

The Site of Protonation in Phosphole Derivatives.  
*1H*-Phospholium Salts Stabilized by Complex Transition Metal Ions

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Sir:

The possible aromatic character of the phosphole system (I) has received considerable attention during the last few years. For example, Brown (1) has estimated by molecular orbital calculations that a planar model of phosphole would have a significant resonance energy and that delocalization would be mainly of the  $p_{\pi}$ - $p_{\pi}$  type as in pyrrole. More recently, Märkl (2) and Quin (3,4) have published nmr data for 1-phenylphosphole and 1-methylphosphole respectively and the results are consistent with some degree of aromatic character in the system. In addition, Mislow (5) has shown that the energy barrier to inversion about the phosphorus atom in 1-isopropyl-2-methyl-5-phenylphosphole (II) has the unusually low value of 16 kcal/mole compared with values of 29-36 kcal/mole for various alkyl and aryl phosphines and has concluded that these results are consistent with  $(3p-2p)_{\pi}$  delocalization and aromaticity in the phosphole ring.

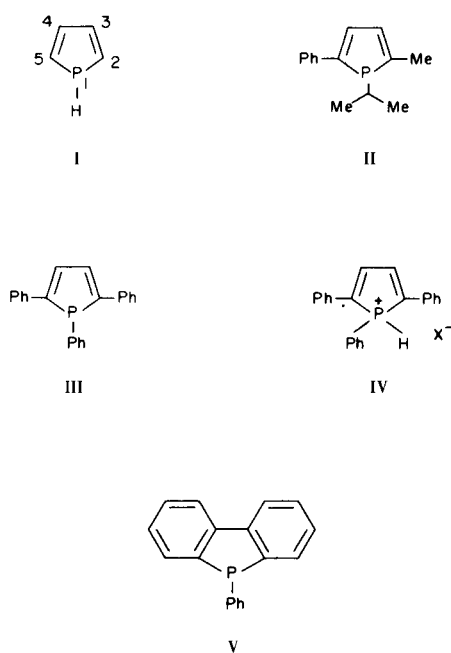
Thus, the sum of this and other evidence (6) indicates that the phosphole system has an electronic structure which is generally of the pyrrole type.

In a detailed report on his investigations of the chemistry and electronic structure of 1-methylphosphole, Quin (4) reported that this compound is not extracted from pentane by 2 *N* hydrochloric acid (unlike other tertiary phosphines) and has a very low  $pK_a$  value of 0.5 compared with a value of  $pK_a = 5.2$  estimated for a non-aromatic model of the phosphole. This value of  $pK_a = 0.5$  is somewhat higher than the value of  $pK_a = -3.8$  estimated for pyrrole (7) although, like pyrrole derivatives, the 1-methylphosphole polymerizes rapidly in aqueous acidic solution. Quin (4) also pointed out that since the site of protonation in pyrroles has been shown to be at the  $\alpha$  or  $\beta$  ring carbon atoms depending upon the substitution pattern (7), similar studies for the phosphole system would be desirable.

In connection with our studies of complexes of phospholes and related compounds with various transition metal systems (to be published as separate papers), we have established that for 1,2,5-triphenylphosphole (III) (TPP), the site of protonation is the phosphorus atom. Furthermore, certain of these 1,2,5-triphenyl-*1H*-phospholium salts (IV)

are remarkably stable, even in air for several hours.

It has been found that the phosphole III, normally a very poor donor, reacts smoothly with pure, dry tantalum (V) chloride under pure nitrogen in rigorously dried benzene to give, in high yield, a complex identified as  $TPP \cdot TaCl_5$  in which the ligand is bound to the metal



through the phosphorus atom. Exposure of this complex in benzene solution to ethanol vapour or to direct addition of very small quantities of ethanol leads to the immediate formation of an orange precipitate. The precipitate may be purified by dissolving it in dry methylene chloride followed by reprecipitation of the solid with dry pentane. The orange solid analyzes very well for  $TPPH^+ TaCl_6^-$  (IV, X =  $TaCl_6$ ) and the same salt may be prepared rapidly and quantitatively by passing dry hydrogen chloride into a dry benzene solution of the complex  $TPP \cdot TaCl_5$ . No phospholium salt of the type  $TPPH^+ Cl^-$  is formed when dry hydrogen chloride is passed into a dry benzene solu-

tion of the phosphole alone although the stronger base triphenylphosphine, as expected, readily forms the salt  $\text{Ph}_3\text{PH}^+\text{Cl}^-$  in excellent yield by this method.

That the phosphole grouping is still intact in the salt  $\text{TPPH}^+\text{TaCl}_6^-$  is shown by the fact that the phosphole III is displaced from the salt by acetonitrile. A peak due to TPP also appears at  $m/e$  312 in the low voltage mass spectrum of the adduct. Aqueous ethanolic hydrolysis of the salt gives some of the phosphole III, some of the corresponding phosphole oxide and some resinous uncharacterized organic material. This shows that the behavior of protonated 1,2,5-triphenylphosphole (III) in water is similar in some respects to the behaviour of 1-methylphosphole (4) and various simple pyrroles in aqueous acid.

