Structure and Stability of Cyano-derivatives of Organochlorophosphate(V) Ions

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The organochlorophosphate(V) ions $[PRCl_5]^-$ (R = Et, C_6F_5, or CCl_3) react with excess AgCN to form $[PEt(CN)_5]^-$, $[P(C_6F_5)Cl(CN)_4]^-$ (one isomer), and $[P(CCl_3)Cl_2(CN)_3]^-$ (all three isomers) respectively; salts containing these ions have been isolated and characterised. Several intermediate chlorocyanophosphates have been detected by ^{31}P n.m.r. spectroscopy and isomeric configurations have been assigned by the method of pairwise interactions. A possible rationalisation of the degree of substitution by cyanide into these and other organochlorophosphates is proposed, based on the relative stabilities of the six-co-ordinate anions and the five-co-ordinate phosphoranes from which they are derived.

Earlier work[1–6] on six-co-ordinate cyanophosphates(V) has been described in a previous paper, in which the first cyano-derivatives of organochlorophosphates were reported.[7] Reaction of excess AgCN with $[PRCl_5]^-$ (R = Ph or Me) led to the formation of $[PPhCl_2(CN)_3]^-$ (all three possible isomers) and $[PMe(CN)_5]^-$ respectively.[7] The isomers of $[PPhCl_2(CN)_3]^-$ were resistant to further substitution, and to hydrolysis, and did not react with tosylamine.[8] This behaviour paralleled that of $[PCl_3(CN)_3]^-$, where the *fac* and *mer* isomers also proved to be extremely stable both to hydrolysis and to further substitution.[4] In an attempt to obtain a more complete understanding of the factors affecting substitution in these complexes, the reactions of AgCN with $[PRCl_5]^-$ (R = Et, C_6F_5, or CCl_3) have been investigated. In this way the effects of both bulky (C_6F_5) and highly electronegative (C_6F_5 or CCl_3) substituents could be examined, and the behaviour pattern of simple alkyl-substituted chlorophosphates(V) could be confirmed.

Experimental

All manipulations, including n.m.r. and i.r. sample preparation, were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. All solvents were degassed on the vacuum line to remove any oxygen present, and stored over molecular sieves. Tetra-alkylammonium salts were dried as described in earlier work.[4] Other starting materials were of the best available commercial grade, and were used without further purification. The preparation of salts containing the ion $[P(C_6F_5)Cl_5]^-$ is described elsewhere.[9] The compound $[NPr^n_4][PEtCl_5]$ was prepared by a similar method to that used for the tetra-n-pentylammonium salt.[10] $PEtCl_4$, prepared by direct chlorination of $PEtCl_2$,[10] was dissolved in a small quantity of CH_2Cl_2, and an equimolar amount of NPr^n_4Cl in the same solvent was added, with constant stirring. The reaction mixture was stirred for 30 min, and then evaporated to dryness *in vacuo*. The white solid obtained was not washed with low-boiling light petroleum in case it dissociated back to the starting materials[10] (Found: C, 42.3; H, 9.4; Cl, 40.7; N, 2.9; P, 7.1. $C_{14}H_{33}Cl_5NP$ requires C, 39.7; H, 7.9; Cl, 41.8; N, 3.3; P, 7.3%). Other organochlorophosphates(V) were prepared *in situ*, as indicated below.

Tetra-n-propylammonium Pentacyano(ethyl)phosphate, $[NPr^n_4][PEt(CN)_5]$.—$PEtCl_4$ (0.48 g, 2.38 mmol) was dissolved in a small amount of CH_2Cl_2 and an equimolar quantity of NPr^n_4Cl (0.53 g, 2.39 mmol) was added, with constant stirring. The reagents were allowed to stir for 1 h before an excess of AgCN (2.50 g, 18.7 mmol) was added, and the mixture then left to stir overnight. The ^{31}P n.m.r. spectrum showed only one signal, at δ −306.2 p.p.m., before the silver salts were removed by filtration. The filtrate was evaporated to dryness *in vacuo* to yield a cream solid (Found: C, 53.8; H, 8.6; Cl, 0.0, N, 16.3; P, 6.6. $C_{19}H_{33}N_6P$ requires C, 60.6; H, 8.8; Cl, 0.0; N, 22.3; P, 8.2%). Carbon and nitrogen analyses were consistently low from several attempts, just as in $[NEt_4][PMe(CN)_5]$,[7] and this was attributed to difficulty in obtaining complete combustion of the cyano-groups. The total absence of chlorine, and the single ^{31}P n.m.r. resonance, which was also obtained when the solid was redissolved in $PhNO_2$, were considered as conclusive evidence for the formation of the compound.

