

Donor Properties of 2-Coordinate Phosphorus in the Phosphorin System: Metal Complexes

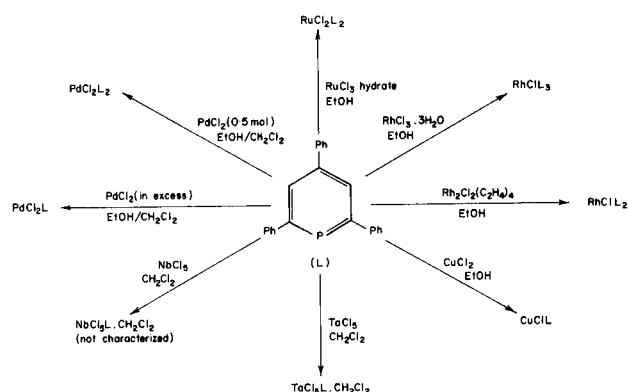
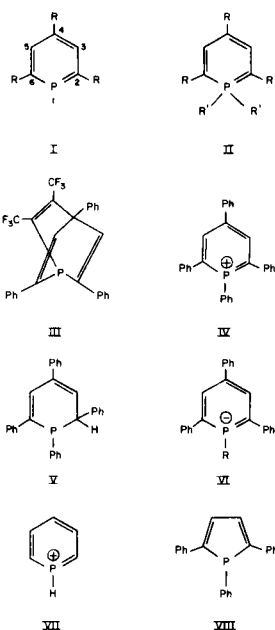
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Received October 3, 1972

Sir:

Since the first reports of simple phosphorin derivatives containing two-coordinate (I, R = Ph) and four-coordinate (II, R = R' = Ph) phosphorus appeared in the literature (1,2), both systems have received considerable attention (3). Superficially, the phosphorin system containing 2-coordinate phosphorus (I, R = H) is very similar to pyridine and, since phosphines normally have appreciable basic character, phosphorins of type I might be expected to have basic properties similar to those of pyridine derivatives. However, Märkl found (4) that 2,4,6-triphenylphosphorin (I, R = Ph) does not form a methiodide on treatment with methyl iodide nor can I (R = Ph) be *P*-alkylated with triethyloxonium fluoroborate. Märkl also found (5) that I (R = Ph) will not react with the powerful electrophile dimethyl acetylenedicarboxylate although triphenylphosphine reacts with this ester in ether virtually instantaneously at -50° (6). Furthermore, the phosphorin I (R = Ph) seems to be reluctant to react with benzyne (7) although it does react (5) at 100° with the powerful dienophile hexafluoro-2-butyne in a Diels-Alder type of 1,4-addition to the phosphorin ring to give the phosphabarrelene derivative III.



In short, experimentally, the phosphorin system appears to have little, if any, nucleophilic character although it should be mentioned that cationic structures of type IV may be prepared indirectly (8) by hydride abstraction from the cyclic phosphine V using trityl perchlorate. On the contrary, I (R = Ph) reacts readily as an electrophile with organometallic reagents such as organolithium compounds (4,7,9,10) and Grignard reagents (10) to give anionic products of type VI. Clearly, the phosphorin system behaves in an entirely different manner from pyridine.

The structure of phosphorins of type I has been the subject of several investigations. Thus, a crystallographic study (11) of 2,6-dimethyl-4-phenylphosphorin showed that the heterocyclic ring is planar and that both the P-C bonds and the C-C bonds are intermediate in character between single and double bonds. In a series of papers, Schweig, *et al.* (12-15) have thoroughly investigated the electronic structure of phosphorins of type I by CNDO/2 calculations (12,14) and by photoelectron spectroscopic studies of suitable phosphorin derivatives (13,15). In summary, these studies have shown that, in compounds of type I, there is a major phosphorus $3p_z$ contribution to the π bonding with a significant d_{π} contribution, the highest occupied orbital is a π orbital (unlike pyridine in which it is the lone pair orbital), the phosphorus lone pair has more s character than that of the nitrogen atom in pyridine, and the phosphorus lone pair occupies a more

diffuse, partly delocalized, and less directional orbital than that of pyridine. Furthermore, the sequence of π orbitals is different in the phosphorin system from that in the pyridine system. Finally, recent CNDO/2 studies (14) regarding the basicity of the phosphorus atom in phosphorins of type I indicate a pK_a value of about -10 for the phosphorinium ion VII although Schweig points out (14) that protonation at C_2 in the phosphorin I ($R = H$) should occur more readily than at the phosphorus atom.

Thus, theoretical predictions and the available experimental evidence indicate negligible basic character for phosphorins of type I. However, as part of our studies (16) of the donor properties of unsaturated, potentially aromatic phosphorus heterocycles towards inorganic systems, we have investigated the reactions of the readily available 2,4,6-triphenylphosphorin (I, $R = Ph$) with several transition metal systems (17) in a wide variety of oxidation states where complex formation with phosphines by donation of an electron pair from the phosphorus atom normally occurs.

