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# REACTIVITY OF CONJUGATED BASES OF HYDRIDOPHOSPHORANES SYNTHESIS OF NEW PHOSPHORANES INVOLVING P-P BONDS

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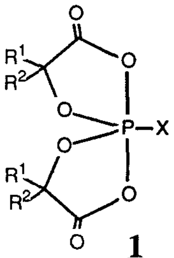
## Summary

Reaction of the hydridophosphoranes ( **1a** and **2** ) with chlorophosphines RR'PCl or with a pentacoordinated chlorophosphorane **7** in the presence of triethylamine gave new phosphorus-phosphorus bonded compounds in good yields. They have been characterized by means of nmr and elemental analysis.

## INTRODUCTION

In the chemistry of phosphorus compounds having a high coordination number at the phosphorus atom, now only a few new types of compounds are described each year. However, in recent years there has been much interest in compounds containing a phosphorus - phosphorus bond with highly coordinated phosphorus atoms (1-4), the two phosphorus atoms included in a cyclic (1,2) structure, or compounds in which one phosphorus atom is outside of the ring system (4).

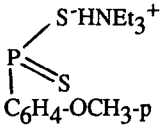
We recently synthesized (6) a serie of compounds with the general formulae **1**.



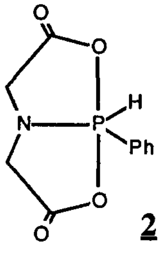
**1**

X = H, OH,
$O^-HNEt_3^+$, $S^-HNEt_3^+$, $Se^-HNEt_3^+$ ,
$CS_2^-HNEt_3^+$, $NTos^-HNEt_3^+$ ,
SMe, SeMe, $CH_2Ph$ , NHPh , ....

**1a** : $R^1 = R^2 = Me,\ X = H$
**1b** : $R^1 = R^2 = Me,\ X = S^-HNEt_3^+$
**1c** : $R^1 = R^2 = Me,\ X = Se^-HNEt_3^+$
**1d** : $R^1 = R^2 = Me$, X =



$P(=S)(S^-HNEt_3^+)(C_6H_4\text{-}OCH_3\text{-}p)$



**2**

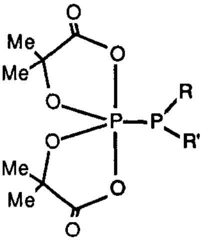
Going further on, we attempted starting with the hydridophosphorane **1a** or with the bicyclic model **2**, to prepare compounds with a phosphorus-phosphorus bond, either $\lambda^5P$-$\lambda^5P$ or mixed valence diphosphorus compounds.

We previously described (6) a first diphosphorus compound **1d** bearing an extracyclic $\lambda^5$P - $\lambda^5(\sigma^4)$P bond, obtained by reacting **1a** with 2,4-bis- (4 methoxyphenyl)- 1,3,2,4- dithia diphosphetane- 2,4- disulfide (Lawesson's reagent) in the presence of triethylamine. Structure elucidation was based upon $^{31}$P nmr, $^{13}$C nmr, $^{1}$H nmr, and microanalysis.

