# Synthetic and Spectroscopic Studies of Phosphoranides $[PR(CN)_2X]^-$ and the Crystal and Molecular Structure of $[NEt_4][PPh(CN)_2Cl]$†

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Several new phosphoranides of the type $[NR_4][PR'(CN)_2X]$($R'$ = Me, Et, Ph, or $C_6F_5$; X = Cl, Br, I, or NCS) have been synthesised, and characterised by means of $^{31}P$ n.m.r. spectroscopy, elemental analysis, and (in some cases) i.r. spectroscopy. These are the first simple phosphoranides to be prepared with an organo group bound directly to phosphorus. Determination of the crystal structure of $[NEt_4][PPh(CN)_2Cl]$ has shown a monomeric distorted ψ-trigonal bipyramidal geometry for the anion, with the phenyl group equatorial and one very long P–Cl axial bond, as observed previously in the $[PCl_4]^-$ ion. Halide ions did not form phosphoranides with $PBu^t(CN)_2$, $PMe_2(CN)$, or $PPh_2(CN)$.

The first hypervalent anionic phosphorus(III) complex, or phosphoranide, $PBr_4^-$, was isolated (as its $NPr^n{}_4^+$ salt) in 1969;[1] the *X*-ray crystal structure of this compound was determined by Sheldrick, and reported in 1981.[2] Several other phosphoranides have subsequently been described,[2–14] particularly by Martin,[3] Schmidpeter,[2,4–6] Riess,[7] Dillon,[2,6,8,9] and their co-workers. In simple non-cyclic systems, however, no phosphoranides with an organo group R attached to phosphorus have been described in detail,[7] and the anions have either been tetrahalogeno-derivatives such as $PBr_4^-$,[1,2] $PCl_4^-$,[6] $PF_4^-$,[12–14] or $PClF_3^-$,[14] or have had one or more cyano-groups present.[2,4–6] We report the synthesis and characterisation of a series of phosphoranides $[PR(CN)_2X]^-$ (R = Me, Et, Ph, or $C_6F_5$; X = Cl, Br, I, or NCS), with an organo-group R on phosphorus in each case. The crystal structure of the compound $[NEt_4][PPh(CN)_2Cl]$ has been determined; the results show a monomeric anion with a distorted ψ-trigonal bipyramidal geometry. The phenyl group occupies an equatorial site, as expected from electronegativity considerations, and there is a very long P–Cl axial bond, similar to that observed previously in the $PCl_4^-$ ion.[6] No acceptor properties towards halide ions were shown by $PBu^t(CN)_2$, $PMe_2(CN)$, or $PPh_2(CN)$.

## Experimental

All manipulations including n.m.r. sample preparation were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Chemicals of the best available commercial grade were used, in general without further purification except for tetra-alkylammonium salts, which were dried as described previously.[15]

(*a*) *Preparation of* $PR(CN)_2$ (R = Me, Et, Ph, $C_6F_5$, or $Bu^t$) *and* $PR_2(CN)$ (R = Me *or* Ph).—The dicyanophosphines were prepared by a 2:1 molar ratio reaction between AgCN and either $PRCl_2$ (R = Me, Et, Ph, or $Bu^t$) or $PRBr_2$ (R = $C_6F_5$) in MeCN (R = Me or Et) or $CH_2Cl_2$ (R = Ph, $C_6F_5$, or $Bu^t$); $P(C_6F_5)Br_2$ was synthesised by the Grignard reaction of $C_6F_5Br$ and magnesium with an equimolar quantity of $PBr_3$. The compound $PEt(CN)_2$ has not been previously reported in the literature and analytical figures for it are included in Table 1. The cyanophosphines $PR_2(CN)$ were similarly prepared by 1:1 reactions between $PR_2Cl$ (R = Me or Ph) and AgCN in $CH_2Cl_2$.