Tetra-n-propylammonium and Tetraethylammonium Chlorotetracyano(pentafluorophenyl)phosphate, $[NPr^n_4][P(C_6F_5)Cl(CN)_4]$ *and* $[NEt_4][P(C_6F_5)Cl(CN)_4]$.—$[NPr^n_4][P(C_6F_5)Cl_5]$[9] (0.39 g, 0.69 mmol) was dissolved in a small amount of CH_2Cl_2. AgCN (0.47 g, 3.51 mmol) was added with constant stirring. The mixture was allowed to stir for 3 h before the silver salts were filtered off. The filtrate was evaporated to dryness *in vacuo*, yielding a fine cream-coloured solid (Found: C, 47.8; H, 5.4; Cl, 5.5; N, 9.1; P, 5.9. $C_{22}H_{28}ClF_5N_5P$ requires C, 50.4; H, 5.4; Cl, 6.8; N, 13.4; P, 5.9%). Again the carbon and nitrogen analyses were rather low, although better carbon figures were obtained for the tetraethylammonium salt, which was similarly obtained as a viscous red liquid, which turned to a red solid in the inert atmosphere box, by reaction of excess (> 5 : 1) AgCN with equimolar amounts of $P(C_6F_5)Cl_4$ and NEt_4Cl in CH_2Cl_2 (Found: C, 45.3; H, 3.8; Cl, 7.5; N, 12.8; P, 5.1. $C_{18}H_{20}ClF_5N_5P$ requires C, 46.2; H, 4.3; Cl, 7.6; N, 15.0; P, 6.6%).

Tetra-n-propylammonium Dichlorotricyano(trichloromethyl)phosphate, $[NPr^n_4][P(CCl_3)Cl_2(CN)_3]$.—Equimolar quantities of $P(CCl_3)Cl_4$[9] and NPr^n_4Cl were dissolved in $PhNO_2$, and an excess (>5:1) of AgCN was added, with stirring. The reaction mixture was allowed to stir for 2 h, the silver salts were filtered off, and the filtrate distilled *in vacuo* to remove most of the $PhNO_2$. The remaining liquid was treated with low boiling (303—313 K) light petroleum and decanted four times to yield a cream-coloured solid (Found: C, 39.6; H, 6.0; Cl, 34.7; N, 10.6; P, 5.9. $C_{16}H_{28}Cl_5N_4P$ requires C, 39.7; H, 5.8; Cl, 36.6; N, 11.6; P, 6.4%). A similar product was obtained from a 3 : 1 molar ratio reaction.

Tetra-n-propylammonium Trichlorodicyano(trichloromethyl)phosphate, $[NPr^n_4][P(CCl_3)Cl_3(CN)_2]$.—This compound was prepared from a 2 : 1 molar ratio reaction of AgCN with $[NPr^n_4][P(CCl_3)Cl_5]$, formed *in situ* as above. The cream-coloured solid product was isolated (Found: C, 36.4; H, 5.3; Cl, 38.7; N, 7.2; P, 5.6. $C_{15}H_{28}Cl_6N_3P$ requires C, 36.5; H, 5.7; Cl, 43.1; N, 8.5; P, 6.3%). Its identity was confirmed by ^{31}P n.m.r. (see Results and Discussion section).

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer, as described previously.[11] Chemical shifts were measured relative to external H_3PO_4, with the downfield (higher frequency) direction taken as positive. Microanalyses[11,12] and i.r. spectra[10] were also obtained as in earlier papers.