## RESULTS AND DISCUSSION

### I - Mixed valence diphosphorus compounds

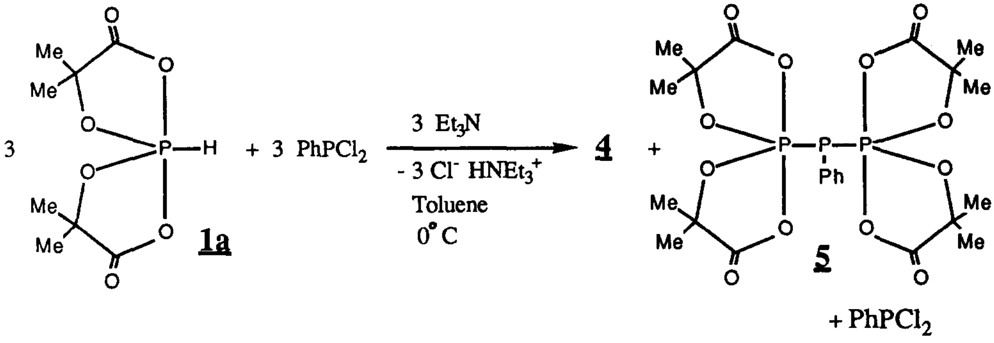
a) Reaction of the hydridophosphorane **1a** with chlorophosphines RR'PCl occurs instantaneously in toluene and in the presence of $Et_3N$ and results in the formation of the corresponding phosphorus-phosphorus bonded compounds **3** and **4**.



**3** R = R' = Ph

**4** R =Ph, R' =Cl

To obtain compound **4** it was found necessary to react the hydridophosphorane and dichlorophosphine in a 1:2 ratio ; use of a 1:1 stoechiometry leads to the formation of **4**, **5** and unreacted $PhPCl_2$ according to equation 1.



Equation 1

The unreacted dichlorophosphine in the 1:2 stoechiometric process is easily separated from compound **4** by treating the solution with pentane from which **4** precipitates as a white powder.

In compounds **3** and **4**, one phosphorus atom does not belong to the cyclic system and the phosphorus atoms have coordination numbers of 5 and 3. Evidence for the presence of the P - P bond is the observed $^{1}J_{PP}$ coupling constant in their $^{31}$P nmr spectra (see Table 1).

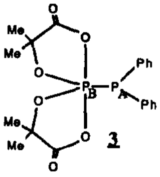
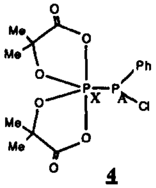
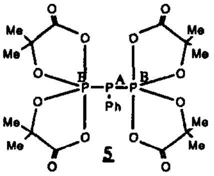
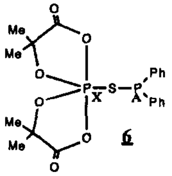
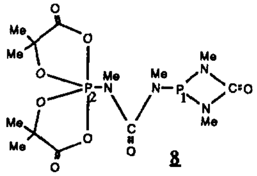
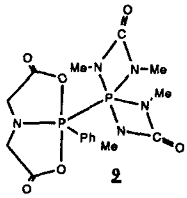
| COMPOUNDS | $^{31}$P nmr<br>$\delta$ ( $J_{PP}$ Hz ) | Analysis | | |
|---|---|---|---|---|
| | | | Calculated | Found |
|  3 | $\delta_A = 1.35$ ( 322.2 ) | C | 57.14 | 55.92* * |
| | $\delta_B = -28.4$ ( 322.2 ) | H | 5.23 | 5.46 |
| | | P | 14.76 | 14.98 |
|  4 | $\delta_A = 63.1$ ( 401.7 ) | C | 44.40 | 44.24 |
| | | H | 4.53 | 4.56 |
| | $\delta_X = -33.5$ ( 401.7 ) | P | 16.36 | 16.39 |
|  5 | $\delta_A = 15.6$ ( 260.9 ) | C | 45.69 | 45.90 |
| | | H | 5.05 | 5.30 |
| | $\delta_B = -33.5$ (260.9 ) | P | 16.07 | 15.54 |
|  6 | $\delta_A = 28$ $^2J_{PP} = 44.5$ | C | 53.10 | 52.75 |
| | | H | 4.90 | 5.25 |
| | $\delta_X = -34.5$ $^2J_{PP} = 44.5$ | P | 13.69 | 13.78 |
| | | S | 7.09 | 6.70 |
|  8 | $\delta_1 = 88.2$ | C | 38.36 | 38.45 |
| | | H | 5.52 | 5.88 |
| | $\delta_2 = -59.7$ | N | 12.78 | 12.68 |
|  9 | $\delta_A = -40.9$ (749.6 ) | C | 43.54 | 44.29 |
| | | H | 4.80 | 5.36 |
| | $\delta_B = -68.1$ ( 749.6 ) | | | |