(*b*) *N.M.R. and Synthetic Studies of the Phosphoranides.*—Initially an excess of the anion, $X^-$, in the form of a solution of its tetra-alkylammonium salt, was added to a solution of $PR(CN)_2$ in an inert organic solvent until the maximum upfield (low-frequency) shift, or limiting shift, of the $^{31}P$ n.m.r. resonance was produced. (Formation of phosphoranides is known to cause an upfield shift of the resonance of the precursor phosphine.[7]) When these experiments had shown that phosphoranides could be obtained in each case for R = Me, Et, Ph, or $C_6F_5$ and X = Cl, Br, I, or NCS, the reactions were repeated in a stoicheiometric (1:1) ratio of reagents, and the products were isolated by removal of the solvent *in vacuo*. Elemental analyses of the new compounds, obtained as in earlier work,[16,17] are given in Table 1. Phosphorus-31 n.m.r. spectra were recorded on a Fourier-transform spectrometer at 307.2 K, as described previously;[15] chemical shifts are expressed relative to 85% $H_3PO_4$, with the downfield (higher-frequency) direction taken as positive. I.r. spectra were also obtained as described in previous work.[16]

(*c*) *Crystal Structure Determination for* $[NEt_4][PPh(CN)_2Cl]$.—Crystals were sealed under argon in Lindemann capillaries.

*Crystal data.* $C_{16}H_{25}ClN_3P$, $M = 325.8$, monoclinic, $a = 10.111(3)$, $b = 15.550(3)$, $c = 12.011(3)$ Å, $\beta = 104.61(2)°$, $U = 1827.4(7)$ Å$^3$ (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, $\lambda = 1.541\,78$ Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $Z = 4$, $D_c = 1.18$ g cm$^{-3}$, $F(000) = 696$, $\mu(\text{Cu-}K_\alpha) = 25.3$ cm$^{-1}$.

*Data collection.* Approximate crystal size 0.58 × 0.42 × 0.38 mm, Nicolet $P2_1$ diffractometer, ω—2θ scan mode with variable scan width, $2\theta \leqslant 130°$ ($\pm h$, $+k$, $+l$), graphite-monochromated Cu-$K_\alpha$ radiation. 3 103 Independent reflections measured, giving 2 624 with $I > 2\sigma(I)$; absorption correction using the azimuthal scan method[18] (maximum, minimum transmission factors 0.79, 0.37). Three standard reflections monitored regularly showed variations $< \pm 1\%$.

*Structure solution and refinement.* Direct methods followed by normal heavy-atom procedures. Full-matrix least-squares refine-

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† Tetraethylammonium chlorodicyanophenylphosphate(III).