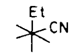
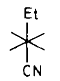
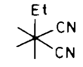
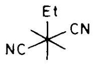
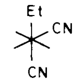
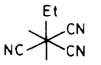
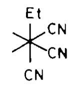
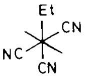
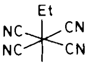
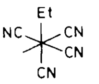
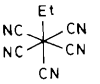
Results and Discussion

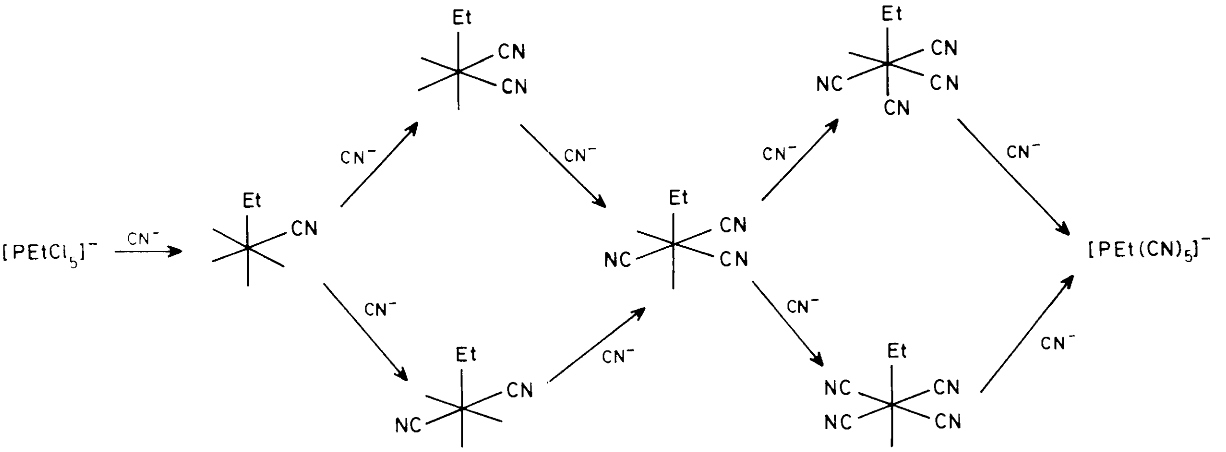
(i) *Substitution into* $[PEtCl_5]^-$.—This ion has been isolated previously as its tetra-n-pentylammonium salt;[10] the most negative chemical shift obtained in $PhNO_2$, even in the presence of excess tetra-n-pentylammonium chloride, was −137.1 p.p.m., which was extrapolated to a 'limiting shift' of −138.0 p.p.m. There is a strong possibility that the anion is dissociated to some extent in this system, however, in agreement with u.v. evidence from other workers for partial formation only of $[PEtCl_5]^-$ when $PEtCl_4$ was treated with either NMe_4Cl or PEt_3Cl_2,[13] and with the chemical shifts of other four-, five-, and six-co-ordinate phosphorus(v) compounds.[14] In support of this hypothesis, addition of $NPr^n{}_4Cl$ to $PEtCl_4$ in CH_2Cl_2 caused a maximum upfield shift of −160 p.p.m., and even this value may not be the true 'limiting shift' of the $[PEtCl_5]^-$ ion. The compound $[NPr^n{}_4][PEtCl_5]$ was successfully isolated as a white solid (Experimental section). For cyanide substitution studies it was normally prepared *in situ* by adding $NPr^n{}_4Cl$ to a solution of $PEtCl_4$ in CH_2Cl_2 until the maximum observable shift was attained.

When a small amount of AgCN was added to this solution, a new signal was discerned, attributed to one of the two possible isomers of the first substitution product $[PEtCl_4(CN)]^-$. Addition of more AgCN caused the appearance of further upfield resonances, which could be assigned to particular members of the series $[PEtCl_{5-n}(CN)_n]^-$, as shown in Table 1. Excess AgCN ($\geqslant$5.1 molar ratio) led to a single resonance ascribed to the $[PEt(CN)_5]^-$ ion, which was isolated in a quantitative reaction as its $NPr^n{}_4{}^+$ salt. This compound, redissolved in $PhNO_2$, also gave a single ^{31}P resonance at −306.2 p.p.m. Its i.r. spectrum (Nujol mull) showed a medium intensity CN absorption at 2 180 cm^{-1}. The anion was quite stable to hydrolysis, and did not decompose on exposure to the laboratory atmosphere overnight, or on the addition of five drops of water to the n.m.r. sample. An attempt to prepare a salt containing the ion $[PEtCl_2(CN)_3]^-$ by a 3:1 molar ratio reaction between AgCN and $[NPr^n{}_4][PEtCl_5]$ led to a mixture of species in solution, since the ^{31}P n.m.r. spectrum showed additional resonances from one isomer of each of the dicyano- and tetracyano-species. No further efforts were therefore made to obtain separate chlorocyanophosphates in this instance. The behaviour in this system is very similar to that found for cyanide substitution into $[PMeCl_5]^-$, the main difference being the observation of two of the three possible isomers for $[PRCl_3(CN)_2]^-$ where R = Et, and only one where R = Me.[7]