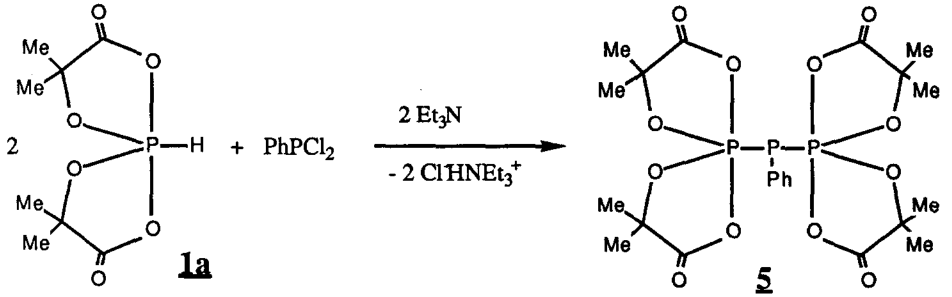
Table 1 : $^{31}$P nmr data and elemental analysis of the new compounds

* * see remark in the experimental part

b) Compounds with a P - X - P skeleton

1) X = P

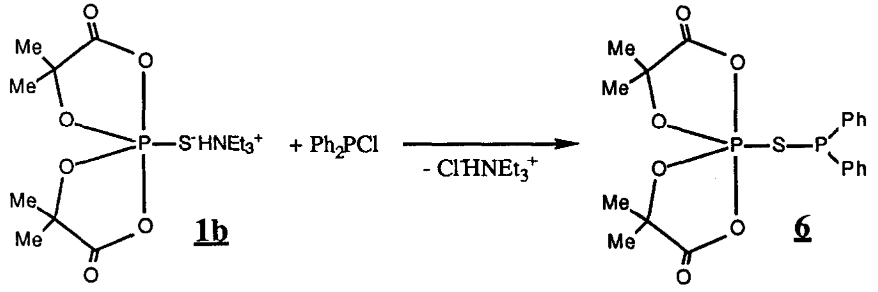
Reacting two hydridophosphoranes **1a** with one equivalent of dichlorophenyl phosphine leaded to compound **5** which bears a $P^V$ - $P^{III}$ - $P^V$ skeleton. The structure of **5** can be deduced from its $^{31}P$ nmr spectrum ( see Table 1 ) which shows an $AB_2$ spin pattern.



**Equation 2**

2) X = S

The same kind of reaction was performed starting with the triethylammonium salt of the thiolophosphorane **1b** and diphenylchlorophosphine. A phosphorus-sulfur-phosphorus bonded structure could be assigned to the reaction compound according to its typical $^{31}P$ nmr AX pattern.



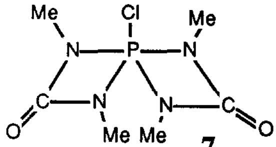
**Equation 3**

With the corresponding salt of selenophosphorane **1c**, the reaction did not lead to well defined products.

II- Compounds with a $\lambda^5P$ - $\lambda^5P$ bond

In 1980 Richman et al.(7) synthesized the first compound containing a $\lambda^5P$ - $\lambda^5P$ bond, the labile P - P bond being stabilized by the fact that both phosphorus atoms were included in a cyclic structure.