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

**Table 1.** Elemental analyses of new phosphorus compounds

| | Found (%) | | | | | Calc. (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | P | X[a] | C | H | N | P | X[a] |
| $[NEt_4][PMe(CN)_2Cl]$ | 50.0 | 9.2 | 15.6 | 11.5 | 13.8 | 50.1 | 8.8 | 15.9 | 11.7 | 13.4 |
| $[NPr_4][PMe(CN)_2Br]$ | 48.6 | 8.3 | 11.3 | 8.6 | 20.4 | 49.5 | 8.6 | 11.5 | 8.5 | 21.9 |
| $[NBu_4][PMe(CN)_2Br]$ | 54.9 | 10.9 | 10.6 | *b* | *b* | 54.3 | 9.4 | 10.0 | 7.4 | 19.0 |
| $[NPr_4][PMe(CN)_2I]$ | 43.2 | 9.4 | 9.6 | 8.2 | 28.7 | 43.8 | 7.6 | 10.2 | 7.5 | 30.9 |
| $[NEt_4][PMe(CN)_2(NCS)]$ | 50.7 | 8.5 | 19.8 | 10.7 | *b* | 50.3 | 8.1 | 19.6 | 10.8 | 11.2 |
| $[PEt(CN)_2]$ | 42.8 | 4.7 | 24.9 | 27.4 | — | 42.9 | 4.5 | 25.0 | 27.6 | — |
| $[NEt_4][PEt(CN)_2Cl]$ | 51.8 | 10.3 | 14.6 | 10.7 | 13.4 | 51.9 | 9.1 | 15.1 | 11.2 | 12.8 |
| $[NPr_4][PEt(CN)_2Br]$ | 50.7 | 8.4 | 10.1 | 8.2 | 20.8 | 50.8 | 8.8 | 11.1 | 8.2 | 21.1 |
| $[NPr_4][PEt(CN)_2I]$ | 45.3 | 8.0 | 9.6 | 6.9 | 29.9 | 45.2 | 7.8 | 9.9 | 7.3 | 29.8 |
| $[NEt_4][PEt(CN)_2(NCS)]$ | 49.9 | 10.4 | 13.8 | *b* | *b* | 52.0 | 8.4 | 18.7 | 10.3 | 10.7 |
| $[NEt_4][PPh(CN)_2Cl]$ | 58.5 | 8.6 | 12.0 | 9.6 | 11.9 | 59.0 | 7.7 | 12.9 | 9.5 | 10.9 |
| $[N(C_5H_{11})_4][PPh(CN)_2Cl]$ | 67.8 | 10.1 | 8.1 | 6.3 | 7.0 | 68.1 | 10.0 | 8.5 | 6.3 | 7.2 |
| $[NEt_4][PPh(CN)_2Br]$ | 49.2 | 8.1 | 9.1 | 7.8 | 21.2 | 51.9 | 6.8 | 11.3 | 8.4 | 21.6 |
| $[NPr_4][PPh(CN)_2Br]$ | 55.4 | 10.0 | 7.0 | 6.7 | 20.6 | 56.3 | 7.8 | 9.9 | 7.3 | 18.7 |
| $[NPr_4][PPh(CN)_2I]$ | 51.3 | 7.3 | 8.4 | 6.4 | 26.3 | 50.7 | 7.0 | 8.9 | 6.5 | 26.8 |
| $[NEt_4][PPh(CN)_2(NCS)]$ | 55.8 | 8.5 | 13.9 | 8.8 | 9.0 | 58.6 | 7.2 | 16.1 | 8.9 | 9.2 |
| $[NPr_4][P(C_6F_5)(CN)_2Cl]$ | 51.4 | 6.2 | 9.0 | 6.2 | 7.4 | 50.9 | 6.0 | 8.9 | 6.6 | 7.5 |
| $[NEt_4][P(C_6F_5)(CN)_2Br]$ | 40.6 | 3.9 | 9.2 | 6.2 | 17.6 | 41.8 | 4.4 | 9.1 | 6.7 | 17.4 |
| $[NPr_4][P(C_6F_5)(CN)_2Br]$ | 43.9 | 5.2 | 7.8 | 6.2 | 15.4 | 46.5 | 5.5 | 8.1 | 6.0 | 15.5 |
| $[NPr_4][P(C_6F_5)(CN)_2I]$ | 42.2 | 4.8 | 7.7 | 5.2 | 22.1 | 42.6 | 5.0 | 7.5 | 5.5 | 22.5 |
| $[NEt_4][P(C_6F_5)(CN)_2(NCS)]$ | 44.9 | 4.8 | 14.7 | 6.7 | 5.5 | 46.6 | 4.6 | 12.8 | 7.1 | 7.3 |

[a] X = Cl, Br, I, or S as appropriate. [b] Not determined.

**Table 2.** Phosphorus-31 n.m.r. data (δ/p.p.m.) for $PR(CN)_2$ and $[PR(CN)_2X]^-$ in $CH_2Cl_2$

| | | $[PR(CN)_2X]^-$ | | | |
|---|---|---|---|---|---|
| R | $PR(CN)_2$ | X = Cl | Br | NCS | I |
| Me | −79.1 | −101.3 | −98.4 | −92.0 | −90.4 |
| Et | −61.3 | −78.0 | −70.9 | −66.2 | −66.2 |
| Ph | −72.6 | −103.3 | −90.4 | −83.8 | −77.5 |
| $C_6F_5$ | −112.9 | −154.7 | −140.2 | −135.5 | −128.9 |

