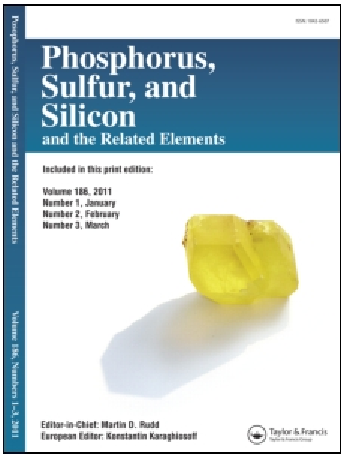

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and ^{31}P N.M.R. Study of Some Novel Phosphoranides

Rusmidah Ali[a]; Keith B. Dillon[a]
[a] Chemistry Department, University of Durham, Durham, U.K.

To cite this Article Ali, Rusmidah and Dillon, Keith B.(1987) 'Synthesis and ^{31}P N.M.R. Study of Some Novel Phosphoranides', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 139 — 142

To link to this Article: DOI: 10.1080/03086648708080541

URL: http://dx.doi.org/10.1080/03086648708080541

Phosphorus and Sulfur, 1987, Vol. 30, pp. 139–142
Photocopying permitted by license only

SYNTHESIS AND ^{31}P N.M.R. STUDY OF SOME NOVEL PHOSPHORANIDES

RUSMIDAH ALI AND KEITH B. DILLON*
Chemistry Department, University of Durham, South Road,
Durham DH1 3LE, U.K.

Abstract Several novel phosphoranides with one or two organo-groups attached to phosphorus and no cyano-groups present have been synthesised for the first time, and identified in solution by ^{31}P N.M.R. spectroscopy. Most of the complexes have been isolated, and further characterised by elemental analysis. Similar ionic derivatives were formed, as expected, by $C_6F_5P(CN)_2$ and $(C_6F_5)_2P(CN)$.

The first hypervalent anionic phosphorus(III) complex, PBr_4^-, was synthesised and isolated (as its n-Pr_4N^+ salt) as recently as 1969;[1] the X-ray crystal structure of this compound was reported in 1981.[2] Several other species of this type have subsequently been described, particularly by Martin,[3] Schmidpeter,[2,4-6] Dillon,[2,6,7] and their co-workers, and by various researchers at the Nice conference.[7-9] Such ions are becoming increasingly important, not only in the chemistry of phosphorus itself, where they may play a key role in nucleophilic substitution reactions at phosphorus(III) centres,[3] but also in coordination chemistry.[10] In simple non-cyclic systems, however, the phosphorus complexes have either been tetrahalogeno-derivatives such as PBr_4^-,[1,2] PCl_4^-,[6] PF_4^-[11-13] or $PClF_3^-$,[13] or have had two or more cyano-groups present.[2,4-6] The only ions of this type with an organo-group R attached to phosphorus also had two cyano-groups in the phosphorus coordination polyhedron,[7,14] the electro-negative groups helping to stabilise the complexes, presumably by delocalisation of negative charge from the phosphorus atom. In keeping with these observations, we have found no acceptor properties towards halide ions under our experimental conditions for t-$BuP(CN)_2$, which has an electron-supplying organic substituent, for the organophosphorus(III) dichlorides $PhPCl_2$ and $MePCl_2$, or for the diorganophosphorus(III) cyanides $Ph_2P(CN)$ and $Me_2P(CN)$.[14]

Attempts to obtain analogues of PCl_4^- and PBr_4^- on a preparative scale were also unsuccessful. The synthesis of PF_4^- was not attempted, although this ion has been identified by both mass spectrometry,[11,12] and by i.r. spectroscopy in an argon matrix,[13] since a suitable source of anhydrous fluoride ions was not available to us. No reaction of PF_3 with Cl^- or Br^- ions was apparent, however, as shown by its unchanged ^{31}P N.M.R. spectrum,[15] even though the $PClF_3^-$ ion has also been reported in an argon matrix.[13] Reaction of PI_3 with tetra-alkylammonium iodides in non-polar solvents led to the formation of P_2I_4 and R_4NI_3, equation (1).[15]

$$2PI_3 + R_4NI \longrightarrow P_2I_4 + R_4NI_3 \qquad (1)$$

This behaviour arises because there is a small amount of P_2I_4 (and I_2) in equilibrium with PI_3 in solution, equation (2), and addition of iodide ions pulls the equilibrium to the right.

$$2PI_3 \rightleftharpoons P_2I_4 + I_2 \qquad (2)$$

There was no evidence for formation of the PI_4^- ion in this system.