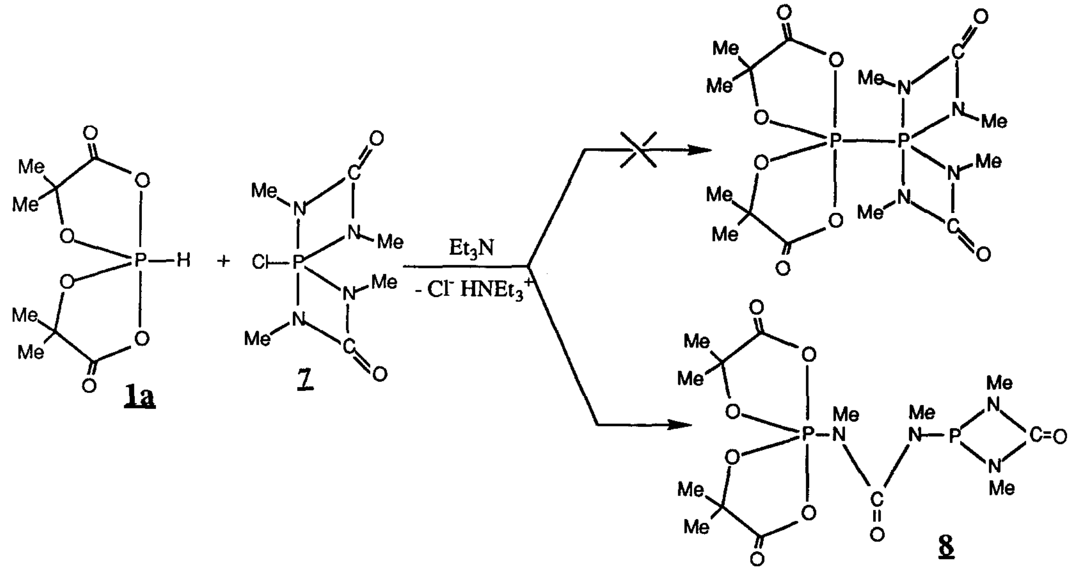
To get $\lambda^5P$ - $\lambda^5P$ compounds starting with our hydridophosphoranes , it seemed us appropriate to use the well known 4 -chloro-1,3,5,7-tetramethyl -1,3,5,7- tetraaza-4$\lambda^5$-phosphaspiro-3,3-heptan -2,6- dione (compound **7** ). This reagent easily available by a two step reaction with NN' dimethylurea and $PCl_5$ (8, 9) allowed Schmutzler and coworkers to prepare a serie of substituted phosphoranes involving this model (10, 11).



**7**

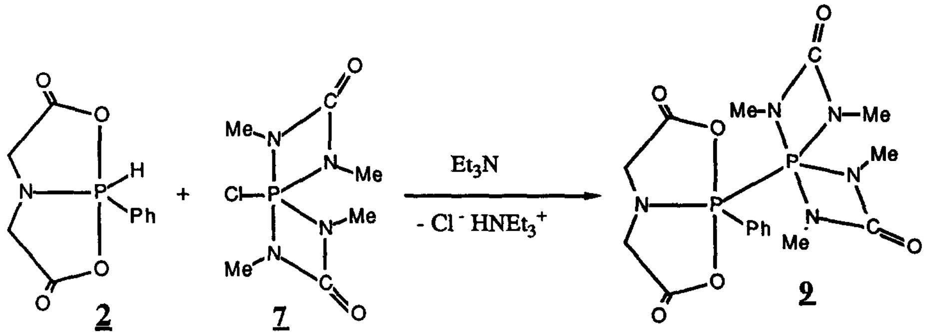
1) The reaction of **1a** onto **7** does not proceed as expected. Instead of the phosphorus-phosphorus bonded compound, we observed the formation of the more stable isomer **8** resulting most probably from a P - P bond cleavage followed by attack on a nitrogen atom. These kinds of side reaction were also observed by Schmutzler et al. in processes involving the same model (12) .Compound **8** was readily obtained as a white powder and was characterized by $^{31}P$ nmr , Infra-red spectroscopy and elemental analysis.

