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Synthesis, Structure and Bonding Properties of 3-Phosphoindoles Analogues of Group 15

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SYNTHESIS, STRUCTURE and BONDING PROPERTIES OF 3-PHOSPHOINDOLES ANALOGUES OF GROUP 15

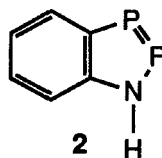
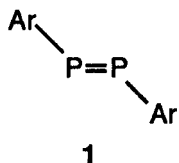
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Abstract We present the synthesis and the characterization of new benzazadiphospholes **3**, **4** and the parent compounds **5** and **6** with a P=As and a P=Sb double bond. The theoretical calculations, the photoelectron spectra and the reactivity of **2** are also discussed.

Compounds featuring double bonding between the heavier group 15 elements and phosphorus are now well known and characterized in details¹.

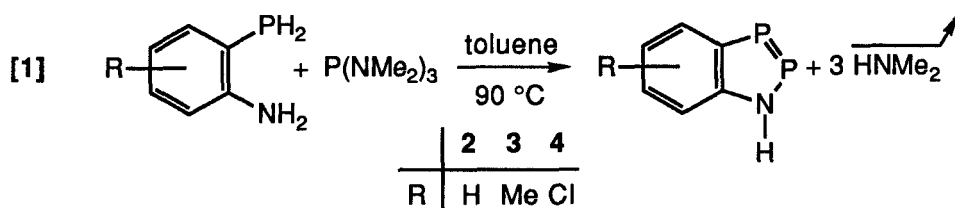
Structural data indicate that **1**, for example, like almost all known diphosphenes, exhibits a trans configuration. We have reported two years ago², the synthesis and the characterization of the first benzazadiphosphole **2** with an intracyclic P=P double bond at the obviously cis configuration. This paper reports the synthesis of the two new benzazadiphospholes **3** and **4** and the corresponding analogues **5**, **6** with a P=As and P=Sb double bond.



I - BENZADIPHOSPHOLES

1 - Synthesis

Our synthetic method is described by the scheme [1] : it is a cyclocondensation of tris(dimethylamino)phosphane with the anilino-2 phosphine, the elimination of three equivalents of dimethylamine results in stable benzazadiphospholes **2**, **3** and **4**



2 - Structural data

The ^{31}P chemical shifts of the benzazadiphospholes are in the range of the two-coordinate phosphorus atoms and are in good agreement with the values found by Niecke and al³. Furthermore the great coupling constant ($J \approx 495 \text{ Hz}$) confirms the double bond between the two phosphorus atoms

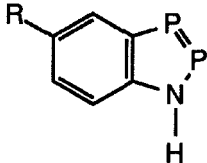
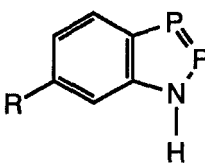
R			
2	H	$\delta_1 = 248 \text{ (d)} ; \delta_2 = 352 \text{ (d)}$ $^1J_{\text{PP}} = 496 \text{ Hz}$	
3	Me	$\delta_1 = 246 \text{ (d)} ; \delta_2 = 358 \text{ (d)}$ $^1J_{\text{PP}} = 494 \text{ Hz}$ 80 %	$\delta_1 = 248 \text{ (d)} ; \delta_2 = 382 \text{ (d)}$ $^1J_{\text{PP}} = 496 \text{ Hz}$ 20 %
4	Cl	$\delta_1 = 245 \text{ (d)} ; \delta_2 = 350 \text{ (d)}$ $^1J_{\text{PP}} = 494 \text{ Hz}$ 70 %	$\delta_1 = 247 \text{ (d)} ; \delta_2 = 349 \text{ (d)}$ $^1J_{\text{PP}} = 494 \text{ Hz}$ 30 %

Table 1 - ^{31}P NMR in toluene

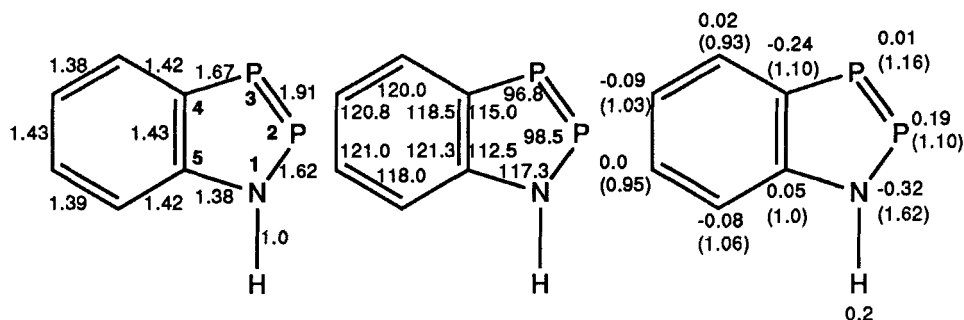
The structure of these compounds is confirmed by ^{13}C NMR and mass spectroscopy.