Isomeric configurations can be assigned to the intermediate chlorocyanophosphates by application of the method of pair-wise interactions,[4,5,7,15,16] although this is more difficult here because of the uncertainty of the shift of the $[PEtCl_5]^-$ ion. As a first approximation, the Et:Cl term was derived as 9.7 p.p.m. from the observed shift of −160 p.p.m. The Cl:Cl, CN:Cl, and CN:CN terms were taken as −24.85, −27.19, and −36.88 p.p.m. respectively from the $[PCl_{6-n}(CN)_n]^-$ series,[4] leaving the Et:CN term as the only unknown. The ion $[PEtCl_4(CN)]^-$ can exist in *cis* and *trans* forms, and since the *trans* isomer has no *cis* Et:CN interactions, its shift can be evaluated as −169.4 p.p.m. This is far from the value observed for the first cyano-substitute, which is therefore deduced to have the statistically more probable[7] *cis* configuration. The Et:CN term may be calculated from its shift as −29.78 p.p.m., and the shifts for all possible isomers evaluated on this basis are shown in column 1 of Table 1. It is readily apparent that the agreement between calculated and experimental values is poor for higher values of *n*. In an attempt to obtain a better value for the shift of the $[PEtCl_5]^-$ ion, the correlation between the ^{31}P shift differences between A^+ and AX (Δ_1) and between A^+ and $AX_2{}^-$ (Δ_2), where A^+ is a phosphonium ion and X is an anionic ligand,[14] was employed, using $\delta(^{31}P)$ $[PEtCl_3]^+$ 129 p.p.m. and $\delta(^{31}P)$ $PEtCl_4$ −24 p.p.m.[10] This procedure gave $\delta(^{31}P)$ $[PEtCl_5]^-$ as −187 p.p.m., and a revised Et:Cl term of 2.95 p.p.m. The Et:CN term is then derived as −9.53 p.p.m. from the shift of *cis*-$[PEtCl_4(CN)]^-$, and the values calculated as a result are shown in column 2. The values in column 3 were obtained by using the

Table 1. Calculated and experimental shifts (p.p.m.) for $[PEtCl_{5-n}(CN)_n]^-$

Isomer	Ion	$\delta(^{31}P)$ Calculated 1	2	3	$\delta(^{31}P)$ Experimental
(A)		−206.5	−206.5	−203.8	−206.5
(B)		−169.4	−196.4	−196.4	—
(C)		−260.4	−233.4	−226.0	−246.6
(D)		−253.0	−226.0	−220.7	−243.5
(E)		−223.2	−223.2	−218.5	—
(F)		−314.2	−260.2	−248.1	−275.7
(G)		−284.4	−257.4	−246.0	—
(H)		−277.1	−250.1	−240.7	—
(I)		−375.4	−294.4	−275.6	−296.6
(J)		−345.6	−291.6	−273.4	−293.6
(K)		−414.2	−333.2	−306.2	−306.2



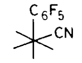
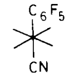
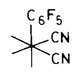
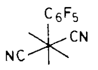
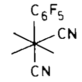
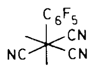
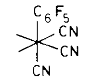
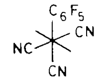
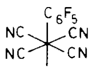
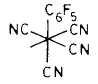
Scheme. Pattern of substitution by CN$^-$ into [PEtCl$_5$]$^-$

revised Et:Cl term and the CN:CN term as −34.84 p.p.m. from [PMe(CN)$_5$]$^-$,[7] giving the Et:CN term as −6.87 p.p.m. from the experimental shift of [PEt(CN)$_5$]$^-$. Column 2 gives the best overall agreement, although there are marked numerical discrepancies in some instances. This is not unexpected, however, in view of the results for other cyanophosphates, which also showed considerable deviations between experimental and calculated values, possibly caused by distortions from regular octahedral geometry.[4,5,7]

