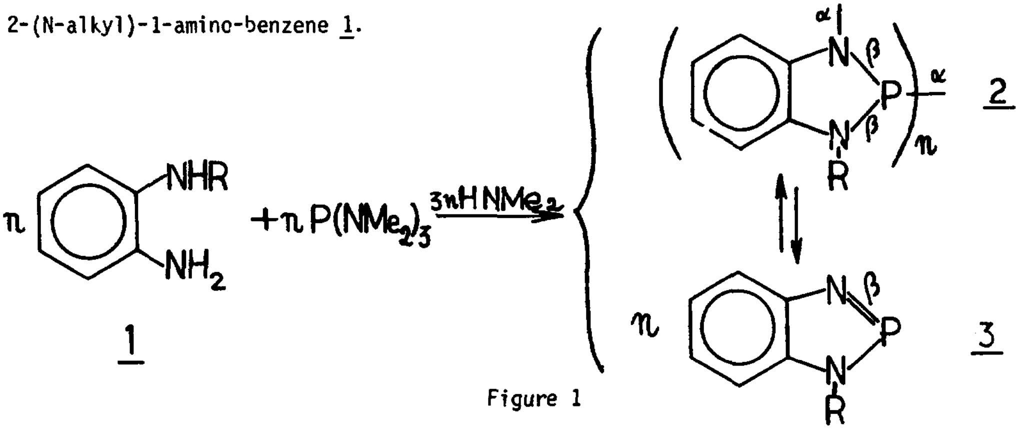


Figure 1

By refluxing in toluene or xylene, P(NMe$_2$)$_3$ reacts with 1 (1:1 ratio) to give a cristalline compound 2, presumably via a dicoordinated phosphorus compound 3. ^{31}P chemical shift in NMR and microanalysis of 2 agree with the proposed structure (11).

Table I

	R	δ^{31}P (ppm)	m.p. °C
2a	Pr	+ 86	194
2b	i-Pr	+ 84	255
2c	s-Bu	+ 81	218
2d	Ph-CH$_2$	+ 89	204

Molecular weights have been determinated by electron impact ionization and by field desorption mass spectrometry : the first method gives n=1 for all the compounds 2, the second one, used in the case of 2b and 2c, shows clearly that compounds 2 exist as the tetrameric form (n=4) already observed in other cases (2) ; the mass spectrum shows, furthermore, weaker peaks characteristic of the trimeric, dimeric and monomeric forms with decreasing intensities (12) ; this fact shows that the P-N bonds α (fig. 1) giving the tetrameric form are weaker than those of the monomeric one, β.

Compounds 2 are slightly soluble in usual solvents ; they do not react with sulfur in benzene solution at room temperature. In boiling benzene it needs several hours to obtain the sulfur compounds ($\delta^{31}P$ = 55ppm) in contrast to many diazadiphosphetidines (3),(4).

Furthermore there is no quaternization by addition of methyl iodide, (3),(6).

All these facts seem to favour the idea that the lone pair on the phosphorus atom is hardly available for donor - acceptor bond formation.

By ^{31}P NMR at variable temperature dicoordinated phosphorus compounds have been observed ($\delta^{31}P$ near 230 ppm) (1),(5).

Table II

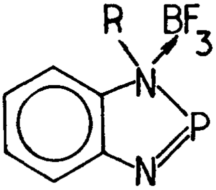
	R	$\delta^{31}P$ (ppm)	
3a	Pr	236	(xylene, 140 °C)
3b	i-Pr	228	(nitrobenzene, 60 °C)
3c	s-Bu	225,8	(xylene, 120 °C)
3d	Ph-CH_2	228	(pyridine, 100 °C)

Above 110 °C in xylene, the existence of a temperature dependent equilibrium, between the tricoordinated phosphorus compound 2 and the dicoordinated phosphorus compound 3 has been proved and demonstrated. For instance, at 120 °C in xylene, the percentage of the 3c monomeric form is 15%, and 30% at 140 °C.

We can notice that this equilibrium is not only temperature dependent but solvent sensitive : for instance, 2c dissolved in nitrobenzene is wholly dissociated at 140 °C, while in xylene, at the same temperature, it is only 30% dissociated.

Recently, an example of $P^{II} \rightleftharpoons P^{III}$ equilibrium has been mentioned (7) but 3 seems to be the first cyclic compound showing this property.

If a Lewis acid (i.e. BF_3 , $AlCl_3$, $ZnCl_2$) is added, at room temperature, to a benzene solution of 2 (proportion 1:1), the ^{31}P NMR spectrum of the solution shows two signals. For instance with BF_3 and 2a-d, we observed an intense signal near 226 ppm and another one weaker near 214 ppm, intensity ratio (5:1), when the signal of 2 disappears.



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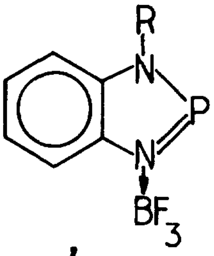

4'

TABLE III

R		F °C	$\delta^{31}P$(ppm)	
			4	4'
a	Pr	145-9	226	214,7
b	iPr	132-4	225,6	214,2
c	S-Bu	104	226,7	214,1
d	Ph-Ch_2	——	224,8	211,7
e	Ph (8)	——		205,9

As the lone pair on phosphorus atom is not available, we think that adduct formation with BF_3 occurs at the nitrogen atoms. The two NMR signals could be attributed to 4 and 4' (13); the fact that tricoordinated nitrogen is generally more basic than the dicoordinated one favours 4 (9). When R = Ph (e), we observe only one signal at 206 ppm assigned to 4' ; in this case the lone pair of the tricoordinated nitrogen atom could be conjugated with the phenyl system and so the complexation by the dicoordinated nitrogen atom could be favoured.

In conclusion, it could be noted :

- the cyclophosphazanes 2 are, at high temperature, in equilibrium with the monomeric form 3 ; the equilibrium is also sensitive to the electrophilicity of the solvent and to the nucleophilicity of the nitrogen atoms ;
- the monomer 3, a dicoordinated phosphorus compound, has been stabilized by complexation with Lewis acids.

Bibliography and notes

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The dicoordinated phosphorus form has been postulated by these authors just from the results of centesimal analysis ; that is in contradiction with the results of fiels descrp-

tion mass spectrometry which shows not only the peak of monomeric form but also the peaks of dimeric, trimeric and higher forms.

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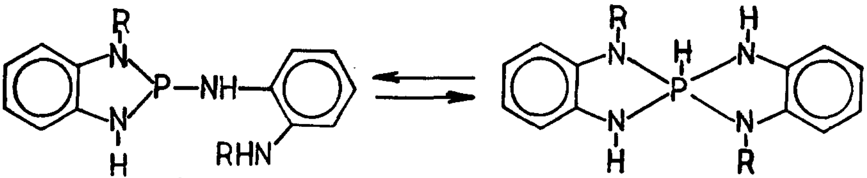
(11) The same reaction run in boiling acetonitrile in 1:2 ratio after elimination of 3 moles of methylamine gives only one P^{III} compound ($\delta^{31}P$ = 99 ppm) while in xylene medium the spirophosphorane 5 is mainly obtained with a little P^{III} species 6. This latter product is probably in equilibrium with 5.



6 5

Such equilibria are known to be solvent sensitive (10).

(12) Molecular weights determinated by ebullioscopy in benzene give n = 2, showing that in boiling benzene these compounds are probably diazadiphosphetidines.

(13) Microanalysis results agree with the formulae 4 or 4'.

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