We have studied the reactivity of these azadiphospholes from

- the abstraction of the H—N proton by a strong base leading to the stable anionic heterocycle
- the cycloaddition [2+4] with 1,3 dienes.

3 - Theoretical calculations and photoelectron spectra

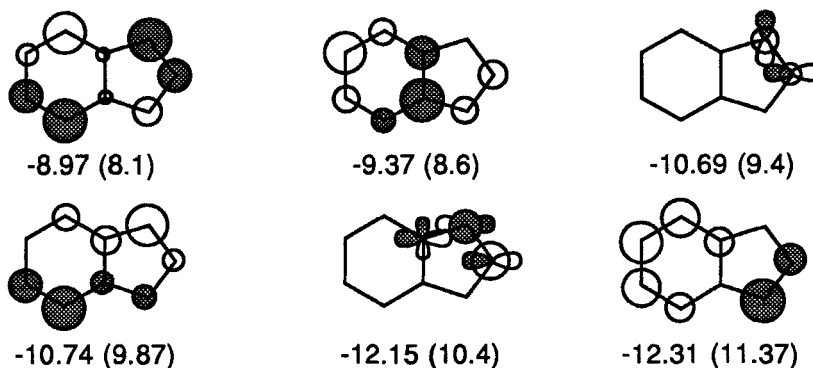
A more detailed analysis of bonding properties of **2** have been done by MNDO calculations. The bonding parameters (bond lengths, angles) after minimization and charge populations calculated without d orbitals are reported in scheme [2]



Scheme [2]

These structures reveal a strong shortening of the single bonds P_3-C_4 and P_2-N_1 ; this last one is intermediate between a $P=N$ (1.54 Å) and a $P-N$ single bond (1.72 Å). The charge populations are in accord with $N_1 \rightarrow P_2$ and $P_3 \rightarrow C_4$ delocalization; the $N-P$ and $P-C$ bonds being strongly polarized, as it was observed by Niecke and al⁴.

The calculated orbitals energies represented scheme [3] give a good interpretation of the photoelectron spectra where the six first ionisation bands are well resolved.



Scheme [3]

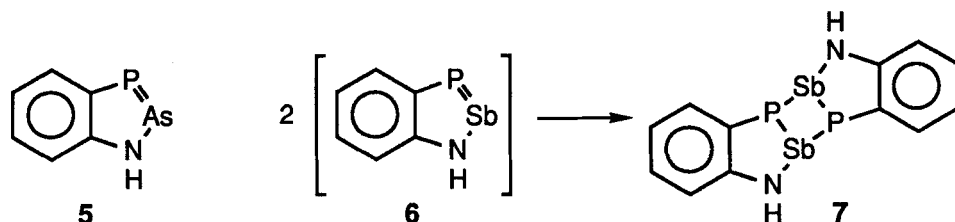
Localisation and orbital energies. The experimental values are in the brackets.

The two first bands (8.1 and 8.6 eV) refer to π orbitals; the lower one

corresponding to a strong localization on the P=P double bond. The third I.P band (9.4 eV) and the fifth (10.41 eV) are associated to the combination of the lone pairs at the two phosphorus atoms.

II - ARSENIC AND STIBENE BENZAZAPHOSPHOLES

We have tried to synthesize the corresponding benzaphospholes **5** and **6** with respectively a P=As and P=Sb double bond



For **5** and **6** the procedure is the same that for **2** using respectively As(NMe₂)₃ and Sb(NMe₂)₃ instead of P(NMe₂)₃ in scheme [1]. The reaction, in both cases, is over at room temperature after one hour.

5 is an orange solid, which is, after isolation, insoluble in all usual solvents. The $\delta^{31}\text{P} = 315$, is the value expected for the two-coordinated phosphorus atom. The mass spectra confirms the monomeric structure $m/e = 197(\text{M}^+)$, 182 (M—NH), 122 (M—As), 91 (M—P—As).

Compound **6** is a brown solid which precipitate in the mixture ; the ^{31}P signal is a singlet at $\delta = 44.5$ and not 600 ppm (expected value for the monomer **6**). The mass spectra confirms the dimer structure. ($m/e = 486$; 488; 490 M^+ with the isotopic distribution % 100, 66.5, 38). So, the stable structure of **6** is the dimer **7**.

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