Despite these limitations, reasonable structural conclusions may be drawn in each case. A *cis* structure (**A**) is indicated for [PEtCl$_4$(CN)]$^-$, as described above. Two isomers were detected for n = 2, and these are assigned configurations (**C**) (δ −246.6) and (**D**) (δ −243.5 p.p.m.) respectively, since the calculated shifts for these species are close together and appreciably more negative than that calculated for isomer (**E**). Only one isomer was detected for n = 3, and the only reasonable structure is (**F**), which can be generated by direct substitution into (**C**) or (**D**) without ligand rearrangement. It is also the statistically most probable isomer for n = 3 if *cis*-[PEtCl$_4$(CN)]$^-$ is formed exclusively. Both isomers were detected for n = 4, and these are assigned structures (**I**) (δ − 296.6) and (**J**) (δ −293.6 p.p.m.) respectively, since the calculated shift for (**I**) is always more negative than that for (**J**). The pattern of substitution is represented in the Scheme, and is identical to that deduced[7] for cyanide substitution into [PMeCl$_5$]$^-$, apart from the result for n = 2. It is apparent from the results that substitution is not governed purely by statistical considerations, and that both ethyl- and cyano-substituents may exert directing effects.

(ii) *Substitution into* [P(C$_6$F$_5$)Cl$_5$]$^-$.—The most negative shift achieved by addition of Cl$^-$ ions to P(C$_6$F$_5$)Cl$_4$ was −240 p.p.m., and salts containing the [P(C$_6$F$_5$)Cl$_5$]$^-$ ion have been isolated.[9] For the cyanide substitution experiments, NPr$^n_4$Cl was added to a solution of P(C$_6$F$_5$)Cl$_4$ in CH$_2$Cl$_2$ until the limiting shift was reached. Successive additions of small amounts of AgCN caused the appearance of several new peaks to higher field of this resonance, which could be assigned to different species in the series [P(C$_6$F$_5$)Cl$_{5-n}$(CN)$_n$]$^-$, as shown in Table 2. Only one isomer was detected for n = 1, but all three possible isomers were found for n = 2 and n = 3. Addition of an excess of AgCN gave just one resonance, which was ascribed to one of the two possible isomers for n = 4. This deduction was confirmed by preparation of both the NPr$^n{}_4{}^+$ and NEt$_4{}^+$ derivatives of the ion [P(C$_6$F$_5$)Cl(CN)$_4$]$^-$ (Experimental section). The NPr$^n{}_4{}^+$ salt before isolation gave a ^{31}P solution signal at −340.0 p.p.m., and the solid redissolved in PhNO$_2$

Table 2. Calculated and experimental shifts (p.p.m.) for [P(C$_6$F$_5$)-Cl$_{5-n}$(CN)$_n$]$^-$

		δ(^{31}P) Calculated			
Isomer	Ion	1	2	3	δ(^{31}P) Experimental
(**A**)		−277.3	−261.9	−275.3	−277.3
(**B**)		−249.4	−249.4	−249.4	—
(**C**)		−322.0	−289.1	−315.9	−315.9*
(**D**)		−314.6	−283.8	−310.6	−307.0
(**E**)		−294.0	−276.6	−290.0	−303.0
(**F**)		−366.6	−316.3	−356.5	−338.6
(**G**)		−346.0	−309.1	−335.9	−332.0
(**H**)		−338.7	−303.8	−330.6	−328.8*
(**I**)		−418.6	−348.8	−402.4	—
(**J**)		−398.0	−341.6	−381.8	−341.6

* Most abundant isomer.