Three different carbonyl absorption bands were observed at 1770, 1740 and 1680 $cm^{-1}$ which are consistent with the proposed structure. The $\nu_{CO}$ value of 1770 is in accord with the C=O included in the four membered ring (13) whereas the value of 1740 corresponds to the carbonyl group of the phosphorane moiety (14). The $\nu_{CO}$ value of 1680 $cm^{-1}$ is consistent with the open part P-N-C(O)-N-P of the molecule (15).



Equation 4

2) A $\lambda^5P$ - $\lambda^5P$ phosphorus compound **9** is obtained according to equation 5 upon reacting equimolecular amounts of **2** and **7** in the presence of triethylamine. The $^{31}P$ nmr spectrum of the crude reaction medium, shows a quasi-quantitative yield. The rather poor stability of compound **9**, however, lowers greatly its yield after extraction, and is also responsible of the fact that the elemental analysis of this compound could not be obtained with a good accuracy (Table 1).



Equation 5

Evidence for the presence of the P-P bond is given by the AB pattern of the $^{31}P$ nmr spectrum (see Table 1) The observed coupling constant (750 Hz) is in our knowledge (one of) the largest known at the moment for compounds with two phosphorus atoms of coordination numbers 5. As it was reported (5) this value is in the range of directly bonded phosphorus atoms, so far it is inconceivable to have $^1J_{PP}$ coupling constants over 700 Hz without a direct P-P bonding.

In 1973, H. Falius and M. Murray (16) found an extremely high $^1J_{PP}$ value of 770 Hz in a four coordinated diphosphorus compound , a difluorodiphosphate anion. This fact was explained according to Finner and Harris (17) by an increased electronegativity of the groups attached to phosphorus which makes the $^1J_{PP}$ more positive.

A single crystal X-ray analysis of **7** (10) and of two other compounds with the same $N_4$ spirocyclic structure obtained by substitution of the chlorine atom of **7** by $NMe_2$ or $N_3$ was performed by Schomburg and coworkers (10). They demonstrated that in each case the extracyclic group is in an equatorial position of the trigonal bipyramid . The same configuration may be proposed for compound **9** the P-P bond is in an equatorial position for both pentacoordinated moieties of the molecule, which can explain (18) the large value observed for the coupling constant.

In summary, the conjugated bases of hydridophosphoranes by their nucleophilic reactivity towards electrophiles provided us an efficient system for smooth formation of phosphorus - phosphorus bonded compounds.Considerable potential exists for the utilisation of some of these compounds as ligands in coordination chemistry by their phosphane functionnality.

## EXPERIMENTAL

* Spectroscopic measurements

$^{31}P$ and $^{1}H$ nmr spectra were recorded in the FT mode on a Bruker AC 80 instrument operating at spectrometer frequencies of 32.44 Mhz for the phosphorus nucleus and 80.13 Mhz for the proton. $^{1}H$ and $^{31}P$ chemical shifts (negative direction upfield) were measured with respect to $Me_4Si$ and 85% $H_3PO_4$ external reference.

* Analysis were performed by the Microanalysis Services of CNRS in Toulouse and Lyon.

**Remark : It has been frequently observed(14a, 20) that for organophosphorous compounds which contain great amounts of carbon (50-70%), the analysis of this element shows an absolute error of up to 2% . This was even shown in the case of compounds perfectly characterized by a single crystal X-Ray structure(14a, 20).

* General procedure

**1a**, **2** and **7** were prepared according to published methods (19, 20, 9). All the reactions were carried out in Schlenk tubes under dry argon atmosphere to prevent the effects of moist air on the sensitive P-P compounds. The solvents were dried and purified by conventional methods and handled under a dry argon atmosphere.