The site of protonation in the salt  $\text{TPPH}^+\text{TaCl}_6^-$  is clearly shown to be the phosphorus atom by examination of the infrared spectrum of a Nujol mull of the salt. This shows a typical (8)  $\text{R}_3\text{P}^+\text{H}$  stretching frequency as a sharp peak of moderate intensity at  $2410\text{ cm}^{-1}$ . This peak also appears (at  $2418\text{ cm}^{-1}$ ) in the infrared spectrum of triphenylphosphonium chloride ( $\text{Ph}_3\text{PH}^+\text{Cl}^-$ ). Moreover, the spectrum of the salt is quite similar (except for small displacements and changes in relative intensities of the peaks) to that of the phosphole III apart from the P-H vibration at  $2410\text{ cm}^{-1}$  and a very intense metal-halogen stretch in the range  $320\text{--}330\text{ cm}^{-1}$  which is typical of the  $\text{TaCl}_6^-$  ion (9).

That the peak at  $2410\text{ cm}^{-1}$  in the infrared spectrum is indeed due to the  $\text{R}_3\text{P}^+\text{H}$  type of stretching is confirmed by forming the salt  $\text{TPPD}^+\text{TaCl}_6^-$  by passage of dry deuterium chloride into a benzene solution of the complex  $\text{TPP}\cdot\text{TaCl}_5$ . In this salt, the P-D stretch occurs at  $1753\text{ cm}^{-1}$  which is typical (8) of such deuterophosphonium salts. X-ray powder diffraction studies show that the salts  $\text{TPPH}^+\text{TaCl}_6^-$  and  $\text{TPPD}^+\text{TaCl}_6^-$  are isostructural.

The salt IV ( $X = \text{TaCl}_6$ ) is moderately stable in air for several hours unless the solid is treated directly with moisture or wet solvents and, in the opinion of the authors, this stability is due mainly to the exceptional stability of the  $\text{TaCl}_6^-$  ion and a favourable lattice energy for crystalline IV ( $X = \text{TaCl}_6$ ). The solid is certainly highly crystalline and gives very intense X-ray powder diffraction patterns.

If the stability of the  $\text{TaCl}_6^-$  ion is an important factor, as the reluctance of the phosphole III to form a hydrochloride under anhydrous conditions would indicate, then analogous salts should be formed with other transition metals which form anions of similar stability. This proves to be the case since the corresponding salt IV ( $X = \text{NbCl}_6$ ) is readily formed by passing hydrogen chloride into a dry benzene suspension of the complex  $\text{TPP}\cdot\text{NbCl}_5$ . The infrared spectrum of the salt  $\text{TPPH}^+\text{NbCl}_6^-$  shows a P-H

stretching vibration at  $2385\text{ cm}^{-1}$  and a characteristic (9)  $\text{NbCl}_6^-$  vibration at  $340\text{ cm}^{-1}$ . However, the salt  $\text{TPPH}^+\text{NbCl}_6^-$  is much more sensitive to atmospheric moisture than  $\text{TPPH}^+\text{TaCl}_6^-$  and hydrolyzes rapidly on exposure to air.

Attempts to prepare the salt IV ( $X = \text{FeCl}_4$ ) met with limited success. A compound showing a P-H stretch at  $2410\text{ cm}^{-1}$  was obtained by treating the phosphole III with a 2:1 excess of ferric chloride in the presence of dry hydrogen chloride. The remainder of the infrared spectrum of this compound is similar in many respects to that of  $\text{TPPH}^+\text{TaCl}_6^-$  in the region  $2600\text{--}600\text{ cm}^{-1}$ , but the salt is extremely sensitive to atmospheric water vapour and, therefore was not analyzed or further purified. Attempts to prepare similar salts stabilized by the ions  $\text{ZnCl}_4^{2-}$ ,  $\text{PtCl}_6^{2-}$ ,  $\text{Ph}_4\text{B}^-$  and  $\text{SbCl}_6^-$  were unsuccessful although, in some cases, interesting complexes were formed.

Similar salts may be obtained from triphenylphosphine and 9-phenyl-9-phosphafluorene (V), and in the latter case, such compounds would be expected since Millar (10) has shown that there is probably very little delocalization of the phosphorus non-bonding electron pair in the central ring of V and it should therefore be a much better donor than the phosphole III.

Thus, it is clear that in salts such as IV, the site of protonation is on the phosphorus atom (11) and these salts are unexpectedly stable. However, it may be that in aqueous acidic solution or with less highly substituted phospholes than III, protonation may occur at a different site. This is currently under investigation.

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(11) We are indebted to a referee for pointing out that what is actually being protonated (for niobium and tantalum) is a phosphole complex of the metal halide. However, in the case of iron (III), where protonation clearly occurs (although no pure complex was isolated), there is no coordination between iron (III) chloride and

the phosphole (12). We therefore feel that the metal plays no part in the protonation process except in so far as the anion appears to stabilize the protonated phosphole once the latter has formed.

(12) D. Budd, R. Chuchman, D. G. Holah, A. N. Hughes and B. C. Hui, to be published.