We find that, under certain circumstances, the phosphorus atom of I ($R = Ph$) can have quite strong donor properties. The preliminary results of this investigation are summarized below.

For example, the phosphorin I ($R = Ph$) forms in methylene chloride an air sensitive, reddish-brown, 1:1 adduct with tantalum (V) chloride and this adduct contains one molecule of solvent (confirmed by mass spectrometry). A similar reaction appears to occur with niobium (V) chloride although the adduct in this case is too air sensitive to characterize unambiguously. Similarly, the phosphorin forms, depending upon reactant proportions, either a 1:1 or a 2:1 air-stable adduct with palladium (II) chloride.

By analogy with numerous tertiary phosphine complexes reported in the literature, the stoichiometries of the adducts reported above clearly indicate complex formation *via* the phosphorus lone pair and, therefore, appreciable donor character for the phosphorus atom in I ($R = Ph$). Even more striking evidence for the tertiary phosphine-like behaviour of I ($R = Ph$) in reactions with transition metal systems is provided by the reactions of the phosphorin with Ru(III), Rh(III), Rh(I) and Cu(II) chlorides. Thus, Ru(III), Rh(III), and Cu(II) are reduced to Ru(II), Rh(I) and Cu(I), respectively, and the reduction is accompanied by complex formation. Furthermore, the phosphorin reacts directly with the dimeric bis-(ethylene)rhodium (I) chloride to give a Rh(I) complex. No reactions of the phosphorin with nickel (II) or rhenium (III) chlorides occur. The reactions outlined above are summarized in the reaction scheme. Satisfactory elemental analyses for all compounds (other than the

Nb(V) adduct) were obtained although it should be noted that good chloride analyses for the Pd(II) adducts were difficult to obtain because these adducts appear to be unusually resistant to hydrolysis.

The syntheses of the complexes mentioned above are very easy to carry out although reaction times are, in general, considerably longer than for the corresponding tertiary phosphine complexes and inert atmosphere (glove-box) conditions are required. Those reactions which result in water-sensitive complexes are best carried out in rigorously dried methylene chloride. For the water-sensitive complexes, a typical experimental procedure was as follows:

The phosphorin I ($R = Ph$) (about 150 mg.) was dissolved in a few ml. of methylene chloride and mixed with a suspension of Ta(V) or Nb(V) chloride in a little methylene chloride (ligand to metal chloride molar ratio 2:1) and heated under reflux for about 24 hours. The brown suspension was then filtered (inert atmosphere) to give maroon crystals of the appropriate complex in 50-70% yield.

Those adducts not sensitive to small amounts of water could be synthesized in ethanol solution. For example, the phosphorin I ($R = Ph$) (about 150 mg.) and Cu(II) chloride dihydrate were mixed in a 1:1 molar ratio in a few ml. of ethanol and heated under reflux for 24 hours. The resulting pale yellow crystals were removed by filtration and proved to be air stable. The Rh(I) and Ru(II) complexes were prepared by small variations in this procedure and, again, yields of 50-70% were obtained. For the palladium complexes, it was convenient to use ethanol or methylene chloride-ethanol mixtures for the solvent.

The infrared spectra of the complexes are very similar to the spectrum of the free ligand except for the presence of typical metal-halogen stretching vibrations in the range 260-345 cm^{-1} depending upon the metal present.

It is interesting to note that 1,2,5-triphenylphosphole (VIII), which is known (16a, 16b) to be a very weak base through interaction of the lone pair with the π system, will not reduce Rh(III) (16d) although it will reduce Cu(II) to Cu(I) with complex formation. It therefore appears from this work that, under certain conditions, the phosphorin system can have quite strong donor character and can exhibit typical tertiary phosphine behaviour. It is therefore probable that some initial strong interaction between the normally very weakly basic phosphorin and the transition metal species perturbs the electronic structure of the phosphorin such that lone-pair electron donation can then occur.

This work is currently being expanded to include studies of the parent phosphorin I ($R = H$) (20).

Acknowledgment.

We wish to thank the National Research Council of Canada for generous financial support. We also gratefully acknowledge a gift of tetrakis(hydroxymethyl)phosphonium chloride from Hooker Industrial Chemicals.

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- (17) There appears to be only one report in the literature (18) regarding the interaction of a phosphorin of type I with a transition metal system. Thus, treatment of chromium(O) hexacarbonyl with I (R = Ph) leads to the formation of 2,4,6-triphenylphosphorin-chromium(O) tricarbonyl for which it has been shown (19) that the phosphorin is π -coordinated to the chromium. The chromium(O) system, is however, particularly suited to the formation of π complexes with aromatic systems.
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