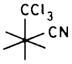
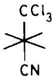
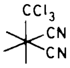
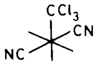
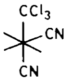
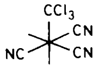
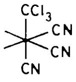
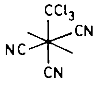
gave a similar resonance at −341.6 p.p.m. Its solid-state spectrum consisted of a broad resonance with a maximum at −341.0 p.p.m. The solution spectrum was unaffected by exposure of the sample to the atmosphere overnight, or by the addition of five drops of water, showing the stability of the phosphate(V) ion to hydrolysis. The i.r. spectrum (Nujol mull) showed a broad medium intensity CN band at 2 180 cm^{-1}. The NEt_4^+ analogue similarly gave a solution resonance at −340.0 p.p.m. before isolation, and a signal at −341.7 p.p.m. when redissolved in $PhNO_2$. It, too, was stable to hydrolysis. Its i.r. spectrum was recorded in CH_2Cl_2 solution, using a KBr cell; it gave a sharp, strong CN band at 2 180 cm^{-1}, with weaker absorptions at 2 150, 2 130, and 2 030 cm^{-1}.

The pairwise interaction method was applied to this system also, to try to deduce the isomeric configurations of the intermediate chlorocyanophosphates and of the final product. The C_6F_5:Cl term was derived as −10.3 p.p.m. from the limiting shift of −240.0 p.p.m. for the $[P(C_6F_5)Cl_5]^-$ ion.[9] If the Cl:Cl and CN:Cl terms are taken from the $[PCl_{6-n}(CN)_n]^-$ series,[4] the shift of the *trans* isomer of $[P(C_6F_5)Cl_4(CN)]^-$ is evaluated as −249.4 p.p.m. The observed spectrum did not show a signal close to this value, suggesting that the first substitution product is again the statistically more probable *cis* isomer. Hence the C_6F_5:CN term can be derived as −40.58 p.p.m., and if the CN:CN term is taken as −36.88 p.p.m.[4] the shifts for all the possible isomeric forms up to $n = 4$ are as given in column 1 of Table 2. If the CN:CN term is taken from the shift of the $[PMe(CN)_5]^-$ ion as −34.84 p.p.m.,[7] the C_6F_5:CN term can be evaluated as −25.18 p.p.m. from the shift of the only possible isomer (**J**) of $[P(C_6F_5)Cl(CN)_4]^-$ to be formed by substitution into all three isomers of $[P(C_6F_5)Cl_2(CN)_3]^-$ without ligand rearrangement. This is also the statistically more probable product. Column 2 of Table 2 gives the shifts calculated on this basis. Alternatively, the C_6F_5:CN term can be derived as −38.58 p.p.m. from the shift of the most abundant isomer of $[P(C_6F_5)Cl_3(CN)_2]^-$, which is taken as the one with both CN groups *cis* to each other and to the C_6F_5 group, structure (**C**). This is the statistically most probable isomer for $n = 2$, and is also the one for which calculations consistently give the most negative shift. The values calculated as a result are in column 3 of Table 2.

Not surprisingly the numerical agreement is at best only moderate, but isomeric configurations may be assigned with reasonable confidence in this series. The single isomer for $n = 1$ is deduced to have a *cis* structure (**A**), as explained above, in agreement with statistical predictions and with the results for other organochlorophosphate(V) systems. All three isomers were detected for $n = 2$, and these are assigned structures (**C**), (**D**), and (**E**) respectively, in accordance with the order of calculated shifts. The most abundant isomer is (**C**), in agreement with statistical predictions for substitution into (**A**). For $n = 3$ the ions are assigned structures (**F**), (**G**), and (**H**) respectively from the shift order. Rather surprisingly the most abundant isomer was (**H**) rather than (**F**), showing that the substituents already present exert directing effects, as observed in substitution by cyanide into other organochlorophosphate species.[7] The unique isomer found for $n = 4$ is assigned structure (**J**) rather than (**I**), not only from the shift value and statistics, but also because, as indicated above, (**J**) is the only possible single substitution product from all of the precursors (**F**), (**G**), and (**H**) without ligand rearrangement.