**Table 3.** Positional parameters for $[NEt_4][PPh(CN)_2Cl]$

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Cl | 0.254 5(1) | 0.533 9(1) | 0.616 2(1) |
| P | 0.198 5(1) | 0.470 5(1) | 0.818 5(1) |
| C(1) | 0.187 2(2) | 0.426 5(1) | 0.959 4(2) |
| N(1) | 0.169 3(2) | 0.407 2(1) | 1.045 0(1) |
| C(2) | 0.376 8(2) | 0.445 4(1) | 0.848 3(2) |
| N(2) | 0.491 2(2) | 0.430 0(2) | 0.868 9(2) |
| C(3) | 0.126 2(2) | 0.374 2(1) | 0.737 8(1) |
| C(4) | 0.008 3(2) | 0.384 3(1) | 0.650 3(1) |
| C(5) | −0.056 2(2) | 0.313 5(2) | 0.590 9(2) |
| C(6) | −0.001 8(2) | 0.232 9(1) | 0.616 9(2) |
| C(7) | 0.116 4(2) | 0.222 1(1) | 0.702 4(2) |
| C(8) | 0.180 5(2) | 0.292 1(1) | 0.763 2(1) |
| N | 0.321 0(1) | 0.319 2(1) | 0.416 9(1) |
| C(11) | 0.176 2(2) | 0.337 8(1) | 0.425 0(1) |
| C(12) | 0.065 4(2) | 0.324 9(2) | 0.315 8(2) |
| C(21) | 0.358 8(2) | 0.376 1(1) | 0.326 5(1) |
| C(22) | 0.337 7(3) | 0.470 0(1) | 0.337 9(2) |
| C(31) | 0.412 9(2) | 0.337 2(1) | 0.535 2(1) |
| C(32) | 0.562 6(2) | 0.319 6(1) | 0.548 4(2) |
| C(41) | 0.336 4(2) | 0.226 6(1) | 0.381 0(2) |
| C(42) | 0.312 7(2) | 0.158 9(1) | 0.464 5(2) |

ment with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions with individual isotropic thermal parameters. The function $\Sigma w(|F_o| - |F_c|)^{19}$ was minimised with weights given by $w = 1/[\sigma^2(F_o) + 0.0002 F_o^2]$. Final $R$ and $R'$ values are 0.034 and 0.036. Calculations were carried out using SHELX 76[19] on the PDP 20 at the GBF, Braunschweig. Atomic scattering factors and $f', f''$ were from refs. 20 and 21 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

## Results and Discussion

(*a*) *Phosphorus*-31 *N.M.R. Measurements*.—The limiting shifts obtained by addition of excess of $X^-$ (X = Cl, Br, I, or NCS) to $PR(CN)_2$ (R = Me, Et, Ph, or $C_6F_5$) in $CH_2Cl_2$ as solvent, together with the shifts of the precursor cyanophosphines $PR(CN)_2$, are given in Table 2. Formation of phosphoranides takes place in all of these systems; the order of upfield (lower-frequency) displacement[7] of the resonance of $PR(CN)_2$ by $X^-$ is $I^- \leqslant NCS^- < Br^- < Cl^-$ in each case, the largest movement being shown for $[P(C_6F_5)(CN)_2Cl]^-$. Some variation of the limiting shift with cation was observed in a few instances, although this effect was not investigated systematically in every case. For example, the limiting shift for addition of $NEt_4Cl$ to $PPh(CN)_2$ was −100.0 p.p.m. in $CH_2Cl_2$, while $N(n\text{-}C_5H_{11})_4Cl$ in the same solvent caused a limiting shift of −103.3 p.p.m. Similarly, $NEt_4Br$ and $NPr_4Br$ with $PPh(CN)_2$ gave limiting shifts in $CH_2Cl_2$ of −82.3 and −90.4 p.p.m. respectively. With $PMe(CN)_2$, however, $NR_4Cl$ (R = Et, Pr, or n-$C_5H_{11}$) all gave limiting shifts of −101.3 p.p.m. in $CH_2Cl_2$. In general the largest upfield movements observed in $CH_2Cl_2$ as solvent are listed in Table 2. No phosphoranide formation was observed on addition of excess of $NR_4X$ (X = Cl, Br, or I) to $PBu^t(CN)_2$, $PMe_2(CN)$, or $PPh_2(CN)$, since the positions of their $^{31}P$ n.m.r. resonances were unaffected. The reactions of these phosphines with $NEt_4NCS$ were not investigated, since anion formation appeared unlikely in view of the above results.

