

Evidence for Delocalization in Phosphole Anions from their ^{31}P N.M.R. Spectra

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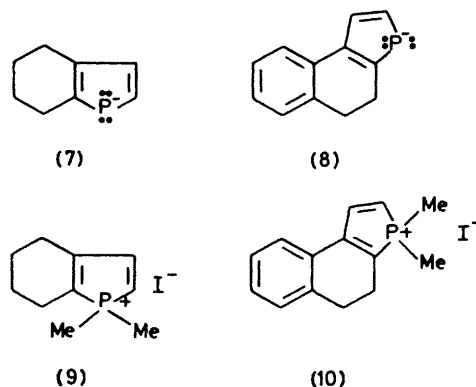
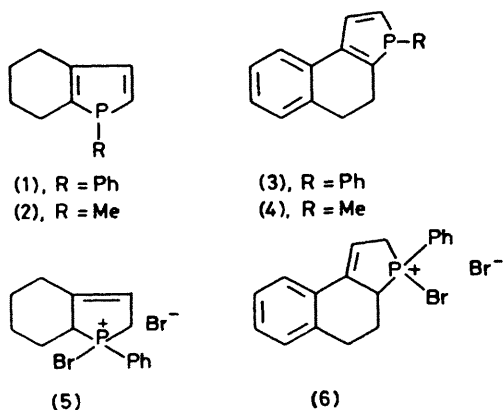
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Summary The phosphorus nucleus in potassium phospholides is strongly deshielded (about 80 p.p.m. downfield from H_3PO_4), consistent with considerable double-bond character for the di-co-ordinate phosphorus.

THEORY has predicted¹ that phosphole anions, which are isoelectronic with thiophen, should be more strongly delocalized than the widely discussed² parent phospholes, but no experimental data bear on this point.³ We have obtained the first ^{31}P n.m.r. spectra for a metallic phospholide; the results can be interpreted on the basis of the system having considerable π -character in the C-P bond as a result of the enhanced delocalization.

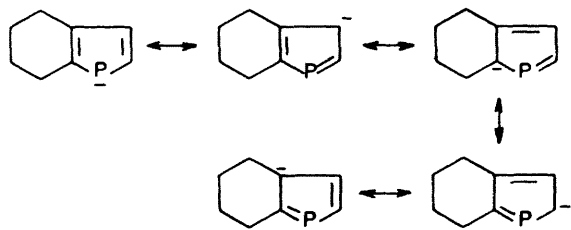
Our study employed two new multicyclic phospholes, (1) and (3), which are more stable and easier to handle than monocyclic phospholes. Both were prepared by the reaction⁴ of 1,5-diazabicyclo[5.4.0]undec-5-ene with the cycloaddition products (5) and (6) derived from the reaction of PhPBr_2 with 1-vinylcyclohexene and 1-vinyl-3,4-dihydronaphthalene, respectively. These phospholes, to be described in more detail elsewhere, had ^{31}P n.m.r. shifts (Fourier transform; ^1H decoupled) of $\delta +10.5$ and $+12.8$ p.p.m., respectively (downfield from 85% H_3PO_4).

Phenyl cleavage with potassium⁵ in tetrahydrofuran (THF) (25 °C) gave the phosphole anions (7) and (8). These reactions were complete in 30 min, forming dark red-brown solutions. ^{31}P N.m.r. measurements were made directly on the THF solutions, giving shifts of $\delta +73.3$ p.p.m. for (7) and $\delta +81.7$ p.p.m. for (8). These values are by far the most downfield ever recorded for a potassium phosphide; most are upfield of H_3PO_4 , the only other positive value we are aware of being that of $(\text{Me}_2\text{CH})_2\text{P}^-$ (+23.2 p.p.m.).⁶ To confirm that the species being observed in the n.m.r. experiments were in fact the phosphole anions, the solutions were quenched with excess of methyl iodide. The red colour was rapidly discharged, giving pale yellow solutions with a precipitate of KI. From the solutions of (7) and (8) were isolated the phospholium salts (9) and (10), respectively, which proved to be identical to the methiodides formed from the new *P*-methyl-phospholes (2) and (4).



