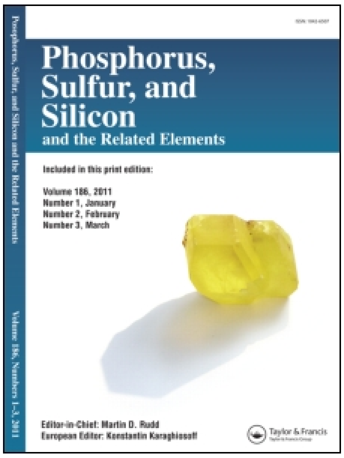

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# $^{31}$P N.M.R. studies of some pseudo-halogeno-derivatives of phosphorus

Robert M. K. Deng[a]; Keith B. Dillon[a]; Andrew W. G. Platt[a]
[a] Chemistry Department, University of Durham, Durham, U.K.

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# $^{31}$P N.M.R. STUDIES OF SOME PSEUDO-HALOGENO-DERIVATIVES OF PHOSPHORUS

ROBERT M.K. DENG, KEITH B. DILLON* AND ANDREW W.G. PLATT
Chemistry Department, University of Durham, South Road,
Durham DH1 3LE, U.K.

Abstract Several new pseudo-halogeno phosphorus species, including isomeric N- and O-bonded cyanato-derivatives of the $PCl_6^-$ ion, cyano-derivatives of $RPCl_5^-$ ions (R = Ph or Me), and organo-phosphorus (III) cyanide adducts $RP(CN)_2X^-$ (R = Me, Et, Ph or $C_6F_5$; X = Cl, Br or I) have been prepared in solution, and identified by means of $^{31}$P n.m.r. spectroscopy. Isomeric configurations in the six-coordinate species have been assigned by the method of pairwise interactions.

## INTRODUCTION

There are many $^{31}$P chemical shift values in the literature for pseudo-halogeno-derivatives of phosphorus, particularly for phosphorus (III), phosphoryl or thiophosphoryl species.[1,2] Less is known about derivatives of $PX_6^-$ ions, however; some fluoro-anions with pseudohalides present have been identified in solution,[3,4] and shift data for azido-, cyano- and thiocyanato-derivatives of $PCl_6^-$ have been reported,[5-8] as well as results for azido- and thiocyanato-derivatives of some chlorofluorophosphate ions.[9] The method of pairwise interactions, originally proposed for tetrahedral species[10] but since applied to octahedral complexes of niobium,[11] antimony[12] and tin[13,14] as well as phosphorus, has proved very valuable for assigning isomeric configurations, especially where chemical reasons preclude the preparation of individual compounds. No cyanato-complexes, or six-coordinate pseudohalogenophosphate (V) species with an organo-group present, have been described.

Several anionic derivatives of phosphorus (III) halides or cyanides $[P(CN)_nX_{4-n}]^-$ (n = 0 or 1, X = Cl or Br; n = 2 or 3, X = Cl, Br or I) have also been prepared, and some of their crystal structures determined, as salts with suitable large cations.[15-17] The results are very interesting in that $P(CN)_3X^-$ (X = Br or I) form symmetrical dimers with halogen bridges,[15] $PBr_4^-$ crystallises in an unsymmetrical dimeric arrangement,[16] $P(CN)_2Br_2^-$ is monomeric with equatorial CN groups and equidistant axial bromines,[16] but both $P(CN)_3Cl^-$ and $PCl_4^-$ are monomeric, with a very long P-Cl axial bond of 262.5 and 285.0 pm. respectively.[17] No similar species with an organo-group attached to phosphorus have been reported previously.

## RESULTS AND DISCUSSION

Two families of cyanato-derivatives of $PCl_6^-$ have been obtained in solution by different preparative routes, assigned to N- and O-bonded isomers respectively on the basis of their chemical shifts. The pairwise interaction method has allowed the assignment of isomeric configurations in each case.

The reaction of AgCN with the organophosphate (V) ions $RPCl_5^-$ (R = Ph[18] or Me[19]) has also been investigated. Even in the presence of excess cyanide, substitution into $PhPCl_5^-$ proceeds only as far as the isomeric forms of $PhPCl_2(CN)_3^-$, similar to the behaviour of $PCl_6^-$, where both isomers of $PCl_3(CN)_3^-$ proved very resistant to further substitution.[8] Complete replacement of the chlorines by cyanide is possible in $MePCl_5^-$, however. This difference in behaviour may possibly be due to the $\pi$-bonding capability of phenyl groups. It has been suggested that the stability of $PCl_3(CN)_3^-$ compared with $PCl_3(N_3)_3^-$ or $PCl_3(NCS)_3^-$ may be caused by the presence of enough ligands high in the spectrochemical series to lower the energy of the unoccupied 3d $t_{2g}$

orbitals on phosphorus, and allow π interactions between lone pairs on the chlorine atoms and these vacant orbitals.[8] This would strengthen the P-Cl bonds, making them resistant to substitution. Support for this suggestion is provided by the lack of reaction between $[PCl_4(bipy)]^+$ and $LiN_3$, since bipy is also high in the spectrochemical series, and the cations $[PCl_{4-n}(N_3)_n$-$(bipy)]^+$ $(0 \leqslant n \leqslant 4)$ are readily prepared by an alternative route.[20] The phenyl group with its π system could facilitate this process when sufficient CN groups are present, whereas the methyl group may well activate the six-coordinate complex to further substitution. If these trends are followed for six-coordinate complexes of other elements, an important extension of crystal field arguments to main group chemistry may be established.

Several of the intermediate isomeric chlorocyanophosphates $RPCl_{5-n}(CN)_n^-$ have also been identified in solution; the pairwise treatment did not give very good agreement for these species, as found previously in the $[PCl_n(CN)_{6-n}]^-$ series,[8] possibly because of distortions from regular octahedral geometry. Nevertheless isomeric configurations could still be assigned in most instances.

The phosphorus (III) adducts $RP(CN)_2X^-$, (R = Me, Et, Ph or $C_6F_5$; X = Cl, Br or I), have been prepared in solution, and a marked upfield shift relative to $RP(CN)_2$ is found in each case; several of the compounds have been isolated as tetra-alkylammonium salts. The crystal structure of $Et_4N^+$ $PhP(CN)_2Cl^-$ has been determined by Dr. W.S. Sheldrick,[21] and shows a distorted structure similar to that of $PCl_4^-$, with an equatorial phenyl group and a long (281.0 pm.) axial P-Cl bond. This kind of compound may well be similar to intermediates in the reaction paths for nucleophilic addition or substitution at $PX_3$[16,17] or $RPX_2$ molecules, and is therefore of considerable importance in trying to rationalise the reactions of both inorganic and organo-phosphorus (III) species.

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