(iii) *Substitution into* $[P(CCl_3)Cl_5]^-$.—A concentrated solution of $[NPr^n_4][P(CCl_3)Cl_5]$ was prepared by adding NPr^n_4Cl to a solution of $P(CCl_3)Cl_4$ in $PhNO_2$ until the limiting shift of −196.6 p.p.m. was reached.[9] New upfield resonances were observed on successive small additions of AgCN, and were assigned to species in the $[P(CCl_3)Cl_{5-n}(CN)_n]^-$ series as shown in Table 3. In addition, signals were detected from the decomposition products $P(CCl_3)Cl_2$ (δ 149.6 p.p.m.) and $P(CCl_3)(CN)_2$ (δ −90.1 p.p.m.). In this system all possible isomers for $n = 1$, 2, and 3 were detected, and, in marked contrast with the systems described previously, the two signals for $n = 1$ were of approximately equal intensity. No further substitution occurred on addition of excess AgCN. The compound $[NPr^n_4][P(CCl_3)Cl_2(CN)_3]$ was isolated as a cream-coloured solid from reactions of $[NPr^n_4][P(CCl_3)Cl_5]$ with either excess (> 5:1) AgCN or a 3:1 molar ratio of the cyanide. The solid from the reaction with excess AgCN, redissolved in $PhNO_2$, showed signals from all three possible isomers, in *ca.* 44 (δ −258.9), 28, and 28% relative intensities. Exposure of this solution to the laboratory atmosphere for 3 h caused no change in the resonance positions, indicating that the ions are resistant to hydrolysis. The solid from the 3:1 ratio reaction showed peaks at δ −258.1 and −262.1 p.p.m., and the signal of the third isomer was not detected, possibly because of overlapping resonances. The i.r. spectrum (Nujol mull) showed a medium intensity, sharp CN band at 2 180 cm^{-1}, with weaker absorptions at 2 310 and 2 020 cm^{-1}. A solid product was also successfully isolated from a 1:2 molar ratio reaction with AgCN (Experimental section). It gave solution signals at −239.6 (strong) and −247.7 (weak) p.p.m. when redissolved in either CH_2Cl_2 or $PhNO_2$, showing that at least two of the isomers for $n = 2$ were present in the product. No signals were observed for species with $n = 1$ or $n = 3$. Its i.r. spectrum contained a weak, broad CN band with maximum absorption at 2 180 cm^{-1}.

Table 3. Calculated and experimental shifts (p.p.m.) for $[P(CCl_3)Cl_{5-n}(CN)_n]^-$

Isomer	Ion	δ(^{31}P) Calculated 1	δ(^{31}P) Calculated 2	δ(^{31}P) Experimental
(**A**)		−221.9	−217.8	−221.9
(**B**)		−206.0	−206.0	−210.7
(**C**)		−254.6	−244.2	−249.3
(**D**)		−247.2	−238.9	−243.6
(**E**)		−238.6	−232.4	−241.2*
(**F**)		−287.2	−270.7	−262.9
(**G**)		−278.6	−264.2	−261.3
(**H**)		−271.3	−258.9	−258.9*

* Most abundant isomer.

The pairwise interaction method was again applied to assign isomeric configurations (Table 3). If the Cl:Cl, CN:Cl, and CN:CN terms are taken from the $[PCl_{6-n}(CN)_n]^-$ system,[4] and the CCl_3:Cl term as 0.55 p.p.m. from the limiting shift of the $[P(CCl_3)Cl_5]^-$ ion,[9] the shift of the *trans* isomer (**B**) of $[P(CCl_3)Cl_4(CN)]^-$ can be calculated as -206.0 p.p.m., in reasonable agreement with the resonance observed at -210.7 p.p.m. The signal at -221.9 p.p.m. is therefore assigned to the *cis* isomer (**A**), enabling the CCl_3:CN term to be evaluated as -17.73 p.p.m. The shifts for all the species with $n = 2$ or 3 may then be derived, as shown in column 1. Alternatively if the CN:CN term is taken as -34.84 p.p.m. from the result[7] for $[PMe(CN)_5]^-$, and the CCl_3:CN term as -13.59 p.p.m. from the shift of the most abundant isomer of $[P(CCl_3)Cl_2(CN)_3]^-$, which is deduced to have structure (**H**), the values in column 2 are obtained. [The calculated shift for isomer (**H**) is always less negative than those of (**G**) or (**F**), so this assignment seems reasonable.]