We have now succeeded in synthesising simple phosphoranides with either one or two organo-groups present and no cyanide ligands, by introducing electronegative C_6F_5 groups into the phosphine starting material. These species may be readily identified in solution by their ^{31}P N.M.R. shifts, which are to lower frequency (higher field) of those of the parent phosphine. By this means novel complexes have been obtained, not only from the halogenophosphines $C_6F_5PCl_2$, $(C_6F_5)_2PCl$ and $(C_6F_5)_2PBr$, but even from the thiocyanatophosphine $C_6F_5P(NCS)_2$. By adding an excess of the ligand X^- (X = Cl, Br, I or NCS) in the form of the R_4N^+ salt to the phosphine, the 'limiting shifts' of the phosphoranides could be established in solution, although these were found to vary markedly in some instances with the size of R. It was not possible, however, to obtain chloride ion adducts of bromophosphines, or thiocyanate adducts of halogenophosphines, in this way, since substitution occurred in preference to addition, as exemplified in equation (3) for reaction between $(C_6F_5)_2PCl$ and Et_4NNCS. Phosphoranides were also formed, as expected, on addition

$$(C_6F_5)_2PCl + Et_4NNCS \longrightarrow (C_6F_5)_2P(NCS) + Et_4NCl \qquad (3)$$

of X^- ions (X = Cl, Br, I or NCS) to either $C_6F_5P(CN)_2$ or $(C_6F_5)_2P(CN)$.

Most of the complexes described above have been isolated from solutions containing 1:1 molar ratios of the reactants as either solids or viscous liquids, and have been further characterised by elemental analysis and (in some cases) i.r. spectroscopy. The products were often thermally unstable, both in the pure state and in solution, so that analyses had to be carried out as quickly as possible after isolation of the compounds. The upfield ^{31}P shift relative to that of the parent phosphine in these phosphoranides generally follows the sequence $I < NCS < Br < Cl$ in systems where all the ions have been prepared.

No adducts with X^- ions were formed under the experimental conditions by $(C_6F_5)_2P(NCS)$, showing that it is a poorer acceptor than the corresponding bromo- or chloro-phosphines. The compound CCl_3PCl_2 also showed no acceptor properties towards X^- ions, indicating that C_6F_5 is a better stabilising electronegative group for phosphoranides than CCl_3.

Formation of hypervalent compounds of the types described above may be of considerable significance in rationalising the mechanisms of nucleophilic substitution reactions at phosphorus-(III) centres.[3,6] The results presented here show that a much larger range of phosphoranides than known previously may be synthesised, and that most of the compounds are sufficiently stable to be isolated, at least on a short-term basis. The formation of transient intermediates of similar structure in substitution reactions, even by phosphorus(III) compounds with less electronegative substituents present, is thus highly probable. Support for this conclusion is provided by the X-ray crystal structures of the PCl_4^-[6] and $[PhP(CN)_2Cl]^-$ ions,[7,16] which both have one very long P-Cl axial bond of 2.85 and 2.81Å respectively. A similar very long P-Cl bond in the crystal structure of a phosphoranide has been reported by Schmutzler and co-workers.[8]

ACKNOWLEDGEMENTS

We thank the Universiti Teknologi Malaysia for the award of a research studentship (to R.A.), and J. Lincoln for technical assistance.

REFERENCES

1. K.B. Dillon and T.C. Waddington, Chem. Commun., 1317 (1969).
2. W.S. Sheldrick, A. Schmidpeter, F. Zwaschka, K.B. Dillon, A.W.G. Platt and T.C. Waddington, J. Chem. Soc. Dalton Trans., 413 (1981).
3. I.Granoth and J.C. Martin, J. Am. Chem. Soc., 100, 7434 (1978).
4. A. Schmidpeter and F. Zwaschka, Angew. Chem. Int. Edn. Engl., 18, 411 (1979).
5. W.S. Sheldrick, F. Zwaschka and A. Schmidpeter, Angew. Chem. Int. Edn. Engl., 18, 935 (1979).
6. K.B. Dillon, A.W.G. Platt, A. Schmidpeter, F. Zwaschka and W.S. Sheldrick, Z. anorg. allgem. Chem., 488, 7 (1982).
7. R.M.K. Deng, K.B. Dillon and A.W.G. Platt, Phosphorus and Sulfur, 18, 93 (1983).
8. G. Bettermann, H. Buhl, R. Schmutzler, D. Schomburg and U. Wermuth, Phosphorus and Sulfur, 18, 77 (1983).
9. B. Garrigues, Phosphorus and Sulfur, 18, 455 (1983).
10. J.-M. Dupart, A. Grand, S. Pace and J.G. Riess, J. Am. Chem. Soc., 104, 2316 (1982).
11. J.G. Dillard and T.C. Rhyne, J. Am. Chem. Soc., 91, 6521 (1969).
12. T.C. Rhyne and J.G. Dillard, Inorg. Chem., 10, 730 (1971).
13. P. Wermer and B.S. Ault, Inorg. Chem., 20, 970 (1981).
14. R.M.K. Deng and K.B. Dillon, in preparation.
15. K.B. Dillon, M.G.C. Dillon and A.W.G. Platt, unpublished work.
16. W.S. Sheldrick, R.M.K. Deng and K.B. Dillon, in preparation.