Loss of phenyl from P^{III} to form phosphide anions can be accompanied by either upfield or downfield small displacements of the ^{31}P chemical shift (*e.g.*, Ph_3P $\delta -5.4$, Ph_2PK -12.4 ,⁷ $\Delta\delta = -7.0$; Pr_2PPh $\delta +9.3$, Pr_2PK $+23.2$,⁶ $\Delta\delta = +13.9$ p.p.m.). Not only are the shifts we have observed for the phosphole anions unique in being so far downfield,⁸ but also the $\Delta\delta$ value accompanying phenyl

cleavage is extraordinarily large [(1) → (7), +64.5 p.p.m.; (3) → (8), +68.9 p.p.m.]. Both features are readily explained by a significant contribution to the phosphole anion of delocalized structures such as those exemplified for (7) in the Scheme. The C-P π -bond character given the anions



SCHEME

accounts for the pronounced ^{31}P deshielding. This follows readily from ^{31}P data for the few systems known to contain di-co-ordinate phosphorus with double-bond character [*e.g.*,

phosphabenzene,⁹ $\delta(^{31}\text{P}) +211$ p.p.m.; mesityl-P=CPh₂,¹⁰ $\delta(^{31}\text{P}) +233$ p.p.m.].

The postulated charge delocalization should result in these phosphole anions being unusually stable, and this was demonstrated by attempted quenching of a THF solution of the anion (8) with excess of absolute ethanol. The red colour was not discharged, and the only change in the ^{31}P n.m.r. spectrum was an upfield shift of a few p.p.m. of the $\delta +81.7$ signal due to the new solvent composition. This suggests that the conjugate acid of the phosphole anion has an acidity similar to or greater than that of ethanol ($\text{p}K_{\text{a}}$ 15.9 in water¹¹). The extent of stabilization of the phosphole anion is revealed by comparing this value with $\text{p}K_{\text{a}}$ values for simple dialkylphosphines (33.7–36.3⁷) or diphenylphosphine (21.7, for whose anion delocalization has also been proposed⁷).

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¹ G. Kaufmann and F. Mathey, *Phosphorus*, 1974, 4, 231.

² For the most recent discussion of phosphole bonding, see N. D. Epiotis and W. Cherry, *J. Amer. Chem. Soc.*, 1976, 98, 4365.

³ When complexed to Mn in the phosphacymantrene system [$\text{R}_2\text{PMn}(\text{CO})_3$], the phosphole anion has been attributed some 'aromatic' character, largely because it undergoes electrophilic substitution on carbon (F. Mathey, *Tetrahedron Letters*, 1976, 4155).

⁴ F. Mathey and R. Mankowski-Favelier, *Org. Magnetic Resonance*, 1972, 4, 171.

⁵ E. H. Braye, I. Capelier, and R. Saussez, *Tetrahedron*, 1971, 27, 5523.

⁶ B. W. Bangerter, R. P. Beatty, J. K. Kouba, and S. S. Wreford, *J. Org. Chem.*, 1977, 42, 3247.

⁷ K. Issleib and R. Kümmel, *J. Organometallic Chem.*, 1965, 3, 84.

⁸ ^{31}P Shifts have been reported for phospholide anions when π -complexed, as in the phosphacymantrene system; these shifts are upfield of H_3PO_4 , and obviously are influenced by the bonding in the complex (F. Mathey, A. Mitschler, and R. Weiss, *J. Amer. Chem. Soc.*, 1978, 100, 5748).

⁹ A. J. Ashe, III, R. B. Sharp, and J. W. Tolan, *J. Amer. Chem. Soc.*, 1976, 98, 5451.

¹⁰ T. C. Klebach, R. Lourens, and F. Bickelhaupt, *J. Amer. Chem. Soc.*, 1978, 100, 4886.

¹¹ P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1960, 82, 795.