For all systems where phosphoranide formation had been demonstrated in solution, the products were isolated from 1:1 stoicheiometric reactions between $PR(CN)_2$ and $NR'_4X$. Analyses of the compounds, which were obtained either as solids or viscous liquids, are given in the Experimental section. The i.r. spectra of the solid products (Nujol mulls) showed

**Table 4.** Bond lengths (Å) and angles (°) in $[PPh(CN)_2Cl]^-$

| | | | |
|---|---|---|---|
| P–Cl | 2.810(1) | C(1)–P | 1.855(2) |
| C(2)–P | 1.791(2) | C(3)–P | 1.832(2) |
| N(1)–C(1) | 1.129(3) | N(2)–C(2) | 1.146(3) |
| C(4)–C(3) | 1.385(2) | C(8)–C(3) | 1.393(2) |
| C(5)–C(4) | 1.383(3) | C(6)–C(5) | 1.373(3) |
| C(7)–C(6) | 1.375(3) | C(8)–C(7) | 1.378(2) |
| C(1)–P–Cl | 172.1(1) | C(2)–P–Cl | 80.6(1) |
| C(2)–P–C(1) | 91.6(1) | C(3)–P–Cl | 88.3(1) |
| C(3)–P–C(1) | 94.2(1) | C(3)–P–C(2) | 100.1(1) |
| N(1)–C(1)–P | 171.8(2) | N(2)–C(2)–P | 179.0(2) |
| C(4)–C(3)–P | 117.5(1) | C(8)–C(3)–P | 123.4(1) |
| C(8)–C(3)–C(4) | 119.1(1) | C(5)–C(4)–C(3) | 120.4(2) |
| C(6)–C(5)–C(4) | 120.0(2) | C(7)–C(6)–C(5) | 120.3(2) |
| C(8)–C(7)–C(6) | 120.2(2) | C(7)–C(8)–C(3) | 120.1(1) |

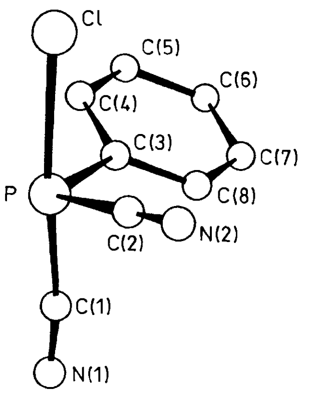

**Figure.** The geometry of the anion in $[NEt_4][PPh(CN)_2Cl]$

**Table 5.** Comparison of bond lengths (Å) and angles (°) in chlorophosphate(III) anions

| | $[PCl_4]^-$ (ref. 6) | $[PPh(CN)_2Cl]^-$ (this work) | $[P(CN)_3Cl]^-$ (ref. 6) |
|---|---|---|---|
| $(P–Cl)_{ax.}$ | 2.850(4) [Cl(1)]<br>2.118(4) [Cl(2)] | 2.810(1) | 2.625(1) |
| $(P–Cl)_{eq.}$ | 2.049(4)<br>2.044(4) | | |
| $(P–CN)_{ax.}$ | | 1.855(2) | 1.915(5) |
| $(P–CN)_{eq.}$ | | 1.791(2) | 1.785(4)<br>1.781(5) |
| $Cl_{ax.}–P–Z_{ax.}$ | 171.4(2) (Z = Cl) | 172.1(1) (Z = CN) | 168.2(1) (Z = CN) |
| $Cl_{eq.}–P–Cl_{eq.}$ | 100.0(2) | — | — |
| $(CN)_{eq.}–P–Z_{eq.}$ | — | 100.1(1) (Z = Ph) | 98.0(2) (Z = CN) |
| $Cl(1)_{ax.}–P–Cl_{eq.}$ | 89.4(1)<br>89.6(1) | —<br>— | —<br>— |
| $Cl(2)_{ax.}–P–Cl_{eq.}$ | 95.7(3)<br>96.3(2) | —<br>— | —<br>— |
| $Cl_{ax.}–P–Z_{eq.}$ | —<br>— | 80.6(1) (Z = CN)<br>88.3(1) (Z = Ph) | 82.7(1) (Z = CN)<br>82.8(1) (Z = CN) |
| $(CN)_{ax.}–P–Z_{eq.}$ | — | 91.6(1) (Z = CN)<br>94.2(1) (Z = Ph) | 89.9(2) (Z = CN)<br>89.1(2) (Z = CN) |