Although the numerical agreement is again only moderate, the configurations of the species with $n = 2$ or 3 may be assigned with some confidence from the theoretical shift sequences in each instance, and are as indicated in Table 3. Interestingly, this system differs considerably from the $[P(C_6F_5)Cl_{5-n}(CN)_n]^-$ system in that both isomers for $n = 1$ are formed in approximately equal amounts, and the most abundant isomer for $n = 2$ has structure (**E**) rather than (**C**), although (**H**) was found to be the most abundant isomer for $n = 3$ in both cases. The CCl_3 group thus appears to have a greater *trans* influence than C_6F_5, labilising the *trans* chlorine to some extent and facilitating substitution in this position, so that the statistical pattern of substitution is not followed. Indeed, if the isomers for $n = 1$ are considered as being formed in equal amounts, it is apparent that both statistical and electronic factors will lead to (**E**) as the most abundant isomer for $n = 2$, since substitution by CN^- into *trans*-$[P(CCl_3)Cl_4(CN)]^-$ can only lead to structure (**E**) without ligand rearrangement. Isomer (**H**) is not the most favoured isomer statistically for $n = 3$, showing that directing effects of the substituents already present are again important, and confirming that the pattern of substitution is not statistically determined.

(iv) *General Considerations.*—The relative stability of the isolated compounds to hydrolysis has been indicated; this parallels the behaviour of $[PCl_3(CN)_3]^-$ (both isomers),[4] $[PMe(CN)_5]^-$, and $[PPhCl_2(CN)_3]^-$ (all three isomers).[7] It was suggested in earlier work that CN^-, being a ligand high in the spectrochemical series, could lower the energies of the vacant t_{2g} $3d$ orbitals on phosphorus and make them available for π donation from lone pair orbitals on Cl (or CN) substituents,[4] and this still appears to be the most plausible explanation. In order to rationalise the different final substitution products for reaction of cyanide with $[PRCl_5]^-$, however, it is necessary also to consider the relative stabilities of the six-co-ordinate anions and their five-co-ordinate phosphorane precursors. The only reasonable substitution mechanism for a six-co-ordinate phosphate(v) anion is a dissociative one, *i.e.* it will react *via* a five-co-ordinate rather than *via* a seven-co-ordinate intermediate, since there are insufficient suitable low-energy orbitals for forming seven σ bonds. Since the P–CN bond is stronger than the P–Cl bond, this may be expressed in the general equations (1) and (2) for formation of $[PRCl_{5-n}(CN)_n]^-$ from $[PRCl_{6-n}(CN)_{n-1}]^-$, where (1) will be the rate-determining step.

$$[PRCl_{6-n}(CN)_{n-1}]^- \rightleftharpoons PRCl_{5-n}(CN)_{n-1} + Cl^- \qquad (1)$$

$$PRCl_{5-n}(CN)_{n-1} + CN^- \dashrightarrow [PRCl_{5-n}(CN)_n]^- \qquad (2)$$

Hence substitution depends on the lability of the P–Cl bond in the dissociation equilibrium (1). If the group R is electronegative, this will assist in delocalising the negative charge on phosphorus and in stabilising the anion to dissociation. Thus equilibrium (1) will be shifted to the left and substitution will be more difficult. The point is well illustrated by the difference in behaviour when R = CCl_3 and when R = Me or Et. With the electronegative substituent CCl_3, the anion becomes very resistant to further substitution when $n = 3$. For the electron-supplying groups Me and Et there is no such stabilisation of the anion, and complete substitution up to $[PR(CN)_5]^-$ is possible.

The phenyl group is also more electronegative than methyl or ethyl, and its behaviour parallels that of the CCl_3 group, with substitution terminating when $n = 3$. The more difficult system to rationalise is that when R is C_6F_5, since this ligand is evidently more electronegative than C_6H_5, yet substitution proceeds a stage further to give one isomer of the $[P(C_6F_5)Cl(CN)_4]^-$ ion. A possible explanation is that the spatially larger C_6F_5 group facilitates the dissociation of a chloride ion to form the phosphorane, so that equilibrium (1) is forced more to the right. The superposition of a steric effect on the normal electronic effects may thus distort the expected substitution behaviour.

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