Preparation of **3**

To a stirred solution of 0.72 g (3.1 $10^{-3}$ mole) of **1a** and 0.69g(3.1 $10^{-3}$ mole) of $Ph_2PCl$ in 10 ml of toluene , 0.8 ml (~ 2 equivalents) of $Et_3N$ were added dropwise at 0°C via a syringe . After complete addition , the reaction mixture was stirred for 5-10 minutes. After completion of the reaction shown by the $^{31}P$ nmr spectrum of an aliquot, the hydrochloride was filtered through a celite layer and the solvent removed under vacuo. The residue was treated with pentane to afford a white powder 0.72 g (56% yield). $^{1}H$ ($C_6D_6$) d : 8 - 6.8 (m, $10H^+$, $C_6H_5$) 1.23 and 1.29 ( $12H^+$, $CH_3$)

Preparation of **4**

1.19 g (5 $10^{-3}$ mole) of **1a** and 2 equivalents of $PhPCl_2$ 1.80 g (1 $10^{-2}$ mole)in 10 ml of toluene were treated with 0.8 ml of triethylamine. **4** was extracted as a white, very hygroscopic powder 1.63 g (82% yield ) as preceedingly, treatment of the residue with pentane permitted us to separate the remaining dichlorophenylphosphine . $^{1}H$ ($CDCl_3$) : d 8.2-7.0 (m, 5 $H^+$, $C_6H_5$) 1.45 and 1.37 (12 $H^+$, $CH_3$ )

Preparation of **5**

1.72 g of **1a** (7.26 $10^{-3}$ mole) and 0.65 g (3.63 $10^{-3}$ mole) of $PhPCl_2$ in 10 ml of toluene were treated with 1.2 ml of triethylamine.1.33 g of **5** (64% yield) were extracted as a white rather unstable powder . $^{1}H$ ($C_6D_6$) : d 8.0 - 6.8 (m, 10 $H^+$, $C_6H_5$) 1.16 and 1.37 (24 $H^+$, $CH_3$).

Preparation of **6**

1.015 g of **1a** (4.3 $10^{-3}$mole) and 0.14 (4.3 $10^{-3}$ eq.gr.) of sulfur dispersed in 10 ml toluene. 1 ml of $Et_3N$ (~ 1.5 equivalents) is introduced dropwise with a syringe, a slightly exothermic reaction occurs and compound **1b** separates as a precipitate. 0.95 g. (4.3 $10^{-3}$mole) of $Ph_2PCl$ is then added to the stirred dispersion of **1b** with a syringe . The medium in a first step became clear , then the hydrochloride precipitated. Extraction of **6** (1.36g 70% yield) was made by the same technique $^{1}H$($C_6D_6$ ) : d 8.5-6.3 (m, 10 $H^+$, $C_6H_5$) 1.26 and 1.13 (12 $H^+$, $CH_3$)

Preparation of **8**

To 1.15g (4.9 $10^{-3}$mole) of **1a** and 1.16g (4.9 $10^{-3}$mole) of **7** dissolved in 10 ml of THF, 1.36 ml ( ~2 equivalents) of $Et_3N$ was added . 1.35 g of **8** (63 % yield) were obtained by the same procedure as before.

$^1H(C_6D_6)$ : d 2.82-2.4 (m, 12 $H^+$, $NCH_3$) 1.22 and 1.47 (12 $H^+$, $CH_3$)

Preparation of **9**

0.714g (2.98 $10^{-3}$ mole) of **2** and 0.712g of **7** (2.98 $10^{-3}$ mole) were dissolved in 10 ml freshly distilled THF. 0.5 ml of $Et_3N$ ( ~ 1 eq.) was added to the stirred solution at 0°C. The hydrochloride was separared by filtration through a celite layer under argon protection, and the solution was evaporated. 0.5g of **9** was isolated as a white very unstable and hygroscopic powder (38% yield). 1H NMR ($C_6D_6$) : d 8.0-7.0 (m, 6 $H^+$, $C_6H_5$); 3.46 (s, $NCH_2$ ), 3.45 (d, $^3J_{HP}$ = 10Hz, $NCH_3$), 3.42 d $^3J_{HP}$ = 9 Hz , $NCH_3$) 16 $H^+$ for these three signals.

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