displacement of the bands in the CN stretching region (2 350—1 950 $cm^{-1}$) compared with those of the precursor cyanophosphine, and in some instances the appearance of an additional band, confirming that the products were not mixtures of the starting materials. The redissolved compounds gave either similar or smaller (higher-frequency) $^{31}P$ n.m.r. shifts than the limiting values, showing that some dissociation to $PR(CN)_2$ and $NR'_4X$ may occur in solution. In a few instances where sufficient material was available, solid-state $^{31}P$ n.m.r. spectra were recorded. These gave broad resonances with similar shift values, although the presence of small amounts of impurities such as $PRO(CN)Cl$ and $PRO(CN)_2$ was sometimes deduced from the spectra. These appeared as sharp peaks superposed on the broad background resonance. For example, $[NPr_4][PEt(CN)_2Br]$ gave a limiting shift of $-70.9$, a broad solid-state resonance at $-67.8$, and a shift of $-66.2$ p.p.m. when the solid product was redissolved in $CH_2Cl_2$.

(*b*) X-*Ray Structure Determination of* $[NEt_4][PPh(CN)_2Cl]$.—Positional parameters are given in Table 3 and bond lengths and angles in Table 4. The geometry of the anion is shown in the Figure. The *X*-ray analysis of the anion $[PPh(CN)_2Cl]^-$ shows it to display a basically ψ-trigonal bipyramidal structure, in which, however, the axial P–Cl bond distance of 2.810(1) Å is remarkably long in comparison with the P–Cl bond length of 2.039(1) Å to three-co-ordinated phosphorus in $PCl_3$.[22] This chlorine atom is not involved in any intermolecular interaction to a second phosphorus at a distance of less than the sum of the van der Waals radii (3.70 Å). A similar P–Cl distance of 2.850(4) Å was reported for one of the axial bonds of the anion in $[NEt_4][PCl_4]$.[6] We interpreted the structure of $[PCl_4]^-$ as representing a 'frozen' intermediate[23] along the reaction path of nucleophilic addition of $Cl^-$ to $PCl_3$. As evidenced by the comparison of molecular dimensions for chlorophosphate(III) anions given in Table 5, an identical reasoning may be applied to the anion structure in $[NEt_4][PPh(CN)_2Cl]$. The axial P–CN distance of 1.855(2) Å is significantly lengthened with respect to the equatorial P–CN distance of 1.791(2), which falls within the range 1.77–1.80 Å observed for $P(CN)_3$ itself in the solid state.[24] An even longer axial P–CN distance of 1.915(5) Å is observed in the anion $[P(CN)_3Cl]^-$, which reflects the relative strength of the axial P–Cl bond [2.625(1) Å] in this trigonal bipyramidal structure. A narrow $Cl_{ax.}–P–(CN)_{eq.}$ angle of 80.6(1)° is found in $[PPh(CN)_2Cl]^-$, as for the analogous parameters in $[P(CN)_3Cl]^-$.

(*c*) *General Conclusions.*—We have shown that simple phosphoranides $[PR(CN)_2X]^-$ may be synthesised for R = Me, Et, Ph, or $C_6F_5$ and X = Cl, Br, I, or NCS, and may be readily recognised in solution *via* their $^{31}P$ n.m.r. shifts. This lends credence to the participation of such species as intermediates in nucleophilic substitution reactions at organophosphorus(III) centres, even if the compounds are not stable to isolation in many instances. Formation of stable phosphoranides is favoured by electronegative ligands such as $CN^-$, and by electron-withdrawing organo groups, presumably because this assists in the delocalisation of the formal negative charge on phosphorus. No complexation was observed of halide ions with $PBu^t(CN)_2$, which could be due to either electronic or steric factors, or with $PMe_2(CN)$ or $PPh_2(CN)$, probably because of the reduction in the number of electronegative ligands present, compared with $PR(CN)_2$. Determination of the crystal structure of $[NEt_4][PPh(CN)_2Cl]$ has shown a distorted ψ-trigonal bipyramidal anion with a very long axial P–Cl bond, similar to that observed in the $[PCl_4]^-$ ion,[6] which may be interpreted as representing a 'frozen' intermediate[23] along the reaction pathway for nucleophilic addition to a phosphorus(III) centre.

## Acknowledgements

We thank the British Council for the award of a Postgraduate Technical Training Grant (to R. M. K. D.).

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*Received* 11*th April* 1989; *Paper* 9/01476D